

# Photoluminescence studies of CdTe films and junctions

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## Abstract

Device quality CdTe films and junctions have been studied using low-temperature photoluminescence (PL) measurements. The behavior of the PL was studied as a function of the measurement temperature and excitation intensity. The CdTe films and junctions were prepared under various deposition conditions to determine the effect of film deposition and solar cell fabrication parameters, such as the effect of oxygen, and chloride treatment. A PL band located at 1.232 eV has been attributed to the presence of oxygen. This band is present only in as-deposited samples excited at the CdTe surface. Samples annealed in the presence of CdCl<sub>2</sub> exhibit a single PL band located at 1.42 eV. A model explaining the behavior of these bands is presented.

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## 1. Introduction

The photovoltaic properties of CdS/CdTe heterojunction-based solar cells greatly depend on recombination levels formed in the components of the heterojunction, and especially the presence of the recombination levels at the interface of the heterojunction. These localized states can be due to structural defects in the metal's sublattice (Cd), in the chalcogen sublattice (S, Te), interstitial defects, or by means of controlled doping of the components of the heterojunction, during the deposition process, or during post-deposition annealing in various environments. Photoluminescence studies of CdS/CdTe heterojunctions from the CdTe side and the CdS/CdTe interface can reveal radiative states due to different impurities and potentially explain their role and influence on solar cell performance. The role of impurities such as oxygen and chlorine has been previously studied but the results are sometimes contradictory. For example while it has been suggested that oxygen does not behave as a p-type dopant in CdTe, it is also believed that oxygen increases the density of acceptors. This paper describes

work aimed at correlating the PL characteristics of CdS/CdTe junctions to two of the most commonly used impurity elements, chlorine and oxygen.

## 2. Experimental

Thin films of CdTe, and solar cell structures (i.e. CdS/CdTe heterojunctions without the back contact) were prepared on SnO<sub>2</sub> coated borosilicate glass using previously described processes [1]. Briefly, the transparent conductors were prepared in the form of a bi-layer (SnO<sub>2</sub>:F/SnO<sub>2</sub>) using MOCVD. The chemical bath deposition (CBD) process was used for the preparation of CdS films at a temperature of 85 °C. Cadmium telluride films were deposited using the close-spaced sublimation process (CSS). For this study, CdTe was deposited in inert (He), or O<sub>2</sub>-containing ambient at a substrate temperature in the range of 580–600 °C. Following the CdTe deposition some of the structures were subjected to the typical CdCl<sub>2</sub> heat treatment [1]. The key process variations will be identified in the Results and discussion sections that follow. The PL measurements were carried out using an Ar-Ion Laser (Coherent Innova 70) with maximum output power of 200 mW at 488 nm, the wavelength used for these measurements. The incident beam power, before

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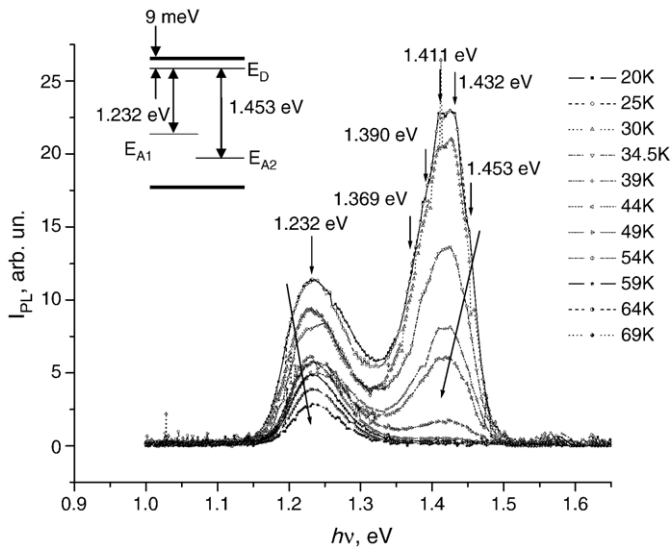


Fig. 1. The temperature dependence of the PL spectra of CdTe deposited in He/O<sub>2</sub> ambient (SnO<sub>2</sub>/CdS/CdTe structure excited from the CdTe side). Inset to Fig. 1: photoluminescence excitation scheme.

the focusing lens was 50 mW. A grating-based monochromator (SPEX-500M) and a Ge detector (model EO-817L — North Coast Scientific Corporation) were used for signal detection. The samples were cooled using a RMC Cryosystems (Model 22HC) closed-loop cryostat with a CTI-Cryogenics (Helix Technology Corporation) 8001 Controller and 8300 Compressor. The lowest stable sample temperature was  $15 \pm 0.5$  K, using a LakeShore 805 Controller. The excitation intensity was varied using neutral density filters. The typical range of temperatures used for the measurements was 15–100 K. Photoluminescence spectra were obtained by exciting the samples either at the CdTe surface, or at the CdTe/CdS interface (i.e. the samples were excited through the glass substrate), with the former providing information on the bulk characteristics of CdTe, and the latter being influenced by the interdiffusion between the two semiconductors (and the formation of the mixed CdS<sub>0.5</sub>Te<sub>0.5</sub> crystal). The energetic resolution for the measurements was 0.5–3 meV.

### 3. Results and discussion

It is known that the behavior of band gap states can vary with temperature and excitation intensity depending on the characteristics of the recombination levels (capture cross section and concentration). The properties of the band gap states can influence the recombination of carriers through the CdTe junctions, and as a result the efficiency of the CdS/CdTe solar cells. It is reasonable to expect that the recombination levels in CdTe layers and especially in the interface layer of the heterojunctions will be influenced by diffusion of S atoms from the CdS layer during the deposition and annealing processes [2]. In order to establish the influence of the impurity atoms diffused in CdTe, the PL spectra have been obtained from the “free” CdTe surface and from the interface of the heterojunctions, as indicated in the previous section. Ample information about the localized states energetic spectrum in

CdTe and in the CdS/CdTe junction interface can be obtained from the PL spectra studied at low temperatures (<78 K) and at different excitation conditions.

#### 3.1. As-deposited CdTe PL — CdTe prepared in O<sub>2</sub> ambient

The 20 K PL spectrum obtained by exciting the CdTe side of a sample for which the CdTe film was deposited in He/O<sub>2</sub> ambient consists of two bands with maximum intensities located at 1.232 eV and 1.420 eV as shown in Fig. 1. The 1.420 eV has a complex structure and further analysis of the envelope of this band, resolved peaks located at 1.453, 1.432, 1.411, 1.390 and 1.369 eV. The 1.453 eV band has been previously ascribed to a D–A pair, with the levels being formed in the metal’s sublattice [3]. Based on the 21 meV LO phonon energy for this material, the rest of the peaks listed are believed to be the phonon replicas of the 1.453 PL band [4]. A similar PL band has been previously found as a result of radiative recombination with plasmon participation [5]. The characteristic of plasmon formation is the increase on the energetic interval between the maxima of the radiative bands with increasing excitation intensity. As shown in Fig. 2, the equidistant distribution of the maxima (21 meV) is preserved along with the excitation intensity increase by more than one order of magnitude. It can therefore be concluded that the structural peculiarities of the 1.420 eV band measured from the CdTe surface are LO phonon replicas ( $\hbar\omega \approx 21$  meV) of the 1.453 transition. It should be mentioned that the 1.420 eV band is active only for temperatures below 55 K, and therefore it can be assumed that for temperatures higher than 55 K the donor level responsible for this band is completely ionized ( $kT \sim 4.7$  meV).

The second PL band with maximum intensity at 1.232 eV has a simple contour, a characteristic of a D–A transition. The Gaussian type behavior of the 1.232 eV band can be clearly seen at temperatures above 55 K, where the intensity of the 1.420 band decreases. The intensity of this band (1.232 eV) begins to saturate at high excitation intensities. Based on these two characteristics, one can ascribe the 1.232 eV band to radiative

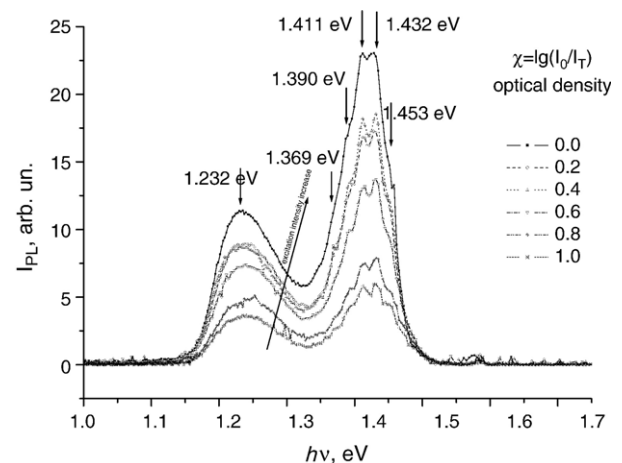


Fig. 2. The excitation intensity dependence of the same CdTe sample shown in Fig. 1 (deposited in He/O<sub>2</sub> ambient; SnO<sub>2</sub>/CdS/CdTe structure excited from the CdTe side);  $T = 20$  K.

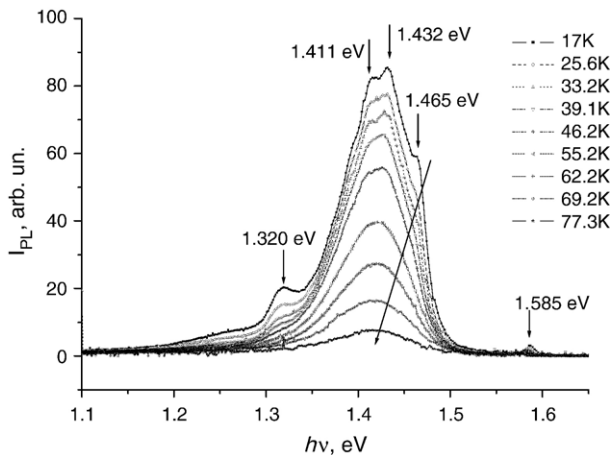


Fig. 3. The temperature dependence of the PL spectra of CdTe deposited in He ambient, (SnO<sub>2</sub>/CdS/CdTe structure excited from the CdTe side); heterojunction, deposited in He ambient only, as-deposited (from CdTe side).

recombination via a D–A complex. The thermal activation energy of this band has relatively low value of approximately 9 meV. For temperatures above 55 K the temperature extinguishing of this band (1.232 eV) increases, resulting in an increase of the activation energy by more than 2 times (~21 meV).

These results can be explained by presuming that both the 1.420 and 1.232 eV bands are results of electron recombination via the same donor level ( $E_D$ ) with the holes localized at two acceptor levels ( $E_{A1}$  and  $E_{A2}$ ) as shown in the inset of Fig. 1. For temperatures above 55 K where the  $E_D$  level is thermally ionized, level  $E_{A1}$  is transformed in the recombination level for the non-equilibrium electrons. So the recombination mechanism: electron-acceptor level predominate in the formation of the 1.232 eV band.

### 3.2. As-deposited CdTe PL — CdTe prepared in O<sub>2</sub>-free ambient

In order to further understand the origin of the 1.232 eV band, the PL spectra for CdTe films prepared in O<sub>2</sub>-free ambient (He) were also measured. Fig. 3 shows the temperature dependence of the PL spectra obtained by exciting the CdTe surface. A comparison of the results shown in Figs. 1 and 3 reveals that the spectra differ by the fact that in the 1.232 eV region there appears to be just a trace of a signal, while a new band is clearly visible at 1.320 eV (more on this band in a subsequent section). The broad peak that dominates this spectrum, consists of two bands: (a) the band at 1.432 eV and its LO phonon replicas (which was also present in Fig. 1), and (b) a second new band with maximum intensity at 1.465 eV. The latter has been previously assigned to a radiative annihilation of excitons bound to structural defects [6]. Corwine et al. have correlated this band to the presence of oxygen in CdTe [7]. Since, as can be seen in Fig. 3 this band is present in CdTe layers grown in an O<sub>2</sub>-free (inert) ambient, the origin of this band is believed to be due to structural defects in CdTe. It should also be noted that the intensity of

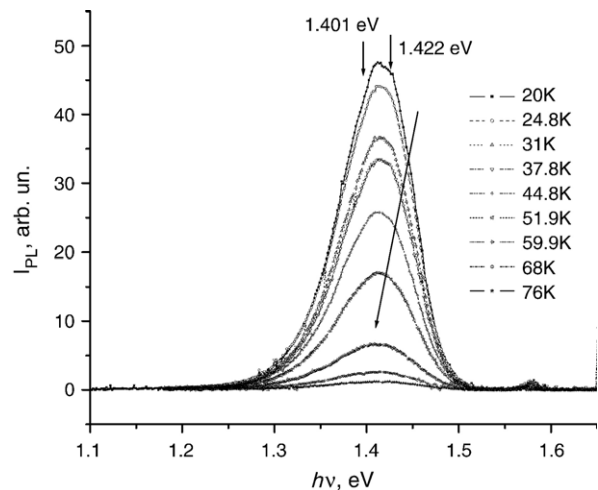


Fig. 4. The temperature dependence of the PL spectra of CdTe layer, component of the SnO<sub>2</sub>/CdS/CdTe heterojunction, deposited in He/O<sub>2</sub> ambient, annealed in presence of CdCl<sub>2</sub> (from CdTe side).

the 1.465 band increases linearly with the excitation intensity; the increase of 2 orders of magnitude questions its excitonic origin.

### 3.3. Heat-treated CdTe PL — CdTe prepared in O<sub>2</sub> ambient

Annealing in the presence of CdCl<sub>2</sub> results in significant changes in the PL spectra measured from the CdTe. Fig. 4 shows the PL spectra of CdTe prepared in He/O<sub>2</sub> ambient. The spectrum at 20 K consists of one band with peak energy at 1.422 eV and its LO phonon replica at 1.401 eV. The interaction with phonons decreases with increasing temperature, and at temperatures above 37 K the PL spectrum consists of a single, Gaussian-shaped band. The maximum intensity of the PL band decreases with increasing temperature, and appears to be completely eliminated at temperatures above 80 K. This temperature dependence of the intensity of the 1.422 eV PL

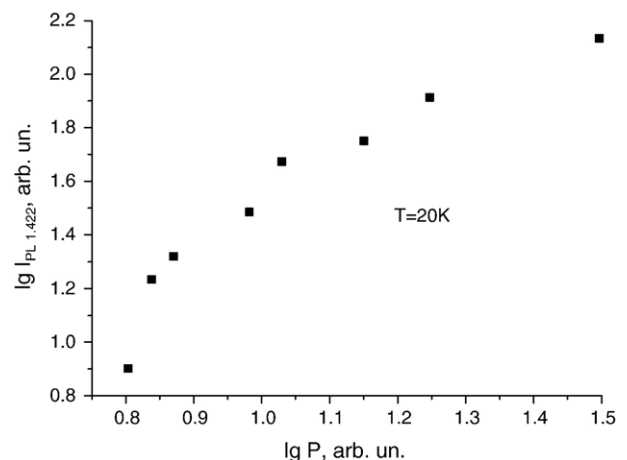


Fig. 5. The excitation intensity dependence of the 1.422 eV PL band of CdTe layer, component of the SnO<sub>2</sub>/CdS/CdTe heterojunction, deposited in He+O<sub>2</sub> ambient, annealed in CdCl<sub>2</sub> (from CdTe side) T=20 K.

band can be described by a function for the recombination luminescence as follows:

$$I = \frac{I_0}{1 + A \cdot \exp \frac{\Delta E}{kT}} \quad (1)$$

The donor's thermal activation energy is equal to 12 meV in the 20–50 K temperature range, and the difference between the activation energy of the acceptor level and the binding energy of the D–A pair is equal to 23 meV. So, as a result of thermal annealing in CdCl<sub>2</sub> along with the decrease of the concentration of structural defects in the Cd sublattice, a new diagram of the recombination levels is formed, which dominates the PL spectra. Specifically the radiative channel which forms the path in the near IR region (1.23–1.24 eV) is closed and the transitions in the 1.42 eV band are amplified.

The intensity of the 1.422 eV PL band at low temperatures ( $T \approx 20$  K) is linearly dependent on the excitation intensity as shown in Fig. 5. At higher temperatures the same dependence shows a saturation behavior for the excitation beam intensity increase (Fig. 6). This dependence points at a recombinational mechanism for the CdTe layer annealed in CdCl<sub>2</sub>. Thermal annealing of the CdTe structures in CdCl<sub>2</sub> results in the decrease of the concentration of the states localized in the CdTe surface layer which are screening the electron–hole bonds. This fact is experimentally seen by the appearance of the free exciton PL band at low temperatures ( $T \sim 16$  K) with maximum intensity at 1.585 eV.

#### 3.4. As-deposited CdS/CdTe PL — CdTe prepared in O<sub>2</sub> ambient

The PL spectrum from the interface of the CdS/CdTe heterojunction in the 15–90 K temperature range is shown in Fig. 7, revealing two PL bands: one having the maximum intensity at 1.332 eV and another around 1.50 eV (15 K). The temperature increase results in the shift of the PL maxima to lower energies. The thermal shift of the 1.332 eV band is

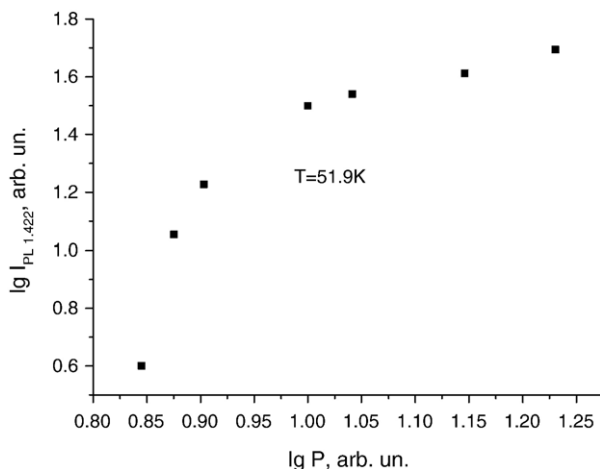


Fig. 6. The excitation intensity dependence of the 1.422 eV PL band of CdTe layer, component of the SnO<sub>2</sub>/CdS/CdTe heterojunction, deposited in He+O<sub>2</sub> ambient, annealed in CdCl<sub>2</sub> (from CdTe side)  $T = 51.9$  K.

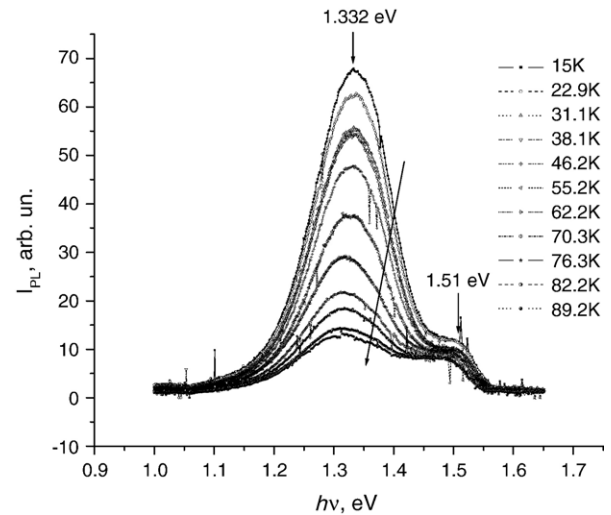


Fig. 7. The temperature dependence of the PL spectra of CdTe layer, component of the SnO<sub>2</sub>/CdS/CdTe heterojunction, deposited in He+O<sub>2</sub> ambient, as-deposited (from CdS/CdTe side).

$\sim 4 \cdot 10^{-4}$  eV/K, which correlates well with the thermal coefficient of the band gap [8]. The 1.332 band, as it was shown previously, is present in the PL spectrum of the CdTe layers deposited in inert ambient (Fig. 3). Considering the CdTe band gap at low temperature ( $T < 15$  K) is approximately equal to 1.60 eV [3], and the impurity level is formed by the oxygen atoms with approximately 10 meV activation energy, the sum of the acceptor level thermal activation energy and the D–A pair binding energy will be 0.106 eV. So, based on the PL spectra presented in Figs. 1 and 7, it can be seen that the structural defects from the interface of the heterojunction form two acceptor levels, which in ensemble with the oxygen impurity atoms change the radiative character of the CdTe layer. As a result the 1.232 and 1.432 bands, present in the CdTe surface PL

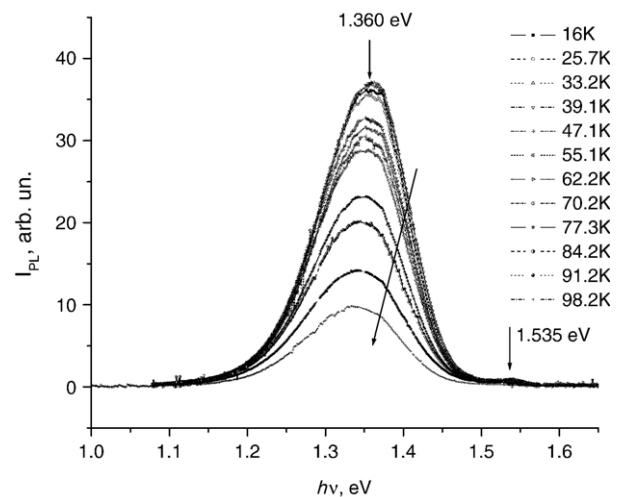


Fig. 8. The temperature dependence of the PL spectra of CdTe layer, component of the SnO<sub>2</sub>/CdS/CdTe heterojunction, deposited in He+O<sub>2</sub> ambient, annealed in CdCl<sub>2</sub> (from CdS/CdTe side).



are extinguished and the intensive 1.31–1.34 eV band arises. At the same time a weak band of 1.50–1.52 eV appears.

The intensity of the 1.332 eV band increases linearly with the intensity of the excitation beam and for relatively weak excitations (less than  $10^{18}$  photons/cm<sup>2</sup>); it saturates for higher beam intensities, which is characteristic of D–A complexes. Therefore a possible model for the interface PL can be proposed: the oxygen impurity is forming a shallow donor level, and the structural defects from the interface of the heterojunction form acceptor levels.

### 3.5. Heat-treated CdS/CdTe PL — CdTe prepared in O<sub>2</sub> ambient

Annealing of the CdS/CdTe structures in CdCl<sub>2</sub>, results in the CdS/CdTe interface PL spectrum shown in Fig. 8. There is a dominant band with maximum at 1.360 eV, and a weaker threshold of a band located approx. at 1.535 eV. So, by annealing of the heterojunctions in CdCl<sub>2</sub> a wide spectrum of levels is formed at the interface of the heterojunctions, which include the levels characteristic for the free annealed CdTe surface (the 1.42 eV band spreads in the 1.3–1.5 eV region) and the levels characteristic for the structural defects from the interface of the heterojunction formed from the difference of the lattice constant of CdS and CdTe layers (the 1.3 eV band spreads in the 1.1 eV up to 1.45 eV). The intensity of the second PL band in the spectra of as-deposited CdS/CdTe (1.5–1.52 eV) decreases considerably after the heat treatment process and only a weak trace of it can be noticed. The intensity and temperature dependence measurement and analysis of the 1.3 eV band for annealed samples suggest that D–A transitions are present. The donor activation energy for this case is less than 8 meV and an acceptor with activation energy of about 45 meV.

The samples deposited in inert ambient and annealed show the same PL behavior from the interface of the junction. The as-deposited samples have an interface PL consisting of a very broad band, stretching from 1.0 eV to 1.5 eV, with a diffused maxima in the 1.4 eV region. The difference between the O<sub>2</sub>/He and He-only samples is the shift of the interface PL band to higher energies by 20–40 meV.

## 4. Conclusions

Based on the analysis of the PL spectral distribution, and the peak energies' dependence on the excitation intensity and temperature, a radiative mechanism is being suggested. For the

D–A radiative mechanism, the donor levels appear localized at approx. 9–12 meV from the minimum of the conduction band and the acceptor levels are formed by structural defects from the CdTe layer.

One of the causes of the appearance of 1.232 eV band in unannealed samples (deposited in oxygen ambient) is definitely the oxygen presence. It is proposed that the recombination scheme for this band consists of two acceptor levels and a donor level, having different activities with respect to sample temperatures.

The interface PL for annealed and unannealed samples, deposited in different ambients appears to be due to defects in the CdTe interface layer.

The origin of the 1.42 eV band present in annealed and unannealed samples is attributed to some structural defects characteristics for CdTe only and it is most probably attributed to Cd vacancies [9].

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