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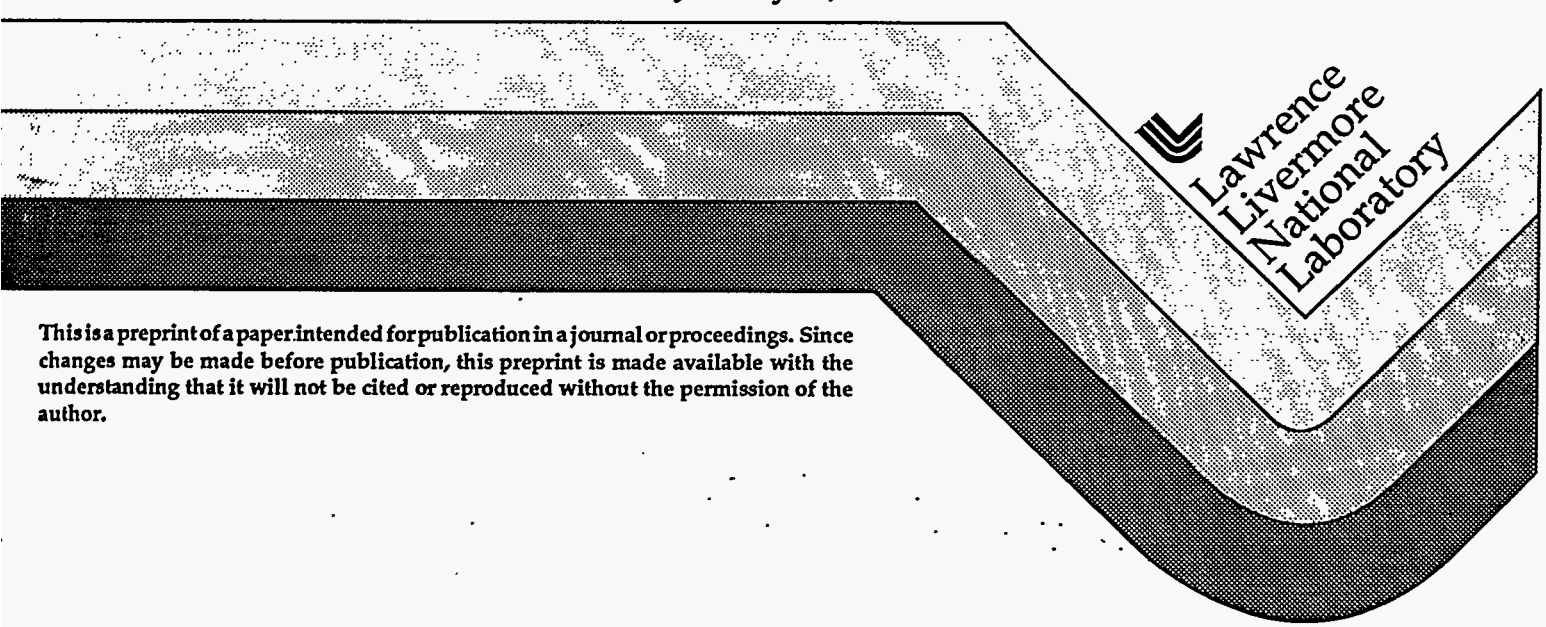

TIGHT-BINDING MOLECULAR DYNAMICS SIMULATIONS ON POINT DEFECTS DIFFUSION AND INTERACTIONS IN CRYSTALLINE SILICON

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ABSTRACT

Tight-binding molecular dynamics (TBMD) simulations are performed (i) to evaluate the formation and binding energies of point defects and defect clusters, (ii) to compute the diffusivity of self-interstitial and vacancy in crystalline silicon, and (iii) to characterize the diffusion path and mechanism at the atomistic level. In addition, the interaction between individual defects and their clustering is investigated.

INTRODUCTION

Ion implantation is now a standard technique in the processing of Si-based microelectronics. Further advances in ion beam processing, however, necessitate a strong improvement in our basic understanding of defect production, defect diffusion, defect-defect and defect-impurity interactions, amorphization and microstructure evolution. Such an improved fundamental understanding can be obtained by computer simulations, where a validated advanced materials modeling tool is employed. Molecular dynamics (MD) methods are very well suited to provide good models to study irradiation-induced defects. In fact, they offer an atomistic picture of the above phenomena, by describing the complete dynamics of both defects and the host matrix. A crucial issue for MD simulation is the model adopted for the interatomic interactions. Classical MD is a valuable tool when dealing with collision cascades and subsequent collisions taking place at a long length and time scale. However, fully empirical interatomic potentials have a limited reliability when used to compute formation energies of point-defects, binding energies of clusters of defects or diffusion phenomena. On the other side, first-principle MD simulations (which are more fundamental and accurate) are in practice limited to a small number of atoms (of the order of 100) and to very short simulation times ($\sim$ ps) because of their heavy computational workload.

In the present work, we apply tight-binding molecular dynamics (TBMD) to the study of point defects and their clusters in Si. In the TBMD scheme, the forces among atoms are derived from the underlying electronic structure, as in first–principles MD. The electronic structure is, however, computed by means of a semi-empirical tight-binding (TB) model, thus dramatically reducing the computational expense. A detailed description of TBMD can be found elsewhere.[1,2] The TB scheme warrants good modeling of the covalent chemical bonding in crystalline Si. This feature is a key issue when dealing with defects, whose formation and diffusion in a crystalline host matrix result in rather large bond-breaking and re-bonding.

This paper is organized as follows. We first provide some details of the TBMD model, then present and discuss the results on single point defects and their diffusion, followed by discussions of interstitial and vacancy clusters and final conclusions.

COMPUTATIONAL METHODOLOGY

In this work, we make use of the Kwon et al.[3] TB model for silicon (KBWHS). Here the short-ranged repulsive potential U_{rep} as well as the scaling functions for the TB hopping integrals are improved compared to the previous Goodwin et al.[4] parameterization (GSP). More specifically, the form of U_{rep} is embedded-atom like, while in the GSP model only two-body interaction were considered. Furthermore, different scaling functions for the TB hoppings are introduced according to the orbital symmetry in a close agreement to first-principles calculations. The resulting TBMD scheme is more accurate, as demonstrated in Table I that will be discussed in the next section.

Most of the results presented here have been obtained using large cubic periodically-repeated simulation supercells containing 216 atoms plus (minus) the number of interstitial (vacancy) defects involved. Typical simulations for annealing and relaxation are performed a few picoseconds. The diffusivities are currently calculated using the 64 atoms cell and with a simulation time up to 100 ps. The formation energy E^f is defined as the energy difference between the defected system and the perfect system with same number of atoms. The binding energy for a cluster of size N is defined as $E^b_N = E^f_{N-1} + E^f_1 - E^f_N$, where E^f_1 is the formation energy of a single defect, and E^f_{N-1} and E^f_N are the formation energies for clusters of size $N-1$ and N, respectively.

Defect	LDA	KBWHS	GSP	SW
Vacancy	3.65	3.69	3.96	2.64
T interstitial	3.5	4.39	4.40	4.84
H interstitial	3.3	4.93	5.90	6.58
(110) dumbbell	3.2	3.80	5.04	3.65

TABLE I - Formation energies (eV) of single point defects in crystalline Si obtained using TBMD of Kwon et al. (KBWHS) and Goodwin et al. (GSP), compared with local density approximation (LDA) results and Stillinger-Weber potential (SW).

RESULTS AND DISCUSSION

Single Point Defects

The formation energies of single vacancy and interstitial defects in silicon are calculated by TBMD at low temperature. The interstitial defects considered are the hexagonal site (H), the tetrahedral site (T) and the (110) dumbbell (two atoms share one common lattice site), which are believed to be the most important interstitial defects in crystalline silicon from previous studies.[5-8] The initial structures of each type mentioned above are set up in a perfect Si crystal, TBMD is then performed to relax the structures until they reach their energy minimum. The formation energies are finally calculated. The vacancy formation energy is computed by taking out one atom from its lattice site and relaxing the crystal to reach its energy minimum. The results of the formation energies are summarized in Table I, and compared to data obtained from first-principle local density approximation (LDA) calculation, GSP and classical (SW) molecular dynamics. The comparisons show that, among the four methods, the formation energy of single vacancy using the

TB parametrization by Kwon et al.[3] (KBWHS) agrees best with the LDA calculation. The KBWHS model predicts the same structure as LDA calculation for the energetically most favorable interstitial defect, i.e., the (110) dumbbell, with close formation energies. Note that although the SW model also gives close formation energy for (110) dumbbell, the resulting structure is different from LDA results.[5] The bond length of the dumbbell from the KBWHS model is 2.41Å, about 10% smaller than the LDA result.

Although the KBWHS model gives different formation energies for the tetrahedral and hexagonal interstitials when compared to the LDA results, the diffusion path of the (110) dumbbell defect is rather similar to that obtained by LDA calculation.[6] During a TBMD simulation performed at $T = 1000K$, the dumbbell was found to move into the closest tetrahedral interstitial position along the (110) chain and then move back to a (110) dumbbell at the second nearest neighbor lattice site, as shown in Fig.1. The migration energy for this process can be estimated to be $E^m \approx 0.6eV$, i.e., of the order of the energy difference between the formation energy of the dumbbell and the tetrahedral interstitial.

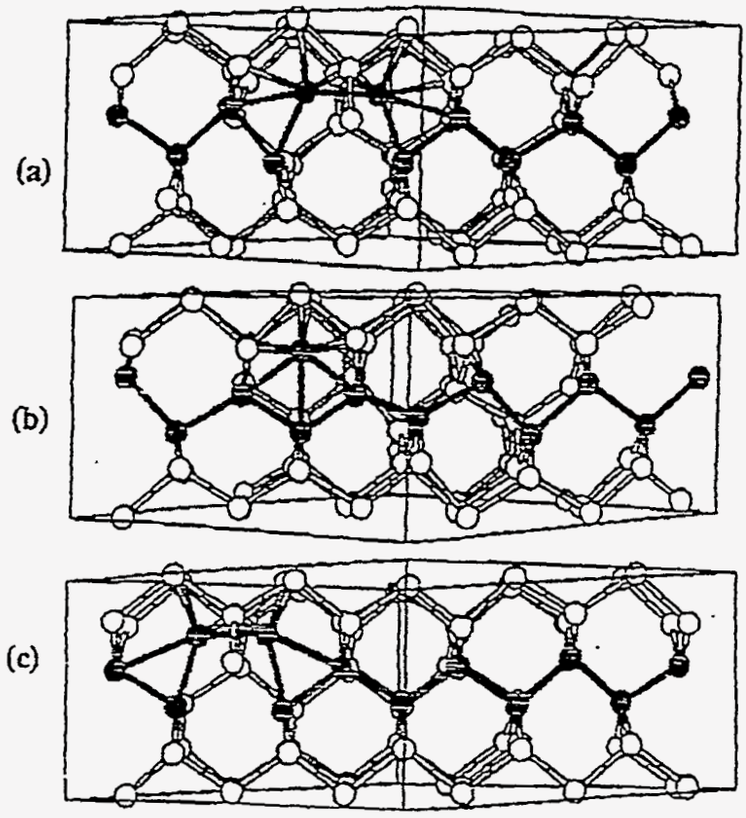

FIG.1 - Diffusion path of a (110) dumbbell defect as observed during a TBMD simulation at 1000K. (a) starting configuration; (b) intermediate configuration (the dumbbell has moved to a tetrahedral position); (c) final configuration (the dumbbell structure is recovered at the second nearest neighbor site of (a)).

Vacancy relaxation shows Jahn-Teller distortions: the four nearest neighbor atoms of the vacancy do not relax symmetrically. One atom moves towards the center of the vacancy by about 40% of the nearest neighbor distance; the other three atoms move equivalently towards each other, in the near inward direction, to form an equal lateral triangle, with a displacement of 15%. To roughly estimate the migration energy, the energy difference of a perfect vacancy and a vacancy with a neighbor atom moved to the bond center (which corresponds to the saddle point for diffusion) is calculated, and the migration energy is estimated to be $0.4eV$. This is only an approximate value since no relaxation is allowed. A more accurate way to obtain the migration energy is from the Arrhenius plot of the diffusivities, which is in progress.

Experimentally, the self-diffusion coefficients exhibit Arrhenius behavior over a wide temperature range, with an activation energy of $4.8eV$.[10] If the diffusion is induced by a mechanism involving either interstitials or vacancies, the activation energy should correspond to the sum of the formation energy and the migration energy of the responsible defect. Based on our calculations, the activation energy for interstitial-mediated and vacancy-mediated diffusion is $3.8 + 0.6 = 4.4eV$ and $3.7 + 0.4 = 4.1eV$ respectively.

Finally, we have computed the diffusivity of the vacancy and dumbbell defects at finite-temperature of ~1500K, obtaining $\sim 7\ 10^{-7}$ cm^2s^{-1} and $\sim 5\ 10^{-8}$ cm^2s^{-1} respectively. These values are smaller than the SW data reported in Ref.[5].

Interstitial Clusters

Individual interstitial defects can interact with each other during the damage annealing process after ion implantation to form defect clusters. Under large dose irradiation conditions, they can further develop extended microstructures such as {311} defects and dislocation loops. In order to understand the role of defects in transient enhanced diffusion, it is of great importance to study their formation and binding energies.

We have studied a di-interstitial cluster formed through the interaction of two (110) dumbbells. The simulations show that two (110) dumbbells, either parallel or perpendicular to each other, at nearest neighbor sites attract and form a stable configuration given by one (110) dumbbell plus a neighboring tetrahedral interstitial. This di-interstitial has a formation energy of $E^f = 5.44eV$ and a binding energy of $E_2^b = 2.17eV$. The di-interstitial cluster found here is different from that obtained using the SW potential, where the di-interstitial is formed by two tetrahedral interstitials at nearest neighbor sites with a binding energy of $1.6eV$.[5] The latter di-interstitial structure is found to be unstable in our TBMD and found to change quickly into the stable configuration of one (110) dumbbell with a neighboring tetrahedral interstitial at 300K.

Finally, tri- and tetra-interstitial clusters have also been studied. The tri-interstitial cluster is found to be formed by two perpendicular (110) dumbbells (slightly distorted) sharing a common lattice site with a binding energy of $1.68eV$. And the tetra-interstitial cluster is found to be formed by two di-interstitials at nearest neighbor sites with a binding energy of $0.83eV$. The study of larger size interstitial clusters is in progress.

Vacancy Clusters

The vacancy clusters are formed by taking atoms away from adjacent sites in the Si crystal. The system is then allowed to relax and reach its energy miminum to obtain the binding energy. Fig.2 shows the binding energies compared to those from the SW calculation,[5] as well as an experimental data point for the di-vacancy.[9] The di-vacancy binding energy obtained from our TBMD calculation is in close agreement with the experimental data. An important feature shown in both curves is that the binding energy

reaches a maximum at a certain cluster size, 4 for KBWHS and 5 for SW. This implies that the vacancy clusters with this particular size are most stable during the defect annealing process. Finally, we would like to point out that, based on our observations, the strain field of the vacancy and its clusters are more extended compared to those of the interstitials.

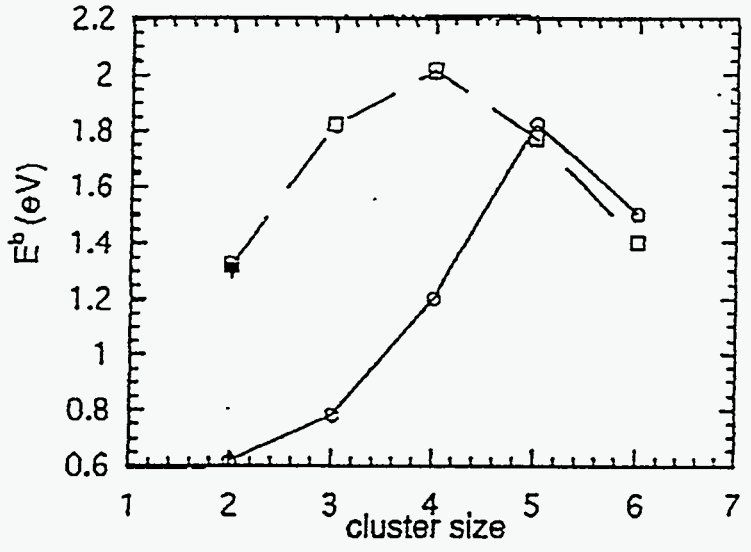

FIG.2 - TBMD binding energy E^b (eV) for a vacancy cluster as function of the cluster size (open squares). Experimental (full triangle) and SW (open circles) data are shown for comparison.

CONCLUSIONS

Based on our results presented above and the comparisons with LDA calculations and available experimental data, we find that the tight-binding KBWHS model provides a valid tool to study teh ground state of neutral point defects in crystalline silicon. Using this model, we are able to not only characterize the static structures of point defects and their clusters, but also to describe ther dynamic diffusion in crystalline silicon at atomistic level. A striking observation from the interstitial cluster studies is that the binding energy goes down as the cluster size goes up. This naturally raises the question regarding the formation of large interstitial clusters, such as the extended defect {311} observed in experiments. This points to a direction of our future study, i.e., to understand how the {311} and other extended defects are nucleated in crystalline silicon.

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