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Mesoscopic Fluctuations in the Distribution of Electronic Defects near the Surface Layer of $\text{Cu}(\text{In,Ga})\text{Se}_2$

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Abstract

High-resolution cathodoluminescence spectroscopic imaging (CLSI) has been employed to study the radiative recombination processes in $\text{Cu}(\text{In,Ga})\text{Se}_2$ (CIGS) films used in solar cells. Mesoscopic fluctuations of the electrostatic potential explain the observed behavior for the radiative transitions identified in the emission spectrum. We show evidence for passivation of grain boundaries near the surface layers of these films. In addition, our results suggest different point-defect physics for the surface layers. These studies have been primarily performed on the CIGS films used in the recently achieved world-record efficiency cell at NREL (19.2%) as a reference to understand differences in performance for the CIGS. However, most of the results are applicable to the standard CIGS deposited by the three-stage process and differences are subtle.

I. Introduction

$\text{Cu}(\text{In,Ga})\text{Se}_2$ (CIGS) is one of the most promising semiconductors for high-efficiency thin-film solar cells. Indeed, at the National Renewable Energy Laboratory a record efficiency of 19.2% has been recently established for CIGS solar cells, which represents the absolute record efficiency for thin-film solar cells. Most of CIGS films for cells exceeding efficiencies of 15% are deposited by the three-stage process, which involves an initial physical vapor deposition of $(\text{In,Ga})_2\text{Se}_3$ (first stage) and its sequential exposure to Cu, and (In,Ga) during the second and third stages, respectively, in the presence of a Se overpressure [1]. The microstructure of the resulting CIGS film is shown in Fig. 1. We observe the μm -size grains commonly found in CIGS films deposited by this sequential physical vapor deposition. The most interesting observation for the studies addressed in this manuscript, as discussed later, is the existence of a *substructure* with apparently larger grains near the free surface of the film. As previously suggested by the authors, this substructure seems to be characteristic of CIGS deposited by the three-stage process, originated from differences in the In and Ga diffusion in the third stage.

In this contribution, high-resolution cathodoluminescence spectroscopic imaging (CLSI) has been used to study the radiative recombination processes in CIGS films. In accordance with previous photoluminescence measurements [2,3], we have found that the emission spectrum of these ternary chalcopyrite compounds is extremely sensitive to deviations from stoichiometry. Although all the CIGS films used in photovoltaics are Cu deficient, those near stoichiometry show characteristic excitonic and donor-to-acceptor (DAP) transitions. Deviations from stoichiometry in the direction of In(Ga) excess result in degenerate and compensated CIGS.

Surprisingly, these are the ternary chalcopyrite compounds that provide the best performance for photoconversion. In such semiconductors, the radiative recombination process has been described by Shklovskii and Efros [4] from fluctuations of the electrostatic potential. CLSI will be applied to spatially resolve these fluctuations and investigate the radiative recombination processes at the interfaces affecting the photovoltaic effect, represented by grain boundaries (GBs) and the surface layers near the CdS/CIGS interface.

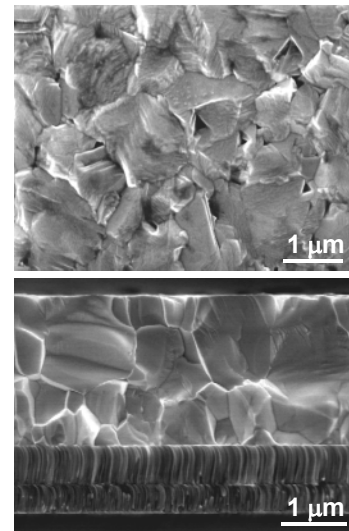


FIG. 1. Microstructure of the CIGS thin film used in the world-record efficiency (19.2%) solar cell.

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 CIGS, the spectra were acquired with an infrared InGaAs CCD, with acquisition times set to 17 ms for each individual pixel. The measurements were performed at temperatures between 15 and 300 K and electron-beam energies (E_b) between 10 and 20 keV. Measurements with very high spatial resolution were performed at $E_b = 2.5$ keV, which required longer acquisition times. Only line scans were recorded in this mode.

III. Results and Discussion

The effects of excitation power (represented by the electron-beam current) on the emission spectrum of CIGS are shown in Fig. 2. We see a pronounced shift to higher

photon energies with excitation carrier density, considerably more than expected for a conventional DAP transition, which is a few millielectron-volts at most. Furthermore, the effect of temperature is the opposite of the observed for a DAP recombination. As suggested by Shklovskii and Efros for degenerated and compensated semiconductors, the recombination processes are dominated by quasi-DAP (QDAP) transitions resulting from fluctuations in the electrostatic potential. The energy of emitted photons in QDAP transitions might be described by [4]:

$$h\nu_{\text{QDAP}} = h\nu_{\text{DAP}} - 2\Gamma, \quad (1)$$

where $h\nu_{\text{QDAP}}$ and $h\nu_{\text{DAP}}$ are the photon energies of the QDAP transition and the equivalent DAP recombination, respectively, whereas Γ corresponds to the amplitude of potential fluctuations. Γ increases with the total concentration of ionized impurity centers and decreases with the carrier-density excess.

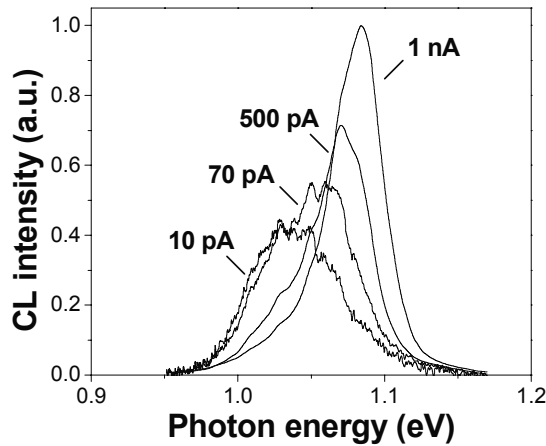


FIG. 2. Effect of excitation density (represented by the electron-beam current) on the emission spectrum of CIGS thin films. $E_b = 15$ keV, $T = 17.0$ K.

An estimate of the actual amplitude Γ (under low excitation density) is represented by the shift of the energy for the QDAP transition by decade of electron-beam current (β), as illustrated in Fig. 3.

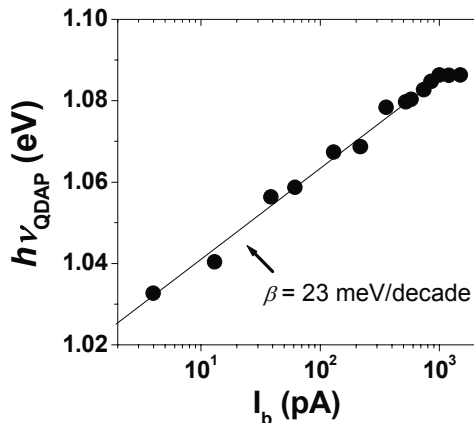


FIG. 3. Photon energy of the quasi-DAP transition as a function of the electron-beam current.

It has been observed that β increases with acceptor/donor concentration and compensation in these ternary chalcopyrite semiconductors (CuInSe_2 , Cu(In,Ga)Se_2 , and CuGaSe_2) [2,3]. For the best-performance CIGS cell, β is estimated to be +23 meV/decade. However, the spectra shown in Fig. 2 were acquired under continuous excitation on an area of $100 \mu\text{m} \times 100 \mu\text{m}$, similar to photoluminescence measurements. Obtaining *images* of the fluctuations of the electrostatic potential in CIGS requires performing CLSI measurements at different electron-beam currents (different excitation densities) to estimate β for each individual pixel in the secondary-electron image, as illustrated in Fig. 4. From these distributions, we have confirmed that mesoscopic fluctuations of the electrostatic potential are present in CIGS, with considerable nonuniformities in the donor(acceptor) concentration and compensation, represented by a range of variation for β of about +30 meV/decade.

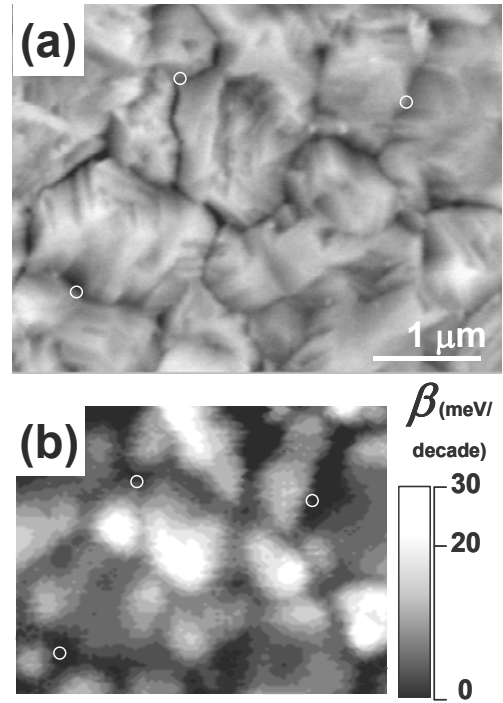


FIG. 4. Secondary-electron image of a CIGS thin film (a) and distribution of β (b) estimated from CLSI measurements performed at different electron-beam currents. $E_b = 10$ keV, $T = 17.5$ K. The points on (a) and (b) are for assistance in the correlation of both images.

One of the most relevant results is that the energy of the QDAP recombination from grain boundaries is practically independent of the excitation density ($\beta \approx 0$). Guided by these results, measurements with very high resolution ($E_b = 2.5$ keV, $I_b = 250$ pA) were performed

across grain boundaries on cross sections of the CIGS films. As shown in Fig. 5. a1, b1, and c1 are the spectra measured at different positions along an individual grain boundary (indicated on Fig. 5b), whereas a2, b2, and c2 are spectra in locations adjacent to those within the adjacent grain. The photon energy of the QDAP transition is at its minimum at and all along the grain boundary. The shift of this transition to higher energies within the grain is a consequence of the potential fluctuations in CIGS, as shown above. Both the minimum energy for the QDAP recombination and the very low values for β observed at GBs are difficult to reconcile with the recombination processes described by the theory of fluctuating potentials. This suggests, on the other hand, that the electronic structure of GBs has to be such that it efficiently reduces the density of the carrier excess. This is evidence for passivation of grain boundaries in CIGS because the minority carriers (electrons) excited in the CIGS do not diffuse and recombine at GBs.

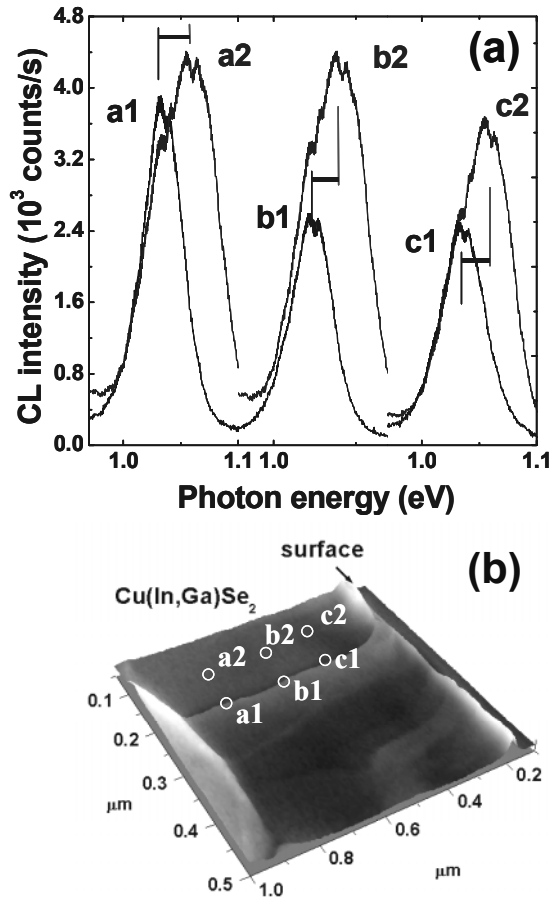


FIG. 5. Emission spectra recorded at different locations along an individual grain boundary and in the adjacent CIGS grain (a) and corresponding topographic image where the points of acquisition are indicated (b).

The third topic of interest is the electronic structure of surface layers in CIGS. The existence of interfaces 100 to 200 nm deep below the free surface has been confirmed by transmission electron microscopy [5,6]. Because the surface layer is within the depletion region of the solar cell, it might have important effects on the cell performance. Cathodoluminescence measurements of the surface layers are difficult because of the high resolution needed to spatially resolve these layers and the location of these layers either near the free surface (in CIGS thin films) or forming an interface with the CdS and ZnO buffer layers (in fully processed solar cells). Figure 6 shows a sequence of emission spectra measured from a very high-resolution line scan crossing the surface layer. We observe a shift to lower energies for the QDAP transition as the electron beam approaches the free surface. This would support a higher amplitude of the potential fluctuations V near the surface, confirming a different point-defect physics for these layers. However, we should be aware that the excitation density provided by the electron beam decreases near the surface because of surface-recombination effects and the loss of primary high-energy electrons through the free surface of the film. Because of the dependence of the excitation and the photon energy for the QDAP transition (see Fig. 2), a shift to lower energies will be observed, whether the surface region has a different point-defect physics or not. Therefore, interpretation of CLSI results must be made carefully. We have an additional argument in support of an electronically distinct surface layer and it is that this shift is not *continuous* along the line scan. A discontinuity is observed near 200 nm in depth. More measurements are currently being performed to investigate the electronic structure of this subinterface.

In the introduction, we pointed out the existence of a *substructure* with apparently larger grains near the surface of the film (see Fig. 1). Cross-sectional CLSI measurements suggest compositional differences between those grains near the molybdenum, which provides the back contact for the cell, and grains with a free surface. Furthermore, the interface between grains in the *substructure* seems to be in an intermediate composition between the adjacent grains. The results and conclusions derived from our investigations are only applicable to grains containing a free surface. Mesoscopic fluctuations in the distribution of electronic defects have been confirmed for the near-surface *substructure*. Furthermore, we have some evidence that passivation of grain boundaries is only effective near the surface. The impact of such diverse electronic behavior on the cell performance has to be assisted by modeling of CIGS cell characteristics, under development in the CIGS research community.

These studies have been primarily performed on the films used in the recently achieved world-record efficiency cell (19.2%) as a reference to understand differences in performance for the CIGS. Most of the differences found between this film (our current baseline) and other CIGS films are subtle. The main difference we have found, if any, is on the distribution of potential fluctuations near grain boundaries that might be related to the mechanisms

involved in the configuration of their electronic structure. However, factors other than the electronic structure of the CIGS, such as the CdS/CIGS interface or the surface passivation provided by the final deposition of ZnO, must be considered as important aspects affecting the final performance of the cell.

IV. Conclusions

In summary, mesoscopic fluctuations of the electrostatic potential have been *imaged* by cathodoluminescence spectroscopic imaging in CIGS thin films used in high-efficiency solar cells. Nonuniformities in the distribution of acceptor(donors) seem to have a beneficial effect on the cell performance, maybe by an *effective* spatial separation of electrons and holes. We have shown some evidence for the passivation of grain boundaries in the near-surface grain *substructure* and a distinct electronic structure for the surface layers in CIGS. These investigations have been made possible by the development of a cathodoluminescence system of high-sensitivity and ultrafast spectrum acquisition.

Acknowledgments

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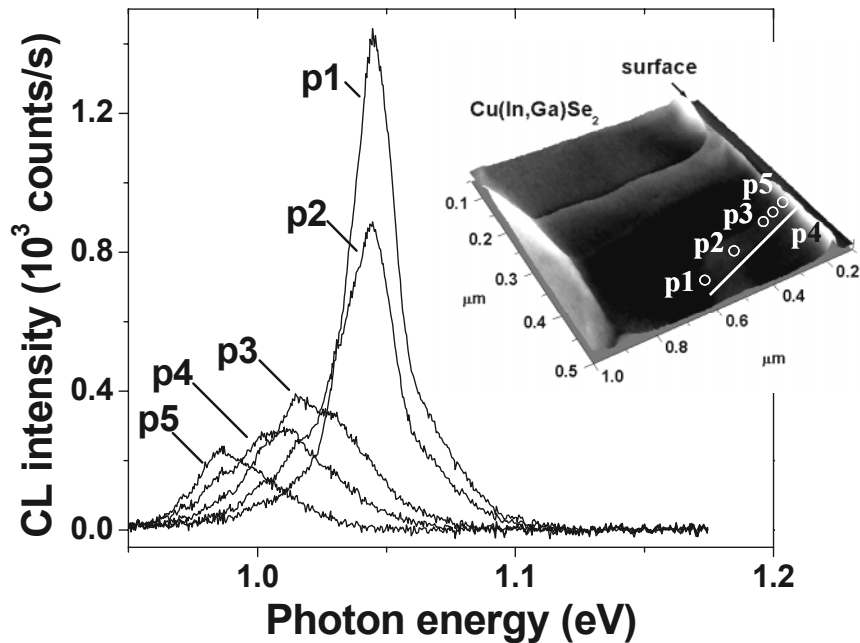


FIG. 6. Emission spectra acquired as a function of the distance to the surface. $E_b = 2.5$ keV, $I_b = 250$ nA, $T = 19.5$ K. The inset corresponds to the topography of the CIGS, displaying the line scan and the points of the spectra shown in the figure.

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