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The structural and optical characterization of thin-film ZnTe/CdSe heterojunctions

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The thin-film ZnTe/CdSe heterojounctions were prepared onto glass substrates covered with a transparent conducting SnO_2 layer. ZnTe (d=74-771 nm) and CdSe (d=843-1322 nm) thin films were deposited by thermal evaporation (cvasi-closed volume technique) under vacuum. Deposition conditions: deposition rate r_d=15 Å/s; substrate temperature, T_s=300 K-500 K; source temperature, T_{ev}=1000 K-1300 K. Structural investigations, performed by X-ray diffraction technique, and atomic force microscopy, showed that studied samples are polycrystalline and have a zinc blende (ZnTe) or wurtzite (CdSe) structure. Transmission and absorption spectra were studied (in the spectral range 300-1400 nm) both for component films and heterojounctions.

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1. Introduction

In the last years, the investigations on the heterojunctions based on II-VI semiconducting compounds in thin polycrystalline films have been much intensified. [1-8]

Thin film heterostructures for modern solid-state devices can be prepared by a variety of methods which lead to samples with different characteristics [4-8].

Thin-film ZnTe/CdSe heterojunctions are widely prepared for some important applications in modern technologies of solid-state devices such as solar cells, light-emitting diodes, transistors, photodetectors, etc. [1,8-10]. The main advantage of polycrystalline based devices lies on their very low cost production [1,8,11].

The fundamental parameters and characteristics of these heterojonctions are characterized by a very sensitive and complex dependence on the microstructure, preparation method and deposition conditions of the component films [1, 4 - 6, 8].

In this paper, the microstructural and optical properties of ZnTe and CdSe films component of In/CdSe/ZnTe/SnO_2/glass heterostructures in comparison with those of CdSe and ZnTe films separately deposited in same conditions onto glass substrates, are studied.

Consequently, we study the structural and optical properties of ZnTe deposited films onto ITO substrates in comparison with those of ZnTe films deposited, in the same conditions, onto glass substrates. Also, micorstructural and optical characteristics of CdSe films deposited onto ZnTe films in comparison with those of CdSe films deposited onto glass substrates were investigated.

2. Experimental

The thin-film ZnTe/CdSe heterojonctions were prepared by successive deposition of component films. The quasi-closed volume technique under vacuum was used [3,5,12].

For measurements the following procedure was used: simultaneously, in similar deposition conditions, two films were prepared: a film for preparation of heterojonction and a film of same compound deposited onto separated substrate (control sample).

The structural and optical properties samples were studied for both thin films simultaneously deposited.

The values of source temperature (T_{ev}) were: 1050 K (for deposition of CdSe thin films) and 1250 K (for deposition of ZnTe thin films). The substrate temperature was varied from 290 K to 490 K, and deposition rate was about 15 Å/s.

Film thickness (determined by an interferential method [9]) was: d = 74 nm - 771 nm for ZnTe thin films and d = 843 nm - 1322 nm for CdSe thin films.

The component films and heterojonctions structure was investigated by X-ray diffraction (XRD) technique (using a DRON2 diffractometer and CuK_α radiation). The surface morphology was studied by means of atomic force microscopy (AFM).

In order to study their current-voltage characteristics ZnTe/CdSe heterojonctions were prepared by deposition onto glass substrates of SnO_2 thin films (obtained by thermal oxidation of vacuum evaporated Sn films), then successive deposition of ZnTe and CdSe thin films and finally, an indium thin film (top electrode).

Optical transmission and reflection spectra (in the wavelength range from 300nm to 1400nm) were recorded using a double beam spectrometer PMQII (C.Zeiss, Jena) and an ETA-STC (Etaoptik Steag) spectrometer.[13,14]

The absorption coefficient, α, was calculated from expression [4,12,13].

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

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

In investigated heterojonctions, ZnTe films (for this compound, energy bandgap is about 2.30 eV) play role of a window layer while CdSe (having energy bandgap E_g=1.75 eV) is the absorber compound [1,9,15-17].

The SnO_2 thin films have been prepared by thermal oxidation, in air, of Sn films.

Sn films, with thickness between 1.15 μm and 1.55 μm, have been deposited in vacuum onto glass substrates, maintained at room temperature. After preparation Sn films were subjected to a heat treatment, in air, consisting of a heating (with a rate of about 10K/min), followed by an annealing for two hours at a temperature 550K, and finally a cooling (over 10 K/min) to the room temperature.

The measurements of Hall and Seebeck coefficients show that ZnTe films have p-type electrical conduction and CdSe films have n-type electrical conduction [1,4,9].

3. Results and discussion

3.1. Structural characteristics

Figs. 1 and 2 show the typical XRD patterns for two thin-film samples deposited onto glass substrates (substrate temperature was, T_s=293K, deposition rate was, r_d=15 Å/s). The studied films are polycrystalline [18,19].

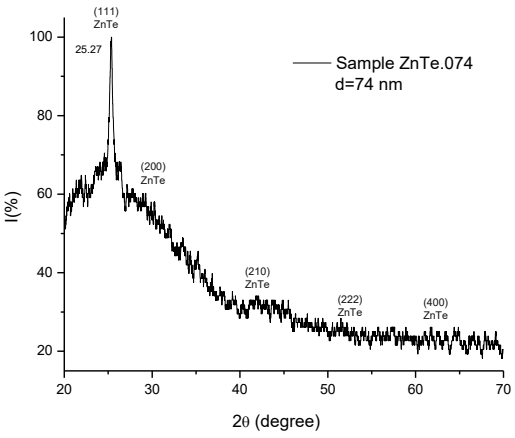

Fig. 1. XRD pattern for thin film ZnTe.074 (d=74 nm).

It was found that ZnTe thin films with smaller thickness (d<0.3 μm) have also an amorphous phase. The crystalline structure was found to be cubic (zinc blende) for ZnTe films and hexagonal (wurtzit) for CdSe films [2,10,16].

The film crystallites are highly oriented. For ZnTe films, the (111) planes are parallel to the substrate surface. For CdSe films, the (002) planes are parallel to the substrate.

The values of some structural parameters determined from XRD patters, are indicated in Table 1.

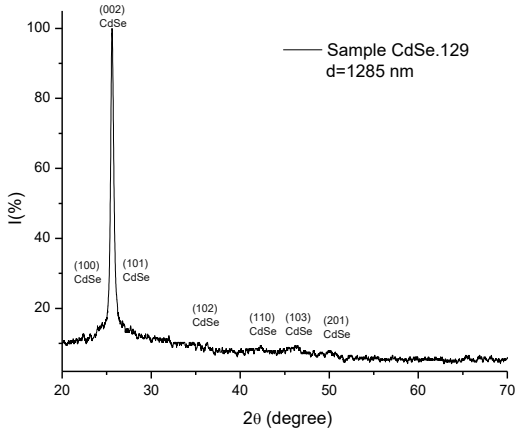

Fig. 2. XRD pattern for thin film CdSe.129 (d=1285 nm).

Fig. 3 shows the XRD pattern for heterojonction ZnTe/CdSe (CdSe film was deposited onto ZnTe film). In this case the degree of preferred orientation of CdSe films is diminished.

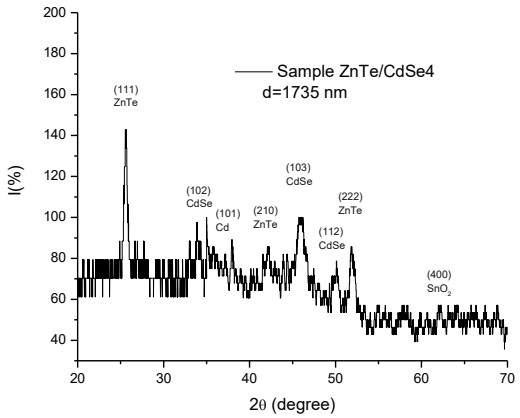

Fig. 3. XRD pattern for thin film ZnTe/CdSe 4 (d=1735 nm) heterojonction.

AFM images show that all the films have a grain-like and pinhole-free microstructure.

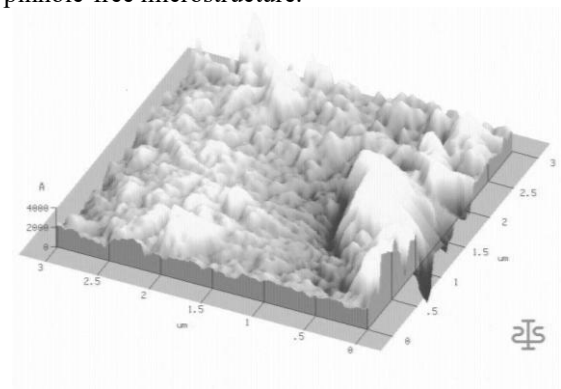

Fig. 4. AFM image for a SnO_2.027 thin film (d=270 nm) R_{rms}=136.10nm, R_{abs}=97.13 nm.

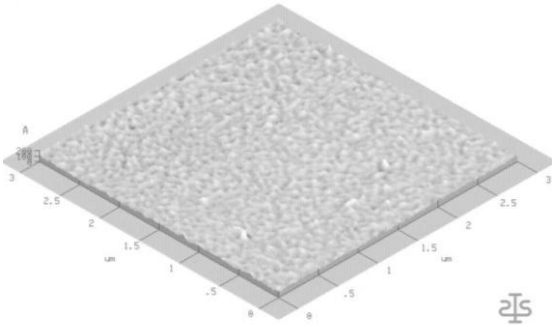

Fig. 5. AFM image for a ZnTe.007 thin film (d=74 nm) deposited onto glass substrate (T_s=300 K, T_{ev}=1120 K) R_{rms}=1.94 nm, R_{abs}=1.41 nm.

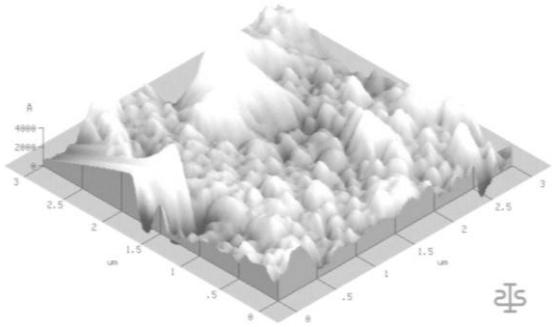

Fig. 6. AFM image for a ZnTe thin film (d=270 nm) deposited onto SnO_2/glass substrate (T_s = 300 K, T_{ev}=1120K) R_{rms}=139.73nm, R_{abs}=101.21nm.

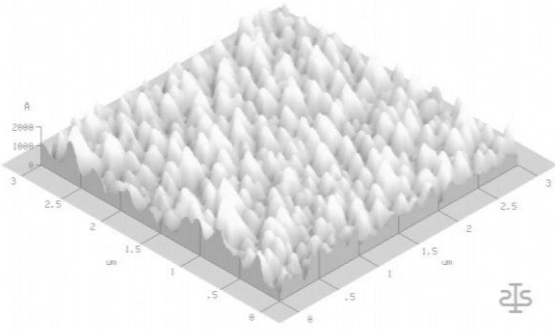

Fig. 7. AFM image for a CdSe.084 thin film (d=843 nm) deposited onto glass substrate (T_s= 300 K, T_{ev}= 1050 K) R_{rms}=41.88 nm,R_{abs}=33.43 nm.

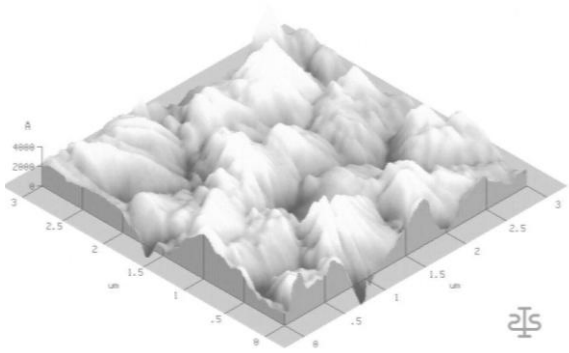

Fig. 8. AFM image for a CdSe thin film (CdSe.084) deposited ontoZnTe film/SnO_2 film/glass substrate (d=1187 nm, T_s=300 K, T_{ev}=1050 K), R_{rms}=130.51 nm, R_{abs}=102.57 nm.

If CdSe films are deposited onto ZnTe films the crystallite size becomes greater. This fact is probably due to lateral grows of the initial crystallites until coalescence.

We remark that the films directly deposited onto glass substrates are characterized by low surface roughness (Figs. 4, 5 and 7). For films deposited onto glass covered with other films the crystallites have greater size.

The topography of the ZnTe films deposited onto SnO_2 coated glass film is very different from that of ZnTe films deposited onto glass substrates.

The most interesting feature of these films is that we observed a smaller density of crystallites.

It is known that electronic transport in polycrystalline thin films is strongly influenced by intercrystalline boundaries, which have a space charge domain due to the interface [4,11]. Energy band bending occurs, and potential barriers to the charge carrier transport result. From this point of view the increasing in the crystallite size has a positive impact because this process determines an decrease of intercrystallite boundary domains [1,11,15,20].

The surface roughness plays an important role in nucleation and growth processes of thin films.

The average roughness, R_{abs} increases from 1.41 nm to 54.27 nm and the root mean square roughness, R_{rms}, increases from 1.94 nm to 69.25 nm, when the films thickness increases between 74 nm – 1187 nm.

Table 1. Structural parameters of ZnTe and CdSe films calculated from XRD patterns.

Sample	d (nm)	(hkl)	2θ (deg.)	d_{hkl} (Å)	a (Å)	c (Å)	$\beta_{2\theta}$ (mrad)	D (nm)
ZnTe.007	74	(111)	29.34	3,895	6,746	-	5,81	24.5
CdSe.084	843	(002)	29,57	3,886	-	7.76	4.48	37.0
		(103)	53,53	2,191	4.75	-	4.12	42.8

d, film thickness; (hkl), Miller indices of the planes; θ, Bragg angle; d_{hkl}, interplanare spacing; a and c lattice parameters, $\beta_{2\theta}$ fullwidth at half-maximum of diffraction peaks; D, crystallite size calculated from Debye-Scherrer formula [19,22,23].

Table 2. Surface parameters of SnO_2, ZnTe and CdSe thin films determined from AFM images.

Compound	SnO_2	ZnTe	CdSe	ZnTe	CdSe
Substrate nature	glass	glass	glass	Glass/SnO_2 film	Glass/SnO_2 film/ZnTe film
Thickness d(nm)	270	74	843	-	-
RMS Roughness (nm)	136.10	1.94	41.88	139.73	130.52
AVE Roughness (nm)	97.13	1.41	33.43	101.21	102.57

The films have a grain-like surface morphology (Table 2). The crystallite size strongly increases for CdSe films deposited onto ZnTe films. The surface morphology the heterojonctions thin film structure was investigated by atomic force microscopy (AFM).

3.2. Optical properties

The intercrystalline boundaries are one of the dominant factors controlling both the electrical and optical properties of polycrystalline films and, hence the performance of various devices made out of them [1,6-8,18-21]. It is well-known, that estimation of crystallite boundary effects from electronic transport measurements is, generally, very difficult [11,22]. Under these conditions the investigation of optical absorption spectra may provide useful information on the crystalline boundary effects on polycrystalline semiconducting films.

Reflection spectra for SnO_2/ZnTe/CdSe system is illustrated in Fig. 9.

It was seen that reflection coefficient strongly increases after deposition of ZnTe films onto SnO_2/glass substrate. On the other hand, the deposition of CdSe onto ZnTe/SnO_2/glass determines a decrease of reflection coefficient. This behaviour is advantageous for different applications of respective heterojonctions [1,11].

The transmission spectra for ZnTe films have a sharp fall at the, band edge, which show that the film possesses a good stoichiometry and crystallinity (curve 4, Fig.10). For ZnTe films deposited onto glass covered with a SnO_2 the transmittance is smaller. This behaviour can be determined from segregation of tellurium atoms at the crystallite boundary, where they form microcrystallittes (tellurium crystals present a high absorption in studied wave length range [12,16,24].

According to expectation, the transmission coefficients of the films deposited onto uncovered glass are higher than those of films studied as a component of heterojonctions. The sharp transmission edge at a wavelength that corresponds to the energy of forbidden gap indicates that respective films have a stoichiometric composition (curves 4 and 5, Fig. 10) [11,23].

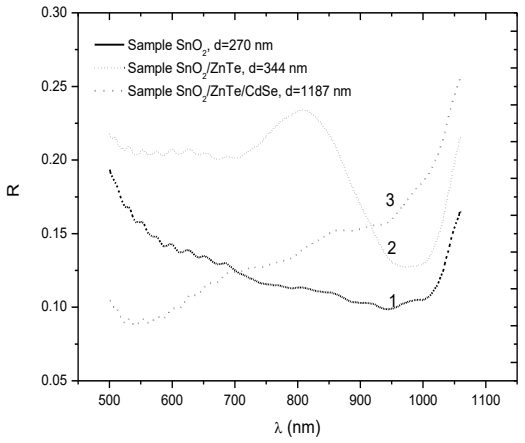

Fig. 9. Reflection spectra for SnO_2/ZnTe/CdSe systems Curve 1: SnO_2 film deposited onto glass substrate; Curve 2: ZnTe film deposited onto SnO_2 coated glass substrate; Curve 3: CdSe film deposited onto a ZnTe coated glass +SnO_2 film substrate.

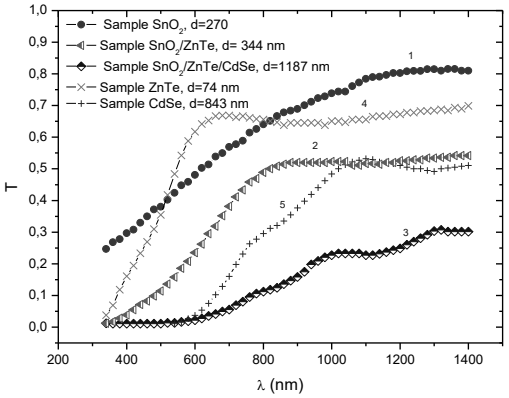

Fig. 10. Transmission spectra for SnO_2/ZnTe/CdSe in heterostructure: Curve 1 SnO_2 film glass substrate; Curve 2: ZnTe film deposited onto SnO_2 coated glass substrate; Curve 3 CdSe film deposited onto a ZnTe coated glass +SnO2 film substrate; Curve 4 ZnTe thin film deposited onto glass substrate; Curve 5 CdSe thin film deposited onto glass substrate.

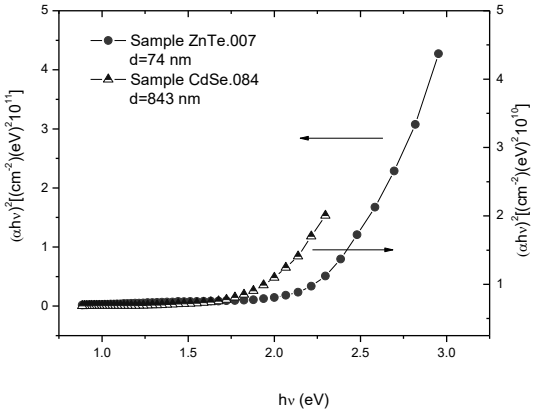

Fig. 11. Spectral dependence of the absorption coefficient $(\alpha h\nu)^2=f(h\nu)$ for sample ZnTe.007 and for sample CdSe.084.

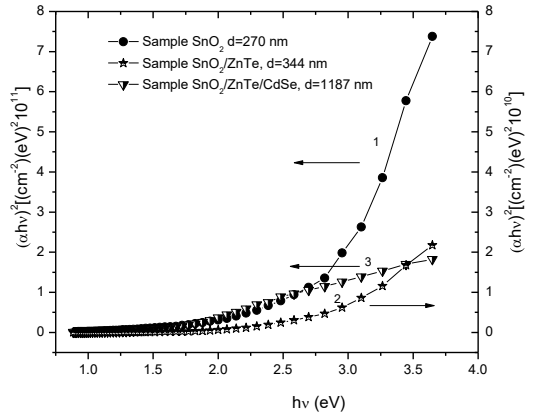

Fig. 12. Spectral dependence of the absorption coefficient $(\alpha h\nu)^2=f(h\nu)$ Curve 1: SnO_2 film deposited onto glass substrate; Curve 2: ZnTe film deposited onto SnO2 coated glass substrate; Curve 3 CdSe film deposited onto a ZnTe coated glass + SnO_2 film substrate.

By taking into account optical band-to-band transitions ZnTe and CdSe are considered to be direct semiconductors [2,10,16]. Therefore, the energy dependence of absorption coefficient, α, near the fundamental absorption band edge for band-to-band transitions is described by expression.[11-13,24]

$$\alpha \cdot h\upsilon = A_a\left(h\upsilon - E_g\right)^{1/2} \qquad (2)$$

where $h\upsilon$ is incident photon energy, A_a denotes a characteristic parameter (independent of photon energy) for respective transitions, and E_g is energy bandgap.

For SnO_2 have been evidenced both allowed direct and indirect, but the optical band gap for SnO_2 has greater values (E_g=3.7 eV).

Therefore, in the wavelength range 400-1400 nm this compound has a good transparence.

Transmission and absorption spectra were studied (in the spectral range 340-1400 nm) both for component films and heterojonctions.

The optical energy gap, E_g, was determined by extrapolating the linear portions of $(\alpha h\upsilon)^2 = f(h\upsilon)$ dependences to $(\alpha h\upsilon)^2 = 0$. For studied samples the optical bandgap values ranged between 1.95 eV and 2.40 eV, which are in good agreement with the values of bandgap width reported for ZnTe and CdSe crystals (for ZnTe crystals, the optical bandgap values ranged between 2.00 eV-2.20 eV and for CdSe crystals these values varied between 1.65 eV and 1.90 eV) (Fig. 11 and 12).

The values of energy bandgap determined from absorption spectra (supposing that allowed direct band-to-band transitions are predominate) are similar. It is know that effects of polycrystalline structure of films on the optical properties are small.

In comparison with a single crystals, the absorption spectra of polycrystalline films have a little additional peak for photon energies less that the energy bandgap.

Current-Voltage characteristics

The static current-voltage characteristics depend on the structure of component films.

Typical current-voltage (I-V) characteristics are presented in Fig. 13. The contacted area of the component films was about 1 cm^2. At low forward voltage the I-V characteristics are almost linear. For higher values of the voltage the current is an exponential function of the voltage.

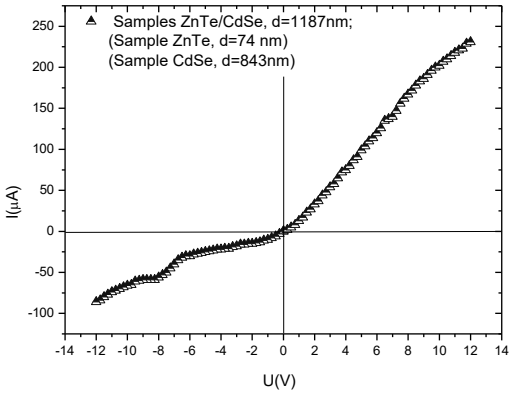

Fig. 13. Typical current-voltage characteristic of ZnTe/CdSe heterojonctions.

The reverse biased heterojounctions had not current saturation. We consider that the trapping sites at the crystallite boundaries strongly influence the electronic transport mechanism through heterojounction.

A detailed discussion on the current-voltage characteristics will presented in other paper.

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