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OPTICAL BEHAVIOR OF MULTILAYERED CdTe/Cu THIN FILMS DEPOSITED BY STACKED LAYER METHOD

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In this paper the experimental results concerning the absorption and photoluminescence spectra in the wavelength range 650 – 1100 nm for CdTe/Cu multilayered thin films are presented. Films with thickness about 900 nm were evaporated under vacuum onto unheated optical glass substrates using the stacked layer method. During deposition process, the substrates holder periodically passed in front of two separately evaporation sources for CdTe and Cu, having the temperatures of 925 K and 1200 K respectively. The XRD structural analysis revealed a cubic CdTe structure, with crystallites preferentially oriented with (111) plane parallel to the substrate, without additional peaks for Cu or Te structures. The energy gap value of 1.48 eV, deduced from absorption spectra, is in good agreement with those for bulk CdTe crystal. The obtained results indicate that this deposition technique may reduce the Te excess and improve the structure and optical properties of CdTe thin films for optoelectronic devices technology.

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Keyword: CdTe films, Layered structures, Optical properties

1. Introduction

Cadmium telluride (CdTe) is one of the leading thin film photovoltaic materials due to their optimum energy band gap (about 1.5eV) and light absorption coefficient (>10^4 cm^{-1}) for visible solar radiation. In the low-cost CdTe-based solar cells, a transparent conducting CdS thin film is used as CdTe partner for formation of the heterojonction. A CdS thin film, p-type CdTe and an ohmic contact are subsequently deposited onto transparent conducting oxide-coated soda-lime glass. The reported efficiency of these solar cells, about 16% [1-5] is lower that those predicted (close to 30% [6]). So, the study regarding the optimization of the properties of device component films and their fabrication technique is still necessary.

Among the growth techniques for large-area and low-cost deposition for CdTe thin films, the vacuum evaporation method is often preferred due to large possibility to modify the deposition conditions. In order to obtain efficient CdS/CdTe heterojonctions by this technique, a high growth temperature during the deposition of CdTe thin films is necessary [7, 8]. However, this may deteriorate the properties of CdS thin-film substrate, so a lower temperature (less than 400 ^{o}C) for deposition of CdTe films is recommended [9]. But an essential problem in deposition of CdTe thin films at lower substrate temperatures is the control of film stoichiometry. Depending on the preparation conditions the films may contain in excess one or other of the constituents, a fact that strongly influences their structural and physical properties. A possibility to decrease such excess is to introduce into the films, during their preparation or by post-deposition treatment, some chemical elements in a convenient approach [5, 10-13].

Our previous studies on the structure and optical properties of CdTe thin films evaporated onto unheated glass substrates revealed some tellurium excess in respective films, which strongly influenced their physical properties. The respective films present a quasi-amorphous structure and a

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greater optical absorption in comparison with films deposited onto heated substrates. Also, the optical band gap energy calculated for CdTe films with Te excess is lower (about 1.43 eV) in comparison with those for stoichiometric CdTe films [14,15]. Tellurium excess in CdTe thin films prepared by different methods has been also observed by other researchers [16-18]. To decrease the Te excess from these films, their doping with some metal atoms which replace the Cd vacancies was proposed [11,13].

S. Jimenez-Sandoval et al. [13,19] have been established that the addition of copper into the sputtered thin films of the semiconductor alloy $Cu_xCd_{1-x}Te$ does not affect the CdTe crystalline structure and lattice constant and inhibits the formation of tellurium aggregates. Taking into account these results, in present paper the effect of Cu-doping on the structure and some optical properties of evaporated onto unheated glass substrates CdTe thin films are investigated.

2. Experimental

The studied samples were thermal evaporated onto glass slides at room temperature by quasi-closed volume technique [20, 21].In order to assure the uniform Cu-doping, an experimental set-up similar to those for the deposition of multilayered thin films was used: the film substrates, placed to a rotating disk, successively passed with constant rotating rate, r, of 50 rpm., over the separate evaporation sources for CdTe (T_{CdTe}= 925K) and Cu (T_{Cu} = 1200 K).Two vertical cylindrical Pyrex tubes close the space between each source and substrate holder in order to limit the deposition space and to confine the vapor steam from each source. To determine the thickness of individual layer of Cu and CdTe deposited in each step, both Cu/Cu, CdTe/Cu and CdTe/CdTe multilayered films were simultaneously obtained. A particular arrangement of film substrates on the rotating holder were used in this purpose.

The interferometrically measured thicknesses of CdTe/Cu samples were 910 nm and 380. The thicknesses, l, of Cu and CdTe individual layers deposited in each step were about 7.6 nm and 10.4 nm respectively and were estimated with relation l = d/r.t ,where t is deposition time and d denotes the total thickness of Cu/Cu and CdTe/CdTe samples respectively.

The crystalline structure of the films was investigated by standard X-ray diffraction (XRD) technique, using Cu Kα radiation. For the optical studies, normal-incidence reflectance, R, and transmittance, T, in the vicinity of fundamental absorption edge were recorded using a STEAG-ETA-OPTIK UV-VIS spectrometer. The absorption coefficient,α, has been calculated from the relation [22]:

$$\alpha = (1/d)\ \ln [(1-R)^2/T]\ , \tag{1}$$

3. Results and discussion

3.1. Structural characteristics of the films

Fig. 1 shows the typical diffraction pattern for as deposited CdTe/Cu films. The sharp diffraction peak observed at 23.7 ^{o} correspond to (111) planes of the cubic CdTe structure [23]. No diffraction peaks associate with metallic Cu,Te or other compounds were observed. This indicates that respective multilayered structures present a single phase with highly oriented CdTe crystallites with the (111) planes parallel to the substrate. The [111] direction is the close -packing direction of the zinc-blende structure and this type of ordering is often observed in polycrystalline CdTe films grown on amorphous substrates [24]. The XRD patern from Fig. 1 indicates an improvement of the crystalline quality of studied samples in comparison with quasi-amorphous structure of CdTe/CdTe sample deposited in the similar conditions. This structural improvement is most likely due to the Cu atoms which reduce the concentration of Cd vacancies.

3.2. Optical properties

Optical absorption spectra for CdTe/Cu films as function of photon energy was studied. The typical spectral dependence of the absorption coefficient in the wavelength range of CdTe fundamental absorption edge (650 -1100 nm.) are presented in Fig. 2. Also, the dependence $(\alpha h\nu)^2 = f(h\nu)$ for the same sample is shown in Fig. 3. The liniar aspect of curve from Fig. 3 indicates that absorption in the high absorption range takes place through direct band-to-band transitions [25]. By extrapolating the liniar portion of respective plot to $(\alpha h\nu)^2 = 0$, the optical band gap energy was determined. The obtained value of 1.48 eV is in good agreement with that for bulk CdTe reported in the literature.

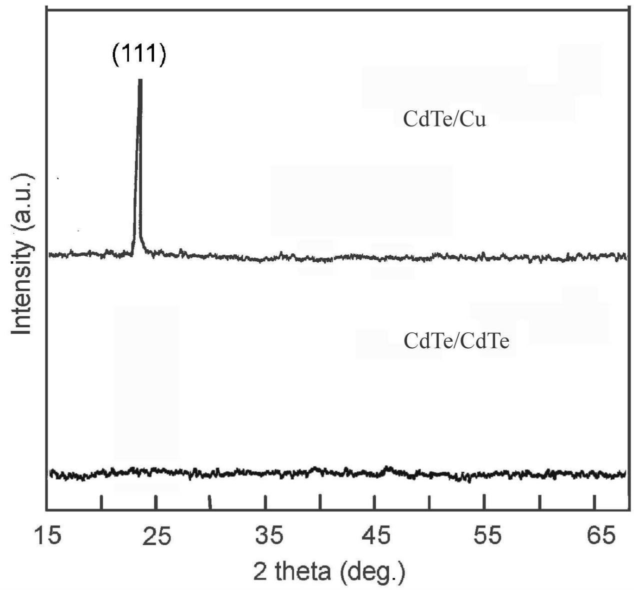

Fig. 1. Typical XRD patterns for studied samples: top – CdTe/Cu sample revealing (111) plane of CdTe; bottom – CdTe/CdTe sample.

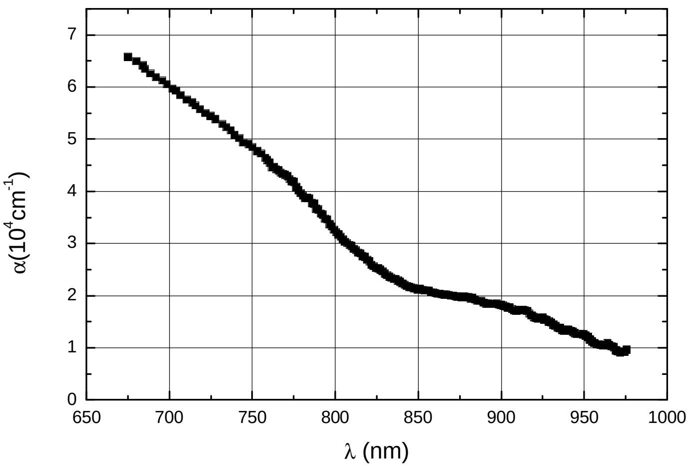

Fig. 2. Typical spectral dependence of absorption coefficient for CdTe/Cu samples.

For some samples, the low temperature photoluminiscence (PL) spectra was carried.Such measurements are a very powerful non-destructive technique used for the caracterization of semiconductors. The photoluminiscence was measured at 80 K using an He-Ne laser (633 nm) at a power density of 1.6×10^{22} quanta /cm^2.s. In Fig. 4 the typical PL spectrum obtained for CdTe/Cu samples is shown .

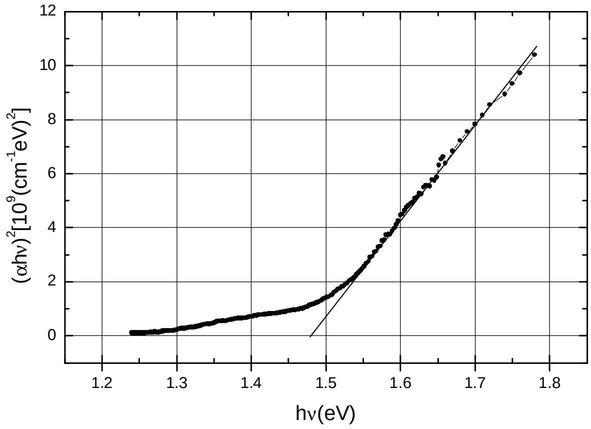

Fig. 3. The dependence $(\alpha h\nu)^2 = f(h\nu)$ corresponding to sample from Fig. 2.

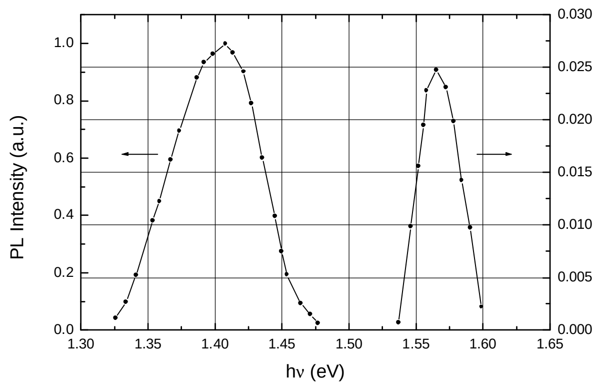

Fig. 4. PL spectrum of CdTe/Cu film at 80 K.

Two maxima located at 1.41 eV and 1.57 eV were observed. The photoluminiscence emission band around 1.57 eV may by considered to be an exitonic band [26,27]. The weaker intensity of this maximum indicates a low life time of exiton determined by the high level of defects and impurity from respective sample.These act as nonradiative recombination centers determining a dramatic decrease of the luminiscence intensity. The 1.41 eV photoluminiscence emission band may be atributed to donor-acceptor pair (DAP) recombination. This band, commonly seen in CdTe , was found to vary in shape and intensity depending on growth techniques and dopants. Usualy, this band is ascribed to intrinsic defect or impurities [6,28]. In our case, the 1.43 eV band may be correlated with native defects due to Cd vacancies and copper impurity acting as acceptor in DAP.

4. Conclusions

The effect of Cu-doping on the structure and optical properties of the CdTe thin films evaporated onto unheated substrates was investigated.

It was established that the incorporation of Cu into CdTe films inhibits the formation of Te aggregates which are commonly observed in such films and improves the crystalline quality of the films.

The value of 1.48 eV obtained for energy band gap for CdTe/Cu films by optical absorption measurements showed that addition of cooper into the films diminishes the effect of tellurium excess on the band gap of CdTe films deposited onto unheated substrates.

The obtained results revealed that deposition of alternate layers of CdTe and Cu may by a promising method for elimination of tellurium excess from CdTe films and for improving of the physical properties of such films used in optoelectronic device technology.

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