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Study of photo- and thermally-induced changes in Ge-As-S thin films by spectroscopic ellipsometry[♣]

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The effect of illumination and post-illumination annealing on the optical properties and thicknesses of thin (~ 150 nm) films of $Ge_{30.8}As_{5.7}S_{63.5}$ and $Ge_{32}As_5S_{63}$ glasses belonging to Ge_2S_3-AsS_3 system was studied by means of spectroscopic ellipsometry in the spectral range 300 - 820 nm. The amorphous films were prepared by thermal evaporation onto glass substrates. The ellipsometric measurements were performed after each technological step, i.e. on the freshly deposited samples and after their UV-illumination and subsequent thermal annealing at a temperature of 350^{o}C. Illumination of the films caused a considerably increase in the film thickness (12-13 %) and a large change in the optical constants. An effect of photo-bleaching was observed; the increase in the optical gap energy E_g was as large as ΔE_g= 240 meV and 400 meV for the $Ge_{30.8}As_{5.7}S_{63.5}$ and $Ge_{32}As_5S_{63}$ films, respectively. Annealing lead to a further increase of the E_g value, by ~100 meV, and to a contraction of the film volume. The observed effects were attributed to photo-induced structural change in the Ge-As-S amorphous network.

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1. Introduction

In certain physical properties of thin chalcogenide films, remarkable photo- and thermally-induced changes can be observed, which can be irreversible or reversible. Studying these phenomena is of great interest for future applications of chalcogenide films as IR transmitting materials [1] and as opto-mechanical devices for nano-technologies [2], etc.

Our previous studies have shown that “giant” photo-induced changes can be provoked in some compositions of the Ge_2S_3-As_2S_3 system [3,4]. According to [5], a change in the optical band gap energy E_g larger than ~200 meV is accepted as “giant”. Also, it has been shown that in films with appropriate compositions from this glassy system, the magnitude of the irreversible photo-induced change increases with decreasing film thickness down to 600 nm [6]. There is still an open question as to the magnitude of the irreversible photo-induced changes, if the film thickness decreases down to ~100 nm.

Here, we present results on the study of the effect of illumination and post-illumination annealing on the optical properties of ~ 150 nm thin films evaporated from $Ge_{30.8}As_{5.7}S_{63.5}$ and $Ge_{32}As_5S_{63}$ glasses belonging to the Ge_2S_3-AsS_3 system, using spectral ellipsometry (SE) measurements. These compositions were chosen because our earlier experiences have shown the most pronounced photo-induced changes for them [3,4]. Spectral ellipsometry was applied as a tool for studying the changes in the optical properties, generated by technological treatments, of the thin films. The photo- and thermally-induced changes can be exquisitely traced, due to the extremely high sensitivity of the ellipsometric parameters to any alteration of the film structure. There are scarce data in the literature concerning the optical properties of ternary chalcogenide thin films.

2. Experimental

Our films were thermally evaporated onto Corning 7059 glass substrates from the previously synthesized $Ge_{30.8}As_{5.7}S_{63.5}$ and $Ge_{32}As_5S_{63}$ glasses. The thickness was controlled by a quartz oscillator, MIKI-FFV. Furthermore, the thickness of these films was more precisely determined from ellipsometric data analysis. For the $Ge_{30.8}As_{5.7}S_{63.5}$ composition, the film thickness was 148.2 nm, while for the $Ge_{32}As_5S_{63}$ film it was 155.6 nm.

The deposited films were exposed to a high pressure Hg lamp (500 W) through an IR cut off filter, for 45 min. The power density was ~160 mW/cm^2. After illumination,

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After each technological step, i.e. deposition, illumination and subsequent thermal annealing, the films were measured using a Rudolf Research ellipsometer, in the spectral region 300-820 nm (4.13–1.51 eV). The accuracy of the polarizer, analyzer and incidence angles was within ±0.01°. Since the glass substrates were about 2 mm thick, with frosted back-side surfaces, the reflection from the substrate back surface was successfully separated by measuring the samples at an angle of light incidence of 50°. The optical parameters, refractive index (*N*), extinction coefficient (*k*), absorption coefficient (α), and optical band gap energy (E_g), and the thicknesses of the films were evaluated from the SE data analysis. The accuracy of the film thickness was ±0.2 nm, while that of the *N* and *k* values was ±0.005.

3. Results and discussion

In Figs. 1(*a*) and 1(*b*), the spectral dependence of the optical constants *N* and *k*, respectively, for films with the two investigated compositions are presented. In general, these films possess good transparency down to 500 nm (Fig. 1*b*), below which the absorption increases. Illumination of the films causes a decrease in both the *N* and *k* values.

After subsequent annealing, the *N* values were as their initial ones, while *k* values showed a weak tendency to further decrease. The observed decrease of *k*, and correspondingly the absorption, in the treated films is in accordance with our previous results [6], where a large enhancement of the transmission by illumination or annealing was registered for $Ge_{32}As_5S_{63}$ films.

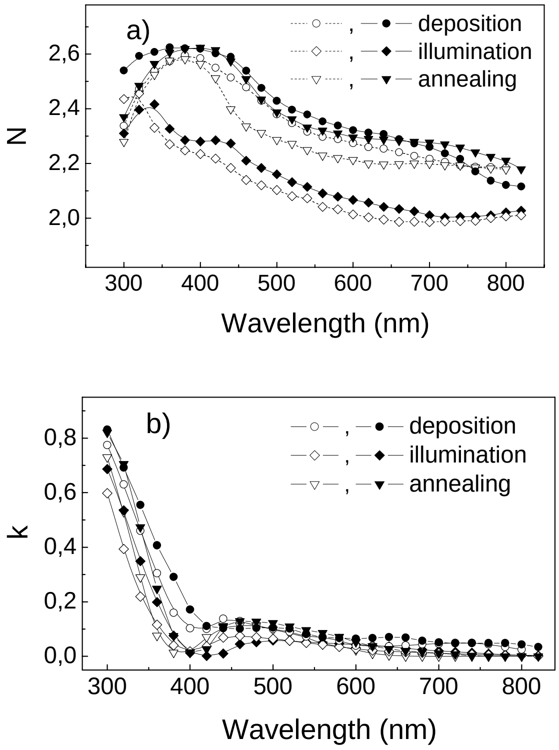


Fig. 1. Dispersion curves of the refractive index N (a) and extinction coefficient k (b) for $Ge_{30.8}As_{5.7}S_{63.5}$ (empty symbols) and $Ge_{32}As_5S_{63}$ (full symbols) thin films, after different technological steps.

The other noticeable effect was the change in the film thickness upon illumination and annealing. The results are summarised in Fig. 2, where the thickness of the films is given after each technological step. In all cases, the thickness of the illuminated films becomes larger. Obviously, during illumination photo-expansion of the film volume occurs and the registered thickness increase is about 12-13 %. After annealing the illuminated films, a contraction of the film volume takes place and, as a result, the film thickness becomes even smaller that that for the as-deposited state. This thermo-contraction is well expressed and is about 14-15 %.

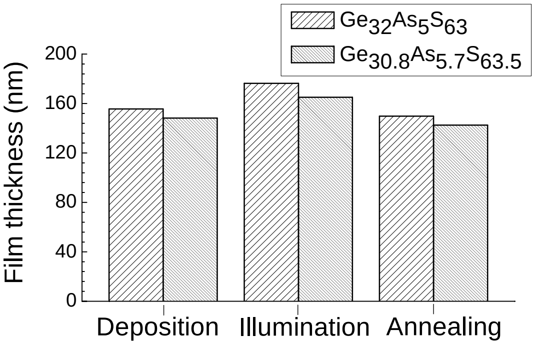
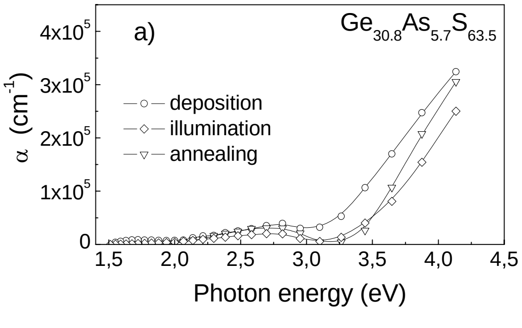


Fig. 2. The thicknesses of $Ge_{30.8}As_{5.7}S_{63.5}$ and $Ge_{32}As_5S_{63}$ thin films, determined after deposition, illumination and post-illumination annealing.

The absorption coefficient α was calculated from the relation $\alpha=4\pi k/\lambda$. In Fig. 3, the obtained values are presented in dependence on the photon energy $h\nu$. A trend of the absorption edge to move toward higher energies (blue shift) by illumination and post-illumination annealing is clearly seen. The optical band gap energy value was elucidated from the corresponding Tauc plot [7] $(\alpha h\nu)^{1/2}$ versus photon energy ($h\nu$), by extrapolation of the linear part of the plot (not shown). The intercept of the line with the energy axis gives the E_g values. These values, obtained with an accuracy of ±0.05 eV, are summarized in Table 1. The different E_g values for both compositions of the as-deposited films are equalized by the treatments, as they increase after illumination and become even larger upon subsequent post-illumination annealing. The increase in the band gap energy shows that illumination causes "giant" photo-bleaching, reflected in a change of E_g as large as ΔE_g =240 meV and 400 meV for the $Ge_{30.8}As_{5.7}S_{63.5}$ and $Ge_{32}As_5S_{63}$ films, respectively. The photo-bleaching is accompanied by a large photo-expansion.



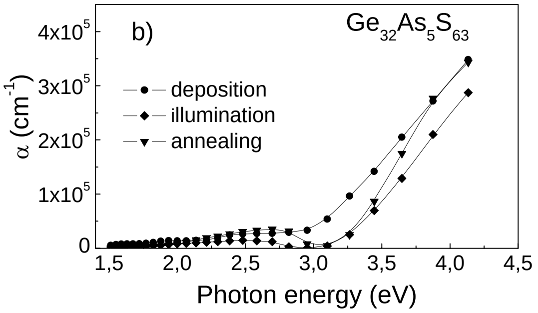


Fig. 3. Absorption coefficient vs. photon energy of $Ge_{30.8}As_{5.7}S_{63.5}$ (a) and $Ge_{32}As_5S_{63}$ (b) thinf ilms after different technological steps.

For comparison purposes, Table 1 also gives the optical constant values at a wavelength of λ=632.8 nm. After illumination, the smaller N value together with the increased film thickness (Fig. 2) are direct evidence of structural changes, due most probably to rearrangement of the chemical bonds leading to an enhancement of the film volume, a lowering of the film density and an increase in the optical band gap energy. Apparently, annealing yields further structural ordering.

Table 1. Optical constants N and k, measured at λ=632.8 nm, and the optical band gap energy E_g of $Ge_{30.8}As_{5.7}S_{63.5}$ and $Ge_{32}As_5S_{63}$ thin films.

Procedure	N	k	E_g (eV)
$Ge_{30.8}As_{5.7}S_{63.5}$			
deposition	2.26	0.04	2.66
illumination	2.00	0.02	2.90
annealing	2.20	0.01	3.07
$Ge_{32}As_5S_{63}$			
deposition	2.31	0.07	2.50
illumination	2.05	0.04	2.90
annealing	2.29	0.03	3.06

It is known that formation of heteropolar bonds in untreated films proceeds under illumination, leading to structural ordering. Consequently, the observed increase in E_g after illumination and post-illumination annealing may be attributed to a decrease in the degree of disorder, which causes a lowering of the defect levels and localized states (unsaturated bonds) in the band gap. The observed decrease in the absorption in the films under illumination and post-illumination annealing supports this suggestion.

The above results show that illumination causes photo-bleaching and photo-induced expansion in the films. Post-illumination annealing leads to a further increase in the optical band gap energies (thermo-bleaching), which is less pronounced than photo-bleaching. Contrary to the effect of illumination, annealing causes a large thermo-contraction of the films.

The observed light-induced decrease of the refractive index (Fig 1 and Table 1), and the increases in film thickness, provide evidence for structural changes in the film volume, causing a reduction in the film density. The volume expansion could be explained in terms of changes in the nearest neighbors' atomic distances, by the formation of heteropolar Ge-S and As-S bonds [8]. These bonds are more energetically favorable than homopolar Ge-Ge, As-As and S-S bonds, existing in the as-deposited films. As a result of the formation of covalent heteropolar bonds, the nearest neighbor atomic distances of Ge-Ge and As-As decrease, simultaneously with an increase in the nearest neighbor atomic distance of S-S [8,9]. Since the largest changes are suggested to proceed in the sulfur atomic surroundings [8], this may explain the overall volume expansion registered in $Ge_{30.8}As_{5.7}S_{63.5}$ and $Ge_{32}As_5S_{63}$ films after illumination.

Another possible explanation for the observed photo-bleaching and photo-expansion could be the excitation of electrons by illumination across the band gap [10], followed by atomic displacements as a result of Coulomb interactions. The photo-generation of charge carriers may lead to either expansion or compression, depending on the film thickness; by decreasing the film thickness the repulsive electron interaction becomes dominant [11]. This could also be a reason for the observed photo-expansion in the studied films with 148-155 nm thicknesses. This process could simultaneously proceed with the chemical bonding arrangements discussed above.

It is widely accepted that thermally induced changes in the optical properties of amorphous Ge-chalcogenides are accompanied by structural improvements, reflected in reductions in the absorption, as is observed in the annealed films (Fig. 1*b* and Table 1). The bond arrangement in the as-deposited films is close to a random one, and the formation of all possible bonds is only statistical [12]. Formation of heteropolar Ge-S and As-S bonds proceeds during illumination. This is consistent with the photo-induced changes in the refractive index and in optical band gap of the illuminated films. For a well annealed film, the chemically ordered arrangement is characterized by the maximization of heteropolar bonds (Ge-S bonds, even at the expense of As-S bonds). Since, in the annealed films, the number of heteropolar bonds should be higher than that in as-deposited and illuminated films, the structure of an annealed film is better ordered, resulting in an optical band gap energy increase. On the other hand, a larger number of heteropolar bonds increases the bond ionicity [12], leading to a stronger Coulomb interaction expressed in thermo-contraction, as is the case for the films studied.

5. Conclusions

Changes in the optical constants and thicknesses of thin $Ge_{30.8}As_{5.7}S_{63.5}$ (155.6 nm) and $Ge_{32}As_5S_{63}$ (148.2 nm) films, by illumination and post-illumination annealing, have been established from spectroscopic ellipsometry measurements. The observed "giant" increase in the optical bandgap energy values (ΔE_g = 240 meV and 400 meV for $Ge_{30.8}As_{5.7}S_{63.5}$ and $Ge_{32}As_5S_{63}$, respectively) by illumination is evident in the photo-bleaching effect. By annealing, the film structure undergoes further ordering and a thermo-bleaching effect takes place. The photo-induced volume expansion (a 12-13 % increase in the film thickness) and thermo-induced contraction (an ~15 % reduction in the film thickness) are explained by the formation of heteropolar chemical bonds, changing the sulfur atomic surroundings and the nearest neighbor atomic distances.

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