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ON THE ELECTRICAL AND OPTICAL PROPERTIES OF NANOCRYSTALLINE CdTe THIN FILMS*

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In the paper, the experimental results regarding the temperature dependence of the electrical conductivity in the temperature range 300 – 550 K, the transmission spectra in the 500 – 1400 nm wavelength range and reflexion spectra in the 1.5 – 6.5 eV photon energy range, as well as the effect of the heat treatment on the spectra, for CdTe thin films having a nanocrystalline structure are presented. The CdTe films (d = 100 nm – 1700 nm) were prepared by the quasi-closed volume technique. The substrate temperature ranged between room temperature and 600 K and the source temperature ranged from 1000K to 1270 K. The XRD investigations revealed that, depending on the deposition conditions, both the textured and quasiamorphous CdTe films may be obtained. The films deposited onto unheated substrates with greater source temperature present a quasiamorphous structure and an excess of tellurium atoms, which precipitate in crystalline form during the heat treatment. It was found that these films present an irreversible temperature dependence of the electrical conductivity and a decrease of film transmitance. These results are correlated with the film recrystallisation during the annealing process. The effect of the heat treatment on the transmission and reflection spectra of the films is also investigated.

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1. Introduction

From the chalcogenide semiconductor class, cadmium telluride is of continuing promising contenders for use in a large scale for the thin film devices technology (i.e. solar cells, IR and γ detectors, field effect transistors, etc.) [1–5]. The efficiency of these devices is strongly determined by the electrical and optical properties of the component films. A study of these properties and their dependence on the preparation conditions presents a great importance because it permits to establish the best growth conditions for obtaining films which to assure a highly and stable efficiency of respective devices. In the last decade, the experimental investigations on the electrical and optical properties of CdTe films obtained by different techniques were intensified [6–14]. From the methods used for the preparation of CdTe films, the thermal evaporation in vacuum is often preferred because it offers large possibilities to modify the deposition conditions and so to obtain films with determined structure and properties. One of the preparation methods, which use the thermal evaporation in vacuum, is the quasi-closed volume technique. It permits to change the deposition conditions by varying the temperature of both the substrate and evaporation source and also by the modification of the shape and the volume of the chamber, which delimit the deposition space [15]. Using such a deposition technique, we have obtained both the textured and quasiamorphous CdTe films. It was found that the structure strongly influences the electrical and optical properties of the films. In the present paper we report some experimental results regarding the electrical and optical properties of nanocrystalline CdTe films obtained by the above-mentioned method.

2. Experimental

CdTe thin film samples were deposited onto glass substrates under vacuum by physical vapour deposition technique in a limited deposition space. The deposition chamber consisted in a Pyrex vessel of special shape closed at the top by the heater-substrates holder system (Fig. 1). More details on the experimental setup and on the deposition technique are given in Ref. [15].

The temperature of the evaporation source, T_{ev}, was varied between 1000 K and 1270 K and the substrate temperature, T_s, ranged from room temperature to 600 K.

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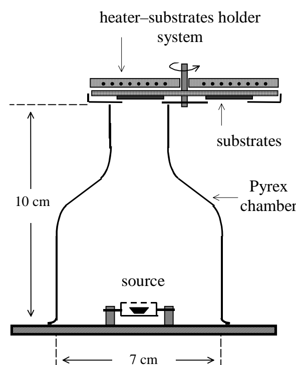

Fig. 1. The experimental setup used for the film deposition.

After preparation, a number of samples were heat-treated by annealing in air at rate of 1–2 K/min, from room temperature to final 475 K, which was maintained for 30 min. Then the sample was cooled down at the same rate.

The film thicknesses, d, measured with an interference microscope, ranged between 100 nm and 1700 nm. The film structures were investigated by standard X-ray diffraction (XRD) technique using CoK_α radiation (λ=0.1790 nm).

For the electrical measurements, samples with planar geometry have been used. Vacuum deposited indium thin films were used as electrodes. The electrical conductivity, σ, was determined according to the relation $\sigma = l/(R.d.b)$, where $l = 2$ mm is the distance between the electrodes, b =1 cm was the width of the film and R represents the electrical resistance of the film, measured by a standard d.c. method, using a KEITHLEY 6517A electrometer.

For the study of the optical properties, normal-incidence transmittance, T, and near-normal-incidence reflectance, R, at room temperature were recorded in the wavelength range 500-1400 nm and 350 – 550 nm respectively.

3. Results and discussion

3.1. Structural characteristics of the films

The analysis of the XRD patterns for the studied samples revealed a strong dependence of the structural characteristics of the films on the deposition parameters, primarily on the deposition rate (the source temperature). In Fig. 2 typical diffraction patterns for the samples deposited at different source temperatures are presented. The patterns in Fig. 2 (a,b) correspond to samples deposited at lower or moderate source temperature, while those from Fig. 2 (c) are typically for films deposited at greater source temperature (>1100 K). As it may be seen from Fig. 2 (a), the pattern of the film deposited at lower source temperature presents a sharp diffraction peak at $2\theta \cong 27.7^0$ which corresponds to (111) planes of the cubic CdTe structure [16]. This proves that in these films the microcrystallites have a preferential orientation with the (111) plane parallel to the substrate. The calculated average crystallite size of such films is about 10 nm [15]. It is found that the structure of these films does not change essentially after a heat treatment. Therefore, the structure of such films is stable and not affected by the annealing.

With increasing of the source temperature, in the XRD patterns of respective samples appear additional peaks at 2θ of about 46.1^o and 54.6^o, which correspond to diffraction from (220) and (311) planes of the CdTe cubic phase respectively [16] (Fig. 2(b)). Also, it may be observe that the respective diffraction pattern exhibits an additional broad peak at $2\theta \cong 32.1^0$. This peak corresponds to the reflection on (101) planes of the hexagonal Te structure [15]. This indicates that the increase of source temperature determines an excess of tellurium atoms in the respective films.

The structure of the films deposited at T_{ev} greater than 1100 K is more influenced by the source temperature. As it may be seen from Fig. 2(c), the structure of the as deposited film is quasiamorphous. The respective XRD pattern exhibits the weak broad (111), (220) and (311) peaks which indicate the existence of fine grained CdTe crystallites in respective film. The post-deposition

heat treatment determines a significant improvement of the film structure as a consequence of the recrystallization process. As it may be seen from Fig. 2(d), the recrystallized films have the structure of CdTe cubic phase, with a random orientation of the microcrystallites. It may be also seen that respective films exhibit Te excess, which aggregates in crystallite form as a consequence of the heat treatment.

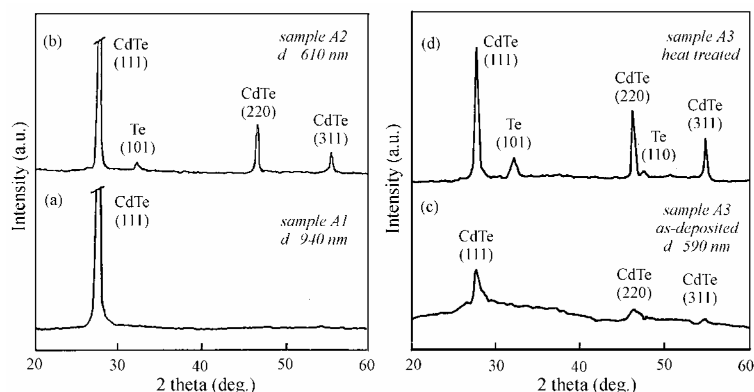

Fig. 2. XRD patterns (Co K_α radiation) of three representative CdTe films deposited at different source temperature: (a) T_{ev}= 1020 K; (b) T_{ev}= 1100 K; (c) T_{ev}= 1270 K; (T_s=300 K).

It was found that the structures of the CdTe thin films deposited at the same conditions as above but onto heated (up to 600 K) substrates do not differ essential by those presented. It results that the principal characteristics of the studied nanocrystalline CdTe films are the textured structure for those deposited with lower source temperature and a quasiamorphous structure with Te excess for the films deposited with greater source temperature.

The presence of some amount of free Te atoms in the respective films influence not only the film structure but also their electrical and optical properties, as it will be seen in next paragraphs.

3.2. Electrical properties

In Fig. 3, the temperature dependences of electrical conductivity are presented during heating-cooling cycles within the temperature range 290 K – 550 K, for the films deposited with different source temperature. As it may be observed, for the films deposited at lower source temperature, this dependence is linear and reversible. The values of electrical conductivity of as deposited films, σ_c, and that determined at room temperature after heating-cooling cycles, σ_t, are almost the same (of order of $10^{-6}\ \Omega^{-1}m^{-1}$) (Fig. 3(a)). The films which contain Te excess present an irreversible temperature dependence of electrical conductivity in the first heating-cooling cycle (Fig. 3 (b,c)). The values of σ_c for these films are of one or two orders of magnitude higher than those, which have an oriented nanocrystalline structure. Also, as it results from Fig. 3(b, c) the values of σ_t for these films depend on the temperature at which the film annealing is stopped. If the film annealing is stopped before the appearance of the complete irreversible shoulder, the value of σ_t for the respective sample is higher than σ_c (Fig. 3(c)). When the film cooling begins after the shoulder formation end, the σ_t is lower than σ_c (Fig. 3(b)).

The irreversible temperature dependence of the electrical conductivity for respective films is supposed to be due to the changes in film structure during the annealing process. Indeed, as it was shown above, these films contain a large amount of free Te atoms not bonded in the CdTe lattice. These free Te atoms trap electrons on their available chemical bond and create acceptor states [17]. In this way, the charge carrier density in these films is greater in comparison with that of the stoichiometric sample. Consequently, the electrical conductivity of the respective films will be greater, fact that explains the greater value obtained for their σ_c.

With increasing temperature during annealing process, precipitation of the free Te atoms in the film with a greater amount of Te excess begins. This process determines at its beginning an important increase of carrier concentration (hence of σ) due to the trapped electrons release. Then, at higher temperatures, as a consequence of the recrystallisation process, the number of free Te atoms gradually decreases and therefore decreases the acceptor state density.

As a result of these two opposite processes, the electrical conductivity of the film begins first to increase and then to decrease, determining the formation of the shoulder in the curve $\ln \sigma = f(10^3/T)$.

After complete crystallization of the tellurium excess, the film structure becomes stable and the temperature dependence of electrical conductivity in subsequent heating-cooling cycles becomes reversible.

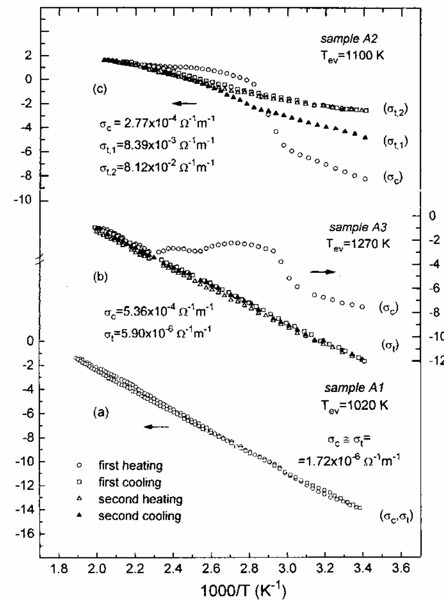

Fig. 3. Typical temperature dependence of electrical conductivity during heating-cooling cycles for CdTe films deposited at different source temperature.

Depending on the preparation conditions, especially on those that determine the amount of free Te atoms, the irreversible variation of σ is more or less pronounced.

3.3. Optical properties

The optical properties of nanostructured CdTe films are also influenced by the Te excess. In Fig. 4 the transmission spectra (relative to uncovered substrate) in the wavelength range of CdTe fundamental absorption edge (500 – 1400 nm), for CdTe films deposited at different source temperatures are presented. Curve (b) corresponds to sample *A2* having the structural characteristics showed by pattern (b) in Fig. 2. Curve (c) corresponds to sample *A3* with structure characterized by the pattern in Fig. 2(c). For comparison, the transmission spectra of a CdTe film deposited at conditions that favor the growth of large (of about 70 nm) and oriented crystallites are shown in Fig. 4(a). As it may be seen, the absorption edges for samples *A2* and *A3* are less steep and the transmittance decreases with increasing source temperature. These behaviors may be correlated with the structural characteristics of the respective films. It is known that the films with a large grain sizes and strong orientation of the crystallites shown an optical behavior similar to that of single-crystal material [18 – 20]. In the case of our nanostructured samples, the film crystallites having smaller sizes, one can expect a lower transmittance of such films. Moreover, the presence of the free Te atoms in the samples deposited at greater source temperature determines a supplemental decrease of the film transmittance due to the numerous staking faults, disorder and defects in structural bonding introduced by these atoms. Also, the stronger absorbance of tellurium in the studied spectral range [21] contributes more to the decrease of the film transmittance.

On the other hand, as it was shown in the previous paragraph, the tellurium excess creates a high concentration of the acceptor states in respective films. The electronic transitions from these acceptor levels to the conduction band should induce an increase of the light absorption in the long wavelength side of the fundamental absorption edge. This may explain the less slope of the absorption edge observed in the transmission spectra for sample *A2* and *A3*.

For certain samples, the transmission spectra were plotted before and after heat treatment of the films. In Fig. 5 such spectra are presented for the sample *A2*. As it can be seen, after the heat treatment the film transmittance decreases. It was found that this decrease is more significant for the films deposited at greater source temperature. We consider that the lower transmittance of heat-treated films is due primarily to the precipitation of Te excess and to the high absorption coefficient of tellurium in this spectral region. As it is known, the heat treatment leads to an increase of the crystallite sizes and an improvement of the film crystallinity [18]. So it could be expected after heat treatment the film transmittance to be greater. But in the case of our CdTe samples, the annealing process not only increases the CdTe crystallite sizes but also increases the size of Te microcrystallites

which may be grow in the respective film still during the deposition process. Moreover, during the annealing process, in the films with greater Te excess, some further precipitation of this excess may take place. If one takes into account the higher value of the Te absorption coefficient, it indicates that in the heat-treated films the Te microcrystallites have an important role in the light absorption. In this way, it is possible that the transmittance of the CdTe films with greater Te excess to decrease after the heat treatment.

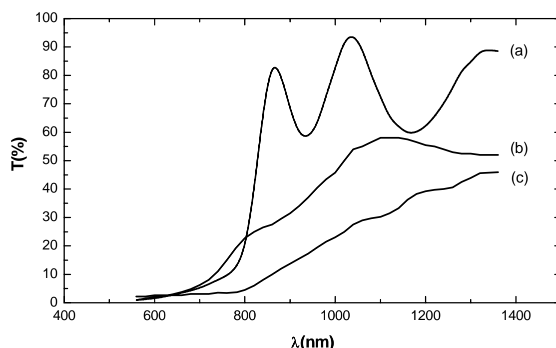

Fig. 4. Typical transmission spectra for the CdTe films deposited at different conditions
(a) T_s=580 K;T_{ev}= 1020 K; d= 650 nm; (b) T_s=300 K;T_{ev}= 1100 K; d= 610 nm;
(c) T_s=300 K;T_{ev}= 1270 K; d= 590 nm.

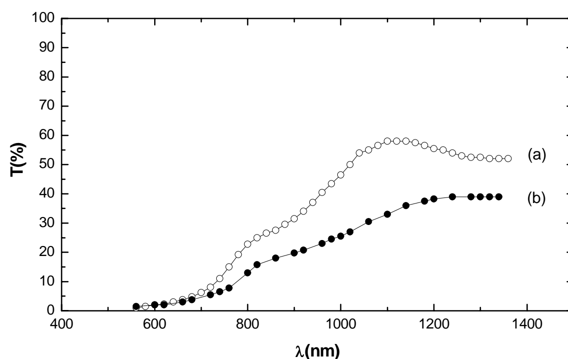

Fig. 5. Effect of the heat treatment on the transmision spectra:
(a) before heat treatment; (b) after heat treatment (sample *A2*).

It was also studied the effect of heat treatment on the film reflection spectra in the photon energy range 1.5 – 6.5 eV. In Fig. 6 the reflection spectrum is presented plotted before (curve a) and after (curve b) heat treatment of the sample *A3*. It may be observed a significant improvement of the shape of the spectrum after film annealing. The sharpness of the interference fringes indicates a decrease of surface roughness and an important improvement of the film crystallinity. It may be also seen in respective spectra a reflection minimum at photon energy of about 3,45 eV, which is better pronounced in the spectrum of the heat-treated film. This minimum can not be attributed to the interference picture. More possible is that these minimums indicate the presence of an absorption peak in the respective region. Such absorption peak was reported by Myers et al. [22] for bulk CdTe and was attributed to the electronic transitions, which occur at the L point of the Brillouin zone. Therefore, the above mentioned reflection minimum is ascribed to such electron transitions. The more pronounced minimum from the spectrum of the heat-treated sample shows that after heat treatment the studied films have, in respective spectral region, optical behavior similar to that of bulk CdTe.

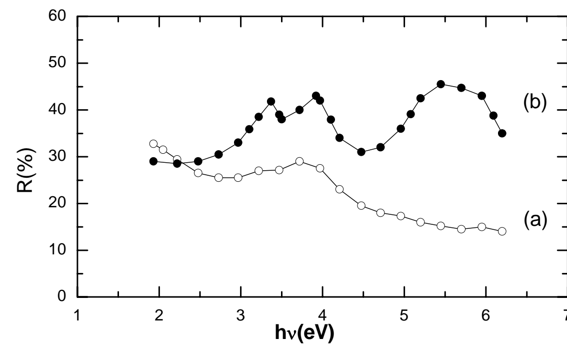

Fig. 6. Effect of the heat treatment on the UV reflection spectra:
(a) before heat treatment; (b) after heat treatment (sample *A3*).

4. Conclusions

Using the quasi-closed volume technique, CdTe thin films with nanocrystalline structure were obtained. By XRD studies it was established that the film structure were primarily influenced by the source temperature. A greater source temperature (> 1100 K) determines a higher amount of free Te atoms in the films and a quasiamorphous structure. The films with Te excess are characterised by higher values of electrical conductivity and an irreversible temperature dependence of these during heating-cooling cycle. These films have a lower transmitance in the long wavelength side of the fundamental absorption edge.

The heat treatment determines a reversible $\ln \sigma = f(1/T)$ dependence, a decreasing of the film transmittance and an improvement of UV reflectance. These behaviors are primarily determined by the film recrystalisation and by the precipitation of Te excess during the annealing process.

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