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 these 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 $E_g(x) = E_{g0} + ax + bx^2$ 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.

PACS: 71.55.Gs; 73.61.-r; 68.47.Fg

1. Introduction

The II-VI compounds CdTe and ZnTe form a complete series of solid solutions with cubic zinblende 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 from 1.5 eV in CdTe to 2.3 eV in ZnTe by controlling the room temperature band gap of these materials can be tuned of solid solutions with cubic zincblende structure [1]. The II-VI compounds CdTe and ZnTe form a complete series of 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 these 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 $E_g(x) = E_{g0} + ax + bx^2$ 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.

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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 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.
BAND GAP ENERGY IN ZN-RICH $Zn_{1-x}Cd_xTe$ THIN FILMS GROWN BY R.F. SPUTTERING

$\text{FIGURE 1. XRD patterns of } d_1 \sim d_6 \text{ samples annealed at 300}^\circ\text{C.}$

$d_7 \text{ as-grown sample. As the grown films show poor crystalline quality (broad XRD peaks), all the } Zn_{1-x}Cd_xTe$ samples $d_n \text{ were thermal annealed in a } N-H_2 \text{ atmosphere at a temperature of } 300^\circ C \text{ ($T_{300}^\circ C$), during 30 minutes ($t_{30}$). Higher values of $T_{300}^\circ C$ and $t_{30}$ 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 transmission electron microscope (TEM) to determine the crystalline structure and particle size of the $d_7 \text{ as-grown sample. The TEM images and selected area electron diffraction (SAED) patterns were taken using a JEOL 2010 microscope operating at 200 KeV. The specimen, for TEM observation, was prepared using conventional mechanical grinding polishing, and dimpling, followed by Ar ion milling at an acceleration voltage of 3 KeV and an incidence angle of 3$^\circ$. 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 \(a_{CdTe} = 6.4813\ \text{Å}\) for the CdTe lattice constant [12], and \(a_{ZnTe} = 6.0675\ \text{Å}\) for the ZnTe lattice constant, obtained from XRD patterns of the sample \(d1\). From diffractograms 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 \(d(\text{OD})/d(\nu)\) versus the photon energy \(h\nu\) 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 \(2\theta = 25.403°, 41.96°, \) 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

\[\text{FIGURE 2. XRD pattern of } d7 \text{ as-grown sample.}\]

\[\text{FIGURE 3. TEM picture taken at 200 KeV of the } d7 \text{ as-grown sample.}\]

\[\text{FIGURE 4. The SAED patterns of the } d7 \text{ as-grown sample.}\]
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.
mium concentration in the Zn\textsubscript{1−x}Cd\textsubscript{x}Te based in the virtual crystal approximation theory is: 

\[
E_g(z) = E_g(ZnTe) + a x + b x^2
\]

From the expression of the virtual crystal theory 

\[
E_g(z) = (1-x)E_g(ZnTe) + x E_g(CdTe) - bx(1-x)
\]

\(a\) and \(b\) are related by the equation 

\[
a = E_g(CdTe) - E_g(ZnTe) - b.
\]

From the fitting of our experimental results, we obtain 

\(a = -0.664\text{ eV},\) \(i.e., E_g(x) = 2.27489 - 0.664 x.\) The value of \(E_g(CdTe)\) measured for this work and reported in a previous work \[16\] is 

\[1.51 \pm 0.01 \text{ eV}.\]

This result becomes interesting because both parameters \(a\) and \(b\) scan, in practice, all the values in the range \((0 - 0.76)\text{ eV.}\) 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 crystal structure corresponding to the zincblende 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 

\(E_g = 2.2748 \text{ eV (x = 0)}\) to 

\(E_g = 2.2226 \text{ eV (x = 0.0811)}\) 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 

\(E_g = 2.27489 - 0.664 x\) for low values of \(x (x < 0.1).\)

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\begin{table}
\centering
\caption{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.}
\begin{tabular}{|c|c|c|c|}
\hline
SAMPLE & \(x(Cd)\) & \(E_g(\text{eV})\) & \(a_{111}(\text{Å})\) \\
\hline
\(d1\) & 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 \\
\hline
\end{tabular}
\end{table}

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