

Efficiency-Limiting Defects in Silicon Solar Cell Material

JEFF BAILEY, SCOTT A. MC HUGO, HENRY HIESLMAIR, and
EICKE R. WEBER

Department of Materials Science and Mineral Engineering, University of
California, Berkeley, Berkeley, CA 94720

The precipitation rate of intentionally introduced iron during low-temperature heating is studied among a variety of single-crystal and polycrystalline silicon solar cell materials. A correlation exists between the iron precipitation rate and the carrier recombination rate in dislocation-free as-grown material, suggesting that diffusion-length-limiting defects in as-grown material are structural defects which accelerate iron precipitation. Phosphorous diffusion gettering was found to be particularly ineffective at improving diffusion length after intentional iron contamination in materials with high iron precipitation rates. We propose that intragranular structural defects in solar cell silicon greatly enhance transition metal precipitation during cooling from the melt and become highly recombination-active when decorated with these impurities. The defects then greatly impair diffusion length improvement during phosphorus gettering and limit carrier lifetimes in as-grown material.

Key words: Defects, silicon efficiency, solar cell

INTRODUCTION

The efficiency of a silicon solar cell depends to a large extent on its bulk minority-carrier diffusion length, especially for low-diffusion-length silicon. Among the variety of cell fabrication techniques, the highest-efficiency cells are consistently produced from high-diffusion-length material, typically single-crystal float-zone (FZ) silicon.¹ Less expensive alternatives to FZ material exist (Czochralski [CZ] silicon and various types of large-grained polycrystalline silicon)^{2,3} but they typically exhibit lower diffusion lengths and higher defect densities than FZ silicon, and therefore yield less efficient solar cells mainly due to increased bulk carrier recombination.

Yet, even between solar cells made from single crystals, differences in as-grown diffusion length and cell efficiency exist. For example, Czochralski silicon cell efficiencies are typically lower than FZ efficiencies and are rivaled by the highest cell efficiencies from cast polysilicon silicon.⁴ This suggests that minority-carrier diffusion-length-limiting defects are

present in Czochralski silicon that are not present in FZ material, and that similar defect concentrations are found in CZ and polysilicon.

Many factors may cause low diffusion lengths in these materials. Dissolved transition metals decrease carrier lifetime through Shockley-Read-Hall recombination,^{5,6} although they are rarely found in concentrations high enough to account for observed low diffusion lengths in solar cell silicon. However, the recombination activity of dislocations in silicon is believed to be a strong function of the degree to which the dislocations are decorated by transition metals.^{7,8} Since dislocations appear in some materials with densities as high as 10^8 cm^{-2} ,⁹ it would appear possible that dislocations limit diffusion length in silicon that contains them. Furthermore, grain boundaries in large-grained silicon can reasonably be ruled out as efficiency-limiting defects.¹⁰ Additionally, FZ silicon growth-related microdefects, known as swirl defects¹¹⁻¹⁴ which can be identified with Cu decoration and preferential etching,¹⁵⁻¹⁷ have a pronounced effect on diffusion length in FZ materials.¹⁸

In polycrystalline silicon, defects include grain boundaries, dislocations, and transition metals. Which

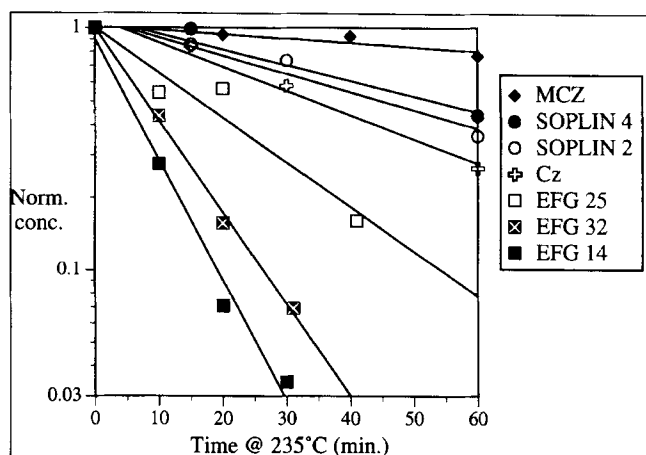


Fig. 1. Concentration of unprecipitated iron in a subset of samples, normalized to the concentration after quenching, as a function of 235°C heating time.

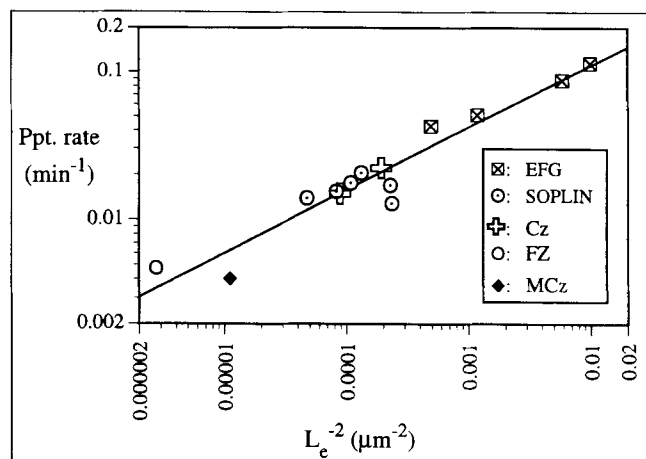


Fig. 2. Iron precipitation rate (inverse of precipitation time constant) vs as-grown minority-carrier recombination rate for all samples.

of these defects account for the poor performance of polysilicon silicon is unclear. As mentioned above, dislocations certainly play a role, but the effects of intragranular microdefects are unknown. A high density ($\sim 10^{12} \text{ cm}^{-3}$) of microdefects has been detected in polysilicon via Cu decoration, preferential etching and contrast in electron beam induced current (EBIC) images.¹⁹ EBIC contrast demonstrates the ability of these microdefects to lower diffusion length when sufficiently decorated, although their effects in as-grown material and processed cells were not determined.

Previously, Gilles and Weber demonstrated that by controllably precipitating intentionally added interstitial iron in oxygen-precipitated Czochralski silicon, information is made available about the concentration of structural defects.^{20,21} (Iron is preferred because it is the most technologically important metallic impurity and, compared to Cu, is a slow diffuser at room temperature. Iron will diffuse considerably above about 200°C, thus allowing highly controlled precipitation.) High densities of structural defects (e.g., oxygen precipitates, dislocations) increase the rate of iron precipitation, which is thus roughly pro-

portional to the defect concentration.²² Recently, Bailey and Weber²³ used this technique of iron precipitation rate studies in EFG polysilicon to identify a high concentration of intragranular microdefects in both dislocated and dislocation-free material. Present in concentrations near 10^{11} cm^{-3} , these defects provide an alternative to dislocations as the diffusion-length-limiting defect in EFG silicon.

In this paper, we report the results of similar experiments extended to a wider variety of polycrystalline and single-crystal materials. We display a relationship of the interstitial iron precipitation rate to the carrier recombination rate in the as-grown state and the response of these materials to phosphorous diffusion gettering after intentional iron contamination. P-N junctions in silicon solar cells are typically formed by a phosphorus diffusion, which is intended to getter transition metals out of the bulk. The degree to which the diffusion length increases after phosphorus diffusion in intentionally contaminated material can provide additional information about the recombination activity of structural defects, namely the degree of impurity decoration of the defects.

EXPERIMENTS

The materials chosen for this study included EFG ribbon polycrystalline silicon from ASE Americas, cast polycrystalline silicon from Bayer Corporation produced by the solidification by planar interface (SOPLIN) technique, Siemens solar Czochralski silicon, magnetic Czochralski material (MCZ), and FZ silicon. EFG and cast polycrystalline silicon are common substrates for lower cost solar cells. MCZ silicon is single crystal material grown by the Czochralski method with an applied magnetic field to suppress melt convection. Carrier lifetimes in MCZ material are known to rival those in FZ silicon.^{25,26}

Iron was diffused into samples of each material at 1050°C for one hour, after which the samples were rapidly quenched to room temperature in ethylene glycol. This prevents essentially all precipitation of iron during cooling,²⁰ and results in a high concentration (10^{15} cm^{-3}) of interstitial iron uniformly distributed through the thickness of the wafer. Essentially all of the dissolved iron forms immobile Fe-B pairs with substitutional boron after several hours.^{26,27} The iron concentration was measured as the concentration of Fe-B pairs using deep level transient spectroscopy (DLTS). Diffusion length measurements of all samples were obtained via the surface photovoltage (SPV) technique.^{28,29} Iron precipitation kinetics were observed by measuring the Fe-B concentration between periods of 235°C heating. This temperature was chosen to compare data with Gilles et al.²⁰ After each heating, several microns of the surface were chemically etched to eliminate any possible surface-related precipitation effects.

Gettering experiments were performed on MCZ and FZ silicon and large-grained dislocated and dislocation-free EFG. Samples of each material were satu-

rated with iron at 750, 850, and 950°C and quenched to room temperature. The iron solubility at these temperatures is roughly 10^{12} , 10^{13} , and 10^{14} cm⁻³, respectively.³⁰ The gettering step consisted of a phosphorus diffusion (POCl₃ source) for 2 h at 950°C, followed by a 750°C anneal in N₂ for 2 h and a chemical etch to remove the surface diffused region. The diffusion length was measured in each sample by SPV in the as-grown state, after contamination, and after P-gettering. DLTS was used to measure residual dissolved Fe after gettering.

RESULTS

Iron precipitation curves for a subset of samples are shown in Fig. 1, containing results for one MCZ, one CZ, two SOPLIN, and three EFG samples. A summary of results for all samples is shown in Fig. 2, showing the relationship between as-grown carrier recombination rate (proportional to $1/L^2$, where L is the minority-carrier diffusion length $\sqrt{D_n \tau}$) and iron precipitation rate (inverse of precipitation time constant). Several points are notable about the data in Fig. 2. The greater uniformity in diffusion length and precipitation rate among SOPLIN material compared with EFG is apparent, as is the similarity between CZ and SOPLIN silicon. The most notable feature, however, is the strong correlation between the iron precipitation rate and the carrier recombination rate in the as-grown state among all materials.

Table I shows the effects of intentional contamination and phosphorus gettering on the diffusion length in FZ, MCZ, and EFG silicon. While the FZ and MCZ regain most of their original diffusion length after the gettering step, the EFG samples hardly recover at all, even in the dislocation-free samples. No dissolved Fe was detected after gettering in these samples with DLTS. This result demonstrates the greater susceptibility of EFG polysilicon to diffusion length degradation after metal contamination, even in large-grained dislocation-free material. The data labeled "MCZ-850 (no P)" are for a control sample subjected to iron contamination at 850°C and an identical thermal cycle as the gettering step but without the phosphorus source. The diffusion length increase after heat treatment in the control sample is only very slight, demonstrating that the recovery of the FZ and MCZ gettering samples is caused by the removal of iron during the phosphorus gettering rather than the thermal cycle alone.

DISCUSSION

Precipitation Kinetics

Bailey and Weber²³ described the accelerated iron precipitation kinetics in EFG silicon as a competition between dislocations and other unidentified intragranular microdefects. The same correlation between diffusion length and iron precipitation rate was observed in EFG material alone and can be attributed to the fact that dislocations are recombination-active in EFG silicon and are known to act as nucleation

sites for iron precipitation. The data shown here, however, express what appears to be a more general trend in which the diffusion length in low-dislocation-density silicon is correlated with the concentration of defects that enhance iron precipitation. This is a strong suggestion that, as in as-grown EFG silicon, microdefects in dislocation-free silicon are the lifetime-limiting defects.

To understand the quantitative relationship between the minority-carrier recombination rate and low-temperature iron precipitation rate, it is useful to consider two points. First, since structural defects in any one of the as-grown materials may be fundamentally different from those in another, the recombination properties of all defects cannot be expected to be identical, especially since the recombination activity of a defect is also a strong function of its level of impurity decoration.^{7,8,18,19} Second, Ham showed that the precipitation rate of a solute scales linearly with the density of precipitation sites.²² So if the carrier lifetime is dominated by recombination at these sites, then the recombination rate should also be proportional to the defect density and the precipitation and recombination rates should be proportional to one another. Such a relationship is not observed in Fig. 2; however, the recombination rate has a greater than linear dependence on the observed precipitation rate. Therefore, while the evidence clearly shows a higher intragranular defect density in as-grown low-lifetime silicon, it is likely that defects in this material are characterized by a greater level of impurity decoration than the defects in high-lifetime silicon. An alternative explanation—that a higher concentration of dissolved metallic impurities exists in low-lifetime materials—can be rejected for the following reason: a high defect density entails a high metallic impurity precipitation rate, which in turn entails few dissolved

Table I. Effects of Intentional Iron Contamination at Three Temperatures and Subsequent Phosphorus-Diffusion Gettering on Minority-Carrier Diffusion Length for Three Types of Materials

Material/Fe Diffusion Temp.	L _n As-Grown (μm)	L _n after Fe Diffusion and Quench (μm)	L _n After P Gettering (μm)
EFG/750°C	82.9	15.9	19.1
EFG/850°C	100.5	0.4	17.3
EFG/950°C	69.7	6.5	21.5
MCZ/750°C	272	48.9	115
MCZ/850°C	274	23.7	149
MCZ/950°C	271	16.4	195
MCZ/850°C (no P)	226	24.7	50.2
FZ/750°C	232	48.4	201
FZ/850°C	230	24.5	161
FZ/950°C	211	16.5	132
EFG/850°C (dislocated)	20.2	14	12

Note: "No P" indicates no phosphorus was used during the gettering heat treatment.

impurities after cooling from the melt. This relationship has been demonstrated in EFG silicon, in which the highest dissolved Fe and Cr concentrations in as-grown material are found in regions with the highest diffusion length.³¹

It is noteworthy that the similar efficiencies of solar cells from CZ and cast silicon are expressed here as essentially identical iron precipitation rates and as-grown diffusion lengths. While the nature of the actual intragranular defects will depend on the details of the growth methods and may be different, the defect concentrations appear to be similar in the two materials. Based on their iron precipitation rates, MCZ and float zone silicon show the lowest bulk defect concentration and highest as-grown diffusion length; FZ material typically produces solar cells with the highest efficiency. EFG silicon shows accelerated iron precipitation even in dislocation free regions, and typically yields even lower peak cell efficiencies than CZ or cast silicon.

At least part of the difference in precipitation rates among these materials can be accounted for by differences in total oxygen concentration. CZ silicon was found to contain 18 parts per million (ppma) dissolved oxygen as measured by room temperature Fourier transform infrared (FTIR) ("new ASTM" standard F121-83)³² and MCZ material only 6.3 ppma. Record carrier lifetimes of nearly 10 μ s have been measured in oxidized high-resistivity MCZ silicon.^{24,25} The superior lifetimes in some MCZ silicon compared to both CZ and even FZ material have been previously attributed to lower densities of grown-in point defects in MCZ silicon,³³ believed to result from the suppression of convection and oscillatory flow in the melt by the applied magnetic field.³⁴ The defects responsible for the observed differences in both carrier lifetime and iron precipitation rate between CZ and magnetic CZ must be structural defects—very likely oxygen-related microprecipitates. The results presented here reveal a substantial reduction in bulk structural defect concentrations between standard CZ and magnetic CZ silicon, due no doubt in part to the difference in total oxygen concentration.

An explanation for the nature of microdefects in EFG silicon comes from a model for the formation of SiC microprecipitates in carbon-rich EFG, presented by Kalejs.³⁵ The dominant impurity in EFG silicon is substitutional carbon, present in a concentration near 20 ppma, and the oxygen concentration is less than 0.2 ppma. Gettering at carbon-based microdefects in EFG material had earlier been proposed to explain changes in carrier lifetime after high-temperature annealing.^{36,37} Also, carbon-related defects in silicon are thermally stable,³⁸ making dissolution of these defects extremely unlikely.

The oxygen concentration in SOPLIN silicon was found to be 4.5 ppma, even less than MCZ silicon and one-fourth the concentration in CZ material. Therefore, the similar iron precipitation rates in CZ and SOPLIN material cannot be understood by simple comparison of oxygen concentrations and indicate an

alternative defect formation mechanism in SOPLIN cast silicon to that in high-oxygen materials.

Phosphorus Gettering

The impaired gettering efficiency of EFG silicon is further confirmation of the presence of intragranular defects even in dislocation-free material. Given the accelerated iron precipitation kinetics in EFG silicon, this important result demonstrates the difficulty with which precipitated transition metals are redissolved and gettered in EFG silicon. Presumably the dissolved iron present after the indiffusion and quench precipitated at the beginning of the phosphorous diffusion stage had it not it would have been gettered as it was in the FZ and MCZ samples. Moreover, little dependence of the final diffusion length on the iron contamination temperature was observed. It appears that a concentration as low as 10^{12} cm⁻³ is sufficient to saturate the electrical activity of the iron precipitation sites.

Low-diffusion-length regions of as-grown EFG silicon are also highly resistant to diffusion length improvement with phosphorus gettering, even without intentional metal contamination.³⁹ The similarity of this observation to the experimental results reported here further suggest that the structural intragranular defects in EFG silicon are already decorated with precipitated metallic impurities that enhance their recombination activity. Moreover, our results taken together allow the following model to be proposed: intragranular structural defects in solar cell silicon greatly enhance transition metal precipitation during cooling from the melt, become highly recombination active when decorated with metallic impurities, greatly impair diffusion length improvement during phosphorus gettering, and limit carrier lifetimes in as-grown material without high densities of dislocations.

CONCLUSIONS

Although EFG silicon can be effectively hydrogen-passivated during processing,⁴⁰ defects responsible for the high iron precipitation rate in EFG silicon may constitute its greatest impediment for improved cell efficiency. Compared with defect concentrations in other silicon photovoltaic materials, this concentration is high; no other material was identified that exhibited as high an iron precipitation rate seen in dislocation-free EFG. Additionally, dislocation-free EFG responded poorly to P-gettering treatments compared with FZ and MCZ silicon. This suggests that polysilicon microdefects precipitate metallic impurities even in the presence of standard gettering mechanisms; thus they must be seriously considered as potential causes for low-diffusion-length regions in fully processed material.

In revealing the presence of structural bulk defects and their effect on minority-carrier diffusion length, this study provides a model that helps explain the superior electrical properties of float-zone and MCZ silicon and the lower solar cell efficiency of cells made

from either inexpensive polycrystalline or dislocation-free CZ silicon. Iron precipitation kinetics are seen to be a useful method for silicon solar cell materials characterization in which structural defects that normally escape detection in other characterization techniques are easily revealed. Additionally, phosphorus gettering is shown to provide a means for determining the precipitation site stability of structural defects in a variety of silicon solar cell materials.

ACKNOWLEDGMENT

The authors are indebted to Semiconductor Diagnostics, Inc. for the SPV equipment used in this study. They also thank Juris Kalejs, Fritz Wald, and Bill Sawyer of ASE Americas, F. Koch of Bayer, and Kim Mitchell of Siemens Solar for supplying material and for many stimulating discussions. Finally, the insightful talks with Ulrich Gösele are greatly appreciated. This work was supported in part by NREL contract XD-2-11004-C.

REFERENCES

1. M.A. Green, *Semicond. Sci. Technol.* 8, 1 (1993).
2. F.V. Wald, *Solar Energy Mater.* 23, 175 (1991).
3. *MRS Bulletin* 18 (1993).
4. S. Narayanan, S.R. Wenham and M.A. Green, *IEEE Trans. Electron Dev.* 37, 382 (1990).
5. W. Shockley and J.W.T. Read, *Phys. Rev.* 87, 835 (1952).
6. R.N. Hall, *Phys. Rev.* 87, 387 (1952).
7. V. Higgs and M. Kittler, *Appl. Phys. Lett.* 63, 2085 (1993).
8. M. Kittler, W. Seifert and V. Higgs, *Phys. Stat. Sol. (a)* 137, 327 (1993).
9. R. Gleichmann, B. Cunningham and D. Ast, *J. Appl. Phys.* 58, 223 (1985).
10. D.P. Singh and P.S. Basak, *Indian J. Pure and Appl. Phys.* 29, 717 (1991).
11. T. Abe, T. Samizo and S. Maruyama, *Jpn. J. Appl. Phys.* 5, 458 (1966).
12. A.J.R. De Kock, *Appl. Phys. Lett.* 16, 100 (1970).
13. P.M. Petroff and A.J.R. De Kock, *J. Cryst. Growth* 30, 117 (1975).
14. A.J.R. De Kock, *Defects in Semiconductors*, eds. J. Narayan and T.Y. Tan (Amsterdam: North-Holland, 1981), p. 309.
15. T.F. Ciszek, *J. Electrochem. Soc.* 120, 94 (1973).
16. X. Zong, Y. Chen, H. Cao, X. Gu and J. Zheng, *Chin. J. Semicond.* 3, 413 (1982).
17. T. Yamauchi, Y. Tsumori, T. Nakashizu, H. Esaka, S. Takao and S. Shinoyama, *Jpn. J. Appl. Phys.* 2, Lett. 31, L439 (1992).
18. T.H. Wang, T.F. Ciszek and T. Schuyler, *Solar Cells* 24, 135 (1988).
19. S.A. McHugo and W.D. Sawyer, *Appl. Phys. Lett.* 62, 2519 (1993).
20. D. Gilles, E.R. Weber and S. Hahn, *Phys. Rev. Lett.* 64, 196 (1990).
21. D. Gilles, E.R. Weber and S. Hahn, *Semiconductor Silicon* 90, 697 (1990).
22. F.S. Ham, *J. Phys. Chem. Solids* 6, 335 (1958).
23. J. Bailey and E.R. Weber, *Phys. Stat. Sol. (a)* 137, 515 (1993).
24. S.K. Pang, A. Rohatgi, B.L. Sopori and G. Fiegl, *J. Electrochem. Soc.* 137, 1977 (1990).
25. S.K. Pang and A. Rohatgi, *Appl. Phys. Lett.* 59, 195 (1991).
26. H. Lemke, *Phys. Stat. Sol. (a)* 64, 215 (1981).
27. L.C. Kimerling and J.L. Benton, *Physica* 116B, 297 (1983).
28. L. Jastrzebski, W. Henley and C.J. Nuese, *Solid State Technol.* 35, 27 (1992).
29. J. Lagowski, P. Edelman, M. Dexter and W. Henley, *Semicond. Sci. Technol.* 7, A185 (1992).
30. E.R. Weber, *Appl. Phys. A* 30, 1 (1983).
31. J.P. Kalejs, L. Jastrzebski, L. Lagowski, W. Henley, D. Schielein, S.G. Balster and D.K. Schroder, *Proc. 12th European PV SEC*, Amsterdam, 1994. Independent confirmation by the authors.
32. *ASTM Annual Book of Standards*, 10.05, 191 (1989).
33. T. Higuchi, E. Gaylord, G.A. Rozgonyi and E. Shimura, *Appl. Phys. Lett.* 53, 1850 (1988).
34. T. Munakata and I. Tanasawa, *J. Cryst. Growth* 106, 566 (1990).
35. J.P. Kalejs and B. Chalmers, *J. Cryst. Growth* 79, 487 (1986).
36. J.P. Kalejs and L.A. Ladd, *Appl. Phys. Lett.* 45, 540 (1984).
37. R. Gleichmann, J.P. Kalejs and D.G. Ast, *Mater. Res. Soc. Symp. Proc.* 36, 181 (1985).
38. Q. Sun, K.H. Yao, J. Lagowski and H.C. Gatos, *J. Appl. Phys.* 67, 4313 (1990).
39. R. Murphy and B.L. Sopori, *Mater. Res. Soc. Spring Mtg.*, 1995, Symp. B, San Francisco, CA, 1995.
40. P. Sana, A. Rohatgi, J.P. Kalejs and R.O. Bell, *Appl. Phys. Lett.* 64, 97 (1994).