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Photoinduced absorption edge shift of $As_{20}Se_{60}Tl_{20}$ films

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ABSTRACT

$As_{20}Se_{60}Tl_{20}$ bulk material was prepared firstly then thermal evaporation method was used to prepare $As_{20}Se_{60}Tl_{20}$ films. Illumination effect at room temperature for the mentioned films has been studied within the homogeneous glass-forming region. The prepared film samples were amorphous, this is depicted by X-ray chart. Optical properties have been studied using spectrophotometric measurements. The absorption edge was shifted to shorter wavelengths due to light exposure or photobleaching effect. It was found that the extinction coefficient and the optical band gap have opposite character after illumination.

1. Introduction

Chalcogenide films have been the subject of systematic investigation for many years because of the changes in physical and chemical properties which occur in these samples after exposure and annealing [1–8], and because of the potential applications of these effects in areas such as submicron lithography, optical memories, holography and imaging [3,6].

Chalcogenide glasses exhibit a wide variety of photoinduced phenomena that enable them to be used as optical imaging or storage media. Registering media based on these chalcogenide vitreous semiconductors have shown good results in many applications [9–15], high density information recording, holography, diffractive optics. Such media provide a resolution capability of the order of several nanometers due to their amorphous structure and ability to produce surface relief after exposure and treatment. Reversible photobleaching or photodarkening [16], one of the most interesting phenomena in chalcogenide and glassy samples with light exposure, is the reversible change in optical and some other properties induced and recovered by illumination and annealing, respectively.

It is assumed that photobleaching is closely related to the structural and electronic properties of chalcogenide glasses. Many researchers have studied it for the past years, but the origin of it is still unknown. The AsSeTl chalcogenide glasses are semiconducting, infrared transmitting, and have gained much industrial and research interest.

When Tl is added to glassy AsSe alloys the glass-forming region of AsSeTl is considered to be wide [17,18]. Other studies were needed to discuss the properties of new wide glass-forming region for AsSeTl alloys. Some other properties for AsSeTl bulk alloys had been studied [19–21]. No information is available in the literature about properties of thin $As_{20}Se_{80-x}Tl_x$ films except our earlier studies of structural, optical and electrical properties of $As_{20}Se_{80-x}Tl_x$ films [22–24].

In this letter, a study of illumination effect on amorphous $As_{20}Se_{60}Tl_{20}$ films will be introduced. For As-containing films, the absorption edge was shifted to shorter wavelengths (i.e. photobleaching occurred [1]). It was observed that the optical transmittance edge of a- $As_{20}Se_{60}Tl_{20}$ films shifted to shorter wavelength. with illumination of band gap light.

2. Experimental

The amorphous bulk material of $As_{20}Se_{60}Tl_{20}$ was prepared from highly pure arsenic, selenium and thallium (99.999% purity) loaded into a fused silica tube with inner vacuum 10^{-6} Torr. Alloying of the elements was accomplished by putting the sealed tubes in a furnace with a rocking mechanism. The rocked motion ensures that a complete mixing of the materials takes place. To assure complete chemical reactions between the constituents, the furnace temperature program was adjusted first at 350 °C for 4 h, secondly at 650 °C for 2 h and at last to 875 °C for 16 h. Rapid quenching in ice-water bath was used to obtain the bulk

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amorphous material. Thin films were prepared by the thermal evaporation of bulk material onto cleaned silicate glass as a substrate using an Edward coating unit model E 306A under a vacuum of 10^{-6} Torr at room temperature. The deposition parameters were kept constant so that comparison of results could be made under identical conditions. Film thickness *d* was controlled at 900 nm using a quartz crystal monitor and confirmed by an interferometric method [25]. Chemical composition of chalcogenide films of $As_{20}Se_{60}Tl_{20}$ was carried out using energy dispersive X-ray spectroscopy to estimate element distribution through the obtained films. The atomic percentage ratios of the $As_{20}Se_{60}Tl_{20}$ in the bulk form were found to be 21.06, 60.18 and 18.76 for As, Se and Tl, respectively. The small deviation between the composition of the bulk and the evaporated films was kept constant using a low evaporation rate of approximately 0.5 nm s^{-1}. X-ray diffraction (XRD) technique was used to investigate the structure of the prepared films using Philips diffractometer (type 1710) with Cu anode. At room temperature, both transmittance T and reflectance R patterns were measured for the amorphous films at normal incidence in the spectral range of wavelength (400–950 nm) using a computerized SHIMADZU UV-1100 double beam spectrophotometer with 10nm steps to study the illumination effect on optical properties $As_{20}Se_{60}Tl_{20}$. Exposure was realized using a 500 W tungsten lamp. The ambient temperature of the illumination process was controlled and kept at 32 °C. The exposure time was experimentally established for different illumination times from 0 to 420 min.

3. Results and discussion.

3.1. XRD patterns

Fig. 1(a) shows the XRD of $As_{20}Se_{60}Tl_{20}$ thin film. One can confirm that the produced film is amorphous due to the absence of sharp diffraction peaks and the presence of hump.

Small peaks were observed after illumination due to some degree of arrangement, see Fig. 1(b).

3.2. Optical properties

3.2.1. Transmittance and reflectance measurements

Spectral variations of transmission and reflection for the $As_{20}Se_{60}Tl_{20}$ films deposited onto glass substrate were measured over the wavelength range 400–950 nm.

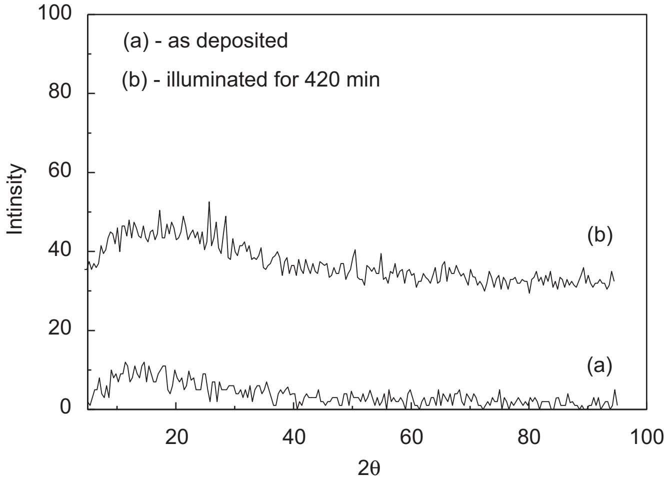

Fig. 1. XRD of thin $As_{20}Se_{60}Tl_{20}$ films: (a) as deposited and (b) illuminated for 420 min.

Fig. 2. shows transmission vs. wavelength as a function of illumination time.

Study of the optical constants in the vicinity of the absorption edge has yielded significant information on the role of various atoms in the chalcogenide network. Spectral dependence of the optical transmittance (T) as a function of both the illumination time (from 0 to 420 min) and wavelength are depicted in Fig. 2. In general, the transmittance increases with increasing in the illumination time. It is clear that the exposure of the films leads to a shift of the optical transmittance edge to shorter wavelength and an increase of the transmittance value. This photoinduced effect is the so-called photobleaching. It is shown in Fig. 2. That, the as-deposited state, shifts to the illuminated states.

3.2.2. Absorption and extinction coefficient

Optical absorption coefficient α was calculated from the following relation [26]:

$$T=(1-R)^2e^{-\alpha d} \tag{1}$$

where *R* and *T* are the spectral reflectance and transmittance and *d* is the film thickness. Optical absorption coefficient α is given by an approximate formula:

$$\alpha=\frac{1}{d}\ln\frac{(1-R)^2}{T} \tag{2}$$

The calculated absorption coefficient vs. wavelength as a function of illumination time is depicted in Fig. 3. One can observe that α increases with increase in photon energy, and decreases with illumination time.

Extinction coefficient of the $As_{20}Se_{60}Tl_{20}$ film was calculated by using the following relation:

$$K=\alpha\lambda/4\pi \tag{3}$$

The calculated values of extinction coefficient vs. wavelength as a function of illumination time were illustrated in Fig. 4. It could be noticed that *k* decreases with increase in wavelength and decreases with illumination time.

3.2.3. Calculation for energy band gap

Absorption edges of semiconductors correspond to the threshold for charge transition between the highest nearly filled band and the lowest nearly empty band. According to inter-band absorption theory, optical band gap of the films can be calculated using the following relation [27]:

$$(\alpha h\nu)=A(h\nu-E_g)^r \tag{4}$$

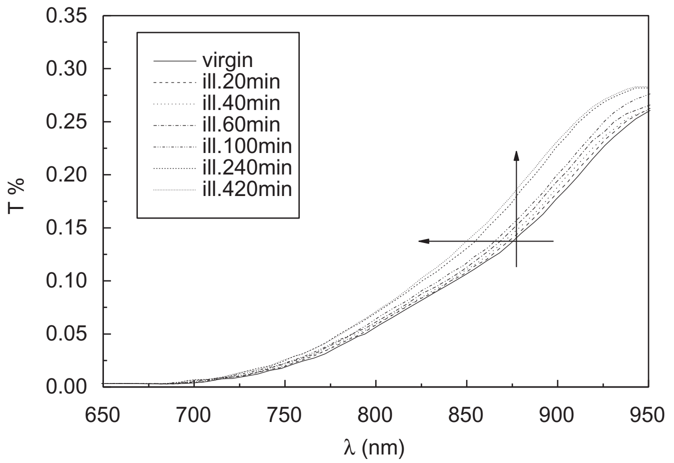

Fig. 2. Optical transmission vs. wavelength of $As_{20}Se_{60}Tl_{20}$ films as a function of illumination time.