Vacancy-vacancy interaction in silicon studied using atomic potentials

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Vacancy-vacancy (V-V) interaction in Si is studied using the modified Stillinger-Weber atomic potential, under both strained and unstrained conditions. The potential is chosen out of a total of four potential forms by considering Si self-diffusion via vacancies. Monte Carlo simulations are performed on a $12\times12\times12$ lattice. Both simulated annealing and steepest descent are applied while relaxing the lattice. The results obtained do not agree well with experimental observations regarding V-V interaction energy, indicating that electronic relaxations are present that are not accounted for in the atomic-potential method. The dominant mode of coalescence with and without strain is compared by evaluating barriers for coalescence.

I. INTRODUCTION

In the present paper results are presented for vacancy-vacancy (V-V) interaction in silicon using the atomic potentials developed for Si.[1-3] The results for the two cases, viz., with and without strain are compared. Section II describes the choice of potentials for the present studies. Section III describes the method used for the energy calculations for various configurations, while Sec. IV discusses the results obtained.

II. CHOICE OF POTENTIALS

Calculation of defect energies has been carried out using *ab initio* methods in the case of silicon.[4] Migration of the interstitial also has been traced, and corresponding energy barriers were determined.[4] It is pointed out that zero migration energy for the Si self-interstitial, particularly under electron bombardment, is a result of atomic as well as electronic relaxation. Classical atomic potentials cannot account for electronic relaxation effects and hence are not suitable to describe a process involving such relaxation. Such an attempt would lead to overestimation of the relevant energies. Nonetheless, complex situations encountered in defect-defect interactions would involve a large number of atoms, and for performing *ab initio* calculations, will pose a formidable task. Atomic potentials are expected to give relatively crude estimates of the parameters and a qualitative picture of the process involved in such circumstances. In this paper, use of atomic potentials is made in the same spirit.

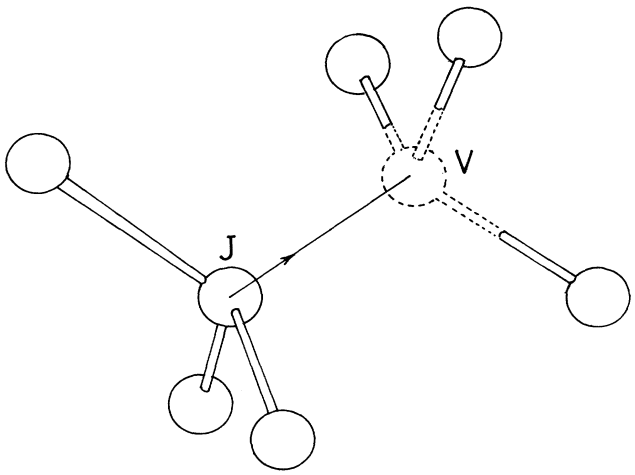

FIG. 1. The situation considered for motion of a single vacancy in a diamond lattice. The vacancy is at position V and the jumping atom is at position J. Positions of atoms are unrelaxed in the figure.

Four different atomic potentials for Si were tested on the configurations involving vacancy migration in bulk Si. Figure 1 depicts the situation. Potentials tested were taken from Tersoff[1] (T), Stillinger and Weber[3] (SW) and Biswas and Hamann "old"[2] (BHO) as well as Biswas and Hamann "new"[2] (BHN).

As a test case in this paper, these four potentials are used to calculate the migration energy of the Si vacancy in bulk Si. These potentials have different forms and different criteria for the choice of parameters. Particularly, BHO and BHN use distorted Si lattices as well as different structures, while fitting the parameters; also, the SW potential uses the criteria to describe liquidlike properties correctly, which essentially involves very many configurations of Si. Thus it is expected that distortions involved during vacancy migrations could be properly represented by these potentials.

III. COMPUTATIONAL PROCEDURE

In order to calculate various energies and simulate the migration of the vacancy, a $12\times12\times12$ unit cell with periodic boundary conditions was chosen. Testing of various potentials was done for the situation shown in Fig. 1. The vacancy is created approximately at the center of the unit cell and the migration barrier was computed by displacing one of the near neighbors of the vacancy toward the vacancy. Thus, in Fig. 1, J is the atom jumping toward the vacancy V.

The energy calculations were performed by allowing relaxation of the atoms up to the third neighbor from the vacancy and the migrating atom. An increasing number of relaxing atoms beyond the third neighbor did not change the energies significantly and, in particular, energy differences. The two-body and three-body terms were evaluated up to the fifth neighbor from the atom under consideration. A total-energy calculation was typically done for a set of about 108 atoms that included displaced and undisplaced atoms during the relaxation procedure.

During the initial test runs, it was observed that depending on the initial position of the atoms, various local-minimum-energy configurations are encountered after relaxation, separated by energy barriers. A Monte Carlo–like procedure was found suitable since the Boltzmann factor included therein allowed the crossing of the barriers with appropriate weightage. Therefore, relaxation was carried out, using the steepest-descent method along with the simulated annealing.[5] Thus the motion of the atoms takes place under the bias of the local force as well as the random force due to the surrounding heat bath. A similar method was employed by Rossky *et al.*,[6] where a Monte Carlo (MC) procedure was used. In the present case, the convergence is obtained faster than in the case where, along with steepest descent, only the MC method is used. Relaxation also was tried, using only the steepest-descent method, followed by a random "kicking" of the atoms (that helped crossing the barrier around the local minimum), and performing the steepest descent again. Repetition of this procedure also led to the minimum value obtained by other methods. The convergence in this method is comparable to the case of the steepest descent with annealing method.

All four potential forms were used to calculate the migration barrier. It was observed that each of the potentials favored a split-vacancy configuration. The formation energies for a single vacancy for T, BHO, BHN, and SW potentials were 2.75, 4.32, 3.70, and 2.88, respectively, in eV, while the corresponding split-vacancy energies were 3.25, 4.75, 4.13, and 3.20 in eV. Thus, clearly, none of the potentials could correctly represent the ground state of the vacancy. The split-vacancy configuration involves the migrating atom midway between the position J and V in Fig. 1. Under this condition, bonds are stretched and bent around the midway atom. It is found in the case of these potentials that elastic properties of Si are not represented properly by any of the potentials for large-angle deviations. Thus, for the split-vacancy position, the net energy gain due to the increased number of neighbors in the two-body term is not offset by the three-body repulsive term, which results in a favorable situation. The difference between the relaxed vacancy and the relaxed split vacancy was found to be minimum for the SW potential (0.3 eV). This potential was then used to study the vacancy-vacancy interaction by appropriately modifying the three-body parameters.

The two-body form of the potential is

$$V(r_{ij})=\epsilon f_2(r_{ij}/\sigma)\ , \tag{1}$$

with

$$f_2(r)=\begin{cases} A(Br^{-p}-r^{-q})\exp[(r-a)^{-1}], & r<a \\ 0, & r\geq a \end{cases} \tag{2}$$

whereas the three-body form was chosen as

$$V_3(\mathbf{r}_i,\mathbf{r}_j,\mathbf{r}_k)=\epsilon f_3\left[\frac{\mathbf{r}_i}{\sigma},\frac{\mathbf{r}_j}{\sigma},\frac{\mathbf{r}_k}{\sigma}\right], \tag{3}$$

with

$$f_3(\mathbf{r}_i,\mathbf{r}_j,\mathbf{r}_k)=h(r_{ij},r_{ik},\theta_{jik})+h(r_{ji},r_{jk},\theta_{ijk}) +h(r_{ki},r_{kj},\theta_{ikj})\ , \tag{4}$$

where θ_{jik} is the angle between r_j and r_k subtended at vertex i, etc. Note that $(r_{ij},r_{ik},\theta_{jik})$ is formally equivalent to $V_2(r_{12},r_{13},\theta_1)$ in the three-body expression used by Biswas and Hamann,

$$h(r_{ij},r_{ik},\theta_{jik})=\lambda\exp[\gamma(r_{ij}-a)^{-1}+\gamma(r_{ik}-a)^{-1}] \times(\cos\theta_{jik}+\tfrac{1}{3})^2 \tag{5}$$

ϵ and σ are energy and length scaling factors while the other parameters are chosen so that (i) at low pressures, the diamond structure is the stable structure compared to the simple-cubic (sc), face-centered-cubic (fcc), and body-centered-cubic (bcc) structures; and (ii) the melting point and the liquid structure, inferred from the molecular-dynamical simulations using this potential, are in reasonable accord with the experimental observations.

It may be noted that, due to the $\cos\theta+\frac{1}{3}$ term in the potential, equilibrium cohesive energy is not affected by changing the parameters of the three-body potential. The parameter λ in the SW potential was chosen to be 1.75 times the original parameter to strengthen the restoring force against bond bending. This new choice was based upon the condition that the single-vacancy migration barrier should be comparable to the experimentally observed one. Thus, with this choice, the lowest-energy state for the single vacancy was indeed the one, with neighbors around the vacancy being relaxed toward the vacancy, while the barrier for migration was encountered midway between the J and V positions in Fig. 1. The barrier is 0.33 ± 0.04 eV for the migration process. We note that a similar increase of the three-body term strength, by a factor of 2.5, was found necessary in the later work[7] of Biswas *et al.* relating to amorphous Si.

IV. VACANCY-VACANCY INTERACTION

In order to simulate the interaction and relative migration behavior between two vacancies, the configuration shown in Fig. 2 was used. In this situation two vacancies (at sites a and e) are four neighbors apart along the $\langle 110\rangle$ direction. At this distance vacancies already find themselves within the mutual strain fields. Due to the limitations posed by computing power, larger separations between vacancies could not be tackled. This is likely to cause an underestimation of the net strain energy due to the two vacancies. However, it is observed that the energy-barrier calculation is not much affected due to distant neighbors, typically beyond fourth neighbors.

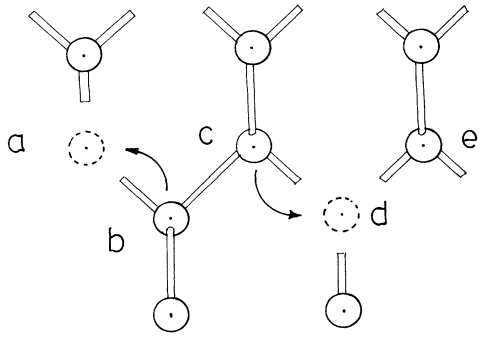

FIG. 2. The typical divacancy configuration with vacancies at the a and d positions. The vacancy arrives at d from position e, which is a four-neighbor distance away from a along the $\langle 110 \rangle$ direction. Similarly, d is at the three-neighbor and c is at the two-neighbor distance away.

Watkins and Corbett[8] have reported the vacancy migration behavior among divacancies, using electron paramagnetic resonance (EPR) data of the annealing studies made on electron-bombarded Si. They have estimated the binding energy of the divacancy to be 1.6 eV. In the present case, this energy is estimated to be less than 0.4 eV and is found to be a function of parameters in the three-body potential. The binding energy increases to 1.2 eV, on increasing λ in the three-body potential term, three times the original value.

Within the limitations of the atomic potential used, it is found that the migration barrier is a function of vacancy-vacancy separation. When vacancies are four neighbors apart along the $\langle 110 \rangle$ direction, the barrier for migration toward the vacancy from e to d in Fig. 2 is 0.2 eV, while from the third-neighbor position toward vacancy (d to c), it is only 0.07 eV. Moreover, the vacancy at the second-nearest neighbor, i.e., at c, is not a stable configuration. The vacancy jumps directly from the third-neighbor position to the first-neighbor one, involving the motion of two atoms simultaneously. As shown in Fig. 2, the atom at the first-neighbor distance moves toward the vacancy (b toward a) while simultaneously the atom at the second-neighbor distance moves toward the vacancy at the third-neighbor position (i.e., c toward d). Thus both vacancies move toward each other and combine occupying sites at b and c. When λ was increased to three times the original value, the barrier for the two-atom jump increased to 0.43 eV for migration from the third neighbor with simultaneous double-atom jump. However, it was still the minimum among all other available paths for the vacancy-vacancy combination.

V. EFFECT OF STRAIN ON THE MIGRATION BEHAVIOR

In order to study the effect of in-plane strain, as experienced, for example, during the growth of Si epitaxial film on a lattice-mismatched substrate, the lateral dimension [i.e., in the (001) plane], was increased by 2.5%. The lattice was relaxed to obtain a 4.5% vertical compression as the minimum-energy configuration. Thus the Poisson ratio obtained for the present potential is 0.55, which is close to the experimentally observed value of 0.63 for Si along the $\langle 001 \rangle$ direction.

Table I contains different energies for vacancies in strained unstrained lattices. It was observed that in general the migration under strain is different than when there is no strain. In particular, the double-atom jump is no more the path for vacancy coalescence when the vacancies are a three-neighbor distance apart. Thus the barrier for migration from d to c is 0.46 eV. The barrier is further decreased to 0.1 eV for migration from c to b in Fig. 2. When lateral strain was increased, the barriers also were increased. Moreover, the vacancy-vacancy coalescence behavior obtained so far did not show any anisotropic behavior. Thus, in some of the cases tried here, with respect to the vacancy at a in Fig. 2, the second vacancy was placed at other near neighbors of the atom at position c (e.g., in the $\langle 1\bar{1}0 \rangle$ direction). The nature and magnitudes of barriers encountered in this situation were similar to the ones described earlier.

From the point of view of the kinetic aspects of misfit dislocation formation, we note from Table I that the binding energy for vacancies initially separated by three neighbors along the $\langle 110 \rangle$ direction in the absence of strain is 0.3 eV, while it is 0.51 eV with a 2.5% lateral strain. The coalescence of these vacancies in a strained

TABLE I. Different energies for single and double vacancies, calculated using the (SW) potential with modified (1.75 times the original value) parameters under both, unstrained and strained lattices.

	Formation energy single vacancy eV	Migration energy single vacancy eV	Binding energy vacancy-vacancy[a] eV	Limiting barrier during coalescence eV
Without strain	2.80	0.33	0.30	0.33
2.5% tensile strain	2.54	0.13	0.51	0.46

[a] This is calculated as the difference between energies when two vacancies are three neighbors apart and when they are coalesced.

lattice will indeed be the lowest-energy state possible, as indicated from the comparison above. The coalescence is, however, an activated process under strain with activation energies from 0.13 eV (for single-vacancy migration, which is expected to be faster in the strained case since the barrier without strain for the same process is 0.33 eV) to 0.46 eV at different stages of coalescence with a 2.5% lateral strain. Atomistic computer simulations by Ghaisas and Madhukar[9] show that due to the strain relaxation at the edge of the clusters in the growth of the lattice mismatched layer, vacancies or interstitials in the growing layers are introduced that can act as a precursor to the formation of dislocations. Thus the dislocation formation also will be an activated process. From the present study, however, it is not clear how a larger number of vacancies (greater than 2) will behave, from the preferred directionality point of view. The anisotropy in the coalescence will be important in generating the line defects. In the present study, due to the limitations on the computational strength, this aspect could not be considered.

Finally, it may be noted that a recent version of Tersoff's potential[10] indeed gives the single vacancy as the ground state. However, due to the customization and neglect of electronic effects, the reliability in the physical processes described by the use of these potentials is difficult to evaluate.

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