CHARACTERIZATION OF THE INTERSTITIAL VOIDS IN THE STRUCTURAL MODEL OF AMORPHOUS SILICON DERIVED FROM THE DIAMOND-LIKE LATTICE

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The simulation of interstitial void evolution in a model of crystalline silicon subjected to topological disordering revealed that the void size distribution broadens and shifts towards smaller mean diameter size, when the lattice disordering increases. The size distribution is not gaussian and the mean diameter of the voids is lower than the crystalline value. The calculation of the structure factor corresponding to void configuration evidences the absence of the short and long range order and point out to the presence of the medium range order.

1. Introduction

Amorphous silicon (a-Si) is a particularly interesting material. With the advent of the hydrogenated amorphous silicon, this non-crystalline semiconductor became the most promising material for solar energy conversion. a-Si was the subject of considerable effort devoted to the measurement of its structure, optical, electrical and vibrational properties [1-5]. Recently, the possibility to have the elemental silicon in several allotropic forms, like carbon, has been demonstrated [6]. Yonezawa et al. [7] have shown that the radiative recombination rate is enhanced in amorphous silicon nanostructures and, therefore, the disorder is important for light emitting silicon.

The fundamental properties of amorphous silicon require a detailed knowledge of the atomic scale structure. As opposite to the crystalline case, there are limitless possible disordered structures but no experimental techniques that provide atomic resolution similar to crystallography [8]. The way to get information on the amorphous structure is to calculate the one-dimensional radial distribution function (RDF) [9]. Nevertheless, the information obtained from RDF is an average on all atomic configurations in the material. The structural models, either hand-built or computer generated, greatly enlarge the information on the structure of the disordered materials, especially when used conjointly with the experimental RDFs [9].

The amorphous state of germanium and silicon was thought, firstly, in terms of the microcrystalline models, and then in terms of the continuous network models [10]. Later, Wooten, Winer and Weaire [11] used a simple algorithm for the systematic computer generation of disordered network models, starting with the simulated diamond structure (FC-2), and successfully rearranging it by special elementary processes. On the basis of the generated models the mentioned authors have investigated the topological conditions that lead to crystallization [12].

Last years, an increased attention was paid to the problem of structural voids in the disordered materials with the purpose to explain some properties of the glasses. Thus, Elliott [13] explained the structural origin of the first sharp diffraction peak in the diffracted intensity curves of several glasses through the void-based model, while Jensen et al. [14] suggested that voids are important for the interpretation of the positron annihilation lifetime data in non-crystalline chalcogenides.

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The presence and the role played by the structural voids in various metal-semiconductor alloys as e.g. Ge-Mo and Ge-Au, are still under debate and several models based on the Monte Carlo – Metropolis and reverse Monte-Carlo methods have been discussed [15,16]. Recently, Gaskell [17] has reviewed the structural network glasses and has shown that ordered (microcrystalline) and random models have both strengths and weaknesses. Halm et al. [18] have shown that in many liquid alloys there are strong fluctuations of density at the atomic scale and they can be ascribed to the specific distribution of the voids.

In this paper we report the results of the calculation of interstitial void size distribution in a model of amorphous silicon derived from the crystalline lattice of silicon by introducing step by step special topological modifications, called deformon states.

2. Topological defects in a perfect tetrahedrally bonded lattice. Model of amorphous silicon

If two neighboring atoms in crystalline silicon are interchanged after breaking and re-forming only three bonds (one common bond and two bonds with the neighbors) then one gets deviant bonds embedded into a perfect lattice. The distortion energy of the deviant bonds rapidly decreases by the relaxation of the lattice around the interchanged atoms. The final state of distortion defines a diffuse defect in the silicon lattice. This can be considered as a topological defect, and Popescu [19] proposed to be called a *deformon* state, or simply *deformon*.

The schematical illustration of the change of the positions of two atoms while preserving all covalent bonds in the lattice, characteristic to the deformon state, is shown in Fig. 1.
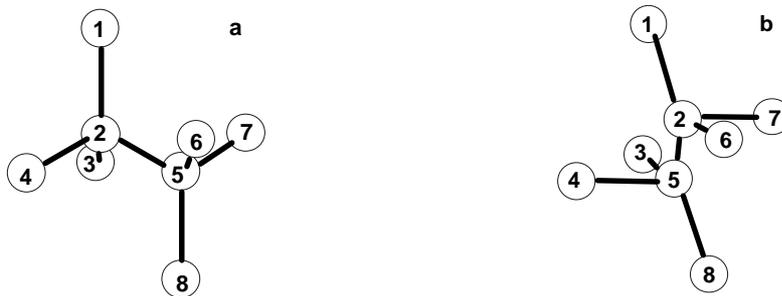
Fig. 1. The topological changes involved in the deformon state; a. initial state; b deformon state.

The modelling was carried out on a hand-built model of crystalline silicon with 300 atoms. A number was attached to each atom in the original crystallite. The coordination of every atom was listed in a coordinate table and the covalently bonded neighbours were listed in a neighbour table. Firstly, only one deformon was introduced in the centre of the model by switching two bonds. The analysis of the topological defect thus formed has shown that in the crystalline lattice characterized by 6-fold chair-like rings of atoms do appear four 5-fold rings and six 7-fold rings of atoms.

After introducing the defect state, the whole crystal (whose atom coordinates were subsequently measured on the model) was energetically relaxed, without boundary conditions, by using a Monte Carlo computer procedure and bond bending and bond stretching potentials after Keating [20] with the elastic force constants given by Martin [21].

The Keating potential is a simple sum of bond-stretching and bond-bending potentials:

$$V = \frac{1}{2} \sum_{i(j)} \frac{3\alpha}{8d^2} (\left| \vec{x}_i - \vec{x}_j \right|^2 - d^2)^2 + \sum_{i(j,k)} \frac{3\beta}{8d^2} \left| (\vec{x}_i - \vec{x}_j)(\vec{x}_k - \vec{x}_i) - d^2 \cos\gamma \right|^2 \quad (1)$$

where α and β are the bond-stretching and bond-bending force constants, respectively, and d is the strain-free equilibrium bond length in the crystal. For Si $d = 0.235$ nm. The sum i is over all atoms, j over the nearest neighbours of i, and k over all nearest neighbours not including j. γ is the ideal tetrahedral angle: $109^{\circ}28'$. The bond stretching force constant is $\alpha = 48.5$ pJ and the ratio $\beta/\alpha = 0.285$.

The Keating potential provides a good semiempirical description of the bonding forces with only two parameters. Central bond-stretching forces are not enough for stabilizing a tetrahedrally bonded structure, hence the bond-bending term is essential.

In the first stage of modelling we introduced a second deformon in the same simulated lattice and the new state of distortion was determined after the relaxation of the whole model. Then, we continued the process by introducing new deformons: 3, 5, 12, 15, 20, 25, 30, 33, 38, 45, 50, 55, 60, 64, 69, 75, 80, 85, 89, 95, 100, 105, 110, 115, 125, 130 and 138 deformons for the final state of the crystalline model. After every new group of deformons introduced in the lattice, the coordinate table and the neighbor table were updated. The relaxed network in every case was analysed in detail.

Fig. 2 shows the variation of the distortion energy per mole of silicon as a function of the number of deformons introduced in c-Si model. It is remarkable the synergic effect induced by a high number of deformons. The total distortion energy increases non-linearly. The increase of distortion energy is not proportional to the number of deformons, but shows a tendency to saturation.
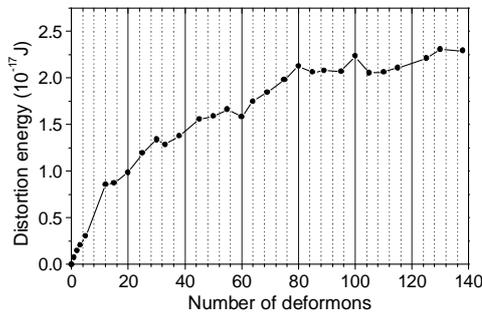
Fig. 2. The distortion energy of the c-Si model vs the number of deformons.

3. Method for the calculation of the void-size distribution

An interstitial void in a lattice or network is defined as that region situated in-between the atoms, that corresponds to the sphere of maximum diameter, which can be introduced in the free space delimited by the atomic neighbourhood [22]. The void size distribution represents the distribution of the diameters of all the spheres that can be introduced in the lattice or network without a notable superposition (partial superposition of around 5-10 % of the diameter was permitted, thus accounting for eventually non-spherical, elongated voids). A special computer program run in FORTRAN was devised to this purpose.

4. Results

4.1 Void distribution. Characterization
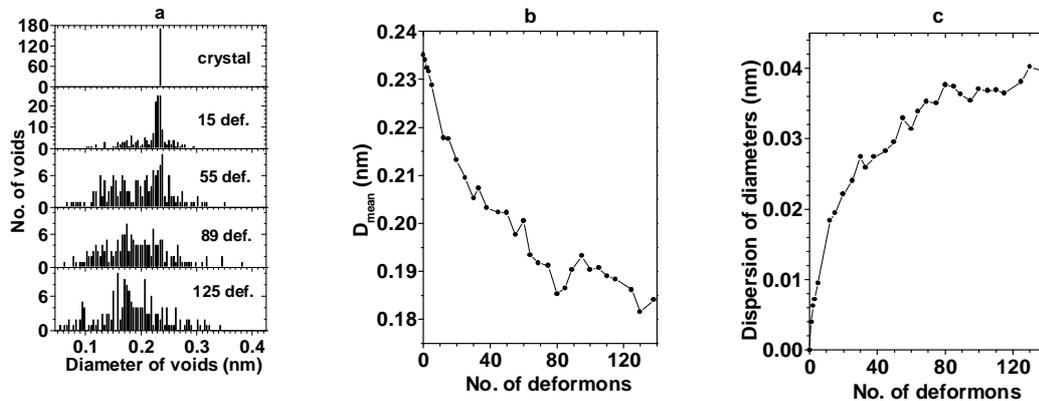
Fig. 3. a. The distribution of the void diameters; b. the mean diameter of voids versus the number of deformons introduced in the silicon lattice; c. the dispersion (r.m.s.) of the void diameters as a function of the number of deformons introduced in the silicon lattice.

Fig. 3 shows the characteristic of the void system in the silicon model. The distribution of the void diameters (a) broadens and moves towards small values when the model becomes disordered by introducing more deformons into the lattice. The mean diameter (b) moves down to a value of ~ 0.18 nm. In the same time the r.m.s. deviation of the void diameter (c) increases up to values of ~ 0.04 nm. It seems that the model tends to a limit of disorder when no four – fold rings of atoms are permitted. This rule was imposed to our model during the disordering procedure.

4.2 Structural characterization of the silicon model and of its voids

The structure factor of the silicon model with various numbers of deformon is shown in Fig. 4a. Fig. 4b shows the theoretical interference function calculated for a model defined by the void centres, where the void centers consist of silicon atoms. The most important feature of the void assembly is the vanishing of the oscillations specific to crystalline lattice (for a large range of the scattering vector) and those specific to short-range order (for high values of scattering vectors).
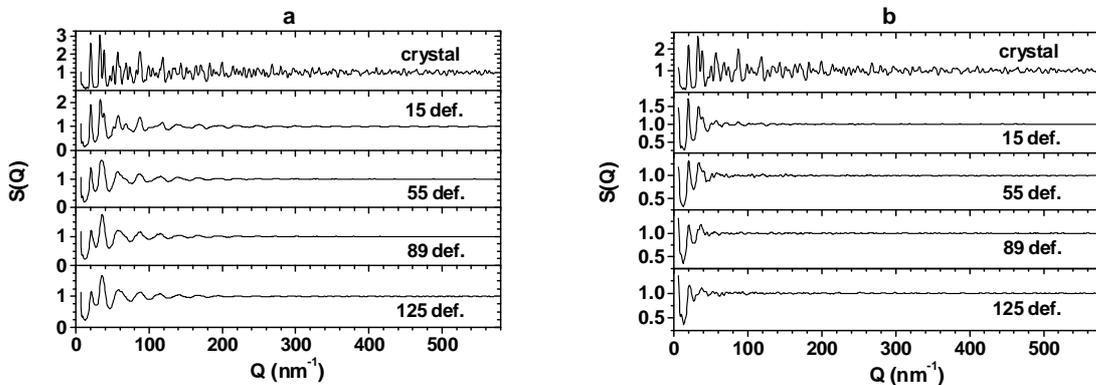
Fig. 4. a. The structure factor of the model with various number of deformons; b. Theoretical interference function calculated for a model defined by the void centres.

The differential radial distribution function of the silicon model and of its image of voids were calculated and represented in Fig. 5 for different number of distorting deformons in the silicon lattice. While the atom DRDF is in good agreement with the experimental function, the void DRDF show less pronounced structural details. The existence of a low and broad maximum around the value of 0.37 nm speaks in favour of some ordering of the voids around the network atoms.
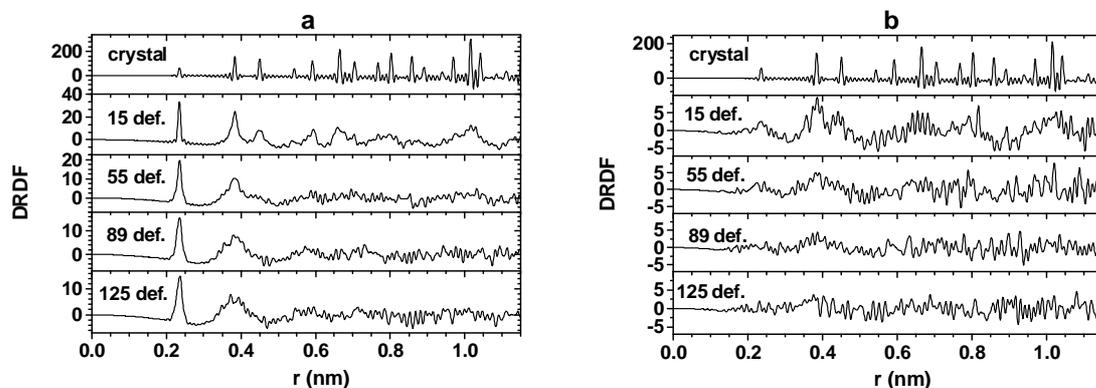
Fig. 5. a. Differential radial distribution function of the silicon model; b. Differential radial distribution function of the model defined by the void centres.

The void configuration could be not completely at random. Some ordering probably exists and this can be related to the medium range order in the amorphous material. The extension of this order has been analysed by determining the network of possible bonds between voids and calculating the hypothetical distribution of dihedral angles between voids. The results are shown in Fig. 6. As easily observed, the dihedral angle correlation is rapidly lost when the number of deformons in the c-Si increases. The complete loss of dihedral angle correlation means that the voids are rather correlated at distances larger than 0.54 nm, corresponding to the average distance between the end voids that define the dihedral angle.
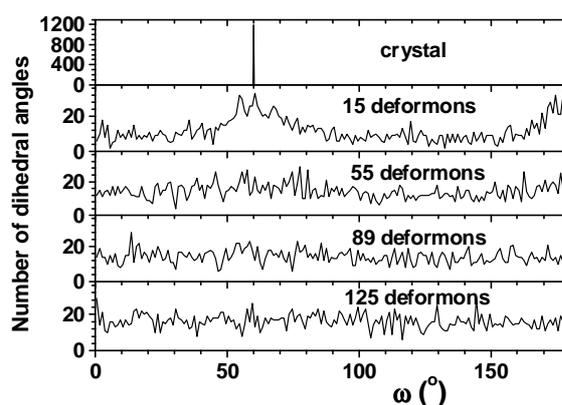
Fig. 6. Dihedral angle distribution in the system of voids.

5. Discussion

The interstitial void distribution in a model of amorphous silicon is an important parameter related to the properties of silicon. Nakhmanson [23] has shown that the main properties of amorphous silicon can be understood by supposing that a network of intimately related nanovoids and crystalline grains defines the structure of the material. The size and distribution of voids and nanocrystallites control the electronic density of states in the material, and, therefore, the optical and electrical properties. Well ordered crystallites define voids with a narrow size distribution. In such configurations the doping of the material is possible because the flexibility of the network is lower. Non-uniform distribution of the strained sp^3 bonds is useful for the appearance of *n* or *p* type centres, especially when doping atoms are added [24].

A general concept of nano-heteromorphism for complex glasses has been developed by Minaev [25]. This concept could be extended to elemental glasses: the glass consists of nanostructural units formed by group of atoms with a low mean distortion of the inter-atomic bonds. This seems to be also the case of the amorphous silicon.

6. Conclusions

The void morphology, size distribution and spatial configuration have been analyzed in a model for amorphous silicon derived from the perfect crystalline lattice of silicon by introducting in it a large number of deforming states. The voids seem to be ordered at the intermediate scale. The void structure is relevant to the physical properties of the material. Work is in progress for comparing the void configuration in this model with the continuous random network models for amorphous silicon.

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