Photoluminescence Studies on Cu and O Defects in Crystalline and Thin-film CdTe

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ABSTRACT

Polycrystalline thin-film CdTe is one of the leading materials used in photovoltaic solar cells. One way to improve device performance and stability is through understanding how various process steps alter defect states in the CdTe layer. Low-temperature photoluminescence (PL) studies show a 1.456-eV PL peak in single-crystal CdTe that is likely due to a Cu$_i$-O$_{Te}$ defect complex. A similar peak, observed in as-deposited glass/SnO$_2$:F/CdS/CdTe thin-film structures, strongly suggests a common origin. The 1.456-eV peak is also seen in a thin-film sample after performing the CdCl$_2$ treatment needed for high efficiencies.

INTRODUCTION

CdTe is of special interest in the photovoltaic (PV) industry because of its nearly ideal band gap of ~1.47 eV at room temperature. Advancement in the efficiency of polycrystalline CdTe/CdS solar cells has occurred mostly through refinement of processing techniques rather than by understanding how the processing techniques are affecting the defect states in the CdTe, and thus enhancing current transport in the device. The effects of copper- and oxygen-related impurities are of prime interest in CdTe PV devices because these elements have been intentionally introduced into device processing techniques to improve device performance. In most devices, Cu is intentionally incorporated during the back-contact process. However, even before this final process step, Cu is present in the CdTe layer as a native impurity, as well as introduced during the CdCl$_2$ treatment. Thus, even if Cu were eliminated from the final contacting process, Cu-related defects would still be present in the device and would influence the overall device performance. Oxygen is included in the chamber atmosphere during the CdTe film growth. This has been shown to reduce the pinhole density [1], so that the subsequent back-contact process does not shunt the device, and to stimulate the growth of smaller grains in the film [2]. Studies on completed devices show that solar cells made with O$_2$ present during the film growth have a higher efficiency than those that do not incorporate oxygen [3]. Additionally, it has been noted that an oxygen-containing ambient during CdCl$_2$ processing improves device efficiency [4].

Oxygen and copper are introduced simultaneously into thin-film CdTe solar cells during the CdTe growth stage: oxygen in the ambient gas and copper as a residual source impurity. It is very likely that these two species will interact to form defect complexes involving both Cu and O. Most previous defect studies on CdTe have investigated the effects of Cu or O separately [5]. Those studies that include both Cu and O either did so unintentionally [6] and did not consider that both species were present during defect assignment, or included other species, such as Cl, which may influence the interaction of the Cu and O [7]. In the present study, care was taken to separate the individual effects of Cu or O on CdTe from the effect of the Cu and O combination. These studies were performed primarily on single-crystal CdTe, with an emphasis on the PL.
transitions in the intermediate region from 1.3-1.5 eV, and the results were then compared to similar analysis of thin-film CdTe: (1) as-grown and (2) after CdCl₂ treatment.

EXPERIMENTAL DETAILS

Single-crystal CdTe samples were manufactured by Keystone Crystals (Butler, Pennsylvania) via the vertical Bridgman technique. These crystals were grown with 6N-purity starting materials and were then mechanically polished by the manufacturer with progressively smaller aqueous Al₂O₃ grits down to 0.01 µm. All crystals in this study came from the same crystal batch to reduce sample-to-sample variation. Additionally, no chemical etching treatments were performed prior to Cu deposition and/or annealing treatments. Hall measurements using the van der Pauw technique indicated that these crystals are p-type with carrier concentration 3 – 5 x 10¹⁴ cm⁻³ and mobility 30 – 60 cm²/V-s.

For the Cu diffusion study, high purity (99.999%) Cu metal was e-beam deposited from a graphite crucible onto single-crystal CdTe. Samples with and without Cu were annealed in 10% H₂ / 90% N₂ (forming gas), N₂, 20% O₂ / 80% N₂ (air-like), or pure O₂. Annealing was performed at 400°C for 1 h with the various flowing gases in a 5-cm single-zone glass tube inside a tube furnace (total flow rate ~3 L/min). For all annealing ambients, multiple Cu-coated and uncoated control samples were prepared for direct luminescence comparison.

Polycrystalline thin-film CdTe samples were prepared via two different growth processes. Two CdTe sample sets were deposited by close-spaced sublimation (CSS): one produced by the National Renewable Energy Laboratory (NREL) [8], and one made with an in-line process at Colorado State University (CSU) [9]. Another CdTe sample set was deposited by vapor-transport deposition (VTD) at a third fabrication laboratory. The structure of all samples was glass/SnO₂:F/CdS/CdTe. Measurements were taken after CdTe deposition (i.e., no CdCl₂ process) from the film surface on all three samples. Additional measurements were taken on the VTD sample after a wet CdCl₂ process was performed, similar to the one described in Ref. 8.

Photoluminescence data were taken at 4.5 K using a helium closed-cycle cryostat. In general, the data were taken shortly after sample preparation. A 20-mW HeNe laser (λ = 632.8 nm, or E = 1.960 eV) was used for excitation. PL spectra were collected by a spectrometer with a diffraction grating of 600 grooves/mm and a 512-pixel CCD. These spectra were analyzed by fitting the measured spectra to a series of Gaussian curves. This process enhanced the distinction between primary transitions and their longitudinal optical (LO) phonon replicas (the LO phonon energy in bulk CdTe is 21 meV [10]). The measurement uncertainty in the zero-phonon transitions was about 1 meV. For intensity-dependent PL, neutral density filters were used to reduce the intensity of the laser beam incident on the sample.

Theoretically derived defect energy levels were obtained from first-principles band structure calculations using VASP code [11] within the local density approximation. The defects under consideration required use of a 512-atom supercell, and periodic boundary conditions were applied.

RESULTS

Figure 1a shows single-crystal CdTe samples without intentional Cu that were annealed in different ambients: forming gas, nitrogen, or oxygen. A non-annealed sample is also shown for comparison. In all four samples, there was a set of peaks between 1.535 and 1.55 eV with two
Figure 1. PL of CdTe single crystals annealed in different ambients. Curves are offset for clarity. (a) Samples without intentional Cu were annealed in forming gas (10% H₂ / 90% N₂), N₂, or O₂. A non-annealed sample is also shown. (b) Samples with 10 nm Cu were annealed in forming gas, N₂, air-like gas (20% O₂ / 80% N₂), or O₂.

phonon replicas. The excitonic transitions in the N₂- and O₂-annealed samples were very similar to those for the non-annealed sample. There was a dominant peak at 1.587 eV and a "shoulder" at 1.591 eV. When CdTe was annealed in forming gas, however, the 1.587 eV peak disappeared, and the 1.591 eV peak became dominant. Because an anneal in forming gas is thought to make the surface more stoichiometric, the 1.587 eV excitonic peak may be related to an off-stoichiometry defect. The non-annealed and N₂-annealed samples also exhibited a peak at 1.475 eV, which was previously identified as a Y-dislocation [12].

The PL spectra changed dramatically when Cu was deposited prior to annealing, with the biggest difference in the PL band from 1.35 – 1.53 eV (Figure 1b). The nitrogen-annealed sample had a broad, smooth peak in this region, whereas the other samples had distinct zero phonon lines (ZPLs) and phonon replicas. The relative sharpness of a ZPL and associated phonon replicas is related to the type of defect involved in the PL transition. This can be determined by the Huang-Rhys factor, S, which measures the degree to which a defect couples to the lattice [13]. The Huang-Rhys factor ranges from small (≲ 1) to large (≳ 10) values, where small values of S are typical for excitonic and shallow defect states and large values of S are consistent with deep defects. Moderate values of S (1 ≤ S ≤ 10) are indicative of defects or defect complexes with intermediate-level activation energies, and these PL transitions have ZPLs and phonon replicas that are distinct but not as sharp as excitonic transitions. The Cu samples annealed in forming gas, air-like gas, and O₂ had PL transitions in the 1.35 – 1.53 eV region with moderate values for the Huang-Rhys factor.

The Cu samples annealed in an oxygen or air-like ambient had a unique feature in the PL at 1.456 eV (Figure 1b). This PL transition is not seen in any of the samples that do not include Cu (Figure 1a) or in the Cu samples annealed in forming gas (reducing atmosphere) or nitrogen. Since this peak is only seen when both copper and oxygen are incorporated together, this peak is likely associated with a defect complex involving Cu and O. Relating this PL peak to a defect complex is certainly consistent with its intermediate Huang-Rhys factor.

PL was taken on as-deposited glass/SnO₂:F/CdS/CdTe samples, one grown by an in-line CSS process at CSU, one by CSS at NREL, and one by VTD (Figure 2a). The two CSS-grown samples had a peak at 1.456 eV, although the ZPL and phonon replicas are less pronounced in the CSU sample. This difference in sharpness of the 1.456-eV peak is similar to the difference between the air-annealed and pure O₂-annealed single-crystal Cu samples, and suggests that less O₂ is incorporated during CSU’s growth process. The NREL CSS sample had an additional peak
at 1.489 eV, but the CSU CSS sample did not exhibit this PL peak. The sample grown via VTD had a peak at 1.463 eV with replicas very similar to those associated with the 1.456-eV peak for the NREL CSS sample, only shifted by ~7 meV. This small shift in PL peak position may be due to differences in the physical properties of the CdTe caused by the different growth method. The as-deposited VTD sample also had a peak at 1.481 eV. When the NREL CSS and the VTD samples were annealed in N\textsubscript{2} at 400°C for 1 h, however, the intensities of their respective peaks at 1.489 and 1.481 eV decreased dramatically (Figure 2b). This is a good indication that the 1.489 and 1.481 eV peaks have a different origin than the 1.456 and 1.463 eV peaks. Finally, PL was taken on a CdCl\textsubscript{2}-treated VTD sample (Figure 2c). This sample exhibited a peak at 1.456 eV. The shift from 1.463 to 1.456 eV could be due to a change in the physical characteristics of the CdTe following the CdCl\textsubscript{2} treatment, or it could be the result of Cu impurities and the O\textsubscript{2}-containing atmosphere from the treatment that helped accentuate the peak at 1.456 eV.

Intensity-dependent PL was performed on the O\textsubscript{2}-annealed Cu sample (Figure 3a) to further understand the nature of the 1.456-eV peak. The dependence of the PL peak position with laser excitation can be used to separate donor-acceptor pair (DAP) transitions from a band-to-defect transition. For a DAP transition, the position of a PL peak is given by:

$$E_{PL} = E_g - (E_D - E_A) + \frac{e^2}{\varepsilon r},$$

where $E_g$ is the band gap (1.606 eV at 4.5 K), $\varepsilon$ is the static dielectric constant, $r$ is the average distance between the donor and acceptor, and $E_D$ and $E_A$ are the donor and acceptor levels, respectively, measured from the valence band minimum (VBM). As excitation intensity increases, there will be more photons incident on the crystal, and donors and acceptors that participate in the transition will, on average, be closer together. From equation 1, therefore, the PL energy for a DAP will shift to higher values as laser excitation increases. For band-to-defect transitions, however, there is no Coulomb interaction, and the position of the PL peak is expected to remain constant with increasing laser excitation. The 1.456-eV peak seen in Figure 3a does not shift to higher energies with laser power, and hence, it can be ascribed to a band-to-defect transition. The intensity independence requires that the donor or acceptor level involved have an ionization energy of 150 meV.

The as-deposited thin-film samples were also studied using intensity-dependent PL (Figure 3b-d). For both CSS-grown samples, the peak at 1.456 eV was intensity-independent. This suggests a band-to-defect transition, likely the same one seen in the O\textsubscript{2}-annealed Cu single-crystal sample. For the VTD-grown sample, the 1.463-eV peak was also intensity-independent. In contrast, the 1.489- and 1.481-eV peaks in the NREL CSS and the VTD samples, respectively,
Figure 3. Intensity-dependent (0.5 –9.5 W/cm²) PL at 4.5 K of: (a) single-crystal CdTe Cu-coated sample annealed in 100% O₂, (b) as-deposited thin-film CSS CdTe made at NREL, (c) as-deposited thin-film CSS CdTe made at CSU, (d) as-deposited thin-film VTD-grown CdTe, and (e) thin-film VTD-grown CdTe after a wet CdCl₂ treatment.

shifted to higher energy with increasing laser excitation. This is indicative of a DAP transition, and is further evidence that these peaks are not related to the peaks seen at 1.456 and 1.463 eV. The intensity-dependence of the CdCl₂-treated sample (Figure 3e) indicated that the position of its 1.456-eV peak did not shift with increasing power, and is likely a band-to-defect transition.

First-principles band structure calculations were performed to determine a plausible assignment for the 1.456-eV defect present only when both Cu and O are present together. In the case of p-type CdTe, the formation energy of Cu_i is lower than for CuCd defects, and hence, Cu_i is more likely to form. In O-free CdTe, Cu_i is most likely to position itself next to a Te site, forming a donor level at ~10 meV below the conduction band minimum (CBM) [14]. One easily formed oxygen defect is OTe, and this isovalent defect has an energy of ~200 meV above the CBM. A Cu_i-OTe defect complex was investigated numerically by placing an OTe defect at the center of a 512-atom supercell and a Cu_i initially placed next to it. In this scenario, the Cu_i defect was allowed to move within a 64-atom subcell in the center of the supercell. The Cu_i defect preferred to locate next to the OTe with a binding energy between the two of about 0.96 eV, indicating that the two are likely to form a defect complex. The calculated ionization energy for a Cu_i-OTe donor complex converges to a value of about 125 meV below the CBM. This is in good agreement with experimental results yielding a defect with energy of 150 meV from the band.

CONCLUSIONS

A PL peak at 1.456 eV was seen in single-crystal CdTe only when Cu and O were introduced simultaneously. A similar PL peak was seen in thin-film CdTe structures both before and after
CdCl₂ treatment, although the degree to which the peak was present varied by sample manufacturer. Intensity-dependent PL identifies this as a band-to-defect transition, where the ionization energy of the defect is ~150 meV. The intermediate value of the Huang-Rhys factor is consistent with a defect complex. Theoretical calculations, consistent with experimental observations, indicate that the defect is most likely a donor complex Cuᵢ-OTₑ.

The implications of the formation of a Cuᵢ-OTₑ donor complex may be very significant. Although OTₑ may serve to reduce recombination through elimination of mid-gap Vᵣₑ defects, a relatively shallow donor level in p-type material can also reduce device efficiency. If current processing techniques are introducing a Cuᵢ-OTₑ defect, this may in part explain why the Cu concentration in thin-film CdTe devices is on the order of 10¹⁸ cm⁻³ whereas the hole concentration is closer to 10¹⁴ cm⁻³ [15].

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