PERGAMON

Unusual atomic arrangements in amorphous silicon

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Abstract

The existence of small bond angles (like those of triangles and squares) in amorphous silicon networks were studied by the tight-binding molecular dynamics method, by analyzing the statistical data of Si–Si–Si fragments inside large molecules, and also by the Reverse Monte-Carlo simulation method. The influence of small bond angles on the electronic density of states was revealed.
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Numerous diffraction measurements [1–5] and computer simulation studies [6–16] have been carried out on amorphous silicon (a-Si) in recent decades in order to retrieve information about the atomic scale arrangement. In 1985, a continuous random network model of a-Si (WWW model) was constructed by Wooten et al. [6] who carried out Monte-Carlo (MC) simulations using the classical empirical Keating potential. This defect-free network includes five-fold and sevenfold rings in addition to the sixfold rings of the diamond-like structure. Since then, several computer generated models have been constructed using various classical empirical potentials [7–9] or by applying different quantum mechanical methods [10–16], yet, despite this the WWW model is still considered to be the best three-dimensional atomic scale representation of a-Si. The WWW or modified WWW models were applied for electronic structures calculations and the results from these works suggest that the covalently bonded a-Si structures are not completely disordered. The bonds between atoms and the coordination numbers are similar to the crystalline phase.

1. Tight binding molecular dynamics simulations

We have developed a tight binding molecular dynamics (TB-MD) computer code to simulate the real preparation procedure of an amorphous structure, which is grown by atom-by-atom deposition on a substrate. Note that this differs from most other molecular dynamic (MD) studies where the amorphous networks are formed by rapid cooling from the liquid state. Our MD method was successfully used for the description of the amorphous carbon growth [17]. The TB Hamiltonian of Kwon et al. [18] was used to describe the interaction between silicon atoms. All the parameters and functions of the interatomic potential for silicon were fitted to the results of the local density functional calculations. The TB potential reproduces the energies of different cluster structures, the elastic constants, the formation energies of vacancies and interstitials in crystalline silicon. The characters of the local to the extended (Anderson) transition in a-Si was also successfully described using this TB Hamiltonian [19].

In our simulations a rectangular diamond lattice cell containing 120 silicon atoms was employed to mimic the substrate. The simulation cell was open along the (111) direction (positive z-axis) and periodic boundary conditions were applied in x, y directions. The kinetic energy of the

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atoms inside the substrate were rescaled at every MD step ($\Delta t = 0.5$ fs) in order to keep the substrate at a constant temperature. In the deposition process the frequency of the atomic injection was on average $1/125$ fs^{-1}. Six structures were constructed with an injection time of 25 ps, and with an average bombarding energy of $E_{beam} = 1$ eV and 5 eV, at $T_{sub} = 100$ K substrate temperature and with 5, 10, and 20 ps relaxation time after injection. The structures of different models consist almost of the same number of atoms (between 162 and 177), with a thickness of about 13 Å. Bulk densities are between 2.3 and 2.5 g/cm^3. The void-free WWW network [6] has a similar density value.

The results for the ring statistics were surprising and unexpected as the networks prepared by our MD method consist of a significant number of squares. Furthermore, triangles are also present in the atomic arrangements. Most of the theoretical models for a-Si do not contain such structural fractions. The question remaining is, whether triangles and squares formed by fourfold coordinated Si atoms are artificial configurations due to the TB potential used or whether there is any other experimental evidence for small bond angles inside the a-Si network.

2. Cambridge structural database

There is no direct experimental method for determining atomic distributions in three dimensions. One way of ascertaining these 'natural' configurations in a-Si would be to consider the configuration of silicon fragments embedded inside large molecules. The surroundings of Si atoms could be considered as a 'white noise' around such fragments. A possible solution for this would be to use the Cambridge Structural Database (CSD) [20]. The CSD is the world's largest database of experimentally determined crystal structures containing the results of X-ray and neutron diffraction studies. We have collated 2559 Si–Si–Si fragments from CSD [21]. After analyzing the structural data it appears that equilateral triangles and near planar squares can also be natural local configurations inside the atomic arrangements of a-Si, as 68 squares and 29 triangles were found in this database [21].

3. Reverse Monte-Carlo simulation

The potential independent Reverse Monte-Carlo (RMC) modeling [22] has already been shown to be a powerful tool for interpreting amorphous structures, especially of a-Si [4, 23]. For the present case, a rather specific series of RMC calculations has been carried out. Our aim was to establish whether bond angles drastically different from the canonical value of 109.5° are necessary to reproduce the neutron diffraction data of Ref. [4]. (We wanted the TB-MD simulations to mimic the sample preparation method that

had been carried out in the studies described in Refs. [2,4], and therefore, if comparability was to be maintained, we had to stick to the diffraction data obtained in these works.) The RMC calculations were started from a 512 atom WWW model and only very small displacements (of the order of 0.002 Å) were permitted. Structural properties, like the static structure factor, $S(Q)$, the pair correlation function, $g(r)$ and the cosine distribution of bond angles, $B(\cos \theta)$, were monitored regularly, after about each 50000 accepted displacements. Results obtained at the 2nd, 5th and 10th stages will be presented here.

In many cases, the exact position of the border between the first and the second neighbor shell (i.e. the maximum value of the bond length) cannot be clearly defined. Usually, results of diffraction measurements on amorphous samples have this problem because the first two main peaks in the radial distribution function obtained by Fourier transformation overlap slightly. A possible solution would be to consider the largest Si–Si distance which has ever been measured in compounds. Among the structural data of CSD, the majority of measured Si–Si distances are less than 2.6 Å; only four out of the 5118 bonds (0.1 %) are somewhat larger than 2.6 Å.

Fig. 1 shows structure factors for the RMC model at the three stages mentioned above in comparison to the experimental data of Ref. [4]. There is one region, at the second (main) maximum, where there are visible changes corresponding to the advance of the calculation. It is clear that a sufficiently good fit is achieved only at the 10th monitored stage (after about 500000 accepted displacements). The corresponding pair correlation functions are given in Fig. 2. There are two regions where the evolution of the model can be easily spotted, where the height of the first maximum is decreasing, and where the shoulder just following the second maximum is developing. Note that
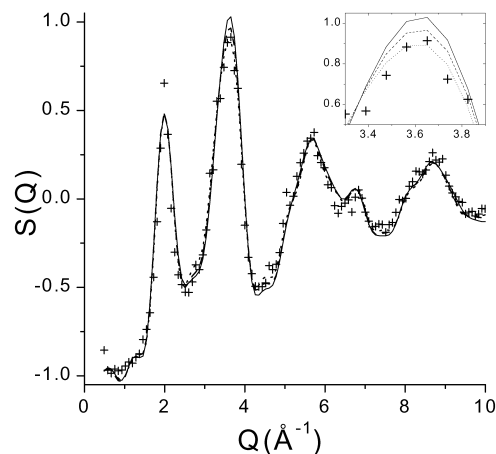

Fig. 1. The structure factor of the RMC model after 100000 (solid line), 250000 (dashed line) and 500000 (dotted line) accepted small displacements. Symbols: experimental data of Ref. [4]. The inset shows the region around the main (second) maximum.
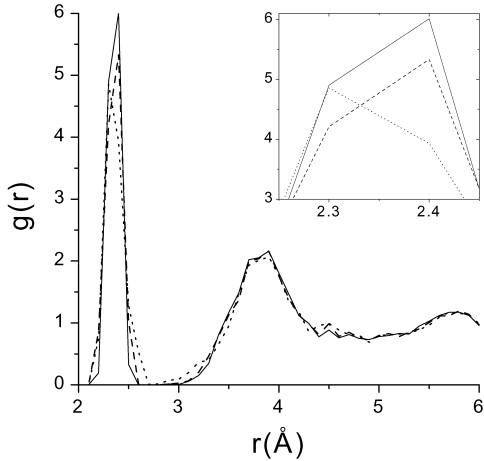
Fig. 2. The pair correlation function of the RMC model after 100000 (solid line), 250000 (dashed line) and 500000 (dots) accepted small displacements. The inset shows the region of the first maximum.

only the $g(r)$ for the 10th stage can be accepted as consistent with the experiment. After 500000 accepted displacements, the $S(Q)$ and $g(r)$ curves show no significant variation.

Fig. 3 displays the cosine distribution of bond angles for the three stages discussed above. It is clear that up to the 5th stage, no real deviation from the original WWW angle distribution is observed and even at the 10th stage, where consistency with the experimental $S(Q)$ is achieved, there is only a little change in the shape of the $B(\cos \theta)$ curve. This small, but visible alteration, however, has to be considered necessary for describing diffraction data for vapor deposited a-Si samples. At 500000 completed displacements the smallest angle, of which only a handful can be found in our model, becomes as small as about 74°, which represents a 35° deviation from the ideal tetrahedral value. As it will be

shown below, the appearance of these low bond angles has a profound effect on the electronic density of states (EDOS). Note that the latest diffraction data [5] were taken on a sample prepared via another method. Accordingly, the results of the same RMC procedure produce slightly different features, such considerable deviations of the bond angle do not seem to be essential for the reproduction of the experimental structure factor. A detailed comparison of structures of differently prepared a-Si samples will be the subject of a later publication.

All of these three independent pieces of evidence support the possible existence—of a small number—of triangles and squares in a-Si structures.

4. Density of states calculations

The AM1 [24] quantum chemical cluster calculations were also carried out in order to find out whether the presence of triangles and/or squares cause variations in terms of the electronic properties. The EDOS of the WWW model and the modified WWW models containing triangles and squares were calculated. The first cluster (a part of the WWW model) contained about 100 fourfold coordinated Si atoms and a sufficient number of hydrogen atoms saturating the dangling bonds on the boundary of the cluster. This system can be taken as a reference system, as it contains no significant deviation from a locally nearly perfect tetrahedral order. Based on this network, we constructed other clusters adding silicon (and hydrogen) atoms which formed one, two and three fused or individual triangles and squares. Significant differences were observed in terms of the EDOS: additional higher energy states appeared in the mobility gap, which are localized on the triangle(s) and square(s). Fig. 4 displays computed EDOS's of the first (reference) cluster and of another one which contains one triangle. The new highest energy peak at the top of the valence band clearly
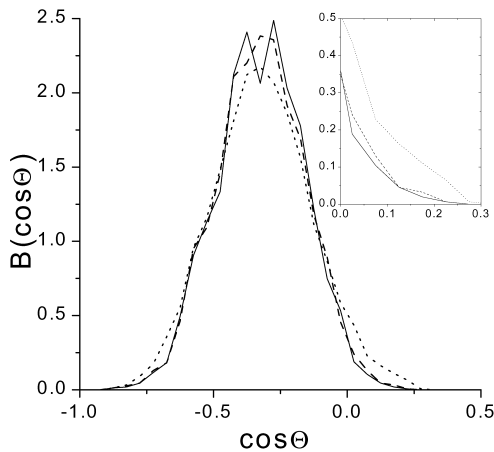

Fig. 3. The cosine distribution of bond angles in the RMC model after 100000 (solid line), 250000 (dashed line) and 500000 (dots) accepted small displacements. The inset shows the region of the smallest angles.
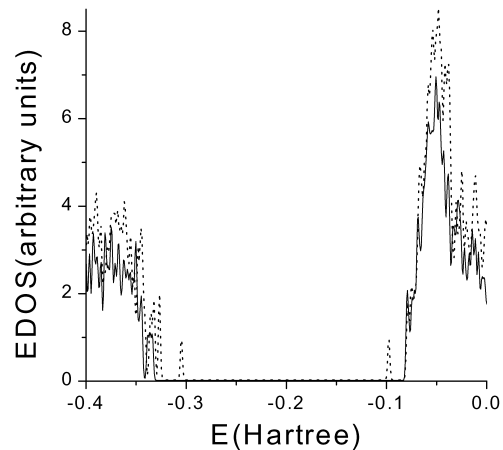

Fig. 4. The EDOS's of the reference cluster (solid line) and of another cluster containing one equilateral triangle (dashed line).

demonstrates the above finding. Fig. 5 shows the EDOS computed for the central part of the RMC structural model obtained at the 10th stage, as compared to the EDOS of the reference (WWW) cluster. (Note that the starting atomic arrangement of the present RMC calculation was also the WWW model.) The similarity (in terms of the EDOS) between the RMC model (which is consistent with the experimental structure factor) and the WWW model with one triangle is striking. It has to be emphasized that the new states in the gap correspond to a bond angle of about 74° in the RMC model, which is consistent with the findings obtained for the modified WWW model. It was more or less well established before, that the deformation of the tetrahedral angles gives rise to the appearance of extra states in the mobility gap. Here, it is demonstrated that these states are due exclusively to bond angles that are smaller than the tetrahedral ones. In the RMC models, bond angles larger than the tetrahedral one are also formed.

5. Conclusions

We have developed a tight-binding molecular dynamics computer code to simulate the preparation procedure of a-Si networks, grown by the technique of vapor deposition. In our simulations, triangles and squares are present in the obtained atomic configurations obtained. The results of two other separate studies based on experimental findings, like the statistical analysis of the Si–Si–Si fragments in large molecules and the Reverse Monte Carlo simulations, also support the possible existence of triangles and squares formed by Si atoms. For the proper interpretation of experimental (neutron diffraction) data on evaporated a-Si, it is necessary that small bond angles, of the order of 75°, are present. The standard AM1 semi-empirical Hartree–Fock calculations show that these arrangements provide higher
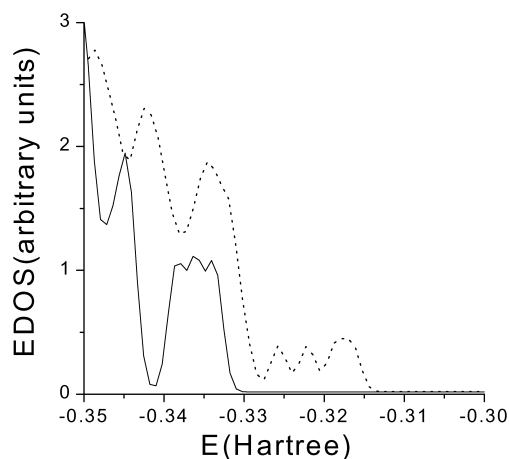

Fig. 5. The critical part of the EDOS's of the reference cluster (WWW model) (solid line) and of the RMC structure at the 10th stage (dashed line).

energy states in EDOS which are localized on these local structures. We consider triangles and squares as a new type of defects inside a-Si. These defects are highly energetic and should only appear rarely in a-Si. This is especially so for the three-membered rings. Nevertheless, the fragments like triangles and/or squares have never been considered in EDOS calculations or with unsolved problems such as the breaking of weak bonds by prolonged illumination, which is the major mechanism for the light-induced defect creation [25–27].

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