Journal of Optoelectronics and Advanced Materials, Vol. 7, No. 4, August 2005, p. 1965 - 1969

OPTICAL PROPERTIES OF TERNARY CHALCOGENIDE THIN FILMS WITH SnTe

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Thin films of As_2Se_3 - $GeSe_2$ - SnTe system are investigated. The present investigation is a continuation of our previous study on the possibilities to obtain amorphous thin films by evaporation and condensation in three component systems based on $GeSe_2$ and As_2Se_3 with SnTe as a third component. The aim is to trace the influence of the third component on the thin film structure and optical absorption. Results from the study show that the optical band gap E_g^{opt} determined both by Tauc plot and Urbach relation reveal a decrease of E_g with increasing SnTe content.

(Received June 1, 2005; accepted July 21, 2005)

Keywords: As_2Se_3-$GeSe_2$-SnTe, Amorphous materials, Chalcogenide glasses, Thin film, Optical properties, Band gap structure

1. Introduction

In recent years there has been a great deal of interest in the study of chalcogenide glasses from the point of view of basic physics as well as of device technology. They are suitable material for optical elements [1], optical memory disks [2], functional elements in integral-optic systems [3], IR-fibres [4] that show high flexibility and chemical durability [5] etc. The Ge-Se-As based glasses are promising optical material due to their optical characteristics - a wide spectral region of transmittance up to 14 μm [6], relatively high values of refractive index ($2 \leq n \leq 3.7$), low optical losses and non-linear dispersion of n. Therefore much work has been done on both bulk and thin film samples of glassy chalcogenides regarding electrical and optical properties and on alloys of different compositions of selenium, germanium and arsenic with respect to the amorphous-crystalline transition structure etc. It is well known that thermal relaxation occurs in these glasses when following an instantaneous change in temperature (during the quenching process) as a glassy substance relaxes from a state of higher enthalpy towards an equilibrium state of lower enthalpy.

It has been observed that the variations of composition and annealing conditions for glassy chalcogenide semiconductors have a significant influence on the band gap and on the optical properties. Studies of the band gap of the bulk As-Se-Ge system have been performed previously [7].

The optical characterization of thin films often requires the use of highly refined computer numerical techniques applied to both optical transmission and reflection spectra. In contrast, a relatively simple and straightforward method for determining the optical constants, using only the transmission spectra, has been proposed by Swanepoel [8], which is also particularly useful because it accounts for a possible lack of film-thickness uniformity.

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In the present study we investigate the effect of the addition of SnTe in amorphous system where the ratio of $GeSe_2/As_2Se_3$ was kept constant.

2. Experimental

Bulk glasses from As_2Se_3- $GeSe_2$ - SnTe system were prepared following standard melt-quenching technique described in [9].

The samples studied in the present work were As_2Se_3 - $GeSe_2$ - SnTe amorphous thin films deposited by vacuum thermal evaporation (Leybold LB 370), with a residual gas pressure of 1.33×10^{-4} Pa. The process was carried out at constant geometry of the experimental setup with 0.09 m distance between the evaporator and the glass substrate and an vaporizer area of 1.2×10^{-5} m^2. The evaporation was performed in temperature range 850 - 1000 K, monitored by a Ni-Ni/Cr thermocouple. The substrates were conveniently rotated during the deposition process, by means of a rotary holder, which allows deposition of thin films with remarkably uniform thickness. The film compositions investigated in the present study are $(As_2Se_3)_x(GeSe_2)_{90-x}$ $SnTe_{10}$ and $(As_2Se_3)_x(GeSe_2)_{80-x}$ $SnTe_{20}$ where the SnTe content was kept constant and the ratio $As_2Se_3/GeSe_2$ was varied 1:1, 1:2,3.

Auger electron spectroscopy (AES) was applied for thin films composition determination. The results show that the compositions of the thin films are close to that of the bulk source materials within the accuracy of the method, ± 1 at. %.

The thin film structure and arrangement wac defined by TEM and SAED study by means of electron microscope, EM-400 Philips. The thickness of the layers ranges from 680 to 900 nm.

The normal-incidence transmission and reflection spectra were measured in the range 400-2500 nm by use of a double beam, computer-controlled spectrophotometer Perkin Elmer, Lambda 25. All optical measurements were performed at room temperature.

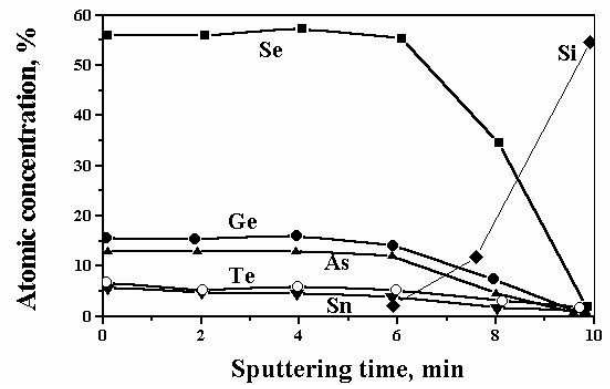

Fig. 1. Auger electron diagram of the sample with composition $(As_2Se_3)_{24}(GeSe_2)_{56}(SnTe)_{20}$.

3. Results and discussion

It was established that the conditions of vacuum evaporation used enable preparation of homogeneous amorphous thin films. The film composition corresponds to that one of the precursors used as confirmed by the Auger electron spectroscopy data (Fig. 1). The TEM and SAED analysis showed that tin telluride content influences the level of the atomic arrangement in the amorphous thin films but the films remain amorphous as it is revealed by the microscopic study (Figs. 2 and 3).

The optical absorption coefficient, α is calculated using the relation:

$$\alpha = 1/d \, [\ln (1-R)^2 / T] \quad (1)$$

where, d is the thickness, T is the transmittance and R the reflectivity. The energy variation of the absorption coefficient gives an indication of the distribution of the density of states in the energy

gap. The absorption-edge spectra of the amorphous samples are seen to consist of two regions, namely power-law and Urbach-regions. In the region with energies higher than 2.5 eV, the absorption coefficient shows a parabolic variation on the photon energy, while up to 2.5 eV, it depends exponentially on the photon energy [10],

$$\alpha = \alpha_0 \exp(h\nu/E_0) \quad (2)$$

where α_0=const and E_0 is the so-called Urbach slope. This Urbach parameter is often regarded as a disorder parameter since the exponential absorption edge can be attributed to transitions between the valence band tail states and the conduction band [11]. Variations in the width of the exponential region, E_0, provide information about the relative changes of the structural disorder induced by an additive [12]. The optical band gap, E_g, of amorphous materials [10] is usually defined as the energy at which α has a value between 10^4–10^5 cm^{-1}.

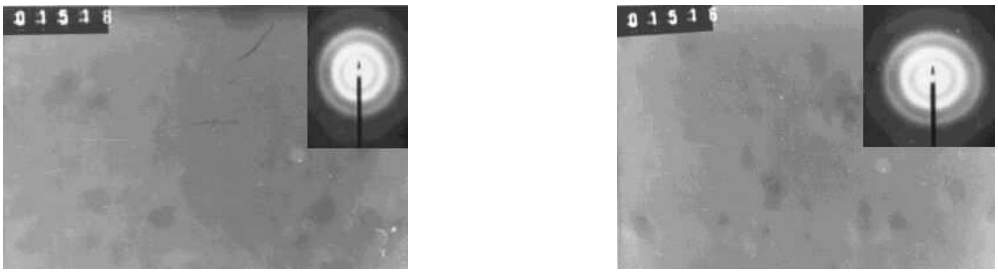

Fig. 2. Electron diffraction pattern of the sample with composition a) $(As_2Se_3)_{24}(GeSe_2)_{56}(SnTe)_{20}$ b) $(As_2Se_3)_{80}(SnTe)_{20}$.

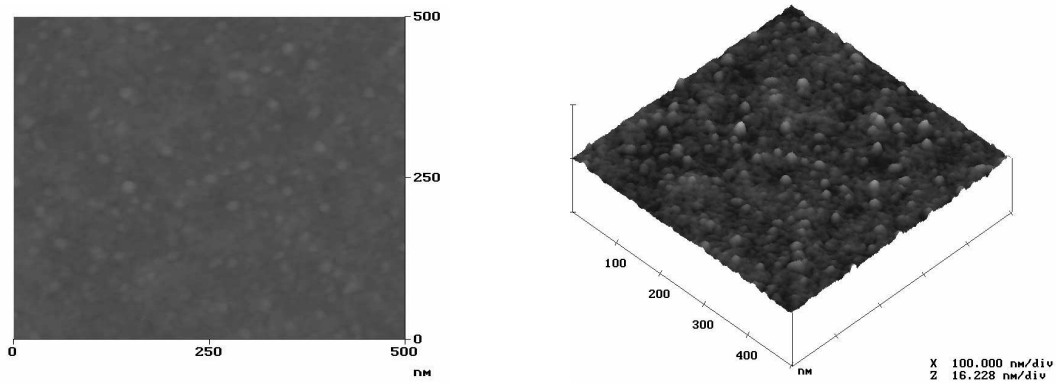

Fig.3. AFM images of the $(As_2Se_3)_{40}(GeSe_2)_{40}(SnTe)_{20}$ thin film.
a) top-view image b) three D image.

The spectral dependences of the absorption coefficient (α) of films with constant SnTe content are plotted in Fig.4,a,b. It is seen that α decreases as $GeSe_2$ concentration increases when the SnTe concentration is constant in the film. The relation observed is due to the lower metallic character of the $GeSe_2$ bonds compared to the bonds in the SnTe compound. However, in general the values obtained are not very much different showing that no substantial changes in the structure are expected with additives in the As_2Se_3 host matrix.

Fig. 5 depicts the Tauc plot that is spectral dependence of the square root of absorption coefficient and energy. The optical band gap values determined from Urbach relation and from the Tauc plot are summarized in Table 1. The results show that the Eg values increase with $GeSe_2$ content. It is related to the bigger optical band gap of $GeSe_2$ compared to this of As_2Se_3 (Eg of $GeSe_2$ = 2.3 eV; Eg of As_2Se_3= 1.7 eV) and to the increase of the structure disorder. The gihger

SnTe content leads to a decrease in E_g values due probably to the stronger metal character of the chemical bonds in the SnTe compound.

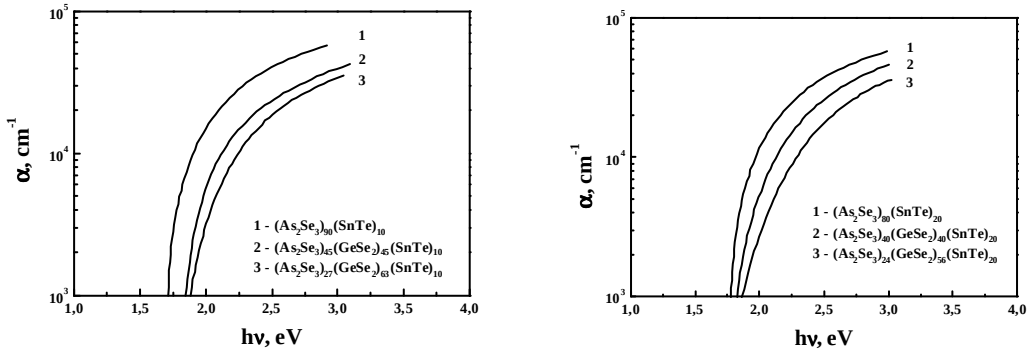

Fig. 4. Spectral dependence of the absorption coefficient by different ratio $As_2Se_3/GeSe_2$
a) 10 mol.% SnTe content b) 20 mol.% SnTe content

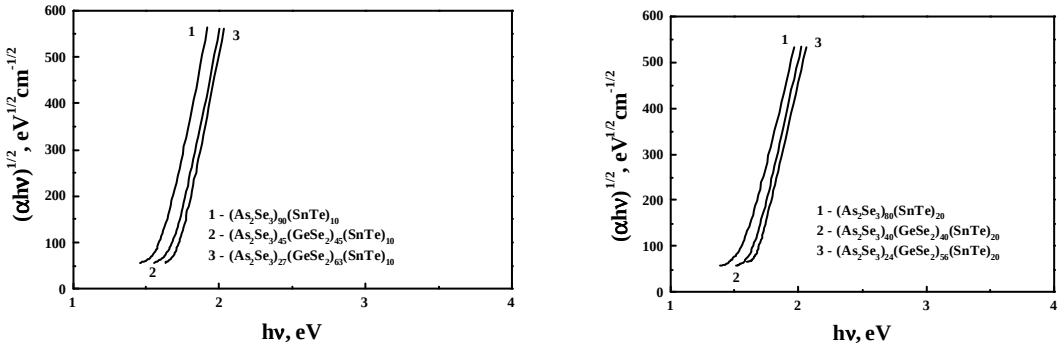

Fig. 5. Tauc's procedure for the ternary system by different ratio $As_2Se_3/GeSe_2$
a) 10 mol.% SnTe content b) 20 mol.% SnTe content

Table 1. The band gap in the ternary system

№	composition	E_g^{opt}, eV	E_g^{04}, eV
1	$(As_2Se_3)_{90}(SnTe)_{10}$	1.58	1.71
2	$(As_2Se_3)_{45}(GeSe_2)_{45}(SnTe)_{10}$	1.66	1.85
3	$(As_2Se_3)_{27}(GeSe_2)_{63}(SnTe)_{10}$	1.68	1.87
4	$(As_2Se_3)_{80}(SnTe)_{20}$	1.52	1.78
5	$(As_2Se_3)_{40}(GeSe_2)_{40}(SnTe)_{20}$	1.60	1.82
6	$(As_2Se_3)_{24}(GeSe_2)_{56}(SnTe)_{20}$	1.63	1.85

4. Conclusions

The results from optical properties investigation of As_2Se_3 – $GeSe_2$ – SnTe films can be summarized as follows:

- Thin As_2Se_3 – $GeSe_2$ – SnTe films prepared by vacuum evaporation are amorphous irrespective of SnTe concentration;
- The films are transparent in VIS and near IR spectral region. The absorption edge shifts to longer wavelengths with increase the ratio of $GeSe_2/As_2Se_3$ and when SnTe content is increased. The phenomena are due to the increase of the metallic atoms number in the film;
- The increase of the $GeSe_2$ content leads to a complication in the thin films structure and rearrengment in the host glassy matrix.
- The optical band gap of As_2Se_3 – $GeSe_2$ – SnTe films depends on the composition. The increase in SnTe reduces the optical band gap values.

$GeSe_2$

Acknowledgment

The authors thank to the Ministry of Education & Science (National Science Fund) for the financial support of this work under Projects X 1203 and X 1204 and POEMES, Centre of Excellence.

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