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Structure and Optical Characterization of $Zn_xCd_{1-x}Te$ Thin Films Prepared by the Close Spaced Vapor Transport Method

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Structure and optical characterization of $\text{Zn}_x\text{Cd}_{1-x}\text{Te}$ thin films prepared by the close spaced vapor transport method

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Zinc cadmium telluride ($\text{Zn}_x\text{Cd}_{1-x}\text{Te}$) solid solution films with $0 \leq x \leq 0.12$ were deposited by the close spaced vapor transport method and characterized using photoluminescence, x-ray diffraction, and scanning electron microscopy. The two former techniques indicate that films with high crystalline quality can be prepared with moderate substrate temperatures and low argon pressures. Under these conditions deposition rates of up to 1000 \AA/s are achieved and Zn concentration in the film is the same as that of the source. The electron micrographs show grain sizes comparable to the film thickness.

I. INTRODUCTION

$\text{Zn}_x\text{Cd}_{1-x}\text{Te}$ is a variable band-gap II-VI compound semiconductor for which solid solutions across the entire compositional range can be prepared.¹⁻³ 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 alloy composition. In particular, $\text{Zn}_x\text{Cd}_{1-x}\text{Te}$ thin films are of current interest because of their promising application as the top device in high-efficiency thin film tandem solar cells.⁴

$\text{Zn}_x\text{Cd}_{1-x}\text{Te}$ thin films have been most commonly prepared by vacuum evaporation techniques. Epitaxial growth by molecular beam epitaxy (MBE) on several types of substrates has been achieved at moderate substrate temperatures (200–300 °C) and low deposition rates ($\sim 1 \text{ \AA/s}$).⁵⁻⁷ Several techniques have been used to characterize the properties of these films; in particular, photoluminescence (PL) is known to be a useful technique to characterize the crystalline quality of semiconductors in either thin-film or bulk forms. In MBE $\text{Zn}_x\text{Cd}_{1-x}\text{Te}$ thin films, the near band edge PL spectra at low temperature ($< 12 \text{ K}$) show free and bound exciton lines for $x = 0$ and 1 but only broader bound exciton peaks for other compositions.⁵ At energies below that of the band gap weaker and broader emission bands are observed due to extrinsic recombination originated at defect or impurity levels, the intensity of these bands increases as the Zn concentration increases.^{3,6}

Recently, $\text{Zn}_x\text{Cd}_{1-x}\text{Te}$ thin films have been prepared by the close spaced vapor transport (CSV T) method.⁴ It was found that values of x in the deposited films equal to those in the source can be achieved either by deposition at atmospheric pressure of an ambient gas, with a small temperature difference ($< 10 \text{ }^\circ\text{C}$) between the source and substrate or by

deposition at low ambient pressures ($< 0.5 \text{ Torr}$) with any desired temperature difference between the source and substrate. The electrical properties of these films were analyzed as a function of deposition parameters, but no optical properties were reported.⁴

In the present study, $\text{Zn}_x\text{Cd}_{1-x}\text{Te}$ thin films were prepared under various conditions by the CSV T method and analyzed using PL, x-ray diffraction (XRD) and scanning electron microscopy (SEM). The composition range investigated was $0 \leq x \leq 0.12$. The cross-section SEM micrographs show that most of the grains have dimensions comparable to the thickness of the films. The PL measurements show that under optimal deposition conditions, the spectra of our CSV T films only contain sharp lines originated from the recombination of excitons. The results are similar to those observed in epitaxially grown $\text{Zn}_x\text{Cd}_{1-x}\text{Te}$ films.^{5,6} This indicates that the crystalline quality within grains in the polycrystalline CSV T films is comparable to that of epitaxial films which generally have a low density of point defects. Under these deposition conditions, deposition rates as high as 1000 \AA/s were typical. This is roughly 1000 times the rate of MBE for comparable quality. The origins of the various emission lines in the PL spectra were deduced from a detailed analysis of the dependence of the spectrum on the temperature and excitation intensity.

II. EXPERIMENTAL

The CSV T apparatus used in this investigation has been previously described.⁸ The source materials were polycrystalline alloys grown by a modified Bridgman technique. All films were deposited on 7059 Corning glass substrates under

Ar ambient gas at a pressure of 0.5 Torr. The source temperature (T_f) was 700 °C in all depositions, and the substrate temperature (T_s) was varied between 450–600 °C. Under these conditions a deposition time of 30 min produced films with thicknesses of about 200 μm . Measurement of Zn concentration was made using an electron microprobe. The PL measurements were carried out in a typical PL apparatus described elsewhere.³

The XRD data was obtained in a C-graphite monochromatized copper $K\alpha$ radiation at 800 W. To avoid extrinsic stress, due to the difference in thermal expansion between film and substrate, the $\text{Zn}_x\text{Cd}_{1-x}\text{Te}$ films were removed from the substrate and powdered together with a crystalline silicon piece for XRD analysis. The silicon lines were used as an internal standard for the determination of the lattice parameter of the compound. To achieve better precision, a high-angle Si diffraction line (422) was used as the calibration in the 2θ scale and the lattice parameter of the alloy was the average value obtained from their (440) and (531) diffraction lines, these being the two nearest lines to the Si (422) line.

III. EXPERIMENTAL RESULTS

A. SEM

Figure 1 shows a cross-section view of a $\text{Zn}_{0.03}\text{Cd}_{0.97}\text{Te}$ film prepared at $T_s = 550$ °C and $T_f = 700$ °C. The thickness of the film is about 200 μm for 30 min of deposition. It is observed that the size of the grains is comparable to the film thickness. The surface roughness of the film is of the order of 10 μm . The darker region underneath the film corresponds to the glass substrate. Similar conclusions were obtained for

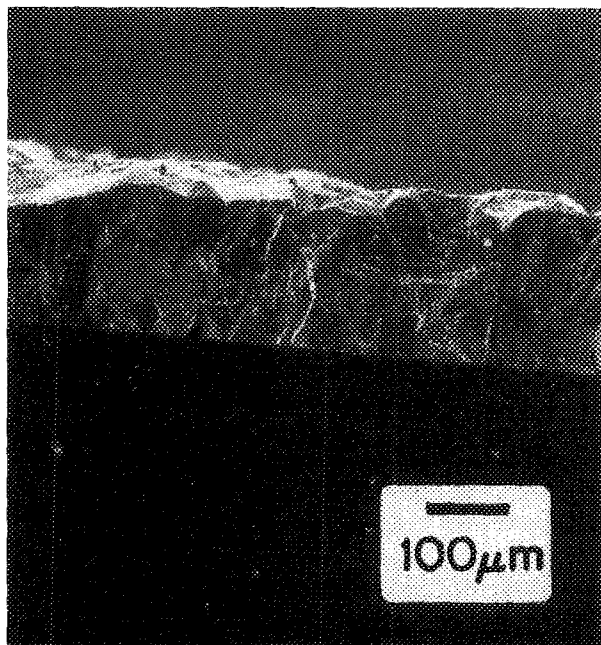


FIG. 1. Cross-section micrograph of a $\text{Zn}_{0.03}\text{Cd}_{0.97}\text{Te}$ film prepared at $T_s = 500$ °C and $T_f = 700$ °C. Notice that the average grain size is comparable to the thickness of the film.

films with other compositions. It is also observed that the average grain size is not affected significantly by either the changes in T_s in the range of 450–650 °C or by the rate of deposition.

B. PL

Figure 2 displays the low-temperature (12 K) PL spectra for three $\text{Zn}_x\text{Cd}_{1-x}\text{Te}$ films with $x = 0$ (a), $x = 0.03$ (b), and $x = 0.12$ (c); for all compositions, the spectra show dominant emission at about 780, 770, and 745 nm, respectively, and weaker emission at longer wavelengths. From the temperature dependence and excitation intensity these lines are identified as due to recombination of excitons. Notice that for the films with $x = 0$ and $x = 0.03$, the exciton recombination spectra show sharper and well resolved lines. As the Zn concentration increases these lines broaden and become a wide emission line as is seen in the sample with $x = 0.12$. Similar broadening effects in the bound exciton (BE) peaks have been observed in thin films⁵ and bulk-alloyed semiconductors.^{3,9} A qualitative explanation is offered based on the compositional fluctuations of the cations atoms.⁹

The broad emission band centered at about 865 nm for pure CdTe has been previously associated with the recombination of electron-hole pairs at levels produced by impurities and/or crystal imperfections.^{10,11} By analogy with the pure crystal, the same origin is attributed to the broad emission bands at 855 and 830 nm in the spectra of samples with $x = 0.03$ and $x = 0.12$, respectively. Notice that the relative intensity of the bands increases as the Zn concentration increases. The latter suggests that the levels involved in this recombination may be related with structural defects produced by the substitution of the Cd by Zn atoms. Also notice that the broad defect bands in films with $x = 0$ and $x = 0.03$ is modulated by several well resolved lines separated by approximately 21 meV, which is the energy of LO phonon in CdTe. Thus these lines correspond to a zero-order transi-

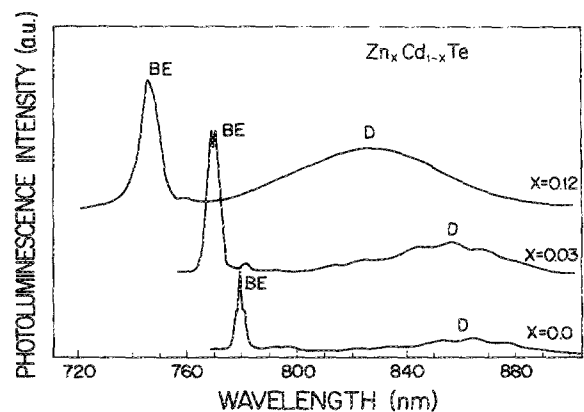


FIG. 2. Low temperature (12 K) PL spectra for three $\text{Zn}_{0.03}\text{Cd}_{1-x}\text{Te}$ films with $x = 0$ (a), $x = 0.03$ (b), and $x = 0.12$ (c) prepared at $T_s = 550$ °C. The emission at 780, 770, and 745 nm in (a), (b), and (c), respectively, correspond to recombination of excitons bound to impurities or crystalline imperfections.

tion, probably a donor-to-acceptor transition (D-A)¹² followed by several phonon replicas. The multiple phonon replicas in films with lower values of x is an indication of a longer phonon diffusion length. There can be less phonon scattering because there is less chemical disorder when the Zn content is small and/or there is a higher degree of crystallinity when there is less Zn. Note that in addition to these phonon replicas, for all three cases the first phonon replica of the bound exciton lines is observed at the low energy side of the main line.

Figures 3(a) and 3(b), respectively, show the PL spectra in the excitonic region for pure CdTe and $Zn_xCd_{1-x}Te$ ($x = 0.03$) films recorded at various temperatures. In both cases all peaks move to longer wavelengths and their intensities decrease with increasing temperature. The peak shift is due to the shrinkage of the band gap with increasing temperature; and the decrease in their intensity is most likely related to the reduction in the density of excitons bound to crystalline imperfections. Since the binding energy of exciton to lattice imperfections depends on the type of imperfection, the temperature dependence of the intensity and position of the bound exciton lines can be used to identify the origin of the levels involved in the transition. The fact that the lines at 777.5 and 768.5 nm in the 12-K PL spectra of films with $x = 0$ and $x = 0.03$, respectively, can be observed at higher temperatures suggests that their origin is possibly due to the superposition of donor–valence band (D-h) recombination with the recombination of excitons bound to donor sites (D,X).³ It is known that the lines due to the recombination of excitons bound to neutral acceptors (A⁰,X) are wider than the (D,X) lines and that their intensities decrease very rapidly with increasing temperature.¹³

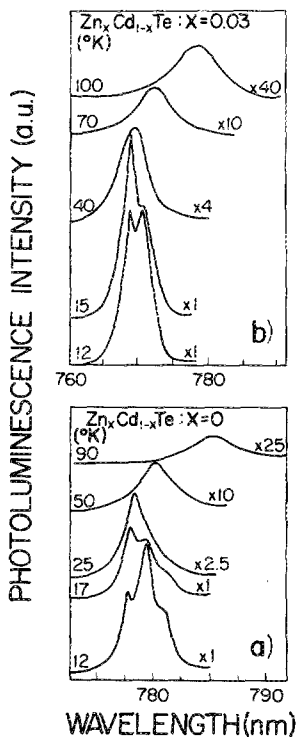


FIG. 3. PL spectra in the excitonic region for a pure CdTe (a) and a $Zn_{0.03}Cd_{0.97}Te$ (b) film recorded at various temperatures. The films were prepared at $T_s = 550^\circ C$.

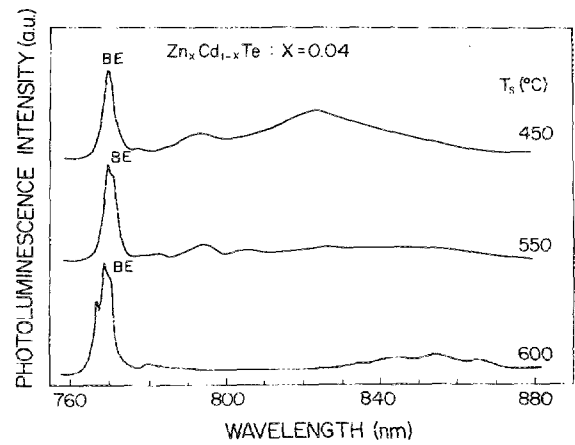


FIG. 4. PL spectra for three $Zn_xCd_{1-x}Te$ films prepared from the same source alloy having $x = 0.04$. The substrate temperatures were $450^\circ C$ (a), $550^\circ C$ (b), and $600^\circ C$ (c). In all three cases the source temperature was $700^\circ C$.

Thus the lines at 779 and 781 nm in the spectrum of the CdTe film are assigned to an (A⁰,X) transition. The same origin is proposed for the line at 771 nm in the PL spectrum of the $Zn_{0.03}Cd_{0.97}Te$ film. The positions of the (D,X) and (A,X) lines reported in this paper for the CdTe film are in good agreement with other studies.^{14,15}

Figure 4 shows the PL spectra in the range of 760–880 nm for three $Zn_xCd_{1-x}Te$ ($x = 0.04$) films prepared at fixed $T_f = 700^\circ C$ and at different T_s : $450^\circ C$ (a), $550^\circ C$ (b), and $600^\circ C$ (c). Similar to the spectra of Fig. 2 the dominant emission occurs in the bound exciton region for all T_s . However, the spectra of samples prepared at higher T_s show that the excitonic emission is composed by several well resolved sharper lines. For $T_s = 450^\circ C$ the broad bound exciton emission band suggests a distribution in the exciton binding energy perhaps due to the interaction of the exciton trapping levels which apparently occur at larger densities at this T_s . Also notice that the relative amplitude of the emission at wavelengths above the bound exciton region increases with decreasing T_s , indicating that better crystalline quality is obtained in films prepared at higher substrate temperatures.

Figure 5 shows the dependence of the room-temperature energy gap of the $Zn_xCd_{1-x}Te$ ($0 < x < 0.12$) films as a function of: (a) the Zn content in the film and (b) the lattice constant. The Zn concentration and the lattice parameter were determined by electron microprobe and x-ray diffraction, as was described in Sec. II of this paper. The room temperature energy gap was obtained by adding 0.013 eV to the energy position of the observed line in the room-temperature PL spectra. The energy of 0.013 eV corresponds to the difference between the donor level and the bottom of the conduction band.³

In both plots of Fig. 5, the relation is approximately linear in the compositional range previously investigated. The compositional dependence of E_g for MBE $Zn_xCd_{1-x}Te$ films has been previously reported as also having a quadratic dependence on x over the entire compositional range. Nevertheless, the contribution to the E_g value of the x^2 term for

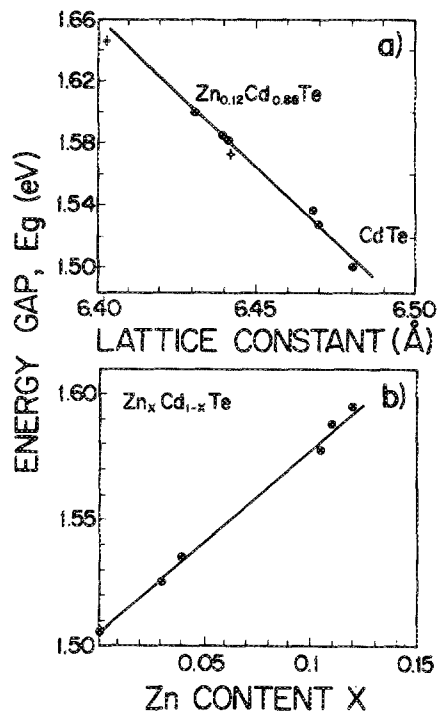


FIG. 5. Dependence of the room temperature energy gap for the $Zn_xCd_{1-x}Te$ ($0 < x < 0.12$) films as a function of: (a) the Zn content and (b) the lattice constant. The crosses correspond to data points reported for single crystal samples (Ref. 16). All samples were prepared at $T_s = 550^\circ C$.

$x < 0.15$ is less than 2%.⁵ A linear relation between E_g and the lattice constant has been previously observed in several II–VI bulk ternary alloys,¹⁶ such as $Mn_xCd_{1-x}Te$, $Hg_xCd_{1-x}Te$ and $CdSe_xTe_{1-x}Te$. The crosses in Fig. 5(a) correspond to the two data points for $Zn_xCd_{1-x}Te$ single crystals reported in Ref. 16. Extrapolating the fitted straight line in Fig. 5(a), it is found that for a lattice constant of 6.100 Å, reported value for ZnTe,¹⁷ the corresponding E_g is 2.3 eV, which is in agreement with the reported values between 2.26 and 2.35 eV.^{17,18}

IV. DISCUSSION AND CONCLUSIONS

In agreement with a previous work,⁴ the present study shows that good quality $Zn_xCd_{1-x}Te$ films can be prepared by the CVST method. Films with a Zn concentration similar to that in the source were prepared following the deposition parameters established before⁴ for low pressure (< 0.5 Torr) transport.

A PL measurement offers the means to evaluate the crystalline quality of II–IV compounds. Radiative emission due to extrinsic recombination at levels associated with crystalline imperfections can be identified in the PL spectrum, therefore the amplitude of these lines in relation to the intensity of the lines due to the recombination of free or bound exciton lines provides a qualitative way to assess the degree of crystallinity.

In the spectra of Fig. 2, the relative intensity of the emission at wavelengths above near band gap increases with increasing Zn concentration, which indicates an increase in

the density of crystalline imperfections. The observations are valid for spectra in Fig. 4 where the decrease in T_s increases the emission from states related to defects or deeper impurity levels. Thus, we have found that, according with the PL spectra, the crystalline quality of $Zn_xCd_{1-x}Te$ thin films degrades with both increasing Zn concentration and with decreasing T_s , below $600^\circ C$.

In the PL spectra of bulk CdTe and $Zn_xCd_{1-x}Te$ crystals prepared from liquid solidification peak at about 50 meV below the energy corresponding to the exciton lines is generally observed. In pure CdTe this peak appears at about 800 nm and it has been associated with radiative transitions involving levels produced by cadmium vacancies.¹⁹ In the $Zn_xCd_{1-x}Te$ crystal the PL spectra shows a peak at about the same energy below the excitonic lines. However, its origin is not yet clear. In our CdTe and $Zn_xCd_{1-x}Te$ films prepared by vapor condensation on substrates at much lower temperatures, the cadmium vacancies-related emission is almost undetectable.

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