Journal of Non-Crystalline Solids 358 (2012) 2060–2062

Contents lists available at SciVerse ScienceDirect

Journal of Non-Crystalline Solids

journal homepage: www.elsevier.com/locate/jnoncrysol

Advances in understanding the defects contributing to the tail states in pure amorphous silicon

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ARTICLE INFO

Article history:
Received 17 August 2011
Received in revised form 7 January 2012
Available online 13 March 2012

Keywords:
Amorphous semiconductors;
Electronic density of states;
Localized mobility gap

ABSTRACT

The tight-binding molecular dynamics simulations and reverse Monte Carlo structural modeling method were applied in order to investigate the existence of small bond angles (like those in triangles and squares) in amorphous silicon networks. The influence of small bond angles on the electronic density of states was analyzed. The presence of a number of smaller bond angles is necessary for a proper reproduction of the neutron diffraction data of amorphous silicon. Semiempirical Hartree–Fock calculations show that these arrangements provide higher energy levels in electronic density of states which are localized on these local structures. Accepting this result we must reconsider the electronic density of states of amorphous semiconductors. The localized mobility gap has structure i.e. two characteristic peaks can be found inside the tail. First larger peak belongs to the squares while the peak at larger energy is formed by triangles.

1. Introduction

Considering electron transport, optical properties like transparency and related effects, etc. in semiconductors, Electronic Density of States (EDOS) is one of the most important properties. Plenty of different theoretical methods exist to derive the EDOS in crystalline case. They are usually based on Block electron theory. Results obtained are usually displayed in inverse space (k space or reciprocal k-space). In the EDOS of crystalline semiconductors there is a well-defined energy interval where we cannot find states at any k value. These gaps are about 1–2 eV in crystalline semiconductors. In amorphous materials there is no periodicity and the Block electron theory is useless. Hence it is impossible to define reciprocal k-space. Only the number of states versus energy is a useful relationship. In all handbooks (i.e. [1]) we can find the following general description for the electronic density of states of pure amorphous semiconductors, see Fig. 1. The first surprise is that in the crystalline physics learned empty gap practically disappeared! Not empty gap – called mobility gap (tail) – could be found. These energy levels contain localized electron states. The rest of states around gap are delocalized and the interface between localized and delocalized states is the mobility edge. What is the origin of such localized states in the impurity-free amorphous semiconductors? The usual answer is just “disordered structure” and no detailed atomic scale description can be found in the literature.

Several calculations on the band structure of amorphous silicon which is the model material of IVth column semiconductors have been reported. Most of cases Continuous Random Network model of Wooten et al. [2] (WWW model) were applied for atomic scale configuration. Wooten's coordination defect-free model of a-Si having periodic boundary conditions contains bond angles in the internal between about 90°and 150°. The classical empirical Keating potential was applied for this Monte Carlo type construction which interaction has a quadratic energy term of the difference between cosine bond angle and cosine ideal bond angle. This term avoids the large deviation from the canonic value of bond angle. The network includes fivefold, sixfold, and sevenfold rings. Several other computer generated models have been constructed using various classical empirical potentials or by applying different quantum mechanical methods [3–13]. Despite of these efforts the WWW model is still considered to be the best three-dimensional atomic scale representation of a-Si (and a-Ge) structure. We also used WWW model for the derivation of charge fluctuation in a-Si and observed that the angle deviation from the ideal bond angle plays the most important role in the charge accumulation on each silicon atoms and the bond length fluctuation is practically negligible [14].

2. Our amorphous silicon structure models

2.1. Tight binding molecular dynamics simulation

A tight binding molecular dynamics (TB-MD) computer code has been developed to simulate the real preparation procedure of amorphous structures, which is grown by atom-by-atom deposition on a substrate. Note that our method differs from most other molecular dynamics (MD) studies where the amorphous networks have been formed by rapid cooling from the liquid state. No laboratory where

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doi:10.1016/j.jnoncrysol.2012.01.056

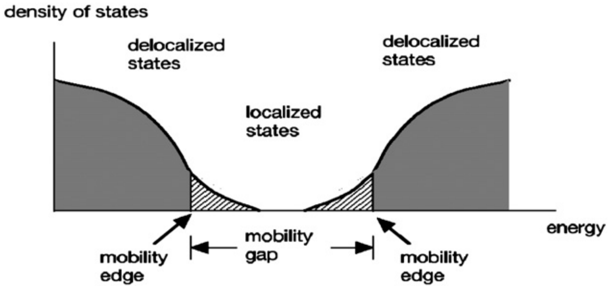

Fig. 1. Traditional description of electronic density of states in amorphous semiconductors.

amorphous samples from the elements of column four could be prepared on this way! Our MD method had been successfully used for the description of the amorphous carbon growth earlier [15]. In silicon case, the TB Hamiltonians of Kwon et al. [16] and T. J. Lenosky [17] have been used to describe the interaction between silicon atoms. All parameters and functions of the interatomic potential for silicon were fitted to the results of the local density functional calculations. These TB models reproduce the energies of different cluster structures, the elastic constants, the formation energies of vacancies and interstitials in crystalline silicon. Surprising results have been found in the ring statistics in both cases [18]. The networks prepared by our models have a significant number of squares. Furthermore, triangles are also present in the atomic arrangements. Most of the theoretical models for a-Si do not contain such structural fractions.

2.2. Reverse Monte Carlo simulation

Using our neutron diffraction data on evaporated amorphous silicon sample [19] RMC computer simulation study have been carried out. Potential independent reverse Monte Carlo (RMC) modeling has already been shown to be a powerful tool for interpreting disordered structures. The unconstrained simulation contained a large number of bond angles of 60°. First, we considered this result to be artifact. For the next stage, a rather specific series of RMC calculations has been carried out. Our aim was to establish whether bond angles drastically different from the canonical value of 109.5° are necessary to reproduce the neutron diffraction data of [20]. The RMC calculations were started from a 512 atom WWW model and only very small displacements (of the order of 0.002 A) were permitted during the Monte Carlo simulation. Bond angles was monitored regularly, after about each 50,000 accepted displacements. The computer program stopped after 500,000 accepted steps. The step development demonstrates that we can get better and better fit to the measured diffraction data if some bond angles get smaller and smaller (At the beginning the smallest bond angle was about 90°).

2.3. Additional information to amorphous silicon structures

There is no direct experimental method for determination the atomic distributions in three dimensions. During the growth of amorphous structures it might be expected that covalently bonded atoms tend to form ‘natural configurations’. A systematic analysis of structural data has been carried out using the Cambridge Structural Database (CSD) [21–22], this being the world's largest database of experimentally determined crystal structures containing the results of X-ray and neutron diffraction studies and three-dimensional atomic coordinates. We have collated from the CSD the experimentally determined structural data of molecules containing Si–Si–Si fragments. The environment of silicon atoms might be considered as ‘white noise’ around such fragments. A search found near 3000 targets. In the angle distribution of Si–Si–Si parts, two well-defined and unexpected regions have been found i.e. we observed triangles and squares as natural configurations of silicon atoms. We consider these results that an experimental evidences for the existence of Si–Si–Si triangles and Si–Si–Si–Si squares.

3. Density of states calculations

Quantum chemical cluster calculations at the AM1 level have been carried out in order to find out whether the presence of triangles and/or squares cause variations in terms of the electronic properties [20]. The electronic density of states (EDOS) of a part of WWW model and the modified WWW models containing triangles and squares were calculated. The first cluster (a part of the WWW model) contained about 100 fourfold coordinated Si atoms and a sufficient number of hydrogen's saturating the dangling bonds on the boundary of the cluster. This system can be taken as a reference system, as it contains no significant deviation from a locally nearly perfect tetrahedral order. Based on this network, we constructed other clusters by adding silicon (and hydrogen) atoms which formed one, two and three fused or individual triangles and squares. Significant differences were observed in terms of the electronic DOS: additional higher energy states appeared inside the gap, which are localized on the triangle(s) and square(s). There atomic scale arrangements construct the localized part of the mobility gap and form a shape of the electronic density of states having two important peaks.

4. Conclusion

Our atomic scale structure investigations of tetrahedrally bonded amorphous silicon confirm that threefold and fourfold rings are also basic atomic arrangements of such materials. We consider triangles and squares as new types of defects. These defects are highly energetic. Accepting this result we must reconsider the electronic density of states of amorphous semiconductors. The localized mobility gap has structure i.e. two characteristic peaks can be found inside the tail. First larger peak belongs to the squares while the peak at larger energy is formed by triangles (Fig. 2). In the earlier investigation of electron transport, hopping conductivity, optical properties, etc. the tail was considered usually as an exponential or Gaussian decaying function. Triangles and/or squares have never been considered in any band structure calculations although they play important role in several phenomena.

Acknowledgment

I am indebted to my coworkers: Laszlo Pusztai and Krisztina Kadas (Institute for Solid State Physics and Optics, Budapest, Hungary) and Krisztian Kohary (University of Exeter, UK). This work has been supported by the Hungarian–Japanese Intergovernmental S&T Programme (Grant No. TÉT_10-1-2011-0021) and by the New Hungary Development Plan Project No. TAMOP-4.2.1/B-09/1/KMR-2010-0002.

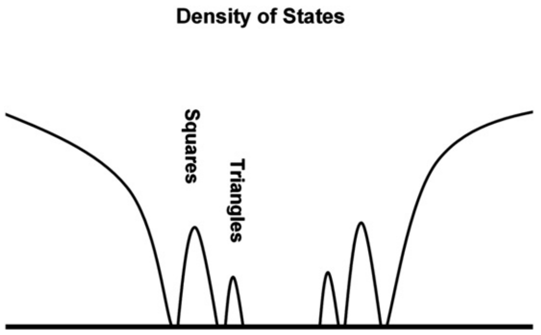

Fig. 2. Electronic density of states of amorphous semiconductors containing two significant peaks belonging to the triangles and squares.

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