Band gap energy in Zn-rich $Zn_{1-x}Cd_xTe$ thin films grown by r.f. sputtering

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Ternary $Zn_{1-x}Cd_xTe$ semiconducting thin films were grown on 7059 Corning glass substrates at room temperature by co-sputtering from a ZnTe-Cd target. The visible Cd-area onto ZnTe target was varied to cover 0% - 4% of the total area. The optical and structural properties of the films were analysed as a function of the Cd concentration (x) on the layers. The sharp diffraction lines indicate mainly the ZnTe in cubic phase. When the cadmium was incorporated into the ZnTe lattice, the band gap energy (E_g) decreased from 2.2748 eV (x=0) to 2.2226 eV (x= 0.081). We found a linear relationship between E_g and (x) in the interval of (x) studied, that predicts a value of the bowing parameter b in the $E_g(x) = E_{go} + ax + bx^2$ relationship, which coincides with the value of b calculated by making the same study for Cd-rich CdZnTe. This result becomes interesting given the large number of values reported for b and a for $E_g(x)$ of this ternary material.

Keywords: II-VI semiconductors; thin films; ZnCdTe; radio frequency sputtering.

Películas semiconductoras de $Zn_{1-x}Cd_xTe$ fueron crecidas por la técnica de co-erosión catódica de radio frecuencia sobre substratos de vidrio Corning 7059 a temperatura ambiente a partir de un blanco de ZnTe-Cd. Pequeñas laminillas de Cd fueron colocadas sobre la superficie del blanco cubriendo un área del 0% - 4%. Las propiedades ópticas y estructurales de las películas fueron analizadas en función de la concentración de Cd (x). El patrón de difracción de rayos-X nos indica preferentemente la fase cúbica del ZnTe. Cuando el cadmio es incorporado dentro de la red del ZnTe, la brecha de energía (E_g) decrece desde 2.2748 eV (x = 0) hasta 2.2226 eV (x = 0.081). A partir de los datos obtenidos se encuentra una relación lineal E_g vs (x) en el intervalo de (x) estudiado, el cual predice un parámetro de curvatura b en la relación $E_g(x) = E_{g0} + ax + bx^2$, que coincide con el valor de b calculado para el mismo estudio en las películas de $Zn_{1-x}Cd_xTe$. Este resultado es interesante dado el gran número de valores reportados para b y a de E_g para este material ternario.

Descriptores: Semiconductores II-VI; películas delgadas; ZnCdTe; erosión catódica.

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1. Introduction

The II-VI compounds CdTe and ZnTe form a complete series of solid solutions with cubic zincblende structure [1]. The room temperature band gap of these materials can be tuned from 1.5 eV in CdTe to 2.3 eV in ZnTe by controlling the alloy composition [2]. The large band gap of the solar cells is either used in fluorescent plastic concentrators [3], or in high-efficiency thin films in tandem solar cells [4]. For instance, in this last application the importance of the variation of E_g with (x) lies in the possibility of growing layers of $Zn_{1-x}Cd_xTe$ with different (x) value, in the entire range $0 \leq x \leq 1$; in this way E_g changes from 1.5 eV to 2.3 eV. This stratified arrange allows a tandem solar cell to absorb a larger fraction of the solar spectrum energy. $Zn_{1-x}Cd_xTe$ thin films have been prepared by different techniques, and depending on the growth system and on the growing parameters used, either epitaxial [5, 6] or polycrystalline thin films with different grain sizes can be deposited, leading to variations of their optical and electrical properties [7–9].

In the last decade, there has been an increased interest in the preparation and study of the physical properties of $Zn_{1-x}Cd_xTe$ solid solution. The functional dependence of the band gap energy E_g with the concentration of Cd has not been, until now well, determined; and although different coefficients have already been proposed for the quadratic expression that describes them, this E_g function has been validated only if all the entire range $0 \leq x \leq 1$ is utilized. The objective of this work is to vary the concentration of Cd in the lattice of the $Zn_{1-x}Cd_xTe$ ternary compound growth by means of a radio frequency (r.f.) sputtering system, in order to modulate E_g as a function of (x). From the experimental results, we found a linear relationship between E_g and (x), which predicts values of the coefficients of the quadratic expression of E_g consistent with those values previously reported by Zelaya *et al.* [10] on Cd-rich CdZnTe.

2. Experimental details

Polycrystalline ZnCdTe films were grown on 7059 Corning glass substrates, at room temperature, in a radio frequency (r.f.) sputtering system. The r.f. power used in the growth process was 30 W, and the distance between the target and the substrate was 4 cm. The final vacuum reached, before the argon introduction, was 5×10^{-6} Torr. During the growth, the total argon pressure on the chamber was of 10 m Torr. A time deposition of 3 hours was used. The extra Cd atoms were introduced in the samples by co-sputtering from a ZnTe target with pieces of elemental cadmium (99.999% pure) placed onto it. The ZnTe (99.999% pure) target had an area of 20.27 cm^2. The Cd area on the target was varied to cover the 0%, 0.5%, 1%, 2%, 3%, and 4% (samples d_n) of the total area of ZnTe target [11]. These films with increasing Cd content were denoted from *d1* to *d6*, respectively. In order to study the influence of the oxygen during the growth, the sample d6 was grown in a mixture of oxygen-argon pressure,

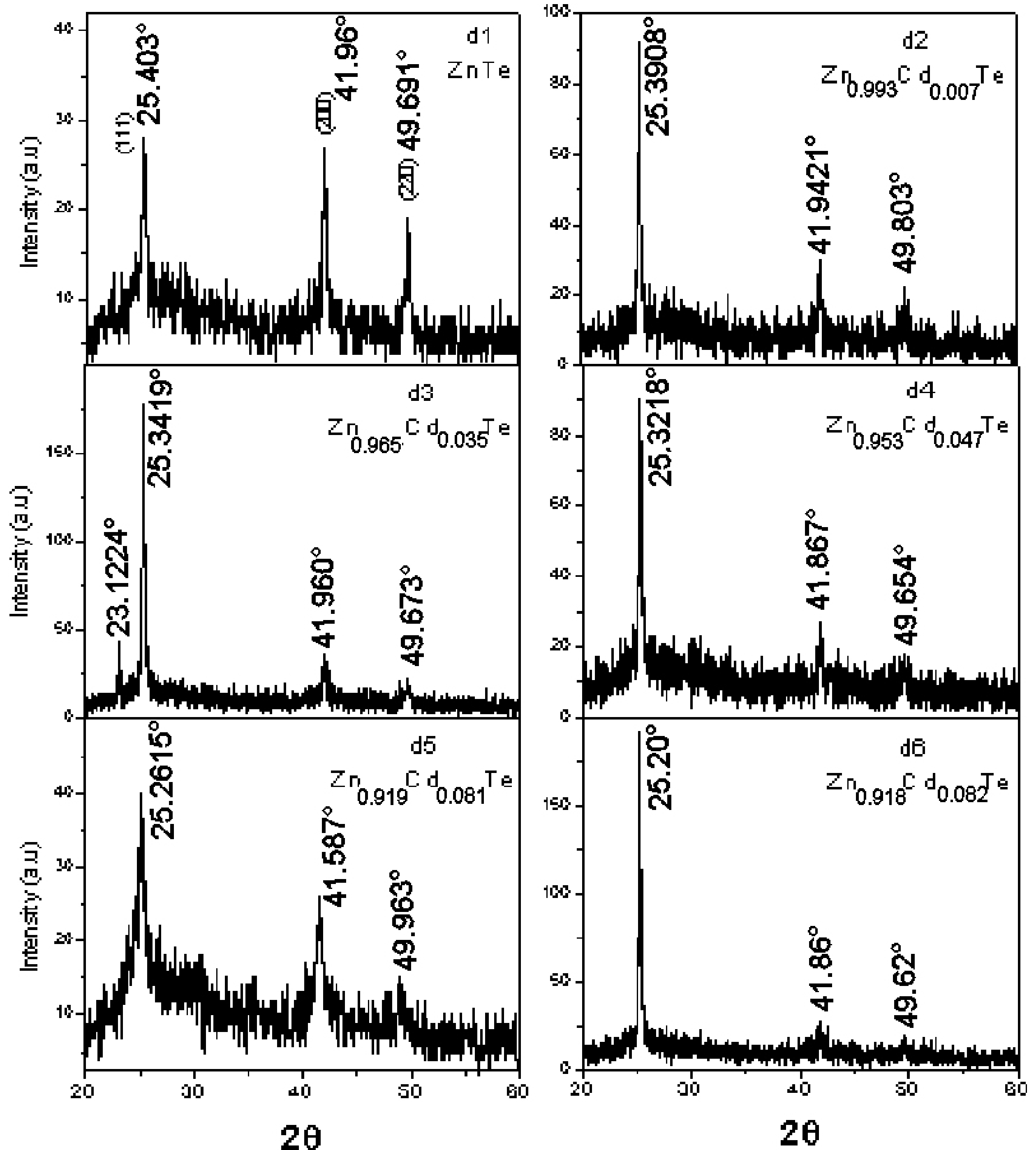

FIGURE 1. XRD patterns of $d1 - d6$ samples annealed at 300°C.

d7 as-grown sample. As the grown films show poor crystalline quality (broad XRD peaks), all the $Zn_{1-x}Cd_xTe$ samples d_n were thermal annealed in a $N-H_2$ atmosphere at a temperature of $300°C$ ($T_{300°C}$), during 30 minutes ($t_{30\prime}$). Higher values of $T_{300°C}$ and $t_{30\prime}$ affect sensitively the thickness of the films.

The crystalline structure of the films was determined from X-ray diffraction (XRD) patterns, measured with an X-ray SIEMENS D5000 diffractometer. We also used a transmissions electron microscope (TEM) to determine the crystalline structure and particle size of the *d7* as-grown sample. The TEM images and selected area electron diffraction (SAED) patterns were taken using a JEOL 2010 microscope operating at 200 KeV. The specimen, for TEM observation, was prepared using conventional mechanical grinding polishing, and dimpling, followed by Ar ion milling at an acceleration voltage of 3 KeV and an incidence angle of 3°. The cadmium concentration was checked from the nominal value through the determination of the lattice constant by XRD. The composition was determined assuming the validity of a linear depen-

dence between the lattice constant and the (x) fraction of cadmium (Vegard's law), using a_{CdTe} = 6.4813 Å for the CdTe lattice constant [12], and a_{ZnTe} = 6.0675 Å for the ZnTe lattice constant, obtained from XRD patterns of the sample *d1*. From diffractogrames the lattice parameter a_x for each samples, (x) can be determined from the linear relation:

$$x = \frac{a_x - a_{ZnTe}}{a_{CdTe} - a_{ZnTe}}.$$

The thickness of the films were in the range of 1000-1500 Å, as measured by the interferometric method. UV-VIS optical absorption spectra of the films were measured by employing a UNICAM 8700 spectrophotometer over the 190-900 nm range of wavelength. Band gap energy (E_g) measurements were carried out through the maximum of the curve of the numerical derivative of the optical absorption coefficient with respect to the photon energy, *i.e.*, as the absorption coefficient is proportional to the optical density (OD), one can directly plot d(OD)/d(hν) versus the photon energy hν to obtain E_g.

3. Results and discussion

XRD patterns of $d1 - d6$ samples annealed at 300 °C are shown in Fig. 1. The *d1* sample corresponds to the composition of a pure ZnTe polycrystalline film. The diffraction peaks characteristic for the cubic structure of ZnTe (zincblende) [13] are observed at 2θ = 25.403°, 41.96°, and 49.691° corresponding to the (111), (200), and (220) planes, respectively. The sharp diffraction line indicates a good crystalline quality with the (111) preferred crystalline orientation of all the films. In general, in sputtered films, the (111) direction is the preferred orientation of the ZnTe crystallites. For samples *d1* to *d6* are at some different angular position, in these films there is a spectral shift toward smaller diffraction angles, due to the substitution of Cd atoms for Zn atoms in the ZnTe matrix. From XRD patterns of the *d1-d6* samples the cadmium concentration was obtained. The cadmium content in the ZnCdTe lattice of this ternary compound was (x) = 0.0, 0.0071, 0.035, 0.0465, 0.0811, and 0.0820 corresponding to *d1, d2, d3, d4, d5,* and *d6* samples, respectively. Beside the (111), (200) and (220) diffraction lines in the *d3* sample a small peak also appears at 23.122°; this line have not been identified, yet. However it is probable that it could be attributed to a tellurium oxide compound. XRD patterns of the *d7* as-grown sample, show an amorphous structure, therefore cadmium concentration could not be measured.

The XRD pattern of the *d7* as-grown sample is shown in Fig. 2. The diffractogram is the typical of an amorphous material. A picture of the TEM-magnification of this sample can be observed in Fig. 3. A statistical analysis of the particle size measured directly on the picture yields an average value of 10.0 ± 2.5 nm. The SAED pattern of the $d7$ as-grown sample can be observed in Fig. 4. The well-defined rings in

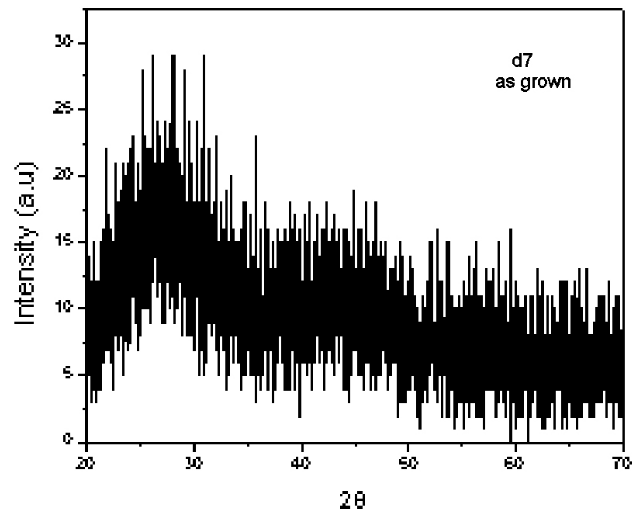

FIGURE 2. XRD pattern of $d7$ as-grown sample.

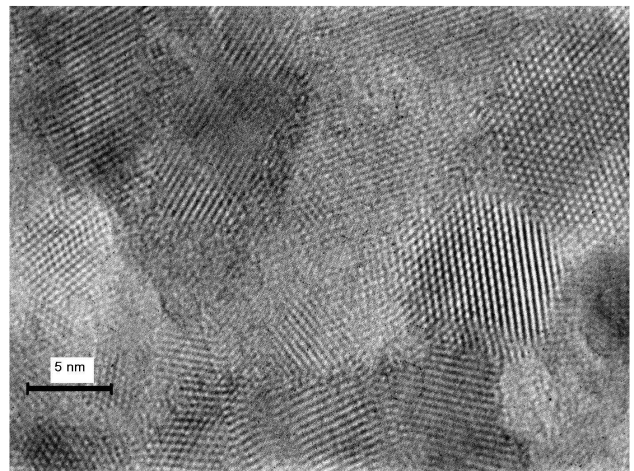

FIGURE 3. TEM picture taken at 200 KeV of the $d7$ as-grown sample.

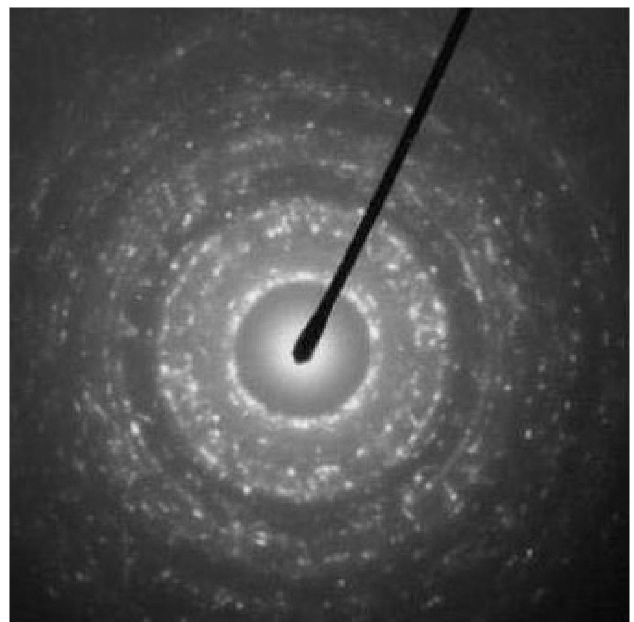

FIGURE 4. The SAED patterns of the *d7* as-grown sample.

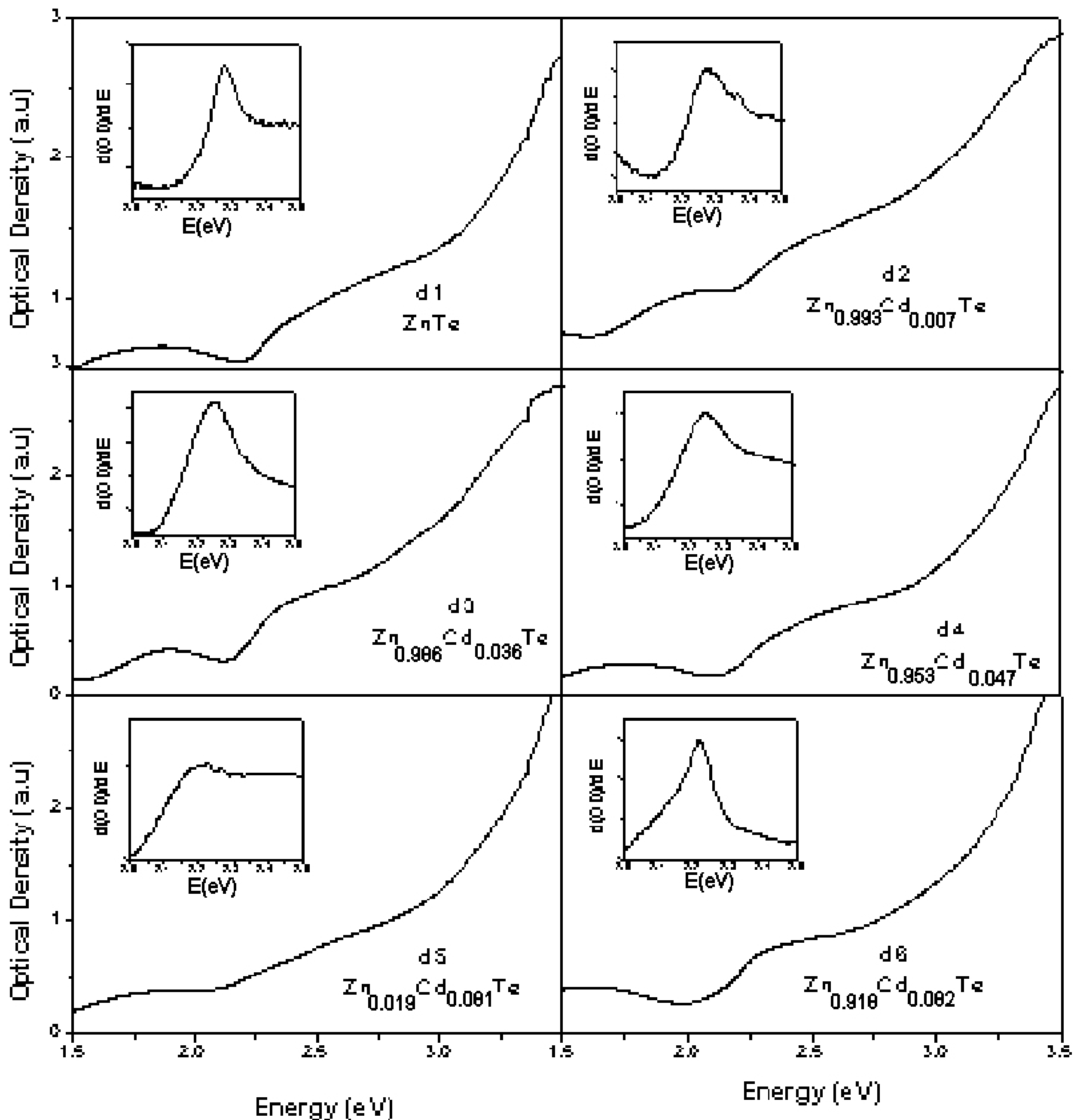

FIGURE 5. Optical density (OD) as a function of the photon energy ($h\nu$) measurements in the $Zn_{1-x}Cd_xTe$ films. The inset shows the (OD) first derivative with respect to E_g (eV).

the pattern undoubtedly demonstrate the polycrystalline nature of the film [14]. The experimental result evidences that the effects of the electron-beam exposure on the films during the TEM measurement process were: first, the nanocrystallization of the amorphous material; and second, the increase of the grain size from amorphous to nanocrystalline films.

From the optical absorption spectra, the E_g values of *d1-d6* films were determined. Figure 5 shows the optical density (OD) as a function of the photon energy ($h\nu$) measurements in the $Zn_{1-x}Cd_xTe$ films. The inset shows the first derivative of (OD) with respect to $h\nu$. The peak, at about 2.2748 eV, is due to the electronic transitions from the fundamental band edge. The position of the peak has been used to estimate the band gap energy [15, 16]. In this figure it is observed that the position of the peak shifts toward smaller energy values when the cadmium concentration increases in the ZnCdTe ternary compound. We found that the band gap energy decreases from 2.2748 eV (x = 0) to 2.2226 eV (x = 0.081). The E_g value of the *d7* film was not determined due to the amorphous nature of the sample. Table I shows the values of the cadmium concentration and lattice constant determined through the XRD patterns, and the values of the energy band gap determined from the absorption spectra of the *d1-d6* samples.

TABLE I. Results of the cadmium concentration and the lattice constant determined by XRD patterns and the band gap energy values determined from the absorption spectra of the $d1 - d6$ samples.

SAMPLE	x(Cd)	E_g(eV)	a_{111}(Å)
$d1$	0.00	2.2748	6.0676
$d2$	0.007	2.2729	6.0705
$d3$	0.0350	2.2550	6.0820
$d4$	0.0465	2.2356	6.0868
$d5$	0.0811	2.2226	6.1011
$d6$	0.0820	2.2208	6.1014

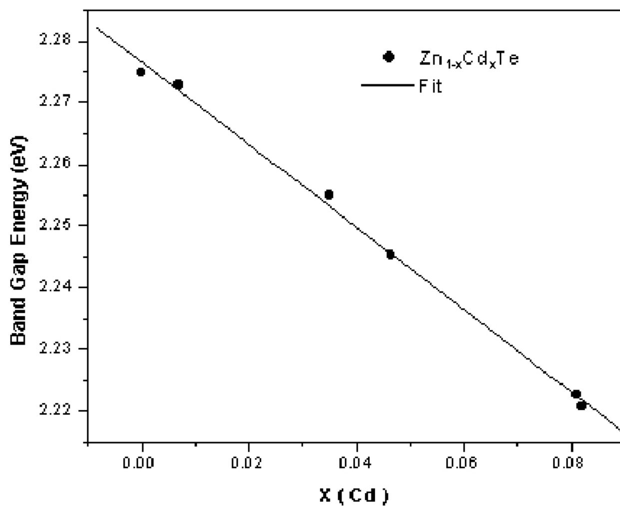

FIGURE 6. Band gap energy as a function of the cadmium concentration in the $Zn_{1-x}Cd_xTe$ films.

Figure 6 shows the band gap energy E_g versus cadmium concentration in the $Zn_{1-x}Cd_xTe$ films. The quadratic expression for the dependence of E_g with (x), based in the virtual crystal approximation theory is: $E_g(x)$=E_{go}+ax+bx^2. In our case E_{go} represents the E_g value, when $x = 0$, *i.e.*, E_g of ZnTe. For $x < 0.1$ one has the approximated expression E_g(eV) $\approx E_g$(ZnTe) $+ ax$. From the expression of the virtual crystal theory E_g = (1-x)$E_{g(ZnTe)}$ + $xE_{g(CdTe)}$ - bx(1-x), a and b are related by the equation $a = E_{g(CdTe)}$ - $E_{g(ZnTe)}$ - b. From the fitting of our experimental results, we obtain a = -0.664 eV, *i.e.*, $E_g(x)$ = 2.27489 - 0.664 x. The value of $E_{g(CdTe)}$ measured for this work and reported in a previous work [16] is 1.51 $\pm$ 0.01 eV. In this way, one obtains b = 0.10 $\pm$ 0.01 eV. This value of b is the same calculated by the same analysis in Cd-rich CdZnTe films [10]. This result becomes interesting because both parameters a and b scan, in practice, all the values in the range (0 - 0.76) eV. The slope of the straight line outlined from $E_{g(CdTe)}$ to $E_{g(ZnTe)}$, *i.e.*, along the entire range $0.0 \leq x \leq 1.0$, is 0.76 eV. All the values of a and b reported result in approximately 0.76 eV [17]. Our two values a and b also add 0.76 eV.

4. Conclusions

Polycrystalline $Zn_{1-x}Cd_xTe$ semiconductor thin films were obtained by co-sputtering from a ZnTe-Cd target under controlled conditions. The ZnCdTe ternary compound possesses a crystalline structure corresponding to the zincblenda cubic phase of the ZnTe. When the cadmium concentration increases in the $Zn_{1-x}Cd_xTe$ ternary lattice compound, the band gap decreases from E_g = 2.2748 eV (x = 0) to E_g = 2.2226 eV (x = 0.081). From the behaviour of the band gap energy E_g with cadmium concentration in the $Zn_{1-x}Cd_xTe$ films, we propose a lineal equation of the form E_g = 2.27489 - 0.664x for low values of x ($x < 0.1$).

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