Hydrogen in silicon: Fundamental properties and consequences for devices

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The interactions between hydrogen and silicon are investigated based on first-principles calculations. After a comprehensive overview of various configurations attention is focused on the energetics and dissociation of Si–H bonds. An examination of the dissociation mechanism of Si–H bonds suggests an explanation for the observed difference in stability between hydrogen and deuterium at dangling bonds. Connections between the phenomena at surfaces, interfaces, and in amorphous materials will be pointed out. © *1998 American Vacuum Society.*
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I. INTRODUCTION

It was recently demonstrated that incorporation of deuterium (D), rather than hydrogen (H), at the Si/SiO$_2$ interface leads to significant improvements in the lifetime of metal-oxide-semiconductor (MOS) transistors.[1] It had previously been observed that scanning tunneling microscope (STM) desorption of hydrogen or deuterium from Si (100) surfaces exhibits a similarly large isotope effect.[2] These observations have generated a wave of new interest and activity in the role of hydrogen in passivating surface and interface states. The hydrogen/deuterium issue poses some profound physics questions, in particular: what is the mechanism behind such a giant isotope effect? We will propose an explanation, based on the vibrational properties and dissociation paths of the Si–H and Si–D bonds.

First, however, we will give an overview of some fundamental properties of hydrogen configurations in silicon, based on the information that can be extracted from state-of-the-art first-principles calculations. These studies provide important insights in the formation and dissociation of Si–H bonds. Various ways to test the proposed explanation for the isotope effect will be suggested, and we will discuss the connection between the phenomena at surfaces, interfaces, and in amorphous materials. We will also discuss how investigations of hydrogen interactions with Ge can shed light on the basic mechanisms.

II. THEORETICAL APPROACH

The important role played by hydrogen in crystalline silicon (c-Si), amorphous silicon (a-Si) and polycrystalline silicon is well recognized. Hydrogen significantly improves the electronic quality of the material, an effect that is usually understood in terms of passivation of dangling bonds.[3] To put these models on a firmer basis, quantitative information is required on the energetics of the various processes and reactions. Such information is very difficult to obtain directly from experiment, but it can be generated using computational techniques. The computational results presented here have all been obtained using a state-of-the-art first-principles approach, based on density-functional theory, *ab initio* pseudopotentials, and a supercell geometry. Details of the method can be found in review papers such as Refs. 4, 5, and 6.

III. ENERGETICS OF HYDROGEN INTERACTIONS WITH SILICON

Using the first-principles techniques described above, we studied a large number of configurations of hydrogen in crystalline Si (c-Si). The results were discussed in Ref. 7; they are summarized in Fig. 1. The calculated values provide direct information about the relative stability of different configurations.

The configurations listed in Fig. 1 were derived for *crystalline* Si. It is clear that the details of configurations and energetics may be different in an *amorphous* network. Still, the values obtained for c-Si provide a good starting point for discussion of hydrogen in a-Si. An example of such applications was given in Ref. 8.

Reference 7 contains a full discussion of all the information included in Fig. 1. Here we only discuss two configurations: isolated interstitial hydrogen, and hydrogen dimers. Hydrogen interactions with dangling bonds will be discussed in the next section.

A. Isolated interstitial hydrogen

Isolated interstitial hydrogen occurs either at the bond center (BC) or at the tetrahedral interstitial site in c-Si. The former geometry is the lowest-energy configuration for H in the positive (H$^+$) and neutral (H^0) charge states; the latter is more favorable for H in the negative charge state (H$^-$). Isolated hydrogen occurs in the positive charge state in p-type material, while it has the negative charge state in n-type material. The energies of H$^+$ and H$^-$ depend on the position of the Fermi level, but can be obtained from the energy of H^0 once the donor and acceptor levels are known; these levels have been obtained experimentally as well as theoretically, as discussed in Ref. 9. For H^0 at the BC site, the energy is

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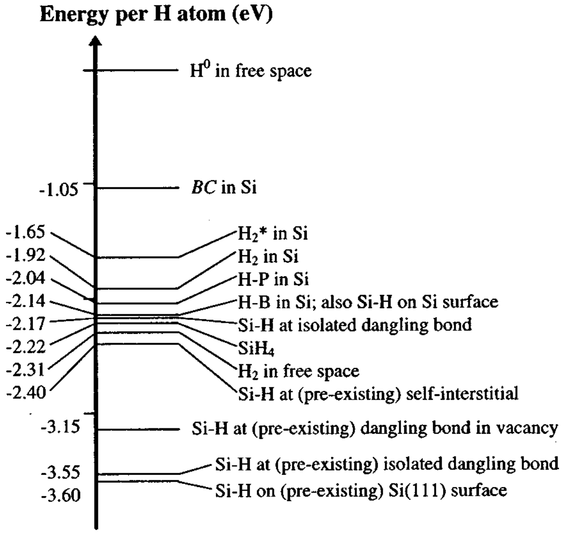

FIG. 1. First-principles energies for various configurations of H in Si. The zero of energy corresponds to a free H atom. The energy values were determined with first-principles pseudopotential-density-functional calculations, and include zero-point energies.

1.05 eV below the energy of H^0 in free space, as shown in Fig. 1. This value agrees with an analysis of solubility data in c-Si.[10]

Interstitial hydrogen is known to diffuse very quickly through silicon; the migration barrier E_M is the energy difference between the saddle-point energy along the path, E_S, and the energy at BC: $E_M = E_S - E_{\mathrm{BC}}$. Hydrogen diffusion experiments in c-Si[11] indicate that the migration energy E_M is about 0.5 eV.

The energy of the BC configuration indicates that interstitial H is not very stable in c-Si; indeed, in crystalline Si, the stability of BC hydrogen has been derived from deep-level transient spectroscopy measurements, showing that the BC configuration is only stable at temperatures below 100 K.[12] Given its high mobility, isolated hydrogen quickly diffuses to sites of higher stability, forming complexes with other hydrogens, with impurities, or with defects. However, variations on the basic bond-center configuration are possible that provide a higher stability. Indeed, the formation energy of the BC configuration involves a balance between energy gain due to Coulomb interaction between the proton and the electron density in the bond, and energy cost due to elastic energy required to move the Si atoms outwards. If the Si atoms were initially spaced further apart, the energy *gain* due to the formation of the three-center bond would still be the same, but the energy *cost* involved in moving the Si atoms would be lower, leading to a net increase in stability of the configuration. Such an expansion of the Si–Si bond is, of course, quite possible in a-Si, corresponding to the insertion of H in weak Si–Si bonds, or in polycrystalline silicon, corresponding to insertion of H in strained bonds near grain boundaries. A particular application to hydrogen-induced metastable donors in polycrystalline silicon has been described in Ref. 13.

B. Hydrogen molecules and molecular complexes

H_2 molecules can easily form in silicon; the binding energy is somewhat smaller than its value in free space, but still large enough to make interstitial H_2 one of the more favorable configurations hydrogen can assume in the lattice. Another configuration involving two hydrogen atoms is the so-called H_2^* complex, in which a host-atom bond is broken and one hydrogen atom is inserted between the two atoms, in a BC position, while the other hydrogen occupies an antibonding site.[14] This configuration is somewhat higher in energy than the H_2 molecule, but it may play an important role in diffusion, in metastability, as well as in nucleation of larger hydrogen-induced defects.

H_2 molecules have commonly been assumed to be present in many semiconductors. Direct experimental observations were lacking, however, due to the challenging nature of the measurement. H_2 has no dipole moment, rendering it invisible to infrared spectroscopy. In addition, the concentrations of H_2 pose a sensitivity problem.

Recently, two studies were reported in which Raman spectroscopy was used to study interstitial H_2 in Si[15] and in GaAs.[16] The results from these studies seem contradictory: in GaAs,[16] the vibrational frequency of the stretch mode is found to be significantly lower, by 227 cm^{-1}, than the value in H_2 gas. The results for Si,[15] on the other hand, show virtually no lowering of the vibrational frequency. In order to resolve this apparent conflict and to further our understanding of the physics of H_2 incorporation we have performed a first-principles computational study of interstitial H_2 in a number of different semiconductors: Si, GaAs, InAs, and GaN (in the zincblende structure).[17]

These investigations show that incorporation of H_2 in an interstitial position results in a lowering of the binding energy, an increase in the bond length, and a lowering of the vibrational frequency. The calculated lowering of the frequency for H_2 in GaAs agrees with the experimental value obtained in Ref. 16. For silicon, an even larger shift was obtained, a result that is also consistent with the physics of the interaction between H_2 and the semiconductor. This result conflicts with the experiments of Ref. 15, suggesting that the species observed in that experiment was not interstitial H_2.

IV. HYDROGEN INTERACTIONS WITH DANGLING BONDS

A. Energetics of the Si–H bond

The energetics of the Si–H bond in bulk (crystalline or amorphous) Si, or on the Si surface, had not been explored until recently. It had mostly been assumed that the bond strength would be similar to that in a silane (SiH_4) molecule; this approach ignores effects of the crystalline environment and possible distortions of the bonding configuration. As a first step, a study was performed for Si–H bonds in a crystalline environment.[18] The resulting energies are included in Fig. 1.

The energy of a Si–H bond can be defined by answering

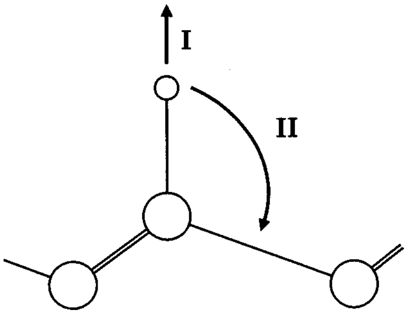

FIG. 2. Schematic representation [projected on a (110) plane] of a Si–H bond and the neighboring Si atoms. Si atoms are represented by large circles, and the H atom by a small circle. Two paths for removing the H atom from the Si–H bond (leaving a dangling bond behind) are indicated; path I moves the H atom towards a tetrahedral interstitial site, path II moves the H atom towards a neighboring bond-center site.

the question: how much energy is needed to remove the H atom from a Si–H bond (leaving a dangling bond behind) and placing the hydrogen in an interstitial (BC) position? Various geometries were used to investigate the structure and energy of the Si–H bond.[18] The first geometry was that of the hydrogenated vacancy; here the H atoms are close enough to significantly interact, and the energy of the Si–H bond was found to be -3.15 eV (see Fig. 1). A second geometry placed a dangling bond in a larger void, created by the removal of four Si atoms; this produced an energy of -3.55 eV. The 0.4 eV difference between the two results is due to H–H repulsion effects.

A different way of defining an energy for the Si–H bond is to assume that one starts from crystalline silicon and a hydrogen atom in free space, and that the energy to create a dangling bond needs to be taken into account; this defines a *formation energy*. For an ''ideal'' Si–H bond (meaning it is located at a dangling bond which is isolated from other dangling bonds, with no H–H repulsion) the formation energy was found to be -2.17 eV. The difference with the energy at -3.55 eV discussed above is that one includes the formation of a dangling bond while the other does not; the difference is $-2.17-(-3.55)=1.38$ eV, a value which constitutes an estimate for the formation energy of a dangling bond in c-Si.

Reference 8 contains a discussion of how these energy values relate to diffusion processes in amorphous silicon.

B. Dissociation mechanisms of Si–H bonds

The path followed by the hydrogen atom during the breaking of a Si–H bond plays an important role in the dissociation mechanism. Several pathways can be considered.[18] The H atom can move along the direction of the Si–H bond away from the Si atom (see Fig. 2); however, this is unlikely to be the most favorable path, for two reasons: (a) the initial rise in energy in that direction is high, as indicated by the high vibrational frequency (around 2000 cm^{-1}) for the Si–H stretch mode; (b) this path eventually leads to a position of the H atom in the interstitial channel, which is not the lowest energy site for H in the neutral or positive charge state (in c-Si) (see Sec. III A). Both of these arguments actually favor a path (path II in Fig. 2) in which the H atom stays at approximately constant distance from the Si atom to which it is bound: (a) the barrier in that direction is much lower, as indicated by the vibrational frequency (around 650 cm^{-1}) for the Si–H wagging mode; (b) this path leads to a H position near the BC site, which is the stable site for H^0 (and also for H^+) in crystalline Si.

The intermediate state, with the H atom in a bond-center site next to the dangling bond, is 1.5 eV higher in energy than the Si–H bond, to be compared with the 2.5 eV it costs to remove the H to a position far away from the dangling bond. Even before the H atom reaches this intermediate position, however, two energy levels are introduced into the band gap (near the valence band and near the conduction band), enabling the complex to capture carriers; after changing charge state there is virtually no barrier to further dissociation. The barrier for dissociation can therefore be significantly reduced when carriers are present. Such carriers are available under many circumstances: at the surface, in a STM desorption experiment; or at an Si/SiO_2 interface, during device operation of the MOS transistor; or in a-Si, in the form of light-induced carriers. An interesting consequence of the features of this dissociation path will be discussed below.

C. Hydrogen versus deuterium for passivation of dangling bonds

Some very exciting results were recently published on the different characteristics of hydrogen and deuterium (D) for passivation of Si dangling bonds. The phenomena were first studied in the context of passivation of dangling bonds on Si surfaces; specifically, the Si (100)-(2×1) surface can be perfectly passivated by hydrogen (or deuterium). It was demonstrated that desorption of hydrogen from this surface can be achieved, with atomic resolution, by irradiation with electrons emitted from a STM tip.[19] When the experiment was repeated with deuterium,[2] a very strong isotope effect was observed: the deuterium desorption yield was much lower (up to two orders of magnitude) than the hydrogen desorption yield.

Lyding *et al.*[1] built upon these observations to conduct an experiment in which the difference between H and D was studied in the context of passivation of defects at the Si/SiO_2 interface. This interface lies at the heart of Si MOS transistor technology. The interface exhibits a high degree of perfection, but any remaining defects (usually considered to be dangling bonds) can be passivated by hydrogen, which is accomplished by an intentional hydrogenation during processing. Unfortunately, some degradation occurs over time, mostly due to hot-electron effects. Significant improvements in the lifetime of MOS transistors were observed when deuterium, rather than hydrogen, was incorporated at the Si/SiO_2 interface.[1] Similar to the surface desorption experiments, this indicates that the Si–D bond is more resistant to hot-electron excitation than the Si–H bond.

This is surprising, because the isotopes are entirely equivalent from an electronic point of view: indeed, the static electronic structure of the Si–H and Si–D bonds is identical. The difference must therefore be attributed to dynamics. Based upon the discussion of the dissociation mechanism presented above, we have proposed a mechanism which provides a natural explanation for the difference in dissociation rates.[20] The dissociation of Si–H bonds has been proposed to proceed via multiple-vibrational excitation by tunneling electrons (at least in the low-voltage regime).[21] This mechanism would apply both to desorption from the surface and to the Si/SiO$_2$ interface. Electrons excite Si–H vibrational transitions with a rate proportional to the tunneling current. The extent to which vibrational energy can be stored in the bond depends on the lifetime, i.e., on the rate at which energy is lost by coupling to phonons. Because the lifetime of H on Si is long,[22,23] efficient vibrational excitation is expected. In the analysis by Shen *et al.*[21] it was assumed that the vibrational energy is deposited in the *stretch* mode of the Si–H bond, which has a frequency around 2100 cm^{-1}. The same assumption is usually implicitly made in discussions of dissociation of Si–H bonds.

It is very important to consider, however, that both the vibrational lifetime and carrier-enhanced dissociation mechanisms are most likely controlled by the Si–H *bending* modes, as discussed in Sec. IV B. The vibrational frequency of the bending mode for Si–H is around 650 cm^{-1}, and the estimated frequency for Si–D is around 460 cm^{-1}. This estimate agrees well with the value obtained from infrared absorption in a-Si films by Lucovsky *et al.*[24,25] This frequency turns out to be very close to the frequency of bulk TO phonon states at the X point (463 cm^{-1}).[26] We therefore expect the coupling of the Si–D bending mode to the Si bulk phonons to result in an efficient channel for deexcitation. While it is quite possible to reach a highly excited vibrational state in the case of Si–H, this will be more difficult for Si–D. Deuterium should therefore be much more resistant to STM-induced desorption and hot-electron induced dissociation, due to the relaxation of energy through the bending mode.

As discussed in Sec. IV B, the bending mode also provides a likely pathway for dissociation in the presence of carriers. We have found that when the displacement of H from its equilibrium position reaches about 0.8 Å, gap levels emerge from the conduction and the valence band. Capture of carriers in these levels results in immediate dissociation. The bending-mode excitation pathway is therefore attractive because of the potential for carrier-enhanced dissociation, in addition to the fact that the overlap of the Si–D bending mode frequency with Si bulk phonons provides a natural explanation for its reduced dissociation rate.

Specific predictions for experimental observations, based on the explanation proposed here, will be discussed in the next section.

V. PREDICTIONS

We now discuss a number of predictions based on our proposed model of the Si–H and Si–D dissociation.

A. Thermal versus carrier-induced desorption

The large isotope effect will not be observed during thermally stimulated desorption. Indeed, in thermal equilibrium the bulk phonons will be excited to the same extent as the Si–D vibrations; the bulk then does not act as a ‘‘sink’’ for the vibrational energy in the Si–D modes, and desorption of H and D should proceed at the same rate.

B. Silicon versus germanium

The validity of the model could be examined by performing experiments on hydrogen desorption from Ge. The frequency of the Ge–H bending mode is only slightly lower (by less than 100 cm^{-1}) than for Si–H.[27] The Ge bulk phonon spectrum, on the other hand, is *very* different from Si: the highest frequency is around 300 cm^{-1}.[26] Ge–H as well as Ge–D bending modes therefore have frequencies *above* the bulk Ge phonons, implying a long lifetime for both. In other words, for Ge one would not expect to see the large isotope effect (large difference in desorption between H and D) that is observed for Si.

C. Temperature dependence of the desorption rates

The strength of the coupling of the Si–H vibrational mode to bulk modes decreases with decreasing temperature.[28] This means that the vibrational lifetime of the Si–H vibrational excitations increases at lower temperatures; in our model this implies that the Si–H bond will dissociate more easily. The difference in desorption rates between H and D should therefore increase at low temperature. This has indeed been observed in STM experiments as a function of temperature.[29]

Since carrier-induced dissociation of Si–H bonds is expected to be enhanced at lower temperatures, device degradation should become worse. This somewhat counterintuitive result has been confirmed in experiments on low-temperature operation of MOS devices, in which device degradation was found to be exacerbated at 77 K.[30]

D. Amorphous silicon

It is tempting, of course, to suggest that the enhanced stability of Si–D as compared to Si–H at Si surfaces and Si/SiO$_2$ interfaces would also apply to Si–D bonds in a-Si, and could be used to address metastability and degradation problems. To our knowledge, no conclusive experiments on this issue have been performed. To observe an effect, it may be necessary to have most or all of the hydrogen in the sample replaced by deuterium; as long as any Si–H bonds are present, they may be the first to dissociate, leading to severe degradation even in the presence of deuterium. Further work in this area should be worthwhile.

VI. SUMMARY

An overview of computational results for hydrogen interacting with silicon has been presented. The energetics of various configurations in c-Si were studied in detail and summarized in Fig. 1. Particular attention was paid to the dissociation mechanism of the Si–H bond, since it has important repercussions for the stability of hydrogen versus deuterium in passivating dangling bonds. Specific predictions to test the validity of our proposed explanation for the large isotope effect have been given.

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