Silicon-hydrogen bonding and hydrogen diffusion in amorphous silicon

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(Received 13 June 1994; revised manuscript received 22 November 1994)

The mechanisms for hydrogen diffusion in amorphous silicon are investigated in the context of first-principles results for silicon-hydrogen interactions. For quantities such as the hydrogen chemical potential and the Si-H bond energy, a comparison between theory and experiment provides insight into the microscopic structures as well as the basics of the diffusion process.

I. INTRODUCTION

Hydrogen passivation of dangling-bond defects leads to a significant improvement in the electronic properties of amorphous Si (a-Si). The behavior of hydrogen in the amorphous material, however, is quite complex and not fully understood. Hydrogen diffusion through the material is known to be affected by the doping level[1] and by the presence of free carriers.[2] In addition, hydrogen motion has been shown to be correlated to the *formation* of both metastable and equilibrium defects.[3] A central process in these phenomena is the breaking of a silicon-hydrogen bond, in which hydrogen is promoted from a stable configuration (in which it is strongly bonded to a Si atom) to a higher-energy interstitial position (in which it is mobile and can easily move through the lattice). A quantitative model of hydrogen bonding and diffusion is complicated by an apparent inconsistency between the experimental data and the expected Si-H energetics. We have recently carried out a comprehensive first-principles investigation of silicon-hydrogen bonding in Si.[4] Here, we build upon those results to address the inconsistent energetics and to identify its origin.

The motion of H through a-Si can be described by a diffusion coefficient

$$D_H = D_0 \exp(-E_A/kT). \qquad (1)$$

In undoped samples, the activation energy E_A is 1.4–1.5 eV; in doped samples the activation energy is smaller, 1.2–1.3 eV.[1] A framework for describing H diffusion through a-Si has been developed by several groups.[5-9] The key energies that play a role in the diffusion process are illustrated in Fig. 1(a). The quantity $E_{\text{Si-H}}$ represents the energy of a Si-H bond. μ_H is the chemical potential of H atoms. E_{BC} is the energy of an isolated interstitial H atom at its most stable site in the network; by analogy with crystalline Si (c-Si) this is taken to be at the bond-center (BC) site.[10] E_S, finally, is the energy corresponding to the saddle point of migration of an interstitial H atom. Figure 1(b) illustrates the expected broadening of the energy levels in hydrogenated amorphous Si (a-Si:H) due to the atomic disorder.[6,7]

The hydrogen chemical potential, μ_H, determines the occupancy of various configurations: states with energies below μ_H are (mostly) occupied with hydrogen, those above are (mostly) empty. The energy difference between mobile hydrogen (energy E_S) and μ_H determines the number of hydrogen atoms that can participate in diffusion. The diffusion activation energy E_A (1.4–1.5 eV in undoped material) should therefore be associated
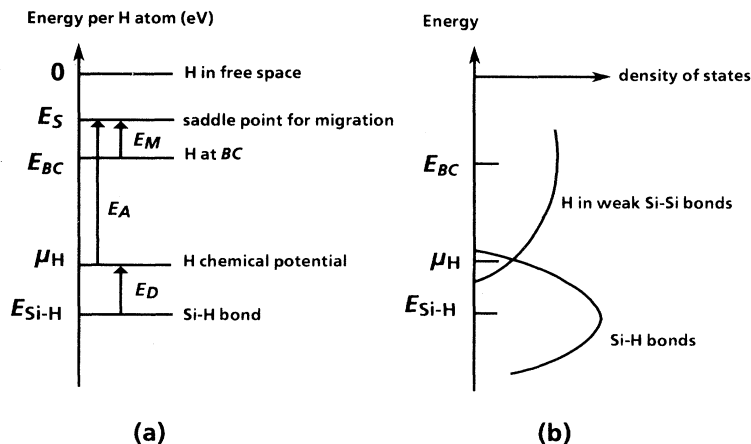

FIG. 1. (a) Energies relevant for H interactions with silicon. The various quantities are described in the text. (b) Schematic hydrogen density of states distribution in a-Si, corresponding to the level scheme in (a). The broadening of the levels is due to the disorder in the amorphous network (after Ref. 6).

with $E_S - \mu_H$.[6]

Estimates about other energies in Fig. 1 can also be made. Hydrogen diffusion experiments in c-Si,[11] as well as H diffusion in a-Si when all deep traps are saturated,[8] indicate that the migration energy $E_M = E_S - E_{BC}$ is about 0.5 eV. On the other hand, first-principles calculations of the adiabatic energy surface[10] indicate that E_M is only about 0.2 eV. We will therefore assume a range of values, 0.2–0.5 eV, for E_M. Analysis of solubility data in c-Si places E_{BC} at about 1 eV below the energy of a H atom in free space,[12] a value which agrees well with a theoretical prediction.[13] Finally, the energy difference between E_{Si-H} and μ_H can be associated with the dangling-bond formation energy, since the removal of H from Si-H results in a dangling bond; measurement of equilibrium defect densities indicated that $E_D = \mu_H - E_{Si-H}$ is about 0.2–0.5 eV.[6,14]

Inspection of these values leads to the energy inconsistency: based on the numbers quoted above, the energy difference between E_{BC} and E_{Si-H} should be around 1.5 eV or less; hence, the energy E_{Si-H} would be less than 2.5 eV below the energy of a free H atom. This energy is much smaller (by more than 1 eV) than one would expect based upon estimates of binding energies of Si-H bonds, e.g., in a silane (SiH$_4$) molecule. Indeed, it takes 3.92 eV to remove the first H atom from an SiH$_4$ molecule (i.e., SiH$_3$-H).[15]

One explanation that has been proposed for this inconsistency assumes that H would predominantly be bonded in strong Si-H bonds on void surfaces, and that transport would take place along these internal surfaces.[16] The transport level would then be ≈ 1.5 eV above the Si-H energy, meaning that it would lie significantly lower than in c-Si (as implied in Fig. 1). Besides the problem that there is no evidence that the void structure in a-Si could allow for long-range diffusion in this fashion, we will see that our theoretical results do not support this mechanism.

In order to examine the validity of the framework described by Fig. 1, and to address the apparent inconsistent energetics, we perform an analysis based upon the values obtained from first-principles calculations. A key result is that the chemical potential derived from the diffusion model agrees with the theoretical calculation, and therefore suggests that the diffusion model is not the source of the energy inconsistency. We have recently performed a comprehensive study of Si-H bonding structures and energetics.[4,13] Those calculations were performed for hydrogen in crystalline Si, and did not explicitly deal with amorphous networks. However, it can be argued that the relevant bonding structures depend mostly on the local environment, and are largely insensitive to the large-scale structure of the network. We, therefore, feel that the first-principles results from Refs. 4 and 13 can be usefully applied to the amorphous case.

The next section (Sec. II) describes the theoretical notions of binding energy and formation energy of Si-H bonds, and establishes a link with the hydrogen chemical potential. Section III discusses the connection with experimental observations, and Sec. IV summarizes the paper.

II. FORMATION ENERGY AND CHEMICAL POTENTIAL

The theoretical values from Refs. 4 and 13 which are relevant for our present investigation are depicted in Fig. 2. We have chosen the zero of energy to correspond to the energy of a neutral H atom in free space. The stable site for the interstitial H is at the bond center (BC),[10] with an energy of -1.05 eV, referred to the energy of a neutral H atom in free space.[13]

The level at -3.55 eV corresponds to the energy required to remove a hydrogen atom from an ideal Si-H bond, leaving a dangling bond behind. This quantity can be associated with the *binding energy* of H to a dangling bond. It is derived by calculating the energy for a Si-H bond in a Si environment, and subtracting the energy of the same configuration with the H removed (which results in a dangling bond). This theoretical definition of the level indicates that it is equivalent to the E_{Si-H} level defined above. For the purpose of calculating this quantity, we placed the Si-H bond in a configuration in which there is no interaction with other H atoms. A hydrogenated vacancy would not fulfill this condition, since the H atoms are close enough together to experience H-H repulsion effects;[4] the "ideal" value was, therefore, calculated for a void configuration. This energy at -3.55 eV is actually quite similar to the energy for H at a dangling bond on a Si(111) surface [for which we found a theoretical value of -3.60 eV (Ref. 13)]; it is somewhat smaller than the value in an SiH$_4$ molecule (3.92 eV, Ref. 15).

A key energy value, not previously considered, is the *formation energy* of a Si-H bond, referred to bulk Si. We will show that this value is directly connected to the hydrogen chemical potential. This energy is listed in Fig. 2 at -2.17 eV, and is derived by calculating the energy for the Si-H bond embedded in a Si environment, and subtracting the energy of the H atom and of the Si atoms, assuming that all Si atoms are part of a bulk environment. The difference with the binding energy discussed above is that the energy of the dangling bond does not enter into the calculation here. Note that the difference between the binding energy and the formation energy is $-2.17 - (-3.55) = 1.38$ eV; this value constitutes an es-
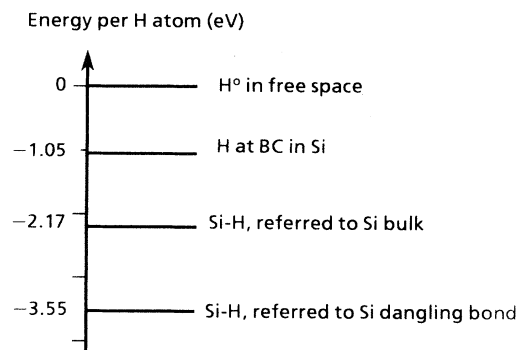
Energy per H atom (eV)

FIG. 2. Selected first-principles energies for Si-H bonds in Si, from Refs. 4 and 13. The zero of energy corresponds to a free H atom.

timate for the formation energy of a dangling bond in c-Si.

We now argue that this value for the formation energy of an Si-H bond, referred to bulk Si, can be associated with the position of the hydrogen chemical potential, μ_H. To understand the connection, we need to describe the significance of μ_H in the case of a-Si. First of all, it is important to realize that μ_H should *not* be located at E_{Si-H}, which is the energy level corresponding to Si-H bonds. Instead, the chemical potential will be located at an energy which corresponds to a minimum in the density of states. The density of states illustrated in Fig. 1(b) has contributions from two types of states: around E_{Si-H}, there is a distribution of Si-H bond energies; at higher energies, we find a distribution of energies for interstitial hydrogen, associated with distortions in weak Si-Si bonds. Hydrogen can move between these two types of configurations: starting from an Si-H bond, hydrogen can move into a weak Si-Si bond, leaving a dangling bond behind. Thus,

$$Si-H \leftrightarrow Si-H-Si + Si_{db}, \qquad (2)$$
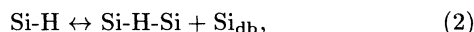
where "db" stands for dangling bond. The Si-H-Si bond can, in turn, convert to a Si-H bond plus a dangling bond; this does not affect the discussion here.

The chemical potential μ_H has to be located at a minimum in the density of states, between the weak-bond and Si-H bond levels. This follows from an energy-minimization argument: if μ_H were higher, a larger number of H atoms in weak Si-Si bonds would be formed, costing energy; if μ_H would be lower, additional H atoms would be removed from Si-H bonds, creating dangling bonds, which also costs energy. The minimum energy situation therefore occurs for μ_H located at the minimum in the density of states. This location is consistent with the observation that a-Si contains a relatively low number of dangling bonds; most bonds in the structure are satisfied, either because they are part of Si-Si bonds or by forming Si-H bonds. Furthermore, this location of μ_H corresponds to the condition that the formation energy of a Si dangling bond in a-Si:H is zero. Indeed, μ_H lies at the level where the formation energy of a Si-H-Si bond is equal to the formation energy of a Si-H bond; if we associate an energy with each of the terms in Eq. (2), this leads to the conclusion that the formation energy of the Si dangling bond in a-Si:H must be zero.

This connection between μ_H and the energy level where the formation energy of a Si dangling bond in a-Si:H is zero immediately provides a connection with Fig. 2, where we found that the level at -2.17 eV corresponds to zero formation energy for the dangling bond. Our arguments in the preceding paragraphs have shown that the hydrogen chemical potential, μ_H, corresponds to the level where the formation energy of the dangling bond in a-Si:H is zero. We thus find that μ_H should be identified with the level corresponding to the formation energy of an Si-H bond, which we calculated to be at -2.17 eV. This immediately allows us to derive a theoretical value for the activation energy E_A: $E_A = E_S - \mu_H = (E_S - E_{BC}) + (E_{BC} - \mu_H) = [0.2...0.5] + (1.12) = [1.32...1.62]$ eV, where the range takes into account the uncertainty in $E_S - E_{BC}$. We note that this value agrees well with

experimental numbers for the diffusion activation energy, E_A.

It is interesting to note that the formation energy of the Si-H bond is actually very close to the calculated formation energy of the Si-H bond on the Si(111) surface $(-2.14$ eV), as well as to the formation energy of SiH$_4$ $(-2.22$ eV), all expressed with respect to Si bulk.[13] The consistency of all of these values strengthens our identification of this level with the hydrogen chemical potential. We also note that placing μ_H at -2.17 eV is in good agreement with a rough estimate made in Ref. 7 based on an entirely different approach.

III. DISCUSSION

Our identification of the energy level corresponding to the chemical potential μ_H is consistent with the experimental activation energy. However, it seemingly leads to a different problem, namely, the fact that the energy difference between μ_H and E_{Si-H} becomes equal to $-2.17 - (-3.55) = 1.38$ eV, i.e., the formation energy of a dangling bond in c-Si. This value is unphysically large for a-Si for two reasons: (1) In order for the assumption of thermal equilibrium to be valid, hydrogen needs to be able to redistribute among the various states at the temperatures of interest; an energy of 1.38 eV would be too large to allow exchange of hydrogen between Si-H bonds and the chemical potential at typical diffusion temperatures. (2) The dangling-bond creation process in a-Si involves excitation of a H atom out of an Si-H bond, which once again would cost 1.38 eV; however, experimental observations give a value below 0.5 eV.[14]

Both concerns can be addressed by establishing that the E_{Si-H} level is *higher* in a-Si than in c-Si. We apply the following arguments.

(1) The value of 1.38 eV was derived for a dangling bond in *crystalline* silicon; the value in *amorphous* Si can be significantly lower. To our knowledge first-principles calculations of the formation energy of a dangling bond in a-Si are lacking; however, empirical-potential simulations[17] produced a dangling-bond formation energy of 0.6 eV, i.e., substantially lower than the value in c-Si.

(2) The E_{Si-H} energy in c-Si corresponds to a single level; in a-Si, however, disorder causes broadening [as schematically indicated in Fig. 1(b)]. Excitation of a hydrogen out of a Si-H bond can occur out of each of the states in this broadened distribution, and states with energies closer to μ_H will be easier to excite.

(3) The calculated E_{Si-H} energy at -3.55 eV corresponded to a Si-H bond at which the H is sufficiently far from any other H atoms to avoid repulsion. H-H repulsion raises the E_{Si-H} energy; for instance, in a hydrogenated vacancy in c-Si H-H repulsion raises the Si-H binding energy by 0.4 eV.[4] Evidence of hydrogen clustering, which would contribute to repulsion effects, exists in a-Si:H.[18,19]

(4) In addition, mechanisms that facilitate the interchange between states at E_{Si-H} and μ_H can be invoked. For instance, exchange of diffusing H atoms with

H bonded in Si-H atoms may occur with lower activation barriers than needed for excitation of a single H out of an Si-H bond; evidence for such a mechanism was found in experiments, where deuterium was exchanged with hydrogen.[20] In addition, we have found that the barrier for dissociation of a Si-H bond may be significantly reduced in the presence of free carriers.[4] The *suppression* of H diffusion when the free carrier density is reduced[2] is consistent with this mechanism.

IV. SUMMARY

In summary, we have provided specific definitions for various quantities that enter in the description of hydrogen diffusion in a-Si, and we have associated calculated values from first-principles theory with these quantities. The hydrogen chemical potential μ_H is associated with the formation energy of Si-H bonds, expressed with respect to Si bulk. The Si-H bond energy level (E_{Si-H}) is placed at a distance below μ_H, corresponding to the formation energy of a dangling bond. We have provided arguments why H atoms can readily move between the μ_H and E_{Si-H} levels in a-Si, thus maintaining the equilibrium picture that underlies the description of diffusion. The resulting framework is consistent with experiment, and obviates the need for more contrived explanations, such as diffusion along interconnected void surfaces. While explicit first-principles calculations on amorphous networks are still necessary to obtain the specifics of the energy distributions, the basic identification of the observed quantities with calculated numbers has now been accomplished.

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