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Defect-induced dissociation of H_2 in silicon

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Ab initio molecular-dynamics simulations of intrinsic defects and hydrogen in crystalline silicon reveal an unexpected process with considerable implications. The vacancy (V) and the self-interstitial (I), both rapid diffusers in c-Si, dissociate interstitial H_2 molecules with a substantial gain in energy: $V+H_2 \rightarrow \{V,H,H\} + 4.0$ eV and $I+H_2 \rightarrow \{I,H,H\} + 1.7$ eV. The dissociation of H_2 is caused by the lattice strain associated with the defect, and occurs whenever H_2 molecules are in the vicinity of strained Si-Si bonds. After the dissociation, the two H's may either bind to the defect that caused the strain or diffuse away from it. The calculated Frenkel pair formation energy is 8.2 eV. The reaction $H_2+H_2 \rightarrow \{V,H_4\}+I$ releases less than 0.1 eV, suggesting that H_2's in otherwise perfect Si will not generate intrinsic defects. [S0163-1829(98)51918-2]

The properties of hydrogen in c-Si have been studied for over 20 years[1,2] because H affects the electrical and optical properties of the material. H removes much of the electrical activity associated with extended defects (dislocations or grain boundaries) and point defects (such as vacancies, dopants, and other impurities). H activates substitutional carbon, and shifts the gap level(s) associated with some transition metals.[3] It also enhances the diffusivity of interstitial oxygen.[4,5] H interacts with the host crystal, leading to the formation of localized defects (bond-centered hydrogen, hydrogen dimers) as well as extended defects such as platelets. Proton implantation may also result in layer-splitting.[6] Many properties of a sample depend on how much H it contains, how it was introduced, and on the history of the sample (heat treatments, implantation, etching, etc.). In this present paper, we focus on interstitial molecular hydrogen (H_2) and two rapidly diffusing intrinsic defects: the vacancy (V) and the self-interstitial (I).

The stability of interstitial H_2 in Si was predicted by two groups independently.[7,8] The molecule is at the tetrahedral interstitial (T) site, oriented along a $\langle 100 \rangle$ direction. Its activation energy for rotation is small (less than 0.1 eV). Its activation energy for diffusion has been predicted[1,2] to be of the order of 0.8 to 1.0 eV. The other dimer, H_2^*, was predicted a few years later, also by two groups independently.[9,10] In this defect, the two H's are not bound to each other. Instead, one Si—Si bond is replaced by two Si—H bonds, with the four atoms on the same trigonal axis. The first H atom is near a bond-centered position bound to an $\sim sp^3$ hybridized Si atom. The second H atom is antibonding to the other Si atom, which is $\sim sp^2$ hybridized. Theoretical predictions for the relative stability of H_2 and H_2^* depend on the method and the author. The calculated energy differences[11–13] vary from 0.5 eV in favor of H_2^* to 0.5 eV in favor of H_2. Our calculations favor H_2^*, as will be discussed elsewhere.[14]

Experimental evidence for H_2^* was first obtained by infrared absorption spectroscopy (FTIR) in proton-implanted samples.[15] H_2 has been more difficult to detect. The first report[16] was a nuclear magnetic resonance (NMR) study of deuterium associated with platelets. The signal was very similar to the signal from isolated D_2 seen by NMR in deuterated amorphous Si. A Raman study[17] identified H_2 in c-Si. The signal was first proposed to be due to isolated interstitial molecules, but was later proved[18] to correspond to nearly-free H_2 associated with platelets.

Raman studies have revealed[19] that some interstitial H_2 is also found in these samples. At room temperature, the H–H stretching frequency is 3601 cm^{-1}, substantially lower than that of free H_2 (4160 cm^{-1}). This implies that the H–H bond is much weaker in Si than in free space. The intensity of the interstitial H_2 signal is reduced upon illumination, while the amplitude of the platelet-related H_2 signal increases. Photoluminescence (PL) studies[20] have also identified isolated H_2 and H_2^* in high-purity Si. Both species have an acceptor level ($-/0$) in the gap near the conduction band minimum. H_2 molecules in Si have also been detected[21] by FTIR in the vicinity of interstitial oxygen (O_i). There is evidence[22,23] that H is attracted to O_i, and it is not known how many H's are around each oxygen interstitial under the conditions of the experiment, and how O_i affects the Si—H interactions.

Hydrogen strongly interacts with V's. The four possible $\{V,H_n\}$ complexes ($n=1,\ldots,4$) have been calculated[24,25] and observed[25] in proton-implanted samples. The same experiments also show a complex identified as $\{I,H,H\}$. The complexes denoted by curly brackets are described in detail in the papers cited.

The present work deals with the interactions between interstitial H_2 and V and/or I in c-Si. The results are obtained with the *ab initio* tight-binding molecular-dynamics (MD) method of Sankey and co-workers.[26] The host crystal is represented by periodic supercells containing 64 Si atoms (63 with V, 65 with I). A time step of 0.2 fs is used with H in the cell, and 2.0 fs without H. Many calculations are done with the Harris energy functional, but the key results were verified self-consistently.[27,28] Both techniques predict very similar results (the energies given below are the self-consistent ones). Note that our study deals only with the interactions between V or I and molecular H_2, but these are not the only possibilities. V's and I's interact with each other (recombination, formation of V_n or I_n aggregates) and with impurities (impurity-V or impurity-I pairs). These situations are not considered here. Our key results are as follows.

(a) Isolated interstitial H_2 is stable in c-Si. In agreement with other authors,[11–13] we find that the potential energy minimum corresponds to a $\langle 100 \rangle$ orientation, with the center of mass of the molecule at the T site. MD runs at room temperature show H_2 vibrating and rotating about its center of mass.

(b) H_2 spontaneously dissociates when placed inside a vacancy or even inside the much larger ring hexavacancy.[29] It cannot remain in molecular form inside such a defect. The configuration is not a local minimum of the potential energy. The only minima have two Si—H bonds.

(c) The potential energy difference between V infinitely far from H_2 and $\{V,\mathrm{H},\mathrm{H}\}$ is 4.0 eV. The potential energy difference between I infinitely far from H_2 and $\{I,\mathrm{H},\mathrm{H}\}$ is 1.7 eV. The gains in energy come from the formation of Si—H bonds and the reduction of the strain associated with the original defect. We found two configurations for $\{I,\mathrm{H},\mathrm{H}\}$. The stable one is that observed by Bech Nielsen *et al.*[15] The metastable one is 0.4 eV higher and has I at a puckered bond-centered site with both H bound to it.

(d) When V (or I) and H_2 are at a large separation d, the only possible state is H_2 plus V (or I). As d becomes smaller, deeper minima of the potential surface become accessible. They correspond to configurations with two Si—H bonds near or at V (or I). When d is very small, the energy barrier separating the molecular from the dissociated states disappears and H_2 melts. When H_2 is third- or fourth-nearest neighbor to V (or I), MD simulations at room temperature (several thousand time steps) show that H_2 first vibrates and rotates, as V (or I) reorients and changes shape. Then, the molecule dissociates. Several configurations roughly equivalent in energy can be realized, but they all have two Si—H bonds in a locally distorted surrounding.

(e) The V and I formation energies are 4.0 and 4.2 eV, respectively, giving a Frenkel pair formation energy of 8.2 eV.

(f) The reaction $H_2+H_2 \rightarrow \{V,H_4\}+I$ releases only 0.06 eV. This implies that two H_2's in an otherwise perfect Si host are unlikely to generate intrinsic defects. The reaction involving H_2 and V or I are much more energetic.

Our calculations imply that interstitial H_2 is stable only when it is surrounded by perfect or near-perfect Si—Si bonds. If H_2 is near stretched, distorted, or otherwise weak Si—Si bonds, it dissociates with a substantial gain in energy. The result is the formation of two Si—H bonds and a reduction of the strain associated with the defect. The further H_2 is from strained Si—Si bonds, the longer it remains in molecular form. Some consequences of our results are as follows.

I. Whenever rapidly-diffusing intrinsic defects such as V or I encounter interstitial H_2, they dissociate the molecule. This is accompanied by a large release of energy. If the final result is the complex $\{V,\mathrm{H},\mathrm{H}\}$ complex, the gain is 4.0 eV. If it is $\{I,\mathrm{H},\mathrm{H}\}$, the gain is 1.7 eV. Both of these complexes have been observed.[25] However, there are also metastable minima of the energy with two interstitial H's bound to the crystal very near V or I. Then, the gain in energy is less.

MD simulations at higher temperatures (typically above 500 K) show that the result of the $V+H_2$ (and to a lesser extent $I+H_2$) interaction can also be the release of one or two H interstitials. The energy released by the dissociation of H_2 becomes kinetic energy for H, and at higher temperatures, it is sufficient for H to escape from the defect. Since most methods of hydrogenation inject V's or I's into the crystal, this could explain why H_2 in c-Si has been detected only with great difficulty and when very high concentrations of H are present.[19,20]

II. Hydrogenation from a gas source at a few hundred degrees Celsius is very inefficient, *except* in the presence of surface damage.[30] Secondary-ion mass spectrometry studies show that while no hydrogenation occurs from the exposure of a perfect surface to an H_2 gas (1 h, 400 °C), delicately rubbing the Si surface with a cotton swab and a 0.3 micron grit results in substantial H penetration (6–8 μm) under the same conditions.[31] Since damaging the surface strains Si—Si bonds, H_2 can readily dissociate and bind to the surface. The result is a reservoir of H at the surface, from where it can diffuse into the bulk. Cho[32] and co-workers found the adsorption energy barrier for H_2 on a perfect Si surface to be 0.8 eV. Our calculations show that H_2 dissociates with no barrier if strained Si—Si bonds are present.

III. A number of gettering procedures lead to the injection of V's (such as Al gettering) or I's (such as P gettering) into the bulk. If some H_2 is already present in the bulk, the injection of V's or I's will transform H_2 into 2 H's which can passivate various centers. In this case, it becomes impossible to separate gettering from passivation.

IV. The diffusivity of H is often measured by monitoring the passivation of B acceptors as a function of depth. Some authors have reported very high values for the diffusivity of H, while others find much smaller numbers under apparently similar conditions.[1] Our results suggest the following explanation. If the hydrogenation itself injects vacancies (plasma exposure, for example) and if the sample contains H_2's, the rapidly diffusing V's will dissociate them, releasing a species that can passivate acceptors. This makes it appear that H has diffused very fast, while in fact vacancies diffused and freed H from a molecular state already present in the bulk. On the other hand, in a sample which contains little H_2, the same treatment produces passivation only near the surface. The activation energy for diffusion[33] of the neutral vacancy, 0.45 ± 0.04 eV, is remarkably close to that of hydrogen, 0.48 eV. However, both V^{++} and V^{--} have much lower activation energies for diffusion and should interact with H_2 as well. The history of the sample affects the interpretation of the data.

V. The diffusion of vacancy-hydrogen pairs has been proposed[30,34] to explain the unexpectedly efficient passivation of poly-Si solar cells. An alternative explanation is that V's (or I's) diffuse, dissociate H_2 molecules in the bulk, allowing H's to passivate defects in their vicinity.

VI. In proton-implanted samples, the $\{I,\mathrm{H},\mathrm{H}\}$ complex has been detected[25] but not (at least, not yet[35]) the simpler

$\{I,\mathrm{H}\}$ complex. This suggests that I's may often be interacting with *two* hydrogen atoms simultaneously. Our results show that I dissociates H_2 at room temperature. A 5000 time-steps simulation produces a complex $\{I,\mathrm{H},\mathrm{H}\}$ very similar to the one observed.

VII. Si samples grown in a hydrogen ambient contain high concentrations of hydrogen. Such samples have been electron-irradiated at room temperature and studied by FTIR.[36] Before irradiation, only a few, weak, Si—H lines are seen. After irradiation, a very dramatic increase in the number and amplitude of the IR lines is observed. This implies that the hydrogen present in the material changed from an optically invisible state to one where many Si—H bonds are seen. Our results provide a process by which this can occur.

We are not aware of situations comparable to that described here. Rapidly diffusing intrinsic defects break up stable and (mostly) invisible H_2 molecules in the bulk of Si. This releases free H's, which in turn changes the electrical and optical properties of the sample. Such a process is not likely to be important in equilibrium, when the concentration of V's and I's is low.[37] However, it could be critical in nonequilibrium situations when a flux of V's or I's is present: etching (including exposure to a hydrogen plasma), deposition of an Al back contact, an n^+ layer, or an antireflection coating, precipitation of O_i's, ion implantation, rapid thermal anneals, and others.

Finally, the reaction $\mathrm{H}_2+\mathrm{H}_2 \rightarrow \{V,\mathrm{H}_4\}+I$ releases too little energy to be a dominant player in the formation of extended defects. The reactions involving H_2 and V (or I) release 4.0 eV (or 1.7 eV) and are much more likely candidates for such reactions.

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