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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 CdCl₂ 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 heterojunctionbased 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

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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 SnO2 coated borosilicate glass using previously described processes [\[1\]](#page--1-0). Briefly, the transparent conductors were prepared in the form of a bi-layer $(SnO_2: F/SnO_2)$ 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 $O₂$ -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 $CdCl₂$ heat treatment [\[1\].](#page--1-0) 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

Fig. 1. The temperature dependence of the PL spectra of CdTe deposited in $He/O₂$ ambient (SnO₂/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 ± 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 CdSTe 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 [\[2\]](#page--1-0). 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 $O₂$ ambient

The 20 K PL spectrum obtained by exciting the CdTe side of a sample for which the CdTe film was deposited in $He/O₂$ 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 [\[3\]](#page--1-0). 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 [\[4\].](#page--1-0) A similar PL band has been previously found as a result of radiative recombination with plasmon participation [\[5\]](#page--1-0). 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∼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_2 ambient; SnO₂/CdS/CdTe structure excited from the CdTe side); $T=20$ K.

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