NREL/CP--413-5064

DE92 016424

NREL/CP-413-5064
DE-92016424

Second Workshop
Role of Point Defects/Defect Complexes
In Silicon Device Fabrication

August 24-26, 1992

Breckenridge, Colorado

Workshop Chairman
Bhushan L. Soporì

Sponsored by

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WORKSHOP THEME

MONDAY, AUGUST, 24, 1992

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

B. L. Sopori

**National Renewable Energy Laboratory
1617 Cole Boulevard
Golden, CO 80401**

Fabrication of high-efficiency solar cells on low-cost silicon substrates requires processes that ameliorate the effects of high concentrations of certain impurities and crystal defects. Solar cell process design must include defect engineering for (i) minimization of defects, (ii) removal of impurities from the active device regions or their redistribution into less detrimental configurations, and (iii) passivation of defects. These processes require extensive knowledge of gettering, defect passivation and defect annihilation, much of which currently exists 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.

The workshop on the Role of Point Defects in Silicon Device Processing (to be held annually) constitutes an integral part of the NREL/DOE Silicon Materials Research Program. The purpose of the workshops is to review new research results and develop coherent concepts of defect engineering as they apply to solar cell process design and material growth.

This paper will briefly review the concepts of defect engineering that may be used to produce high-efficiency solar cells in a cost-effective manner.

NOTES

SESSION 1:

MONDAY, AUGUST, 24, 1992

**DEFECTS AND IMPURITIES IN COMMERCIAL
PHOTOVOLTAIC SILICON SUBSTRATES**

DEFECTS AND IMPURITIES IN SOLAREX CAST POLYCRYSTALLINE SILICON

S. Narayanan

**630 Solarex Court
Frederick, MD 21701**

Cast polycrystalline silicon has emerged as the dominant substrate for solar cells. In this paper, the steady improvement of the quality of Solarex polycrystalline silicon since its commercialization will be reviewed. The defects, impurities present in Solarex material will be discussed. The interaction of the defects and impurities during thermal treatments will be briefly discussed.

NOTES

EFFECTS OF IMPORTANT IMPURITIES AND DEFECTS IN EFG SOLAR CELLS

F. V. Wald

**Mobil Solar Energy Corporation
4 Suburban Park Drive
Billerica, MA 01821**

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 early on, 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.

All this then brings up the question how these various processes influence dislocations, and why impurity based processes are generally not clearly demonstrable.

The paper will present some further results from more recent investigations at Mobil Solar to demonstrate the phenomena discussed above. In particular some recent results using photoluminescence will be shown, along with more recent EBIC studies, and DLTS results, which nevertheless show that by and large the view presented above is still correct, in spite of the fact that the solar cell efficiencies have markedly improved over the years.

NOTES

**THE NONCONTACT LASER/MICROWAVE PHOTOCONDUCTANCE
TECHNIQUE:
HOW FAR CAN WE PUSH IT!**

A. Buczkowski, F. Shimura and G. Rozgonyi

**Department of Materials Science and Engineering
North Carolina State University
Raleigh, NC 27695-7916**

A noncontact laser excitation/microwave reflection transient photoconductance (LM-PC) technique is a commonly used tool for recombination lifetime characterization. However, the analysis of photoconductance decay, particularly for bare, untreated silicon with a long diffusion length, can be quite a complex task. Thus, most often oxidized wafers with passivated surface states are used for measurements. In our approach, we take this apparent disadvantage of the procedure and put to work for us in order to independently determine surface and bulk energy states. An algorithm for separation of surface and bulk recombination effects has been developed¹ wherein the surface recombination component of lifetime is 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 is 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. Furthermore, since the surface lifetime is effected by wafer thickness and carrier mobility, the mobility can be extracted in a noncontact fashion via measurements of effective lifetime on a wafer which is processed into two samples with different thicknesses.²

Since trapping and recombination processes are influenced by temperature via change in occupancy status of deep energy levels, the question of whether these properties can be calculated from the temperature dependence of surface recombination velocity and bulk recombination lifetime has been addressed.^{3,4} We will discuss the theory for a convenient, high throughput, nondestructive DLTS method

based on *recombination* processes and then compare it to conventional, *emission* based DLTS analysis. To this end data for silicon samples intentionally doped with metals during crystal growth is shown. Differences between techniques, their respective advantages, and experimental problems in noncontact deep level determination are discussed.

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Cz SILICON: AN IMPURITY/DEFECT PERSPECTIVE

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

Single crystal Si photovoltaic (PV) manufacturing based on Czochralski (Cz) grown ingots is fully integrated at Siemens Solar Industries, namely, polysilicon and other materials enter the facility and are fabricated into completed PV cells and modules. Improvements in Si module performance accrue from reducing cell-to-cell variations and improving individual cell performance. Impurities and defects in 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. Typical Cz Si ingots are 5.3 inches in diameter and boron-doped, 1 ohm-cm resistivity. Total area (104 cm²) commercial Si cell efficiencies approach 16% with active area efficiencies above 18%.

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. In addition, slip dislocations propagate back into the grown ingot. Optical beam induced current (OBIC) images identify the presence of the slip dislocations. The degradation of the cell short-circuit current J_{sc} , open-circuit voltage V_{oc} , and fill factor by the slip dislocations will be described in the paper.

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. Fourier transform infrared (FTIR) absorption analysis indicates oxygen concentrations of 30 ppm or 1.5×10^{18} cm⁻³. Minority carrier lifetimes of 4 microseconds in as-grown ingots increase to 15 to 20 microseconds in completed devices as determined by photoconductivity decay measurements at Sandia Laboratories and calculations based on the diode reverse saturation current J_0 , implying defect gettering or passivation during device processing. In addition, using float zone Si wafers, cell processing demonstrated the ability to maintain

minority carrier lifetimes above 1 msec. No transition metal impurities in the Si were identified using deep level transient spectroscopy (DLTS) measurements at Siemens Central Research above the detection limit of 4×10^{12} traps/cm³.

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

CHARACTERIZATION OF HEM MULTICRYSTALLINE SILICON

F. Schmid
Crystal Systems, Inc.
27 Congress Street
Salem, MA 01970

HEM multicrystalline silicon is characterized by large vertical columnar grains that are uniform in size from top to bottom and center to edge. The resistivity is uniform across the cross section and decreases with ingot height because of segregation of B. HEM silicon is processed in vacuum of .1 Torr and has a low oxygen content ranging from 5.3 to 2.3×10^{17} atom/cm³ from bottom to top. The carbon content is uniform from bottom to top at 5×10^{17} atom/cm³. HEM silicon was processed in an inert atmosphere and the oxygen and carbon concentration remained at about the same levels. In situ annealing was also performed and increased the average precipitate density.

NOTES

SESSION 2:

MONDAY, AUGUST, 24, 1992

POINT DEFECTS AND POINT DEFECT PROCESSES

FUNDAMENTAL PROPERTIES OF POINT DEFECTS: THE ROLE OF THEORY

S.K. Estreicher

Physics Department
Texas Tech University
Lubbock, TX 79409-1051

Solar grade silicon contains a large number of "point" defects which are introduced into the material during growth or processing. Many of those defects are electron-hole recombination centers and are therefore undesirable. Examples include intrinsic defects (such as self-interstitials or vacancies), interstitials (oxygen, copper, titanium and many others), and substitutional impurities (chalcogen, heavy transition metal impurities, etc.). Some defects are found in several charge and/or spin states, and have different properties in each state. Others tend to form complexes.

Standard "remedies" are known to cure the recombination problem in a few cases. Some transition metals (*Au*) can be gettered toward an unimportant part of the crystal. However, not much is known about the diffusion mechanism(s). Many deep levels can be passivated by hydrogen (or copper), but the details of the interactions are often unknown. In other cases, nothing works: For example, *Ti* can neither be gettered nor passivated. One is left wondering why hydrogen passivates so easily the deep levels of *Au* but not those of *Ti* or *V*? 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 provide only a part of the needed information. The defect under study must have some observable property (e.g., IR or Raman activity, non-zero spin, etc.) and its concentration must be high enough (typically, $\geq 10^{16} \text{ cm}^{-3}$). Then, information about the symmetry of the defect, the species involved, and some microscopic properties can be obtained. On the other hand, "first-principles" or "ab-initio" calculations are becoming reliable enough to help experimentalists analyze their data and even predict the behavior of point defects. Much of what is understood today about hydrogen passivation phenomena is the result of a close collaboration between experiment and theory. In a number of cases,

theory is the only way to approach a problem.

In this short paper, I will discuss some aspects of the theory and list what properties of point defects can or cannot be calculated. This will be illustrated with examples of recent calculations dealing with interactions difficult to access experimentally for a variety of reasons.

**RECONSTRUCTION OF GRAIN BOUNDARIES IN SILICON
BY POINT DEFECT INJECTION**

UNAVAILABLE AT TIME OF PRINTING

NOTES

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

P. Mascher

Centre for Electrophotonic Materials and Devices
Department of Engineering Physics, McMaster University
Hamilton, Ontario, Canada L8S4L7

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

Positron lifetime and Doppler-broadening experiments as well as Fourier-transform infrared spectroscopy (FTIR) were performed on a variety of six-inch wafers. Measurements were done at several locations across the wafers which were cut from the seed-, middle-, and tail-sections of two boules grown at different pull-speeds.

In as-grown material, the positron response typically 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, i.e., $\leq 10^{16} \text{ cm}^{-3}$. After a two-step heat treatment, FTIR showed that significant amounts of oxygen (4-8 ppma) had precipitated in wafers taken from the seed-sections of the boules but not in any of the other wafers. The positron data did not reflect this distinctive difference, however, both lifetime and Doppler-broadening results strongly indicate the creation of vacancy-type defects at concentrations in the low to medium 10^{16} cm^{-3} range.

Recent studies [1] 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.

[1] S. Dannefaer, T. Bretagnon, K. Abdurahman, D. Kerr, and S. Hahn to appear in "Defect Engineering in Semiconductor Growth, Processing and Device Technology", MRS 1992 Spring Meeting, San Francisco.

NOTES

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

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

Center for Positron Studies, Department of Physics, The 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 vacancy-type defects in Czochralski grown silicon wafers annealed at different temperatures. By using a variable energy positron beam and gamma-ray spectroscopy, we have obtained the depth profiles (from surface down to about 1 μm deep) of defects for an epitaxial Si $\langle 100 \rangle$ wafer, an as-grown wafer, and for wafers annealed at different temperatures. There are significant differences in the depth profiles of these wafers. From the depth profiles measured for the Si $\langle 100 \rangle$ epilayer and as-grown wafer, we calculate a higher concentration of defects in the top 0.5 μm layer of the as-grown wafer. At about 1 μm , both of these wafers "look" equally good from the point-of-view of the density of defects. The differences in the top 0.5 μm layer of the as-grown wafer arise due to the trapping of positrons in near-surface defects and positronium formation near the surface. The depth profile is sensitive to thermal processing of the wafer. Following a 4-hour anneal at 1100°C, the depth profile changes so as to provide a lower density of defects in the top 2000 Å and a much higher density of "defects" in the > 2000 Å region of the wafer. We discuss the observed temperature dependence of the depth profiles in terms of the oxygen precipitation in the > 2000 Å region of the wafer. We also present results for the radial variation in the density and nature of the vacancy-type defects in the as-grown wafer. These results are obtained from the bulk positron lifetime measurements made by axially displacing a positron source on the wafer. It is observed that (a) the 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 for the effects of

thermal treatment on the bulk positron lifetime measurements on these wafers.

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

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

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, $2 \times 10^{15} \text{cm}^{-2} \text{P}^+$ 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 TiSi_2 silicided junctions exhibited equal amounts of transient enhanced diffusion behavior, the junction depths under CoSi_2 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 TiSi_2 or CoSi_2 silicidation. However, enhanced removal of the loops was observed under both TiSi_2 or CoSi_2 , with essentially complete removal of the defects under CoSi_2 after 5 min at 900°C. The observed diffusion and defect behavior strongly indicate that implantation damage induced excess interstitial concentrations are significantly reduced by the formation and presence of CoSi_2 , and to a lesser extent TiSi_2 . 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.

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MODELING OF THE COUPLED DIFFUSION OF PHOSPHORUS WITH POINT DEFECTS

S. T. Dunham

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

The diffusion of substitutional dopants in silicon 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. In this paper, we develop and analyze models for the coupled diffusion of dopants and point defects, demonstrating that they can model phosphorus diffusion profiles quantitatively. We begin by describing 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.

NOTES

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**

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 (cleaning by $\text{NH}_4\text{OH}/\text{H}_2\text{O}_2/\text{H}_2\text{O}$ chemical mixture solution) is known to be effective in reducing the amount of dust. However, most of the small particles left after the SC1 cleaning cycles have shown to be pits formed during the SC1 cleaning. It is suggested that such pits originate from some grown-in defects in the Si crystals. These grown-in defects (called "COPs" meaning crystal-originated particles) have been shown to affect the thin gate oxide integrity. Since these defects are induced during solidification process, various researchers believe they are point defect clusters. Even though both COPs and D-defects (one of two well-known point defects) appear to share many common features, their direct structural correlations have not yet been made. In addition, it is not clear how both defects lead to oxide failures. In this study, using oxide breakdown voltage and time-dependent-dielectric breakdown measurements, emission microscopy for

multilayer inspection and a focus ion beam system, thermal wave modulated optical reflectance (mapping and imaging modes), positron annihilation spectroscopy and chemical etching/optical microscopy, we investigated:

- effects of D-defects upon oxide integrity
- possible oxide failure mechanism due to D-defects
- 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-defect 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 to that of the D-defects; and
4. both thermal wave imaging and positron annihilation spectroscopy data indicate that D-defects are not of interstitial nature, and allow us to infer that the D-defects are vacancy-related defects.

POINT DEFECTS, CARBON AND OXYGEN IN EFG SILICON

J. P. Kalejs

**Mobil Solar Energy Corporation
4 Suburban Park Drive
Billerica, MA 01821**

Relationships among point defects, carbon and oxygen in formation of microdefects in silicon crystals grown from the melt are examined for polycrystalline material. Crystal growth variables influencing microdefect formation mechanisms are discussed in detail for the case of silicon sheet grown by the Edge-defined Film-fed Growth (EFG) technique. Experimental evidence for intrinsic point defect participation with carbon and oxygen to form complexes is presented and candidates proposed for nucleation sites for several types of carbon-related and vacancy-based microdefects in the as-grown EFG silicon lattice.

NOTES

SESSION 3:

TUESDAY, AUGUST, 25, 1992

IMPURITY GETTERING FOR SILICON SOLAR CELLS

IMPURITY ANALYSIS OF SILICON BY SPV METHOD

J. Lagowski
Center for Microelectronics Research
University of South Florida

Surface photovoltage (SPV) minority carrier diffusion length measurement has been utilized for over three decades in the monitoring of recombination center defects in semiconductors. Recent refinements in this low excitation level technique extends SPV application to noncontact, no wafer preparation, rapid measurement of surface impurities at concentrations as low as 10^8 atoms/cm² and bulk impurities at concentrations of 10^9 atoms/cm³. The signature of individual defects, generally lost in lifetime-related methods, can be obtained using thermally and optically stimulated defect reactions. The procedure will be discussed on an example of the omnipresent iron. The recombination enhanced dissociation of iron-boron pairs differentiates iron from other metal impurities and enables reliable iron detection at very low concentration.

NOTES

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

**K. Mishra
MEMC Electronic Materials, Inc.
501 Pearl Drive
St. Peters, MO 63376**

The effects 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, FeB, Cr_i, and Mo (in decreasing order) are effective lifetime killer in p-type silicon. Further, the effects of FeB and CrB pair dissociation on minority carrier lifetime are compared and contrasted. While a decrease in diffusion length is commonly observed with FeB dissociation, an increase was seen after thermal dissociation of CrB. Kinetics of CrB formation following 200°C dissociation anneal was also studied. The formation of CrB pairs continues for more than three months in samples with resistivity of 50 ohm cm. This time period is approximately ten times larger than the formation of FeB in similar resistivity samples.

NOTES

GETTERING OF TRANSITION METALS

UNAVAILABLE AT TIME OF PRINTING

NOTES

PRECIPITATION AND GETTERING OF HEAVY METAL DURING IC PROCESSING

L. Jastrzebski

**Center for Microelectronics Research
College of Engineering
University of South Florida
Tampa, FL 33620**

Precipitation and gettering of the most common heavy metal contaminants during IC processing: Fe, Cr, Ni and Cu will be discussed. Fe and Cr behaviors are different from Ni and Cu in terms of gettering efficiencies and optimum gettering conditions. These differences are attributed to the differences in solubility and diffusivity of these impurities. Gettering approaches such as external stress (polysilicon or mechanical damage) on the back of silicon wafers, chlorine in oxidizing ambient and phosphorous diffusions will be reviewed, mechanisms discussed and results for various heavy metals illustrated. The results obtained indicate that the removal of nonprecipitated Ni and Cu can be reasonably easily achieved by gettering sinks, while removal of Fe and Cr is rather difficult. Unfortunately these two impurities in a nonprecipitated state have a strong effect on reduction of the lifetime of silicon. The most promising procedure for Fe gettering seems to be phosphorous diffusion with an optimized temperature cycle.

NOTES

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**

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.

NOTES

PHOSPHORUS AND ALUMINUM GETTERING FOR HIGH EFFICIENCY POLYCRYSTALLINE SILICON SOLAR CELLS

A. Rohatgi

**University Center of Excellence for Photovoltaics
Research and Education
Georgia Institute of Technology
Atlanta, GA 30332**

This paper reports on the fabrication and analysis of one of the highest efficiency solar cells made on cast polycrystalline silicon to date. A combination of optimized aluminum and phosphorus gettering and oxide passivation was used in the process sequence to obtain a record high 17.7% efficient one sun solar cell on polycrystalline silicon. A deep phosphorus diffusion at 930°C was performed followed by a partial etch-back of the n⁺ region. Optimum aluminum treatment for polysilicon cells included 1.2 μm thick Al deposition followed by 850°C/35 minute drive-in. Solar cells fabricated on single crystal float zone silicon using the identical process sequence gave 19.6% efficient cells. In addition to achieving the high efficiency cells, the beneficial effects of optimized gettering, oxide passivation, and emitter sheet resistance on the performance of polycrystalline cells have been investigated and quantified, cell model calculations were performed ignoring the grain boundary effects but using a measured effective carrier lifetime in the cell. A good correlation was found between the measured and calculated cell data, suggesting that in this properly gettered large grain cast polysilicon, intragrain defects, rather than the grain boundaries, dominate the cell performance. Model calculations are extended to outline an approach towards achieving greater than 20% efficient polysilicon solar cells which emphasizes the need for surface texturing, gettering, and reduced back surface recombination.

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PANEL 2:

TUESDAY, AUGUST, 25, 1992

GETTERING IN SILICON SOLAR CELLS

MECHANISMS OF GETTERING BY P AND Al

T. Y. Tan

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

Any metallic impurity gettering mechanism is based on the segregation phenomenon. The detailed mechanisms are, however, different for different impurities and different gettering methods employed. P in-diffusion getters interstitial (i) and interstitial-substitutional (i-s) metallic impurities. In the P diffused region, the high electron concentration provides the stabilization force for concentrating the metallic atoms via their negatively charged state configurations which are substitutional in nature. During P in-diffusion to high concentrations, Si self-interstitials (*I*) are injected into Si substrate regions beyond the P diffusion front, leading to an *I* supersaturation. This *I* supersaturation effectively leads to a decreased solubility of the s species and an increased solubility of the i species of the i-s impurity, e.g., Au. In this way, the concentration of s in the Si bulk is decreased via rapid migration of the i species which is subsequently stabilized in the P diffused region in a s configuration. Gettering of interstitial metallic (M_i) impurities by Al is probably via a quite different mechanism: the formation of M_xAl solution or intermetallic compound at the Al-Si interface. In cases that such M_xAl solution or compound defines a M_i solubility smaller than the M_i concentration in Si, a continuous non-vanishing M_i flux toward the Al layer exists and the M_i species is gettering by Al until the solubility of M_i in Si defined by the M_xAl solution or intermetallic compound is reached, or Al is totally exhausted.

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SESSION 4:

TUESDAY, AUGUST, 25, 1992

PASSIVATION OF IMPURITIES AND DEFECTS

**H IN CRYSTALLINE Si:
A FEW RECENT RESULTS ON DEFECT PASSIVATION**

M. Stavola*

**Sherman Fairchild Laboratory
Lehigh University
Bethlehem, PA 18015**

A survey of the following recent developments on the hydrogen passivation of defects in Si will be given:

- (i) In most early studies of the stability of H-passivated dopants, the annealing kinetics were not first order and were difficult to analyze. Recently, the dissociation energies of several dopant-H complexes have been accurately determined by measuring the recovery kinetics of the dopant activity in reverse biased diodes.[1]
- (ii) Dopants and deep defects can be passivated throughout the bulk of Si samples that are a few mm thick by annealing in H₂ at high temperature (1250°C) and quenching.[2] This passivation method presents new opportunities for studies of the microscopic properties of complexes that include deep defects and H. Preliminary EPR and FTIR results on Pt-diffused Si into which H has been introduced will be described.

* supported by ONR grant No. N00014-90-J-1264

[1] T. Zundel and J. Weber, Phys. Rev. B39, 13549 (1989).

[2] I. Velcarisoa, M. Stavola, D.M. Kozuch, R.E. Peale and G.D. Watkins, Appl. Phys. Lett. 59, 2121 (1991).

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SPIN DEPENDENT PHOTOCURRENTS IN SILICON SOLAR CELLS

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

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. Except for some work in a-Si:H devices, the potential analytic capabilities of this technique for studying photovoltaic devices have been largely undeveloped. In this talk I will describe the experimental methodology of SDT, and briefly describe some of the theories offered to explain prior results. 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 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 at 300 K, we have recently begun to extend our work to lower temperatures and other cell structures in order to identify all of the major recombination centers in this material.

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ATOMIC HYDROGEN INTERACTION WITH DISORDERED REGIONS IN SILICON

S. Ashok and K. Srikanth*

Department of Engineering Science and Mechanics and
Center for Electronic Materials & Processing
The Pennsylvania State University
University Park, PA 16802

The interaction of atomic hydrogen (H) with disordered regions in Si created by ion implantation has been studied in view of applications involving reactive ion etching (RIE), device isolation by implantation and local lifetime control in power devices. Unlike other studies that relate to hydrogenation in ion-implant doped Si, the focus of this work is the migration of H and its electrical interaction defects in *as-implanted* layers. Both surface and buried regions of disorder were created by implanting Ar at 20 keV and 380 keV respectively, over a dose range of 10^{12} - 10^{15} cm⁻². We have addressed issues relating to acceptor deactivation and deep-level passivation, and show that disordered regions - surface as well as subsurface - directly inhibit the penetration of H. Irrespective of the method of hydrogenation or disorder generation, it is shown from spreading resistance, SIMS and electrical measurements that disordered regions directly suppress the penetration of hydrogen into the bulk c-Si. Further, it is unequivocally proven that the hydrogen-soaked disordered region acts as a *source* of *atomic* hydrogen upon thermal processing. Our study also gives evidence of passivation of defects created by high-energy H implantation by subsequent low-energy atomic hydrogen treatment.

* Present address: Texas Instruments, Semiconductor Process & Design Center, P.O. Box 655012, MS 944, Dallas, TX 75265.

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