PHOTOINDUCED ANISOTROPY IN AMORPHOUS CHALCOGENIDE THIN FILMS

V.M.Kryshenik,V.I.Mikla*, I.P.Mikhalko

Institute for Solid State Physics & Chemistry, Voloshina Str.54, 88000 Uzhgorod, Ukraine
E-mail address: mikla@iss.univ.uzhgorod.ua (V.I.Mikla)

Optical anisotropy have been investigated in As_xS_{1-x} non-crystalline chalcogenides by means of wave guiding technique. Conventional photoinduced anisotropy (birefringence) is considered. The mechanism for photoinduced anisotropy was proposed. The layer-like formation has been proposed to contain quasi-crystalline active entities (like clusters) which tend to align in accordance to polarization states of illumination.

1. Introduction

Glasses and amorphous solids are inherently isotropic. For chalcogenides, a group of sulfur, selenium and tellurium compounds, there exist techniques for producing optical anisotropy. These techniques for creature anisotropic amorphous structures may be divided into two categories. The first category may include the preparation procedure of amorphous films. Up to now only oblique deposition technique [1] was reported to be appropriate for these purposes in thin film forms. In our earliest publications [2,3] we have shown that even in the case of amorphous thin films prepared by conventional vacuum thermal evaporation intrinsic (initial) optical anisotropy is inherent. Moreover, chalcogenide glasses are known to exhibit a variety of photoinduced phenomena [4-8]. Among these phenomena the photoinduced anisotropy [7] has aroused considerable interests for fundamental point of view and for a technical reasons. The phenomenon consists in appearance of optical anisotropy when these materials were exposed to linearly polarized light. A number of systems have been investigated in such an aspect. To explain this phenomenon different models have been proposed. Among them based on the intrinsic negative defects of chalcogenide glasses [9], on the orientation of normal bonding orbitals [10], and on the basis of more extended structural sites [11,12]. Due to the fact that the physical mechanisms of the phenomenon remain controversial, there exists a need for additional experimental data.

In this article it has been shown that amorphous chalcogenide films exhibit photoinduced optical anisotropy (birefringence). Optical anisotropy may be erased by exposure to unpolarized (circularly polarized) band gap light. Here we used a wave guiding technique, which has been proven to be profitable for investigations of optical properties in thin films. Note that materials examined here were limited to amorphous As-S system, but the features described below appeared common to chalcogenide glasses.

2. Experimental

The experiments were carried out on amorphous As_xS_{1-x} ($0.20 \leq x \leq 0.43$) film samples prepared by standard vacuum evaporation. Glassy As_xS_{1-x} alloys being the source material were prepared by conventional melt-quenching procedure.

The As_xS_{1-x} alloys were then vacuum deposited onto a microscopic glass substrate. The substrate was pre-cleaned before deposition. The As_xS_{1-x} alloys were deposited at a substrate temperature of 300 K. The deposited arsenic content is relatively uniform (within 0.5%) over the film thickness. A typical evaporation rate was 3-4 nm s^{-1}. The film thickness ranged from 0.9 to 1.2 μm.

A prism-coupling technique was used to measure the refractive index, birefringence and thickness of amorphous films. The experimental arrangement is the following. A guided wave of 633 nm (or 1150 nm) was generated with a GaP prism. The latter was pressed appropriately to the film. Only slight

absorption (especially for the λ=1150 nm) is characteristic for the films at these wavelengths. Thus, it may be neglected while determining the effective refractive index. To avoid possible photostructural changes at 633 nm wavelength, the probing light intensity was reduced to sufficiently low values. The wave guiding technique provides significant advantages over traditional techniques, e.g. the elipsometric method. The benefits of the technique include ability to determine independently refractive index in the film plane (from propagation constants measured from TE-optical modes) and perpendicularly to it (from TM-modes). The experimental arrangements for the observation of the resonance coupling angles and the parameters' measurement of several modes TE- and TM-polarizations was performed. If few modes were presented and the number of observed modes of both polarizations have been ≥3, the unknown n and Δn are overdeterminated. Thus this method is self-consistent. The accuracy of the refractive index measurements is $\delta n/n=10^{-4}$. Ar^+ laser (λ=514.5 nm) was used to photoinduce birefringence in amorphous films. Most of the experiments were carried out at room temperature.

3. Results

The inherent optical anisotropy (initial birefringence) of as-evaporated amorphous films was earlier defined in [2,3] as $\Delta n=n_z-n_y<0$, where n_z and n_y were refractive indices measured with the light in which the electric field runs perpendicularly to the film plane and in the films plane, respectively. The probing beam (TE- or TM- optical mode) was propagated in the film plane along the axis x (hereafter x, y and z are the Cartesian coordinate). The refractive index in the film plane was uniform, i.e. $n_x=n_y$. The parameter of the inherent optical anisotropy Δn did not depend on the choice of the probing beam wavelength (λ=633 nm or λ=1150 nm).

As it should be expected variation of the substrate temperature during deposition influence optical parameters. Thus, n_y (or n_x) linearly increases with increasing the substrate temperature T_s approaching the value of refractive index typical for that one in the bulk glass (n = 2.6 for $As_{0.4}S_{0.6}$). Naturally, more homogeneous in structural and chemical senses and thermodynamically stable structure is formed during deposition onto a heated substrate.

Some comments may be needed here for the samples. All thin film samples investigated are amorphous independently on treatment procedure, i.e. annealing, illumination or dark resting at room temperature. This is strongly supported by electron diffraction data as well as by Raman scattering spectra.

The consideration conventional photoindused anisotropy in such samples can be easily produced when the "fresh"(after the attainment the optical isotropy state produced by the preliminary radiation of unpolarized light) or annealed samples were subjected to linearly polarized band gap light. By alternating the polarization states of light one can induce or erase birefringence (Fig.1). The erasure can be produced also by circularly polarized light (see inset, Fig.1). A linearly polarized inducing Ar^+ (λ=514.5 nm) laser beam was incident perpendicular to the film plane (along the axis z). The inducing and erasing cycles for consideration birefringence can be produced repeatedly many times. If the annealed sample is illuminated by the linearly polarized light with orthogonal electric vector direction the so-called reversible birefringence appears the magnitude of which is the distance between points A-B, C-D, E-F… (Fig.1).

Fig.2 shows the initial parts of the inducing curves of reversible birefringence for different exposure values. We are defined the reversible photoindused birefringence as $\Delta n=n_y-n_x$ now. Nearly the same behavior is characteristic to the annealed films. The only difference between Figs. 1 and 3 is the level to which the birefringence is erased. That is between the points B-D-F-… points of Fig.1 and the corresponding points for annealed films.

At it is seen from the compositional dependence for as-evaporated and annealed films (Fig.4), two curves show the similar character up to 30 % As.

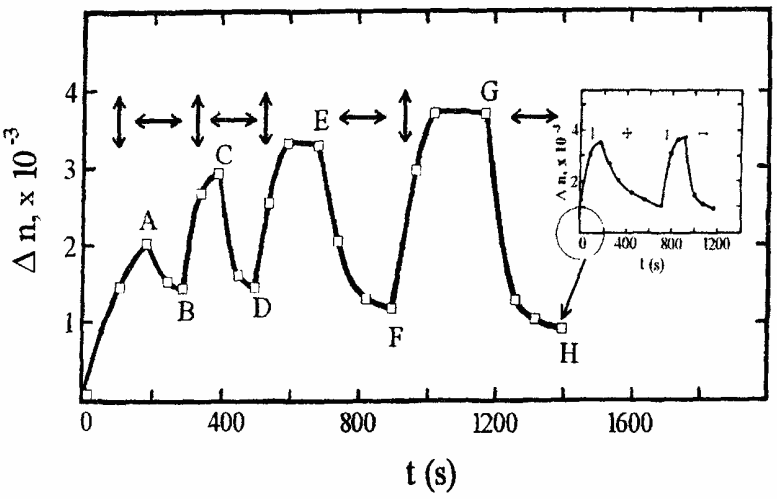

Fig.1. Inducing and erasing photoinduced birefringence $\Delta n = n_z - n_y$ in amorphous $As_{0.4}S_{0.6}$films by alternating polarization state of linearly polarized light. The vertical and horizontal arrows denote the polarization state from λ=514.5 nm laser beam (I=60 mW cm^{-2}). The insert shows the erasing by circularly polarized light.

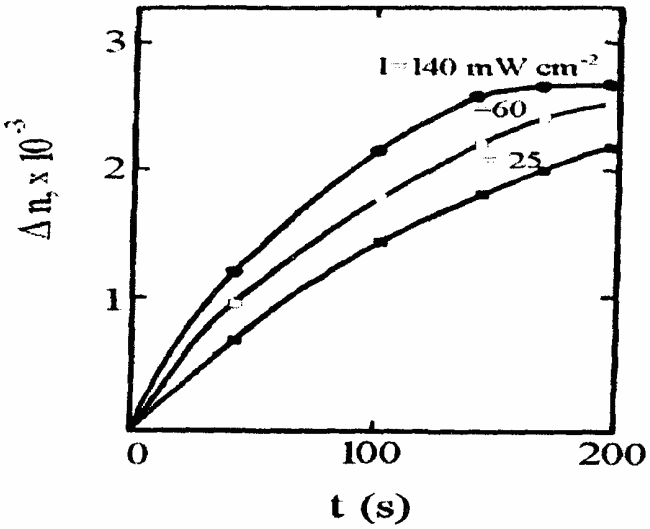

Fig.2. Exposure-time dependence of photoinduced reversible birefringence for intensities shown.

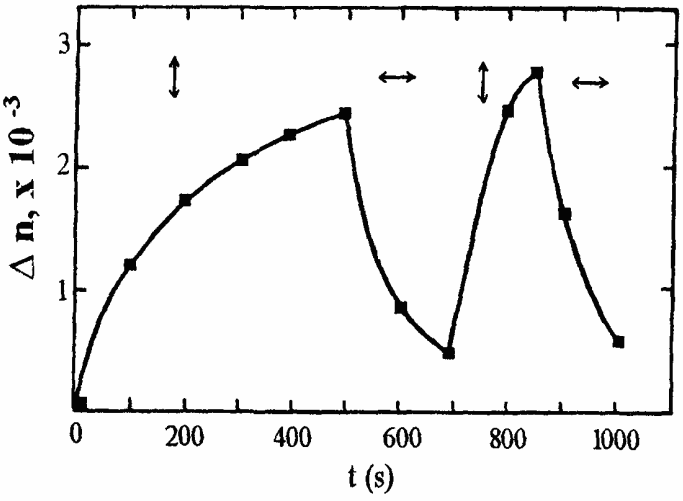

Fig.3. Inducing, erasing and reinducing photoinduced birefringence, $\Delta n = n_z - n_y$, in annealed $As_{0.4}S_{0.6}$ amorphous films.

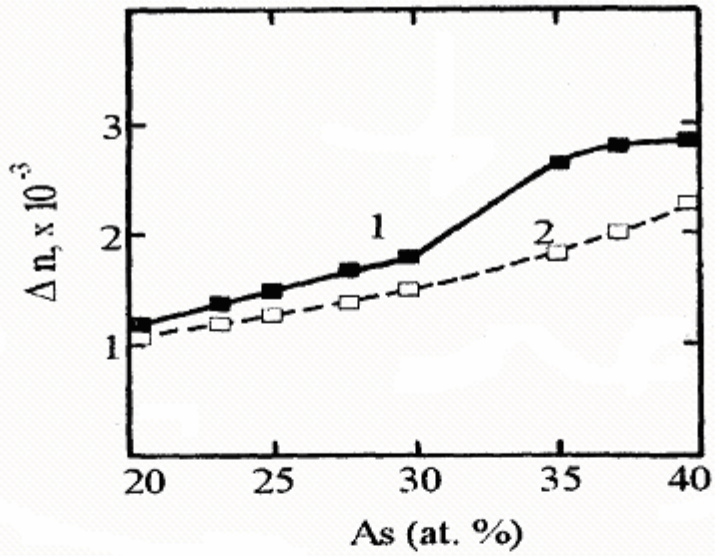

Fig.4. Compositional dependencies of maximal possible reversible photoinduced birefringence in "fresh" (1) and annealed (2) $As_{0.4}S_{0.6}$ amorphous films shown.

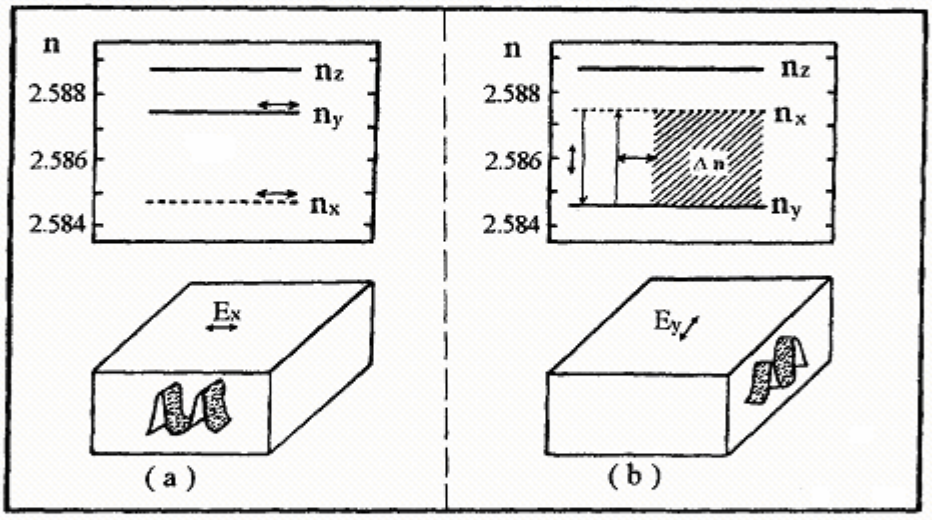

Fig.5. Schematic illustration of oriented layer clusters, which may be produced by a linearly polarized light of respective orientation. For simplicity, only parts of oriented clusters are illustrated. The upper part of Figures shows the refractive indices and the transitions between the mutually orthogonal states (shadowed area), respectively

4.Discussion

Photoinduced anisotropy is induced by a definite external factor (irradiation by a polarized light). For the photoinduced anisotropy we can suppose that there exists a structural distinction of irradiated and unirradiated samples.

It is interesting to consider a relationship between the magnitude Δn: for As_2S_3 the crystalline birefringence is –0.5. The conventional photoinduced birefringence of the amorphous films is ~1/100 of the latter and ~1/10 of the intrinsic anisotropy mentioned in [2,3].

We assume that as-deposited As_xS_{1-x} films contain horizontal layer structures with quasi-crystalline clusters. This seems to be supported by the following. In As_2S_3 crystals, it is demonstrated that $n_{\parallel}^c > n_{\perp}^c$, where $n_{\parallel}^c$ and $n_{\perp}^c$ are the refractive indices with electric fields parallel and perpendicular to the layer plane. Therefore, the layer clusters in fresh

films may be responsible for the intrinsic anisotropy [2,3]. However, more additional experiments, especially by means of structural-sensitive techniques are needed for further suggestions.

Fig.5 illustrates well the photoinduced anisotropy. In the upper part of Fig.5 the refractive index values are given. The lower part of the aforesaid Figure shows the orientation of quasi-crystalline clusters forming the layers respective to the orientation of an electric vector of linearly polarized light. These layers are seen to be oriented perpendicularly to the electric vector.

5. Summary

The photoinduced anisotropy (birefringence) in amorphous As_xS_{1-x} films has been investigated. A set of a new experimental data concerning the reversible photoinduced anisotropy in arsenic chalcogenide films has been used to show that a satisfactory description of the phenomenon can be explained on the basis of the simple structural model. The microscopic model assumed that activated layer clusters reorientation can be produced in accordance to polarization state of the inducing bandgap light illumination.

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ФОТОСТИМУЛЬОВАНА АНІЗОТРОПІЯ В ТОНКИХ ПЛІВКАХ АМОРФНИХ ХАЛЬКОГЕНІДІВ

В.М.Кришеник, В.І.Мікла, І.П.Михалько

Інститут фізики і хімії твердого тіла,

Ужгородський національний університет, Ужгород, 88000, вул. Волошина,54

Здійснено дослідження оптичної анізотропії в некристалічних халькогенідах As_xS_{1-x} з використанням хвилеводного методу. Обговорюються експериментальні дані з наведеної світлом анізотропії (двопроменезаломлення) в досліджуваних плівках. Запропоновано механізм прояву фотостимульованої анізотропії. Розглядаються шаруватоподібні квазікристалітні утворення кластерного типу, що активуються згідно до поляризаційних характеристик опромінюючого світла.