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Small bond angles in amorphous silicon: are they a new type of defect?

S. Kugler [a,*], K. Kohary [a,b], K. Kádas [a], L. Pusztai [c]

[a] Department of Theoretical Physics, Budapest University of Technology and Economics, H-1521 Budapest 1521, Hungary
[b] Department of Materials, University of Oxford, Parks Road, Oxford, OX1 3PH, UK
[c] Research Institute for Solid State Physics and Optics, P.O. Box 49, H-1525 Budapest, Hungary

Abstract

The reverse Monte Carlo structural modeling method and tight-binding molecular dynamics simulations were applied in order to investigate the existence of small bond angles (like those in triangles and squares) in amorphous silicon networks. The influence of small bond angles on the electronic density of states was also analyzed. It is shown that the presence of a small number of bond angles around 75° is necessary for a proper reproduction of the experimental structure factor of vapor deposited amorphous silicon.
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A large number of computer simulation studies [1–12] have been carried out on amorphous silicon (a-Si) during the past two decades with the aim of retrieving information about atomic scale particle arrangements. A continuous random network (CRN) model of a-Si (WWW model) was constructed by Wooten et al. [1] in 1985 who carried out Monte Carlo (MC) simulations using the classical empirical Keating potential. This is a harmonic approximation of atomic interactions which is valid for small distortions of bond angles and bond lengths. The potential energy is proportional to the square of difference between cosine of the actual bond angle and cosine(109.47°). This term prevents large deviations from the crystalline local bond structure. The defect-free WWW network includes fivefold and sevenfold rings in addition to the sixfold rings of the diamond-like structure. A comparison of radial distribution functions for a-Si re-scaled model and a-Ge experimental result was carried out and there was no serious discrepancy. Since then, several computer generated models have been constructed using various classical empirical potentials [2–4] or by applying different quantum mechanical methods [6–12], yet, despite these efforts, the WWW model is still considered to be the most realistic available atomic scale network of a-Si. The WWW or modified WWW models have been widely applied for electronic structure calculations and for other physical studies.

The main goal of the present contribution is to show that bond angle distortions larger than found in the WWW-model are necessary for a quantitative description of the experimental structure factor of (evaporated) amorphous Si. For this, extensive reverse Monte Carlo calculations are reported in the next section. Tight-binding molecular dynamics and electronic structure calculations, both supporting the above argument, are described in Sections 2 and 3 and in Section 4, conclusions are drawn.

1. Reverse Monte Carlo simulations

The potential independent reverse Monte Carlo (RMC) modelling [13] has already been shown to be a powerful tool for interpreting amorphous structures. Our earlier neutron diffraction measurement and RMC computer simulation study [5] have been carried out on amorphous silicon (a-Si). The unconstrained simulation contained a large number of small bond angles, i.e. 60°. At that time, we considered this result as an artifact due to the absence of suitable geometrical constraints. For the present case, a rather specific series of RMC

* Corresponding author. Tel.: +36-1 463 2146; fax: +36-1 463 3567. *E-mail address:* kugler@eik.bme.hu (S. Kugler).

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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 [5]. 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 50 000 accepted displacements. Results obtained at the 2nd and 10th stages will be presented here.

Fig. 1 shows structure factors for the RMC model at the two stages mentioned above in comparison to the experimental data of [5]. There is one region, at the second (main) maximum, where there are visible changes corresponding to the advance of the calculation. A sufficiently good fit of the experimental data is achieved only at the 10th monitored stage (after about 500 000 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 observed, where the height of the first maximum is decreasing, and where the shoulder just following the second maximum is developing. Note that only the $g(r)$ for the 10th stage can be accepted as consistent with the experiment. After 500 000 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. 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 500 000 completed displacements the smallest angle, of which only a handful can be found in our model, becomes as small as

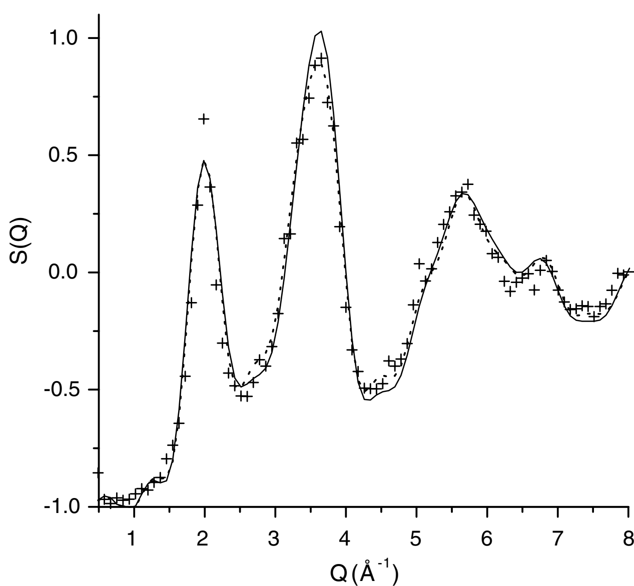

Fig. 1. The structure factor of the RMC model after 100 000 (solid line) and 500 000 (dotted line) accepted small displacements. Symbols: experimental data of [5].

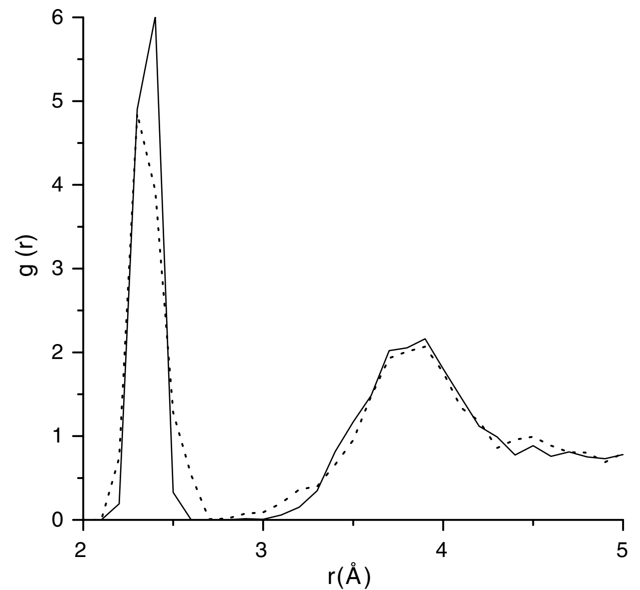

Fig. 2. The pair correlation function of the RMC model after 100 000 (solid line) and 500 000 (dots) accepted small displacements.

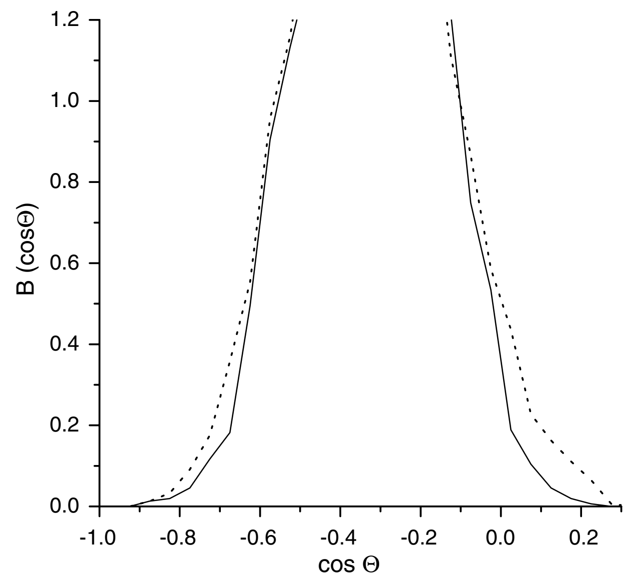

Fig. 3. The cosine distribution of bond angles in the RMC model after 100 000 (solid line) and 500 000 (dots) accepted small displacements.

about 74°, which represents a 35° deviation from the ideal tetrahedral value.

2. 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 dynamics (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 [14]. The TB Hamiltonian of Kwon et al. [15] was used to describe the interaction between silicon atoms. All 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.

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 (1 1 1) direction (positive z-axis) and periodic boundary conditions were applied in x, y-directions. The kinetic energy of the atoms inside the substrate were re-scaled 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 $E_{\text{beam}} = 1$ and 5 eV, at $T_{\text{sub}} = 100$ K substrate temperature and with 5, 10, and 20 ps relaxation time after injection [14]. 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 to 2.5 g/cm^3. Crystalline silicon and void-free WWW network [1] has a similar density value. One of the models is shown in Fig. 4.

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. Recently we repeated the simulation using an other TB Hamiltonian [16] and similar conclusions were obtained.

After analyzing the structural data due to Si–Si–Si fragments from the Cambridge structural database (CSD) it appears that equilateral triangles and near planar squares may also be natural local configurations inside the atomic arrangements of a-Si, as 68 squares and 29 triangles were found in this database [17].

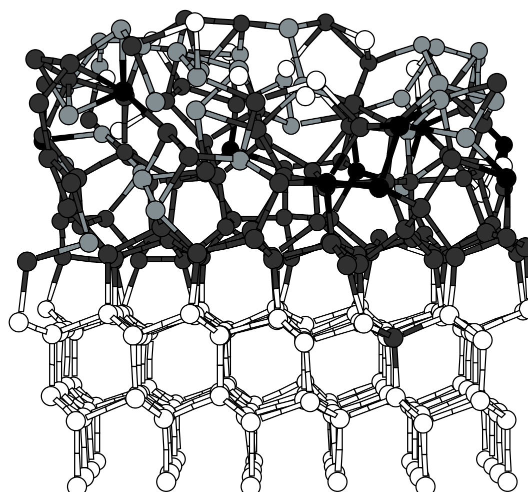

Fig. 4. One of the models is shown constructed by tight-binding molecular dynamics simulation. Bottom part is the substrate and top part is the amorphous network.

3. Density of states calculations

Quantum chemical cluster calculations at the AM1 level [18] 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 electronic density of states (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 hydrogens 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 by 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. 5 displays computed EDOSs 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 demonstrates the above finding. Fig. 6 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 bond angles of about 74° in the RMC model, which is consistent with the findings

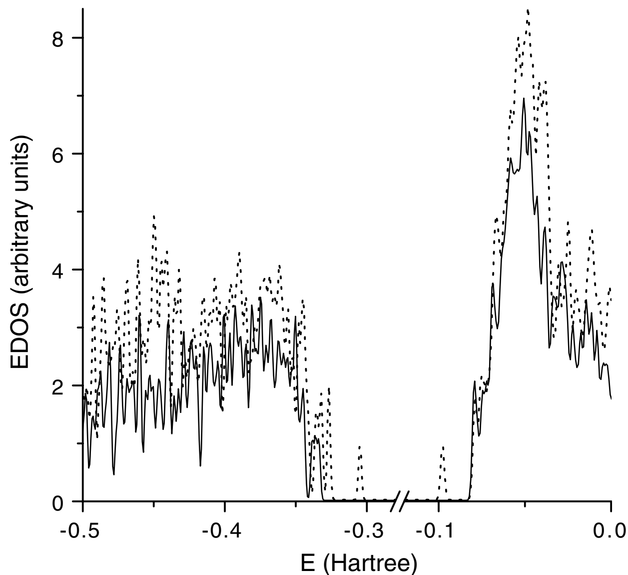

Fig. 5. The EDOSs of the reference cluster (solid line) and of another cluster containing one equilateral triangle (dashed line).

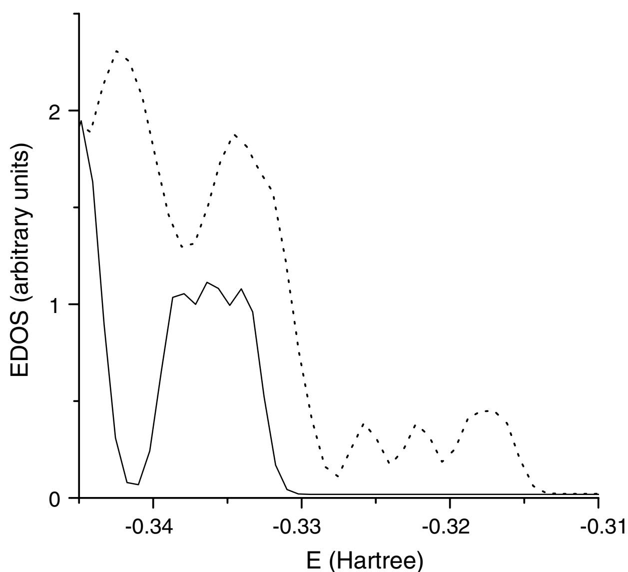

Fig. 6. The critical part of the EDOSs of the reference cluster (WWW model) (solid line) and of the RMC structure at the 10th stage (dashed line).

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.

4. Conclusions

For the proper interpretation of experimental (neutron diffraction) data on evaporated samples, it is *necessary* that small bond angles, of the order of 75°, are present which angles are not included in WWW model. In other words, the (potential-free) Reverse Monte Carlo simulations do not object the *possible* existence of triangles and squares formed by Si atoms in a-Si. A tight-binding molecular dynamics computer code was developed for simulating the preparation procedure of a-Si networks, grown by the technique of vapor deposition. In our simulations, triangles and squares are present in the atomic configurations. Standard AM1 semi-empirical Hartree–Fock calculations show that these arrangements provide higher 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 the case for the three-membered rings. Nevertheless, triangles and/or squares have never been considered in EDOS calculations or with unsolved problems such as the breaking of weak bonds [19,20].

Acknowledgements

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