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A new model for the structure of chalcogenide glasses: The closed cluster model

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ABSTRACT

A new model is proposed for the structure of low atomic coordination chalcogenide glasses. The closed clusters model is based on the various types of clusters, packed by van der Waals forces in a molecular-type packing. Arguments are given to support the new model, taken as example the typical chalcogenide glass As_2S_3.

1. Introduction

The problem of the structure of chalcogenide glasses remains up to – day one of the most challenging problem in the chalcogenide field of research. While crystalline state is well known, the glassy or amorphous state is still subject of debate. Many phenomena, specific to non-crystalline state of the amorphous chalcogenides, cannot be explained satisfactorily without a sound theory for the structure of the glass. What is particular in the case of binary glasses is their low atomic coordination (the mean coordination of the atoms is 2.4 in As_2Ch_3 glasses, Ch = chalcogen).

In the old models of glassy structure Vaipolin et al. [1] supposed a wavy structure of the glassy chalcogenides. Later, it was supposed, especially for thin films, a structure with molecular entities (e.g. As_4S_4 or/and As_4S_6 molecules) [2]. Thereafter, Popescu [3] gave experimental arguments for the existence of disordered layered domains in As_2Ch_3 glasses. In 2002 Tanaka [4] opened again the problem in a disputable article with the title ‘Does charged defects exists in chalcogenides?’ Adriaenssens [5] riposted immediately by writing a well documented article in favour of the charged defects.

More recently Banik [6–8] wrote several articles that discuss the optical and electrical properties, including electro-absorption. In these articles the main emphasis is put on the so-called *barrier-cluster model* of chalcogenide glasses. In this paper we try to demonstrate that the structure of chalcogenide glasses based on closed clusters is not only possible but, also, very probable. The closed clusters model offers an explanation for many glass properties.

2. Old models

2.1. Model with waved layers

Based on the radial distribution functions calculated from the experimental diffraction patterns of the As_2S_3, As_2Se_3 and As_2Te_3 glasses, and on the observation according to which the structure of a crystalline layer could be considered as a deformed layer of a close packing of chalcogen atoms linked to arsenic atoms, Vaipolin and Porai-Koshits [1] proposed a model for the arsenic chalcogenide glass with layers similar to those from crystal but waved.

2.2. Model with waved layers and mixed rings of atoms

Tsuchihashi and Kawamoto [9,10] demonstrated that the As_2S_3 glass density is less than that of crystal by 8%. This difference was ascribed to the open structure of the glass as opposite to the

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crystal. Careful measurements have shown that the quasi-distance between layer-like configurations deduced from FSDP position is 5.0 Å in glass while in crystal is 4.8 Å. Based on these observations the authors propose a structural model for the glass made of triangular pyramids of AsS_3 linked through corners. The rings thus formed have not exclusively 6 members, but five, seven or eight member rings can be integrated in the layers. The model of distorted layer structure with mixture of rings with different number of members explains the disappearance of the coordination situated at 4.25 Å, specific to orpiment crystal (this distance is an intra-ring distance in 6 member regular rings of orpiment) and the lower density of the glass if compared to the crystal (due to waved layers that repel each other according to the van der Waals force requirement).

2.3. Model with small molecular clusters

An alternative explanation of the structure of the chalcogenide glasses was based on the packing of structural units. De Neufville [2] proposed a structural model based on As_4S_4 (As_4Se_6) molecules for freshly deposited amorphous As_2Ch_3 chalcogenides. The X-ray patterns exhibit narrow FSDPs which indicate a molecular correlation range of ~40 Å in analogy with the dense random packing of a hard sphere glass. This sharpness decreases sharply to the bulk glass value through cross-linking during annealing or illumination. Apling et al. [11] simulated a molecular glass having as basic unit the As_4S_6 molecule. The simple model is described by a random sphere packing calculated by assuming an effective molecular diameter of 6.4 Å and a packing fraction of 0.532. The model gives excellent fit to FSDP but there are obvious deficiencies in the mid range of k or Q (the scattering vector in the diffraction pattern). The sharpness of the FSDP in the model is easily adjusted by varying the packing fraction and altering the effective molecular diameter to maintain the overall density.

3. Closed clusters. The series of nano-pie clusters

Based on the self-organization phenomenon we have developed a new model for the binary chalcogenide glasses (As_2S_3, As_2Se_3). In this model the structural configurations consist of closed clusters of different size and spatial extension. At first, different extended di-layered clusters with closed ends have been built and relaxed by computer. The basic idea was that in a non-equilibrium melt, during cooling the best stable configuration is the packing of layers that connect each other by the ends, so that configurations of two parallel layers are formed. The more or less extended disordered layers make easily couples after a certain extension dictated by the cooling rate. Thus closed extended clusters do appear, that leads to covalent linking of the layer ends. Thus no dangling bonds remain in the structure. The clusters will pack similarly to the packing of small molecular clusters, by van der Waals interaction.

Various extended clusters were built by physical plastic units that simulates the arsenic (three legs unit) and chalcogen (two legs unit). The approximate coordinates of the atoms, measured directly on the model, and the first coordination sphere for each atom were used as input data for energy relaxation in the frame of a Monte-Carlo – Metropolis procedure. For As_2S_3 model the equilibrium distance between atoms are $r_o = 2.27$ Å, the angle between As bonds: $\alpha_o^{As} = 98.7°$ (an average value, after Rubinstein and Taylor [12]) and $\alpha_o^{S} = 106°$ for the angle on sulphur. For the simplicity of the Monte-Carlo calculations we introduced in the model a common mean angle on As and S of 101.1°. The structure of minimum free energy (minimum distortion energy of the bonds) has been calculated with the use of the force constants taken from the literature and valence force field approximation proposed by Keating [13]. In the force field model, the forces between covalently bonded atoms are approximated by non-linear stretching forces, as a function of deviation of inter-atomic bonding distance from the ideal distance corresponding to crystals and parabolic function for bond bending forces for small deviations from the ideal bonding angle in crystal. Due to its small contribution (large clusters) the entropy term in energy was neglected. For the bond stretching force (As–S) the interaction potential was taken as $V_S = A(r^2 - r_o^2)^2$ with A = 86.7 meV/Å^4. The bond bending potential, $V_B = B(\alpha - \alpha_o)^2$, was centered on the mean equilibrium bond angle and the force constant was taken $B = 24.03$ meV/rad^2. The force constants were approximated on the basis of Raman results published by Ludvig et al. [14] and Shastri et al. [15]. After relaxation every model has been described by bonding distance fluctuations, bonding angle fluctuations, diameter, thickness, interlayer distance, structure factor and pair distance distribution histograms. Of high importance is the value of the free energy per atom that distinguishes between different types of clusters and gives an indication on the stability of the closed clusters. Fig. 1 shows the relaxed clusters.

The smallest cluster in this family is the so-called crown cluster. It is formed by two parallel sixfold rings of AsS_3 pyramids linked each to other. The total number of atoms is 30 (12 As and 18 S). Its mean free energy per atom is: 1.582 meV. The width of the bonding angle distribution in the model is 20.44°.

The smallest nano-pie cluster is formed by attaching six rings around the central one in the crown. The total number of atoms is 120 (48 As and 72 S). The mean free energy per atom is 0.1718 meV. The width of bonding angle distribution = 6.186°. The medium size nano-pie is built from 180 atoms (72 As and 108 S). The free energy per atom is 0.2142 meV. The width of the bonding angle distribution is 7.982°. The large pie cluster is derived from the small pie cluster by adding 12 new rings around the central core with 6 rings. The total number of atoms is 270 (108 As and 162 S). The free energy per atom is: 0.318 meV. The width of the bonding angle distribution is 9.42°.

A cluster with small nano-pie size, and 175 atoms, formed by three parallel layers was modeled. The bond angle distribution was got considerably broader than that of the relaxed two-layer cluster. The cluster is very deformed. The free energy per atom of the cluster is 0.6042 meV. The width of the bonding angle distribution is 11.35°.

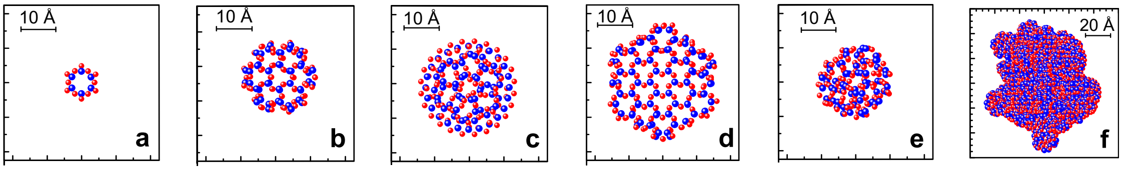

Fig. 1. (a) The small crown-like cluster ($As_{12}S_{18}$); (b) The small nano-pie cluster (120 atoms); (c) The medium nano-pie cluster (180 atoms); (d) The large cluster (270 atoms); (e) The triple layer pie cluster (175 atoms); (f) tentative model for the binary arsenic glasses (1140 atoms).