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

Final Report
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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 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 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 passivated 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.](image-url)
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
Si, vibrational lines due to HD and D₂ 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 H₂ 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>20K 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 H₂ and D₂ must also be freely rotating and that their IR transitions are seen only when the molecules are in the J=1 rotational state (T₂ in tetrahedral symmetry). Thus only ortho-H₂ and para-D₂ 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 H₂ and D₂, which were taken previously as evidence for a static defect, are fit well by a T₂ to T₂ 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 H₂ in Si. Furthermore, the vibrational properties of an O-H₂ center in Si that has been studied recently [25] can be explained as those of a rotating interstitial H₂ molecule perturbed by the field of a nearby O atom [26]. The separate ortho and para O-H₂ complexes each gives an oxygen vibrational line and H₂ 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 (1250ºC) 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
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 PtH\(_2\) defects were then determined from their vibrational spectra. From these data, the approximate level positions of the PtH and PtH\(_2\) defects were determined by the comparison of the PtH and PtH\(_2\) 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 PtH\(_2\) 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
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 PtH$_2$ 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 $\sim 10^{15}$ cm$^{-3}$ for layer thicknesses of only $\sim 3$ µm. (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 PtH$_2$ 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
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 PtH$_2$ complexes are shown in Fig. 6.

**IV. Conclusions**

Our studies of interstitial H$_2$ in Si have established that H$_2$ acts as a nearly free rotator in Si, and have solved vexing puzzles about the experimental properties of H$_2$ 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

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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 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 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.

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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