Optical and opto-electronic properties of polycrystalline Cd$_{0.96}$Zn$_{0.04}$Te thin films

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Received 20 November 2002, revised 10 January 2003, accepted 1 February 2003
Published online 15 June 2003

Key words Cd$_{0.96}$Zn$_{0.04}$Te, thin films, vacuum evaporation, XRD, spectroscopic ellipsometry, photoluminescence.

PACS 78.20.-e

Cd$_{0.96}$Zn$_{0.04}$Te thin films are deposited onto thoroughly cleaned glass substrates (Corning 7059) kept at room temperature by vacuum evaporation. The films are found to have good stoichiometry as analyzed by Rutherford Backscattering Spectrometry. The films exhibited zinc blende structure with predominant (111) orientation. The surface morphology of the films is studied by Atomic Force Microscopy. The rms roughness of the films evaluated by AFM is 3.7 nm. The pseudodielectric-function spectra, $\varepsilon(E) = \varepsilon_1(E) + i \varepsilon_2(E)$ at room temperature are measured by spectroscopic ellipsometry. The measured dielectric function spectra reveal distinct structures at energies of the $E_1$, $E_{1+\Delta}$ and $E_2$ critical points. The band gap energy of the films measured by optical transmittance measurement is 1.523 eV. The PL spectrum of the films shows intense emission due to free and bound exciton recombination and no emission associated with crystal imperfection and deeper impurity levels. The PL line shapes give indications of the high quality of the layers.

1 Introduction

There is much current interest in II-VI ternary compound semiconductors for use in a variety of solid-state devices. Cd$_{1-x}$Zn$_x$Te is a technologically important II-B-VIA compound semiconductor, in which Zn occupies Cd sites. Due to the band gap engineering of Cd$_{1-x}$Zn$_x$Te, this alloy has a great potential in opto-electronic devices, such as solar cells, optical windows, photodetectors, light emitting diodes, optical memory devices and X-ray and gamma ray detectors [1,2,3]. With the particular composition of $x = 0.04$, Cd$_{0.96}$Zn$_{0.04}$Te nearly lattice match with Hg$_{1-y}$Cd$_y$Te (MCT) for all values of y, so it is mainly used as the substrate material for the growth of MCT infrared focal plane arrays (IRFPAs) [4]. Recently, room temperature deposited Cd$_{0.96}$Zn$_{0.04}$Te thin film is used as the surface passivation layer for MCT infrared detectors [5,6].

Photoluminescence (PL) measurements have proven to be a sensitive and non-destructive technique for examining the quality of the material. PL spectroscopy of compound semiconductors and ternary alloys allows identification of point defects, including substitutional impurities (donors, acceptors) and native, or intrinsic defects. In ternary alloys, the observation near-band-edge emission also provides approximate determination of the band gap energy ($E_g$), and thus the composition [7].

Spectroscopic Ellipsometry (SE) is an excellent technique for investigating the optical response of semiconductors [8,9]. SE can be used as a tool for characterizing and understanding the physical properties of materials, particularly used in conjunction with other techniques. SE is very sensitive to surface irregularities such as surface roughness, interdiffusion and interlayer formations in multilayer thin film systems [10,11]. Though much work has been done on the optical properties of Cd$_{1-x}$Zn$_x$Te ($0 < x < 1$), only a few reports are

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available on the optical characterization of Cd$_{1-x}$Zn$_x$Te thin films using spectroscopic ellipsometry [12]. The present work deals about the optical and opto-electronic properties of Cd$_{0.96}$Zn$_{0.04}$Te thin films by spectroscopic ellipsometry, optical transmittance measurement and photoluminescence.

![Rutherford Backscattering Spectrum of Cd$_{0.96}$Zn$_{0.04}$Te thin films.](image1)

![X-ray diffraction spectrum of Cd$_{0.96}$Zn$_{0.04}$Te thin films.](image2)

2 Experimental

The Cd$_{0.96}$Zn$_{0.04}$Te alloy was prepared from its own constitutional elements. Appropriate weights of the individual elements (purity 99.999%) were mixed together, charged in a quartz ampoule and sealed under a vacuum of $10^{-5}$ Torr. The sealed quartz ampoule with the charge was placed in a rotating furnace. The
temperature of the furnace was raised gradually to 1100°C and left at this temperature for about 36 hours. After that, the ampoule was slowly cooled to room temperature at a rate of 30°C/h [13]. The Cd_{0.96}Zn_{0.04}Te ingot was taken out from the ampoule and made into fine powder and used for evaporation.

The Cd_{0.96}Zn_{0.04}Te thin films were prepared by vacuum evaporation onto thoroughly cleaned glass substrates (Corning 7059) kept at room temperature. Tantalum boat was used as the source and the pressure inside the evaporation chamber was better than 10^{-5} Torr. The thickness and composition of the films were evaluated using Rutherford backscattering spectrometry (RBS). A beam of 2.24 MeV from a He source was used and the detector was positioned at a scattering angle of 170°. The studies were carried out on a film of typical thickness 302 nm since 300 nm is the optimum thickness for the surface passivation layer to MCT IRFPAs [5]. The thickness of the films were also measured by α-STEP (TENCOR, α-Step Instrument), this also gives the average surface roughness value. Structural analysis was made using a Philips X-ray diffractometer with Cu Kα radiation (λ = 0.1542 nm) at 40 kV and 20 mA in the scanning angle (2θ) from 20° to 60°. The surface microstructure of the films was investigated by an ex-situ atomic force microscopy (AFM) (PSI, Autoprobe CP Model). The AFM images were acquired in the tapping mode and in the repulsive force regime with a force constant of 1 nN between the AFM cantilever tip and sample surface. Optical properties of Cd_{0.96}Zn_{0.04}Te thin films were studied by optical transmittance measurement and spectroscopic ellipsometry (SE). The optical transmittance was recorded using a UV-VIS-NIR (SHIMADZU 3101 PC) spectrophotometer in the wavelength range 400-2000 nm. The SE equipment was of the polariser-sample-rotating analyzer type (DVA-36VW-A, Mizojiri Optical Co. Ltd.). A 150 W xenon lamp was used as the light source. The SE data were measured over the photon energy range 1.3 – 5.5 eV at room temperature. The angle of incidence was set at 75° with a polarization azimuth of 45°. The photoluminescence spectrum of Cd_{0.96}Zn_{0.04}Te thin films was recorded at 25 K with a Jobin Yvon (Ramanor U1000) spectrometer and a photomultiplier. Mechanically chopped radiation from Ar laser (514.5 nm) is used as the excitation source. The sample is enclosed in a glass-walled Dewar of circular cross section and mounted on a copper block, which is in thermal contact with the cryogen used, either liquid nitrogen/helium. To ensure accurate determination of sample surface temperature, 1 m Torr He gas is introduced into the sample Dewar as a thermal exchange gas after a base pressure of 10^{-6} Torr is reached. Emitted radiation from the sample surface is detected by a cooled photomultiplier tube (S-1) in conjunction with a high-resolution monochromator and a Lock-in amplifier. Output from the lock-in amplifier is fed to a computer, which also controls the wavelength settings of the monochromator through a stepper motor.

3 Results and discussion

The vacuum evaporated polycrystalline Cd_{0.96}Zn_{0.04}Te thin films were found to be smooth, uniform and have very good adhesion to the substrate surface. Rutherford backscattering spectrum of Cd_{0.96}Zn_{0.04}Te thin film is shown in Fig. 1. The films were found to have a very good stoichiometry as analyzed by RBS simulations (Cd:
The thickness of the Cd$_{0.96}$Zn$_{0.04}$Te thin film evaluated by RBS was 302 nm, which agrees well with the thickness measured by α-Step surface profilometer (303 nm).

The X-ray diffraction pattern of vacuum evaporated Cd$_{0.96}$Zn$_{0.04}$Te thin films is shown in Fig. 2. The films were found to exhibit three diffraction peaks associated with (111), (220) and (311) orientations, of which the intensity of the (111) orientation is very predominant. The lattice constant (a), the grain size (D) and the dislocation density ($\delta$) of the Cd$_{0.96}$Zn$_{0.04}$Te thin films were evaluated as 0.6459 nm, 0.152 $\mu$m and $4.33 \times 10^{13}$ m$^{-2}$ respectively. The values are in good agreement with the earlier reports [14,15,16].

Ex-situ atomic force microscope (AFM) has been used independently to access surface quality of the vacuum evaporated Cd$_{0.96}$Zn$_{0.04}$Te thin films. Fig. 3 shows the large scale (1 $\mu$m × 1 $\mu$m) three-dimensional AFM image of Cd$_{0.96}$Zn$_{0.04}$Te thin films. The root mean square (rms) roughness evaluated from AFM measurement of the vacuum evaporated Cd$_{0.96}$Zn$_{0.04}$Te thin film is 3.7 nm. The average roughness of the film measured by α-Step surface profilometer was 3.9 nm.

The complex dielectric function, $\varepsilon(E) = \varepsilon_1(E) + i \varepsilon_2(E)$, can describe the optical response of any homogeneous medium at all photon energies ($h\nu$). The real ($\varepsilon_1$) and imaginary ($\varepsilon_2$) parts of the complex dielectric function are connected by the following Kramers–Kronig relationships [17].

\begin{equation}
\varepsilon_1(E) = 1 + \frac{2}{\pi} \int_0^\infty \frac{\varepsilon_2(E')}{E'^2 - E^2} dE'.
\end{equation}

\begin{equation}
\varepsilon_2(E) = \frac{2E}{\pi} \int_0^\infty \frac{\varepsilon_1(E')}{E'^2 - E^2} dE'.
\end{equation}

Fig. 4 shows the pseudodielectric function spectra, $\varepsilon(E) = \varepsilon_1(E) + i \varepsilon_2(E)$, of vacuum evaporated Cd$_{0.96}$Zn$_{0.04}$Te thin films. The SE spectra of the films revealed distinct structures, which arise owing to interband transition. This structure originates from transitions at $E_0$ edge. It is very difficult to find the $E_0 + \Delta_0$ related transitions in the optical spectra of Te-based II-VI compounds (CdTe and ZnTe) [18]. The present measurements did not show evidence of the $E_0 + \Delta_0$ structure in the spectra. The structures found in the 2.6 to 5.00 eV energy range are due to $E_1$, $E_1 + \Delta_1$, and $E_2$ transitions. The peak at $E_1$ (lower energy) is due to the $\Lambda_3 - \Lambda_1$ transition along the (111) axis. The $E_1 + \Delta_1$ peak arises due to spin-orbit splitting of the valance band in the $\Lambda$ direction. The peak at $E_2$ has been attributed to the $X_5 - X_1$ transition at the X-point of the Brillouin Zone [12]. The origin of these distinct structures is due to interband transitions [18,19,20,21].

Optical constants, such as the complex refractive index $n^* = n(E) + i k(E)$, absorption coefficient $\alpha(E)$ and normal-incidence reflectivity $R(E)$, can be easily calculated from the SE $\varepsilon(E)$ data [18,22,23]. The real refractive index $n(E)$ and extinction coefficient $k(E)$ can now be written as

\begin{equation}
n(E) = \left[ \frac{[\varepsilon_1(E)^2 + \varepsilon_2(E)^2]^{\frac{1}{2}} + \varepsilon_2(E)}{2} \right]^{\frac{1}{2}}
\end{equation}

\begin{equation}
k(E) = \left[ \frac{[\varepsilon_1(E)^2 + \varepsilon_2(E)^2]^{\frac{1}{2}} - \varepsilon_2(E)}{2} \right]^{\frac{1}{2}}
\end{equation}

The absorption coefficient $\alpha(E)$ and normal-incidence reflectivity $R(E)$ can be expressed as

\begin{equation}
\alpha(E) = \frac{4\pi}{\lambda} k(E)
\end{equation}
\[ R(E) = \frac{(n(E) - 1)^2 + k(E)^2}{(n(E) + 1)^2 + k(E)^2} \]  \hspace{1cm} (6)

where, \( \lambda \) is the wavelength corresponding to the photon energy (E).

![Graph](image)

**Fig. 4** Pseudodielectric-function spectra for the vacuum evaporated Cd\(_{0.96}\)Zn\(_{0.04}\)Te thin films.

![Graph](image)

**Fig. 5** Spectral dependence of n(E) for the vacuum evaporated Cd\(_{0.96}\)Zn\(_{0.04}\)Te thin films obtained from SE.

Fig. 5 shows the numerically calculated spectral dependence of n(E) for the Cd\(_{0.96}\)Zn\(_{0.04}\)Te thin films deposited at room temperature. They are obtained from Eq.3 for n(E). In n(E), the clear peaks at E \sim 2.94 \text{ eV}, E \sim 3.80 \text{ eV} and E \sim 4.7 \text{ eV} have been related to \( E_1 \), \( E_{1+\Delta} \) and \( E_2 \) transitions respectively. From Eqns 6,7,8 the values of \( k(E) \), \( \alpha(E) \) and \( R(E) \) were calculated respectively. We observed \( E_1 \), \( E_{1+\Delta} \) and \( E_2 \) transitions for the \( k(E) \), \( \alpha(E) \) and \( R(E) \) values. The critical point values (\( E_1 \), \( E_{1+\Delta} \) and \( E_2 \)) obtained from SE data for the optical constants (\( \varepsilon_r \), \( \varepsilon_i \), \( R \), n, k and \( \alpha \)) are comparable with the earlier report [12] and the critical point values are tabulated in Table 1.
Table 1  The interband transition energies obtained from SE data of Cd_{0.96}Zn_{0.04}Te thin films.

<table>
<thead>
<tr>
<th>Film Thickness t_f</th>
<th>E_1 (eV)</th>
<th>E_1+Δ (eV)</th>
<th>E_2 (eV)</th>
<th>Δ_1 (eV)</th>
<th>Spectrum</th>
</tr>
</thead>
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<tr>
<td></td>
<td>2.67</td>
<td>3.20</td>
<td>4.50</td>
<td>0.53</td>
<td>ε vs. hv</td>
</tr>
<tr>
<td></td>
<td>3.20</td>
<td>3.99</td>
<td>4.96</td>
<td>0.79</td>
<td>ε vs. hv</td>
</tr>
<tr>
<td></td>
<td>2.94</td>
<td>3.80</td>
<td>4.70</td>
<td>0.86</td>
<td>n vs. hv</td>
</tr>
<tr>
<td>302 nm</td>
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<td>3.83</td>
<td>5.03</td>
<td>0.54</td>
<td>k vs. hv</td>
</tr>
<tr>
<td></td>
<td>3.45</td>
<td>4.31</td>
<td>5.29</td>
<td>0.86</td>
<td>α vs. hv</td>
</tr>
<tr>
<td></td>
<td>3.52</td>
<td>4.01</td>
<td>4.96</td>
<td>0.49</td>
<td>R vs. hv</td>
</tr>
</tbody>
</table>

Fig. 6  Optical transmittance spectra of the vacuum evaporated Cd_{0.96}Zn_{0.04}Te thin films (t_f = 302nm).

Fig. 6 shows the optical transmittance spectra of Cd_{0.96}Zn_{0.04}Te thin films in the wavelength range 400 – 2000 nm. The transmittance of the films is high at higher wavelength region. The transmittance spectra of the films show interference patterns with a sharp fall of transmittance at the band edge, which indicates the crystallinity of the films. The variation of transmittance with wavelength is given by the relation [24]

\[ T = \frac{16n_n n_s n^2 \exp(-\alpha t)}{R^2 + R_s^2 \exp(-\alpha t) + 2R_s R_r \exp(-\alpha t) \cos(4\pi nt / \lambda)} \]  

(7)

where, \( \alpha \) is the absorption coefficient and \( n, n_a \) and \( n_g \) are the refractive indices of the film, air and substrate respectively. The maxima and minima in the transmittance versus wavelength (T-λ) plot occur when,

\[ \frac{4\pi nt}{\lambda} = M\pi \]  

(8)

where, \( M \) represents the order number and \( t \) the thickness of the film. The refractive index \( n \) of the films has been computed using the relation [25,26] given below,

\[ n^2 = \frac{n_h^2 + n_l^2}{2} + 2n_h n_l T^\prime + \left[ \frac{(n_h^2 + n_l^2 + 4n_h n_l T^\prime)^2}{4} - n_l^2 n_h^2 \right]^{1/2} \]  

(9)

where, \( T^\prime = (T_{\text{max}}-T_{\text{min}})/(T_{\text{max}}+T_{\text{min}}) \). \( T_{\text{max}} \) and \( T_{\text{min}} \) represent the envelopes of the maximum and minimum positions of the T-λ curve.
The extinction coefficient $k$ and the absorption coefficient $\alpha$ of the films were calculated from the relations,

$$k = \frac{\ln(1/T)}{4\pi t} \quad (10)$$

and

$$\alpha = \frac{4\pi k}{\lambda} = \frac{\ln(1/T)}{t} \quad (11)$$

where, $t$ is the film thickness. The calculated values of $n$ and $k$ for the Cd$_{0.96}$Zn$_{0.04}$Te films were plotted as a function of photon energy and are shown in Fig. 7. The value of refractive index $n$ is found to decrease with increase of photon energy. The absorption coefficient ($\alpha$) is related to the band gap energy ($E_g$) by using the relation [27],

$$\alpha = (h\nu - E_g)^{1/2} / h\nu \quad (12)$$
Fig. 8 shows the plot of $(\alpha h \nu)^2$ versus $h \nu$ of the Cd$_{0.96}$Zn$_{0.04}$Te films. The optical band gap values were obtained by extrapolating the linear portion of the plot of $(\alpha h \nu)^2$ versus $h \nu$ to $\alpha = 0$. The band gap value of the film is found to be 1.523 eV. The value is in good agreement with the earlier reports [14,12]. The optical constants such as $n$ and $k$ determined by optical transmittance measurements were comparable with that of the values determined by SE.

![Photoluminescence spectrum of Cd$_{0.96}$Zn$_{0.04}$Te thin films recorded at 25 K.](image)

A photoluminescence (PL) measurement offers the means to evaluate the crystalline quality of II-VI compounds. A typical photoluminescence spectrum recorded at 25 K between 1.565 to 1.650 eV of Cd$_{0.96}$Zn$_{0.04}$Te films is shown in Fig. 9. Based on the origin of the emission lines, the PL spectrum can be divided into three regions, (i) the exciton region for wavelengths $\lambda$ lower than 775 nm (>1.60 eV) (ii) the free-to-bound and bound-to-bound level transitions for intermediate $\lambda$ and (iii) emission at $\lambda > 820$ nm (<1.51 eV) associated with crystal imperfections and deeper impurity levels [27]. In the first region, emission lines due to free and bound excitation recombination are observed. In the intermediate region, PL spectrum of Cd$_{0.96}$Zn$_{0.04}$Te films shows excitation peaks at 1.5692 eV and 1.5712 eV due to transitions between donor and acceptor levels (D,A) and free electrons and acceptor (F,A) levels. The emission at 1.5976 eV and 1.6193 eV are due to acceptor-to-bound ($A^0,X$) and donor-to-bound ($D^0,X$) recombinations respectively. The lines due to the recombination of excitons bound to neutral acceptors ($A^0,X$) are wider than the donor to acceptor ($D^0,X$) lines [28]. We did not observe any significant emission for $\lambda \geq 820$ nm, which is an indication of high crystalline quality [27,29,30,31]. The exciton line widths in Cd$_{0.96}$Zn$_{0.04}$Te thin film sample are somewhat broader than for pure CdTe and pure ZnTe due to alloy broadening [32], but still indicate good overall quality.

4 Conclusions

Polycrystalline Cd$_{0.96}$Zn$_{0.04}$Te thin films were deposited onto well-cleaned glass substrates kept at room temperature by vacuum evaporation. X-ray diffraction trace of the films showed the zinc blend structure with predominant (111) orientation. The rms roughness of the films evaluated by atomic force microscopy was 3.7 nm. The pseudodielectric functions $\varepsilon(E) = \varepsilon_1(E) + i \varepsilon_2(E)$ of polycrystalline Cd$_{0.96}$Zn$_{0.04}$Te thin films has been determined by spectroscopic ellipsometry at room temperature. The spectra of various optical constants obtained from the SE $\varepsilon(E)$ data ($\varepsilon_1$, $\varepsilon_2$, $R$, $n$, $k$ and $\alpha$) revealed three distinct critical points ($E_1$, $E_1+\Delta$, and $E_2$). The band gap energy of the films determined by transmittance measurement was 1.523 eV at room
temperature. The PL spectrum recorded at 25 K indicates a high crystalline perfection of the samples investigated. As a result of that, the PL spectrum shows emission lines due to the recombination of free excitons in their ground state level, and no emissions associated with structural and/or deep impurity levels.

Acknowledgements One of the authors, M. Sridharan, would like to thank Korea Advanced Institute of Science and Technology (KAIST), Taejon 305 701, Korea, for the award of Visiting Research Student Fellowship and for permitting him to work in the Department of Electrical Engineering and Computer Science, KAIST, Taejon, Korea.

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