# What is the origin of tail states in amorphous semiconductors?

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**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. Semi-empirical Hartree–Fock calculations show that these arrangements provide higher energy states in electronic density of states which are localized on these local structures. We consider that smaller bond angles are a new type of defects. These defect states are highly energetic and they are the origin of tail in amorphous semiconductors.

## 1. Introduction

In condensed matter physics, the electronic density of states (DOS) of a system describes the number of states at each electron energy level. The states can be occupied or unoccupied. A DOS of zero means that no states can be occupied at that energy level. These states form a so-called gap. The DOS is one of the most important properties of condensed materials considering electron transport, optical properties like transparency and related effects, etc. We must have information on it for electronic application as well. In crystalline case having translational symmetry plenty of different calculation methods exist to derive the DOS. They are usually based on Block electron theory. Huge number of such papers appeared containing electronic density of states calculations and results are usually displayed in inverse space (k space or reciprocal k-space), inside the first Brillouin zone of the lattice showing symmetry labels (see e.g.[1], page 204 for Si, page 207 for Ge and page 209 for GaAs). In the electronic DOS of crystalline semiconductors there is an energy interval where we can not find states at any k value. These gaps are about 1-2 eV in crystalline semiconductors. If the maximum energy of occupied and the minimum energy of unoccupied states belong to the same k than we say that this semiconductor has direct gap, opposite case this is an indirect gap semiconductor [1].

There is no periodicity in amorphous materials. Hence there is no reciprocal k-space. Block electron theory does not work! Should band gap occur in amorphous materials as it exists in crystalline case? The answer is yes but it is a little bit different. Only the number of states versus energy is the useful relationship. How to determine? The most common possibility is the cluster calculation which has two important steps. First, a good atomic configuration is needed so one must make a convenient computer modeling. Molecular Dynamics and Monte Carlo simulations are usually used for obtaining an atomic scale configuration. This structure allows us to carry out an electron energy calculation. Hartree-Fock ab initio or semi-empirical methods usually applied for deriving the DOS of

noncrystalline semiconductors, but there are some others like density functional method or tight-binding model. So far the Hartree-Fock approximation seems to be the best method to calculate the electron energies although this method overestimates the gap.

In all handbooks we can find the following general description for the electronic density of states of pure amorphous semiconductors, see figure 1. The first surplice is that from the crystalline physics learned empty gap disappeared! Not empty gap called mobility gap (tail) can be found containing localized electron states which states do not exist in any pure crystalline semiconductors. The rest of states around gap are demoralized and the interface between localized and demoralized states is the mobility edge. A natural question: what is the origin of such states in the impurity-free amorphous semiconductors? The usual answer is "disorder". That's it no detailed description can be found in the literature.
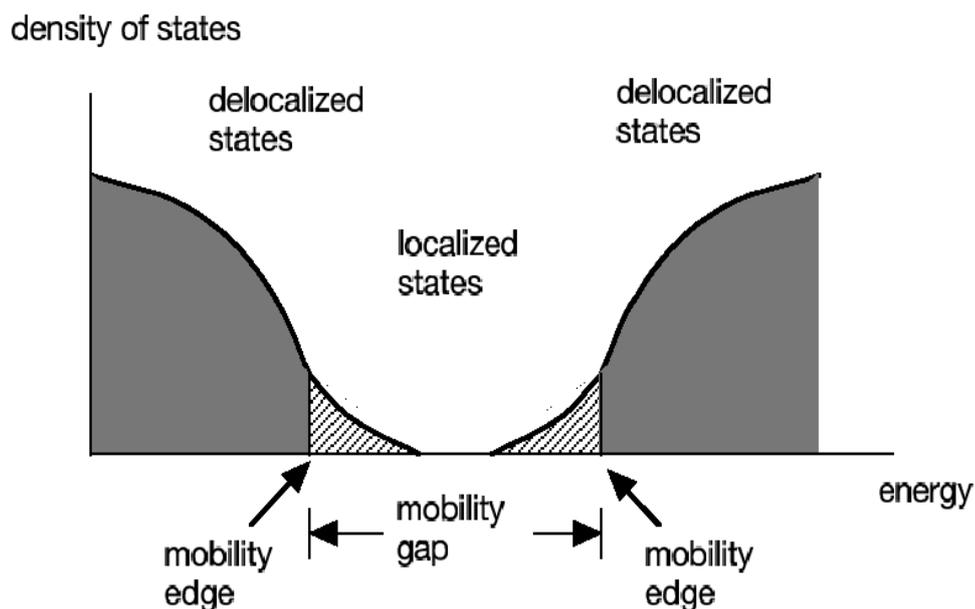


**Figure 1**. Traditional description of electronic density of states in amorphous semiconductors

There are several calculations on the band structure of amorphous silicon which is the model material of IVth column semiconductors. Most of cases Continuous Random Network model of Wooten et al. [2]. (WWW model) were applied for structural atomic scale configuration. Wooten's model of a-Si having periodic boundary conditions contains bond angles in the internal between about $90^o$ and $150^o$. The classical empirical Keating potential was applied for the 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 coordination defect-free network includes fivefold and sevenfold rings in addition to the six fold rings of the diamond-like structure. Since then, several computer generated models have been constructed using various classical empirical potentials or by applying different quantum mechanical methods [3-11]. Despite this effort the WWW model is still considered to be the best three-dimensional atomic scale representation of a-Si structure. We also used WWW model for the derivation of charge fluctuation in a-Si [12]. We 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 negligible in a-Si [12]. We got the similar conclusion for tetrahedrally bonded a-C [13]. (My/our all papers cited here can be downloaded from my homepage: http://www.phy.bme.hu/~kugler/pub2.html)

## 2. Our amorphous silicon structure investigations

We have developed a tight binding molecular dynamics (TB–MD) computer code to simulate the real preparation procedure of amorphous structures, which is grown by atom-by-atom deposition on a substrate. Note that our differs from most other molecular dynamics (MD) studies where the amorphous networks are formed by rapid cooling from the liquid state. No laboratory where amorphous samples from the elements of column four could be prepared! Our MD method was successfully used for the description of the amorphous carbon growth first [14,15]. Later on the TB Hamiltonian of Kwon et al. [16] was 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. The TB potential reproduces the energies of different cluster structures, the elastic constants, the formation energies of vacancies and interstitials in crystalline silicon. A surprising result was found in the ring statistics [17]. We defined a ring as a closed path, which starts from a given atom walking only on the first neighbor bonds. The size of a ring is the number of atoms in a closed path. 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.

Having our neutron diffraction data on evaporated amorphous silicon sample [18,19] 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 amorphous structures. The unconstrained simulation contained a large number of bond angles of 60 degrees. At that time, we considered this result might be artifact. For the next case, 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 degrees are necessary to reproduce the neutron diffraction data of [20,21]. The RMC calculations were started from a 512 atom WWW model and only very small displacements (of the order of 0.002Å) 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 angle get smaller and smaller. (At the beginning the smallest bond angle was about 90 degrees).

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'. 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) [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. A search found more than 2000 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.

## 3. Density of states calculations

Quantum chemical cluster calculations at the AM1 level were carried out in order to find out whether the presence of triangles and/or squares cause variations in terms of the electronic properties [19 20, 21]. 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.
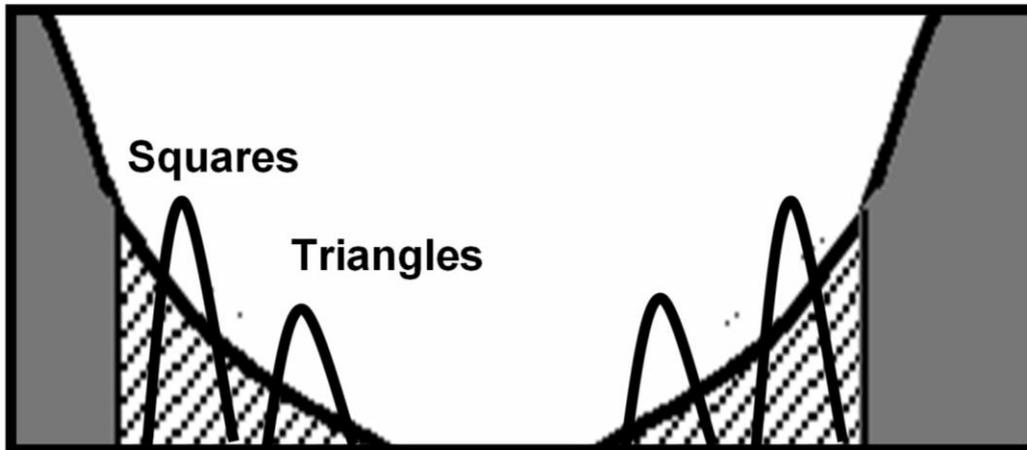


**Figure 2**. Electronic density of states of amorphous semiconductors containing two significant peaks belonging to the triangles and squares.

## 4. Conclusion

Our atomic scale structure investigations of tetrahedrally bonded amorphous semiconductors 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 (figure 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.

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