

STRUCTURAL CHARACTERISTICS AND STRUCTURAL MODIFICATIONS OF NON-CRYSTALLINE SEMICONDUCTORS

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The general problems of the non-crystalline solid structure are discussed. A new definition of the non-crystalline materials is proposed. Various levels of structural modification of non-crystalline semiconductors are considered: the levels of short- and medium-range order, morphology and the defects' subsystem. It is shown that there are possible two mechanisms for the formation of the medium-range order in non-crystalline semiconductors, depending upon the structural network rigidity.

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1. Introduction

One of the main steps in the development of the solid state physics in the second half of the twentieth century was the emergence and the growth of the new field, that is, the physics of non-crystalline semiconductors. Advances in physics of non-crystalline semiconductors are founded on the basic works of B. Kolomiets, N. Mott, W. Spear, R. Grigorovici and many others. In parallel with the experimental and theoretical research of non-crystalline semiconductors, and often ahead of it, the practical application of those new materials was proceeding further. The success in that field was greatly due to the name of Stanford Ovshinsky and to the Company: Energy Conversion Devices (ECD) founded by him together with Iris Ovshinsky in 1960. The purpose of ECD was to develop the researches on the use of non-crystalline semiconductors in various stages of storage and control of information in relation to the concept of energy conversion. The ECD company developed and introduced into production threshold and memory switches, integrated circuits of memory matrix on the base of chalcogenide glassy semiconductors, high efficient solar cells on the base of hydrogenated amorphous silicon, rewritable CD-ROMs and other devices. However, commercial activity as well as research activity is taking place in the absence of anything like a complete understanding of the atomic structure of disordered solids. At the same time a knowledge of atomic structure is necessary both for understanding the basic properties of a material and from the point of view of the possibilities to change the structure in order to control the properties of non-crystalline semiconductors.

2. Structural characteristics of solids

The distinctive feature of crystals is a long-range order in the arrangement of the atoms. As a rule, non-crystalline substances are determined as materials, which do not have a long-range order. The negative character of that definition is not only contrary to the common rule, that is, to define from the general to the particular but has very little useful data. In this connection at first it is necessary to answer the question: which characteristics of the atomic structure are necessary and sufficient for defining the non-crystalline state of a solid?

The simplest case from the standpoint of a structure is an ideal single crystal. In order to describe completely its structure it is enough to know the structure of an elementary cell or the short-range order of the arrangement of atoms. For a whole definition of any real single crystal it is

necessary to add a defects' subsystem. For describing the structure of polycrystals in addition to short-range order and defects, it should be taken into consideration the morphology of the material, that is, crystal size distribution, crystal texture, formation of spherulites and so on.

As for non-crystalline solids in order to describe their structure it should be taken into consideration the four levels of structural characteristics: short-range order of atomic arrangement, medium-range order of atomic arrangement, morphology and defects' subsystem (Table 1).

Table 1. Structural characteristics of solids.

Structural subsystems	Solid states			
	ideal single crystal	real single crystal	polycrystal	non-crystalline solid
short-range order	+	+	+	+
defects' subsystem	-	+	+	+
morphology	-	-	+	+
medium-range order	-	-	-	+

As one can see in the Table 1, the amount of characteristics necessary to describe the structure of the substance increases with the growth of its complexity. Where one characteristic for describing the structure of an ideal single crystal is sufficient, it is necessary to use four characteristics to describe the structure of non-crystalline solids. From this point of view it is evident that the more complete definition of non-crystalline solids can be formulated in comparison with the definition based on the absence of long-range order in the atomic arrangement. Non-crystalline solids are the materials that require the use of the parameters of short and medium range orders of atomic arrangement, morphology and defects' subsystem when the full description of their structure is made.

3. Levels of structural modification of non-crystalline semiconductors

In the first investigations concerning non-crystalline semiconductors B. Kolomiets established [1] that the most essential feature of these materials is their weak sensitivity to impurities. In spite of some solutions found later (for example, chemical modification of chalcogenide glassy semiconductor films [2], doping of hydrogenated amorphous silicon [3]), the problem of control over the properties of non-crystalline semiconductors and the problem of reproducible synthesis of non-crystalline semiconductors with prescribed properties still remain pressing.

As an alternative to the control over semiconductor properties by doping, the method of the structural modification of non-crystalline semiconductor properties has been proposed [4]. It consists in the control of the properties by changing the structure of a material without changing its chemical composition. At first the method was developed for chalcogenide glassy semiconductors and used the changes of atomic structure at the level of a medium-range order.

Along with this, as it has been shown above, there are four levels of structural characteristics necessary for common description of structure of non-crystalline solids. Therefore, structural changes are possible not only at the level of a medium-range order, but also at the other levels of structural characteristics mentioned above. In that way one can conclude that on the whole there exist four levels of structural modification distinguished by various changes of material structure, namely [5]: the level of short-range order, the level of medium-range order, the level of morphology and the level of defects' subsystem (Table 2). Let us analyze the possibility and efficiency of structural changes at

the various levels in covalent semiconducting elements belonging to Groups IV – VI of the periodic Table and also in a number of their systems.

Table 2. Levels of structural modification.

Level of structural changes	Characterization of sensitive properties	Groups (examples) of sensitive properties	Influence on the other structural characteristics
Short range order	All properties	All properties	Medium-range order Morphology Defects' subsystem
Defects' subsystem	Properties dependent on the distribution of the density of localized states and on the Fermi level position	Electrical, photoelectric (field dependent conductivity)	–
Morphology	Properties dependent on macroheterogeneity	Electrical, optical (AC conductivity)	Defects' subsystem
Medium range order	Properties associated with rearrangement of structural units	Mechanical properties, phase transitions (viscosity, hardness, Young modulus, temperature and activation energy of crystallization)	Morphology Defects' subsystem

4. Short-range order and defects' subsystem levels

The structural changes at the level of short-range order lead to variations of all basic properties of a material. For example, polymorph crystalline modifications of carbon (diamond, graphite, carbene) possess fundamentally different physico-chemical properties because of the different hybridizations of electron orbitals and different atomic structures at the short-range order level. Amorphous carbon films incorporate structural units of different allotropic modifications, with the relative content of these units determined by film growth modes and varying widely for the same preparation method. Correspondingly, the coordination of atoms varies (between 2 and 4) together with the other parameters of the first coordination sphere [6]. When the films of amorphous hydrogenated carbon (a-C:H) are obtained by rf-sputtering in an argon-hydrogen atmosphere, then, by simply changing the substrate temperature and discharge power may produce films, in which the optical gap varies by two orders of magnitude (between 0.02 eV for graphite-like films and 1.85 eV for films with predominance of the diamond-like phase); and the dark conductivity varies by more than 10 orders of magnitude (between 7 and $2 \times 10^{-10} \Omega^{-1} \text{ cm}^{-1}$) [7].

Carbon has long been considered the only (and unique in this respect) element among those considered here which exists in allotropic crystalline modifications of diamond (sp^3 hybridization) and graphite (sp^2 hybridization). The discovery of carbenes (sp hybridization) in 1960 [8] only served as much more evidence of the unique properties of carbon. At the same time, it should be noted that there have been reports that the short-range order may change substantially under certain conditions for other elements as well. For example, cubic α and β modifications of crystalline selenium with

atom coordination numbers of, respectively, 4 and 6 were obtained in electron beam induced crystallization of thin films [9, 10]. The monopoly of carbon on the possibility of existence of forms with different hybridizations of electron orbitals and, consequently, with different atom coordination numbers was radically broken up by a series of investigations [11, 12]. New forms of silicon which appeared under the certain conditions in films of amorphous silicon and in *a*-Si:H were discovered in these studies: silicine with *sp* hybridization of electron orbitals and atom coordination 2 and a form with *sp*² hybridization and atom coordination 3.

Thus, in the considered group of covalent semiconducting materials (periods 2 — 5, Groups IVA — VIA of the periodic Table), structural changes at the short-range order level are observed for the elements belonging to Group IVA, periods 2 and 3 (C, Si), and Group VIA, period 4 (Se), i.e., for the three elements out of the considered nine. We should also note the increase in the first coordination number from 2 to 3 in tellurium melt (at 600 °C), with the covalent nature of chemical bonds being preserved [13] and the changes at the short-range order (bond length) in glassy GeS₂ under high pressure [14]. The mentioned elements show no fundamental distinctions in electron shell structure or the other parameters from the rest of the considered elements. In view of the above facts, it seems reasonable to assume that the structural changes at the short-range order level are not unique only for carbon, but they are characteristic to all of the considered covalent semiconducting materials.

The structural modification on the level of a short-range order not only determines the considerable changes in the properties of a material but also influences upon the others groups of structural characteristics, namely: the medium-range order, the morphology, the defects' subsystem (see Table 2). Thus, in [14] it was shown that caused by the applied high pressure the changes in tetrahedron structure of glassy GeS₂, that is, the changes of short-range order, lead to the change of tetrahedrons' mutual packing, that is, to the change of medium-range order. And more essential changes of all the structural characteristics should be expected at the transition from the tetrahedral coordinated network to the layer structure or to the linear polymers.

The changes in the defects' subsystem are possible under the influence of either sample fabrication conditions or under the action of various external factors and are manifested as the changes in the spectrum of localized states in the gap, which, in turn, leads to the changes in material properties (Table 2). The effect of amorphous silicon pseudo-doping that depends upon the sample preparation conditions has been observed in [15, 16]. A significant change in the spectrum of localized states in *a*-Si:H, resulting from a change in the relative content of Si-H, Si-H₂, and Si-H₃ complexes, was achieved by treating samples with ultraviolet radiation [17]. The effect of weak electric and magnetic fields on quasimolecular defects and properties of vitreous selenium, arsenic triselenide, and materials of the selenium-tellurium system was observed in [18, 19]. Later the same results were obtained for sulfur and arsenic trisulfide [20].

Thus, this level of structural modification is observed experimentally both in a tetrahedral material with rigid covalent structural network (*a*-Si:H) and in vitreous materials of group VI and V-VI chalcogenide glasses. The above result suggests that the structural modification at the defects' subsystem level is inherent, like the structural modification at the short-range order level, in all of the considered non-crystalline semiconducting materials. At the same time the changes of a materials' structure at the level of a defects' subsystem at the first approach should not influence upon the other structural characteristics, namely: short- and medium-range orders, morphology.

5. Morphology and medium-range order levels

It is well known that the necessary condition for obtaining a non-crystalline solid is thermodynamically the non-equilibrium process of its synthesis. In conformity with the basic concepts of the synergetic theory, the non-equilibrium conditions of material formation result in the appearance of heterogeneity due to self-organization process. Thus, general considerations suggest the presence of heterogeneity in all of the non-crystalline solids.

The macroheterogeneities (columns, globules, cones, etc. with the size, as a rule, of dozens of nanometers and more) in films of non-crystalline materials are also called morphological inhomogeneities. A certain morphology (column structure) was observed in *a*-Si:H films by Knights and Lujan [21]. Later, it was demonstrated [22-25] that the presence of macroheterogeneity is a

characteristic feature of amorphous tetrahedral semiconductors (a-Si-H, a-C:H, a-Si_xC_{1-x}:H) and there was established a relationship between the averaged morphological parameters (for example, cross dimensions of columns), spectra of electron states, and material properties (Table 2). At the same time, while the presence of certain morphology (macroheterogeneity) in films of tetrahedral non-crystalline semiconductors has been firmly established, a “structureless” smooth surface is commonly observed in vitreous materials. Considering that the presence of heterogeneity lays in the nature of non-crystalline solids themselves, one can conclude that in glassy materials there exists microheterogeneity, which points to the manifestation of not the morphology, but medium-range order. However, such a conclusion implies the answer to a number of questions, namely: why are the two classes of non-crystalline semiconductors characterized by various kinds of heterogeneity? What factors cause the limit between them and where such boundary pass? Let’s make an effort to answer these questions.

Medium-range order is linked with the correlation between atom positions in the range of up to one or a few nanometers. The first attempt to explain the presence of medium-range order one is the microcrystalline model by Lebedev [26], though historically this model arose before the introduction of the term “medium-range order”. In 1987 Lucovsky [27] defined the medium-range order as regular distribution of dihedral angles for a distance of about ten atoms. At the last years a number of paracrystalline models were used to explain the medium-range order in amorphous silicon and chalcogenide glasses. In these models the medium-range order is explained by the presence of nanoclusters [28, 29], crystalline grains embedded in a disordered matrix [30, 31] or crystal-like configurations with distorted arrangement of atoms [32]. There also exist a number of other approaches to explain the medium-range order.

The above-noted models can be divided into two groups. In the first group the ordered regions determining the medium-range order are the part of the surrounding matrix (or they are linked with each other) without breaking the continuous covalent network. In the second group between the ordered regions there are the limits at which structural network breaks. The possibility for the first or the second group to be realized in a specific non-crystalline material depends upon the flexibility of its structural network. In the first case the network must exhibit certain flexibility and flexible bonds are present. In view of the above facts, there are reasons to assume that the limit in question corresponds to the rigidity threshold of the structural network [33-35] at which the average number of force constants per atom becomes equal to the number of degrees of freedom. Phillips [34] determined the critical coordination number corresponding to the rigidity threshold of the structural network for chalcogenide glasses: $N_c = 2.4$. For the systems Ge — Se, Ge — S, As — Se, and As — S, the rigidity threshold is shown by the dashed line in Table 3 [5]. However, the experimental studies of these systems [36, 37] have shown that the rigidity threshold actually lies at higher average coordination numbers. It was demonstrated [38] that the reason for the discrepancy between the calculated and experimental values of the rigidity threshold comes from the fact that the ionic component and metallization of chemical bonds are neglected. The rigidity threshold obtained for the above-mentioned systems with account of the ionicity of chemical bonds is shown in Table 3 by the solid line.

On the right hand side of that line there are placed the materials in which the formation of the ordered regions determining the medium-range order (microheterogeneities) is made possible without breaking the continuous covalent network. In these materials it is possible the structural modification at the level of medium-range order but there are not macroheterogeneities (morphology). Changing the medium-range order without changing the short-range order mainly affects the macroscopic properties of a material (viscosity, micro-hardness, Young modulus – see Table 2).

Table 3. Medium range order and morphology levels.

Columns		$A^{IV}_x (A^V_x) B^{VI}_{1-x}$ systems							Column
		Value of X							VI A
IV A	V A	0,60	0,50	0,40	0,33	0,25	0,20	0,11	
Ge					GeSe₂	GeSe₃	GeSe₄	GeSe₈	Se
4					2.66	2.50	2.40	2.22	2
4					2.40	2.30	2.24	2.12	2
Ge			GeS	Ge₂S₃	GeS₂	GeS₃	GeS₄	GeS₈	S
4			3.00	2.80	2.66	2.50	2.40	2.22	2
4			2.73	2.49	2.30	2.23	2.19	2.10	2
	As	As₃Se₂	AsSe	As₂Se₃	AsSe₂	AsSe₃	AsSe₄	AsSe₈	Se
	3	2.60	2.50	2.40	2.33	2.25	2.20	2.11	2
	3	2.53	2.42	2.31	2.25	2.19	2.16	2.09	2
	As	As₃S₂	AsS	As₂S₃	AsS₂	AsS₃	AsS₄	AsS₈	S
	3	2.60	2.50	2.40	2.33	2.25	2.20	2.11	2
	3	2.49	2.38	2.26	2.22	2.17	2.14	2.08	2

- - - - - rigidity threshold in the case of purely covalent bonds;
 ————— rigidity threshold in the case when bond ionicity is taken into account;
 e.g. **2.25** - average coordination number, N_c ;
 e.g. **2.25(italics)** - $N_c(1 - I_c)$, where I_c – mean coefficient of bond ionicity.

At the same time, the properties governed by the electronic structure (electronic spectrum) of a material, which depend mainly on the short range order, exhibit only relatively small changes. On the left hand side of the pointed line there are the materials, in which the formation of the ordered regions leads to the break of continuous covalent network and the formation of limits between microheterogeneities. While synthesizing such materials, some microheterogeneities can reach the size of macroheterogeneities forming the specific morphology. Thus in the considered materials the structural modification is made possible both at the level of medium-range order and at the level of morphology. Morphology changes affect the properties sensitive to macroheterogeneities (Table 2).

6. Conclusions

There is proposed a more complete definition of non-crystalline solids – the materials that require the use of the parameters of short and medium range orders, morphology and defects' subsystem for the full description of their structure.

There are considered the possibility and efficiency of the four levels of structural modification of non-crystalline semiconductors: short-range order, medium-range order, morphology and defects' subsystem levels. Based on the performed analysis there has been made the conclusion that the structural modification at the short-range order and defects' subsystem levels can be applied to all the non-crystalline covalent semiconducting materials. Structural modification at the medium-range level is also made possible for all the considered materials, but the mechanisms of the medium-range order formation are different depending upon the structural network rigidity. The limit between the two mechanisms of the medium-range order formation is the rigidity threshold of the structural network calculated with account of the ionicity of chemical bonds. The morphology level of structural

modification can be applied only to the materials with the structural network rigidity higher than the above-mentioned rigidity threshold.

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