PHASE-CHANGE OVONIC SWITCHING.
A MODELLING INVESTIGATION OF THE STRUCTURAL TRANSITION

M. Popescu[*], F. Sava, A. Anghel, A. Lörinczi, I. Kaban[a], W. Hoyer[a]

National Institute of Materials Physics, Bucharest – Magurele, Romania
[a]Technical University Chemnitz, Institute of Physics, Chemnitz, Germany

The transition from amorphous to a more ordered structure was simulated in the frame of a model with disordered As_2Te_3 layers containing Si and Ge. The layers are interlinked by Si(Ge)-Te-Si(Ge) bonds. By breaking the bonds between layers and elimination of Si and Ge from the disordered layers a new phase is obtained. The Si and Ge remains isolated as dimmers or as small clusters in-between the layers.

1. Introduction

The ternary or quaternary systems Si-As-Te and Ge-Si-As-Te have very interesting features from the viewpoint of both basic physics and technological applications. They are good ovonic materials for memory devices. Si(Ge) – As – Te consists of mixed combinations of tetravalent, trivalent and divalent bonding and exhibits a large structural flexibility for constructing continuous random networks, yielding a large glass formation region in which various physical constants are controlled. For example, the energy gap can be tailored in the range 0.6-2.5 eV, which covers the energy gap of conventional crystalline semiconductors: Ge (0.66 eV), Si (1.0 eV), Ga As (1.4 eV) and Ga P (2.25 eV). This means that the system is suitable for exploring the atomic and electronic properties of random bonding in solids. Due to the importance of the system, amorphous samples of this composition have been prepared on the space station in microgravity environment [1] and the pressure effect on the electrical and optical properties has been investigated [2].

The phase change technology based on the so-called ovonic materials, developed by Ovshinsky [3,4] earlier in '70, is now one of the most important technology for memory devices and applications in computers, CD, DVD, etc.. The amorphous ovonic material characterised by phase-changes under the influence of electrical field or optical beam is based essentially on a combination of As, Te and other covalent semiconductors. The amorphous alloy must crystallise very rapidly, and, to be able to become again amorphous under the influence of the electrical field and optical beam with parameters different from those used for crystallisation. Many papers have been dedicated to ovonic phase change materials but in spite of the tantamount studies and researches, their structure, transformations and physical properties are not completely understood [5-11]. In parallel stuidies were conducted on various chalcogenides based on Te atoms that are good candidates for ovonic switching materials [12-26].

In this paper we report the results of a modelling approach of the ovonic switching material: $Si_{12}Ge_{10}As_{30}Te_{48}$. The structural phase change in this material has been modelled on the basis of an original idea.

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[*] Corresponding author: mpopescu@infim.ro

2. Experimental

The glassy alloy of composition $Si_{12}Ge_{10}As_{30}Te_{48}$ has been prepared from raw materials of 5 n purity, by heating the powdered elements weighted in right proportions, and encapsulated in quartz ampoules. The quartz ampoules have been cleaned and outgased in vacuum at 900 ^{o}C. Before heating the ampoule was evacuated at 1 X 10^3 Pa for 30 minutes, then sealed. The synthesis was carried out in a rotating furnace at the temperature of 650 ^{o}C for 24 h. The glassy sample was obtained by rapid cooling of the alloy when the ampoule was thrown in cold water.

The experimental measurements have been performed by X-ray diffraction using a conventional $\theta - \theta$ diffractometer in the Laboratory of X-ray diffraction of the Institute of Physics, TU Chemnitz, Germany. An X-ray tube with molybdenum target has been used in order to reach high scattering vector, thus improving the resolution of the radial distribution function calculated from the diffraction pattern. The sample was prepared by transforming several chunks of glass in fine powder, using a porcelain mortar and a pestle. The powder was pressed in a support of rectangular shape with the dimensions: 2×3 cm^2. The thickness of the powder sample was 2 mm. In order to eliminate the influence of the support on the X-ray diffraction pattern, we have carried out the measurement on the support without powder. This measurement has been used to correct the final pattern registered with the pressed powder in the sample support.

All the measurements have been carried out at room temperature.

3. Results

The X-ray diffraction pattern of $Si_{12}Ge_{10}As_{30}Te_{48}$ has been corrected for various factors: Compton scattering, air scattering, absorption, and polarisation. After normalisation, the reduced intensity function, i(s), (s=2sin(θ)/λ) of the investigated ovonic glass has been calculated. This curve is represented in Fig. 1.
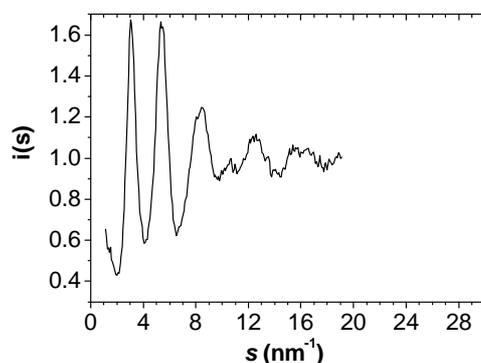

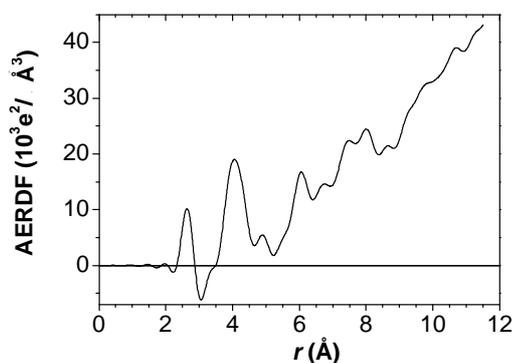Fig. 1. The reduced intensity curve of the glass $Si_{12}Ge_{10}As_{30}Te_{48}$ (Mo K$_\alpha$ radiation).

Fig. 2. The atomo-electronic radial distribution function of glassy $Si_{12}Ge_{10}As_{30}Te_{48}$

The curve is characterised by two intense, relatively narrow diffraction peaks followed by other broader peaks of low intensity. The first sharp diffraction peak (FSDP), typical for a large number of glasses and amorphous chalcogenide films, is practically absent. A very faint peak in the position of Q=4πsinθ/λ = 0.952 Å^{-1}, corresponding to the quasi-distance of 6.600 Å could be observed on the diffraction curve.

In Fig.2, the atomo-electronic radial distribution function (AERDF) for $Si_{12}Ge_{10}As_{30}Te_{48}$ has been calculated form the reduced intensity curve (Fig.1), by a Fourier transformation.

The AERDF is characterised by well-defined peaks. The first peak is situated at 2.623 Å.

This maximum corresponds to the first order distances, or bonding distances, in the glassy alloy. In this positions the main contributions could be that of Ge-Te and As-Te bonds: 2.59Å and 2.58 Å, respectively.

A weak dehybridization of the bonds, specific to amorphous networks with distorted bonds, that leads to longer bonding distances, could explain the differences between the experimental bonding distance and the crystallochemical bonding lengths. From the area under the first maximum we have calculated, taking into account the major contribution of the As-Te pairs, the mean co-ordination number of 2.4.

The second peak in the AERDF is situated at 4.062 Å and from the area under this peak one estimates the mean co-ordination number in the second sphere of co-ordination: $N_2 = 4.91$. The N_2 for crystalline As_2Te_3 is 4 and for amorphous germanium (or silicon is 12). If one calculates the position of the second neighbour peak on the basis of a model with dominance of the As-Te bonds, one gets 3.95 Å, a value approaching the experimental value. The second peak in AERDF is much broader than the first peak because the contribution of different distances in the second co-ordination is situated in a much larger range.

All the experimental data support the idea that the most important bonds in the $Si_{12}Ge_{10}As_{30}Te_{48}$ glass are those specifics for amorphous As_2Te_3.

4. Modelling

Taking into account the experimental results obtained on $Si_{12}Ge_{10}As_{30}Te_{48}$ glass we have developed a model for the structure of this glass and for the possible transformation during excitation (heating or illumination) of the material.

The initial model consists of an arrangement of three disordered layers of type As_2Te_3. These layers are doped randomly with silicon and germanium. The model has 202 atoms. Silicon and germanium takes the places of tellurium atoms. They bind two neighbouring layers through the intermediation of the tellurium atoms released from the bonds occupied by Ge or Si. Thus two disordered As_2Te_3 type layers are linked by square bridges Si – Te -Si(Ge)-Te. The model was relaxed by computer using the standard Monte Carlo-Metropolis procedure and appropriate force constants. The results, after 600 billions of iterations with a variable step, are shown in Fig. 3a and 4a. In the following simulation step we modelled the phase transformation induced by external factor acting on the glass. The excitation of the stressed bonds in the glass lead to breaking and reforming the bonds in a new configuration. The breaking of the bonds between disordered layers is most probable due to the stressed bonds Si-Te and Ge-Te. Tellurium takes the place of germanium (or silicon) in the layers and forms strong As-Te bonds that fit the network of type As_2Te_3. The remaining Si and Ge atoms form separated dimmers or small clusters in-between the As_2Te_3 layers. The model of the new phase was relaxed by computer and is shown after relaxation in Fig. 3b. The structural data calculated from the model are shown in Fig. 4.
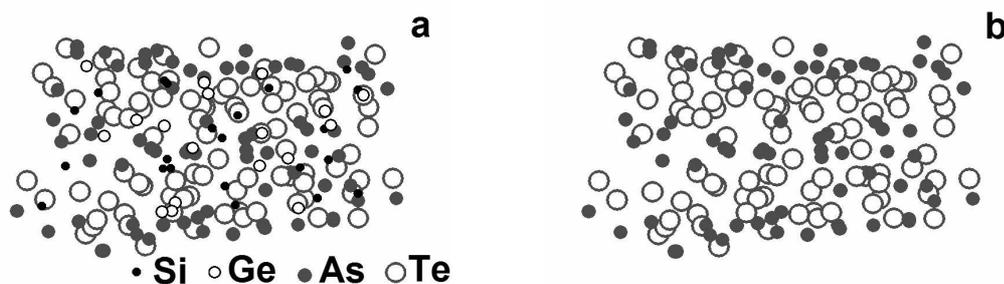

Fig. 3. The model of $Si_{12}Ge_{10}As_{30}Te_{48}$ glass (a) and the model of the new phase got by structural transformation (b). In the last case the Si and Ge atoms are not shown.

It is interesting to remark (Fig. 3) that the structure of the models is strongly different in the original state and phase-transformed state. In the last model the formation of waved layers could be followed.
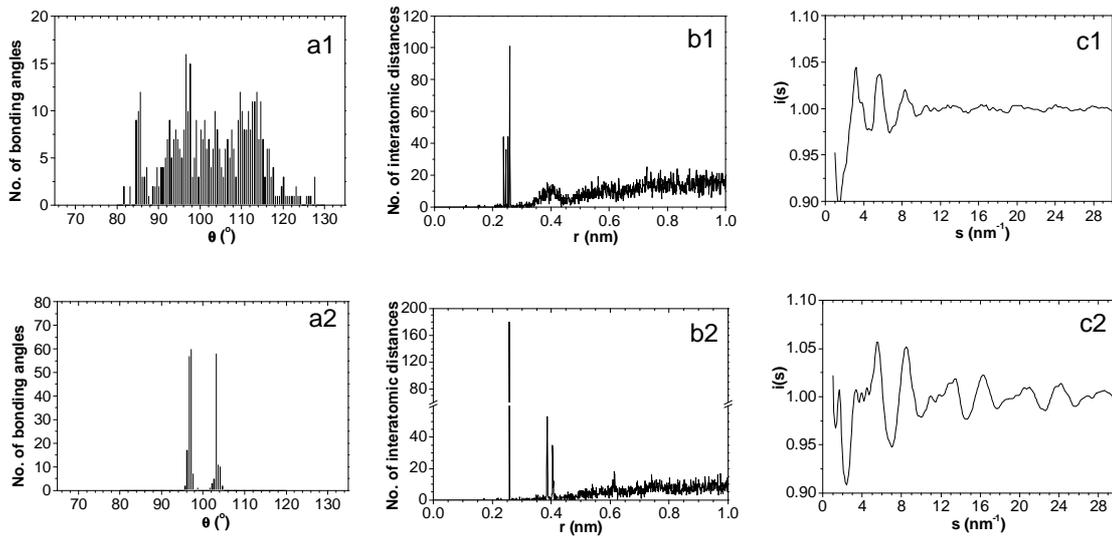

Fig. 4. The structural data calculated from the spatial model with interconnected layers (initial phase) (1) and from the model with decoupled layers and interstitial Ge, Si atoms (2). a – bond angle distribution; b – histogram of pair distance distribution; c – structure factor

Fig. 4-a shows the bond angle distribution in both models. When the quasi-layers with silicon and germanium are bonded between them, the angle distribution is very large. The bonding angles extend from 82 to 128 $^{\circ}$. The structure is stressed and its total free energy is very high: 4.396 $\times 10^{-5}$ eV. For the phase-transformed model, the angles are situated in a narrow distribution around the values for 98° and 105° for As, respectively Te. The free energy of the model strongly diminishes: 5.403×10^{-5} eV.

In the radial distribution function, the model with interlinked layers shows a broad distribution of the peaks, centred on the positions got from the experimental radial distribution function. The second peak is very broad. The model with decoupled layers shows a split second peak based on two narrow distributions of distances (Fig. 4-b2).

The structure factor of the model with interlinked layers does not show a first sharp diffraction peak. Nor the experimental structure factor exhibits a significant FSDP.

After transformation, the new phase shows an intense FSDP in the structure factor (Fig. 4-c2), situated at 0.169 Å^{-1}, that corresponds to a quasi-distance of 5.903 Å and an interlayer distance of 7.261 Å.

Melting and quenching the phase obtained by annealing the glass would induce the reverse transformation to a higher free energy state.

5. Discussion

The structure of the quaternary glass $Si_{12}Ge_{10}As_{30}Te_{48}$ is given by a random network of atoms linked by covalent bonds. The atoms retain the covalence known from their crystalline compounds. Nevertheless the As-Te bonds are favoured. The composition with As_{30} and Te_{48}, approaching As_2Te_3 composition, supports the idea that the main configuration in this glass is based on As_2Te_3. Therefore the idea to embed Si and Ge in As_2Te_3 layers seemed attractive. Interconnection of the As_2Te_3 layers containing Si and Ge atoms is possible if Si(Ge)-Te-Si(Ge)

bonds are considered in-between the layers. The phase change under heat consists in the separation of the layers by breaking the interlayer bonding and elimination of Ge and Si from the As_2Te_3 layers.

Thus, the new phase becomes more ordered and more stable than the initial phase. A possible return back to the old glassy phase is possible only by strong excitation (melting and quenching). Regarding the interlayer distance, after decoupling the layers during the formation of the new phase, an expansion is produced in the material in order to reach the distance specific to van der Waals forces and to allow for accommodation of the Si (Ge) clusters.

The structure of complex glasses seems to be complex. As early as 1969, R. Roy and V. Caslavska [27] demonstrated the di-phasic structure of switching and memory device glasses. A clear phase separation can be followed in Fig. 5. Two-phase glass of composition 25% As, 15 %Ge, 40% Te, 20% Ga looks inhomogeneous in the electron microscopy picture (Fig. 5).
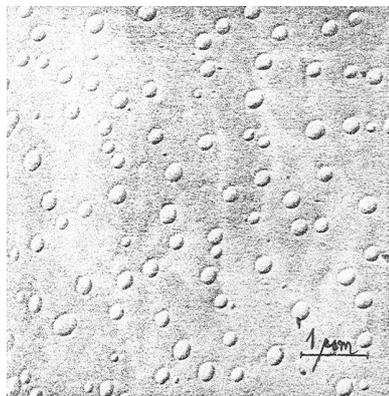

Fig. 5. Carbon/platinum replica of 25% As, 15% Ge, 40% Te, 20% Ga glass etched in fumes of HNO_3 (magnif. 13.000 ×), after [27].

The minor phase is disseminated in the main matrix as small grains (~0.1 – 0.2 μm in diameter). We believe that this phase corresponds to Ge-Ga clusters while the glassy matrix is based on As_2Te_3. During switching the Ge-Ga clusters increases on the account of the matrix and they could eventually pass over the percolation threshold, thus determining a strong modification of electrical conduction. By switching back, the ball-like minor phase is partially dissolved into the matrix and the ball size decreases, thus triggering the material in the non-conductivity state (the material moves toward a structure situated below the percolation threshold of the minor phase).

The diphasic, finaly interpenetrating structure, has been earlier shown to be characteristic of other important electric glasses [28]. C. A. Angell remarked the recognition of polymorphism within the glassy state [29] and P. H. Gaskell [30] showed that there is a growing evidence that the structure of glasses and crystals may be more similar even at medium-range level than had been supposed.

The above discussed literature results gives a strong support to our model of switching based on structural transformations in a complex glass.

Firstly, before switching the initial (Si-Ge)-(As-Te) glass has a non-conducting structure based on di-phasic structure: one Si-Ge rich glass (minor phase) and other As-Te rich glass (major phase).

During switching the phase based on As-Te transforms in a glass more nearer to the As_2Te_3 glass, while Si-Ge is released and diffuses to form bigger Si-Ge clusters. Thus a conducting materials is obtained. When an erasure impulse is given to the material, it melts and returns to the initial more disordered glass (non-conducting).

The switching can be repeated indefinitely for very short triggering times, if aging, i.e. strong cluster separation and growth, does not take place.

6. Conclusions

The structure of $Si_{12}Ge_{10}As_{30}Te_{48}$ glass has been determined. A model of the glass, based on disordered A_2Te_3 layers with Si and Ge situated on the tellurium sites and interlinked layers through tellurium has been built and relaxed by a computer-assisted procedure. The phase change in this

material was simulated. During strong electrical pulse the links between layers break and the tellurium atoms occupy the right places within the disordered As_2Te_3 layers. The new structure exhibits low distortion energy and is more stable than the original one. Thus a phase change explanation could be done. This change can be (or not) related to crystallisation.

The change of structure is made only by small displacements of the atoms after bond breaking. The transformation is, therefore, very rapid. No diffusion at long distances is needed.

Acknowledgement

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