Hydrogen Diffusion in Silicon from Tight-Binding Molecular Dynamics

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We present the first tight-binding molecular dynamics simulation of hydrogen diffusion in silicon for $800 < T < 1800$ K. We show that the diffusion law deviates from the high-temperature Arrhenius plot below $T = 1200$ K, and we compute the diffusion coefficient in a region where no experimental data are available. The diffusion mechanism and path are observed during very long simulations. We demonstrate that hydrogen diffuses through jumps, avoiding low valence-charge-density regions. Observation of jumps between non-nearest-neighbor bond-center sites is reported, and the role of the phonon spectrum of silicon is discussed.

Hydrogen in semiconductors has long been considered an outstanding and lively field of solid state physics. Its importance is related to the capacity of hydrogen (H) to affect optical and electrical properties of semiconductor materials and to the fact that it is present in nearly any step of processing of Si or III-V compounds. Moreover, H is often intentionally inserted into a host and used to passivate defect states. When present in a semiconductor device, H may diffuse and affect the transport properties of the electrically active region. This is in most cases a disturbing situation that makes the control of the electric field in the active region quite troublesome. A detailed comprehension at an atomistic level of the hydrogen diffusion mechanism is therefore a basic issues to understand the physics of hydrogenated semiconductors.

Most of the experimental and theoretical investigations on H diffusion have been in fact focused on crystalline (c) or amorphous Si [1]. As regards c-Si, despite the huge amount of work dedicated to this problem, the full characterization of hydrogen motion and diffusivity mechanism is still a matter of discussion. In Fig. 1 we collect the experimental [2–8] and theoretical data [9], reporting the variation of the hydrogen diffusion coefficient D with temperature. In the low-temperature region ($T < 800$ K) the experimental measurements of D (performed with different techniques and relative to different charge states of hydrogen) show a sizable spread [3–8]. On the other hand, at higher temperatures ($T > 1000$ K) both the experimental data by Van Wieringen and Warmoltz [2] (VWW) and the first-principle simulation by Buda et al. [9] (CP) indicate a linear variation of $\ln D$ against inverse temperature. This trend can be reproduced by the Arrhenius law [2] $D(T) = D_0 \exp(-E_A/k_B T)$, where $D_0 = 9.41 \times 10^{-3}$ cm^2 s^{-1} and $E_A = 0.48$ eV (activation energy). The extrapolation (dash-dotted line in Fig. 1) down to intermediate temperatures shows larger and larger deviations from measurements (apart from the puzzling almost exact matching of Seager et al. [4] and Tavendale et al. [6] room temperature data).

Also the diffusion mechanism and path are not well established. Both Hartree-Fock [10,11] and density-

functional-theory [12] (DFT) calculations have been performed in the cluster and supercell geometry for both neutral and charged H. The main question there addressed was the determination of the equilibrium site for interstitial hydrogen in c-Si at zero temperature. According to all of the calculations, the bond-center (BC) site—the midpoint of a Si-Si bond—turns out to be the minimum energy position. However, conflicting estimations [10–12] have been given for the energy of other interstitial sites (e.g., the hexagonal, tetrahedral, C, and M sites, where M indicates a site located midway between a BC and a hexagonal site and C indicates a site midway between two M sites). This prevents the determination of a unique picture for hydrogen diffusion in c-Si as deduced from $T = 0$ K calculations of diffusion path and activation energies. In order to bypass the limitations of static calculations, Buda et al. [9] have performed a first-principles molecular dynamics (MD) simulation of hydrogen (in the H$^+$ state)
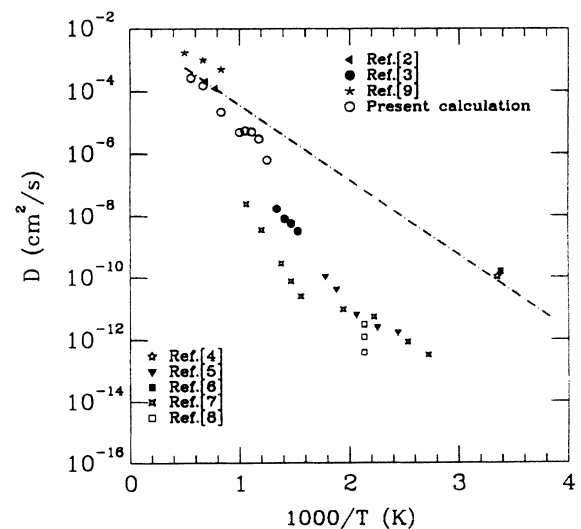

FIG. 1. Diffusion coefficient for hydrogen in c-Si. Open circles: present calculation. Other symbols: experimental and theoretical data from Refs. [2–9]. Dash-dotted line: Arrhenius-like extrapolation of VWW data (see text) from Ref. [2].

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in crystalline silicon. They have calculated the diffusion coefficient for $1200 < T < 1950$ K finding a rather good agreement to VWW experimental data [2] (see Fig. 1). The high-temperature behavior has been confirmed by another DFT total energy calculation by Blöch et al. [13] based on rate theory. Moreover, Buda et al. [9] have demonstrated that the diffusion mechanism is jumplike between highly symmetric interstitial sites and that the inclusion of dynamical effects substantially modify the picture emerging from zero temperature calculations. Two possible paths of diffusion have been proposed in Ref. [9]: (i) a twofold-coordinated path in which jumps between twofold-coordinated BC and M sites were observed; and (ii) a onefold-coordinated path in which hydrogen moves in the regions of low valence charge density. The two paths have been proposed to alternate during the diffusion, but it was not possible to estimate their relative occurrence frequency.

The accurate investigation by Buda et al. [9] is, however, limited to very high temperatures ($T > 1200$ K) and to very short simulation times (4 ps) because of the high computational workload of that first-principles MD. These limitations leave unanswered some important questions: (i) understanding why the diffusion coefficient undergoes such a dramatic change (almost 4 orders of magnitude) in the small temperature interval $900 < T < 1200$ K; (ii) fixing the range of validity for the $D(T) = 9.41 \times 10^{-3} \exp[(-0.48 \text{ eV})/k_B T]$ cm^{2}s^{-1} Arrhenius extrapolation; and (iii) collecting hydrogen trajectories during long simulations in order to fully characterize the diffusion path. To these aims we have performed tight-binding molecular dynamics (TBMD) simulations of hydrogenated c-Si for $1800 < T < 800$ K. As discussed elsewhere (see Ref. [14] and references therein), TBMD is a simulation scheme where the interatomic forces governing the atomic trajectories are derived from the underlying electronic structure of the simulated system through the Hellman-Feynman theorem. The electronic structure is calculated at every time-step of the MD run by means of a semiempirical tight-binding (TB) Hamiltonian. The resulting computational framework is quantum mechanical and has both the required accuracy to deal with covalent materials with directional bonds and a reduced computational workload. This, in turn, allows for large-scale simulations. The reliability of TBMD simulations has been established either for elemental [15–17] or compound [18] semiconductors and for carbon-based materials [19].

In the present work we make use of the sp^3 Goodwin et al. [14] Hamiltonian to model Si-Si interactions. As for the Si-H interactions, we have determined the tight-binding (TB) parameters by using a selected set of properties of the SiH$_4$ molecule. The difference between the diagonal elements for Si-Si interactions was derived from Ref. [14], whereas the equilibrium values of two off-diagonal Si-H elements (i.e., $ss\sigma$ and $sp\sigma$), as well as the H-H and Si-Si diagonal hopping integrals, have been de-

termined by fitting the energy of the first (a_1^+) and second (t_2^+) bonding and the first antibonding (t_2^-) level and the frequency of the symmetric bending mode (SB). Just the $1s$ orbital was used for H. The full set of TB parameters used in this work is shown in Table I, while in Table II we report the results of the present parametrization for the SiH$_4$ molecule together with experimental data [20]. The fitted Si-H hopping integrals have been scaled upon the interatomic distance according to the Goodwin et al. model [14]. The repulsive potential [14] for Si-H pairs has been obtained by the difference between the universal binding curve of the Si-H bond [21] and the band-structure energy per bond, as calculated with the above TB parameters.

The reliability of our model Hamiltonian was further tested by performing static total-energy calculations of interstitial hydrogen in c-Si at zero temperature. As previously found in first-principles calculations [9–12], the BC site turned out to be the minimum-energy site for hydrogen. Within the numerical accuracy of the present model ($\sim$0.1 eV/atom) the hexagonal site is almost degenerate with BC and, relative to BC, all the other interstitial configurations have energy higher by an amount ranging between 0.2–0.8 eV with the following sequence: M, TD, C. Similar results are found in Refs. [9,12]. Since conflicting estimations exist for the energy of the M, C, TD, and hexagonal sites, we cannot further comment about our set of energies. However, it is worth noticing that, despite the present TB model being quite simple, the correct gauge for interstitial energies is well reproduced. Moreover, we have found that hydrogen causes relevant structural relaxations in the host lattice. In particular, when placed in BC position, the two first neighboring Si atoms are symmetrically and radially displaced by 0.4 Å. The relaxations of the second and third shells of Si atoms were also calculated and were found to be much smaller, as in Ref. [12]. On the other hand, we have found that relaxation of Si atoms is negligible when placing H at tetrahedral or hexagonal sites. Both these features result in rather good agreement with DFT calculations by Van de Walle et al. [12]. Finally, we remark that we have calculated the equilibrium Si-H bond length to be 1.6 Å, when H is placed at the antibonding position. Again, this is in excellent agreement to both experimental data [22] and previous calculations [23]. The above extensive tests of accuracy make us confident that the present tight-binding model is reliable for attempting to study dynamical properties.

TABLE I. TB parameters (in eV) for Si-Si, Si-H, and H-H interactions used in the present work. We used the notation after Ref. [24].

	E_s	E_p	$ss\sigma$	$sp\sigma$	$pp\sigma$	$pp\pi$
Si-Si	−14.843	−6.548	−1.820	1.960	3.060	−0.870
Si-H			−2.815	4.265		
H-H	−8.758					

TABLE II. Energy levels (eV) and vibrational frequencies (meV) for SiH_4.

	a_1^+	t_2^+	t_2^-	SB	S
Expt. (Ref. [20])	−18.20	−12.70	−5.40	15.00	33.66
Present work	−18.20	−12.70	−5.40	14.16	34.47

Finite-temperature simulations of diffusion were performed with a periodically repeated cubic supercell containing 64 Si atoms and 1 hydrogen. The density of the sample was fixed to the experimental value for c-Si. The classical equations of motion have been integrated by means of the velocity-Verlet algorithm with a time step $\delta t = 0.5 \times 10^{-15}$ s and $\delta t = 1 \times 10^{-15}$ s for $T > 1000$ K and $T < 1000$ K, respectively. Taking full advantage of the reduced computational workload of the present TBMD, we have been able to follow hydrogen during a simulation as long as 25 ps for $T > 1000$ K. A special effort was required for the simulation at $T < 1000$ K: Here we followed the diffusion for much longer times (up to 300 ps). The observation was preceded at each temperature by a careful equilibration (2.5 ps).

In Fig. 1 the results of the present investigation are shown as open circles. The diffusion coefficient was calculated from the mean square displacement (MSD) of the hydrogen atom. We can clearly see that at very high temperatures the agreement with VWW data is excellent. This is the most striking proof of reliability for our TBMD simulation. On the other hand, for $T < 1200$ K we observe a sizable deviation from the Arrhenius law as obtained by extrapolation [2,9,13] of VWW data. The trend shown by our calculations proves that between 1200 and 900 K the variation of $\ln D$ as a function of inverse temperature deviates from $D(T) = 9.41 \times 10^{-3} \exp[(-0.48 \text{ eV})/k_B T] \text{ cm}^2 \text{s}^{-1}$. Such a trend matches the high- and low-temperature sets of experimental data. According to our analysis, the extrapolation of the high-temperature Arrhenius plot down to room temperature turns out to be questionable.

The mechanism and path of diffusion have been deduced by carefully analyzing the hydrogen trajectories collected during the simulations. In Fig. 2 we report the H trajectory as obtained at 1200 K for 25 ps. The time evolution is represented with a suitable site labeling. The silicon lattice (thick sticks) is represented at rest, omitting the thermal motion of Si atoms for the sake of clarity. Figure 2 is representative of most of the diffusive features observed at any temperature. A clear picture emerges from it: H moves *via* a jumplike mechanism visiting preferentially BC sites. This picture is in qualitative good agreement with the previous findings by Buda *et al.* [9]. We can, however, give more details about the diffusive behavior, thanks to the larger statistics we have accumulated. First of all, we can observe that the time spent in the neighborhood of equivalent BC sites may significantly
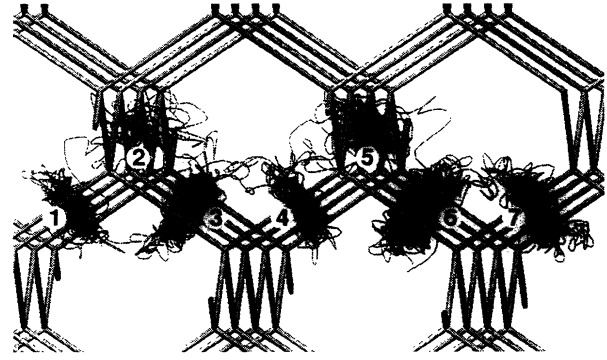

FIG. 2. Hydrogen trajectory at $T = 1200$ K during a 25 ps long simulation. Silicon lattice (thick sticks) is represented in its equilibrium configuration. The time evolution of the H position is given by the following sequence of jumps: 6-7-6-5-2-1-3-4.

differ from case to case (this corresponds to a more or less entangled trajectory). H diffusion is, in fact, a sequence of *stop-and-go* processes in which the pauses can have different durations. Moreover, forward and backward jumps are equivalent and occur with the same frequency. A second important peculiarity is related to the diffusive path: In Fig. 2 (and, similarly, in all of our simulations) we see that H avoids the regions of low valence charge density. In other words, we did not observe the onefold-coordinated path discussed in Ref. [9]. This result holds both at high and low temperature and does not depend upon the initial position of hydrogen from which the trajectory was generated. We must conclude that, according to our simulations, the onefold-coordinated path is a rather infrequent event. However, we remember that in Ref. [9] they considered H^+ diffusion, whereas in the present calculation the charge state of H is given by the instantaneous occupation of its $1s$ orbital. A third relevant information that we can extract from Fig. 2 refers to the length of the jumps: We have observed jumps between BC sites lying at a distance longer than the first nearest-neighbor one (jump between site 5 and 2 in Fig. 2). As a general trend, we found that the higher the temperature was, the longer the maximum jump length was.

This conclusion is confirmed by Fig. 3 where we report the MSD of H at three different temperatures. First, we notice that the frequency of jumps decreases with temperature. This feature is particularly evident for $T \leq 850$ K. This temperature corresponds to the minimum thermal energy (~ 70 meV) required to excite the highest optical phonons (~ 65 meV) in silicon, corresponding to the stretching mode of a Si-Si bond. When such vibrations are not thermally activated, the diffusion is not encouraged because the BC site is an energetically favorite site for H. However, we believe that it is not the only factor responsible for the dramatic change in the diffusion coefficient around $T = 1200$ K. In fact, one clearly sees that the squared absolute length
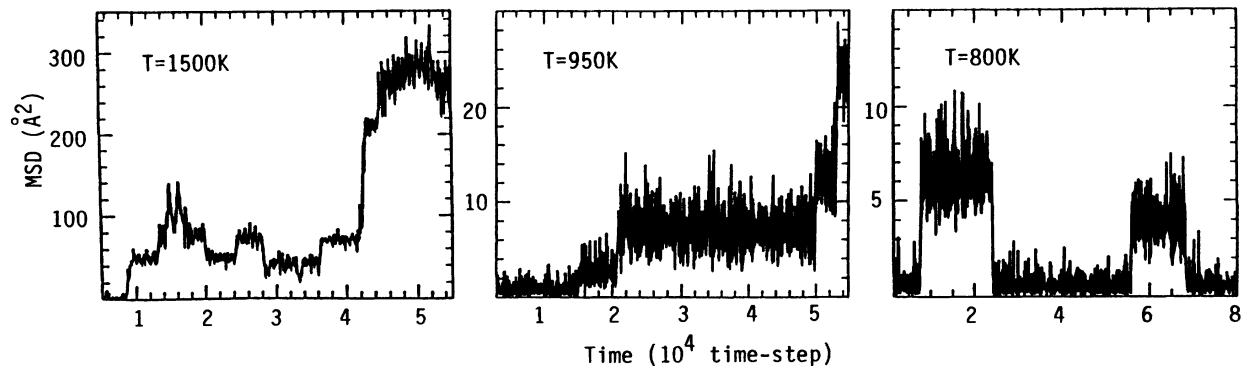
FIG. 3. Mean square displacement (MSD) of H at three temperatures. The $T = 800$ K panel represents a section of a longer simulation (3×10^5 time steps).

of the jumps (that correspond to the height of the steps in the MSD plot) changes by about 1 order of magnitude from $T = 1500$ K (left panel) to $T = 950$ and 800 K (central and right panels). This indicates that the drop in temperature causes the quenching of the longer jumps. We propose that the combination of these two mechanisms is the origin of the deviation from the high-temperature Arrhenius law [2,9,13] for $T < 1200$ K.

In summary, we have presented the first TBMD simulation of H diffusion in c-Si over a wide range of temperatures ($800 < T < 1800$ K). The agreement to high-temperature experimental data and first-principles simulations is excellent. Moreover, we have demonstrated that the diffusion law differs from $D(T) = 9.41 \times 10^{-3} \exp[(-0.48 \text{ eV})/k_B T] \text{ cm}^2 \text{s}^{-1}$ for $T < 1200$ K. A full characterization of the diffusion path has been given as well, and different diffusion mechanisms have been proposed.

[1] S. J. Pearton, W. Corbett, and M. Stavola, *Hydrogen in Crystalline Semiconductors*, Springer Series in Materials Science Vol. 16 (Springer-Verlag, Berlin, 1992).

[2] A. Van Wieringen and N. Warmoltz, Physica (Utrecht) 22, 849 (1956).

[3] T. Ichimiya and A. Furuichi, Int. J. Appl. Radiat. Isot. 19, 573 (1968).

[4] C. H. Seager and R. A. Andersen, Appl. Phys. Lett. 53, 1181 (1988).

[5] A. Mogro-Compero, R. P. Love, and R. Schubert, J. Electrochem. Soc. 132, 2006 (1985).

[6] A. J. Tavendale, A. A. Williams, D. Alexiev, and S. J. Peraton, Mater. Res. Soc. Symp. Proc. 104, 285 (1988).

[7] S. J. Pearton, J. Electron. Mater. 14a, 737 (1985).

[8] N. M. Johnson, D. K. Biegelsen, and M. D. Moyer, Appl. Phys. Lett. 40, 882 (1982).

[9] F. Buda, Guido L. Chiarotti, R. Car, and M. Parrinello, Phys. Rev. Lett. 63, 294 (1989).

[10] A. Amore Bonapasta, A. Lapiccirella, N. Tomassini, and M. Capizzi, Europhys. Lett. 7, 145 (1988).

[11] P. Deak, L. C. Snyder, and J. W. Corbett, Phys. Rev. B 37, 6887 (1988).

[12] C. G. Van de Walle, P. J. H. Denteneer, Y. Bar-Yam, and S. T. Pantelides, Phys. Rev. B 39, 10791 (1989).

[13] P. E. Blöch, C. G. Van de Walle, and S. T. Pantelides, Phys. Rev. Lett. 64, 1401 (1990).

[14] L. Goodwin, A. J. Skinner, and D. G. Pettifor, Europhys. Lett. 9, 701 (1989); C. Z. Wang, C. T. Chan, and K. M. Ho, Phys. Rev. B 39, 8586 (1989).

[15] G. Servalli and L. Colombo, Europhys. Lett. 22, 107 (1993).

[16] R. Virkkunen, K. Laasonen, and R. M. Nieminen, J. Phys. Condens. Matter 3, 7455 (1991).

[17] C. Z. Wang, C. T. Chan, and K. M. Ho, Phys. Rev. Lett. 66, 189 (1991).

[18] C. Molteni, L. Colombo, and L. Miglio, Europhys. Lett. 24, 659 (1993).

[19] C. H. Xu, C. Z. Wang, C. T. Chan, and K. M. Ho, J. Phys. Condens. Matter 4, 6047 (1992); S. Goedecker and L. Colombo, Phys. Rev. Lett. 73, 122 (1994).

[20] M. Cardona, Phys. Status Solidi (b) 118, 463 (1983).

[21] J. H. Rose, J. Ferrante, and J. R. Smith, Phys. Rev. Lett. 47, 675 (1981).

[22] S. T. Picraux and F. L. Vook, Phys. Rev. B 18, 2066 (1975).

[23] N. M. Johnson, C. Herring, and D. J. Chadi, Phys. Rev. Lett. 56, 769 (1986).

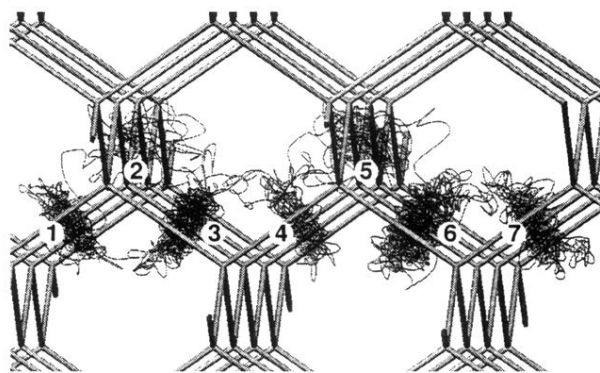[24] J. C. Slater and G. F. Koster, Phys. Rev. 94, 1498 (1954).

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