

PHOTOINDUCED SCALAR AND VECTOR EFFECTS IN OBLIQUELY DEPOSITED a-As₂S₃ THIN FILMS

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The influence of the columnar microstructure on the photoinduced scalar and vector effects in obliquely deposited a-As₂S₃ films has been examined. For this purpose, the optical constants of non-illuminated and Ar⁺ laser illuminated As₂S₃ films, prepared at different vapour incidence angles, were determined from spectrophotometric measurements. Also, the kinetics of the photoinduced optical anisotropy in obliquely deposited samples was studied by means of a computerized polarimetric set-up. It is established that the scalar effect of photorefractive and the vector effect of the photoinduced birefringence are greatest in a-As₂S₃ films prepared at the highest angle of incidence, which are characterized by the largest free volume in their structure. On the basis of the results obtained, the important role of the columnar microstructure in the occurrence of photoinduced transformations in arsenic chalcogenides has been discussed.

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1. Introduction

The exposure of amorphous As₂S₃ thin films to linearly polarized light produces optical anisotropy, which results in linear dichroism and birefringence [1]. These so-called vector effects occur simultaneously with the well-known scalar effects of photodarkening and photorefractive, but it is not clear yet whether the origins of the both phenomena are similar or not [2]. A variety of models for the mechanism of photoinduced scalar and vector effects in amorphous chalcogenides have been published, most of them being speculative [3]. Generally, it is believed that the scalar effects are mainly due to light-induced inter-atomic bond breaking and the creation of a large number of new defects, while the vector effects are usually explained by alignment and re-orientation of the native defects of the glass [4]. In the proposed models, however, poor attention has been paid to the role of the film microstructure on the occurrence of photoinduced transformations, leading to the observed optical changes.

Our recent investigations have shown that vacuum deposited a-As₂S₃ films are characterised by a columnar structure and a granular surface morphology [5]. Both the surface and internal microstructure are strongly influenced by the vapour incidence angle i.e. the angle between the vapour beam direction and the substrate normal. Increasing the latter from 0 to 80° leads to a considerable change in the optical, mechanical and other structure related properties of the films [6]. It can be expected that the observed structural peculiarities would also affect the photoinduced transformations in vacuum deposited a-As₂S₃ thin films. This makes the obliquely deposited samples very suitable subjects for studying the role of microstructure during the action of light.

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It is the aim of the present paper to follow the influence of columnar microstructure on the photoinduced scalar and vector effects in obliquely deposited a-As₂S₃ thin films.

2. Experimental details

The experiments were performed with thin films obtained by thermal evaporation of high purity As₂S₃ in a standard high-vacuum unit, maintaining 5×10^{-4} Pa residual pressure. A resistively heated Ta crucible with a special design [7] was used as an evaporation source. It allowed the sublimation and evaporation of As₂S₃ without local overheating, thus preventing undesirable effects of thermal decomposition. The substrates used were BK-7 glass plates, exhibiting a negligible absorption in the visible and near IR wavelength region. The deposition rate was about 0.5 nm/s at an evaporation temperature of 240 °C. The vapour incidence angle was varied between 0 and 80°. The deposition at every angle of incidence was performed in a separate vacuum cycle. The usual thickness of the films was 1500 nm.

The exposure was done by an Ar⁺ laser ($\lambda=488$ nm) with a light intensity on the specimen surface of 33 mW/cm². For studying the scalar effect of photodarkening and photorefraction, the a-As₂S₃ films were illuminated by the laser until saturation, i.e. to the moment when further illumination did not lead to a new shift of the absorption edge. The times of irradiation of the samples prepared at normal and oblique deposition was determined experimentally, and were 45 and 60 min., respectively. The transmission spectra of irradiated and non-irradiated films were recorded using a high-precision Cary 5E spectrophotometer in the wavelength range 400-1300 nm. The optical constants (refractive index n and absorption coefficient k) and physical thicknesses of the films were evaluated using a method similar to Swanepoel's "minimax" envelope technique [8]. The uncertainties in the optical parameters were sufficiently low, $\Delta n, \Delta d \approx 1\%$.

The kinetics of the photoinduced anisotropy was followed by means of a computerised polarimetric set-up, which measured the Stock's parameters of light in real time [9]. On this basis, the intrinsic and light induced dichroism and phase delay were evaluated. The latter allowed estimation of the values of birefringence, provided the film thickness was known. The sensitivity of the polarimetric set-up was 0.01 in dichroism and 0.1 degree in phase delay. The exposure was performed by the Ar⁺ laser, and the kinetics of the photoinduced anisotropy was monitored by a probe beam of a He-Ne laser ($\lambda = 633$ nm).

3. Results and discussion

Fig. 1 presents the spectral dependence of the refractive indices of non-illuminated (full symbols) and illuminated (opened symbols) a-As₂S₃ films, deposited at 0°, 30°, 50° and 70°. As seen, the increase of the vapour incidence angle leads to a decrease of the refractive index values, the lowest being for the sample deposited at 70°. Obviously, this is due to the microstructure of the obliquely deposited films, which are built up of individual columns inclined to the substrates, and an appreciable void volume [6]. Evidently, the number of voids is greatest in the film prepared at 70°. Also, similarly to previous data [2], the refractive indices of all samples studied increased as a result of irradiation.

The influence of the microstructure of a-As₂S₃ films on the scalar effect of photorefraction is demonstrated in fig. 2, which shows the dependence of the light-induced refractive index change Δn on the vapour incidence angle, α . It is seen that the photoinduced change of the refractive index increases with the angle of incidence, and is greatest for sample deposited at 70°. Therefore, the photoinduced transformations associated with the scalar effect of photorefraction proceed with the highest efficiency in As₂S₃ films which are characterised by the largest free volume. Most probably, the microstructure of this kind of sample provides a lot of free space where bond breaking and atom movements are facilitated. Simultaneously, it was found that the vapour incidence angle does not influence substantially the degree of the photoinduced change of the absorption coefficient i.e., the degree of photodarkening. This was confirmed by the results obtained for the optical band gap energy values of the samples studied, determined according to Tauc's law [10] from the spectral dependences of the linear absorption coefficient. It was established that for unexposed As₂S₃ films, prepared at normal and oblique deposition angles, E_g had values of 2.41 ± 0.02 eV. After irradiation, E_g decreased to 2.32 ± 0.02 eV for all samples.

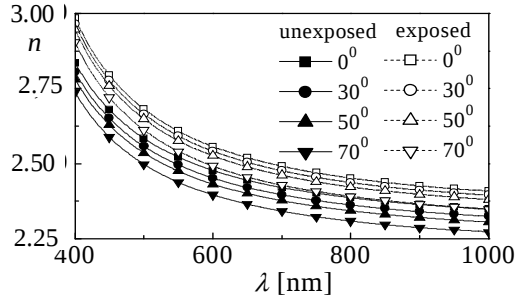


Fig. 1. Spectral dependence of n of 1500 nm thick a-As₂S₃ films, deposited at 0°, 30°, 50° and 70°.

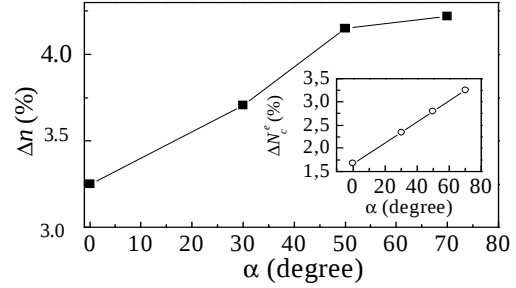


Fig. 2. Dependence of Δn and ΔN_c^e (inset) on the angle of incidence in 1500 nm thick a-As₂S₃ films.

Therefore, the influence of columnar microstructure of obliquely deposited a-As₂S₃ films is more pronounced on the scalar effect of photorefraction than on the photodarkening one.

In order to obtain information about the photoinduced structural transformations in the samples studied, the refractive index dispersions of exposed and unexposed a-As₂S₃ were fitted by the Wemple-Didomenico [11] relation:

$$n^2 = 1 + \left(E_d E_0 / (E_0^2 - (\hbar\omega)^2) \right), \quad (1)$$

where $(\hbar\omega)$ is the photon energy and E_0 and E_d are single oscillator fitting constants, that measure the oscillator energy and strength respectively. By plotting $(n^2 - 1)$ against $(\hbar\omega)^2$ and fitting a straight line, E_d and E_0 were determined for non-illuminated and illuminated films. Special attention was given to the dispersion energy E_d , the variation of which is assumed [12] to be due to the change of the nearest neighbour atomic configurations. It has been pointed out that E_d obeys the simple empirical relation [11]:

$$E_d = \beta N_c Z_a N_e, \quad (2)$$

where β is a constant, the value of which in covalent crystalline and amorphous materials is estimated to be 0.37 ± 0.04 eV, N_c is the coordination number of the cation nearest neighbour of the anion, Z_a is the formal chemical valence of the anion, and N_e is the total number of the valence electrons per anion.

Assuming that the change of E_d is primarily a coordination number effect [11], we calculated the effective As coordination number N_c^e in illuminated and non-illuminated As₂S₃ films, vacuum deposited at different angles of incidence. The dependence of the photoinduced change of this parameter on the vapour incidence angle is shown as an inset in fig. 2. As seen from the figure, the value of ΔN_c^e increases with α and is greatest for sample deposited at 70°. Therefore, it can be concluded that the light induced changes in the local atomic configurations proceed with the highest efficiency in this As₂S₃ film, which is characterised by the largest free volume. Thus, the results obtained demonstrate the important role of microstructure on photoinduced transformations in vacuum deposited a-As₂S₃ films.

It should be mentioned here that the method used could not be applied for films deposited at angles higher than 70° because of their very strong light scattering. Obviously, in this case the development of a suitable method for obtaining the optical constants determination is required. Our investigations in this respect are in progress.

The influence of the columnar microstructure on the occurrence of the vector effects is demonstrated in Fig. 3, which presents the kinetic curves of the photoinduced birefringence in a-As₂S₃ thin films, deposited at 0°, 70° (a) and 80° (b). As seen from fig. 3a, the maximal achieved value of this vector effect was greater in obliquely deposited samples than in normally deposited ones. Also, the time for achieving this value was lower, which means that the photoinduced transformations in this sample proceeded with a higher efficiency. Obviously, the most pronounced

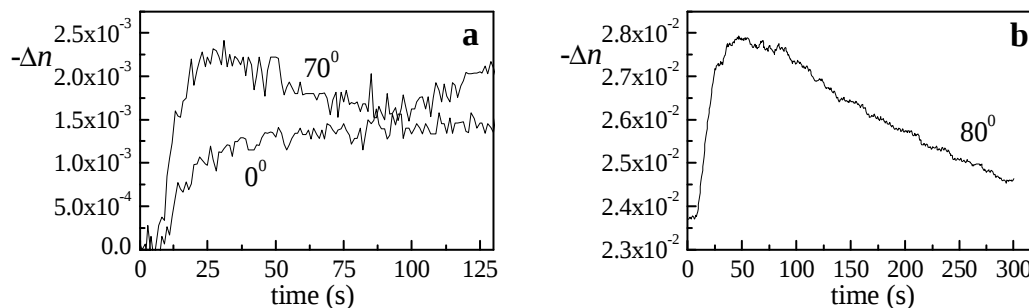


Fig. 3. Kinetic curves of light-induced birefringence in 1500 nm thick a-As₂S₃ films, deposited at 0°, 70° (a) and 80° (b) angles of incidence.

columnar structure in obliquely deposited films promotes in some way the occurrence of photoinduced anisotropy. This suggestion is confirmed by the results for the As₂S₃ film deposited at a much higher angle - 80°, presented in Fig. 3b. It is seen that this sample exhibited a considerable intrinsic birefringence, of the order of 0.02, which is most probably due to the strong anisotropy in the film microstructure. Simultaneously the photoinduced birefringence was about two times greater than in the sample prepared at a 70° angle of incidence.

Finally, it should be mentioned that similarly to the scalar effect of photodarkening, no substantial influence of the vapour incidence angle on the occurrence of the vector effect of photoinduced dichroism was found.

4. Conclusions

The results of this study showed that the photoinduced changes in the optical properties of vacuum deposited a-As₂S₃ thin films are influenced by the vapour incidence angle. It was established that the scalar effect of photorefraction and the light induced change of the effective As coordination number were greatest in the films prepared at the highest angle of incidence. Obviously, the more pronounced columnar structure of these samples provided a lot of free space where the bond breaking and atom movements were facilitated. Simultaneously, the columnar structure As₂S₃ films prepared at high angles of incidence presupposes the existence of intrinsic optical anisotropy, which plays an active role in the occurrence of the photoinduced vector effect of birefringence. Therefore, it can be concluded that the microstructure of obliquely deposited As₂S₃ films affects the degree of both scalar and vector effects. Thus, the results obtained demonstrate the possibility for controlling photoinduced processes in arsenic chalcogenide thin films by varying the vacuum deposition conditions, which may be of some technological interest.

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