

THEORY OF HYDROGEN INTERACTIONS WITH AMORPHOUS SILICON

CHRIS G. VAN DE WALLE* and BLAIR TUTTLE**

*Xerox Palo Alto Research Center, 3333 Coyote Hill Road, Palo Alto, California 94304; vandewalle@parc.xerox.com

**Department of Physics, Computational Electronics Group, Beckman Institute, University of Illinois, Urbana, IL 61801

ABSTRACT

We present an overview of recent results for hydrogen interactions with amorphous silicon (α -Si), based on first-principles calculations. We review the current understanding regarding molecular hydrogen, and show that H_2 molecules are far less inert than previously assumed. We then discuss results for motion of hydrogen through the material, as relating to diffusion and defect formation. We present a microscopic mechanism for hydrogen-hydrogen exchange, and examine the metastable $\equiv SiH_2$ complex formed during the exchange process. We also discuss the enhanced stability of Si-D compared to Si-H bonds, which may provide a means of suppressing light-induced defect generation.

INTRODUCTION

We have recently witnessed a resurgence of interest in the properties of hydrogen in semiconductors in general, and in amorphous silicon in particular. Several exciting developments have spurred this renewed interest: focusing on α -Si, they include new information about Si-H bond dissociation, hydrogen diffusion, and new models for light-induced defect generation; the potential for more stable defect passivation by using deuterium instead of hydrogen; and progress in the ability to experimentally observe interstitial H_2 molecules. First-principles computations have significantly contributed to our understanding of hydrogen-related phenomena. In this paper we will focus on recent work closely connected to the issues outlined above. The computational results 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.

In the first part of the paper, we will focus on hydrogen molecules. We will review experimental observations of interstitial H_2 molecules in crystalline and amorphous semiconductors, and describe the theoretical framework for understanding the physics of incorporation of a strongly bound molecule in a semiconducting environment.

The second part of the paper will deal with hydrogen motion, as occurs in diffusion and in light-induced defect generation. We first discuss an exchange process between trapped and interstitial H that plays a significant role in diffusion. We have determined a low-energy pathway for exchange which involves an intermediate, metastable $\equiv SiH_2$ complex with both H atoms strongly bound to the Si atom. The energy barrier for the exchange is less than 0.2 eV, consistent with observations of hydrogen-deuterium exchange in α -Si:H(D) films. We also discuss potential implications of the $\equiv SiH_2$ complex for metastability and defect generation. On the issue of stability of Si-H bonds, finally, we discuss the dissociation path and the connection to vibrational properties. We then show how these insights into the microscopic mechanisms immediately explain the enhanced stability of Si-D bonds.

METHODS

We have performed comprehensive and systematic calculations for hydrogen interactions with silicon using a state-of-the-art first-principles approach based on density-functional theory in the local-density approximation [1]. We employ a plane-wave basis set and a supercell geometry, with *ab initio* pseudopotentials for the semiconductor host atoms [2, 3]. Relaxation of host atoms was always included, and 32-atom supercells were typically used. This approach has produced reliable results for bulk properties of many materials, as well as properties of surfaces, interfaces, impurities, and defects. More details about the application of the method to the study of hydrogen can be found in Refs. [4], [5], and [6]. We estimate the uncertainty on the energies quoted here to be ± 0.1 eV.

HYDROGEN MOLECULES

It has been known for some time that H_2 molecules are one of the more stable forms of hydrogen in many semiconductors. This knowledge was based on computational studies (see, e.g., Ref. [4, 5, 7]) as well as on interpretation of experimental data. Direct observation of H_2 molecules proved very challenging, however, because of sensitivity problems in techniques such as NMR (nuclear magnetic resonance) and vibrational spectroscopy. Recently, however, great progress has been made in this area.

A thorough understanding of the incorporation of H_2 in the lattice is essential for the many technologically important processes that involve hydrogen: passivation of defects at the Si/SiO₂ interface; the “smartcut” process for producing silicon-on-insulator structures [8]; passivation and generation of defects in amorphous silicon; etc. In amorphous silicon, it has long been known that much more hydrogen is incorporated than is strictly needed for defect passivation. Work by Norberg *et al.* [9] suggests that a significant fraction of this hydrogen could be in the form of interstitial molecules. For many of these processes, it is essential to understand how H_2 interacts with existing defects or contributes to the formation of new defects; one aspect of such interactions is also addressed in the section on **Hydrogen Motion**.

Experimental observation of interstitial H_2 in crystalline semiconductors

Vibrational spectroscopy provides an excellent tool for observing hydrogen-related centers in semiconductors, but the lack of a dipole moment in the symmetric H_2 molecule makes it difficult to observe with infrared (IR) spectroscopy. Even if the interaction with its environment induces a dipole moment in the molecule, it is expected to be very weak. Raman spectroscopy, on the other hand, is not hampered by the inversion symmetry of the molecule.

Recently, impressive progress has been made in the experimental observation of H_2 molecules in crystalline semiconductors. Hydrogen molecules have been detected with Raman spectroscopy in GaAs [10] and Si [11]. In both cases, the vibrational frequency of the stretch mode was found to be significantly lower than the frequency in H_2 gas. More recently, the vibrational modes of interstitial H_2 in Si have also been observed with IR spectroscopy [12, 13]; at 10 K, a value of 3618 cm^{-1} was found, in excellent agreement with the Raman results. In Si, care has to be taken to distinguish between truly interstitial H_2 molecules, and H_2 in small voids or near platelets; the latter exhibit a vibrational frequency close to H_2 in vacuum [14].

First-principles calculations of interstitial hydrogen molecules

We have performed first-principles computational studies of interstitial H_2 in a number of different semiconductors: Si, GaAs, InAs, and GaN (in the zincblende structure) [15]. 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. These effects can be attributed to the immersion of the molecule in a low-density electron gas near the interstitial site. Indeed, the decrease in binding energy and corresponding lowering of the vibrational frequency correlate with the charge density near the interstitial site. Our calculated lowering of the frequency for H_2 in GaAs and in Si agrees well with the experimental values [10, 11], and with other recent calculations by Hourahine *et al.* [16] and by Okamoto *et al.* [17].

For each of the semiconductors, we placed H_2 in various interstitial configurations, in a number of different orientations. For the lowest-energy configurations, a series of calculations was subsequently carried out for different bond lengths in order to obtain a potential energy curve for determination of the vibrational frequencies, including both harmonic (ω) and anharmonic ($\Delta\omega$) terms. The vibrational frequencies turned out to be remarkably insensitive to the orientation of the molecule. We also calculated the difference between the energy of interstitial H_2 in the semiconductor and the energy of H_2 in vacuum; for c-Si, this energy difference ΔE is 0.8 eV per molecule.

Our systematic investigation of H_2 in different semiconductors allowed us to extract trends and investigate the underlying mechanisms. The vibrational frequency decreases along with the lattice constant a of the semiconductor – up to a point. For large a there is little direct interaction between the H_2 molecule and the host atoms; the relaxation of the host atoms is small and its effect on the vibrational frequency is negligible. The interaction increases as the lattice constant goes down, resulting in lower values of the vibrational frequency ω , larger values of the anharmonicity, $\Delta\omega$, and higher values of ΔE . Repulsion between H atoms and host atoms (which would lead to a stiffening of the force constant and an increase in frequency) does not seem to play any significant role, until the lattice constant becomes smaller than that of silicon. In fact, immersion of the molecule in the semiconductor charge density leads to a weakening of the bond. This trend obviously breaks down for semiconductors with a very small lattice constant, such as GaN. In this case strong repulsion occurs between the molecule and the host atoms; in essence, there is not enough room in the interstitial cage to accommodate the molecule, resulting in a large value of ΔE and an increased value of ω .

These insights allow us to predict that in amorphous silicon, the vibrational frequencies corresponding to interstitial H_2 would probably correspond to a broad band, reflecting the slightly different environments at the different interstitial sites. The width of this band would probably make detection by vibrational spectroscopy very difficult.

Diffusion of H_2

We also performed calculations for diffusion of interstitial H_2 in c-Si. We found that the saddle point occurs at the hexagonal interstitial site, with a migration barrier of 0.95 eV. An alternative diffusion mechanism for H_2 diffusion consists of dissociation of the molecule, followed by atomic diffusion. Results obtained in Ref. [5] indicate that dissociation of H_2 into two neutral interstitial hydrogen atoms costs 1.74 eV. Dissociation into an H^+H^- pair would cost 1.34 eV. It is conceivable that the dissociation energy could be even lower, for

instance, if additional energy can be gained from conversion of one of the charge states, or maybe through a catalytic interaction with an impurity.

Still, the migration barrier of 0.95 eV for H_2 to diffuse as a molecule seems low enough to form a viable channel for diffusion under many circumstances. This value agrees well with the observed diffusion of interstitial H_2 reported in Ref. [12]. Markevich and Suezawa [18] also derived an activation energy for diffusion of a hydrogen-related species responsible for the formation of O-H complexes in *c*-Si; their value was 0.78 ± 0.05 eV. Based on other evidence, they argued that this species was interstitial H_2 molecules.

We also mention that during the Raman experiments of Leitch *et al.* [11] a decrease of the interstitial H_2 signal was observed during the measurement, indicating that the H_2 molecules are either diffusing or dissociating [19]. Since this effect is observed even at 4 K, it must be attributed to the interaction of (above band-gap) light with the molecule, either directly or through the generation of carriers.

Hydrogen molecules in amorphous silicon

Much of what we discussed above for H_2 in crystalline silicon is likely to apply to amorphous silicon as well. The presence of H_2 molecules in *a*-Si had been considered previously, but mainly in the context of molecular hydrogen trapped in voids or microbubbles [20, 21]. Device-quality hydrogenated amorphous silicon typically contains up to 15% hydrogen – a concentration that is much larger than the amount of hydrogen needed to passivate defects. The configuration in which this massive amount of hydrogen is incorporated has been debated for a long time.

Norberg and coworkers [9] have recently performed deuteron and proton nuclear magnetic resonance (NMR) measurements on high-quality plasma-enhanced CVD *a*-Si films, showing that a significant fraction of the hydrogen in these samples (2% or more) is not involved in Si-H bonds. On the basis of their measurements they conclude that nearly all of this non-bonded hydrogen is present as isolated H_2 molecules, located in centers of atomic dimensions, perhaps in the analogue of T_d -sites in crystalline silicon. These molecules are *not* the small population of densely packed molecules in the occasional microvoids. Norberg has also found that the photoelectronic quality of the *a*-Si films increases as the fraction of non-bonded hydrogen increases. The non-bonded hydrogen also appears to be in the vicinity of light-induced defects, suggesting the molecular hydrogen may play a role in Staebler-Wronski degradation [22]. We will return to this issue in the section on **Hydrogen Motion**.

One may wonder whether molecular hydrogen could play any role in structural rearrangements or electronic defect formation. In this context, we point out the following experimental result for crystalline silicon: Heating boron-doped *c*-Si in H_2 gas at temperatures exceeding 900°C allows hydrogen to diffuse into the material. When the sample is quenched to room temperature, some of the hydrogen is found to passivate boron acceptors, but the majority of hydrogen atoms (about 70%) are found in a different configuration, which was recently identified to be H_2 molecules [23]. Annealing of the sample at 175°C results in the dissociation of the H_2 molecules and formation of additional H-B complexes. The B acceptors probably play a role in the H_2 dissociation; still, these findings indicate that H_2 molecules can dissociate at modest temperatures. Estreicher *et al.* [24] recently pointed out that interaction of H_2 with vacancies or self-interstitials also leads to dissociation of the molecule, with a substantial gain in energy.

Regarding diffusion, both experiment and theory now point towards an activation en-

ergy for H_2 diffusion in *c*-Si of less than 1.0 eV. This makes molecular hydrogen far more mobile than previously assumed. This result presumably applies also to *a*-Si, although it is hard to predict how the disorder in the network will affect the diffusion.

HYDROGEN MOTION

Interstitial hydrogen can diffuse through crystalline silicon with an activation energy of about 0.5 eV [4, 25]. Hydrogen interacts strongly with other impurities as well as with defects in the crystal. The strongest of these interactions is with silicon dangling bonds, where Si-H bonds are formed with bond strengths up to 3.6 eV [5, 6], similar to those in silane. Silicon dangling bonds thus form deep traps for hydrogen. In *a*-Si:H hydrogen diffusion is understood to occur by the dissociation of Si-H bonds, producing interstitial hydrogen; the latter diffuses rapidly along interstitial sites until trapped at a dangling bond or other defect site. The measured activation energy for hydrogen diffusion in *a*-Si:H is about 1.5 eV [26].

Exchange of deeply trapped and interstitial hydrogen

Hydrogen exchange between deeply trapped and mobile states plays an important role in the diffusion process [27, 28]. If such exchange takes place by first dissociating a Si-H bond and subsequently placing another H at the dangling bond, the activation energy would be high. Experimentally, however, the exchange is known to proceed very efficiently, based on observations of deuterium replacement of hydrogen [27, 29, 30, 31]. Unraveling the microscopic mechanisms by which a neutral interstitial hydrogen can exchange with a deeply trapped hydrogen was a challenge we tackled with first-principles calculations.

Our calculations focused on hydrogen trapped at an isolated Si-H bond in bulk crystalline silicon [32]. To isolate a Si-H bond, we create a small void in the silicon crystal following the procedure outline in Ref. [33]. The local environment in this model, including the open void above the Si-H bond, is similar to the environment of deeply trapped, isolated Si-H bonds in explicit simulations of *a*-Si:H [6]. Recent *ab initio* total energy calculations also indicate that the bond strengths of isolated Si-H bonds in *a*-Si:H are similar to those in our *c*-Si model [6]. In addition, the interactions governing the energetics of the exchange process seem to be fairly localized in nature (as illustrated by the insensitivity to relaxations beyond second-nearest neighbors); we therefore suggest our results apply to an amorphous environment as well.

The main result is that H-H exchange can proceed with an energy barrier of less than 0.2 eV. The first part in the process consists of an interstitial H atom approaching the Si-H bond, resulting in a hydrogen in a bond-center (BC) site next to the Si-H bond. The H-H exchange then proceeds via an intermediate, metastable state, in which *both* H atoms are equally bonded to the Si atom, a configuration which we label $\equiv SiH_2$. In this configuration the two atoms can easily rotate; the H atom that was originally deeply bound can then jump to a BC position and diffuse away, completing the exchange.

Figure 1 displays the exchange process schematically. Note that Figure 1 includes neither all the atoms of the supercell nor all the atoms relaxed in our simulations. We use the following notation: hydrogen at a bond-center site is labeled H-BC; for the isolated dangling bond we use DB, and if it is passivated by hydrogen we use H-DB or Si-H, interchangeably; for hydrogen in a BC site next to a DB site, we use (H-BC,H-DB); finally, if H-BC is far from a DB site we use (H-BC)+(H-DB).

Figure 1(a) is a schematic of the fully relaxed (H-BC,H-DB) complex which is the starting point for the exchange. The energy of the (H-BC,H-DB) complex is 0.15 eV higher than the energy of (H-BC)+(H-DB). This modest increase in energy does not constitute much of a barrier for an interstitial H atom to approach the Si-H bond.

The exchange of the H-BC with the H-DB involves a concerted motion of the two H atoms, along with relaxations of all the Si atoms. First, we move the H atom from BC towards H-DB, fixing this H at a number of positions along a path labeled "Path I" in Fig. 1(a). Path I leads to an intermediate $\equiv\text{SiH}_2$ configuration, as shown in Fig. 1(b). The energy barrier along Path I is ~ 0.06 eV. Our calculations for this configuration established that $\equiv\text{SiH}_2$ is actually a metastable configuration (i.e., a local minimum in the energy surface).

The energy of the $\equiv\text{SiH}_2$ complex is 0.01 eV lower than the (H-BC,H-DB) complex. An investigation of the electronic structure reveals that along path I the highest occupied eigenlevel descends from near the conduction-band edge to near mid-gap, at which point the eigenstate is localized on the silicon and both hydrogens. We found that the H atoms in the $\equiv\text{SiH}_2$ complex can "rotate" with relative ease around the [111] direction of the original Si-H bond, as sketched in Fig. 1(b). We calculated the energy barrier for the re-orientation of the $\equiv\text{SiH}_2$ complex to be smaller than 0.04 eV. To complete the exchange, the original H-DB moves into a BC site along a path which, by symmetry, is the reverse of path I, with the same energy barrier.

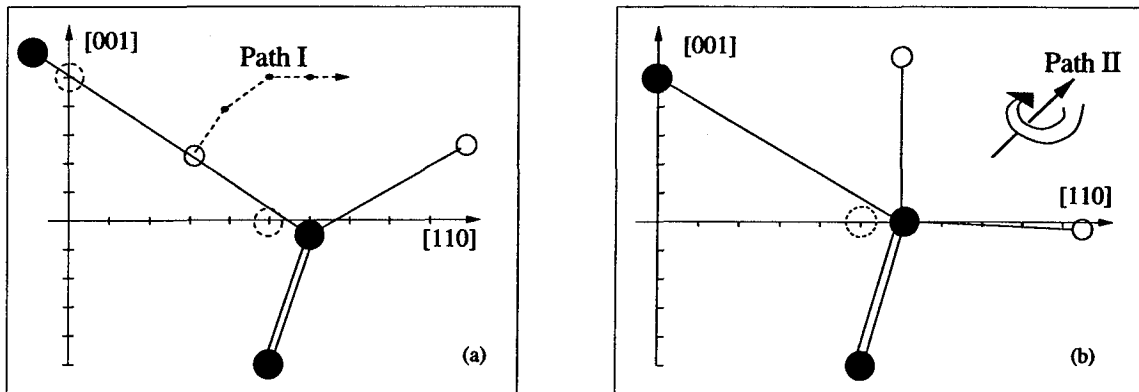


Figure 1: Schematic illustration of the hydrogen-hydrogen exchange process. A dangling bond at atom Si2 passivated by a H atom (H-DB). The small open circle represents a hydrogen atom; the large filled circles represent silicon atoms. The solid lines represent bonds in the plane of the page [the $(1\bar{1}0)$ plane]; the double lines indicate bonds to the Si3 and Si4 atoms, which lie in front of, resp. behind, the plane of the page. (a) The bond-centered H atom moves by the path labeled I towards the dangling-bond region, resulting in a metastable $\equiv\text{SiH}_2$ complex. The dotted circles represent the initial position of the silicon atom. The solid circles show the position of the Si atoms in the (H-BC,H-DB) complex. (b) In the $\equiv\text{SiH}_2$ complex the two H atoms can "rotate" around the [111] direction, as schematically illustrated by Path II. To complete the exchange, the originally deeply bound H atom moves to a new BC position, along a path that is the equivalent of Path I.

Considering the full exchange process, we find that the energy barriers along Paths I and II in Fig. 1 are both smaller than 0.1 eV. Since the migration barrier for interstitial H is about 0.5 eV [4, 25], the barriers along paths I and II can easily be overcome at the modest temperatures at which interstitial H is mobile. The activation energy of the exchange process is therefore dominated by the energy cost of 0.15 eV needed to place the interstitial (transport-level) hydrogen in a (H-BC,H-DB) state.

In the course of our investigations we explored a number of possible paths and exchange mechanisms other than the one reported in Fig. 1. For instance, we examined the possibility that as the H-BC moved towards the dangling-bond region, the H-DB would simultaneously move to one of the two neighboring BC sites. We found that such a process would encounter energy barriers over 0.8 eV. We conclude that having at least one H to passivate the dangling bond at any time is essential to a low-energy exchange. Only mechanisms which consistently maintain at least one H passivating the dangling bond will be competitive with those reported in Fig. 1.

It should be noted that our calculations apply to *neutral* interstitial H exchanging with a deeply bound H. Interstitial hydrogen can occur in different charge states [4, 5]. In the positive charge state H still prefers the BC site, and we expect only minor modifications to the exchange path described above. In the negative charge state, H prefers to sit in open interstitial positions, and the exchange mechanism (if present) may be quite different.

Exchange: experiments

Detailed experimental information about the exchange process in amorphous silicon has been obtained in hydrogen-deuterium tracer diffusion experiments in *a*-Si:H(D) [29, 30]. To explain the data, Branz *et al.* found it essential to take deep trap levels into account, in addition to shallow traps and a transport level; in addition, it was found that (1) there is significant exchange between the transport level and the deeply trapped hydrogen and (2) the energy barriers for H-H(D) exchange are much smaller than the barriers for long-range diffusion (1.5 eV). Kemp and Branz [30] proposed that H-D (or H-H) exchange occurs via an intermediate state with two H atoms bonded to a Si atom, i.e., where the Si atom is over-coordinated. They also noted that the energy of this intermediate state has to be nearly degenerate with the energy of an isolated Si-H plus a transport-level hydrogen. The properties of the $\equiv\text{SiH}_2$ emerging from our calculations are entirely consistent with the mediatory complex suggested by Kemp and Branz [30]. We find an energy difference of 0.14 eV between $\equiv\text{SiH}_2$ and (H-BC)+(H-DB). The consistency of our present results with the experimentally based constraints for hydrogen exchange suggests that we have captured important features of the exchange mechanisms for H in *a*-Si:H.

The $\equiv\text{SiH}_2$ complex and light-induced defect generation

In this study, we have examined the $\equiv\text{SiH}_2$ complex which involves a five-fold coordinated silicon atom. Overcoordination defects are known to be present in bulk silicon; they have also been suggested to be an important intrinsic defect in *amorphous* silicon [6, 34]. The present complex differs from over-coordinated defects found in bulk silicon. In the $\equiv\text{SiH}_2$ complex, the underlying silicon defect is a 3-fold coordinated atom. The overcoordinated silicon complex occurs when two hydrogen atoms are placed in the dangling-bond region. A similarity between the 5-fold coordination defect studied in the context of *a*-Si and the $\equiv\text{SiH}_2$ complex is that both result in a deep level which is rather localized on

several atoms [6, 34, 35].

The $\equiv\text{SiH}_2$ in the *c*-Si model discussed above is a locally stable configuration, but the barrier to go to the (H-BC,H-DB) configuration is less than 0.1 eV high; the $\equiv\text{SiH}_2$ would therefore not be stable for a long time. It is conceivable that certain sites in *a*-Si would provide a slightly greater stability of this complex, due to increased flexibility of the surrounding network.

One might speculate that the $\equiv\text{SiH}_2$ complex will be a precursor for generation of H_2 , leaving a dangling bond behind. In fact, our calculations indicate that such a configuration, in which the H_2 is still close to the dangling bond, is close in energy to the $\equiv\text{SiH}_2$ complex (within 0.1 eV). A full determination of the barrier between the two configurations was beyond the scope of our study; however, preliminary investigations suggested the barrier was about 1.0 eV high [36].

We suggest that the $\equiv\text{SiH}_2$ complex might play a role in defect formation. Since the complex is electrically active, light or free carriers could enhance the dissociation of the complex which may lead to formation of a dangling bond and an H_2 molecule. This H_2 molecule may diffuse away (again potentially assisted by light), leaving behind a dangling bond, i.e., an electrically active defect.

It is well accepted that hydrogen plays a role in light-induced defect formation. Explanations of this effect need to include a mechanism for generating mobile hydrogen (usually attributed to excitation from Si-H bonds due to photo-induced carriers), as well as a mechanism for trapping the hydrogen in the final state. Recently, Branz [37] proposed a model in which two mobile H atoms collide, forming an immobile complex containing two Si-H bonds. Biswas and Pan [38] proposed specific configurations for this final configuration based on molecular dynamics simulations. Here we speculate that H_2 molecules could also be candidates for the final state. Instead of requiring two mobile hydrogens to come together, a single mobile hydrogen (which has left a dangling bond behind) could approach an Si-H bond, forming the $\equiv\text{SiH}_2$ complex. Photo-generated carriers could promote the reaction to form H_2 plus a second dangling bond. The H_2 may then diffuse away from the dangling bond. Alternatively, two mobile H atoms may come together (as in the Branz model) and form an H_2 molecule.

Thermal annealing of light-induced defects proceeds with an activation energy of about 1.1 eV [22]. Recent experiments in *c*-Si (see Ref. [23], discussed above) indicate that annealing at 175°C dissociates most of the H_2 present in a quenched sample; this anneal temperature would be consistent with an activation energy of 1.1 eV.

While this suggestion for H_2 involvement in light-induced defect generation is not nearly as developed as the comprehensive model proposed by Branz [37], we feel that the information that has recently become available about the behavior of H_2 in silicon should prompt a careful examination of the role H_2 may play in defect generation.

Dissociation mechanisms of Si-H bonds; H/D isotope effect

A few years ago it was discovered that Si-D bonds behave very differently from Si-H under electronic excitation: Si-D were found to be orders of magnitude harder to break. This giant isotope effect was first observed for Si-H bonds on Si surfaces [39, 40], and quickly applied to passivation of defects at the Si/SiO₂ interface in MOS transistors [41]. Since hydrogenated amorphous Si suffers from carrier- and light-induced degradation, it should be expected that the observed enhanced stability of Si-D as compared to Si-H would also apply to Si-D bonds in *a*-Si. Experimental observations of the enhanced stability of deuterated

a-Si under light exposure were recently reported by Wei *et al.* [42] and by Sugiyama *et al.* [43]. Replacing hydrogen with deuterium has also been reported to greatly reduce the PL degradation of porous silicon [44].

These observations may seem surprising, because H and D 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. We have proposed a mechanism which provides a natural explanation for the difference in dissociation rates [45]. 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) [46]. 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 [47, 48], efficient vibrational excitation is expected. The question then is: why would Si-D behave qualitatively differently?

The path followed by the hydrogen (or deuterium) atom during the breaking of a Si-H (Si-D) bond turns out to play a crucial role in the dissociation mechanism. It was often implicitly assumed that dissociation would proceed by moving the H atom away from the Si along the direction of the Si-H bond away from the Si atom; 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 2100 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). Both of these arguments actually favor a different path 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 bending mode; (b) this path leads to H positions closer to the Si atom, which are more favorable for H^0 and H^+ in *c*-Si. A detailed examination of these dissociation paths was recently presented in Ref. [49].

The vibrational lifetime is thus mostly controlled by the Si-H *bending* modes, as discussed above. 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} . The latter frequency turns out to be very close to the frequency of bulk TO phonon states at the X point (463 cm^{-1}) [50]. 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. These qualitative differences between H and D have recently been confirmed in tight-binding molecular dynamics studies by Biswas *et al.* [51]. 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.

We also point out that displacements along the “bond-bending path” cause energy levels to be 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 as in a scanning tunneling microscope (STM) desorption experiment; at an Si/SiO₂ interface, during device operation of the MOS transistor; or in *a*-Si, in the form of injected or light-induced carriers.

CONCLUSIONS

In summary, we have discussed a number of areas in which first-principles calculations have recently provided new insights into microscopic mechanisms relevant for hydrogenated amorphous silicon. We pointed out that theory as well as experiments on crystalline silicon indicate that H_2 molecules may play a more important role than previously thought, because they diffuse and dissociate more easily than had been assumed. With relevance for hydrogen diffusion, we have determined a low-energy exchange mechanism between interstitial and deeply bound hydrogen, which requires an activation energy of only 0.15 eV. The microscopic mechanism involves an intermediate $\equiv SiH_2$ complex. Finally, we have discussed dissociation of the Si-H bond and our explanation for the enhanced stability of Si-D.

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