JOURNAL OF OPTOELECTRONICS AND ADVANCED MATERIALS Vol. 9, No. 10, October 2007, p. 3088 - 3092

Structural transition and intermediate (Boolchand) phase in amorphous thin films of the As_2S_3-GeS_2 system

K. PETKOV, M. POPESCU[a,*], A. LŐRINCZI[a], F. SAVA[a], S. ZAMFIRA[b], M. LEONOVICI[c]
Central Laboratory of Photoprocesses of the Academy of Sciences of Bulgaria, Sofia, Bulgaria
[a]*National Institute of Materials Physics, P. O. Box MG. 7, 077125 Magurele, Ilfov, Romania*
[b]*University "Transylvania" Dept. of Precision Mechanics and Mechatronics, 29 Bd. Eroilor, 5036-Brasov, Romania*
[c]*Physics Department, Faculty of Physics, University of Bucharest, Romania*

The structure of the chalcogenide glass films of composition As_2S_3-GeS_2 has been investigated bu X-ray diffraction. The relation between the quasi-distance as evidenced from the first sharp diffraction peak, and the composition ration has been estabilished. The Boolchand (intermediate) phase was found ro be characterized by large structuro-compositional fluctuations.

(Received July 5, 2007; accepted October 1, 2007)

Keywords: As_2S_3-GeS_2, Boolchand phase, Amorphous films, FSDP, Structure

1. Introduction

The chalcogenide glasses are promising optical materials due to transparency in infrared and to the good thermal, mechanical and chemical properties [1]. The glasses are characterized by low optical losses. The modifications that appear in thin films of the system As-Ge-S as a result of the exposure to light have been the object of numerous papers. The experimental data have shown that the optical properties and the solubility of glasses depend on the ratio of their components [14-19]. The structural modifications are strongly related to their optical properties. The results of the researches achieved up to now [18-19] show that the largely accepted idea related to the photodarkening after light exposure, are confirmed for all the films of the investigated systems. The Tanaka's hypothesis, according to which the ternary system As-Ge-S is characterized by photoinduced structural transformations, which are mostly expressed for the compositions with the mean coordination number $z = 2.6 \div 2.7$, is still controversial.

An analysis of the series of compositions from As-Ge-S system, for different values of the mean coordination number is important to shed more light on the topological threshold and intermediate phase in the system.

2. Experimental

The initial compositions of the system $As_xGe_{40-x}S_{60}$ (x=0, 10, 20, 30, 40) have been prepared by melting the chemical components in stoichiometric proportions: arsenic, germanium and sulphur, with the purity better than 99.999, in quartz ampoules sealed under vacuum of 10^{-3} Pa at 970 °C for 12 hours for glasses with germanium and at 870 °C for 10 hours for glasses of composition $As_{40}S_{60}$.

The evaporation has been achieved in molybdenum crucible under a vacuum of $6 \div 8 \times 10^{-4}$ Pa, and the substrates were held at room temperature, mounted on a rotating calotte. The deposition rate was controlled through the modification of the intrinsic oscillation frequency of a piezoelectric crystal during the evaporation process. Thin chalcogenide films (thickness: 1500 nm) were deposited on silicon wafers and on silica and graphite substrates by the evaporation of bulk samples with the rate $0.5 \div 1$ nm/s. The composition of the bulk materials as well as thin films has been determined in a scanning microscope provided with micro analyser RX (JOEL Superprobe 733, Japan). The preparations have been carried out in the Central Laboratory of Photo processes of the Academy of Sciences of Bulgaria, Sofia, in the frame of the Bilateral Cooperation with National Institute R&D for Materials Physics, Bucharest, Romania.

The fluctuations of composition of both bulk and thin films samples are lower than 1%, i.e. the compositions are maintained in the range of instrumental accuracy.

3. Structural measurements on the amorphous chalcogenide films

The structures of the samples from the system As-S-Ge have been determined by X-ray diffraction. The diffraction patterns have been recorded in a diffractometer of type TUR-M62 provided with copper target tube (λ = 1.54178 Å) and proportional counter in the detection system.

The working parameters of the diffractometer have been: tube voltage of 40 kV, and current of 20 mA. The exit slit of the X-ray tube was 1.75 mm and that in front of the detector was 1.09 mm.

The recording of the intensity curves as a function of the scattering angle was carried out in angular steps of 0.05^o (theta). For every angular position the registration time of the X-ray quanta scattered by the sample was 40 s.

The measured angular interval was situated between 1 and 13^o (theta), and this range corresponds to the so-called first sharp diffraction peak (FSDP).

The X-ray diffraction diagrams of the investigated samples are presented in Figs. 1 a, b, c, d.

A detailed analysis of the first sharp diffraction peak shows that the parameters that characterize the FSDP are functions of the film composition (Table 1).

After the transformation of the abscissas from theta angles to scattering vectors Q ($Q = 4\pi\sin\theta/\lambda$), there were calculated the positions of the maxima on the scale of quasi-distances as well as the integral width.

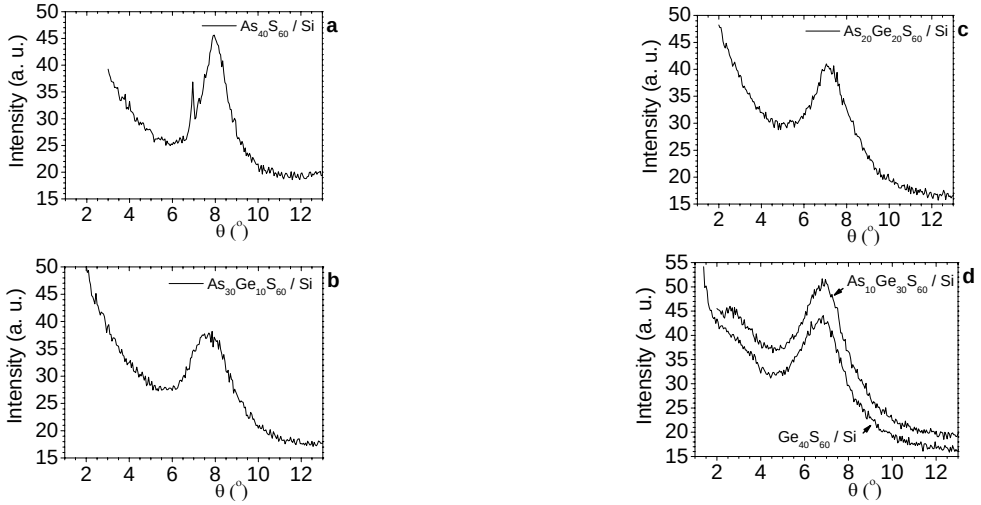


Fig. 1. X-ray diffraction diagrams of the $As_xGe_{40-x}S_{60}$ thin films in the angular range of the first sharp diffraction peak.

Table 1. The characterization of the FSDP measured on the amorphous films of $As_xGe_{40-x}S_{60}$.

Material	$\beta_{integral}$ (Å^{-1})	$Q_{max\ integral}$ (Å^{-1})	$d_{integral}$ (Å)	$\beta_{1/2}$ (Å^{-1})	$Q_{1/2}$ (Å^{-1})
$Ge_{40}S_{60}$	0.3557	0.9721	6.4634	0.3138	0.9638
$As_{10}Ge_{30}S_{60}$	0.3626	0.9792	6.4168	0.3137	0.9798
$As_{20}Ge_{20}S_{60}$	0.3255	1.0215	6.1507	0.2843	1.0335
$As_{30}Ge_{10}S_{60}$	0.3240	1.0991	5.7167	0.2946	1.1022
$As_{40}S_{60}$	0.2141	1.1343	5.5391	0.1841	1.1344

4. The analysis of the system $As_xGe_{40-x}S_{60}$ from the point of view of the intermediate or medium range order

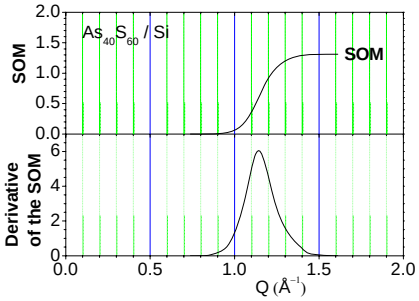
With the aim to analyse in detail the intermediate order expressed in the profile of the FSDP, we have performed the smoothening of the diffraction curves and have calculated the first order derivative, as well as the first, second and third order momenta of the FSDP profiles.

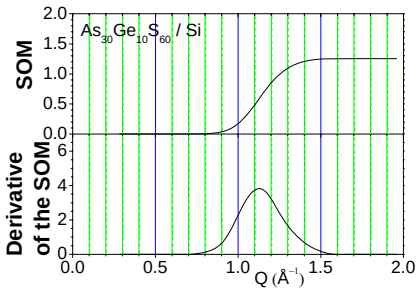
From the behaviour of the first order derivative it is concluded that every FSDP of the system is characterized by a significant asymmetry. After our opinion this feature proves the particularity of the packing of the quasi-layers, supposed to be the main structural configuration in the samples: besides the narrow distribution of the layer packing that corresponds to FSDP position, it appears a minor amount of denser layer packing with a little bit lower quasi-distance. These packings may be due to more ordered layers that form the structural packing configurations or due to special pie-like clusters, packed similarly to the ones modelled recently by us [20].

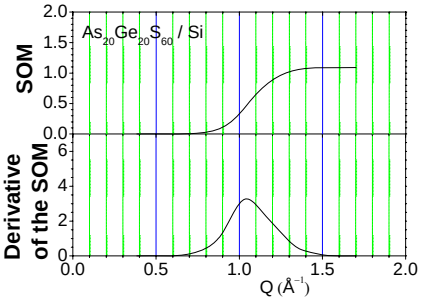
The first order momentum defines the mass centre of the diffraction line. The second order momentum represents the variance of the diffraction line. The third order momentum defines the deviation from symmetry (squeezing) of the diffraction line profile.

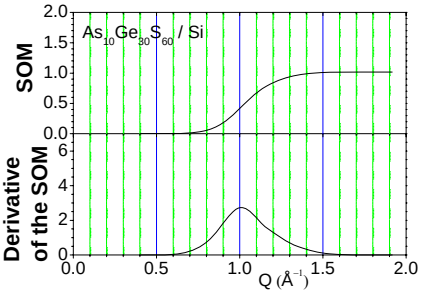
Fig. 2 and 3 shows the second order momentum - $\int Q^2 I(Q)dQ / \int I(Q)dQ$ - and third order momentum - $\int Q^3 I(Q)dQ / \int I(Q)dQ$ - of the FSDP, measured on the investigated samples.

On the basis of the results of the calculation of the FSDP's momenta, there were drawn the plots of the momenta as a function of the mean coordination number, N_{av}, of the amorphous films (Fig. 4, 5). One can conclude that the samples that correspond to the Boolchand phase show lower values of the FSDP momenta, if compared to the theoretical positions corresponding to a linear variation in the investigated series.









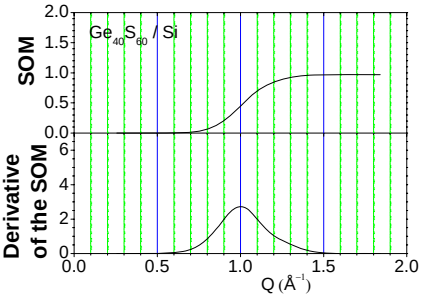
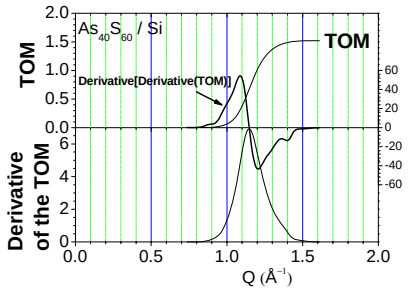
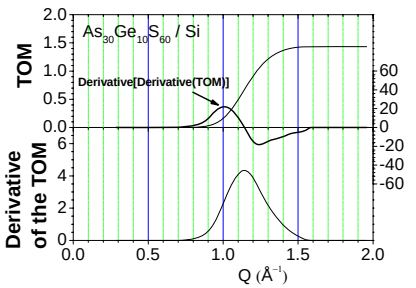
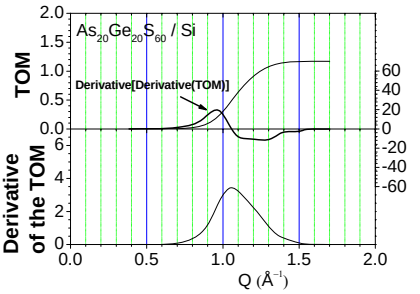
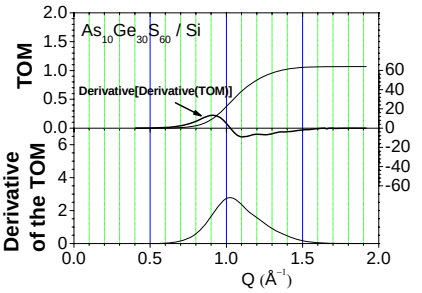


Fig. 2. The curves of the second order momenta (SOM) and their derivative of the FSDP in the $As_xGe_{40-x}S_{60}$ films.









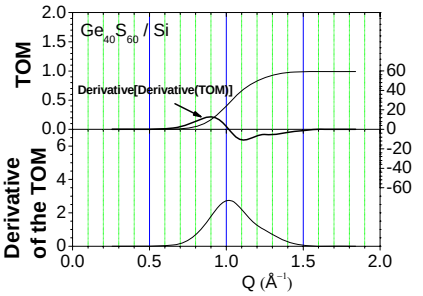


Fig. 3. The curves of the third order momenta (TOM) and their derivative of the FSDP in the $As_xGe_{40-x}S_{60}$ films.

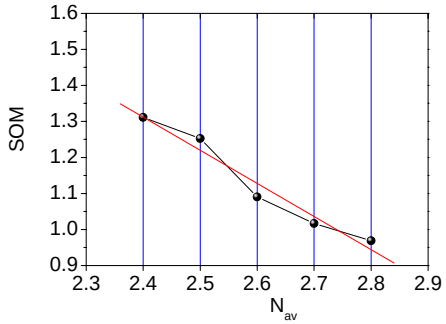


Fig. 4. Second order momentum (SOM) as a function of the mean coordination number of the $As_xGe_{40-x}S_{60}$ films.

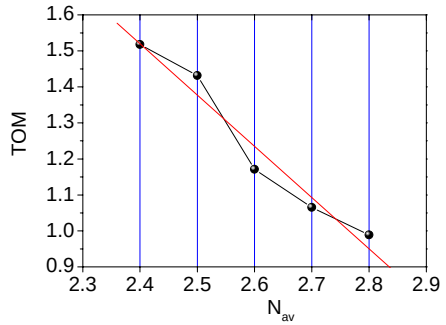


Fig. 5. Third order momentum (TOM) as a function of the mean coordination number of $As_xGe_{40-x}S_{60}$ films.

Figs. 6 a, b show the evolution of the position and quasi-distance associated to every FSDP as a function of the mean coordination number, N_{av}, of the $As_xGe_{40-x}S_{60}$ films.

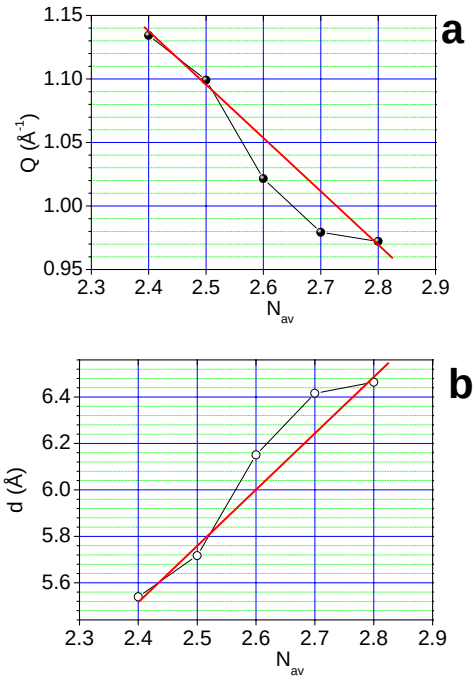


Fig. 6. a) Position and b) quasi-distance associated to every FSDP as a function of the mean coordination number, N_{av}.

One observes that the FSDP position (Fig. 6a) exhibits a linear dependence on N_{av}. The deviation from the linearity is proper to the samples that correspond to the range where the Boolchand phase was supposed to exist.

A higher deviation of the FSDP towards smaller angles (that corresponds to the increase of the interlayer quasi-distance, specific to the domains with quasi-disordered layers, Fig. 6b) proves that the compositions with intermediary phase are less disordered from the crystallographic point of view, but exhibit some ordering of the constituent clusters.

The integral breadth of the FSDP as a function of the mean coordination number is presented in Fig. 7. Here the deviation of the integral breadth of the FSDP from the linear function defined by the sample at the limit of composition, which correspond to maximum ordering, proves a worse ordering in the intermediary phase.

Fig. 8 indicates the variation of the mean size of the amorphous structural domains as a function of N_{av}. The domains are situated around the values 15 ÷ 20 Å, which correspond to the packing of 3 ÷ 4 disordered films.

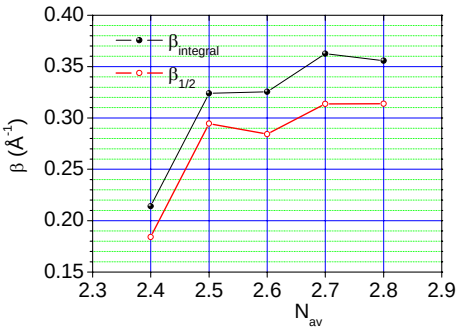


Fig. 7. The integral breadth (B_{int} and $B_{1/2}$) as a function of the mean coordination number, N_{av}.

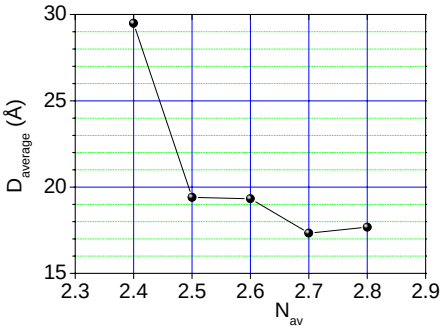


Fig. 8. The average size of the amorphous domains (amorphites) as a function of the mean coordination number, N_{av}.

5. Conclusions

A relation was established between quasi-structure and the mean coordination number of the thin amorphous chalcogenide films from the system As-Ge-S.

The compositions that correspond to Boolchand phase are evidenced by the structural parameters that deviate from the normal linear behaviour in the series of compositions with different mean coordination numbers.

The ternary phases are inhomogeneous from the structural point of view showing fluctuations in the distribution of nanophases. The intermediate (Boolchand) phase is characterized by high structuro-compositional fluctuations.

The intermediate order in the samples is directly related to the mean coordination number of atoms in the amorphous material.

References

[1] A. Zakery, J. Optoelectron. Adv. Mater. **7**(3), 1143 (2005).
[2] M. L. Trunov, J. Optoelectron. Adv. Mater. **7**(3), 1223 (2005).
[3] D. Strand, J. Optoelectron. Adv. Mater. **7**(4), 1679 (2005).
[4] N. P. Eisenberg, M. Manevich, A. Arsh, M. Klebanov, V. Lyubin, J. Optoelectron. Adv. Mater. **7**(5), 2275 (2005).
[5] D. Lezal, J. Zavadil, M. Prochazka, J. Optoelectron. Adv. Mater. **7**(5), 2281 (2005).
[6] A. Andriesh, J. Optoelectron. Adv. Mater. **7**(6), 2931 (2005).
[7] J. Dikova, J. Optoelectron. Adv. Mater. **7**(6), 2945 (2005).
[8] I. Stratan, D. Tsiublyanu, I. Eisele, J. Optoelectron. Adv. Mater. **8**(6), 2117 (2006).
[9] S. Kokenyesi, J. Optoelectron. Adv. Mater. **8**(6), 2093 (2006).
[10] J. S. Sanghera, I. D. Aggarwal et al. J. Optoelectron. Adv. Mater. **8**(6), 2148 (2006).
[11] M. Popescu, J. Optoelectron. Adv. Mater. **8**(6), 2164 (2006).
[12] M. Popescu, J. Optoelectron. Adv. Mater. **8**(2), 755 (2006).
[13] D. Savastru, S. Miclos, R. Savastru, J. Optoelectron. Adv. Mater. **8**(3), 1165 (2006).
[14] E. Vateva, M. Nikiforova, E. Skordeva, J. Non-Cryst. Solids **77-78**, 1133 (1985).
[15] Gan Fuxi, Mao Xilai, Wang Hao, Yang Peihong, J. Non-Cryst. Solids **56**, 303 (1983).
[16] E. Vateva, P. Minkov, E. Skordeva, D. Arsova, M. Nikiforova, J. Non-Cryst. Solids **90**, 481 (1987).
[17] Ke. Tanaka, Phys. Rev. B **39**, 1270 (1989).
[18] K. Petkov, B. Dinev, J. Mater. Sci. **29**, 468 (1994).
[19] K. Petkov, P. J. S. Ewen, J. Non-Cryst. Solids **249**, 150 (1999).
[20] M. Popescu, F. Sava, A. Lorinczi, J. Optoelectron. Adv. Mater. **6**(3), 883 (2004).

*Corresponding author: mpopescu@infim.ro