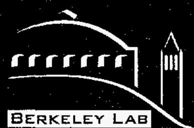
CONF-961202--113

LBNL-39712
UC-410



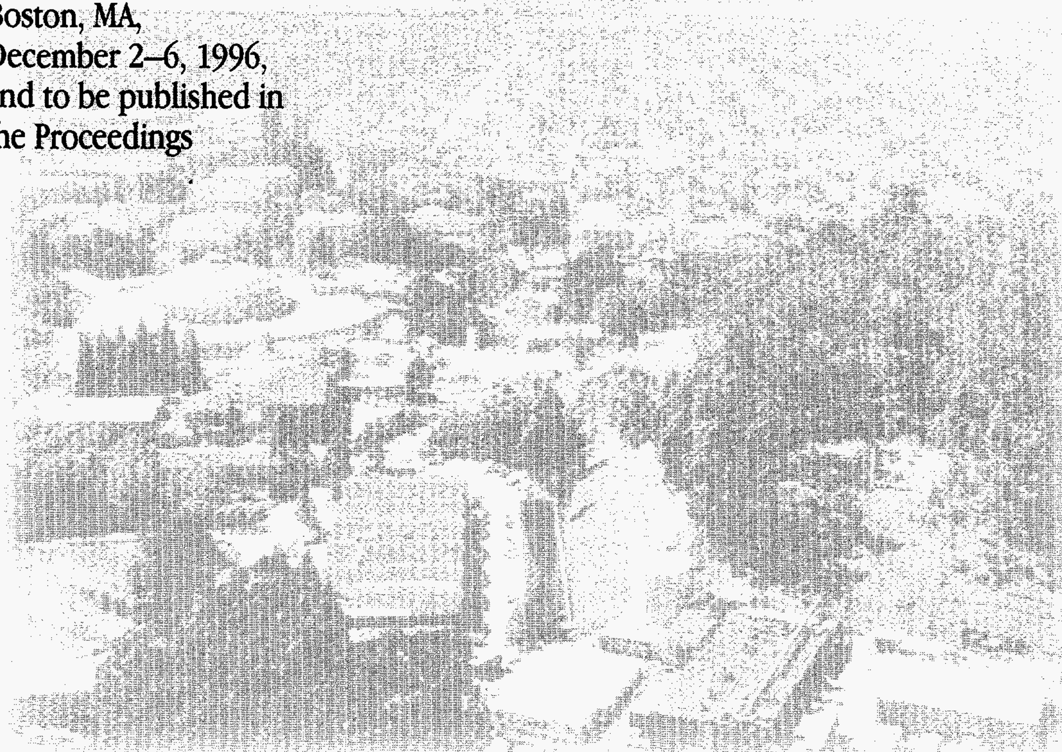
ERNEST ORLANDO LAWRENCE BERKELEY NATIONAL LABORATORY

Interactions of Structural Defects with Metallic Impurities in Multicrystalline Silicon

RECEIVED
JUN 2 3 1997
OSTI

S.A. McHugo, H. Hieslmair, E.R. Weber, M.D. Rosenblum, and J.P. Kalejs
Accelerator and Fusion Research Division

November 1996
Presented at the *Materials Research Society Symposium*, Boston, MA, December 2–6, 1996, and to be published in the Proceedings



DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

DISCLAIMER

This document was prepared as an account of work sponsored by the United States Government. While this document is believed to contain correct information, neither the United States Government nor any agency thereof, nor The Regents of the University of California, nor any of their employees, makes any warranty, express or implied, or assumes any legal 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 its 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, or The Regents of the University of California. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof, or The Regents of the University of California.

This report has been reproduced directly from the best available copy.

Ernest Orlando Lawrence Berkeley National Laboratory is an equal opportunity employer.

LBNL-39712
LSBL-359
UC-410

INTERACTIONS OF STRUCTURAL DEFECTS WITH METALLIC IMPURITIES IN MULTICRYSTALLINE SILICON

S.A. McHugo
Advanced Light Source
Ernest Orlando Lawrence Berkeley National Laboratory
University of California, Berkeley, California 94720

H. Hieslmair, E.R. Weber
Department of Materials Science and Mineral Engineering
University of California, Berkeley, California 94720

M.D. Rosenblum, J.P. Kalejs
ASE Americas Inc.
Billerica, Massachusetts 01821

MASTER

*This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Sciences Division, of the U.S. Department of Energy, under Contract No. DE-AC03-76SF00098.

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

DISCLAIMER

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

Light Source Note:
Author(s) Initials SAM 11/22/96 Date
Group Leader's initials [illegible] 12/1/96 Date

INTERACTIONS OF STRUCTURAL DEFECTS WITH METALLIC IMPURITIES IN MULTICRYSTALLINE SILICON

LSBL- 359

S.A. McHugo *, H. Hieslmair**, E.R. Weber**, M.D. Rosenblum*** and J.P. Kalejs***

* Advanced Light Source, Lawrence Berkeley National Laboratory, Berkeley, CA 94720
** Dept. of Materials Science and Mineral Eng., University of California, Berkeley, CA 94720
*** ASE Americas Inc., Billerica, MA 01821

ABSTRACT

Interactions between structural defects and metallic impurities were studied in multicrystalline silicon for solar cell applications. The objective was to gain insight into the relationship between solar cell processing, metallic impurity behavior and the resultant effect on material/device performance. With an intense synchrotron x-ray source, high sensitivity x-ray fluorescence measurements were utilized to determine impurity distributions with a spatial resolution of $\approx 1\mu m$. Diffusion length mapping and final solar cell characteristics gauged material/device performance. The materials were tested in both the as-grown state and after full solar cell processing. Iron and nickel metal impurities were located at structural defects in as-grown material, while after solar cell processing, both impurities were still observed in low performance regions. These results indicate that multicrystalline silicon solar cell performance is directly related to metal impurities which are not completely removed during typical processing treatments. A discussion of possible mechanisms for this incomplete removal is presented.

INTRODUCTION

Multicrystalline silicon is one of the most promising materials for terrestrial solar cells. The material's low cost and good efficiency make it cost competitive without inherent environmental disposal difficulties. An important property of this material is that once the material's minority carrier diffusion length (L_n) drops below the material's thickness, the cell efficiency is drastically reduced. L_n values of as-grown multicrystalline silicon are typically shorter than the material's thickness which necessitates steps for material improvement. These low L_n values have been attributed to the presence of dislocations and microdefects [1-2]. Furthermore, the carrier recombination rate of these defects is intensified when metal impurities are precipitated at or decorating the defects [3-7]. Therefore, it is critical to getter impurities from the material as well as inhibit contamination during growth and solar cell processing.

Standard solar cell processing steps such as phosphorus in-diffusion for p-n junction formation and aluminum sintering for backside ohmic contact fabrication intrinsically possess

gettering capabilities [8-12]. These processes have been shown to improve L_n values in regions of multicrystalline silicon with low structural defect densities but not in highly dislocated regions, suggesting that if impurities are present at these dislocations they are not effectively gettered [1,2,13-15]. Recent Deep Level Transient Spectroscopy (DLTS) results indirectly reveal higher concentrations of iron in highly dislocated regions [16] while further work suggests that the release of impurities from structural defects, such as dislocations, is the rate limiting step for gettering in multicrystalline silicon [16-18]. The work presented here directly demonstrates the relationship between metal impurities, structural defects and solar cell performance in multicrystalline silicon. Additionally, a brief discussion is presented on the thermodynamics and kinetics of impurity release from structural defects.

EXPERIMENT

Edge-defined Film-fed Growth (EFG) multicrystalline silicon in the as-grown state and after full solar cell processing was used in this study. Standard solar cell processing steps were carried out at ASE Americas Inc. The materials possessed oxygen concentrations of $< 10^{17}$ cm^{-3}, carbon concentrations of $\approx 8x10^{17}$ cm^{-3} and boron doping levels of $1x10^{15}$ cm^{-3}. As-grown cast multicrystalline silicon was also used for comparison. Prior to analysis, as-grown materials were etched to remove $\approx$ 5 μm from both the front and backside. Fully processed samples were etched with a metal etchant to remove the front and backside contacts followed by a silicon etch of $\approx$ 15μm from both the front and backside in order to remove the heavily phosphorus doped region and the aluminum doped backside layer. Samples were subjected to a piranha cleaning ($5:H_2SO_4$, $1:H_2O_2$ @ 120°C) for 15 minutes, prior to all Surface Photovoltage (SPV) and X-Ray Fluorescence (XRF) micro-probe measurements. This treatment has been shown to effectively remove organics and metal impurities from silicon surfaces [19]. SPV measurements, a standard technique for measurement of diffusion length [20-22], quantified L_n values over an entire 10x10 cm solar cell wafer. XRF measurements used a synchrotron x-ray source emanating from a bending magnet at beamline 10.3.1 of the Advanced Light Source, Lawrence Berkeley National Laboratory. The sample was not under vacuum, so only elements with Z greater than silicon could be detected, which includes all metal impurities of interest. Multi-layer mirrors arranged in a Kirkpatrick-Baez orientation focused the x-rays down to $\leq$ 1μm. The typical sampling depth for metal impurities in silicon is $\approx$ 50μm. Standard samples with known amounts of various impurities ranging from Al to Zn were used to quantify the impurity concentration in the

multicrystalline silicon samples. This allowed for micron-scale mapping of metal impurities with sensitivities far surpassing conventional mapping techniques. Structural defect densities were determined by preferential etching and surface analysis using a Scanning Electron Microscope (SEM) in secondary electron mode. Mapped areas were exactly relocated between the XRF and SEM to allow for direct comparison of impurity and structural defect distributions.

RESULTS AND DISCUSSION

Minority carrier diffusion length (L_n) values were measured on a number of as-grown EFG samples using SPV. Typical L_n values ranged from 10-100μm. XRF studies of this material as well as other as-grown multicrystalline silicon materials reveal the presence of Fe and Ni. The observation of Fe in as-grown multicrystalline silicon are in accord with indirect measurements of other work [16]. An XRF map of Fe is shown below in Figure 1a.

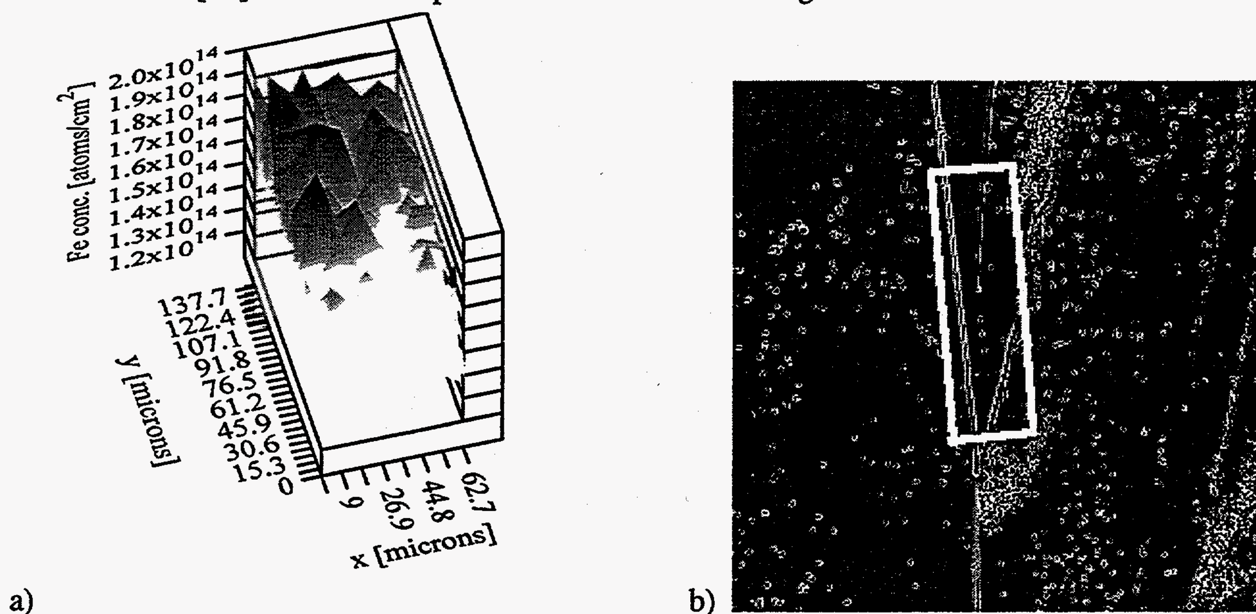


Figure 1: a) X-Ray Fluorescence map of Fe in an EFG multicrystalline silicon sample b) SEM micrograph of a preferentially etched EFG sample showing dislocations and grain boundaries. The XRF scan area of Figure 1a is denoted by the white box.

Following the XRF mapping, the sample from Figure 1a was preferentially etched and analyzed with an SEM in secondary electron mode as shown in Figure 1b where the lines delineate grain boundaries and the pits are etched out dislocations. By comparison of Figures 1a and b, it is apparent that the Fe is primarily present along two grain boundaries. This is direct evidence that metal impurities agglomerate at structural defects in multicrystalline silicon. One would expect this agglomeration in as-grown material since any impurities present during the slow cool from crystal growth would prefer to precipitate at the highly disordered core of a grain boundary. This

defect seems to provide an extraordinarily low energy site for Fe which, in general, would be required in order to trap impurities at high growth temperatures when the impurities are highly mobile and the impurity supersaturation is low. This concept has been shown for Cu precipitation at structural defects in single and multicrystalline silicon [7,23].

SPV measurements of L_n were also taken on fully processed EFG, as shown in Figure 2.

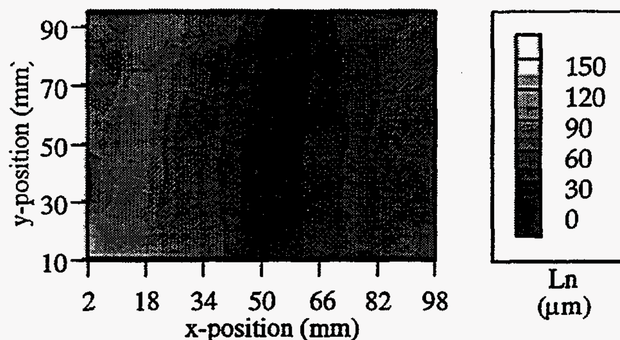


Figure 2: SPV map of L_n across a 10x10 cm EFG solar cell after complete solar cell processing. Of particular interest is the one poorly performing region down the center of the wafer which is along the growth direction. This region has drastically reduced the solar cell efficiency by ≈ 3% absolute. XRF line scans were taken across this poor region as well as other good regions. A summed spectra taken from the poor region, shown in Figure 3, shows the presence of Ni and Fe.

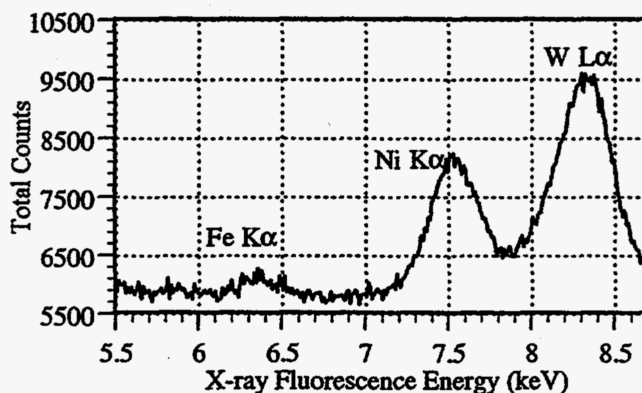


Figure 3: XRF spectra of a fully processed EFG solar cell. This spectra is the sum of 228 spectra taken over a line scan through the low L_n regions in Figure 2.

For this scan, 228 points in 1.25 μm steps were taken with a 5 minute dwell time at each point. The W Lα is a stray signal from the apparatus. XRF scans taken in good regions detected neither these impurities nor any other impurities. The Ni was approximately uniformly distributed while the Fe signal was too weak at any point for spatial resolution. This is direct proof that metal impurities are not adequately gettered during typical solar cell processing steps.

Considering the results presented here and other past work [16-18], which show incomplete gettering for lengthy anneal times such that impurity diffusion from the original site to the gettering layer should be sufficient, it is highly probable that these impurities are not gettered from this material because of sluggish impurity release from defects. Previous work on this subject [24] suggested the diffusion of impurities away from precipitates can slow the dissolution process of a precipitate such that this process cannot be considered as the exact opposite of impurity precipitation, as originally suggested [25]. However, this mechanism of dissolution sluggishness is an important factor only for very slowly diffusing impurities which is not the case for Ni, Fe or Co in silicon at usual processing temperatures.

The surface reaction rate must also be considered as possibly retarding impurity release. If one considers the metal to be in the form of metal silicide at the structural defect, then a simple analysis would indicate that the dissolution rate is dictated by the metal silicide-silicon reaction rate. Based on metal impurity diffusion into silicon from metal silicide sources [26], there is no indication that the surface reaction rate at this interface is slower than impurity diffusion away from the silicide and into the silicon. However, the metal silicide could be stabilized by the structural defect's strain field such that dissolution is not comparable with metal in-diffusion studies. Additionally, the assumption that the impurity is in the form of a silicide may not be correct. Rather, the metal may reside in a dissolved state where the defect acts as a region of higher solubility than the surrounding matrix, essentially existing as a segregation-type gettering mechanism just as aluminum or phosphorus gettering but within the material. Also, the metal may be in the form of a metal carbide or metal oxide which would completely alter the surface reaction rates and metal solubilities in the matrix.

CONCLUSIONS

This work reveals metal impurities agglomerated at structural defects in multicrystalline silicon used for solar cells. These impurities are seen to remain in poorly performing regions of finished solar cells, indicating the cell processing steps inadequately getter these impurities. A strong possibility exists that impurity release from structural defects is the rate limiting step for gettering in this material. It is argued that the release process is slow because the impurities are either stabilized at the structural defects in the form of metal silicides or dissolved impurities or they are in the form of a metal carbide or metal oxide.

ACKNOWLEDGMENTS

The authors would like to thank S.M. Myers, F.G. Kirscht, A.C. Thompson and T. Heiser for wonderfully enlightening conversations. This work was supported by the Director, Office of Energy Research, Office of Basic Energy Sciences, Materials Sciences Division, of the U.S. Department of Energy, under Contract No. DE-AC03-76SF00098.

REFERENCES

1. B.L. Sopori, L. Jabstrzebski, T. Tan and S. Narayanan: in *Proc. of the 12th European Photovoltaic Solar Energy Conference,* Netherlands, 1994, p. 1003
2. S.A. McHugo, J. Bailey, H. Hieslmair and E.R. Weber: in *1994 IEEE First World Conf. on Photovoltaic Energy Conversion,* Waikoloa, Hawaii, U.S.A., 1994, p. 1607
3. C. Cabanel and J.Y. Laval, J. Appl. Phys. **67**, 1425 (1990)
4. V. Higgs and M. Kittler, Appl. Phys. Lett. **63**, 2085 (1993)
5. M. Kittler, W. Seifert and V. Higgs, Phys. Stat. Sol. (a) **137**, 327 (1993)
6. T.H. Wang, T.F. Ciszek and T. Schuyler, Solar Cells **24**, 135 (1988)
7. S.A. McHugo and W.D. Sawyer, Appl. Phys. Lett. **62**, 2519 (1993)
8. L. Baldi, G. Cerofolini and G. Ferla, J. Elec. Chem. Soc. **127**, 164 (1980)
9. W. Schröter and R. Kühnapfel, Appl. Phys. Lett. **56**, 2207 (1990)
10. E.Ö. Sveinbjörnsson, O. Engström and U. Södervall, J. Appl. Phys. **73**, 7311 (1993)
11. R.D. Thompson and K.N. Tu, Appl. Phys. Lett. **41**, 440 (1982)
12. M. Apel, I. Hanke, R. Schindler and W. Schröter, J. Appl. Phys. **76**, 4432 (1994)
13. M. Loghmarti, R. Stuck, J.C. Muller, D. Sayah and P. Siffert, Appl. Phys. Lett. **62**, 979 (1993)
14. O. Porre, M. Stemmer and M. Pasquinelli, Materials Science and Eng. B24, 188 (1994)
15. S.A. McHugo, H. Hieslmair and E.R. Weber: in *Defects in Semiconductors 18, International Conference on Defects in Semiconductors,* edited by M. Suezawa and H. Katayama-Yoshida, Sendai, Japan (1995) p. 1979
16. S.A. McHugo and E.R. Weber: in print, Applied Physics A, 1996
17. M. Seibt and W. Schröter: *6th Workshop on the Role of Impurities and Defects in Silicon Device Processing,* Aug. 1996
18. S.A. McHugo, H. Hieslmair and E.R. Weber: ibid 17
19. M.M. Heyns, S. Verhaverbeke, M. Meuris, P.W. Mertens, H. Schmidt, M. Kubota, A. Philipossian, K. Dillenbeck, D. Gräff, A. Schnegg and R. de Blank, Mat. Res. Symp. Proc., vol. 315, p. 35, (1993)
20. E.O. Johnson, J. Appl. Phys. **28**, 1349 (1957)
21. A.M. Goodman, J. Appl. Phys. **32**, 2550 (1961)
22. J. Lagowski, A.M. Kontkiewicz, L. Jabstrzebski and P. Edelman, Appl. Phys. Lett. **63**, 2902 (1993)
23. B. Shen, T. Sekiguchi, J. Jablonski and K. Sumino, J. Appl. Phys. **76**, 4540 (1994)
24. H.B. Aaron and G.R. Kotler, Met. Trans. **2**, 393 (1971)
25. G. Thomas and M.J. Whelan, Phil. Mag. **6**, 1103 (1961)
26. E.R. Weber, Appl. Phys. A **30**, 1 (1983)