

Research on the Hydrogen Passivation of Defects and Impurities in Si Relevant to Crystalline Si Solar Cell Materials

**Final Report
16 February 2000–15 April 2003**

M. Stavola
*Lehigh University
Bethlehem, Pennsylvania*



NREL

National Renewable Energy Laboratory

1617 Cole Boulevard
Golden, Colorado 80401-3393

NREL is a U.S. Department of Energy Laboratory
Operated by Midwest Research Institute • Battelle • Bechtel

Contract No. DE-AC36-99-GO10337

Research on the Hydrogen Passivation of Defects and Impurities in Si Relevant to Crystalline Si Solar Cell Materials

**Final Report
16 February 2000–15 April 2003**

M. Stavola
*Lehigh University
Bethlehem, Pennsylvania*

NREL Technical Monitor: R. Matson

Prepared under Subcontract No. ACQ-9-29639-02



NREL

National Renewable Energy Laboratory

1617 Cole Boulevard
Golden, Colorado 80401-3393

NREL is a U.S. Department of Energy Laboratory
Operated by Midwest Research Institute • Battelle • Bechtel

Contract No. DE-AC36-99-GO10337

NOTICE

This report was prepared as an account of work sponsored by an agency of the United States government. Neither the United States government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or 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 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. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States government or any agency thereof.

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: 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>



Table of Contents

Summary	1
I. Introduction	2
II. Interstitial H ₂ Molecule in Si	3
III. Transition-Metal-Hydrogen Complexes in Si	5
A. Level Positions from the Fermi Level Dependence of the Vibrational Spectra	7
B. Multiple Internal Reflection	7
C. Structures of the Transition-Metal-H Complexes	8
IV. Conclusions	9
References	10
Papers Partially supported by NREL	12
Reports Supported by NREL Contract	12
Ph.D Theses Based on Work Partially Supported by NREL Contract	12

List of Figures

Figure 1. The Interstitial H ₂ Molecule in Si	2
Figure 2. Spectra measured as a function of temperature for the 3265.0 and new 3191.1 cm ⁻¹ absorption lines assign-ed to the interstitial HD molecule in Si	4
Figure 3. Effect of stress on the 2642.6 cm ⁻¹ line of D ₂ in Si. The vertical lines show the positions of the vibrational lines and the relative intensities given by the fit of our model (a T ₂ to T ₂ transition in tetrahedral symmetry) to the data	5
Figure 4. IR absorption lines assigned to the neutral charge states of the PtH and PtH ₂ complexes in Si	6
Figure 5. Multiple-internal-reflection geometry used for IR measurements of thin hydrogenated Si surface layers	8
Figure 6. Structured of the PtH (left) and PtH ₂ (right) complexes in Si	9

Research on the Hydrogen Passivation of Defects and Impurities in Si Relevant to Crystalline Si Solar Cell Materials

Summary

Hydrogen is commonly introduced into Si solar cells to reduce the deleterious effects of defects and increase the minority carrier lifetime. Nonetheless, the methods by which hydrogen is introduced during processing and hydrogen's subsequent interactions with defects remain poorly understood. The goal of this experimental research program is to increase the understanding, at a microscopic level, of hydrogenation processes and passivation mechanisms for crystalline-Si photovoltaics.

In our experiments, vibrational spectroscopy has been used to study the properties of the interstitial H₂ molecule in Si and the transition-metal-hydrogen complexes in Si. The interstitial H₂ molecule is formed readily in Si when hydrogen is introduced. Our studies establish that interstitial H₂ in Si behaves as a nearly free rotator, solving puzzles about the behavior of this defect that have persisted since the discovery of its vibrational spectrum. The transition metals are common impurities in Si that decrease the minority carrier lifetime and degrade the efficiencies of solar cells. Therefore, the possibility that transition-metal impurities in Si might be passivated by hydrogen has been of long interest. Our studies of transition-metal-H complexes in Si help to establish the structural and electrical properties of a family of Pt-H complexes in Si, and have made the Pt-H complexes a model system for understanding the interaction of hydrogen with transition-metal impurities in Si.

A promising method to introduce H into Si solar cells in order to passivate bulk defects is by the post-deposition annealing of an H-rich, SiN_x surface layer. Unfortunately, it has been difficult to detect directly the H introduced by this method because of its small concentration. A novel method that combines IR spectroscopy with marker impurities that can trap H in the Si has been developed, based upon our fundamental studies of the Pt-H complexes in Si, to determine the concentration and depth of H introduced by processes commonly used to hydrogenate Si solar cells.

I. Introduction

The silicon substrates used for the fabrication of solar cells contain impurities and defects that limit device performance. Hydrogen is commonly introduced into Si solar cells where it reduces the deleterious effects of defects and increases the efficiency of solar cells by a few percent [1-4]. In spite of the importance of hydrogenation processes, the microscopic properties of many hydrogen-containing defects in Si remain poorly understood. In work supported by this contract, experiments have been performed to provide new microscopic information about the structures and properties of hydrogen-containing defects in Si and the mechanisms by which hydrogen interacts with impurities and defects.

Vibrational spectroscopy has proved to be an excellent probe of hydrogen-containing defects and has been used in our studies [5]. Multiple-internal-reflection methods have been used to provide enhanced sensitivity for the study of thin hydrogenated surface layers. Uniaxial stress is used in conjunction with IR absorption spectroscopy to provide information about defect symmetry and structure.

Interstitial H_2 molecules form readily in Si when hydrogen is introduced. The recent discovery of vibrational lines due to H_2 in Si [6,7] has led to new opportunities to probe the properties of interstitial H_2 . Our studies show that H_2 in Si act as a nearly free rotator (Sec. II), solving persistent puzzles that have arisen in recent years concerning the microscopic behavior of this defect [8-10].

Transition-metal impurities in Si decrease the minority carrier lifetime and degrade the properties of solar cells. Hydrogen interacts with transition-metal impurities and modifies their

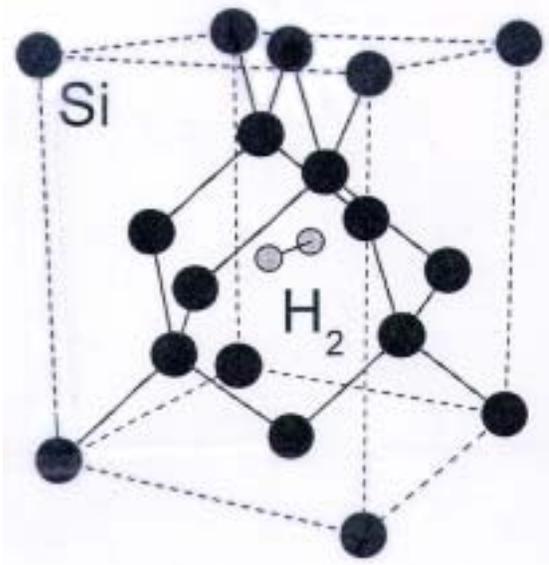


Fig. 1. The interstitial H_2 molecule in Si.

electrical properties [11]. Therefore, the possibility to passivate metal impurities in Si with hydrogen has been of long interest for solar-cell applications. Infrared absorption spectroscopy has been used to probe the properties of Pt-H complexes in Si (Sec. III) [12-14]. The Pt-H complexes have become a model system for understanding the interaction of H with transition-metal impurities in Si. Furthermore, our fundamental studies of the transition-metal-hydrogen complexes have led to a novel method to characterize the hydrogen introduced into Si by processes used to fabricate solar cells (Sec. IV) [15].

II. Interstitial H₂ Molecule in Si

In the early 1980s, isolated H₂ molecules in semiconductors (Fig. 1) were suggested to play an important role in the diffusion of hydrogen and in H-related defect reactions [16-18]. However, in spite of its proposed importance, the H₂ molecule in a semiconductor was not observed directly until recently when vibrational lines for the H₂, HD, and D₂ molecules in GaAs [19] and Si [6,7] were discovered. These new experimental results have motivated a number of experimental and theoretical studies of the vibrational properties of interstitial H₂ in semiconductors [20-24]. In spite of these exciting recent advances, a number of experimental and theoretical results for H₂ molecules, especially in Si, led to contradictory conclusions. A particularly controversial issue concerned whether the H₂ molecule in Si is a nearly free rotor or whether there is a substantial barrier to rotation. In work supported by this contract, vibrational spectroscopy combined with uniaxial stress has been used to probe the structure and microscopic properties of H₂ in Si and has led to a definitive solution of the puzzles associated with this defect [8-10].

The H₂ molecule in Si gives only a single, sharp, H₂-vibrational line at 3618.4 cm⁻¹ and no evidence for an ortho-para splitting in its IR absorption spectrum [6]. To explain the absence of an ortho-para splitting, it was suggested that there must be a barrier that prevents rotation of the molecule [20]. Uniaxial stress results for the 3618.4 cm⁻¹ line of interstitial H₂ in Si were interpreted in terms of an orientationally degenerate defect with low symmetry, reinforcing the suggestion that the H₂ molecule is static [24]. However, several theoretical calculations for H₂ at a tetrahedral interstitial site in Si find that different orientations have similar energies [9,20-22], making it surprising that the H₂ molecule does not rotate. Furthermore, recent molecular dynamics calculations indicate that the H₂, HD and D₂ molecules in Si behave as nearly free rotators, bouncing within the interstitial region [23]. In addition to the 3618.4 cm⁻¹ line for H₂ in

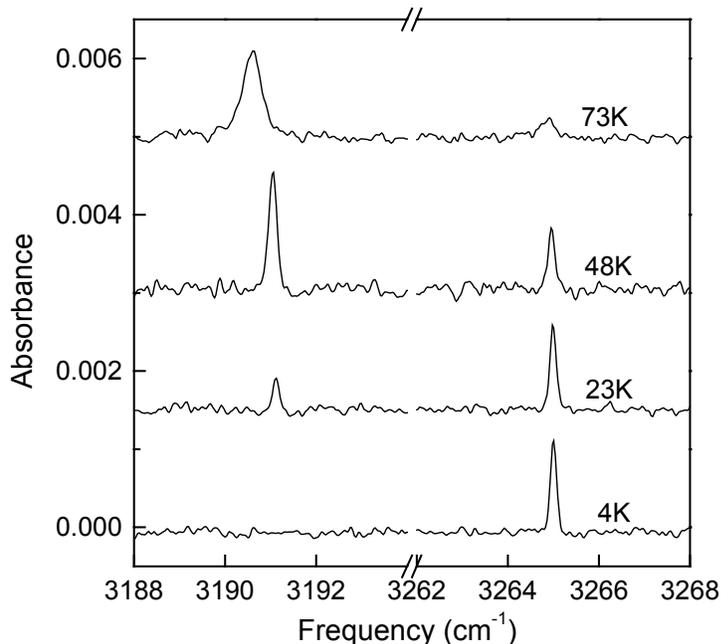


Fig. 2. Spectra measured as a function of temperature for the 3265.0 and new 3191.1 cm^{-1} absorption lines assigned to the interstitial HD molecule in Si.

Si, vibrational lines due to HD and D_2 were discovered at 3265.0 and 2642.6 cm^{-1} (4.2K), respectively, by IR absorption [6] and Raman spectroscopies [7].

The telling experimental clue that interstitial H_2 in Si is actually freely rotating is our discovery of a new vibrational line at 3191.1 cm^{-1} for the HD molecule in Si (Fig. 2) [8]. This line appears for sample temperatures above $T > 20\text{K}$ and lies 73.9 cm^{-1} below the 3265.0 cm^{-1} line previously observed for HD. This 73.9 cm^{-1} energy is in fact close to the $J = 0$ to $J = 1$ rotational transition energy for a free HD molecule. From selection rules learned from the ro-vibrational transitions of HD, it follows that H_2 and D_2 must also be freely rotating and that their IR transitions are seen only when the molecules are in the $J=1$ rotational state (T_2 in tetrahedral symmetry). Thus only ortho- H_2 and para- D_2 are seen, explaining the puzzling absence of an ortho-para splitting in the IR spectrum. Several additional anomalous properties are also automatically explained. Uniaxial stress results for H_2 and D_2 , which were taken previously as evidence for a static defect, are fit well by a T_2 to T_2 transition in full tetrahedral symmetry (Fig. 3) [10]. This assignment, and the observed isotope independence of the stress splittings, provides a strong confirmation of the rotational motion of interstitial H_2 in Si. Furthermore, the vibrational properties of an O- H_2 center in Si that has been studied recently [25] can be explained as those of a rotating interstitial H_2 molecule perturbed by the field of a nearby O atom [26]. The separate ortho and para O- H_2 complexes each gives an oxygen vibrational line and H_2 vibrational lines with distinctive properties.

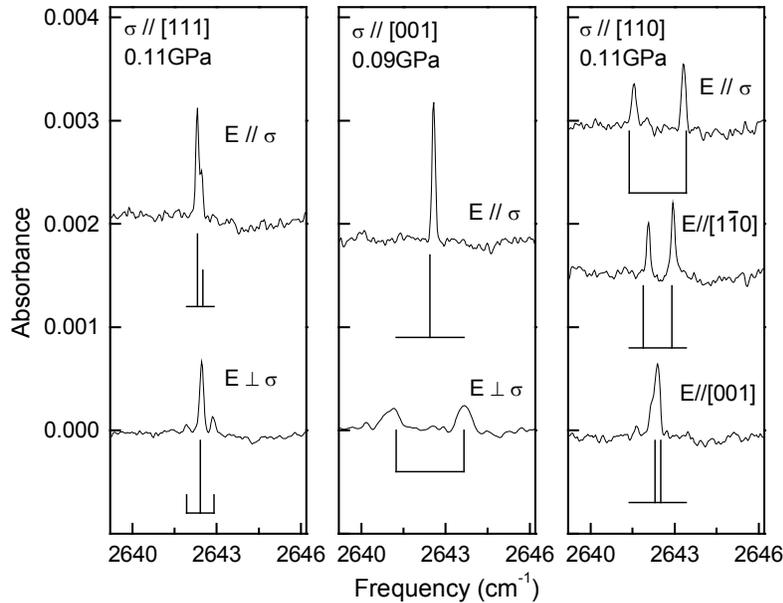


Fig. 3. Effect of stress on the 2642.6 cm^{-1} line of D_2 in Si. The vertical lines show the positions of the vibrational lines and the relative intensities given by the fit of our model (a T_2 to T_2 transition in tetrahedral symmetry) to the data.

III. Transition-Metal-Hydrogen Complexes in Si

In early studies of the hydrogen passivation of deep-level defects, it was discovered that exposure of Si samples to a hydrogen-containing plasma can eliminate many of the electrical levels associated with transition metal impurities [11,27]. This effect continues to be of great importance for the passivation of defective Si materials like the multicrystalline Si used to make solar cells. Until recently, little was known about the microscopic properties of the hydrogenated defects or the mechanism of passivation. Several recent studies provide new insight and have made the transition-metal-H complexes in Si model systems for the study of hydrogen's interaction with deep-level impurities in semiconductors [14,28]. These recent studies also show that the hydrogenation of transition metal impurities is more complicated than the early studies suggested and that families of electrically active defects that include a metal impurity and different numbers of H atoms can be formed.

In a series of experiments performed by our group at Lehigh, H was introduced at high temperature (1250°C) into Si doped with a transition-metal impurity [12-14]. In this way, H could be introduced throughout bulk samples, producing a sufficient number of defects to study with

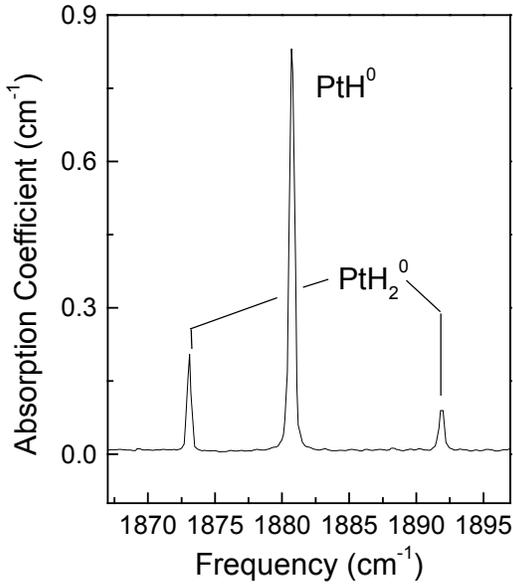


Fig. 4. IR absorption lines assigned to the neutral charge states of the PtH and PtH₂ complexes in Si.

structure-sensitive methods like EPR and vibrational spectroscopy. A few hydrogenated transition metal impurities (PtH, PtH₂, AuH and AuH₂) were identified and structures for the defects were proposed, providing valuable input for theoretical calculations. Fig. 4 shows the vibrational lines of the neutral charge states of the PtH and PtH₂ complexes in Si.

Independently, a few groups have introduced H by wet chemical etching (at room temperature) into thin surface layers of Si doped with metal impurities. Deep level transient spectroscopy (DLTS) was used to study the electrical properties of the hydrogenated transition metals [14,28,29]. Unfortunately, it was not known whether the transition-metal-H complexes produced by different methods and studied by different techniques were indeed the same defects. Correlating the results of our structure-sensitive IR studies with the electrical measurements made by DLTS has been one of the achievements of the research supported by this contract [14].

Experiments on the transition-metal-hydrogen complexes in Si have been performed in collaboration with J. Weber's group (formerly at the Max Planck Inst., Stuttgart, and now at the TU Dresden). Our goal was to determine whether the transition-metal-H complexes in Si that were produced by different methods, and studied by vibrational spectroscopy by our group [12-14] and by DLTS by Weber's group [28,29], are indeed the same defects. The problem has been that typical sample characteristics for DLTS experiments, which probe the electrical properties of a defect, and typical sample characteristics suitable for EPR and vibrational spectroscopy experiments, are usually incompatible. Therefore, it has been difficult to take full

advantage of what seem to be complementary results because it has remained uncertain that the different techniques do, indeed, probe the same defects.

A. Level Positions from the Fermi Level Dependence of the Vibrational Spectra

We have determined the approximate electrical level positions associated with the vibrational lines of the transition-metal-H complexes so that these levels can be correlated with the results of DLTS experiments [14]. To do this, we have taken advantage of the fact that the H-stretching bands associated with different charge states of the same defect are shifted by about 20 cm^{-1} , making it possible to monitor the relative populations of different charge states for different positions of the Fermi level.

For these experiments, we prepared samples with different Fermi level positions by compensating n- and p-type samples with deep level defects (transition metals or electron-irradiation produced centers) whose levels are known. The relative populations of the different charge states of the PtH and PtH₂ defects were then determined from their vibrational spectra. From these data, the approximate level positions of the PtH and PtH₂ defects were determined by the comparison of the PtH and PtH₂ levels to the Fermi level in the sample.

The results of these experiments link the levels observed by DLTS to specific defect structures, and also allow the vibrational lines of the transition-metal-H complexes to be associated with specific charge states. It has also been possible to calibrate the IR absorption intensities of the PtH and PtH₂ complexes with these experiments so that the concentrations of these defects can be determined from their vibrational spectra [14].

B. Multiple Internal Reflection

The thin, hydrogenated surface layers that are produced by etching for DLTS experiments are unsuitable for typical vibrational absorption measurements made with the spectrometer light at normal incidence because of the sensitivity limits of the technique. To enhance the sensitivity of IR absorption measurements so that thin surface layers could be studied, we have developed the capability to make multiple-internal-reflection (MIR) measurements for Si samples at liquid He temperature [14]. For MIR experiments, the ends of a rectangular sample are beveled at a 45° angle. The spectrometer light is introduced through one of the beveled faces so as to be

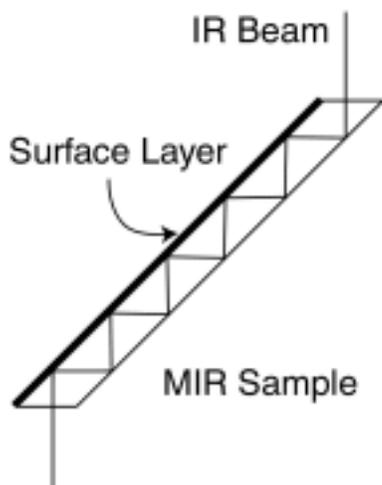


Fig.5. Multiple-internal-reflection geometry used for IR measurements of thin hydrogenated Si surface layers.

multiply reflected many times from the internal surfaces of the sample before it exits from the opposite beveled face (Fig. 5). In such measurements, the interaction of the light with the near surface regions of the sample is greatly increased.

For our experiments, Si samples that contained Pt impurities were hydrogenated by a wet chemical etching treatment, i.e., with the typical sample preparation method used for DLTS measurements. The vibrational lines previously assigned to the PtH and PtH₂ complexes were observed in these Si:Pt MIR samples that had been hydrogenated by etching [14]. The estimated concentrations of Pt-H complexes that were detected is $\sim 10^{15} \text{ cm}^{-3}$ for layer thicknesses of only $\sim 3 \text{ }\mu\text{m}$. (This concentration is roughly 100 times smaller than the typical sensitivity limit of IR absorption measurements.) These results support the assignment of Pt- and H-containing defects seen previously by IR absorption and DLTS to the same PtH and PtH₂ complexes.

C. Structures of the Transition-Metal-H Complexes

We have obtained experimental results that challenge the currently accepted structural model for the transition-metal-H complexes in Si. In previous models, it has been proposed that the H atom in, for example, the PtH complex in Si is attached to one of the Pt atom's Si neighbors [30]. If this were true, the H-stretching lines for the complexes would show characteristic fine structure in their IR spectra due to the naturally abundant isotopes of Si. We have made IR measurements with high signal to noise ratio that show that this fine structure is

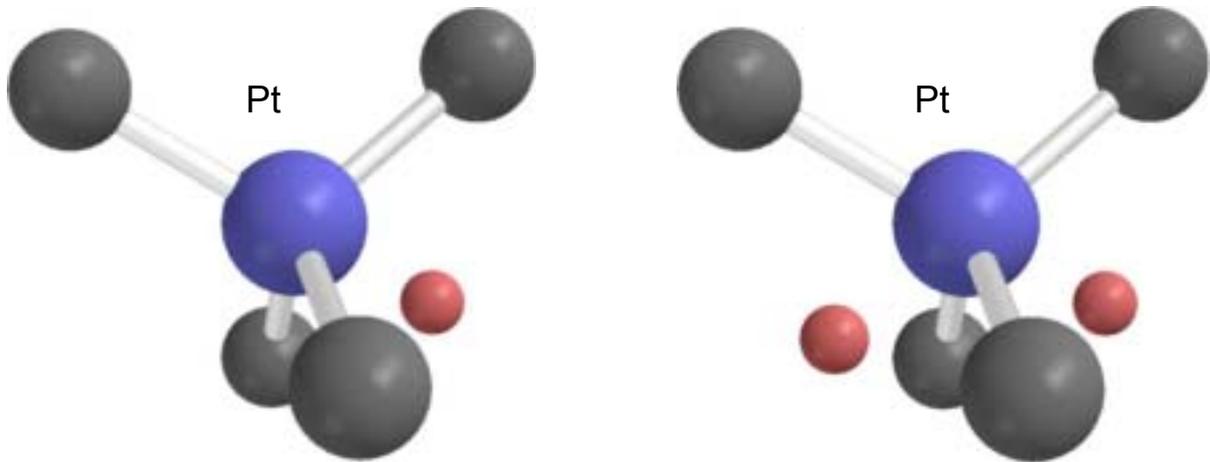


Fig. 6. Structures of the PtH (left) and PtH₂ (right) complexes in Si.

absent from the H-stretching absorption lines and, therefore, that the H atom in the PtH complex is not bonded to Si [31]. Our results favor a structure with the H atom bonded directly to the Pt impurity. Structures for the PtH and PtH₂ complexes are shown in Fig. 6.

IV. Conclusions

Our studies of interstitial H₂ in Si have established that H₂ acts as a nearly free rotator in Si, and have solved vexing puzzles about the experimental properties of H₂ in Si that have persisted for several years [8-10]. Our studies of the transition-metal-hydrogen complexes in Si show that IR absorption and DLTS studies do indeed study the same defects [14]. These results have allowed us to calibrate the IR absorption lines of the Pt-H complexes so that the concentration of the defects can be determined from the intensities of the IR lines. Our results also provide experimental support for new structural models for the Pt-H complexes [31].

Furthermore, our work on the fundamental properties of the transition-metal-hydrogen complexes in Si has provided us with a sensitive new method to study the introduction of hydrogen into Si by processes used to fabricate solar cells [15]. A commonly used method to introduce H into Si solar cells in order to passivate bulk defects is by the post-deposition annealing of an H-rich, SiN_x layer that is deposited onto the Si to act as an antireflection coating [32-35]. It previously has been difficult to characterize the small concentration of H that is

introduced by this method. In our continuing work funded by NREL award AAT-2-31605-4, we use IR spectroscopy coupled with Pt impurities introduced into Si-test samples to act as model traps for hydrogen. The Pt-H complexes can be sensitively detected by the multiple-internal-reflection methods developed in the present studies and their intensities have been calibrated so the concentration of H introduced into the Si bulk can be determined [14]. These novel methods to sensitively detect H in Si, based on the results of fundamental studies supported by the present contract, have the potential to provide new microscopic information about processes used to hydrogenate Si solar cells [15].

References

1. C. H. Seager, D. S. Ginley, and J. D. Zook, *Appl. Phys. Lett.* **36**, 831 (1980).
2. J.I. Hanoka, C.H. Seager, D.J. Sharp, and J.K.G. Panitz, *Appl. Phys. Lett.* **42**, 618 (1983).
3. B.L. Sopori, X. Den, J.P. Benner, A. Rohatgi, P. Sana, S.K. Estreicher, Y.K. Park, and M.A. Roberson, *Solar Energy Materials and Solar Cells* **41/42**, 159 (1996).
4. R. Lüdemann, *Mater. Sci. Eng. B* **58**, 86 (1999).
5. M. Stavola, in *Identification of Defects in Semiconductors*, Semiconductors and Semimetals, Vol. 51B, edited by M. Stavola (Academic, Boston, 1999), p. 153.
6. R.E. Pritchard, M.J. Ashwin, J.H. Tucker, and R.C. Newman, *Phys. Rev. B* **57**, 15048 (1998).
7. A.W.R. Leitch, V. Alex, and J. Weber, *Phys. Rev. Lett.* **81**, 421 (1998).
8. E E. Chen, M. Stavola, W.B. Fowler, and P. Walters, *Phys. Rev. Lett.* **88**, 105507 (2002).
9. W.B. Fowler, P. Walters, and M. Stavola, *Phys. Rev. B* **66**, 075216 (2002).
10. E E. Chen, M. Stavola, W.B. Fowler, and J.A. Zhou, *Phys. Rev. Lett.* **88**, 245503 (2002).
11. Chapt. 3 in S.J. Pearton, J.W. Corbett, and M. Stavola, *Hydrogen in Semiconductors*, (Springer-Verlag, Heidelberg, 1992), p. 28.
12. S.J. Uftring, M. Stavola, P.M. Williams, and G.D. Watkins, *Phys. Rev. B* **51**, 9612 (1995).
13. M.J. Evans, M Stavola, M.G. Weinstein, and S.J. Uftring, *Mater. Sci. Eng. B* **58**, 118 (1999).
14. M.G. Weinstein, M. Stavola, K.L. Stavola, S.J. Uftring, J. Weber, J.-U. Sachse, and H. Lemke, H., *Phys. Rev. B* **65**, 035206 (2002), p. 447, and the references contained therein.
15. F. Jiang, M. Stavola, A. Rohatgi, D. Kim, J. Holt, H. Atwater, and J. Kalejs, *Appl. Phys. Lett.*, submitted.
16. A. Mainwood and A.M. Stoneham, *Physica* **116B**, 101 (1983).
17. J.W. Corbett, S.N. Sahu, T.S. Shi and L.C. Snyder, *Phys. Lett.* **93A**, 303 (1983).

18. R.N. Hall, *J. Electron. Mat.* **14a**, 759 (1985).
19. J. Vetterhöffer, J. Wagner, and J. Weber, *Phys. Rev. Lett.* **77**, 5409 (1996).
20. B. Hourahine, R. Jones, S. Öberg, R.C. Newman, P.R. Briddon, and E. Roduner, *Phys. Rev. B* **57**, 12666 (1998).
21. Y. Okamoto, M. Saito, and A. Oshiyama, *Phys. Rev. B* **56**, 10016 (1997).
22. C.G. Van de Walle, *Phys. Rev. Lett.* **80**, 2177 (1998).
23. S.K. Estreicher, K. Wells, P.A. Fedders and P. Ordejón, *J. Phys.: Condens. Matter* **13**, 6271 (2001).
24. J.A. Zhou and M. Stavola, *Phys. Rev. Lett.* **83**, 1351 (1999).
25. R.E. Pritchard, M.J. Ashwin, J.H. Tucker, R.C. Newman, E.C. Lightowers, M.J. Binns, S.A. McQuaid, and R. Falster, *Phys. Rev. B* **56**, 13118 (1997).
26. E E. Chen, M. Stavola, and W.B. Fowler, *Phys. Rev. B* **65**, 245208 (2002).
27. S.J. Pearton and A.J. Tavendale, *Phys. Rev. B* **26**, 7105 (1982).
28. J. Weber, in *Proc. 24th Int. Conf. on the Physics of Semiconductors*, edited by D. Gershoni, World Scientific, 1999.
29. J.-U. Sachse, J. Weber, E.Ö. Sveinbjörnsson, *Phys. Rev. B* **60**, 1474 (1999).
30. R. Jones, B.J. Coomer, J.P. Goss, B. Hourahine, and A. Resende, *Solid St. Phenom.* **71**, 173 (2000).
31. M. Stavola, M.J. Evans, and G. Shi, unpublished.
32. A. Rohatgi, P. Doshi, J. Moschner, T. Lauinger, A.G. Aberle, and D.S. Ruby, *IEEE Trans. Electron. Dev.* **47**, 987 (2000).
33. A. G. Aberle, *Sol. Energy Mater. Sol. Cells* **65**, 239 (2001) reviews the SiN_x passivation of c-Si solar cells and includes a historical overview.
34. F. Duerinckx and J. Szlufcik, *Sol. Energy Mater. Sol. Cells* **72**, 231 (2002).
35. B. L. Sopori, Y. Zhang, and R. Reedy, *Proc. 29th IEEE-Photovoltaic Specialists Conference*, New Orleans, May 2002, edited by R. D. McConnell (Report No. NREL/EL-590-32461).

Papers partially supported by NREL Contract No. ACQ-9-29639-02

1. Lifetimes of hydrogen and deuterium related vibrational modes in silicon, M. Budde, G. Lupke, E Chen, X. Zhang, N.H. Tolk, L.C. Feldman, E. Tarhan, A.K. Ramdas, and M. Stavola, Phys. Rev. Lett. **87**, 145501 (2001).
2. Pt-H complexes in Si: Complementary studies by vibrational and capacitance spectroscopies, M.G. Weinstein, M. Stavola, K.L. Stavola, S.J. Uffring, J. Weber, J.-U. Sachse, and H. Lemke, Phys. Rev. B **65**, 035206-1 (2002).
3. Key to understanding interstitial H₂ in Si, E E. Chen, M. Stavola, W.B. Fowler, and P. Walters, Phys. Rev. Lett. **88**, 105507 (2002).
4. Rotation of molecular hydrogen in Si: Unambiguous identification of ortho-H₂ and para D₂, E E. Chen, M. Stavola, W.B. Fowler, and J.A. Zhou, Phys. Rev. Lett. **88**, 245503 (2002).
5. Ortho and para O-H₂ complexes in silicon, E E. Chen, M. Stavola, and W.B. Fowler, Phys. Rev. B **65**, 245208 (2002).
6. Dynamics of interstitial H₂ in crystalline silicon, W.B. Fowler, P. Walters, and M. Stavola, Phys. Rev. B **66**, 075216 (2002).

Reports supported by NREL Contract No. ACQ-9-29639-02

1. Transition-metal-hydrogen complexes in Si: Do structure-sensitive spectroscopies and DLTS study the same defects? 10th (NREL) Workshop on Crystalline Silicon Solar Cell Materials and Processes, Report No. NREL/BK-520-28844, Copper Mountain, CO, Aug., 2000, p. 159.
2. Interstitial H₂ in Si: A nearly free rotator after all, M. Stavola, E E. Chen, W.B. Fowler, J. A. Zhou, and P. Walters, 12th (NREL) Workshop on Crystalline Silicon Solar Cell Materials and Processes, Report No. NREL/BK-520-32717, Breckenridge, CO, Aug. 2002, p. 155.

Ph.D. Theses based on work partially supported by NREL Contract No. ACQ-9-29639-02

1. Identification of Hydrogen-Containing Defects in the III-V Nitrides and in Si from Advanced Applications of Vibrational Spectroscopy, Marcie G. Weinstein, Lehigh University, 2000.
2. Infrared Studies of the Rotational Motion of Interstitial H₂ and the Vibrational Lifetimes of H-decorated Lattice Defects in Si, E Elinor Chen, Lehigh University, 2002.

REPORT DOCUMENTATION PAGE			Form Approved OMB NO. 0704-0188	
Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.				
1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE September 2003	3. REPORT TYPE AND DATES COVERED Final Report 16 February 2000–15 April 2003		
4. TITLE AND SUBTITLE Research on the Hydrogen Passivation of Defects and Impurities in Si Relevant to Crystalline Si Solar Cell Materials: Final Report, 16 February 2000–15 April 2003		5. FUNDING NUMBERS PVP32601 ACQ-9-29639-02		
6. AUTHOR(S) M. Stavola				
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) Department of Physics Lehigh University Bethlehem, Pennsylvania 18015		8. PERFORMING ORGANIZATION REPORT NUMBER		
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) National Renewable Energy Laboratory 1617 Cole Blvd. Golden, CO 80401-3393		10. SPONSORING/MONITORING AGENCY REPORT NUMBER NREL/SR-520-34821		
11. SUPPLEMENTARY NOTES NREL Technical Monitor: Richard Matson				
12a. DISTRIBUTION/AVAILABILITY STATEMENT National Technical Information Service U.S. Department of Commerce 5285 Port Royal Road Springfield, VA 22161		12b. DISTRIBUTION CODE		
13. ABSTRACT (<i>Maximum 200 words</i>): The goal of this experimental research program is to increase the understanding, at a microscopic level, of hydrogenation processes and passivation mechanisms for crystalline-Si photovoltaics. In our experiments, vibrational spectroscopy was used to study the properties of the interstitial H ₂ molecule in Si and the transition-metal-hydrogen complexes in Si. The interstitial H ₂ molecule is formed readily in Si when hydrogen is introduced. Our studies establish that interstitial H ₂ in Si behaves as a nearly free rotator, solving puzzles about the behavior of this defect that have persisted since the discovery of its vibrational spectrum. The transition metals are common impurities in Si that decrease the minority-carrier lifetime and degrade the efficiencies of solar cells. Therefore, the possibility that transition-metal impurities in Si might be passivated by hydrogen has long been of interest. Our studies of transition-metal-H complexes in Si help to establish the structural and electrical properties of a family of Pt-H complexes in Si, and have made the Pt-H complexes a model system for understanding the interaction of hydrogen with transition-metal impurities in Si. A promising method to introduce H into Si solar cells to passivate bulk defects is by post-deposition annealing of an H-rich, SiN _x surface layer. Unfortunately, it has been difficult to detect directly the H introduced by this method because of its small concentration. A novel method that combines IR spectroscopy with marker impurities that can trap H in the Si was developed, based on our fundamental studies of the Pt-H complexes in Si, to determine the concentration and depth of H introduced by processes commonly used to hydrogenate Si solar cells.				
14. SUBJECT TERMS: PV; hydrogenation process; crystalline-Si; vibrational spectroscopy; solar cell; multiple-internal-reflection; minority carrier; deep-level transient spectroscopy (DLTS); transition-metal-hydrogen; Pt-H complexes		15. NUMBER OF PAGES		
		16. PRICE CODE		
17. SECURITY CLASSIFICATION OF REPORT Unclassified	18. SECURITY CLASSIFICATION OF THIS PAGE Unclassified	19. SECURITY CLASSIFICATION OF ABSTRACT Unclassified	20. LIMITATION OF ABSTRACT UL	