Proton Diffusion in Crystalline Silicon

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An *ab initio* molecular-dynamics simulation of high-temperature proton diffusion in crystalline silicon is presented. This is the first time dynamical effects have been included explicitly in the simulation of this system. We find that the diffusion proceeds via a jumplike mechanism. Because of dynamical effects the diffusion path is substantially different from that inferred from static total-energy calculations. The calculated diffusion coefficient and its temperature dependence are in good agreement with the available experimental data. It is suggested that scattering experiments may distinguish between different diffusion paths.

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The behavior of hydrogen in crystalline silicon (*c*-Si) has been the object of extensive experimental and theoretical investigations because of its technological importance, arising mostly from the ability of H to passivate defect-related electronic states.[1]

A detailed microscopic understanding of the H diffusion process represents a basic achievement toward a general interpretation of the phenomena associated with its incorporation into *c*-Si. However, a controversial picture emerges from the available experimental data on the equilibrium sites[2-4] and diffusivity,[5-9] and the ability of theoretical calculations to clarify these issues has been limited.

Equilibrium sites have been investigated by means of channeling experiments on implanted deuterium samples.[2,3] These results show a dependence on deuterium preferred sites from temperature implantation and/or annealing treatment. Nevertheless, at low temperature in as-implanted samples, H appears to be mainly located at the bond-center (BC) site.[3] However, the interpretation of these data is difficult due to the large amount of damage induced by the high-energy implantation (10-13 keV). Indirect support to the BC configuration comes from the muon-spin-rotational spectra for anomalous muonium recently presented by Kiefl *et al.*[4]

A controversial picture emerges from measurements of diffusion coefficients performed with various techniques.[1] Especially in the low-temperature regime (<800 K) the data show a spread of orders of magnitude,[5-8] as is evident in Fig. 1 where some of these data are reported. In the high-temperature regime ($T>1000$ K) the only existent data are, to our knowledge, those of Van Wieringen and Warmoltz[9] (VW). These authors found by a direct permeability measurement that the diffusing species consisted mainly of atomic hydrogen, either neutral of positively charged, with a very high mobility ($D \simeq 2\times10^{-4}$ cm^2/sec at $T \simeq 1470$ K) and a thermal activation barrier of 0.48 eV within a 10% error. Different estimates of the thermal activation barrier in the range 0.6-0.8 eV have been given by other authors,[5,10] using data at lower temperatures. These data correspond to diffusion coefficients that are orders of magnitude smaller than the values obtained by extrapolating to low T the VW data. Very recently, however, Seager and Anderson[8] presented low-temperature (around 300 K) diffusivity data that agree with the Arrhenius extrapolation of the VW results. These data would confirm the high mobility of H in Si. The above discussion once again demonstrates the difficulty in interpreting the experimental data, and underlies the necessity for a deeper theoretical understanding of the phenomena.

A large theoretical effort based on cluster[11,12] and supercell[13] calculations has been recently devoted to the prediction of the energetically favored sites at zero tem-

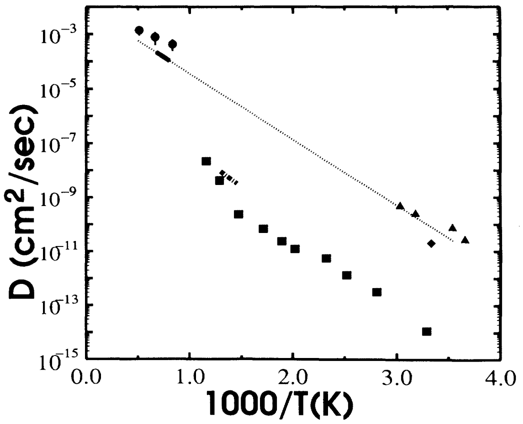

FIG. 1. Diffusion coefficient for hydrogen in *c*-Si as a function of inverse temperature. Solid circles: present calculation for H$^+$. Error bars are indicated by vertical bars. Solid line: $D=9.41\times10^{-3}\exp[(-0.48\text{ eV})/k_BT]$ cm^{2}sec^{-1} as obtained by VW (see text) in the temperature range 1240-1480 K; extrapolation outside this range is given by the dotted line. Dash-dotted line: $D=4.2\times10^{-5}\exp[(-0.56\text{ eV})/k_BT]$ cm^2 sec^{-1}, tritium diffusion from data in the temperature range 670-770 K (Ref. 5). Squares: experimental data from Ref. 6. Diamond: experimental measurement at room temperature from Ref. 7. Triangles: experimental diffusivity values in Au Schottky-barrier sample (Ref. 8).

perature. The most relevant result of these calculations is that hydrogen, in both the H^+ (Refs. 12 and 13) and H^0 (Refs. 11–13) charge state, prefers to sit in regions of high valence charge density (HD region). In this region the energetically favorite location is the BC site, according to all of the calculations. The rather accurate investigation of Ref. 13 reports the M (Ref. 14) site to be almost degenerate in energy with the BC one. All of the HD configurations are characterized by a large relaxation of the Si atoms close to hydrogen. In contrast, for hydrogen situated in sites lying in the low-valence-charge-density (LD) region only small distortions are induced. These site, however, are energetically unfavorable being, on average, at an energy more than 0.5 eV higher than the HD sites.[13]

On the basis of these $T=0$ calculations prediction of the diffusion path and of the thermal activation energy has been attempted. In particular, for H^+ the authors of Ref. 13 predict that the most likely diffusion path connects adjacent BC sites through the intermediate C (Ref. 15) site. The energy barrier for this path is estimated to be less than 0.2 eV. Note that the predicted diffusive path lies entirely in the HD region and is accompanied by a large and concerted ionic relaxation. The LD-region paths which lead to small ionic distortions were discarded as energetically unfavorable.

However, it is very difficult to infer unambiguously from static calculations the dynamical behavior of H. In addition, a theoretical prediction of the value of the diffusion coefficient has never been attempted so far, making a direct contact with experiment difficult. For this reason we have performed an *ab initio* molecular-dynamics[16] (MD) simulation of H in *c*-Si. Although H in Si can exist in various charge states, here we confine ourselves to consideration of the H^+ case only, which has been argued[8,13,17] to be the dominant one in a *p*-doped material. We consider only the high-temperature regime where quantum effects are negligible. Our main conclusions are as follows: (i) The diffusion mechanism is jumplike between highly symmetric interstitial sites. (ii) The compound diffusion coefficient D is in agreement with the VW high-temperature experimental data. (iii) The inclusion of dynamical effects substantially modifies, at least in the high-temperature regime, the picture of the diffusive paths inferred by $T=0$ total-energy calculations.

As discussed at length in Ref. 16(b) the *ab initio* MD method allows one to combine a statistical mechanical approach, necessary to obtain dynamical information, with the accuracy of the state-of-the-art electronic structure calculations in the computation of the interatomic forces. In our simulation both the proton and the silicon atoms are treated as classical particles. We use a periodically repeated fcc supercell containing 128 silicon atoms and 1 proton. Full details of the calculation will be given elsewhere.[18] We fix the lattice constant at $a=5.43$ Å. *Ab initio* norm-conserving pseudopotentials of the Kleinman-Bylander[19] form were constructed from the pseudopotentials of Ref. 20 retaining s nonlocality only for silicon and treating H as purely local. Plane waves, for the expansion of Kohn-Sham orbitals, were included up to a cutoff of 6 Ry. The supercell Brillouin zone (BZ) was sampled by the use of the Γ point. The choice of these parameters gives an accurate description of the H^+ energy surface as we have explicitly checked by performing calculations on smaller cells using larger energy cutoffs (up to 12 Ry) and increasing the number of points in the BZ summation. Using the same accuracy of our high-T simulations, the computed $T=0$ energy surface, allowing a full relaxation of the atomic coordinates, is overall similar to that obtained in Ref. 13. In particular, we find, as in Ref. 13, that BC is the lowest-energy configuration. Relative to BC, the configurations C, Hex, and Td have energies of 0.3, 0.5, and 0.9 eV to be compared with the values of ≤ 0.2, 0.4, and 1.0 eV of Ref. 13. The generalized equations of motion of Ref. 16(a) were integrated using a time step $\Delta t \simeq 1.2\times10^{-16}$ sec and an electronic "mass" parameter $\mu=200$ a.u. With this choice the atomic motion deviates from the Born-Oppenheimer surface by less than 0.03 eV/atom after 4 psec, our largest observation time. Many runs have been performed in a temperature range varying from 1000 to $\simeq 1950$ K.

The mean-square displacement of the proton, given by $\langle [r_H(t)-r_H(0)]^2\rangle$, gives a diffusion coefficient D of the order of 10^{-4} cm^2/sec at $T\simeq 1200$ K, thus confirming the high mobility observed in the experiment of VW. In Fig. 1 we report our results for D at three different temperatures, one of which would correspond to an overheated crystal. The agreement of the simulation with the experimental VW data is remarkable, considering that the theory does not take into account the presence of defects, possible molecular formation, or other factors that could hinder the diffusion process.

A detailed analysis of the diffusive path of the proton has been performed in all of the simulation runs at the various T. The study of the pair correlation function $g_{\mathrm{HSi}}(r)$, averaged over different time intervals, allowed us to determine the lattice positions visited by H^+ in its diffusive motion. This is illustrated in Fig. 2 where we report a segment of a proton trajectory representative of some general diffusive features observed in many different runs at the same and at different T. For clarity the thermal motion of the silicon atoms is omitted and only a small portion of the total MD cell is reported. In the insets we show the $g_{\mathrm{HSi}}(r)$ computed in different segments of the trajectory. The $g_{\mathrm{HSi}}(r)$'s corresponding to the passage of H^+ through regions close to the various symmetry sites differ from one another both in their shape and in the coordination shells. For example, in the BC position one has the sequence of coordination shells {2:8:20}, while in the M site one has {2:16}. The shape

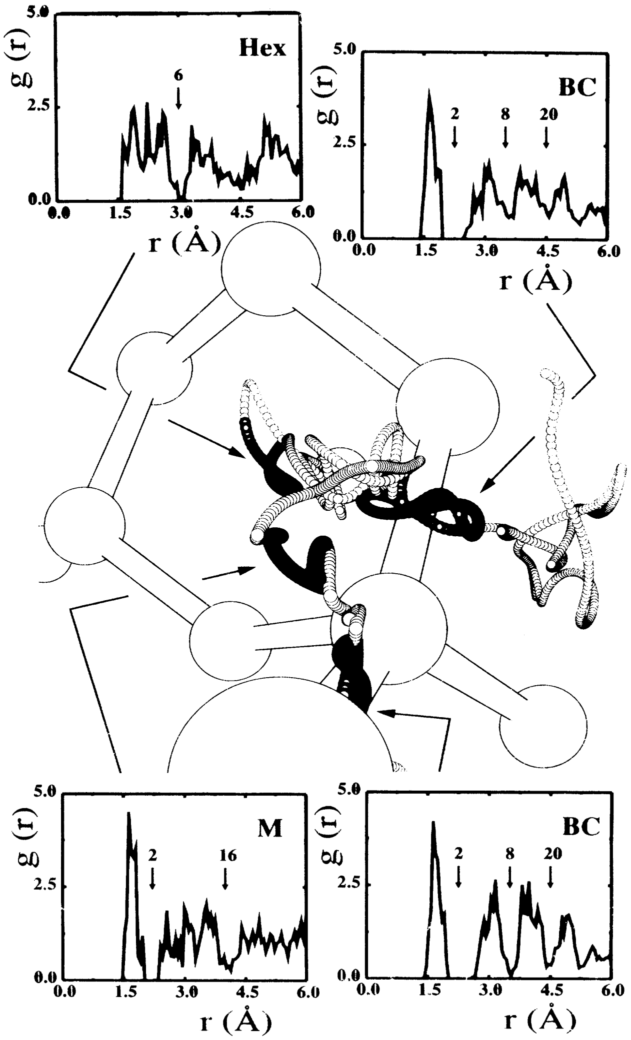

FIG. 2. H^+ trajectory at 1200 K for about 0.7 psec. The large balls represent the silicon atoms in the perfect crystalline positions; only a few bonds are shown. The small balls correspond to the hydrogen position reported every $5\Delta t$ ($\Delta t \simeq 1.2 \times 10^{-16}$ sec). The cross term of the pair correlation function $g_{\mathrm{HSi}}(r)$, relative to the passage of H^+ in the darkened regions indicated by the arrows, and the average coordination numbers are reported in the insets.

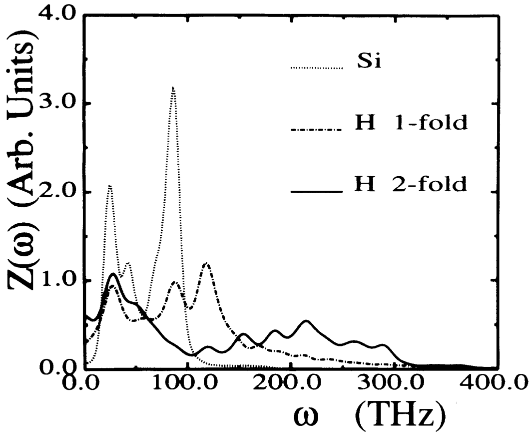

FIG. 3. Phonon density of states at $\simeq 1000$ K. Dotted line: silicon. Dash-dotted line: H^+ in the onefold path (see text). Solid line: H^+ in the twofold path (see text).

of the $g_{\mathrm{HSi}}(r)$ reflects both the hydrogen motion within a particular site and the silicon motion. The first peak of the $g_{\mathrm{HSi}}(r)$ in the insets relative to the BC configuration occurs at $\simeq 1.6$ Å, indicating an average relaxation of the nearest two silicon atoms of about 0.5 Å. From the sequence of the $g_{\mathrm{HSi}}(r)$'s shown in Fig. 2 one can observe that H^+ is moving from one BC site to another, passing through an M site and a hexagonal (Hex) site. This means that the proton follows a path in which it explores alternately the HD region (BC, M) and the LD region (Hex). However, the proton resides longer in the twofold-coordinated sites (BC, M) than in the Hex site. This kind of analysis shows that the diffusion mechanism is jumplike.

In general we have detected, as the most likely, a path in which the proton jumps from a twofold (BC, M) coordinated site to another by using the Hex and/or the tetrahedral (Td) as intermediate sites. We will call this path the twofold-coordinated path indicating with this the fact that the proton spends most of its time in twofold-coordinated sites. In other segments of the trajectory, the proton has been observed to follow a path lying completely in the LD region. This path proceeds via jumps from a near antibonding (AB) site (about 1.6 Å from a silicon atom) to another one, going through Td or Hex sites. We call this the onefold-coordinated path since the proton spends most of its time in onefold-coordinated sites (AB). However, these two paths can alternate during the same simulation run. We are not able at this stage to give a precise estimate of the relative occurrence frequency of the two paths. Scattering experiments could distinguish between these two situations. Indeed these two paths are characterized by a significant difference in the velocity-velocity correlation function $Z(t)$ of the proton. We report in Fig. 3 the power spectra of $Z(t)$ for H^+ diffusing in the onefold and in the twofold paths, respectively. In the latter case the spectrum exhibits higher-frequency components. In the same picture we also show the computed silicon spectrum which closely reproduces the measured phonon density of states for the pure system.[21]

The reason why the proton does not follow the strictly HD path resulting from $T=0$ calculations can be traced to the large difference in mass between H and Si. When the H^+ motion is fast, as is the case at these high temperatures, the heavy Si ions cannot adiabatically follow the proton. Thus the lattice may not have the time to undergo the large relaxation needed for the HD sites to become energetically favorable. When this happens the proton prefers to move through regions of low energy for the undistorted lattice. This explains the observation of the onefold-coordinated path.

From the slope of a linear fit to the three data points in Fig. 1 we obtain an activation energy $E_A = 0.33 \pm 0.25$ eV. Within this rather large error bar, this value is in reasonable agreement with 0.48 eV obtained from the only existing experimental data[9] in the same temperature range. It has to be noted that, due to the complexity of the H^+ diffusive motion illustrated above, it does not seem correct to identify E_A with a single energy barrier. It seems more adequate to consider E_A as an average barrier seen by the diffusing proton along its path.

In summary, we have presented the first *ab initio* MD study of the diffusion of a proton in *c*-Si at high temperatures. This work demonstrates that dynamical effects substantially modify the picture emerging from $T = 0$ results. In particular, we observed that the proton follows diffusive paths different from the HD path and, as a consequence, sees a higher activation energy. Our results for the diffusion coefficient agree well with experiments in the studied range of temperatures, and confirm the high mobility of the proton in *c*-Si. Finally, we suggest that scattering experiments can help to establish the nature of the diffusive path.

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