Are the triangles and the squares possible local atomic arrangements in the structure of amorphous silicon?

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Abstract

During the preparation of amorphous structures covalently bonded atoms tend to form their 'natural configurations'. The measured radial distribution function is only a one-dimensional representation of the spatial atomic distribution, therefore efforts to develop new techniques for analyzing the atomic scale structure in three dimensions ('local natural configurations') are continuously being made. One way of ascertaining these natural configurations in a-Si is to consider the configuration of silicon fragments embedded inside large molecules. Insights into the structure of a-Si have been made by analyzing local configurations found in silicon fragments in large molecules. The source for these data is the Cambridge Structural Database (CSD). Out of almost 2600 Si–Si–Si fragments analyzed, a considerable number contain Si atoms in triangular or almost planar square arrangements. © 2002 Elsevier Science B.V. All rights reserved.

PACS: 61.43.Dq

1. Introduction

Knowledge of the arrangement of atoms is an essential prerequisite for understanding the physical and chemical properties of amorphous materials. Amorphous silicon (a-Si) has received particular attention since it is the archetype of covalently tetrahedrally bonded amorphous structures [1]. The structure of a-Si has been studied by different diffraction techniques which yield the radial distribution function (RDF) containing integrated information about the amorphous structures. The RDF is only a one-dimensional representation of the spatial atomic distribution in three dimensions. The lack of periodicity causes that the structure cannot be determined in the sense that it is possible in crystalline cases from diffraction measurements. Some experimental investigations have been made on a-Si using electron diffraction [2], high-energy X-ray diffraction [3] and X-ray absorption [4], but the neutron diffraction technique gives the most accessible information on the structure [5–7]. Covalently bonded amorphous semiconductors are not completely disordered. The bonds between atoms are similar to the crystalline phase and the co-ordination numbers are usually the same. Comparing amorphous form of silicon to a perfect crystal, the first- and second-neighbor peaks are broadened but

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their positions are the same, while the third peak disappears in the measured RDF. The absence of the third peak confirms that there is no characteristic dihedral angle, i.e., the angle between second-neighbor bonds. These are the most important conclusions of diffraction measurements.

Several computer-generated models have been constructed in different ways [7–16]. Traditional Monte Carlo (MC) method using a Keating potential has been applied to construct a well-known continuous random network (CRN) model for amorphous silicon [8]. The second method, molecular dynamics (MD), also needs a local potential to describe the interaction between atoms. The most common characteristic of the existing models of a-Si is that the local order is similar to the crystalline case. However, the models invariably contain five- and seven-membered rings of atoms, unlike the diamond structure which contains only six-membered rings. Some models also contain underco-ordinated (3) and overco-ordinated (5) atoms.

A new version of the MC method, the reverse Monte Carlo (RMC) simulation was applied for constructing large models of a-Si [7]. For generating atomic configurations RMC is the only consistent simulation method with the experimental structure factor which has no dependence on the atomic interaction potential.

2. Method

During the growth of amorphous samples it might be expected that covalently bonded atoms tend to form 'natural configurations'. The only question is what the possible 'natural configurations' are? There is no direct experimental method having atomic resolution for determining the atomic distributions in three dimensions; therefore efforts to develop new techniques for analyzing the atomic scale structure are continuously being made. One way of ascertaining these natural configurations in amorphous silicon is to consider the configuration of silicon fragments embedded inside large molecules. The environment of silicon atoms might be considered as 'white noise' around such fragments. We carried out a system-

atic analysis of structural data using the Cambridge Structural Database (CSD) [17], this being the world's largest database of experimentally determined crystal structures containing the results of X-ray and neutron diffraction studies. CSD is designed as a critically evaluated numerical resource, containing three-dimensional atomic coordinates. We have collated from the CSD the experimentally determined structural data of molecules containing Si–Si–Si (and Ge–Ge–Ge) fragments. Our recent search found 2559 targets. The results of this search are presented here.

3. Results

Since in one Si–Si–Si fragment two bond lengths belong to one bond angle, therefore we have 5118 bond lengths. The overwhelming majority of bond lengths and bond angles fall in the expected region, i.e., around 2.35 Å and 109.47°. The minimum bond length is 2.217 Å while the maximum is 2.647 Å. Except for one fragment, the bond angles lie inside the interval 53.9–145.8°. The average bond length and bond angle are 2.365 Å and 107.10°, respectively. A histogram of the bond angle distribution is shown in Fig. 1. The large peak around 109.47° corresponds to the main peak in the RDF of a-Si. However, there are some significant peaks in the interval 75–96° which is an unexpected region (314 angles). Most of them belong to a near planar square arrangement.
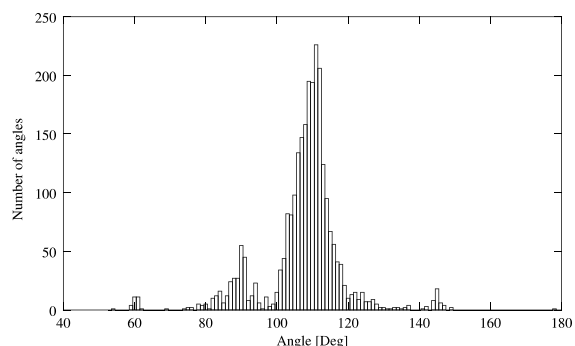

Fig. 1. The histogram of bond angle distribution. A large peak around 109.47° and two unexpected regions in the interval 75–96° and around 60° can be found.

Sixty-eight such squares were found in the database. Bond angles around 60° can also be found corresponding to nearly equilateral triangles. In Fig. 1 only 29 angles are displayed around 60°, instead of 87 because when the Si1–Si2–Si3 angle has been obtained, the search stops, so Si2–Si3–Si1 and Si3–Si1–Si2 angles are not considered. This is the other unexpected region.

We have also collated the experimentally determined structural data of molecules containing Ge–Ge–Ge fragments. Searching on the CSD an order of magnitude less different targets have been found. It means the statistics are not as good as with the Si–Si–Si case. We analyzed the bond angles distribution and we obtained similar conclusion, i.e., germanium atoms are able to form triangles and near planar square local arrangements as natural configuration of such atoms.

The histogram of 5118 Si–Si bond lengths has a normal shape but shows a shoulder at larger values as it is shown in Fig. 2. A weak correlation can be observed between bond lengths and bond angles, i.e., an increase of bond angle corresponds to a decrease of bond length. For clarification the bond lengths are divided into two parts; the first set (shaded) includes bonds forming three- and four-membered rings while the second set contains the remainder. The average of first set is equal to 3.41
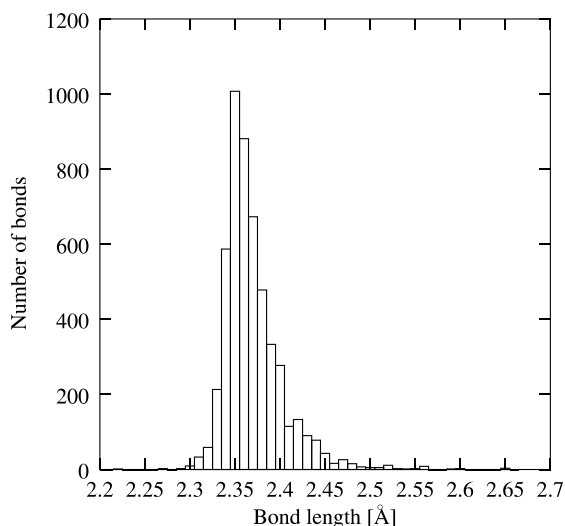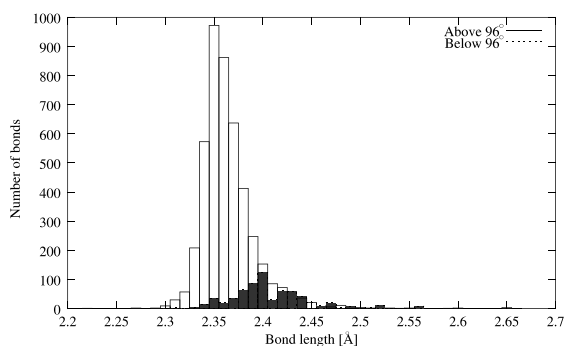

Fig. 3. Two histograms. 5118 bond lengths are divided into two sets: the first set includes bonds forming three- and four-membered rings (shaded histogram) while the second larger set has the remainder (thin solid line). As seen the three- and the four-membered rings have longer average bond lengths and this subpeak forms a shoulder of the main peak.

Å. As can be seen in Fig. 3, the three- and four-membered rings having lower bond angles than near tetrahedral have longer average bond lengths and this subpeak forms a shoulder of the main peak. Such a shoulder has also been found in measured RDFs of a-Si and has remained unexplained. The first-neighbor peak has structure and the bond angle is a sufficient parameter to describe this.

Last, the histogram of the second-neighbor distances are displayed in Fig. 4. There is a small peak around 2.35 Å because the second-neighbor distances due to triangles are simultaneously bond lengths. The peak around 3.4 Å belongs to diagonal of near planar squares.
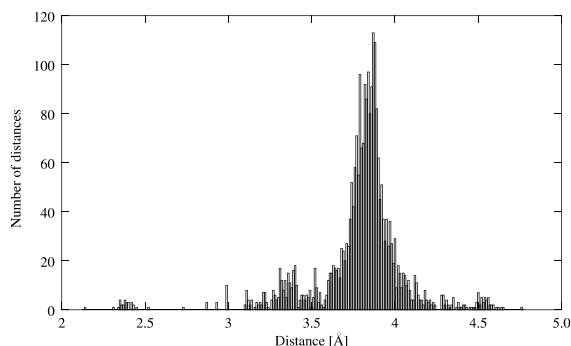

Fig. 2. The histogram of 5118 bond length distribution. The peak has a normal shape but shows a shoulder at larger values.

Fig. 4. The histogram of second-neighbor distances. The peak around 3.4 Å belongs to diagonal of near planar squares.

4. Conclusion

In conclusion, we have presented the results of a large number of diffraction measurements from molecules containing silicon fragments. The most surprising result is that the networks we got have a significant number of three-membered rings, i.e., triangles are present in the atomic arrangement. Furthermore, near planar squares can also be found. Most of the theoretical models for a-Si do not contain such a part of the structure. Our neutron diffraction measurement carried out on pure evaporated amorphous Si sample at ILL, Grenoble and evaluated by RMC method shows similar conclusion [7]. RMC simulation generating atomic configurations are consistent with the experimental data! Similar conclusion has been obtained by our tight-binding molecular dynamics simulation [18–20]. These computer simulations of a-Si growth on substrate suggest that the equilateral triangles and near the equilateral triangles and near planar squares can be natural local configurations inside the atomic network of a-Si.

There are three independent evidences which support the existence of triangles in a-Si structures! Fragments corresponding to equilateral triangles or near planar squares have not been considered in electronic density of states calculations or in problem such as the breaking of weak bonds by prolonged illumination which is a major mechanism for the light-induced defect creation [21].

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