Annealing Behavior of the Photoluminescence Lines in CdTe and Znx Cd1-x Te Single Crystals

David D. Allred
allred@byu.edu

A. Reyes-Mena

Jesus González-Hernández

Elías López-Cruz

Worth P. Allred

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ANNEALING BEHAVIOR OF THE PHOTOLUMINESCENCE LINES IN CdTe AND $Zn_x Cd_{1-x}$ Te SINGLE CRYSTALS

J. GONZALEZ-HERNANDEZ*, A. REYES-MENA*, ELIAS LOPEZ-CRUZ+, D.D. ALLRED# AND WORTH P. ALLRED&
*Departamento de Física, Centro de Investigación y de Estudios Avanzados del IPN. Apdo. Postal 14-740, 07000 México, D. F.
+Departamento de Física del Instituto de Ciencias, Universidad Autónoma de Puebla, Apdo. Postal J-48, Puebla 72570, Pue. México.
#Physics and Astronomy Department, Brigham Young University, Provo, UT.
&Galtech Semiconductor Materials Corp., Mt. Pleasent, UT.

ABSTRACT

The main lines in the photoluminescence spectra of $Zn_x Cd_{1-x}Te$ single crystals grown by a modified Bridgman method in the compositional range of $0 \leq X \leq 0.25$ have been identified. All crystals show only near-band-edge emission. To assist in the identification, various samples with different compositions were annealed under a Cd atmosphere. In the pure crystals, the prominent (A°,X) bound exciton line, as well as the doublet at longer wavelengths, disappear after the annealing. In contrast, the treatments do not change significantly the PL spectra of the mixed crystals.

INTRODUCTION

Large area cadmium telluride (CdTe) and zinc cadmium telluride ($Zn_x Cd_{1-x}$ Te) single crystal substrates have many potential applications in the fabrication of electronic and optoelectronic devices [1]. Interest in this wide-gap material has also developed due to its chemical compatibility and close lattice match to the important infrared detector material HgCdTe. However, the understanding of the native defects and their complex with residual impurities is important in order to have a better control of both their optical and electrical properties. In the last few years numerous studies on the photoluminescent (PL) properties of CdTe crystals have been reported [2-5] and only few on $Zn_x Cd_{1-x}Te$ [6-8].

In the present paper we report on the PL from as-prepared and Cd vapor annealed $Zn_x Cd_{1-x}Te$ ($0 \leq X \leq 0.25$) single crystals. For all the investigated values of x, the prominent emission lines occur in the exciton region indicating a high crystalline quality. In pure CdTe crystals, the 15K PL spectra exhibit two main lines in this region at 778.2 nm (1.5934eV) and 779.5 nm (1.5907eV). The former line occurs in the energy range where recombination of excitons bound to shallow neutral donors (D°,X) has been reported [9]. Our studies on annealed CdTe samples under Cd atmosphere indicate that the 1.5907 eV line is related with recombination of excitons bound to cadmium vacancies [5]. We also observed that in the mixed crystals exciton recombination mainly occurs via neutral donor states.

EXPERIMENTAL

All samples were grown from the melt by a modified Bridgman method at Galtech Semiconductor Materials Corporation. The composition of the $Zn_x Cd_{1-x}Te$ samples was determined from electron microprobe analysis and from the energy of the main exciton line observed in the 15K PL spectra [6]. All as-prepared crystals were unintentionally doped and have an approximate room-temperature resistivity of $5X10^6$ and $8X10^8$ Ω cm for the mixed and pure crystals, respectively. All spectra in the as-prepared samples were taken on (110) cleaved surfaces at 15K. The laser power, from an argon ion laser, impinging on the sample was of 0.5 mW with the laser beam focused using cylindrical optics. The PL emission was spectrally analyzed with a double monochromator, with slits set to achieve a resolution of less than 1A.

Annealing was carried out in a sealed quartz ampoule under Cd saturated isothermal conditions at 600°C for two hours. Before the PL was measured all annealed samples were chemically etched to remove the surface damage. The chemical treatment was as follows: immersion in a 1% bromine in methanol solution for 30 seconds followed by a 60 seconds immersion in a solution of 3.5M KOH in 1 liter of H_2O.

RESULTS AND DISCUSSION

Figure 1 shows typical 15K PL spectra for three as-prepared $Zn_xCd_{1-x}Te$ cleaved surfaces with x=0, 0.10 and 0.25. All three spectra are plotted with the same abscissa. Considering the origin of the emission lines, the PL spectra in the figure can be divided into three regions: a) the exciton region, for wavelengths near the band-gap; b) the free to bound (F-A) and bound to bound (D-A) transitions, for intermediate λ's and, c) emission at longer λ's associated with crystal imperfections and deeper impurity levels [6,10]. This latter emission generally appears in the PL spectra as a broad band at approximately 50 to 100 nm above the exciton lines. Notice that none of the three spectra in Fig. 1 shows any significant emission in this latter region, which is an indication of high crystalline quality.

The identification of the emission lines in the intermediate region, as due to electron-acceptor and donor-acceptor transitions has been reported in a previous study [11].

In the exciton region, free exciton recombination results in the emission of photons with an energy 10.5 meV less than the band gap, which, at 15K is at 772 nm (1.606 eV), 743.5 nm (1.668 eV) and 695.9 nm (1.7819eV) for x=0, 0.10 and 0.25, respectively. This line is denoted by (X)n=1 in the figure. The existence of several different donors and acceptors in CdTe has already been pointed out [12]. Free excitons can get trapped by the potential of the impurities becoming bound excitons. The two main lines in the exciton region of our pure CdTe crystals at 778.2 nm (1.5934 eV) and at 779.5 nm (1.5907 eV) have been identified as due to the recombination of excitons bound to shallow neutral donors (D°,X) [9] and to neutral acceptor (A°,X) states, respectively.

The identification of the 1.5907 eV line as due to a (A°,X) process is based on the changes observed in the PL spectra induced by the annealing under Cd atmosphere, which are shown in Fig. 2. The complete PL spectra as well as the resolved exciton regions are shown for as-prepared (a) and for annealed (b) samples. As can be seen, two drastic changes occur upon annealing: one is that the lines in the range of 790-800 nm denoted by (F-A) and (D-A) have been drastically reduced and the other is the disappearance of the (A°,X) line. The broader bands found at 790--800nm are generally accepted to involve deep acceptorlike levels associated with a complex center[3], and more recently their origin has been related with cadmium vacancies [13]. In a recent publication Seto et al [5] have seen that, under similar annealing conditions, the intensity of a bound exciton

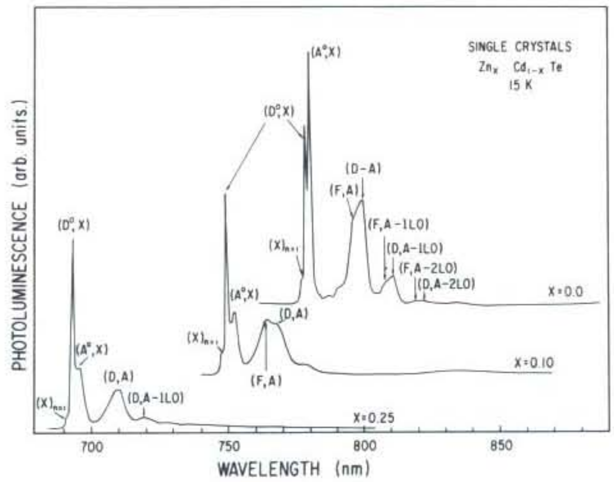

Fig. 1. Photoluminescence spectra of $Zn_xCd_{1-x}Te$ single crystals with x=0, 0.10 and 0.25. Details on the assignments and identification of various lines can be found in the text.

line at 1.5896 eV in their 4.2K PL spectra of high quality p-type CdTe is drastically reduced after the annealing; their results strongly suggest that this line can be ascribed to the recombination of excitons trapped at Cd vacancies. Our results in annealed CdTe crystals under a Cd atmosphere provide further evidence for the previously proposed assignments for the PL bands in the region of 790-800 nm as well as for the origin of the (A°,X) line at 1.5907 eV. The identification of the 1.5907 eV line is also consistent with its temperature dependence because the PL intensity of acceptor-bound excitons decreases very rapidly with increasing temperature [11].

Figure 3 shows the PL spectra of an as-prepared (a) and Cd vapor annealed (b) $Zn_xCd_{1-x}Te$ with x=0.09. Similar to the pure CdTe crystals, the PL spectra of the as-prepared mixed crystals show a dominant near-band-edge emission. In the exciton region the line at 753.2 nm (1.6463eV) has the same exciton binding energy of 2 meV as the line labeled with (D°,X) in the PL spectra of pure CdTe, lending evidence that this feature is due to the same transition in both cases. The line at 756 nm (1.6402 eV) has been identified with a (A°,X) transition based on a variety of evidence. In the first place, the exciton binding energy of 7.5 meV is close to the calculated binding energy of excitons bound to acceptors of 7 meV [14]. In the second place, this line is thermally quenched at temperatures exceeding 50K. This assignment is also in agreement with previous observations in other alloyed compound semiconductors showing that the (A°,X) lines are much more sensitive to alloying and that the linewidth increases at a rate much greater than that of the (D,X) levels [15]. We have observed that in the exciton region, the PL spectra of the mixed crystals look very similar regardless of x in the range investigated.

The result of the annealing under Cd atmosphere for $Zn_xCd_{1-x}Te$ crystals is quite different than that observed in the pure crystals. In the

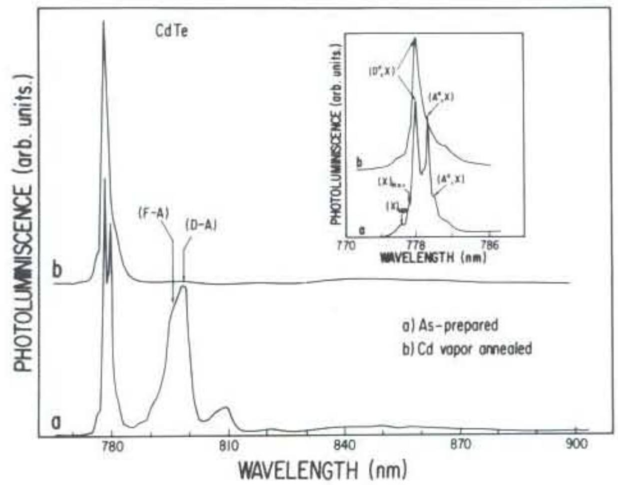

Fig. 2. Photoluminescence spectra of a CdTe single crystal, before (a) and after (b) annealing at 600C/2hrs. in a saturated Cd vapor atmosphere. The insert shows the resolved exciton region.

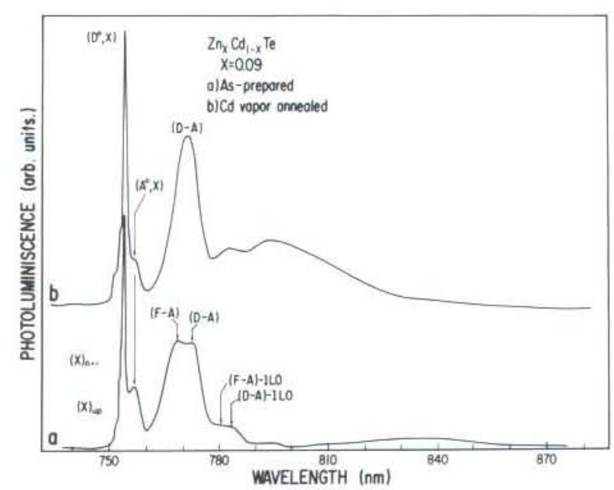

Fig. 3. Photoluminescence spectra of as-prepared (a) and Cd vapor annealed (b) $Zn_xCd_{1-x}Te$ single crystals with x=0.09.

mixed crystal a small decrease in the amplitude of the (A°,X) line and a change in the shape of the broader emission line located at about 20-30 nm above the exciton range are observed. Before annealing the well defined doublet labeled as (F-A) and (D-A) becomes a single line with a position at 769.5 nm (1.6114 eV) in between the (F-A) and (D-A) doublet. From the dependence on temperature and excitation intensity we have identified this line with a (D-A) transition. We have also observed that as a result of Cd annealing a new broad emission band appears at about 795 nm (1.5597 eV) probably originated at deeper defect levels created during the thermal annealing, however, further studies are needed in order to have a better understanding about the origin of this band.

Based on the annealing behavior of the PL spectra of CdTe and $Zn_x Cd_{1-x}Te$ crystals, one can conclude that, in contrast to pure CdTe, the free to bound, the bound to bound and the (A°,X) bands in the mixed crystals are probably not related with recombination involving cadmium vacancy levels. These results provides further support for the observation that Zn addition to CdTe improves crystal quality [16,17], particularly reducing the density of group II (Cd or Zn) vacancies.

CONCLUSIONS

The photoluminescent properties of $Zn_x Cd_{1-x} Te$ single crystals for $0 \leq X \leq 0.25$ have been studied. To assist in the identification of the lines in the spectra, as-prepared and annealed (under Cd atmosphere) samples were measured. In all crystals, the dominant emission occurs at the near-band-edge region, indicating good crystalline quality. In the pure crystal, the two main exciton lines are identified with recombination of excitons at neutral shallow donors (778.2 nm) and at neutral donors (779.5 nm). The assignment of the latter line was deduced from its annealing behavior under a saturated Cd atmosphere. We also observed that the doublet in the wavelength range of 790-800 nm disappears after the annealing, which indicates that the levels involved in that transition are also related to cadmium vacancies.

In the as-prepared mixed crystals, we observed that the PL spectra is qualitatively similar regardless of the values of x. By analogy with the pure crystal, the main exciton line is identified with a (D°,X) transition and a weak (A°,X) line is also observed. From the observed changes in the PL spectra of Cd annealed mixed crystals, we concluded that the main lines in the spectra are not related with transitions involving Cd vacancies.

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