THEORY OF HYDROGEN REACTIONS IN SILICON

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ABSTRACT

We report first-principles total-energy calculations for H atoms in a Si lattice. Our results for single H atoms are presented in the form of total-energy surfaces, providing immediate insight in stable positions and migration paths. We examine the stability of different charge states (H^+, H^0, H^-) as a function of Fermi-level position, and its implications for H diffusion in p-type vs. n-type material. The results are used to scrutinize and supplement existing understanding of experimental observations. We also study the cooperative interactions of several H atoms, and propose a novel mechanism for H-induced damage.

INTRODUCTION

In the last few years, a variety of experimental data have revealed a wealth of fascinating phenomena associated with H in crystalline Si. It has been found that H can passivate all of the shallow acceptors, causing a dramatic increase in the resistivity of p-type material. In contrast, only weak passivation has been observed in n-type material. It was also found that H, in addition to passivating existing defects, actually induces defects as well.[1] Understanding of these phenomena has been rather limited[2] largely because reliable theoretical results for the properties of H in crystalline Si have been lacking. An excellent review of the existing literature was recently published by Pearton, Corbett and Shi.[3]

Here we report the application of state-of-the-art theoretical techniques to describe the properties of H in Si. Our studies cover two major topics. First, we examine the behavior of a single H atom in the Si lattice. We establish the stable configurations and migration paths for a H atom in its various charge states, including sites and paths that involve strong reactions with the Si network. In particular, we have not limited ourselves to an investigation of the interstitial regions, but also present information for the bond-center position. The latter involves significant relaxation of the silicon atoms, but proves to be the minimum energy position for hydrogen in the positive or neutral charge state. Hydrogen in this position introduces an energy level in the upper part of the band gap, and thus exhibits donor-like behavior. When hydrogen is moved from the bond-center site to the interstitial region, its energy level moves rapidly through the band gap, and acquires acceptor-character. The new and unexpected insights provided by these investigations show that the two distinct paths associated with different charge states of the H will lead to strikingly different phenomena in the presence of dopants. We also determine the relative stability of the different charge states as a function of Fermi-level position, and investigate the consequences for H diffusion and reactions in intrinsic, p-type and n-type material.

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In the second part of our investigations, we explore the phenomena that may arise from precipitation of two or more H atoms. This includes the interaction of the H atoms with each other, leading to molecule formation, as well as the cooperative reactions of several H atoms with the Si network. In particular, we will propose a mechanism for H-assisted defect formation, which may be responsible for the observations of H-induced damage.

METHODS

Our calculations[4] are based on local-density-functional theory[5] in the LDA, using *ab initio* norm-conserving pseudopotentials for Si, and the Coulomb potential for H. These techniques have established their reliability in numerous studies of point defects and impurities in Si and III-V compound semiconductors. Details of the calculational approach are presented elsewhere.[6]

In order to present our results for a single H atom in a Si lattice, we have developed a novel technique to generate energy surfaces.[7] The energy surface gives the value of the total energy as a function of the coordinates of the H impurity. For each position of the impurity, the surrounding Si atoms are completely relaxed. In our construction of the energy surface, we exploit the fact that this surface has the symmetry of the perfect crystal. It can therefore be expanded in a set of basis functions which exhibit this symmetry. A small set of energy values at representative points is then sufficient to determine the expansion coefficients.

RESULTS

Energy Surfaces

While it is impossible to pictorially represent the energy surface (a four-dimensional object) as a function of all three dimensions, our choice of data points and our fitting procedure assure that we take the full three-dimensional character into account. Fig. 1 shows contour plots of the energy surface for the H^+ restricted to the (110) plane through the atoms. Fig. 2 shows the energy surface for the H^+ restricted to a (110) plane parallel to the plane in Fig. 1 and lying half-way between equivalent planes through the atoms. Special points in the energy surface are labeled as follows: B is the bond-centered position, T is the tetrahedral interstitial site, H is the hexagonal interstitial site at the center of a six-fold ring, and C is at the center of a rhombus formed by three adjacent Si atoms and the nearest tetrahedral interstitial site. The points C' are symmetry-related points along equivalent paths. The point M in Fig. 2 is located midway between two C-sites, or alternatively can be defined as lying on a line perpendicular to the Si-Si bond, midway between the bond center and the neighboring hexagonal interstitial site. Note that the Si relaxations for each position of the H atom are different but are not displayed in the figures.

The energy surfaces for H in the positive, neutral, and negative charge state exhibit a number of common features. There are two distinct regions in which the H atoms exhibit significantly different behavior. The first region is the region of high electron density, including the bond-center site (B in Fig. 1), the sites C, M, etc. In this region, the nearby Si atoms relax strongly. For example, when the H atom is placed at the B site, the adjacent Si atoms relax out by 0.4 Å for a net gain in energy of more than 4 eV. Furthermore, in this high-density region, there is an H-related level in the upper part of the energy gap. Its

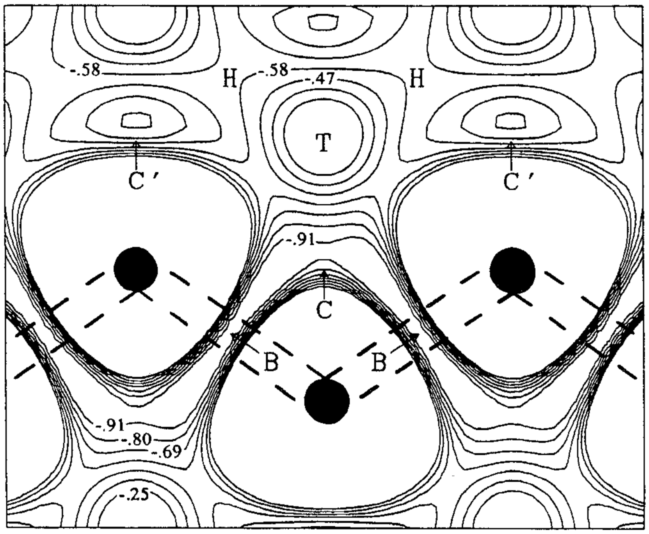

Fig. 1. Contour plot in the (110) plane through the Si atoms of the total energy surface for H^+ in Si. The atomic positions are indicated by solid dots, as well as the points T (Tetrahedral interstitial site, chosen as reference, E=0), H (Hexagonal interstitial site, E=-0.61 eV) B (Bond center, E=-1.04 eV), and C (at the center of a rhombus formed by three adjacent Si and the nearest T, E=-0.93 eV). The energy difference between adjacent contours is 0.11 eV.

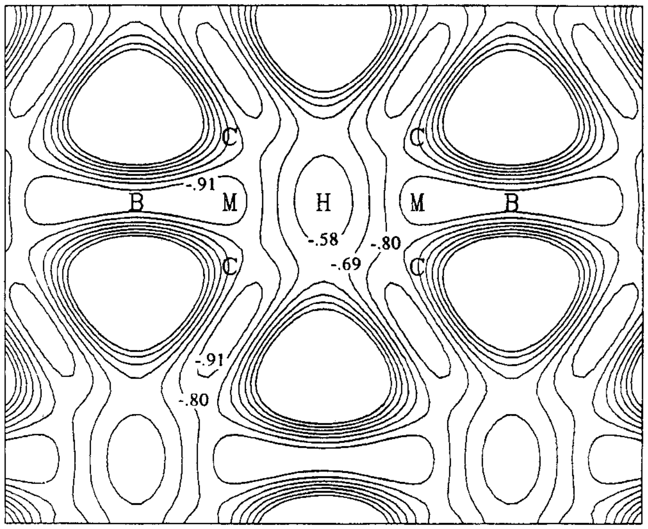

Fig. 2. Same as Fig. 1, but for a plane through B, C, H and M. The M point is located midway between a bond center and the nearest hexagonal interstitial site.

precise position changes only by ~0.1 eV as a function of charge state. The second region consists of the low-electron-density "channels" and includes the high-symmetry tetrahedral (T) and hexagonal (H) interstitial sites. In this region, the Si atoms in the vicinity of H relax very little if at all. Furthermore, the H-related level is now significantly lower and occurs as a resonance just below the top of the valence bands.

From Fig. 1, we see that the lowest energy positions for the H^+ occur in the high-density regions of the crystal, with the global minimum at the bond-center site. The energy rises sharply when the hydrogen atom is displaced from the bond center along the bond direction towards one of the Si atoms. In contrast, the energy surface is very flat in directions perpendicular to the bond. This can be seen also in Fig. 2, which depicts the energy surface in a plane containing the bond center and a hexagonal interstitial site. Here we can study the behavior around the M-site, which Corbett *et al.*[8] proposed as the minimum-energy location for *neutral* H in Si. We find that all points between B and M on this line have approximately the same energy. The following picture then emerges for the migration path: The lowest energy position is at B with similar energy configurations perpendicular to the Si-Si bond. To move through the crystal, the proton has to move through a saddle point located close to C, with a barrier height of 0.12 eV.

We have also generated the energy surfaces for H in the neutral and negative charge states. For neutral H, the same features and relative positions of local minima can be recognized as in the case of H^+. The high-density path is again favored, but the low-density path is less than 0.1 eV higher. Thus, H^0 seems to be able to move rather freely through the network with very small energy barriers. For the case of negative H, the tetrahedral interstitial site is the lowest in energy, with the energy rising sharply outside the low-density regions. The barrier to migration along a path through the low-density region and going through the hexagonal interstitial site is 0.3 eV.

Stability of Charge States

We now examine the *relative energies* of the different charge states of the H, in order to determine the lowest-energy state. These relative energies depend on the position of the Fermi level, with which electrons are traded in order to alter the charge state of the defect. In p-type material, we find that the lowest-energy state is H^+ in the high-density region; thus, H^+ diffuses via the high-density path and exhibits donor-like behavior. This result confirms the suggestion that the passivation of p-type material is a direct result of compensation, i.e. electrons from neutral H-atoms annihilate the free holes in the valence band.[2] Pairing between H^+ and negative acceptors follows compensation. For n-type material, our results are more sensitive to the intrinsic uncertainties of the methods. Experimentally, weak passivation of donors has been observed, but there is no evidence for direct compensation. In our theoretical approach, the corrections to the LDA energy levels make the error bar too large to distinguish between H^- and H^0 as the stable state in n-type material, allowing the distinct possibility that H^0 is the more stable charge state. Thus, it is not possible at this point to confirm or rule out the suggestion[2] that H^- does not form and that passivation of n-type Si occurs only via pairing.

Interactions of Multiple H atoms

So far, we have only discussed the properties of a single H atom in crystalline Si. Important effects can also occur due to the precipitation of several H atoms in a small region. First, we examine H_2 molecule formation. Hydrogen atoms in the + or - charge states will of course avoid each other, so formation of H_2 molecules must only be considered for the neutral charge state. We have found the minimum energy position for the molecule straddling the tetrahedral interstitial site, oriented in the <100> direction, with the atoms separated by 0.94 Å (to be compared with 0.75 Å in vacuum). The barrier along the migration path is ~1 eV. We calculate a binding energy of ~2 eV per molecule.

Another phenomenon consists of the cooperative interaction of several H atoms with the Si lattice, and is related to the issue of damage induced by hydrogenation.[1] A possible mechanism for defect formation involves Si atoms being removed from the defect region, with the resulting dangling bonds tied off by H atoms. Our calculations show that passivation of a dangling bond by an interstitial H atom results in an energy gain of ~2.2 eV per Si-H bond.[9] This value is sufficiently large to allow removal of Si atoms at the edge of the defect, which are bound by only two or three bonds to the rest of the network. This process will have to compete with molecule formation; however, the resulting defect structure is quite stable. We also note that H_2 formation is suppressed if the diffusing H are charged, while Si-H bond formation can still proceed.

Nucleation of the proposed extended defect can occur at any vacancy; such a vacancy can itself be formed by H-assisted defect generation. Vacancy-interstitial pair creation can be exothermic, provided enough H atoms are available to tie off the dangling bonds. Because of the kinetic difficulties of actually bringing in four H atoms around a Si site, single defect creation will be a rare process. The mechanism described above for extending the defect provides a likely explanation for the observed hydrogen-induced damage.

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