The Role of Point Defects and Defect Complexes in Silicon Device Processing

Summary Report and Papers

Workshop Chairman: B. L. Sopori
Second Workshop
Breckenridge, Colorado
August 24-26, 1992

Prepared by: B. Sopori and T.Y. Tan
with contributions from Session Chairmen

National Renewable Energy Laboratory
1617 Cole Boulevard
Golden, Colorado 80401-3393

A national laboratory of the U.S. Department of Energy
Managed by Midwest Research Institute
for the U.S. Department of Energy
under contract No. DE-AC36-83CH10093

Prepared under Task No. PV421101

August 1994

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

MASTER

NOTICE: This report was prepared as an account of work sponsored by an agency of the United States government. Neither the United States government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States government or any agency thereof.

Printed on paper containing at least 50% wastepaper and 10% postconsumer waste

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

Second Workshop Role of Point Defects/Defect Complexes in Silicon Device Processing

Contents

<u>Papers Received:</u>	Page
WORKSHOP THEME: DEFECT ENGINEERING CONCEPTS FOR LOW-COST HIGH EFFICIENCY SOLAR CELL PROCESS DESIGN	
Bhushan Sopori.....	11
IMPORTANT IMPURITIES AND DEFECTS IN EFG SOLAR CELLS	
Fritz Wald	15
THE NONCONTACT LASER/MICROWAVE PHOTOCONDUCTANCE TECHNIQUE: HOW FAR CAN WE PUSH IT!	
A. Buczkowski, F. Shimura and George Rozgonyi.....	19
CZ SILICON: AN IMPURITY/DEFECT PERSPECTIVE	
K. W. Mitchell.....	27
CHARACTERIZATION OF HEM MULTICRYSTALLINE SILICON	
C. P. Khattak, Frederick Schmid, Bhushan Sopori and W. K. Schubert.....	33
FUNDAMENTAL PROPERTIES OF POINT DEFECTS: THE ROLE OF THEORY	
Stefan Estreicher	41
RECONSTRUCTION OF GRAIN BOUNDARIES BY POINT DEFECT INJECTION	
Dieter Ast.....	47
THE ROLE OF POSITRON ANNIHILATION SPECTROSCOPY IN THE STUDY OF DEFECTS IN CRYSTALLINE SILICON	
Peter Mascher	55
DEPTH AND RADIAL PROFILES OF DEFECTS IN CZOCHRALSKI-GROWN SILICON FOLLOWING THERMAL PROCESSING	
A. K. Issar, R. C. Hyer, N. Hozhabri, S. C. Sharma, M. F. Pas, S. Kim and T. Shaffner	65
POINT DEFECT INJECTION DURING CO AND TI SILICIDATION OF PHOSPHORUS IMPLANTED SILICON	
Jeff Honeycutt, J. Ravi and G. A. Rozgonyi.....	79
MODELING OF THE COUPLED DIFFUSION OF PHOSPHORUS WITH POINT DEFECTS	
Scott Dunham	89
EFFECTS OF D-DEFECTS IN CZ SILICON UPON THIN GATE OXIDE INTEGRITY	
Sookap Hahn, J. G. Park, S. P. Choi, G. S. Lee, Y. J. Jeong, S. Kwak, C. K. Shin, W. L. Smith and P. Mascher	99
POINT DEFECTS, CARBON AND MICRODEFECTS IN EFG SILICON	
Juris Kalejs.....	107
MECHANISMS OF GETTERING BY EXTENDED DEFECTS BY P AND BY AL	
T. Y. Tan and U. M. Gosele	111

IMPURITY ANALYSIS OF SILICON BY SPV METHOD J. Lagowski, M. Dexter and P. Edelman.....	115
EFFECTS OF METALLIC IMPURITIES IN CZ-SI: A MINORITY CARRIER LIFETIME STUDY BY SURFACE PHOTOVOLTAGE (SPV) METHOD Kamal Mishra.....	121
PRECIPITATION AND GETTERING OF HEAVY METALS DURING IC PROCESSING L. Jastrzebski	131
TEMPERATURE DEPENDENCE OF THE EXTERNAL GETTERING EFFICIENCY IN CAST SEMICRYSTALLINE SILICON MATERIALS L. A. Verhoef and P. P. Michiels.....	137
PHOSPHORUS AND ALUMINUM GETTERING FOR HIGH EFFICIENCY POLYCRYSTALLINE SILICON SOLAR CELLS A. Rohatgi, P. Sana, R. Ramanachalam, and W. B. Carter	143
PASSIVATION OF IMPURITIES IN SI BY ANNEALING IN H ₂ Michael Stavola, G. D. Watkins, P. M. Williams and S. Uffring	149
SPIN DEPENDENT PHOTOCURRENTS IN RIBBON SOLAR CELLS C. H. Seager, E. L. Venturini and W. K. Schubert.....	155
ATOMIC HYDROGEN INTERACTION WITH DISORDERED REGIONS IN SILICON S. Ashok and K. Srikanth.....	165

SECOND WORKSHOP

SUMMARY

The silicon substrates used for commercial solar cells consist of low-cost single crystal Czochralski (CZ), cast ingots and ribbon materials. Despite their different growth techniques, their photovoltaic properties appear to be quite similar. For example, the typical efficiencies of the cells fabricated on these substrates are in the range of 12 - 14%. These efficiencies are limited by the defects and impurities in the material. However, the influence of impurities and defects can be mitigated by processes such as impurity gettering and defect passivation. These defect engineering approaches are extensively used in the IC industry, and there are indications that they can also be valuable for silicon solar cells. Hence, the theme of this workshop was to identify defect engineering approaches that offer a promise of improving the efficiency of silicon solar cells fabricated on low-cost substrates.

Session 1 discussed characteristics of various commercial photovoltaic silicon substrates, the nature of impurities and defects in them, and how they are related to the material growth. Session 2 on Point defects reviewed the capabilities of theoretical approaches to determine equilibrium structure of defects in the silicon lattice arising from transitional metal impurities and hydrogen were discussed. Session 3 was devoted to a discussion of the surface photovoltage (SPV) method for characterizing bulk wafer lifetimes, and to detailed studies on the effectiveness of various gettering operations on reducing the deleterious effects of transition metals. The salient results of these sessions are summarized below.

Session 1

- The performance of Solarex cells appeared to be limited by intragrain dislocations that can locally reach densities of 10^7 cm^{-2} ; other structural defects consist of grain and subgrain boundaries. Improvement in the casting method led to reduction in the stress in the ingot with a concomitant improvement in the cell performance up to 14%. The standard material exhibits carbon and oxygen concentrations of 10 ppm and 25 ppm, respectively.
- The EFG substrates have high concentration of C with no evidence of precipitation on dislocations. As-grown substrates have low minority carrier lifetime. However, after some process steps, the lifetime ranges from 1 to 4 μs . Metallic impurities consist primarily of Fe, Cr and Ti. A reduction in the resistivity has major impact of rapidly lowering the minority carrier diffusion length. Presence of Fe and Cr does not appear to have any effect on the cell performance but Ti has a strong detrimental effect. Photoluminescence measurements show two lines in regions of high dislocation densities and four in low density regions.
- Siemens Solar utilizes CZ wafers, grown in-house at a higher speed than conventional CZ. Major problem in the growth manifests as a "lost structure" in the form of slip bands. The minority carrier lifetime depends on the thermal history and is typical about 4 μs . Van der Pauw measurements indicate a low mobility of $300 \text{ cm}^2/\text{Vs}$, perhaps limited by the presence of compensating impurities. Slip dislocations result in a loss in the short circuit current; this is attributed to a decrease in the minority carrier diffusion length.

Material with heavy slip shows a trap level at 0.59 eV. Near-term objective is to reduce oxygen to about 20 ppm.

- The HEM method is a directional solidification approach which leads to impurity segregation at the GB's. The growth is carried out at low pressures leading to a low convection that is accompanied by absence of breakdown in Si and SiO₂ interface, and hence a low oxygen content. The minority carrier diffusion length values are highest in the material coming from the middle of the ingot. A discussion of the effects of in situ annealing was presented.

- A non-contact Laser microwave technique was developed by NCSU that operates in a photoconductive decay mode. This technique can separate bulk and surface lifetimes.

Session 2

- Application of positron annihilation spectroscopy (PAS) for evaluation of defects in the silicon was reviewed. The technique relies on the fact that defects act as positron traps, increasing the benchmark lifetime of positrons. Various vacancy complexes exhibit different lifetimes that can also change in the presence of other impurities. Although PAS was shown to identify changes in the lifetime associated with oxygen precipitation, the effect is believed to be related to the behavior of the B-O complex. It is believed that PAS can identify vacancy concentration, introduced by high temperature RTA, in the range of 10¹⁶/cm³. PAS was applied to determine variation in as-grown wafers and upon annealing. Annealing shows some improvement of the material quality at the surface.

- Silicidation of Co and Ti, following phosphorus diffusion, injects high concentrations of vacancies into silicon. These vacancies are responsible for removal of the end-of-range dislocation loops.

- A review of the analysis of dopant diffusion using a model involving coupled diffusion of dopants and point defects was presented. This approach includes both the negative charged P-V and P-I pairs, and seems to provide a good match between the experimental and calculated phosphorus diffusion profiles.

- The D-defects found induce a surface roughness at the Si/SiO₂ and have a detrimental effect on the integrity of the oxide. The density of D-defects increases with pull rate in p-type, 5 Ω-cm, low oxygen, low carbon, material. Failure mechanism is due to roughness associated with the D defect. But it may also be due to etching during SC1 cleaning.

- A review of the capabilities of theoretical approaches to determine equilibrium structure of defects in the silicon lattice arising from transitional metal impurities and hydrogen were discussed.

- Interstitial injection by hydrogen implantation was applied to induce nonconservative motion of grain boundaries to yield columnar grains of low electrical activity at the grain boundaries. Density of states at GB's, determined from the characteristics of the TFT's, fabricated on such films, was quite low. Thick films of these characteristics are grown in a two-step process in which a thin seed layer is first grown and reconstructed, followed by a second deposition. Suitability of these films as poly emitters on EFG cells is being investigated.

Session 3

- Recent refinements in the SPV technique have resulted in a method which is very sensitive to small lifetime variations and, because of capacitive coupling, can be applied to unprocessed wafers. While it appears to be the method of choice for as-grown material, it can also be conveniently used to monitor the effect of gettering operations which involve junction formation or back contact alloying. However, it was shown that using SPV and optical dissociation of boron/metal pairs; the effects of Fe or Cr on wafer lifetime. This is a clever use of fundamental defect properties to study device degradation.

- Fe, Ni, Cu, Cr, Mo, and Ti were the principal transition metals of concern. Several gettering procedures were discussed, including: 1. Phosphorus diffusion, 2. Al back contact formation, 3. Backside damage gettering, and 4. Front surface oxidation. It was pointed out repeatedly that the p-base cells, steps 1 and 2 were essentially inevitable, so that it behooved cell processors to manipulate their processing sequences to maximize the removal of transition metal impurities.

- The studies on P-diffusion generally showed that extended drive-in times maximized the gettering effects on base lifetime, but this can drastically lower blue light cell response because the resulting thick emitter essentially functions as a "dead" layer with poor photoresponse. There was some discussion of the etchback method used to alleviate this problem, and there was disagreement as to the controllability and cost effectiveness of this solution. Studies showed that the gettering effectiveness of P-diffusion was generally higher for faster diffusing metals. While this is not an unexpected result, the exact mechanism for P-diffusion gettering has yet to be elucidated; interstitial injection appears to be a good candidate for the driving force behind this effect.

- Gettering during Al back contact formation was also discussed. Studying this effect demands some caution, since significant Al-indiffusion will set up a back surface field which will raise cell efficiency in good lifetime material independent of any gettering effect. Less work on this method was reported, although it was shown that the optimum Al drive-in temperature was 850°C (for poly). There appears to be little hard information available on the physical mechanism of gettering by this method. It was pointed out that studies where the chemical content of Al back contact layers was analyzed after alloying, might help define just which impurities reach this layer during sintering (if they reach this layer at all).

- There was also some discussion of internal gettering methods. Precipitated oxygen was identified as an important site for the gettering of Fe. Data was also presented to support the common assumption that transition metals will precipitate at the cores of dislocations and grain boundaries. This fact provides the rationale for the backside damage gettering technique. However, it is clear that the degree of electrical activity of metals precipitated at dislocation cores varies with metal type and annealing environment, so that much more work must be done to define how effective this process might be in a real solar device with a given spectrum of impurities.

Panel 1

Impurity/Defect Issues in Commercial Photovoltaic Silicon

Chairman: Kim Kimerling, MIT
Members: Dieter Ast, Cornell University
Scott Dunham, Boston University
George Rozgonyo, North Carolina State University

The first general discussion of Sessions 1 and 2 of the Workshop was intended to provide broad coverage of all the issues related to the impurities and defects in solar cell substrates and their effects on the cell performance. For this reason, the in-depth aspects of many issues brought up were to be covered in a discussion session later. For the purpose of conducting the discussion in an orderly manner, it was structured into five topics, each containing a number of aspects, as follows:

- (1) Crystal Growth
 - ambient (O), (C)
 - growth rate: K_{eff} , defects
 - heat treatment
 - (O), (C)
 - (δ) 700-1000°C
 - as-grown vs. device
- (2) Dislocations
 - nucleation/multiplication
 - grain boundary motion vs. residual stress
 - electronic states
 - annihilation reactions
 - metallization, diffusion
 - climb
- (3) Grain Boundaries
 - reconstruction/passivation
 - impurity segregation
 - textures
 - enhanced diffusion
 - H_2
 - P, Al
- (4) Electrical Activity
 - definition
 - $E_T f(T, \phi_{hv}, E_F, \epsilon, \dots)$
 - local reconstruction
 - gettering, passivation
 - lifetime
 - vs. ρ ($< \Omega\text{-cm}$)
 - equilibrium
 - contacts, diffusion
 - annihilation
 - textured interface
 - measurement
 - non-exponential decay
 - mapping

- (5) Variation in Performance
- homogeneity over large areas
 - cell to cell

The following highlights were summarized in accordance with the above listed topics:

- (1) Crystal Growth
EFG materials can contain over 10ppm C, due to the graphite die used. In oxygen ambient, Cr was gettered away; oxygen also passivates dislocation cores, e.g., eliminated a 0.2eV deep level, but it does not passivate precipitates. The thermal equilibrium segregation coefficients of most metals in Si (that of their concentration in solid vs. that in liquid Si) is extremely small, on the order of 10^{-5} - 10^{-8} . Therefore, provided the pulling rate is not too high, the incorporation of metallic impurities into crystalline Si is ignorable. The EFG Si pulling rate is quite large and is made more susceptible to metal contamination.
- (2) Dislocations
There are two different theories as to the cause of the electrical activity of dislocations (i) metal atoms surrounding dislocation core; and (ii) unreconstructed dislocation core configurations, primarily that of jogs (and/or kinks). Experimental evidences show that metal atoms can activate dislocation states.
- (3) Grain Boundaries
Reconstructed and/or passivated grain boundaries were not electrically active.
- (4) Electrical Activity
Electrical activity results from unpaired electrons of metal atoms and dangling Si bands at defects. Gettering removes metal atoms and passivation by H eliminate unpaired electron bonds. Decreased lifetime in low resistance materials is probably due to metal contaminants.
- (5) Variations in Performance
- No essential discussions.

Panel 2

Gettering in Silicon Solar Cells

Chairman: Teh Tan, Duke University
Members: Leendert Verhoef, R&S Netherlands
Eicke Weber, University of California-Berkeley

Gettering technology stems from the IC industry where it is widely used to improve leakage-limited fabrication yield of devices. Gettering effects have also been observed in solar cell fabrication processes, in controlled as well as uncontrolled experiments, resulting in improved solar cell efficiencies. Therefore, it appears that the time is ripe for a serious consideration of incorporating gettering as a strategy for solar cell efficiency improvements. However, the demands on gettering in solar cells are different from that in IC devices. for IC fabrications, every effort has been made to preserve the Si quality and

assure processing line cleanliness. Hence, gettering serves as only a final, continuous, in-processing cleaning step for removing unintentionally introduced metallic impurities away from the device active regions, i.e., the wafer front surface region of a thickness less than ~10 μ m. Gettering needs are quite different for solar cells because:

- (1) The whole Si wafer must be the gettered region;
- (2) for economic reasons, a variety of different types of silicon substrate materials of quite different quality (crystallinity, impurity levels) were used; and
- (3) also for economic reasons, processing lines and processing may not have been in a desired clean state.

Thus, the role of gettering is more demanding on its coverage in solar cell than in IC fabrications. On the other hand, because of the shorter processing cycle, the required sustaining ability of gettering in solar cell fabrications is not as stringent as in IC fabrications.

The following topics were addressed in this discussion session:

- (1) When and where to apply gettering? As-grown materials or device processing?
- (2) What is to be accomplished by gettering (removal of impurities only or include the reconstruction of existing extended defects)?
- (3) What gettering methods are feasible for solar cells?
- (4) What are the gettering mechanisms?

A consensus was reached that it is best to apply gettering during device processing. The inclusion of gettering steps mandates a modification of the normal device processing sequence. Because solar cell processing is relatively uncomplicated, process compatibility does not seem to be a serious issue. It is emphasized that the solar cell fab line must be maintained to a certain degree of cleanliness, which is fortunately less stringent than that of an IC fab line.

Because of their high migration activation energies, rare earth metals (Ti, V, Mo, etc.) are next to impossible to be gettered, and the noble metals (Au, Pt, etc.) are very difficult to getter. Therefore, these metals must be avoided in the as-grown crystals and in the solar cell fab process. Fortunately, these metals do not normally exist either in as-grown Si crystals or in a fab line. In agreement with the IC case, the transition metals Ni, Cu, and Fe appear to be the major contaminants that normally exist in the as-grown materials and in the solar cell fab line. These metals are the impurities that need to be gettered although it is still not known which metal is the dominant contaminant. It is highly desirable that evaluation of the commercial solar cell materials be performed to identify such impurities. It is seemingly premature to consider extended defect rearrangement by gettering or point defect injection scheme, for in-cast and EFG materials. The dominant factor determining the structures and densities of dislocations is still thermal stress during crystal growth. Elimination of thermal stress during crystal growth and/or by post-growth annealing has a much larger effect at this stage.

Because of the long lasting reversible configuration of certain metal-dopant pairs, e.g., vB, which can disassociate or associate at quite low temperatures, it may be worthwhile to begin addressing the long-term reliability of solar cells.

The desirable gettering methods for solar cell fabrication are combinations of a few external gettering (EG) schemes. For example, P indiffusion and Cl gettering have already been used to improve solar cell efficiencies, which are, fortunately, part of solar cell fab process even if gettering is not intended; HCl gettering may be an addition. In contrast to the IC fabrication case, intrinsic or internal gettering (IG) schemes is not desirable. However, IG related phenomena still need to be considered. For using CZ Si for solar cell fabrication, the oxygen precipitate related IG centers are to be avoided. This may be done by reducing the SiO₂ nucleation rate by reducing oxygen content and/or by high temperature wafer annealing before solar cell processing. For cast and EFG materials, it is noted that IG centers, in the form of grain boundaries and dislocations, naturally exist. They must be passivated.

Most opinions about gettering mechanisms follow those briefly summarized by Tan and Gosele in general and by Weber for gettering Fe by IG in particular. For gettering by Al, the additional possibilities that Al may directly passivate dislocations or indirectly passivate defects by generating H₂ from H₂O have been pointed out.

There was general agreement that the most urgent need is to identify the dominant lifetime limiting defect(s). It was further agreed that grain boundaries and dislocation can have low electrical activity owing to bond reconstruction and/or H passivation.

Panel 3

Passivation of Impurities and Defects in Silicon Solar Cells

Chairman: Stefan Estreicher

Members: H. Branz, C. Seager, M. Stavola

Hydrogen and other rapidly diffusing species interact with a variety of impurities and other defects, and with the lattice itself. These interactions are basically of a chemical nature, i.e., involving covalent interactions. Hydrogen binds to a weak Si bond or to an impurity. As a result, a complex is formed, interactions are stabilized, energy levels associated with the initial defect shift, and the complex often becomes electrically inactive.

The panel discussion covered the following five areas:

- passivation of point defects
- passivation of extended defects
- hydrogen diffusion
- hydrogenation techniques
- other issues

The discussion brought out the following important issues that require further attention of the PV community:

(1) Hydrogen Interactions With Localize Deep Centers

The emphasis clearly is on transition metals, but other centers (vacancies) have also been discussed. There is good experimental evidence that hydrogen interacts with

many metals, but nothing is known about the details of the interactions, the passivation mechanisms, or the stability of the complexes. Particularly puzzling is why some important transition metals (Ti, V) are not passivated. Recent experimental work involving high-temperature hydrogenation and recent theoretical data have opened the door toward fundamental advances.

(2) Hydrogen and Extended Defects

Hydrogen is believed to passivate undecorated dislocations and grain boundaries. However, even this is controversial. The case of decorated dislocations is poorly understood. Metallic precipitates at dislocations interact with hydrogen and are (at least partially) passivated. Even the phenomenology is unclear, and a database is incomplete.

(3) Hydrogen Diffusion

Hydrogen diffusion profiles do not show the classical erfc behavior or even the behavior expected for particles diffusing in a field of traps. The near-surface region of a plasma-exposed sample contains hydrogen in amounts far greater than that of known solubility of hydrogen in silicon (10^{21}cm^{-3}). Hydrogen related platelets and/or bubbles are new and are not well identified.

H diffusion in the field induced by the in-diffused, phosphorous, hydrogen may play a crucial role which is not understood. The critical parameters that control H diffusion are not known. These important issues will require attention.

(4) Other issues that were briefly discussed include:

- multiple phases of H at point defects
- H-enhanced diffusion of interstitial oxygen
- passivation-induced defects
- passivation through overlayers
- passivation by F, Li, and Cu
- backside passivation

Panel 4

**Approaches to Material Quality Enhancement
of Photovoltaic Silicon Substrates**

Chairman: Fritz Wald, Mobil Solar
Members: Juris Kalejs, Mobil Solar
Kim Mitchell, Siemens Solar Industries
Mohan Narayanan, Solarex Corp.

This discussion session was concerned with materials quality improvement for improving solar cell efficiencies. The bottom line is economy, measured in dollars/watt, which dictates a desirable 22-24% solar cell efficiency and a minimum cost on Si substrates.

Presently in the solar cell industry, based on CZ or casting techniques, materials recycling and minimizing cutting loss, etc. have been employed as means for lowering the Si cost. However, other approaches involving improved material quality can certainly help in additional cost reductions. The latter approach requires further understanding of the material properties. Improved lifetime in low resistivity CZ Si is needed and characterization effort should certainly be helpful.

For cast Si, low lifetime areas need to be eliminated. This can probably be done by further minimization of thermal stress during growth, supplemented by P diffusion gettering and H₂ passivation. Furthermore, it seems that better control of C and O contents are also needed.

The quality of the EFG material can perhaps be improved by growing thinner material for which a smaller intra grain dislocation density is expected.

A provocative thought is to use floating zone (FZ) Si for solar cell fabrications, as this material is free from extended defects and excess impurities. However, there has not been an agreement of the cost involved. Opinions differ from being economical (for large scale production) to noneconomical.

In addition, a feed-stock price issued has been raised. Current PV materials industry enjoys a very low feed-stock cost because the IC industry rejects have been included in the feed-stock. Anticipating a large increase in feed-stock consumption by the PV materials industry, say, by a factor of 10³-10⁴, this advantage would disappear.

Panel 5

Solar Cell Processing Design Considerations Involving Defect Engineering

Chairman: Peter Iles, Applied Solar Energy Corp.
Members: James Gee, Sandia National Laboratories
Ajeet Rohatgi, Georgia Institute of Technology

The purpose of this discussion is to try to establish when and how to apply defect engineering to PV processing. Bearing in mind that solar cell materials will always have variable qualities, we see that defect engineering will always be an issue. Since the role of impurities and defects as lifetime/solar cell efficiency killers and their removal/gettering has been addressed in previous sessions, the present session focused on process parameters and process sequences on gettering, passivation, and defect control in bulk and surfaces. Therefore, the main discussion topics are:

- (1) Materials specifications
- (2) Defect engineering opportunities in current PV technology
 - Phosphorus diffusion
 - Al gettering
 - H₂ passivation
 - Other

(3) Future opportunities

It is agreed upon that a reasonable materials specification should include: (i) resistivity; (ii) defect types and densities; (iii) concentrations of the inert impurities C and O; (iv) concentrations of the electrically active metal species, including transition metals, noble metals and rare earth metals; and (v) minority carrier lifetime. It was emphasized that since lifetime represents the overall quality of the material (a result of all other factors such as doping, impurity, and defects) it may finally be the factor that can be used to correlate with solar cell efficiencies appropriately fabricated. For this reason, it is worthy of considering measuring lifetime after certain critical solar cell fabrication steps, e.g., P diffusion for junction formation and gettering.

For the P diffusion-gettering step, a specification will be dependent upon the specifics of the Si material and solar cell process sequence. However, generally, the following aspects will be crucial: (i) temperatures; (ii) time; (iii) P surface concentration; (iv) ramp rate (may be premature); (v) diffusion ambient; (vi) diffusion source material; and (vii) etch back after diffusion.

For the Al gettering-passivation process, temperature, times, Al layer thickness, Al source material (paste/evaporated) and ambient conditions should be specified.

It is not clear whether the hydrogen passivation process will still be needed for the Si bulk if P and Al gettering processes were already implemented. However, it seems clear that interface passivation will be beneficial, which probably can be done at the end processing the cells and at low temperatures; e.g., -450°C .

DEFECT ENGINEERING CONCEPTS FOR LOW-COST HIGH EFFICIENCY SOLAR CELL PROCESS DESIGN

Bhushan L. Sopori
National Renewable Energy Laboratory
1617 Cole Boulevard
Golden, Colorado 80401

ABSTRACT

Fabrication of high-efficiency solar cells on low-cost silicon substrates requires processes that can mitigate the influence of crystal defects and high concentrations of impurities present in these materials. Defect engineering concepts involving gettering, defect passivation, and defect annihilation could be applied to improve the material quality and boost the cell performance. However, this information currently resides primarily in the realm of microelectronics. The NREL/DOE Silicon Materials Program is aimed at acquiring up-to-date information in these areas and understanding the basic mechanisms of point defect processes and their application to quality enhancement of PV silicon substrates. This paper presents a brief discussion of practical implementation of these concepts in a way that can minimize the cost of cell fabrication.

INTRODUCTION

During the last decade, a number of new methods have been developed for growing low-cost silicon for photovoltaic applications. These include casting, ribbon growth, fast-pulled Czochralski, and thin-silicon-film. Solar cells fabricated on these materials yield efficiencies in the range of 13%-15% under Global AM1.5 illumination. However, these efficiencies are considerably lower than 16%-18% required to meet the DOE cost goals for photovoltaic (PV) energy. In the past, efforts to reach the DOE cost goals were primarily directed at improving the crystal growth processes. However, it is expected that further improvements through crystal growth cannot occur without increasing the cell cost. Hence, further improvements in the cell performance must come from post-growth quality enhancement methods such as gettering, defect annihilation, and defect passivation. In order to improve the cell efficiencies without a significant increase in the cell cost, such treatments must be incorporated as a part of the cell fabrication sequence.

DEFECT ENGINEERING TO IMPROVE CELL PERFORMANCE (Theme of the Workshop)

The high concentrations of impurities and defects in solar cell substrates are primarily a result of economic considerations in keeping the substrates costs low. For example, high crystal growth rates needed for high throughput necessitate large thermal gradients, which are generally accompanied by large stresses. Thermal stresses above the yield stress result in formation dislocation. Likewise, high impurity content in the substrate can be due to the use of (inexpensive) low-grade poly feedstock, and impurity transport from low-cost furnace parts. Higher efficiency cells can be fabricated on these substrates only if the substrate quality can be improved during the cell processing. This requires treatments like gettering, defect annihilation, and passivation that must be included as a part of the cell fabrication. Development of such processes relies heavily on defect engineering whereby impurities and defects can be restructured into less harmful configurations. Solar cell process designers face a major new challenge in fabricating high efficiency devices without significantly increasing the cell fabrication costs.

These new challenges are being anticipated by the Crystalline Silicon Materials Research Program of NREL/DOE which heavily emphasizes basic research on post-growth quality enhancement of low-cost silicon substrates. The various areas under this program include research on the basic mechanisms of impurity gettering, defect/impurity passivation, and defect annihilation. A major effort of the program is to introduce the photovoltaic community to the significance of point defect processes in gettering, defect passivation, and defect annihilation; areas that are already well recognized in the IC industry. The results of this research are expected to lead to suitable processes for the fabrications of higher efficiency solar cells on low-cost substrates.

Although a great deal of information about defect engineering already exists from microelectronics devices, it cannot be directly applied to the fabrication of solar cells using low-cost substrates. For example, in the IC industry the role of gettering is primarily to remove process included impurities; in solar cell fabrication the objective is to utilize these methods for improving the material quality. In addition, it is expected that processes like gettering may not take place formly in solar cell substates because they have non-uniform distributions of defects and impurities. Furthermore, in order to minimize the added costs of such processes, they must be included in the cell fabrication processes.

The purpose of this workshop is to review new research results from both the microelectronics and photovoltaic fields, and to develop coherent approaches to defect engineering that can be appalled to solar cell process design and material growth.

DEFECT ENGINEERING PROCESSES

IMPURITY GETTERING:

Many commercial PV silicon substrates have high concentrations of carbon and/or oxygen. It is observed that dissolved C and O do not directly limit the cell performance. However, when present in high concentrations, these impurities can precipitate at certain parts of the ingot, which can reduce the minority carrier diffusion length. In IC processing, a high concentration of oxygen is used for internal gettering to clean up the surface region for device fabrication. Unfortunately, there is no evidence that these impurities could be exploited for some type of internal gettering for solar cells. It is tempting to consider internal gettering for solar cells. In such an approach, the bulk defects such as dislocation and grain boundaries may act as gettering centers.

Solar cell substrates also contain relatively high concentrations of metallic impurities such as Fe, Cu, Cr, and Ni. These impurities could be gettered using schemes typically prevalent in the IC processing such as phosphorous gettering, Chlorine gettering, and Backside gettering. The choice of a specific gettering process clearly depends on the nature of the impurities to be gettered, the compatibility of the process with conventional cell fabrication steps, and the cost of such a process step. Phosphorous gettering appears to be quite effective for all heavy metal (Fe, Ni, Cu, and Cr) impurities and, hence, quite suitable for solar cells. Since nearly all silicon solar cells use boron-doped substrates that require phosphorous diffusions for junction formation, phosphorous gettering could conceivably be included as a part of the junction formation process. HCl gettering, typically used in conjunction with oxidation processes, has not been adequately investigated for its effectiveness in solar cells. Likewise, backside damage gettering has not been attempted for solar cell fabrication.

Gettering characteristics of phosphorus diffusion are well recognized. However, a detailed process description is not known. It is known that gettering occurs in part because of the formation of dislocations near the surface, a result of heavy stress induced by high concentrations of phosphorus in silicon. Although it can be speculated that gettering is influenced by the injection of interstitials/vacancies, a well organized theory is not available.

DEFECT ANNIHILATION:

It has been determined that dislocations present in PV silicon substrates could be frozen in high-energy configurations. Such a defect density can be lowered by thermal treatments such as annealing. Experimental results have shown that annealing at 1200°C can reduce dislocation density by an order of magnitude in some polycrystalline substrates. It is also expected that the injection of point defects can bring about a non-conservative motion of defects. However, high temperature thermal treatments can also introduce a variety of other undesirable effects. For example, thermal treatments that reduce dislocation density in the regions of high density have been found to increase dislocation densities in low density regions. It is also known that high temperature treatments of material containing high concentrations of carbon and/or oxygen can lead to precipitation, which in turn can significantly lower the minority carrier lifetime. These precipitates can also increase the junction leakage current, thus lowering Voc and the FF of the cell. The total effect of thermal treatments needs to be studied further.

DEFECT PASSIVATION:

Passivation of crystal defects and impurities by hydrogen is now well recognized as a potential process for improving solar cell efficiency. Among several methods for hydrogenation, low-energy ion implantation has worked quite effectively. A major issue in hydrogenation is related to the fact that high concentrations of hydrogen are needed to produce bulk hydrogen concentration sufficient to passivate defects. Such high concentrations of hydrogen have been found to produce defects in silicon which lower the minority carrier lifetime. As a result, hydrogen introduced from the junction side of a solar cell can also have deleterious effect on the cell performance due to the formation of defects near the junction. This has prompted much interest in back-side hydrogenation.

It is also found that the diffusivity of hydrogen in some solar cell substrates can be quite high due to a newly discovered mechanism involving the formation of mobile hydrogen-vacancy complexes. This mechanism has been applied to develop a back-side hydrogenation technique that circumvents many difficulties associated with front side hydrogenation. This mechanism of hydrogen diffusion can also be invoked in other processes such as PECVD of silicon nitride. Back-side hydrogenation has been successfully applied to finished commercial cells resulting in the improvement in the cell performance.

SOLAR CELL PROCESSING INCLUDING QUALITY ENHANCEMENT PROCESSES:

An important issue in implementing quality enhancement processes is that they should not significantly add to the cell fabrication costs. Clearly, the best scenario would be to make these processes a part of the cell fabrication schedule. Figure 1 illustrates two quality enhancement processes that may be easily incorporated into a cell fabrication sequence.

- **Gettering during junction formation:**

Although it is clear that some gettering occurs during junction formation, the requirements for gettering and junction formation are not likely to fully overlap. Effective gettering will require long time and high temperatures, leading to deep junctions and high recombination velocities at the emitter surface. The latter are due to high concentrations of gettered impurities and defects introduced by extensive phosphorus diffusion. The approach that is currently used in the laboratory to overcome this problem is to etch back the near-surface region after phosphorus diffusion.

There can be significant differences in the procedures used for impurity gettering applied to single crystal IC material and those applied to solar cell material (typically polycrystalline), containing other grown-in defects. Metallic impurities such as Cu and Ni may precipitate at defect sites during crystal growth, making their gettering less effective. In such a case, the precipitates need to be dissolved prior to gettering. It is also conceivable that the diffusivity of the impurities in the

defected regions may be significantly lower than in the rest of the material. This effect can be important for solar cells since defect distributions can be very non-uniform in these materials.

Another mechanism that can have a significant effect on the cell performance is the impurity gettering/release due to internal defects such as dislocations and grain boundaries. The internal defects are expected to serve as gettering centers; however, some degree of impurity segregation is likely to have occurred during growth. Consequently, the effective of this process will depend upon the degree of impurity segregation as well as the impurity release characteristics of the defects. If the defects can act as gettering centers, it may be possible to passivate the decorated defects by hydrogen at a later stage.

- **Passivation of defects and impurities:**

Figure 1 also shows passivation and AR coating deposition could be combined into one process step. Recent results have shown that deposition of a silicon nitride coating by PECVD process may be producing passivation. It is also likely that molecular hydrogen treatments prior to and during an AR coating deposition may produce sufficient passivation. Recently it was shown that enhanced diffusion of hydrogen can occur in some solar cell materials. We believe that this feature could be applied to use hydrogen passivation as a by-product of such process steps as AR coating, and metallization. Further funding of hydrogen passivation is necessary to develop such a process.

CONCLUSION:

Implementation of defect engineering approaches in solar cell processing has the potential to produce high efficiency devices on current commercial silicon substrates. Basic research is necessary to understand the application of defect engineering concepts to solar cell substrates. Although much can be learned from microelectronics technology, silicon solar cells pose unique problems, such as material non-uniformities. It is expected that current research programs can provide an impetus for academic institutions, National Labs, and industry to work together on these issues.

Figure 1
Possibilities of incorporating quality-enhancement processes at various cell fabrication steps

IMPORTANT IMPURITIES AND DEFECTS IN EFG SOLAR CELLS

Fritz V. Wald
Mobil Solar Energy Corp.
Billerica, Mass. 01821-3980

Abstract:

Fairly early on in the development of EFG silicon material it was shown that of the many defects present, the dislocations are by far the most detrimental. That view has remained essentially unchanged for the past ten years. Also, it was demonstrated that substantial precipitation is not an important contributor to property changes during processing of the material, but that phosphorous diffusion, Al back contact formation, and in particular hydrogen passivation, all improve material properties during processing, as does the addition of CO during growth. In this paper, we revisit some of the questions.

1. Introduction:

During a previous coordination meeting at Sandia Labs in 1988, the basic research needs of Mobil Solar with respect to materials science were described as shown in Table 1. As can be seen there, the fundamental defect questions pertinent to the material at various stages were open, and we felt that addressing them might further enhance the capabilities of EFG material with respect to the production of efficient solar cells.

In the meantime, materials production has changed to the more productive octagon format, and the solar cell processing has also changed, so that efficiencies have improved significantly over the 1988 situation (1). That leads us to evaluate again whether the questions raised in 1988 are still pertinent in 1992.

2. Basic Studies Since 1988.

To address the question of the low resistivity material first, it must be said that little progress has been made. We still don't understand why the currents in EFG solar cells are reduced, when the resistivity is decreased. But, as can be seen from Table 2, the problem still exists, and an oxygen content in the material also is still beneficial. We have also evaluated two hypotheses relative to this problem. One related to the size of the boron atom, the other one related to the possibility of micro defect generation at high doping levels. Both were found not to be pertinent. (2,3) Insofar as the importance of dislocations vis- -vis impurities in limiting the lifetime of the material is concerned, we have been able to show that several metals, even when introduced into the melts at fairly high concentrations, are surprisingly benign. (4,5,6,) Ti, on the other hand, has been proven to be quite damaging (7) and further studies on Mo, and V are still underway. At present it is believed that the differences in behaviour are related to the diffusion coefficients, which dictate the capability for being gettered during processing.

The role of dislocations in all this is still quite unclear, as it is still presumed that they might be both damaging by themselves, but aiding in the gettering process. The latter is difficult to reconcile with the fact that studies by TEM, conducted over several years by Prof. Ast at Cornell University, established conclusively the absence of precipitation under virtually all conditions of processing.

Recent studies using photoluminescence, however, clearly established the presence of the four well known luminescence peaks ascribed to dislocations in silicon (8). Since there are suggestions that such peaks only occur if impurities are present, it seems still possible that the dislocations act as gettering centers, without necessarily causing precipitation.

These dislocations, can be substantially hydrogen passivated, and then become quite benign in their electrical effects on solar cells, an observation of long standing at Mobil Solar (9), which so far has not been contradicted, although the exact mechanism of passivation is by no means clear.

3. Conclusions:

The general conclusion from the work at Mobil Solar would have to be that the defects that limit the lifetimes either after growth, or after hydrogen passivation, are still not clearly defined. The only exception to this statement is found in the behavior of Ti, when it seriously contaminates the material. In that case, definite decreases in lifetimes can be seen.

References:

1. F.V. Wald, Solar Energy Materials 23, 175, (1991)
2. C. Dube, M. Prince and F.V. Wald : Proceedings of the 11th European P.V. Solar Energy Conference, Montreux, 1992, To be published.
3. S. McHugo and W.D. Sawyer, to be published.
4. B.R. Bathey, R.O. Bell, C.E. Dube, J.P. Kalejs, F.V. Wald, Proceedings, 4th International Photovoltaic Science and Engineering Conference, Sydney, Australia, 1989, p.117.
5. B.R. Bathey, C.E. Dube, J.P. Kalejs and F.V. Wald, Proceedings of the 21st IEEE Photovoltaic Specialists Conference, Kissimmee, Florida, 1990, p.687.
6. S.H. Park, D.K. Schroeder, and J.P. Kalejs, Proceedings of the 22nd IEEE Photovoltaic Specialists Conference, Las Vegas, Nevada, 1991, p. 864.
7. J.T. Borenstein, B.R. Bathey, J.P. Kalejs, J.I. Hanoka, and N. O. Pearce, *ibid.*, p.1006.
8. W.D. Sawyer and J. Michel, Proceedings of the 16th Conference on Defects in Semiconductors, Edited by Gordon Davies et al. Materials Science Forum, Vols. 83-87, Trans Tech Pubs. Zurich, 1992, p.291.
9. J.I. Hanoka in: Hydrogen in Disordered and Amorphous Solids, Edited by G. Bambakidis et al., Plenum Publishing Corp, 1986, p.81.

Basic Research Needs - MSEC

As Grown Minority Carrier Lifetime in p-type EFG Material :

0.26 - 1 μ sec (Yablonovitch, Bellcore 1988)

Upgrading by :

[Oxygen Addition During Growth
Phosphorus Gettering During Diffusion
Hydrogen Passivation]

↓

Minority Carrier Lifetime in EFG Cells :

8 - 40 μ sec (Yablonovitch, Bellcore 1988)
(Rohatgi, Georgia Tech. 1988)

Basic Question : Which are the states that dominate lifetime in the as - grown material ?

Basic Research Needs - MSEC

Corollary Question :

How do the three upgrading steps used interact with the basic lifetime limiting states to deactivate them ?

We have some evidence that all three upgrading steps interact with dislocations :

1) J.L. Hanoka, R.O. Bell and B.R. Bathey in :
The Electrochemical Society, Extended Abstracts 81-1
p.955, Spring Meeting, Minneapolis, Minnesota 1981

2) C.E. Dube' and J.L. Hanoka
Appl. Phys. Letters 45, 1135 (1984)

Basic Question : Are Dislocations the major (only ??)
Lifetime Limiting Species ?

Basic Research Needs - MSEC

In EFG Material
Decreasing p-type resistivity from 2 - 5 Ω .cm
to 0.7 Ω .cm does not show the expected
efficiency gain.

TABLE I
MEASURED

SAMPLE	R(Ω CM-CM)	PP(%)	Jsc(MA/CM ²)	Voc(V)	FF
02-7-6	0.7	13.67	28.86	0.608	0.779
02-5-3		13.52	28.65	0.609	0.774
02-17-3	1.6	13.48	29.44	0.598	0.766
02-16-8		13.57	29.77	0.597	0.763
02-33-4	4.5	13.68	30.63	0.583	0.766
02-29-7		13.65	30.50	0.586	0.764

TABLE II

CALCULATED, 33.5 μ SEC LIFETIME (ROHATGI 1988)

R(Ω CM-CM)	PP%	Jsc(MA/CM ²)	Voc(V)	FF
0.7	14.9	31.3	619	(0.77)
1.6	14.6	31.6	606	(0.76)
4.5	14.1	31.8	585	(0.76)

TABLE 1:

Basic Research questions Pertinent to Mobil Solar's EFG
Material, as Stated in 1988.

ID	Run # 04G41-G	Nom. 2	ohm*cm	CO
Voc(mV)	Isc(mA/cm-2)	FF(%)	Eff.(%)	
21 Cell Average	596	30.6	78	14.3
Best Cells				
010	605	31.0	78	14.6
016	600	31.2	78	14.5
015	599	30.9	79	14.5
002	599	30.9	78	14.4
004	599	31.0	78	14.4
	Run # 03T41-3	Nom. .75	ohm*cm	CO
39 Cell Average	604	28.3	76	13.0
Best Cells				
39	607	28.8	77	13.5
24	609	28.7	77	13.4
31	607	28.6	78	13.5
11	608	28.3	78	13.4
13	609	28.8	76	13.4
	Run # 03T41-3	Nom. .75	ohm*cm	No CO
43 Cell Average	593	27.8	74	12.2
Best Cells				
84	603	28.3	77	13.1
59	597	28.5	76	12.9
51	595	28.2	76	12.7
90	597	28.0	77	12.8
80	599	28.0	75	12.6

TABLE 2:

**Recent Results on Low and Intermediate Resistivity EFG
Material and the Effects of Oxygen.**

The Noncontact Laser/ Microwave Photoconductance Technique: How Far Can We Push It!

A. Buczkowski, F. Shimura and George Rozgonyi

Dept. of Materials Science & Engineering
North Carolina State University
Raleigh, NC 27695-7916

ABSTRACT

We have extended the range of application of the laser excitation/ microwave reflection transient photoconductance (LM-PC) technique beyond its use as a non-contact tool for determining the effective recombination lifetime. An algorithm for separation of surface and bulk recombination effects has been developed wherein the surface recombination component of lifetime was determined by extrapolating the tail portion of the carrier decay curve to the carrier axis. Although the slope of this curve depends on both surface and bulk properties, it has been shown that the y-intercept depends only on the surface component of lifetime. As a result, a wide range of surface lifetimes, corresponding to surface recombination velocities from 10^2 cm/s to 10^5 cm/s, and bulk lifetimes from a few microseconds to several hundred microseconds can be measured. Since trapping and recombination processes are temperature dependent due to changes in occupancy status of deep energy levels, the question of whether these levels can be calculated from the temperature dependence of surface recombination velocity and bulk recombination lifetime has been addressed. The theory for a convenient, high throughput, nondestructive DLTS method based on *recombination* processes has been developed and then compared to conventional *emission* based DLTS analysis. Experimental data for silicon samples intentionally doped with metals during crystal growth is shown. Differences between the conventional and laser/microwave techniques, their respective advantages, and experimental problems in noncontact deep level determination are discussed.

INTRODUCTION

Deep Level Transient Spectroscopy (DLTS) [1, 2], based most often on capacitance transient measurements performed at low temperature, is one of the most recognized and widely used tools for electronic characterization of defects. It can be applied for comprehensive determination of defect properties like defect concentration, emission and capture rates and the energy position within the semiconductor bandgap, as well as for positive structural/ chemical identification of defects, especially when combined with other analytical methods. However, in spite of its usefulness, the necessity for preparation of special test samples, often with evaporated metal contacts defined by a photolithography process, is an inherent inconvenience of the technique. Moreover, in case of high quality crystals, where defect concentration is very low, its applicability is limited since the observed signal is directly proportional to the trap number probed within the device space charge region. Therefore, there is a great interest in establishing a procedure for noncontact electrical characterization of defects, not requiring any specific sample preparation, which at the same time could overcome mentioned limitations. Several attempts to reach this objective have already been made and depending on the measurement set-ups, the names microwave-DLTS [3], laser/ microwave DLTS (LM-DLTS) [4, 5], and surface photovoltage DLTS (SPV-DLTS) [6] were introduced. These techniques are based on the observation of transient conductance/ voltage decays at different temperatures after sample excitation by photons. In most cases, measurements were carried out on GaAs wafers characterized with relatively high trap density, in a time interval where the signal decays were governed by re-emission of carriers

from traps, filled during the photon pulse, instead capture of carriers by traps. However, in Ref. 4 silicon samples were measured where the observed signal decay was primarily affected by recombination lifetime, related to both electron and hole captures but not to carrier emission. Since recombination and emission processes base on the same physical principles, it is reasonable to address the question whether the recombination lifetime-based DLTS can be the complimentary tool to the classical DLTS (c-DLTS) technique. The goal of this paper is to present some theoretical and experimental verification to the on-going discussion on this interesting matter. The theoretical discussion has been limited to the problem of determination of deep level energy associated with the defect. A laser excitation/ microwave reflection photoconductance (LM-PC) technique was used in experimental part of this work.

ANALYSIS AND RESULTS

Deep energy level analysis preformed using the noncontact LM-PC technique is different in many aspects from the approach taken in c-DLTS. One of the major differences is the temperature range for measurements; typically, in c-DLTS, temperatures much below 0°C are required whereas in LM-PC the temperature range above 100°C is applicable. Additionally, in spite of the fact that the recombination and emission processes are based on the same physics, the volume associated with collected information is different. In case of the emission/capture-based c-DLTS, the volume probed is limited to the space charge region established by the voltage bias on the sample, typically a layer a few microns thick, located just beneath the sample surface. In contrary, the recombination process occurs within the entire wafer volume. Furthermore, recombination is influenced by the top and bottom surface with flaws of different properties. The measured recombination lifetime in LM-PC, therefore, is an "effective" lifetime consisting two components; the bulk and the surface. Thus, the separation of components is an important step in the deep level analysis. It is at this point worth mentioning that the transient decay observed in the photoconductance experiment is not exponential since it is described by an infinite series of exponential decays, as given by Eqn. 1:

$$N(t) = A \sum_{n=1}^{\infty} B_n \exp\left(-\frac{t}{\tau_n}\right) \quad (1)$$

where $N(t)$ represents the integrated number of excess carriers present within the examined sample, observed as photoconductance. Each term in Eqn. 1 is characterized with its own time constant dependent on bulk lifetime, τ_{bulk} , surface recombination velocity, S , wafer thickness, d , and ambipolar carrier diffusion coefficient, D_{amb} . However, with time, the first term in the series becomes dominant and an exponential decay with the effective lifetime constant is established. The surface recombination component of the effective lifetime is determined by extrapolating the tail portion of the carrier decay curve to the y-axis. Although the slope of this curve depends on both surface and bulk properties, the y-intercept depends only on the surface component of lifetime, as it was shown in Ref. 7 and is sketched in Fig. 1. Thus, the LM-PC measurement in the desired temperature range followed by separation analysis leads to both, the surface and the bulk lifetime vs. temperature which can serve as the basis for the deep energy level analysis.

Before practical implementation it is useful to study the influence of recombination center energy on lifetime vs. temperature relationship in theoretical way. This relation is routinely used for the construction of the Arrhenius plot, the slope of which is related to deep energy levels. First, surface recombination velocity, which is a surface counterpart of the bulk lifetime will be addressed.

Fig. 1 Simulated decay profile showing the y-intercept point related to the surface component of lifetime

Fig. 2 Bandgap model of the near surface region

Based on the analysis of A. Many et al. [8], and F. Berz [9], for a low injection approximation the surface recombination velocity as given by Eqn. 5.83 in Ref. 8 is:

$$S = \frac{\sqrt{K_n K_p} N_t (n_b + p_b)}{2 n_i \left[\cosh \left(\frac{E_t - E_i}{k T} - u_0 \right) + \cosh (v_s + u_b - u_0) \right]} \quad (2a)$$

$$u_b = \frac{E_F - E_i}{k T}, \quad v_s = \frac{V_s}{k T / q}, \quad u_0 = \ln (K_p / K_n) \quad (2b)$$

It should be noticed that the S function is nonexponential. In addition, the surface recombination velocity is not solely dependent on trap properties as expressed by trap energy, concentration, and capture cross section, but is also modified by the surface potential V_s defined in Fig.2. In fact, the influence of the surface potential is crucial; a small change in V_s can change the surface recombination by several orders of magnitude. The surface potential value can be calculated from a self-balance requirement for the charge associated with filled surface traps and the compensating near-surface charge of opposite sign, as discussed in details in Ref. 10. Selected results of calculations for surface recombination velocity as a function of temperature with trap energy level as a parameter and corresponding instantaneous curve slope interpreted as an activation energy are presented in Figure 3a and b, respectively. p-type semiconductor and acceptor traps are shown in the figure but a similar conclusion can be drawn for n-type semiconductor and donor traps, although quantitative results are dependent on selected configuration. It can be seen that, in general, the curves are nonexponential and their slopes when interpreted as an energy are not constant. Moreover, even though some segments of exponential behavior can be selected, the slope within these segments is not always equal to the deep energy levels of surface states. Thus, although the curve shape is affected by the trap energy and can be used for trap characterization, it cannot be directly interpreted as the trap energy.

Fig. 3 Theoretical surface recombination velocity (a) and its slope (b) as a function of temperature with surface trap energy as a parameter

In order to study the energy of recombination centers associated with bulk defects the separation algorithm can be applied or surface recombination velocity can be decreased to a negligible level by wafers oxidation. In either case the recombination lifetime formula derived from the Shockley-Read-Hall (SRH) theory can be used to describe the bulk lifetime. Under single recombination center and low excitation level assumptions, the lifetime is significantly affected by defect-induced recombination centers located within the forbidden gap, characterized by the center concentration, energy level and both electron and hole captures, as given by Eqn. (3):

$$\tau_{\text{SRH}} = \frac{\tau_p (n_0 + n_1 + \Delta n)}{p_0 + n_0 + \Delta n} + \frac{\tau_n (p_0 + p_1 + \Delta n)}{p_0 + n_0 + \Delta n} \quad (3)$$

with

$$n_0 = \frac{n_i^2}{p_0} \quad \tau_n = \frac{1}{\sigma_n v_{\text{th}} N_T} \quad \tau_p = \frac{1}{\sigma_p v_{\text{th}} N_T}$$

$$n_i = \sqrt{N_c N_v} \exp\left(-\frac{E_c - E_v}{2kT}\right) \quad n_1 = n_i \exp\left(\frac{E_T - E_i}{kT}\right) \quad p_1 = n_i \exp\left(\frac{E_i - E_T}{kT}\right)$$

$$v_{\text{th}} = 1.93 \times 10^7 \left(\frac{T}{300}\right)^{0.5} \quad N_c = 6.2 \times 10^{15} T^{1.5} \quad N_v = 3.52 \times 10^{15} T^{1.5}$$

In general, these parameters should be experimentally determinable and the noncontact lifetime measurements should be a suitable technique for this purpose. The lifetime formula, however, is more complicated than the simple expression describing carrier emission given by Eqn. (4):

$$e_n = \sigma_n v_{\text{th}} N_c \exp\left(-\frac{E_c - E_t}{kT}\right) \quad (4)$$

and so we can expect the lifetime-based analysis to be. This is because the expression for lifetime includes more than one exponential term as opposed to the expression for emission, as at least two captures are required to complete carrier recombination transition via flaws. Moreover, Eqn. 3 does not represent an exponential nor a linear sum of exponential terms, as it contains an exponential nominator modified by an exponential denominator.

Fig. 4 Theoretical bulk recombination lifetime (a) and its slope (b) as a function of temperature with surface trap energy as a parameter

This modification is especially strong at high temperature and for low resistivity samples. In Fig. 4, the results of theoretical lifetime calculations and corresponding instantaneous lifetime slope, interpreted as energy, with doping concentration as a parameter are presented. For the arbitrarily selected data there is a wide temperature range where the deep energy levels can satisfactorily be recovered. However, when the absolute energy of traps decreases, i. e. levels are closer to the middle of the bandgap, a higher measurement temperature is required and it is more difficult to recover the correct energy value. Therefore, the algorithm for deep energy level analysis based on the slope of the lifetime has a limited range of applicability. In this case a curve fitting method can be applied; however, the uniqueness of the values obtained in this manner is questionable since for each trap four parameters can be independently varied. Although this inherent problem of the fitting method is not fully solved yet, it is believed that the proposed solution is relatively unique as the action of each fitting parameter is different, especially, if many fitting points within wide range of temperatures is available.

In order to verify the algorithm a set of samples intentionally contaminated with Cr, Fe and Au metals during Czochralski crystal growth was studied. Recombination lifetime was measured with noncontact photoconductance technique using the laser/ microwave Lifetech-88[®] system from 20°C to 220°C temperature range, at 4°C step. The bulk and surface lifetime components were obtained using the separation algorithm described in Ref. 7. Measurement results for selected metals are presented in Fig. 5 a and b where the surface recombination velocity and the bulk lifetime are shown as a function of temperature, respectively.

Fig. 5 Temperature dependent surface recombination velocity (a) and bulk lifetime (b) for samples doped with heavy metals (gold, chromium and iron)

For comparison, the p+n junctions made by ion implantation were measured with conventional DLTS technique and trap properties as specified in Table I were obtained. Then, the theoretical lifetime as predicted by the SRH theory was calculated using the data obtained with the c-DLTS technique. Since only the electron capture cross section was determined in the DLTS measurement and for lifetime calculations both, electron and hole capture cross sections are required, the missing capture cross section was selected to obtain the best agreement between experiment and theory.

Fig. 6 Experimental and simulated with SRH theory bulk recombination lifetime with two levels fitted for the best agreement

However, even though the hole capture cross section was independently varied the agreement between the experimental and SRH lifetime was not acceptable. In order to obtain better match it was additionally necessary to introduce a second trap level and to change some of the c-DLTS trap properties. As an example, the comparison of temperature relationship measured with the LM-PC technique and calculated in accordance to the SRH theory is presented in Fig. 6 for the sample doped with iron. Full set of fitting parameters for the three metals studied is specified in Table I. Since for every metal at least two energy levels were identified with one being very close to middle of the bandgap it was not possible to obtain energy directly from the lifetime vs. temperature curve slope but instead the fitting procedure was applied. It was practically verified that only hole capture

cross sections for both identified traps can be varied within relatively wide range without significant influence on lifetime. The influence of other six fitting parameters was more critical and relatively unique. However, this problem has to be re-addressed in future along with further improvement in collected data precision, i.g. the temperature step has to be decreased and measurement noise reduced. It also seems that deconvolution of multiple exponential lifetime dependence prior to fitting procedure should increase the final accuracy.

Table I. Comparison of data measured with the conventional DLTS and data received by curve fitting based on Shockley-Read-Hall theory to the experimental lifetime measured by the noncontact LM-PC technique

		Cr		Fe		Au	
		c-DLTS	LM-PC	c-DLTS	LM-PC	c-DLTS	LM-PC
N_{t1}	[cm ⁻³]	$1.7 \cdot 10^{13}$	$4.6 \cdot 10^{11}$	$4.7 \cdot 10^{13}$	$3.5 \cdot 10^{13}$	$1.1 \cdot 10^{13}$	$2.0 \cdot 10^{13}$
E_{t1}	[eV]	0.25	0.27	0.2	0.21	0.0	0.03
σ_{p1}	[cm ⁻²]	-	$5.3 \cdot 10^{-15}$	-	$4.8 \cdot 10^{-17}$	$1.3 \cdot 10^{-16(a)}$	$2.0 \cdot 10^{-16}$
σ_{n1}	[cm ⁻²]	$4 \cdot 10^{-17(a)}$	$1.5 \cdot 10^{-17}$	$6 \cdot 10^{-15(a)}$	$2.2 \cdot 10^{-14}$	$2.8 \cdot 10^{-14(a)}$	$2.1 \cdot 10^{-14}$
N_{t2}	[cm ⁻³]	-	$3.8 \cdot 10^{13}$	-	$2.1 \cdot 10^{13}$	-	$1.4 \cdot 10^{13}$
E_{t2}	[eV]	-	0.02	-	0.058	0.22	0.22
σ_{p2}	[cm ⁻²]	-	$1.7 \cdot 10^{-17}$	-	$1.3 \cdot 10^{-16}$	-	$4.4 \cdot 10^{-16}$
σ_{n2}	[cm ⁻²]	-	$4.4 \cdot 10^{-18}$	-	$2.0 \cdot 10^{-14}$	$1.5 \cdot 10^{-13(a)}$	$3.6 \cdot 10^{-14}$

(a) Ref. 2

SUMMARY

Temperature dependence of recombination effective lifetime measured in noncontact way with laser/ microwave photoconductance technique was analyzed for deep energy level determination. After the effective lifetime separation into its surface and bulk component surface and bulk traps were independently analyzed. It was found that although surface traps affect the surface recombination velocity vs. temperature curve, its slope interpreted as energy is not directly related to trap location within the energy bandgap. In case of the bulk traps the slope of temperature dependence can be a basis for the trap energy analysis; however, due to interfering process of thermal carrier generation, the range of determinable energies is limited to relatively middle and shallow traps. In this case instead of lifetime slope analysis the fitting procedure can be applied. In this way at least two traps were identified for each contaminating metal, although the conventional DLTS was able to find only one of them. Further improvement of the technique is expected when a deconvolution technique of multi exponential terms will be applied however, a greater number of more accurate data points is required for this purpose.

ACKNOWLEDGEMENTS

The authors would like to thank A. Agarwal of NCSU and A. Salih of GI for conventional DLTS measurements, and T. Kusama of Semitex and T. Abe of SEH for supplying the Lifetech-88 system and metal-doped silicon wafers, respectively.

REFERENCES

- ¹ D. V. Lang, J. Appl. Phys. **45**, 3023 (1974).
- ² D.K. Schroder, *Semiconductor Material And Device Characterization*. (Wiley, New York, 1990).

- ³ Y. Fujisaki, Y. Takano and T. Ishiba, Jap. J. Appl. Phys. **25**, L874 (1986).
- ⁴ Y. Kirino, A. Buczkowski, Z. Radzimski, G. Rozgonyi and F. Shimura, Appl. Phys. Lett., **57**, 2832 (1990).
- ⁵ M. S. Wang and J. M. Borrego, (1990), "*Contactless Deep Level Transient Spectroscopy Using Microwave Reflection*", eds. P. Bristowe et al., Materials Research Society Symposium Proceedings, **209**, 523, (1991 Materials Research Society, Pittsburgh)
- ⁶ J. Lagowski, A. Morawski and P. Edelman, "*Non-Contact, Wafer-Scale Deep Level Transient Spectroscopy Based on Surface Photovoltage*", presented at the MRS Meeting, December 1991, Boston, MA, to be published in the Conference proceedings
- ⁷ A. Buczkowski, Z. Radzimski, G. Rozgonyi and F. Shimura, J. Appl. Phys., **69**, 6495 (1991).
- ⁸ A. Many, Y. Goldstein, and N. B. Grover, *Semiconductor Surfaces*, North-Holland Publishing Company, Amsterdam, 128, (1965).
- ⁹ F. Berz, in *Surface Physics of Phosphors and Semiconductors*, eds. C. G. Scott and C. E. Reed, Academic Press, London, 143, (1975).
- ¹⁰ A. Buczkowski, G. Rozgonyi and F. Shimura, "*Effect of Ultraviolet Irradiation on Surface Recombination Velocity in Silicon Wafers*", submitted to Jap. J. Appl. Phys.

CZ SILICON: AN IMPURITY/DEFECT PERSPECTIVE

K. W. Mitchell
Siemens Solar Industries
Camarillo, CA 93010

Abstract

Impurities and defects in Czochralski (Cz) Si are evidenced directly in the form of slip dislocations or indirectly in their impact on the minority carrier lifetime and solar cell device properties. Impurities may be introduced from the source materials or during processing. Due to the nature of Cz crystal growth, high levels of oxygen are present which impact the minority carrier lifetime through their interaction with defects and impurities. Present commercial Si cell efficiencies of 16% are expected to exceed 20% through identification and reduction of electrically active defects.

I. INTRODUCTION

Siemens Solar Industries (SSI) processes tens of millions of wafers per year sliced from in-house grown, 5.3 inch diameter, <100>-oriented Cz Si ingots, boron-doped to achieve 1 ohm-cm resistivity. To maintain this level of production, hundreds of tons of Si are processed. The quality of incoming poly-Si source material varies in doping, bulk impurities and surface oxides and contaminants. In addition, due to the nature of Cz growth and impurity segregation, the oxygen, dopant, impurity and defect distributions vary from the top to the bottom of the ingot and, thus, from wafer to wafer [1]. Utilizing this Cz Si material, photovoltaic device manufacturing at SSI has achieved total area (104 cm^2) commercial Si cell efficiencies approaching 16% with active area efficiencies above 18%. Identification and reduction of defects and impurities which degrade cell performance will result in commercial Si cell efficiencies above 20%.

Crystalline defects in Cz Si can exist in many forms: point, line, plane, or volume geometries [1]. Intrinsic point defects consist of vacancies and self-interstitials. Examples of extrinsic point defects are substitutional and interstitial impurity atoms, including dopant atoms. Edge dislocations, screw dislocations, and dislocation loops are examples of line defects. Stacking faults and twins are plane defects. Finally, volume defects may be in the form of precipitates and voids. The type, distribution, and interactions among these defects define the electronic properties of the bulk Si wafer. This paper presents the preliminary results of a study to understand the nature and impact of impurities and defects on Cz Si in order to improve cell performance.

II. SLIP DISLOCATIONS

One cause of reduced cell performance is the generation of slip dislocations in the bottom portions of ingots caused by "lost structure" which results from a perturbation during growth such as an oxide flake in the melt colliding with the growing ingot or an interruption of furnace power. The remaining portion of the ingot, due to loss of crystal structure, is remelted and not processed into cells. Slip dislocations also propagate back into the grown ingot as described below [2].

Normal growth conditions result in "full term" ingots, which at the end of growth are properly tapered as they are removed from the Si melt. Fig. 1, a plot of cell I_{sc} as a function of wafer location in the ingot, shows uniform performance throughout the ingot. The left to right direction represents moving from the bottom towards the top of the ingot with about 12 wafers per cm of ingot length. The other cell parameters, V_{oc} and FF, show identical trends.

For a "lost structure" ingot, Fig. 2, similar in layout to Fig. 1, shows that I_{sc} decreases in the bottom portion of the ingot. Similar losses occur in V_{oc} and FF. The primary cause of this performance decrease is the presence of slip dislocations. In the graph, the origin for the wafer location is the point of initial occurrence of lost structure in the ingot. The data thus indicates that the slip dislocations propagate back into the grown ingot. Optical beam induced current (OBIC) measurements confirm the presence of the slip dislocations.

The light current-voltage (I-V) curves (under 100 mW/cm² ASTM 1.5 global spectrum) for Type A (no slip dislocations) and Type B (slip dislocations present) are compared in Fig. 3. The Type A cell is 15.6% efficient with a 32.9 mA/cm² J_{sc} , 621 mV V_{oc} , and 0.763 FF based on a 103.5 cm² total area. In contrast, the Type B cell is 14.0% efficient with a 30.6 mA/cm² J_{sc} , 607 mV V_{oc} , and 0.754 FF. The comparison of the spectral response curves for Type A and Type B cells in Fig. 4 shows the loss of long wavelength response for cells with slip dislocations present, implying a reduced effective minority carrier diffusion length for the Type B cells.

III. IMPURITY/DEFECT ANALYSIS OF Cz Si

Optical and electrical measurements and processing studies have provided a preliminary assessment of the behavior of impurities and defects in Cz Si. In the absence of slip dislocations, the minority carrier lifetime of the Cz wafers depends on the nature of the electronic defects, which is presently not well understood [3]. Measured Hall Effect room temperature hole mobility values of 300 cm²/V-sec for 3×10^{16} cm⁻³ compared to literature values above 400 cm²/V-sec for the same doping level imply an increased number of scattering centers [4]. Fourier transform infrared (FTIR) absorption analysis indicates oxygen concentrations of 30 ppm or 1.5×10^{18} cm⁻³. In literature, these high oxygen contents have been

Fig. 1. I_{sc} versus wafer position for a "Full Term" Cz ingot.

Fig. 2. I_{sc} versus wafer position for a "Lost Structure" ingot.

Fig. 3. Light I-V curves for Type A and Type B Si cells.

Fig. 4. Spectral Response for Type A and Type B Si cells.

correlated with reduced minority carrier lifetimes [5]. Impurities as well as oxygen are introduced from the dissolution of the quartz crucible into the Si melt. Thus, reducing the oxygen content in the wafer to the range of 20 ppm will also reduce impurities and improve the electronic properties of the Cz wafers.

The minority carrier lifetime is influenced by thermal processing. Minority carrier lifetimes of 4 microseconds in as-grown Cz Si ingots increase to 15 to 30 microseconds in completed devices as determined by photoconductivity decay measurements at Sandia Laboratories [6] and calculations based on the diode reverse saturation current J_0 , implying defect gettering or passivation during device processing. Over-exposure of the Cz Si wafers to the temperatures above 900 C, which are characteristic of float zone Si device processing, degrades the minority carrier lifetime. For example, Sandia Laboratories found that increasing the emitter diffusion temperature for the Cz Si wafers from 900C to 950C reduced the effective bulk diffusion length from 160 micrometers to 80 micrometers.

Cell processing is also a potential source of impurity contamination. Using float zone Si wafers, minority carrier lifetimes above 1 millisecond were maintained through cell processing, implying no impurities are introduced which degrade carrier lifetime. In a separate study at Siemens Central Research, using deep level transient spectroscopy (DLTS), no transition metal impurities in Cz Si were identified above the detection limit of 4×10^{11} traps/cm³.

IV. DISCUSSION

Further study is required to understand the way in which defects and impurities interact and control minority carrier recombination and cell performance in Cz Si. The assistance of other research groups in the characterization of this material is solicited.

ACKNOWLEDGEMENTS

The contributions of my colleagues at SSI, especially the characterization efforts of Don Aldrich, Wes Chesarek, and Jim Walle, are acknowledged. The material and device analyses at Sandia Laboratories were carried through James Gee. The DLTS studies at Siemens Central Research were performed by A. Endros.

REFERENCES

1. F. Shimura, Semiconductor Silicon Crystal Technology, Academic Press, New York, 1989.
2. K. W. Mitchell, D. L. Aldrich, J. R. Walle, D. G. Gretlein, K. L. Pauls, R. Probst, J. M. Gee, J. D. McBrayer, Proc. 10th European Photovoltaic Solar Energy Conference, Lisbon, Portugal, 1991, pp. 310-312.
3. T. F. Ciszek, Proc. 20th IEEE Photovoltaic Specialists Conf., Las Vegas, Nevada, 1988, pp. 31-38.
4. S. M. Sze, Physics of Semiconductor Devices. Wiley-Interscience, New York, NY, 1969.
5. B. L. Sopori, see Ref. 3, 1988, pp. 591-596.
6. P. A. Basore and B. R. Hansen, Proc. 21st IEEE Photovoltaic Specialists Conf., Kissimmee, Florida, 1990, pp. 374-379.

CHARACTERIZATION OF HEM MULTICRYSTALLINE SILICON

C. P. Khattak and F. Schmid
Crystal Systems, Inc.
Salem, Massachusetts 01970

B. L. Sopori
National Renewable Energy Laboratory
Golden, Colorado 80401

W. K. Schubert
Sandia National Laboratories
Albuquerque, New Mexico 87185

Abstract

Multicrystalline silicon ingots produced by the Heat Exchanger Method (HEM™) have shown nearly vertical grain boundaries orientation and diffusion lengths up to 230 μm . The distinguishing feature of HEM silicon is the low oxygen concentration (2 to 5 ppm) for the standard solidification cycle under vacuum. Even when directional solidification was carried out under inert atmosphere, the oxygen concentration increased only slightly and when a non-oxide ceramic was utilized, the oxygen concentration reduced to less than 1 ppm. Optical examination of samples showed precipitate twins and dislocation arrays which could not be correlated with directional solidification parameters.

Introduction

The Heat Exchanger Method (HEM™) has been adapted for the production of large square cross-section silicon ingots for photovoltaic applications[1-3]. Silicon ingots of 44 cm square cross section weighing 80 kg have been produced with large grain size and nearly vertical grain boundaries orientation[4,5]. Characterization of silicon for photovoltaic applications as a function of position within the ingot has shown[6] that the diffusion length for the central region of the ingot was 230 μm . It is recognized in the industry that high performance solar cells can be fabricated from HEM silicon and that further improvements can be achieved by controlling the defects and non-metallic impurities. This paper discusses the characteristics of HEM silicon, the effect of atmosphere on the carbon and oxygen concentration in silicon, and the formation of defect complexes and precipitates.

Processing by HEM

A high-purity silica crucible supported with graphite plates is placed in an HEM furnace and loaded with off-semiconductor grade silicon meltstock and dopant alloy. The furnace chamber is evacuated to 0.1 torr, heat is applied by the graphite resistance heater and the charge is melted. After stabilization of the

charge, heat is extracted from the entire bottom of the crucible with the heat exchanger system. Solidification of silicon progresses from the bottom of the crucible to the top surface with a slightly convex solid-liquid interface. Controlled directional solidification is achieved and the last material to solidify is in the top corners of the square crucible. After solidification is complete, the ingot is cooled in the furnace.

The distinctive features of processing silicon by HEM are that solidification of the ingot takes place in a high-purity silica crucible. The crucible is heat treated so that it delaminates from the ingot during cooldown and therefore prevents the ingot from cracking[1,7]. In the standard HEM cycle, the furnace chamber is evacuated so that the pressure is approximately 0.1 torr. After solidification is achieved, the ingot is still in the heat zone and can be *in situ* annealed by decreasing the furnace temperature below the melting point of silicon and reducing the temperature gradient with the heat exchanger system.

While 80 kg silicon ingots of 44 cm square cross section have been produced, a smaller development HEM furnace was utilized to produce the experimental ingots. These ingots were 33 cm square cross section weighing 45 kg. The solidification time was approximately 10 hours and the total cycle time was about 48 hours. Ingot #217K was processed by the standard HEM cycle. Ingot #222K was similar to 217K but after solidification, it was *in situ* annealed prior to cooldown. For ingot #199K a standard cycle was adopted but processing was carried out under an inert gas atmosphere instead of vacuum. Ingot #206K was similar to #199K except that the ingot was annealed prior to cooldown.

Carbon and Oxygen Concentration

Multicrystalline silicon samples from various ingots were characterized by Fourier transform infrared (FTIR) spectroscopy for carbon and oxygen concentration, and the data is shown in Table I. From the data it can be seen that oxygen concentration for HEM silicon is significantly less than typical values (in the range of 20-30 ppm) for silicon produced by other processes. For ingots #217K and #222K where solidification was carried out under vacuum, the oxygen concentration in the silicon is lower than for samples from 199K and 206K where inert gas atmosphere was utilized. The oxygen concentration of samples processed under inert gas atmosphere is also lower than for silicon produced by other techniques. This is attributed to the fact that HEM solidification was carried out under stabilizing temperature gradients with low temperature gradients in the liquid and minimal convection. The SiO generated due to reaction of molten silicon with the silica crucible is minimized. This is confirmed by the minimal grooving of the crucible at the solid-liquid interface position.

The primary source of oxygen in silicon is from the silica crucible. By suppressing the reaction between molten silicon and the silica crucible, oxygen incorporation in the HEM silicon is minimized. Processing under vacuum further reduces the oxygen concentration of silicon.

An experiment was carried out in which a non-oxide ceramic crucible was used with silicon nitride coating. Characterization of silicon produced from this crucible (#239K) showed that the oxygen concentration was less than 1 ppm.

TABLE I. CARBON AND OXYGEN CONCENTRATION FOR MULTICRYSTALLINE HEM SILICON SAMPLES FOR VARIOUS PROCESSING CONDITIONS.

Ingot #	Position in Ingot	Carbon (ppm)	Oxygen (ppm)	Comments
217K	bottom	9.7	5.3	standard cycle (vacuum)
	middle	10.6	4.9	
	top	9.5	2.3	
222K	bottom	5.8	3.5	same as 217K and <i>in situ</i> annealed
	middle	6.8	3.1	
	top	13.0	1.5	
199K	middle	10.0	6.2	processed under inert atmosphere
206K	middle	4.7	9.7	processed under inert atmosphere and annealed
239K	middle	11.8	0.7	non-oxide ceramic crucible with silicon nitride coating

Defect Arrays

The primary objective of defect analysis was to investigate differences in the nature of crystal defects and precipitates that could be correlated to the growth conditions. Samples from each group were polished, defect etched and examined under TEM, SEM and optical microscope. The TEM analysis did not show any differences in the nature of defects and precipitates were not detected by TEM. Figure 1 shows an optical examination of a precipitate pit surrounded by dislocation arrays for an etched sample which corresponded to the standard HEM cycle. A sample from the ingot processed under inert atmosphere showed dislocations bound by twins with perpendicular orientation of twin lines and random distribution of shallow dislocations. The precipitate density was low and randomly distributed (Figure 2). A sample from an ingot processed under inert atmosphere and annealed prior to cooldown showed a large number of precipitates without any set orientation. Parallel twin lines were observed with dislocations between these twins (Figure 3). SEM examination of precipitates is shown in Figure 4. Precipitates, twins and dislocations have been observed in all HEM silicon samples. A correlation between these defects and growth conditions can only be carried out after systematically evaluating a large number of samples.

FIGURE 1. OPTICAL EXAMINATION (200X) OF A PRECIPITATE PIT AND DISLOCATIONS FOR A SAMPLE CORRESPONDING TO STANDARD HEM SILICON.

CS# 199k

CS# 199k

FIGURE 2. OPTICAL EXAMINATION SHOWING TWINS AND DISLOCATIONS FOR AN HEM SAMPLE PROCESSED UNDER INERT ATMOSPHERE.

FIGURE 3. A SAMPLE OF HEM SILICON PROCESSED UNDER INERT ATMOSPHERE AND *IN SITU* ANNEALED SHOWING RANDOM DISTRIBUTION OF PRECIPITATES AND PARALLEL TWIN LINES.

FIGURE 4. SEM EXAMINATION OF PRECIPITATES IN HEM SILICON.

Lifetime Measurements

Wafers from different positions in ingots #217K and #222K were evaluated for photoconductance decay (PCD) illuminated lifetime measurements after POCl_3 diffusion and oxidation at 900°C . The data is shown in Figure 5. This data shows that higher lifetime values are obtained for wafers from the middle of the ingot and that difference in lifetime for the wafers from annealed and unannealed ingots is not significant. The wafers from the top and bottom sections of the ingots showed a degradation in the minority carrier lifetime as compared to the middle of the ingot.

FIGURE 5. PCD ILLUMINATED LIFETIME AS A FUNCTION OF POSITION FOR STANDARD (217K) AND ANNEALED (222K) INGOTS.

Summary

Silicon ingots of 44 cm square cross section, 80 kg are produced by HEM directional solidification under vacuum so that large grains with vertical orientation of grain boundaries are obtained. The distinguishing feature of HEM silicon is the low oxygen concentration attributed to solidification under low temperature gradients in the liquid and stabilizing temperature gradients in the heat zone. Even when directional solidification is carried out under inert gas atmosphere, the oxygen concentration in HEM silicon increases only slightly. The silica crucible was the source of oxygen and when a non-oxide ceramic crucible was utilized, the oxygen concentration was reduced to less than 1 ppm level.

Characterization of HEM silicon ingots showed that the highest lifetime is for wafers from the middle of the ingot with some deterioration in lifetime for the top and bottom sections of the ingot. Optical examination of etched samples showed precipitates, twins and dislocation arrays. However, these defects could not be correlated with changes in growth atmosphere or other growth parameters. It is necessary to evaluate a large number of samples to correlate the defects with processing parameters.

References

1. C.P. Khattak and F. Schmid, *Proc. 13th IEEE Photovoltaic Specialists Conf.* (IEEE, New York, 1978) p. 137.
2. F. Schmid and C.P. Khattak, *Opt. Spectra* 15(5) 65 (1981).
3. C.P. Khattak and F. Schmid, in *Silicon Processing for Photovoltaics II*, C.P. Khattak and K.V. Ravi, eds., (North Holland, New York, 1987) p. 153.
4. C.P. Khattak, F. Schmid, D.W. Cunningham and J.G. Summers, *Proc. 22nd IEEE Photovoltaic Specialists Conf.*, (IEEE, New York, 1991).
5. C.P. Khattak and F. Schmid, *Proc. 6th International Photovoltaic Science and Engineering Conf.*, (Oxford & IBH Publ., New Delhi, India, 1992) p. 117.
6. T.M. Bruton, J.G. Summers, B.E. Lord, A.M. Mitchell, D.W. Cunningham, A.E. Hughes, K.C. Heasman, B.M. Neville and M. Lesniak, *Proc. 22nd IEEE Photovoltaic Specialists Conf.* (IEEE, New York).
7. C.P. Khattak and F. Schmid, *Am. Ceram. Soc. Bull.* 57, 609 (1978).

FUNDAMENTAL PROPERTIES OF POINT DEFECTS: THE ROLE OF THEORY

Stefan K. ESTREICHER

Physics Department, Texas Tech University — Lubbock, TX 79409-1051

Abstract

Many point defects in silicon trap charge carriers and are therefore undesirable for photovoltaic applications. Examples include intrinsic defects (self-interstitials or vacancies), interstitials (O , C , Ti , ...), and substitutional impurities (chalcogen, heavy transition metals, ...). Some defects are metastable and/or bistable, others exhibit negative-U properties, or tend to form complexes. Standard "remedies" (gettering and passivation) are known to increase the lifetime of charge carriers. But the processes involved must often be optimized by trial-and-error, and sometimes do not work at all. A pre-requisite to the optimization of solar cell performance is to *understand* the microscopic mechanisms involved in order to be able to *control* the reactions. Experimental techniques often provide only a part of the needed information. Further, they are restricted to those states of a given defect that have an observable property *and* are present in high enough concentrations. On the other hand, "first-principles" or "ab-initio" calculations are becoming reliable enough to predict the behavior of point defects. Theory provides much help in the interpretation of experimental data and, in some cases, is the only way to approach a problem.

I. GENERAL PROPERTIES OF POINT DEFECTS

1. "Point" defects?

Solar grade silicon contains many imperfections ranging from extended structures (dislocations, grain boundaries, etc.) to localized defects such as vacancies or interstitials. A "point defect" is a localized structure such as an isolated impurity *including* the rearrangement of the lattice around it. Small complexes are often also referred to as "point" defects. Most of them are incorporated involuntarily into the crystal during growth or processing.

If the energy levels of such a defect are located deep in the fundamental gap,^[1] they are electron or hole traps, reduce the lifetime of charge carriers, and must be avoided. Among the most dreaded traps for charge carriers are some transition metal impurities such as Ti or V . Even a tiny amount of such impurities - say 10^{-12} cm^{-3} or so - is enough to reduce substantially the efficiency of a solar cell.^[2]

One increases the lifetime of charge carriers by physically displacing the undesirable impurities to an unimportant region of the crystal (gettering) or chemically neutralizing them (passivation). The former process involves the high temperature diffusion of an impurity (Au , for example) toward a gettering center. The latter process normally involves atomic hydrogen that binds to the defect, or to an imperfect host atom bond near the defect. This allows relaxations to take place, stabilizes the interactions, and shifts the energy levels - hopefully all the way to a band. Silicon dangling bonds (at vacancies, grain boundaries, etc...) and some impurities, such as substitutional Au , are efficiently passivated^[3] by atomic H . Other point defects, however, stubbornly refuse to be gettered

or passivated (interstitial Ti is one of the most notorious examples), or form complexes with H that are themselves traps for charge carriers, such as the $\{H, V\}$ pair.^[4]

Even in situations where a recipe to remove a deep center exists, our understanding of the phenomena taking place is often limited. Little is known about the mechanism(s) involved in Au diffusion. Why would a 6th-row *substitutional* impurity such as Au diffuse so much easier than a 4th-row *interstitial* such as Ti ? While the passivation by hydrogen of *shallow* impurities is rather well understood,^[5] much less is known about the interactions between hydrogen and deep centers, except perhaps the vacancy. Other elements capable of passivation are also often present: Interstitial copper is one example. Again, little is known about its role. Finally, vacancies and self-interstitials are easily created at various steps of processing, including hydrogenation. Since the barrier for diffusion of vacancies is lower than that of hydrogen, it is possible that vacancies participate directly or indirectly in many reactions as well.

This lack of fundamental knowledge limits the technological approaches to trial-and-error methods, with or without the benefits of an educated guess. In order to optimize the efficiency of photovoltaic devices, a microscopic understanding of the phenomena discussed above is necessary. This understanding can only emerge from a combination of experimental and theoretical studies.

2. Complications

Many localized defects in Si are metastable, bistable, and/or have negative-U properties. Depending on the position of the Fermi level, on external fields, or even on the temperature or illumination, the same defect can exhibit very different properties.

a) Metastability: The potential energy surface of a defect in a given charge (and spin) state has more than one minimum. The lowest-energy configuration is "stable", and the other configurations are "metastable". The geometry as well as the electrical and optical properties in the various states may be totally different. If the energy difference between the states is small, two (or more) "versions" of the same defect coexist. One example is interstitial H^0 , which is stable in the bond-centered (BC) configuration and metastable at the tetrahedral interstitial (T) site.^[6] The $\{Fe, Al\}$ pair in silicon^[7] has two configurations, one with trigonal and the other with tetragonal symmetry. The $\{C, P\}$ pair has at least four distinct configurations.^[8] There are numerous other examples.

b) Bistability: The potential energy surface of a defect has different lowest-energy minima in different charge states. One recently discovered example is the $\{H, P\}$ pair in silicon:^[9] $\{H, P\}^0$ is electrically inactive and H is antibonding to one of the four Si nearest neighbors to P , in the now familiar configuration $\{P \cdots Si - H\}^0$. The P atom is three-fold coordinated while Si is nearly sp^2 hybridized with H bound to the dangling p orbital on the trigonal axis. After capture of a hole, P^+ becomes isoelectronic to Si , and the lowest-energy configuration has H near the BC site: $\{P \cdots H - Si\}^+$.

c) Negative-U behavior: A defect with one odd electron may be unstable against the capture of a second electron or the loss of the odd electron.^[10] If the Hubbard correlation energy U resulting from spin pairing exceeds the energy loss due to the Coulomb repulsion between the two electrons, the defect is said to have negative-U properties. In other words, the defect can trap two electrons (or holes), with the second bound more strongly than the first. A well-known example is the vacancy, which is unstable in the spin doublet V^+ and V^- states, and stable in the spin singlet V^{++} , V^0 , and V^{--} states.^[11] Some authors have recently suggested that interstitial H may also have negative-U properties.^[12] However, this is still the matter of debate among theorists as well as experimentalists.

II. MICROSCOPIC STUDIES

The complicated behavior of many deep center defects makes it necessary to use as many different study tools as possible. Experimental and theoretical approaches complement each other in many ways.

Experimental studies are limited to defects that exist in sufficiently high concentrations, typically of the order of 10^{16} cm^{-3} or so, and have some observable property: infrared or Raman activity, non-zero spin, presence of an electrically active level in the gap, etc. However, only one charge state of a defect may have an odd electron and be EPR active, or one of several configurations have a level in the gap and give a DLTS signal, etc.

The type of properties that can be measured include the symmetry of the defect, some vibrational frequencies, the hyperfine parameters, the positions of levels in the gap relative to the bands, the electrical activity, and so on. Species identification can be obtained from isotope substitutions or other means.

Within the past ten years, several theoretical techniques^[13,14] designed to study defects in covalent materials have been developed or improved to the point where a true partnership with experiment is possible. The type of quantities that can be calculated are equilibrium geometries (including lattice relaxations of one or two host atom shells around the defect), electronic structures, configurations of the metastable state(s), barriers for diffusion, vibrational modes, and a number of ground state properties such as charge distributions and dipole moments, spin and charge densities, etc. At this time, there is no widely applicable method able to calculate excited states for systems as large and complex as the ones under consideration here. Therefore, the conduction band and the position of deep defect levels in the gap are at best qualitatively described.

The most widely used theoretical tools belong to one of three groups of techniques:

- (a) semiempirical^[15] Hartree-Fock (HF), such as MNDO or MINDO/III,
- (b) ab-initio or near ab-initio HF, such as PRDDO,^[16]
- (c) first-principles density functional theory within the local density approximation.^[17]

The increased speed, disk space, and availability of supercomputers and, more recently, of high-power workstations, was an important factor in these developments and will certainly contribute to the removal of some of the current limitations and uncertainties.

These techniques and their strengths, weaknesses, and limitations have recently been reviewed.^[14] The methods tend to agree on the fundamental ground state features of many defects. For example, almost all theorists agree that the BC site is the stable site for H^0 in Si , or that the equilibrium geometry of the $\{H, B\}$ pair is $B \cdots H - Si$. However, disagreements persist in most finer features.

Errors can creep in because of the limited size of molecular clusters or supercells used to describe the host crystal, of the neglect of electron correlation (HF) or of approximate electron exchange and correlation (DFT), of the use of small basis sets (HF) or of a small number of plane waves (DFT with supercells), of inadequate parametrizations (semiempirical HF), and other factors. Some of the uncertainties – such as the ones due to limited cluster, supercell, or basis set size – will be corrected as more powerful computers become available. Other problems, such as electron correlation or excited states, are more tricky and are bound to stay with us for a while.

Finally, some limitations result not from the lack of computer power or intrinsic limitations of the theory, but from our incomplete understanding of the dynamics of the systems. For example, how much time does the lattice have to relax while an impurity diffuses? Specialized techniques such as molecular dynamics^[18] can treat some of these issues, but they have limitations of their own.

Other difficulties are related changes of state: it is very difficult to calculate the relative stability of different charge or spin states of a given defect.

III. EXAMPLE: INTERSTITIAL Ti

A dramatic reduction in the lifetime of charge carrier results from the presence of even trace amounts of Ti . This interstitial diffuses very slowly (if at all) even at high temperatures and hydrogenation does not appear to affect its deep levels. We have calculated^[19] the barriers for diffusion of interstitial Ti in the 0 (spin triplet) and +1 (spin quartet) charge states and compared them to that of Cu^+ . We also studied $Ti-H$ interactions.

Interstitial Ti is stable as a Ti^+ spin quartet species at the T site in the silicon lattice. Its 3d states split into t_2 and e :

Note that interstitial Ti^0 has spin 1, i.e., the fourth electron pairs with another electron in one of the three t_2 states. This makes Ti^0 an orbital triplet, and a Jahn-Teller distortion would necessarily result. This has not been considered in our calculations.

At the T site, titanium binds to ten Si atoms: the amount of covalent overlap amounts to 1-electron covalent bonds between Ti and its four Si nearest-neighbors (degree of bonding = 0.5) and slightly less (degree of bonding = 0.3) between Ti and its six second nearest-neighbors. The needed charge density comes from weakened $Si-Si$ bonds all around the impurity. Thus, interstitial Ti looks like an "octopus" attached to everything in its neighborhood rather than an atomic-like interstitial.

The calculated barrier for diffusion is 3.29 eV for Ti^+ (spin quartet) and 2.25 eV for Ti^0 (spin triplet). The large difference in these barriers results from the way the 3d orbitals are populated at the saddle point, the hexagonal interstitial (H) site. The total density of Ti^0 is localized on the impurity and cigar-shaped while that of Ti^+ is considerably more delocalized and more spherical in shape. As a result, Ti^0 is able to squeeze much easier through the lattice than Ti^+ . A plot of the total Ti charge density at the H site is shown below (the direction of diffusion is horizontal) Our value for the diffusion barrier of Cu^+ along the same path is 0.24 eV. Note that the electronic structure of Au^+ is similar to that of Cu^+ : $5d^{10}$ vs $3d^{10}$. The closed d shell results in minimal overlap between the ion and the lattice and a much lower barrier for diffusion, dominated by the size of the diffusing species rather than by covalent interactions.

The calculated binding energy of interstitial Ti^+ and H^0 is 2.20 eV, and Ti^+ is indeed a strong trap for H^0 . However, this interaction is not sufficient to passivate all the deep levels of Ti^+ . As shown below, the 1s level of H^0 couples to *one* of the half-filled t_2 levels of Ti^+ , leaving two odd electrons. This implies that Ti^+ will not be passivated unless *three* hydrogen interstitials bind to it, forming $(TiH_3)^+$. This is an unlikely outcome given the fact that almost *all* of the Ti present would need to be passivated in this manner in order to improve significantly the lifetime of charge carriers. Further, in p -type samples in which hydrogen is believed to be stable in the H^+ charge state, a long-ranged Coulomb repulsion may prevent the two species from coming near each other.

Acknowledgements

The author acknowledges the support of the Robert A. Welch Foundation.

References

- [1] See e.g., 'Deep centers in semiconductors', ed. S.T. Pantelides (Gordon & Breach, New York, 1986).
- [2] J.R. Davis Jr., A. Rohatgi, R.H. Hopkins, P.D. Blais, P. Rai-Choudhury, J.R. McCormick, and H.C. Mollenkopf, IEEE Trans. Electron. Dev. 27, 677 (1980).
- [3] S.J. Pearton and A.J. Tavendale, Phys. Rev. B 26, 7105 (1982).
- [4] T. Sadoh, H. Nakashima, and T. Tsutushima, J. Appl. Phys. 72, 520 (1992).
- [5] For a recent review, see S.J. Pearton, J.W. Corbett, and M.J. Stavola, 'Hydrogen in crystalline semiconductors' (Springer-Verlag, Berlin, 1992).
- [6] S.K. Estreicher, Phys. Rev. B 36, 9122 (1987); C.H. Chu and S.K. Estreicher, Phys. Rev. B. 42, 9486 (1990).
- [7] J.J. Van Kooten, G.A. Weller, and C.A.J. Ammerlaan, Phys. Rev. B 30, 4564 (1984); A. Chantre and D. Bois, Phys. Rev. B 31, 7979 (1985).
- [8] L.W. Song, B.W. Benson, and G.D. Watkins, Phys. Rev. B 33, 1452 (1986); A. Chantre and L.C. Kimerling, Appl. Phys. Lett. 48, 1000 (1986).
- [9] S.K. Estreicher, C.H. Seager, and R.A. Anderson, Appl. Phys. Lett. 59, 1773 (1991).
- [10] G.D. Watkins, in 'Defects in semiconductors', ed. J. Narayan and T.Y. Tan, (North Holland, 1981).
- [11] See the chapter by G.D. Watkins in Ref. 1.
- [12] C.G. Van de Walle, P.J.H. Denteneer, Y. Bar-Yam, and S.T. Pantelides, Phys. Rev. B 39, 10791 (1989); K.J. Chang and D.J. Chadi, Phys. Rev. B 40, 11644 (1989).
- [13] C.G. Morgan-Pond, J. Electron. Mat. 20, 399 (1991).
- [14] S.K. Estreicher, MRS Symp. Proc. 240, 643 (1992).
- [15] See e.g., G.G. DeLeo, W.B. Fowler, T.M. Sudol, and K.J. O'Brien, Phys. Rev. B 41, 7581 (1991); P. Deak, L.C. Snyder, and J.W. Corbett, Phys. Rev. B 37, 6887 (1988).
- [16] See e.g., S.K. Estreicher, Phys. Rev. B 40, 8545 (1989); S.K. Estreicher, L. Throckmorton, and D.S. Marynick, Phys. Rev. B 39, 13241 (1989).
- [17] See Ref. 12 and R. Jones, J. Phys. C 21, 5735 (1988).
- [18] R. Car and M. Parrinello, Phys. Rev. Lett. 55, 2471 (1985).
- [19] D.E. Woon, D.S. Marynick, and S.K. Estreicher, Phys. Rev. B 45, 13383 (1992).

RECONSTRUCTION OF GRAIN BOUNDARIES BY POINT DEFECT INJECTION

Dieter G. Ast; Material Science and Engineering, Cornell University, Ithaca NY 14853-1501.

ABSTRACT:

Point defects injected into poly-Si preferentially anneal out at grain boundaries. The sinking of these point defects enables the non-conservative motion of grain boundary dislocation leading to a large increase in the atomic mobility of the boundary. The result is grain growth, coupled with reconstruction of the boundary into low(er) energy configuration(s).

Electrical measurements show that reconstruction improves the hole and electron mobility and lowers the density of grain boundary states. Investigations of poly-Si subjected to increasing amount of point defect injection, and hence reconstructed to different degrees, show a corresponding decrease in the electronic density of grain boundary states. It is found that this decrease in electrical activity correlates well with the decrease in the diffusivity of dopant atoms along grain boundaries, a property also controlled by the core structure of the boundary.

In thick films, it is difficult to obtain high volume supersaturations of point defects. We therefore use thin, reconfigured, CVD poly-Si films as templates to grow thick, up to 20 μm , thick films. The structure of these films, and the conversion efficiency and DLTS signature of p-i-n devices fabricated in these films are strongly influenced by the degree to which the seed layer was reconstructed.

When such undoped, reconstructed films are hydrogenated, a thin surface layer - 0.5 μm thick - with very high conductivity forms, resulting in a decrease of the overall resistance of about four orders of magnitude in n-type contacted films. The initial high resistance can be restored by removing 0.5 μm from the resistor surface or by annealing the samples for 15 min at 550 $^{\circ}\text{C}$.

INTRODUCTION:

A well established, but not well understood, property of Si is that the grain size in polycrystalline Si can *not* be significantly increased through strain induced recrystallization. This behavior significantly differs from metals, such as iron, where straining followed by heat treatment can result in grain growth on the order of centimeters.

Comparable grain growth in poly-Si would permit the fabrication of efficient solar cells on low cost substrates. Therefore, the recrystallization behavior of Si has been studied extensively.

One possible reason for the different behavior of Si relative to metals is that Si has a strong preference to form "special" boundaries characterized by low a low Σ ¹ value and multiple twinning [1,2].

This tendency is so strong that a grain boundary may dissociate into two boundaries, each of which "encloses" an intermediate crystal orientation. Although the grain boundary area is nearly doubled, the overall energy is lower since the symmetrical boundaries formed have lower energies (as low as 1/60 of the surface energy). Examples of this process are shown in Fig. 1 a,b.

It is interesting to note that a study of strain induced grain growth in Al [4] found that low Σ boundaries are considerably more difficult to move than general boundaries. This suggests, but does not prove, that the slow grain growth in Si is linked to the preferred formation of special boundaries.

Fig. 1a,b; see text.

INJECTION OF POINT DEFECTS INTO POLY-SI

Because strain induced recrystallization in Si is essentially absent, alternative methods to promote grain growth are of interest. One of these methods is the injection of point defect.

Undoped CVD poly-Si has a very small grain size, on the order of 1000 Å. During the fabrication of thin film transistors (TFTs) in this material, we noticed that the TFT transfer properties improved when HCl was removed [5]².

This observation suggested that point defects generated during oxidation, the concentration of which increases when HCl is removed were responsible for the improvement. In poly-Si, the "sinking" of these point defects at grain boundaries permits the grain boundary dislocations comprising the boundary to exert non-conservative motions, resulting in an increase in the atomic mobility of the grain boundary. The result is both grain growth and the reconfiguration of the boundary into a low energy configuration (that is a configuration with few or no broken bonds). Since a boundary without broken bond tends to be electrically inactive [2], this reconstruction also lowers the electrical activity of the grain boundary³.

¹ The Σ value of a boundary is the inverse of the fraction of common lattice sites if the crystal is hypothetically extended into the adjacent grain. It is a volume property which has been used to construct geometric properties of grain boundaries (see Bollmann [3]) but which has - contrary to frequent assertions - no clear cut relation to the energy of of grain boundaries in Si.

² HCl is added to remove transition metal impurities. An second, less stated, reason is the removal of Si-self interstitials that otherwise tend to plate out as oxidation induced stacking faults

³ A more detailed analysis shows that the amount of broken bonds is controlled by symmetry and

Based on this analysis, we set out to intentionally *maximize* the amount of point defect injection into Si using deep oxidation cycles free of chlorine containing gases.

Typically, to fabricate a 1000 Å thick poly Si film, we start with a 5000 Å thick poly-Si CVD film (deposited from silane) and oxidize the top 4000 Å of this film, leaving just 1000 Å of the original film in the form of poly-Si. Next, the oxide is removed with HF. The remaining 1000Å poly-Si layer is used as a starting material for the fabrication of CMOS TFT circuits [7,8,9] or as a template for the growth of thick poly-Si films [10].

Below, we discuss three aspects of such films: i) the relationship between the density of grain boundary states and dopant diffusivity along grain boundaries ii) the influence of thin, reconstructed seed layers on the properties of subsequently grown thick poly-Si films and iii) the unusual hydrogenation behavior of some of these films.

DENSITY OF GRAIN BOUNDARY STATES AND DOPANT DIFFUSIVITY IN RECONSTRUCTED POLY-SI FILMS.

Undoped poly-Si has a very high electrical resistivity as the few carriers available are trapped at midgap, grain boundary induced, states. As the doping is increased, more traps are being filled, increasing the barrier height at the boundary. Eventually, doping reaches the level where the Fermi level will "depin" from the grain boundary states. At that stage, additional carriers provided by doping become available for conduction and the resistivity of poly-Si falls steeply by several orders of magnitude over a narrow doping range. The dopant level at which this happens is a measure of the density of grain boundary states (see Seto [11] and Baccarani et al [12]).

Fig. 2, see text.

In a TFT using an undoped channel, a comparable change in carrier concentration can be induced in the near surface regime by changing the gate voltage. Again, the source drain conduction increases dramatically, once the Fermi level is "depinned" from the grain boundary states [7,8]. The gate voltage at which this happens is a quantitative measure of the density of grain boundary states. For a detailed analysis of this complex topic see [8].

In addition, the diffusion of dopants along grain boundaries can be accurately measured, since the active channel length in a poly-crystalline Si TFT differs markedly

not by the Σ value of the boundary [6]. For example, tilt boundaries with 110 median boundary planes can be constructed without broken bonds for any boundary angle - as long as the boundary is symmetric. Broken bonds invariably appear when the boundary is asymmetric. EBIC investigations show that symmetric boundaries are not electrically active but that even small deviations from symmetry introduce electrical activity into a boundary [1,2]

from the mask dimensions, due to the enhanced diffusion of dopant atoms along grain boundaries out of the implanted source drain regions underneath the gate ⁴.

In a TFT activated at 1000 °C, the phosphorus typically migrates about 2 μm under the gate. This reduces the electrical channel length of a nominal 5 μm gate device to 1 μm , increasing the "apparent" channel mobility by a factor 4. By making a series of TFT with different gate length on a wafer, the diffusivity of dopant atoms along grain boundaries can be extracted accurately [8].

Analysis of the electrical characteristics of TFTs fabricated in increasingly reconstructed poly-Si therefore permits to deduce the relationship between the spatially averaged density grain boundary states (an electronic quantity) and the spatially averaged diffusivity of dopant along grain boundaries (a structural property related to the "free volume" at the grain boundary).

The measured relationship is shown in Fig. 2. Note that density of grain boundary states correlates linearly with the diffusion length. This very interesting finding can be explained by noting that boundaries free of broken bonds tend to have tighter core structures.

INFLUENCE OF RECONSTRUCTED POLY-SI LAYERS ON ELECTRONIC PROPERTIES OF SUBSEQUENTLY GROWN THICK POLY-SI FILMS.

Because it is difficult (with any technique) to generate a high *volume* supersaturation of point defects in thick films, we have used thin, reconfigured films as seed layers to grow 20 μm thick poly-Si films, at 1080 °C, in a commercial diclorosilane reactor.

Figs. 3 and 4 show cross-sections, very lightly etched with Wright-Jenkins defect etch, of two such films. Samples 321, Fig. 3, used an unreconfigured, 1 μm thick, poly-Si film, deposited by CVD from silane at 670 °C as a seed layer. Sample 243, Fig. 4, started with a 2.5 μm thick seed layer deposited at 670 °C which was oxidized 6 times at 1150 °C. After each oxidation, the oxide was removed with HF. The poly Si layer thickness was then build up by the deposition of about 0.5 μm of additional poly at 620 °C which was oxidized once more ⁵.

Inspection of Figs. 3 and 4 show that although the growth condition of the epitaxial film were identical, the grain configuration of the films is remarkably different. Films grown with reconfigured seed layers tend to develop large (up to 6 μm wide) columnar grains, separated by straight(er) boundaries, and contain far fewer defects in the grain interior.

To assess the electrical properties of such films we fabricate p-i-n test structures, consisting of p doped and n-doped (by ion implantation) fingers on the surface of these films. These devices are not meant to be solar cells but give an indication of the photoelectrical properties of the film.

⁴ In single crystal Si, the effect is very much smaller and only plays a role in submicron devices

⁵ The minimum thickness of the seed layer is set by the in-situ etch back - to insure a clean surface - prior to switching diclorosilane reactor into the deposition mode

The I-V characteristics prior to hydrogenation of three test structures employing three different seed layers are shown in Fig. 5. Sample 113, which shows the lowest conversion efficiency used a seed layer deposited at 620 °C which was oxidized once. Sample 311 used a seed layer deposited at 670 °C which was oxidized four times with oxide removal between each oxidation. The short circuit current of this sample is one order of magnitude higher than that of sample 113.

Fig. 3, see text

Fig. 4, see text

Deep level transient spectroscopy of these devices, see Fig. 6, indicates that the 260 K peak in sample 113 is caused by non-interacting traps, located 0.395 eV above the valence band and a cross-section of $9.3 \cdot 10^{-17} \text{ cm}^2$. This peak rapidly disappears when the sample is hydrogenated.

Fig. 5, see text

Fig. 6, see text

The magnitude of 225 K peak in sample 113 depends logarithmically on the duration of the filling pulse which is characteristic of interacting traps such as traps along dislocations lines. The peak corresponds to an electron trap, 0.456 eV below the conduction band, with a cross-section of $3.3 \cdot 10^{-13} \text{ cm}^2$. This trap disappears slower with hydrogenation. After extensive hydrogenation, the DLTS spectrum of sample 113 becomes similar to that of sample 311. For more details see [10].

HYDROGENATION OF RECONSTRUCTED BOUNDARIES.

To learn more about the hydrogenation of such boundaries we measured changes in the resistance of undoped poly-Si resistor test structures contacted with either n-type or p-type implanted contacts. These test structures are similar to TFTs but lack a gate electrode.

If a sample with n-type contacts is exposed to a hydrogen plasma, the resistivity, on the time scale of seconds, falls by orders of magnitude, see Fig. 7. The original resistance can be restored by annealing the sample at 500 °C. This cycle can be repeated many times.

Etching shows that the high conductivity layer is confined to about 0.5 μm thick surface layer, see Fig. 8. No corresponding changes are observed in resistors with p-type contacts [13].

This findings are not understood at this time. A working model (which we are testing with TEM) assumes that the grain boundary near the surface has a different structure

(possibly due to the incorporation of oxygen) and that this grain boundary traps ionized hydrogen, resulting in a positive near surface space charge.

Fig. 7, see text

Fig. 8, see text

FUTURE WORK

We have recently begun a study with Ted Kamins at H-P Labs on the structure, transport properties, etching behavior and reconfiguration of poly Si-Ge. It is hoped that the availability of three different bond lengths, Si-Si, Si-Ge, and Ge-Ge makes it easier for the grain boundary to assume a low energy configuration during reconstruction and also that the process occurs at a lower temperature.

Poly-Si emitters are widely used in the IC industry in bipolar transistors. Their most attractive feature for solar cells is that their use would facilitate "in situ" junction formation during growth of ribbon silicon⁶. To investigate such emitters, we are starting a joint research project with Mobil Solar.

ACKNOWLEDGEMENTS:

Funding for this work was provided by DOE through a grant from the Materials Division and through DOE/Sandia.

⁶ In ribbon Si, the surface is generally not accessible between 1410 and about 700 °C (the lower limit of dislocation mobility) since the temperature profile must be carefully controlled to avoid residual thermal stresses, requiring heat shields and after-heaters. Below 700 °C, plastic deformation by dislocation movement ceases and the ribbon becomes more accessible. At this stage, the ribbon surface temperature is too low to thermally diffuse dopants into the ribbon, but is compatible with the in-situ deposition of a poly-Si emitter

REFERENCES:

- [1] D.G. Ast and B. Cunningham "Structural Characterization of Defects in Solar Silicon"; Chapt. 7, in *Silicon Processing For Photovoltaics I*, Eds. C.P. Khattak & K.V. Ravi, (North Holland, 1985)
- [2] D.G. Ast "Grain Boundaries in Semiconductors", in *Concise Encyclopedia of Semiconducting Materials & Related Technologies* Eds S. Mahajan and L.C. Kimmerling, (Pergamon Press , 1992).
- [3] W. Bollmann *Crystal Lattices, Interfaces, Matrices* (Imprimerie des Bergues, Carouge, Geneva, 1982) ISBN 2-88105-000-X
- [4] J.W. Wyrzykowski and M.W. Grabski, *Mater.Sci* 17 (1983) 445
- [5] R.E. Proano and D.G. Ast, "Effects of the presence/absence of HCl during gate oxidation on the electrical and structural properties of polycrystalline thin film transistors", *J.Appl.Phys*, 66(5) (1989) 2189
- [6] M.D. Vaudin, B. Cunningham and D.G. Ast "The Structure of Second and Third Order Twin Boundaries in Silicon", *Scripta Metall.*, 17 (1983) 191
- [7] R.E. Proano, R.S. Misage and D.G. Ast, "Development and Electrical Properties of Undoped Poly- crystalline Silicon Thin-Film Transistors", *IEEE Transactions on Electron Devices*, 36 (2) (1989) 1915
- [8] Roberto Enrique Proano " Polycrystalline Silicon Thin Film Transistors for Active Matrix Guest-Host Liquid Crystal Displays" , Ph.D. Thesis, Cornell U, (1990).
- [9] R.E. Proano, R.S. Misage, D. Jones, D.G. Ast, "Guest-Host Active Matrix Liquid-Crystal Display Using High-Voltage Polysilicon Thin Film Transistors" *IEEE-ED* 38, No 8 (1991) 1781
- [10] C.B. Moore and D.G. Ast, "A study of the Effects of Thermal Oxidation and Hydrogen Passivation on CVD Polysilicon PIN Solar Cells Using DLTS", *Proc. 22nd IEEE Photovoltaic Specialist Conf. II*, (1991), 853
- [11] J.Y.W. Seto, *J.Appl.Phys* 46 (1975) 5247
- [12] G. Baccarani, B. Ricco and G. Spadini, *J.Appl.Phys* 49 (1978) 5565
- [13] C.B. Moore and D.G. Ast, "Anomalous Behavior in the Resistivity of n-i-n Polysilicon Resistors after Hydrogenation", to be published in *MRS Symposia Proc.*, Vol. 262, April 1992

THE ROLE OF POSITRON ANNIHILATION SPECTROSCOPY IN THE STUDY OF DEFECTS IN CRYSTALLINE SILICON

Peter Mascher

Centre for Electrophotonic Materials and Devices,
Department of Engineering Physics, McMaster University,
Hamilton, Ontario, Canada L8S 4L7

ABSTRACT

After a brief review of the contributions positron annihilation spectroscopy has made over the past years to the characterization of defects in silicon the paper concentrates on recent results obtained on Czochralski-grown wafer material.

Both positron lifetime and Doppler broadening experiments show that, after heat-treatment, vacancy-type defects are retained in the wafers at concentrations in the low to medium 10^{16} cm^{-3} range. However, there seems to be no obvious correlation between oxygen precipitation as measured by Fourier-transform infrared spectroscopy and the positron results.

Recent studies of rapid thermal annealed (RTA) samples have shown the concentration of retained vacancy-type defects to be even higher than in furnace annealed samples. In lightly doped materials the vacancies are predominantly trapped by oxygen interstitial clusters and these complexes appear to have temperature dependent configurations which can be quenched-in through RTA.

INTRODUCTION

Positron annihilation has in recent years become an increasingly valuable tool for the study of defect structures in semiconductors. Positrons are specifically (but not exclusively) sensitive to even the smallest open-volume defects such as mono- and divacancies, their agglomerates, and vacancy-impurity pairs. While much progress has been made in the defect characterization by positron annihilation spectroscopy (PAS) in compound semiconductors, this paper will concentrate on the contribution PAS has made to the understanding of defect-structures in silicon.

After a brief review of the technique and some fundamental results, recent experiments on Czochralski (Cz) - grown wafer material will be discussed with the intention to indicate specific areas of application for PAS in technology-related research areas. Much more complete reviews of the technique can be found in references [1, 2].

GENERAL REVIEW OF THE POSITRON ANNIHILATION TECHNIQUE

In Fig. 1 is shown a schematic representation of the three fundamental positron annihilation experiments. When positrons are emitted from the (most frequently used) ^{22}Na positron source their kinetic energies show a characteristic β^+ -

distribution with a maximum energy of about 0.54 MeV. The positrons therefore penetrate deep into the sample (for silicon up to about 200 μm) where they become thermalized. Obviously, such a positron source is only suitable for bulk studies and cannot efficiently be used for studies of thin films or surfaces. For such studies variable energy positron beams have been developed where the positron kinetic energy can be tuned so that all positrons are stopped within a thin layer of interest [3].

Fig. 1 Schematic representation of the fundamental positron annihilation experiments.

When the positron annihilates with an electron, the centre-of-mass of the electron-positron pair will have a certain non-zero momentum which is essentially determined by the momentum of the electron since the positron is thermalized. This, in turn, means that there is a small deviation from collinearity between the annihilation quanta (to preserve momentum), and also that there is a small Doppler shift of the energy of the γ -quanta. One may measure the deviation from collinearity (angular distribution) of the annihilation quanta or the energy distribution. The two experimental methods only differ in their intrinsic resolution power, angular correlation (measuring directly the momentum distribution) being at least 5 times better than Doppler broadening, but the latter technique has the advantage of being orders of magnitudes faster.

In a positron lifetime experiment, on the other hand, one determines the time elapsed between the emission of the positron (as signalled by a 1.28 MeV γ -quantum) when ^{22}Na undergoes β^+ decay and its annihilation, as signalled by the emission of the annihilation quanta. This time is typically between zero and 5 ns, and by recording the annihilations for many individual positrons one obtains the so-called lifetime spectrum.

Extensive calculations of the positron wavefunction and annihilation rates, λ , have been performed for metals as well as for semiconductors [4,5]. In all cases the calculations show that the positron wavefunction is peaked in the interstitial regions between the atoms. This result is expected when one considers that the crystal potential which excludes the electrons from the interstitial region will have the opposite effect on the positron.

Lattice defects in non-perfect materials can act as positron traps. Again, extensive calculations [6,7] have shown that trapping mainly occurs at open-volume defects, but there are some experimental indications for trapping at interstitial-type defects; particularly in Cz-Si [8]. The trapping process into a given defect is strongly influenced by its charge state since only neutral and negatively charged defects act as efficient positron traps due to the positive charge of the positron.

The introduction of defects will result in a lifetime spectrum of the general form

$$S(t) = \sum_i I_i \lambda_i \exp(-\lambda_i t), \quad (1)$$

where I_i is the intensity of the i 'th lifetime component and $\lambda_i \equiv 1/\tau_i$ is the annihilation rate of this component.

Contrary to that, analysis of Doppler broadening data is normally restricted to an averaging process, although various deconvolution approaches have been attempted. A commonly utilized parameter is the S (shape) parameter which is defined as the fraction of all the recorded counts inside a certain "window" of energy, usually chosen so that $S \approx 0.5$ for maximum sensitivity. Generally, trapping by defects of vacancy type leads to a narrowing of the distribution, (i.e., an increase of the S-parameter) as compared to the bulk state, and one would expect the opposite trend if trapping by interstitial-type defects occurs.

In Tables 1 and 2 are summarized the characteristic positron lifetimes for a number of fundamental and impurity-related defects in silicon.

Table 1. Positron Lifetimes in Silicon

Positron State	Bulk	V	$(V_2)^{0,-}$	Larger vacancy agglomerates
$\tau(\text{ps})$	218	270 ± 3	321 ± 4	350 - 520
Experiment	Thermal equilibrium ($\rightarrow 1500\text{K}$) [9]		n-irradiation @RT[15]	Plastic deformation @800°C [16]
	e--irradiation @ 20K [10,11]			e--irradiation @ 373K [17]
	He implantation @ 15K [12]			
	p-irradiation @ 15K [13]	e--irradiation @ RT [14]		

In addition to information about distinct positron states, i.e., trapping centres, a lifetime spectrum contains information about the concentration of these centres. In order to establish the link between the directly measured quantity, i.e., the intensity, I_i , of a certain component and the defect concentration one usually applies the so-called trapping model [21]. This leads to the calculation of the trapping rate(s), κ_i , the rate(s) at which the positrons make the transition from the bulk into the trapped state(s). The trapping rate then is related to the defect concentration, C_D , through

$$\kappa_D = \nu_D C_D, \quad (2)$$

where ν_D is the specific trapping rate given by

$$\nu_D = v + \sigma_D, \quad (3)$$

with v the thermal velocity of the positrons and σ_D the trapping cross-section of the defect.

Typically, defects present in concentrations above 0.1 ppma lead to measurable responses. The trapping rate for neutral defects in silicon is of the order of 10^{15} s^{-1} per unit fractional defect concentration [14] but increases significantly if the defect is negatively charged, especially at low temperatures (according to a T^{-n} dependency). At low temperatures ($\leq 30 \text{ K}$) negatively charged defects in the 10^{15} cm^{-3} concentration range can therefore contribute significantly to the trapping of positrons.

Table 2. Positron Lifetimes in Impurity Complexes in Silicon

Positron State	$(P_x \cdot V)^{0,-}$	$(V_2O)^{0,-}$	$(O \cdot V)^-$	$B_S \cdot V \cdot O_I$	O_I -clusters
$\tau(\text{ps})$	247-270	270 ± 3	225 ± 2	271 ± 15	≤ 100
Experiment	p-irradiation @RT[18]	e-irradiation @RT[14]			
	e-irradiation @ 20K[11]	H-, He- implantation @ 15K[12,13]		heat-treated Cz-Si [20]	
	e-irradiation @ RT[19]				

DEFECT CHARACTERISTICS IN CZ-SILICON WAFERS

In this section of the paper is given an overview of the results of several systematic investigations by PAS of Cz-Si wafer material. The experimental details, if not given explicitly, can be found in the respective publications.

Table 3 is a summary of positron lifetime results obtained on as-received wafers taken from the seed-, middle-, and tail-sections of two boules grown at different pull speeds [23].

Table 3: Positron lifetime data for the as-received state of two groups of wafers grown at different pull speeds. The values in brackets indicate the standard deviations across the respective wafer rather than experimental uncertainties

WAFER	PULL SPEED (mm/min)	POSITION IN BOULE	I_1 (%) ($\tau_1 = 113$ ps)	τ_2 (ps)
NL-028		SEED	11.1 (1.3)	221 (1)
NL-290	0.85	MIDDLE	11.3 (1.0)	221 (1)
NL-592		TAIL	11.4 (1.2)	221 (1)
IHS-008		SEED	9.1 (0.5)	222 (1)
IHS-193	1.26	MIDDLE	7.4 (0.7)	222 (1)
IHS-260		TAIL	8.5 (0.6)	222 (1)

If one now makes the assumption, as is usually done, that the short-lived τ_1 component is actually the bulk lifetime modified by trapping into defects which give rise to the longer-lived τ_2 component, one can use the simple trapping model [21] to calculate what the bulk lifetime should have been. This approach is important because the bulk lifetime is a materials parameter (it is essentially determined by the average valence electron density in the "perfect" crystal) which should not be affected by the presence of positron traps. The established value for silicon is $\tau_B = 218$ ps [22]. The calculated values for τ_B in this set are around 205 ps, which is significantly shorter, and thus causes doubt as to the applicability of the trapping model in its simple form. On the other hand, the value of the main lifetime component, τ_2 , is very close to the expected value for the bulk lifetime. This, together with the above mentioned discrepancy was taken as a corroboration of a model in which the short-lived component, τ_1 , reflects a distinct positron state as opposed to the modified bulk lifetime. This state can be associated with positrons trapped at interstitial-oxygen clusters where the local electron density is about twice that for silicon. A detailed analysis of the trapping process involved is given in [8]. The small difference between τ_2 and τ_B rendered attempts to resolve a vacancy-related component inconclusive, most likely due to too small a contribution to the spectrum.

After a two-step heat treatment (750°C/4 hrs + 1050°C/6 hrs in N₂) Fourier-transform infrared spectroscopy (FTIR) showed that significant amounts of oxygen (4-8 ppma) had precipitated in the wafers taken from the seed-sections of the boules but not in any of the other wafers. The positron results did not reflect this distinctive difference; however, the analysis procedure outlined above now leads to characteristically different results. First, even without any marked change in the behaviour of the short-lived component the value of τ_2 increases by about 3 to 5 ps, depending on the specific wafer. Second, the quality of such a fit to the lifetime

spectra deteriorates. Both effects indicate that an additional lifetime component now is necessary to properly describe the experimental data. In addition, the increase in τ_2 strongly suggests that this component could be vacancy-related since such traps would contribute a lifetime, $\tau_D > \tau_B$. Using a high-resolution lifetime spectrometer it was indeed possible to resolve three significant components through unconstrained fits. The "new" lifetime had values of 270 ± 15 ps in excellent agreement with the literature-values for defects with monovacancy character in silicon.

Table 4 is a summary of the results of such an analysis for all six wafers after heat-treatment [24]. Under the assumption that the defects giving rise to τ_D are neutral, the κ -values in the Table correspond to concentrations in the low 10^{16} cm^{-3} range [11,14].

Table 4: Positron lifetime data after annealing of two groups of wafers grown at different pull speeds. The values in brackets indicate the standard deviations across the respective wafer rather than experimental uncertainties

WAFER	I_1 (%) ($\tau_1 = 90\text{-}110$ ps)	I_D (%) ($\tau_D = 270$ ps)	κ (ns ⁻¹)
NL-028	8.9 (2.2)	11.8 (4.2)	0.11 (0.05)
NL-290	7.8 (2.2)	16.6 (2.5)	0.16 (0.03)
NL-592	8.1 (2.2)	15.8 (2.1)	0.15 (0.03)
IHS-008	9.5 (0.6)	19.0 (2.1)	0.20 (0.03)
IHS-193	9.4 (0.6)	19.5 (1.4)	0.20 (0.02)
IHS-246	9.0 (0.7)	18.1 (2.2)	0.18 (0.03)

To obtain some information about the local environment of the observed vacancies, the S-parameter values of the Doppler-broadening experiments before and after annealing were compared. Contrary to the case of unassociated vacancies, where a strong increase in S is found [10], the behaviour of the S-parameter in the presence of defect complexes is much more difficult to predict. This is so, because impurities (in our case mainly oxygen and interstitial silicon) close to the vacancy may modify the S-parameter by introducing electrons with higher momentum than the host's. Figure 2 shows the comparison for wafer IHS-193. Although the effect is much smaller than the one observed in the lifetime data, the increase in S with annealing is consistent with the introduction of vacancy-type defects.

Fig. 2 S-parameter as a function of measuring position across wafer IHS-193 (see Table 3) before and after annealing.

The observation that there seems to be no obvious correlation between the interstitial-oxygen concentration, $[O_I]$, as determined by FTIR and the positron response was corroborated by recent experiments on P-doped (10-15 Ω cm) wafers subjected to a multi-step heat-treatment process [25]. Figure 3 shows the intensity, I_{short} , of a typical interstitial cluster-related component, the trapping rate, κ , into a

Fig. 3 Positron lifetime parameters (I_{short} , κ) and interstitial-oxygen loss as a function of thermal processing. $[O_I] = 18.2 \pm 0.6$ ppma before processing.

vacancy-type defect, and the loss in interstitial oxygen as a function of thermal processing. Despite the significant amount of oxygen precipitation during stages 3-5, the positron parameters remain essentially constant.

The results presented above as well as several other studies indicate either that vacancies play only a minor role in the oxygen precipitation process or that they are not retained during the typically slow cool-down from the processing temperatures. Recent experiments [26] on rapid thermal annealed (RTA) wafers indeed show that it is possible to retain significantly higher vacancy concentrations after such heat treatment than after conventional furnace anneal. In Fig. 4 are shown the defect lifetime, τ_2 and the corresponding trapping rates, κ_2 , into these defects.

Fig. 4 Trapping rate, κ_2 , and defect lifetime, τ_2 , for as-grown RTA treated (●) and CES-6 (▲) pre-treated B-doped Cz-Si. CES-6 is a multi-step heat-treatment process [26].

There are two most interesting observations to be made. First, the effect of RTA on the defect lifetime is a general decrease in its value from 270 ps to about 240 ps (at 900°C). Second, the trapping rate increases rather abruptly to a constant level about two times higher than for the as-grown material.

Realizing that such an increase in the trapping rate is directly related to an equivalent increase in the defect concentration, it was suggested in [26] that due to the fast cool-down of the RTA-treated wafers, high temperature configurations of the grown-in vacancy-impurity complexes can be quenched in. These are missing in the

slowly cooled wafers thus accounting for the increase in κ with RTA. The observed change in the lifetime value from 270 ps to 240 ps then indicates that the high-temperature configuration corresponds to a somewhat "squeezed" vacancy-impurity complex.

The importance of these experiments lies in the fact that it may be possible through RTA to access high-temperature defect configurations and distributions by PAS without having to resort to experimentally difficult experiments in thermal equilibrium. This clearly is very encouraging and further experiments of this nature are currently in preparation.

CONCLUSIONS

Positron annihilation is a technique particularly suited to study open-volume, i.e., vacancy-type defects. The accessible concentration range is $5 \times 10^{15} \leq C_D \leq 10^{18} \text{ cm}^{-3}$, depending on the charge state of the defect (i.e., neutral or negative).

In as-grown Cz-Si wafer material, the positron response typically is quite uniform across the wafer diameter and consists of components from small oxygen-related clusters and "perfect" bulk silicon only. Possible contributions from vacancy-type defects are near the detection limit of the technique.

After conventional heat-treatment, there seems to be no obvious correlation between $[O]$ (from FTIR) and the positron response, however, the concentration of vacancy-type defects tends to increase slightly to values in the low to medium 10^{16} cm^{-3} range.

Recent studies of RTA samples have shown the concentration of retained vacancy-type defects to be even higher than in furnace annealed samples. In lightly doped materials the vacancies are predominantly trapped by oxygen interstitial clusters and these complexes appear to have temperature dependent configurations which can be quenched-in through RTA.

ACKNOWLEDGEMENTS

The wafers discussed in this paper were supplied by Siltec Silicon, California; Siltron Inc., Korea (both in collaboration with Dr. Sookap Hahn); and by Mitel S.C.C., Canada (in collaboration with Alain Comeau).

I am grateful to Professor Steen Dannefaer for the permission to use his RTA data prior to publication.

The research programme at McMaster University is being supported through grants from the Natural Sciences and Engineering Research Council of Canada and the Ontario Centre for Materials Research.

REFERENCES

- 1) Positrons in Solids, ed. P. Hautojärvi, Springer Verlag, 1979.
- 2) Positron Solid State Physics, eds. W. Brandt and A. Dupasquier, North-Holland, 1983.
- 3) P.J. Schultz and K.G. Lynn, Rev. Mod. Phys. 60, 701 (1988).
- 4) M.J. Puska, J. Phys.: Condens. Matter 3, 3455 (1991).
- 5) M.J. Puska and C. Corbel, Phys. Rev. B38, 9874 (1988).
- 6) M.J. Puska, S. Mäkinen, M. Manninen, and R.M. Nieminen, Phys. Rev. B39, 7666 (1989).
- 7) M.J. Puska, C. Corbel, and R.M. Nieminen, Phys. Rev. B41, 9980 (1990).
- 8) S. Dannefaer and D. Kerr, J. Appl. Phys. 60, 1313 (1986).
- 9) S. Dannefaer, P. Mascher, and D. Kerr, Phys. Rev. Lett. 56, 2195 (1986).
- 10) W. Fuhs, U. Holtzhauer, S. Mantl, F.W. Richter, and R. Sturm, Phys. Stat. Sol. (b) 89, 69 (1978).
- 11) J. Mäkinen, C. Corbel, P. Hautojärvi, P. Moser, and F. Pierre, Phys. Rev. B39, 10162 (1989).
- 12) S. Mäkinen, H. Rajainmäki, and S. Linderöth, Phys. Rev. B44, 5510 (1991).
- 13) S. Mäkinen, H. Rajainmäki, and S. Linderöth, Phys. Rev. B42, 11166 (1990).
- 14) P. Mascher, S. Dannefaer, and D. Kerr, Phys. Rev. B40, 11764 (1989).
- 15) S. Dannefaer, G.W. Dean, D. Kerr and B.G. Hogg, Phys. Rev. B14, 2709 (1976).
- 16) S. Dannefaer, N. Fruensgaard, S. Kupca, B.G. Hogg and D. Kerr, Can. J. Phys., 61, 451 (1983).
- 17) Motoko-Kwete, D. Segers, M. Dorikens, L. Dorikens-Vanpraet, P. Clauws, and I. Lemahieu, Appl. Phys. A49, 659 (1989).
- 18) P. Mascher, D. Kerr, and S. Dannefaer, Phys. Rev. B35, 3043 (1987).
- 19) J. Mäkinen, P. Hautojärvi, and C. Corbel, J. Phys.: Condens. Matter 4, 5137 (1992).
- 20) S. Dannefaer, W. Puff, P. Mascher, and D. Kerr, J. Appl. Phys. 66, 3526 (1989).
- 21) R.N. West, Adv. Phys. 22, 263 (1977).
- 22) S. Dannefaer, Phys. Stat. Sol. (a) 102, 481 (1987).
- 23) P. Mascher, W. Puff, S. Hahn, K.H. Cho, and B.Y. Lee, Materials Sci. Forum 83-87, 413 (1992).
- 24) P. Mascher, W. Puff, S. Hahn, K.H. Cho, and B.Y. Lee, Mater. Res. Soc. Proc. 262 (1992).
- 25) P. Mascher and A. Comeau, presented at the 6th Canadian Semiconductor Technology Conf., Ottawa, Canada, 1992.
- 26) S. Dannefaer, T. Bretagnon, K. Abdurahman, D. Kerr, and S. Hahn, Mater. Res. Soc. Proc. 262 (1992).

DEPTH AND RADIAL PROFILES OF DEFECTS IN CZOCHRALSKI-GROWN SILICON FOLLOWING THERMAL PROCESSING

A. K. Issar, R. C. Hyer, N. Hozhabri, and S. C. Sharma *

Department of Physics, University of Texas at Arlington, Arlington, Texas 76019

and

M. F. Pas, S. Kim, and T. Shaffner

Texas Instruments Incorporated, Dallas, Texas 75265

We present results on the depth and spatial profiles of defects in Czochralski grown silicon wafers annealed at different temperatures. By using a variable energy positron beam, we have measured depth profiles of defects for epitaxial Si $\langle 100 \rangle$, as-grown wafer, and wafers annealed at different temperatures. We observe a high concentration of defects in the top 0.5 μm layer of the as-grown wafer. At about 1 μm , the as-grown and the Si $\langle 100 \rangle$ epilayer "look" equally good from the point-of-view of the density of defects. Following a 4-hour anneal at 1100 $^{\circ}\text{C}$, the depth profile changes so as to provide a lower density of defects in the top 2000 $\text{\AA}$ and a much higher density of "defects" in the interior of the wafer. From the bulk positron lifetime measurements, we observe that: a) density of the vacancy-type defects increases with displacement from the center to edge of the wafer, b) both monovacancies and divacancies are present at the center of the wafer, and c) mostly monovacancies are present at the edge of the wafer. We compare these results with the minority carrier diffusion lengths that are measured to be smaller near the edge than those measured in the central part of the wafer. We also present results on hydrogen and helium containing microvoids in a-C:H and irradiated aluminum, respectively.

* to whom correspondence should be addressed

INTRODUCTION

Positron Annihilation Spectroscopy (PAS) is a nondestructive technique that is sensitive to the vacancy-type defects at 10^{15} cm^{-3} level in semiconductors. The technique is capable of providing information on the depth and spatial profiles of defects in silicon wafers. Of particular interest to the photovoltaic research are potential applications of PAS in the characterization of defects (vacancies, microvoids, etc.) and in the investigations of the role of hydrogen in a-Si:H. In the recent years, we have applied PAS to study defects in the Czochralski grown silicon ^{1, 2}, GaAs epilayers grown at low temperatures by Molecular Beam Epitaxy ^{3, 4}, and chemical vapor deposited diamond films ^{5, 6}. Here we present results for the depth and spatial profiles of defects in Cz-grown silicon by implanting variable energy positrons at different depths and measuring the Doppler broadening in the annihilation gamma-ray energy spectra and also by conducting the positron lifetime measurements by axially displacing a ²²Na positron source on the as-grown wafer. We also present results for the effects of thermal treatment on the bulk positron lifetimes in the Cz-grown wafers. Finally, we present results from our recent study of hydrogen in a-C:H and in microvoids in irradiated aluminum. Some positron lifetime experiments on a-S:H have already been reported ⁷ and additional PAS work on a-Si:H could provide information useful to the photovoltaic research.

EXPERIMENTAL DETAILS

Bulk Measurements : Qualitatively, an energetic positron from a radioactive source enters a solid and rapidly (within picoseconds) thermalizes by losing its kinetic energy. In a defect-free solid, a thermalized positron behaves like a "free" particle; the positron density distribution is pretty much uniformly distributed throughout the crystal with a small enhancement in positron density in the interstitials. The ultimate fate of the thermalized positron is annihilation with one of the electrons of the crystal. The annihilation of a positron-electron pair results in the emission of two gamma rays. The energy of each gamma ray is 0.511 MeV. The annihilation process is characterized by the positron lifetime and electron momentum distribution. Both of these characteristics provide information about lattice defects in the crystal. The negatively charged lattice vacancies are efficient traps for the positively charged positrons. The characteristics of a trapped positron are markedly different from those of a free positron in a crystal. For example, the lifetime of a positron trapped in a lattice vacancy in silicon is almost 16 % longer than the lifetime of a free positron in

defect-free silicon. The positron lifetime is also influenced by the size of the defect; the lifetime of a positron trapped in a divacancy in silicon is 20% longer than the lifetime of a positron in a monovacancy. The momentum distribution of the positron-electron pair, measured by the Doppler shift method, also gets narrower whenever the positrons annihilate from vacancy-traps. Thus by measuring changes in the positron lifetime and/or the electron momentum distributions, we can study concentrations of both monovacancies and divacancies. PAS can also detect oxygen precipitates in silicon due to the fact that positrons preferentially sample interstitials in which the local electron density can be significantly altered by the presence of the precipitates. The positron lifetime measurements can also provide useful information about hydrogen in a-Si:H due to an enhanced probability for annihilation in collisions with the hydrogen molecules in a microvoid.

Depth Profile Measurements : The variable energy positron beam has recently emerged as a powerful surface probe. This technology has enabled studies of surface properties, in particular, studies of atomic scale disorder in the near-surface region ($\sim$ few μm deep). These measurements are based on a strong positron-surface interaction and on remarkable changes in the annihilation characteristics upon positron trapping in defects. The data from these experiments, conducted by implanting monoenergetic positrons at varying depths, are analyzed by solving the positron diffusion equation that provides results for: 1) the positron diffusion length which changes because of positron-trapping in defects, and 2) defect depth profile in the sample.

The specific details on the various interactions of the low energy positrons and PAS experiments can be found elsewhere.⁸ Here we provide only a brief description. Our variable energy positron beam spectrometer consists of a magnetically guided positron beam, a high-purity Ge solid state detector, a NaI(Tl) gamma-ray energy detector, and computer controlled multichannel analyzer. Moderated positrons are transported through a curved beam-line by a focussing magnetic field and accelerated to desired energies up to 30 keV just prior to being implanted into the sample maintained under high vacuum (10^{-7} torr). Positrons thermalize within picoseconds and diffuse through the sample. While diffusing, positrons experience trapping in defects with a probability that depends on the concentration and nature of the defects. It is also possible that a certain number of the positrons will escape to the surface. Upon returning to the surface, positrons become trapped in open volume defects on the surface and/or form positronium. The positron-electron annihilation gamma-rays are recorded by using Ge and NaI(Tl) detectors and are analyzed for the S parameter (= area

under a central narrow region divided by the total area under the background-corrected annihilation peak) and for the valley-to-peak ratio (area under the Compton distribution divided by the area under the photo-peak), respectively. The S parameter is sensitive to defects and to changes in the valence electron distribution. The positron lifetime spectra are measured by using a fast-fast lifetime spectrometer and analyzed by Positronfit Extended.⁹ In layman's terms the positron lifetime measurement is based on the following: the positron source ($^{22}\text{NaCl}$) emits a gamma-ray of energy = 1.28 MeV at the instant of positron emission. The detection of this gamma ray marks "zero-time". The subsequent annihilation of the positron with one of the electrons of the material produces two gamma rays, each of energy = 0.511 MeV. The time interval between the "zero-time" and one of the annihilation gamma rays, is the lifetime of the positron.

RESULTS AND DISCUSSION

Depth Profile of Defects

The S parameters measured for the as-grown Cz-silicon, Si <100> epilayer, and Cz-Si annealed at 1100 °C for 4 hrs are plotted against positron energy in Fig. 1.

Figure 1(a). The S parameter of the Doppler broadening spectrum vs positron energy for as-grown Cz-Si wafer. The solid curve represents fit of the positron diffusion equation.

Figure 1(b). The S parameter of the Doppler broadening spectrum vs positron energy for Si <100> epilayer. The solid curve represents fit following the positron diffusion equation.

Figure 1(c). The S parameter vs positron energy for Cz-Si annealed at 1100 ° C for 4 hrs.

In the case of the as-grown wafer, the S parameter decreases from a high value of 0.420 ± 0.001 at the surface to a value of 0.412 ± 0.002 at about $5000 \text{ \AA}$. Beyond $5000 \text{ \AA}$, the S parameter remains at 0.411 ± 0.001 , which also happens to be the S parameter measured for implantations $\geq 300 \text{ \AA}$ in the Si $\langle 100 \rangle$ epilayer shown in Fig. 1(b). The high S parameter in the top $0.5 \text{ }\mu\text{m}$ of the as-grown wafer arises from positron trapping in defects and/or positronium formation. There is an appreciable number of defects in the top $5000 \text{ \AA}$ layer. Deeper than $5000 \text{ \AA}$, the wafer appears to be as good as the epilayer. Except for a near-surface layer of thickness $\leq 300 \text{ \AA}$, the S parameter for the epilayer is independent of the positron implantation depth. These data show that : 1) the defect density in the epilayer is uniform from $\sim 300 \text{ \AA}$ down to $1 \text{ }\mu\text{m}$ and it is much lower than the density of defects in the upper $0.5 \text{ }\mu\text{m}$ layer of the as-grown wafer, and 2) the S parameters measured for the implantation depths $\geq 0.5 \text{ }\mu\text{m}$ in the as-grown Cz-wafer approach a value measured for the epilayer. Fig. 1 (c) shows changes in the depth-profile after 4 hr anneal at $1100 \text{ }^\circ\text{C}$. Except for a high point on the surface, the measured S parameter remain at 0.412 ± 0.002 for depths down to about $2000 \text{ \AA}$. For depths $> 2000 \text{ \AA}$, the S parameter gradually increases to 0.419 ± 0.003 at $5000 \text{ \AA}$, and remains at this high value up to about $1 \text{ }\mu\text{m}$. As a result of annealing, the top $2000 \text{ \AA}$ layer of the as-grown wafer appears to "look like" the epilayer. This is possibly related to the so-called oxygen denuded zone in the wafer. Whereas oxygen can escape from the near surface region, the oxygen precipitates in the deeper regions of the wafer are expected to remain. Based on the staining analyses using Leo's etch, we estimate that the diameter of the oxygen precipitates in the annealed wafer can be as large as few hundred $\text{\AA}$. Since such large precipitates produce substantial strain in the lattice, the S parameter behavior for the positron implantations between $2000 \text{ \AA}$ and $1 \text{ }\mu\text{m}$ could be used to study oxygen precipitation.

An analysis of the S parameter data by using the following well-known one-dimensional positron diffusion equation can provide quantitative information: ¹⁰

$$D_+ d^2c(z)/dz^2 - d/dz (v_d c(z)) - (k_t n_t(z) + \lambda_b) c(z) + P(z, E) = 0 \quad (1)$$

where $c(z)$ is the positron volume density at depth z , v_d is the field dependent positron drift

velocity, $n_t(z)$ is the atomic fraction of the defect density, k_t is the specific positron trapping rate, λ_b is the positron bulk annihilation rate, and D_+ is the positron diffusion coefficient related to the positron diffusion length by $L_+ = (D_+/\lambda_b)^{1/2}$. The positron implantation profile is given by

$$P(z, E) = (m/z_0) (z/z_0)^{m-1} \exp(- (z/z_0)^m), \quad (2)$$

where $z_0 = 1.13 \bar{z}$, $\bar{z} = (\alpha_p / \rho) E^n$ is the mean implantation depth at energy E in keV, ρ is the density of the sample in g/cm³, $\alpha_p = 3.32 \mu\text{g/cm}^2 \text{ keV}^{1.6}$, $m = 2$, and $n = 1.6$. In this analysis, the measured S parameters are represented by

$$S(E) = \sum_l S_l f_l + S_{\text{surf}} f_{\text{surf}}, \quad (3)$$

where f_l is the fraction of the positrons in l^{th} layer, f_{surf} is the fraction of the positrons returning to the surface, S_l is the value assigned to the l^{th} layer, and S_{surf} is characteristic of the surface. As an example, we summarize in Table 1 the results obtained from the fit of the positron diffusion equations (eqs.1-3) for the as-grown, epilayer, and annealed wafers.

TABLE 1

Analysis of the S parameter data (Fig. 1) following eqs. (1)-(3).

Sample	S_{surf}	S_{top}	S_{bulk}	$(L_+)_{\text{top}}$ (Å)	$(L_+)_{\text{bulk}}$ (Å)
Cz-Si Wafer	0.42 fixed	0.4253 ± 0.0026	0.4097 ± 0.0009	1185 ± 432	2710 ± 977
Cz-Si (annealed)	0.42 fixed	0.3631 ± 0.0063	0.4199 ± 0.0010	1269 ± 123	722 ± 240
Epilayer	0.3994 ± 0.0015		0.4115 ± 0.0010	100	2773 ± 440

Spatial Profile of Defects

The radial dependence of the positron lifetime parameters in Cz-Si are shown in Fig.2.

Figure 2 (a). Relative intensity of the trapped positrons vs radial position on the as-grown Cz-Si wafer. The center and edge of the wafer are at 0 and 7.5 cm, respectively.

Figure 2 (b). Lifetime of the trapped positrons vs radial position on the as-grown Cz-Si wafer. The center and edge of the wafer are at 0 and 7.5 cm, respectively. The lifetimes for the positrons trapped in a monovacancy and in a divacancy are indicated.

Figure 2 (c). The shortest lifetime vs radial position on the as-grown Cz-Si wafer. The center and edge of the wafer are at 0 and 7.5 cm, respectively. The free-positron lifetime in Si is indicated.

The longer-lived component of lifetime τ_2 results from annihilations of positrons trapped in the vacancy-type defects. The intensity of this component (I_2) is a measure of the density of the defects. The changes in the shorter lifetime τ_1 also arise from positron trapping in defects.¹¹ Positron lifetime in defect-free silicon has been measured¹² (0.220 ± 0.002) ns and theoretically calculated¹³ (0.219 ns). Similarly the lifetime of positrons trapped in a monovacancy in silicon has been measured¹² (0.266 ± 0.002) ns and theoretically calculated¹³ (0.254 ns). The calculated value of the positron lifetime in a divacancy in silicon is 0.306 ns. There is an excellent agreement between our measurements and these previous results. Based on these data, we conclude that: 1) there is a radial variation in the concentration and nature of vacancies, 2) there are mostly monovacancies at the edge, 3) monovacancies and divacancies are present at the center, and 4) the vacancy concentration increases towards the edge of the wafer. This is in agreement with our observation that the minority carrier diffusion length near the edge of the wafer is smaller than the diffusion length at the center of the wafer. The data for the minority carrier diffusion length are shown in Fig. 3. Whereas the observations of the high values of I_2 (high vacancy concentrations) and shorter diffusion

lengths near the edge of the wafer are in agreement, the diffusion lengths near the center of the wafer, where lower values of I_2 are measured, do not increase.

Figure 3. The diffusion length for the minority carriers vs radial position for the Cz-Si wafer.

Effect of Thermal Treatment

In Fig. 4 we show the spatial variation in the bulk positron lifetime parameters on a wafer that had been annealed at 900 °C.

Figure 4 (a). Relative intensity of the trapped positrons vs radial position on the as-grown Cz-Si annealed at 900 °C. The center and edge of the wafer are at 0 and 7.5 cm, respectively.

Figure 4 (b). Lifetime of the trapped positrons vs radial position on the Cz-Si wafer annealed at 900 ° C. The center and edge of the wafer are at 0 and 7.5 cm, respectively.

Figure 4 (c). Lifetime of the short-lived component vs radial position on Cz-Si wafer annealed at 900 ° C. The center and edge of the wafer are at 0 and 7.5 cm, respectively

Obviously, the spatial variation in the density and nature (monovacancy vs divacancy) of the defects, seen in the case of the as-grown wafer, has almost disappeared. The density of the defects in the case of the wafer annealed at 900 °C is approximately equal to the density of the defects measured near the center of the as-grown wafer. Additionally, from a comparison between the values of the longer lifetimes measured for the as-grown and 900 °C annealed wafers, it appears that the latter contains both monovacancies and divacancies. Additional positron lifetime measurements on wafers annealed at different temperatures for varying durations are needed to better understand the effects of thermal processing. The effect of the 1100 °C anneal on the depth profile has already been shown in Fig. 1.

Hydrogen in Microvoids in a-C:H and Irradiated Aluminum

In order to demonstrate that the positron annihilation spectroscopy can be used to study hydrogen contained in a-Si:H, we present preliminary data from a series of experiments that we have recently conducted on a-C:H thin films and irradiated aluminum. The a-C:H thin films were grown by chemical vapor deposition ^{5, 6, 14} and the aluminum single crystals were irradiated by α -particles. ¹⁵ This irradiation creates microvoids in the aluminum lattice which are filled with helium gas. In the case of the a-C:H thin films, we observe four lifetime components in the positron lifetime spectra. An intermediate lifetime component (~ 0.22 ns) originates due to positron annihilations in the silicon substrate on which about 10 μ m thick a-C:H films were grown. Two long-lived components of lifetimes = ~ 0.9 ns and 3 ns originate from the so called pick-off annihilations of positronium inside the hydrogen containing microvoids. The shortest-lived component of lifetime ≤ 0.1 ns reflects the trapping of the positrons in defects in the films. It is the longest-lived component that allows a determination of the radius of the microvoid (~ 2 to 5 Å).

Further details on the pressure of the gas in the microvoids can be obtained from an analysis of the temperature dependencies of the positron lifetime parameters. Some of our data on α -irradiated Al are shown in Fig. 5. The observed variations in the positron lifetime parameters with temperature have contributions primarily from the temperature dependence of the density of the gas contained in the microvoids, possible physisorption of the atoms/molecules on the internal surfaces of the microvoid, and the surface of the microvoid. An analysis of the aluminum data, taking into consideration these effects, provides 63 Å for

the radius of the spherical microvoid filled with helium at pressures ranging from 1.23×10^3 atm at 150 K to 3.18×10^3 atm at 295 K. In the case of a-C:H, we observe a much larger effect; there is a change of about 45 % in both the positron lifetime and its relative intensity between 295 K and 10 K. Although some of the quantitative differences between the Al and a-C:H data can be attributed to the expected differences in the PVT of helium vs hydrogen, a better understanding awaits additional work.

Figure 5. Lifetime of positrons trapped in helium-filled microvoids in α -irradiated Al.

In conclusion, the positron annihilation spectroscopy is a technique that is sensitive to lattice defects in silicon. This technique has provided the depth (surface to 1 μm deep) and spatial profiles of the vacancy-type defects in the Cz-grown silicon wafers subjected to thermal processing. It has also been used to study the average size of the microvoids and the density of the gases in the microvoids in a-C:H and irradiated aluminum. The technique has the potential for providing useful information about defects and hydrogen in a-Si:H.

Research supported, in part, by a grant by Texas Instruments.

REFERENCES

1. S. C. Sharma, R. C. Hyer, N. Hozhabri, M. F. Pas, and S. Kim, *Appl. Phys. Lett.* **62**, 1939 (1992).
2. S. C. Sharma, N. Hozhabri, R. C. Hyer, T. Hossain, S. Kim, F. O. Meyer, III, M. F. Pas, and A. E. Stephens, *MRS Proceedings*, **262**, 45 (1992).
3. N. Hozhabri, R. C. Hyer, S. C. Sharma, J. Y. Ma, R. N. Pathak, and K. Alavi, *J. Vac. Sci. Technol.*, B **10**, 788 (1992).
4. N. Hozhabri, S. C. Sharma, K. Alavi, R. N. Pathak, and J. Y. Ma, submitted for publication, (1992).
5. S. C. Sharma, C. A. Dark, R. C. Hyer, M. Green, T. D. Black, A. R. Chourasia, D. R. Chopra, and K. K. Mishra, *Appl. Phys. Lett.* **56**, 1781 (1990).
6. R. C. Hyer and S. C. Sharma, submitted for publication (1992).
7. V. G. Bhide, R. O. Dusane, S. V. Rajarshi, A. D. Shaligram, and S. K. David, *J. Appl. Phys.* **62**, 108 (1987).
8. P. J. Schultz and K. G. Lynn, *Rev. Mod. Phys.* **60**, 701 (1988).
9. P. Kirkegaard, M. Eldrup, O. E. Mogensen, and N. J. Pedersen, *Comp. Phys. Commun.* **23**, 307 (1981).
10. A. van Veen, H. Schut, J. de Vries, R. A. Hakvoort, and M. R. Ijpma, in *Positron Beams for Solids and Surfaces*, eds. P. J. Schultz, G. R. Massoumi, and P. J. Simpson, AIP Conf. Proc. 218, 171 (1990).
11. S. C. Sharma, S. Berko, and W. K. Warburton, *Phys. Lett.* **58 A**, 405 (1976).
12. S. Dannefaer, *J. Phys. C*, **15**, 599 (1982).
13. M. J. Puska and C. Corbel, *Phys. Rev. B* **38**, 9874 (1988).
14. S. C. Sharma, M. Green, R. C. Hyer, C. A. Dark, T. D. Black, A. R. Chourasia, D. R. Chopra, and K. K. Mishra, *J. Mater. Res.* **5**, 2424 (1990).
15. N. Hozhabri, J. Ma, S. V. Naidu, C. I. Eom, S. C. Sharma, P. M. G. Nambissan, and P. Sen, *Nucl. Instru. Meth. in Phys. Res. B* **56/57**, 578 (1991).

Point Defect Injection During Co and Ti Silicidation of Phosphorus Implanted Silicon

J.W. Honeycutt, J. Ravi and G.A. Rozgonyi

Department of Materials Science and Engineering

North Carolina State University

Raleigh, NC 27695-7916

ABSTRACT

The effects of Ti and Co silicidation reactions on point defect concentrations in silicon have been investigated from the perspective of local point defect dynamics, dopant diffusion and extended defect dissolutions[1,2], and compared with other silicidation studies[3,4]. After silicidation of unannealed 40 keV, $2 \times 10^{15} \text{cm}^{-2}$ P⁺ implanted junctions by rapid thermal annealing at 900°C for 10-300 seconds, secondary ion mass spectrometry depth profiles of phosphorus in silicided and non-silicided junctions were compared. While non-silicided and TiSi₂ silicided junctions exhibited equal amounts of transient enhanced diffusion behavior, the junction depths under CoSi₂ were significantly shallower. End-of-range interstitial dislocation loops in the same silicided and non-silicided junctions were studied by planview transmission electron microscopy. The loops were found to be stable after 900°C, 10 seconds annealing in non-silicided material, and their formation was only slightly affected by the TiSi₂ or CoSi₂ silicidation. However, enhanced removal of the loops was observed under both TiSi₂ and CoSi₂, with essentially complete removal of the defects under CoSi₂ after 5 min at 900°C. The observed diffusion and defect behaviour strongly indicate that implantation damage induced excess interstitial concentrations are significantly reduced by the formation and presence of CoSi₂, and to a lesser extent TiSi₂. The observed time-dependent defect removal under the silicide films suggests that vacancy injection and/or interstitial absorption by the silicide film continues long after the silicide chemical reaction is complete.

INTRODUCTION

Ion implantation damage induced transient enhanced diffusion (TED) of ion implanted boron[5-7] phosphorus[7,8], and to a lesser degree, arsenic[7] junctions are issues of great concern in ultra shallow junction technology. Interestingly, the ranking of dopants in order of the experimentally observed TED effects, i.e. B>P>As, is in the same order as the ranking of oxidation enhanced diffusion (OED) effects, and the interstitialcy components of the dopant diffusivities. Excess interstitial concentrations created by knock-on events during implantation coalesce in the end-of-range region during annealing to form extrinsic dislocation loops, similar in effect to the growth of oxidation stacking faults due to the excess interstitials generated during oxidation. These end-of-range dislocation loops, which generally require high temperature annealing to remove, are known to degrade leakage currents in junctions when located in the depletion region[9,10]. Considerations of damage removal/dopant diffusion tradeoffs in shallow junction processing have been discussed recently by Fair[11]. One of the important dopant redistribution issues to be resolved is the possibility that point defects are injected into silicon during silicidation reactions. Several papers have demonstrated that implantation damage in Si in the form of interstitial dislocation loops[10, 13-17] can be profoundly affected by silicidation, presumably due to vacancy injection during silicidation. Others have also attributed dopant diffusivity perturbations during silicidation of shallow junctions to point defect injection. Hu[12]

observed enhanced diffusion of Sb and B doped buried layers during 950°C, 10 hour annealing of a thick sputter deposited TaSi_x layer. The secondary ion mass spectrometry (SIMS) profiles in our recent report on enhanced diffusion of Sb doped buried layers[18] during CoSi₂ and TiSi₂ formation were inaccurate due to surface roughening and insufficient etching of the silicide films, and we therefore recanted those results[13]. Wittmer et al. also recently noted possible errors[4] in the SIMS dopant profiles in their recent report on enhanced diffusion of buried layers during Pd₂Si formation[3], but Rutherford Backscattering (RBS) results[4] seem to confirm these findings. The idea that silicidation reactions generate point defects is not really surprising, since the only other two common silicon thin film growth processes involving silicon-consuming chemical reactions on the wafer surface, i.e. oxidation and nitridation, are known to perturb point defect concentrations[19] via observations of enhanced/retarded dopant diffusion and growth/shrinkage of stacking faults. However, until now, only one direct correlation[3] has been found between diffusion perturbations and defect removal in silicided shallow junctions. The removal of end-of-range damage by silicidation strongly implies that the implantation induced interstitial concentrations are significantly reduced by the silicidation process, by vacancy injection or otherwise. One therefore would infer that in addition to removal of end-of-range defects, damage induced TED effects should also be suppressed if the junction annealing is performed concurrently with silicide formation in a single annealing step, rather than the typical two-step process where junction annealing is performed prior to silicidation. Due to their low resistivities and good thermal stabilities, CoSi₂ and TiSi₂ are the silicides of choice for shallow junction contact formation, and were thus chosen for these studies. Phosphorus was chosen as the dopant because it exhibits substantial TED and has not been investigated extensively as a shallow junction dopant. Maex, et al.[20] have shown that As is thermodynamically unstable under both CoSi₂ and TiSi₂, so if concurrent silicidation suppresses transient diffusion, the possibility of using P as an alternative n⁺ junction dopant is deserving of further investigation.

EXPERIMENTAL

Czochralski grown 30 Ω-cm, 4 inch diameter silicon wafers were RCA cleaned, followed by P⁺ implantation at 40 keV to a dose of 2x10¹⁵ cm⁻². Following cleaving of implanted wafers into halves, and etching in 10:1 buffered oxide etch to remove native oxide, 23 nm Ti or 13 nm Co were evaporated through a shadow mask onto a portions of the wafers, which upon annealing resulted in silicided and non-silicided regions. These thicknesses were chosen to result in a silicon consumption about 50 nm, corresponding to the projected range of 40 keV phosphorus ions in silicon, and within the current constraints of ULSI shallow junction technology. Consuming equal amounts of silicon also allows comparisons to be drawn between Co-Si and Ti-Si reactions as sources or sinks for point defects. Pairs of Ti and Co half-metallized samples were then simultaneously rapid thermally annealed at 900°C in flowing nitrogen for times ranging from 10-300 seconds, to simultaneously anneal the implantation damage (including solid phase epitaxial regrowth of the amorphized surface), diffuse and activate the phosphorus, and form the silicide thin film. It should be noted that before ramping to 900°C in the Heatpulse RTA system, a standard 400°C 10 second pre-anneal was performed to avoid thermal stresses induced plastic deformation. The Co₂Si and CoSi phases form from Co-Si reactions at 350-500°C[21], whereas only slight reaction is expected at 400°C for Ti-Si[22]. Following etching of unreacted Ti and Ti-O-N in 1:1:5 NH₄OH:H₂O₂:H₂O, determination of the silicide phases formed was accomplished by x-ray diffraction (XRD) on a Rigaku diffractometer. The silicide layers, which XRD confirmed to be TiSi₂ or CoSi₂ in all cases, were then etched in concentrated (49%) HF. The depth of silicon consumed by the silicide was determined with a stylus profilometer, measuring the step height across the border between etched silicided and non-silicided regions. SIMS depth profiles of phosphorus in non-silicided and etched silicided regions were performed on a Cameca IMS-3F using a 5keV Cs⁺ beam. The phosphorus profiles measured on silicided samples after etching were

shifted to the right on the depth scale by the measured amount of silicon consumption to allow direct comparison of phosphorus profiles between silicided and non-silicided samples, as referenced to the original silicon surface. Cross-sectional and planview transmission electron microscopy (TEM) investigations of residual implant damage in annealed samples were performed on a Hitachi H-800 electron microscope operating at 200 kV. Dislocation loop densities were measured on 50,000X micrographs of the specimens in three different areas, covering a total area of about $7.5 \mu\text{m}^2$.

RESULTS

Fig.1 shows SIMS phosphorus concentration profiles illustrating the lack of time dependence of diffusion in non-silicided P implants during RTA at 900°C for times of 10 to 300 seconds. Implantation damage induced TED is evidenced by an essentially time-independent deviation from the as-implanted concentration profile beginning where the concentration drops to about $3 \times 10^{19}/\text{cm}^3$, at a depth of about $0.1 \mu\text{m}$. Since the 10-300 second profiles match closely, the phosphorus motion is indeed a transient effect occurring over a time of less than 10 seconds. Kim, et al. have previously shown that the time constant for TED is less than 15 seconds in 40 keV, $1 \times 10^{15}/\text{cm}^2$ P^+ implants[7]. These observations of TED are consistent with the widely accepted view that Si lattice atoms are knocked deeper into the material by collisions with the incoming implanted species, and some of them are incorporated into the lattice in the form of self-interstitials. These excess self-interstitials then temporarily enhance diffusion of dopants with substantial self-interstitialcy components (B and P), until finally the large excess interstitial concentration in the end-of-range region is reduced by the diffusion and recombination of interstitials in the bulk or at the surface, as well as their agglomeration into interstitial dislocation loops.

XRD spectra showed that, as expected, the Ti and Co films reacted with Si during 900°C RTA to form TiSi_2 and CoSi_2 . Fig. 2 shows the effects of the concurrent TiSi_2 and CoSi_2 formation on transient phosphorus diffusion at 900°C for 10 seconds. Comparison of silicided vs. non-silicided profiles reveals that while TiSi_2 formation exerts little effect on the phosphorus diffusion in the underlying silicon, a significant reduction in the junction depth of about 50 nm is observed under CoSi_2 . In order to determine if this effect is due simply to consumption of the near-surface region of the phosphorus profile by the CoSi_2 , 68 nm of Si was etched from an as-implanted sample, partially masked from the etchant with wax, using a 1:3:10 mixture of $\text{HF}:\text{HNO}_3:\text{CH}_3\text{COOH}$ followed by annealing at 900°C for 10 seconds. The resulting phosphorus profile closely matches the non silicided and TiSi_2 silicided profiles. Therefore, the transient diffusion indeed occurs because of implantation induced point defects present beyond the projected range, and the consumption of the near surface region by the CoSi_2 is not itself responsible for reducing the junction depth. This result complements the findings of Kim, et al.[7], who etched a 40 keV, $2 \times 10^{14}/\text{cm}^2$ BF_2^+ implanted wafer to a depth of about 80 nm (far beyond the end-of-range dislocations) and observed no transient diffusion at 900°C . These combined results confirm that the source of interstitials is in the end-of-range region, and not in the bulk nor within the originally amorphous layer.

SIMS profiles of non-silicided and silicided samples annealed for 20-300 sec at 900°C were very similar to the 10 sec results shown in Fig.2, i.e. TED was not influenced by TiSi_2 silicidation, but was significantly reduced by CoSi_2 silicidation. It should also be noted that the extremely high phosphorus concentrations of above $10^{21}/\text{cm}^3$ for CoSi_2 for times ≥ 60 seconds are probably an artifact of SIMS surface transient effects, and/or the etching of the CoSi_2 in HF, which may leave behind a P-rich surface residue that becomes difficult to remove for annealing times ≥ 60 seconds. The presence of residual Co was confirmed in the 60 sec sample by monitoring the Co signal during SIMS profiling. The P concentration at the CoSi_2/Si interface in the 900°C , 60 sec CoSi_2 sample was investigated by performing SIMS analysis without removing the silicide

film. Quantification of phosphorus concentration in the silicide was achieved in a manner described in [23], using separate phosphorus implanted Si and CoSi₂ standards for determining sputter rates and relative sensitivity factors. The resulting SIMS phosphorus profile of the 60 sec CoSi₂ sample revealed an interfacial phosphorus peak of about $10^{20}/\text{cm}^3$.

The effects of concurrent silicidation on the formation and removal of end-of-range damage were studied by planview TEM. Figure 3 shows planview TEM micrographs of the end-of-range interstitial dislocation loops under bare, Ti silicided, and Co silicided surfaces after annealing at 900°C for 10 and 300 seconds. Comparison of the micrographs in Fig. 3(a,d) reveals that the dislocation loops are very stable at 900°C in the non-silicided samples, with no readily observable change (at this magnification) in the loop size or density over the entire 10-300 sec time range. The observed stability of the end of range loops is consistent with the work of Jones, et al.[24], who found that end-of-range loops in 50 keV, $1 \times 10^{15}/\text{cm}^2$ P⁺ implanted material could not be removed even after annealing at 900°C for 72 hours. The stability of the defects may be related to the generation of self-interstitials by the motion of phosphorus in the high concentration region[25]. As shown in Fig. 3(a-c), there is little noticeable effect of Ti or Co silicidation on dislocation loop size or density after 10 second annealing. At 300 seconds however, the dislocation loops have been essentially annihilated under CoSi₂ (one defect is shown) and have also been reduced both in size and density under TiSi₂ (see Fig. 3 d-f).

Quantitative analysis of the dislocation loop densities in each of the 10-300 sec non-silicided and silicided samples was performed by examination planview TEM micrographs. By counting the number of loops contained in three separate $2.5 \mu\text{m}^2$ areas of each TEM specimen and dividing by the area, the dislocation loop densities were calculated. The defect densities were found to be uniform to within $\pm 10\%$. Fig. 4 is a plot of the measured defect densities for 10-300 sec annealing. The end-of-range dislocation loops under silicided surfaces behave according to classical precipitation kinetics -- nucleation and growth of "precipitates" from the supersaturation of interstitials (loop density increases, 10~60 sec), followed by growth of large defects at the expense of smaller ones and diffusion controlled dissolution of the defects (loop density decreases, ~60-300 sec). In addition to changes in dislocation loop densities, the loop sizes are noticeably reduced under the silicide layers at $t \geq 100$ seconds, and as noted above are essentially dissolved at 300 seconds under CoSi₂. This decrease in the loop size strongly suggests that non-conservative climb is the mechanism for the loop removal, as opposed to glide of the dislocations out of the crystal.

DISCUSSION

The above observations of suppressed transient diffusion and enhanced end-of-range damage removal in concurrently silicided phosphorus junctions strongly suggest that the near-surface point defect concentrations are modified by the formation and/or presence of the silicide. It should be re-emphasized that the reduced junction depths observed under CoSi₂ silicided junctions are not due to consumption of the high concentration near-surface region which acts as the chemical source of phosphorus, since the usual TED was observed under TiSi₂, and after chemically removing even more silicon (68 nm) than was consumed by the CoSi₂ (43 nm). Out diffusion of P into CoSi₂ is not responsible either, since as shown in Fig.1 the junction depth remains very stable during 10-300 seconds annealing at 900°C. Furthermore, the PREDICT process simulator, which contains accurate TED models, very accurately predicts the experimental phosphorus junction depths for the 10-60 sec concurrent CoSi₂ silicidation process. PREDICT (correctly) omits TED diffusivity enhancements for concurrent Co silicidation processes, so the agreement between SIMS and simulation also suggests that the reduced junction depths are due to silicidation induced reduction of the implantation induced excess interstitial concentrations which produce TED. Interstitial concentrations therefore must be reduced either by vacancy injection at the Co silicide interface followed by recombination of excess interstitials with the injected vacancies, or by direct absorption of the excess interstitials by the Co silicide film.

To understand the relationships between silicide formation and TED, it is useful to consider the relative kinetics of the processes which occur during concurrent silicidation, namely the amorphous layer regrowth, silicide formation, and the time regime over which TED occurs. From the literature on the kinetics of these processes, it was estimated that at 900°C it takes about 0.04 sec to regrow a 100 nm amorphous layer on [100] Si [26], 0.002 sec to grow 50 nm of CoSi₂ from CoSi/Si[27], and 0.2 sec to grow 50 nm of TiSi₂ from Ti/Si[28]. (The values for amorphous layer regrowth and silicide formation times at 900°C were extrapolated from the lower temperature data given in the respective references.) The time constant for phosphorus TED at 900°C from the present results is ≤10 sec. For Co, the silicide layer forms first, followed by completion of the amorphous layer regrowth, and finally completion of the TED transient. It is difficult to imagine a flux of point defects propagating across an amorphous layer, so TED is apparently affected by the mere presence of the CoSi₂ film (not only its formation) after the amorphous layer recrystallizes. The observations of enhanced dissolution of dislocation loops under both CoSi₂ and TiSi₂ after extended annealing times also suggest that the silicide film acts as a source of vacancies and/or a sink for interstitials even after the silicidation reaction is complete. Other observations of point defect related phenomena occurring under non-advancing thin film interfaces include the correlation of Ahn, et al.[29] of enhanced Sb diffusion and extrinsic stacking fault shrinkage rates to the stress levels in deposited nitride layers. In addition, Moynagh, et al.[30] recently proposed vacancy generation from CoSi₂ after observing enhanced diffusion and electrical activation of As in Si during out-diffusion from pre-formed As-implanted CoSi₂ layers. Similar diffusion enhancements of As from CoSi₂ were also observed by Jiang, et al. [31].

It was shown above that concurrent silicidation exerts little effect on the early stages of end-of-range damage formation. However, the enhanced dissolution of end-of-range dislocation loops long after the silicide reaction is complete suggests that a non-advancing CoSi₂/Si or TiSi₂/Si interface has a much greater capacity for removing implantation damage than an exposed or native oxide covered Si surface. The removal of dislocation loops can occur only by either dislocation glide or non-conservative climb motion. As will be discussed in another paper [32], the possibility that enhanced glide motion of the loops is responsible for their removal under silicide films was dismissed, based on that fact that the forces on dislocations exerted by film stress are too small[33], and the image forces[34] exerted on dislocations due to the silicide films are actually repulsive. Therefore, non-conservative climb of the dislocation loops must be enhanced by the silicide films via one of the following mechanisms: (1) emission of self-interstitials from dislocations followed by their absorption at the silicide/silicon interface; (2) emission of self-interstitials from dislocations followed by their recombination with vacancies generated by the silicide; or (3) vacancy generation by the silicide and dislocation climb via direct absorption of vacancies by the loops.

Previously proposed mechanisms of point defect generation during thin film chemical reactions have commonly been based on the identity of the dominant diffusing species during the reaction, which may not always be a correct assumption, as pointed out by Fahey and Dutton[35]. However, one should also consider that atomic motion is not halted when the chemical reaction is complete, although the film composition and volume remain constant. This continued diffusion is, in fact, manifest in silicide agglomeration phenomena[36,37], the mechanism of which could conceivably be directly related to vacancy injection or interstitial absorption. Interestingly, a thin Si-rich surface layer has been reported to form on thin epitaxial CoSi₂ layers[38], the thickness of which increases with increasing annealing temperature. Similar results were obtained in our laboratory by Auger electron spectroscopy (AES) sputter depth profiling of 250 nm thick CoSi₂ films formed at 900°C. Thick films were used for this experiment because the thinner films above were probably agglomerated, which would result in inaccurate AES profiles. As shown in Fig. 5, a silicon-rich surface layer was observed after 900°C 120 sec RTA. Out diffusion of Si from the substrate, possibly via grain boundary diffusion, is undoubtedly the mechanism for the formation of this surface silicon rich film, which could account for injection of vacancies or absorption of

excess interstitials by a non-reacting CoSi_2 film. Interestingly, CoSi_2 films usually have grain sizes of the order of the film thickness, whereas C54 TiSi_2 films normally have much larger grains. Therefore, if agglomeration or the formation of a thin silicon-rich surface film on the silicide via grain boundary diffusion of silicon atoms is responsible for vacancy injection or interstitial absorption, one might expect such a phenomenon to be more effective for a small-grained silicide (CoSi_2) than for large grained silicides (TiSi_2), in accordance with the present observations.

CONCLUSIONS

The results of an investigation of the time-dependent effects of concurrent TiSi_2 and CoSi_2 silicidation on ion implantation damage, manifested in the form of transient enhanced diffusion and end-of-range dislocation loops, have been presented. CoSi_2 silicidation was shown to cause suppression of the transient diffusion of phosphorus and enhanced removal of end-of-range interstitial dislocation loops. Although TiSi_2 silicidation exerts no effect on transient diffusion, enhanced removal of end-of-range defects was observed, with a significantly smaller effect than that of CoSi_2 . The observed suppression of transient diffusion under CoSi_2 was shown by experiment and simulation not to be caused by dopant loss to the silicide, and therefore must be due to a reduction of the implantation induced excess interstitial concentrations, resulting from the formation or presence of the CoSi_2 . Several possible explanations for the observed dislocation loop removal based on enhanced glide and climb processes under silicide films were examined. The only logical explanation for the observed effects seems to be vacancy injection and/or interstitial absorption at silicide/silicon interfaces. Since the CoSi_2 formation is likely to have proceeded completely on the amorphized silicon prior to recrystallization, and since the onset of dislocation loop removal occurred long after the Co-Si reaction was complete, we proposed that the suppressed interstitial concentrations are a result of vacancy emission or interstitial absorption by the CoSi_2/Si interface after completion of the silicidation reaction. A similar post-reaction mechanism for point defect injection/absorption may exist for TiSi_2 based on the fact that delayed dislocation loop removal was also observed, but no effect on transient diffusion.

REFERENCES

- [1] J.W. Honeycutt and G.A. Rozgonyi, *Appl. Phys. Lett.* **58**(12), 25 March 1991
- [2] J.W. Honeycutt, J. Ravi and G.A. Rozgonyi, *MRS Symp. Proc.* **262**, 1992.
- [3] M. Wittmer, P.M. Fahey, G.J. Scilla, S.S. Iyer and M. Tejwani, *Phys. Rev. Lett.* **66**, 632 (1991).
- [4] M. Wittmer, P.M. Fahey, J. Cotte, S.S. Iyer and G.J. Scilla, *Phys. Rev. B*, **45**, 383 (1992).
- [5] S. Solmi, R. Angelucci, F. Cembali, M. Servidori, and M. Anderle, *Appl. Phys. Lett.* **51**, 331 (1987).
- [6] M. Mikaye and S. Aoyama, *J. Appl. Phys.* **63**, 1754 (1988).
- [7] Y. Kim, H.Z. Massoud, and R.B. Fair, *J. Elec. Mat.* **18**, 143 (1989).
- [8] M.D. Giles, *J. Electrochem. Soc.* **138**, 1160 (1991).
- [9] S.D. Brotherton, J.P. Gowers, N.D. Young, J.B. Clegg, and J.R. Ayres, *J. Appl. Phys.* **60**, 3567 (1986).
- [10] D.S. Wen, P. Smith, C.M. Osburn, and G.A. Rozgonyi, *J. Electrochem. Soc.* **136**, 466 (1989).
- [11] R.B. Fair, in *Semiconductor Silicon 1990*, H. Huff, K.G. Barraclough, and J. Chikawa (eds.), (The Electrochemical Society, Pennington, NJ, 1990), p. 429.
- [12] S.M. Hu, *Appl. Phys. Lett.* **51**, 308 (1987).
- [13] I. Ohdomari, K. Takano, T. Chikyow, H. Kawarada, J. Nakanishi, and T. Ueno, *MRS Symp. Proc.* **54**, 63 (1986).

- [14] K. Maex, R. DeKeersmaecker, C. Claeys, J. Vanhellemont, and P.F.A. Alkemade, in *Semiconductor Silicon 1986*, H. Huff, T. Abe, and B. Kolbesen (eds.), (The Electrochemical Society, Pennington, NJ, 1986), p. 346.
- [15] D.S. Wen, P.L. Smith, C.M. Osburn, and G.A. Rozgonyi, *Appl. Phys. Lett.* **51**, 1182 (1987).
- [16] K. Maex and L. Van den Hove, *Mat. Sci. Eng.* **B4**, 321 (1989).
- [17] W. Lur, J.Y. Cheng, C.H. Chu, M.H. Wang, T.C. Lee, Y.J. Wann, W.Y. Chao, and L.J. Chen, *Nucl. Instr. Meth.* **B39**, 297 (1989).
- [18] J.W. Honeycutt and G.A. Rozgonyi, *Appl. Phys. Lett.* **58**, 1302 (1991).
- [19] P.M. Fahey, P.B. Griffin, and J.D. Plummer, *Rev. Mod. Phys.* **61**, 289 (1989).
- [20] K. Maex, G. Ghosh, L. Delaey, V. Probst, P. Lippens, L. Van den Hove, and R.F. De Keersmaecker, *J. Mat. Res.* **4**, 1209 (1989).
- [21] A.E. Morgan, E.K. Broadbent, M. Delfino, B. Coulman, and D.K. Sadana, *J. Electrochem. Soc.* **134**, 925 (1987).
- [22] I.J.M.M. Raaijmakers, L.J. van IJzendoorn, A.M.L. Theunissen, and K.B. Kim, *MRS Spring Meeting, Symp. B.*, San Diego (1989).
- [23] S.F. Corcoran, C.M. Osburn, N. Parikh, R.W. Linton, and D.P. Griffis, *J. Vac. Sci. Tech.* **A7**, 3065 (1989).
- [24] K.S. Jones, S. Prussin, and E.R. Weber, *J. Appl. Phys.* **62**, 4114 (1987).
- [25] P. Fahey, R.W. Dutton, and S.M. Hu, *Appl. Phys. Lett.* **44**, 777 (1984).
- [26] L. Cspregi, E.F. Kennedy, T.J. Gallagher, J.W. Mayer, and T.W. Sigmon, *J. Appl. Phys.* **48**, 4234 (1977).
- [27] L. Van den Hove, R. Wolters, K. Maex, R. DeKeersmaecker, and G. Declerck, *J. Vac. Sci. Tech.* **B4**, 1358 (1986).
- [28] C.A. Pico and M.G. Lagally, *J. Appl. Phys.* **64**, 4957 (1988).
- [29] S.T. Ahn, H.W. Kennel, J.D. Plummer, and W.A. Tiller, *J. Appl. Phys.* **64**, 4914 (1988).
- [30] P.B. Moynagh, A.A. Brown, and P.J. Rosser, *J. Phys.* **C4**, 187 (1988).
- [31] H. Jiang, C.M. Osburn, P. Smith, Z.-G. Xiao, D. Griffis, G. McGuire, and G.A. Rozgonyi, *J. Electrochem. Soc.* **139**, 196 (1992).
- [32] J.W. Honeycutt and G.A. Rozgonyi, to be submitted to *J. Appl. Phys.*
- [33] L. Van den Hove, Ph.D. Thesis, Katholieke Universiteit Leuven, Belgium (1988).
- [34] J. Narayan and K. Jagannadham, *J. Appl. Phys.* **62**, 1694 (1987).
- [35] P. Fahey and R.W. Dutton, *Appl. Phys. Lett.* **52**, 1092 (1988).
- [36] Z.G. Xiao, G.A. Rozgonyi, C.A. Canovai, and C.M. Osburn, *MRS Symp. Proc.* **202**, 101 (1991).
- [37] T. Nolan, R. Beyers, and R. Sinclair, *MRS Symp. Proc.* **202**, 95 (1991).
- [38] F.D. Schowengerdt, T.L. Lin, R.W. Fathauer, and P.J. Grunthaner, *Appl. Phys. Lett.* **54**, 1314 (1989).

Fig. 1 SIMS depth profiles of P in Si after concurrent Co silicidation during RTA at 900°C for 10-300 sec.

Fig. 2 SIMS depth profiles of P in Si after 900°C, 10 sec RTA, with and without concurrent Ti and Co silicidation.

Fig. 3 Planview TEM micrographs of end-of-range dislocation loops under bare (a,d), TiSi₂ silicided (b,e), and CoSi₂ silicided(c,f) surfaces after 900°C, 10 sec (a-c) and 300 sec (d-f) RTA.

Fig. 4 End-of-range dislocation loop density under bare and silicided surfaces as a function of RTA time at 900°C .

Fig. 5 AES depth profile of 250 nm thick CoSi_2 formed by RTA at 900°C for 120sec, showing Si rich surface region.

MODELING OF THE COUPLED DIFFUSION OF PHOSPHORUS WITH POINT DEFECTS

S. T. Dunham

Department of Electrical, Computer and Systems Engineering,
Boston University, Boston, MA 02215

In this paper, we develop and analyze models for the coupled diffusion of dopants and point defects. We begin by considering a general model for phosphorus diffusion via dopant/defect pairs assuming local equilibrium for electronic processes, but not for chemical processes. Using this system, along with parameters based on experimental data previously reported in the literature, we test common model assumptions. Our analysis concludes that dopant/defect pairing reactions are near local equilibrium, but that defect recombination reactions are not. We then use a simplified model, based on the assumption that the pairing reactions are near equilibrium to simulate phosphorus profiles. By including diffusion of phosphorus via negatively-charged phosphorus/vacancy pairs, in addition to diffusion via phosphorus/interstitial pairs which dominates in intrinsic material, we are able to match experimental phosphorus diffusion profiles with surface concentrations ranging from intrinsic to solid-solubility at 900 and 1000°C, while remaining consistent with the broad range of previously observed behavior of phosphorus and point defects in silicon.

1 Introduction

The diffusion of substitutional dopants takes place via interactions with point defects (interstitials and vacancies). Most impurities have been reasonably well modeled by systems which consider equilibrium point defect concentrations, but phosphorus has long shown apparently "anomalous" behavior such as "kink and tail" diffusion profiles and "base push" effects. Although a number of models have been proposed to explain these effects, the most commonly used quantitative models are based on vacancy interactions [1] and are inconsistent with a large range of observations which show that phosphorus diffuses primarily with interstitials [2] and that the "base push" and related effects are caused by interstitial supersaturation [3, 4]. In addition, these models use a phenomenological approach, with different models for the peak and tail regions, and thus are inadequate for modeling process interactions or two- and three-dimensional effects.

Recently, several authors have observed that the qualitative aspects of the phosphorus kink and tail arise naturally from the coupled dopant/point defect system and have developed models to account for observations of enhanced dopant diffusion [5-13]. All of these proposed models follow the basic formalism laid out by Mathiot and Pfister [5] in which dopants are assumed to diffuse only when paired with point defects. However, they differ dramatically in the assumptions made in simplifying the general system to one which is suitable for numerical solution. The goal of this paper is to determine appropriate assumptions for modeling of coupled diffusion of dopants with point defects and develop a model which is capable of quantitatively matching experimental results.

2 General Coupled Diffusion Model

The system in which a dopant diffuses via interactions with point defects can be described by a set of reactions. First, there are the dopant/defect pairing reactions:

where P^+ represents ionized phosphorus atoms, I and V represent interstitials and vacancies, (PI) and (PV) represent dopant/defect pairs, and i represents the charge state of the defect or pair ($-$, 0 , $+$, etc.). Next, the recombination and generation of Frenkel pairs must be considered,

In addition, the pairs can interact directly with the opposite type defect to produce a reaction which is equivalent to a pair dissociation followed by defect recombination:

Finally, two opposite type pairs can recombine leaving two unpaired dopant atoms,

There are also ionization or charge exchange reactions for each of the charged species. Because electronic interactions are much faster than the atomic diffusion processes, we will assume that all of the ionization reactions are near equilibrium. Thus, for example, the concentrations of interstitials and phosphorus/interstitial pairs in the various charge states are given by

$$C_{I^i} \cong K_I^i \left(\frac{n_i}{n} \right)^i C_{I^0} \quad \text{and} \quad C_{(PI)^{i+1}} \cong K_{PI}^i \left(\frac{n_i}{n} \right)^i C_{(PI)^+}, \quad (5)$$

where the K 's represent equilibrium constants.

For our analysis, we assume that there is local charge neutrality and complete impurity ionization. We also ignore band-gap narrowing effects and use Boltzmann statistics. In addition, we assume that charged defects and pairs can be ignored in determining the Fermi level.

There are a couple of other simplifying assumptions which have been commonly made in the literature. First, it is often assumed that the dopant/defect pairing reactions are near equilibrium [5-9,14], which implies that

$$C_{(PI)^{i+1}} \cong K_{P/I}^i C_{P^+} C_{I^i} \cong K_{P/I}^i K_I^i \left(\frac{n_i}{n} \right)^i C_{P^+} C_{I^0}, \quad (6)$$

where $K_{P/I}^i$ is the equilibrium constant for the pairing of phosphorus with interstitials in charge state i (Equation(1)). An equivalent expression can be written for vacancy pairing. Another assumption sometimes used in modeling coupled diffusion is that the defect recombination reactions are also near equilibrium [6, 9, 12, 13],

$$C_I C_V \cong C_I^* C_V^*. \quad (7)$$

We will begin without making these last two assumptions and use the more general analysis to assess whether these assumptions appear to be justified given parameter values calculated from published experimental data.

Based on these reactions, we can write five continuity equations for the diffusion and reaction of substitutional dopants, interstitials, vacancies, dopant/interstitial pairs and dopant/vacancy pairs. The full set of equations are described in Reference [15]. There are a large number of parameters required to quantify the coupled dopant/defect system; however, many of the parameters can be

Table 1: Parameters used for 1000°C phosphorus diffusion simulations as determined from published experimental results.

Parameter	Value
D_I	$1.3 \times 10^{-7} \text{cm}^2/\text{s}$
D_V	$1.2 \times 10^{-9} \text{cm}^2/\text{s}$
C_I^* (intrinsic)	$2.3 \times 10^{13} \text{cm}^{-3}$
C_V^* (intrinsic)	$2.4 \times 10^{15} \text{cm}^{-3}$
$D_{(PI)^+} K_{P/I}^0 C_{I^0}^*$	$9.6 \times 10^{-15} \text{cm}^2/\text{s}$
$D_{(PI)^0} K_{P/I}^0 K_{PI}^- C_{I^0}^*$	$4.9 \times 10^{-15} \text{cm}^2/\text{s}$
K_I^+	0.53
K_I^-	0.06
K_V^+	0.09
K_V^-	1.52
$K_V^{\equiv}$	0.11

calculated based on previously reported experimental results. Table 1 summarizes the parameter values at 1000°C as determined from the literature.

Isoconcentration diffusion studies [16] were used to determine the dependence of the effective dopant diffusivity on Fermi level or electron concentration. Since the isoconcentration data do not allow us to determine the concentration of pairs and their diffusivities independently, we assume that the diffusivities of the pairs are independent of their charge state.

The relative importance of interstitial versus vacancy pair diffusion can be determined by experiments which use oxidation or nitridation to alter the point defect concentrations. From such experiments, it is found that phosphorus diffuses primarily via interstitial mechanisms under intrinsic conditions [2]. We will therefore neglect diffusion via phosphorus/vacancy pairs in our initial simulations, although diffusion with vacancies is likely to be more significant in heavily doped n -type material and is included in our simulations in Section 3.

The locations of defect charge states in the energy gap, which determine the relative numbers of defects in those states as a function of Fermi level, have been calculated for vacancies from electron paramagnetic resonance (EPR) studies [17] and for interstitials from enhanced diffusion in heavily doped material [18]. The defect energy levels can be used to calculate the equilibrium constants for the defect charging reactions which are given in Table 1 for 1000°C.

The values for the average diffusivity and equilibrium concentration of interstitials and vacancies in intrinsic material have been estimated based on analysis of metal diffusion and silicon self-diffusion [19, 20]. The values at 1000°C are listed in Table 1. Since there is no experimental determination of the relative diffusivities of the defects in different charge states, we assume the defect diffusivities to be independent of charge state.

In addition to these equilibrium parameters, we need kinetic parameters in order to consider nonequilibrium conditions. We can estimate forward reaction rate coefficients for each reaction from a simple kinetic approximation,

$$k_{AB} = 4\pi r(D_A + D_B) \exp\left(\frac{-\Delta E}{kT}\right), \quad (8)$$

where D_A and D_B are the diffusivities of the reactants and ΔE is the energy barrier for the reaction. As an example, for an interaction radius of $r \cong 5 \text{ \AA}$, the diffusion-limited recombination rate (no barrier) for Frenkel pairs would be $k_{I/V} \cong 8 \times 10^{-14} \text{ cm}^3/\text{s}$ at 1000°C .

Using the parameter values in Table 1, we solve the coupled diffusion of dopants defect and pairs numerically using PDECOL, a general partial differential equation solver from the ACM Algorithms Distribution Service [21]. For boundary conditions, we assume a constant phosphorus dose (no flux at surface) and assume that the surface regrowth velocity for both defects is large enough that $C_I \cong C_I^*$ and $C_V \cong C_V^*$ at $x = 0$.

We begin by considering the coupled diffusion of I^0 , V^0 , $(PI)^+$ and P^+ (a subset of the possible charge states) and the applicable parameters above. We assume that there is no barrier to defect recombination, dopant/defect pairing or dopant-mediated recombination and that the diffusivity of both defects and pairs is independent of charge state. We choose the equilibrium constant for the pairing reaction ($K_{P/I}^0$) such that $D_{(PI)} = D_I$. Figure 1 shows an example of the results of such a simulation for a 5 min diffusion at 1000°C . The resulting phosphorus profile manifests the characteristic kink as well as greatly enhanced diffusion in the tail region. The interstitial and vacancy concentrations are also shown and the interstitial enhancement in the bulk, which gives rise to base push effects is present.

We can also use this simulation to test whether it is appropriate to assume that the pairing reactions and/or recombination reactions are near equilibrium. Figure 1 also plots values of $C_{(PI)^+}/(C_{I^0}C_{P^+})$ and $C_{I^0}C_{V^0}$, which should be constant if the associated reactions are near equilibrium. It is clear that, for this system, the pairing reaction is very near local equilibrium for times of interest to VLSI fabrication, and thus that Equation (6) is valid. This relation remains valid even for the rate of the pairing reaction reduced by up to a factor of 100 below the diffusion limited value.

In contrast to the pairing reaction, even including pair/defect recombination (or dopant-mediated recombination) and assuming no barrier to recombination and fast surface recombination, the defect recombination process does not appear to be rapid enough to maintain local equilibrium between the defects. That is, Equation (7) does not hold as C_IC_V significantly exceeds $C_I^*C_V^*$ near the kink region where the gradient in dopant and defect concentrations is the greatest, which contradicts the assumption made by Morehead and Lever [6, 9] and Morris *et al.* [12] in their analysis.

3 Comparison to Experiment and Discussion

Since it appears that the dopant/defect pairing reaction is near equilibrium, we can reduce the number of differential equations and parameters needed to describe the system, solving just three continuity equations (for dopant, interstitials and vacancies). In the remainder of this work, the simulations will utilize this simplified model as implemented in a modified version of SUPREM IV [14].

Correctly modeling the changes in diffusion as a function of dose or surface concentrations is one of the most difficult challenges for high concentration diffusion modeling. In contrast to previous

Figure 1: Simulations of dopant and defect concentrations for simple coupled phosphorus diffusion model after 5 minutes at 1000°C. Normalized plots of $C_{(PI)}+ / C_{I^0}C_{P^+}$ and $C_{I^0}C_{V^0}$ are used to test whether the pairing and defect recombination reactions, respectively, are near local equilibrium. The initial dopant profile is included for reference.

comparisons of coupled diffusion models to experimental data [7-12], we compare our models to experimental profiles over the full range of surface concentrations from intrinsic to solid-solubility using a single set of parameters at each temperature considered.

There has been some disagreement over whether there is a large barrier to I/V recombination. Measurements of enhanced and retarded diffusion during oxidation have resulted in contradictory conclusions. Antoniadis and Moskowitz [22] found apparently slow recombination suggesting a large barrier, while more recent measurements by Guerrero *et al.* [23] suggest that there is at most a small barrier to recombination. We have shown in previous work [24], and it has also been observed by Richardson and Mulvaney [25] for a similar system, that relatively rapid I/V recombination (small or negligible barrier) is required in order for simulations to approximate experimental profiles.

Although observations of enhanced and retarded diffusion during oxidation and nitridation show that the diffusion of phosphorus in intrinsic material is dominated almost totally by interstitial mechanisms [2], the same is not necessarily true in heavily doped material. Phosphorus/vacancy pairs have been found to have an acceptor level well within the band gap [26, 27]. Since the number of negatively-charged pairs increases in proportion to the square of the electron concentration, diffusion via negatively-charged vacancy pairs may be dominant near solid-solubility, while contributing less than 2% to diffusion in lightly-doped material.

In order to test the simplified model for coupled diffusion, we conducted a series of simulations and compared the results to an extensive series of experimental data reported by Yoshida *et al.* [28, 29]

Table 2: Optimized parameters for phosphorus diffusion at 900 and 1000°C for the two model assumptions analyzed.

Parameter	Optimized Values			
	900°C		1000°C	
	No PV pairs	(PV) ⁻ pairs	No PV pairs	(PV) ⁻ pairs
$D_{(PI)^0} K_{P/I}^0 K_{PI}^- C_{I^0}^*$ (cm ² /s)	5.3×10^{-16}	7.0×10^{-16}	6.0×10^{-15}	5.4×10^{-15}
$D_{(PV)^-} K_{P/V}^0 K_{PV}^- C_{V^0}^*$ (cm ² /s)	—	1.1×10^{-17}	—	1.2×10^{-16}
$k_{I/V}$ (cm ³ /s)	1.3×10^{-14}	2.7×10^{-14}	3.3×10^{-14}	1.7×10^{-14}

and Matsumoto and Niimi [30]. The experimental profiles all resulted from diffusion from SiO₂ doped with various levels of phosphorus and produced surface concentrations that were constant with time. The doping profiles were all measured using differential conductivity and anodic oxidation.

Currently, published phosphorus isoconcentration data is insufficient to reliably determine the extent to which phosphorus diffuses with negatively-charged pairs and only at 1000°C is there even sufficient data to estimate the contribution due to neutral pairs. Therefore, the values of these parameters were chosen to best match the experimental data. In addition, since there is no accurate estimate of the bimolecular recombination rate, the effective rate of Frenkel pair recombination was also allowed to vary. These parameter values were determined by minimizing the difference between the simulated and measured profiles using a Levenberg-Marquardt optimization code (PROFILE [31]) and the results are summarized in Table 2. The rest of the parameters, including all point defect parameters and intrinsic diffusivities are based on the sources cited in Section 2.

Our first set of comparisons assumes that diffusion occurs only via positive and neutral interstitial pairs and that vacancy pairs can be neglected (Figures 2 and 3). This model is similar to that utilized in our previous work [24] and by Richardson and Mulvaney [10]. In both earlier works, a reasonable fit was obtained to a single profile by assuming rapid recombination, but the simulations significantly underestimated diffusion in the peak region. The problem is much more severe when fitting profiles over a range of peak concentrations, and it is clear from Figure 2 that without considering phosphorus/vacancy pairs, the coupled diffusion model is unable to account for the experimental results. Note that since the effective recombination rate was optimized to match the data, very fast recombination is insufficient to produce the experimentally-observed high concentration diffusion profiles in contrast to assertions made by Richardson and Mulvaney [25].

Figure 3 shows the effects of including diffusion via negatively-charged phosphorus/vacancy pairs. It is clear that the coupled diffusion model does an excellent job of matching the experimental results over the full range of doping levels.

We can make a number of observations from the simulation results. First, the values calculated for $D_{(PI)^0}$ at 1000°C are very similar to those derived from isoconcentration experiments [16] (Table 1), supporting the validity of the calculated parameters. Second, based on the parameters listed in Table 2, diffusion via (PV)⁻ pairs doesn't equal diffusion via (PI)⁰ pairs until the doping reaches 3

Figure 2: Active phosphorus concentration profiles based on simulations of diffusion at 900 and 1000°C, neglecting diffusion via PV pairs. Diffusion times are 4h at 900°C and 2h with the exception of the highest dose at 1000°C for which the diffusion time was 1h. The data is as reported by Yoshida *et al.* [28, 29] and Matsumoto and Niimi [30].

or $4 \times 10^{20} \text{ cm}^{-3}$ for the model which includes $(\text{PV})^-$ pairs. Third, the calculated values for effective recombination rate are quite similar to the diffusion-limited values estimated from Equation (8) ($1.3 \times 10^{-14} \text{ cm}^3/\text{s}$ at 900°C and $8 \times 10^{-14} \text{ cm}^3/\text{s}$ at 1000°C), which implies that there is little or no barrier to Frenkel pair recombination. The recombination rates are large enough to play an important role in determining the diffusion profiles, but as discussed in Section 2, are not large enough to maintain the Frenkel pair recombination reaction near equilibrium in regions of maximum dopant and defect gradient.

We can consider the role of the Frenkel pair recombination rate in more detail by trying to match this same data using a recombination rate which is fast enough to maintain $C_I C_V \cong C_I^* C_V^*$ throughout the bulk, even in the kink region. Using the model which includes negatively-charged phosphorus/vacancy pairs with constant pair diffusivity (which does an excellent job of matching the experimental data as shown in Figure 3), we increased the recombination rate by over two orders of magnitude (which was large enough so that the $C_I C_V$ product remained within 10% of the equilibrium product for all the profiles). As for previous simulations, the other parameters were optimized to best match the experimental data. It is clear from Figure 6, which shows the best fit for the 900°C data, that the deviation of $C_I C_V$ from $C_I^* C_V^*$ has a dramatic effect on the doping profiles and that it is not possible to match the experimental results using this model if the recombination rate is assumed to be very large. Just as neglecting bulk recombination greatly overestimated the tail diffusion [24], assuming very rapid defect recombination greatly underestimates the tail diffusion. By considering negatively-charged phosphorus/interstitial pairs instead of phosphorus/vacancy pairs, it is possible to generate profiles which manifest the characteristic kink and tail features while assuming fast bulk recombination. However, as for the model without

Figure 3: Active phosphorus concentration profiles based on simulations of diffusion at 900 and 1000°C, including diffusion via $(PV)^-$ pairs. The data is as reported by Yoshida *et al.* [28, 29] and Matsumoto and Niimi [30].

vacancy pairs shown in Figure 2, even with optimized parameters, the simulations do not correctly account for the changes in profile shape with doping concentration observed experimentally.

4 Conclusions

In this work, we have developed models for the coupled diffusion of dopants and point defects which can account quantitatively for phosphorus diffusion profiles over the full range of doping levels. Starting with a general model for the coupled dopant/defect system assuming that electronic, but not chemical, processes are near local equilibrium, we simulated the phosphorus system using published values of point defect and dopant parameters combined with estimates of the kinetic parameters. We found that the assumption that dopant/defect pairing reactions are near local equilibrium is justified, but that even with dopant-mediated recombination and with no barriers to recombination, point defect recombination is not fast enough to bring the interstitial and vacancy concentrations to near local equilibrium in regions of large dopant concentration gradient.

Utilizing our conclusion that the dopant/defect pairing reactions remain near equilibrium, we derived a simplified model which we compared to an extensive set of published experimental phosphorus diffusion profiles at 900 and 1000°C. We found that when we included diffusion via negatively-charged phosphorus/vacancy pairs, the model was able to account for the experimental data over the full range of peak doping concentrations, from intrinsic to solid-solubility.

In the analysis, the effective recombination rate for Frenkel pairs was used as an optimization parameter, and the best results were obtained for recombination rates that were similar to those estimated using a simple diffusion-limited kinetic approximation. This result is consistent with recent calculations of the recombination rate based on enhanced and retarded diffusion, which

Figure 4: Active phosphorus concentration profiles based on simulations of diffusion for 4h at 900°C, including diffusion via $(PV)^-$ pairs and assuming rapid bulk recombination so that $C_I C_V \cong C_I^* C_V^*$. The data is as reported by Yoshida *et al.* [28, 29] and Matsumoto and Niimi [30].

conclude that there is little or no barrier to recombination. Since a constant effective recombination rate was assumed, the results presented here may be improved by consideration of a concentration-dependent recombination rate arising from pair/defect reactions. We also found that using a much higher recombination rate, which was sufficient to keep $C_I C_V \cong C_I^* C_V^*$, resulted in simulated profiles which could not be reconciled with the experimental data.

In summary, the model considered in this paper correctly predicts the rapid diffusion in the peak region observed at high concentrations as well as the dependence of tail diffusion on peak doping level, while remaining consistent with experimental evidence that intrinsic phosphorus diffusion is dominated by interstitials. Since published values for point defect parameters and intrinsic diffusivity are used, the model also is consistent with the broad range of point defect related behavior observed in silicon and appears to have achieved the goal of developing a quantitative model for the coupled diffusion of phosphorus with point defects that is suitable for process simulation applications.

Acknowledgements

This work was supported by a SEMATECH Center of Excellence grant #90-MC-503 and NSF grant #ECS-9009591.

References

- [1] R. B. Fair, in *Semiconductor Silicon 1977*, ed. by H. R. Huff and E. Sirtl, Electrochemical Society, 968 (1977).

- [2] P. Fahey, G. Barbuscia, M. Moslehi and R. W. Dutton, *Appl. Phys. Lett.* **43**, 683 (1983).
- [3] P. Fahey, R. W. Dutton and S. M. Hu, *Appl. Phys. Lett.* **44**, 777 (1984).
- [4] K. Nishi and D. A. Antoniadis, *J. Appl. Phys.* **59**, 1117 (1986).
- [5] D. Mathiot and J. C. Pfister, *J. Appl. Phys.* **55**, 3518 (1984).
- [6] F. F. Morehead and R. F. Lever, *Appl. Phys. Lett.* **48**, 151 (1986).
- [7] B. Mulvaney and W. Richardson, *Appl. Phys. Lett.* **51**, 1439 (1987).
- [8] M. Orlowski, *Appl. Phys. Lett.* **53**, 1323 (1988).
- [9] F. F. Morehead and R. F. Lever, *J. Appl. Phys.* **66**, 151 (1989).
- [10] W. Richardson and B. Mulvaney, *J. Appl. Phys.* **65**, 2243 (1989).
- [11] B. Mulvaney and W. Richardson, *J. Appl. Phys.* **67**, 3197 (1989).
- [12] E. Rorris, R. R. O'Brien, F. F. Morehead, R. F. Lever, J. P. Peng and G. R. Srinivasan, *IEEE Trans. CAD* **9**, 1113 (1990).
- [13] D. Mathiot and S. Martin, *J. Appl. Phys.* **70**, 3071 (1991).
- [14] M. E. Law and R. W. Dutton, *IEEE Trans. CAD* **7**, 181 (1988).
- [15] S. T. Dunham, *J. Electrochem. Soc.* **139**, 2628 (1992).
- [16] J. S. Makris and B. J. Masters, *J. Electrochem. Soc.* **120**, 1253 (1973).
- [17] G. D. Watkins, in **Lattice Defects in Semiconductors 1974**, ed. by F. A. Huntley, Inst. Phys. Conf. Ser. 23, London, 1975.
- [18] M. D. Giles, *IEEE Trans. CAD* **8**, 460 (1989).
- [19] G. B. Bronner and J. D. Plummer, *J. Appl. Phys.* **61**, 5286 (1987).
- [20] T. Y. Tan and U. Gösele, *Appl. Phys.* **A37**, 1 (1985).
- [21] N. K. Madsen and R. F. Sincovec, *ACM Trans. Math. Soft.* **5**, 327 (1979).
- [22] D. A. Antoniadis and I. Moskowitz, *J. Appl. Phys.* **53**, 6788 (1982).
- [23] E. Guerrero, W. Jüngling, H. Pötzl, U. Gösele, M. Grasserbauer and G. Stingeder, *J. Electrochem. Soc.* **133**, 2181 (1986).
- [24] S. T. Dunham and R. A. Meade, in **Second International Symposium on Process Physics and Modeling in Semiconductor Technology**, G. Srinivasan, J. Plummer and S. Pantelides, eds. (Electrochem. Soc. Proc. **91-4**, Pennington, NJ, 1991) pp. 287-303.
- [25] W. Richardson and B. Mulvaney, *Appl. Phys. Lett.* **53**, 1917 (1988).
- [26] G. D. Watkins and J. W. Corbett, *Phys. Rev.* **134**, A1359 (1964).
- [27] L. C. Kimerling, *Inst. Phys. Conf. Ser.* **31**, 221 (1977).
- [28] M. Yoshida, *Jap. J. Appl. Phys.* **18**, 479 (1979).
- [29] M. Yoshida, E. Arai, H. Nakamura and Y. Terunuma, *J. Appl. Phys.* **45**, 1498 (1974).
- [30] S. Matsumoto and T. Niimi, *Jap. J. Appl. Phys.* **15**, 2077 (1976).
- [31] G. J. L. Ouwerling, *The PROFILE/PROF2D User's Manual*, Delft University of Technology, 1987.

EFFECTS OF D-DEFECTS IN CZ SILICON UPON THIN GATE OXIDE INTEGRITY

S. Hahn¹, J.-G. Park², S.-P. Choi², G.-S. Lee², Y.-J. Jeong², Y.-S. Kwak², C.-K. Shin², W.L. Smith³, and P. Mascher⁴

1. Department of Materials Science and Engineering
Stanford University, Stanford, CA 94305, USA
Tel (415) 723-3268
Fax (415) 725-4034
2. Samsung Electronics, Quality Control Division
Kihung Plant, Kihung, Kyungki-do, Korea
3. Therma-Wave, Inc. 47320 Mission Falls Court
Fremont, CA 94539, USA
4. Department of Engineering Physics, McMaster University
Hamilton, Ontario, Canada L8S 4M1

ABSTRACT

In this study, using oxide breakdown voltage and time-dependent-dielectric breakdown measurements, thermal wave modulated reflectance (both mapping and imaging modes), positron annihilation spectroscopy and chemical etching/optical microscopy, we investigated:

- o effects of D-defects upon oxide integrity
- o possible oxide breakdown mechanism due to D-defects, and
- o nature of D-defects.

Our data show that: (1) D-defects in the Si substrate affect both oxide breakdown voltage and time-dependent-dielectric breakdown characteristics of thin gate oxide; (2) D-defects can induce rough Si/SiO₂ interfaces during various DRAM processes - an increase in the interface roughness is the main cause for poor oxide integrity; (3) the variation of monovacancy-type defects with respect to the high temperature thermal annealing closely matches that of D-defects; and (4) D-defects are not of an interstitial nature and are possibly vacancy-related.

INTRODUCTION

Since particles on Si wafer degrade VLSI device performance, many efforts have been made to reduce the number of particles. The minimum size of the particles to be eliminated has been related to the linewidth of the VLSI devices. It has been supposed that the particles counted by widely used laser particle counters are dust on the wafers. Therefore, the cleaning process of wafers has been studied mainly to find the ways to remove the particles. The SC1 cleaning [1] (cleaning by NH₄OH/H₂O₂/H₂O chemical mixture solution) is known to be effective in reducing the amount of dust. However, J. Ryuta and coworkers have recently claimed that most of the small particles left after the SC1 cleaning cycles are not dust on the wafers but pits formed during the SC1 cleaning [2]. It is suggested that such pits originate from some grown-in defects in the Si crystals. These grown-in defects (called "COP," meaning cystal-originated particles) have been shown to affect the thin gate oxide integrity [2]. Since these defects are induced during solidification process, various researchers

believe they are point defect clusters. Point defects in silicon single crystals have been studied very extensively; two types of crystal defects are well known, namely, A- and D-defects. A-defects were reported as silicon interstitial dislocation loops by transmission electron microscopy (TEM) observation [3]. In contrast, it is difficult to confirm the composition of D-defects. Abe recently investigated such defects in detail by a technique involving inner diffusions of vacancies or of interstitial silicon atoms after annealing in various kinds of ambient [4]. He reported that D-defects contained a vacancy agglomerate. However, these point defects cannot be recognized directly. A copper decoration method is usually used, but the content of the point defects can change during annealing around 1273°K; it is very difficult to count their densities. Yamagashi and coworkers reported developing the preferential etching method to delineate D-defects without involving a heat treatment at high temperature [5]. They claimed that:

- o D-defects appeared as "flow patterns" after the preferential etching treatment.
- o D-defects affect oxide integrity; higher defect density leads to lower average breakdown voltage and poorer time-dependent-dielectric breakdown characteristics.
- o D-defect density depends upon crystal pull rate; the higher the crystal pull rate, the higher the defect density.
- o D-defect density and COP density are linearly correlated.

EXPERIMENTAL

The samples used in this investigation were p-type (res., ~5 ohm-cm), (100)-oriented, 150 mm diameter Cz Si wafers with interstitial oxygen concentration, O_i , of (12.5 ± 0.5) ppma (ASTM F121-81). Carbon concentration, C_g , of these wafers was typically below instrument sensitivity limit ($\leq$ 0.05 ppma). In order to investigate effects of D-defects upon thin gate oxide integrity, two different types of experiments were carried out in this study, namely, Test I and Test II.

In Test I, we used only the wafers specially prepared by one specific commercial material supplier. These wafers were chosen from four ingots grown with four different average pull speeds (0.4, 0.5, 0.55 and 1 mm/min, respectively). After modified RCA cleaning, as-received wafers were submitted into Mb DRAM processes. Subsequently, the wafers were further processed with gate oxidation (oxide thickness ~23 nm), polysilicon deposition, $POCl_3$ diffusion and patterning to fabricate test device structures for gate oxide integrity test. Both oxide breakdown voltage and time-dependent dielectric breakdown characteristics were measured with HP 4142 B Semiconductor Device Analyzer. After the oxide integrity test, these device structures were further characterized by using emission microscope for multilayer inspection (EMMI) and a focus ion beam system (FIB). Finally, these samples were preferentially etched to observe flow pattern defects with Secco etchant for 30 min.

In Test II, the wafers from four commercial wafer vendors (Vendors A, B, C, and D) were used. First, some of the as-received wafers were tested with Secco etching for 30 min. to determine the flow pattern defect density, and with PAS lifetime method to determine the various vacancy-related defect lifetime signatures inside the bulk of the samples. The remainder of as-received wafers was annealed at 1200°C for 2 h in O_2 diluted with N_2 ambients. The annealed wafers were characterized by both Secco etching and PAS lifetime methods in order to get potential correlations between flow pattern defects and vacancy-related defects.

The positron lifetime spectra were obtained using state of the art spectrometers with time resolution FWHM of between 205 and 230 ps. Each spectrum contained at least 6×10^6 counts. The positron sources were rather weak, typically $3.5 \mu C_i$ of $^{22}NaCl$, deposited on thin (1-3 μm) Al-foil. Numerical analysis of the lifetime data was performed using the programs PATFIT 88 [6] or PFPOSFIT [7];

agreement of results on test spectra was always found to be within statistical uncertainty. After correlation for annihilations in the Al-foil and the NaCl itself, all of the spectra contained three lifetime components, the longest of which, however, was an essentially constant term of about 1.5 ns with no more than 0.3% intensity. This term could easily be separated from the actual spectra, leaving two significant terms from the samples themselves.

RESULTS AND DISCUSSION

1. Effects of Crystal Pull Rate Upon Oxide Integrity

Figs. 1 and 2 show effects of crystal growth rate upon average oxide breakdown field strength, oxide breakdown yield and time-dependent-dielectric breakdown (TDDB) characteristics. In Fig. 1, the breakdown yield is defined as the percentage of MOS devices whose breakdown field strength is larger than 6 MV/cm. Both figures clearly demonstrate that wafers from the ingot grown with fast pull speed growth program exhibit poorer oxide integrity compared to those from the crystal grown by slow pull speed growth program.

2. Oxide Breakdown Mechanism Due to D-Defects

Miyashita and coworkers [8] recently reported that there are two types of surface microdefect clusters, namely, undecorated and metal-decorated clusters, and that only metal-decorated surface microdefect clusters can act as weak spots in oxide, thus contributing to low oxide breakdown distribution. Our experience during this investigation shows that a big drop in average oxide breakdown field strength (≥ 3 -4 MV/cm) is generally observed whenever there are line problems due to metallic impurities, whereas rather small changes in the breakdown field strength (at most 1-1 1/2 MV/cm) occur due to D-defects. Therefore, we believe the degradation in oxide integrity due to D-defects is not likely caused by metal decoration.

In this study, using both EMMI and FIB, we further characterized defect morphologies which cause the B-mode breakdown failure. Cross section SEM micrograph displays that almost all the D-defects induced oxide failures are originated from etch pits. Based upon these experimental data, the D-defect induced oxide breakdown mechanism can be considered as follows. D-defects create shallow etch pits on wafer surface during DRAM processes that include various etching and oxidation steps. These etch pits degrade interface roughness between Si and SiO₂. The rough surface causes accelerated local field concentration at the edge of etch pits under the biased voltage, which in turn leads to B-mode type oxide failures (Fig. 3).

3. Nature of D-Defects

As described in the Experimental Section above, both as-received and high temperature (at 1200°C for 2h in O₂ diluted with N₂ ambients) annealed wafers from four different commercial material supplies were further analyzed by both thermal waver imager and PAS lifetime method. After both thermal wave imager and PAS lifetime measurements, we etched off 60 μm of wafer surface layer by the mixed etchant, and the flow pattern defect density was measured via the preferential etching procedure.

In PAS lifetime measurement, two types of positron lifetimes have been observed for all the wafers, both as-received and annealed (besides 218±2 ps characteristic lifetime from perfect Si lattice).

One type is shorter lifetime ($\tau_1 = 113 \pm 15$ ps), which has been reported to be associated with positrons

trapped at interstitial-type clusters (some researchers call these defects "oxygen-related defects" [9]. The intensity of this lifetime component is rather small ($I_1 = 6.13\%$) and does not change significantly, even after the anneal at 1200°C .

Another type is longer lifetime ($\tau_2 = 273$ ps), which is known to be associated with positrons trapped at monovacancy-type defect clusters. The intensity variation of this lifetime component due to the high temperature anneal at 1200°C for the wafers from the four commercial Si material vendors A, B, C, and D is shown in Fig. 4. In addition, we also include the variation of flow pattern defect density due to the same high temperature anneal as a comparison. The data in Fig. 4 show that high temperature anneal affects monovacancy-type defect (τ_2) component intensity. A substantial decrease in τ_2 -component intensity was observed for the wafers from Vendors A and B, whereas a small decrease or no recognizable changes in τ_2 -component intensity was observed for the wafers from Vendors C and D. In addition, interesting correlations between τ_2 -component intensity and D-defect density have been observed. A big drop in τ_2 -component intensity corresponds to a large reduction in D-defect density, whereas a small change in τ_2 -component intensity leads to a small change in D-defect density. The real causes for this interesting difference in defect behavior among four commercial vendors have not been completely understood. One possibility is a difference in the crystal growth procedure (and subsequent thermal anneal procedures) used. Subsequent TW imager measurements for these samples show that TW image data for the wafers with high D-defect density generally contain numerous dark TW defects, indicating that the recombination time [of the electron-hole (e-h) pairs injected by the laser in the TW apparatus] is greater at the dark defect sites than it is in the surrounding regular Si lattice. We note that these dark defect images are distributed inhomogeneously. We also note that some defects are bright instead of dark. It is believed from previous other studies [8] that the higher-than-background TW signal results from strong e-h recombination at D-defects that are metal-contaminated. Additional studies are under way to confirm this effect.

The PAS observation of longer lifetime in the presence of D-defects is important to explain the characteristic dark appearance of the D-defects in the TW image. No other Si defects have ever been observed to exhibit lower-than-background TW signal, consistent with the unique increase in e-h lifetime at the D-defect site. All other known Si defects cause decreased e-h lifetime and correspondingly high-than-background TW signal.

Therefore, based upon both PAS lifetime and preliminary TW dark defect image data, we infer that D-defects are not interstitial defect clusters but vacancy-type defect clusters.

SUMMARY

In this study, using oxide breakdown voltage and time-dependent-dielectric breakdown measurements, thermal wave imaging, positron annihilation spectroscopy and chemical etching/optical microscopy, we investigated:

- o effects of D-defects upon oxide integrity
- o possible oxide breakdown mechanism due to D-defects
- o nature of D-defects

Our experimental data show that

1. the crystal pull rate affects both oxide breakdown field strength (related to the B-mode type failures) and time-dependent-dielectric breakdown characteristics of thin gate oxide. The

degradation of these device characteristics is caused by D-defects in the Si substrate;

2. D-defects can induce rough Si/SiO₂ interfaces during various DRAM processes. An increase in the interface roughness accelerates the local field stress concentration and eventually leads to lower breakdown field strength and poor time-dependent-dielectric breakdown characteristics;
3. thermal annealing at 1200°C for 2h in O₂ diluted by N₂ atmosphere decreases the D-defect density and the concentration of monovacancy-type defects (by positron annihilation spectroscopy lifetime technique). The variation of monovacancy-type defects with respect to the high temperature thermal annealing closely matches the D-defects; and
4. both thermal wave imaging and positron annihilation spectroscopy data indicate that D-defects are not of interstitial nature, and allows us to infer that the D-defects are vacancy-related defects.

REFERENCES

1. W. Kern and D.A. Puotinen, *RCA Rev.* 31:207 (1970).
2. J. Ryuta, E. Morita, T. Tanaka, and Y. Shimanuki, *Jpn J. Appl. Phys.* 29:L1947 (1990).
3. H. Föll, U. Gösele, and B.O. Kolbesen, in: "Semiconductor Silicon 1977," H. R. Huff and E. Sirtl, eds., Electrochemical Society, Princeton (1977), p. 565.
4. T. Abe, *Ohyo Butsuri* 59:272 (1990) [in Japanese].
5. H. Yamagishi, I. Fusegawa, N. Fujimaki, and M. Katayama, *Semicond. Sci. Technol.* 7:A135 (1992).
6. P. Kirkegaard, N.J. Pedersen, and M. Eldrop, RISO-M-2740, Riso National Laboratory 1989, DK-4000 Roskilde, Denmark.
7. W. Puff, *Comput. Phys. Commun.* 30:359 (1983).
8. M. Miyashita, H. Hiratsuka, and Y. Matshushita, in: "Defects in Silicon-II," ECS PV 91-6, W. M. Bullis, F. Shimura, and U. Gösele, eds., Pennington, NJ (1991), p. 407.
9. S. Dannefaer and D. Kerr, *J. Appl. Phys.* 60:1313 (1986).

Fig. 1 Effects of crystal pull rate upon average oxide breakdown field strength and MOS oxide breakdown yield.

Fig. 2 Effects of crystal pull rate upon time-dependent-dielectric breakdown.

Fig. 3 Oxide breakdown mechanism due to D-defects.

Fig. 4 Intensity variation of monovacancy-type defect component by PAS lifetime method due to high temperature anneal at 1200°C for the wafers from the four commercial Si material vendors A, B, C, and D. In addition, the variation of flow pattern defect density due to the same high temperature thermal anneal is shown.

POINT DEFECTS, CARBON AND MICRODEFECTS IN EFG SILICON

J. P. Kalejs
Mobil Solar Energy Corporation
4 Suburban Park Drive, Billerica, MA 01821, USA

Microdefect formation conditions in polycrystalline silicon grown by the Edge-defined Film-fed Growth (EFG) are compared to those for FZ and cast polycrystalline silicon. Models are reviewed for microdefect formation and the role of intrinsic point defect participation with carbon to form carbon-related and vacancy-based microdefects in the as-grown EFG silicon lattice is discussed.

1. Introduction

Polycrystalline silicon, grown for use in low-cost solar cell manufacture by ingot casting, i.e., directional solidification, and in sheet (ribbon) form, contains a variety of defects, dislocations, grain boundaries and twins, as well as high levels of carbon [1]. These are inhomogeneously distributed, and greatly complicate the study the influence of point defects on material structure and properties. Information on point defects in the as-grown crystal is commonly deduced from the study of etch pits and Cu decoration [2,3]. The most ubiquitous microdefects, the B- and D-defects, cannot usually be imaged in transmission electron microscopy. Their role in governing material electronic properties is indirectly inferred from study of material responses in high temperature processing [4].

The EFG solidification process imposes conditions on defect formation which differ from those in most other silicon growth techniques [5]. Sheet thicknesses can be as low as 200-400 microns, the interface temperature gradients are very high (~1000 C/cm) and cooling rates are extremely rapid, and the melt is supersaturated in carbon. Interstitial oxygen levels can be varied from below the detection level to about $1 \times 10^{17}/\text{cm}^3$. Crystal growth parameters affecting microdefect formation for EFG are contrasted to other silicon melt growth techniques in Table 1. The consequences of constraints placed on microdefect formation by these crystal growth factors are reviewed in this paper, and formation mechanisms for microdefects examined. Experimental evidence supporting these microdefect models for EFG silicon was presented previously [6].

2. Crystal Growth Variables

This section highlights the role of the critical crystal growth parameters listed in Table 1 that are known to impact on microdefect formation processes.

Table 1. Comparison of Growth Variable Ranges for Single Crystal FZ and Polycrystalline Ingot Cast Silicon
Silicon With EFG Silicon Sheet

<u>Variable</u>	<u>FZ Silicon</u>	<u>Ingot Cast Silicon</u>	<u>EFG Silicon</u>
Growth Speed V (cm/min)	0.02-1.0	0.1-0.5	2
Interface Temp. Gradient G (°C/cm)	300	200	1000
Interface Cooling Rate VG (°C-min)	6-300	20-100	2000
V/G (cm ² /°C-min)	6x10 ⁻⁵ - 3x10 ⁻³	5x10 ⁻⁴ - 2.5x10 ⁻³	1x10 ⁻³
MicroDefect Regimes			
B-Swirls (low carbon) (cm ² /°C-min)	$1 \times 10^{-4} \leq \frac{V}{G} \leq 1.3 \times 10^{-3}$		
D-Defects (low carbon) (cm ² /°C-min)	$\frac{V}{G} > 2 \times 10^{-3}$		
Substitutional Carbon C _S (at/cc)	$\leq 1 \times 10^{16}$	$\sim 1-5 \times 10^{17}$	$\sim 1 \times 10^{18}$
Interstitial Oxygen O _I (at/cc)	$\leq 1 \times 10^{16}$	$\sim 5-10 \times 10^{17}$	$\leq 1 \times 10^{17}$
C _S /O _I Ratio	~ 1	0.1-1	≥ 10

The EFG process has an order of magnitude higher cooling rate, VG, than other growth techniques, and this scales down denuded zone size, proportional to (VG)⁻¹, both near the sheet surfaces and also around extended defects such as dislocations or grain boundaries. In spite of the close proximity of crystal surfaces and higher densities of extended defects, microdefects and dislocations can be clearly distinguished from one another by etch pit size [6]. They coexist on length scales of the order of a few microns to support the validity of the above scaling law for denuded zone dimensions.

The ratio V/G is comparable for all of the techniques listed in Table 1. Microdefect patterns in FZ growth change with increasing V/G, from swirl-like formations for the B-swirls to a homogeneous distribution in the case of D-defects [3]. There is a gap in V/G values between the B-swirl and D-defect growth regimes. A considerable body of empirical evidence has been obtained [3,4] to argue for assignments of different types of point defects to these microdefects - Si_I for B-swirls and Si_V for D-defects.

The third important factor which influences the microdefect formation regimes in FZ silicon is the carbon concentration. The maximum V/G to which the B-swirl regime extends increases with increasing carbon concentration and the limiting V/G values given in Table 1 shift to higher magnitudes [3]. This is attributed to an increase of Si_I supersaturation caused by the carbon and to decreases in the temperature gradient. The latter increases the cooling duration and allows more annealing time to promote agglomerate dissolution and excess point defect annihilation. The carbon concentrations investigated in FZ growth span a limited and comparatively low range, from 1×10^{15} to $3 \times 10^{16}/\text{cm}^3$, and there is no data for higher carbon levels. The supersaturated carbon levels in EFG sheet, up to $1 \times 10^{18}/\text{cm}^3$, must be expected to play a dominant role in affecting point defect equilibria and microdefect formation. Perhaps on account of the very high carbon levels, a speed dependence for microdefect formation in EFG material has not been observed.

3. Microdefect Considerations

The basis of arguments supporting one prominent model [2,3] for microdefect formation processes is the assumption that excess Si_I are generated in the initial stages of crystallization of a perfect silicon lattice just below the freezing temperature. This Si_I supersaturation decays as the crystal cools. Under some conditions it is argued [3] that this decrease is rapid enough such that at intermediate cooling temperatures, say in the range of 1000-1100 C, the Si_I and Si_V concentration profiles cross and that vacancies become the dominant point defects in the crystal at room temperature. Hence, the observed disappearance of B-swirls and onset of D-defect formation as V/G increases in FZ crystals is a consequence of an accelerated decay of the Si_I supersaturation, and replacement by Si_V as the dominant point defect. Carbon and SiC precipitation influence Si_I and Si_V concentrations, both during growth and in post-growth annealing, in opposing ways. Substitutional carbon contracts the lattice and generates Si_I , while precipitation of carbon as SiC requires Si_I .

The central finding of experimental studies investigating point defect behavior in EFG silicon [6] is that the as-grown EFG lattice responds as if it contains excess sinks for Si_I . A model that is consistent with these experimental studies and with the known constraining factors from crystal growth requires that these excess trapping centers for Si_I are present already in the high temperature stage for EFG. Carbon-based defects, formed at solidification or immediately after, are proposed as the sites that will accelerate depletion of an initially large Si_I supersaturation in EFG silicon during cooling. This will hasten the onset of vacancy domination, and achieve Si_I undersaturation in the EFG lattice already at high temperatures, similarly to

that proposed for FZ crystals rich in D-defects [3]. Evolution of several types of microdefects then proceeds in parallel in EFG as the crystal cools: either at sites which continue to act as traps for Si_I , or through agglomeration processes at other available nucleation sites, e.g., dislocation cores, carbon-oxygen and multivacancy complexes. This results in a lattice which contains both carbon-based microdefects and the D-defects, and these defects contribute toward the shallow etch pit densities observed in as-grown EFG material. It is not ruled out that Si_I -rich agglomerates formed at the carbon-based microdefect sites in EFG silicon are not also the B-swirls common to FZ silicon.

The results from platinum and gold diffusion, as well as from positron annihilation experiments provide limits to vacancy and vacancy-cluster type microdefect concentrations in silicon. Platinum recombines with single vacancies only, and does not give information on vacancy clusters. This approach suggests an upper bound to the single vacancy concentration is about $1 \times 10^{12}/\text{cm}^3$ for EFG silicon. Positron annihilation [7] is sensitive to total numbers of vacancies, hence is more suitable for detecting clusters, and has an estimated lower limit of detection of 10^{14} to $10^{15}/\text{cm}^3$. These limits bracket a range of total vacancy concentrations that are consistent with the etch pit counts observed in EFG silicon crystals, which are typically in the range of 10^7 - $10^8/\text{cm}^3$. For an etch pit density near the maximum observable, $10^9/\text{cm}^3$, for example, the total vacancy concentration would range from $10^9/\text{cm}^3$ if the pits contained single vacancies, to $10^{13}/\text{cm}^3$ if they were to contain 10^4 vacancies per cluster.

Acknowledgements

I would like to thank W.D. Sawyer of Mobil Solar, and H. Zimmermann of Duke University, for providing details of preliminary results on positron annihilation and platinum diffusion, respectively, prior to publication.

References

- [1] See papers in Silicon Processing for Photovoltaics, Volumes I and II, edited by C.P. Khattak and K.V. Ravi (Elsevier, Amsterdam, 1987).
- [2] H. Foell, U. Goesele and B.O. Kolbesen, J. Crystal Growth 52, 907(1977).
- [3] P.J. Roksnoer, J. Crystal Growth 68, 596(1984).
- [4] T. Abe and M. Kimura, in Semiconductor Silicon 1990, edited by H.R. Huff, K.G. Barraclough and J. Chikawa (Electrochemical Soc., Pennington, 1990), p. 105.
- [5] J.P. Kalejs in Ref.[1], Volume II, Ch 4.
- [6] J.P. Kalejs, J. of Crystal Growth (in press) 1992.
- [7] W.D. Sawyer, private communication.

Mechanisms of Gettering by Extended Defects, by P and by Al

T. Y. Tan and U. M. Gösele

Department of Mechanical Engineering and Materials Science
Duke University, NC 27708-0300

Introduction

Gettering in Si serves the purpose of removing unwanted metallic impurities from the device active regions. When existing in Si in atomic form, metallic impurities are minority carrier recombination-generation centers which, via shortening of carrier lifetimes, decrease the efficiency of photovoltaic devices and increase the leakage current of switching/memory transistors in integrated circuits (IC). In an excessive amount, metals serve to nucleate extended defects (mainly oxidation-induced stacking faults) in fabricating IC using single crystal Si, and then in turn precipitate out as silicides which give rise to extremely large leakage current to cause the devices to fail. Modern Czochralski (CZ) Si contain only minute amount of metals that are actually not harmful to devices. Thus, if the IC processing is truly clean, there shall be no need for gettering. Since such a clean state is extremely difficult and expensive to attain, gettering is a more practical way of improving IC fabrication leakage limited yield. For photovoltaic devices, the cost requirement is even more stringent. Therefore, gettering appears to be an attractive alternative to improve the materials quality and the device efficiency. However, because of the already high contamination level in the low cost solar cell grade Si materials, the requirements on gettering may be even more stringent than that in IC fabrications. In this paper we provide a brief description of mechanisms of gettering, mainly with knowledge obtained from IC processing.

Metal Atom Segregation

In using gettering, a gettered and a gettering region must be both present. The gettered region is the device active region from which the unwanted metallic impurity atoms must be removed. The gettering region, positioned adjacent to the gettered region, is where the metal atoms will be moved to and stabilized at. During IC device operation, the gettering region may either still be present or removed. For solar cell operations, the gettering regions should probably be removed beforehand.

The most fundamental physical basis of gettering is the segregation property of the metallic atoms in the gettering and gettered regions. Let the *effective* Gibbs free energy of incorporating a metal atom M in the device active Si region be $g_M^f(\text{Si})$ and that in the gettering region be $g_M^f(\text{G})$, the thermal equilibrium concentrations of M in the two regions satisfy

$$\frac{C_M^{\text{eq}}(\text{Si})}{C_M^{\text{eq}}(\text{G})} = \exp \left[- \frac{g_M^{\text{eq}}(\text{Si}) - g_M^{\text{eq}}(\text{G})}{k_B T} \right], \quad (1)$$

where k_B is Boltzmann's constant and T is the absolute temperature. The physical meaning of Eq. (1) is that, in thermal equilibrium, the M concentration in the gettered region (Si) will be substantially smaller than that in the gettering region (G) for the condition

$$g_M^f(\text{Si}) \gg g_M^f(\text{G}) \quad (2)$$

holding. Note that, provided a steady state is reached, Eq. (1) also holds for M concentrations being undersaturated or supersaturated. During the gettering process, the flow of M atoms is from the gettered region to the gettering region.

Equation (1) points out whether the gettering process can be effective on an energetic basis. The actual gettering process is a dynamic one in which kinetic factors are also involved. For example, M segregation relies on M diffusion. Thus, it will be easier to getter interstitial M species, M_i , because of their high diffusivity; very difficult to getter substitutional M species, M_s , because of their low diffusivity, or precipitated M species, M_p , because they are not mobile and hence a precipitate dissolution process must also be involved; and somewhat in between for an interstitial-substitutional (i-s) M species, M_i - M_s , for which the slow moving M_s species may be converted to the fast moving M_i species. Therefore, because of the inherent differences in the behaviors of the different M species, there shall be no universal gettering scheme. For example, defect based gettering schemes¹ have been found to be effective in gettering unintentionally introduced impurities Fe, Ni, Cu, etc. in IC fabrications but not in gettering the i-s species Au already introduced into Si. On the other hand, P indiffusion gettering is more effective for Au but not for Fe, Ni, Cu, etc.

Gettering by Extended Defects

Gettering by creating the extended defects dislocations and some form of precipitates in device inactive Si regions,¹ in particular that of intrinsic gettering,² is a part of standard IC fabrication processes for gettering unintentionally introduced Fe, Ni, Cu, etc. These impurities are i species and therefore diffuse fast, so that there do not appear to be a kinetic barrier preventing their being gettered at the appropriate gettering sites. However, it has been shown that, during the gettering annealing, for Fe there is no preferential segregation to the intrinsic gettering sites created.³ This indicates that $g_M^{\text{eq}}(\text{Si}) \approx g_M^{\text{eq}}(\text{G})$ holds for Fe_i at high temperatures. During cooling after annealing, however, Fe precipitates form at the gettering sites, i.e., there is an effective satisfaction of Eq. (2).

Gettering by P

P indiffusion provides the most effective way to getter an already incorporated i-s species, e.g., Au,⁴ which occurs at the annealing temperature, apparently for two reasons. First, in the heavily P doped region,

where V^- is a negatively charged Si vacancy (which populates the P diffused region in abundance), appears as a very effective process for stabilizing Au atoms in the P diffused region (the gettering region) because $g_{\text{Au}_i}^f \gg g_{\text{Au}_s}^f$ holds, i.e., Eq.(2) satisfies. Second, P indiffusion to a high concentration injects Si self-interstitials (I) into the gettered regions.⁵ Via the reaction

the Au_s atoms in the gettered region are quite effectively turned into Au_i atoms which then migrate rapidly to the gettering region to be stabilized according to reaction (3).

For an i-s species similar to Au but already in precipitated form, ASi, it is expected that P indiffusion may also provide the driving force for the precipitate dissolution:

wherein it is assumed that the process does not encounter a large volume change issue.

Gettering by Al (also by Sn?)

It seems that gettering by Al will be most effective above 577°C, the Eutectic temperature (T_e) of the Al-Si system. Above T_e , Al exists in two (or one) liquid Al-Si solutions for which the solubility of a M species is a few tens percent of the total weight or number of atoms of the solution. Consider that the typical M solubility in Si at the gettering temperature should probably be on the order of ppm, the value of Eq. (1) is on the order of 10^{-5} . This provides a tremendously large driving force for M to be segregated into the liquid Al-Si solution, provided that the M atoms are fast moving species, e.g., an i species. Below 577°C, Al and Si form a solid solution in which the Cu, Ni, and Fe solid solubilities is typically ~0.05%. Though somewhat smaller than those in the liquid Al-Si solutions, this M solubility value still is a factor very much in favor of M being segregated out into the Al (solid) solution.

It is interesting to mention, in analogy to Al, also the possibility of using Sn for gettering purposes. Tin forms a simple Eutectic system with Si with T_e of 232°C, thereby allowing gettering to proceed at a temperature lower than that of using Al. The M solubility situation in the Sn-Si liquid solution is quite similar to that of the Al-Si case.

Conclusions

Gettering in Si relies upon the impurity atom segregation phenomenon. Because of the different nature of the impurities and the gettering methods, there are some fundamental differences. Consequently, in order to apply the most effective gettering scheme, the nature of the metallic species must be first determined. There is no universal gettering scheme.

1. *Impurity Diffusion and Gettering in Silicon*, Mater. Res. Soc. Proc. vol. 36 (Mater. Res. Soc., Pittsburgh, Pa, 1985).
2. T. Y. Tan, E. E. Gardner, and W. K. Tice, *Apl. Phys. Lett.* 30, 175 (1977).
3. D. Gilles, E. Weber, and S. Hahn, *Phys. Rev. Lett.* 64, 196 (1960).
4. D. Lecrosnier, J. Paugam, G. Pelous, F. Richov, and M. Salvi, *J. Appl.* 52, 5090 (1981).
5. F. F. Morehead and R. F. Lever, *Appl. Phys. Lett.* 48, 151 (1986).

IMPURITY ANALYSIS OF SILICON BY SPV METHOD

J. Lagowski, M. Dexter and P. Edelman
Center for Microelectronics Research
University of South Florida
Tampa, FL 33620

Abstract

Surface photovoltage (SPV) minority carrier diffusion length measurements have been utilized for more than three decades in the monitoring of recombination center defects in semiconductors. Recent refinements extend this low excitation level technique to long diffusion lengths larger than the wafer thickness. Corresponding sensitivity for a non-contact, no wafer preparation measurement of metal impurities is 10^9 atoms/cm³. A metal identification procedure is discussed for iron and chromium in B-doped p-type silicon. The procedure is based on differences in thermal and optical dissociation of Fe-B and Cr-B pairs.

Introduction

Transition metals dissolved in silicon introduce deep level recombination centers which degrade the minority carrier diffusion length, L , and affect certain bipolar devices [1]. In the form of precipitates, metals can cause localized leakers and gate oxide breakdown which is of special concern in sub-micron VLSI technology [2]. In $0.5\ \mu\text{m}$ technology, the corresponding limits for Fe, the most common metal impurity, are 10^{10} atoms/cm² on the surface and 2×10^{11} atoms/cm³ in the bulk [2].

Monitoring of metals at such low concentrations is not a simple issue. To meet the demands of the IC fab environment, monitoring must be done in a very fast, non-contact manner in which no wafer preparation is needed [2]. This rules out the use of analytical techniques as well as Deep Level Transient Spectroscopy (DLTS). Minority carrier recombination lifetime measuring techniques have been employed for this purpose. Among them, the SPV method for non-contact diffusion length measurement [3,4] has attracted a great deal of attention as a quantitative method operating at a low excitation level limit and separating the bulk recombination lifetime, τ , from the surface recombination, S .

We outline two aspects of SPV especially relevant to the analysis of metal impurities: (1) the extension to L values larger than the wafer thickness which shifts the SPV metal detection limit in wafers down to 10^9 atoms/cm³; and (2) a metal (Fe and Cr) identification procedure. Details of the SPV apparatus and probe arrangement for non-contact measurements are available in Reference 4. The present discussion uses, as an example, the case of p-type silicon, thus, electrons are the minority carriers.

SPV Measurement of Large L Values

Surface photovoltage, ΔV , is a change of the surface potential barrier under illumination. The surface depletion region commonly present on p-type silicon wafers constitutes a preferable condition. Illumination produces excess minority carriers which accumulate in the surface space charge region and/or are trapped by the surface states. Rigorous theoretical treatment is available [5,6] for "small signal" SPV whereby ΔV is much lower than $kT/q \approx 26$ mV at room temperature. In an experimental arrangement, the incident photon flux, ϕ , of the monochromatic light is pulsed by a chopper with a frequency, ω . This creates, in the wafer, a corresponding AC signal of excess minority carriers near the surface, $\Delta n(t)$, and of the SPV $\Delta V(t)$ as shown in Figure 1. This AC signal is picked up by a semi-transparent pick-up electrode capacitively coupled and, therefore, not in contact with the wafer. By reducing the magnitude of the photon flux, the small signal SPV range is reached whereby ΔV is directly proportional to ϕ . As shown in Figure 2, the photon flux in this range is typically below 10^{13} photons/cm²s. Corresponding excess minority carrier density, Δn , is as low as 10^9 cm⁻³.

Figure 1

Figure 2

In this low excitation level range the recombination parameters are independent of the photon flux. The concentration of recombination centers, N_i , can be determined from the diffusion length, $L^{-2} = D^{-1} \sum C_i N_i$ where D is the minority carrier diffusivity value and C_i is the effective electron capture cross section of the center. Values of C are known for the donor levels of interstitial Fe and Cr as well as for corresponding metal-Boron pairs [7,8].

In a theoretical treatment of SPV, an overall charge neutrality condition is a starting point:

$$Q_{sc} + Q_s = 0 \quad (1)$$

where Q_{sc} is the space charge density and Q_s is the surface state charge density. Illumination produces a small disturbance which can be expressed as

$$\Delta Q_{sc} = (\partial Q_{sc} / \partial V_s) \Delta V + (\partial Q_{sc} / \partial \Delta n) \Delta n \quad (2a)$$

$$\Delta Q_s = (\partial Q_s / \partial V_s) \Delta V + (\partial Q_s / \partial \Delta n) \Delta n \quad (2b)$$

where V_s is the surface potential barrier height and Δn is the excess minority carrier concentration beneath the surface just outside the surface space charge region. This space charge region extends over a distance much smaller than the diffusion length and the light penetration depth.

From Equations (1) and (2), the small signal photovoltage becomes:

$$\Delta V = C_0 \cdot \Delta n \quad (3)$$

where $C_0 = -(\partial Q_{sc} / \partial n + \partial Q_s / \partial n) / (\partial Q_{sc} / \partial V_s + \partial Q_s / \partial V_s)$. The terms $\partial Q_s / \partial n$ and $\partial Q_s / \partial V_s$ are related to changes in the surface state charge and are often small, especially if the light chopping frequency is high in comparison with the inverse of the surface state time constant. These terms, however, even if significant, do not affect the SPV method operating in a small signal linear range.

The value of Δn in Equation (3) is obtained from a steady state solution of the continuity equation as given in Reference 5. An overall expression relating ΔV to the absorption coefficient, α , of a silicon wafer of thickness, T , illuminated from the front side, and with the surface recombination values S_f and S_b on the front and the back surfaces, respectively, is:

$$\Delta V = \phi_{eff} C_0 C_1^{-1} D^{-1} \frac{\alpha L^2}{\alpha^2 L^2 - 1} [(S_b \alpha L - D/L) \sinh(T/L) + (\alpha D - S_b) \cosh(T/L)] \quad (4)$$

where $C_1 = (S_f S_b L/D + D/L) \sinh(T/L) + (S_f + S_b) \cosh(T/L)$ and ϕ_{eff} is the photon flux entering the wafer, i.e., corrected for the reflectivity.

It may be worth mentioning that a different approach has recently been proposed [9] for calculation of the SPV based on balancing electric currents in analogy to p-n junctions. This calculation yielded super-linear dependence of ΔV on the photon flux, ϕ , in a low photon flux range. This is in disagreement not only with all other SPV theories, but also with well-established experimentally linear SPV behavior in the low intensity range (see Figure 2).

In the SPV method, ΔV is measured for a series of α values corresponding to different wavelengths of the incident light and $\Delta V(\alpha)$ is used for the determination of L . Goodman's

original treatment [3] was intended for short diffusion lengths small as compared to the wafer thickness. Under such conditions $\sinh(T/L) \approx \cosh(T/L) \approx e^{T/L}/2$ and Equation (4) can be simplified and rewritten as:

$$\phi_{\text{eff}}/\Delta V = C_0^{-1} (S_f + D/L) (1 + \alpha^{-1}L^{-1}) \quad (5)$$

It is apparent from Equation (5) that the L value is obtained from the plot of $\phi_{\text{eff}}/\Delta V$ vs. α^{-1} as an intercept of the plot extrapolated to $\phi_{\text{eff}}/\Delta V = 0$. This procedure, illustrated in Figure 3, has become commonly used in SPV diffusion length measurements. However, by definition, it is not valid for diffusion lengths comparable to or longer than the wafer thickness.

As shown in Figure 3, for $L > T$ the plot $\phi_{\text{eff}}/\Delta V$ vs. α^{-1} is no longer a straight line, but rather its slope increases with the increasing light penetration depth. This behavior is typical for large values of surface recombination on the back surface, S_b , exceeding 10^4 cm/s as commonly found on silicon surface. Determination of diffusion length in this case requires a different "new" procedure based on fitting experimental data to the full Equation (4) rather than to the simplified Equation (5). The new procedure requires knowledge of the wafer thickness.

The procedure is simplified by the fact that, for high back surface recombination, L is determined from the dependence ΔV vs. α^{-1} without knowledge of the specific S_b value. The results of the new procedure are illustrated in Figure 4 whereby experimental data are given for p-type MCZ silicon, with $L = 800 \mu\text{m}$, gradually thinned from 3 mm to $300 \mu\text{m}$. It is seen that the new procedure give $L \approx 800 \mu\text{m}$ for all thicknesses. On the other hand, the old procedure, based on Equation (5), yielded incorrect L values decreasing with the sample thickness. This L behavior is in excellent agreement with a computer modeling of the old procedure which assumes $S \geq 5 \times 10^4$ cm/s. It is evident that an apparent decrease of L in thin wafers results from the use of the incorrect procedure, and it should not be taken as a limitation of the SPV method.

Figure 3

Figure 4

It must be emphasized that the uncertainty for L determination increases with an increasing L/T ratio. For $L/T = 2$, this uncertainty can exceed 10%, especially if the L value is $10^3 \mu\text{m}$ or higher. In order to reduce the uncertainty, a very accurate SPV measuring procedure must be used which incorporates statistical noise reduction via averaging of the results of multiple measurements. For example, using signal averaging and a new procedure, one can reliably measure changes of L below 5% on clean 5" to 8" wafers with a diffusion length of $800 \mu\text{m}$. According to Equation (4) of Reference 4, this would correspond to changes in the interstitial iron concentration of $1.6 \times 10^9 \text{ atoms/cm}^3$.

Identification of Metal Impurities

In p-type B-doped silicon, transition metal impurities form, at room temperature, donor-acceptor pairs which can be dissociated by short (minutes) annealing at temperatures of about 200°C . After quenching to room temperature, metals are left in a metastable interstitial position. Iron-boron pairs have an energy level 0.1 eV above the valence band and an electron capture cross section about ten times smaller than that of the isolated interstitial Fe^+ donor level about 0.4 eV above the valence band. Thus, a dissociation of Fe^+-B^- pairs creates recombination centers about ten times more efficient than the pairs themselves. In SPV measurements, this process is manifested by a reduction of the diffusion length value after 200°C annealing. Calibrating data are available which relate the iron concentration to diffusion length values, L_0 and L_1 , measured before and after annealing, respectively [7].

Chromium exhibits a different recombination behavior than that of Fe wherein Cr-B pair dissociation results in an increase of the diffusion length [8]. This contrasting behavior of Fe and Cr is shown in Figure 5 in which SPV maps of the diffusion length differences before and after 200°C annealing are shown for p-type B-doped silicon wafers. The wafers were contaminated with Fe and Cr by scratching them on the back with Fe and Cr wires to form respective letters. Contaminants were then driven into the bulk by 1150°C RTP annealing. It is evident that areas containing Fe are white which corresponds to an L decrease after pair dissociation, while areas containing Cr are black which denotes an L increase after pair dissociation. This contrasting behavior is the basis for identification of Fe and Cr impurities.

Iron can be uniquely identified in silicon using optical activation rather than the 200°C annealing. It is well known that Fe^+-B^- pairs dissociate at room temperature under strong illumination due to the recombination-enhanced process. Photo-generated excess electrons captured by the pairs liberate an energy of about 1 eV which is larger than the pair binding energy of 0.89 eV. For Cr-B pairs, the energy liberated during electron capture is only about 0.8 eV, i.e., it is smaller than the pair binding energy. Accordingly, Cr-B pairs cannot be optically dissociated.

Using optical and thermal pair dissociation, it is, therefore, possible to determine Fe and Cr concentrations in p-type silicon even if both impurities are simultaneously present. A quantitative description of this procedure is given in Reference 10.

Figure 5

Acknowledgements

This work was supported by grants from the Florida High Technology and Industry Council, AT&T Microelectronics, and Semiconductor Diagnostics.

References

1. L. Jastrzebski, Materials Science and Engineering B4, 113 (1989).
2. W. Henley, L. Jastrzebski and N. Haddad, to be published in the proceedings of the MRS Spring Meeting, April 1992, San Francisco.
3. A.M. Goodman, J. Appl. Phys. 32, 2550 (1961).
4. J. Lagowski, P. Edelman, M. Dexter and W. Henley, Semicond. Sci. Technol. 7, A185 (1992).
5. E.O. Johnson, Phys. Rev. 111, 153 (1958).
6. D.R. Frankl and E.A. Ulmer, Surf. Sci. 6, 115 (1966).
7. G. Zoth and W. Bergholz, J. Appl. Phys. 67, 6764 (1990).
8. K. Mishra, elsewhere in these proceedings.
9. S.C. Choo, L.S. Tan and K.B. Quirk, Solid St. Electronics 35, 269 (1992).
10. J. Lagowski, M. Dexter and P. Edelman, to be published.

EFFECTS OF METALLIC IMPURITIES IN CZ-Si: A MINORITY CARRIER LIFETIME STUDY BY SURFACE PHOTOVOLTAGE (SPV) METHOD

Kamal Mishra
MEMC Electronic Materials, Inc.
501 Pearl Drive, St. Peters, Mo 63376

ABSTRACT

The effect of metallic impurities (Fe, Cr, Mo, Cu and Ni) in p type CZ-Si on minority carrier lifetime has been studied using SPV. Samples intentionally doped with metals during crystal growth were prepared. It was found that defects associated with Fe_i, CrB, Cr_i, and Mo, in decreasing order of effectiveness, degrade lifetime in p type Si. Further, the effects of FeB and CrB pair dissociation on minority carrier lifetime were compared and contrasted. While a decrease in minority carrier lifetime is commonly observed with FeB dissociation, an increase was seen after thermal dissociation of CrB. Kinetics of CrB formation following 200C dissociation anneal was also studied. The formation of CrB pairs continues for more than three months in samples with resistivity of 50 ohmcm. This time period is approximately thirty times larger than that observed in case of FeB pair association.

INTRODUCTION

Transition metals such as Fe, Cr, Cu and Ni are fast diffusers in silicon and contamination by these impurities may occur during various stages of device processing involving thermal treatments. It is well established that metallic impurities cause degradation of yield and reliability of VLSI circuits. As a result there has been ever growing interest in understanding the behavior of metallic impurities in silicon (1-9). Weber (1,2) reviewed solubility and diffusivity of most of transition metals. Rohatgi and coworkers (10) reported the effect of metallic impurities doped during crystal growth on the efficiency of silicon solar cells. The efficiency of solar cells may be determined by several factors including grown-in impurities, process induced- defects and resistances. The present study was undertaken to determine the effect of various metallic impurities on minority carrier lifetime. The samples were doped with metallic impurity during crystal growth.

Another important aspect of this work concerns the identification of metallic impurities in silicon. The identification of metals at a sub- ppb level is only possible by techniques such as Deep Level Transient Spectroscopy (DLTS) and Electron Paramagnetic Resonance (EPR). Recently, quantitative identification of Fe in Si by SPV (8) has emerged as a fast and sensitive method involving no sample preparation. In this paper, it is shown for the first time that SPV can also be used to identify Cr in p type Si. Earlier, Conzelmann and coworkers studied the properties of Cr in silicon using DLTS, EPR and photoluminescence(9). The energy levels at $E_c-0.23$ and $E_v +0.27$ eV were attributed to Cr and CrB related defects.

EXPERIMENTAL

The metal doped p type samples were grown by Czochralski method. Most of the samples were boron doped, 30-50 ohmcm, and $\langle 100 \rangle$ orientation. In addition, few Cr doped samples with low resistivity (1-2 ohmcm) were also grown. Typical concentration of intentionally added metal impurity ranged between 0.2×10^{13} and 5×10^{13} atoms/cc. The concentration of metals in samples were calculated using segregation coefficients. These coefficients have previously been determined using DLTS and Neutron Activation Analysis (10,11). In addition, selected Fe and Cr doped samples were analyzed, in this study, using DLTS.

Samples, 2mm in thickness, were cut from various axial locations from these doped crystal. Thermal donor annihilation of these samples was conducted, after cleaning in RCA 1 and RCA 2 baths, prior to heat treatment in a clean furnace in the presence of oxygen to avoid any unintentional contamination of samples. Lifetime values in the absence of any intentionally added metals were at least ten to twenty times higher than that observed in cases of metal doped samples. No unintentionally added impurity was detected using DLTS.

The SPV method of determining minority carrier lifetime utilizes a very low ($\Delta p/p = 10^{-5}$) level of excitation. The constant flux method employed in this study has been described in reference 12. The advantage of this method is that it measures true bulk lifetime without any extensive surface preparation to lower surface recombination velocity. Relatively thick samples (2 mm) used in this study allowed the measurement of diffusion length up to 1200 microns without limitations imposed by surface recombination velocity at the back surface.

The dissociation of metal-acceptor pairs (FeB, CrB) was conducted by heat treating samples at 200C for 10 min. followed by quenching in water. The optical dissociation of FeB pairs was achieved by illuminating the samples using 250 Watt W-halogen lamp for a period of less than one minute.

RESULTS AND DISCUSSION

Intentionally Doped Samples

The energy levels of various metallic impurities in Si studied in this work are presented in Table I. Figures 1-4 show the relationship between the concentration of various metallic impurities and lifetime as measured by SPV. Due to axial segregation of metals, the impurity concentration in a crystal varies by a factor of approximately five to six from seed end to tang end. The data for each metal impurity reported in these figures corresponds to the samples taken from various locations in the ingot. The linear relationship between concentration and the inverse of minority carrier lifetime was found to hold even when the concentration of a metallic impurity such as Fe and Cr was varied over two order of magnitude.

Generally, transition metal cations such as Fe, Cr and Mn form stable "metal-acceptor" pairs in p-Si. Since the binding energy estimated from a two-point charge Coulombic interaction is

only 0.5 eV (5,12,13) these pairs can be easily dissociated by a low temperature anneal ($T < 200$ C). These thermodynamic expectations have been experimentally verified using EPR and DLTS measurements. In case of Fe and Cr doped samples, FeB and CrB controlled lifetime is also

TABLE I: ENERGY LEVELS OF VARIOUS METALLIC IMPURITIES IN SILICON.

DEFECT	ENERGY LEVEL	REMARK
Fe_i	$E_v + 0.40$ eV	Ref.4,6,8
FeB	$E_v + 0.10$ eV	Ref.4,8
Cr_i	$E_c - 0.23$ eV	Ref.9,10
CrB	$E_v + 0.27$ eV	Ref.9,10
Mo	$E_v + 0.30$ eV	Ref.10
Cu	$E_v + 0.08$ eV	Ref.15, only in FZ fast quenched samples, anneals out at 200 C.
Ni	$E_v + 0.16$ eV	Ref.15, only in FZ samples

FIGURE 1 The effect of Fe and FeB on minority carrier lifetime.

FIGURE 2 Effect of Cr and CrB on minority carrier lifetime.

Figure 3 Effect of Mo on minority carrier lifetime

FIGURE 4 Effect of Cu and Ni on minority carrier lifetime.

reported (Figures 1 and 2). In accordance with previous findings(8), FeB controlled lifetime is approximately fifteen times larger than Fe_i controlled lifetime. On the other hand, in case of Cr doped samples, lifetime values increased by a factor of ten after pair dissociation. It seems that CrB ($E_v = 0.27\text{eV}$) is more efficient recombination center than Cr_i ($E_c - 0.23\text{eV}$, also see below). The effect of Mo on minority carrier lifetime is shown in Figure 3. On comparing the results in Figure 1-3, it seems that Fe_i is by far the most efficient lifetime killer impurity followed by CrB, FeB, Cr_i and Mo.

The effects of Cu and Ni on minority carrier lifetime are shown in Figure 4. The behavior of these impurities differ from those reported in figure 1-3 in that no linear relationship was observed between the concentration of metallic impurity and the inverse of lifetime. It is known that Cu and Ni are extremely fast diffusers in Si and can not be quenched in CZ-Si because they precipitate out as their respective silicides (1) at any available high energy defect sites. It could be possible that these metal silicides precipitates act as recombination centers, the formation of which would depend upon the thermal history of samples. Thus, no trends in lifetime were observed from the seed end to the tang end.

Identification of Cr contamination

Earlier Zoth (8) reported a fast and quantitative method of detecting Fe in p-Si using SPV. It is

proposed here to identify Cr in p type Si using SPV. The principle of identification of Cr contamination relies on the fact that CrB pairs can be easily dissociated at low temperature anneal (9), and that capture cross sections for Cr_i and CrB related Shockley Reed recombination centers differ significantly. As reported in Figure 2, CrB defect site is approximately ten times more effective recombination center than Cr_i defect site. It should be noted that the lifetime time effects as a result of pair dissociation in case of Cr doped samples differ from that seen in Fe doped samples, i.e., an increase in lifetime in the presence of Cr as opposed to the decrease in lifetime in the presence of Fe. Also, FeB pairs can easily be dissociated optically. The "recombination enhanced dissociation" of FeB pairs (4,5) optically can be achieved even at sub zero temperatures whereas CrB cannot be dissociated optically. An example of thermal and optical dissociation of FeB and CrB pairs is presented in Figure 5. In principle, quantitative analysis of Cr in the presence of other impurities such as Fe should be possible.

FIGURE 5 Effect of thermal anneal(200C,10 min) and illumination on the diffusion length of Fe and Cr doped samples.

Association Time Spectroscopy (ATS): CrB pair formation:

The progress of pair formation reaction following "200 C, 10 min" dissociation anneal was monitored by measuring the diffusion length over a period of six months. These data are reported in Figure 6. The samples used in Figure 6 were taken from same crystal with resistivity ranging from 30-50 ohmcm. The concentration of Cr varied by a factor of five in these samples. The concentration of Cr_i and CrB can be calculated from the diffusion length values. The kinetics

formation in samples with 1-2 ohmcm resistivity was found to be lower than that observed by Park et al. (16) using edge defined film fed growth (EFG), i.e., two days vs. nine days reported in ref 16.

Figure 7 Association time constants for CrB and FeB as a function of boron concentration.

SUMMARY

The effect of Fe, Cr, Mo, Cu and Ni on minority carrier lifetime has been determined. It was observed that under the experimental conditions Fe, CrB, FeB and Mo, in decreasing order, are effective lifetime killer in p-Si. In general, Cu and Ni do not affect minority carrier in CZ-Si as these fast diffusing metals easily precipitate out.

It has also been shown for the first time that contactless, fast SPV method of determining minority carrier lifetime can be used to identify Cr contamination in p type silicon. Dissociation/association behavior of CrB pairs differs from FeB. FeB pairs can be dissociated optically as well thermally whereas CrB dissociation can be achieved only thermally. As a result of pair dissociation in case of FeB, lifetime decreases by a factor of ten to fifteen. On the other hand,

pair dissociation in case of CrB results in a tenfold increase in minority carrier lifetime. Association time constant for CrB reaction was found to be approximately thirty times higher than that for FeB formation.

ACKNOWLEDGEMENTS

The author would like to thank Dr. Walter Huber for the many valuable discussions in the course of this work. Thanks are also due to Jerry Moody for supplying the metal doped samples needed for this study.

REFERENCES

1. E.R. Weber, Appl. Phys. A 30, 1 (1983).
2. E. Weber and H. G. Riote, J. Appl. Phys. 51, 1484 (1980).
3. G.W. Ludwig, H.H. Woodbury, Solid State Phys. 13, 223 (1962).
4. K. Graff and H. Pieper, J. Electrochem. soc. 128, 669 (1981).
5. L.C. Kimmerling and J.L. Benton, Physica 116B, 297 (1983).
6. S.D. Brotherton, P. Bradley, and A. Gill, J. Appl. Phys. 57, 1941 (1985).
7. H. Lemke, Phys. Status Solidi A 64, 215 (1981).
8. G. Zoth and W. Bergholz, J. Appl. Phys. 67, 6764 (1990).
9. H. Conzelmann, K. Graff and E.R. Weber, Appl. Phys. A 30, 169 (1983).
10. A. Rohatgi, J.R. Davis, R.H. Hopkins and P.G. McMullin, Solid State Electronics 26, 1039 (1983).
11. D.E. Hill, H.W. Gutsche, M.S. Wang, K.P. Gupta, W.F. tucker, J.D. Dowdy and R.J. C Crepin, Photovoltaic Specialists Conference, IEEE, 1976, p112.
12. J. Lagowski, P. Edelman, M. Dexter and W. Henley, Semicond. Sci. Technol. 7, A185 (1992).
13. L. C. Kimmerling, Solid state Electronics 21, 1391 (1978).
14. K. Wunstel and P. Wagner, Appl. Phys. A27, 207 (1982).
15. G. Zoth and W. Bergholz, in Diagnostic Techniques for Semiconductor Materials and Devices, edited by J.L. Benton, G.N. Maracas and P. Rai-Choudhury (Electrochemical society, Pennington, NJ, 1991) p.88.
16. S. H. Park, D.K. Schroder and J.P. Kalejs, in Diagnostic Techniques for Semiconductor Materials and Devices, edited by J.L. Benton, G.N. Maracas and P. Rai-Choudhury (Electrochemical society, Pennington, NJ, 1991) p.119.

PRECIPITATION AND GETTERING OF HEAVY METALS DURING IC PROCESSING

L. Jastrzebski
Center for Microelectronics Research
University of South Florida
Tampa, FL 33620

Abstract

The development of optimized gettering procedures, designed to improve the quality of photovoltaic silicon is the goal of the photovoltaic industry. This work reviews recent developments in gettering procedures used by the IC industry which could lead to optimization of gettering schemes used for photovoltaic silicon. Several procedures will be compared with emphasis on recent developments.

Introduction

The IC industry uses gettering to prevent formation of heavy metal precipitates in device-active regions during the cooling which follows high temperature steps. The presence of these defects results in an increase of junction leakage, soft junction breakdown and gate oxide integrity problems. Gettering is designed to reduce the amount of heavy metals present in the bulk of silicon wafers at diffusion/oxidation temperatures (e.g., phosphorous and chlorine gettering) and to provide preferential sites for heavy metal precipitation during cooling which follows high temperature steps (e.g., poly-silicon, backside damages or oxygen precipitates in internally gettering wafers). It should be emphasized that only dissolved heavy metals are gettering, those that have already precipitated cannot be gettering. From a practical standpoint, the major benefit of gettering manifests itself as a reduction of large variations of device characteristics which is reflected in yield fluctuations present in processes using non-gettering wafers. Gettering seldom significantly improves the properties of the best wafers, but it substantially improves the yield of poor wafers as shown in Figure 1 which presents the average yield of a CMOS line for gettering and non-gettering wafers as a function of time [1]. During a period of heavy metal contamination in this line, the yield of non-gettering wafers was affected much more than that of gettering wafers.

The most common heavy metal contaminates in IC processing lines are Fe, Ni, Cu and Cr [2]. Their gettering behaviors can be divided into two categories wherein Fe and Cr are difficult to getter while Ni and Cu precipitate easily, even at the wafer surface, and are easily removable by any gettering process. As pointed out by Weber [3], this difference in gettering properties is most likely related to the differences in the solubility and diffusivity of heavy metals.

Chlorine Gettering

With the exception of gold, this method proved its effectiveness in the early seventies in the gettering of various heavy metals [4]. Both HCl and TCA are common sources used for chlorine gettering. The formation of volatile metal chlorides, due to the reaction between chlorine and heavy metals on the surface of silicon wafers, is believed to be responsible for the gettering process.

Initially, it was believed that HCl removes only those heavy metals left on the silicon wafer surface (e.g., by wet chemical cleaning) which prevents the formation of nucleation sites for process-induced stacking faults. Subsequent work showed that chlorine gettering also getters heavy metals present in the bulk, resulting in an improvement in diffusion length [5]. The gettering efficiency improves with an increase of the oxidation temperature as shown in Figure 2 where the diffusion length is plotted as a function of oxidation temperature for 20 minutes dry oxidation with 1% HCl [5]. The most efficient gettering takes place during dry oxidation and is significantly reduced if steam is used as the oxidation ambient.

Figure 1. Yield in CMOS line as a function of time for non-gettered and gettered (IG) wafers [1]. Notice the smaller yield reduction in the gettered wafers during the period of high concentration.

Figure 2. Diffusion length as a function of temperature (a) oxidation in the presence of HCl and (b) phosphorous diffusion [5].

Phosphorous and Boron Gettering

During phosphorous gettering, a gettering sink is formed by diffusion or implantation of phosphorous into the back of the silicon wafer. The gettering takes place at the highest temperature of the heat cycle, as well as during the subsequent cooling. The most efficient source is POCl_3 . The oxidation "soak" following diffusion is required to improve the gettering efficiency. Gettering efficiency increases with an increase of the phosphorous diffusion temperature [5]. The observed improvement of diffusion length is presented in Figure 2 [5].

Phosphorous gettering is efficient in the removal of the majority of heavy metals including Fe. Two mechanisms have been proposed to explain the efficient gettering of Fe by phosphorous. One assumes an enhancement of Fe solubility in the phosphorous-doped layer due to the pairing of negatively-charged Fe atoms with positively-charged phosphorous atoms [6]. The Fe atoms become negatively charged due to the shift of the Fermi level in the heavily phosphorous diffused region. The second model assumes coupling of local currents of self-interstitial and metals [7]. This phenomena accounts for the improvement of gettering efficiency when, subsequent to the phosphorous diffusion, the oxidation "soak" is performed.

The most recent work carried out by Nadahara, et. al. [8] showed that the effectiveness of Fe gettering by a phosphorous layer depends on two factors: the concentration of phosphorous; and an equilibrium constant, K , which describes the equilibrium established between the solubility of Fe in the bulk of silicon, Fe(dissolved), and the phosphorous-diffused layer, Fe(gettered):

$$\text{Fe(dissolved)} / \text{Fe(gettered)} = K / P \quad (1)$$

The ratio between gettered and non-gettered Fe, as a function of temperature and phosphorous concentration, is shown in Figure 3 [9]. This data allows one to predict the efficiency of the gettering process, i.e., for a phosphorous concentration of $5 \times 10^{16} \text{ cm}^{-2}$ at 800°C , 99 out of 100 Fe atoms will be gettered. For a given phosphorous concentration, a reduction of temperature improves this ratio. This ratio depends on the solubility of Fe in the phosphorous layer and is described by the constant K whose temperature dependance is presented in Figure 4. When the temperature is decreased from 1000°C to 800°C , the amount of Fe dissolved in the phosphorous layer (for the same phosphorous concentration) increases by 100 times. The mechanism responsible for this phenomena is not fully understood at the present time. A practical implication of this data is far reaching since it points to an optimum phosphorous gettering cycle, namely, the highest diffusion temperature to achieve the highest phosphorous concentration, plus oxidation soak, followed by slow/equilibrium cool down to 800°C . All processing should be done in an oxidizing ambient. By equilibrium cooling, we define the cooling rate which allows heavy metals enough time, at a given temperature, to diffuse to the gettering sink through the thickness of the silicon wafer.

Figure 3. Ratio between gettered and non-gettered Fe and phosphorous concentration for various temperatures [9].

Figure 4. The dependance of equilibrium coefficient (describing solubility of Fe in phosphorous-doped layer) on diffusion temperature [9].

Recent experiments have shined a new light on the gettering of Fe by boron [10]. The study of boron-implanted silicon, intentionally contaminated with Fe prior to and after annealing of implantation damage, showed that Fe gettering by boron takes place only if the implantation damage is also annealed during gettering. In samples implanted with boron, in which the implantation damage was annealed prior to the Fe contamination, gettering of Fe by boron did not occur.

Backside Damage Gettering

A gettering sink for backside damage gettering is created by poly-silicon or nitride deposited on the back of the silicon wafer or by mechanical damage introduced by sand blasting or laser melting. During cooling of the silicon wafer, when heavy metals become supersaturated, the crystallographic defects introduced into the backside of the wafer act as nucleation sites for heavy metals precipitation. In photovoltaic poly-silicon, crystallographic defects present in the bulk perform gettering of heavy metals during the cooling which follows crystal growth or during subsequent processing used for solar cell fabrication. This leads to decoration of crystallographic defects and an increase of their electric activity.

Although there are some differences between the gettering properties of various backside damages in relationship to the role played by point defects, as a general rule, gettering of Ni and Cu can be easily achieved while Fe gettering by backside damage is very difficult. Figure 5 shows the results reported for gettering of Ni, Cu and Fe [11-12]. Cu and Ni are the most efficiently getterted by poly-silicon, light backside damage introduced by sand blasting is not as efficient. Fe is not getterted by any of these backside damages.

Figure 5. Lifetime/diffusion length in wafers intentionally contaminated with Cu [12], Ni [11] and Fe [11] (non-contaminated, contaminated without gettering, with poly-silicon, and with backside damage introduced by sand blasting). Notice the efficient backside gettering of Cu and Ni and no effect on Fe.

Discussion: Implication to Photovoltaic Poly-silicon

The results presented above showed that Ni and Cu can be getterted by any gettering sink, while getterting of Fe is more difficult. During cooling, when a sufficient degree of supersaturation is reached, Ni and Cu easily precipitate on crystallographic defects. Fe tends to stay dissolved in silicon. This has a profound implication for photovoltaic silicon: During the cooling which follows crystal growth, the majority of Ni and Cu will precipitate on crystallographic defects, thereby decorating them and increasing their electric activity while the majority of Fe will stay as an interstitial impurity or Fe-acceptor pair, therefore, giving a large number of very efficient recombination centers and reducing the diffusion length. It appears that efficient getterting of Fe can only be performed by HCl or phosphorous diffusion. It should be emphasized that only non-precipitated heavy metals can be getterted, therefore, removal of already precipitated heavy metals, via a special heat treatment designed to dissolve the precipitates, should be performed.

At the present time, it is not clear what exact temperature treatment is required to achieve dissolution of heavy metal precipitates. If a well defined silicide phase has been formed, then the eutectic temperature should be exceeded. Table 1 summarizes the eutectic temperatures for various heavy metals [13]. It ranges between 700°C for Cu and 1340°C for Ti. Recent data

published by R. Falster, et. al. [14] showed that Ni precipitates can dissolve around 600°C which indicates that Ni precipitate dissolution can take place at temperatures significantly below the eutectic temperature of 990°C. This data indicates that some precipitates can dissolve when temperatures exceed the solubility temperature for a given heavy metal concentration in the bulk of silicon, even for temperatures below the eutectic temperature. At this time, however, it is also not clear what role point defects play in the dissolution process. An important issue for future investigation is an understanding of this phenomena so an effective gettering of heavy metals already present in precipitated form can be designed.

Table 1
Eutectic Temperatures for Various Metal-Silicon Systems

	<u>Cu</u>	<u>Ni</u>	<u>Fe</u>	<u>Mu</u>	<u>Cr</u>	<u>Ti</u>
Temperature (°C)	700	990	1210	1145	1340	1340

References

1. L. Jastrzebski, R. Soydan, J. McGinn, R. Kleppinger, M. Blumenfield, G. Gillespie, N. Armour, B. Goldsmith, H. Henry, and S. Vecrumba, J. Electrochem. Soc. 134, 1018 (1987).
2. Nikkei Microdevices, May 1990, p. 54 (in Japanese).
3. E. Weber, elsewhere in these proceedings.
4. C.W. Pearce, Semiconductor Silicon 1981, edited by H.R. Huff, et. al., Electrochem. Soc. Softbound Proceed. Series, p. 705 (1981).
5. L. Jastrzebski, Semiconductor Silicon 1990, edited by H.R. Huff, et. al., Electrochem. Soc. Softbound Proceed. Series, p. 614 (1990).
6. D. Gilles, W. Bergholz and W. Shroter, Phys. Rev. B41, 5770 (1990).
7. W. Shroter and R. Kuhnopf, Appl. Phys. Lett. 56(22), 2207 (1990).
8. S. Nadahara, M. Watanabe, K. Yamabe, Solid State and Material Conf., August 1990, Conf. Proceedings.
9. S. Nadahara, "SPV Workshop," Tokyo, Japan, July 1991 (in Japanese).
10. Y. Niki, S. Nadahara and M. Watanabe, Defect Control in Semiconductors, Vol. 1, edited by K. Sumino, North Holland, p. 329.
11. M. Miyazaki, M. Sano, S. Sadamitsu, S. Sumita, N. Fujino, and T. Shiraiwa, Jap. J. Appl. Phys. 28, L519 (1989).
12. T. Abe, "SPV Workshop," Tokyo, Japan, July 1991 (in Japanese).
13. E.R. Weber, Appl. Phys. Lett. A30, 1 (1983).
14. R. Falster, et. al., Material Research Soc. Meet, April 1992, San Francisco, CA, proceedings in press.

TEMPERATURE DEPENDENCE OF THE EXTERNAL GETTERING EFFICIENCY IN CAST SEMICRYSTALLINE SILICON MATERIALS

L.A. Verhoef and P.P. Michiels
R&S Renewable Energy Systems B.V.
P.O. Box 45, 5600 AA Eindhoven, The Netherlands

ABSTRACT

The effectiveness of P-diffusion induced (PDI) and Al-induced gettering on different types of cast semicrystalline Si are compared. The optimum PDI gettering temperature of 900 °C is not very sensitive to the type of Si involved. The optimum temperature of 700 °C for Al-induced gettering in cell processing without H-passivation is significantly lower than that of PDI gettering. This suggests that by Al-induced gettering different impurities are being removed than by PDI gettering. In solar cell processing, these optimum temperatures may well shift because of subsequent processing steps like H-passivation.

INTRODUCTION

On most semicrystalline silicon materials, gettering is required in the solar cell processing scheme to achieve cell efficiencies larger than 15 %. We define external gettering as the process of reallocation of impurities out of the bulk into the Si wafer surface region. In the past, external gettering has been studied extensively on monocrystalline silicon and a clear model of the mechanisms involved has been developed.

External gettering on semicrystalline silicon, being a less well-defined material, has led to the following phenomenological results. Martinuzzi's group has shown that P-diffusion induced (PDI) gettering on Photowatt's POLYX material yields appreciable enhancements of minority-carrier diffusion lengths [1]. We have shown that comparable effects can be achieved by Al-induced gettering on Wacker SILSO material [2]. Green's group has shown that cell efficiencies of 17.8 % are attainable by combining PDI gettering and Al-film deposition and annealing [3]. Despite these good results, there is no clear microscopic picture on the mechanisms taking place during gettering in semicrystalline Si, nor is it known which impurities are gettering out of this material.

The potential effects of each gettering treatment depend on the type of semicrystalline Si and its thermal history, the type of impurity sink applied and the time and temperature of the treatment. In this paper we will address some features of

external gettering of metals by P diffusion and Al doping. The interaction of both treatments with various types of cast materials and with subsequent processing will be discussed.

EXPERIMENTAL RESULTS

Monocrystalline silicon

The gettering mechanisms have been reviewed recently [4]. A simple model to explain the external gettering-efficiency of impurities as a function of temperature was proposed. At low temperatures gettering is limited by the diffusion of the impurity. At high temperatures the efficiency is limited by the ratio of the solubility of impurities in the high-doped part of the wafer and the impurity-solubility of the low-doped bulk. This ratio (the segregation coefficient) depends on the gettering layer at the surface of the wafer during the heat treatment. In n^+ -type silicon this solubility is higher by typically one order of magnitude than in p^+ -type silicon [5,6]. With the segregation coefficient being known, the efficiency of gettering can be calculated from the thickness of the wafer, the impurity diffusivity at the gettering temperature and the annealing time [6]. It should be noted that a large 'solubility' in high-doped layers can result from solid-state dissolved impurities but also from silicide-formations and metal ion-pairing with P and other effects. PDI gettering results in a marked increase of minority-carrier diffusion length on intentionally Au doped wafers, see Fig. 1 [4]. These results agree well with the model mentioned above and show a typical optimum gettering temperature of 900 °C.

Only a few results on the gettering of transition metals by Al or Al-doped layers are known. At temperatures just below the eutectic (540 °C) it was shown that enormous amounts of Cu (10^{21} cm⁻³) could be gettered into an evaporated Al film [7]. In a similar experiment, gettering by Al-doped layers (prepared by screenprinting, alloying, and etching) was demonstrated [2]. These layers exhibited solubilities of Cu and Ni over 10^{19} cm⁻³. Other metal films can also getter impurities. In Fig 1. the temperature dependence of gettering by a deposited Ni film is shown [4].

Semicrystalline silicon

Experiments on POLYX material have shown that the optimum temperature for PDI gettering is between 800 and 900 °C, depending on the quality of the starting material [8]. In combination with a hydrogen passivation treatment the diffusion temperature became less important [9].

In our own experiments we have compared the lifetime-improvement (as measured by microwave decay) by PDI gettering on 3 different cast semicrystalline silicon materials at 800, 850 and 900 °C for

1, 2 and 4 hours. In all materials we have seen an improvement of the lifetime. On Wacker SILSO gettering at 900 °C for 1 hr yielded an increase in the diffusion length by 10 %, see Fig. 1. The two other materials required 4 hours at this temperature for equivalent improvements. After diffusion and gettering, all wafers were processed to solar cells employing hydrogen passivation. Only in the Wacker SILSO groups annealed at 900 °C, this resulted in improved final cell efficiency. In the other materials, no significant improvement and in some cases even reduction of cell efficiency was observed in the gettered groups compared to standard groups without gettering.

Gettering of impurities with Al-films at temperatures below the eutectic (577 °C) were shown to be beneficial on those regions of POLYX material where the dislocation density is larger than 10^4 cm^{-2} [8]. No optimum temperature was determined. An Al-doped BSF layer made by screenprinting, alloying, and etching can also be used as a gettering layer in a subsequent anneal [2]. The diffusion length of complete cells made on Wacker SILSO versus Al-induced gettering temperature is shown in Fig. 1. The optimum temperature at gettering times of 1 hr is 700 °C. In another paper we have shown that this optimum treatment can effectively

Figure 1. Improvement of minority carrier diffusion length vs gettering temperature for P-induced gettering, Ni-film gettering on monocrystalline silicon and P-induced and Al-induced gettering on semicrystalline silicon. The optimum temperature and gettering efficiency apparently depends on both treatment and material.

be combined with hydrogen passivation [10]. However, it is unknown whether in such combined gettering-passivation scheme 700 °C is the optimum temperature.

DISCUSSION

Silicon material

No difference in efficiency between different cast materials has been observed after PDI gettering at 900 °C. This suggests that the segregation coefficient of this treatment as well as the diffusivity of the impurities gettered are similar, leading to the tentative conclusion that similar metallic impurities are being gettered. A clear optimum temperature of 900 °C for PDI gettering is deduced. The identity of the impurities which are gettered is not clear since direct detection is hampered by the low concentrations (typically 10^{12} to 10^{14} cm⁻³) involved [10]. Thus a direct comparison of the influence of impurities present in or gettered out of the cast various materials is not possible. The segregation coefficient of PDI gettering is determined mainly by the very high-doped (dead) layer via mechanisms like silicide formation, ion-pairing or Fermi-level shifting and is therefore independent of the Si material used.

Al-induced gettering is effective on SILSO, POLYX en mono. The optimum temperature of 700 °C for SILSO differs drastically from that of PDI gettering. We therefor surmise that these two treatments may be gettering different impurity species from the wafer and may thus be complimentary [10].

Interaction with H-passivation

One of the side effects during P diffusion (and probably also during Al-alloying and gettering) is the generation of point defects and silicon self-interstitials. Grain boundaries themselves are also known to emit point defects at elevated temperatures. In the models developed for gettering in mono-silicon, these effects are not incorporated. Apart from the two limiting factors for gettering, i.e. the segregation coefficient and the impurity diffusivity, the generation of physical-defect related recombination centers may limit the effect of gettering on the diffusion length. This diffusion length is normally used as a criterium to optimize gettering and not the impurity-concentration distribution in the wafer.

In processing steps following the gettering treatment the diffusion length may be reduced by thermal stress or by unintentional wafer contamination or may be enhanced by hydrogen passivation. One therefore needs to optimize the impurity-removal and defect creation by gettering and the subsequent impurity contamination and defect passivation by cell processing and hydrogenation in combination with each other.

An example of the need for combined optimization was observed in our own PDI gettering experiments: directly after gettering, a clear optimum exist for all materials. Upon hydrogenation such optimum is only present for the Wacker SILSO material. Higher temperatures or longer gettering times could possibly result in the other materials.

CONCLUSIONS

P-diffusion induced gettering seems to be effective on all three types of cast semicrystalline Si. We tentatively conclude that equivalent metallic impurity species are being removed out of the wafer bulk by this treatment. The difference in optimum gettering temperature of Al and P suggests that both treatment may getter different impurity species.

In general it is necessary to optimize gettering temperatures and times within the solar cell processing scheme. Not the lifetime directly after the gettering treatment determines whether an optimum has been reached, but the final cell efficiency. This is especially important in multi-step processing schemes which employ other lifetime-improving techniques such as H-passivation.

ACKNOWLEDGEMENTS

We thank R. Steeman and J. Eijkelboom of the Netherlands Energy Research Foundation ECN for performing microwave decay measurements and R.J.C. van Zolingen of R&S for stimulating discussions.

REFERENCES

1. I. Perichaud et.al., in: Conf. Record of the 21st IEEE Photovolt. Specialists. Conf. (IEEE, New York, 1990), p. 737
2. L.A. Verhoef et. al., Mat. Sci. and Engin. B7, 49 (1990)
3. S. Narayanan, S.R. Wenham and M.A. Green, IEEE TED 37, 382 (1990)
4. J.S. Kang and D.K. Schroder, J. Appl. Phys. 65, 2974 (1989)
5. R.N. Hall and H. Racette, J. Appl. Phys. 35, 379 (1964)
6. D. Gilles, Mat. Res. Soc. Spring Meeting, San Fransisco, 27 April - 1 May, 1992, in press
7. R.D. Thompson and K.N. Tu, Appl. Phys. Lett. 41, 440 (1982)
8. S. Martinuzzi et.al., in: Conf. Record of the 20th IEEE Photovolt. Specialists Conf. (IEEE, New York, 1990), p. 1575
9. I. Perichaud and S. Martinuzzi, in: Conf. Record of the 22nd IEEE Photovolt. Specialists Conf. (IEEE, New York, 1990), p. 877
10. L.A. Verhoef et.al. Appl. Phys. Lett. 57, 2704 (1990)

Phosphorus and Aluminum Gettering for High Efficiency Polycrystalline Silicon Solar Cells

A. Rohatgi, P. Sana, R. Ramanachalam, and W. B. Carter
University Center of Excellence for Photovoltaics
Georgia Institute of Technology
Atlanta, Georgia 30332

1. Introduction

Polycrystalline silicon solar cells have become a strong contender for terrestrial applications. Several investigators [1] have reported polycrystalline silicon cell efficiencies in the range of 14.5-16.8%, with one group [2] reporting efficiency in excess of 17%. In spite of recent accomplishments in polycrystalline cell efficiency, exact identification and role of efficiency limiting defects and mechanisms in polycrystalline cells are not fully understood. Extensive research has been conducted on this topic using single crystal silicon but little has been done on polysilicon. Polycrystalline silicon quality suffers from the presence of grain boundaries and point defects such as vacancies, interstitial, transition metal impurities, oxygen, carbon and their complexes. Therefore, what has been learned on single crystal silicon cannot be applied blindly to polysilicon. Gettering and passivation techniques need to be developed, understood, and optimized for polycrystalline materials. Both phosphorus and aluminum gettering treatments are not only desirable but highly compatible with silicon cell processing because phosphorus gettering forms the n^+ -emitter and aluminum treatment results in the formation of the p^+ back-surface-field (BSF) of n^+ - p - p^+ solar cells. The objective of this paper is three folds: improve basic understanding of phosphorus and aluminum gettering in silicon, fabricate and analyze high efficiency polycrystalline silicon solar cells, and provide guidelines for achieving $\geq 20\%$ efficient polycrystalline silicon solar cells.

2. Basic Understanding of Phosphorus and Aluminum Gettering

This section reviews some facts and issues related to the phosphorus and aluminum gettering in silicon and discusses some results in an attempt to improve the understanding of the effect of these two treatments.

2.1. Phosphorus gettering of metallic impurity

Phosphorus gettering is better understood than the aluminum process. In order to prove that phosphorus treatment actually getters or removes harmful metallic contaminants from the silicon bulk, a study was conducted [3] by incorporating Mo, Ti, and Cr transition metals in both single and polycrystalline silicon by contaminating the silicon melt during the Czochralski growth. It is important to recognize that Mo is a very slow diffuser with diffusion constant $D < 10^{-14} \text{ cm}^2/\text{s}$, Ti is an intermediate/slow diffuser with $D \sim 8 \times 10^{-10} \text{ cm}^2/\text{s}$ and Cr is a fast diffuser with $D \sim 10^{-7} \text{ cm}^2/\text{s}$. Table I shows the metallurgical impurity

content of the ingot which was determined by the spark source mass spectroscopy.

Deep-level or the electrically active impurity concentrations at different locations on the as-grown polycrystalline and single-crystal wafers and cells were determined. The averages of these values are compiled in Table I. The data show that the electrically active Mo, Ti, and Cr concentration in single crystal is 100%, 40%, and 23% respectively, of

Table I. Average impurity concentrations in single and polycrystalline silicon ingots and cells

Ingot ID	Metallurgical Concentration cm^{-3}	Electrically Active Concentration in As-grown wafer cm^{-3}	Electrically Active Concentration in Solar Cell (near junction) cm^{-3}
Ti-210-Single	1.0×10^{14}	$(3.8 \pm 0.5) \times 10^{13}$	$(4.0 \pm 0.5) \times 10^{12}$
Ti-102-Poly	1.1×10^{14}	$(4.6 \pm 2) \times 10^{13}$	$(6.0 \pm 2.0) \times 10^{12}$
Cr-004-Single	1.0×10^{15}	$(1.5 \pm 0.5) \times 10^{14}$	undetectable
Cr-227-Poly	1.4×10^{15}	$(8-200) \times 10^{12}$	undetectable
Mo-207-Single	2.0×10^{12}	$(2.3 \pm 0.2) \times 10^{12}$	$(2.2 \pm 0.3) \times 10^{12}$
Mo-215-Poly	2.0×10^{15}	$(2.4 \pm 0.3) \times 10^{12}$	$(2.3 \pm 0.2) \times 10^{12}$

metallurgical impurity content. The reduction in the deep-level concentration is attributed to precipitation or complexing following crystal growth. A further reduction in the deep-level concentration of Ti and Cr, near the junction, occurs due to phosphorus diffusion during cell fabrication. Cr concentration near the junction decreases by more than three order of magnitude and falls below the DLTS detection limit, which was $\sim 4 \times 10^{11} \text{ cm}^{-3}$ for these samples. Ti concentration reduces by about a factor of 10 near the junction but recovers after $20 \mu\text{m}$ into the bulk due to diffusion limited gettering toward the junction. However, the Mo concentration remains unaffected, a result ascribed to the very low diffusion constant of Mo in silicon compared to Ti and Cr.

The DLTS data for the polycrystalline material exhibit considerably more variability than for the single-crystal silicon, particularly in the case of Cr. This is due to the changes in the impurity concentration near microstructural features. In general, the impurity concentration is reduced in the vicinity of meandering grain boundaries, while the concentration near the straight-sided twin boundaries or within the grain interiors remains nearly unaffected. All grain boundaries do not affect the impurity concentration equally. The reduction in deep-level concentration was found to be species-dependent. In the case of fast diffuser Cr, as much as a 20-fold reduction near some grain boundaries was observed [3]. However, for Ti the depression in electrical activity was less than a factor of two, and in the case of very slow diffuser Mo there was no noticeable change in electrical activity that could be related to impurity-grain boundary interaction.

The above data clearly shows that phosphorus treatment effectively getters or removes fast diffusers, partially getters intermediate diffusers, and is unable to getter very slow diffusers like Mo. It is interesting to note that the efficiency of phosphorus gettering of metallic contaminants is very similar for single and polycrystalline silicon. The model for phosphorus gettering is well understood [4] and involves injection of silicon interstitials into the bulk which kick out metallic contaminants from the substitutional to interstitial sites which diffuse toward the n^+ -sink and form phosphorus-impurity complexes or pairs by reoccupying the vacant substitutional sites created by the high temperature phosphorus treatment.

2.2. Effect of aluminum treatment on silicon

Unlike POCl_3 treatment, the effect of aluminum treatment on silicon is not well understood. Al treatment usually involves deposition of 1-2 μm thick aluminum followed by a high temperature drive-in. Although several investigators [2] have reported the beneficial effect of Aluminum treatment on the polycrystalline silicon cell performance, it is not clear whether this effect is the result of gettering, defect passivation, or simply the formation of p^+ -BSF which can reduce SRV and increase the effective bulk lifetime in the base. There are a number of unconfirmed speculative models in the literature including (a) aluminum treatment passivates grain boundaries by removing dangling bonds (b) atomic hydrogen evolves during the aluminum treatment which can passivate bulk defects (c) aluminum diffuses rapidly through the grain boundaries and forms p - p^+ high-low junction to reduce grain boundary recombination velocity (d) aluminum treatment getters metallic contaminants and its gettering efficiency improves in the presence of dislocations and (e) aluminum gettering is complimentary to phosphorus gettering. In spite of the lack of understanding, aluminum treatment is attractive because it is inexpensive, non-toxic, and forms p^+ -BSF.

In order to understand the effect of aluminum process, we performed aluminum treatment on high quality 500 Ω -cm single crystal silicon wafers by depositing 1-2 μm thick aluminum followed by a 1000 $^\circ\text{C}/3\text{hr}$ drive-in in a high quality clean furnace as well as in a contaminated furnace. The minority carrier lifetime in these as-grown wafers was 3-5 msec. Figure 1 shows that the aluminum treatment in the clean furnace had no major effect on the lifetime, which remained about 2-3 msec. This indicates that Al-treatment is not beneficial when dealing high quality wafers in a clean processing environment. However, Figure 1 also shows that when processing is done in the contaminated furnace, there is a definite improvement in the lifetime. In this experiment, half of the wafer that was not coated with aluminum had a lifetime of only ~ 500 μsec due to furnace contamination but the Al-coated half had a lifetime of ≥ 1 msec. This experiment shows that aluminum treatment can at least mitigate the process-induced degradation of lifetime. Note that the Al-coated half had a lifetime that was less than the starting lifetime of 2-5 msec, indicating that the aluminum treatment was helpful in this experiment but was not able to completely restore the lifetime to the original value.

Aluminum treatments were also performed on 0.8 Ω -cm polysilicon obtained from Osaka Titanium which showed an optimum drive-in temperature of 850 $^\circ\text{C}$ (Figure 2).

Since it was difficult to decouple the lifetime and BSF effects due to low lifetime in polysilicon, we plotted the V_{oc} in Figure 2 which contains both the effects.

More research and analysis needs to be done to understand the exact aluminum gettering mechanism and the reason for the optimum gettering temperature. Below the 850 °C drive-in, the V_{oc} increases with increasing drive-in temperature because of two reasons: first the Al gettering efficiency increases with the temperature, and secondly the thickness and effectiveness of the BSF increases with the increased temperature. The decrease in V_{oc} beyond 850 °C is probably due to the fact that defective materials like polysilicon cannot stand very high temperature processing without lifetime degradation.

3. Fabrication of High Efficiency Polycrystalline Cells

Phosphorus and aluminum gettering conditions were optimized to achieve high efficiency polycrystalline silicon cells. In order to take advantage of the intense gettering without the harmful effects of the emitter dead layer, a deep phosphorus diffusion at 930 °C for 25 min. was performed followed by a partial etch-back of the n^+ -region. Optimum aluminum treatment for polysilicon cells involved 1-2 μm thick Al deposition followed by 850 °C/35 min drive-in. Oxide passivation was found to be effective in the cells made on these OTC polysilicon wafers. A 5 min. oxide passivation was done during the aluminum drive in oxygen ambient. A combination of optimum phosphorus and aluminum gettering, oxide passivation, and double layer antireflection coating resulted in record 17.7% efficient polycrystalline silicon solar cells under one sun illumination.

Model calculations were performed to match the performance of the 17.7% efficient cell using the PC-1D program with reasonable and realistic input parameters. Table II shows that the model calculations are in a very good agreement with the experimentally measured cell parameters, in spite of ignoring the grain boundary defects and effects. A measured effective bulk lifetime of 25 μsec was used in the model calculation. This indicates that in a properly gettered large grain polycrystalline cells, intragrain defects are probably more important than the grain boundary defects in dictating the cell performance. Slight differences in the measured and modeled lighted I-V parameters may be due to the assumption of flat surfaces and assumed SRV values.

Table II. Comparison of the calculated and measured cell parameters of the high efficiency polycrystalline silicon

Comparison of Model and Exp.	$J_{sc}(\text{mA}/\text{cm}^2)$	$V_{oc}(\text{mV})$	FF	Eff. %
Measured Parameters	35.60	626	0.7921	17.7
PC-1D Model	35.50	621	0.8136	17.9

4. Modeling and Directions for High Efficiency Polycrystalline Silicon Cells

After matching the measured cell parameters of the 17.7% efficient polycrystalline cell, attempts were made to change the cell design and material properties to provide guidelines for achieving even higher efficiencies. Figure 3 shows the effect of changing some of the design parameters on the performance of the cell. Increase in the carrier lifetime from 25 to 100 μsec increases the absolute efficiency by less than 0.5% for this cell with 1 μm deep unpassivated BSF. Therefore additional gettering will not do much for this cell unless BSF or BSRV are improved. Figure 3 shows that some gettering is very important because efficiency increases rapidly with lifetime (τ) up to a lifetime value of about 40 μsec . Beyond $\tau = 40 \mu\text{sec}$ relative improvement in cell efficiency becomes very small. Model calculations show that even with the increase in the bulk lifetime value up to 1 msec, an efficiency of only 18.6% can be realized with this cell structure. Figure 3 also shows that surface texturing alone, using slats or grooves with a pitch of 100 μm and slat angle of 60° , can raise the efficiency of this cell to 18.9%. Finally, Figure 3 demonstrates that a combination of reduced BSRV, increased base doping, and front surface texturing can produce $\geq 20\%$ efficient polycrystalline silicon cells.

5. Summary

Both aluminum and phosphorus gettering are important and highly compatible with polycrystalline silicon cell processing. Gettering mechanism and the ability of phosphorus treatment to remove impurities is well understood. However, more research is needed to understand the role of aluminum treatment in gettering or passivating impurities and defects in polycrystalline silicon. Preliminary results indicate that aluminum process can getter process-induced contaminants and improve polycrystalline cell performance, specially when the material quality is not so good and the process environment is not very clean. Optimization of phosphorus and aluminum gettering resulted in a record high 17.7% efficient polycrystalline silicon cells. In order to achieve $\geq 20\%$ efficient polycrystalline cells, we not only need to identify lifetime killers and develop gettering and passivation techniques, but we also need to conduct such research in conjunction with cell design and fabrication in order to take full advantage of the gettering-induced improvements in polycrystalline materials.

References

- [1]. H. Watanabe, "Improvements in Large Area Multicrystalline Silicon Solar Cells", in Proceedings of the 6th International Photovoltaics Science and Engineering Conf., pp. 745-752, 1992.
- [2]. S. Narayanan, et al, "17.8-Percent Efficiency Polycrystalline Silicon Solar Cells", IEEE Transaction on Electron Devices, Vol. 37, No. 2, pp. 382-384, 1990.
- [3]. A. Rohatgi et al, "Impurity Effects on Polycrystalline Silicon Solar Cells", in Proceedings of the 16th IEEE PVSC, pp. 411-416, 1982.
- [4]. W. Schroter, and R. Kuhnappel, "Model Describing Phosphorus Gettering of Transition Elements in Silicon", Appl. Phys. Lett., 56(22), pp.2207-2209, 1990.

Fig 1. The effect of Al diffusion on SRH lifetime

Fig 2. The effect of Temperature on Voc

Fig 3. The Effect of Resistivity, Texturing, and BSRV

on Polysilicon Cell Performance

PASSIVATION OF IMPURITIES IN Si BY ANNEALING IN H₂

Michael Stavola, G.D. Watkins, P.M. Williams, and S. Uftring
Physics Bldg. 16, Lehigh University, Bethlehem, PA 18015

ABSTRACT

In this paper the passivation of impurities in silicon by annealing in H₂ gas is described. A fraction of the shallow acceptors are passivated throughout the bulk of a Si sample that is several mm thick by annealing in H₂ gas at 1280°C and quenching. Complexes of H with deep defects can also be formed in this way. It is now possible to make samples with a sufficient number of hydrogen passivated deep defects to study by structure sensitive techniques such as IR absorption or EPR spectroscopy.

I. INTRODUCTION

Most recent work on H in semiconductors [1-3] has focussed on defect-passivation in a plasma that contains atomic hydrogen. Here, new examples where annealing in an H₂ ambient leads to significant H incorporation and impurity-H complex formation are discussed. (i) Acceptors in Si can be passivated by annealing in H₂ at elevated temperatures (900°C-1280°C) and then quenching rapidly. [4-6]. (ii) Transition metal-H complexes are also formed by similar heat treatments. [7, 8]

Although H passivation from H-containing plasmas dominates recent work, there are a number of cases where H₂ in growth and annealing ambients has been shown to lead to H incorporation and/or defect passivation. In elemental hosts, Hall [9] and Haller and coworkers [10] have discovered several H-related species in Ge that had been grown in H₂. Si grown in an H₂ atmosphere is also known to contain a number of H-related defects.[11] In experiments performed by the Sievers group,[12,13] annealing Si in H₂ gas led to the formation of impurity-H complexes.

II. PASSIVATION OF SHALLOW ACCEPTORS

In our experiments, Si samples were sealed in quartz ampules that had been evacuated and then filled with 0.6 atm of H₂ gas at room temperature. The sealed ampules were annealed at temperatures between 900°C and 1280°C and then quenched to room temperature by withdrawing the ampule from the furnace and dropping it into ethylene glycol at room temperature.

IR spectra of bulk, acceptor-doped Si samples (with N_A of the order of 10^{16} cm^{-3}) that had been annealed in H_2 are shown in Fig. 1. The H-stretching features have frequencies and absorption strengths similar to those reported for acceptor-H complexes in samples that were doped with concentrations greater than 10^{18} cm^{-3} by ion-implantation and then passivated by exposure to an H_2 plasma.[14] Absorption strengths in the H_2 -soaked, uniformly doped samples that are comparable to thin, heavily doped layers implies acceptor passivation well into the bulk of the H_2 -soaked samples. To confirm that the passivation was uniform throughout the sample thickness, we remeasured the IR absorption after grinding 1 mm from the surfaces of an H_2 treated, B-doped sample that was initially 3 mm thick. Vibrational absorption due to B-H centers was observed with a strength consistent with the 1 mm thickness of the thinned sample and a uniform distribution of centers throughout the sample.

Fig. 1. IR spectra measured near liquid He temperature for acceptor-doped, Si samples that had been annealed in H_2 gas at 1280°C for 30 min. and then quenched to room temperature. The acceptor concentrations are 6×10^{16} , 1×10^{16} , and $0.7 \times 10^{16} \text{ cm}^{-3}$ for the B, Al, and Ga doped samples, respectively.

To determine [B-H] from the strength of the IR absorption at 1903 cm^{-1} we have reexamined previous results [15] for a B-implanted sample that had been passivated in an H_2 plasma. The calibration is given by,

$$[\text{B-H}]/A = 2.5 \times 10^{15} \text{ cm}^{-1}. \quad (1)$$

Here, A is the integrated absorption coefficient for the 1903 cm^{-1} band in units cm^{-2} . With the calibration given by Eq. (1) we find that $[\text{B-H}] = 4.6 \times 10^{15}$ and $5.0 \times 10^{14} \text{ cm}^{-3}$ for samples with $[\text{B}] = 1.7 \times 10^{17}$ and $1.6 \times 10^{16} \text{ cm}^{-3}$, respectively. Hence, approximately 3% of the B is passivated by the anneal in H_2 at 1280°C . For the Al doped sample we find

$[Al-H] = 1.3 \times 10^{15} \text{ cm}^{-3}$ and that 8% of the Al is passivated. The more complete passivation of Al is consistent with this complex's greater binding energy. [16]

We have explored the role of the temperature and duration of the H_2 -soaking treatment on the concentration of B-H complexes that are formed. In Fig. 2 are plotted the concentrations of B-H complexes formed vs. the reciprocal of the temperature of the H_2 anneal for the sample doped with $[B] = 1.7 \times 10^{17} \text{ cm}^{-3}$. The open circles are for 30 min. anneals and the closed squares are for 120 min anneals. At 1100°C , increasing the duration of the anneal increases the strength of B-H absorption only slightly. At 900°C , increasing the duration of the anneal increases the B-H absorption by roughly a factor of 2 indicating that H has not fully diffused through the sample during the 30 min anneal. The dashed line shown in Fig. 2 is the best fit to the data. (At 900°C , the data for the 120 min anneal was used.) If we use the calibration of the B-H absorption given in Eq. (1), the temperature dependence of $[B-H]$ for our samples is given by

$$[B-H] = 1.2 \times 10^{19} \exp(-1.04 \text{ eV}/kT) \text{ cm}^{-3} \quad (2)$$

Also shown in Fig. 2 is the hydrogen solubility determined by Van Wieringen and Warmoltz [17], $S_H = 4.8 \times 10^{21} \exp(-1.88 \text{ eV}/kT) \text{ cm}^{-3}$. While $[B-H]$ is greater than the VWW value by only a factor of 1.3 at 1280°C , the B-H concentration in our samples annealed at 900°C exceeds the VWW value by a factor of 10. The activation energies in Eq.(2) and the solubility determined by VWW differ by nearly a factor of 2.

Fig. 2. The integrated absorption coefficient, A , for the H-stretching vibration of the B-H complex vs. the reciprocal of the annealing temperature for Si samples with $[B] = 1.7 \times 10^{17} \text{ cm}^{-3}$ that were annealed in H_2 , and then quenched. The concentration scale on the right is related to A by Eq.(1) in the text. The solid line is the solubility of H in pure Si determined by Van Wieringen and Warmoltz.

When H was introduced into n-type Si doped with P or As in the mid- 10^{16} cm^{-3} range by annealing at 1280°C in H_2 gas and quenching, IR absorption bands at 1555 and 1561 cm^{-1} that have been assigned to P-H and As-H complexes [18] were not detected. We conclude that shallow donors are not passivated as efficiently as acceptors by the introduction of H into our samples at high temperatures.

II. PASSIVATION OF DEEP LEVELS

Previous studies of H-passivated shallow impurities are made possible, in part, by the high solubility of the dopant. In order to have a sufficient number of centers in the micron-thick, H-passivated layers that are typical of plasma exposed samples, the dopant concentration must be large, i.e. $> 10^{18}\text{ cm}^{-3}$. The study of hydrogen-passivated deep impurities has been hampered by their lower solubility ($\sim 10^{16}\text{ cm}^{-3}$) which does not lead to a sufficient total number of hydrogen-passivated centers in thin, plasma-passivated layers for easy examination by structure sensitive techniques such as IR absorption or EPR. Our results summarized above show that H can be introduced throughout the bulk of a semiconductor sample and that the total number of centers introduced will permit structure-sensitive studies of species with solubilities that are decades smaller than is typical of common dopants.

In recent experiments complexes of Pt and H have been formed in bulk Si samples for study by EPR [7] and IR absorption [8]. Pt was diffused into n-type Si at 1250°C . Subsequently, these samples were annealed in H_2 at 1250°C and quenched to room temperature. In EPR measurements [7], a new spectrum characteristic of a defect with C_{2v} symmetry has been found. From hyperfine splittings observed in the spectrum it has been determined that there are one Pt atom and two hydrogen atoms in the center. The change in the hyperfine splittings upon substitution of D for H confirms this interpretation.

The EPR data lead to a tentative model in which the Pt atom is displaced from its lattice site and is bonded to two of its Si neighbors. This leaves two Si dangling bonds which are terminated by hydrogen atoms.

In these same samples, several new IR absorption bands are also found in the H-stretching region (Fig. 3). The shift in the vibrational frequencies upon the substitution of D for H confirms that these are H vibrations. These bands are not found in samples into which no Pt has been diffused or in samples into which other metal impurities have been diffused; these results provide evidence that the new spectra are indeed related to Pt.

Fig. 3. An IR absorption spectrum (measured near 4 K with 0.2 cm^{-1} resolution) for a Pt-diffused Si sample that was subsequently annealed in H_2 at 1250°C . [8]

In our ongoing work we are attempting to correlate the spectral features in the EPR and IR spectra and to determine the microscopic properties of the complexes of Pt with H. We are also exploring the H-passivation of other deep centers with some success.

III. CONCLUSION

In recent work it has been shown that acceptor impurities in bulk Si samples can be passivated by annealing in H_2 at high temperature and quenching. [4-6] H is incorporated at concentrations that are above the solubility determined by Van Wieringen and Warmoltz. [17] Such passivation techniques that result in H incorporation throughout bulk samples have the promise of allowing us to develop a detailed, microscopic understanding of H-passivated deep levels. There are now a few examples [7,8,12,13] where annealing Si in H_2 gives rise to a sufficient number of centers that include H and a deep level defect for study with structure-sensitive probes like IR absorption and EPR.

REFERENCES

1. Hydrogen in Semiconductors, ed. J.I. Pankove, and N.M. Johnson, (Academic, San Diego, 1991).
2. Hydrogen in Semiconductors, ed. M. Stutzmann and J. Chevallier, (North Holland, Amsterdam, 1991).
3. S.J. Pearton, J.W. Corbett, and M. Stavola, Hydrogen in Crystalline Semiconductors, (Springer-Verlag, Heidelberg, 1992).
4. I.A. Veloarisoa, D.M. Kozuch, R.E. Peale, M. Stavola, and G.D. Watkins, Bull. Am. Phys. Soc. 36, 945 (1991).
5. S.A. McQuaid, R.C. Newman, J.H. Tucker, E.C. Lightowlers, R.A.A. Kubiak, and M. Goulding, Appl. Phys. Lett. 58, 2933 (1991).
6. I.A. Veloarisoa, M. Stavola, D.M. Kozuch, R.E. Peale, and G.D. Watkins, Appl. Phys. Lett. 59, 2121 (1991).
7. P. Williams and G.D. Watkins, unpublished.
8. S. Uftring, M. Stavola, P. Williams, and G.D. Watkins, unpublished.
9. R.N. Hall, Inst. Phys. Conf. Ser. No. 23, 190 (1975).
10. E.E. Haller, in ref. 1, p. 351; ref. 2, p. 351.
11. G.R. Bai, M.W. Qi, L.M. Xie, and T.S. Shi, Solid State Commun. 56, 277 (1985); M.W. Qi, G.R. Bai, T.S. Shi, and L.M. Xie, Mat. Lett. 3, 467 (1985) and references contained therein.
12. K. Muro and A.J. Sievers, Phys. Rev. Lett. 57, 897 (1986).
13. R.E. Peale, K. Muro, A.J. Sievers, Shallow Impurities in Semiconductors, ed. G. Davies, (Trans Tech, Switzerland, 1991), p. 141.
14. M. Stavola, S.J. Pearton, J. Lopata, and W.C. Dautremont-Smith, Appl. Phys. Lett. 50, 1086 (1987).
15. M. Stavola, S.J. Pearton, J. Lopata, and W.C. Dautremont-Smith, Phys. Rev. B 37, 8313 (1988).
16. T. Zundel and J. Weber, Phys. Rev. B 39, 13549 (1989).
17. A. Wieringen and N. Warmoltz, Physica 22, 849 (1956). The solubility given in this reference is for H₂. We double the reported values to obtain the solubility for atomic H.
18. K. Bergman, M. Stavola, S.J. Pearton, and J. Lopata, Phys. Rev. B 37, 2770 (1988).

SPIN DEPENDENT PHOTOCURRENTS IN RIBBON SOLAR CELLS

C. H. Seager, E. L. Venturini and W. K. Schubert
Sandia National Laboratories
Albuquerque, N. M. 87185

ABSTRACT

Spin Dependent Transport (SDT) is a method of identifying recombination centers which employs a microwave resonance condition to affect the recombination rate of minority carriers in a device. When this technique is used to analyze the diffusion-limited currents produced by long-wavelength optical excitation, it has the potential to chemically identify the major recombination sites in solar cells. We have used this resonance technique to analyze short circuit photocurrents in Edge-defined film-Fed Growth (EFG) ribbon silicon solar cells. At room temperature, our observed photocurrent resonances have zero-crossing g values and linewidths which are similar to SDT observations made on the trans-barrier currents in silicon bicrystals, and electron spin resonance signals seen in damaged silicon, and polycrystalline silicon. These dangling-bond-like SDT signals depend on cell illumination levels in a way that suggests that the values of recombination velocity at electrically active linear boundaries decrease with illumination intensity. Hydrogen processed cells show markedly smaller SDT response, consistent with the passivation of Si dangling bond defects. While most of our SDT observations have been made on n^+/p EFG cells, we suggest that measurements made at low temperatures on other cell structures might uncover resonances due to other recombination centers in this material.

INTRODUCTION

Identifying the recombination centers which control minority carrier lifetime is an important step in the process of optimizing the performance of low-cost photovoltaic devices. Techniques like Electron Beam Induced Current (EBIC)¹ and its light beam counterpart, LBIC¹, can reveal spatially localized defect arrays such as grain boundaries or dislocations, but do not provide information about the chemical identity of the actual recombination centers. Deep Level Transient Spectroscopy (DLTS) can sense deep electron or hole trap levels in the depletion region of a junction device², but literally hundreds of different trap energies have been catalogued in materials like Si and GaAs, so identification of the specific contaminant may prove difficult.

Beginning in the early 1970's, a spin resonance-based transport technique variously identified as SDT (spin dependent transport) or SDC (spin dependent conductivity) has been demonstrated in single crystal silicon^{3,4}, silicon

bicrystals^{5,6}, and Si transistors^{7,8}. In this measurement the photoconductivity, trans-barrier current, or dark junction current is measured as a resonance condition is established for paramagnetic defects which control the sample current. Because the (usually unique) magnetic resonance properties of the transport controlling defect are probed, this measurement has a high degree of chemical specificity.

Our work will demonstrate the use of this technique to probe the nature of minority carrier recombination in silicon ribbon solar cell structures. The results show that one relatively well understood recombination center, the silicon dangling bond, is present in these devices, and that the density of dangling bonds can be substantially reduced by hydrogen in-diffusion. We show that our SDT signal-to-noise ratio at 300K is close to that necessary to detect any spin-saturable recombination center which obeys the simple model first proposed by Lepine³; At 76K our signal to noise ratio should easily permit us to observe SDT resonances which obey this model. Despite this fact, we see only resonances associated with the dangling bond at these lower temperatures. These studies represent the first application of this method to understanding recombination mechanisms in a production photovoltaic device made from crystalline silicon.

EXPERIMENTAL

The cells measured here were cut from large EFG ribbon Si n⁺/p solar devices⁹. Edge-fed film-defined growth silicon is a high purity, solar grade material obtained by pulling a continuous liquid ribbon from a carbon crucible through a carbon die. Because of the high stress levels present during the cooling process, coherent or higher order twin boundaries with associated dislocation arrays form along the growth axis of the ribbon. Many of these structures are active recombination planes and are easily observed in EBIC analyses¹⁰. Hydrogen passivation¹⁰ of these structures greatly reduces this EBIC activity and produces increases in ribbon solar cell short circuit currents of ~4-6%. In ribbon cells with minority carrier diffusion lengths, X_L , of 50-60 μm , the average spacing of EBIC active boundaries is typically 10 per cm. Given these parameters, we estimate that ~5 - 10% of short circuit cell currents are lost at grain boundaries, assuming that all photocarriers generated within X_L are swept into these defects and undergo non-radiative recombination. While this estimate makes the H passivation results¹⁰ seem sensible, it has also been noted that the bulk diffusion length, measured away from active boundaries, shows significant improvement as well.

Small (~3 X 3 mm) scribed and broken pieces of fabricated cells (with no AR coating) were inserted into a TE102 X-band microwave cavity located in a standard electron spin resonance apparatus. The cavity and sample could be cooled to 76K. The available microwave power was 150-250 mW. Illumination was provided by a quartz halogen source with spectral selection via Corning glass filters. Short circuit photocurrent was monitored with a Keithley 427

current amplifier; its output was lock-in detected at the 0.2-3 KHZ magnetic field modulation frequencies used for standard derivative detection.

RESULTS

Figure 1 shows the photoconductivity derivative spectra obtained at 300K for a non-hydrogen-processed EFG cell with red light (Corning 2-58 filter, $\lambda_{\min} = 600 \mu\text{m}$) illumination. Because of the fairly small signal size, a 4 Gauss p-p magnetic field modulation was employed; recent experience¹¹ with SDT in Si bicrystals leads us to believe that this signal may be seriously overmodulated at this p-p value. At this modulation level the derivative of the current resonance is symmetric about $g = 2.003 \pm .001$, has a ~ 10 G p-p width, and corresponds to a decrease in the photocurrent; it closely resembles the Si dangling bond resonances seen in a-Si:H¹², damaged¹³, and polycrystalline Si¹⁴.

Under these signal conditions $\Delta I_{sc}/I_{sc} \approx -4 \times 10^{-6}$, an estimate which is uncertain by perhaps a factor of 2 due to our ignorance of the true lineshape. Cooling the sample to 76K reduces the short circuit photocurrent by a factor of 3, but the value of $\Delta I_{sc}/I_{sc}$ at $g=2.003$ remains roughly equal to its 300K value. No other resonances were observed at either temperature despite many field scans at other H values.

Table 1 shows ΔI_{sc} at 300K versus microwave power for several samples. No attempt was made to control sample temperature during these measurements and full microwave power does raise the cell an estimated 5-15°C above the ambient dewar temperature. We see that, while ΔI_{sc} is a sublinear function of power at the highest power levels, we are not able to saturate the spin system in any of our samples. Thus, our above estimate of $\Delta I_{sc}/I_{sc}$ is only a lower bound to the infinite power value. We also note that there is almost no modulation frequency dependence of ΔI_{sc} .

We observe that the spectral composition of the incident light has a large effect on the SDT signal. Using a Corning (blue) 2-60 filter we were able to generate photocurrent from carriers produced in the n+ emitter. When we compare the signal produced by blue light with that produced at equal I_{sc} levels by red light, we find no observable blue-light-SDT response within the noise levels ($\sim \pm 15\%$) present at the rather small photocurrents employed. We also observe no dark SDT signal with small forward or reverse junction biases; in addition, the light-induced SDT response did not seem to be a noticeable function of cell bias. All of these observations indicate that the SDT response is primarily due to resonance induced variations of the minority carrier lifetime in the p-type base of the cell.

While our observed photocurrents were (within a few %) linear in the illumination intensity (not shown), a noticeable dependence on I_{sc} is observed when the normalized value of the resonance induced current decrease, $\Delta I_{sc}/I_{sc}$, is plotted, as illustrated in Figure 1. This is particularly true for EFG cells that have been hydrogen passivated. Figure 1 shows that this treatment not only reduces the SDT response, but also enhances the dependence

Figure 1. The peak to peak values of the resonance induced variation of short circuit photocurrent, ΔI_{sc} , normalized by I_{sc} and plotted versus I_{sc} . Open circles are for an untreated EFG ribbon silicon solar cell; closed circles; a hydrogenated EFG cell. The inset shows a derivative ΔI_{sc} spectra recorded for an untreated cell with red light illumination and 4 G p-p magnetic field modulation.

of $\Delta I_{sc}/I_{sc}$ on cell current. Since these cells were passivated before being scribed and broken, the difference in response between baseline and H passivated cells indicates that dangling bonds at the broken edges are probably not an important source of our SDT signals. The data shown in Figure 1 were replicated by other virgin and H passivated cells.

DISCUSSION

Previous treatments¹⁵⁻¹⁷ of minority carrier recombination at grain boundaries suggest that the recombination velocity, S , is typically an exponential function of the barrier height, i.e.:

$$S \propto \sigma_n e^{\phi_B/kT} \quad (1)$$

where σ_n is the capture cross-section for an electron at a positively charged boundary in p-type material, and ϕ_B is the potential barrier height. This expression is generally valid for $\phi_B < 0.25$ eV. For parallel grain boundaries with average separation X_B , it is not hard to show, using the formalism of reference (17), that the spatially averaged minority carrier population is:

$$n_{ave} = n_{\infty} (1 - (2X_L/X_B)(S/(S+1))), \quad (2)$$

where n_{∞} is the steady state minority density far away from a boundary, and S (now dimensionless) is expressed in units of (D_n/X_L) where D_n is the minority carrier diffusion coefficient. If $S \Rightarrow S + \Delta S$ at resonance, and n_{∞} does not change, we find that:

$$\frac{\Delta I_{sc}}{I_{sc}} = - \frac{2X_L}{X_B} \frac{S}{(S+1)^2} \frac{\Delta S}{S}, \quad (3)$$

where we have assumed that $\Delta I_{sc}/I_{sc}$, the fractional change in diode photocurrent, $= \Delta n_{ave}/n_{ave}$. It is reasonable to assume that the only term in Equation (1) that varies at resonance is σ_n , so that $\Delta S/S$ in Equation (3) may be replaced with $\Delta \sigma_n/\sigma_n$. To explain the variation of $\Delta I_{sc}/I_{sc}$ seen in Figure 1 we remind the reader that, above some threshold light intensity, S starts to drop and eventually becomes a linearly decreasing function¹⁷⁻¹⁹ of

illumination level (or equivalently of I_{sc}). We now refer to a plot of the S dependence of equation (3) shown in Figure 2. We suppose that in unhydrogenated EFG material a distribution of boundaries exists with S values both above and below $S = 1$ (corresponding to $\approx 10^4$ cm/sec). This distribution is outlined with a solid rectangle in the figure. Under these conditions, any decrease in S caused by illumination (shown by dashed lines) does not shift the average value of $\Delta I_{sc}/I_{sc}$ very much, since the RHS of Equation (3) is relatively constant for $0.2 < S < 5$. At large I_{sc} values, however, the center of gravity of the distribution of S values will shift to the left of $S = 1$, and some decrease in $\Delta I_{sc}/I_{sc}$ will be seen, as experimentally observed.

Previous studies have shown^{10,20} that hydrogenation reduces grain boundary S values by 1-2 decades, presumably by rendering boundary trap states electrically inactive. We see from Figure 2 that when most boundary S values lie below 1, decreases of S with illumination will lead to almost linear decreases in $\Delta I_{sc}/I_{sc}$ with increasing illumination ($\propto I_{sc}$), as observed (Figure 1).

Equation (3) predicts that the magnitude of $\Delta I_{sc}/I_{sc}$ will be:

$$\frac{\Delta I_{sc}}{I_{sc}} < \frac{2X_L}{X_B} \frac{1}{4} \cdot \frac{\Delta \sigma_n}{\sigma_n} \quad (4)$$

for the distribution of S values shown in Figure (1) for unhydrogenated cells. Recent studies of SDT in silicon bicrystals have inferred that $\Delta \sigma_n/\sigma_n \geq 2 \times 10^{-3}$ for carrier recombination at Si dangling bonds¹¹. This rather large value may be associated with recombination of correlated e-h pairs at dangling bond arrays found at dislocation or grain boundary cores and has been predicted theoretically by Kaplan et al.²¹. Using $X_L = 50 \mu m$ and $X_B = 0.1$ cm, Equation (4) yields $\Delta I_{sc}/I_{sc} < 5 \times 10^{-5}$. This upper limit is consistent with the experimental values that we observe. We note that these fractional alterations of the photocurrent are well above the prediction of the Lepine model ($\sim 7 \times 10^{-6}$) at 300K. Note that this model applies to uncorrelated recombination at isolated impurities. In the present case we anticipate that both electrons and holes may be simultaneously trapped at higher order twin boundaries giving rise to pair recombination.

An alternative explanation for the increased dependence of $\Delta I_{sc}/I_{sc}$ on I_{sc} seen for hydrogenated cells may lie in the mechanism for the light sensitivity of grain boundary potential barriers. It has been shown that these barriers begin to decrease when the captured minority carrier currents become comparable to the steady state flux of majority carriers which are captured and emitted by unfilled majority carrier traps¹⁷. If some process (hydrogenation in this case) substantially reduces this trap state density, essentially all of the majority carrier traps may be filled in the dark state, leaving boundaries which are very light sensitive, despite their rather low barrier heights. At present experimental bicrystal studies which bear on this issue have not been carried out.

Figure 2. The S variation of Equation 3 plotted versus S . The upper solid rectangle shows a hypothesized range of S values for unhydrogenated EFG cells in the dark; the upper dashed rectangle shows the range of S values at an arbitrary illumination level. The rectangles at the lower left show possible S ranges for dark and illuminated EFG cells which have been hydrogenated.

Because of the uncertainty in boundary parameters for EFG material, these arguments must be, by necessity, somewhat qualitative. In our view, they are reasonably consistent with the hypothesis that our SDT signals arise from Si dangling bonds at higher order twin boundaries, and that this loss mechanism represents only a small fraction of e-h recombination in this material. What can be said about the remaining recombination events? We have scanned other regions of magnetic field to search for defects having responses above and below those shown in Figure (1). No other detectable SDT resonances were found at 300K or 76K. For p-p SDT linewidths in the 5-15 Gauss range, Lepine-like signals (from uncorrelated e-h recombination) would be near to our 300K noise level, but well above our 76K resolution assuming that spin relaxation times are long enough for us to reach microwave spin saturation. These observations do not rule out the presence of recombination at other centers, such as transition metal impurities. For a Lepine-like signal to be present, it is necessary that the impurity be paramagnetic before minority carrier capture. It is conceivable that this paramagnetic state could only exist for Fermi level positions in the upper half of the forbidden gap. To check for this possibility we are beginning measurements on EFG cells with n-type bases.

CONCLUSIONS

We have observed SDT resonances in the short circuit current from EFG ribbon silicon solar cells. These signals represent a microwave-induced decrease of the diffusion current collected in the p-type base region, and have g values similar to spin resonance data attributed to dangling silicon bonds in silicon bicrystals, damaged and polycrystalline silicon. Hydrogenation strongly affects the magnitude and current dependence of these signals in a fashion that appears consistent with prior studies which indicate that this process reduces the number of electrically active dangling bonds at grain boundaries. These and other studies indicate that dangling bond defects at electrically active boundaries are responsible for less than 10% of the recombination losses in untreated ribbon cells. While SDT signatures of other defects controlling recombination have not been detected, we suggest that experiments with n-type base solar cells could result in the identification of Lepine-like SDT signals arising from uncorrelated e-h recombination at other sites in these materials. Of course, it is also possible that the silicon dangling bond is the only major recombination center in these materials. This would be consistent with observations of H passivation of isolated dislocations in the bulk of EFG ribbon cells and the generally large increases in bulk lifetime seen after hydrogenation.

ACKNOWLEDGEMENTS

The authors would like to thank J. Kalejs for providing samples of EFG ribbon silicon diodes and for useful conversations concerning the properties of this material. This research was supported by the U. S. Department of Energy under contract No. DE-AC04-76DP00789.

TABLE I

Values of the SDT variation, ΔI_{sc} , at various microwave power densities and short circuit current levels for unhydrogenated and hydrogenated ribbon Si solar cells.

CELL#	TYPE	I_{sc} ($\times 10^{-4}$ A)	PWR (arb. units)	ΔI_{sc} (arb. units)	$\Delta I_{sc}/PWR$
2	unhyd.	4.5	1.0	7.4	7.4
"	"	"	0.5	4.9	9.8
"	"	"	0.25	2.3	9.2
"	"	"	0.10	1.03	10.3
"	"	0.48	1.0	1.28	1.28
"	"	"	0.5	0.7	1.4
3	hydrog.	1.0	1.0	1.60	1.60
"	"	"	0.5	1.23	2.46
"	"	"	0.25	.60	2.40
"	"	8.8	1.0	3.00	3.00
"	"	"	0.5	1.97	3.93
"	"	"	0.25	1.27	5.07

REFERENCES

1. For a comparison of these techniques, see: C. H. Seager, J. Appl. Phys. 53, 5968 (1982)
2. G. L. Miller, D. V. Lang, and L. C. Kimerling, Ann. Rev. Mater. Sci. 1977, pp. 377-448.
3. D. Lepine, Phys. Rev. B6, 60 (1972).
4. G. Mendz and D. Haneman, J. Phys. C.11, L197 (1978).
5. P. M. Lenahan and W. K. Schubert, Solid State Comm. 47, 423 (1983).
6. P. M. Lenahan and W. K. Schubert, Phys. Rev. B30, 1544 (1984).
7. I. Solomon, Solid State Comm. 20, 215 (1976).
8. F. C. Rong, E. H. Poindexter, M. Harmatz, W. R. Buchwald, and G. J. Gerardi, Solid State Comm. 76, 1083 (1990).

9. F. V. Wald, in *Crystals: Growth, Properties, and Applications 5*, edited by J. Grabmaier (Springer, Berlin, 1981), pp. 147-198.
10. J. I. Hanoka, C. H. Seager, D. J. Sharp, and J. K. G. Panitz, *Appl. Phys. Lett.* 42, 618 (1983).
11. C. H. Seager, E. L. Venturini, And W. K. Schubert, unpublished.
12. I. Solomon, D. Biegelsen, and J. C. Knights, *Solid State Comm.* 22, 505 (1977).
13. V. V. Kveder, A.E. Koshelev, T. R. Mchedlidze, Yu. A. Osipyan, and A. Shalynin, *Zh. Espk. Teor. Fiz.* 95, 183 (1989).
14. W. B. Jackson, N. M. Johnson, and D. K. Biegelsen, *Appl. Phys. Lett.* 43, 195 (1983).
15. H. C. Card and E. S. Yang, *IEEE Trans. Electron Devices* Ed-24, 397 (1977).
16. J. G. Fossum and F. A. Lindholm, *IEEE Trans. Electron Devices* Ed-27, 692 (1980).
17. C. H. Seager, *J. Appl. Phys.* 52, 3960 (1981).
18. L. L. Kazmerski, *J. Vac. Sci Technol.* 20, 423 (1982).
19. This can be inferred from the logarithmic dependence of ϕ_B on light intensity seen in the model and data of references 17 and 18.
20. C. H. Seager, D. J. Sharp, J. K. G. Panitz and J. I. Hanoka, *J. de Physique* 43, C1-103 (1982).
21. D. Kaplan, I. Solomon, and N. F. Mott., *Journal de Physique* 39, L51 (1978).

ATOMIC HYDROGEN INTERACTION WITH DISORDERED REGIONS IN SILICON

S. Ashok and K. Srikanth
Department of Engineering Science & Mechanics
The Pennsylvania State University
University Park, PA 16802

Abstract

The interaction of atomic hydrogen (H) with disordered regions in Si created by ion implantation has been studied. The focus of this work is the migration of H and its electrical interaction with defects in *as-implanted* layers. Surface as well as buried regions of disorder were created by implanting Ar at 20 keV and 380 keV over the dose range $10^{12} - 10^{15} \text{ cm}^{-2}$. From spreading resistance, SIMS and electrical measurements, the disordered regions are shown to strongly inhibit the penetration of H into the bulk crystalline Si. It is also established that the hydrogen-soaked disorder region can act as a *source* of *atomic* hydrogen during subsequent thermal processing.

Introduction

The role of atomic hydrogen (H) in crystalline Si (c-Si) has been a subject of intense interest in recent years, and in particular dopant deactivation and defect passivation under hydrogen plasma or low-energy hydrogen implantation have been widely investigated [1]. Acceptor deactivation is a singularly dominant effect, with the hole concentration dropping by 3-4 orders of magnitude at the surface and the reduction extending over several μm from the surface. Unlike other studies that have dealt with dopant-implanted and annealed layers, here we have studied the role of H, specifically its interaction with ion damage and migration through and from as-implanted layers. The practical import of this study arises from the rather routine use of H-containing gases in reactive ion etching (RIE) of Si, and the concurrent presence of in-situ ion damage or residual damage from earlier implants. The post-processing anneal behavior of hydrogenated ion damage layer also could be very different from that of the layer with no hydrogenation. Further, ion damage is used for applications such as device isolation in integrated circuits and spatially selective minority carrier lifetime control in power thyristors [2]. A recent report shows also that hydrogen implants can be successful in suppressing the precipitation of oxygen in the top device layer of SIMOX (Separation by IMplanted OXYgen) process for Si SOI (Silicon On Insulator) [3]. An understanding of the influence of H on disordered regions in Si will hence help identify and evaluate future applications involving hydrogenation. We present results on the hydrogen interaction based on spreading resistance, SIMS and electrical measurements of Schottky diodes fabricated on H-treated Si samples.

Experimental

p-type Si samples of (100) orientation were cut and cleaned by conventional techniques. Since the cleaning process itself could inject H into Si [4], all the samples were subjected to a rapid thermal anneal (RTA) at 800 °C for 20 s in order to remove the effects of this stray hydrogenation. Disordering of the Si was done by a variety of techniques: 20 keV Ar implants (dose range 10^{13} - 10^{15} cm⁻²), 100 nm of sputter-deposited a-Si and 200 nm CVD-deposited poly-Si, for surface disordering; 380 keV, 2×10^{15} cm⁻² Ar implants for subsurface disordering.

Atomic hydrogen treatment was done using two different techniques. In the first, a Commonwealth Scientific Ion Beam System with a Kaufman-type ion source was used to implant H at an energy of 0.4 keV and current density of 1 mA/cm². The implant time was typically 10 mins. The second method involved an electron cyclotron resonance (ECR) plasma, generated at 2.45 GHz with 400 W of microwave power fed into the 6 in. orifice of the chamber. The hydrogen pressure, flow rate and duration of hydrogenation were 0.12 mTorr, 2.8 sccm and 1 hour respectively. The hydrogenation steps were usually performed with no intentional substrate heating.

Following the hydrogenation, an SiO₂ capping layer was magnetron sputter-deposited on selected samples to enable precise spreading resistance (SR) measurements starting right from the H-exposed Si surface. In order to discern the effects of high-temperature anneals on the H-soaked disordered regions, RTA was carried out in a Heatpulse 210 system. For electrical measurements, Al Schottky contacts were formed on the front hydrogenated surface.

Results

Figure 1 gives the carrier concentration profiles of H-implanted Si, without and with preceding Ar implantation. Curve (a) displays extensive deactivation of the boron acceptor up to 6 μ m into the bulk, with the surface concentration reduced by over two orders of magnitude relative to the bulk concentration of 2×10^{15} cm⁻³. Such behavior is well known and expected [1] [5]. Under identical hydrogenation conditions, the p-Si sample that had earlier been implanted with Ar to a dose of 10^{13} cm⁻² displays considerably reduced depth as well as extent of deactivation as seen in curve (b). A more drastic change is evident under a higher Ar dose of 10^{15} cm⁻² (curve (c)). In fact, the change due to hydrogenation is hardly noticeable in the latter case. For comparison, SR measurements of samples with Ar implant alone and no hydrogenation were obtained, and they display flat carrier concentration profiles as expected.

The decreasing trend in acceptor deactivation with Ar implantation dose, as seen in the SR data of Figure 1, may be attributed to (1) the trapping of H by the disordered region, (2) formation of H₂ molecules at this region, or (3) suppression of the dopant deactivation mechanism by the ion damage. In order to elucidate the role of the Ar-implanted layer in inhibiting acceptor deactivation by H, we replaced hydrogen with deuterium and carried out SR and SIMS

measurements. The SR profiles are similar to those of Figure 1, while the SIMS profiles of deuterium (D) reveal that the Ar implantation damage prevents the entry of D in Si. As seen in Figure 2, the concentration of D rapidly drops away from the surface, with the depth of penetration into Si reducing with the Ar implant dose. Thus it is conclusively seen that Ar ion damage directly *suppresses the penetration* of deuterium into bulk Si, and not merely affect the acceptor deactivation mechanism.

FIGURE 1. HOLE CONCENTRATION PROFILES OBTAINED FROM SPREADING RESISTANCE MEASUREMENT ON p-Si (a) WITH 0.4 keV H ONLY, (b) WITH 20 keV, 10^{13} CM $^{-2}$ Ar IMPLANT FOLLOWED BY 0.4 keV H, AND (c) WITH 20 keV, 10^{15} CM $^{-2}$ Ar IMPLANT FOLLOWED BY 0.4 keV H.

The SIMS plot of Figure 2 also discloses that the penetration of H can be suppressed when the surface disorder is created with a deposited poly-Si layer. In contrast to the disordered samples, the control sample shows penetration of D deep inside the Si. These results are also consistent with the corresponding SR profiles.

The effect of *subsurface* disordering on H penetration was studied with the 380 keV Ar implant that gives a damage region extending from about 0.3 μ m to 0.5 μ m. From the SR profiles (not shown) one observes deactivation of acceptors in the undamaged near-surface region up to 0.3 μ m, but again suppression of acceptor deactivation and hence H migration beyond the damaged region [6].

The transport properties of metal-semiconductor contacts (Schottky barrier) are a sensitive measure of near-surface damage and deactivation [7], and we had earlier shown that H-

treatment of p-Si following Ar ion implantation damage could result in ultrahigh barrier heights [8]. In comparing the thermal anneal recovery of the Ar-implanted samples without and with H-treatment, it was found that the electrical recovery of the I-V characteristics was also inhibited by the presence of hydrogen in the disordered region. In order to understand this phenomenon, we subjected the Ar-implanted and hydrogenated [(Ar + H)] samples to RTA anneal. Figure 3 gives the SR profiles of the ECR hydrogenated 10^{15} Ar sample subjected to RTA at 500 °C for 40 s. The control sample (no Ar implant) with ECR hydrogenation is seen to give complete reactivation of the acceptors after the RTA. For the disordered regions replete with hydrogen, acceptor deactivation is negligible prior to anneal (not shown in figure), but a greatly enhanced deactivation profile is generated upon RTA and persists for different anneal times. Since molecular hydrogen cannot deactivate acceptors, it is evident that atomic hydrogen is generated from the hydrogen-soaked regions under rapid thermal anneal. Thus at least part of the hydrogen in the hydrogenated, disordered region should be present in *atomic* form, thereby causing this region to act as a source of H during the RTA.

This sustained acceptor deactivation occurring under RTA is observed for anneal temperatures ranging over

FIGURE 2. SIMS PROFILES OF 0.4 keV DEUTERIUM IMPLANTED SAMPLES: (a) CONTROL (C-Si ONLY), (b) WITH 20 keV, 10^{13} CM⁻² Ar IMPLANT, (c) WITH 20 keV, 10^{15} CM⁻² Ar IMPLANT, AND (d) WITH 200 nm OF POLYCRYSTALLINE Si.

350-800 °C and for durations up to a minute. As seen in Figure 3, there is up to a four decade decrease in hole concentration for the heavily doped case and more than a two decade change for the lightly doped p-Si. The depth of deactivation seems to depend weakly on the substrate resistivity.

Similar RTA experiments with the hydrogenated, buried disordered regions (380 keV Ar + H)

show H in-diffusion as well as effusion from the buried layer. Additional details of the results can be found elsewhere [6].

FIGURE 3. HOLE CONCENTRATION PROFILES OBTAINED FROM SPREADING RESISTANCE MEASUREMENTS ON p-Si SAMPLES WITH 10^{15} Ar IMPLANT, ECR HYDROGENATION AND RAPID THERMAL ANNEAL (500 °C, 40 s) WITH (a) BULK $\rho = 38-63$ OHM-CM, (b) BULK $\rho = 8-10$ OHM-CM, AND (c) BULK $\rho = 0.006-0.002$ OHM-CM. ALSO SHOWN IS THE PROFILE OF A 8-10 OHM-CM p-Si SAMPLE WITH ECR HYDROGENATION ONLY, SUBJECTED TO A 600 °C, 15 s ANNEAL.

Summary

We have shown that Ar ion implantation damage suppresses the penetration of hydrogen into p-type Si. The electrical characteristics of Schottky diodes and spreading resistance profiles indicate that the hydrogenated, disordered layer could affect the thermal anneal recovery of the electrical properties by acting as a source of *atomic* hydrogen. In essence, disordered regions act as *sinks* for atomic hydrogen during hydrogenation, and as *sources* within the substrate during subsequent thermal processing.

References

1. J.I. Pankove and N.M. Johnson, Hydrogen in Semiconductors, Academic Press, New York, 1990.
2. B.G. Svensson, A. Hallen and B.U.R. Sundqvist, *Mat. Sci. Engg.* **B4**, 285 (1989).
3. B. Mizuno, M. Kubota, N. Nomura and H. Iwasaki, *J. Appl. Phys.* **62**, 2566 (1987).
4. C.H. Seager, R.A. Anderson and J.K.G. Panitz, *J. Materials Res.* **2**, 96 (1987).
5. T. Zundel, T. Mesli, A.J. Muller and P. Siffert, *Appl. Phys.* **A48**, 31 (1989).
6. K. Srikanth and S. Ashok, *J. Vac. Sci. Technol.* **A10**, 1118 (1992).
7. S.A. Ringel, H.-C. Chien and S. Ashok, *Appl. Phys. Lett.* **49**, 728 (1986).
8. S. Ashok and K. Giewont, *Jap. J. Appl. Phys.* **24**, L533 (1985).

REPORT DOCUMENTATION PAGE

Form Approved
OMB NO. 0704-0188

Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.

1. AGENCY USE ONLY (Leave blank)		2. REPORT DATE August 1994		3. REPORT TYPE AND DATES COVERED Conference Summary Report	
4. TITLE AND SUBTITLE The Role of Point Defects and Defect Complexes in Silicon Device Processing				5. FUNDING NUMBERS C: NA TA: PV421101	
6. AUTHOR(S) B.L. Sopori, T.Y. Tan					
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)				8. PERFORMING ORGANIZATION REPORT NUMBER	
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) National Renewable Energy Laboratory 1617 Cole Blvd. Golden, CO 80401-3393				10. SPONSORING/MONITORING AGENCY REPORT NUMBER TP-413-7064 DE94011876	
11. SUPPLEMENTARY NOTES NREL Technical Monitor: NA					
12a. DISTRIBUTION/AVAILABILITY STATEMENT				12b. DISTRIBUTION CODE UC-1263	
13. ABSTRACT (Maximum 200 words) This report is a summary of a workshop held on August 24-26, 1992. Session 1 of the conference discussed characteristics of various commercial photovoltaic silicon substrates, the nature of impurities and defects in them, and how they are related to the material growth. Session 2 on point defects reviewed the capabilities of theoretical approaches to determine equilibrium structure of defects in the silicon lattice arising from transitional metal impurities and hydrogen. Session 3 was devoted to a discussion of the surface photovoltaic method for characterizing bulk wafer lifetimes, and to detailed studies on the effectiveness of various gettering operations on reducing the deleterious effects of transition metals. Papers presented at the conference are also included in this summary report.					
14. SUBJECT TERMS point defects ; defect complexes ; silicon ; devices ; photovoltaics ; solar cells				15. NUMBER OF PAGES 175	
				16. PRICE CODE A08	
17. SECURITY CLASSIFICATION OF REPORT Unclassified	18. SECURITY CLASSIFICATION OF THIS PAGE Unclassified	19. SECURITY CLASSIFICATION OF ABSTRACT Unclassified	20. LIMITATION OF ABSTRACT UL		