



Airy pattern on narrow photoluminescence spectrum of band to band recombination in CdTe:Te thin films



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ARTICLE INFO

Keywords:

Thin films

CdTe

Sputtering deposition

X-Ray, Optical characterization

ABSTRACT

Semiconductor CdTe:Te films were deposited by means of rf sputtering on glass substrates. The excess of Te gave place to a high number of Cd-vacancies (V_{Cd}) producing p-type CdTe films. The density of carriers produced a high strength surface electric field which allowed obtain the bandgap value employing modulated transmittance spectroscopy. The obtained bandgap value of 1.40 ± 0.01 eV was confirmed by absorption spectroscopy measures. The density of holes is so high that bandgap renormalization is observed. Photoluminescence (PL) measurements were carried out with the down-converted 883.2 nm (1.403 eV) line of the 441.6 nm wavelength of a He-Cd laser. This energy allows to produce a resonant excitation of the CdTe:Te films, in such a way that electrons from the conduction band (CB) can be just excited to the valence band (VB). The resonant excitation produced a PL spectrum of band to band electron-hole recombination showing discrete energy emissions that follow the pattern of oscillations corresponding to the Airy model for a quantum triangular potential well. The average width of signals of the higher energy oscillations is 12 ± 3 μ eV and separation between energy levels is of the order of 12 ± 3 μ eV.

1. Introduction

The high absorption coefficient and optical bandgap value of the semiconductor CdTe had kept alive the interest on this material for many years. Even when recent technological advances had allowed obtain commercial CdTe based solar cells with increased efficiency and lab cells with a record value of 21% it is still far from the theoretical limit established by the detailed balance approximation [1]. The efficiency improvement in CdTe based solar cells had detonated an increasing demand for it then it is necessary to develop alternatives to the slow traditional purification processes used nowadays [2]. Beside its application in the production of solar cells, CdTe is used in the fabrication of radiation detectors for astrophysical and medical applications [3] and high resolution imaging devices [4], among others. For these optical applications it is important to understand the reflection, absorption, and transmission processes of the light along with the photon emissions produced under excitation by means of light, heat, electric field, etc. In particular to improve the efficiency of CdTe based solar cells it is of paramount importance to understand the diverse processes associated with hole carriers [5]. In the past our group has characterized diverse aspects of the photoluminescence (PL) spectrum of CdTe

films such as multiphonon emissions [6], the influence of Cadmium vacancies on it [7], the dependence of the energy bandgap on temperature [8], and more recently, the donor–acceptor pair effects on it [9]. Now, we are reporting the sharp photoluminescence (PL) of a p-type CdTe:Te polycrystalline film with a bandgap value (E_g) of 1.40 ± 0.01 eV, which occurs when the excitation source is the 883.2 nm line (1.404 eV) obtained by down conversion of the 441.6 nm light of a He-Cd laser. The similar values between the energies of the bandgap and PL excitation line produces a resonant excitation in the CdTe films. The CdTe films were deposited by the RF sputtering technique employing an additional source of Te in order to obtain samples with a high content of Te. The surface states associated with the presence of cadmium vacancies produced an approximated triangular well with an electric field normal to the surface. It is worth to mention that the lower band gap value, as compared with that of a CdTe single crystal, is due to the high density of carriers associated to the Te content. The CdTe films were characterized by X-ray diffraction, X-Ray fluorescence spectroscopy and room temperature absorption, Raman, modulated transmission and PL spectroscopies. The hole density was obtained from Hall effect measurements. The band to band PL emission is accompanied at lower and higher energies than E_g by oscillations of

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intensity which follow an Airy pattern characteristic of quantum confinement in a triangular potential well.

2. Experimental

The Te rich CdTe sample was grown on a 7059 Corning glass substrate at room temperature (RT) using a balanced magnetron rf 13.5 MHz sputtering system with a water-cooled cathode. The system is monitored employing ion and pirani gauges. A pressure base of 10^{-6} Torr was attained prior to film deposition by employing a diffusion pump backed with a mechanical pump. The working plasma was produced using 10 mTorr of UHP Ar gas. The rf power utilized during the growth process was 30 W with a distance of 4 cm between the target and substrate. The glass substrates were cleaned by a standard technique using detergent and organic solvents. The extra Te atoms were introduced in the samples by co-sputtering from a single CdTe target on which a piece of elemental tellurium of purity of $\sim 99.999\%$ placed above. The cold pressed 1 in. diameter circular target was prepared using CdTe powder material with $\sim 99.999\%$ of purity from CERAC. The effective area of the metallic Te was approximately 2%, this figure is obtained taking in account the small erosion profile associated with the balanced magnetron sputtering process. The thickness of the CdTe film was 250 ± 10 nm as measured with a KLA TENCO P-15 profilometer. The Cd and Te contents in the films were measured by means of X-ray spectroscopy (EDS) using a Voyager II X-ray quantitative microanalysis in an1100/1110 EDX system from Noran Instruments, with an uncertainty of $\pm 1\%$. The determination of Cd and Te content was calibrated by employing CdTe polycrystal with a purity of 99.999% from CERAC. The sign and concentration of carriers were obtained through Hall Effect measurements, performed in a conventional apparatus from GMW magnet systems model 3472-50. The crystalline structure of the films was determined by x-ray diffraction patterns, measured with a diffractometer SIEMENS D5000, the system has an instrumental line-width of 0.05° at 45° in the 2θ scale. The RT optical absorption spectra of the films were measured by using a UNICAM 8700 spectrophotometer. RT Raman spectroscopy was carried out employing a Jobin Yvon Labram micro Raman using the 632.8 nm HeNe laser line as excitation source. PL measurements were carried out at RT using as the excitation source the 441.6 nm (2.808 eV) line of an Omnicrome 2056 He-Cd laser with 35 mW of power. The 441.6 nm line was down-converted to 883.2 nm (1.404 eV) by means of a BBO filter. PL emission was analyzed using a 0.5 m Jovin-Ivon double spectrograph, endowed with a resolution better than 0.05 nm, and detected using a Ag-Cs-O Hamamatsu photomultiplier, with a spectral response in the range 400–1200 nm using standard lock-in technique. The modulated laser light was irradiated onto the sample by a spot radius of 1 mm. The fundamental band gap energy of the CdTe:Te layers was determined by RT modulated transmittance spectroscopy (MTS) employing a standard experimental setup, with modulation light provided by the 632.8 nm wavelength of a He-Ne laser. The chopped laser light was irradiated onto the sample by a spot radius of 1 mm. A 200 W tungsten lamp was dispersed by employing a 20-cm monochromator and used as the probe-light. The transmitted-probe light from the sample was detected by a Si detector, and the signal from the detector was fed to a lock-in amplifier.

3. Results and discussions

CdTe is a material that easily gets self-compensated and generally it is obtained with a slightly p-type conductivity. When it is grown as a single crystal p-type doping levels associated with Te are relatively low; it is reported a merely $2 \times 10^{16} \text{ cm}^{-3}$ value [10]. Higher contents of Te can be attained with deposition processes far from equilibrium such as rf sputtering. Usually as grown CdTe films deposited by rf sputtering from high purity CdTe targets result Te-rich. In order to obtain stoichiometric CdTe films, elemental Cd should be added to the target [11]. In the present case an excess of elemental Te was added to the target to

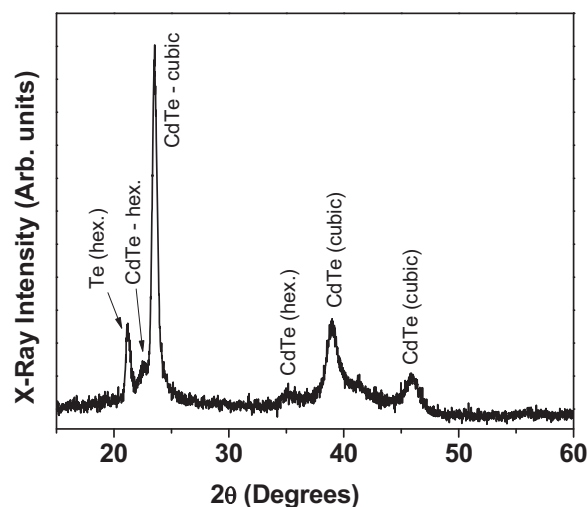


Fig. 1. X-ray diffraction pattern of a CdTe:Te sample where the film has essentially the cubic-zincblende structure. Inclusions of hexagonal-wurtzite CdTe and hexagonal Te are also observed in the sample.

reach a Te rich composition of 53 ± 1 at%. The CdTe with excess of Te is characterized to behave as p-type semiconductor mostly due to the Cd vacancies formation and interstitial Te [12]. The holes density calculated from Hall Effect measurements was $5.0 \pm 0.2 \times 10^{18} \text{ cm}^{-3}$. Fig. 1 displays the X-ray diffraction pattern of the sample studied where a polycrystalline cubic-zincblende structure is mainly displayed plus some hexagonal-wurtzite CdTe and hexagonal Te inclusions. From the width of peaks for low 2θ values in the diffractogram and using the Debye-Scherrer formula an average diameter of 18 ± 2 nm for the grains was calculated. The Bohr radius of CdTe is 7.3 nm, this means that this study lies in the intermediate regime of quantum confinement. The Raman spectrum of the CdTe:Te sample is shown in Fig. 2, clearly signals from CdTe and Te modes are present. The higher intensity of Te modes with respect to those of CdTe is consequence of the very large cross section of Te [13]. The existence of Te rich CdTe is in this way confirmed through these three different techniques. The high doping level due to the Te content is reflected through the presence of a surface electric field easily modulated by the generation of electron-hole pairs associated with the modulated transmission spectroscopy [14]. The bandgap energy (E_g) was calculated from modulated transmission spectroscopy measurements (MTS) by the fitting to the Aspnes model employing a tridimensional critical point [15]. The experimental MT spectrum along with the theoretical fitting is shown in Fig. 3. This value

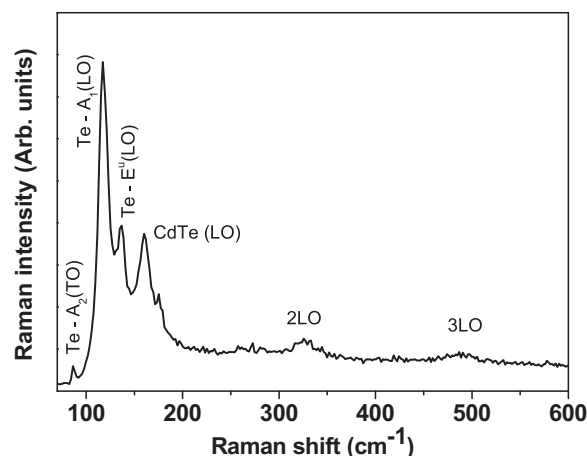


Fig. 2. Raman spectrum of the CdTe:Te thin film where the LO phonon mode plus two overtones and a Te-modes are displayed in the $170\text{--}600 \text{ cm}^{-1}$ range.

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