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AMORPHOUS SEMICONDUCTORS ARE DENSER…

M. Popescu, F. Sava, W. Hoyer[a]

National Institute of Materials Physics, P. O. Box MG. 7, 76900 Bucharest-Magurele,
[a]Institute of Physics, Technical University Chemnitz, D-9107 Chemnitz, Germany

The structure of amorphous materials is still challenging [1]. The most fundamental property, the density, is not well known. We have modelled the structure of amorphous silicon by using a large number of networks with different entangled topology and different distortion of the covalent bonds and have found that the density of the amorphous structure is higher than that of the crystalline phase. This increase of density scales with the square of the root mean square (rms) of the bond angle distortion. We compared our data with other results both from modelling and experiment and have found that the relation density – bond angle distortion holds not only for amorphous semiconductors, but also for other disordered materials, as e.g. oxides, and last but not least for ice and water, a tetrahedral bonded substance. Therefore, a new method for determining the density was suggested: the measurement of the width of the second peak in the radial distribution function that is directly related to the bond angle distortion. The implications of the new findings is extremely important in nanoelectronics for controlling the quality of the amorphous materials and for developing micro-sources of energy, in surface and thin film physics, in colloid science, where thin dense films on the surface of the grains is predicted, in biology for understanding the behaviour of the confined water in tissues, in geological plate tectonics connected to earthquake phenomena, and in astrophysics for understanding the particular structural properties and possible release of a high amount of energy by celestial bodies subjected to temperature changes.

Because of the isotropic nature of amorphous materials, the most that can be determined from a diffraction experiment is the radial distribution function (RDF), which contains one-dimensional information. In order to discern the three-dimensional atomic structure, one must build models and compare them with experiment.

The study of amorphous silicon (a-Si) is of particular interest because it is the canonical system for the study of all covalently bonded amorphous materials and has long served as a test material for comparing theoretical and model calculations involving the role of order and disorder in continuous random networks. Nevertheless, the basic properties of amorphous silicon are not known despite growing technological and scientific interest. One such fundamental property is the density. Early X-ray diffraction data indicated an amorphous density as much as 10 % below that of the crystal, although this was ascribed to the presence of voids in the vapour-deposited films [2]. Brodsky et al. [3] interpreted Rutherford backscattering experiments in combination with surface polarimetry to conclude that a-Si could be up to 1 % denser than crystalline silicon (c-Si), although the measured density of their electron-beam deposited a-Si films was 3 % less than that of c-Si. Later, experimental results on thin implanted layers indicated an a-Si density between 1.7 % and 2.3 % less than the density of the crystal [4]. Attempts to estimate the density of a-Si using molecular dynamic simulations have lead to results on either side of c-Si [5]. Recently, Custer et al. [6] reported measurements of the density of self-implanted silicon layers over a wide range of thickness, regrowth and relaxation conditions. Amorphous silicon was determined to be 1.8 ± 0.1 % less dense than crystalline silicon.

The atomic structure of silicon (and also of germanium and of tetrahedral amorphous carbon [7]) is believed to be that of a roughly fourfold co-ordinated random network where the short-range (local) order is similar to that of the crystalline counterpart [8].

A considerable amount of work, both with classical and quantum techniques has been done to simulate the atomic structure of a-Si (a-Ge). A collection of models is now at our disposal for understanding the amorphous semiconductors with special emphasis on a-Si. Among them the most successful in explaining the experimental data are the continuous random network models and the models derived from the procedure of randomisation initiated by Wooten et al. [9].

We used the procedure of randomisation of the crystalline silicon lattice, followed at every step by an energy relaxation and calculation of the structural parameters.

The starting structure was a perfect crystal with 300 simulated atoms (a second crystal with 455 atoms was also used for randomisation). The fundamental bond switch introduced into the lattice is based on the interchange of two atoms by breaking one common bond and two bonds with the neighbouring atoms, and then reconnecting the bonds, thus maintaining completely bonded the whole assembly. The state of deformation got after the relaxation of the network in the frame of Keating theory of valence force field [10] with the force constants given by Martin [11] has been called a ***deformon state*** and is shown in Fig. 1.

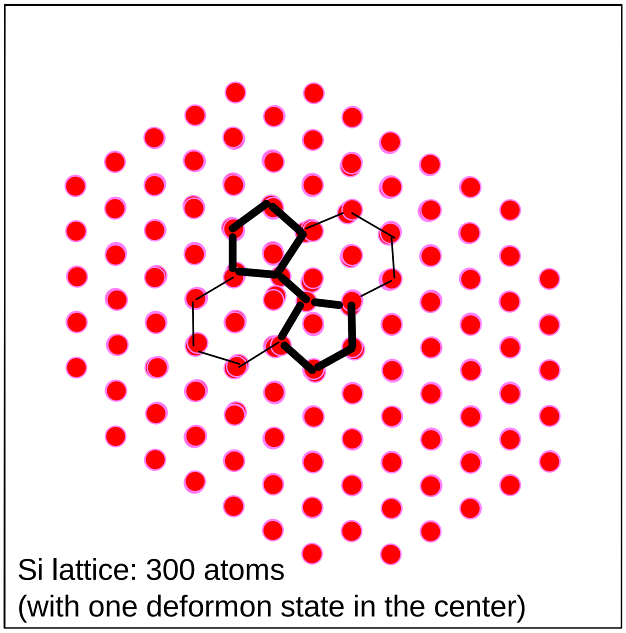

Fig. 1. The projection on the Z-axis of the model of a crystalline lattice of silicon with 300 atoms and one deformon state introduced in the center of the lattice (after energy relaxation).

The deformon states were gradually introduced in the crystalline lattice (up to a maximum number of 138 for the crystal with 300 atoms and only 37 for the crystal with 455 atoms). No fourfold rings of atoms were permitted in the network. Every stage of randomisation was followed by energy relaxation. The results were compared with those got from a computer-generated randomised model for silicon, built by Djordjevic et al. [7], and containing 4096 atoms. Besides, a large continuous random network model with 2052 atoms devised by Popescu, and recalculated for silicon, was also considered [12].

In order to understand the behaviour of the non-crystalline networks we calculated the densities of the models and observed they are perfectly correlated with the rms deviation of the bond angle, θ, in the network. The relative density (ρ/ρ_{cryst}) increases linearly with the square of the width of the bond angle distribution or rmsθ (Fig. 2). This means that more the bonds deviates from the tetrahedral symmetry, more the density increases.

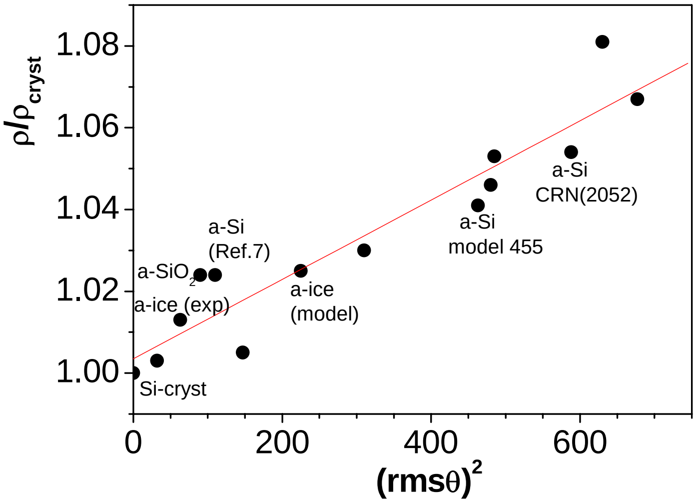

Fig. 2. The relation between the density increase in the network of randomised silicon for various number of deformon states and the square of the rms deviation of the bonding angle from the ideal tetrahedral one (109° 28'). The position of the largest CRN model (2052 atoms) is shown. The corresponding points for solid water (amorphous ice, experiment and model) are given, as well as the position of the experimental point for a-SiO_2 (Ref. 20). The straight line is the linear fit to the points.

When the structure factors and radial distribution functions (RDFs) are calculated for the models, the best agreement with experiment is obtained for the CRN model.

The correlation $\rho/\rho_{cryst} \sim (\mathrm{rms}\vartheta)^2$ seems to be quite general, and the implications are important. Firstly, the relation predicts that the covalently bonded solids must exhibit an increase of density in the amorphous state. Secondly, the density measurements made up to day seem to be misleading, and this can be due to the possible amount of unknown defects, cavities, large voids into materials. Thirdly, it is possible to get the true density of the amorphous homogeneous network without defects by simply measuring the width of the second peak in the radial distribution function.

The estimated increase of density in the amorphous state is for silicon and germanium: 2.1 %.

It is remarkable that the relation $\rho \sim (\mathrm{rms}\vartheta)^2$ is valid even for so different substance as water is. Water has an open locally tetrahedral structure (similar to silicon, germanium or diamond carbon) maintained by a network of highly directional hydrogen bonds [13]. When the ice melts and the temperature gradually increases, then the tetrahedral structure is lost and the density increases. Urquidi et al. [14] have shown, inspired from the high-pressure polymorphs of ice, that the water structure changes through the bond bending and not breaking the hydrogen bonds. Recently, Modig et al. [15] revealed a substantial hydrogen bond distortion, responsible for the gradual loss of second-order spatial correlation at higher temperatures. The model for amorphous ice developed by us [16], confirms the density formula.

There is a number of oxides, as e.g. SiO_2, GeO_2, that can be found in both crystalline and amorphous state. The increase of the density, as a function of the full width at half maximum (FWHM) of the bond angle distribution has been reported in SiO_2 glass by Wei Jin et al. [17] during modelling of the pressure induced structural transformations. Recently, accurate structural data were published [18]. According to these data, during densification of quartz under pressure the bond length slightly increases while the bond angle distribution becomes larger (~15°). It has been shown that both pressure compaction and fast neutron irradiation of amorphous SiO_2 give smaller changes: a reduction in Si-O-Si bond angle together with a small increase in the Si-O bond length [19] and an increase of density with 2.4 % during fast neutron irradiation [20].

We have calculated from the models of randomised silicon the interstitial void size distribution. An interstitial void is defined as the maximum volume of a sphere, which can be placed in between neighbouring atoms. The void diameter distribution is a measure of the free space available in the network. We have found that the relative increase of density in amorphous silicon scales with the decrease of the mean void size in the network. Fig. 3 shows this correlation. If the data are extrapolated to small void size we get the maximum possible increase of density of 30 %.

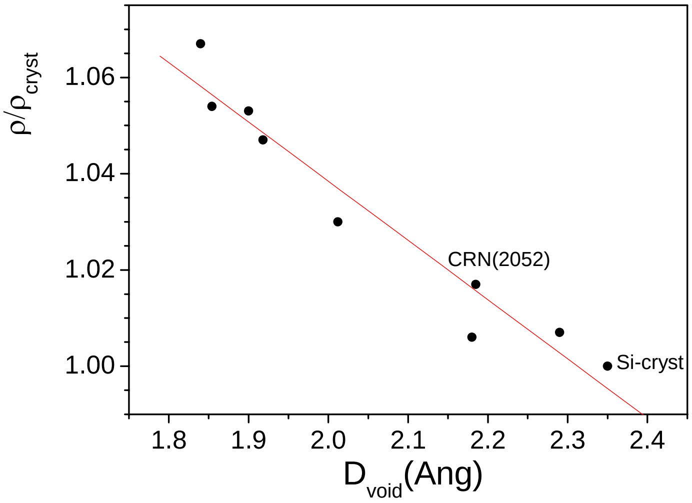

Fig. 3. The relation between the density increase in the randomised silicon lattice (model with various number of deformon states: 1 – 138) and the decrease of the mean diameter of the interstitial voids (in angströms) in the network (the position of the CRN model with 2052 atoms is also shown). The straight line is the linear fit to the points.

The importance of the general formula $\rho \sim (\mathrm{rms}\vartheta)^2$ is both theoretical and practical. In theory, the connection between density and bond bending fluctuations is basically for understanding the dynamics, structure, and stability of the disordered networks. The formula puts at the disposal of the practitioners a procedure for getting information on the quality of the film (and bulk) materials, whenever a perfect material is needed, as e.g. for nanoelectronics. The film surface is characterised by large bond angle distortions and, therefore, for very thin films high density of the surface layer means high density in the whole film. Nevertheless, this effect was not observed experimentally due, probably, to the large amount of defects embedded in the films. In colloid and materials science the density of amorphous particles enhanced by the high ratio surface/bulk it is challenging and rich in consequences related to ion diffusion and sintering. The density increase related to the softening of the covalent bonds is important for understanding the melting process and phase transformations in glasses, metglasses and various alloys.

Another important consequence of our finding is the variability of the amorphous phase on a large scale of bond angle distortions. It is suggested to use the amorphous semiconductors as micro-sources of energy, to be released during transformation between different types of amorphous phases.

As concerning the chemical bonding in solids, it is now clearly assessed that the distortion of the bonds in amorphous semiconductors leads to some increase of the bonding lengths due to loss of hybridisation, while the density increases. This is also the case of high pressure polymorphs of silicon and germanium, as well as the case of SiO_2 and GeO_2. The increase of the bond length is, nevertheless, compatible with the increase of density [20].

An important consequence is related to water [13].

Water, if confined, exhibits a non-homogeneous structure. The surface bonds are more distorted than the inner bonds and, therefore, a more denser layer forms at the surface. This could be relevant for the diffusion in biological cells.

In biology, the correct knowledge of the liquid state of water is important for the tissue cryo-preservation [21]. The change of water density, related to the possibility to control the bond angle distortion, can be of interest for developing techniques for freezing the water in a state with the density approaching that of normal water. This would prevent the tissue alteration. Rapid cooling, with the aim to quench the distorted bonds, is suggested. The water properties at the surface is important for the way in which gases and liquids interact. For example, adsorption of oxygen in our lungs and industrial process of "scrubbing" waste gas are undoubtedly correlated with the structure of the surface layer of water. The decrease in the organised hydrogen bonding at the water surface must lead to an increase of compactness and not to a loosing (it was unrealistically estimated an intermolecular separation in water at the surface of 5 % greater than in the bulk liquid [22])

The interplay between science and technology raises the question about the amount of energy able to be stored in the distorted covalent bonds in amorphous networks and to be released when necessary.

Recently, it was speculated that amorphous ice should appear on many bodies in cosmic space [23].

As a matter of fact, as early as in 1974 [24], a hypothesis has been advanced, according to which the amorphous ice, abundant in comet heads, can be a source of energy originated in the transformation amorphous ice - crystalline ice. The phase transition in ~5×10^7 tons of a-ice can produce enough energy (10^{12} kcal) for determining the cometary outbursts usually observed. As concerned the cosmic water, the possible amorphous water films formed in darkness can expand violently when sunlight is acting, thus causing stone breaking and formation of the powders on the surface of the cosmic bodies.

In geology, water, initially present in the planetary ocean, becomes trapped in sediments, subducted and immobilised in the deep interior [25]. The state of the water, and the phase changing by changing the bond angle distortion and, therefore, the density, can lead to powerful cracks in the earth crust. This effect may explain certain earthquakes and, also, the appearance of volcanic outbursts.

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