Radiation-Induced Formation of H_2^* in Silicon

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Two kinds of hydrogen dimers have been observed in c-Si: the interstitial H_2 molecule and the H_2^* complex. Theory predicts that H_2 and H_2^* are within a few tenths of an eV of each other, but the two centers have never been observed to coexist. Instead, the irradiation of samples rich in H_2 induces its conversion into H_2^*. No such conversion has been thermally induced, and H_2^* is seen only in irradiated material. In the present paper, *ab initio* molecular-dynamics simulations demonstrate in real time how these reactions occur. A vacancy (V) or a self-interstitial (I) break up interstitial H_2, resulting in the $\{V, \mathrm{H}, \mathrm{H}\}$ or $\{I, \mathrm{H}, \mathrm{H}\}$ complex. Then V-I recombination forms H_2^*, as in $\{I, \mathrm{H}, \mathrm{H}\} + V \rightarrow H_2^*$. [S0031-9007(98)08287-8]

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Hydrogen is the most versatile impurity in semiconductors [1,2]. It modifies the electrical and optical activity of the material by passivating many electrically active impurities, changing the electrical activity of others, and forming a range of defects visible by infrared (IR) absorption, Raman spectroscopy, and/or photoluminescence. Hydrogen catalyzes the diffusion of interstitial oxygen in Si, and passivates grain boundaries and (at least some) dislocations. Hydrogen forms monatomic centers at the tetrahedral interstitial (T) site and the relaxed bond-centered (BC) site. It also forms two kinds of dimers, interstitial H_2 molecules at the T site and the H_2^* complex which consists of two Si-H bonds on the same trigonal axis, replacing a Si-Si bond: The first H is near a BC site, bound to a nearly sp^3-hybridized host atom, and the second H is in an antibonding (AB) configuration, bound to a nearly sp^2-hybridized host atom.

Interstitial H_2 molecules, predicted by theory some 15 years ago [3,4], have recently been observed. A Raman study by Murakami *et al.* [5] yielded a broad band at 4158 cm^{-1} in plasma-hydrogenated samples. The authors initially attributed this frequency to interstitial H_2 molecules. However, the signal proved [6] to be associated with molecules trapped in voids associated with platelets. Leitch *et al.* [7] found the Raman signature of isolated interstitial H_2 in similarly hydrogenated samples. At room temperature, the line is at 3601 cm^{-1}, some 500 cm^{-1} below that of free molecules. At 10 K, the lines shifts to 3618 cm^{-1}. No ortho/para splitting was detected, in contrast to similar data in GaAs [8].

Molecular hydrogen was also seen by IR spectroscopy at 10 K in 17-mm-thick samples soaked at high temperatures in a H_2 gas. In phosphorus-doped (Czochralski) CZ-Si [9], two bands at 3789 and 3731 cm^{-1} were assigned to H_2 molecules trapped near interstitial O, and a third band at 3618 cm^{-1} to isolated interstitial H_2. This IR line is seen [10] up to at least 350 °C, and is also seen in boron-doped (floating zone) FZ-Si [11]. In these samples, over 90% of the hydrogen incorporated initially is in interstitial H_2 form. This accounts for the large fraction of "hidden hydrogen"—the difference between the easily detected hydrogen in {B, H} pairs and the total amount seen by secondary-ion mass spectrometry [11].

Recent *ab initio* calculations agree that the stretching frequency of interstitial H_2 in Si is substantially reduced from the free-molecule value [12–14]. Some questions remain regarding the orientation of the molecule in the crystal and its barrier for rotation [13,15,16].

The existence of H_2^* was also predicted by theory [17,18] before the complex was detected [19] by IR spectroscopy in proton-implanted samples. The stretch modes are at 2062 cm^{-1} (for the H near the BC site) and 1838 cm^{-1} (for the H near the AB site). Both IR lines anneal out simultaneously at about 200 °C.

Theorists disagree on whether H_2 or H_2^* is the more stable dimer, but they do agree that they are within a few tenths of an eV of each other. Both complexes should therefore coexist in H-rich samples. Further, since H_2 is still observed at 350 °C while H_2^* anneals out at 200 °C, one could expect a thermally induced transition from H_2^* to H_2. However, the two dimers have never been seen together in the same sample and no thermally induced transition from one to the other was ever observed. Instead, H_2^* has only been seen in irradiated material [11]. Furthermore, the irreversible conversion of H_2 to H_2^* by electron irradiation has now been reported [11,20]. Experimental evidence shows that a transition from H_2 to states involving Si-H bonds is induced by radiation damage. [21] Such states include $\{V, \mathrm{H}, \mathrm{H}\}$ (a vacancy decorated with two H's [22]) and $\{I, \mathrm{H}, \mathrm{H}\}$ (two H's trapped at a self-interstitial [23]).

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In the present paper, we show that the radiation-damage-induced conversion from H_2 to H_2^* follows from two successive reactions equivalent to the recombination of a vacancy (V) and a self-interstitial (I) at the H_2 molecule. During the irradiation, both V and I diffuse rapidly through the material even at low temperatures.

We use the *ab initio* tight-binding molecular-dynamics (MD) method developed by Sankey and co-workers. [24,25] The calculations are done in periodic supercells containing 64 host atoms (± 1 with I or V, and excluding the two H atoms). The basis set consists of a set of valence s and p pseudoatomic orbitals on all of the Si atoms, with cutoff radius $5.0 a_B$ (the cutoff radius for H is $3.6 a_B$). The core electrons are removed by the use of *ab initio* pseudopotentials. The time step in the MD simulations ranges from 0.2 fs (when H is present) to 2.0 fs (when no H is present). Our constant-temperature simulations last 4 000 to 8 000 time steps and start with quenched configurations (that is, the initial configuration is a local minimum of the potential energy). All of the energies quoted below are self-consistent ones, but the longer simulations were done using the Harris energy functional. The approach has been tested for various Si-H systems. For example, the Si-H stretching vibrational modes for the four vacancy-H complexes [26] closely match the experimental values [27].

Our MD simulations of H_2-V (and H_2-I) interactions show [28] that V (and I) readily dissociates the molecules which results in the formation of the $\{V, \mathrm{H}, \mathrm{H}\}$ (and $\{I, \mathrm{H}, \mathrm{H}\}$) complexes. Both complexes have been observed [22,23] in proton-implanted samples. The reaction $V + \mathrm{H}_2 \rightarrow \{V, \mathrm{H}, \mathrm{H}\}$ releases 4.0 eV, while $I + \mathrm{H}_2 \rightarrow \{I, \mathrm{H}, \mathrm{H}\}$ releases 1.7 eV. At the same level of theory, the formation energy of the vacancy is 4.0 eV and that of the self-interstitial is 4.2 eV. Thus, 8.2 eV are available from V-I recombination. Since the energy gain from the reaction of either V or I with H_2 is substantially less than 8.2 eV, one would expect [29] that $\{I, \mathrm{H}, \mathrm{H}\}$ could further react with V, and $\{V, \mathrm{H}, \mathrm{H}\}$ with I. Both reactions could lead to the formation of H_2^*.

Total energy differences indeed predict that the two recombination reactions release substantial amounts of energy: $\{I, \mathrm{H}, \mathrm{H}\} + V \rightarrow \mathrm{H}_2^* + 7.12$ eV and $\{V, \mathrm{H}, \mathrm{H}\} + I \rightarrow \mathrm{H}_2^* + 4.84$ eV. By themselves, these numbers do not prove that the reactions occur. However, MD simulations allow the observation of the dynamics of a system in real time. In such calculations, the electronic energy must be computed at every time step, that is every 0.2 fs in our case. *Ab initio* MD simulations are therefore limited to (real) times of the order of the ps, and the calculation must be set up "just right" in order for a given reaction to be observable. We did observe $\{I, \mathrm{H}, \mathrm{H}\} + V \rightarrow \mathrm{H}_2^*$ in a 4 000 time step MD simulation at $T = 1000$ K. This completes the cycle $\mathrm{H}_2 + I \rightarrow \{I, H, H\}$ followed by $\{I, \mathrm{H}, \mathrm{H}\} + V \rightarrow \mathrm{H}_2^*$, as observed in e^--irradiated samples. A version of the latter simulation reduced to 400 steps is available to the interested reader [30]. In an MD simulation at room temperature, the same reaction had barely begun after 3 000 time steps. We believe that $\{V, \mathrm{H}, \mathrm{H}\} + I$ also occurs, but not within the few picoseconds (real time) that are available to us (at 1200 K, the reaction had not begun after 8 000 time steps).

Figure 1 shows six steps from the simulation. The initial configuration (a) is a local minimum of the potential energy. It consists of a vacancy (schematically represented by a dashed circle) at a third nearest-neighbor site from $\{I, \mathrm{H}, \mathrm{H}\}$. This complex is the one observed by IR in proton-implanted Si [23]. At the end of the simulation, the V-I recombination has taken place, and only H_2^* remains. In (b), atom 1 is on its way toward the vacancy, pushed by atom 2 which will take its place. In (c), atom 1 is in place and V-I recombination is essentially achieved. In (d), we are left with a pair of Si-H bonds parallel to each other, but not on the same $\langle 111 \rangle$ axis. The center of the cell is still heavily distorted. In (e), this region is almost completely reconstructed. Between (e) and (f), the hydrogen atom attached to atom 2 jumps to the correct trigonal axis and H_2^* is formed. This jump occurs via a BC configuration. Note that the last step shown (f) still corresponds to 1 000 K (not a quenched configuration) and the two Si-H bonds oscillate around the trigonal axis. A quench of configuration (f) gives H_2^*.

These results show that interstitial H_2 in Si reacts with V's and I's to form IR-active centers, as observed experimentally [11,20,21]. V's and/or I's are present in the sample in above-equilibrium concentrations during a variety of processes such as electron irradiation, ion implantation, etching, or the deposition of various surface layers. During such processes, V's and I's diffuse very rapidly and interact with defects. The interactions with H_2 are particularly energetic. In a sample containing hidden hydrogen, now identified as interstitial H_2 molecules, the interactions result in the formation of Si-H bonds in centers such as $\{V, \mathrm{H}, \mathrm{H}\}$ (when V's dominate, such as during etching or nitridation), $\{I, \mathrm{H}, \mathrm{H}\}$ (when I's dominate, such as the deposition of Au or n^+ layers), or H_2^* (when both V's and I's are abundant, such as during electron irradiation).

At temperatures higher than 200 °C, the H_2^* complex thermally dissociates, and the net result of the interaction of H_2 with radiation damage is the transformation of the molecule into interstitial H, which suddenly appears in the bulk of the material. There have been reports of anomalously high diffusivity of H, assumed to be vacancy enhanced [31,32]. The present results show that if hidden H_2 is *already present* in the bulk, it will become electrically and optically active following the injection of V's and/or I's. This will make it appear that H diffused very fast from the surface, while in fact only V's and I's diffused.

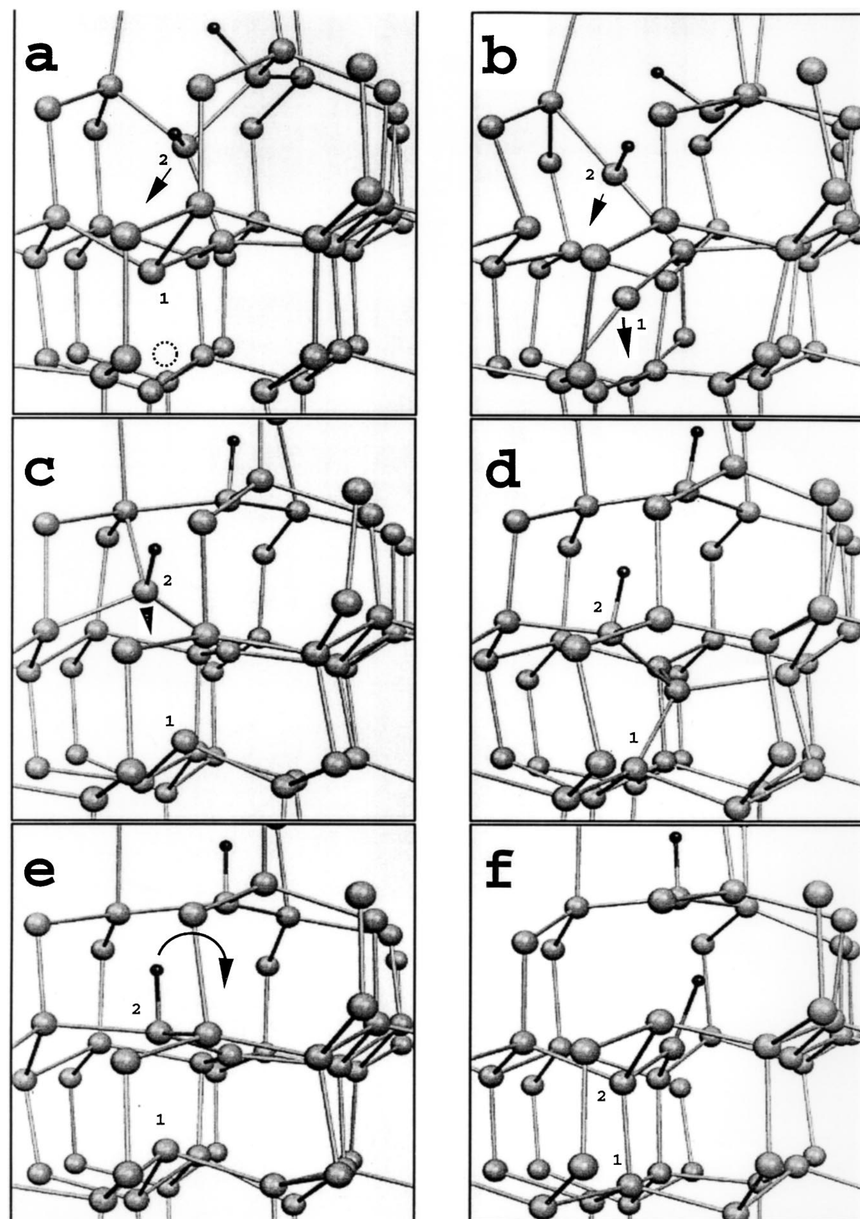

FIG. 1. Six of the 4 000 time steps MD simulation at 1 000 K showing the reaction $\{I, \mathrm{H}, \mathrm{H}\} + V \rightarrow \mathrm{H}_2^*$. Some of the host atoms in the cell are not shown. The initial configuration (a) is a local minimum of the potential energy, and the vacancy is schematically shown as a dashed circle. The last configuration (f) is H_2^* (at 1 000 K, the two H's are oscillating around the trigonal axis). The arrows show the main directions of motion. A movie of the reaction is available [30].

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