A national laboratory of the U.S. Department of Energy
Office of Energy Efficiency & Renewable Energy

National Renewable Energy Laboratory
Innovation for Our Energy Future

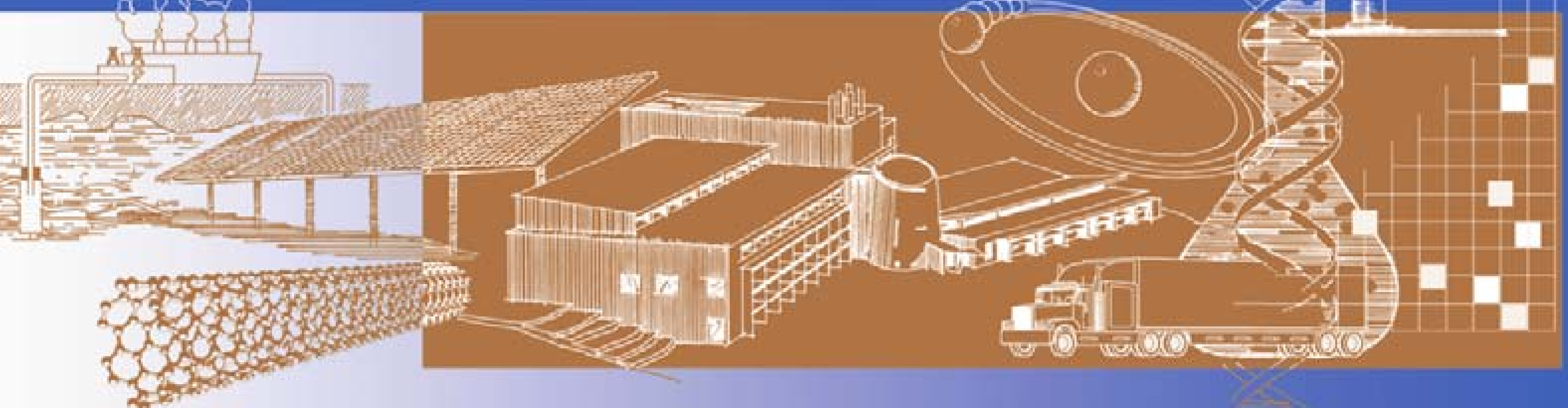
Subcontract Report
NREL/SR-520-44088
September 2008

Precipitate Dissolution and Gettering under Vacancy Injection in Silicon

Final Subcontract Report
21 March 2006 – 15 January 2008

T.Y. Tan and N. Li
Duke University
Durham, North Carolina

NREL is operated by Midwest Research Institute ● Battelle   Contract No. DE-AC36-99-GO10337



Precipitate Dissolution and Gettering under Vacancy Injection in Silicon

Final Subcontract Report
21 March 2006 – 15 January 2008

T.Y. Tan and N. Li
Duke University
Durham, North Carolina

NREL Technical Monitor: Fannie Eddy

Prepared under Subcontract No. XEJ-6-66132-01

Subcontract Report
NREL/SR-520-44088
September 2008

National Renewable Energy Laboratory
1617 Cole Boulevard, Golden, Colorado 80401-3393
303-275-3000 • www.nrel.gov

Operated for the U.S. Department of Energy
Office of Energy Efficiency and Renewable Energy
by Midwest Research Institute • Battelle

Contract No. DE-AC36-99-GO10337

Available electronically at http://www.osti.gov/bridge

Available for a processing fee to U.S. Department of Energy
and its contractors, in paper, from:
U.S. Department of Energy
Office of Scientific and Technical Information
P.O. Box 62
Oak Ridge, TN 37831-0062
phone: 865.576.8401
fax: 865.576.5728
email: mailto:reports@adonis.osti.gov

Available for sale to the public, in paper, from:
U.S. Department of Commerce
National Technical Information Service
5285 Port Royal Road
Springfield, VA 22161
phone: 800.553.6847
fax: 703.605.6900
email: orders@ntis.fedworld.gov
online ordering: http://www.ntis.gov/ordering.htm

Printed on paper containing at least 50% wastepaper, including 20% postconsumer waste

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 $\rho=10^{11}$ 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]

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

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]

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

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

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 gettering 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.

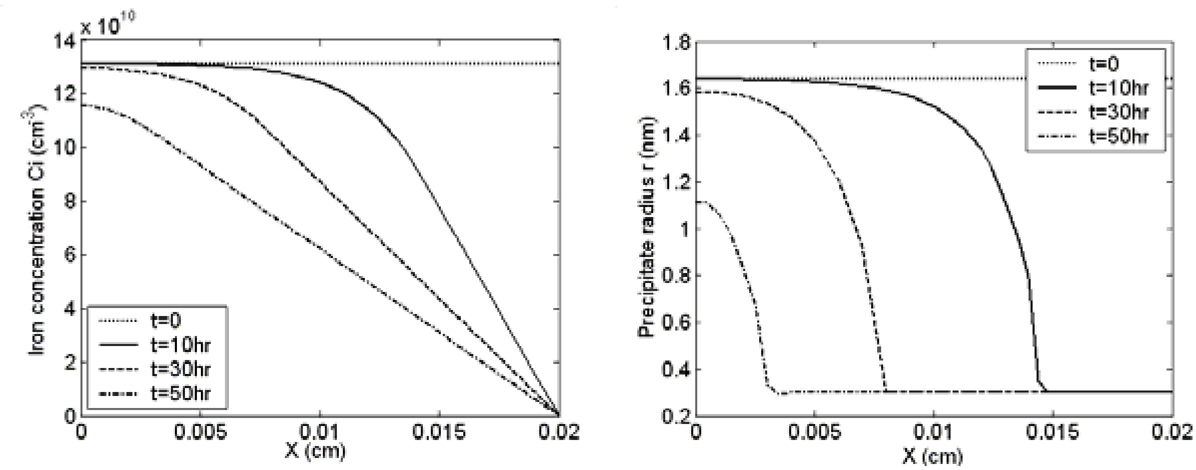


Fig. 1. Simulation results of gettering dissolved interstitial Fe (left) and $FeSi_2$ precipitates (right) from the Si matrix by a 2μm thick Al-Si liquid layer at the wafer backside (200 μm position) by thermal annealing at 700°C.

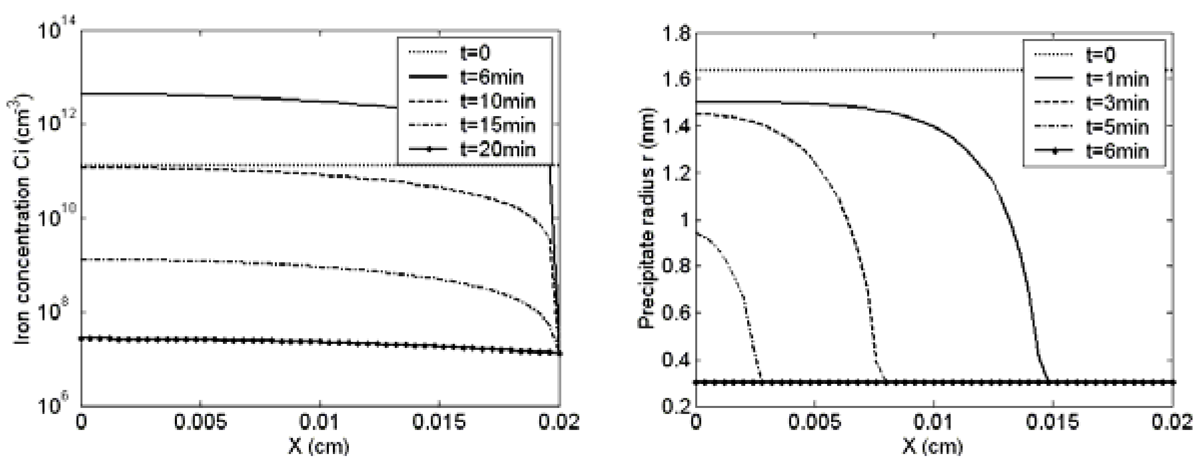


Fig. 2. Simulation results of gettering dissolved interstitial Fe (left) and $FeSi_2$ precipitates (right) for the case of Figure 1 by optical processing.

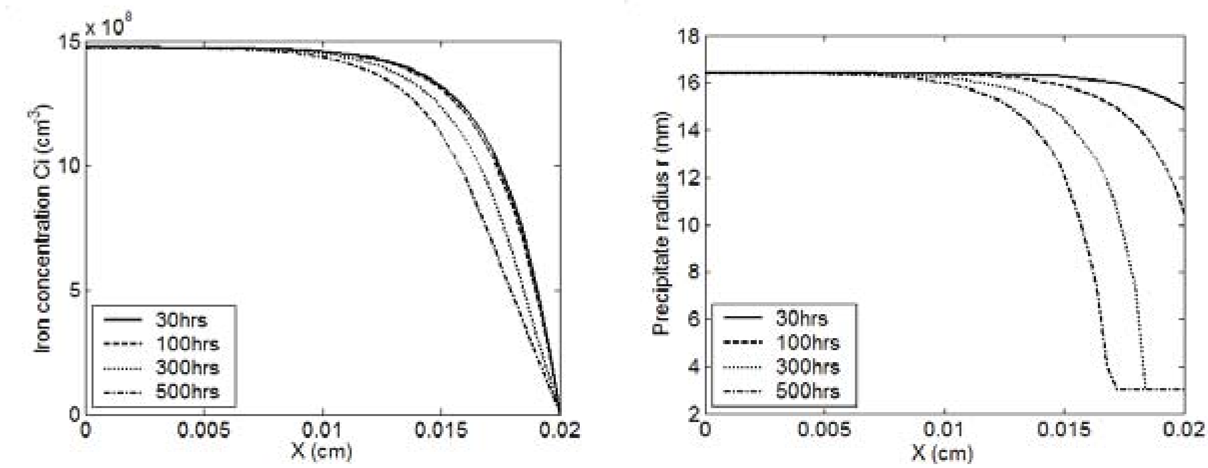


Fig. 3. Simulation profiles of dissolved iron concentration (left) and the profiles of precipitate radii (right) of a hypothetical precipitate case that the misfit y is positive, for which the generation of *V* or consumption of *I* or both will result from precipitate dissolution. Under the condition 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.

REPORT DOCUMENTATION PAGE	*Form Approved* *OMB No. 0704-0188*

1. **REPORT DATE** *(DD-MM-YYYY)*	2. **REPORT TYPE**	3. **DATES COVERED** *(From - To)*
September 2008	Subcontract Report	21 March 2006 – 15 January 2008

4. TITLE AND SUBTITLE
Precipitate Dissolution and Gettering under Vacancy Injection in Silicon: Final Subcontract Report, 21 March 2006 - 15 January 2008

5a. CONTRACT NUMBER
DE-AC36-99-GO10337

5b. GRANT NUMBER

5c. PROGRAM ELEMENT NUMBER

6. AUTHOR(S)
T.Y. Tan and N. Li

5d. PROJECT NUMBER
NREL/SR-520-44088

5e. TASK NUMBER
PVA72401

5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
Duke University - Office of Research Support
334 North Building, Box 90077
Durham, North Carolina 27708

8. PERFORMING ORGANIZATION REPORT NUMBER
XEJ-6-66132-01

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
National Renewable Energy Laboratory
1617 Cole Blvd.
Golden, CO 80401-3393

10. SPONSOR/MONITOR'S ACRONYM(S)
NREL

11. SPONSORING/MONITORING AGENCY REPORT NUMBER
NREL/SR-520-44088

12. DISTRIBUTION AVAILABILITY STATEMENT
National Technical Information Service
U.S. Department of Commerce
5285 Port Royal Road
Springfield, VA 22161

13. SUPPLEMENTARY NOTES
NREL Technical Monitor: Fanny Eddy

14. ABSTRACT *(Maximum 200 Words)*
Using a deposited Al layer, optical processing at a temperature below the Si-Al eutectic temperature of T_{eu}=577^{o}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 hours are needed when using thermal annealing at 700^{o}C. Possible mechanisms involved in optical-processing gettering are proposed: 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 precipitates, physical modeling and numerical simulations uncover and test the conditions for the mechanisms to be effective. The mechanisms are effective if 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 if the Fe atom migration energy barrier is reduced by ~0.15 eV by radiation at the higher temperature. On the other hand, for gettering a precipitate species for which the Si lattice will shrink concomitantly with the dissolution of precipitates, the vacancy-injection mechanism will not only be ineffective but should also have a detrimental effect.

15. SUBJECT TERMS
PV; optical processing; gettering; multicrystalline silicon vacancy injection; radiation-enhanced solubility; radiation-enhanced diffusion; metal impurity atoms; precipitate dissolution;

16. SECURITY CLASSIFICATION OF: a. REPORT	b. ABSTRACT	c. THIS PAGE	17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
Unclassified	Unclassified	Unclassified	UL		19b. TELEPHONE NUMBER *(Include area code)*

Standard Form 298 (Rev. 8/98)
Prescribed by ANSI Std. Z39.18

F1146-E(09/2007)