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Structural and optical properties of Cu-doped CdTe films with hexagonal phase grown by pulsed laser deposition

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Cu-doped CdTe thin films were prepared by pulsed laser deposition on Corning glass substrates using powders as target. Films were deposited at substrate temperatures ranging from 100 to 300 °C. The X-ray diffraction shows that both the Cu-doping and the increase in the substrate temperature promote the presence of the hexagonal CdTe phase. For a substrate temperature of 300 °C a CdTe:Cu film with hexagonal phase was obtained. Raman and EDS analysis indicate that the films grew with an excess of Te, which indicates that CdTe:Cu films have p-type conductivity. Copyright 2012 Author(s). This article is distributed under a Creative Commons Attribution 3.0 Unported License. [http://dx.doi.org/10.1063/1.4721275]

I. INTRODUCTION

CdTe is a direct bandgap material with a value of 1.5 eV and an absorption coefficient > 10^5 cm⁻¹ in the visible region, which means that a layer thickness of few micrometers is sufficient to absorb 90% of incident photons. As grown CdTe thin films can exhibit n or p-type electrical conductivity, it has been established that cadmium excess yields n-type while telluride excess yields p-type conductivity.¹ CdTe thin-film solar cell is one of the most promising candidates for photovoltaic energy conversion. The maximum theoretical efficiency for a CdTe/CdS solar cell, at standard spectrum, is about 30%.² In this system a p-type CdTe film plays the role of absorber layer. One of the limitations to increase the efficiency is the difference between the crystal structure of CdTe and CdS that are cubic and hexagonal,³ respectively, because a large density of defects is generated in the interface. A way of reducing this would be to grow the two layers with the same phase. Because the stable phase of CdS is the hexagonal phase is very important to obtain CdTe in hexagonal phase. CdTe polycrystalline films can be prepared by several growth techniques such as close-space sublimation (CSS),⁴ chemical deposition,⁵ sputtering,⁶ pulsed laser deposition (PLD),⁷ vapor transport deposition (VTD), physical vapor deposition (PVD), spray deposition⁸ among others. Some of these techniques, such as CSS, VTD, PVD requires a high growth temperature. Due to the high deposition temperature, the CdTe films are deposited with Cd deficiency, giving rise to p-type conductivity. PLD has some advantages over other techniques, for instance; the high energy atoms and ions in the laser-induced plasma plume produces a higher surface mobility which makes it possible to grow high quality films at relatively low substrate temperature.⁸ In this work we report on the influence of the substrate temperature on the structural and optical properties of CdTe:Cu films grown by PLD. Undoped and Cu-doped CdTe films at low deposition temperature (100-300 °C) with high crystalline quality and excess of Te were obtained. For a substrate temperature of 300 °C a CdTe:Cu film with hexagonal structure and p-type conductivity was obtained.

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TABLE I. Cd and Te concentrations, crystal size, thickness and bandgap ($E_g$) of CdTe and CdTe-Cu films.

| Sample     | Cd (%)  | Te (%)  | Cd:Te ratio | Crystal size (nm) | Thickness (μm) | $E_g$ (eV) |
|------------|---------|---------|-------------|-------------------|----------------|------------|
| CdTe-300   | 42.9    | 57.1    | 0.75        | 28                | 5.03           | 1.49       |
| CdTe:Cu-100| 48.45   | 51.55   | 0.94        | 39                | 2.95           | 1.34       |
| CdTe:Cu-200| 48.30   | 51.70   | 0.93        | 40                | 4.63           | 1.39       |
| CdTe:Cu-300| 49.43   | 50.57   | 0.98        | 37                | 3.52           | 1.41       |

FIG. 1. XRD patterns of undoped and Cu-doped CdTe films grown at different substrate temperature. Note that the growth temperature and the Cu-doping promote the presence of CdTe in hexagonal phase.

II. EXPERIMENTAL DETAILS

Undoped and Cu-doped CdTe films were grown on Corning glass substrates by modified PLD, this technique uses powders enclosed in a glass ampoule as target. The details of the deposition system are described elsewhere. The films were prepared using a Nd:YAG laser at 1064 nm with a pulse width and frequency of 5 ns and 10 Hz, respectively. The materials employed were powders of CdTe and Cu$_2$Te with a purity of 99.99%. The powders composition used was 1 wt% Cu$_2$Te + 99 wt% CdTe. The powders were mixed by ball milling. Films were grown at substrate temperatures ranging from 100 to 300 °C. The background pressure in the deposition chamber was $10^{-4}$ Torr and the vacuum in the chamber was maintained during the growth. The distance between source material and substrates was 2.2 cm. The growth time was 10 min. The samples were labeled according to the substrate temperature (Table I). Four samples were prepared and studied: three Cu-doped CdTe films and one undoped CdTe film grown at 300 °C used as reference (CdTe-300 sample). The crystalline structure was determined by X-ray diffraction (XRD), with a Siemens D5000 diffractometer, using
FIG. 2. SEM images of the surface morphology of CdTe and CdTe:Cu films grown by PLD.

III. RESULTS AND DISCUSSION

XRD patterns of the undoped and Cu-doped CdTe films are shown in Fig. 1. It can be seen that all samples present two common peaks located at 23.68° and 39.26°, these peaks may correspond to the cubic or hexagonal CdTe phase and the diffraction planes are (111)C/(002)H and (220)C/(110)H, respectively. Because the CdTe stable phase is the cubic it is proposed that the CdTe-300 and CdTe:Cu-100 samples have cubic structure. The diffractogram 1c) presents three peaks located at 23.68°, 39.26° and 42.64°, the peak located at 42.64° corresponds to the hexagonal CdTe phase and the diffraction plane is (103)H, which indicates that probably the CdTe:Cu-200 sample has the hexagonal phase. The diffractogram 1d) exhibits six diffraction peaks at 22.36°, 23.68°, 25.38°, 32.76°, 39.26° and 42.64°, the peaks located at 22.36°, 25.38°, 32.76° and 42.64° correspond to the hexagonal CdTe phase and the diffraction planes are (100)H, (101)H, (102)H and (103)H. Due to the presence of these four peaks corresponding to the hexagonal phase, the peaks located at 23.68° and 39.26° can be assigned to the hexagonal phase and the diffraction planes are (002)H and (110)H. Therefore, the CdTe:Cu-300 sample has the hexagonal CdTe phase. It is important to note that the diffractograms of the CdTe-300 and CdTe:Cu-100 are very similar, while the diffractograms of the CdTe:Cu films grown at 200 and 300 °C present additional diffraction peaks which correspond to hexagonal phase. From XRD patterns it can be seen that both the incorporation of copper in the CdTe
structure and the increase in the substrate temperature cause the presence of hexagonal CdTe in films grown by pulsed laser deposition. The crystallite size was calculated from XRD using the Scherrer formula: 

$$d = \frac{0.9 \lambda}{B \cos \theta_B}$$

where $d$ is the crystallite diameter, $\lambda$ is the wavelength (1.5406 Å), $B$ is the full width at half maximum (FWHM) of the peak and $\theta_B$ is the Bragg angle. The crystallite size is between 28-40 nm (see Table I).

Fig. 2 shows the surface morphology of undoped and Cu-doped films grown at different substrate temperature. The CdTe-300 sample presents grains of arbitrary shape (Fig. 2(a)). The Fig. 2(b) shows the morphology of CdTe:Cu-100 sample which presents grains with circular shape and different grain size ranging from 100 nm to 1.2 μm. The CdTe:Cu-200 sample (Fig. 2(c)) has a smooth morphology with few particles on the surface, these particles have sizes ranging from 150 to 620 nm. The Fig. 2(d) shows the surface morphology of CdTe:Cu-300 sample, which presents a smoother surface composed of flakes. Note that the substrate temperature plays a role very important on the surface morphology of CdTe thin films grown by PLD. It should be note here that SEM images show the grain size while XRD gives the crystallite size and can be different. The XRD and SEM analysis indicate that the grains are composed of small crystallites.

Fig. 3 shows representative Raman spectra for the undoped and Cu-doped CdTe films grown at different substrate temperature. All spectra showed the CdTe longitudinal optical (LO) mode at the frequency of 166.5 cm$^{-1}$ and their second order (2LO) mode at 333 cm$^{-1}$, characteristic of CdTe.\(^6\) The LO modes of cubic and hexagonal phases of CdTe can coincide at the same frequency,\(^13\) so these measurements agree with those of XRD. The features located at 123 and 142 cm$^{-1}$ correspond to the phonon vibrations $A_1$ and $E_1$ modes, respectively, in the hexagonal Te structure.\(^6\)\(^,\)\(^14\) The Te characteristic signals appears well defined in 2a) and 2c) spectra and weaker but still noticeable in 2b) spectrum. The Raman measurements indicate that undoped and Cu-doped CdTe films grew with an excess of Te. In order to check this fact EDS measurements were performed. In Table I...
are compiled the atomic concentrations for Cd and Te obtained from EDS analysis as well as the Cd:Te ratio. It can be appreciated that all samples grew with an excess of Te. The Cd:Te ratio of the undoped CdTe-300 sample has a value of 0.75, whereas the Cd:Te ratio for the CdTe:Cu-300 sample was 0.98, note that the last sample presents lower Te excess. Both Raman and EDS measurements indicate that films grew with Te excess. It is accepted that CdTe films with Te excess have p-type conductivity.1

The Fig. 4 shows the transmittance spectra of the CdTe films. The transmission is practically zero in the visible region. The absorption coefficient (α) was calculated for each film by the equation:15

\[ T = (1 - R)^2 \exp(-\alpha d) \]

where \( T \) is the transmittance, \( R \) the reflectance and \( d \) the film thickness. The thickness for the samples is found in Table I. The absorption coefficient was used to determine the bandgap (\( E_g \)) using the relation \( a h\nu \approx (h\nu - E_g)^{1/2} \), where \( h\nu \) is the photon energy, as shown in the inset of Fig. 4. The bandgap of undoped CdTe film has a value of 1.49 eV, which agree well with the 1.5 eV bandgap of CdTe at room temperature.1 The bandgap of Cu-doped CdTe films increases from 1.34 to 1.41 eV (Table I). Comparing the bandgap value of the CdTe-300 and CdTe:Cu-300 samples, it can be observed that the Cu-doping reduces the bandgap (from 1.49 to 1.41 eV) of the CdTe films. The decreasing of the bandgap probably can be attributed to the incorporation of Cu ions in the lattice giving rise to acceptor levels in the bandgap. The acceptor levels become degenerate and merge in the valence band causing the valence band to extend into the forbidden region, which reduces the bandgap, a similar behavior has been observed in other II-VI materials.16
IV. CONCLUSIONS

CdTe:Cu films with hexagonal phase at low deposition temperature were obtained by PLD. The structural, compositional and optical properties of CdTe:Cu films were investigated as a function of the substrate temperature and the Cu-doping. The structural analysis indicates that the Cu-doping and the increase in the growth temperature promote the presence of hexagonal CdTe phase. The Raman and EDS measurements indicate that undoped and Cu-doped films grew with an excess of Te, this indicates that the films probably have a $p$-type conductivity. For a substrate temperature of 300 °C a $p$-type CdTe:Cu film with hexagonal phase was obtained.

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