Tight-Binding Molecular-Dynamics Study of Defects in Silicon

C. Z. Wang,^{(1),(2)} C. T. Chan,⁽¹⁾ and K. M. Ho^{(1),(2)}

⁽¹⁾*Ames Laboratory-U.S. DOE, Iowa State University, Ames, Iowa 50011*

⁽²⁾*Department of Physics and Microelectronics Research Center, Iowa State University, Ames, Iowa 50011*

(Received 17 September 1990)

A tight-binding molecular-dynamics scheme is shown to have the efficiency and accuracy to study complex Si systems. We first establish the reliability of the scheme by showing that simulation results of liquid Si are nearly identical to *ab initio* (Car-Parrinello) results. The ability of the method to study complex systems is demonstrated by calculating defect formation energies and atomic configurations around vacancies and self-interstitials, with simulation unit cells of up to 512 atoms. The calculated formation energies compare well with first-principles results.

PACS numbers: 61.70.Bv, 61.20.Ja

The modeling and simulation of covalent materials have long been the prime concern of many authors since a good theoretical understanding of these technologically important materials is essential for better design and control of semiconductor devices. First-principles techniques such as the local-density-functional formalism are well developed, and have already produced a wealth of significant results. However, the computational cost is prohibitive for large systems, and we are severely limited by the number of atoms one can afford to treat in the unit cell. Even though recent breakthroughs such as the Car-Parrinello method¹ have made molecular-dynamics calculations possible within the local-density-functional regime, the simulation is still limited to a small number of atoms and a short simulation time. On the other hand, there are quite a number of empirical interatomic potentials that have been proposed for covalent materials like Si and C.²⁻⁴ These potentials include three-body terms which are often fitted to calculated phase diagrams or other properties of the crystals. Computational cost is not a problem here, but these potentials do not always give correct descriptions for properties that are not explicitly included in the fitting data base. Electronic structure information cannot be obtained, nor can we expect these classical potentials to give phenomena that are quantum mechanical in nature (e.g., Jahn-Teller-type distortions around vacancies). For a large class of problems which require more atoms than first-principles techniques can handle and demand more accuracy than classical potentials can provide, we will either have to wait for the next generation of computers to do *ab initio* computations, or have to stretch classical simulations to beyond their normal range of validity. It is thus imperative to have a scheme that is powerful enough to treat a few hundred atoms while accurate enough so that we can trust the results.

In this paper, we will show that a molecular-dynamics simulation scheme using a tight-binding potential model (hereafter referred to as tight-binding molecular dynamics or TBMD) has the desirable efficiency and accuracy for describing complex Si systems. The method can help

to bridge the gap between first-principles and classical-potential simulations. The tight-binding scheme is computationally efficient since it employs a minimal basis (e.g., four orbitals per atom for Si) and the Hamiltonian matrix elements are parametrized. The tight-binding Hamiltonian, though simple, contains the very essence of the physics of the directional bonding. It is quite obvious that our scheme, being an empirical method, is much faster than *ab initio* techniques, but its accuracy and reliability need to be established. The best way to do so is to compute some properties that are of physical interest, and have accurate first-principles results to compare with. These properties also must not be part of, or trivial consequences of, the fitting data base, so that the predictive power of the method can be tested. This is the reason that we present in this paper simulation results of liquid Si and the formation energy and relaxation of atoms around point defects in crystalline Si. We will show that the TBMD scheme gives results that compare very favorably with *ab initio* calculations. Since we can handle over 500 atoms in our simulations, there is no need to impose symmetry constraints nor combine with elastic theory in our defect-relaxation calculations. These problems are also chosen because they are interesting and important topics in their own right.⁵

In the TBMD scheme, the Hamiltonian governing atomic motions is

$$H = \sum_i \frac{p_i^2}{2m} + \sum_n^{\text{occupied}} \langle \psi_n | H_{\text{TB}} | \psi_n \rangle + \sum_{i>j} \phi(r_{ij}), \quad (1)$$

where the first term is the kinetic energy of ions, the second term is the electronic energy calculated from a parametrized tight-binding Hamiltonian H_{TB} , and $\phi(r_{ij})$ in the third term is a pairwise potential representing the ion-ion repulsion and the correction for double counting the electron-electron interaction in the second term. Further details of the TBMD scheme can be found elsewhere.^{6,7}

In the present study, we adopt the tight-binding Hamiltonian H_{TB} and the pairwise potential $\phi(r_{ij})$ proposed by Goodwin, Skinner, and Pettifor,⁸ which is very simi-

lar to the earlier formulation of Chadi⁹ and Harrison¹⁰ except that the tight-binding hopping parameters and the pairwise potential are scaled by an extra exponential function in addition to the original power-law scaling functions. It has been shown by Goodwin, Skinner, and Pettifor that this tight-binding potential model reproduces well the first-principles-calculated Si bulk phase diagram as well as giving correct ground-state structures of small Si clusters.⁸ The ability of this model to describe nicely various ground-state ($T=0$) properties of crystalline Si has also been tested, where the calculated structural, vibrational, elastic, and anharmonic properties of Si in the diamond structure compare well with experimental and *ab initio* results.¹¹

To show that the model is also accurate enough to study Si systems far from the ground-state tetrahedral geometry, we have performed molecular-dynamics simulation studies of liquid Si and compared our results with those recently obtained from the first-principles Car-Parrinello method.¹² Constant-temperature-constant-volume MD simulation has been performed with a 64-Si-atom cubic cell and with periodic boundary conditions. The density of the sample is chosen to be 2.53 g/cm³.² The time step used in the simulation is 1.07×10^{-15} s and the electronic structure Hamiltonian is solved for the zone-center point. After careful thermalization, 8000 MD steps (corresponding to 8.56 ps) have been used to perform the statistical average for the properties of liquid Si at $T=1780$ K. We note that the simulation can be done for more atoms, a longer time, and better $\mathbf{k}$ -point sampling. The current simulation parameters are chosen to resemble closely the simulation condition of the Car-Parrinello results,¹² so that the comparison of results is most meaningful. In Fig. 1, the TBMD result of the radial distribution function $g(r)$

FIG. 1. Radial distribution function of liquid Si. Inset (quoted from Ref. 12): The *ab initio* molecular-dynamics simulation result (solid line) and experimental results (dotted and dash-dotted lines) for the purpose of comparison.

is presented, where we observe a sharp nearest-neighbor peak followed by an oscillatory tail of value of about 1. The agreement of our results with the Car-Parrinello result and experimental data (see inset) is excellent. Integration of $g(r)$ to its first minimum at $r=3.12$ Å yields a coordination number of 6.5, which agrees well with the experimental value of 6.4,¹³ and the Car-Parrinello simulation result of 6.5.¹² Angular distribution functions and electronic density of states of liquid Si from our TBMD scheme are also in excellent agreement with Car-Parrinello simulation results. From our results, we obtain a value of 0.43 eV/atom for the latent heat of fusion, close to the experimental value of 0.47 eV/atom.¹⁴ Details of the results will be published elsewhere.¹¹

Having established the reliability of the TBMD scheme, vacancies and interstitials in crystalline Si are studied using supercells with 64, 216, and 512 Si atoms, respectively, plus one defect. Periodic boundary conditions are imposed on all three directions. Both tetrahedral and hexagonal interstitials are studied. The ground-state configuration of the defects is obtained by relaxing the atomic positions using the tight-binding molecular-dynamics scheme. In Table I, our results for the formation energies of the fully relaxed defects are compared with first-principles calculations.¹⁵⁻¹⁸ We note that different authors have arrived at slightly different defect formation energies, due to the use of different computational techniques (e.g., Green's function or supercell) and different approximations for treating the lattice relaxation induced by the defects. Our present results are within the range of the first-principles results.

The tetrahedral symmetry around the vacancy is found to be broken by the relaxation of the atoms adjacent to the defect. Distortions of the nearest-neighbor atoms consist of a tetragonal Jahn-Teller-type distortion superimposed on a radial distortion towards the vacancy so that the dangling bonds around the vacancies are bent to pair the atoms up along the [110] direction, as illustrated in Fig. 2. The tetragonal distortion around the Si vacancy agrees with the electron-paramagnetic-resonance data of Watkins¹⁹ and the theoretical calculations of Baraff, Kane, and Schlüter.²⁰ The inward relax-

TABLE I. Comparison of calculated point-defect formation energies with the first-principles [local-density approximation (LDA)] calculation results (Refs. 15-18). The values in parentheses are the formation energies of the unrelaxed defects. All energies are in units of eV. T-inter. and H-inter. denote tetrahedral and hexagonal interstitials, respectively.

Defect	64 atoms	216 atoms	512 atoms	LDA
Vacancy	3.67 (5.02)	3.96 (5.82)	4.12 (6.03)	3.6-5.0
T-inter.	4.39 (6.42)	4.40 (6.54)	4.41 (6.55)	4.3-6.2
H-inter.	5.78 (10.08)	5.90 (10.32)	5.93 (10.35)	5.0-6.0

FIG. 2. Lattice distortions around the vacancy in crystalline Si. The dangling bonds around the vacancy are bent to pair the atoms up along the $[110]$ directions.

ation (towards the “void”) of the atoms around the vacancy is consistent with recent first-principles calculations on the Si vacancy,¹⁶ and should be contrasted with the relaxation of the top layers of Si(111), which relax towards the bulk. Relaxations of the tetrahedral and hexagonal interstitials, on the other hand, are found to push the neighboring atoms away in such a way that the tetrahedral or hexagonal symmetries around the interstitials are preserved. The lattice distortions at the neighborhood of the interstitials are illustrated in Fig. 3.

Since the TBMD scheme can be applied to unit cells containing over 500 atoms, we can obtain defect-induced atomic relaxations not just close to but also relatively far away from the defect. In order to see how rapidly the distortion decays away from the vacancy and the interstitials, we have examined the distortion amplitudes of all the atoms in the supercells as a function of their distance away from the defects. The results obtained from the 512-atom supercell are plotted in Fig. 4. The distortion amplitude of the nearest-neighbor atoms of the vacancy is found to be quite large, about 0.5 Å, but it decays rapidly away from the vacancy and becomes negligibly small at four or five bond lengths away (about 10 Å) from the defect. We note that the vacancy-induced atomic distortions are anisotropic and propagate along a zigzag chain in the $[110]$ direction (see Fig. 2). The atomic distortions caused by the interstitials are also found to decay very quickly and spread to a distance of about five bond lengths away from the interstitial atom. It seems that for the case of interstitials, there are no particular channels along which the distortions are propagated. However, we do find that the second-largest distorted atoms are those bonded along the $[111]$ direction to the atoms next to the interstitials (see Fig. 3), although their distance from the defects is larger than that of those sites on face-center positions. The distortions of other atoms are much smaller.

Finally, we note that the distortion pattern of the 216-atom supercell is almost identical to that of the 512-atom supercell. This fact indicates that our results

FIG. 3. Lattice distortions around the tetrahedral and the hexagonal self-interstitial atoms in crystalline Si.

on the defect relaxation presented above are converged as far as the size of the sample is concerned.

In summary, we have studied liquid Si and the structural properties of point defects in crystalline Si with a tight-binding molecular-dynamics scheme. Our results show that the present scheme is comparable in accuracy to *ab initio* schemes, yet can be applied to unit cells containing over 500 atoms. There exist numerous problems which are computationally too demanding for first-principles techniques while too subtle for classical empirical potentials. This scheme can serve to fill in the

FIG. 4. Lattice distortion amplitudes as a function of distance from the vacancy and interstitials.

gap and help to pave a way for the better understanding of many areas of semiconductor physics.

This work is supported by the director of Energy Research, Office of Basic Energy Sciences, including a grant of computer time on the Cray computers at Lawrence Livermore Laboratory, and by the U.S. Air Force Office of Scientific Research. Ames Laboratory is operated for U.S. Department of Energy by Iowa State University under Contract No. W-7405-ENG-82.

¹R. Car and M. Parrinello, Phys. Rev. Lett. **55**, 2471 (1985).

²F. H. Stillinger and T. A. Weber, Phys. Rev. B **31**, 5262 (1985).

³R. Biswas and D. R. Hamann, Phys. Rev. Lett. **55**, 2001 (1985).

⁴J. Tersoff, Phys. Rev. Lett. **56**, 632 (1986); Phys. Rev. B **37**, 6991 (1988); Phys. Rev. Lett. **61**, 2879 (1988).

⁵For a recent review see, for example, *Deep Center in Semiconductors: A State-of-the-Art Approach*, edited by S. T. Pantelides (Gordon and Breach, New York, 1986), and references therein.

⁶C. Z. Wang, C. T. Chan, and K. M. Ho, Phys. Rev. B **39**, 8592 (1989).

⁷C. Z. Wang, C. T. Chan, and K. M. Ho, Phys. Rev. B **40**, 3390 (1989).

⁸L. Goodwin, A. J. Skinner, and D. G. Pettifor, Europhys.

Lett. **9**, 701 (1989).

⁹D. J. Chadi, Phys. Rev. Lett. **41**, 1062 (1978); Phys. Rev. B **29**, 785 (1984).

¹⁰W. A. Harrison, *Electronic Structure and the Properties of Solids* (Freeman, San Francisco, 1980).

¹¹C. Z. Wang, C. T. Chan, and K. M. Ho (to be published).

¹²I. Stich, R. Car, and M. Parrinello, Phys. Rev. Lett. **63**, 2240 (1989).

¹³J. P. Gabathuler and S. Steeb, Z. Naturforsch. **34a**, 1314 (1979).

¹⁴A. R. Ubbelohde, *The Molten State of Matter* (Wiley, New York, 1978), p. 239.

¹⁵Y. Bar-Yam and J. D. Joannopoulos, Phys. Rev. Lett. **52**, 1129 (1984); in *Proceedings of the Thirteenth International Conference on Defects in Semiconductors*, edited by L. C. Kimmerling and J. M. Parsey (The Metallurgical Society of AIME, New York, 1984).

¹⁶A. Antonelli and J. Bernholc, Phys. Rev. B **40**, 10643 (1989).

¹⁷R. Car, P. Kelly, A. Oshiyama, and S. T. Pantelides, Phys. Rev. Lett. **52**, 1814 (1984); in *Proceedings of the Thirteenth International Conference on Defects in Semiconductors* (Ref. 15).

¹⁸G. A. Baraff and M. Schlüter, Phys. Rev. B **30**, 3460 (1984).

¹⁹G. D. Watkins, in *Deep Center in Semiconductors: A State-of-the-Art Approach* (Ref. 5), p. 147-183.

²⁰G. A. Baraff, E. O. Kane, and M. Schlüter, Phys. Rev. B **21**, 3563 (1980); **21**, 5662 (1980).