

# Self-organization in amorphous semiconductors and chalcogenide glasses

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It is shown that self-organization in non-crystalline networks of amorphous semiconductors, as well as in non-crystalline chalcogenide materials is rather a rule than an exception. The fundamental principles are stated on the basis of few examples. The most extended order in glasses is given by the uniform distribution of large stochastic clusters.

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## 1. Introduction

The problem of more order existing into the amorphous semiconductors was put in the early times of structural modeling of amorphous semiconductors by Prof. Radu Grigorovici. He affirmed [1] that “continuous network models of amorphous semiconductors are unavoidably characterized by fluctuations and non-randomness”.

The self-organization of one or more entities occurs when the total energy of the system is minimized to result in a more stable state. The process of self-assembly inherently implies: 1. some mechanism where movement of entities takes place using diffusion, electrical fields, etc. 2. the concept of “recognition” between different elements that results in self-assembly 3. where the “recognition” leads to the binding of the elements dictated by forces (electrical, covalent, ionic hydrogen bonding, van der Waals, etc.) such that the resulting physical placement of the entities pushes the system in the state of lowest energy.

Self-assembled processes could have a variety of applications. They are important in any case where micro- or nanoscale objects of one type need to be placed or assembled at specific sites on other substrate. Applications could include a) detection and diagnostic b) fabrication of novel electronic/optoelectronic systems, and c) new material synthesis.

In recent years a high interest raised in the developing concept and approaches for self-assembled systems for electronic and optical applications. Material self-assembly has been demonstrated in a variety of semiconductors (GaAs, InSb, SiGe...) using Stransky-Kastranov strain-dependent growth of lattice mismatch epitaxial films [2-5]. There is a continuous interest in assembling semiconductor transistors [6], carbon nanotubes [7,8] and quantum wires [9,10], which can be used as active devices for memory and logic applications. The self-organization in amorphous materials seems to be of potential interest for three-dimensional integration of nano-scale devices.

Recently, Lucovsky [11] has reported self-organizations that prevent percolation of network and interfacial bond-strain, which lead to intermediate phases

or Boolchand phases) with low concentration of defects in systems as:  $\text{Si}_3\text{N}_4\text{:H}$ ,  $\text{SiO}_2$  interfaces, Ge-Sb-Te chalcogenide films, etc. Self organizations are correlated with the observation of non-statistical bonding arrangements and the average number of bond-stretching and bond-bending constraints/atom being approximately 3.

The strained networks of tetrahedrally bonded amorphous silicon proved to be important for their unusual properties, including high densities. The density fluctuations, and the existence of very dense regions are the basis for self-organizations in the amorphous networks [12].

Special nanowires and nanotubes have been got in several oxides using growth in ion track membranes [13].

In this paper we discuss the self-organization phenomena and point out the phenomena starting from modeling of structure of non-crystalline tetrahedrally bonded semiconductors (Si, Ge) and of non-crystalline chalcogenides, compared to the experimental data.

## 2. Tetrahedral bonded semiconductors

Continuous random network models (CRN) are ideal networks and can be rarely produced. In fact they must include an enough large amount of free energy due to growing misfit in the compact arrangement of atoms when the volume of CRN increases. This misfit appears e.g. when the crystalline like arrangement of the tetrahedral units in germanium or silicon is substituted by dodecahedral-pentagonal configurations (amorphonic or modified Voronoi polyhedra, introduced for the first time by Prof. Grigorovici [14]), which are incompatible with the long-range order characteristic to crystal. With this idea in mind we tried [15] to see what happens if a model of amorphous silicon, of minimum free energy, is split in two amorphous domains, which, subsequently, were relaxed separately.

Fig. 1 shows the model of the amorphous silicon with 405 atoms where the cutting line between the two domains (amorphites) is clearly evidenced. Table 1 shows the free

energy data after computer relaxation of the model as a whole (M) and for the two separated and relaxed domains (M1 and M2).

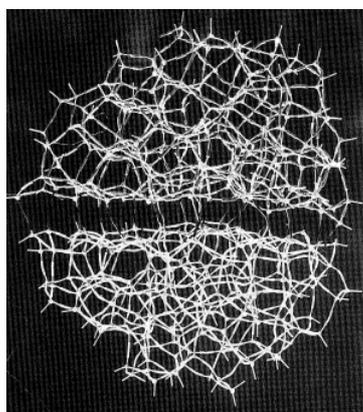


Fig. 1 A continuous random network model with 405 atoms for amorphous silicon. The separation between the two amorphous domains (amorphites) is seen.

As can be seen from Table 1 the splitting of the CRN(405) model for amorphous silicon allows for a significant diminishing of the total free energy of the model.

Many years ago, in a letter to Nature, Prof. Grigorovici [16] evidenced the importance of the energy

balance in the core and at the surface of a CRN cluster of amorphous germanium. Later, he demonstrated [17] that for the surface atoms it is necessary to introduce a contribution of the  $d$ -orbital to  $sp^3$  hybrid orbitals of germanium (silicon) bonds. The character of the bonds is changed by the bonding distortions. Individual bonds are described by orthonormalized  $s-p-d$  hybrids pointing in the right directions and having the right strength, so as to eliminate strain; energy is stored mainly by promoting some of the electrons into  $d$ -orbitals. This type of approach is popular with the crystal chemists, though mostly only bond angle distribution, but not bond lengths are accounted for. Consequently, a new energy term must be introduced, or an approximation based on softening of the Keating force constants must be considered. In the case of amorphous silicon or germanium the bond distortions are accompanied by a slight modification of the electrical charge on atoms. The more bent atoms exhibit higher electrical charge. Guttman [18] has shown that bond stretching and bond bending on silicon atoms in a-Si lead to a mean electrical charge of  $\sim 0.2$  e.u. per atom. The charge transfer from atom to atom in the amorphous network characterized by bonding deformations implies the diminishing of the bending forces because the ionic interactions increase on the account of the covalent ones. Softening of the Keating force constants determines the reduction of free interface energy in spite of the larger distortions of the bonds appeared on the interface between amorphites.

Table 1. The free energy and structural characteristics of the CRN(405) relaxed model of amorphous silicon before and after separation in two domains.

Models (atoms)	Bond stretching energy $\times 10^{-2}$ dyn.Å	Bond bending energy $\times 10^{-2}$ dyn.Å	Total free energy $\times 10^{-2}$ dyn.Å	Bond angle distortion ( $^\circ$ )	rms bond distortion (Å)	rms 2-nd order distance (Å)
M (405)	0.5378	1.620	2.157	10.200	0.072	0.266
M1 (200)	0.1256	0.5593	0.6849	9.100	0.053	0.246
M2 (205)	0.1299	0.5253	0.6552	8.841	0.053	0.245
M1 + M2	0.2555	1.0846	1.3401	8.971	0.053	0.2455

Therefore, we are lead to the idea that the true, realistic model of tetrahedrally bonded amorphous semiconductors must suppose a meander-like structure, where CRN domains of limited size create an entanglement of fine inter-domains boundaries which are extended over all the volume of the material. This new picture for amorphous semiconductors can open the way toward understanding the specific phenomena observed experimentally as e.g. centers of defects different from dangling bonds, hydrogen diffusion, aging, etc. In fact, symmetry breaking in continuous random networks seems to be a natural concept, usually encountered in many phenomena from the nuclear physics to astrophysics.

If the symmetry is broken and several domains are formed, is it possible to get a state of lower free energy, as a consequence of self-organization? The separation of the models in several domains gives rise to boundaries, which must be compared, to the experimentally observed CLO's [16].

During self-organization with the formation of inter-domain boundaries hydrogen diffuses at the surface of the

amorphous domains. The surface is stabilized with low distortion bonds and crystalline-like organization. The formation of a fractal surface that minimizes the free energy of the surface is probably the characteristic feature in this case.

The energy introduced in the self-organized system can shift the equilibrium of the atom network. The amorphous domains can be 're-amorphized' and a new melted/solidified phase with different characteristics can be reached. High-energy irradiation rises the metastability minimum of the amorphous phase, while low energy irradiation can trigger modifications according to which the system descends to a lower metastability minimum. Thus, a fine-tuning by switching to various configurations in a reversible manner can be obtained.

The simulations performed for a-Si point out the natural tendency of the a-Si material to divide in small domains separated by boundaries. The boundary atoms take a structural configuration with low distortion bonds, and crystalline-like (diamond and/or wurtzite) arrangement. A tentative simulation of crystalline-like

arrangement at the boundary between two CRN domains was carried out on a CRN model with 499 atoms, Mixt499 (Fig. 2).

We introduced two silicon layers ( $2 \times 47$  atoms), one layer connected to the amorphite M1 and the other to the amorphite M2 of the CRN (405) model (44 links). Thereafter, the two amorphites were merged by the intermediary of the dangling bonds at the surface of every extended amorphite. A new CRN model with 499 atoms has been thus obtained. This model was relaxed. In the second stage we changed topologically the two layers in order to obtain a crystalline-like configuration (6-fold, chair-like rings), thus simulating the crystallization of a thin region situated in-between the amorphites (Fig. 3 and model Cryst (499) in Table 3). A new relaxation was performed. In the next stages the crystallized region with a thickness of  $\sim 0.5$  nm and the diameter of  $\sim 2.5$  nm was decoupled step by step from the bodies of the amorphites by cutting a percent of the links with amorphites, starting with the most distorted bonds (models: Decoupl. 1-5, Table 3). After relaxation, the structural and energetical parameters were calculated for every step of simulation both for the diamond-like crystalline configuration and for the rest of the amorphites. The results are shown in Table 3.

It is remarkable that bond angle distortion (BAD) in the crystallized layer diminishes step by step when the coupling with the amorphites becomes poorer. This means that the thin crystallite becomes more free of constraints and takes a more and more correct structure. Finally for 75 % reduction of the bonding constraints with the amorphites, the BAD reaches the value of  $2.629^\circ$ . This corresponds to 11 bonds between crystallite and amorphites from a total of 44 bonds acting in the initial

topological configuration. The low value of the BAD is to be compared with the experimental value deduced for CLO's observed in TEM and characterized by Raman scattering:  $BAD \sim 0^\circ$ . The agreement is fairly good.

As resulted from our simulation experiments the main aspect of the formation of a crystallite with low distortion of the bonds is the decoupling of the most part of its bonds with the amorphous network. This is undoubtedly triggered by the presence of the hydrogen, which diffuses and satisfies the dangling bonds appeared during formation of the crystalline thin film. Only in amorphous hydrogenated silicon with enough high concentration of hydrogen it is possible to have such diffusion process with the satisfaction of the dangling bonds and separation of the crystalline configurations in-between the amorphous domains of the material.

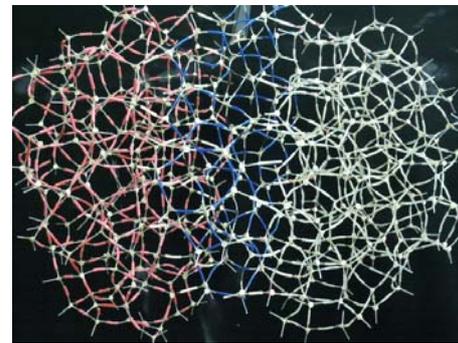


Fig. 2 The model with 499 atoms having an additional double layer between two amorphites.

Table 2. The structural and nergetical parameters for the CRN(499) model for amorphous silicon with crystallized interface.

Model	decoup bonds (%)	rms( $r_1$ ) (Å)	rms( $r_2$ ) (Å)	BAD ( $^\circ$ )		Stretching energy $\times 10^{-2}$ dyn.Å	Bonding energy $\times 10^{-2}$ dyn.Å	Total energy $\times 10^{-2}$ dyn.Å
				Crysta-llite	Amorphite			
Mixt 499	0	0.070	0.265	10.735	9.748	0.5587	1.8400	2.3986
Cryst 499	0	0.068	0.256	6.020	9.715	0.5378	1.6197	2.1575
Decoupl 1	21	0.065	0.255	5.144	9.523	0.4628	1.4578	1.9207
Decoupl 2	38	0.065	0.252	4.457	9.397	0.4281	1.3631	1.7910
Decoupl 3	54	0.062	0.249	4.043	9.340	0.4071	1.3105	1.7176
Decoupl 4	69	0.060	0.246	3.261	9.233	0.3593	1.2371	1.5963
Decoupl 5	75	0.055	0.246	2.629	9.111	0.3080	1.1780	1.4860

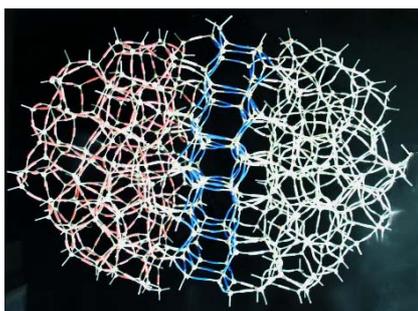


Fig. 3. Model of amorphous silicon (499) atoms with crystallized interface between domains

### 3. Chalcogenide glasses

The films of amorphous chalcogenides condensed under non-equilibrium conditions (vacuum condensation, magnetron sputtering) are important for the study of self-organization. Such films are related to the dissipative structures whose formation is just conditioned by self-organization processes. Many chalcogenides glasses and thin films have been studied [19-58]. Clustering and nano-scale molecular phase separation are known to be an important manifestation of the structural-chemical inhomogeneity in amorphous chalcogenides [59]. The chalcogenides films exhibit intrinsic metastability. This

metastability is the driving force for various structural transformations and relaxation processes, which take place both under the influence of external factors and spontaneously

A peculiarity of the structural transformations in dissipative structures is their stochastic character. The stimulated transition of a structural configuration in a new topological structure is not a deterministic process but a stochastic one.

We have demonstrated on the case of a memory glass, that the structural configurations resulted from the transition crystal  $\rightarrow$  glass and back consists in the stimulations of various type of clusters. Moreover these clusters, subjected to long-time cycling, become more and more spatially shifted, so as to make a network of clusters, relatively stable. This self-organization during cycling is shown in Fig. 4.

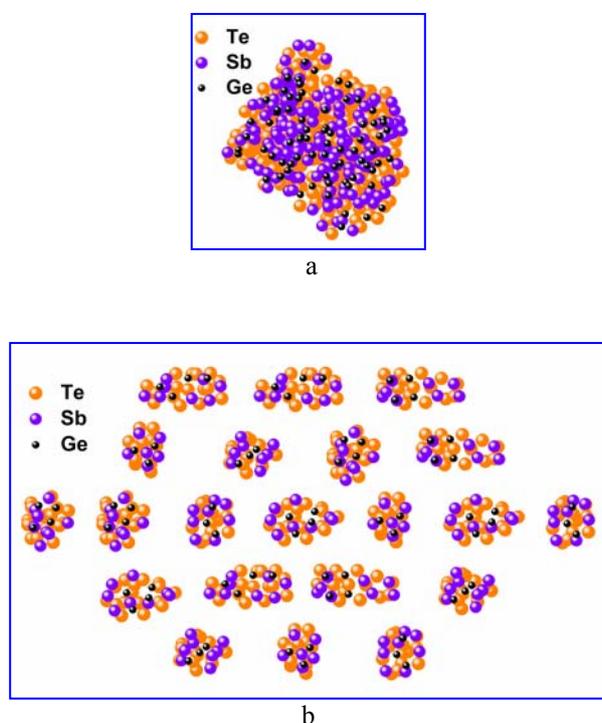


Fig. 4. The change of a large size cluster of atoms (a) towards an array of small clusters (b), which remain stable, after long-cycling of the Ge-Sb-Te phase-change material.

Another example of self-organization is the case of intermediary phase (or Boolchand phase) that was demonstrated to occur in many binary chalcogenide glasses [59]. We have shown by structural modelling that the structure of the intermediate phase is described by small chalcogenide clusters having narrow size distribution of closed clusters (no dangling bonds exist in every cluster). Fig. 5 shows two examples of elementary clusters in the Boolchand phase.

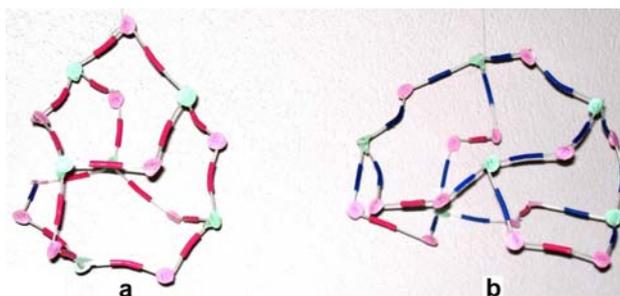


Fig. 5. The clusters of As-S of the same composition, but with different configurations (a, b) that appear in the intermediate phase during self-organization.

#### 4. Conclusions

The self-organization is an important phenomena that acts both in amorphous tetrahedrally bonded semiconductors (Si, Ge) and in chalcogenide films and bulk glasses. This phenomenon leads to the realization of nano-structural clustering and nano-scale molecular phase separation in the disordered material. The self-organization can be regarded as a new kind of order into the non-crystalline materials, besides medium-range order or other more extended types of order.

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