EFFECT OF THALLIUM ON THE OPTICAL PROPERTIES AND STRUCTURE OF THIN As-S-Tl FILMS[✶]

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Thin films from the system $(As_2S_3)_{100-x}Tl_x$ ($0 \leq x \leq 15$) were deposited by thermal evaporation on Si, graphite and optical glass substrates BK-7. From transmission and reflection measurements of the thin films, the refractive index, n, film thickness, d, optical band gap, E_g^{opt}, oscillator energy, E_o and dispersion energy, E_d, before and after exposure to light were determined. The results for optical parameters were analyzed using the Wemple - Di Domenico single-oscillator model and Lorenc-Lorenc equation. It was found that E_g decreases, while n, E_0 and E_d increase for as deposited films with increasing of Tl concentration passing through a maximum at 6 at. % of Tl. After exposure to light, n, E_0 and E_d increase, and E_g decreases for all compositions investigated. The maximum change in n ($\Delta n = 0.16$ at $\lambda = 632.8$ nm) was observed for thin $As_{38}S_{56}Tl_6$ films. From infrared spectroscopy measurements of bulk glasses and thin films we could conclude that when up to 6 at. % of thallium is introduced, As-S-As chains break and a ternary $TlAsS_2$ compound appears at 10 at% Tl.

1. Introduction

Photoinduced changes in amorphous chalcogenides are an object of systematic investigations with a view of better understanding the mechanism of this phenomenon as well as their practical applications [1, 2]. Chalcogenide glasses are of great interest because of their good infrared transmission and electrical properties which make them potentially useful for application such as threshold switching, memory switching, inorganic photoresists, IR transmission and detection through lenses and optical waveguides [3-6].

The addition of network formers or modifiers in glassy As_2S_3 changes its properties and therefore leads to broadening the scope of their applications [7, 8]. In particular, the glasses from the As-S-Tl system are an object of special interest because higher polarizability of thallium ion leads to significant changes in their optical properties. In several papers, the glasses from the system As_2S_3-Tl_2S-Sb_2S_3 have been studied [9-11] and some data about the influence of Tl on the structure and band gap were presented. It was shown that small amounts of Tl strongly modify the covalent network by creation of dispersed Tl-S weak bonds in the glass. As seen from the infrared and Raman spectra, the existence of ternary $TlAsS_2$ compound is quite possible at higher concentrations of Tl_2S

[8,9]. In our previous investigations of bulk samples and thin films from $(As_2S_3)_{100-x}Tl_x$ and $As_{40-x}S_{60}Tl_x$ systems we have found that the inclusion of thallium in As_2S_3 changes some of its physical properties, for example, transition temperature, microhardness and optical constants [12-14]. Recently, the influence of third compounds added to arsenic chalcogenide glasses on their non-linear properties is discussed and some conclusions for their potential applications in optical switching devices are given [15,16].

The present paper is focused on the determination of the optical parameters (n, k, E_g, E_o and E_d) of thin films from the system $(As_2S_3)_{100-x}Tl_x$ ($0 \leq x \leq 15$) and their changes after exposure to light depending on the thallium concentration. Using IR transmission spectroscopy, some data about the structure of the ternary chalcogenide thin films will be presented and applied for the explanation of photoinduced effects in them.

2. Experimental

Glass samples of the ternary As-S-Tl system were synthesized by melt quenching in a quartz ampoule at 700° C for 12 hours and cooling in ice water. Thin films were deposited on Si, graphite and optical glass substrates BK-7, with a rate of evaporation of about 0.5 nm.s^{-1} in a high vacuum of 6×10^{-6} Torr by thermal evaporation of previously weighed quantities of glasses. The composition of the bulk samples as well as the thin films was determined in a scanning electron microscope with an X-ray microanalyser Jeol Superprobe 733 (Japan) at an electron accelerating voltage of 20 kV and a current of 1.4 nA [7]. Exposure was made by a halogen lamp (20 mWcm^{-2}) in air until saturation time was experimentally established for each composition. The transmittance (T) and reflectance (R) were measured by a Carry 5E UV-VIS-NIR spectrophotometer (USA) in the wavelength range of 350 to 2000 nm to an accuracy of $\Delta T = \pm 0.1$ % and $\Delta R = \pm 0.5$ %. Far-infrared spectra were taken using a FTIR spectrometer (BRUKER IFS 55/FRA 106) in the range of 400-150 cm^{-1} with a 2 cm^{-1} resolution and 64 scans.

3. Results

The results from the X-ray microanalysis (Table 1) showed that the compositions of the bulk samples were very close to the expected one while the composition of thin films demonstrated some discrepancies from the bulk samples due to the process of thermal evaporation.

Table 1. Composition obtained from X-ray microanalysis for bulk samples and thin films deposited.

Composition	Expected composition (at %)	Obtained composition (at %)	
		Bulk samples	Thin films
As_2S_3	$As_{40}S_{60}$	$As_{39.1}S_{58.9}$	$As_{41}S_{59}$
$(As_2S_3)_{97}Tl_3$	$As_{39}S_{58}Tl_3$	$As_{38.8}S_{59.5}Tl_{1.7}$	$As_{43}S_{54.6}Tl_{2.4}$
$(As_2S_3)_{94}Tl_6$	$As_{38}S_{56}Tl_6$	$As_{37}S_{57}Tl_6$	$As_{41}S_{54}Tl_5$
$(As_2S_3)_{90}Tl_{10}$	$As_{36}S_{54}Tl_{10}$	$As_{37.8}S_{53.5}Tl_{8.7}$	$As_{34}S_{53}Tl_{13}$

The spectral behavior of the transmittance of as-deposited and exposed thin As-S-Tl films is shown in Fig. 1a. It could be noticed that for unexposed thin films the absorption edge was shifted to longer wavelengths. An effect of photodarkening was observed for all compounds studied after exposure to light.

The refractive index, n, and the thickness, d, of thin As-S-Tl films was calculated from the interference extremes in transmission spectra using Swanepoel's method [17] and a computer program developed by Konstantinov [18]. The spectral dependence of the refractive index, $n(\lambda)$ of unexposed and exposed thin As-S-Tl films is plotted in Fig. 1b. It was found that the value of the refractive index, n, for as-deposited thin films increases with the increase in the thallium concentration up to 6 at% Tl (Fig. 1b) and a decrease of n for 10 at% Tl was observed. After

exposure to light, n increases for all composition and a maximum change was found for a thin film with a composition of $As_{38}S_{56}Tl_6$ ($\Delta n=0.16$, for $\lambda = 632.8$ nm).

The dispersion of the refractive index was analyzed using the Wemple–Di-Domenico (WDD) model [19,20], which is based on the single-oscillator formula:

$$n^2 = 1 + \frac{E_d E_0}{E_0^2 - (h\nu)^2} \qquad (1)$$

where ($h\nu$) is the photon energy, E_0 is the oscillator energy and E_d is the oscillator strength or dispersion energy. The parameter E_d, which is a measure of the intensity of the inter-band optical transition, does not depend significantly on the band gap. The dispersion energy is related to other physical parameters of material through the empirical formula:

$$E_d = \beta N_c Z_a N_e \qquad (2)$$

where N_c is the effective coordination number of the cation nearest-neighbour to the anion, Z_a is the formal chemical valency of the anion, N_e is the total number of valence electrons per anion, and β is a constant (with a value depending on whether the solid is covalent or ionic, $\beta = 0,26 \pm 0,03$ eV and $\beta = 0,37 \pm 0,04$ eV, respectively). Plotting $(n^2-1)^{-1}$ against $(h\nu)^2$ allows us to determine the oscillator parameters (E_0 and E_d) by fitting of the straight line to the points. The extrapolation for $(h\nu) \to 0$ also gives frequency independent refractive index or so called static refractive index, n_0. The data for single-oscillator parameters are presented in Table 2. The dispersion energy E_d increases with the addition of thallium for unexposed thin films. This would mean that the incorporation of Tl in the glass matrix leads to an increase in one or another parameter in right-hand side of equation (2). As found by Wemple and DiDomeniko [19], the oscillator energy E_0 is closely related to the optical band gap energy E_g. The decrease in the values of E_0 when increasing the thallium concentration shows that the optical gap decreases. After exposure by light both E_d and E_0 increase.
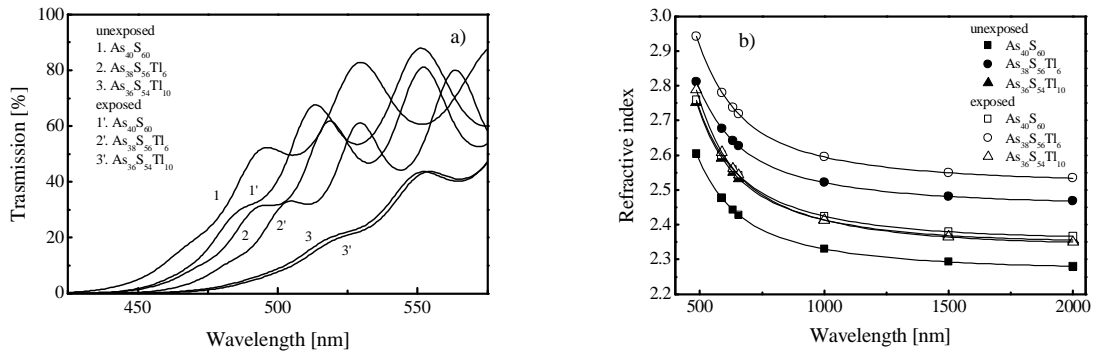

Fig. 1. Optical transmission spectra, T (a) and refractive index, n, vs. wavelength, λ, of unexposed and exposed thin As-S-Tl films.

Table.2. Optical parameters for thin $(As_2S_3)_{100-x}Tl_x$ films ($0 \leq x \leq 15$).

Composition	$\Delta d/d$	Eg (eV)	E_0 (eV)	E_d (eV)	N_c	n_0	$\Delta n/n$	$(\Delta n/n)_{calc}$
As_2S_3 unexposed exposed	1.0%	2.39 2.37	4.77 4.53	19.71 20.44	2.85 2.96	2.27 2.35	3.5%	1.0%
$(As_2S_3)_{97}Tl_3$ unexposed exposed	3 %	2.38 2.37	4.86 4.58	19.88 20.42	2.87 2.96	2.28 2.34	2.6%	3.1 %
$(As_2S_3)_{94}Tl_6$ unexposed exposed	1.3%	2.35 2.34	4.86 4.62	24.37 24.59	3.52 3.56	2.45 2.54	3.3 %	1.2 %
$(As_2S_3)_{90}Tl_{10}$ unexposed exposed	0.3%	2.16 2.14	4.50 4.34	20.72 19.19	3.00 2.79	2.34 2.34	0 %	0.3%

At the high values of the absorption coefficient α, when the condition αd >1 is satisfied, the absorption coefficient, α, should be calculated from the equation:

$$T = (1 - R)^2 \exp(-\alpha d) \tag{3}$$

where T is transmittance, R is reflectance and d is thin film's thickness. Analysis of the strong absorption region ($10^4 \leq \alpha \leq 10^5$) has been carried out using the following well-known quadratic equation or often called Tauc law [21]:

$$(\alpha h\nu) = B(h\nu - E_g^{opt})^2 \tag{4}$$

where B is substance parameter, which depends on electronic transition probability, ($h\nu$) is the photon energy and E_g^{opt} is the so-called Tauc gap. The spectral variation of absorption coefficient plotted as $(\alpha h\nu)^{1/2}$ versus the photon energy ($h\nu$) is shown in Fig. 2.
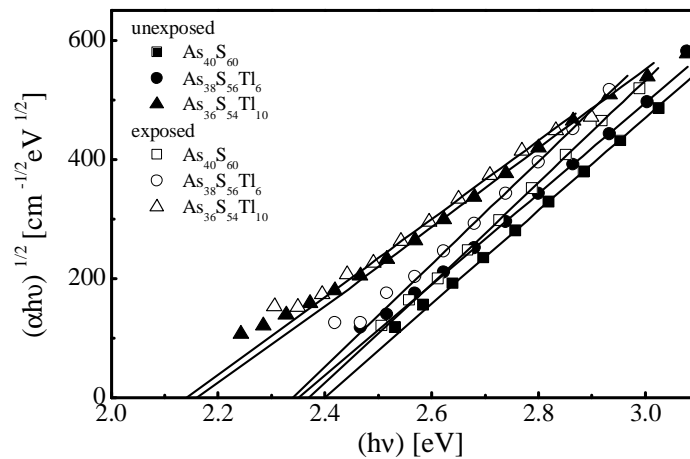

Fig. 2. Plot of $(\alpha h\nu)^2$ versus $h\nu$ for for As-S-Tl films before and after irradiation.
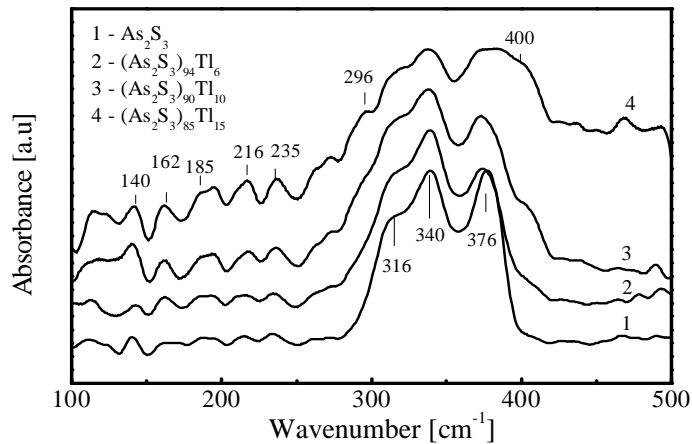

Fig. 3. The infrared transmission spectra of as-deposited thin As-S-Tl films.

The good linear relation of the $(\alpha h\nu)^{1/2}$ vs. ($h\nu$) plot indicates that the absorption mechanism in the As-S-Tl films is non-direct transition [21]. The optical gap E_g^{opt} for non-direct transition can

be obtained from interception $(\alpha h\nu)^{1/2}$ *vs.* $(h\nu)$ with the energy axis at $(\alpha h\nu)^{1/2} = 0$. The variation of E_g^{opt} as a function of Tl content is found to be non-linear and two regions have been observed. In the first region where the thallium concentration is less than 6 at. % , the optical gap dependence on film composition was negligible. The optical gap E_g^{opt} decreases gradually from 2.39 eV for thin $As_{40}S_{60}$ film to 2.35 eV for films with composition $As_{38}S_{56}Tl_6$. For Tl concentration higher than 6 at% we observed a sharp decrease in E_g (down to 2.14 eV for the film composition of $As_{36}S_{54}Tl_{10}$). At the same time, the slope parameter, B, characterizing the absorption edge, decreases from 795 $cm^{-1/2}$ $eV^{-1/2}$ for $As_{40}S_{60}$ to 648 $cm^{-1/2}eV^{-1/2}$ for $As_{36}S_{54}Tl_{10}$, which could be attributed to an increase in the structural disorder in the system.

The infrared spectra of thin films from system $(As_2S_3)_{100-x}Tl_x$ are shown in Fig. 3. The infrared spectrum of thin $As_{40}S_{60}$ film demonstrates three intensity peaks at *ca.* 316, 340 and 376 cm^{-1} in the spectral range 280-400 cm^{-1}. The first two peaks are attributed to asymmetric and symmetric stretching modes of As-S bonds in pyramidal $AsS_{3/2}$ units, respectively, and the last one - to the asymmetric coupling vibration of As-S-As bridges between two AsS_3 pyramids. A weak line at 490 cm^{-1} is observed in the spectra which is attributed to the symmetric stretching vibration of As-S-S-As structural units [22]. Below 250 cm^{-1} numerous different peaks are observed. The bands at 140 and 162 cm^{-1} are due to the asymmetric and symmetric bending modes in pyramids AsS_3, respectively, while at 216 cm^{-1} a ν_1'(As-S-As) mode between the pyramidal AsS_3 units was observed. The peaks at *ca.* 185 and 235 cm^{-1} can be related to the presence of As-As bonds in molecular As_4S_4 structural units. As seen from IR spectra, introducing thallium in As_2S_3 matrix results in progressive changes in the properties of the band at *ca.* 280-400 cm^{-1}. The consequent increase in Tl in thin films leads to the appearance of a new peak at 296 cm^{-1} and the infrared absorption increases at spectral area 390-400 cm^{-1}. The introduction of Tl in As_2S_3 reduces the length of adjacent As-S covalent bonds and is accompanied by local symmetry of pyramidal AsS_3 units. The infrared spectrum of the $TlAsS_2$ crystal observed in [8] includes the following peaks at 280, 310, 330, 380 and 400 cm^{-1}.

4. Discussion

Analyzing the values of the optical parameters n and E_g^{opt} of thin As-S-Tl films it could be concluded that thallium is incorporated into the host matrix with distinct feature dependence on thallium concentration. Depending on the thallium content of the As-S-Tl thin films, two different regions for the values of refractive index, n, and band gap energy, E_g^{opt}, have been observed for the Tl content between 0-10 at. %. The observed non-linear behavior of E_g with Tl concentration was reported for some glasses of the As_2S_3-Tl_2S system [10].

The dependence of the refractive index on the film composition and its changes after exposure by light can be explained on the basis of the Lorentz-Lorentz relationship:

$$\frac{n^2-1}{n^2+1} = \sum N_j \alpha_{p,j} \tag{5}$$

where ε_0 is the vacuum permittivity, N_j is the number of polarizable units of type j per volume unit, with polarizability $\alpha_{p;j}$ and n is the static refractive index, n_0 for $h\nu \rightarrow 0$. The increase in n for thin As-S-Tl films with the increase in the Tl concentration could be explained with the fact that the introduction of Tl cations in the glass matrix of As_2S_3 changes the number of polarizable units and/or new units with higher polarizability are created. Assuming that the lateral dimensions of the film are fixed by the glass substrate and that the density change affects only the number of polarizable units N_j per unit volume and their polarizability $\alpha_{p;j}$ we differentiate eq. (5) with respect to the film thickness, d and the following equation was obtained for the relative changes of the refractive index, $\Delta n/n$ and thickness $\Delta d/d$ after illumination with light:

$$\frac{\Delta n}{n}\left(\frac{d}{\Delta d}\right)^{-1} = \frac{1/6(n^2+2)(n^2-1)}{n^2} \tag{6}$$

From the calculated values for $\Delta d/d$ and eq.(6) we obtained the values $(\Delta n/n)_{calc.}$ listed in Table 2. The difference between the experimental values for the relative changes of n_0 and those derived from eq.(6) indicates that less than 30% of the refractive index change is caused by thickness decrease. This result suggests notable changes in the effective polarizability of the material occurs as arrangement of the bonds after exposure by light.

It was observed that the refractive index, n, the dispersion energy, E_d and the effective coordination number of the cation nearest-neighbour to the anion, N_c have similar behavior depending on the composition of thin As-S-Tl films. The EXAFS [11] of crystalline and amorphous As_2S_3-Tl_2S compounds shows that the increase in the content of Tl_2S reduces the number of nearest and next-nearest neighbours. It could be reasonable to assume that adding thallium affected the cation coordination, as proposed as an explanation for the case of thin films from systems As-S-Ag [23] and As-Se-Cu [24]. Despite the changes of the cation coordination, two things were taken into account. The Tl-S bonds are more ionic and that is why a change in β towards to smaller ionic values takes place. Also, the ionic character of Tl – S bonds should reduce the values of N_e due to the more pronounced s-p splitting in the ionic materials.

The calculated values for E_0 of thin As_2S_3 films is in good agreement with the values found by Tanaka ($E_0 = 4.7$ eV) [25]. As was known, the oscillator energy E_0 seems to vary proportionally to the optical gap. For the calculated values of E_0 and E_g^{opt} a similar dependence has been observed. Both E_g^{opt} and E_0 decrease with increasing the thallium content (see Table 2). It was found that a correspondence exists between E_0 and E_g^{opt} ($E_0 \approx 2E_g^{opt}$) in the amorphous materials. For the system studied, the ratio E_0/E_g^{opt} is between 2-2.1 for all compositions. As was shown, the average bond strength decreases for As-Se-Tl glasses due to the lower binding energy of As-As and Tl-Tl bonds [26]. Furthermore, for As-S-Tl system, a decrease in in E_g^{opt} should be expected with the increase in thallium content which could be explained by the fact that the binding energies of Tl - S, As – As, Tl – As and Tl – Tl bonds should be lower than the As - S and S – S bonds. Therefore, this finding leads to a significantly smaller energy splitting between the states of the valence and conduction bands. The slope parameter B in eq. (4) is assumed to be an indicator of the degree of structural randomness of amorphous semiconductors and could be related to the localized-state tail width ΔE ($B \sim 1/\Delta E$) [27]. The decrease in in the values of B with the increase in the Tl content clearly indicates that the introduction of thallium increases the structural disorder and new localized states in the band gap are created.

The role of thallium as a glass modifier or maybe its role as depolymerizer is evident from the infrared spectra. The structural investigations of as-deposited stoichometric As_2S_3 thin films suggest that these films consist of As_4S_6 molecular spheres, molecular As_4S_4 units or combination from As_2S_3, As_4S_3, As_4S_4, As_4 and chains/or rings S_n (n =1-8). Therefore, as-deposited As_2S_3 films consist of clusters with heteropolar (As-S) and homopolar (As-As and S-S) bonds [28]. According to some authors [8,11], the addition of Tl in arsenic sulfide is expected to create Tl–S bonds by breaking some As-S-As bridges. Because of the more ionic character of Tl - S bonds compared to the As-S bonds, two types of S atoms must be distinguished: the bridging sulfur atoms occurring in As-S_b-As bridges and non-bridging sulfur atoms in As-S_{nb}-Tl bridges. The As-S_{nb} bonds are shorter than As-S_b bonds. This fact leads to splitting of asymmetric stretching mode of AsS_3 pyramids at ca. 310 cm^{-1} and its degeneracy of two modes at 296 and 310 cm^{-1}. Arising of absorption at 390-400 cm^{-1} for thin films with Tl above 6 at.% could be proposed existence structure units of ternary compound $TlAsS_2$ in glass network of thin film with composition $As_{36}S_{54}Tl_{10}$ [8]. This finding in changes in structure could be explain observed dependence in optical parameters n, E_d, E_g^{opt} from composition of thin films. The thin films with thallium concentration below 6 at % Tl atoms breaks glass network and charged As-S_{nb} δ-Tl δ+ are created. Above that concentration we can propose that ternary compound $TlAsS_2$ appears.

5. Conclusions

Bulk samples from the system As-S-Tl with controlled by X-ray microanalysis Tl content were synthesized in a wide range of concentrations. The bulk samples were subjected to X-ray and electron diffraction analysis, which confirmed that only the amorphous phase was present. The

optical properties of as-deposited amorphous $(As_2S_3)_{100-x}Tl_x$ films ($0 \leq x \leq 15$) deposited by thermal evaporation, have been determined from the transmission and reflectance spectra. It was found that the refractive index increases with increasing Tl content in the films. The compositional dependence n was attributed to changes in the bond types and polarizability.

It was found that the dispersion parameter, Ed, increases with the increase in the Tl concentration. According to the model suggested by Wemple, it has been inferred that the increase in E_d points towards an increase in the interaction between the structural layers, hence leading to an increase in the effective coordination number, N_c. It was found that E_g decreases, while n, E_0 and E_d increase for as deposited films with increasing of Tl concentration passing through a maximum at 6 at. % of Tl. After exposure to light n, E_0 and E_d increase, and E_g decreases for all compositions investigated. The maximum change in n ($\Delta n = 0.16$ at $\lambda = 632.8$ nm) was observed for thin $As_{38}S_{56}Tl_6$ films. From infrared spectroscopy measurements of bulk glasses and thin films we could conclude that if up to 6 at. % of thallium is introduced, As-S-As chains break and a ternary $TlAsS_2$ compound appears at 10 at% Tl. The correspondence between E_o and E_g is apparent and is expressed functionally as $E_o = 2.1 E_g$.

The presence of high concentration of localized states in the band structure is responsible for the essential narrowing of the optical band-gap in the case of the amorphous chalcogenide films. The decrease in the optical band-gap may be explained on the basis of the defects introduced in the system due to Tl incorporation.

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