PHILOSOPHICAL MAGAZINE LETTERS, 2001, VOL. 81, NO. 8, 569–574

Possible unusual atomic arrangements in the structure of amorphous silicon

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[*Received in final form 21 March 2001 and accepted 27 March 2001*]

ABSTRACT

Insights into the structure of amorphous Si (a-Si) and hydrogenated amorphous Si (a-Si:H) have been made by analysing local configurations found in Si fragments in large molecules. The source for this data is the Cambridge Structural Database. Out of almost 1800 fragments analysed, a considerable number contain Si atoms in triangular or almost planar square arrangements. It is suggested that the presence of such configurations in a-Si could account for structure in the first peak of the experimentally determined radial distribution function.

Amorphous semiconductors have been the subject of numerous experimental and theoretical works in recent decades. Amorphous Si (a-Si) has received particular attention since it is the archetype of covalently tetrahedrally bonded amorphous structures (Morigaki 1999). Knowledge of the arrangement of atoms is an essential prerequisite for understanding the physical and chemical properties of such materials.

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. Some experimental investigations have been made using electron diffraction (Barna *et al.* 1977, Moss and Graczyk 1979), high-energy X-ray diffraction (Laaziri *et al.* 1999) and X-ray absorption (Di Cicco *et al.* 1990), but the neutron diffraction technique gives the most accessible information on the structure (Bellissent *et al.* 1989, Fortner and Lannin 1989, Kugler *et al.* 1989, 1993).

Covalently bonded amorphous semiconductors are not completely disordered. The bonds between atoms are similar to those of the crystalline phase and the coordination numbers are usually the same. Comparing amorphous semiconductors with a perfect crystal, the first- and second-neighbour peaks are broadened but 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, that is the angle between second-neighbour bonds.

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Philosophical Magazine Letters ISSN 0950–0839 print/ISSN 1362–3036 online
http://www.tandf.co.uk/journals
DOI: 10.1080/0950083011005535 5

Several computer-generated models have been constructed in different ways (Wooten *et al.* 1985, Kelires and Tersoff 1988, Kugler *et al.* 1993, Tóth and Náray-Szabó 1993, Ishimaru *et al.* 1997, Herrero 2000). There are two main methods for structural modelling on an atomic scale. The first is the Monte Carlo (MC) method. The traditional MC method using a Keating potential has been applied to construct a continuous random network model for a-Si (Wooten *et al.* 1985). The second method, molecular dynamics, also needs a local potential to describe the interaction between atoms. Recently a new version of the MC method, namely the reverse Monte Carlo (RMC) simulation, has been developed on the basis of the results of diffraction measurements. This method was applied for constructing large models of a-Si (Kugler *et al.* 1993). For generating atomic configurations the RMC technique is the only consistent simulation method with the experimental structure factor which has no dependence on the atomic interaction potential. 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 undercoordinated (three) and overcoordinated (five) atoms.

There is no direct experimental method for determinating the atomic distributions in three dimensions; therefore efforts to develop new techniques for analysing the atomic-scale structure are continuously being made. During the growth of amorphous structures it might be expected that covalently bonded atoms tend to form 'natural configurations'. One way of ascertaining these natural configurations in a-Si is to consider the configuration of Si fragments embedded inside large molecules. The environment of silicon atoms might be considered as 'white noise' around such fragments.

A systematic analysis of structural data has been carried out using the Cambridge Structural Database (CSD) (Allen *et al.* 1983), this being the world's largest database of experimentally determined crystal structures containing the results of X-ray and neutron diffraction studies. The 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 fragments. A search found 1860 targets. The *R* factor of these data, which represent the error of measurements, has been checked and some of them were greater than 0.1. We ignored these data as the accuracy of these measurements are not considered good enough, leaving 1789 Si—Si—Si fragments.

The results of this search are shown in figure 1. Each point represents a measured bond length as a function of bond angle. Since, in one Si—Si—Si fragment, two bond lengths belong to one bond angle, 3578 points are plotted. The overwhelming majority of these points fall in the expected region, that is around 2.35 Å and 109.47°. The minimum bond length is 2.21 Å while the maximum is 2.64 Å. Except for one fragment, the bond angles lie inside the interval 58.6–145.8°. The average bond length and angle are 2.37 Å and 106.33° respectively. Drawing a line of best fit, a weak correlation can be observed, that is an increase in bond angle corresponds to a decrease in bond length.

A histogram of the bond angle distribution is shown in figure 2. 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. Most of them belong to a nearly planar square arrangement. 51 such squares were found in

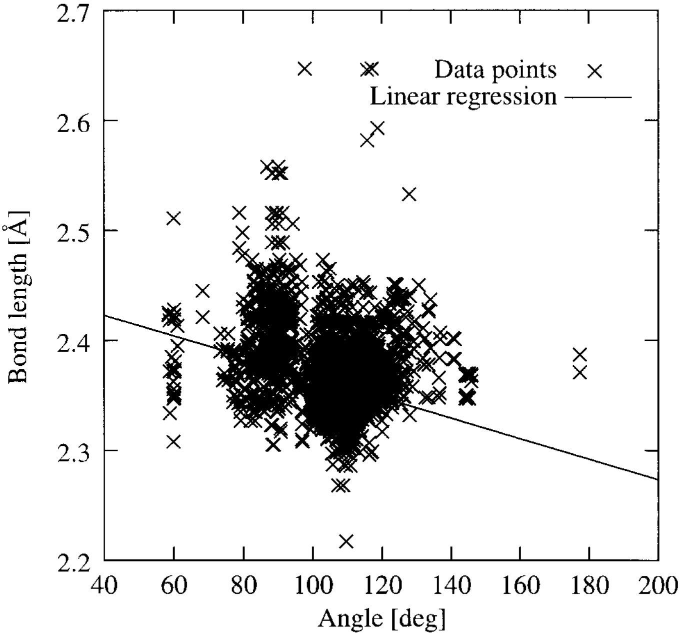

Figure 1. Bond lengths as a function of bond angles. The majority of 3578 points fall around 2.35 Å and 109.47°. The straight line fitted represents a correlation between bond lengths and bond angles.

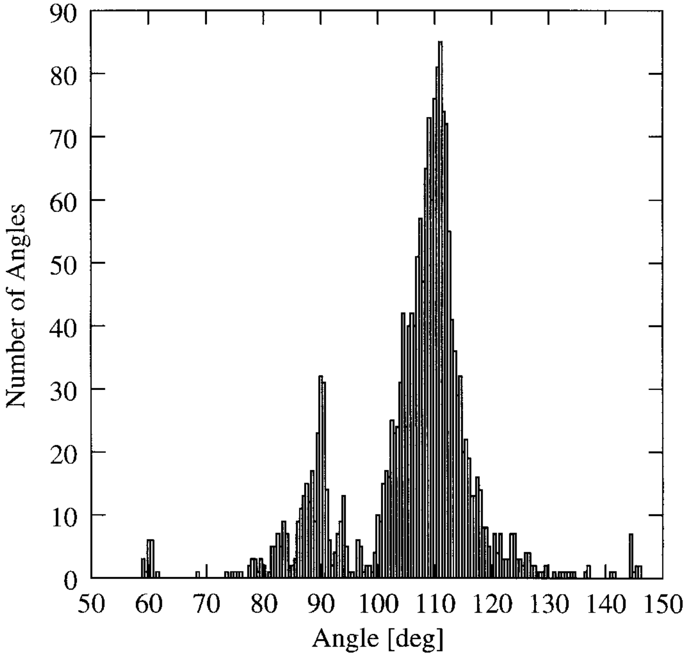

Figure 2. The histogram of bond angle distribution. A large peak at around 109.47° and two unexpected regions in the interval 75–96° and around 60° can be found.

the database. For example *cis*,*trans*,*cis*-1,2,3,4-tetrakis(tri-tert-butylsilyl)-cyclotetrasilane, $C_{48}H_{112}Si_8$ or *cis*-2,5-dichlorododecaisopropylbicyclo(4.2.0)octasilane, $C_{36}H_{84}Cl_2Si_8$, etc., contain a Si_4 fragment in square arrangement. Bond angles around 60° (inside *cis-trans*-1,2,3-tri-tert-butyl-1,2,3-tricyclohexyl-cyclotrisilane, $C_{30}H_{60}Si_3$ or hexakis((2-dimethylaminomethyl)phenyl)-cyclotrisilane , $C_{54}H_{72}N_6Si_3$, etc., molecules) can also be found corresponding to nearly equilateral triangles. In figure 2, only 18 angles are displayed around 60°, instead of 54 because, when the Si(1)–Si(2)–Si(3) angle has been obtained, the search stops; so the Si(2)–Si(3)–Si(1) and Si(3)–Si(1)–Si(2) angles are not considered. This is the other unexpected region although the RMC simulation provides a similar conclusion (Kugler *et al.* 1993).

The histogram of 3578 bond lengths has a normal shape but shows a shoulder at larger values (figure 3). For clarification the bond lengths are divided into two parts: the first set (shaded histogram) includes bonds forming three- and four-membered rings while the second set contains the remainder. As can be seen, the three- and four-membered rings having smaller bond angles than near the tetrahedral angle have longer 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 (see Kugler *et al.* (1993) figure 4). The first-neighbour peak has structure and the bond angle is a sufficient parameter to describe this.

We have also collated the experimentally determined structural data of molecules containing Si—Si—H fragments. Hydrogen is an important component of electronically useful hydrogenated amorphous Si (a-Si : H). On searching the CSD, 120

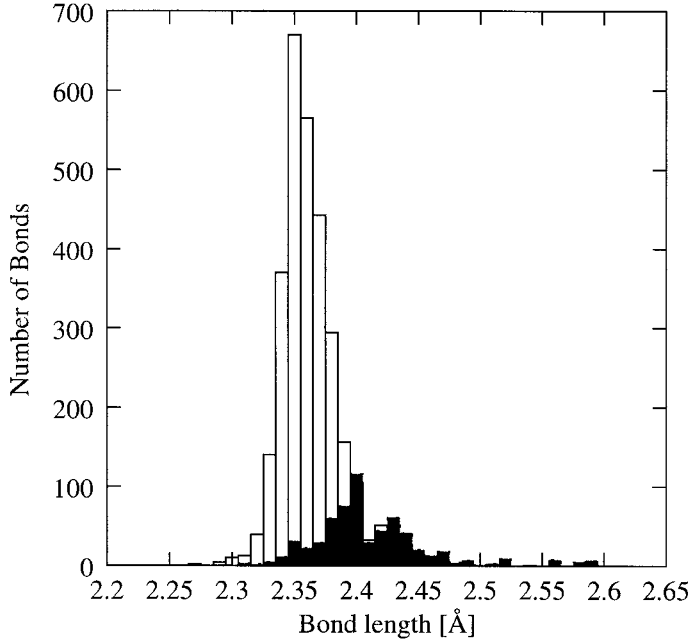

Figure 3. Two histograms. 3578 bond lengths are divided into two sets: the first set includes bonds forming three- and four-membered rings (shaded histogram) while the second larger set has the remainder (white histogram). As seen, the three- and the four-membered rings have longer bond lengths and this subpeak forms a shoulder of the main peak.

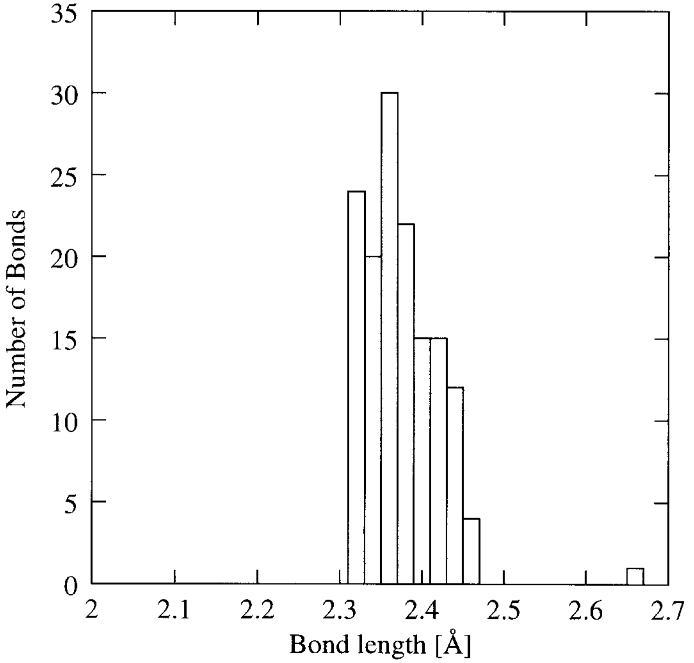

Figure 4. The histogram of second search containing Si—Si—H fragments. The Si—Si bond lengths lie in the interval 2.3–2.48 Å. The average is greater than 2.35 Å, which is the first-neighbour distance in the crystalline case.

different targets have been found, although the statistics are not as good as for the Si—Si—Si case. We have analysed only the Si—Si bond lengths because H is a critical element having a large incoherent cross-section for neutron scattering and a very low cross-section for other diffraction techniques. The results obtained are sometimes inaccurate. The histogram of this second search is shown in figure 4. The Si—Si bond lengths, except for one at 2.67 Å, lie in the interval 2.3–2.48 Å. This H causes an increase in the average length of the Si–Si bond.

In conclusion, we have presented the results of a large number of diffraction measurements from molecules containing Si fragments. In the angle distribution, two well-defined and unexpected regions have been found. Most models of a-Si do not contain such configurations which correspond to three- and four-membered rings. The first-neighbour peak has structure, and its shape is related to the bond-angle distribution. Fragments corresponding to equilateral triangles or nearly planar squares have not been considered in electronic density-of-states calculations or in problems such as the breaking of weak bonds by prolonged illumination, which is a major mechanism for the light-induced defect creation (Shimakawa *et al.* 1995).

ACKNOWLEDGEMENTS

The authors are indebted to Ms Veronika Harmat (Eotvos University, Budapest) for retrieving raw data. This work has been supported by Országos Tudományos Kutatási Alapprogramok (grant T029813, T032193, T033004) and by Hungarian–Japanese intergovernmental co-operation (grant JAP-21/98).

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