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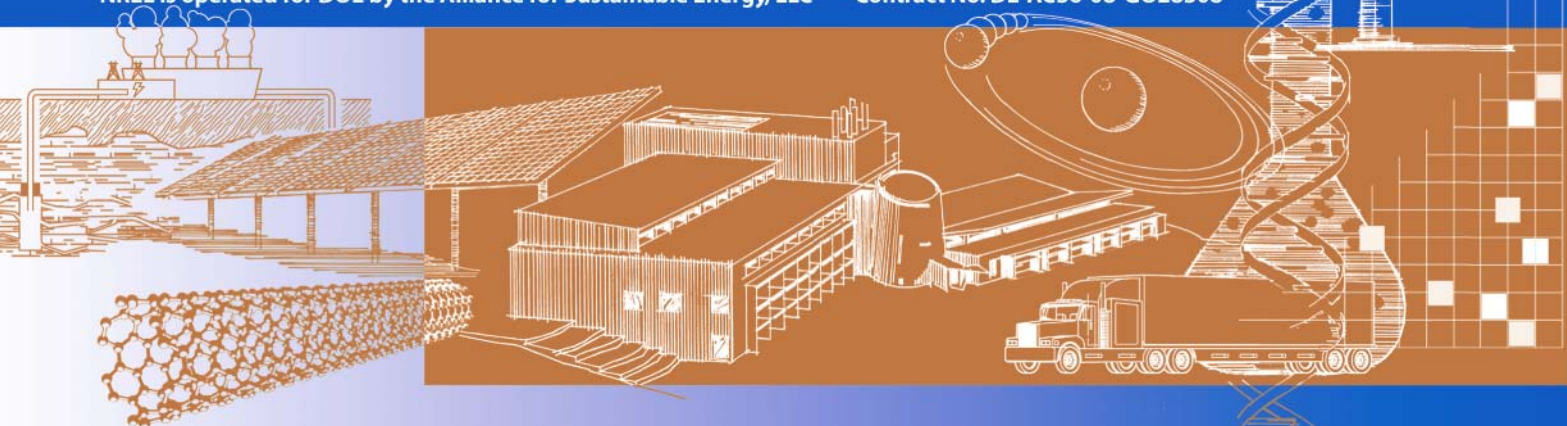# Hydrogenation Methods and Passivation Mechanisms for c-Si Photovoltaics

Final Technical Report
2 January 2002 – 15 January 2008

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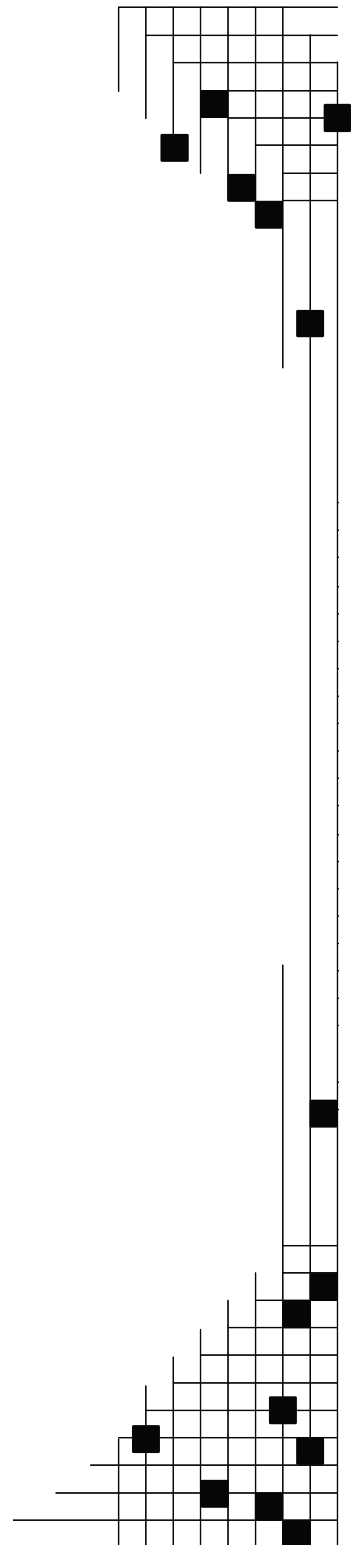*Lubbock, Texas*

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Abstract

The identification, characterization, and passivation of lifetime-reducing defects in solar-grade Si are critical to the optimization of PV devices. We have used first-principles theory in conjunction with experiment to study key defects and their interactions with H. Theory has been used to identify {B,O}, {C,O}, and Fe-related complexes responsible for lifetime reductions in Si solar cells. Experiment has determined the concentration and penetration depth of H introduced by methods used to passivate bulk defects, and different processing strategies have been compared.

I. Introduction

The principal investigators on this project have been funded by NREL to perform experimental and theoretical studies of defect processes important in Si PV materials under a grant titled "Hydrogenation Methods and Passivation Mechanisms for c-Si Photovoltaics."

The identification, characterization, and passivation of lifetime-reducing defects in solar-grade Si are, critical to the optimization of PV devices. While much progress has been achieved using "trial-and-error" optimizations, it is best to understand quantitatively which interactions are actually taking place. First-principles theory and experimental vibrational spectroscopy are powerful tools for the study of key defects and their interactions with hydrogen and other passivating agents.

During this project, *experimental work* has focused on the study of processes used by industry for the hydrogen passivation of defects in the Si bulk and on the defect reactions that occur when solar cells made from mc-Si containing high concentrations of carbon are processed. Si test samples have been subjected to industrial processes, and spectroscopic methods have been used to identify impurities, determine their concentrations and motion, and to monitor defect reactions so that manufacturing processes involving defects and impurities can be better understood and engineered. Experiment has provided quantitative data on the concentration and penetration depth of hydrogen introduced by methods used to passivate bulk defects.

Complementary *theoretical work* has involved predicting defect structures, energetics, electrical activity, vibrational spectra, and interaction with H. Special emphasis was placed on predicting the properties of electrically active defects, ranging from C-O and B-O complexes to transition metal impurities, in particular Fe-related defects responsible for lifetime reductions in Si solar cells. The objective of this joint experimental and theoretical research program was the improvement of processes used to eliminate or passivate lifetime-reducing defects in the Si bulk.

II. Technical Approach

A. Experiment

Hydrogen is commonly introduced into mc-Si solar cells to passivate defects in the Si bulk and improve solar-cell performance.[1-7] A low-cost method to introduce H that is widely used is by the post-deposition annealing of a hydrogen-rich SiN_x layer that is deposited onto the solar cell for use as an antireflection coating. In research supported by NREL, we have made a quantitative determination of the concentration of H that is introduced into a Si model system by the post-deposition annealing of a SiN_x antireflection coating. Infrared (IR) absorption studies were performed by the group of M. Stavola at Lehigh University. The preparation of test samples and plasma-enhanced chemical vapor deposition (PECVD) SiN_x coatings were performed by the research group led by Professor A. Rohatgi at the Georgia Institute of Technology Center of Excellence for Photovoltaics Research. Additional collaborators include J. Kalejs (American Solar Technologies) and G. Hahn (University of Konstanz).

The effect that the post-deposition annealing of a SiN_x layer has on solar-cell performance has been widely studied in order to improve this hydrogenation method.[8-30] A difficulty that has been encountered in such studies is that the concentration of H introduced into the Si bulk under ordinary circumstances is too small to detect and quantify by methods such as secondary ion mass spectrometry (SIMS), even when D is used to improve the detection limit $(\approx 10^{15}$ cm$^{-3})$.[31,32] Therefore, the concentration and penetration depth of H were unknown, and it had remained controversial whether H was even introduced in sufficient concentration to passivate bulk defects.

B. Theory

When applied together, experimental methods for defect identification and first-principles theory provide deep insights into the microscopic mechanisms for defect processes that occur during solar-cell fabrication. In the past few years, first-principles theory has evolved to the point that many predictions are quantitative.

Today's predictions go beyond defect structures, spin states, and energetics to complete vibrational spectra, electrical activity (gap levels), and even the temperature dependence of binding energies. The knowledge of the free energy would allow the calculation of the stability of defects at the operating temperature of the device. The calculated normal-mode frequencies of defects can be directly compared to the measured IR spectra, greatly facilitating defect identification.

Theory also allows the study of impurity and defect interactions in a systematic manner, thus providing critical insight into the behavior of specific impurities in realistic environments, such as Si material containing native defects and a range of impurities and dopants. In particular, precious little is known about the interactions of transition metal impurities (such as Ti, Fe, or Ni) with native defects (vacancies, self-interstitials) and common impurities (H, C, N, O, other transition metals). Some of these interactions are weak, whereas others result in the formation of complexes that are strong recombination centers.

The basic ingredients of first-principles theory[33] are (a) **supercells** (typically ~100 atoms) to represent the host crystal. Periodic boundary conditions are applied to eliminate surface effects, and (b) ab-initio type **pseudopotentials** to remove the core regions from the calculations. The valence **electronic states** are treated self-consistently within density-functional theory.

These tools provide the energy of the system as a function of nuclear coordinates. The Hellmann-Feynman theorem is then used to optimize the geometry of the system without symmetry assumptions. This provides the structure of a defect in its stable and metastable configurations, in various charge and/or spin states, as well as the associated charge and spin-density distributions. Depending on the type of basis set used to expand the electronic states, chemical-type population analyses can also be performed.

Much more information can be obtained from the **dynamical matrix**[34-35] of the system in an equilibrium state. The eigenvalues of this matrix are all the normal mode frequencies of the system. The IR-active local-mode frequencies can be directly compared to the measured ones. This is crucial to the precise identification of defects such as H trapped in the crystal. The typical accuracy for high-frequency modes is about 10-20 cm^{-1}. The normal-mode frequencies can also be used to calculate vibrational free energies and entropies.[36] The eigenvectors of the dynamical matrix are needed to prepare the supercell in thermal equilibrium[37] at a temperature T, which allows meaningful molecular dynamics simulations and study defect reactions and/or diffusion one to perform.

The **electrical activity** of a defect is determined by the existence and location of donor and/or acceptor levels in the gap. Our approach involves scaling the calculated ionization energies and electron affinities to those of a known defect, the "marker."[38] We normally use the perfect crystal itself as a marker, thus removing the "semiempirical" nature of the method (that is, the selection of a "good" marker). In recent work[39] dealing with interstitial Fe and Fe-acceptor pairs in Si, the gap level predictions were often better than 0.1 eV.

These calculations are computer intensive, but the results provide a quantitative link between a specific defect and its electrical, optical, and magnetic signatures. Further, theory predicts the properties of many defects that cannot be observed for a variety of reasons such as too low concentrations, no IR or electrical activity, or the presence of metastable states, which are always difficult to detect. Finally, theory can test if and how passivating species such as hydrogen interact with electrically active defects, or if there is any other means to passivate defects.

III. Results

A. Experiment

1. Method to detect small concentration of H in Si by methods used to fabricate solar cells

To help address questions for which quantitative information about the H concentration would be insightful, we developed a Si model system in which hydrogenated impurities in the Si bulk can be detected by IR spectroscopy with a sensitivity sufficient to determine the concentration of H introduced by the post-deposition annealing of a SiN_x coating.[40,41] For our experiments, Pt impurities, to be used as traps for H, were diffused uniformly[42] into Si samples grown by the floating-zone method. Although Pt is not an impurity that is typically found in solar cells, its properties as a trap for H make it an ideal model trap for our experiments. When Pt in p-type Si traps hydrogen, it forms a neutral PtH^0 complex with an IR line at 1880 cm^{-1} [Fig. 1(a)], whose intensity has been calibrated so that the concentration of hydrogen can be determined.[43,44] The PtH^0 complex is dissociated by annealing at 650 °C so that at temperatures near 750 to 800 °C where H is typically introduced from SiN_x layers, H diffuses rapidly.[34] When a sample cools, the H it contains becomes stably trapped to form PtH^0 complexes that are readily detected by IR spectroscopy. To increase the sensitivity of IR measurements, a multiple-internal-reflection geometry was used (inset, Fig. 1) and spectra were measured at 4.2 K.

2. Concentration and penetration depth of H in Si

Several strategies used recently for introducing H into Si solar cells were examined to provide quantitative information about how effectively impurities are hydrogenated in the Si bulk. We have obtained the following results for the concentration and penetration depth of H in Si:

(a) It was found that H could be introduced into the Si bulk with a concentration up to $\sim 10^{15}$ cm[-3], and that the concentration of H that is introduced is sensitive to processing methods, for example, the SiN_x deposition conditions and annealing procedure.[41] A hydrogen concentration of $[H] \leq 10^{15}$ cm[-3] is an interesting range. This concentration is sufficiently low to be less than the detection limit for SIMS measurements, but sufficiently high to passivate the typical concentrations of traps found in solar cells fabricated from mc-Si.
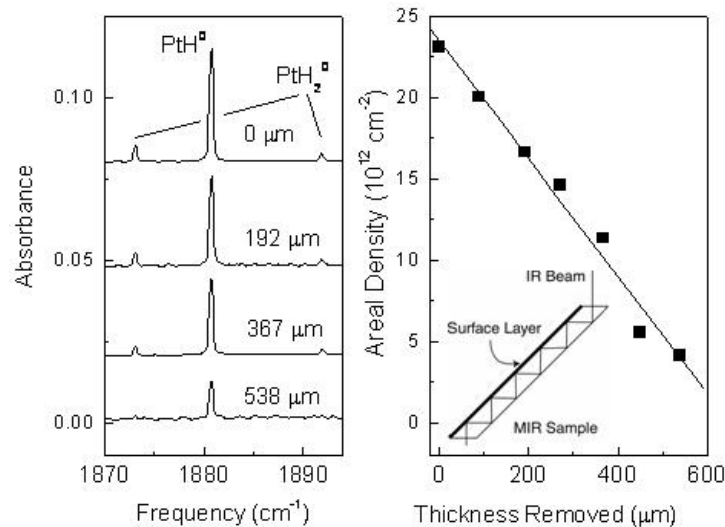
Fig. 1: (a) IR spectra (4.2K) show the vibrational lines of the PtH complex in a hydrogenated Si:Pt sample. To probe the H penetration depth, spectra were measured after layers of the indicated thicknesses had been removed. (b) The areal density of PtH complexes vs. the thickness of the removed layer, derived from the data in (a). The inset shows the multiple internal reflection geometry used for IR measurements to increase sensitivity.

(b) The direct detection of H in our experiments permitted us to determine the penetration depth of H.[40,41] For these experiments, Si samples were mechanically thinned, and the disappearance of the PtH IR line was monitored to determine how far H had diffused into the sample [~600 μm in Fig. 1(b)]. Hydrogenation by the post-deposition annealing of a SiN_x AR coating leads to a H penetration depth that is consistent with the rapid indiffusion of isolated H estimated from the diffusivity determined by Van Wieringen and Warmoltz,[45] rather that a slower, trap-limited diffusion process.

3. IR characterization of SiN_x: role of SiN_x density and the Si/SiN_x interface

SiN_x films deposited with different PECVD reactors and at different deposition temperatures have been found to introduce concentrations of H that vary by more than a factor of 10. The correlation between the SiN_x film density and the effectiveness of the passivation of defects in the Si bulk has been investigated recently.[18,25-29] Denser films have been reported to be more thermally stable and more effective for bulk passivation (as measured, for example, by the internal quantum efficiency of solar cells at long wavelength). While the SiN_x film density can be measured directly, a convenient strategy has been developed by researchers at the Energy Research Center of the Netherlands (ECN) in which IR spectroscopy is used to characterize the SiN_x film properties.[18,25,26] The integrated intensity of a broad Si-N IR absorption band at near 820 cm^{-1} (Fig. 2) was found to be proportional to the SiN_x film density, and an optimum film density has been identified. The positions and intensities of Si-H and N-H IR absorption lines that have been used to characterize the hydrogen content of SiN_x films was also found to be correlated with the intensity of the Si-N IR line and the SiN_x density.

While great progress has been made, several issues remained controversial because it is difficult to provide definitive answers to questions about the SiN_x hydrogenation process when the H that is introduced into the Si bulk cannot be directly detected. For example, some groups believe that the density of the SiN_x film is of primary importance for hydrogenation effectiveness, with more dense films leading to better bulk passivation, while other groups have reported that the SiN_x/Si interface and the hydrogen that can be trapped there are of primary importance.[30]
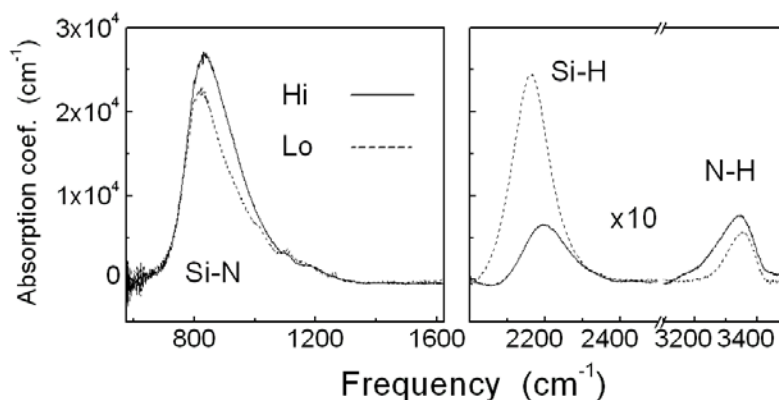
Fig. 2: IR spectra (room temperature) for SiN_x layers approximately 75 nm thick deposited on Si substrates. The Si-N, Si-H, and N-H stretching bands are shown. Spectra drawn with solid lines are for high-density SiN_x films, and spectra drawn with dashed lines are for low-density SiN_x films.

With the hydrogen-detection methods developed at Lehigh, we have been able to make a quantitative comparison of the concentrations of H that are introduced into our Si model system by the post-deposition annealing of high-density and low-density SiN_x films that have been well characterized by IR spectroscopy (Fig. 2).[46] Furthermore, we have performed experiments in which the processing of

the SiN_x/Si interface was varied to compare how properties of the interface and properties of the SiN_x film itself affect the concentration of H that introduced into the Si bulk. For example, for several of our samples, the Si surface was treated with an NH_3 plasma process prior to SiN_x deposition.

The results of our experiments show that the optimization of the quantity of hydrogen that is introduced to passivate defects in the Si bulk requires that neither the properties of the SiN_x film nor the Si/SiN_x interface can be neglected.[46] High-density SiN_x films deposited after a NH_3 pretreatment were found to be most effective for the introduction of hydrogen, introducing 20x more hydrogen than low-density films. If the Si surface did not receive an NH_3 pretreatment prior to SiN_x deposition, the quantity of H that was introduced into the Si bulk was found to be reduced by a factor of 3, even though IR measurements of the Si-N, Si-H, and N-H IR bands of the SiN_x film showed no obvious change in the properties of the SiN_x. Our results also indicated that while pretreatment of the Si surface has a significant effect on the concentration of H that is introduced, H trapped at the Si/SiN_x interface[30] was not the primary source of H introduced into the Si bulk; in our experiments, a high-density SiN_x coating was found to be necessary to optimize the quantity of H that is introduced into the Si bulk during a post-deposition anneal.

Our capability to detect and quantify the very small concentrations of H that are introduced into a Si model system by processes used to manufacture solar cells has led to following achievements:

a. Direct quantitative proof that a sufficient concentration of H to passivate bulk defects in Si solar cells is introduced into the Si bulk by the post-deposition annealing of a SiN_x coating.

b. Comparison of the concentration of H that is introduced as processing parameters are varied, showing that the concentration of H can vary by more than a factor of 10.

c. Determination of the penetration depth of H for processes used to hydrogenate solar cells by industry, showing that H can penetrate several hundred microns into Si.

d. Characterization of SiN_x film density by IR spectroscopy with complementary measurements of the quantity of H introduced into the Si bulk by the post-deposition annealing of these films.

e. Comparison of the relative importance of SiN_x film density vs. properties of the Si/SiN_x interface.

B. Theory

In the past few years, we have studied a wide range of problems related to impurities and defects common in solar cells, hydrogenation and passivation, and the development of advanced theoretical tools for the study of such defects and processes. These issues included the properties of N and N-H interactions,[47] copper and its complexes,[48] substantial advances in the calculations of the vibrational dynamics of defects,[36,39] and their properties at elevated temperatures.[38] More recently, we have identified the B-O complexes responsible for the lifetime reductions in Si solar cells.[49,50] Theory at T=0K predicts that four complexes can form. In terrestrial cells, the mobile $\{O_i,O_i\}^{++}$ pair traps at B_s^- and forms two metastable recombination centers $\{B_s,O_i,O_i\}^+$. In irradiated (space-based) cells, the mobile B_i^+ traps at O_i^0 and forms the recombination center $\{B_i,O_i\}^+$.

Ongoing research involves systematic studies of Fe in Si. This transition-metal impurity is always present in Si PV material and little is understood about its behavior. Indeed, only two centers are well known experimentally: the isolated interstitial (Fe_i) and the Fe-acceptor pair (in mc-Si, this is the $\{Fe_iB\}$ pair). We have recently performed the first total-energy calculations involving Fe-related defects in Si.[46] This work deals with Fe_i, Fe_i-hydrogen interactions, Fe-acceptor, and Fe-donor pairs. In order to understand trends, we considered all the possible acceptors (B, Al, Ga, In, and Tl) and donors (P and As). Our results are very close to the experimental data. In particular, the activation energy for diffusion (0.69eV for Fe_i^+ and 0.76eV for Fe_i^0) match the measured values, as do the calculated donor level and the absence of acceptor level of Fe_i, the binding energies of Fe-acceptor pairs, and other important features.

1. Boron-oxygen complexes

We have calculated from first principles the configurations, thermodynamic gap levels, and binding energies of **acceptor-oxygen complexes** in Si. In terrestrial (non-irradiated) cells, the defect responsible for the reduction in lifetimes is the $\{B_sO_iO_i\}$ complex, which results from the interactions between B_s^- and $\{O_iO_i\}^{++}$. Very similar structures are realized when Ga is substituted for B, but with smaller binding energies (~0.1eV). These Ga-related complexes are unstable above 200K or so.

In space-based (irradiated) cells, two configurations of the $\{B_iO_i\}$ complex (labeled a and b) with similar binding energies could coexist and be the defect(s) responsible for the lifetime degradation. If the vibrational zero-point energy is ignored, $\{B_iO_i\}_a$ is slightly more stable in the neutral and positive charge states than $\{B_iO_i\}_b$. However, if this contribution is included, the energy difference between the two structures becomes smaller, and $\{B_iO_i\}_b$ is slightly more stable than $\{B_iO_i\}_a$ in the positive charge state.

The nudged elastic band method was employed to calculate the transformation barrier between the two structures, yielding an activation energy of ~0.6eV for the 0 and + charge states.

The calculated electric levels of the two structures are close to the range of experimental values reported by various groups. Nevertheless, the presence of two variants of the defect could be verified by vibrational spectroscopy, because the LVMs arising from both structures are distinct.

We have also calculated the **binding free energies** ΔE_b of four acceptor-oxygen complexes in Si, all of which have similar binding energies at T=0K. The free energies were obtained from the (Helmholtz) vibrational free energies. The configurational entropies were calculated analytically with assumed impurity concentrations. The conclusions hold for any $\{A,B\}$ defect complex that dissociates into the products A and B, in any crystal. The key points are the following.

  a) The binding free energy of $\{A,B\}$ varies linearly with temperature, with a slope largely dominated by the difference in configurational entropy between $\{A,B\}$ and A away from B.
  b) There is a temperature T_0 where $\Delta E_b(T_0)=0$. This temperature depends on the concentrations [A] and [B] and the binding energy at 0K. For $T>T_0$, the interaction between A and B becomes repulsive.
  c) The difference in configurational entropy depends on the concentrations [A] and [B] in the sample. Therefore, the binding free energy of a specific complex $\{A,B\}$ at a specific temperature will be different in samples containing different concentrations of A or B. In an Arrhenius plot, this will appear to be a change in the dissociation rate, but is really caused by a difference in the configurational entropy ΔS_{config}.
  d) For a given $\{A,B\}$ complex, the smaller the concentration of A and B, the larger the configurational entropy associated with the dissociated species and the smaller the entropy associated with complex formation. Then, the slope of $\Delta E_b(T)$ is much steeper. The opposite holds if A and/or B exist in high concentrations. In the example discussed in this paper, changing one component of the complex from B_s to B_i changes the relevant concentration from 10^{19} to $10^{14} cm^{-3}$, which roughly triples ΔS_{config}.
  e) An Arrhenius plot of the dissociation reaction produces a straight line, the slope and intercept of which are very close to $-\Delta E_b(0)/k_B$ (not exactly because $\Delta E_b(T)$ is not linear at very low T) and $lnR+ \Delta S_{config} /k_B$ (not exactly because of a small contribution of ΔF_{vib}), respectively. Thus, a carefully controlled series of experiments could provide direct measurements of configurational entropy differences.

2. Fe-related defects

The strongest interactions involve interstitial iron (Fe_i) and vacancy-like defects. In the four cases investigated (vacancy, iron-boron pair, divacancy, and A-center), the most stable complex has Fe inside the void, covalently bound to the host crystal, with a gain in energy of 2.0eV (Fe_sO_i}), 2.7eV ($\{Fe_sB_s\}$),

2.9eV (Fe_s), and 3.0eV ({VFeV}) relative to isolated Fe_i and {OV}, V and {Fe_iB_s}, V and Fe_i, V_2 and Fe_i, respectively.

In the case of Fe_i interacting with V or V_2, a metastable defect is generated, {Fe_iV} or {Fe_iV_2}, respectively. It involves Fe_i trapped off the T-site, along the trigonal axis, but outside V or V_2. The binding energy relative to isolated Fe_i is on the order of 2eV, and the barrier that Fe_i must overcome to reach the stable configuration (Fe_s and {VFeV}, respectively) is on the order of 0.6 and 1.2eV, respectively. The precise values of these energies depend on the charge and spin state.

Upon formation of {Fe_sB_s}, {Fe_sO_i}, Fe_s, and {VFeV}, the donor level associated with interstitial iron (E_v+0.4eV) disappears, and an acceptor level appears at E_c-0.84eV, E_c-0.36eV, E_c-0.41eV, and E_c-0.73eV, respectively. The passivation by vacancies of the donor levels of both Fe_i and {Fe_iB_s} has consequences. For example, an injection of vacancies occurs during the high-temperature anneal that follows the deposition of an SiN_x anti-reflection coating on Si solar cells. This treatment generally improves the efficiency of cells, as H diffuses from the surface layer into the bulk, which results in the passivation of some defect centers. Our results show that vacancy injection could also play a role in this process by passivating the deep-donor activity of Fe_i and {Fe_iB_s}.

All the complexes that contain interstitial iron, namely {Fe_iV}, {Fe_iV_2}, {Fe_iSi_i}, and {Fe_iC_i}, have a donor level in the gap at E_v+0.35eV, E_v+0.25eV, E_v+0.42eV, and E_v+0.67eV, respectively. These levels are close to that of isolated Fe_i (calculated E_v+0.37eV, measured E_v+0.39 to 0.45eV).

The complexes that involve Fe_i and either C_i or a vacancy, namely {Fe_iC_i}, {Fe_iV}, and {Fe_iV_2}, also have a deep acceptor level in the gap, E_c-0.44eV, E_c-0.71eV, and E_c-0.75eV, respectively. In the case of {VFeV}, a double acceptor level at E_c-0.55eV is present. Figure 3 shows the calculated gap levels associated with all the defects considered here, compared to isolated Fe_i and the {Fe_iB_s} pair.
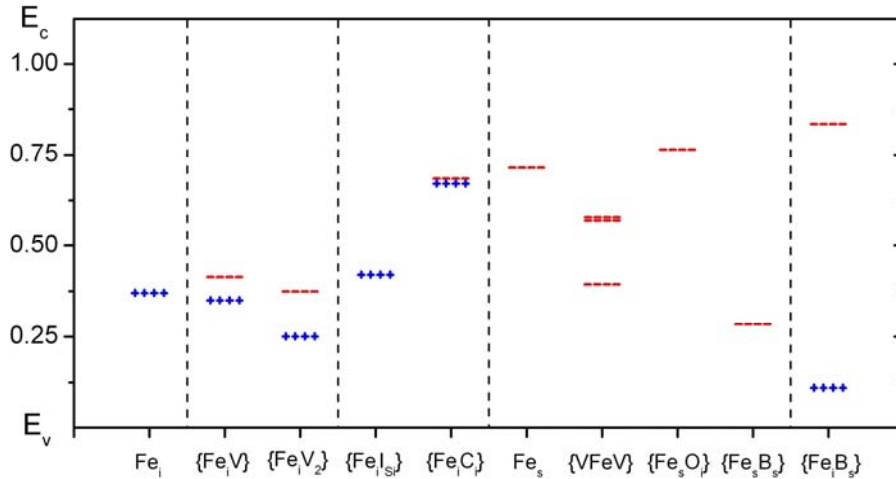

Fig. 3: Calculated donor (+ signs, blue) and acceptor (minus signs, red) levels associated with various Fe-related defects. The double acceptor level of {VFeV} is marked with = signs. The calculated gap levels of Fe_i and {F_iB_s} match the experimental value and the calculated donor level of Fe_s is close to the P11 trap reported by Kaminski et al.

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V. Publications That Acknowledge Suuport from This Contract

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The identification, characterization, and passivation of lifetime-reducing defects in solar-grade Si are critical to the optimization of Photovoltaic devices. We have used first-principles theory, in conjunction with experiment, to study key defects and their interactions with H. Theory has been used to identify {B,O}, {C,O}, and Fe-related complexes responsible for lifetime reductions in Si solar cells. Experiment has determined the concentration and penetration depth of H introduced by methods used to passivate bulk defects, and different processing strategies have been compared.

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