

EFFECT OF ULTRAVIOLET RADIATION ON $\text{Ge}_{27}\text{Sb}_{13}\text{Se}_{60}$ AMORPHOUS FILMS

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The photo-structural transformations induced by ultraviolet (UV) radiation in $\text{Ge}_{27}\text{Sb}_{13}\text{Se}_{60}$ amorphous thin films prepared by thermal evaporation method have been investigated. The mechanical, optical and structural data were investigated before and after irradiation of the fresh and annealed films. The modifications of the film structure and properties depend essentially on the state of the films: fresh or annealed below glass transition temperature.

(Received February 19, 1999; accepted March 2, 1999)

1. Introduction

The infrared transmitting chalcogenide glasses based on selenium are of interest in infrared (IR) optical systems. The physical properties of germanium chalcogenide glasses have attracted much interest for physical and technical reasons. Ge-Sb-Se glasses are attractive candidates for applications requiring low transmission losses, as they are transparent in to IR radiation from 2 to 16 μm [1]. Recently, IR optical fibres have been successfully made from these glasses [2,3]. Glasses rich in germanium exhibit improved thermo-mechanical properties. So it is easily to understood that commercially available optical glasses usually belong to the germanium chalcogenide based systems such as Ge-As-Se and Ge-Sb-Se as e.g. $\text{Ge}_{28}\text{Sb}_{12}\text{Se}_{60}$ (mark: AMTIR 3/TI 1173 IRG 100) [4]. Ge-Sb-Se glasses are p-type semiconductors [5].

Various investigations have been reported on the optical properties [6-8], thermodynamic properties [9], electrical conduction [10,11], photo-electrical properties [12,13] of Ge-Sb-Se glasses. All these properties have been related to the existence of the quasi-binary $\text{GeSe}_2\text{-Sb}_2\text{Se}_3$ system. The glass-forming region was found to extend from 5 to 35 at.% Ge, 5 to 40 at.% Sb and the rest being selenium [14]. The amount of metallic antimony in Ge-Sb-Se glasses can appreciably affect the optical and electrical properties. The optical absorption results in the system $\text{Ge}_{20}\text{Sb}_x\text{Se}_{80-x}$ (where $0 \leq x \leq 40$ at.%) indicate that the absorption mechanism is due to non-direct transition [15]. The optical gap of the as-deposited films was found to decrease monotonically with increasing antimony content, a result that was interpreted by Moharram [15] on the basis of the chemical bond approach proposed by Bicerano and Ovshinsky [16].

The properties in the system Ge-Sb-Se are strongly influenced by the phase transition in the medium-range order at the mean co-ordination number $Z=2.67$, where a transition from a 2D layer structure to a 3D network occurs [17]. That is why the composition situated on the topological threshold ($\text{Ge}_{27}\text{Sb}_{13}\text{Se}_{60}$) is very important for the experimental and applied purposes.

The amorphous films based on Ge, Sb and Se are good candidates for optical recording and information storage media, as well as for memory switches.

Berkes et al. [18] and Tagantsev and Nemilov [19] have observed modification induced by UV radiation in chalcogenide materials. A significant decrease of viscosity and a flowing effect have been discovered. The visible consequence is the smooth topography of the fresh amorphous films.

Ultraviolet light irradiation induces photostructural changes in the antimony chalcogenide films that are manifested in a shift of the optical absorption edge and changes in the dissolution kinetics, allowing the use of such films as optical memory media or in photoresist applications.

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We have studied the effect of the UV light on fresh and annealed thin films of $\text{Ge}_{27}\text{Sb}_{13}\text{Se}_{60}$ composition, situated at the topological threshold, in order to get more insight into the magnitude and the mechanism of its structural transformations induced by annealing and by UV light.

2. Experimental

Thin $\text{Ge}_{27}\text{Sb}_{13}\text{Se}_{60}$ films were deposited on (111) oriented silicon wafers by vacuum evaporation method.

Twin samples were prepared. One of the samples was annealed and one was left fresh. The annealing temperature was below the softening temperature of the films. Afterwards, the half of each sample has been illuminated with an Ultra-Vitalux UV lamp for 90 hours per sample. The UV light was situated in the range 300 to 400 nm and the power density on the sample surface was 0.05 W/m^2 .

X-ray diffraction, microhardness and infrared absorption (IR) measurements have been performed. The thicknesses of the films have been measured with a mechanical profilometer device. There were found $d_{\text{fresh}}=3.2 \mu\text{m}$, $d_{\text{fresh-i}}=3.3 \mu\text{m}$, $d_{\text{ann.}}=3.3 \mu\text{m}$, $d_{\text{ann.-i}}=3.4 \mu\text{m}$.

The X-ray diffraction patterns were recorded in a TUR M62 diffractometer. The X-rays generated by a Ni target tube ($\lambda = 1.6578 \text{ \AA}$) were used in measurements. The microhardness was measured with a PMT-3 apparatus. Indentation loads in the range 5-10 g were used. The Vickers hardness, H_v , in kgf/mm^2 or $\times 10^7 \text{ N/m}^2$ was calculated. The IR spectra were recorded in a spectrometer Spekord.

3. Results and discussion

The general X-ray diffraction pattern, as a function of the diffraction angle, θ , is given in Fig. 1 for one of the films (the freshly deposited film). The amorphous diffraction patterns for the other films look similar and this proves that our samples remain amorphous after annealing and illumination and no indication of the incipient crystallization can be found.

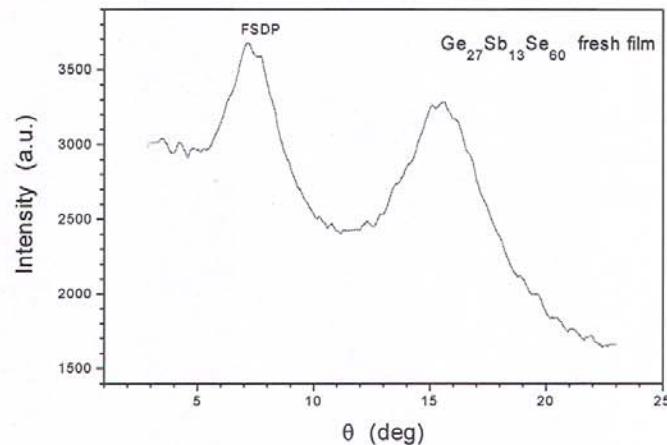


Fig. 1 X-ray diffraction pattern of amorphous fresh film of composition $\text{Ge}_{27}\text{Sb}_{13}\text{Se}_{60}$.

It is known, that the first sharp diffraction peak (FSDP) of an X-ray diagram for an amorphous material is the most sensitive to the medium range order (MRO) structure modifications. So, we have expected to observe some differences in the position and the shape of the FSDPs of our four samples, ascribed to the four different situations (corresponding to four different structure states) mentioned above.

To see more clearly the differences, we have smoothed the curves.

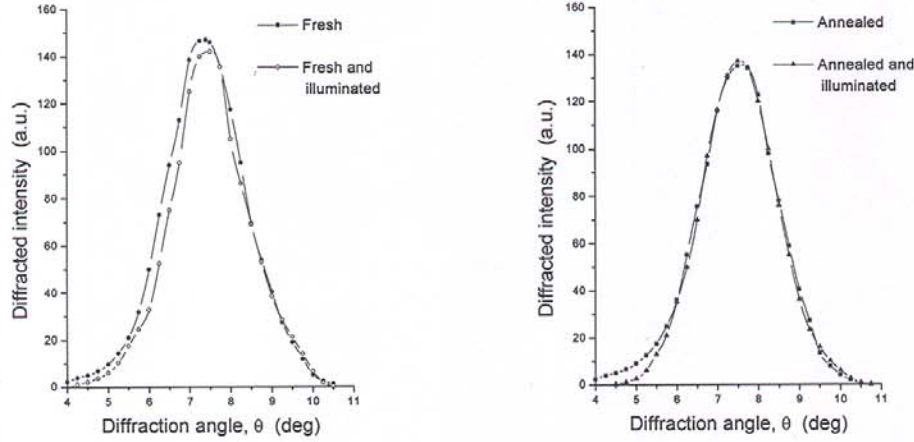


Fig. 2 Modifications of the FSDP induced by UV radiation in Ge₂₇Sb₁₃Se₆₀ amorphous films.

According to the layered model of the amorphous chalcogenide material, the average thickness of the domain built by packing a number of disordered layer configurations can be estimated with the Scherrer's formula:

$$D = \frac{K \cdot \lambda}{\beta \cdot \cos \theta} \cdot \frac{360}{2\pi} \text{ (\AA)}, \quad (1)$$

where $K = 0.9$ is the Debye-Scherrer constant, λ is the X-ray wavelength, θ is the angular position of the FSDP, and β is the width (in 2θ) at the half maximum of the FSDP. The distance between two such amorphous layers is:

$$d = \frac{\lambda}{2 \cdot \sin \theta} \text{ (\AA)}. \quad (2)$$

With D and d it is possible to define $p = \frac{D}{d}$, a kind of measure for the layer packing, which says how many amorphous layers, are in an amorphous domain. We shall call it here "packing"-factor.

The results presented in Fig. 3-6 reveal that the effect of the UV light is much stronger on fresh films than on the annealed films. The UV light induces an increase of the medium range order (MRO) as evidenced by the decrease of the width of the first sharp diffraction peak (Fig. 5). The increase of MRO is maximum for fresh films. If annealed films are compared with the fresh films, then, as expected, heating the film under T_g appreciably increases the MRO.

The main structural information obtained from these diffraction patterns is listed in the Table 1.

Table 1 Structural data obtained from X-ray diffraction measurements on Ge₂₇Sb₁₃Se₆₀ amorphous films.

Amorphous film	θ (deg)	β (deg)	D (\AA)	d (\AA)	$p = D/d$
Fresh	7.387	2.207	19.529	6.440	3.032
Fresh and illuminated	7.462	2.054	20.987	6.382	3.288
Annealed	7.523	2.186	19.722	6.331	3.115
Annealed and illuminated	7.526	2.128	20.260	6.328	3.201

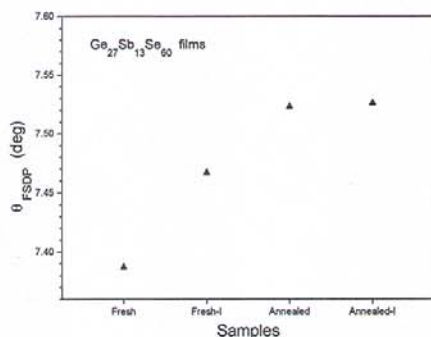


Fig. 3 The position of the first sharp diffraction peak in $\text{Ge}_{27}\text{Sb}_{13}\text{Se}_{60}$ amorphous films before and after UV irradiation. (fresh-I: fresh and illuminated; annealed-I: annealed and illuminated).

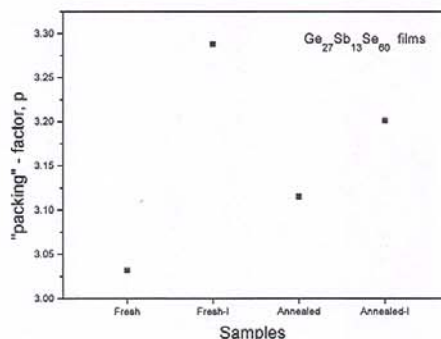


Fig. 4 The "packing"-factor calculated for the amorphous films of $\text{Ge}_{27}\text{Sb}_{13}\text{Se}_{60}$ before and after UV irradiation (fresh-I: fresh and illuminated; annealed-I: annealed and illuminated).

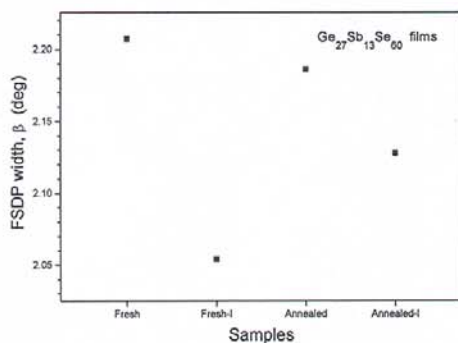


Fig. 5 The width of the FSDP in amorphous films of $\text{Ge}_{27}\text{Sb}_{13}\text{Se}_{60}$ before and after UV irradiation (fresh-I: fresh and illuminated; annealed-I: annealed and illuminated).

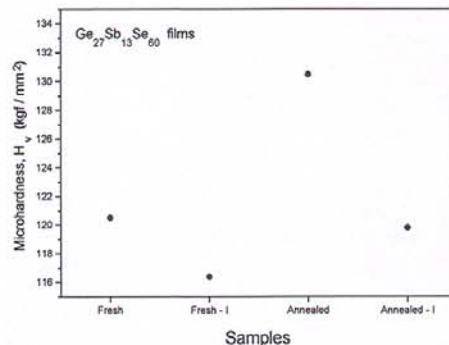


Fig. 6 The microhardness of the $\text{Ge}_{27}\text{Sb}_{13}\text{Se}_{60}$ amorphous films, before and after UV irradiation (fresh-I: fresh and illuminated; annealed-I: annealed and illuminated).

An increase of the θ_{FSDP} induced by the irradiation is observed. This increase can be ascribed to a more compact re-arrangement - the decrease of the interlayer distance (d) - of the layered structure in our chalcogenide materials. The change is much higher for the fresh samples. The annealed structure being already relaxed - FSDP maximum is already shifted to higher angles - it allows less modification possibility for the UV radiation. Because even this small modification exists, let us to suppose, that the action of (UV) light has a different nature on the bond-rearranging in the amorphous materials than that of the action of the heat. The light produces mainly an increase of the contiguous domain thickness, while the annealing has mostly a smoothing-effect on the already formed layers in such an amorphous domain.

The microhardness (H_v) increases by annealing and decreases after illumination in both cases. So, we have a photo-induced softening for these samples. Such softening effect was observed in the Ge-As-S system too [20].

These changes in the mechanical properties can be explained on the basis of Fig. 3-6 by the bonding changes in the complex ternary alloy. The annealing eliminates the major part of the dangling and wrong bonds between atoms. The effect of UV irradiation is more complex. Some bonds are broken by the energetic UV quanta and locally they are reformed in a rapid relaxation process giving rise again to non-equilibrium homo-bonds. In the fresh films this effect is superposed

on a process of photo annealing, i.e. the annealing by light of part of the rich structural defects existing in the amorphous matrix. That is why the decrease in hardness is higher for annealed films than for fresh films.

The refractive indices (n) of the films have been calculated from the infrared reflection spectra, using the following formula

$$n = \frac{\lambda_1 \lambda_2}{2d(\lambda_2 - \lambda_1)}, \quad (3)$$

where d is the film thickness, λ_1 and λ_2 are the wavelengths of two consecutive maxima of the IR reflection diagram.

The average refractive indices calculated for the range of 2600-16500 nm of the IR spectrum are given in Table 2 and in Fig. 7. While the absolute values of the index of refraction is affected by systematic errors estimated at the first decimal digit, the relative variation of n due to annealing and illumination is a much more accurate value that can be discussed and applied with high confidence.

Table 2 The refractive index calculated from the optical transmission data in the Ge₂₇Sb₁₃Se₆₀ amorphous films.

Amorphous film	Refractive index, n
Fresh	2.73
Fresh and illuminated	2.27
Annealed	2.44
Annealed and illuminated	2.37

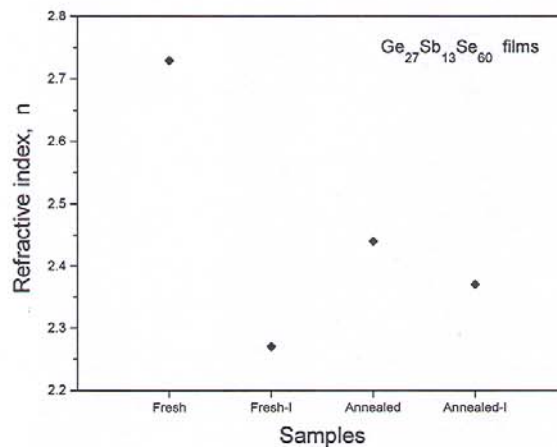


Fig. 7 The refractive index of Ge₂₇Sb₁₃Se₆₀ amorphous films before and after UV irradiation (fresh-I: fresh and illuminated; annealed-I: annealed and illuminated).

A decrease of the refractive index induced by the illumination for both type of samples (fresh and annealed) was revealed. The relative decrease of n for the fresh film is of 16.8 %, while for the annealed film the decrease is of only 2.8 %.

Finally, we would like to point out that Ovshinsky [21] was the first who has shown that the local structural changes in chalcogenide glasses are possible due to high steric flexibility of the structural units containing chalcogens. These changes are the key for the explanation of various optoelectronic properties of the chalcogenide films [22], including our films. The specific optoelectronic phenomena in chalcogenide films were recently explained by Fritzsche [23,24] on the basis of local bonding changes and light induced diffusion "that continue to occur even when an overall dynamic equilibrium and saturation of some microscopic changes are established as a result of competing thermal and light-induced relaxation processes".

4. Conclusions

The investigation of the ternary chalcogenide films of composition $\text{Ge}_{27}\text{Sb}_{13}\text{Se}_{60}$, situated at the topological threshold, led us to the conclusion that the amorphous Ge-Sb-Se films are sensitive to UV-light, and show mechanical, optical and structural changes. The largest photostructural changes are revealed in the fresh samples. The annealed, stabilized samples, show small but significant modifications. In both cases the refractive index decreases and medium-range order increases while the microhardness diminishes, thus evidencing a softening effect induced by UV light in these films.

Acknowledgement

The author is grateful to DAAD for the grant kindly offered to carry out scientific research in the Institute of Physics, Technical University, Chemnitz. The author is thankful to Dr. V. Pamukchieva (Institute of Solid State Physics, Sofia, Bulgaria) for providing the samples.

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