

Measurement of Lattice Vacancy-Type Defects in Crystalline Si by a Au Labeling Technique

A. T. Fiory and N.M. Ravindra

Department of Physics, New Jersey Institute of Technology, Newark, N.J.

R. Kalyanaraman

Department of Physics, Washington University, St. Louis, Mo.

V. C. Venezia

Phillips Research, Leuven, Belgium.

B. L. Sopori

National Renewable Energy Laboratory, Golden, Co.

Vacancy densities and vacancy binding energies have been quantitatively determined by a Au labeling technique for single crystal Si damaged by high-energy ion implantation. When Au is diffused into the defective Si material, Au atoms are preferentially trapped at vacancies and small vacancy clusters. The volume concentration has been quantitatively calibrated to be 1.2 Au atoms per vacancy (denoted as calibration factor $k = 1.2$). The technique is potentially capable of obtaining vacancy concentrations in as-grown and processed solar cell Si material by diffusing Au from the surface. Of particular interest is vacancy injection associated with the formation of Al backside contacts. Introduction and diffusion of the Au species and Au profiling is discussed in the context of applying a Au labeling technique to problems where vacancies play a role in solar cell processing, such as hydrogen passivation and contact formation.

Introduction

Electrically active lattice defects in solar cell Si can be largely passivated by hydrogenation. Vacancies, which contribute 2 acceptor and 2 donors levels, are endemic to most starting Si materials grown by rapid solidification from the melt. Vacancy concentrations are also correlated with oxygen and carbon impurity levels.

During solar cell processing, additional vacancies are injected by the thermal processing to form the backside contact with Al metallization. Vacancies, as well as other defects, act as traps, which affect the diffusion of H in Si. The apparent diffusivity of H in Si is thus material sensitive, as shown in Fig. 1 [1]. The measurements yield an effective trap-limited diffusivity of H. Diffusion of H in the presence of fixed and mobile traps has been modeled by Zhang [2]. Trap concentrations on the order of 10^{13} to 10^{14} cm^{-3} were obtained by fitting diffusion profiles in float zone (FZ) Si. Trap concentrations in the 10^{17} cm^{-3} range can be inferred from model fits to diffusion of H introduced by ion implantation into cast polycrystalline (CP) and edge defined film growth (EFG) solar Si. These traps are likely to include vacancies or vacancy clusters.

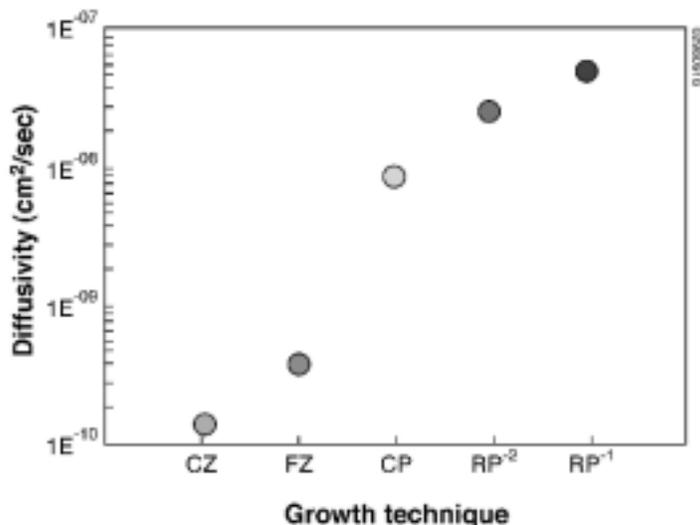


FIG. 1. Apparent diffusivities of H in Si materials grown by Czochralski (CZ), float zone (FZ), cast polycrystalline (CP), and several recrystallized ribbon (RP) methods [Source: Refs. 1, 2].

The vacancies presumably agglomerate to form clusters after thermal processing. A number of methods have been used to sense the presence of vacancies. Positron annihilation S-parameter measurements have been useful for qualitatively profiling the density of open-volume defects [3].

Au Labeling in Implant-Damaged Si

Previous studies of vacancies in Si exploited the selective precipitation of Au at vacancies and vacancy clusters [4-8]. In these works the source of the Au was a surface implanted layer. Figure 2 shows the Au concentration obtained in Si damaged by a 2 MeV, $10^{16} \text{ cm}^{-2} \text{ Si}^+$ implant. The diffusion times at 750 °C are shown in the legend. The Au concentrations are in excess of the Au solid solubility of $2 \times 10^{14} \text{ cm}^{-3}$ at 750 °C. Transmission electron microscopy (TEM) studies indicate the presence of fcc Au precipitates [5]. The Au concentration profiles obtained by RBS and TEM were found to be in good agreement. Importantly, it was shown that the ratio of Au atoms to vacancies,

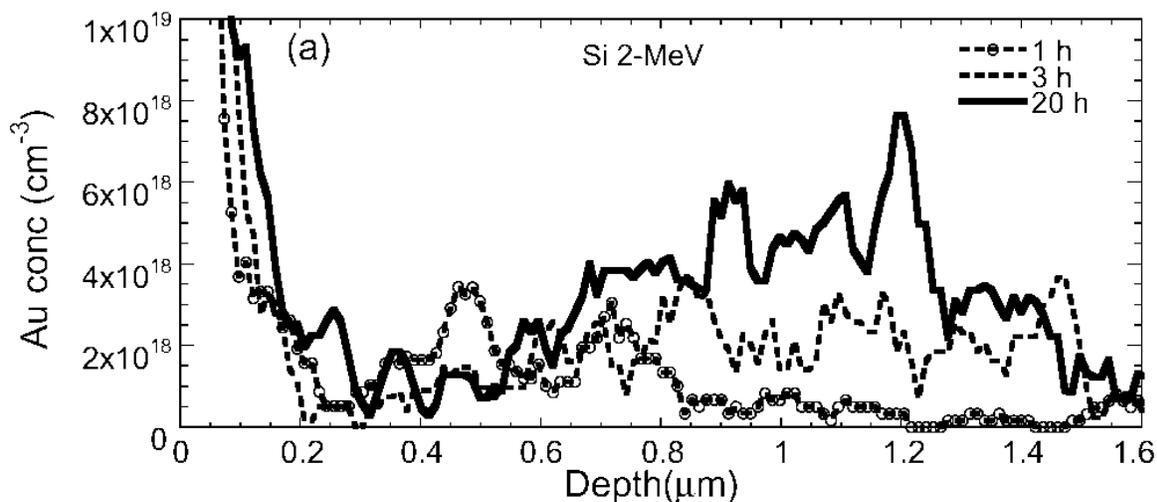


FIG. 2. Au concentration profile in high-energy implanted Si, determined by Rutherford backscattering spectrometry (RBS) with a 2.8-MeV $^4\text{He}^{2+}$ analysis beam [Source: Ref. 8].

i.e., the calibration factor for the Au labeling technique, is given by $k = 1.2$. The characteristic time, τ , for the vacancies to become saturated with Au atoms, was found to scale with vacancies [6] as

$$\tau = 3.2 \times 10^{-11} \text{ cm}^2 \text{ s } [v], \quad (1)$$

where $[v]$ is the areal density of vacancies in the profiled region [8]. Thus data such as the solid curve in Fig. 2, which corresponds to annealing up to saturation of Au in the vacancy region, is a quantitative measure of the vacancy concentration profile in Si.

Au Labeling in Solar Cell Si

A deposited Au film was also used for Au labeling and yielded similar findings as for ion-implanted Au [9]. Au-Si clusters were observed to be formed at the surface, since the film provided an excess quantity of Au, as compared to ion-implanted doses.

Although it requires special sample preparation, one could introduce Au in solar cell Si material by depositing a thin Au film on the surface. The method will entail a surface-clean preparation of the Si surface and deposition under clean conditions to avoid an oxide interfacial diffusion barrier. For studying the effect of Al-diffused contacts, the Al film would be removed by etching prior to the Au deposition.

Au diffusion into the Si is assumed to follow a trap limited diffusion mechanism, where the Au diffusivity varies inversely with the vacancy concentration. The equilibration is also limited by the solubility of Au at the anneal temperature ($2 \times 10^{14} \text{ cm}^{-3}$ at $750 \text{ }^\circ\text{C}$). Assuming a diffusion time of $\tau = 1 \text{ hr}$, the depth, d , to which the Au labeling will reach saturation can be estimated by scaling Eq. (1) as $[V] = [v] / d$, where $[V]$ is the mean volume density of vacancies. This relationship between the depth d and $[V]$ is plotted in Fig. 3.

The model shown in Fig. 3 suggests that a depth of $100 \text{ }\mu\text{m}$ can be probed for a vacancy concentration of 10^{16} cm^{-3} .

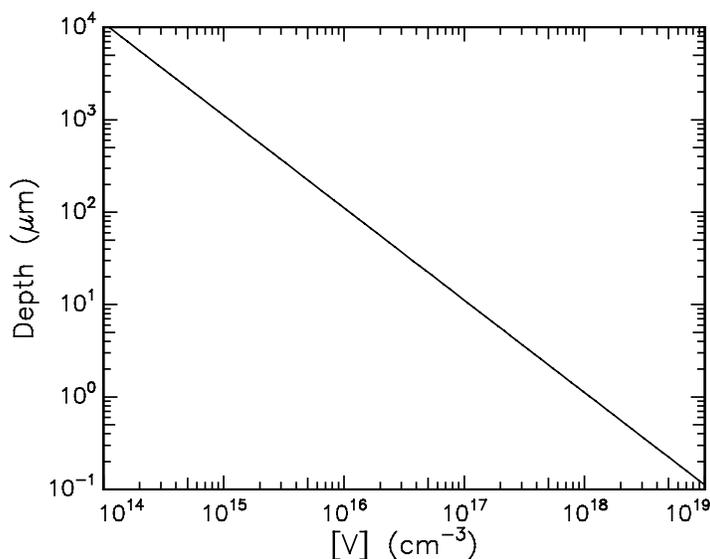


FIG. 3. Relationship between probed depth and vacancy volume concentration for Au diffusion at $750 \text{ }^\circ\text{C}$ for 1 hr. Model is estimated from Au labeling result of Eq. (1).

Au Profile Measurement

Vacancy concentrations may be considerably lower in processed solar Si, when compared to the high-energy ion implanted Si of Refs. 4-9. However, the Au concentration profiles can also be determined by secondary ion mass spectroscopy (SIMS), which has greater sensitivity than the RBS method. The depths probed by SIMS are nominally unlimited, a further advantage over RBS. The sensitivity of SIMS is expected to correspond to a mean Au volume concentration of 10^{15} cm^{-3} [10].

The vacancy concentration near the surface will be perturbed by the Au/Si diffusion reaction. A peak and shoulder structure in the Au profile near surface region is observed with the Au implantation method, as can be seen in Fig 2.

Conclusions

Au labeling has been proposed for quantitatively determining vacancy concentrations in solar cell Si materials. It will be necessary to study whether the thermal treatment required to diffuse the Au would also ripen or perturb the vacancy distribution under study. Such effects were determined to be negligible in the case of vacancies introduced in crystalline Si by ion implantation damage. Controlled deposition of the Au film could provide a reliable and reproducible surface source of Au diffusion. Studies of Al contact formation entail removal of the Al film, to avoid further reaction and eutectic formation, and deposition of a Au film. The Al processing will be restricted to approximately 400 °C, which is below the Al spiking temperature. Study of the redistribution of the Al during the Au diffusion would also be of interest.

References

1. "Silicon Device Processing in H-Ambients; H-Diffusion Mechanisms and Influence on Electronic Properties", B. L. Sopori, Y. Zhang, and N. M. Ravindra, *J. Electron. Mat.* **30**, pp. 1616-1628 (2001).
2. "Modeling hydrogen diffusion for solar cell passivation and process optimization", Y. Zhang, Ph.D. Thesis, New Jersey Institute of Technology (2002).
3. "Impurity and Defect Characterization in c-Si by Positron Beams," K. G. Lynn and M. H. Weber, 10th Workshop on Crystalline Silicon Solar Cell Materials and Processes, pp. 71-82 (NREL, 2000).
4. "Depth profiling of vacancy clusters in MeV-implanted Si using Au labeling", V.C. Venezia, D.J. Eaglesham, T.E. Haynes, A. Agarwal, D.C. Jacobson, H.-J. Gossmann, and F.H. Baumann, *Appl. Phys. Lett.* **73**, 2980 (1978).
5. "Quantification of excess vacancy defects from high-energy ion implantation in Si by Au labeling, R. Kalyanaraman, T. E. Haynes, V. C. Venezia, D. C. Jacobson, H.-J. Gossmann, and C. S. Rafferty, *Appl. Phys. Lett.* **76**, 3379 (2000).
6. Binding energy of vacancy clusters generated by high-energy ion implantation and annealing of silicon", V. C. Venezia, L. Pelaz, H.-J. L. Gossmann, T. E. Haynes, and C. S. Rafferty, *Appl. Phys. Lett.* **79**, 1273 (2001).
7. "Binding energy of vacancies to cluster formed in Si by high-energy ion implantation", R. Kalyanaraman, T. E. Haynes, O. W. Holland, H.-J. L. Gossmann, C. S. Rafferty, and G. H. Gilmer, *Appl. Phys. Lett.* **79**, 1983 (2001).
8. "Quantitative Depth Profiles of Vacancy Cluster Defects Produced by MeV Ion Implantation in Si: Species and Dose Dependence," R. Kalyanaraman, T.E. Haynes, D.C. Jacobson, H.-J. Gossmann, and C.S. Rafferty. *Mat. Res. Soc. Symp. Proc.* **610**, B9.4 (2000).
9. "Evolution of Vacancy Supersaturations in MeV Si Implanted Silicon," V.C. Venezia, Ph.D. Thesis, University of North Texas, Denton, TX (May, 1999).
10. The Au detection limit of $\sim 10^{15} \text{ cm}^{-3}$ of Au is based on SIMS with a Cs beam at 5-keV energy and 60° incident angle (Evans East, private communication).