December 2004 • NREL/SR-520-37181

Subcontractor Report

Research in Hydrogen Passivation of Defects and Impurities in Silicon

Final Report
2 May 2000–2 July 2003

S. Ashok
Pennsylvania State University
University Park, Pennsylvania

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

December 2004 • NREL/SR-520-37181

Research in Hydrogen Passivation of Defects and Impurities in Silicon

Final Report
2 May 2000–2 July 2003

S. Ashok
Pennsylvania State University
University Park, Pennsylvania

NREL Technical Monitor: Richard Matson

Prepared under Subcontract No. ACQ-9-29639-04

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

Table of Contents

Project Objective:

The work consists of hydrogenating Si samples by different methods such as low-energy implantation, electron cyclotron resonance (ECR) plasma and thermal diffusion. The samples will be provided through NREL. The experimental work has been carried out at Penn State involves the study of hydrogen interaction with defects, trapping, migration and formation of complexes. The principal vehicle for the latter study will be ion implantation, and the intent is to understand mechanisms of defect passivation and activation by hydrogen.

Approach/Background:

NREL has implemented a study of hydrogen passivation of impurities and defects in silicon solar cells. The work includes theoretical and experimental components that will be performed at different universities. The theoretical studies will consist of calculation of the structure and parameters related to hydrogen diffusion and interactions of hydrogen with transition metal impurities in silicon. Experimental studies will involve measurements of hydrogen and hydrogen-impurity complexes, and diffusion properties of various species of hydrogen in Si. The experimental work at Penn State includes introduction of hydrogen in a variety of PV Si by ECR plasma, low energy ion implantation and thermal diffusion. The specific tasks will be the evaluation of hydrogen interaction with defects engineered by ion implantation; defect passivation, activation and migration in hydrogenated Si under thermal anneal; electrical activity of hydrogen-impurity complexes. Electrical characterization will entail I-V and C-V measurements, spreading resistance, and deep level transient spectroscopy (DLTS).

Major Accomplishments:

The first experimental study focused on the creation of buried cavity layers in Si by He implantation and thermal anneal, followed by hydrogenation. The ultimate motivation behind this work is evaluation of gettering ability of these nanocavities *and* using hydrogen-soaked cavities as a *source of atomic hydrogen* for passivation of defects elsewhere in the structure.

He implant-induced nanocavity layers have been shown to be most effective for gettering fast-diffusion metals in conventional Si technology. While gettering of the conventional thick (300 μm) Si substrate in PV is a difficult task, we expect our technique to be very effective for the thin c-Si technologies being developed. The work also has bearing on realizing thin crystalline Si films for solar cells using ion-cut and wafer bonding approaches.

The cavities were formed in crystalline Si with (80 keV) He ion implantation. We have been able to form He-induced cavities in Si with He doses as low as 5 x 10^{15} cm^{-2} and subsequent anneal at 800 -1000 ^{o}C. Further, by choice of appropriate energy we can generate either a single layer of cavities or a band of cavities. TEM cross-section of the cavities (formed with 2 x 10^{16} cm^{-2} He implantation and 800 ^{o}C – 30 min. anneal) show regular hexagonal shapes with specific orientation. Sets of samples were subsequently hydrogenated in an ECR hydrogen plasma system [700 W, 250 ^{o}C - 30 min.]. The electrical properties of the cavities - with and without hydrogen – have been evaluated with photoluminescence and deep level transient spectroscopy (DLTS). These results confirm the strong affinity of the cavities for hydrogen, and disclose passivation of the extended defects in the cavities as well as a new strong minority carrier DLTS peak due to the hydrogen-induced damage.

We have also successfully fabricated multiple layers of such He-induced cavity or void regions in Si. Such multi-layered cavity regions are of interest in tailoring the gettering and hydrogen passivation layers in thin film Si for photovoltaics. The generation of these layered cavity regions has been found to depend critically on the implant/anneal sequences employed. For instance, a sequence of three implants with decreasing energy (160 keV, 130 keV and 110 keV) followed by a single 800 C - 1 hour anneal results in the formation of a single void layer. But the same sequence interspersed with 800 C - 1 hour anneal after each implant gives rise to three distinct

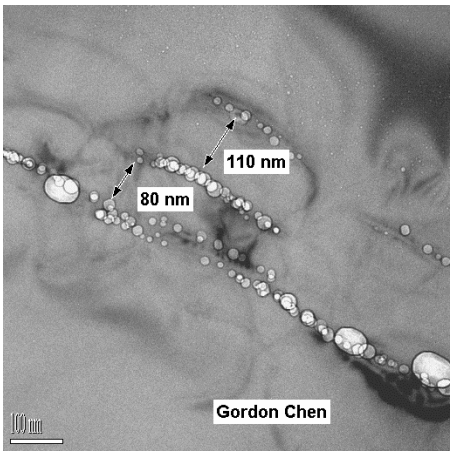


Figure 1 Cavity layers generated by cascade implants with anneal at each step. The depth of the void layer due to the 160 keV implant is 0.91 μm, the 130 keV implant is 0.8 μm and that of 110 keV is 0.7μm.

void layers, with the void density decreasing progressively from the top layer. The void layers and their evolution have been evaluated using SEM and TEM. Under isothermal anneal, the cavity shape changes from a distinct hexagonal geometry to a rounded spheroidal shape as the anneal time is increased. PL spectra at 77 K reveal a broad peak at 0.8 eV for all the He-implanted and annealed samples, attributable to vacancy clusters.

The use of ECR hydrogen plasma on shallow junction formation and low-temperature dopant activition has also been studied. For the thin crystalline Si cells under development, the photovoltaic junction needs to be shallower than normal. While conventional ion implantation is an impractical technique for low-cost PV fabrication, alternatives such as plasma immersion implantation (that does not require mass analyzer, etc.) may prove to be cost-effective and so this study is of relevance to photovoltaics. Experimental as well as theoretical studies have shown that atomic hydrogen in the crystalline Si lattice can reduce the thermal budget for activation anneals, while also enhancing dopant activation. This has been attributed to lattice relaxation, which occurs because of the termination of silicon dangling bonds by hydrogen and charge screening. It has been shown for example that for a phosphorus dopant atom at an interstitial site, the reduction in the activation energy is almost 3.0 eV (depending on the configuration of hydrogen and the vacancy). An earlier study involving the implantation of hydrogen into the region implanted with phosphorus showed a 10% increase in dopant activation when compared to an un-hydrogenated (UH) implanted case. The results from such furnace anneals differ considerably from rapid thermal anneals (RTA), since the thermal budget for RTA is vastly lower.

We studied the influence of plasma hydrogen treatment on p-n junction formation in Si following boron implantation and prior to activation anneal. The dopant activation was evaluated from Spreading Resistance measurements, as a function of anneal temperature for both the hydrogenated and the un-hydrogenated cases. The observed dependence of hydrogen on dopant ctivation and junction depth has been explained by defect evolution in self-implanted silicon, evaluated by DLTS. The results are of interest in forming shallow p-n junctions needed for thin c-Si cells, at low thermal budget.

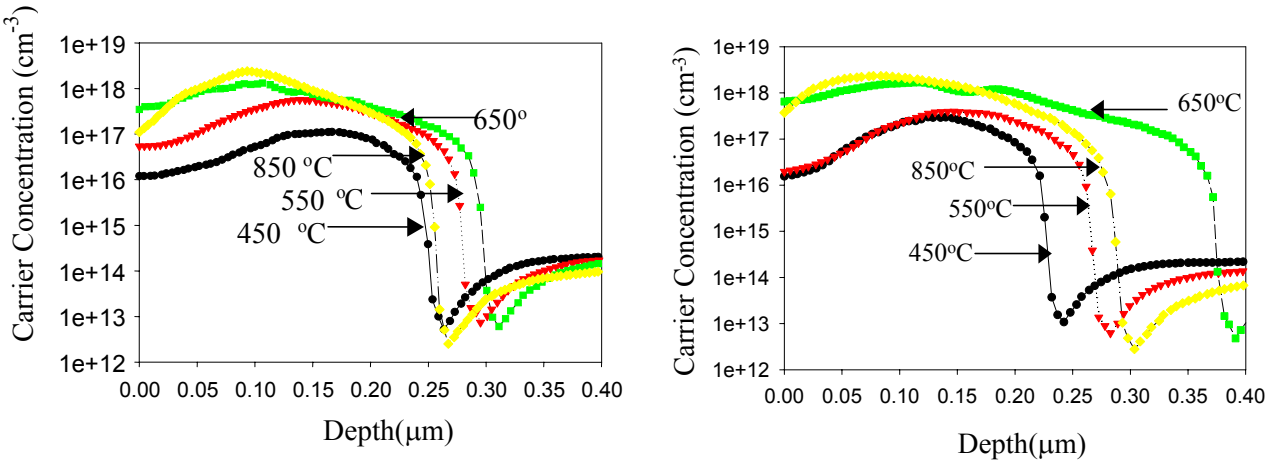
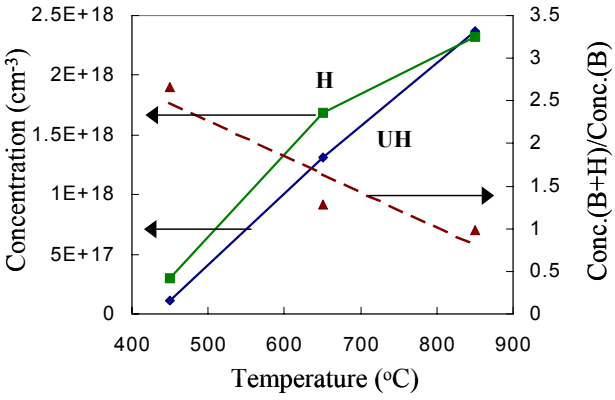


Figure 2. Spreading resistance profiles of the unhydrogenated (UH) sample (left) and hydrogenated (H) samples (right) as a function of RTA temperature. RTA time is 20 s.

Figure 2 shows the spreading resistance profiles (SRP) for hydrogenated (H) and un-hydrogenated (UH) boron implanted samples annealed at various temperatures. The junction depth for both cases increases as a function of anneal temperature up to 650 ^{o}C. However at 850 ^{o}C the junction depth is less than that at 550 ^{o}C for the un-hydrogenated case and 650 ^{o}C for the hydrogenated case. The peak ionized boron concentration in all cases increases monotonically with temperature. Figure 4 shows the junction depths for the H and UH samples. While the junction depths at 450 ^{o}C and 550 ^{o}C for the UH case are greater than the H case, at 650 ^{o}C and 850 ^{o}C, the junction depths for the H case are greater. Pronounced diffusion is observed in the H sample annealed at 650 ^{o}C.

Figure 3 shows the peak carrier concentrations for the H and UH cases, along with the activation enhancement factor of H over UH samples. The hydrogenated samples show enhanced dopant activation at temperatures below 650 ^{o}C, with the effect of hydrogen lost at 850 ^{o}C. We have been able to correlate this



behavior to the ion bombardment-induced interstitial defects, the affinity of H for vacancy sites and hydrogen effusion. Further details are described in the publication cited at the end of the report.

A number of Si FZ wafers and EFG ribbons, received from NREL during this program, were hydrogenated / deuterated with ECR hydrogen plasma as well as standard low-energy ion implantation. The ECR hydrogen and deuterium treatments have been done at 600 W microwave power, 20 W substrate power, 250 ^{o}C substrate temperature, and 30 min. duration. Ion implantation of deuterium was done at room temperature using a Varian 350D ion implanter at an energy of 40 keV, and a dose of 1 x 10^{15} cm^{-2}. These are intended primarily as reference samples to establish the hydrogen profile under normal process conditions, and develop predictive models for optimal hydrogenation conditions for a variety of PV silicon samples used in the industry. From the diffusion profiles of H generated from this work, a hydrogen trapping / detrapping model developed at NREL has been verified. Details of the results can be found in the publication cited below. In a related study, we performed preliminary experiments for forming high-quality thin layers of crystalline as well as poly-Si from hydrogen plasma treatment / wafer bonding approaches. An informal joint research program established with the University of Marseille on ECR hydrogen passivation of large-grain poly-Si was augmented during the PI's sabbatical in France during Spring 2002.

In continuation of this project, further efforts over the next 2-year period will involve carrying out hydrogen plasma passivation of new multicrystalline samples furnished by NREL, and evaluating the influence of hydrogen on He nanocavity *formation* and gettering for solar cells.

Major Publications and Conference Presentations under this Subcontract:

A.N. Nazarov, V.M. Pinchuk, T.B. Yanchuk, V.S. Lysenko, Ya. N. Vovk, S. Rangan, S. Ashok, V. Kudoyarova and E.I. Terukov, "Hydrogen effect on enhancement of defect reactions in semiconductors: Example for silicon and vacancy defects," *International Journal of Hydrogen Energy*, **26**, 521-526 (2001).

Sanjay Rangan, S. Ashok, G. Chen and D. Theodore, “Formation and Characterization of Multi-layered Nanocavities in Silicon with Cascade Helium iIplantation," *Proc. International Conference on Semiconductor and Integrated Circuit Technology*, Shanghai, China, 22-25 Oct. 2001.

S.P. Singh, V. Rao, Y.N. Mohapatra, S. Rangan, S. Ashok, “Electrical Signature of Ion-implantation Induced Defects in n-silicon in the Defect Cluster Regime studied using DLTS and Isothermal Transient Spectroscopies,” Proc. *Materials Research Society Spring Meeting*, San Francisco, 1-5 April 2002, vol. 719, pp. 303-309.

B. Sopori, Y. Zhang, R. Reedy, K. Jones, N.M. Ravindra, S. Rangan and S. Ashok, “Trapping and detrapping of H in Si: Impact on Diffusion Properties and Solar Cell Processing,” Proc. *Materials Research Society Spring Meeting*, San Francisco, 1-5 April 2002, vol. 719, pp. 125-131.

S. Rangan, M. Horn and S. Ashok, “Influence of Hydrogen Plasma Treatment on Boron Implantation,” *J. Vac. Sci. Technol.* **B21**, 781-784 (2003)

S. Rangan, S. Ashok, G. Chen and D. Theodore, “Multi-Layered Nanocavities in Silicon with Cascade Helium Implantation and Anneal,” *Nucl. Instrum. Methods in Physics B 206,* 417-421 (2003).

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

PLEASE DO NOT RETURN YOUR FORM TO THE ABOVE ORGANIZATION.

1. REPORT DATE *(DD-MM-YYYY)*	2. REPORT TYPE	3. DATES COVERED *(From - To)*
December 2004	Subcontractor Report	2 May 2000–2 July 2003

4. TITLE AND SUBTITLE
Research in Hydrogen Passivation of Defects and Impurities in Silicon**:** Final Report, 2 May 2000–2 July 2003

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

5b. GRANT NUMBER

5c. PROGRAM ELEMENT NUMBER

6. AUTHOR(S)
S. Ashok

5d. PROJECT NUMBER
NREL/SR-520-37181

5e. TASK NUMBER
PVA52101

5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
Pennsylvania State University
110 Technology Center
University Park, Pennsylvania 16802

8. PERFORMING ORGANIZATION REPORT NUMBER
ACQ-9-29639-04

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-520-37181

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: Richard Matson

14. ABSTRACT *(Maximum 200 Words)*

This subcontract report describes hydrogenating Si samples by different methods such as low-energy implantation, electron cyclotron resonance (ECR) plasma, and thermal diffusion. The samples were provided through NREL. The experimental work, carried out at Penn State, involved the study of hydrogen interaction with defects, trapping, migration, and formation of complexes. The principal vehicle for the latter study was ion implantation, and the intent to understand mechanisms of defect passivation and activation by hydrogen. NREL implemented a study of hydrogen passivation of impurities and defects in silicon solar cells. The work included theoretical and experimental components performed at different universities. The theoretical studies consisted of the calculation of the structure and parameters related to hydrogen diffusion and interactions of hydrogen with transition-metal impurities in silicon. Experimental studies involved measurements of hydrogen and hydrogen-impurity complexes, and diffusion properties of various species of hydrogen in Si. The experimental work at Penn State included introduction of hydrogen in a variety of PV Si by ECR plasma, low-energy ion implantation, and thermal diffusion. The specific tasks were the evaluation of hydrogen interaction with defects engineered by ion implantation; defect passivation, activation, and migration in hydrogenated Si under thermal anneal; and electrical activity of hydrogen-impurity complexes.

15. SUBJECT TERMS
PV; thin film; module; electron cyclotron resonance (ECR) plasma; ion implantation; hydrogen; thermal diffusion; deep-level transient spectroscopy (DLTS); crystalline; solar cells;

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