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ELLIPSOMETRIC INVESTIGATIONS OF a-As_2S_3 THIN FILMS OBTAINED BY RF MAGNETRON SPUTTERING

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In this paper we report the investigation of optical properties of As_2S_3 amorphous chalcogenide thin films. Arsenic trisulfide is well known amorphous material. As_2S_3 thin films have important applications in optoelectronics. The most usual method of fabrication is thermal evaporation in vacuum which is known for deposition ofa-As_2S_3 films with high probability of oxidation in contact with ambient environment. In this paperwe studied the optical properties of As_2S_3 thin films obtained by a different method as RF magnetron sputtering. Ellipsometric measurements permit the studies of the film optical constants in high absorption spectral domain which give the possibility to determine the own oscillator frequencies. Fitting model based on the well-established exponential absorption inside the band gap tail and Tauc fundamental absorption was used. Thin films of a-As_2S_3 comparison were made on Si and glass substrates.

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1. Introduction

The field of chalcogenide materials have been extensively studied over the past 40 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]. Despite the development of numerous models, the underlying structural or electronic phenomena taking place during photo-induced processes are still under research studies [5-6]. As of today, not one model has been able to account for all modifications taking place in these materials [6-7].

Although recent research on the subject has been abundant, most particularly in As_2S_3 glasses, these studies usually were focusing either on the bulk or the thin films but rarely proposing a systematic comparison between these materials [8-9].

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 [10-12]. Changes in optical properties andphoto-induced structural changes were observed in various films and massive amorphous chalcogenide materials [13-18]. Depending on the experimental conditions and the nature of the changes [19-23], they could be reversible, partially reversible or non-reversible. So

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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 the heat-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. Also it is well known that chalcogenide materials present a high interest in the field of optical integrated components development [8, 24-27]. In this way, in this paper we report the use of ellipsometric method regarding the comparison of the obtained results.

2. Preparation of As-S Thin films

Bulk chalcogenide glasses were synthesized using elements As, S 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 homogeneous mass. The As_2S_3 target was realized by melting the pre-synthesized arsenic trisulfide compound in evacuated up to $5x10^{-6}$ Torr fused silica ampoules. Next, the ampoule was quenching (fast cooling) suddenly by taking it out of the furnace. Re-melting occurs in vacuum in order to obtain 2 inch diameter bars of As_2S_3.Disks with the diameter of 50 mm and 3 mm thickness (Figure.1.) for target realization were catted in lab (not commercial one) from cylindrical bulk material obtained. Plasma was initiated in argon gas flow at the pressure of 5-10 mTorr. The sample was placed at a distance of 7cm from the target. The average deposition time was 60 min for the As_2S_3/Glass thin film and of 180 min for the As_2S_3/Si thin film. Thin films with the thicknesses of 350-1000 nm were obtained from these As_2S_3 targets. Refractive index n, extinction coefficient k, and the thickness of the films, were measured by spectroscopic ellipsometry in the wavelength range of 190-2100 nm (UVISEL, Horiba Jobin Yvon, France).

Fig.1. Target view.

3. Results and discussion

The thin films investigation was realized by the use of electronic microscope Quanta Inspect F50 with electron gun, with field emission - FEG (field emission gun) having the 1.2 nm resolution and X-ray spectrometer dispersive in energy (EDS) with resolution at MnK of 133 eV.

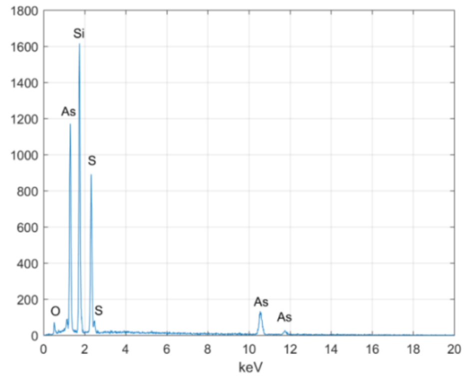
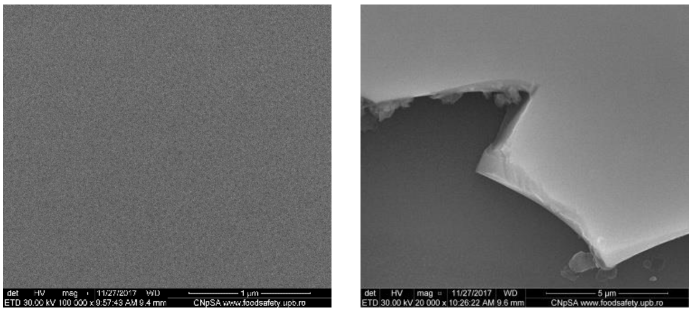


Fig.2. EDS elements presence.

Investigation of elements presenceis shown in the table below:

Table 1. Elements percentage

Element	Weight %	Atomic %	Net Int.	K Ratio
O	2.01	4.47	2.51	0.003
Si	33.3	42.29	348.11	0.1464
S	35.29	39.24	330.61	0.1563
As	29.4	13.99	101.95	0.2771



(a) *(b)*

Fig.3. (a) Amorphous surface view As2S3/Si; (b) Section view of As2S3/Si.

Spectroscopic ellipsometry and reflectivity measurements are used for determination of As_2S_3 film thickness. For determination of the optical properties of the As_2S_3 films, a layer-by-layer growth model was used as presented in Fig. 4.

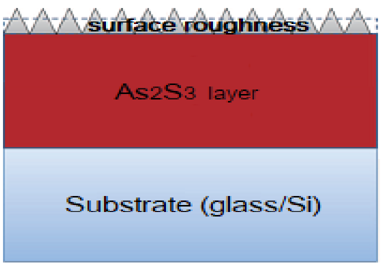


Fig.4. Schematic illustration of 3-layer model for As_2S_3 layer onGlass/Si substrate

We used the UVISEL Spectroscopic Ellipsometer equipment from HORIBA Jobin Yvon in the spectral range 190-2100 nm [28].

All calculations were performed using DeltaPsi vs 2.6 software. Substrate back reflections were eliminated by the use of a regular non-transparent tape.

Experimental data were fitted for the transparence domain in order to find the thickness (Table 2) for both thin films:

Table2. Chalcogenide thin films thickness.

No.	Thin film/Substrate	Thickness	Best fit
1	As_2S_3/Si	1069 nm	190-2100 nm
2	As_2S_3/Glass	366 nm	190-2100 nm

Tan Ψ and cos Δ spectra were modelled until the best fit was obtained (Si and glass).

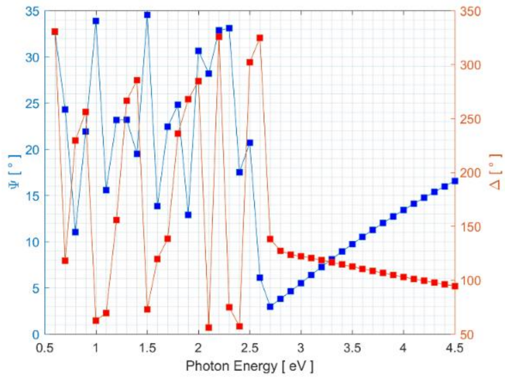


Fig.5. Measured spectroscopic ellipsometry data Ψ and Δ, along with numerical fits from model As_2S_3/Si calculation

Both models for As_2S_3/Si and As_2S_3/Glass had a high quality of fit (Fig. 5 and 6) based on the use of Tauc-Lorentz oscillator.

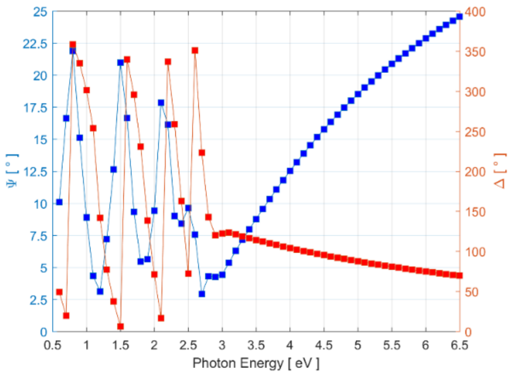


Fig.6.Measured spectroscopic ellipsometry data Ψ and Δ, along with numerical fits from model As_2S_3/Glass calculation

The model consists of a main chalcogenide material layer with a surface roughness layer. The Tauc – Lorentz dispersion law (oscillator) was used for the As_2S_3 layer, while the surface roughness layer was formed by one layer of AsS and voids. The model used is shown in Fig. 7.

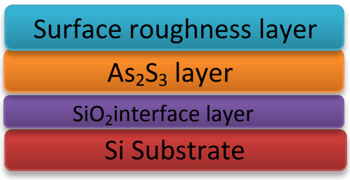


Fig.7.Schematic illustration of 3-layer model for As_2S_3 on Si substrate.

Complex refractive index components (n, k) for As_2S_3/Si, of about 1 μm thick thin film deposited by RF magnetron sputtering on Si substrate, are shown in Fig. 8. The model details of As_2S_3/Si are: thickness: 1069nm ± 10nm, oscillator used: Tauc-Lorentz, number of points: 60, fit quality factor: 9, roughness layer: 2.2nm ± 0.5 nm, band gap: Eg = 1.79 eV.

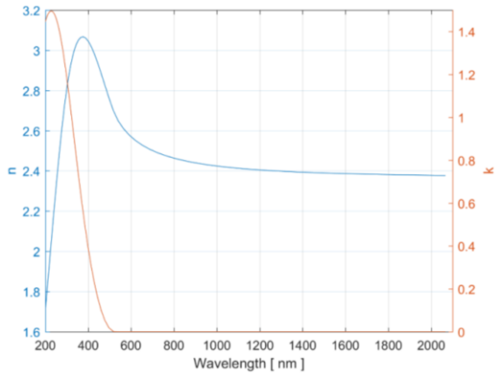


Fig.8.The refractive index and extinction coefficient of magnetron sputtered a-As_2S_3/Si thin film. The thickness of the film was 1069nm ± 10 nm. The measured results were obtained from an ellipsometer within the range of 190-2100 nm (UVISEL, Horiba Jobin Yvon, France).

The model of As_2S_3 deposited by RF magnetron sputtering on Glass substrate is represented in Fig. 9.

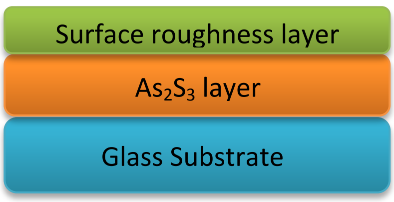


Fig.9.Schematic illustration of 2-layer model for As_2S_3 on Glass substrate.

Refractive index and extinction coefficient for As_2S_3/Glass, of about 350 nm thick thin film deposited by RF magnetron sputtering on glass substrate are shown in Fig. 10. The model details of As_2S_3/Glass are: thickness: 366nm ± 2nm, oscillator used: Tauc-Lorentz, number of points: 60, fit quality factor: 7, band gap: Eg = 2 eV.

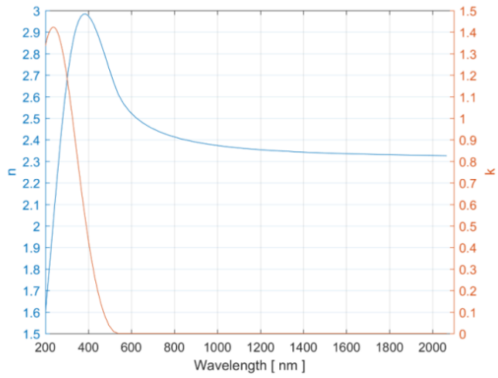


Fig.10. The refractive index and extinction coefficient of magnetron sputtered a-As_2S_3/Glass thin film. The thickness of the film was 366nm ± 2nm. The measured results were obtained from an ellipsometer within the range of 190-2100 nm (UVISEL, Horiba Jobin Yvon, France).

By comparing the results in Figure 8 and 10 it is evident that is no notable difference which denotes the veracity of the spectroscopic ellipsometry method concerning the characterization of optical properties for the amorphous chalcogenide materials.

4. Conclusions

High quality As_2S_3 thin films were synthesized by RF magnetron sputtering.We measured the refractive index and extinction coefficient of a-As_2S_3 thin films deposited on Si and Glass substrates by RF magnetron sputtering using a non-commercial target.

The stoichiometry was correct and the binding energy of the film had no significant amount of O_2 found on the surface. The optical and structural properties agree with previous published results on As_2S_3 chalcogenide materials.

Characterization by scanning electron microscopy showed the percentage of elements presence. Spectroscopic ellipsometry permits the study of the film optical constants in high absorption spectral domain which give the possibility to determine the own oscillator frequencies. However, the uses of fitting models which are presented into ellipsometer data base give enough accuracy. The use of a fitting model based on the well-established exponential absorption inside the band gap tail and Tauc fundamental absorption was a success.

The UVISEL NIR ellipsometer allows the determination of film thickness and optical properties with very high accuracy even where the films have microns thick, and deposited on a transparent substrate.

The comparison of refractive index results for As_2S_3 deposited on Si and Glass substrate reveal no difference which denotes the veracity of the spectroscopic ellipsometry method concerning the characterization of optical properties for the amorphous chalcogenide materials.

Following the successfully realization of RF magnetron sputtered a-As_2S_3 thin films using a non-commercially target, we enlarge the field for more wide and efficient development of integrated optical devices with applications in optoelectronics.

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