Auger-electron spectroscopy investigation of thin Ag-As-S-Se films

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Abstract. The photoinduced changes in the refractive index and optical band-gap of thin As32S34Se34 films photodoped with silver were studied using spectrophotometric methods. The compositional profile of the films was revealed by means of Auger-electron spectroscopy.

1. Introduction
Photodoping of metals into chalcogenide glasses has been of continued interest [1-4] since the first report on the phenomenon in 1924 [5] due to the possibility of its practical application in grey-scale lithography for MEMS [6], photovoltaic cells [7], etc. Industrial applications require that the photodoped layers possess reproducible properties – optical, electrical, mechanical. Reasonably, the reproducibility of the optical properties demands optical homogeneity of the films, which is closely related to the uniform distribution of the metal into the chalcogenide layer. Few papers dealing with the metal distribution in photodoped chalcogenide films have been published [1, 8-9].

We report the results from our study on the optical properties of very thin (0.12 µm) As32S34Se34 films photodoped with silver. Investigations of such thin photodoped chalcogenide layers have not been reported earlier. The claim for compositional homogeneity (i.e. uniform elemental distribution in the depth of the layers) of our films was supported by Auger-electron spectroscopy (AES) profiles.

2. Experimental
Powdered bulk glass of composition As32S34Se34 was placed into a Mo crucible wherefrom thermally evaporated at room temperature under vacuum of 3×10⁻³ Pa. Thin chalcogenide films were deposited in the same vacuum cycle onto bare optical BK-7 glass and Si substrates and onto preliminarily sputtered Ag layers. Optical transmission and reflection measurements in the spectral range 400-2000 nm were carried out by a UV–VIS–NIR spectrophotometer (Cary 05E, USA) both prior to and following illumination of the mono - (chalcogenide) and double layered (chalcogenide/Ag) structures. The samples were exposed to a halogen lamp (20 mW/cm²) for 30 min. The illumination of the double layered structure was conducted through the chalcogenide side until the silver layer (with thickness 17 nm) was consumed.

The optical constants – linear refractive index, \(n\), and extinction coefficient, \(k\) – and the thickness of the films, \(d\), were determined by spectrophotometric measurements. Since the thickness of the layers was 120 nm, the number of interference extrema in the transmittance spectra was insufficient to

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allow application of the envelope method [10]. Hence, double TR methods [11], as described elsewhere [12], were applied. The program used to calculate \( n \) can determine it to an accuracy better than 3% in the transparent region (where \( d/\lambda < 0.3 \)) for an experimental inaccuracy of ±0.1% and ±0.5% in transmittance and reflectance, respectively [13].

The absorption coefficient, \( \alpha \), of the films was calculated from the relation \( \alpha = 4\pi k/\lambda \), where \( \lambda \) is the wavelength. The optical band gap, \( E_{g}^{\text{opt}} \), for direct transitions was derived by Tauc’s law [14]:

\[
(\alpha h\omega)^{1/2} = B(h\omega - E_{g}^{\text{opt}}),
\]

where \( h\omega \) is the photon energy and \( B \), a factor inversely proportional to the localized state bands.

The Auger analysis was implemented by a Riber’s ASC 2000 microprobe at normal incidence of the primary electron beam with energy 3 keV. The elemental composition of the sample’s surface was determined from the registered differentiated Auger-spectra. Ar⁺ ion sputtering was used to measure the elemental depth distribution. A detailed description of the analysis was published in [9].

### 3. Results and discussion

Figure 1 shows the transmittance and reflectance spectra of a double layered As\(_{32}\)S\(_{34}\)Se\(_{34}\)/Ag structure and a Ag-photodoped As\(_{32}\)S\(_{34}\)Se\(_{34}\) layer.

As seen in figure 1a, prior to illumination we have a double layered structure for which the transmittance (curve 3) is below 50% and the reflectance from the glass substrate side (i.e. from the metal layer side) is higher that that from the chalcogenide film side. Upon light exposure, photodiffusion of silver is initiated and eventually a homogenous Ag-doped chalcogenide layer is produced. The transmittance of such a layer (curve 3, figure 1b) in the interference maximum is close toh that of the substrate used and the reflectance in the spectral region of material’s transparency is identical from both the film and substrate sides.

Following the above described procedure for determination of the optical properties, the refractive index and extinction coefficient were calculated and, thence, the optical band-gap was derived. Figure 2 presents the refractive index dispersion for As\(_{32}\)S\(_{34}\)Se\(_{34}\) – undoped and silver doped. Table 1 provides the exact values of \( d, n \) and \( E_{g}^{\text{opt}} \).

It is seen both in figure 2 and table 1 that the refractive index of the layers of the composition studied is almost not influenced by the exposure In fact, the relative photoinduced refractive index increase (1.6%) may be within the accuracy of the method applied for calculation of \( n \). The presence of silver, on the other hand, could increase the refractive index by 11%. The values of \( n \) calculated for the thin films are close to those previously published for 1 µm-layers [15]. Silver dissolution could also be related to the expansion of the film – the thickness of the photodoped layer is more than 6% higher than that of the silver-free one. The reduction of the optical band-gap following silver photodissolution.
is up to 15% and could be related to an increase in the density of the localized states. Our results are in agreement with those obtained for 0.8 µm films from the system Ag/As₃₃S₃₃.₅Se₃₃.₅ (for silver concentration of 25 at.%) published in [4].

Table 1. Optical properties of thin Ag-As-S-Se films; the relative increase of the refractive index in comparison to that of the unexposed, undoped layer of the relevant composition is given in the parentheses.

| Composition     | d, nm | n at 1.55 µm | E_g, eV |
|-----------------|-------|--------------|--------|
| As₁₂S₃₄Se₃₄ un  | 125   | 2.44         | 2.0    |
| exp             | 126   | 2.48 (1.6%)  | 2.0    |
| Ag              | 133   | 2.71 (11%)   | 1.7    |

Figure 3 presents Auger profiles of the undoped and silver-doped As-S-Se layers. The AES profiles reveal uniform distribution of all the elements in the depth of both undoped and silver doped chalcogenide films (figure 3a, c). It should be mentioned, however, that the methods of Auger profiling for the layer of As₃₂S₃₄Se₃₄ and Ag-As₃₂S₃₄Se₃₄ differ from one another. It was found that the analyzing electron beam induced additional silver diffusion into the sample of As₃₂S₃₄Se₃₄ composition. It is seen in figure 3b that for electron bombardment time of 10 minutes the Auger signal originating from silver increases by a factor of two compared to that at the beginning of the analysis. This is known as “electron-induced chemical modification”, which was reported for Ag-Ge(As)-S(Se) glasses [16]. The process could be explained by migration of positively charged silver ions from the non-irradiated parts of the sample in direction to the negatively charged irradiated region. Following these considerations, it becomes clear that the time of electron-beam interaction with matter should be reduced to less than 5 minutes and, consequently, the conventional approach of simultaneously

Figure 2. Refractive index dispersion of thin As₃₂S₃₄Se₃₄ as-deposited undoped (1), undoped exposed (2) and Ag-doped films (3); the values derived from the experimental data (represented by symbols) were fitted by the Sellmayer’s equation (solid lines).

Figure 3. Auger profiles of thin undoped (a) and silver doped As₃₂S₃₄Se₃₄ films obtained by conventional AES analysis (a, b) and crater-edge profiling (c).
analyzing and etching the sample (which requires time of approximately 30 min) appears to be inapplicable to silver doped films. Instead, crater-edge profiling (figure 4) was utilized. The latter approach consists in etching a crater in the studied sample and successively scanning the fabricated edge by an electron beam. Thus, the irradiation duration of each spot to be scanned is reduced to less than 1.5 min and accumulation of silver is prevented. On the other hand, a distortion of the Auger results could arise from preferential sputtering of any of the elements. Following ion bombardment, an “altered layer” is produced at the surface of the film with different composition than that in the depth. Since the thickness of the altered layer is much smaller than the thickness of the whole film [17], our conclusion for homogeneity remains correct.

4. Conclusions
Thin films (~120 nm) of composition As$_{32}$S$_{34}$Se$_{34}$ were produced and photoinduced diffusion of silver was performed. The reflectance spectra reveal no perceptible inhomogeneity of the photodoped layer. It is shown that the refractive index of the latter is up to 11% higher than that of the undoped films. Auger-electron spectroscopy profiles support our assumption that silver has been uniformly distributed in the chalcogenide films.

References
[1] Kalyva M, Siokou A, Yannopoulos S N, Wágner T, Orava J and Frumar M 2009 *J. Non-Cryst. Solids* **355** 1844
[2] Kovalskiy A, Jain H and Mitkova M 2009 *J. Non-Cryst. Solids* **355** 1924
[3] Yeo J B, Yun S D, Kim T W and Lee H Y 2008 *J. Non-Cryst. Solids* **354** 5343
[4] Krbal M, Wágner T, Vlček Mil, Vlček Mir and Frumar M 2006 *J. Non-Cryst. Solids* **352** 2662
[5] Freundlich H and Nathansohn M 1921 *Koll. Zeitschr.* **29** 16
[6] Kovalskiy A, Cech J, Tan C L, Heffner W R, Miller E, Waits C M, Dubey M, Churaman W, Vlček M and Jain H 2009 *Proc. SPIE* **7273** p 72734A
[7] Yoshida N, Harada H and Tanaka K 1997 *Solid State Ionics* **95** 323
[8] Tomova R, Spasov G, Stoycheva-Topalova R and Buroff A 2000 *J. Non-Cryst. Solids* **266-269** 985
[9] Tomova R, Spasov G, Stoycheva-Topalova R and Buroff A 2004 *J. Non-Cryst. Solids* **338-340** 582
[10] Swanepoel R 1983 *J. Phys. E Sci. Instrum.* **16** 1214
[11] Abeles F and Theye M 1996 *Surf. Sci.* **5** 325
[12] Tasseva J, Todorov R and Petkov K 2005 *Nanosciences & Nanotechnologies* **5** ed E Balabanova and I Dragieva (Sofia: Heron Press) p 81
[13] Konstantinov I, Babeva Tz and Kitova S 1998 *Appl. Opt.* **37** 4260
[14] Tauc J 1974 *Amorphious and liquid semiconductors* (New York: Plenum Press)
[15] Tasseva J, Todorov R and Petkov K 2009 *Optoelectron. Adv. Mater.* **11** 1257
[16] Yoshida N and Tanaka K 1997 *J. Non-Cryst. Solids* **210** 119
[17] Pamler W and Röll K 1983 *Surf. Interface Anal.* **5** 105