A novel technique for the structural and energetic characterization of lattice defects in the molecular dynamics framework

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Abstract

We present a technique which allows the direct determination of defect structures and energetics in the molecular dynamics framework. Due to its computational simplicity, it can be applied during the actual molecular dynamics simulation. This allows the monitoring of the evolution of the defect properties as a function of time and/or temperature. We have applied it to deduce a criterion for discriminating the amorphous and crystalline phases of Si, and to study the variation with temperature of the configuration and formation energy of the Si self-interstitial.

1. Introduction

In recent years defect engineering has become an important issue in the fabrication of integrated circuits (IC). Point and extended defects, amorphous pockets and even full amorphous layers can be formed during the implantation stage. They have been shown to affect dopant diffusion and consequently the electrical behavior of the manufactured devices [1]. On the design of new IC generations, with ever shrinking sizes, it is becoming essential the use of process simulators in order to avoid the realization of expensive and time-consuming experiments [2]. To have predictive capabilities, these simulators must include detailed information about the properties of such defects (energetics, interactions, diffusion, etc.). The molecular dynamics (MD) simulation technique has been shown to be a good tool for the determination of defect properties, since the small sizes and time scales often involved usually preclude direct experimental characterization.

The MD method consists of the numerical resolution of the equations of motion for a system
of \( N \) atoms [3]. These equations are discretized in time and solved in a computer by using a suitable integration algorithm. The outcome of the MD simulation in each time-step \( \Delta t \) is the set of positions \( \{r^{N}\} \) and momenta \( \{p^{N}\} \) for all atoms. In classical MD, where empirical interatomic potentials are used, \( N \) can be as high as 1 million atoms and simulations can be carried out for \( 10^6 \) time-steps or even more. It is easy to realize that the amount of generated data is overwhelming. That is precisely why the most difficult task when carrying MD simulation studies is the analysis of the obtained data.

For the structural and energetic characterization of amorphous pockets within the MD framework it is essential to discriminate which atoms in the simulation belong to them and which ones are in perfect crystal positions. Methods usually employed consist of the evaluation of atomic potential energies [4] or angles among atoms [5]. However, as we shall see, these criteria could lead to wrong conclusions. On the other hand, for the determination of the stable configuration and the formation energy of point or extended defects, some relatively complex and time consuming minimization techniques have to be employed, such as the steepest-descent/conjugated-gradient methods, or the cooling down to 0 K [6,7]. We present a novel technique based on time averaging the atom coordinates, which allows determining defect structures and energetics directly off the MD simulation, and thus monitoring the evolution of the defect properties as a function of time and/or temperature. To show the possibilities this technique offers, we have applied it to define a criterion for the identification of the Si amorphous phase and to study the structure and energetics of the Si self-interstitial as a function of temperature.

2. Md simulations

In our simulations we used a system consisting of 576 Si atoms (577 in the case of the self-interstitial study). The dimensions of the computational cell were \( 4a \times 3\sqrt{2}a \times 3\sqrt{2}a \), being \( a \) the Si basic unit cell length (5.43 Å). The MD cell, of approximately the shape of a cube, was bounded by two (100) planes in the \( X \) direction and by four (110) planes in \( Y \) and \( Z \) directions. To describe the Si–Si interactions we employed the Tersoff potential within its third parametrization [8], one of the most commonly used empirical potentials for Si since it has been shown to give a good description of the Si amorphous and liquid phases and point defect properties [9,10]. To minimize finite size effects we used periodic boundary conditions along the three axes. We solved the classical equations of motion using the 4th order Gear predictor–corrector algorithm [11] with a variable time-step.

3. Identification of the amorphous phase

In order to identify disordered zones embedded in crystal Si during MD simulations some methods have been devised. Uttormark et al. employed three different criteria, one of them based on the coordination of the atoms and the other two on the angles they form [5]. These three criteria were successfully used to identify crystalline clusters in a liquid environment, since the coordination in the liquid is around 6, and the angles are strongly distorted with respect to the ones in the perfect crystal lattice. Unfortunately, these criteria are not helpful when considering an amorphous structure. This is due to the fact that the amorphous state has a short range order and shares some of the structural features of the crystalline phase: basically all the atoms are fourfold coordinated and the angular distribution is peaked around 109.5, the typical angle of the diamond lattice. A different type of criterion was used in the MD simulations of structural transformations and defect production in ion implanted Si [4]. In this study, atoms with potential energies 0.2 eV above the ground state of the crystal were identified as amorphous. This criterion is appropriate for determining the damaged regions (amorphous pockets) produced in the crystal lattice by the incoming ion, since the involved atoms are in a state of high potential energy. However, when the amorphous and crystalline phases are in quasi-equilibrium (i.e. the amorphous phase is very well relaxed) this criterion could lead to error. If we apply the energy
criterion in two different samples stabilized at 773 K, one purely amorphous and the other a perfect crystal, 5% of the atoms in the crystal would be considered as amorphous atoms and 24% in the amorphous phase as crystalline ones.

This inconvenience is related to the spreading of the angle and energy distributions for the crystalline atoms due to thermal vibrations. These can be effectively removed by averaging in time the atom coordinates. Fig. 1(a) and (b) show the three-body correlation functions for crystalline and amorphous Si at 773 K, respectively, when the positions of the atoms are averaged in time for 100, 200 and 300 fs. For the sake of comparison, we show as well the distributions without averaging. Note that the cosine angle distributions become narrower in the crystal case, but are not affected in the amorphous case. This is because as thermal vibrations are eliminated in the averaging process, atoms in the crystal tend to its equilibrium position and consequently the angle distributions become narrower. However, in the amorphous case the dispersion in the angular distributions is not due to thermal agitation but to the amorphous structure itself. Consequently, this dispersion is not affected by time averages. This difference in behavior allows us to introduce a criterion to distinguish the amorphous from the crystal phase of Si. This method has been successfully used to study the evolution during annealing of amorphous pockets produced in Si by ion irradiation [12] and the radiation-assisted recrystallization behavior of crystalline seeds embedded in the amorphous phase [13].

4. Si Self-interstitial characterization

To study the variation of the Si self-interstitial properties with temperature we have carried out different MD simulations for several temperature values between 1000 K and 2400 K, the predicted melting point in the Tersoff 3 description of Si [14]. Initially the atoms are set to occupy perfect lattice positions. An extra atom is then introduced in a hexagonal interstitial position, just to keep it as far as possible from their first neighbors in the perfect lattice (if the extra atom is set close to any host atom, an artificially high repulsive energy may be introduced in the cell). By velocity re-scaling during an initial run samples are stabilized at each given temperature. Initial velocities are chosen from a Maxwell–Boltzmann distribution corresponding to each temperature to be simulated. Then the system is allowed to freely evolve in the NVE ensemble until the total simulation time is reached. This time should be long enough to assure that a meaningful part of the phase-space is sampled.

Usually thermal agitation precludes the direct determination of the structure and formation energy of defects when using the MD technique, above all at high temperatures, as can be seen in Fig. 2 for the case of the Si self-interstitial. Each atom vibrates around the local potential energy minimum which occupies. To get a clean configuration from a MD run different methods can be
used. In the cooling down to 0 K the kinetic energy of the system is slowly drained until the total temperature has dropped close to 0 K [6]. In the steepest-descent and/or conjugate-gradient methods atoms are moved along the direction of the maximum variation of the interatomic potential curve [7]. In both cases particles are gradually displaced to their closest local potential minimum, thus eliminating thermal vibrations. Then it is possible to extract clean configurations and formation energies for the defect. However, these techniques are relatively computer demanding, and thus they cannot be applied to every configuration obtained from the MD simulation. Besides, there is not certainty of reaching the global potential minimum instead of a local minimum, and the information regarding the influence of temperature is lost.

The disturbing thermal vibrations can be eliminated by averaging in time the atom coordinates, as we have shown in the previous section. The result of the time average during 1000 simulation time-steps is also represented in the Fig. 2, along with the atom coordinates obtained by cooling down to 0 K using atom velocity re-scaling every 1000 steps for a total MD simulation run of $10^6$ steps. As can be seen, the time average gives a very good approximation to the positions obtained by cooling down to 0 K, but at a much lesser computational cost. Besides, this technique can be applied on the fly, i.e., during the actual MD simulation. Consequently, it is possible to extract the evolution in time of the Si self-interstitial configuration and energetics.

We have carried out time averages on the atom coordinates every 1000 steps at every simulated temperature. Each averaged configuration is compared to the perfect lattice: when an atom is closer than 0.7 Å to a lattice site the atom is associated to that site, otherwise it is labeled as “displaced”. In the same way, lattice sites with no associated atom are labeled as “empty”. This method allows a first classification of the Si self-interstitial configurations. Once each set of averaged atomic positions obtained along the simulation is classified in terms of displaced atoms and empty sites, it is possible to make a statistical study of the morphology and energetics of each interstitial configuration. We have identified four basic interstitial configurations, which are represented in Fig. 3. In the first one shown in Fig. 3(a) there are no empty lattice sites but one displaced atom which occupies a tetrahedral interstitial site. This is the so-called tetrahedral interstitial, usually represented by $T$. Fig. 3(b) shows the dumbbell interstitial ($D$), where two displaced atoms oriented along the $\langle 110 \rangle$ direction share a common lattice site. $T$ and $D$ interstitials are the most studied Si self-interstitial configurations [6,9]. In Fig. 3(c) appears the extended interstitial ($E$), where four displaced atoms and three empty lattice sites lie on a (110) plane. This configuration has been observed to appear during recrystallization from a planar crystal-amorphous interface in MD simulations [15]. Fig. 3(d) shows an interstitial configuration that, to our knowledge, has not yet been reported in the literature. It consists of three displaced atoms and two empty lattice sites. We have observed that it appears as the saddle point between the $D$ and $E$ configurations. Consequently, we will refer to it as $DE$ interstitial. It is worth to note that while the $T$, $D$ and $E$ interstitials are high-symmetry configurations, that is not the case of the $DE$ interstitial.

Fig. 2. $XY$ projection of the trajectories followed by a Si self-interstitial and its neighbors during 1000 simulation steps at 2200 K. Open circles represent the potential energy minima, as obtained by cooling down to 0 K. Crosses are the positions obtained by time averaging the atom coordinates during the 1000 steps.
In Fig. 4(a) we represent the relative concentrations \( C_i \) found in our simulations for each interstitial configuration \( i \) as a function of temperature. As can be seen, relative concentrations of the \( T \) and \( E \) interstitials decrease linearly with temperature, while for the \( D \) and \( DE \) interstitials the concentrations increase linearly. \( C_i(T) \) gives the relative probability of finding the Si self-interstitial in a given configuration at each temperature \( T \). As can be deduced from Fig. 4(a), the most frequent configuration is the \( T \) interstitial at all temperatures. Formation energies \( E_i \) for each interstitial type are calculated by the evaluation of the potential energy of the system containing each given configuration and subtracting that of a perfect crystal with the same number of atoms [6,9]. The potential energy corresponding to a perfect crystal lattice at each temperature is extracted by carrying out the same type of time average done for the system with the extra atom. Formation energies obtained from our simulations are represented in Fig. 4(b) as a function of temperature. Thin solid lines are best linear fits. As can be seen, formation energies decrease linearly with temperature, except for the case of the \( T \) interstitial. It is noteworthy that when extrapolating these lines to \( T = 0 \) K, the formation energy values are in very good agreement with the ones obtained by other authors [9,15]. The thick solid line represents the total formation energy, calculated as \( \sum C_i E_i / 100 \).

5. Conclusions

We have presented a novel technique to be used in MD simulations that allows the structural and energetic characterization of defects in Si. It is based in the time average of the atom coordinates along the simulation. With this simple technique it is possible to extract clean atomic configurations where thermal vibrations have been eliminated, allowing for a direct analysis of the defect structure as well as its associated energy. Advantages are (a) its computational efficiency in comparison to other
techniques routinely used for potential energy curve minimization, (b) the temperature-dependent information is not lost, and (c) the possibility of its application on the fly, which allows studying the variation of the defect properties in time.

We have applied this technique to introduce a criterion for the discrimination between amorphous and crystalline phases of Si, and to the study of the variation with temperature of the Si self-interstitial properties. We have observed that the Si self-interstitial can appear in different configurations, characterized by different formation energies. We have determined the relative probability of a self-interstitial being in a given configuration, which in turn has been found to depend on temperature. This is the reason behind the variation of the self-interstitial formation energy with temperature. A more detailed study on this matter is currently under way.

References