Low Temperature Photoluminescence Spectroscopy of Defect and Interband Transitions in CdSe$_x$Te$_{1-x}$ Thin Films

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We present the defect analysis by photoluminescence (PL) spectroscopy of CdSe$_x$Te$_{1-x}$ thin films, grown with varying Se content by a co-sputtered deposition method. We observe a peak at 1.203 eV in the CdSe$_x$Te$_{1-x}$ film for x = 0.21, which shifts towards higher energies with increase in laser power. This peak was assigned to a donor-to-acceptor (DAP) transition, with a measured j-shift of ~4.7 meV/decade. Temperature dependent PL intensity measurements confirm that the observed DAP peak involves a shallow defect state of binding energy ~34.7 meV. In contrast, a free-to-bound (FB) peak at 1.294 eV involving a shallow defect of binding energy ~18.3 meV was observed in the CdSe$_x$Te$_{1-x}$ film for x = 0.14. Additionally, we observe band edge emission at 1.452 eV and 1.448 eV in CdSe$_x$Te$_{1-x}$ films for x = 0.14 and x = 0.21 respectively. Our analysis shows that the Se concentration not only changes the band gap energy of the resulting CdSe$_x$Te$_{1-x}$ alloy thin film, but also modifies the nature of the dominant observed defect emission.

INTRODUCTION

Initial interest in CdSe as a heterojunction partner for the well-established CdTe absorber layer has led to the development of CdSe$_x$Te$_{1-x}$ as a graded layer at the front side of CdTe solar cells [1-5]. The presence of such an alloy in CdTe solar cells increases the current densities in resulting devices by increasing the cell photo-response for both short- and long-wavelength photons [1, 2]. For the longer wavelengths (> ~850nm), the optical absorption is enhanced from the decrease in the band gap of the CdSe$_x$Te$_{1-x}$ alloy as a result of a band gap bowing effect [6-8]. For shorter wavelengths (< ~500nm), the design yields a substantial optical improvement over the use of the more conventional CdS window layer, for which parasitic optical absorption results in relatively little contribution to the photocurrent. However, the reported open circuit voltage (V$_{oc}$) and fill factor (FF)

are lower than for CdS/CdTe solar cell designs. Photo-generated carrier lifetime is also lower than that in non-alloyed CdTe thin films [3]. This reduction in photo-generated charge carrier dynamics are an indicator of an increase in recombination site density in the $CdSe_xTe_{1-x}$ alloy region. Thus, understanding of the recombination mechanisms in $CdSe_xTe_{1-x}$ is warranted. There have been many studies reported on identification of various kinds of defects within CdTe polycrystalline films along with their influence on optoelectronic properties, and we seek here to establish some of the defect analysis for $CdSe_xTe_{1-x}$ films. The present work focuses on the defect analysis of polycrystalline $CdSe_xTe_{1-x}$ films via low temperature photoluminescence (PL) measurement. Laser power and temperature-dependent measurements reported here revealed the presence of donor-to-acceptor (DAP), free-to-bound (FB), and band edge emission in $CdSe_xTe_{1-x}$ films. We were also able to calculate the thermal quenching of observed defect peaks using temperature-dependent PL intensity.

EXPERIMENTAL DETAILS

Co-sputtered $CdSe_xTe_{1-x}$ thin films, nominally 2 μm in thickness, were deposited on 3mm thick soda-lime glass substrates (NSG Pilkington, USA) pre-cleaned using surfactant solution (Micro-90) facilitated by ultrasonication. The substrate was held at ~ 270°C while rotating at approximately 60 rpm, while CdTe and CdSe were deposited simultaneously utilizing two independently controlled RF sputter sources in a single vacuum chamber (AJA Inc., Japan). [9] The deposition condition was at 10 mTorr, maintained with a flow of 23 sccm of Argon. Depending upon the desired composition of the individual sample films, the sputtering powers of each source was adjusted between 0 and 50 W, and the deposition times ranged from 1.5 - 2.5 hours. Cadmium chloride ($CdCl_2$) treatment was conducted by depositing a small amount of $CdCl_2$-saturated methanol solution (MeOH) on the surface of the samples and annealing at 390°C for 30 minutes under a flow of 500 sccm dry air in a custom-built tube furnace. [9] Residual $CdCl_2$ was rinsed off using MeOH after the annealing process.

Energy dispersive X-ray spectroscopy (EDS), utilizing a Hitachi S-4800 high resolution scanning electron microscope (SEM) equipped with an EDS detector (Oxford Instruments, UK) was used to determine the elemental composition of the alloys. Optical absorbance spectra were acquired with a UV–Vis spectrophotometer (PerkinElmer Lambda 1050). For PL measurements, samples were excited at the film side. For steady-state PL, a 532 nm cw (continuous wave) laser beam (focused beam diameter ≈ 90 μm) was used for the photoexcitation. For room temperature measurements, the PL signal was detected by a Horiba Symphony-II CCD (charged coupled device) detector after a 300 g/mm grating monochromator while a liquid nitrogen cooled Germanium photodiode from Electro-Optical Systems was used for low temperature measurement. Temperature dependent PL measurements were carried out by mounting the sample on the cold finger of a He closed-cycle refrigerator cryostat system from Advanced Research Systems. PL measurements were performed using laser intensities in the range of ~0.15 to 9.9 W/cm^2.

RESULTS & DISCUSSION

Table 1 shows the average fraction of Se in $CdSe_xTe_{1-x}$ alloy estimated by using Energy Dispersive X-ray spectroscopy (EDS). Absorbance and normalized PL spectra taken at room temperature (Figure 1a) show that the band gap of the

$CdSe_xTe_{1-x}$ ternary alloy decreases with Se content in this range, consistent with the previously reported band gap bowing effect. Figure 1b shows that the same trend was observed for the spectra acquired at low temperature. The observed above – band - gap emission (emission at >1.50 eV) at room temperature is unexpected, and unexplained here. We note that for high Se content (x > 0.3) the emission is suppressed or absent, and also that $CdSe_xTe_{1-x}$ films grown by close space sublimation have not shown this PL behavior. Additional analysis is underway to explain the anomalous PL behavior.

Table 1. Fraction of Se in $CdSe_xTe_{1-x}$ alloys obtained from EDS analysis using equation x = % Se / (% Se + % Te)

At% of Se	At% of Te	x %	x in $CdSe_xTe_{1-x}$
(6.0 ± 0.4)	(39.0 ± 0.4)	(13.6 ± 1.4)	0.14
(9.8 ± 0.7)	(38.3 ± 0.6)	(21.0 ± 0.4)	0.21
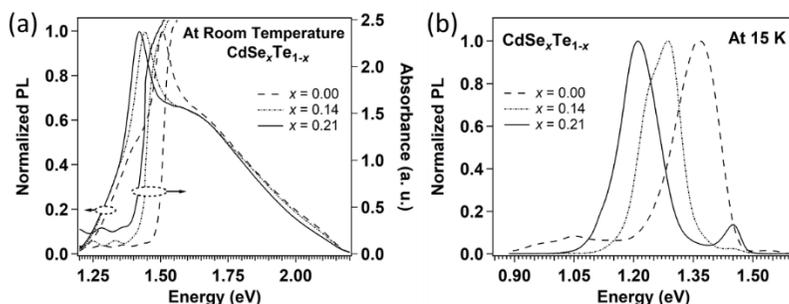
Figure 1. (a) Room temperature absorbance and normalized PL spectra of $CdSe_xTe_{1-x}$ film for varying Se content and (b) PL spectra taken at 15 K.

Since the optoelectronic properties of the $CdSe_xTe_{1-x}$ film are influenced by the presence of native defects, we have performed low temperature PL measurement on these films for x value ranging from 0 to 0.21 to identify the type of defects associated with them. Figure 1b shows that the PL spectra of $CdSe_xTe_{1-x}$ film for x =0 taken at 15 K consists of Z′-band at ∼1.36 eV, and a DAP peak overlapped with its phonon replica around ∼1.53 – 1.55 eV consistent with previous reports [10-14]. Additionally, a broad DAP peak corresponding to a V_{Te}–Te_i complex is also observed at ∼ 1.05 eV [11, 15]. For the alloy samples at 15 K, we observe sharp emission at 1.294 eV and 1.203 eV respectively in $CdSe_xTe_{1-x}$ film with x = 0.14 and x = 0.21 as shown in Figure 1b. Additionally, we observed emission peaks at higher energies, specifically at 1.452 eV and 1.448 eV in $CdSe_xTe_{1-x}$ films with x = 0.14 and x = 0.21, respectively, although the peak intensity is weaker for x = 0.14.

Integrated PL intensity follows power law $I_{PL} = I^k_{Laser}$ with a value of $1 < k <2$ for band-to-band (BB) and excitonic recombination, and $k < 1$ for free-to-bound (FB) and donor-to-acceptor (DAP) recombination [11, 16, 17]. When a semiconductor gets optically excited, photogenerated electrons and holes can be

captured by the ionized donor and ionized acceptor states if present. Recombination of these captured electron and hole emits a photon whose energy not only depends upon the donor and acceptor energy level from band edge but also depends upon the coulomb interaction between donor and acceptor. The energy of a photon emitted via donor-to-acceptor recombination can be described by equation (1), where E_A and E_D are acceptor and donor binding energies respectively, E_g the band gap energy, r the separation between donor and acceptor in DAP [18, 19].

$$E_{DAP} = E_g - E_A - E_D + \frac{e^2}{4\pi\epsilon\epsilon_o r} \qquad (1)$$

As the laser intensity increases, closer donor-acceptor pair recombination dominates, causing a blue shift of the DAP peak. On the other hand, free-to-bound (FB) transition occurs via recombination of a free electron (or hole) with a hole (or electron) bound to a defect state. FB peak does not change with incident laser intensity [20]. To explore the identity of the observed emission peaks, laser power dependent PL measurement were performed as shown in Figure 2a-b. PL spectra were then spectrally integrated to investigate the laser intensity dependent PL (i.e. $I_{PL} = I^k_{Laser}$) of the observed emission peaks. The obtained k < 1 values (Figure 3a-b) for the most prominent peaks -- at 1.294 eV and shoulder peak at 1.241 eV in CdSe$_x$Te$_{1-x}$ film with x = 0.14, and 1.203 eV in the case of x = 0.21-- are the result of defect assisted transitions. The higher energy peaks with k > 1, at 1.452 eV for x = 0.14 and at 1.448 eV for x = 0.21, may be assigned to either band-to-band or excitonic emission. As laser power is increased, the 1.203 eV peak observed in CdSe$_x$Te$_{1-x}$ film with x = 0.21 shifts towards higher energy as shown in figure 2b. This shift is called j-shift. The coulomb interaction in the photon energy which depends upon the separation between donor and acceptor in DAP is responsible for such shift as described in equation (1). As the laser intensity increases, closer donor-acceptor pair recombination dominates causing a blue shift of the DAP peak. The measured j-shift for the 1.203 eV peak was 4.7 meV/decade. So, the 1.203 eV peak is assigned to a donor-to-acceptor peak (DAP), while the 1.294 eV peak observed for x = 0.14 is assigned to a free-to-bound (FB) transition. The nature of 1.241 eV defect peak observed for x = 0.14 is still under investigation. Furthermore, rapid quenching with increasing temperature lead us to attribute the higher energy peaks at 1.452 eV (FWHM ∼ 54 meV) for x = 0.14 and 1.448 eV (FWHM ∼ 46 meV) for x = 0.21 to band-to-band emission. Since defect states dominate at low temperature, observed band edge emission were very weak in intensity. In addition, our analysis shows that the Se concentration not only changes the band gap energy of the resulting CdSe$_x$Te$_{1-x}$ alloy thin film, but also modifies the nature of the dominant observed defect emission. Ma *et al.* reported that an increase in Se content in CdSe$_x$Te$_{1-x}$ can lower the formation energy of some defect states [6]. However, it is still too early to say how Se content determines the type of defects in the CdSe$_x$Te$_{1-x}$ alloy.

In the temperature dependent PL spectra of Figures 4a-b, it has been observed that the 1.452 eV and 1.448 eV peaks quenched very rapidly with

increasing temperature compared to the other peaks. In Figure 5a, a thermal activation energy of ~ 18.3 meV was obtained for the 1.294 eV FB peak in $CdSe_{1-x}Te_x$ film with $x = 0.14$ by using equation (2) [21, 22], where I_o, and C are fitting parameters and E_T is the thermal activation energy. As the probability of hole and electron capture on a donor-acceptor pair varies as $T^{-3/2}$, the thermal activation energy of the 1.203 eV DAP peak in the $CdSe_{1-x}Te_x$ film with $x = 0.21$ was obtained by fitting temperature dependent PL using equation (3) [23-25].
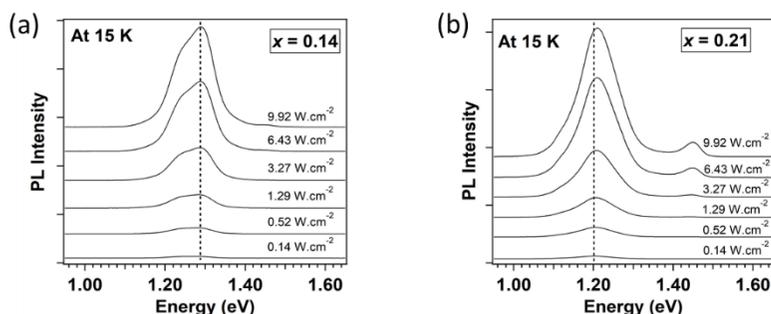
Figure 2. Laser intensity dependent PL spectra of $CdSe_xTe_{1-x}$ film (a) for $x = 0.14$ and (b) for $x = 0.21$ acquired at 15 K sample temperature.
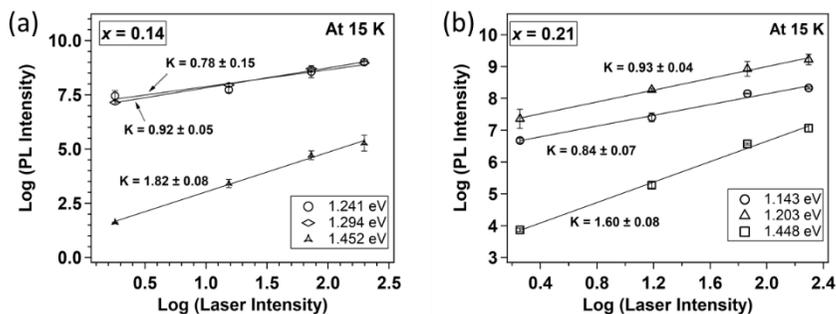
Figure 3. Power law dependency of observed peaks in $CdSe_xTe_{1-x}$ film (a) for $x = 0.14$ and (b) for $x = 0.21$ taken at 15 K.

$$I(t) = \frac{I_o}{1 + C\, e^{-E_T/KT}} \qquad (2)$$

$$I(t) = \frac{I_o}{1 + A\, T^{3/2} + B\, T^{3/2}\, e^{-E_T/KT}} \qquad (3)$$

The obtained value of thermal activation energy for 1.203 eV DAP peak in $CdSe_xTe_{1-x}$ film for $x = 0.21$ was ~ 34.7 meV as presented in figure 5b. Here, A, B, I_o are the fitting parameters, and E_T the thermal activation energy. The thermal activation energy of 34.7 meV suggested that the 1.203 eV DAP peak involved a shallow defect state of binding energy ~ 34.7 meV. The observed DAP (1.203 eV) and band edge

emission (1.448 eV) peaks confirm the involvement of at least one deep level defect state in the DAP recombination process following the equation (1). Identification of the source of observed defects in CdSe$_x$Te$_{1-x}$ alloys using calculated activation energies remains under investigation.
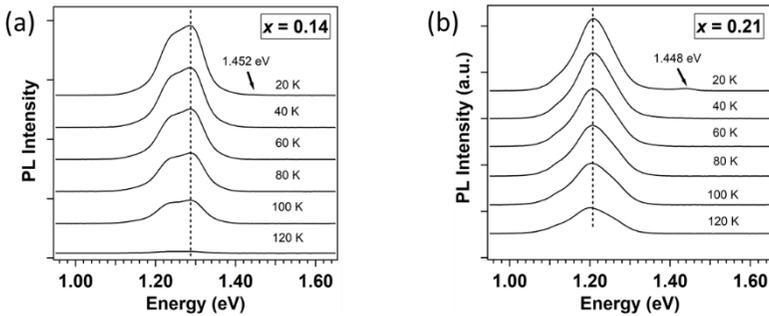
Figure 4. PL spectra of CdSe$_x$Te$_{1-x}$ film at various temperatures (a) for $x = 0.14$ and (b) for $x = 0.21$.
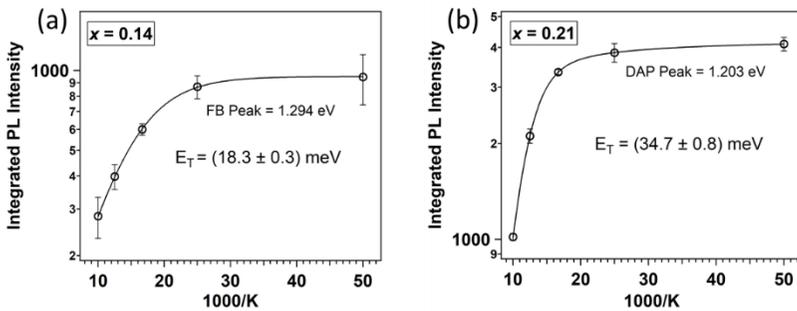
Figure 5. Temperature dependence of PL intensity of CdSe$_x$Te$_{1-x}$ film (a) for $x = 0.14$ and (b) for $x = 0.21$. Fitted curves are shown as solid lines. The calculated activation energies are also shown.

CONCLUSIONS

We have carried out an initial analysis of defects in sputtered CdSe$_{1-x}$Te$_x$ thin film based on PL measurements. PL spectra of CdSe$_{1-x}$Te$_x$ films taken at low temperature show evidence of several native defects. The 1.203 eV peak observed in CdSe$_{1-x}$Te$_x$ with $x = 0.21$ shows a blue-shift with increasing laser power, and the measured j-shift was 4.7 meV/decade – confirming that the 1.203 eV peak corresponds to the DAP recombination. The thermal activation energy of such a DAP peak was determined to be ~ 34.7 meV. Additionally, we observe band edge emission at 1.448 eV in CdSe$_{1-x}$Te$_x$ with $x = 0.21$. Furthermore, we have assigned the 1.294 eV peak, observed for the $x = 0.14$ CdSe$_{1-x}$Te$_x$ thin film, to a free-to-bound transition, and the 1.452 eV peak to band edge emission. The estimated value of thermal activation energy for the 1.294 eV peak was ~ 18.3 meV which shows that FB transition involves a shallow defect state. Furthermore, we have been able to show that the Se concentration not only changes the band gap energy of the resulting CdSe$_{1-x}$Te$_x$ alloy thin film, but also modifies the nature of the dominant

observed defect emission. Since some defects -- e.g. deep level defect states -- are detrimental to the performance of a solar cell, identification of the source of these defect states and their properties are crucial to improve the performance of a solar cell. Therefore, our defect analysis of $CdSe_{1-x}Te_x$ alloys may help the PV scientific community to improve the power conversion efficiency of a [n-type window/($CdSe_{1-x}Te_x$ /CdTe)] or [CdSe/CdTe] solar cell.

ACKNOWLEDGEMENTS

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