Journal of Optoelectronics and Advancced Materials, Vol. 2, No. 5, 2000, p. 667-670

Section 7: Non-crystalline materials

THE EFFECT OF ULTRAVIOLET RADIATION ON THE STRUCTURE OF NON-CRYSTALLINE CHALCOGENIDES

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Amorphous films and bulk glasses of binary and ternary chalcogenides have been subjected to controlled irradiation by ultraviolet (UV) rays. The subsequent transformations were characterized by X-ray diffraction.

Keywords: Amorphous, Chalcogenide, Ultraviolet irradiation, X-ray diffraction

1. Introduction

Amorphous chalcogenide materials, based on binary (e.g. As-S, As-Se) or ternary (e.g. Ge-As-(S,Se), Ge-Sb-(S, Se)) combinations, exhibit a wide variety of physical and chemical changes when illuminated by band-gap light [1, 2].

Among various applications of these chalcogenides, the optical recording of information is of leading importance. The principle underlying optical recording consists in the appearance of large change of certain physical and chemical parameters of the non-crystalline chalcogenides under the action of light, e.g. conductivity in the conventional xerographic process [3], absorption or reflection in the case of structural modifications [4, 5].

The energy of the light quanta situated in the UV spectral range is expected to induce qualitatively new changes in the chalcogenide glasses, because this energy is equal or higher than the chemical bond energy [6].

In this paper we report the results obtained in the investigation of several chalcogenide materials subjected to ultraviolet irradiation.

2. Experimental

Arsenic sulphides and arsenic selenides glassy samples were prepared by melting the corresponding mixture of elements of p.a. purity in quartz ampoules, followed by cooling in air.

Amorphous films of binary or ternary composition arsenic chalcogenides were prepared by thermal vacuum evaporation from targets and deposited on substrates at rates of 10 nm/s.

Some samples were irradiated for 92-140 h with UV radiation emitted by an Ultra-Vitalux lamp (λ=300 ÷ 400 nm and power density 0.1 ÷ 0.2 W/cm^2). Other samples were irradiated by an UV-ROM lamp (λ=336 nm) at a power density of 116 μW/cm^2.

The temperature reached during irradiation did not exceed 40 ºC with the exception of those cases where a controlled raising of temperature were carried out, by changing the distance UV lamp-target, in order to see the combined effect temperature-irradiation.

3. Results. Documented cases

3.1. AsSe films

In AsSe films the first sharp diffraction peak (FSDP) observed in X-ray diffraction diagrams exhibits low intensity. The inter-layer characteristic distance is 5.47 Å and the FSDP width is 1.41º. After UV irradiation FSDP decreases and becomes broader (1.56º) but its position is maintained. This effect speaks in favour of a more disordered structure induced by UV radiation.

3.2. AsSe:Sn films

The AsSe films doped by 5 at% Sn are of interest for applications in magneto-optical recording of information. The interlayer distance calculated from FSDP peak position is 5.50 Å. The FSDP width is 1.40 Å. A partial crystallization was observed in the initially virgin samples. As_4Se_4, realgar-like crystallites were detected. After UV irradiation FSDP decreases significantly and becomes broader: FWHM=1.74º. Meantime, the crystalline peaks characteristic to As_4Se_4 phase disappear. This effect can be regarded as a proof for the photo-amorphization process induced by UV radiation.

3.3. As_2S_3 bulk glass

Bulk samples of glassy As_2S_3 exhibit significant changes of medium range order (MRO), as revealed by the FSDP position and profile, while subjected to UV radiation.

The non-irradiated samples show a FSDP situated at 9.28º (NiK_α radiation), which correspond to the inter-layer distance of 5.14 Å. The FSDP width is FWHM=2.54º. After 26.5 hours of irradiation (at P=116 $\mu W/cm^2$) the FSDP position moves towards lower diffraction angles (θ=9.20º). The new FSDP position corresponds to the interlayer distance of 5.19 Å. The FWHM of the FSDP peak increases up to 2.70º. After irradiation a thin film of As_2O_3 (arsenolite) was detected on the sample surface.

3.4. $As_2Se_3:Sn_{0.8}$ bulk glass

Bulk samples of As_2Se_3 glass doped by Sn were irradiated by UV light for a time interval of 1-4 h in air. As a consequence of UV irradiation, a thin film of As_2O_3 (arsenolite) appeared on the ingot surface. Careful analysis by small angle X-ray scattering revealed a thin oxide film of thickness 165 Å. The thickness of As_2O_3 film increases with the irradiation time.

3.5. Ge-As-S thin films

The non-crystalline germanium-arsenic chalcogenides represent an important class of photoconductors and IR window materials. They are stable and can be easily fabricated by melt-quenching or vacuum evaporation techniques. Thin films of $Ge_xAs_{40-x}S_{60}$ ($0 \le x \le 40$) were nvestigated.

The characteristic distance, d, calculated from the first sharp diffraction peak increases with x and, upon irradiation, this distance decreases for x<19, while it increases for x>19. There was observed an average film contraction of ~5% of the films. This effect is related to the loss of material (chalcogen) during UV irradiation of the films [7].

3.6. Ge-As-Se thin films

The UV irradiation of fresh films of composition $Ge_xAs_{40-x}Se_{60}$ ($0 \le x \le 40$) determines a large decrease of the inter-layer characteristic distance, d, while the irradiation of annealed films determine a small increase of this distance.

One important feature must be mentioned in the case of the x=0 composition (As_2Se_3). In both type of samples (fresh and annealed) irradiated by UV radiation was revealed narrow diffraction lines ascribed to arsenic oxide, As_2O_3 (arsenolite). We have determined in fresh films the mean size of the arsenolite crystallites: ~92 nm. The crystallites are oriented preferentially with the plane (111) along the substrate. In the annealed films the mean size of the As_2O_3 crystallites is larger: ~138 nm but the orientation is the same as in fresh films. The observed difference of crystallization can be explained by the more ordered structure based on layer-like As_2Se_3 clusters, where oxygen from atmosphere substitutes selenium.

3.7. $Ge_{27}Sb_{13}Se_{60}$ thin films

Chalcogenide glasses based on selenium are of interest in infrared (IR) transmitting optical systems. The amorphous films of composition $Ge_{27}Sb_{13}Se_{60}$ have been investigated by X-ray diffraction [8]. The structural data obtained for various annealing and irradiation conditions are given in the table below:

Amorphous film	Θ_{FSDP} (deg)	FSDP width (deg)	D (Å)	Inter-layer distance d(Å)	P=D/d
Fresh	7.378	2.207	19.529	6.640	3.032
Fresh and illuminated	7.462	2.054	20.987	6.382	3.288
Annealed	7.526	2.186	19.722	6.331	3.115
Annealed and illuminated	7.526	2.128	20.260	6.328	3.201

In the table D is the size of a mean cluster of disordered layers in the material and P is the number of disordered layers in a cluster.

An increase of the position angle of the FSDP (θ_{FSDP}) induced by the UV irradiation is observed. This increase can be ascribed to a more compact re-arrangement (corresponding to the decrease of the interlayer distance d) of the layered structure in the chalcogenide materials. The change is much higher for the fresh samples. The annealed structure being already relaxed (FSDP maximum is shifted to higher angles) it allows less possibility of modification during the UV irradiation. Because even this small modification exists, let us to suppose, that the action of UV light has a different nature on the bond re-arranging 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 amorphous domain. 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. The increase of medium range ordering is maximum for the fresh films. Annealing the film under T_g increases appreciably the MRO.

4. Discussion

Long time irradiation by UV light of various chalcogenide samples proved to be a good procedure for evidencing the structural transformations that occur in the disordered network characteristic to non-crystalline chalcogenides. Several type of transformations have been revealed in bulk and thin film amorphous samples: change of the medium range order, as revealed by the significant modifications of the position and width of the first sharp diffraction peak, photo-chemical reactions at the irradiated surface exposed to normal atmosphere, including the formation of arsenic oxide (molecular, arsenolite type) and loss of chalcogen (e.g. sulphur for the documented case 1.5).

The most remarkable phenomenon observed during irradiation by UV light of chalcogenide films is the photo-amorphization. The crystalline molecular phase formed during film preparation can be returned to the amorphous phase. It is supposed that this new effect is facilitated by the photo-chemical reaction with oxygen. Kolobov and Elliott [9] suggested that easiness of photo-amorphization of crystalline As_4Se_4 could be explained by the marginal stability of the As_4Se_4 molecular units due to the presence of strained As-As bonds.

5. Conclusion

The irradiation of non-crystalline chalcogenides by ultraviolet light allows to get new information on the atomic-scale phenomena that are responsible for the change of properties of these optoelectronic materials. Strong modifications of the amorphous network under UV light are related mostly to the rearranging of the atoms at medium range distance. Photo-reaction phenomena are usually superposed and, in the presence of oxygen new compounds more or less disordered can be formed.

Acknowledgement

The authors are thankful to Dr. E. Skordeva and colleagues from the Institute of Solid State Physics, Sofia, for providing some ternary amorphous film samples.

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