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ON THE ELECTRONIC TRANSPORT AND OPTICAL PROPERTIES OF ZnTe THIN FILMS

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ZnTe thin films (d = 0.12 –1.80 μm) were deposited onto glass substrates by the quasi-closed volume technique under vacuum. The structure analysis of the film was performed by X-ray diffraction (XRD) technique and atomic force microscopy (AFM). The films are polycrystalline and have a würtzite (hexagonal) structure. It was experimentally established that films with stable structure can be obtained if they, are subjected to a heat treatment. The spectral dependences of absorption coefficient were calculated in the range 400 - 1400 nm, from transmission spectra. The influence of heat treatment on the shape of the transmission and absorption spectra was studied for samples with different thickness. Optical gap, calculated from the absorption spectra is situated in the range 1.70 eV – 2.40 eV.

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1. Introduction

Zinc telluride (ZnTe) is an important semiconductor material for the development of various modern technologies of solid-state devices (blue light emitting diodes, laser diodes, solar cells, microwave devices, etc) [1-4]. Operated at the temperature of liquid nitrogen, ZnTe is a promising compound for devices used in terahertz regime [4, 5].

A variety of methods have been developed for the preparation of ZnTe thin films such as physical vapour deposition under vacuum, molecular beam epitaxy, organo-metallic chemical vapour deposition, solution growth, spray pyrolysis, etc [2, 6-8].

The dependence of the optical properties on the preparation conditions of the films and post deposition heat treatment is poorly studied for ZnTe films.

In the previous papers [9-13], we have studied electronic transport and optical properties of some II-VI semiconducting compounds (CdSe, CdS, ZnSe).

In this paper, some structural and optical properties of vacuum evaporated ZnTe thin films are investigated as a function of deposition conditions and post deposition heat treatments.

2. Experimental

ZnTe thin films were deposited onto unheated glass substrates by physical vapour deposition under vacuum of high purity ZnTe single crystals. The quasi-closed volume technique was used. The deposition equipment is described in detail in previous papers [9, 10].

The samples under study were prepared using the following deposition parameters: the source (evaporator) –substrate distance was 8 cm; source temperature was 1100 K; deposition rate was about 15 Å/s.

The films thickness was determined by an interferometric method [7] and for investigated samples ranged between 0.12 and 1.80 μm.

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The transmission spectra (in the spectral range of 400-1400 nm) were record (at room temperature) using a double beam spectrophotometer PMQ II type and an ETA-STC spectrometer.

The absorption coefficient, α, was determined by relationship [7, 11, 14]:

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

where d is the film thickness, and R and T represent the reflection and transmission coefficients, respectively.

The dependence of the electrical conductivity on the temperature was studied using surface-type cells [15, 16].

The experimental arrangements were similar to those described in [11-13, 16].

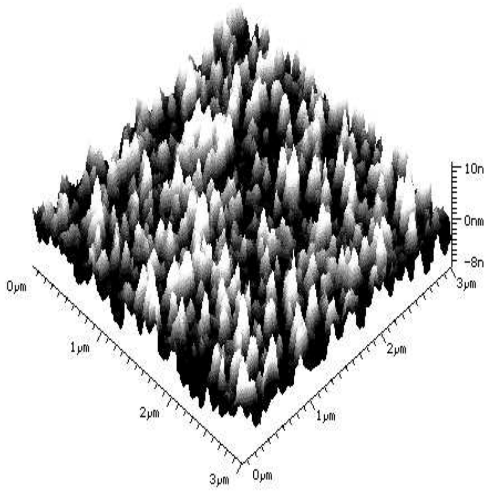
3. Results and discussion

For ZnTe thin films deposited onto unheated substrates we have experimentally established that the samples with stable structure and reproducible electrical and optical properties can be obtained if, after preparation, they are subjected to some heat treatments.

These treatments consist of several successive heating-cooling cycles within a temperature range, ΔT=300-500 K.

The film structure was examined by X-ray diffraction (XRD) technique. The XRD patterns showed that the samples are polycrystalline and have a würtzit (hexagonal) structure. The similar crystalline structure was generally observed for ZnTe single and polycrystals [1, 6, 17, 18].

The surface topography of ZnTe films has been investigated by atomic force microscopy (AFM). Fig. 1 to 3 show the AFM micrographs for three studied films. It can be observed that the microstructural features of respective samples are characterized by high-density columnar structure.



.Fig. 1. AFM image (3 µm*3 µm) for sample b3:
d = 0.99 µm; R_{rms} = 2.73 nm; R_{abs} = 2.17 nm.
(before the heat treatment)

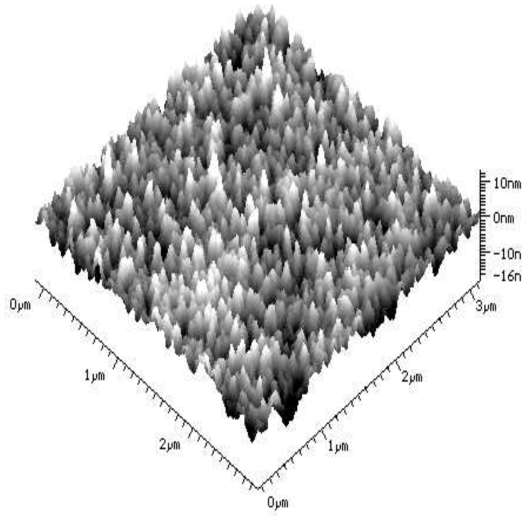


Fig. 2. AFM image (3 µm*3 mµ) for sample a1:
d = 0.56 µm; R_{rms} = 2.15 nm; R_{abs} = 1.67 nm
(after the heat treatment).

The average roughness, R_{abs}, and the root mean square roughness, R_{rms}, have been calculated.

The presence of pin holes in studied films is not observed. It is established from the AFM micrographs that the crystallite size is greater for films with greater thickness. After heat treatment, the preferential orientation of the film crystallites is maintained.

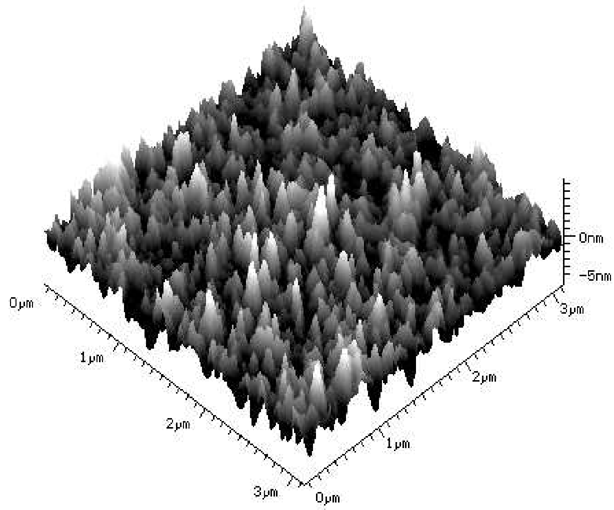


Fig. 3. AFM image (3 μm*3 mμ) for sample a3: d=0.36 μm, R_{rms}=1.47 nm; R_{abs}=1.12 nm.
(after the heat treatment).

The behavior of the lnσ = f (10^3/T) dependences during heat treatment was analyzed for a large number of ZnTe films.

The typical curves obtained are illustrated in Fig. 4. The respective sample was subjected to two successive heating and cooling.

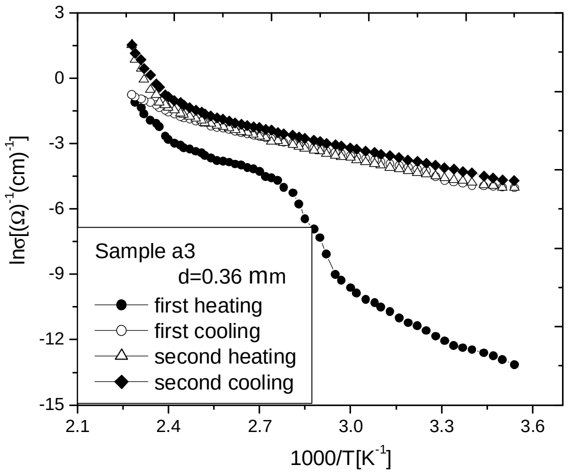


Fig. 4. Temperature dependence of the electrical conductivity during heat treatment for sample a3.

At first heating some structural changes in the films may occur. At first cooling an exponential increase of the electrical conductivity with temperature has been observed. The experiments showed that after 2-4 series of successive heatings and coolings the temperature dependence of the electrical conductivity becomes reversible. This fact indicates the stabilization of the sample structure in the studied temperature range.

For heat-treated samples thermal activation energy of electrical conduction can vary from 0.75 eV to 1.20 eV.

It is known, that the bandgap width for ZnTe crystals ranged between 2.10 eV and 2.22 eV [1, 2, 17].

In the investigated polycrystalline films, the transport phenomena are strongly influenced by crystallite size and characteristics of crystallite boundaries. Consequently, the mechanism of electronic transfer in investigated samples can be explained by applying some models elaborated for the films with poly-crystalline structure [13, 19, 20].

The Seebeck coefficient (measured by using thermal-sondes method [16]) was found to be positive for all studied samples.

This behavior is due to vacancies of Zn atoms in ZnTe crystalline lattice [2, 17].

By studying optical properties (transmission and absorption spectra, refractive index dispersion) of ZnTe films, very valuable information can be obtained about energy band-gap, characteristics of optical transitions, etc [10-12, 14, 21, 22].

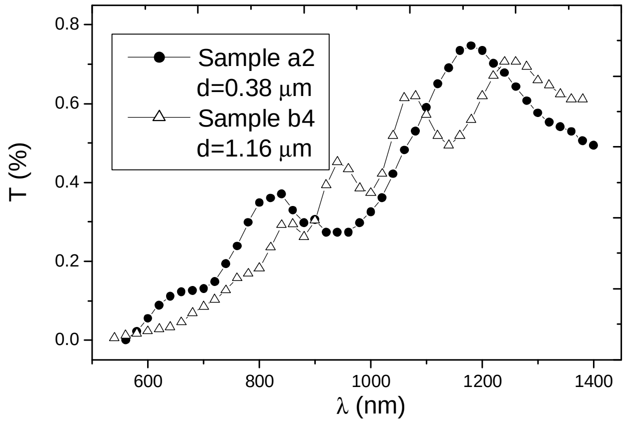


Fig. 5. Transmission spectra for two samples ZnTe films.

The optical transmission spectra as a function of wavelength in the range of were measured for different samples. Fig. 5 shows typical transmissions spectra for two investigated films.

Fig. 6 shows the typical absorption spectra. Generally, the pure compounds in thin films are characterized by sharp absorption edges at photon energies which correspond to the forbidden energy gap of respective semiconductors [7,19, 21].

A slow increase of absorption coefficient on the photon energy indicates a large concentration of structural defects (especially, Zn vacancies).

Experiments showed that heat treatment little influenced the shape of absorption spectra.

The similar results have been reported by Leiderer et al. [23].

In paper [23] the absorption spectra are interpreted in terms of indirect optical transitions in respective films.

The investigated films are characterized by a polycrystalline structure (see Figs.1 to 3). In this case compared to single crystals, the absorption spectrum generally has an additional absorption little peack (which depends on the crystallite size) for photon energy less than band gap energy [13,19].

This additional absorption may be masked in compounds characterized by indirect optical transitions, where the absorption edge is not as steep as in direct gap compounds [2,19,21].

In the domain of fundamental absorption edge, the absorption coefficient, α, for allowed direct transitions, is given by expression [14, 21,22]:

$$\alpha h\nu = A_a(h\nu - E_g)^{1/2} \tag{2}$$

where hν is photon energy, E_g represents the energy bandgap and A_a is characteristic parameter, independent of photon energy, for respective transitions.

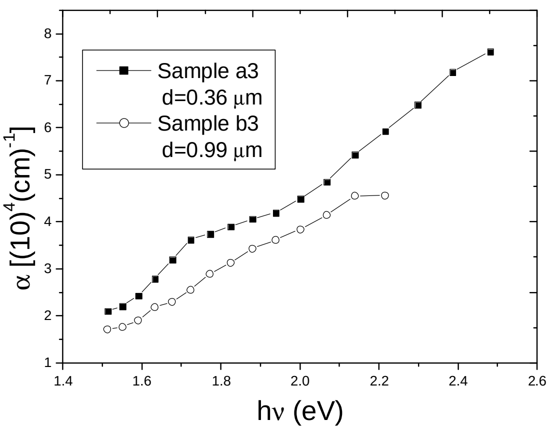


Fig. 6 Absorption spectra for two ZnTe thin films.

According to E_q. 2, in vicinity of fundamental absorption edge, the dependence $(\alpha h\nu)^2 = f(h\nu)$ is linear.

Fig. 7 shows this dependence for two of the studied samples. The values of bandgap width, E_g, can be determined by extrapolating the linear portions of the respective curve to $(\alpha h\nu)^2 = 0$. The values of energy gap, calculated from absorption spectra, ranged between 1.70 and 2.40 eV.

Swanepoel [24], Manifacier et al. [25,26] and other investigators [19,27] have developed a method for extracting the values of refractive index, (n); extinction coefficient (k) and thickness (d) for an absorbing film, deposited onto a transparent substrate, from transmission measurements (if $n^2 \gg k^2$).

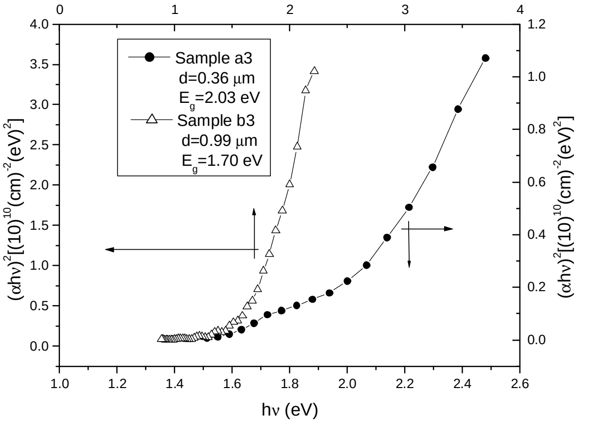


Fig. 7. Dependence $(\alpha h\nu)^2 = f(h\,\nu)$ for two ZnTe thin films.

In this method, is drawn the envelope functions of transmission maxima, T_M, and minima, T_m, which are considered as continuous functions of wavelength λ.

Then the refractive index, of a uniform thin film, for a determined wavelength, is given by [24-27].

$$n=[N+(N^2-n_s^2)^{1/2}]^{1/2} \tag{3}$$

where

$$N=(1+n_s^2)/2+2n_s(T_M-T_m)/(T_M*T_m) \tag{4}$$

The refractive index of the transparent substrate, n_s, is determined by expression [27]

$$n_s=1/T_s+(1/T_s^2-1)^{1/2} \qquad (5)$$

where T_s is the transmission coefficient for free-film substrate.

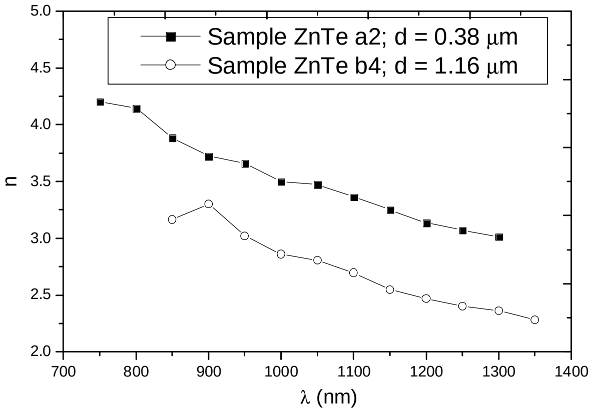


Fig. 8. Dependence n=f(λ) for two samples ZnTe films.

For the substrates, we have found that the transmission coefficient is around 0.93 (consequently, n_s=1.50) and is constant in investigated wavelength range.

For two films, the dispersion of refractive index is presented in Fig. 8.

The dispersion of the refractive index below the interband absorption edge is described by the Wemple-DiDomenico [28, 29] singe-oscillator framework

$$n^2-1=(E_o*E_d)/(E_o^2-(h\nu)^2) \qquad (6)$$

where E_0 and E_d are the oscillator energy and oscillator strength, respectively.

By plotting $(n^2-1)^{-1}$ as a function of $(h\nu)^2$ and fitting a straight line (Fig. 9), E_d and E_0 can be determined from the slope (this is $(E_dE_o)^{-1}$) and the intercept of the line with the ordinate axis, E_0/E_d [28,29].

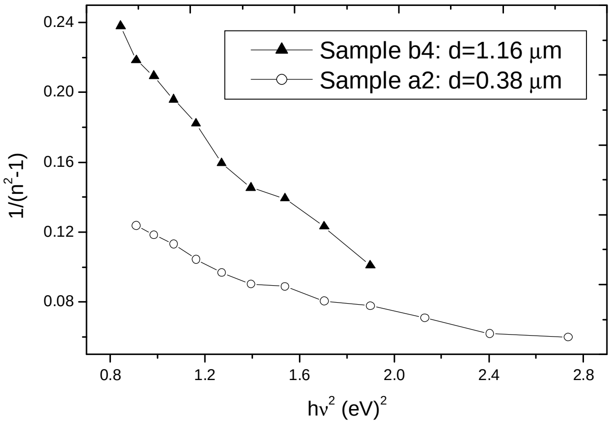


Fig. 9. Dependence $1/(n^2-1)=f[(h\nu)^2]$ for samples ZnTe films.

For a large number of semiconductor compounds in thin films it was found that $E_o \approx 2E_{go}$ (E_{go} is optical band gap) [11,13,28-32].

But, for studied samples, the values of optical band gap determined from this method (E_{go}=1.20-1.80 eV) are smaller than those calculated from absorption spectra.

This difference can be explained taking into account the specific structure of ZnTe films.

4. Conclusions

The studied ZnTe thin films deposited by vacuum thermal evaporation onto unheated glass substrates revealed a polycrystalline structure. It was found that a heat treatment performed after deposition results in the stabilization of film structure and the temperature dependences of the electrical conductivity become reversible.

The values of the energy gap, calculated from the absorption spectra ranged between 1.7 eV and 2.4 eV.

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