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# Molecular-dynamics study on atomistic structures of amorphous silicon

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## Abstract

Structural characteristics of amorphous silicon (a-Si) have been examined by molecular-dynamics calculations using the Tersoff interatomic potential. It was confirmed that the computer-generated atomic configurations reproduce well the structural and dynamical properties of a-Si obtained experimentally. The a-Si networks contained two types of structural defect: threefold coordinated Si atoms (dangling bonds) and fivefold coordinated ones (floating bonds). The average bond length increased with the coordination number. Bond angles were distributed around  $120^\circ$  for the threefold coordinations, suggesting the existence of the atomic clusters constructed by  $sp^2$  bonding. On the other hand, they had peaks at  $\sim 60^\circ$  and  $90^\circ$  for the fivefold coordinated atoms. Partial radial distribution functions revealed that the floating bonds have a tendency to cluster in the a-Si network.

## 1. Introduction

Amorphous silicon (a-Si) is a prototype of tetrahedral amorphous semiconductors with covalent bonding. In addition, a-Si films are of technological importance for electronic applications such as solar cells and display elements. In order to develop these applications, it is important to understand the physical properties of a-Si, so extensive studies on structural, thermodynamic, and electronic properties of a-Si have been carried out. A molecular-dynamics (MD) simulation is a possible way to obtain atomistic information regarding amorphous materials, and much effort has been devoted to construct structural models of a-Si [1–6]. Car and Parrinello [1] and Stich *et al* [2] generated a-Si by rapid quenching from melted Si, employing *ab initio* MD simulations in which the volume of the MD cell was gradually increased by applying negative pressure. The structural, dynamical, and electronic properties of the computer-generated a-Si were in good agreement with those obtained experimentally. However, *ab initio* MD simulations are numerically so intensive that they are limited to a short period of time and small number of atoms.

The main advantage of an empirical interatomic potential is that it is much cheaper to use and can therefore model a larger number of atoms than more robust methods. We have recently performed MD simulations using the Tersoff interatomic potential [7] in order to examine the

validity of this potential for liquid Si (l-Si) [8, 9] and a-Si [10]. In our MD procedures, a-Si networks were generated by simply quenching l-Si without any *ad hoc* procedures. It was confirmed that the computer-generated networks thus obtained reproduce well the structural and dynamical properties of a-Si obtained experimentally [11–13]: the Tersoff potential is applicable for preparing a-Si, though it gives rise to a high melting temperature [8, 9, 14]. In the present study, we carried out MD simulations using the empirical Tersoff potential in order to clarify the local structures of a-Si.

## 2. Simulation procedures

The a-Si networks were prepared by the same computational procedures as described previously [10]. An empirical interatomic potential developed by Tersoff [7] was used in this paper to represent the interactions between Si atoms. A justification of the Tersoff potential for this system was described in [8–10]. MD simulations were performed under constant-*NVT* conditions, i.e. constant-volume and constant-temperature conditions. The 1000 Si atoms were at first placed on the diamond lattice sites in a cubic MD cell with periodic boundary conditions. The size of MD cells was chosen to be  $5a_0 \times 5a_0 \times 5a_0$ , where  $a_0$  is the equilibrium lattice parameter of Si ( $a_0 = 0.357$  nm), corresponding to the experimental density of crystalline Si (c-Si) and a-Si, namely  $2.33 \text{ g cm}^{-3}$ . Then the system was heated up and quenched by rescaling the velocities of the particle. The Newtonian equations of motion were integrated using the velocity form of the Verlet algorithm [15] with a time step  $\Delta t = 2 \times 10^{-3}$  ps. The forces acting on all particles are analytically calculated by taking the deviation of the potential energy with respect to each atomic position.

The adjustable parameters of the Tersoff potential were determined by fitting to a database containing the cohesive energy, lattice constant and bulk modulus of the diamond structure and the cohesive energy of  $\text{Si}_2$  and bulk polytypes of Si. It should be noted that the Tersoff potential is not adjusted to fit to any liquid-phase data. Therefore, this potential overestimated greatly the melting temperature of crystalline Si. To generate the configurations in the liquid state, the initial configuration was melted at 3500 K by periodic velocity scaling during 200 ps ( $10^5 \Delta t$ ). The system showed a highly diffusive behaviour at this temperature and was found to reach equilibrium during this period as judged by the total energies. The melted Si was cooled down to 300 K with a rate of  $5 \times 10^{12} \text{ K s}^{-1}$ . This cooling rate is almost the same as the estimated cooling rates that were achieved in laboratories to prepare a-Si by laser annealing techniques [16]. It should be noted that l-Si is simply quenched without any *ad hoc* procedures such as the application of negative pressure [1, 2] and the enhancement of tetrahedral force component [3, 4] during the cooling procedures as adopted by previous investigations. The as-quenched sample was then annealed for  $10^4$  ps ( $5 \times 10^{16} \Delta t$ ) at 1400 K. After annealing, the samples were quenched to 300 K with a cooling rate of  $5 \times 10^{12} \text{ K s}^{-1}$  before the final structural and dynamical properties were measured.

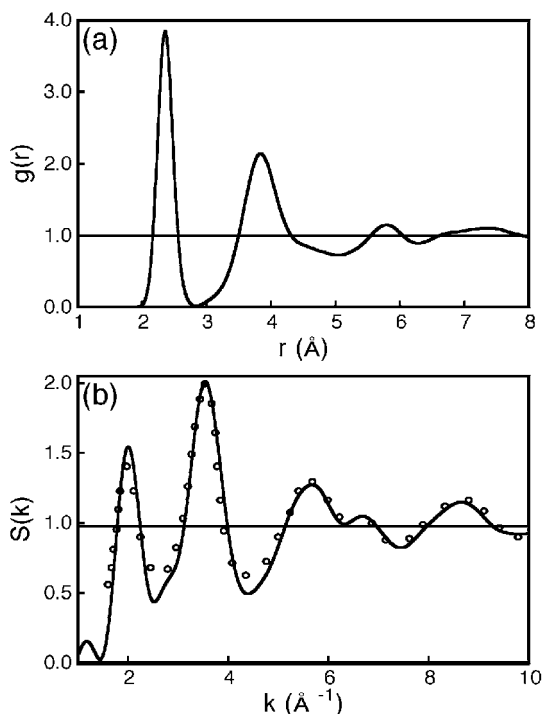
## 3. Results and discussion

Figure 1(a) shows a radial distribution function  $g(r)$  of atomic configurations after annealing. The  $g(r)$  was obtained by averaging over 500 configurations during  $500\Delta t$  (1 ps). We observed no indication of any recrystallization in the time simulated, because the large activation barrier of  $\sim 3.7$  eV lies between the amorphous and crystalline phases [17]. The first and second nearest neighbours exist at 0.235 and 0.386 nm, respectively. It should be noted that the third nearest neighbour peak of crystalline Si (0.450 nm) is not observed, corresponding to the

features of a-Si formed by vapour-phase deposition [11] and sputtering [12]. To compare with the available data of neutron-diffraction scattering [11, 12], the static structure factor  $S(k)$  was calculated by Fourier transforming  $g(r)$ ,

$$S(k) = 1 + 4\pi\rho_0 \int_0^\infty r^2 \{g(r) - 1\} \frac{\sin(kr)}{kr} dr \quad (1)$$

where  $\rho_0$  is the average number density of atoms and  $k$  is the wavenumber of the diffracted wave. Figure 1(b) demonstrates  $S(k)$  corresponding to the  $g(r)$  of figure 1(a). The  $k < 15 \text{ nm}^{-1}$  region contains substantial truncation error and should be disregarded. The result is in excellent agreement with that obtained experimentally from evaporated a-Si (open circles) [12].



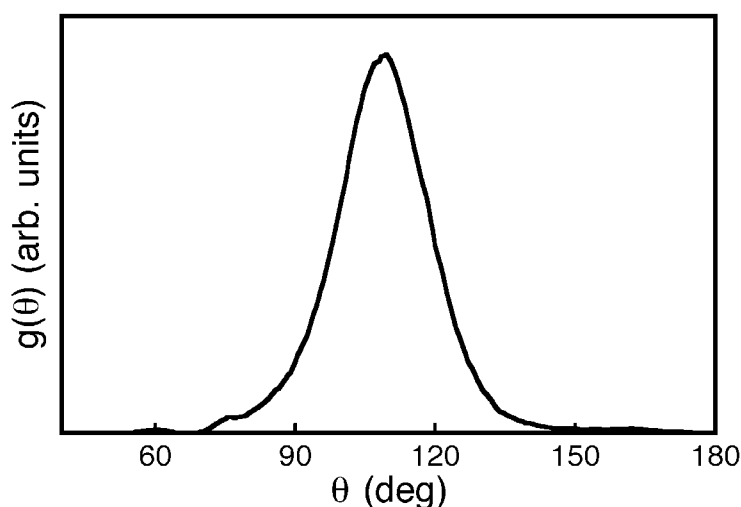
**Figure 1.** (a) Radial distribution function  $g(r)$  and (b) static structure factor  $S(k)$  for the computer-generated atomic configurations. Open circles in (b) indicate an experimental result reported by Fortner and Lannin [12].

The average coordination number, which is estimated by integrating  $4\pi r^2 \rho_0 g(r)$  up to the first minimum in the  $g(r)$ , is 4.07. The computer-generated atomic configuration includes two types of defect: threefold coordinated Si atoms (dangling bonds) and fivefold coordinated ones (floating bonds). The concentrations of the threefold and fivefold coordinated defects are 0.2 and 7.0%, respectively. That is, the dominant structural defect in a-Si is the fivefold coordinated atoms. According to continuous-space Monte Carlo simulations by Kelires and Tersoff [18], the estimated formation energies for fivefold coordinated defects are smaller than those for the threefold coordinated ones, which is consistent with the present MD results. Therefore, it is very probable that both types of defect are present in a-Si. A similar tendency in the distribution of coordination numbers has also been observed in earlier simulations [3, 4, 18, 19].

Typical spin densities, determined by electron-spin-resonance (ESR) measurements, of a-Si films grown by sputtering lie between  $10^{18}$  and  $10^{21} \text{ cm}^{-3}$ , and the dominant ESR active

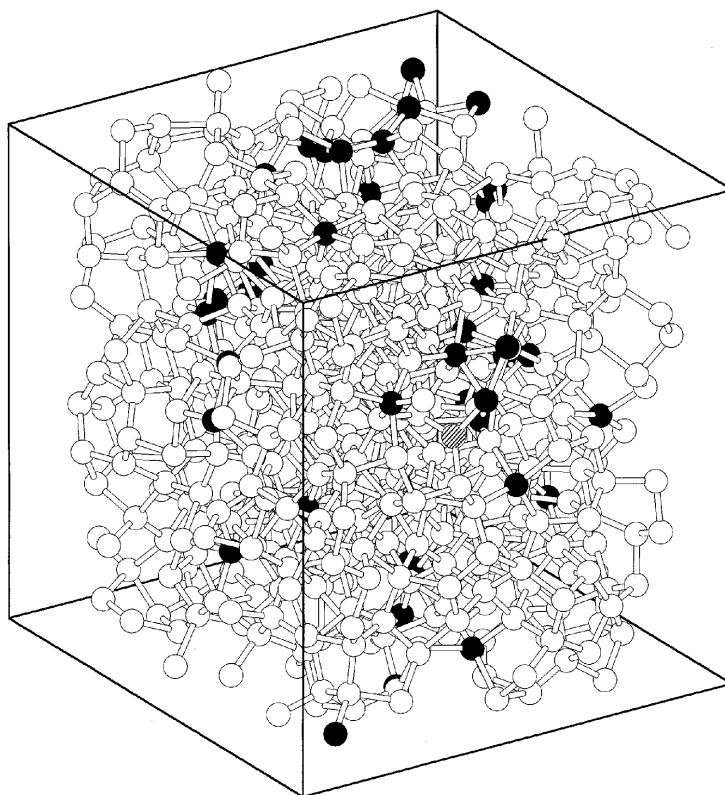
centre is identified as dangling bonds. The a-Si structure obtained by the Tersoff potential includes 0.2% threefold coordinated atoms, corresponding to  $10^{20} \text{ cm}^{-3}$ , which are comparable with experimental values. In addition to the dangling bonds, our simulations show that the floating bond proposed by Pantelides [20] is a possible intrinsic defect in a-Si. If the fivefold sites are ESR inactive, there is no discrepancy between the computer-generated and real a-Si structures. Using a tight-binding approximation with an on-site Hubbard repulsive term  $U$ , Knief and von Niessen [21] have recently discussed the possible defect for the origin of the ESR signals. As a result, they showed that for a realistic value of the Hubbard parameter ( $U = 0.1\text{--}1 \text{ eV}$ ) only dangling bonds give rise to local magnetic moments, whereas floating bonds give only tiny moments: ESR measurements can determine only the concentration of dangling bonds.

Bond angle distributions provide valuable information regarding the local structural units and their connectivity in the amorphous structures. The bond angle distribution function  $g(\theta)$  of atomic configurations is given in figure 2. The cutoff distance to characterize a bond is set at the first minimum position in the  $g(r)$  of figure 1(a). The average position and the standard deviation of bond angles are  $\bar{\theta} = 108.9^\circ$  and  $\Delta\theta = 12.5^\circ$ , respectively. Based on the results obtained by neutron diffraction measurements [12] and Raman scattering spectroscopy [22, 23], it was reported that the bond angle distribution peaks at a nearly tetrahedral angle with  $\Delta\theta = 7^\circ\text{--}13^\circ$ . Good agreement is obtained between the simulated and experimental measured bond-angle variations.



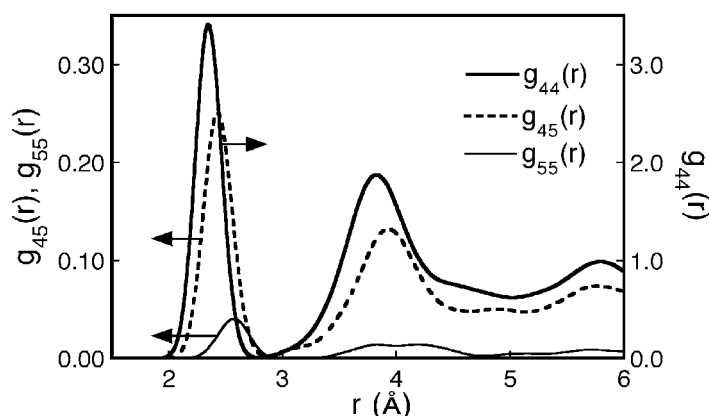
**Figure 2.** Bond angle distribution function  $g(\theta)$  of atomic configurations generated by the Tersoff potential. The cutoff distance is equal to the first minimum position in  $g(r)$  and each distribution is an average over 500 configurations during  $500\Delta t$  (1 ps).

As described above, the present MD approach can represent well the structural features of a-Si obtained experimentally, suggesting that an appropriate amorphous structure is obtained. Therefore, we can discuss more detailed microstructures of a-Si based on the present model. Figure 3 provides a part of the atomic configurations obtained by the present MD simulations. Open spheres indicate fourfold coordinated sites, while defects are denoted by hatched (threefold) and closed (fivefold coordinated sites) spheres. It appears that the fivefold coordinated atoms have a tendency to cluster in the amorphous network.



**Figure 3.** Snapshot of atomic configurations in selected regions of the MD cell. Bonds are defined by neighbours within the first minimum position in the  $g(r)$  of figure 1(a). Hatched, open and closed circles denote the threefold, fourfold and fivefold coordinated atoms, respectively.

Galli *et al* [24] carried out *ab initio* MD studies on liquid and amorphous carbon, and examined their structural properties using the partial radial distribution function  $g_{ij}(r)$  [25]. The  $g_{ij}$  provides information regarding the spatial distributions of defects, therefore we applied this analysis to a-Si (figure 4). The thick and thin solid lines denote the like-defect pair-correlation  $g_{44}$  and  $g_{55}$ , respectively, and the broken line denotes the unlike-defect one  $g_{45}$ . We do not display the partial pair-correlation related to the threefold coordinated sites, because these sites are so few that an accurate statistics cannot be obtained. The average bond length (the location of the first peak) tends to become longer with the increase of the coordination number. A similar behaviour in the bond length is observed in melted Si [9, 26]. Our calculation reveals that the floating bonds show a tendency to cluster (see figure 3). Indeed the ratio  $\int_0^{r_m} g_{55}(r) dr / \{\int_0^{r_m} g_{35}(r) dr + \int_0^{r_m} g_{45}(r) dr\} = 0.19$ , where the integrals are extended from zero up to the first minimum  $r_m$  in the  $g_{ij}$ , is considerably larger than the value  $N_5/N_4 = 0.08$ , which one would obtain for randomly distributed fivefold coordinated atoms ( $N_4$  and  $N_5$  indicate the number of fourfold and fivefold coordinated sites, respectively.) This suggests that the floating bonds are preferably connected to fivefold coordinated atoms rather than fourfold ones. The coordination defects give rise to additional peaks in the electronic density of states of a-Si in the region of the Fermi level, therefore the clustering of floating bonds may be important in understanding electronic properties of a-Si.



**Figure 4.** Partial radial distribution functions  $g_{ij}(r)$  of the Tersoff amorphous network. The  $g_{ij}$  is defined to be the number of particles with coordination  $i$  per unit volume, found at a distance  $r$  from an origin site with coordination  $j$ .

The partial bond angle distributions for atoms with (a) three-, (b) four- and (c) fivefold coordination numbers are displayed in figure 5. For the threefold and fourfold coordinations, the bond angles are distributed around  $120^\circ$  and the tetrahedral angle ( $109.5^\circ$ ), respectively, suggesting the existence of  $sp^2$  and  $sp^3$  bondings in a-Si. Besides the main peak of  $\sim 90^\circ$ , a second peak at  $\sim 60^\circ$  appears in figure 5(c). The distributions in figure 5(c) resemble those in l-Si [8, 9, 26, 27]. Typical examples of the local atomic configurations with (a) under- and (b), (c) over-coordinated Si atoms in a-Si are demonstrated in figure 6. Bonds are defined by neighbours within the first coordination shell in  $g(r)$ . In the Tersoff amorphous structures, all threefold coordinated atoms possess a planar configuration (figure 6(a)), which is consistent with the bond angle distributions of figure 5(a). This feature accords with that of a-Si generated by the Biswas–Hamann potential [28], but our structure contains no dangling bond atoms with a nearly tetrahedral environment reported previously [21]. Interestingly, the fivefold coordinated atoms can be divided mostly into two classes, as indicated in figures 6(b) and 6(c). The former contains a three-member ring, which leads to the  $60^\circ$  peak observed in figure 5(c), while a nearly spiked configuration ( $\sim 90^\circ$ ), as indicated by A–B–C, exists in the latter.

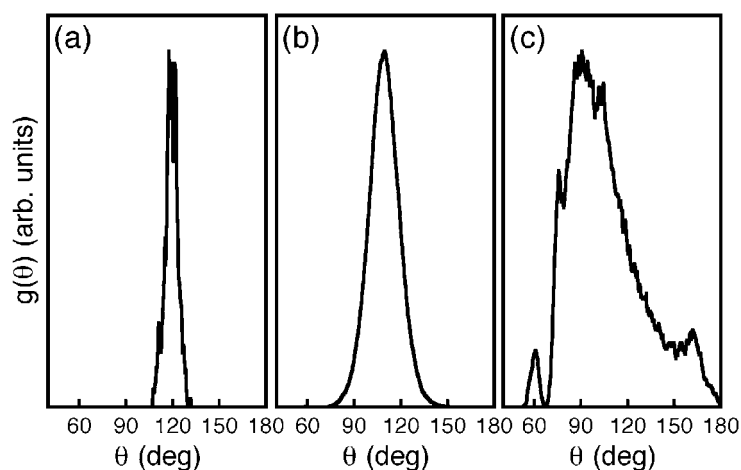
To clarify the dynamical properties of a-Si generated by the Tersoff potential, the phonon density of states  $Z(\omega)$  (PDOS) was calculated by the Fourier transformation of the velocity autocorrelation  $Z(t)$ ,

$$Z(\omega) = \int_0^\infty Z(t) \cos(\omega t) dt. \quad (2)$$

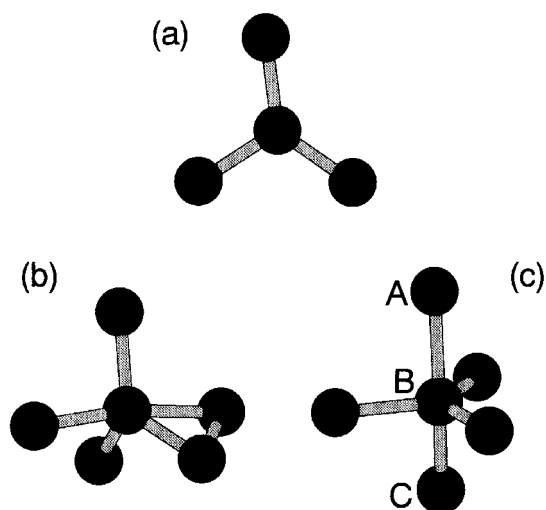
$Z(t)$  is defined as

$$Z(t) = \frac{\langle \mathbf{v}(t) \cdot \mathbf{v}(0) \rangle}{\langle \mathbf{v}(0) \cdot \mathbf{v}(0) \rangle} \quad (3)$$

where  $\mathbf{v}(t)$  is the velocity vector of a particle at time  $t$ . The average in equation (3) was taken over all particles and over different starting times along the equilibrium MD trajectories. Figure 7 indicates the PDOS of the computer-generated a-Si networks. The peaks around 160, 320, 420 and 500  $\text{cm}^{-1}$  correspond to the TA, LA, LO and TO (T: transverse, L: longitudinal, A: acoustic, and O: optical) vibrational mode of c-Si, respectively. These positions are in good agreement with those obtained by neutron diffraction measurements [13] and Raman scattering



**Figure 5.** Partial bond angle distributions for (a) the threefold, (b) fourfold and (c) fivefold coordinated atoms. The bond angles are distributed around  $120^\circ$  for (a) and the tetrahedral angle for (b), while two prominent peaks around  $60^\circ$  and  $90^\circ$  can be observed in (c).



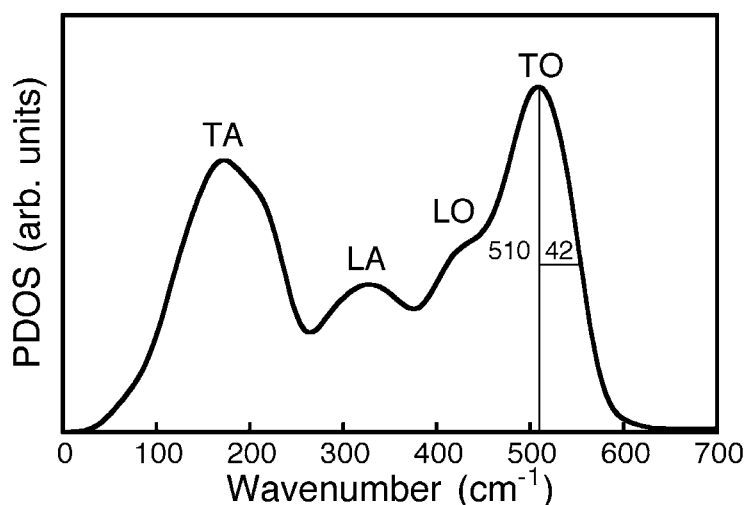
**Figure 6.** Local structural geometries at (a) a dangling bond site and (b), (c) a floating bond site. Bonds are defined by neighbours within the first minimum distance.

spectroscopy [22, 23]. Beeman *et al* [22] have reported that there is a linear relationship between  $\Delta\theta$  and half-width at half-maximum ( $\Gamma/2$ ) of the TO-like peak in a-Si:

$$\Gamma/2 = 7.5 + 3\Delta\theta. \quad (4)$$

To avoid the influence of the LO-like peak at  $\sim 420 \text{ cm}^{-1}$ ,  $\Gamma/2$  in the higher wavenumber region was determined. The calculated  $\Delta\theta$  from  $\Gamma/2$  is  $11.5^\circ$ , almost the same as that estimated from the  $g(\theta)$  of figure 2, and good agreement is obtained between the measured bond-angle variation and that based on Raman estimates [22, 23].





**Figure 7.** Phonon density of states of a-Si generated by the Tersoff potential. This is obtained by the Fourier transformation of the velocity autocorrelation function.

#### 4. Conclusions

The structural properties of a-Si have been examined by using MD simulations. The findings of this study are as follows.

- (1) The structural and dynamical behaviours of a-Si generated by the Tersoff empirical potential were in excellent agreement with those obtained by experiments. This represents that the MD simulations based on the Tersoff potential is sufficient for the structural analysis of a-Si.
- (2) The Tersoff amorphous structures contained defects consisting of the threefold and fivefold coordinated atoms, so-called dangling and floating bonds, respectively. The atoms with the dangling bond possessed a planar configuration with the bond angle of  $120^\circ$ , while the atoms with the floating bond had the peaks at  $\sim 60^\circ$  and  $\sim 90^\circ$ . The fivefold coordinated atoms could be classified into two types: they include a three-member ring or a nearly spiked configuration as a part of the structures.
- (3) The fivefold coordinated defects possessed the longer bond as compared with the threefold and fourfold coordinated atoms, and have a tendency to cluster in a-Si networks.

#### Acknowledgments

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