Journal of Optoelectronics and Advanced Materials Vol. 7, No. 3, June 2005, p. 1293 - 1297

OPTICAL PROPERTIES OF THIN Ge – S – AgI FILMS

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Thin films of glassy $(GeS_2)_{1-x}$ $(AgI)_x$ system have been studied. The films have been prepared from the respective bulk glasses previously synthesized from the elements with constant Ge:S=1:2 ratio and different amount of AgI (x= 5, 10, 15,20 mol.%). The amorphous nature of the films has been proved by X-ray diffraction (XRD) and electron microscope investigation. Spectral distribution of the film transmission has been obtained. Compositional dependence of the basic optical parameters has been derived. The optical energy gap E_g^{Tauc} has been determined from the Tauc plot $\alpha h\nu=B(E_g^{Tauc} - h\nu)^2$ and E_g^{04} from the relationship $\alpha = f(h\nu)$. The values of E_g calculated by both methods show decrease with increasing of silver content. The influence of the third component on the thin film structure and optical absorption has been discussed.

(Received May 19, 2005; accepted May 26, 2005)

Keywords: Germanium chalcogenides, Optical properties, Thin films, Band gap

1. Introduction

Recently, the amorphous semiconductors and particularly the chalcogenide and chalcohalide glasses attract strong scientific interest due to the advantages from practical point of view:

- relatively easy deposition in thin film form due to the absence of long-range order;
- opportunity to design and modify the basic and application-relevant properties in wide ranges by small compositional changes;
- attractive optical application-relevant characteristics: wide region of optical transparency, high refractive index, photoinduced effects, which are accompanied by considerable changes in the value of the optical constants as a result of the structural changes of these materials.

A great number of amorphous chalcogenide and chalcohalide materials are successfully applied or are of potential interest for optical storage media [1- 4], IR optical windows, sensors [5- 7], non-linear optical elements [8], solid state electrolytes [9], etc.

Complicated glasses of Ge-S system have been extensively studied by many authors [10,11]. Ge- chalcogenides have been recognized as promising material for optical application due to the wide range of transparency [12]. Silver iodide as compound is at the boundary between an ionic crystal and a covalent one. The stable high-temperature form of AgI (α-AgI) is prominent ionic conductor. Complicated chalcogenide glasses with AgI additives are known as good transmitters of electricity [13] but also as photosensitive material suitable for IR optics [14].

Thin film evaporation is problematic when thin film of the respective complicated glass is preparing. Among the sulphur containing chalcogenides GeS_2 belongs to glasses composed of the components with drastically different vapour pressure that reflect to the film structure. The presence of AgI into GeS_2 glassy matrix additionally creates problems with thin film preparation. Optical

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properties investigation of the thin films as an important task for materials preparation and characterization in view of the above indicated applications.

The aim of present work is to prepare thin films of synthesized new vitreous $(GeS_2)_{1-x}(AgI)_x$ materials. We report the compositional dependence of the basic optical properties and band gap, correlation between the composition and the optical properties in terms of the chemically ordered covalent network model.

2. Experimental

Bulk samples from the $(GeS_2)_{1-x}$ $(AgI)_x$ system were prepared by melt-quenching technique, using 5N purity elements of Ge and S, and AgI compound (Alfa Aesar, 99,9%). Evacuated ampoules with the initial substances were heated in a rotated furnace with a constant heating rate of 3 K/min up to a final temperature of 1200 K. Glasses were obtained after quenching in a mixture of water and ice.

The glassy state of the obtained bulk samples and thin films was checked by X-ray diffraction by means of diffractometer TUR – M 61 with CuK_α radiation and Ni filter in the 2θ range from 10° to 60°.

Vacuum installation Leybold LB 370, with a residual gas pressure of 1.33×10^{-4} Pa was used for the preparation of the thin films. The conditions of film preparation were: distance source-substrate - 0.12 m, temperature of the evaporation source - 700-800 K. Thin films were evaporated on glass substrates using the respective bulk composition as a source material. The typical thickness was about 0.5 μm as measured by interference microscope.

The composition of the bulk samples and thin films were investigated by Energy – Dispersive X-ray Analysis (EDAX) using scanning electron microscope (JEOL, model JSM 35 CF with x-ray microanalyser – Tracor Northeren TN – 2000). The standards used are from JEOL Ltd; bias of the probe was 2×10^{-9} A and accelerating voltage – 25 keV. The film surface and morphology in depth was examined by SEM (SEM Hitachi, S 4000).

The normal transmittance-incidence and reflection spectra were measured in the range 300-1200 nm by means of a double-beam spectrophotometer (Perkin Elmer, model Lambda-19).

All optical measurements were performed at room temperature.

3. Results

The results of X-ray diffraction investigation show that thin films under study are amorphous as it is seen in Fig.1. The addition of AgI up to 15 mol.% does not cause appearance of any sharp peaks on difractograms. The SEM investigations confirm the homogeneous and smooth surface of the films without any defects (Fig. 2). The composition of the films is found to be close to the initial bulk composition within the accuracy of the method (±1 mol.%).

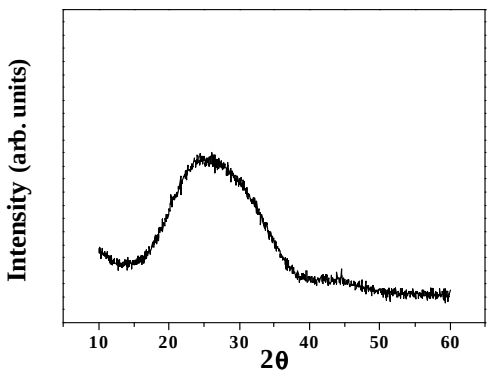

Fig. 1. X-ray diffraction of thin film with composition $Ge_{34}S_{51}(AgI)_{15}$

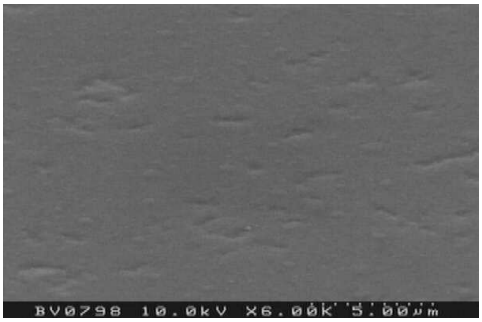

Fig. 2. Electron microscope pattern of thin film with composition $Ge_{34}S_{51}(AgI)_{15}$.

Transmission and reflection spectra of the thin film are measured in the visible and near IR region as a function of the film composition. The spectral dependence of the film transmittance is presented in Fig. 3. The absorption edge shifts continuously to shorter wavelength with increasing AgI content. However, in the films with 20 mol.% AgI the edge is found to be shifted towards longer wavelength. The experimental data indicate that the film transparency changes when AgI is added into the GeS matrix. In the low photon-energy region $400<\alpha<600$ nm a significant decrease in the transparency with AgI content can be easily seen. Films with 20 mol.% AgI show 20 % lower transparency compared with film with 5 mol% AgI while the reflectivity of the films increases, respectively. The recorded reflectivity values at 400 nm (close to absorption edge) are given in Table 1.

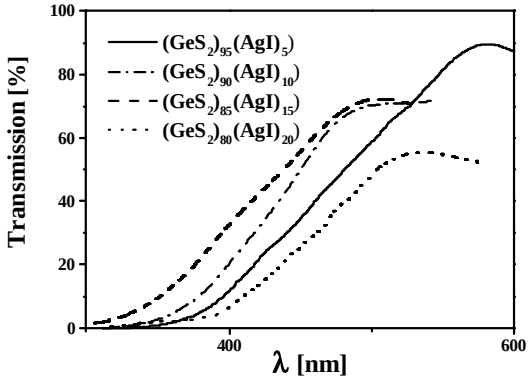

Fig. 3. Spectral dependence of the transmittance of the $(GeS_2)_{1-x}$ $(AgI)_x$ films.

The optical constants of the films can be completely determined when the spectral dependence of the transmittance and reflection are known. If the films are homogeneous, with constant thickness, d, the absorption coefficient can be calculated from the relation: $\alpha=1/d\ [\ln (1-R)^2/T]$, where the thickness, d, the reflectivity, R and the transmission, T, are measured. The optical band gap (E_g) is determined by two methods:

- from the plot $\alpha h\nu=B\ (E_g^{Tauc}-h\nu)^2$ by means of well-known Tauc's procedure
- taking as optical gap, E^{04}, the energy at $\alpha=2\times10^4$ cm^{-1}.

The values obtained are presented in Table 1.

The optical constants of the thin films are calculated from the transmission and reflection spectra, using a computer program Layers [15] based on the Swanepoel method [16] and Fresnell equations. The average coordination number (Z) and the values of basic optical parameters are also listed in Table 1.

Table 1. Optical parameters and E_g of the $(GeS_2)_{1-x}(AgI)_x$ films.

Composition	Z	R_{400} %	k_{400}	n_{400}	E_g^{04} eV	E_g^{Tauc} eV
$Ge_{32}S_{63}(AgI)_5$	2.64	1.3	0.027	2.27	2.48	2.28
$Ge_{30}S_{60}(AgI)_{10}$	2.60	6.1	0.035	2.01	2.44	2.21
$Ge_{28}S_{57}(AgI)_{15}$	2.57	8.8	0.020	2.09	2.38	2.02
$Ge_{26}S_{54}(AgI)_{20}$	2.54	17.2	0.023	2.80	2.27	1.91

4. Discussion

The composition dependence of the optical band gap measured by both methods presented in Fig.4 shows that the values of the optical band gap E_g^{Tauc}, and E_g^{04} decrease as the AgI content increases. The photon energy at $\alpha=10^4$ cm^{-1} is larger that the optical band gap determined by Tauc procedure. The compositional variation of the band gap can be explained in terms of structural arguments.

In the chemical-bond approach to explain the structure and properties of various complicated chalcogenide glasses Bicerano and Ovshinsky [17] have assumed that:

a. atoms of one type are more favourable linked with atoms of a different type ;
b. bonds are formed in sequence of decreasing bond energy until all available vacancies are filled;
c. each atom is coordinated by (8-N) atoms, where N is number of outer shell electrons.

According to this assumption the structure of the investigated films can be presented as consisting of completely cross-linked structural units of GeS_2 and AgI clusters with no excess of sulphur.

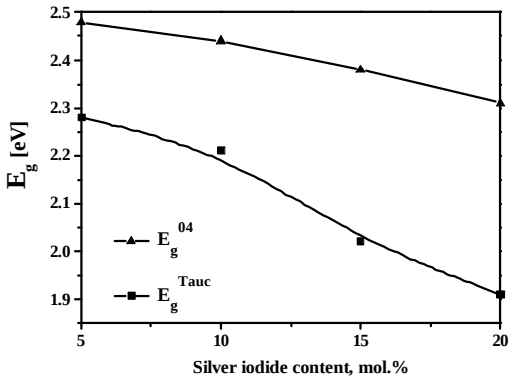

Fig. 4. Compositional dependence of optical band gap (E_g) (the line is drawn to guide the eyes).

The most likely bonds in the films under investigation have bond energy as follows [18]:

Ge – S 551 $kJ.mol^{-1}$
Ag – I 234 $kJ.mol^{-1}$
Ag – S 217 $kJ.mol^{-1}$
S-S 213 $kJ.mol^{-1}$
Ge-Ge 185 $kJ.mol^{-1}$

The bond energies values exclude the application of random covalent network model for structure explanation where Ge-Ge bonds are possible. Bonds such as Ag-S and S-S have also lower possibility of existence due to their lower bond energy. We suggest that most favorable structural units are $GeS_{4/2}$ and AgI. The tetrahedral $GeS_{4/2}$ units are corner bridged with AgI clusters trough three-coordinated silver atoms. The increase in the AgI amount is associated with an increase in the number of AgI clusters and increase in the number of metallic bonds in the film. Thus the lower transparency and bigger reflectivity of films with 20 mol.% AgI can be explained.

The almost linear decrease of the band gap with silver iodide content is attributed also to the structural transformation in the films after AgI introducing. The incorporation of AgI clusters in the Ge-S matrix is connected with an increase of the disorder and an increase in the number of localized states within the band gap. According to Davis and Mott [19] the presence of high density of localized states in the band structure is responsible for lower values of the optical gap. It seems that our experimental data agree well with Davis and Mott suggestion.

5. Conclusions

The investigation of optical properties of $GeS_2)_{1-x}(AgI)x$ thin films shows that optical band gap decreases with the silver iodide introduction into the GeS_2 glassy matrix. The film transparency decreases as silver iodide is introduced due to the stronger metallic character of the chemical bonds. The films structure is most probably built by random distributed $GeS_{4/2}$ and AgI units.

Acknowledgments

This research was supported by the Bulgarian Science Foundation (under contract X - 1404/ 2004 – Young Scientists program, to whom we are deeply indebted.

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