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Precipitate Dissolution and Gettering under Vacancy Injection in Silicon

Final Subcontract Report
21 March 2006 – 15 January 2008

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Duke University
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Subcontract Report
NREL/SR-520-44088
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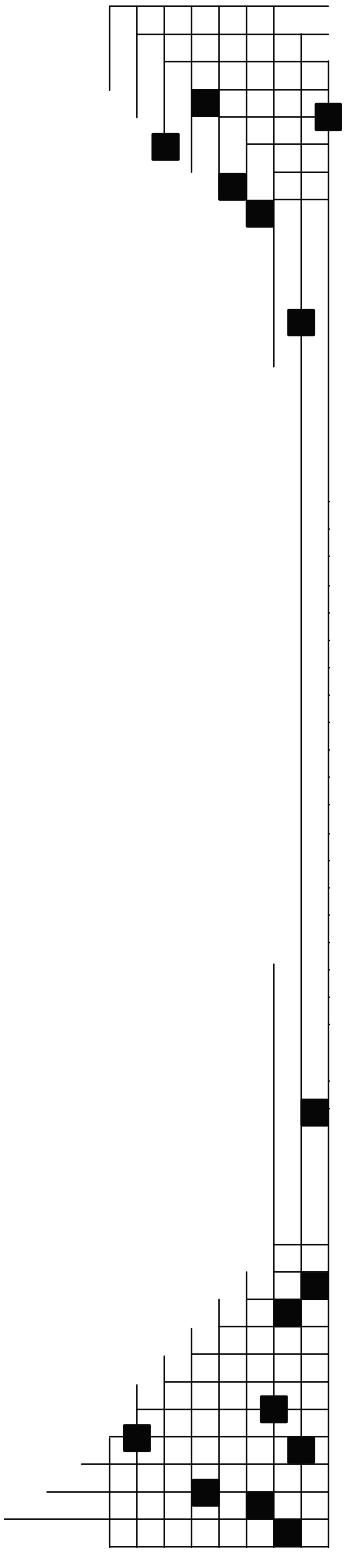

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ABSTRACT

Using a deposited Al layer, optical processing at a temperature below the Si-Al eutectic temperature of T_{eu}=577°C for a few minutes and followed by $T>T_{eu}$ for a few more minutes are able to getter metallic precipitates out of multicrystalline Si. To accomplish the same, a few tens of hrs is needed when using thermal annealing at 700°C. Possible mechanisms involved in optical-processing gettering are proposed. These mechanisms include vacancy injection, radiation-enhanced solubility, and radiation-enhanced diffusion of vacancies and metal impurity atoms. Using $FeSi_2$ as a model case for which the Si lattice expands concomitantly with the dissolution of the precipitates, physical modeling and numerical simulations are carried out to uncover and test the conditions for the mechanisms to be effective. The mechanisms are found to be effective provided that the injected Si vacancies due to alloy formation are nearly all retained inside and evenly distributed throughout the Si bulk at the lower temperature, and that the Fe atom migration energy barrier is reduced by ~0.15 eV by radiation at the higher temperature. On the other hand, for the gettering of a precipitate species for which the Si lattice will shrink concomitantly with the dissolution of the precipitates, the vacancy-injection mechanism will not only be ineffective but should also have a detrimental effect.

INTRODUCTION

It is well known that gettering of metallic impurity precipitates from multicrystalline (mc-) Si using Al is not effective by thermal annealing at the relatively low temperatures of ~700°C for a short time, as is appropriate for solar cell processing. Using $FeSi_2$ as a model precipitate species, we have shown that it will take more than 50 hrs at 700°C to getter them out. We identified the limiting mechanism as the slow precipitate dissolution rate.[1] In that study, the assumed conditions are that Fe was introduced at 900°C to its solubility of ~5.02×10^{13} cm^{-3} and then precipitated out to steady state at 700°C to the density of $\rho=10^{11}$ cm^{-3}. On the other hand, it is also known that, using a deposited Al layer, gettering by optical-processing are able to getter metallic precipitates out of mc-Si with a total time of minutes.[2] Optical-processing gettering consists of two steps: (i) a low temperature step below the Si-Al eutectic temperature of T_{eu}=577°C for several minutes; and (ii) a high temperature step with $T>T_{eu}$ for several minutes. In this report, the possible physical mechanisms responsible for the effectiveness in gettering under optical-processing conditions are proposed. Using $FeSi_2$ as the model impurity precipitate, physical modeling and numerical simulations are carried out to test the effectiveness of these mechanisms by finding the appropriate conditions. The proposed mechanisms include vacancy injection, radiation-enhanced solubility, and radiation-enhanced diffusion of vacancies and metal impurity atoms

We have previously identified the involved physical processes and accordingly modeled the gettering of metals,[1,3-6] including metal dissolution from the precipitates, diffusion of metal atoms to and their stabilization at the gettering sites, and the effect of the precipitate volume misfit with the Si matrix on the gettering effectiveness. In the present problem of optical-processing gettering of Fe and $FeSi_2$ as the gettered metal and precipitates, we assume that the misfit due to precipitate dissolution is accommodated primarily by the point defect vacancies (V).[1] As an initial test of the soundness of our model, numerical simulations were carried out for optical-processing gettering of Fe in Si wafers 200 μm in thickness by a 2 μm thick Al layer at the wafer

backsurface (at the 200 μm position). It is assumed that Fe was introduced at 900°C to its solubility of ~5.02x10^{13} cm^{-3} and then precipitated out to steady state at 700°C to the density of ρ=10^{11} cm^{-3}. For the $FeSi_2$ precipitates the misfit parameter of y=-0.15 is used. The negative y value means that growth of $FeSi_2$ precipitates is associated with a Si matrix volume contraction while their dissolution with a volume expansion. Thus, generation of *V* or consumption of *I* or both will result from $FeSi_2$ precipitate growth, while generation of *I* or consumption of *V* or both will result from $FeSi_2$ precipitate dissolution. Consequently, gettering of Fe will be faster if a *V*-supersaturation exists.

Optical processing occurs at two temperatures, a low temperature $T_L<T_{eu}$ and a high temperature $T_H>T_{eu}$, where T_{eu} is the Al-Si system eutectic temperature of 577°C. Injection of *V* into Si takes place at T_L, which is assumed to be 500°C. At T_L, a solid Al-Si alloy with 0.6 at% Si forms by the migration of Si atoms into Al (not the other way around, because the Al solubility in Si is negligibly small), with each Si atom went into Al leaving one *V* behind in Si. Assuming that alloy formation is complete at T_L, then there will be $C_V = 3x10^{18} cm^{-3}$ *V* injected into Si for the case assuming an Al layer thickness of 2 μm and a Si wafer thickness of 200 μm. Dependent upon the *V* diffusivity in Si at T_L under the optical processing condition, these injected V may either be essentially accumulated at the interface of the Al-Si alloy and the Si bulk, or distributed throughout the Si bulk. Now, the *V* contribution to Si self-diffusion is known to be[7]

$$D_V^{Si} = D_V\left(C_V^{eq} / C_o\right) = 2 \sim 3x10^{22} \exp\left(-4eV / k_B T\right) cm^2 s^{-1}, \quad (1)$$

where $C_o = 5x10^{22} cm^{-3}$ is the Si atom density. There are two sets of data in the literature of the separate D_V and C_V^{eq} values:[7]

$$D_V = 0.1 \exp\left(-2eV / k_B T\right)\ cm^2 s^{-1}, \quad C_V^{eq} = 2x10^{23} \exp\left(-2eV / k_B T\right) cm^{-3}, \quad (2)$$

$$D_V = 6.17x10^2 \exp\left(-0.5eV / k_B T\right)\ cm^2 s^{-1}, \quad C_V^{eq} = 4.86x10^{23} \exp\left(-3.5eV / k_B T\right) cm^{-3}, \quad (3)$$

The values given by Eq. (2) did not allow to obtain the needed optical-processing gettering results, i.e., much longer times are needed. Hence, the values of Eq. (3) are used. If it is assumed that the injected *V* are accumulated at the Al-Si alloy and Si interface, our simulation results showed that it is not possible to complete th gettering process at 700°C on a time scale of minutes. Thus, the injected *V* will be assumed as distributed throughout the Si bulk. This is justified using the D_V value given by Eq. (3), which in fact predicts that the injected *V* will be essentially distributed throughout the Si bulk with the 500°C optical annealing time exceeding a few minutes. This yields also that $C_V / C_V^{eq} \sim 8.15x10^{12}$, which is a huge *V* supersaturation. Furthermore, in order to simulate the complete gettering of the present case, the Fe atom migration energy needs to be reduced by ~0.15 eV (from 0.68 eV), which is assumed to be due to the radiation enhancement. In this simulation the radiation enhanced solubilities of *V* and Fe are not invoked, as it was not needed. As reported previously, Figure 1 shows the result of using thermal annealing only at 700°C, and it is seen that more than 50 hrs is needed to complete the gettering process. Figure 2 shows the results of that of the optical-processing gettering, and it is seen that the getter-

ing process is complete with the processing time of only minutes at 500°C and followed by also minutes at 700°C. In addition, we have performed simulations for the case of a positive misfit y value, which means that precipitate growth is associated with a Si matrix volume expansion while precipitate dissolution is associated with a volume contraction. Figure 3 shows the simulation results of the case with y=+0.15 (instead of -0.15 for iron) under otherwise the same optical-gettering conditions as for the $FeSi_2$ case. This shows that, when optical-gettering, the precipitate dissolution is slowed down from the gettering process of using thermal annealing.

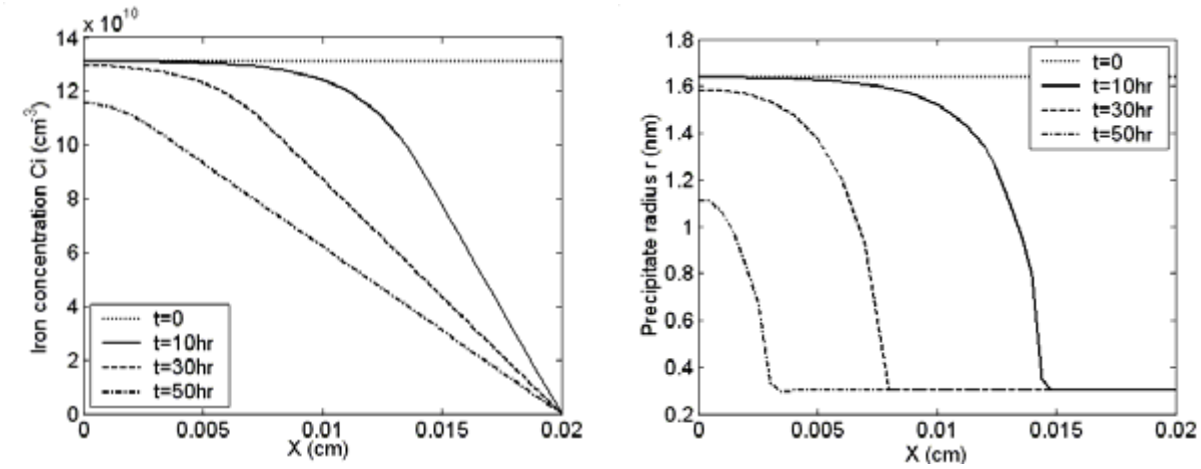

Fig. 1. Simulation results of gettering dissolved interstitial Fe (left) and $FeSi_2$ precipitates (right) from the Si matrix by a 2□m thick Al-Si liquid layer at the wafer backside (200 □m position) by thermal annealing at 700°C.

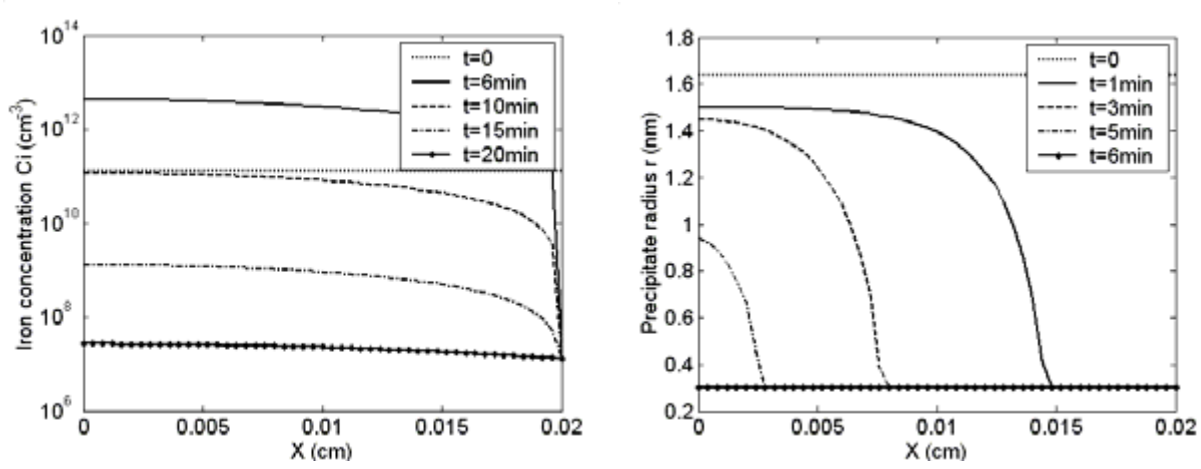

Fig. 2. Simulation results of gettering dissolved interstitial Fe (left) and $FeSi_2$ precipitates (right) for the case of Figure 1 by optical processing.

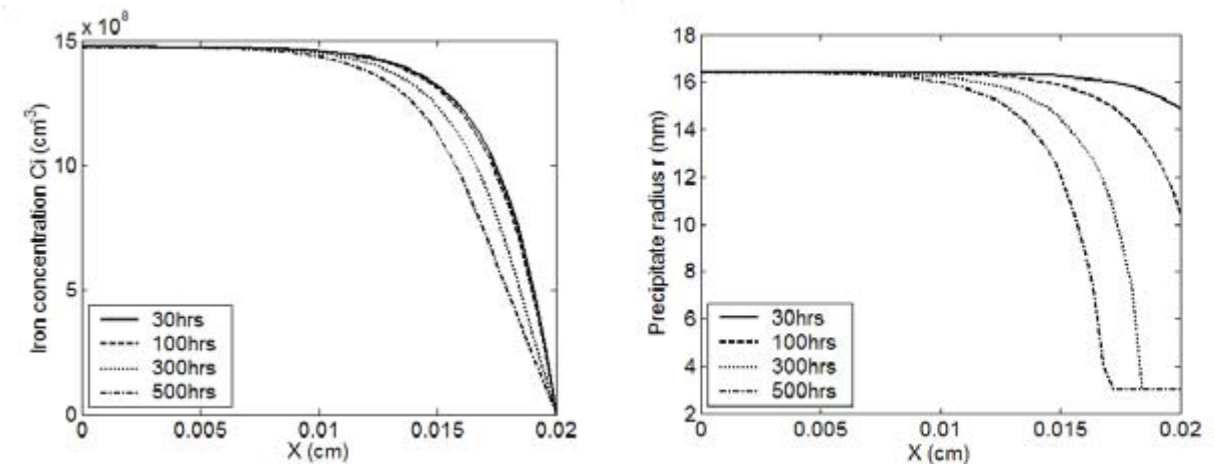

Fig. 3. Simulation profiles of dissolved iron concentration (left) and the profiles of precipitate radii (right) of a hypothetical precipitate case that the misfit y is positive, for which the generation of *V* or consumption of *I* or both will result from precipitate dissolution. Under the condition that optical processing injects V into the Si matrix, the needed gettering time is prolonged from that of the thermal annealing case.

It is obvious that optical-processing gettering involves hereto unconsidered physical mechanisms that introduce new challenges into the impurity precipitation/gettering modeling problem. In this initial modeling study, the mechanisms are proposed and used to demonstrate that they can give rise to improvement in the effectiveness of gettering metallic precipitates provided upon precipitate dissolution the matrix material will expand, and this is the case for $FeSi_2$ which is most common in mc-Si. Should the precipitate species be a species that upon its dissolution the Si matrix material will contract, then the opposite effect can be expected, e.g., some Ni and Cu precipitate species. This is because the proposed mechanisms include Si vacancy injection into the Si matrix to cause a *V* supersaturation, such vacancies will release the compressive strain for the Si matrix expansion case. The opposite holds for the Si matrix contraction case, for which, owing to *V*-supersaturation due to injection, not only should the optical-gettering condition not effective, but also it might well be harmful. Verifications of the mechanism both experimentally and theoretically are needed. For instance the formation of the solid Al-Si alloy should be readily detectable after processing at T_L. Also, if a buried dopant layer is used it should be possible to detect the injected vacancies in the T_H processing step by observing an enhancement in the dopant diffusivity and dopant-*V* pair concentration. Examples of theoretical problems need to be addressed would include: whether the injected *V* did or did not substantially migrate out through the Al-Si alloy layer; obtaining a more precise physical picture of the migration energy barrier reduction through the radiation enhanced diffusion mechanism; and the role of radiation enhanced *V* and Fe solubilities.

REFERENCES

1. N. Li, H. Li and T. Y. Tan, *Extended Abstracts and Papers, 14th Workshop on Crystalline Silicon Solar Cells & Modules: Materials and Processing,* p. 238 (Winter Park, Co., Aug. 11-14, 2004).
2. B. L. Sopori, US Patent No. 6,852,371 B2 (Feb. 8, 2005).
3. P. S. Plekhanov, R. Gafiteanu, U. M. Gösele, and T. Y. Tan, J. Appl. Phys. 86, 2453 (1999).
4. S. M. Joshi, U. M. Gösele, and T. Y. Tan, Solar Energy Materials and Solar Cells 70, 231 (2001).
5. T. Y. Tan, "Impurity Gettering in Silicon" in *Encyclopedia of Materials: Science and Technology*, ed. Subhash Mahajan (Elsevier, Amsterdam, 2001) pp. 4031-4042.
6. P. S. Plekhanov, M. D. Negoita, and T.Y. Tan, J. Appl. Phys. 90, 5388 (2001).
7. T. Y. Tan and U. Gösele, "Point Defects, Diffusion, and Precipitation", in "Handbook of Semiconductor Technology, vol. 1: Electronic Structure and Properties of Semiconductors", eds. K. A. Jackson and W. Schröter (Wiley-VCH, New York, 2000) p. 231-290.

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