The influence of In on photo-induced properties of Ge-Te-In chalcogenide thin films

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Ligth-induced changes in the optical properties of Ge-Te-In thin films have been studied. The refractive index, the absorption coefficient and the optical band gap of the films have been determined before and after exposure by analyzing the material's transmission spectrum. The thin film's nonuniform thickness was accounted for to accurately determine the optical constants. The variations in the optical parameters and bang gap are discussed due to glass structure reorganization after indium introduction.

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1. Introduction

One of main advantages of the chalcogenide materials is the optical transparency in the wide spectral region, high refraction index and low phonon energy [1]. Chalcogenide glasses based on arsenic alloys show very broad optical window but contain arsenic, a toxic element, and this encourages the scientific work in exploration new arsenic-free chalcogenide systems with good IR transparency. The germanium based chalcogenide glasses are very good alternate of infrared transmitting materials with pass bands out to 20 μm depending on the composition. Binary chalcogenide glasses from the Ge-Te systems are currently used as key phase change materials for optical storage media [2, 3]. The composition variation of chalcogenides by doping of the glasses with elements from III or V groups is an effective approach for directing the electrical and optical properties in a desired direction [4, 5].

The present study deals with investigation of the optical properties of amorphous Ge-Te-In thin films. The correlation between the composition, optical properties and thermo-induced changes of these properties is debated.

2. Experimental

Bulk glasses from $(GeTe_5)_{1-x}In_x$ system (indium content, x, was varied from 0 to 20 mol.%) were prepared by melt quenching method. The elements weighed and sealed in evacuated quartz ampoules were heated in furnace with a constant rate up to T=1200 K. Rapid quenching in ice-water bath was used to obtain the bulk amorphous material.

Thin films were prepared by means of B 30.2 Hochvakuum set-up. The films were deposited onto quartz substrates from the bulk ingots at constant deposition conditions: vacuum pressure 3.10^{-4} Torr; distance source/substrate - 0,12 m; evaporation surface - $1,2.10^{-5}$ m^2.

The films were exposed to a xenon lamp (350 W) to study the light induced changes. The light power was maintained stable with uniform intensity to avoid uncertainty in the total supplied energy by using an aperture (1.10^{-4} m^2). The distance lamp – sample was 0.20 m and the time of exposure was 30 minutes. The transmittance and reflectance spectra of the films were recorded by double beam UV–VIS–NIR spectrophotometer (Jasco V 670) at normal incident condition in the spectral range 700 – 2700 nm. The accuracy of wavelength measurement was ±1 nm. All measurements were performed at ambient temperature. Optical constants such as refractive index, extinction coefficient and absorption coefficient have been obtained from the transmission spectra by using suitable approach [6, 7].

3. Results

The recorded spectra showed good transparency of the films in the entire region of investigation (700 - 2700 nm) before and after irradiation with xenon lamp. The transmission edge of as prepared films varies from 950 nm to 1130 nm depending on the composition. After the illumination the transmission edges shift to the longer wavelength. The film thickness calculated before and after irradiation does not show changes in the values.

The optical constants - refractive index, n, and extinction coefficient, κ, were determined by two methods: using fitting procedure based on Swanepoel method and using Pointwise Unconstrained Minimization Approach (PUMA) [8] developed by research group from Department

of Applied Mathematics, Department of Applied Physics of State University of Campinas and Department of Computer Science of University of São Paulo. The second method allows estimating the thickness and the optical constants of thin films using transmission data. PUMA is written in C language and free for non-commercial use only. In this work, PUMA modified method is used counting the substrate to be suitable for chalcogenide films. The results correspond very well to the results obtained by classical Swanepoel method.

The refractive index values calculated at 1600 nm wavelength as a function of the average coordination number are presented on Fig. 1. The average coordination numbers of the samples calculated according equation given in Ref. [9] are listed in Table 1.

Table 1. Average coordination number and absorption coefficient of ternary $(GeTe_5)_{1-x}In_x$ films – fresh and after irradiation.

Composition	Z	$\alpha .10^3$ cm^{-1} before	$\alpha\ 10^3$ cm^{-1} after
$(GeTe_5)_{100}In_0$	2.333	9.18	8.25
$(GeTe_5)_{95}In_5$	2.339	0.99	0.71
$(GeTe_5)_{90}In_{10}$	2.345	0.85	0.72
$(GeTe_5)_{85}In_{15}$	2.352	6.78	7.23
$(GeTe_5)_{80}In_{20}$	2.360	14.43	16.61

The absorption coefficient of thin films can be obtained using the extinction coefficient, k, and the expression from the equation:

$$\alpha = \frac{4\pi k}{\lambda}$$

The values of the absorption coefficient reported in Table 1 are calculated at 1600 nm wavelength. The tendency in absorption coefficient values is identical to those of the refractive index – a decrease after irradiation is observed in films with lower indium content compare to the as prepared films values. With increasing the In content a regular increase of the absorption coefficient before and after treatment is discovered. The biggest absorption coefficient values have been obtained in the samples with 20 % In.

The average coordination numbers of the samples and the obtained values of the extinction coefficient, k, are listed in Table 2.

Table 2. Average coordination number and the extinction coefficient, k, of ternary $(GeTe_5)_{1-x}In_x$ films – fresh and after irradiation.

Composition	Z	k before	k after
$(GeTe_5)_{100}In_0$	2.333	0.113	0.099
$(GeTe_5)_{95}In_5$	2.339	0.012	0.009
$(GeTe_5)_{90}In_{10}$	2.345	0.011	0.009
$(GeTe_5)_{85}In_{15}$	2.352	0.085	0.092
$(GeTe_5)_{80}In_{20}$	2.360	0.018	0.021

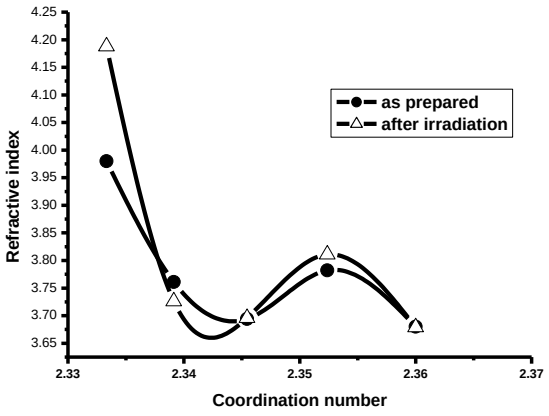

Fig. 1. Dependence of the refractive index from the coordination number.

Using the absorption coefficient, the optical band gap can be calculated by means of Tauc's equation [10]:

$$\alpha h\nu = B\left(h\nu - E_g^{opt}\right)^n$$

where B is a parameter that depends on the transition probability, E_g^{opt} is the optical band gap and n is equal to 2 for indirect transitions. The E_g^{opt} of $(GeTe_5)_{1-x}In_x$ thin films was calculated with an accuracy of ±0.02 eV.

Variations in the band gap values are observed in films with coordination number around 2.34 and 2.36 (Fig.2).

The average coordination numbers of the samples and the calculated values of the optical band gap of ternary system are listed in Table 3.

Table 3. Average coordination number and optical band gap of ternary $(GeTe_5)_{1-x}In_x$ films – fresh and after irradiation.

Composition	Z	E_g^{opt}(eV) before	E_g^{opt}(eV) after
$(GeTe_5)_{100}In_0$	2.333	0.715	0.719
$(GeTe_5)_{95}In_5$	2.339	0.789	0.869
$(GeTe_5)_{90}In_{10}$	2.345	0.822	0.846
$(GeTe_5)_{85}In_{15}$	2.352	0.751	0.747
$(GeTe_5)_{80}In_{20}$	2.360	0.844	0.842

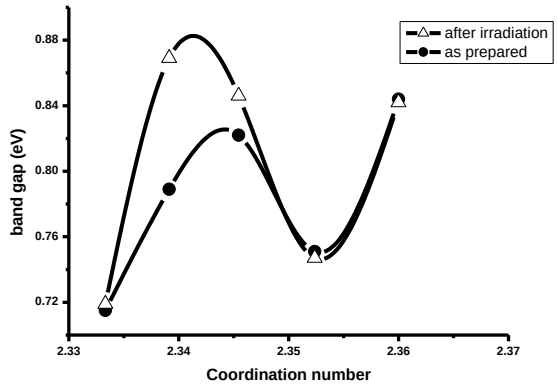

Fig. 2. Dependence of the E_g^{opt} vs. coordination number.

4. Discussion

There is a similarity in the structure of chalcogen elements Se and Te. Each selenium and tellurium atom has six valence electrons, two s and four p electrons. Two of the p electrons contribute to construct a chain structure and the remaining two p electrons become lone-pair electrons. Tellurium is much heavier than selenium, and the strength of the Te-Ge bond is lower than Se-Ge bond so that the optical absorption edge shifts to a higher value compared with Ge-Se-Ga films reported in an earlier work [11]. As a result of this isoelectronic replacement of selenium by tellurium the structure of the film is transformed from a chain-like to trigonal one depending on Te concentration [12]. The decrease of Eg in the samples with higher In content may be caused by the tendency of In atoms to form chemical disordering and to create localized states in the band gap. According to the model of density of states proposed by Mott and Davis [13] the width of the localized states near the mobility edges depends on the degree of the disorder and defects present in the amorphous structure. In particular, it is known that the unsaturated bonds are responsible for the formation of some defects in amorphous solids. Such defects produce localized states in the band gap. The presence of high concentration of localized states in thin films is responsible for low values of optical band gap.

It is known that Ge bonds in chalcogenide glasses are responsible for electron conduction. The small variations in Ge content for the all investigated films may be attributed to the presence of approximately equivalent concentration of covalent bonds in the samples with the same Ge content.

In general, the optical parameters investigated in this work show a tendency of increasing with increase of the indium content as it is shown from the energetic parameter values. Linear increase in E_g^{opt} with increasing indium content has been found with small anomalies of this relation observed around Z = 2.34 - 2.36 for the investigated system.

5. Conclusions

Thin amorphous $GeTe_5In$ films were grown by vacuum thermal deposition from the corresponding bulk glassy materials and characterized with respect to their optical properties. A red shift of the transmission of the films was observed with the addition of In to the glassy matrix.

Pointwise Unconstrained Minimization Approach (PUMA) was applied to estimate the thickness and the optical constants of thin films using transmission data. The introducing of In decreases the refractive index and the extinction coefficient of the system.

A regular increase in the absorption coefficient values before and after treatment is discovered.

The decrease of E_g^{opt} in the samples with higher In content may be caused by the tendency of In atoms to form chemical disordering and to create localized states in the band gap.

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