INFLUENCE OF ILLUMINATION ON THE OPTICAL BANDGAP ENERGY VALUE OF $Ge_xSb_{20-x}Te_{80}$ FILMS

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The influence of light illumination on the optical bandgap energy E_g of chalcogenide thin films with $Ge_xSb_{20-x}Te_{80}$ composition and thicknesses of ~1 μm has been studies by spectral ellipsomerty in the range of 300-820 nm. The studied compositions were chosen within the glass-forming region of the Ge-Sb-Te system. The films were illuminated with a 500 W HBO mercury lamp. Immediately after illumination the E_g values decrease suggesting a structural change in the films. The changes are not stable in time, which is reflected in a gradual increase of bandgap energies toward initial E_g values.

1. Introduction

Recently, the research efforts have devoted to development and investigations of chalcogenide materials suitable for optoelectronics. Special attention is paid to ternary Ge-Sb-Te chalcogenide glasses due to their controllable crystal-to-glass phase transition. These alloys, with a stoichiometry close to the $GeTe-Sb_2Te_3$ pseudobinary line, have been the basis for data recording applications [1,2]. Non-stoichiometric Ge-Sb-Te film compositions are also of practical interest, and their optical and structural properties have recently become subject of investigation [3,4]. Still it is an open question how the structural, mechanical, optical and electrical properties of non-stoichiometric films change by illumination. All these changes appear significantly stronger in thin films obtained by vapour deposition technique and usually they are accompanied by changes in the optical constants.

In this work we present a study of the influence of light illumination on the optical bandgap enrgy values of chalcogenide thin films with non-stoichiometric $Ge_xSb_{20-x}Te_{80}$ composition being within the glass-forming region of the Ge-Sb-Te system. As a tool spectroscopic ellipsometry (SE) in the range of visible light is applied.

2. Experimental details

In this study the non-stoichiometric $Ge_xSb_{20-x}Te_{80}$ composition of the films was chosen with x = 15, 17 and 19. The films were thermally evaporated onto glass substrates from the parent $Ge_xSb_{20-x}Te_{80}$ glasses synthesized from elements of Ge, Sb and Te with 5N purity. The thickness of the films (~1 μm) was controlled in situ by MIKI FFV quartz sensor device.

The as-deposited films were illuminated with a Mercury HBO 500 lamp at a power of 0.42 W/cm^2 without using any filters. During the one-hour light exposure the samples were cooled keeping their temperature below 50 ^{o}C, far from the glass transition temperature.

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Before and after illumination, ellipsometric measurements were carried out on a Rudolf Research ellipsometer in the spectral region of 300-820 nm. Since the glass substrates were about 2 mm thick, the reflection from the substrate backsurface was successfully separated by measuring the samples at an angle of light incidence of 50°. The optical bandgap energy (E_g) values were determined from the absorption coefficient (α) evaluated from the SE data analysis.

The change of the optical bandgap energy with the time was traced by periodical measururements performed on films leaved in air conditions. The results were compared with those obtained before illumination.

3. Results and discussion

In the present work our study is focused only on the change of the E_g values caused by illumination of the films and, therefore, the optical constants, i.e. refractive index (n) and the extinction coefficient (k) for these films are given elsewhere [5,6]. From each measurement these optical constants were determined, and the E_g values were evaluated by using the Tauc relationship [7] $\alpha \sim (E-E_g)^\eta$, where η is 2, being typical for chalcogenide glasses, and α is the absorption coefficient equal to $\alpha = 4\pi k/\lambda$. The E_g evaluation procedure is given in details in ref. [5[.

Before illumination the optical bandgap, noted as E_{g0}, shows a linear dependence for the investigated compositions. The corresponding E_{g0} values are given in Fig. 1. With increasing the Ge content, or correspondingly with decreasing the Sb content, the E_{g0} value increases but it remains less than 1 eV. Such low bandgap energies are reasonable since the films contain high amount of Te (80 at. %). For films with even twice-smaller Te content, the E_{g0} value has been reported to be slightly higher than 1 eV [8].
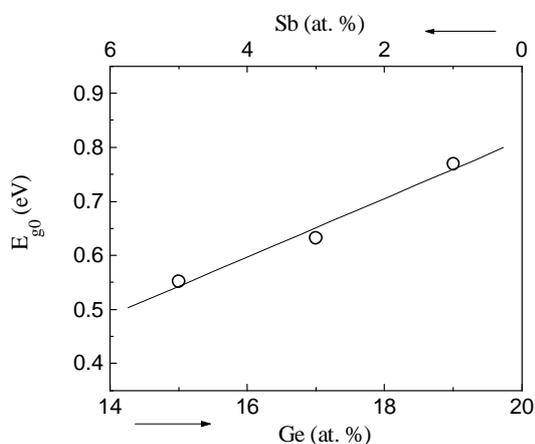

Fig. 1. Compositional dependence of the optical band gap energy (E_{g0}) of $Ge_xSb_{1-x}Te_{80}$ films.

It is known that in the band gap of chalcogenide systems the conduction band depends mainly on the amount and strength of the heteropolar chemical bonds, while the valence band tail defines by the amount of chalcogenide atoms [9]. Therefore, in our case the valence band tail remains the same, since the Te content is constant (Te – 80 at. %), while the conduction band will change with the changes of the Ge and Sb contents. With increasing the Ge content the conduction band tail becomes narrower in the result of the increasing amount of stronger Ge-Te bonds at the expense of weaker Sb-Te bonds [10].

In general, low E_{g0} values are indicative of narrow-gap semiconductors with high densities of intrinsic defects. It is expected that such a high defective and disordered structure will predispose to microstructural rearrangements in these $Ge_xSb_{20-x}Te_{80}$ films. Thus one may expect that illumination will provoke changes in the structure leading to change in the optical bandgap energy.

Our experiments have shown [6] that the optical constants slightly change by illumination. This is an indication that the films undergo some structural changes, which seem to be stable with time. However, the analysis of the spectral dependence of the absorption coefficient α, by applying the Tauc relationship [7] and tracing the change of the optical bandgap energy, shows that the film structure goes through a change during illumination but after turning off the light, the film structure aspires to restore its initial state. For all film compositions, a decrease of the bandgap energy value is registered immediately after illumination, while leaving the sample at prolonged atmospheric conditions, the E_g value tends to approach the initial energy level, i.e. the bandgap energy gradually increases with the time of storage. This is illustrated in Fig. 2, where the optical bandgap energy values of the $Ge_{19}Sb_1Te_{80}$ film immediately after illumination and after prolonged stay of the film at atmospheric conditions are given. The initial E_{g0} value (before illumination) is highlighted with a "full symbol" data point. As is seen, the post-illumination value of $E_g = 0.62$ eV slowly increases with time of storage but even after 144 h it does not reach the value obtained for unilluminated film.
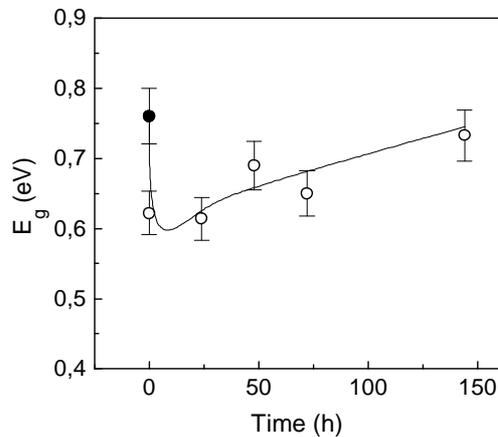

Fig. 2. Optical band gap energy (E_g) of illuminated films with composition of $Ge_{19}Sb_1Te_{80}$ as a function of storage time. The initial E_{g0} value of unilluminated film is expressed with full symbol. The accuracy of E_g determination is given by error bars.

The most pronounced change is observed for films with composition of $Ge_{17}Sb_3Te_{80}$. This is well demonstrated in Fig. 3, where the relative changes in the optical bandgap energy values as a function of storage time are presented. These values are determined as $\Delta E / E_{g0}$, where ΔE is the difference of the bandgap energy value before and after illumination and E_{g0} is the bandgap energy value before illumination.
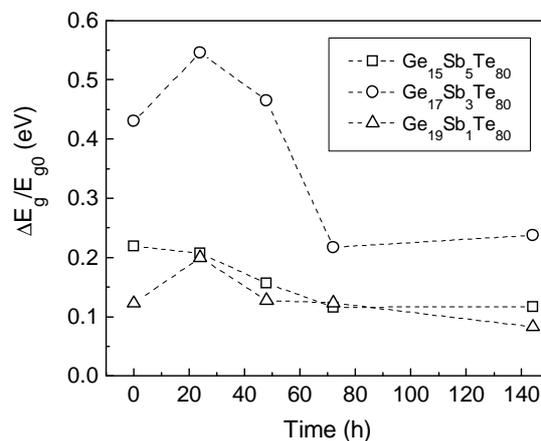

Fig. 3. Relative changes in the optical band gap energy of films with different compositions as a function of storage time.

Different reasons can be responsible for the observed change in the bandgap energy under illumination. One of the reasons could be the increase of the number of homopolar bonds [11], mainly Te-Te, at the expenses of heteropolar Ge-Te and Sb-Te ones, leading to valence band tail broadening and, thus to a decrease of the optical bandgap energy. Another reason could be the generation of charged defects in the band-tails region [12] giving to a contribution of the optical bangap narrowing. Also, some kinds of distortions in normal bonding configurations could take place resulting in enhancement of the interaction between the non-bonding lone-pair p orbital of chalcogenide atoms and in creation of shallow localized states into the bandgap [1,11,13]. Since in our films the concentration of Te atoms is significantly high (80 at. %), the reduction of the optical bandgap energy is most probably due to the intensified lone-pair interactions.

The observed changes are unstable; the film structure relaxes with time with a tendency to return to its initial state. However, the process is only partly reversible. It should be emphasized that the as-deposited films are not subjected to any thermal annealing, and therefore, some degree of irreversible changes in the film structure can be expected.

4. Conclusions

From the spectral ellipsometric data analysis it has been established that illumination leads to a different degree of decrease in the optical bandgap energy values depending on the film composition. Films with composition $Ge_{17}Sb_3Te_{80}$ are most sensitive to the illumination. The observed decrease of the bandgap energy after illumination is evidence that the film structure undergoes rearrangements upon exposure to light. At prolonged stay in atmospheric conditions the films structure tends to recovery, expressed in increasing the bandgap energy toward its initial value.

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