Spatially Resolved Cathodoluminescence of CdTe Thin Films and Solar Cells

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Abstract

We have investigated the spatial distribution of different transitions identified in the emission spectra of CdTe thin films and solar cells by cathodoluminescence spectroscopic imaging (CLSI). Prior to back-contact deposition, the spectra are dominated by excitons (*X*) and donor-to-acceptor (DAP) transitions. After contacting, Cu acceptor states are found in addition to the *X* and DAP recombination processes. A very systematic behavior found in CdTe is that DAP transitions occur preferentially at grain boundaries (GBs). The distribution of these states responsible for the passivation of GBs is not affected by further processing, although additional levels participate in the recombination process. We believe that this stability is one of the reasons for the success of thin-film CdTe solar cells. Estimates of the densities of different donors and acceptors participating in the recombination process are possible from the analysis of the evolution of the emission spectra with the excitation level. It is found that the back contact suppresses some intrinsic acceptors (associated with the A center) near the back-contact interface and, therefore, Cu acceptor states should be responsible for the *p-typeness* of the back surface more than a reduction of compensation. CLSI measurements are shown to be helpful in understanding the physics of back-contact formation.

I. Introduction

Thin-film CdTe solar cells are very promising for future, cost-effective, terrestrial photovoltaics. Photoconversion efficiencies up to 16.5% have recently been attained from CdTe/CdS cells by the improved optical transmission provided by transparent conducting oxides (TCOs) other than SnO_2 [1,2]. Thin-film CdTe solar cells are growing more and more cost effective by virtue of recent progress in conversion efficiency, and stability issues are now of prime importance for their future implementation.

Thin films for high-efficiency cells are produced by physical deposition methods, such as close-spaced sublimation (CSS) and vapor-transport deposition (VTD), which produce a high concentration of native cadmium vacancies (V_{Cd}^-). Electronically, deep energy levels at ε_v + 400 meV and ε_v + 760 meV are attributed to the isolated Cd vacancy [3] and to an acceptor complex involving V_{Cd}^- and an impurity [4], respectively. Donors form complexes with such deep levels, lowering their energies to a relatively deep acceptor with activation energy of 140-150 meV (usually identified as center A) [4,5]. Removal of nonradiative recombination centers and increase of acceptor density by center A formation should be beneficial to the cell performance, and it is believed that this is indeed the main *electronic* effect of the post-deposition treatment in presence of chlorine that is required to attain high efficiency. It has been suggested that Cl_{Te} forms a defect complex with V_{Cd}^- (the chlorine A center [5]) and lowers the energy level of the isolated V_{Cd}^-. Several of these complexes are accessible in the emission spectra of CdTe films. Spectra representative of CdTe thin films for high-efficiency solar cells are shown in Fig. 1. The spectrum consists of transitions involving excitons (*X*), and several donor-to-acceptor (DAP) transitions, where the acceptor states correspond to complexes associated with V_{Cd}^-, such as the center A.

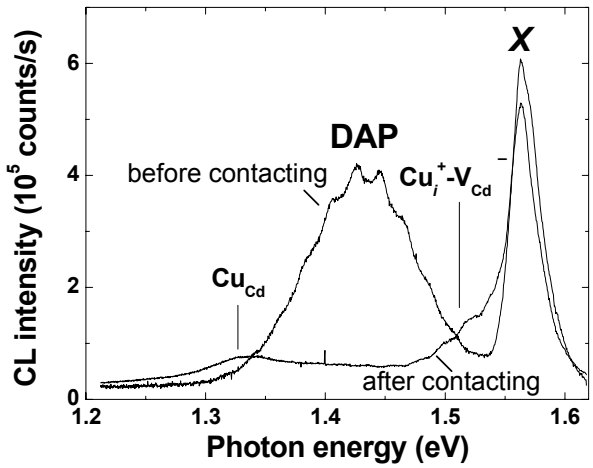

FIG. 1. Effects of Cu diffusion on the emission spectra of CdTe thin films used in high-efficiency solar cells. I_b = 100 pA, E_b = 20 keV, T = 77 K.

Because of the high electron affinity of CdTe, a highly doped p^+-type back surface is required for improving the ohmic characteristics of back contacts. Low-resistance contacts have been effectively achieved through the incorporation of Cu from the back surface of CdTe films. Though beneficial to the cell performance, the long-term cell stability is often compromised. Therefore, diffusion of Cu is considered by many to be a source of instability for CdTe/CdS solar cells. In CdTe, Cu is incorporated interstially as Cu_i^+, in a shallow donor state, or substitutes Cd to form the deep acceptor Cu_{Cd}, with an activation energy of 280-340 meV [6,7]. Complexes involving Cu_i^+ and cadmium vacancies (Cu_i^+- V_{Cd}^-) are relatively shallow acceptors that stabilize isolated V_{Cd}^- and other associated complexes [6,8]. A fundamental understanding of the mechanism of Cu diffusion is thus required for the further improvement in stability of thin-film CdTe solar cells.

The effects of Cu diffusion on the CL spectra of CdTe films are shown in Fig. 1. After Cu diffusion, the DAP emission becomes strongly attenuated by disruption

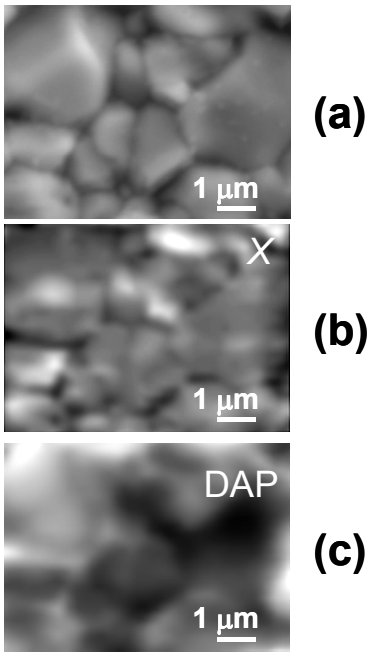

FIG. 2. (a) Secondary-electron image of a CdTe thin film deposited directly on TCO, without the previous CdS-film deposition, and monochromatic CL images for the excitonic (b) and DAP (c) transitions. I_b = 250 pA, E_b = 10 keV, T = 15.7 K.

of the A centers from both incorporation of Cu into V_{Cd}^- to form Cu_{Cd} and formation of Cu_i^+- V_{Cd}^- complexes. Because Cu_{Cd} is a deep acceptor with activation energies of 280-340 meV, the emission around 1.32 eV might be associated with Cu substituting Cd. Additionally, Cu incorporation leads to transitions around 1.52 eV related to Cu_i^+- V_{Cd}^- complexes, which are relatively shallow acceptors.

In this contribution, we explore the spatial distribution of the different transitions identified in the emission spectra by cathodoluminescence spectroscopic imaging (CLSI).

II. Experimental

In the Measurements and Characterization Division at NREL, we have developed a cathodoluminescence system capable of high-sensitivity, ultrafast spectrum acquisition in synchronization with the electron-beam when acquiring a secondary-electron image. This method is named spectroscopic imaging (SI) because the system processes spectroscopic information for each pixel on the secondary-electron image. For CdTe, the spectra were acquired with a cryogenic 1340×400 CCD with acquisition times of 10 ms for each individual pixel. The measurements were performed at temperatures between 15 and 300 K and electron-beam energies (E_b) between 5 and 30 keV.

III. Results and Discussion

In an effort to understand the fundamentals of carrier recombination in polycrystalline CdTe, we have deposited films directly on TCO. Previous combinatorial research in CdS on CdTe structures showed that CdS affects the CdTe emission spectrum and we wanted to avoid this influence in the first place. Figure 2 shows the monochromatic images corresponding to the *X* and DAP emissions for such film. Transitions associated with donor and acceptor complexes occur preferentially at the boundaries. Excitons exhibit an opposite behavior and dissociate at the boundaries, as lateral transport measurements have suggested [9]. The spatial distribution of the *X* and DAP transitions found for CdTe is consistent with the conventional CdTe on CdS used in thin-film solar cells but additional nonradiative recombination complicates the analysis, as we discuss later.

These films are not fully processed devices. Deposition of the back contact is the final stage of processing, and an additional interface is produced at the back surface of the cell. The incorporation of Cu into the CdTe affects the carrier recombination by the introduction of electronic levels related to Cu, as show in Fig. 1.

We explored the distribution of these states by monochromatic images for each of the transitions identified in the spectrum (see Fig. 3). The distribution of the excitonic emission is similar to the one observed prior to back-contact deposition, with the dissociation of excitons at GBs. In contrast, Cu_i^+- V_{Cd}^-, other V_{Cd}^--related (represented by the DAP transitions), and Cu_{Cd} states are highly nonuniformly distributed in the CdTe films. There is a competition between Cu_i^+- V_{Cd}^- and other V_{Cd}^--related complexes for recombination, which is suggested when comparing their mutual distributions. Thus, when the emission associated with Cu_i^+- V_{Cd}^- increases, the one related to other V_{Cd}^- complexes decreases, and vice versa.

In the diffusion of Cu by Cu_i^+- V_{Cd}^- and Cu_{Cd} states, we find that the primary diffuser is represented by Cu_i^+-V_{Cd}^- acceptors as their distribution is progressively more uniform deeper in the CdTe film, as shown by measurements at different electron-beam energies (exciting progressively deeper into the film). The diffusion of these complexes is accompanied by the dissociation of other states involving cadmium vacancies. Cu incorporation as Cu_{Cd} seems to be highly nonuniform and restricted to the

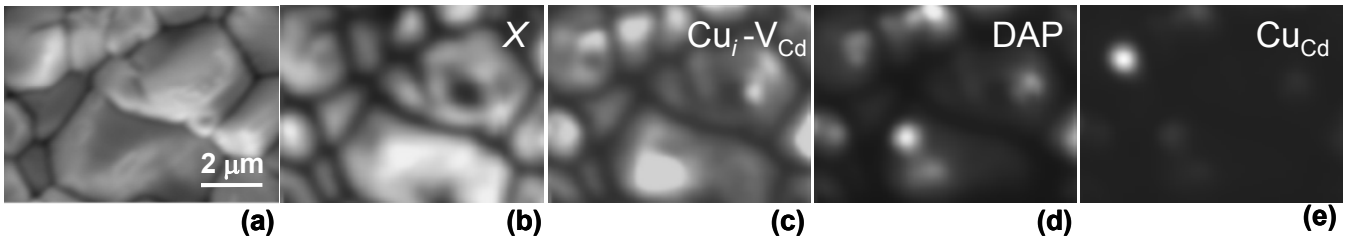

FIG. 3. (a) Secondary-electron image of a CdTe thin film from a fully processed solar cell. (b), (c), (d), and (e) correspond to the transitions identified on the emission spectra (see Fig. 1). I_b = 200 pA, E_b = 20 keV, T = 77 K.

back-contact interface. These results suggest that Cu diffusion is limited for Cu incorporation into cadmium vacancies, whereas Cu_i^+ migration and subsequent complex formation represents most of the electronically active Cu. This is consistent with a high competition between the formation and dissociation of Cu_i^+- V_{Cd}^- and Cu_{Cd} states.

The main effect of Cu diffusion on the electronic structure of boundaries is the introduction of nonradiative recombination centers. For this reason, we have used images of Cu-related emissions normalized to either the excitonic or DAP transitions. These images reveal that Cu diffusion involving Cu_i^+- V_{Cd}^- or Cu_{Cd} along grain boundaries is not favored. This contradicts, at least partially, the commonly accepted assumption that Cu diffusion along GBs should be easier [10,11]. Our measurements support that Cu is not activated as an acceptor at grain boundaries, even though GB Cu diffusion could be preferential. However, we have observed that the DAP transitions are more probable that *X* recombination at the boundaries, and this is independent of the back-contact scheme utilized. The DAP to *X* ratio is thus shown in Fig. 4. These results support that the electronic structure of boundaries settles after the chlorine post-treatment, and further processing does not annihilate the defect complexes responsible for the DAP recombination, even if novel nonradiative recombination centers are introduced. Recently, direct evidence has been shown for grain-boundary depletion in CdTe films by scanning probe microscopy [12]. Dissociation of excitons into free carriers and their subsequent recombination involving donor and acceptor complexes are in agreement with the existence of GB depletion. Therefore, we believe that the DAP-to-*X* ratio distributions are an estimate of the potential barrier at grain boundaries. We hope to perform side-by-side CLSI and SPM measurements to confirm this assumption.

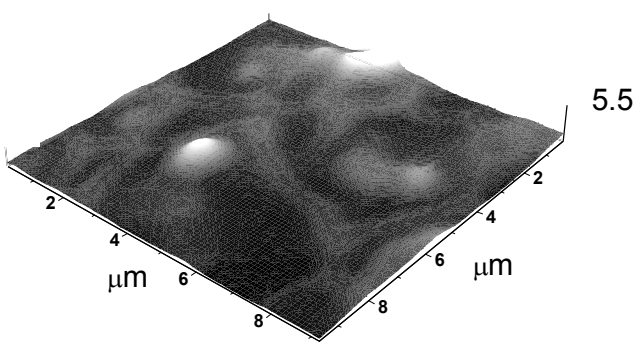

FIG. 4. Spatial distribution of the DAP transition normalized to the excitonic recombination (DAP-to-*X* ratio) obtained from the same area shown on Fig. 3a. For grain boundaries, the probability of radiative carrier recombination via defect complexes is higher than via excitons, independently of other nonradiative recombination processes.

In addition to *imaging* different transitions, we have estimated the densities of different levels participating in the recombination process. This is possible from the analysis of the evolution of the emission spectrum with the excitation level. Figure 5 shows the emission spectrum for a CdTe film, prior and after back-contact deposition (Figs. 5a and 5b, respectively) as a function of electron-beam current [9]. We assume that the DAP recombination is limited by the availability of A centers. Saturation is defined as when the density of carriers excited by the electron beam is comparable to the density of defect complexes involved in a particular transition. In the onset of saturation (S1 on Fig. 5a), the probability for other recombination processes at higher photon energies increases. The shift to higher photon energy of the DAP transition is consistent with the activation of radiative recombination involving the chlorine A center, with an activation energy of 120 meV instead of 140-150 meV for the A center. Increasing the electron-beam excitation (S2 on Fig. 5a) causes this transition to become saturated, and the spectrum is then dominated by excitons. As shown in Fig. 5b, the back contact suppresses the chlorine A centers and, therefore, Cu acceptor states should be responsible for the *p-typeness* of the back surface more than a reduction of compensation.

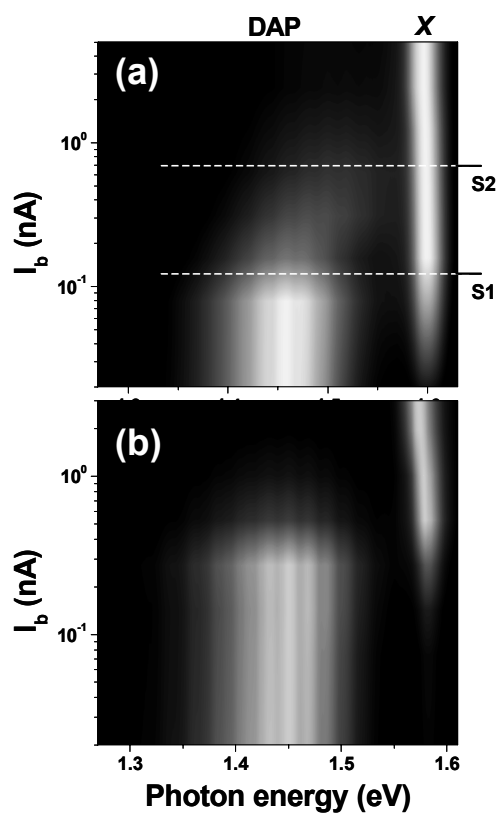

FIG. 5. Effect of excitation (represented by the electron-beam current) on the emission spectrum of CdTe thin films prior to (a) and after (b) back-contact deposition.

IV. Conclusions

In summary, we have used cathodoluminescence spectroscopic imaging to investigate the spatial distribution of different transitions identified in the emission spectra of CdTe thin films and solar cells. Transitions associated to donor and acceptor complexes occur preferentially at the boundaries. Excitons exhibit an opposite behavior and dissociate at the boundaries. Dissociation of excitons into free carriers and their subsequent recombination involving donor and acceptor complexes are in agreement with the existence of a depletion region at grain boundaries. Successive Cu diffusion does not affect substantially their electronic configuration, although nonradiative recombination centers are introduced by the back-contact process. Final contact deposition is found to suppress some of the intrinsic acceptors near the back-contact interface.

Acknowledgments

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