INTERSTITIAL VOIDS IN TETRAHEDRALLY AND IN THREE-FOLD BONDED ATOMIC NETWORKS

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The aim of this letter is to investigate the interstitial voids distribution in simulated networks of disordered silicon and graphitic materials. We have characterised these disordered structures and evidenced the importance of the SW and WWW defects on the structure in the newly obtained netwoks. The voids distributions are related to the posibility to get new materials by filling the voids with different kind of atoms. The change of the parameters of the first diffraction peak (FDP) in amorphous silicon and graphite as a consequence of filling the lattice voids has been determined.

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1. Introduction

In this paper we report the results obtained by computer simulation of modifications induced in a rather perfect silicon lattice by creating Wooten-Winer-Weaire (WWW) defect states without introduction of dangling bonds or other type of defects. Elliott [1-5] has demonstrated that the ordering of the interstial voids around the chalcogen atoms in chalcogenide glasses is essential for the formation of the first sharp diffraction peak (FSDP) in these materials.

On the other hand, we simulated similar defects [6] in ideal graphene layers and we analyzed the general effect of the defects on the structure of graphene packing, especially on the particular first sharp diffraction peak (FSDP) in the calculated X-ray patterns. The Stone-Walls defects were previously studied in [7,8]. Kapko et al. [9] firstly calculated the electronic structure of the amorphous graphene. Pentagonal puckering in a sheet of amorphous graphene was recently demonstrated by Li et al. [10]. The realization of the Zachariasen glass in amorphous graphene was remarked by Kumar et al. [11]. The presence and distribution of voids in these materials is important for the formation of intercalated compounds of the type graphite – alkali combinations. Lastly new materials based on defected graphene layers and disordered alkaline insertions could be predicted.

2. Simulation of the defect states in silicon and graphene lattices.

We used one silicon lattice with 455 atoms and 5 graphene lattices each of them with 150 atoms. In these networks (which are initial perfectly ordered) we have introduced a number of topological defects to obtain disordered networks. Then, these clusters have been energetically relaxed using the Monte-Carlo method in the frame of valence field theory. We consider that these clusters are at temperature of 0 K. The total energy of every silicon atom (which is a measure of

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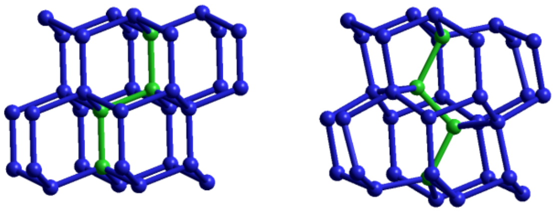
the deviation of Si-Si bond lengths and of bond angles from the specific values of the crystal) was calculated with the formula of Keating [12] using the force constants given by Martin [12]. To calculate the total energy of every carbon atom, energy which accounts for the bending and stretching of the carbon bonds, we used the formula and the force constants given by Jishi [12].

The "Wooten-Winer-Weaire (WWW) defect" is a topological defect of a tetrahedral lattice formed by interchange of two neighbors of two bonded silicon atoms without destroying continuity of the lattice [6]. Figure 1 shows the initial state (a) and WWW defect state (b) of silicon lattice. The bonds between silicon atoms, as a function of the distance from the defect's centre, are more or less deformed. The lattice domain affected by deformation extends up to a distance of 0.66 nm from the centre of defect.



a b

Fig. 1. Silicon lattices with minimum of the energy being in a) crystalline state, b) WWW defect state (four 5-fold rings and sixteen 7-fold rings of atoms)

To obtain an amorphous silicon lattice we introduced 56 WWW defects in crystalline lattice of silicon (Fig. 2) and thus deformation spheres are partial superposed.

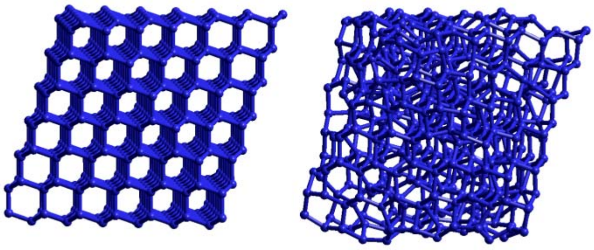


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Fig. 2. Model of silicon lattice (455 atoms) with minimum of the energy in: a) crystalline state, b) amorphous state with 56 WWW defects.

The "Stone–Wales (SW) defect" is a topological defect of graphene lattice like WWW defect [10]. This similarity between two types of defects made Popescu to unify them in a single concept named "deformon". Thrower [13] was first who studied this type of defect in graphite. Figure 3 shows the graphene lattice (150 atoms) (Fig. 3a) and SW defect state of graphene lattice (Fig. 3b). In the case of graphene with one defect, the defect radius is 0.31 nm, and the decrease of the energy is much more rapid than in the case of silicon with one defect

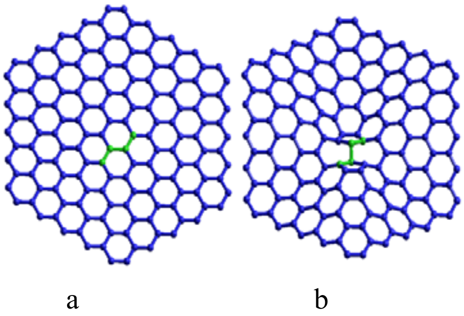

Fig. 3. Top view of graphene lattice with 150 atoms with minimum of the energy in: a) crystalline state, b) the Stone-Wales defect state (two 5-fold rings and two 7-fold rings of atoms.

To obtain amorphous carbon monolayers we introduced 9 or 10 Stone–Wales defects in the two-dimensional lattice of five graphene layers (150 atoms) (Fig. 4). These five amorphous carbon monolayers there packed in an amorphous carbon structure (a-C) (Fig. 5b) and in Fig 5a is presented a graphite lattice.

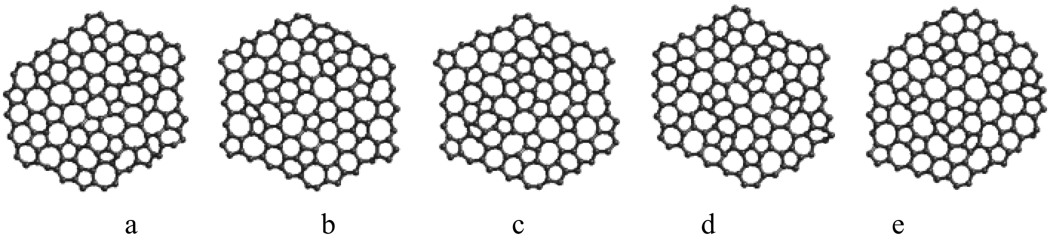

Fig. 4. Disordered layers of graphene used in simulated stacking of amorphous carbon a-c) 10 Stone-Wales defects, d-e) 9 Stone-Wales defects [7].

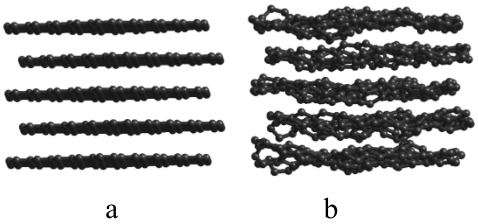

Fig. 5. The lattice model of 750 carbon atoms in a) crystalline state (graphite), b) amorphous state (a-C) (48 SW defects.

3. Voids in silicon and graphene simulated amorphous lattices.

The normalized interstitial voids' radius (r_V) distributions in crystalline and amorphous silicon (455 atoms), respectively in five graphene and in five amorphous carbon layers (5 × 150 atoms) are shown in Fig. 6a, b. While in amorphous silicon the interstitial voids are all spherical, in amorphous carbon layers some are spherical and some are of discoidal shape. In graphene all the interstitial voids are discoidal in shape.

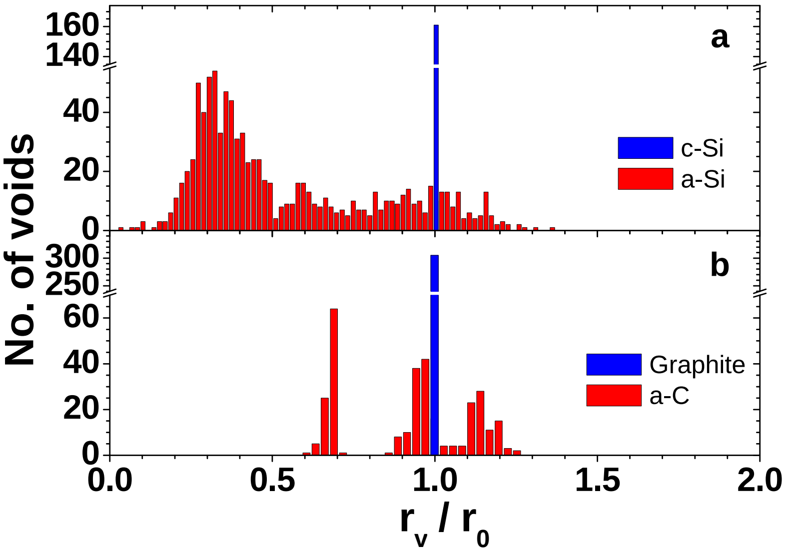

Fig. 6. The normalized voids' radius (r_V/r_0) distribution in crystalline and amorphous silicon (a), in graphene and in amorphous carbon layers of a-C with 48 defects (b) (r_0 is the covalent radius of silicon and carbon: r_0(Si) = 0.117 nm and r_0(C) = 0.071 nm).

The interstitial voids in these two types of lattices are important for understanding the origin of first diffraction peak in the structure factor of amorphous silicon (Fig. 7b) and second diffraction peak of structure factor of a-C (Fig. 8b).

Fig. 7b shows the structure factor of the amorphous silicon model after relaxation. Elliott [3] has demonstrated in a rather seminal paper that the so-called FSDP in glasses depends on the distribution, size and ordering of voids. Popescu and Sava suggested that the voids distribution into an amorphous material is essential in the amplification or vanishing of the first diffraction peak (FDP).

We have simulated the filling of the interstitial voids in amorphous silicon, by introduction in the center of the voids of ions with atomic number identical to that of silicon, without covalent bonds between silicon and ions. The diffraction pattern of the model shows the decrease of the first diffraction peak (FDP) as a measure of filling the voids (Fig. 7b).

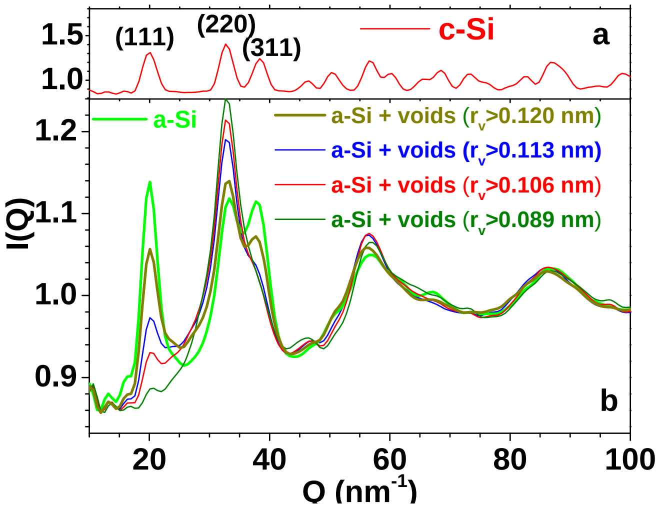

Fig. 7. a) The structure factor of the crystalline silicon model. b) Diffraction pattern of the amorphous silicon model with gradually occupied voids with atoms non-bonded in the lattice. The arrows denote the crystalline peaks.

Further we have simulated, as in the case of silicon, the gradual filling of the interstitial voids in each amorphous layer from a-C with ions having the atomic number approaching that of carbon. In this case the second diffraction peak (SDP) of structure factor of a-C diminishes its height and gradually vanishes (Fig. 8b).

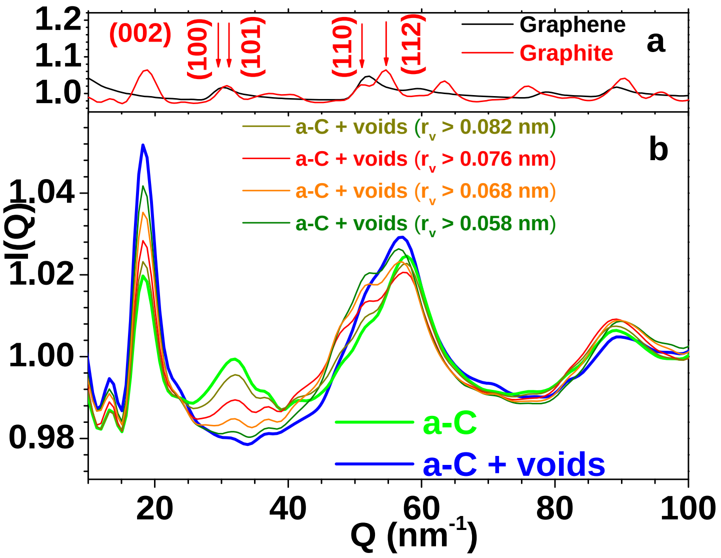

Fig 8. The structure factor of a graphene layer and graphite (a) compared to the structure factor of a-C with 48 defects when an increasing number of interstitial voids of amorphous layers are filled (b). The arrows denote the crystalline peaks.

The first diffraction peak (FDP) (situated at Q ~ 20 nm^{-1}) is a sharp peak and is followed by a smaller peak (situated at Q ~ 32 nm^{-1}) which is very sensible to the filling of voids of the disordered graphene layer. In the same time the FDP increses with the degree of filling the structural voids.

4. Discussion of the results

We have simulated several networks of tetrahedrally bonded networks of silicon and three-fold bonded graphite layers with structural defects. The interstitial voids have been calculated. In silicon simulated networks the distribution of voids are determined by the level of disordering. For a small number of defects the deformation of the network of atoms is strictly localized.

The packing of defected graphenes, followed by filling-up the voids within the graphene layer with atoms having the radius near that of carbon (e.g. lithium or nitrogen) has as main consequence the lowering of the second peak in the diffraction pattern down to its disappearance.

5. Conclusions

The disappearance of the first diffraction peak (FDP) situated at Q = is explained by the filling of the structural voids.

The second diffraction peak situated at Q = when amorphous layer is integrated in a-C gradually vanishes (as in the case of FDP of silicon) when the interstitial voids are filled by ions with the diameter approaching that of carbon (e.g. nitrogen ions or lithium ions). The motivation of this study is to show that the gradual fill of the interstitial voids with virtual atoms have an important effect on some maxima in the structure factor (FDP in the case of a-Si and second maximum in the case of a-G). Our main goal was to show the existence of a direct relationship between the maxima in the structure factor of the amorphous materials and the atoms that define the distribution of the interstitial voids.

Acknowledgements

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