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Particle size reduction of thallium indium disulphide nanostructured thin films due to post annealing

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ABSTRACT

Chalcogenide semiconductors are widely used, due to their versatile structural, optical and electrical properties. They are used in image sensors, energy conversion, non-volatile memory, and waveguides applications. Due to these versatilities in the properties, nanostructured thin films of $TlInS_2$ are successfully prepared by thermal evaporation. The average particle size changes due to thermal treatment are examined by X-ray diffraction (XRD), and transmission electron microscope (TEM). A sharp reduction in the average particle size of the pristine nanostructured films is reported upon annealing processes at 423 K and 523 K. Besides, thermal treatment temperatures induce changes in the dispersion parameters viz oscillator energy, dispersion energy, high-frequency dielectric constant and dielectric constant. Of these, only the oscillator energy decreases with the annealing temperatures while all the other parameters increase. Moreover, the non-linear optical calculations have revealed that the nanostructured $TlInS_2$ films exhibit high third-order nonlinear optical susceptibility of order 10^{-11} esu and strong nonlinear refractive index of order 10^{-10} esu.

1. Introduction

Chalcogenides are semiconductors with a typically band gap of 1–3 eV, depending on composition [1–3]. They show varied responses to optical [3], electrical [4] and thermal stimuli [5]. Moreover, they are used in non-volatile memories [6], photoelectrochemical cells [7], all-optical switching devices [8], photovoltaic devices and solar cells [9,10].

Single crystals of thallium indium disulphide ($TlInS_2$) had extensive studies for their structural, optical [11], photoconductive properties, photovoltaic [9,12]. $TlInS_2$ is a member of $A^{III}B^{III}C_2{}^{VI}$ group of chalcogenide semiconductors. Its crystal structure is reported as a monoclinic system and it consists of sulphur layers surrounded with a sequence, TlInInTl, with all octahedral sites occupied by indium and half of the trigonal-prismatic sites occupied by thallium atoms [13].

Previously, Ozdemir et al. [14] have studied the temperature dependence of dark and photocurrent of $TlInS_2$ single crystals in the temperature range 160–210 K. They have concluded that the changes in the temperature dependent photocurrent results from the change in the density of discommensurations. Moreover, the decreases of photocurrent in the temperature range 175–238 K are attributed to disorder of the structure. Also, Bakirov et al. [15] have studied the electro-absorption properties of $TlInS_2$ single crystals in the temperature range 77–300 K. They have found that $TlInS_2$ has a forbidden band gap energy equals to 2.535 eV. Additionally, the exciton activation energy equals 32 meV. Yonggu et al. [16] have studied the incoherent ellipsometry below energy gap of $TlInS_2$

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single crystals at room temperature. A remarkable increase in the birefringence at energy gap equals 2.4 eV was observed. Furthermore, the band gap exciton transitions were allowed in $E//C^*$ and forbidden in $E \perp C^*$ orientation.

Modern technology requires thin films for the diversity of applications such as optical coating, display devices, and solar cells [17]. Although $TlInS_2$ single crystals have been extensively studied, the effect of annealing temperature on the structure and optical properties of the nanostructured $TlInS_2$ thin films hasn't enough clear studies. Therefore, this paper aims to highlight the effect of thermal treatment at 473 K and 523 K on the microstructure, optical conductivity, third-order nonlinear susceptibility and nonlinear refractive index of nanostructured $TlInS_2$ thin films. All annealed films showed enhanced optical, nonlinear and structural properties. Of these, the annealed film at 523 K has the highest optical conductivity, third-order nonlinear susceptibility and nonlinear refractive index. Moreover, it has a sharp reduction in the average particle size.

2. Experimental

Thallium indium disulfide ($TlInS_2$) is purchased from Sigma-Aldrich and is used without further purifications. Nanostructured $TlInS_2$ thin films are successfully prepared using thermal evaporation technique (Edwards Co., England, model E 306 A). The as-deposited thin films are undergoing thermal treatment at 423 K and 523 K and for 30 min in a high-temperature furnace (type 21,100 tube furnace). The crystal structure of the thin films is investigated via x-ray diffraction technique (XRD; Shimadzu XRD-6000, Japan). XRD patterns are obtained in the range of 2θ from 4° to 90° at room temperature. Cu Kα is used as a radiation source of wavelength $\lambda = 0.15408$ nm, scan rate 2°/min, and operation voltage and current are 50 kV and 40 mA, respectively [18]. Moreover, information on the shape and size of the surface nanoparticles of $TlInS_2$ thin films are obtained via high resolution Transmission electron microscopy (TEM images are obtained by using Tecnai G20, Super twin, double slit TEM operated at 200 kV using lanthanum hexaboride electron source gun with a side-mounted CCD camera with 4k*4k image resolution). Additionally, UV–vis spectroscopy (Shimadzu UV-2101, Japan) is employed to measure reflectance $R(\lambda)$ and transmittance $T(\lambda)$ in a range of wavelengths from 200 to 2500 nm. Subsequently, $T(\lambda)$ and $R(\lambda)$ are computed to calculate refractive index, extinction coefficient, and absorption coefficient via a software program privately developed [19–21].

3. Theory

The microstructural parameters of nanostructured thin films viz the average crystallite size, D, the average dislocation density, δ, the microstrain, M, and stacking fault, SF, can be conducted by estimating the broadening width (β) of the most intensive peak and using the following relations [22,23]:

$$D = \frac{0.94\lambda}{\beta \cos(\theta)} \tag{1}$$

$$\delta = \frac{1}{D^2} \tag{2}$$

$$M = \frac{\beta}{4 \tan\theta} \tag{3}$$

$$SF = \frac{2\pi^2 \beta}{45\sqrt{3} \tan\theta} \tag{4}$$

where θ is the diffraction angle and λ is the wavelength of x-ray incident photons.

The refractive index, n, the absorption coefficient, α, and the extinction coefficient, k, of the thin films can be obtained from the measured values of the transmission $T(\lambda)$ and the reflectance $R(\lambda)$ based on the following relations [24]:

$$n = \left(\frac{4R}{(1-R)^2} - k^2\right)^{1/2} + \left(\frac{1+R}{1-R}\right) \tag{5}$$

$$\alpha = \left(\frac{1}{d}\right)\ln\left[\left(\frac{(1-R)^2}{2T}\right) + \left(\left(\frac{(1-R)^4}{4T^2}\right) + R^2\right)^{1/2}\right] \tag{6}$$

$$k = \frac{\alpha\lambda}{4\pi} \tag{7}$$

where d is the thickness of the thin film.

Both the real part of optical conductivity, σ_1, and the imaginary part, σ_2, are given as functions of the dielectric constants ($\varepsilon_1 = n^2 - k^2$ and $\varepsilon_2 = 2nk$) [20]:

$$\sigma_1 = \omega\varepsilon_2\varepsilon_0 \tag{8}$$

$$\sigma_2 = \omega\varepsilon_1\varepsilon_0 \tag{9}$$

where, ω is the angular frequency and ε_0 is the permittivity of the free space.