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ELLIPSOMETRIC STUDIES OF PHOTOINDUCED CHANGES OF OPTICAL CONSTANTS IN As-Se CHALCOGENIDE

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Abstract. Chalcogenide materials have outstanding optical properties that made them very attractive for memory storage devices, fiber and integrated optics sensors, IR amplifiers and laser sources. The measurements of their optical have encountered several investigations by means of optical transmission technique. However, this technique has limited applications for high values of the absorption coefficient. The ellipsometric method used by us removes this deficiency because it measures the light reflected from samples. The obtained experimental results are fitted by specific ellipsometric models. The obtained optical photoinduced change values in the transparence band gap are in concordance with the measured values obtained from the ellipsometric studies.

Key words: ellipsometry, optical constants, chalcogenide, optical sensor.

1. INTRODUCTION

Chalcogenide materials, including ChG's have been extensively studied over the past 50 years. Most of the data published to date has focused on amorphous (a-) Se, amorphous or crystalline (c-) As_2S_3 or As_2Se_3 [1–2]. To our knowledge, studies relating the variation in chemical compositional to corresponding physical property variation, which specifically examines such changes to linear and nonlinear optical properties, has started to be wide researched [3–4]. Along with the growing interest in these materials for optoelectronic applications comes a need to understand any modification or variation in these properties resulting from their transformation from bulk material, to thin film form [5–6]. Despite the development of numerous models, the underlying structural or electronic phenomena taking place during photo-induced processes are still under research studies [6–7]. As of today, no one model has been able to account for all modifications taking place in these materials [7–8]. Although recent research on the subject has been abundant, most particularly in As_2Se_3 glasses, these studies usually were focusing either on the bulk or the thin films but rarely proposing a systematic comparison between these materials [9–10]. The ellipsometric methods are fast, non-destructive and very sensitive to the presence of surface inclusions and they provide higher accuracy for determination of the refractive index and thickness of thin layers in comparison with the spectrophotometric methods [11–12, 13]. Changes in optical properties and photoinduced structural changes were observed in various films and massive amorphous chalcogenide materials [14–15, 16]. Depending on the experimental conditions and the nature of the changes, they could be reversible, partially reversible or non-reversible. So far there have been proposed several models partly explain the experimental data obtained on chalcogenide glasses. Non-reversible changes can occur in many chalcogenide systems. Reversible changes are typically seen in theheat-treated amorphous layer, as well as in the bulk amorphous materials, also heat-treated. Reversible changes induced by the irradiation of the material may be removed at temperatures in the vicinity of the softening temperature. In this way, in this paper we report the use of ellipsometric method regarding the comparison of the obtained results with the transmittance measurements.

2. PREPARATION OF HIGH OPTICAL QUALITY As-Se THIN FILMS

Bulk chalcogenide glasses were synthesized using elements As, Se (AsSe and As_4Se_3 composition) in quartz ampoules. Precursor elements were loaded in the ampoule, then the ampoule was evacuated and flame soldered. The temperature was raised slowly to the melting temperature of 870–920 °C. The maximum temperature of the liquid melt mixture was maintained for 24 hours along with the rotation about its axis and vibration in order to obtain a homogeneous mass. Next, the ampoule was cooled suddenly by taking it out of the furnace. Some of the synthesized chalcogenide glasses were cut into square parallel plates with dimensions 10×10×4 mm^3 and polished until they achieved a glossy surface suitable for optical measurements. Thin films were obtained by thermal evaporation in vacuum (5×10^{-6} Torr) [4, 17]. Vacuum thermal evaporation is based on the formation of atomic and molecular flows by heating the source material. The flows travel without collisions from the evaporator to the substrate, where the material condenses to form a thin layer. Shape and reciprocal location of the source and substrate determine the thickness distribution. To obtain high quality thin films a special evaporator was developed, which uses indirect heating. Transparent amorphous films were obtained in the 125 ÷ 500 nm thickness domain on glass substrates. It was established a deviation of films composition from the bulk material used for evaporation. The real composition depends on the technological parameters, especially the evaporation speed. The composition of the current films used for experiments was established by EDX method. The films composition obtained from AsSe bulk was of $As_{46.5}Se_{53.5}$. The films composition obtained for As_4Se_3 bulk was of $As_{54}Se_{46}$. The relaxation of the transmission curves was measured during the illumination using a Laser Power Meter Gentec, SOLO-PE.

3. RESULTS AND DISCUSSION

Before the ellipsometric and transmission measurements an experimental setup was developed in order to illuminate the thin films regarding the comparison of the optical constants as a change between the illuminated thin films and non-illuminated ones, as it shown in the Figure 1. It was used an Stocker Yale, Canada, laser diode, with a wavelength of 670 nm and the power of the laser radiation on the thin films surface was of 100 mW.

Experimental data was fitted with Cauchy model for the transparence domain in order to find the thickness and the illumination process lead to a rise of the thin films thickness and roughness as it is shown in Table 1.

Table 1

Chalcogenide thin films thickness

No.	Thin Film	Thickness, Roughness (nm)	MSE	Best Fit
1	As_4Se_3	346 / 2.1	10.56	250–1700 nm
2	As_4Se_3 – illuminated	364 / 4.6	10.44	600–1700 nm
3	AsSe	803 / 3.7	3.13	250–1700 nm
4	AsSe – illuminated	809/ 4.3	13.84	250–1700 nm

Using the spectroscopic ellipsometric method the thin films deposited on glass substrate (amorphous chalcogenide compound) were measured. The measurements were made in the 300–1700 nm domain at 70^o degree angle with a step of 2 nm and with 50 rev/measurement. The “backside reflection” was removed. The experimental data was fitted with the following models Cauchy, GenOSC. Gauss and PSM0.

It can be observed a heaviness trend of the fitting process following the illumination of thin films that reveal changes in the thin films structure.

Long time period transmittance changes occur in As_4Se_3 is due to photo structural change during the illumination process. In AsSe films the transmittance change is lower than the changes occurred in As_4Se_3.

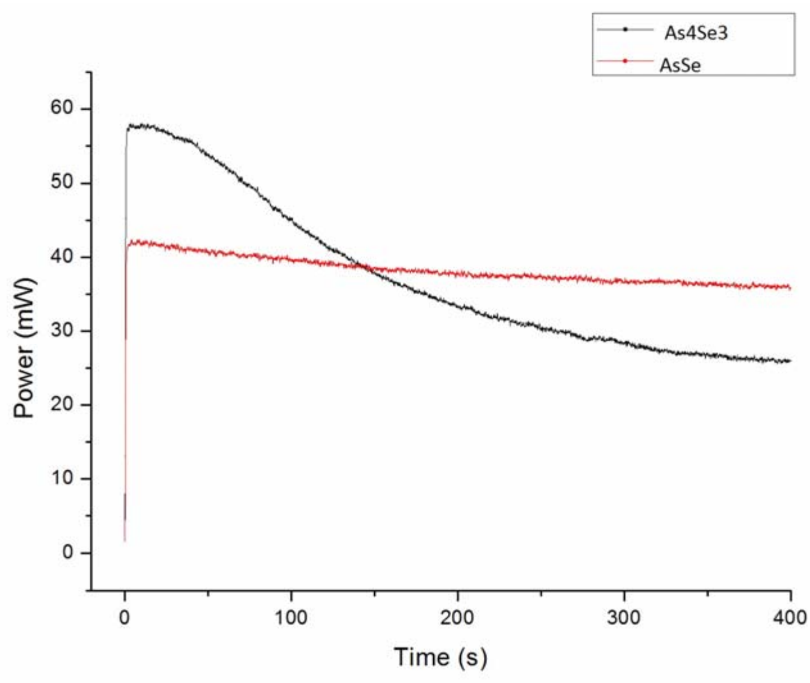

Fig. 1 – Transmittance changes during the 400 s as time of illumination for AsSe and As_4Se_3 films.

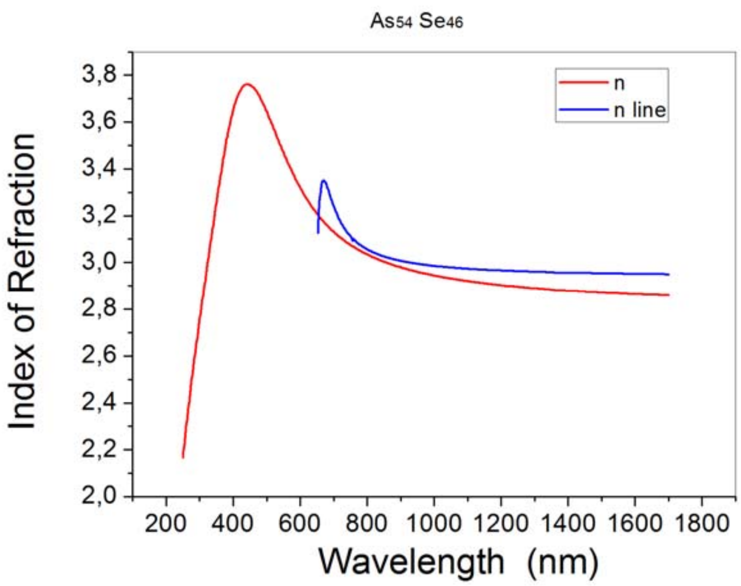

Fig. 2 – Thin film As_4Se_3 index of refraction changes, with (*n*-line) and without illumination (*n*).

The values of refractive index coefficient for films obtained with ellipsometric method from As_4Se_3 bulk are presented in Figure 2. Major changes up to 0.1 are observed in infrared region after the illumination (line). These changes are correlated with the data presented by other authors obtained with optical transmission method. In the short range domain less than 700 nm the refractive index on the contrary is diminished. This result could not be observed by the measurements using the optical transmission method as the light attenuation has a very high value as it can be seen from the Figure 6.

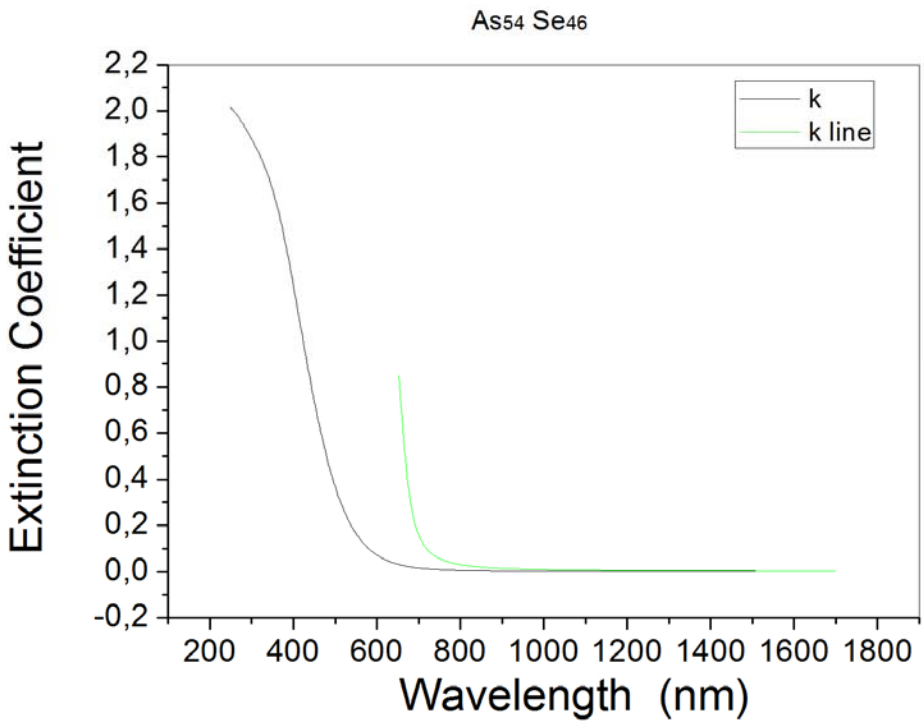

Fig. 3 – Thin film As_4Se_3 extinction coefficient changes, with (line) and without illumination (k).

The extinction coefficient for films obtained from As_4Se_3 bulk material presented in Fig. 3 show a sharp rise for wavelengths less than band gap which is approximately at 600 nm for as-evaporated films. After the illumination (line) a major change of the extinction coefficient occurs. The changes are greater than the changes observed in AsSe films. That is the photoinduced changes of the extinction coefficient and the refractive index coefficient correlated to such changes increase with the increasing content of As in arsenic selenide films.

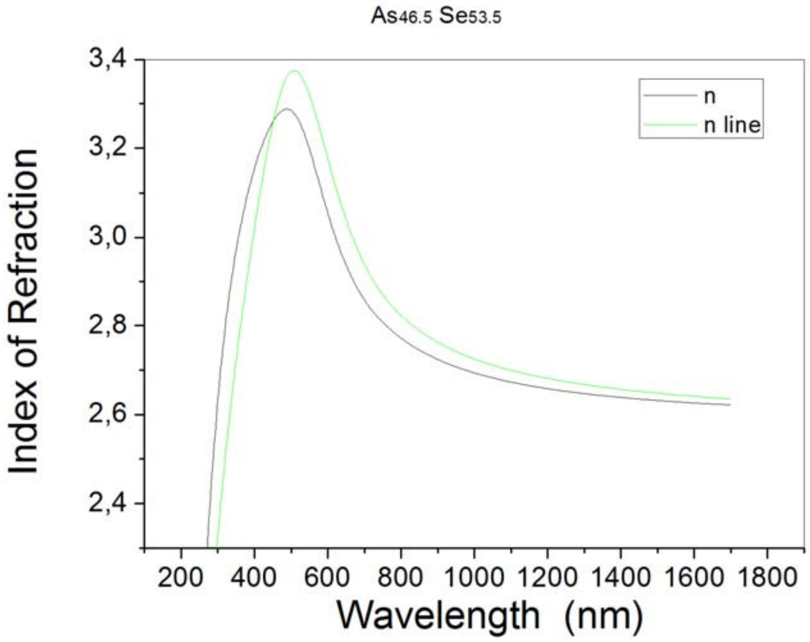

Fig. 4 – AsSe index of refraction changes, with (*n*-line) and without illumination (*n*).

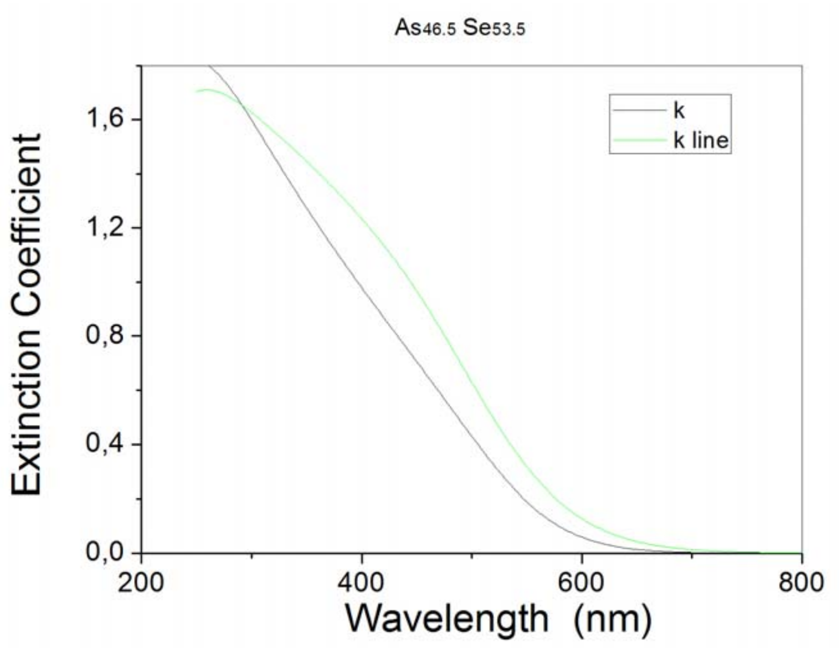

Fig. 5 – AsSe extinction coefficient changes, with (*k*-line) and without illumination (*k*).

For the AsSe compound the measured values of the refractive index are presented in Figure 4. The refractive index in infrared domain increase while in the short range wavelengths, less than 500 nm, the refractive index value decreases after illumination.

The increase of the extinction coefficient after the illumination (line in Fig. 5) means that the transmission is decreased or that the photo darkening phenomenon takes place.

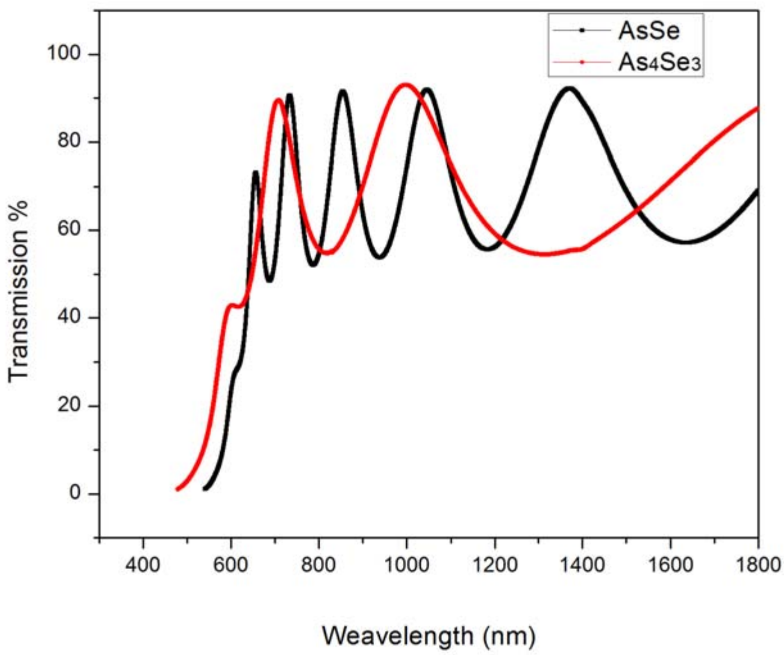

Fig. 6 – Optical transmission changes for As_4Se_3 and AsSe thin films.

Optical transmission curves obtained for the arsenic selenide studied films presented in Fig. 7 show the interference patterns in the infrared range. Transmission peaks is as high as the clear substrate transmission, which prove the high quality without the films scattering. This data can be used for the calculation of refractive index. Low transmission in band gap range of wavelengths (500–600 nm) can be used for the calculation of the extinction coefficient.

4. CONCLUSIONS

A trend of the fitting process provided by the use of spectroscopic ellipsometry method reveal changes in the thin films optical constants. The values of photoinduced changes of the optical constants after illumination were obtained. The changes are higher for films with high content of arsenic.

Ellipsometry method permitted to obtain the optical constants values for the wavelengths where films transmission is low enough. The deduced photoinduced changes are important for plasmonic structure that contains chalcogenide films.

Overall results are important for the development of the structural change models for chalcogenide amorphous material.

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