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**NANO/MESO-SCALE SEPARATION IN SOME  
Ge-As-S GLASSES AND AMORPHOUS FILMS**

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*Atomic force microscopy (AFM) and atomic force acoustic microscopy (AFAM) is used for examination of the role of annealing and illumination of flexible network of  $Ge_{0.12}As_{0.17}S_{0.71}$  amorphous film and rigid network of  $Ge_{0.25}As_{0.30}S_{0.45}$  amorphous film. The virgin state of both films appears to be smooth with the value of smoothness  $S_a$  at around 0.8 nm. Annealing leads to changes in topological smoothness ( $S_a$  increased up to 5 nm in case of S-rich film) attributed to a nano/meso phase separation associated, most probably, with sulfur aggregation in the case of  $Ge_{0.12}As_{0.17}S_{0.71}$  and arsenic aggregation in the case of  $Ge_{0.25}As_{0.30}S_{0.45}$  amorphous film. Illumination of virgin  $Ge_{0.12}As_{0.17}S_{0.71}$  amorphous film leads to less pronounced but similar results as obtained by annealing, while rigid  $Ge_{0.25}As_{0.30}S_{0.45}$  amorphous film is insensitive to used illumination.*

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## Introduction

Mamedov *et al.* [1] showed that three distinct types of networks exist in  $\text{Ge}_x\text{As}_x\text{S}_{1-2x}$  glasses: (i) a floppy network where  $x < 0.11$ , (ii) an intermediate network (phase) where  $0.11 < x < 0.15$  and (iii) a stressed-rigid network where  $x > 0.15$ , see also Qu *et al.* [2]. The structure of floppy network consists of  $\text{S}_8$  units, for example, while the structure of stressed-rigid network consists of  $\text{As}_4\text{S}_4$  and  $\text{As}_4\text{S}_3$  monomers [2]. Recently we showed that in some sulfur-rich  $\text{Ge}_x\text{As}_x\text{S}_{1-2x}$  glasses, where  $0 < x \leq 0.15$ , sub-microcrystalline sulfur exists indicated by melting observed at around 110 and 120 °C using the differential scanning calorimetry (DSC) [3]. From gradient annealing experiments it was observed that in the region of stressed-rigid network, namely for  $x \geq 0.225$ , arsenic clusters must be present in the glassy matrix [3]. Hence, in some  $\text{Ge}_x\text{As}_x\text{S}_{1-2x}$  glasses molecular like sulfur entities even in the form of microcrystalline aggregates are separated from a backbone mainly in floppy network, whereas in stressed-rigid network not only  $\text{As}_4\text{S}_4$  and  $\text{As}_4\text{S}_3$  monomers but also  $\text{As}_n$  aggregates are separated from a backbone. In this communication we present preliminary results of examination whether some intrinsic nano/meso phase separation indices can be observed in an intermediate network (S-rich film- $\text{Ge}_{0.12}\text{As}_{0.17}\text{S}_{0.71}$ ) and in stressed-rigid network (rigid film- $\text{Ge}_{0.25}\text{As}_{0.30}\text{S}_{0.45}$ ), by using atomic force microscopy (AFM) and atomic force acoustic microscopy (AFAM). A comparison with the bulk glasses with corresponding chemical composition ( $\text{Ge}_{0.12}\text{As}_{0.12}\text{S}_{0.76}$ , S-rich bulk and  $\text{Ge}_{0.28}\text{As}_{0.27}\text{S}_{0.45}$ , rigid bulk) is done.

## Experimental

Amorphous films of the thickness around 1  $\mu\text{m}$  were prepared on microscope glass by thermal evaporation from the bulks. The chemical composition of the films was determined using electron microprobe X-ray analyses (Jeol JSM 5500 LV) with the precision of  $\pm 1.5\%$ . As-prepared (virgin – v), annealed (a) and illuminated (i) films (the sequence of treatment was  $v \rightarrow a$  and  $v \rightarrow i$ ) were characterized by optical band gap ( $E_g$ ) see Table I. Annealing was done for 3 hours in dry argon at 208 °C for  $\text{Ge}_{0.12}\text{As}_{0.17}\text{S}_{0.71}$  and at 340 °C for  $\text{Ge}_{0.25}\text{As}_{0.30}\text{S}_{0.45}$  amorphous film. Illumination of virgin films was carried out in dry nitrogen for two hours by “near-over gap” photons with the energy of 2.75 eV for  $\text{Ge}_{0.12}\text{As}_{0.17}\text{S}_{0.71}$  and 1.82 eV for  $\text{Ge}_{0.25}\text{As}_{0.30}\text{S}_{0.45}$  amorphous film. The incident light energy varied from 140 to 170  $\text{mW cm}^{-2}$ . For some more details related to the thin films preparation, treatment and  $E_g$  determination, see Ref. [4]. AFM and AFAM measurements were realized by using Solver Pro M Atomic Force Microscope (NT-MDT; Russia) with high-resolution “Golden” silicon cantilevers CSG-10 (Au coating, cone angle less than 22° and typical force constant 0.1  $\text{N m}^{-1}$ ) were used for all the measurements. The

images were recorded at the scan frequency between 0.5 and 1 Hz for a resolution of  $256 \times 256$  pixel (if not otherwise stated). The smoothness ( $S_a$ ) was calculated according ISO 4287-1997 [5].

Table I Chemical composition and film state (virgin – v, illuminated – i and annealed – a), the optical gap and the smoothness of studied films. The smoothness of the used substrate  $S_a$  equals 0.58 nm.

Film		$E_g$ eV	$S_a$ nm	Film		$E_g$ eV	$S_a$ nm
$\text{Ge}_{0.12}\text{As}_{0.17}\text{S}_{0.71}$	v	2.56	0.75	$\text{Ge}_{0.25}\text{As}_{0.30}\text{S}_{0.45}$	v	1.63	0.81
	i	2.65	2.77		i	1.63	0.79
	a	2.69	4.99		a	1.93	3.59

## Results and Discussion

The case study should be discussed on S-rich  $\text{Ge}_{0.12}\text{As}_{0.17}\text{S}_{0.71}$  film. The images of surface and surface smoothness for different treatment are shown in Fig.1 and Table I. The smoothness ( $S_a$ ) of virgin sample is comparable to the smoothness of substrate glass ( $S_{a\text{-subst}} = 0.58$  nm), however, there are detected sharp inhomogeneities, like domains, in AFAM mode, see small dots in Fig. 1A, B. It means that these domains have different local response on out-of-plane vibration. Based on shift of contact resonance curves [6-8], the surfaces with a higher stiffness as well as lower density generate a response with lower amplitude in AFAM mode, *i.e.* they appear as dark areas. The origin of dark areas (lower amplitude domains) we observed could be twofold: (i) Local decrease in cohesive forces in otherwise chemically homogeneous medium, the case of significant differences in structural arrangement of domains and surroundings, for instance two different structural modifications with identical chemical composition. (ii) Lower density due to different chemical composition of dark area in comparison to surroundings. Origin of observed dark domains (dots) on AFAM image of virgin  $\text{Ge}_{0.12}\text{As}_{0.17}\text{S}_{0.71}$  thin film surface was tentatively assigned to the presence of domains with different chemical composition and lower densities in comparison to plain-fields, namely to presence of microcrystalline sulfur aggregates/clusters. The diameter of these domains is about 50 nm and their contrast is high, as it is demonstrated by AFAM line-scan of the virgin sample, see Fig. 2-AFAM. These particles are spread over the surface occasionally. After the film annealing (up to 208 °C, in inert gas atmosphere) the film surface dramatically changed. The protuberances are growing with the height up to 40 nm and diameter about 300 nm, see Fig. 2-TOPO(A), and the roughness increases 6-times to  $S_a = 4.99$  nm, see Table I. The mechanical characteristics of these domains/protuberances are diffe-

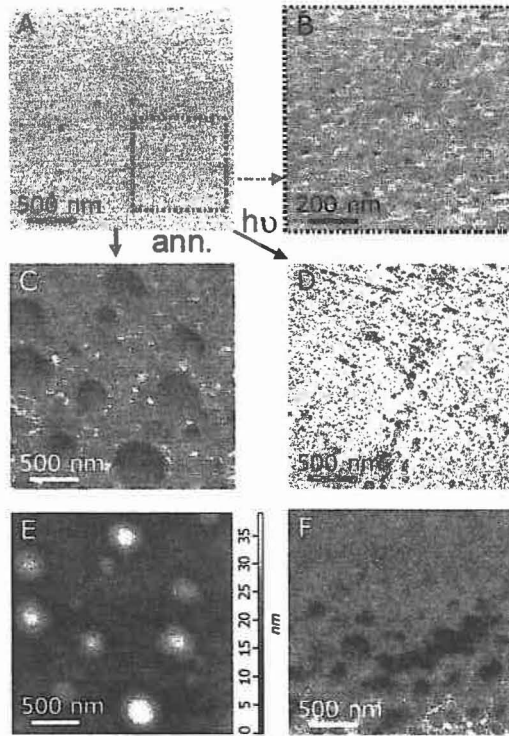


Fig. 1 Surface of S-rich chalcogenide  $\text{Ge}_{0.12}\text{As}_{0.17}\text{S}_{0.71}$  film observed by AFM (figures A to D and F) and AFM (figure E, surface topology). State of sample: A, B – virgin state; C, E – annealed state; D – illuminated, F – fresh fracture of bulk sample with similar chemical composition:  $\text{Ge}_{0.15}\text{As}_{0.15}\text{S}_{0.7}$ , (resolution  $128 \times 128$  pxs)

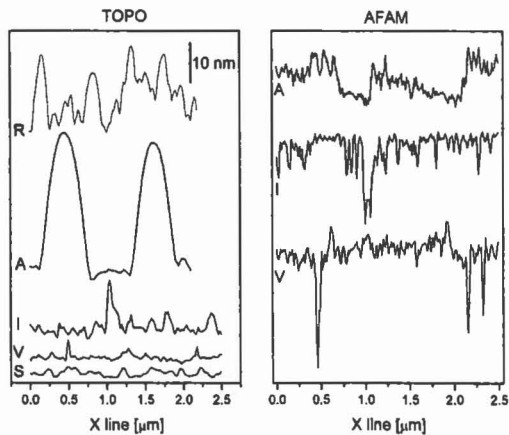


Fig. 2 Typical line-scan in AFM mode (TOPO) and in AFAM mode (AFAM) of S-rich sample  $\text{Ge}_{0.12}\text{As}_{0.17}\text{S}_{0.71}$  in following states: V – virgin; I – illuminated; A – annealed. The symbol S refers to line-scan of substrate glass surface and the symbol R refers to the line-scan of annealed rigid film  $\text{Ge}_{0.25}\text{As}_{0.30}\text{S}_{0.45}$  (R) added here for comparison

rent from plain-fields, and there is proved a good correlation between mechanical — AFAM image and topological — AFM image surface's in-homogeneities, compare Figs 1C and E. Interesting observations are that the contrast of these domains/protuberances is lower and the diameter is much higher in comparison to virgin thin film. These results seem to be consistent with our assignment of the dark domains/protuberances and local chemical in-homogeneities with the presence of microcrystalline sulfur aggregates/clusters. Hence, the annealing-induced growing of sulfur domains dimension reflects only thermally enhanced phase separation. The image of AFAM and TOPO mapping of illuminated S-rich film surface is between that for virgin and annealed sample namely from the point of view of diameter, roughness as well as contrast of in-homogeneities (domains) in comparison to plain-fields as seen in Fig. 1D, line-scans I in Fig. 2 and Table I.

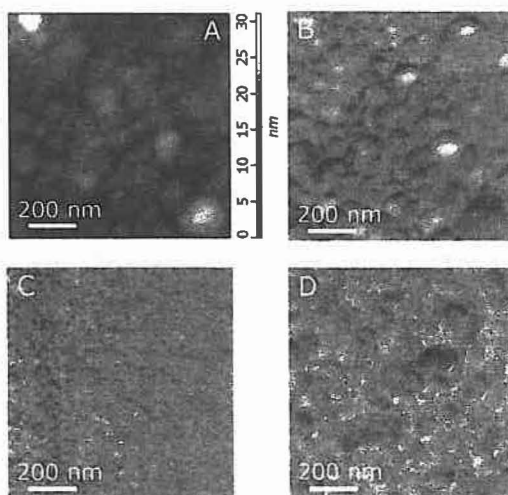


Fig. 3 Surface of rigid  $\text{Ge}_{0.25}\text{As}_{0.30}\text{S}_{0.45}$  film observed in topology and AFAM mode. A – AFM image (topology) and B – AFAM image of annealed film; C – AFAM image of virgin film and D – AFAM image of fresh fracture of the bulk with similar composition

The surface of rigid film ( $\text{Ge}_{0.25}\text{As}_{0.30}\text{S}_{0.45}$ ) has different behavior as illustrated in Fig. 3: (i) For both  $v$  and  $i$  states of rigid film there are not observed surface in-homogeneities in TOPO and AFAM images which are characteristic for virgin and illuminated states of S-rich thin film. (ii) Similar smoothness is observed for virgin and illuminated states of the rigid  $\text{Ge}_{0.25}\text{As}_{0.30}\text{S}_{0.45}$  film, whereas the value of  $S_a$  is increasing at least three-times in S-rich film, see Table I. This finding seems to be consistent with recent observation [4] that the rigid  $\text{Ge}_{0.25}\text{As}_{0.30}\text{S}_{0.45}$  thin film is practically insensitive to illumination by the white light and by the light with energy little exceeding the optical band gap ( $E_g$ ) and it agrees with the results of Brillouin scattering study in Ge-Se glasses [9] indicating that

in stressed-rigid networks the light-induced effects are rather minimized.

The AFAM image of surface of annealed rigid film could be described as containing domains with the diameter of 50-70 nm connected by brighter borders, Fig. 3B. The smoothness of the sample is slightly lower in comparison to annealed S-rich thin film ( $S_a = 3.59$  nm, see Table I) but the distribution of topological protuberances is quite different, see TOPO line-scans A and R in Fig. 2-TOPO. In this case, the protuberances height is lower (up to 20 nm) but they cover nearly whole examined surface, whereas for S-rich sample the protuberances are higher, they crosscut dimensions in  $x$ - $y$  plane are larger but their percent occurrence is smaller within unit area. The domains/protuberances created by annealing are attributed to enhancement of phase separation due to arsenic aggregation, see also [3].

For comparison, we examined also the bulk samples with the chemical composition similar to our amorphous films. The bulk of corresponding glass was broken into pieces and after careful grinding of the bottom side the sample was mounted to the transducer. The AFAM images, taken from fresh fracture area were quite similar with the corresponding annealed thin film, that is (i) for S-rich bulk sample, Fig. 1F, there were observed dark domains with diameter up to about 300-500 nm interconnected to a chain and (ii) the darker domains were observed with diameter 80 nm for rigid bulk sample, Fig. 3D. This result corresponds to the experimental experience that structural arrangement of annealed amorphous films is close to the structural arrangement of the corresponding bulks.

## Conclusion

Our results indicate that: (i) Annealing of the virgin films leads to a nano/meso phase separation indicated by the presence of domains having lower density in comparison with surroundings. Following our recent results [3] we suppose that the domains observed can be attributed to separation of a phase based on microcrystalline sulfur aggregates in the case of S-rich film and to a phase based on growth of arsenic clusters and subsequent arsenic aggregation in the case of rigid film. (ii) Illumination of virgin films leads, in comparison with influence of annealing, to rather gentle nano/meso phase separation in S-rich film, whereas no response is seen in rigid film. This is also in harmony with our most recent results [4] indicating that in S-rich film light induces some structural changes accompanied, for instance, by a blue shift of the optical gap, while the rigid film is practically insensitive to illumination. (iii) In the bulk samples with the chemical composition close to the rigid films studied similar indices of nano/meso phase separation are observed as in the case of annealed amorphous films.

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