RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 51, NUMBER 4 15 JANUARY 1995-II

Energetics of bond-centered hydrogen in strained Si-Si bonds

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(Received 31 August 1994; revised manuscript received 1 November 1994)

The energetics of hydrogen incorporation into strained Si-Si bonds are examined using first-principles density-functional-pseudopotential calculations. It is found that an increase in the bond length of the initial Si-Si bond leads to a lower formation energy for the Si-H-Si configuration. A simple linear relationship, describing the change in formation energy as a function of the Si-Si bond length, is presented, which applies to bond-stretching as well as bond-bending distortions. The results are discussed in the context of hydrogen interaction with grain boundaries in polycrystalline silicon.

Hydrogen is extensively used for passivating deep levels in semiconductors. Hydrogenated amorphous silicon (a-Si:H) is probably the most widespread and well-known application. Hydrogenation is also employed to reduce the defect density in polycrystalline silicon (poly-Si).[1] However, unlike the a-Si case where H is incorporated during growth, dangling-bond defects in poly-Si are passivated by posthydrogenation at elevated temperatures.[2] Recent investigations[3] have revealed an unexpected richness in the phenomena associated with hydrogen in poly-Si, indicating that the behavior of hydrogen extends beyond the simple passivation of dangling bonds. One key experiment was performed on undoped samples that have been hydrogenated until the defect density saturated at a minimum value. It was found that annealing around 160 °C followed by a quench to low temperature produces an enhancement in the conductivity. This enhancement is metastable and decays with time. The temperature dependence of the decay rate indicates that the activation energy for the decay process is $E_A \approx 0.74$ eV. This activation energy allows for the metastable state to have a lifetime on the order of hours at room temperature.[3]

These observations are consistent with a model in which quenching leads to the trapping of H in an electrically active metastable state. The decay of the conductivity is then associated with the release of H from the metastable configuration. The H that is released from the traps returns to a lower-energy state (see Fig. 1); this "reservoir" of H was found in Ref. 3 to have an energy 0.35 eV below that of the metastable state. In this paper we will focus on the microscopic nature of the metastable state. The interactions of H with Si have been investigated in detail;[4] the configurations in the relevant energy range are shown in Fig. 1 (configurations with energies below -2.15 eV are not included in the figure). An isolated, neutral H interstitial in Si resides at the bond-center (BC) site, with an energy 1.05 eV below the energy of H in free space. In this configuration hydrogen acts as a donor, with a level about 0.2 eV below the conduction band.[5–7] The activation energy E_A mentioned above corresponds to the energy difference between the metastable state and the saddle point of the migration path of an interstitial H atom. This saddle point occurs at an energy E_M above the level of the H interstitial at the BC. The activation barrier for migration can be estimated to be between 0.2 and 0.5 eV (the lower number resulting from a first-principles calculation of an adiabatic energy surface,[7] the higher number from high-temperature diffusion experiments[8]). We thus find that the energy of the metastable state is between -1.6 and -1.3 eV.

According to Ref. 4 and Fig. 1 the stability of most Si-H configurations is such that activation energies much higher than 0.74 eV would be required to release hydrogen. In fact, the only configuration which allows for hydrogen to escape at room temperature or below is that of an isolated, interstitial H atom at the BC. In crystalline Si (c-Si), the stability of the BC hydrogen has been derived from deep-level transient spectroscopy (DLTS) measurements. It was found that the BC configuration is only stable at temperatures below 100 K.[5]

In this paper we investigate whether variations on the basic bond-center configuration are possible, which provide a higher stability, and would lower the energy of this configuration to fall in the range from -1.6 to -1.3 eV. The stability of the bond-center configuration arises from the formation of a three-center bond between the H atom and the two Si neighbors.[9] Hydrogen prefers the bond-center location, because the positively charged proton is Coulombically attracted to the high negative charge density due to the electrons in the bond. At the same time, however, the stability is

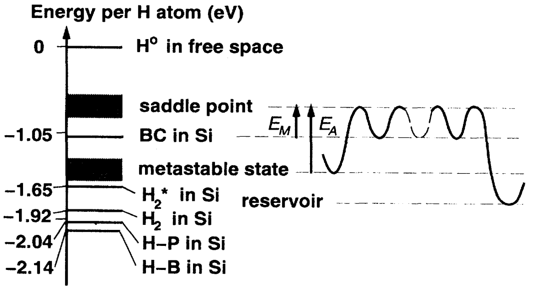

FIG. 1. Schematic diagram depicting first-principles energies of various configurations of hydrogen in silicon, as well as energy as a function of position. The saddle point for migration lies $E_M = 0.2-0.5$ eV above the level of H at the BC. The activation energy $E_A \approx 0.74$ eV obtained from the experiments in Ref. 3 is the energy difference between the metastable configuration and the saddle point. The energy of the metastable state therefore lies between -1.6 and -1.3 eV.

0163-1829/95/51(4)/2636(4)/$06.00

reduced due to the geometric constraints imposed by the surrounding network: in order to provide reasonable Si-H bonding distances, the Si atoms have to move outward from their regular lattice sites in c-Si, raising the elastic energy. Hypothetically, 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. While this hypothesis is incompatible with the nature of pure c-Si, it is an attractive possibility in the case of poly-Si, where bond distortions near the grain boundaries are known to provide a variety of Si-Si bond distances.

It is the purpose of the present paper to quantify the increase in stability of the bond-center configuration as a function of the bond distance in distorted Si-Si bonds. A previous study by Tarnow and Street[10] addressed one aspect of this problem, namely, the effect of shear strain, which was felt to be more appropriate to model bond-angle distortions in a-Si. In the present work we investigate bond-length variations as well as bond-angle variations. We also employ a different geometry in the calculations.

We investigate the stability of the bond-center configuration in a theoretical framework based on pseudopotential-density-functional theory in a supercell geometry; details of the computational approach were discussed in Ref. 7. The calculations are carried out with an energy cutoff of 12 Ry; tests at 18 Ry indicate that the calculated relaxations are essentially converged, and that the differences in formation energy are accurate to within 0.1 eV (and much better than that, for small displacements). Here we are interested in finding out how much the energy of the bond-center configuration is lowered if the Si-Si bond into which the H atom is introduced is initially distorted. This distortion can take two forms: (a) a bond-length distortion, in which the separation between the two Si atoms is increased, while maintaining the orientation of the bond; or (b) a bond-angle distortion, in which the two Si atoms are displaced relative to each other along a direction perpendicular to the bond.

We have chosen the following geometry (illustrated in the inset of Fig. 2) to investigate these distortions: we cut the crystal along a plane perpendicular to the [111] direction, through the center of the Si-Si bonds. The relative displacements of the Si atoms mentioned above are then accomplished by moving these two halves of the crystal with respect to one another. This implies that we are distorting *all* the bonds which are cut by this plane. Also, when we introduce hydrogen into the Si-Si bond, we are introducing it in *all* the bonds which cross this particular (111) plane. This geometry will serve as an adequate approximation for the study of a single Si-H-Si bond, if we can show that the interaction between H atoms in neighboring bonds is small.

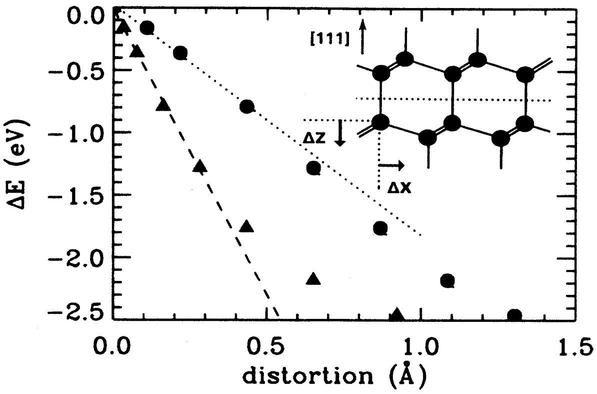

FIG. 2. Lowering in formation energy of the bond-centered Si-H-Si configuration, for a bond-length distortion, as a function of *initial* distortion (circles) and as a function of the change in the *relaxed* bond length (triangles). For small distortions the calculated points can be described by linear fits: 0.18 eV per 0.1 Å (dotted line) and 0.46 eV per 0.1 Å (dashed line). Inset: schematic representation of the configuration used to study incorporation of H into strained Si-Si bonds. A projection of the Si network onto a (110) plane is shown, with the [111] direction along the vertical. Bond distortions are introduced by cutting the crystal along a (111) plane (indicated by dotted lines), and moving the upper half of the crystal with respect to the lower half. The coordinates describing these displacements (Δz for bond stretching and Δx for bond bending) are indicated. Hydrogen incorporation is in the [111] oriented bonds at the interface between the two crystal halves.

The quantity we are interested in is the *difference* in formation energy between H in a Si-Si bond in bulk Si, and in a strained Si-Si bond. The formation energy is defined as the energy difference between the Si-H-Si configuration, and bulk Si plus a free H atom. The formation energy in bulk c-Si serves as the reference with respect to which the changes in formation energy as a function of distortion will be expressed. Since these results involve a *difference* in energies between configurations which both include a hydrogen interaction term, the H-H interaction effects should largely cancel. We have also compared our results for bond-angle strains with those of Ref. 10, which were obtained for an isolated Si-H-Si bond in a 32-atom supercell, and found them to be in good agreement. Finally, we have performed calculations for bond-length distortions in 32-atom supercells with a geometry similar to that employed in Ref. 10, for which interactions between H atoms should play no role. The results are essentially the same as those presented below.

To maintain periodicity in the calculations, the actual geometry is that of a superlattice along the [111] direction. The superlattice included 12 Si atoms and zero or one H atoms. For each configuration, the formation energy was determined by subtracting the energies of the calculations with and without H. This formation energy was then compared with the formation energy of the undistorted configuration. The inset of Fig. 2 defines our choice of coordinates for the various types of distortions investigated here. In the case of a shear strain ($\Delta x \neq 0$) periodicity can only be maintained if *two* interfaces are created in the supercell: one with the Si-Si bonds into which the H atoms are introduced, the other with distorted Si-Si bonds. The latter interface is present in both calculations, with and without hydrogen, and its influence on the formation energy therefore cancels out. For each of the distortions, only the first-nearest-neighbor Si atoms are allowed to relax, both in the absence and in the presence of the H atom.

Figure 2 summarizes our results for bond-stretching distortions. In this case, the Si atoms are displaced along the original bond direction, and the change in the Si-Si bond length, prior to relaxation, is given by Δz (see inset). The circles in Fig. 2 indicate results for the change in formation energy expressed as a function of this *initial* distortion in the Si-Si bond length. If we allow relaxation, the Si atoms around the interface of course tend to move closer together, in order to try and restore the original Si-Si bond length. After relaxation, the change in the bond length will therefore be smaller than given by the *initial* distortion; the triangles in Fig. 2 indicate results plotted as a function of the distortion in the *relaxed* bond length. For the configuration with H inserted in the bond, the Si atoms are of course also relaxed. The change in formation energy, ΔE, is always calculated using energy values for relaxed configurations, both in the absence and in the presence of hydrogen.

For displacements up to $\Delta z = 0.3$ Å (which will turn out to be the physical range of interest), the behavior can be adequately described by a linear fit. Within the accuracy of the calculations, one finds a change in formation energy of 0.18 eV per 0.1 Å of increase in the *initial* (unrelaxed) bond length. In a realistic situation (such as around a grain boundary) one would start from prestrained Si-Si bonds whose *relaxed* bond length is (at least theoretically) known, and one would like to estimate the lowering of the Si-H-Si formation energy as a function of the distortion in this relaxed bond length. As discussed above, this dependence is shown by the triangles in Fig. 2. Once again, we note that for small displacements the points roughly fall on a straight line, where now we find a change in formation energy of 0.46 eV per 0.1 Å of increase in the Si-Si bond length.

It is relevant to ask whether the symmetric Si-H-Si configuration (with H on the bond axis, midway between the two Si atoms), which was the lowest energy state in unstrained c-Si, would undergo any modification in the case of prestrained bonds. While it is safe to assume that H will remain on the bond axis, we have investigated whether the H might prefer to bond to one of the Si atoms preferentially, a tendency which looks plausible in the case of larger Δz values. We found no tendency for the H to assume an asymmetric position, as long as $\Delta z < 0.8$ Å (or $\Delta d < 0.4$ Å), which will turn out to be the range of interest for the grain-boundary problem.

Let us now turn to bond-angle distortions, described by the parameter Δx (see inset of Fig. 2). Here our results are in general agreement with the work of Tarnow and Street.[10] Therefore we focus on the small-displacement regime ($\Delta x < 0.6$ Å), which was not investigated in detail by Tarnow and Street. Larger displacements also favor asymmetric incorporation of the H atom, which is outside the scope of the present investigation. We have only considered distortions for which $\Delta x > 0$; in accordance with Ref. 10, we found such distortions to be more favorable than those with the opposite sign. The calculations show that the lowering in formation energy of the bond-centered Si-H-Si configuration as a function of the coordinate Δx can be described by a parabolic fit: $\Delta E = -0.4(\Delta x)^2$.

It is more illuminating to plot the results for bond-angle distortions as a function of the increase in bond length caused by the initial displacement Δx; the resulting values are shown in Fig. 3. Once again, the circles indicate the change in formation energy as a function of the *initial* change in bond length; the triangles show the change in formation energy as a function of the change in the *relaxed* bond length. The dotted line is a linear fit to the calculated points for *initial* distortions, corresponding to a change in formation energy of 0.20 eV per 0.1 Å. The dashed line is the corresponding fit as a function of change in *relaxed* bond length, leading to a gain of 0.40 eV per 0.1 Å distortion. Both of these fits are remarkably close to the case of bond-stretching distortions. These results allow us to reach the conclusion that, for small displacements, no matter what the origin of the increase in bond length (be it pure bond stretching or bond bending), the formation energy of the Si-H-Si bond will be lowered by ~0.2 eV per 0.1 Å of *initial* displacement, or about ~0.4–0.5 eV per 0.1 Å of distortion in the *relaxed* Si-Si bond.

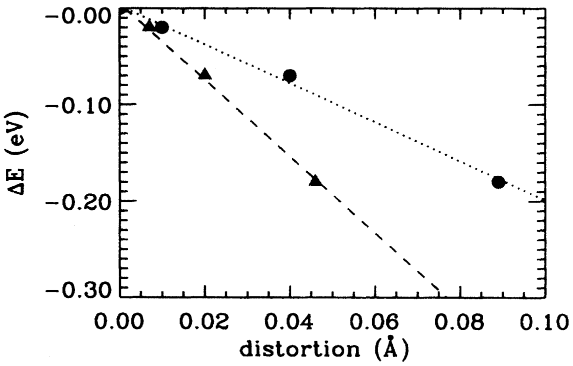

FIG. 3. Lowering in formation energy of the bond-centered Si-H-Si configuration, for a bond-angle distortion, as a function of *initial* (unrelaxed) distortion in Si-Si bond length (circles), and as a function of the change in the *relaxed* bond length (triangles) of the Si-Si bond. For small displacements, the calculated points can be described by linear fits: 0.20 eV per 0.1 Å distortion (dotted line), and 0.4 eV per 0.1 Å change in the relaxed bond length (dashed line).

Now that we have obtained quantitative results for the bond-energy lowering of the Si-H-Si bonds as a function of the distortion of the initial Si-Si bond, it is relevant to inquire about the distribution of bond distortions in practical samples. To our knowledge, this type of detailed information has not yet been obtained experimentally, and first-principles theoretical studies have only been carried out for grain boundaries in Ge.[11,12] For the $\Sigma 5$ and $\Sigma 5^*$ twist boundaries, an *ab initio* molecular dynamics approach produced optimized geometries, for which the distribution of bond lengths was then examined. Atoms in the first layer near the boundary were found to exhibit nearest-neighbor bond lengths ranging from 2.2 Å to more than 2.8 Å; the equilibrium bond length in Ge is 2.45 Å. The distribution was asymmetric, with stretched bonds outnumbering compressed bonds. We note that first-principles calculations have also been carried out for 90° partial dislocations in Si;[13] one may expect that the features of the atomic geometry around dislocations bear some similarity to those around grain boundaries. The results of Ref. 13 indicate that, once again, there is a tendency for bonds to be stretched, by amounts that can exceed 5% of the bond length (i.e., larger than 0.1 Å).

While the statistics on the few cases that have been explicitly computed are insufficient to derive quantitative results, we can clearly draw the qualitative conclusion that the microscopic atomic structure near grain boundaries includes a significant number of bonds with bond lengths exceeding the bulk bond length. Changes in the bond length of 0.1 Å seem common; our theoretical results then indicate that the formation energy of a hydrogen atom inserted in such a stretched bond would be lowered by 0.4–0.5 eV; this is precisely the amount needed to bring the formation energy in the range where it could explain the experimental observations of Ref. 3.

The Si-H-Si configuration has been identified as a donor in *c*-Si, with an energy level approximately 0.2 eV below the conduction band.[5–7] We find that this configuration continues to behave as a donor state if the Si-Si bonds are strained prior to inserting H. However, the donor level moves away from the conduction band as the bond becomes distorted, at a rate of ~0.1 eV per 0.1 Å change in the (relaxed) bond length of the Si-Si bond. The experiments of Ref. 3 are not expected to be sensitive to the precise position of the donor level; indeed, the modification in the conductivity occurs through the introduction of charged defects at the grain boundary, which affect the depletion layers and hence the potential barriers at the boundaries (see Ref. 14).

In summary, we have performed a first-principles investigation of the incorporation of H atoms into strained Si-Si bonds. We find that the distorted structures with an increased bond length exhibit a lower formation energy (i.e., greater stability) for the Si-H-Si configuration. For small bond distortions, caused by either bond stretching or bond bending, the lowering in formation energy can be described by a linear relation: 0.2 eV per 0.1 Å of *initial* increase in the bond length, or 0.4–0.5 eV per 0.1 Å increase in the *relaxed* bond length. For typical distortions in bond lengths near grain boundaries, we find that the formation energy of Si-H-Si bonds is lowered to the point where this configuration is consistent with the observations on electrically active metastable states in poly-Si.

This work was supported by NREL. N.H.N. is pleased to acknowledge partial support from the Alexander von Humboldt Foundation, Federal Republic of Germany.

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