Near-surface defect distributions in Cu(In,Ga)Se_2

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Abstract

The density and distribution of point defects in Cu(In,Ga)Se_2 (CIGS) layers used for solar cell applications is critical to the resulting device performance. These devices are generally thought to be limited by recombination in the space-charge region of the collecting heterojunction. The situation is complicated by the presumed presence of an n-type surface layer on the CIGS absorber. Both the surface inversion and space-charge recombination processes are intimately tied to near-surface point defects. Here, we overview recent results on surface chemistry, transient photocapacitance spectroscopy (TPC) and depth-resolved cathodoluminescence (CL) for polycrystalline device layers from two laboratories, and single crystal epitaxial layers of three orientations. The results are combined with device modeling to provide a picture of the near-surface defect structures in these materials. The TPC results show deep defect levels ~0.7 and 0.9 eV above the valence band. CL shows evidence of subgap radiative recombination, which increases dramatically near the sample surfaces. The results point to a near-surface Cd-containing layer, which could be responsible for the surface carrier type inversion, a near-surface region containing an elevated defect density, possibly near the valence band edge, and deep hole traps near the conduction band. Implementation of the results in a device model provides reasonable fits to the device performances.

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1. Introduction

Photovoltaics based on CuInSe_2, and related materials have the highest performance of any thin film devices [1]. However, many questions remain to be answered concerning their operation. The devices typically consist of polycrystalline Cu(In,Ga)(S,Se)_2 (CIGS) semiconductor alloys deposited on Mo-coated soda-lime glass substrates [2]. The CIGS is coated with CdS by a chemical bath deposition method. Finally, a top transparent conducting oxide contact is applied. The devices are generally limited by recombination of carriers in the space-charge region, although the details of defects involved in this recombination and the properties of the CIGS/CdS heterojunction are still very unclear. In addition to polycrystalline CIGS devices, a limited number of devices have been produced using single-crystal epitaxial layers of CIGS on GaAs. The performance of these devices is generally found to be inferior to that of the polycrystals, in spite of controlled variation in surface orientation and surface polarity based on selection of the GaAs substrate orientation [3].

Recently, a significant amount of comparative data has been obtained through a collaborative research effort, known as the NREL CIS Team sponsored by the US National Renewable Energy Laboratory (NREL). In this paper, we will consider a subset of this data and the incorporation of the results into a computer device model. The results suggest three points. (1) The surface of the CIGS (the top ~2 nm) contains a significant amount of Cd when coated with CdS by chemical bath deposition. This Cd is much more strongly bound to the CIGS than the Cd in the bulk of the CdS and is not removed by HCl etching. It is argued that this Cd has...
replaced Cu atoms or has filled Cu vacancies, leading to a highly n-type surface layer on the CIGS. Most significant, this layer is only a few monolayers thick. The resulting surface inversion is found, based on device modeling to be essential to device performance. Such surface inversion has been suggested previously based on the CIGS/CdS heterojunction band offset [4]. By contrast, the current proposal does not impose any restrictions on the CdS band offset but provides the inversion by the surface Cd layer. (2) There is a higher concentration of subgap defects in the CIGS near the surface of the layer than deeper in the film based on cathodoluminescence (CL) depth profiling. This layer of defects is present in both dip-coated and uncoated films and occurs in the anticipated space-charge region. The defects showing this enhancement are proposed to be acceptors near the valence-band edge. Such acceptor states have been studied extensively before [5]. (3) There are defect states near the conduction band edge, which are distributed throughout the film as well as band tails on at least one band edge which have a measurable effect on the device performance. Modeling suggests that the resulting device performances are consistent with these observations, although the model requires further refinement to fit all of the results in detail.

2. Experimental

CIGS films were prepared by two methods. Polycrystals were produced by coevaporation of the constituent elements onto a heated substrate at the Institute for Energy Conversion at the University of Delaware (IEC) [6] and NREL [1]. The IEC devices have a uniform composition throughout the CIGS layer, while the NREL samples contain significant changes in alloy composition with depth. Single crystals were deposited by a sputtering and evaporation method at the University of Illinois (UIUC) [3]. Substrates for polycrystals were Mo-coated soda lime glass, while epitaxial layers were deposited on (1 0 0), (1 1 1)S, (1 1 1)P and (1 1 0) oriented GaAs wafers. The deposition temperatures were 550–650 °C for polycrystals and 600–740 °C for single crystals. Microchemical and microstructural analyses of the films were carried out by atomic force microscopy (AFM), secondary ion mass spectrometry (SIMS), Auger electron spectroscopy (AES), angle-resolved photoelectron spectroscopy, X-ray diffraction and other techniques. Solar cells were produced and characterized at IEC and NREL by dip-coating of the CIGS with CdS, followed by deposition of In2O3−SnO2 or ZnO transparent conductors. Current−voltage and spectral−response curves were obtained in solar simulators at NREL or IEC. Cathodoluminescence spectroscopy (CLS) experiments were performed in a UHV chamber at the Ohio State University (OSU). CLS experiments detect optical recombination of carriers induced by electron beam generation of electron−hole pairs. Details of the analysis technique may be found in Ref. [7]. An electron beam of variable energy and flux was electronically chopped to improve signal detection. A Carl Leiss single flint prism monochromator dispersed the CL intensity for spectral analysis. Liquid nitrogen cooled Ge and thermoelectrically cooled S-20 detectors coupled to a Stanford Research lock-in amplifier detected the CL emissions. Finally, transient photocapacitance spectroscopy (TPC), discussed in detail elsewhere, [8,9] was used to analyze the devices. This technique is based on detection of the transient capacitance response of the diode to a voltage filling pulse. The capacitance transient arises from release of trapped carriers from defect levels within the depletion region. The response is represented as a single number by integrating over a fixed time window. The difference between transient signals measured in the presence of weak monochromatic light and those in the dark, normalized by the photon flux, gives the photocapacitance signal. TPC as implemented here is primarily sensitive to defects in the upper portion of the energy gap of the semiconductors.

3. Computer device model

While many empirical models of CIGS devices have been attempted, few have proven predictive, although many are diagnostic. More basic and predictive models have been proposed based on the AMPS, ADEPT and SCAPS computer codes. Solar cell simulations presented here used the AMPS computer code developed at the Pennsylvania State University by Fonash et al. This code uses the Newton–Raphson method to solve the Poisson and two continuity equations. Fundamental models such as AMPS are potentially more useful in predicting limitations to device performances than empirical methods. However, they require detailed inputs of two sorts, (1) material parameters and (2) composition depth profiles, to reduce the number of possible fits such that one can say that a given result is representative of the actual device. The experimental observations above provide such input. Furthermore, device results on the same materials allow a direct comparison of AMPS results with the defect studies. For simulations presented here, AMPS parameters were selected based on literature values where reliable values were available. Other inputs were used as fitting parameters but were constrained to reasonable ranges and were varied as little as possible. Similar parameters were used in fitting other device results allowing only the density of the various defect states to change from one simulation to another. Reasonable fits to a variety of devices were obtained. Additional details on the fitting approach may be found in Ref. [10].
4. Results and discussion

4.1. Surface inversion

The extremely smooth surfaces obtained for epitaxial layers on (111) GaAs permit analyses that are not possible with relatively rough polycrystalline films. To study the effect of CdS chemical bath deposition on CIGS surfaces, both metal- and Se-terminated (112)-oriented epitaxial layers were dip coated. It was determined by SIMS analysis that the dip coating process removes the native oxide on the CIGS surface. After characterization of the coated layers, the CdS was removed by diluted HCl etching and the surfaces were reexamined. The results showed residual Cd (and a smaller amount of S) in strongly bound surface sites, not removable by HCl. All of the bulk CdS was removed rapidly by the HCl etch. The residual Cd represented \( \sim 1 \times 10^{14} \) atoms/cm\(^2\), or approximately 0.25 monolayers of Cd. The amount of Cd decreased by approximately a factor of two after an additional 18 h of etching, but was clearly detectable even at this time. The surface morphology of the samples, as determined by AFM, was relatively unchanged by the dip-coating and HCl etching process. Only some rounding of normally sharp corners of surface steps was observed. Thus, it is clear that the residual Cd is not present as large precipitates on the surfaces, but rather must be incorporated into the atomic structure of the surface without changing the gross morphology.

The HCl-etched samples were loaded into either AES or XPS instruments shortly after etching and were reanalyzed. The etched surfaces contain relatively little oxide even after a deionized water rinse and brief air exposure. The residual Cd was clearly detectable in both techniques. Analysis of angle-resolved XPS data suggests that the majority of the Cd is present in the first one to three monolayers of the surface. AES sputter depth profiling removed most of the Cd very rapidly, with complete loss of signal after sputtering of 4–6 nm of the film. However, comparison of the Cd depth profile with the profile of surface C atoms suggests that the Cd was probably restricted to a layer much thinner than this, as suggested by XPS. Typical XPS measurements of the dip-coated and HCl-etched surfaces are shown in Fig. 1. This result shows that there is chemically-distinct Cd in the CIGS and that it is localized very near the surface of the film.

We propose that the strongly-bound Cd atoms, not removable by HCl etching, fill \( V_{\text{Cu}} \) sites in the first few monolayers below the sample surface (or even simply in the exposed surface monolayer itself) and result in n-type surface inversion. Residual S atoms presumably replace Se atoms or fill Se vacancies. S is isovalent with Se so this replacement presumably does not strongly influence the surface electronic properties. Any Cd found below the first few monolayers is presumably of modest importance in comparison to the large amount near the surface. These results are discussed in more detail in Refs. [11,12].

4.2. Surface subgap luminescence

AES analysis of the epitaxial layers suggests the presence of a Cu-poor region extending roughly 100 nm into the film (well beyond the range of strong Cd penetration). A convenient way of studying this near-surface region is CLS. UIUC epitaxial layers and polycrystalline films from NREL were studied at OSU. By adjusting the electron beam energy, the excitation depth can be controlled. The results, discussed in more detail in Ref. [7], show luminescence over a range of energies extending well below the band gap energy. Typical results are shown in Fig. 2. The subgap luminescence is qualitatively similar in the NREL polycrystals and the UIUC epitaxial layers, but decreases more rapidly with electron beam penetration depth in the polycrystals. The
NREL results show distinct oscillations in the resulting spectrum, which are well explained by interference patterns due to reflections from the Mo behind the CIGS. No such oscillations are found in the epitaxial layer, probably because it is grown on GaAs, which is transparent to the wavelengths in question. Consequently, no interference patterns are expected. The band-gap emissions in the NREL samples are significantly stronger than in the epitaxial layers. The subgap emissions are consistent with a broad peak centered at 0.9 eV energy. None of the subgap emissions were found to depend strongly upon the energy gap of the CIGS absorber material under test.

Variation in the primary beam energy from 0.5 to 5 keV shows that the intensity of the subgap emission increases relative to the band-edge emission near the film surface, especially in the epitaxial layers. No significant change in the qualitative behavior of the emissions was found for uncoated, dip-coated, or dip-coated and HCl-etched samples, suggesting that the subgap emissions were not significantly modified by CdS dip coated layer. This is consistent with the above results concerning the depth of the effects of the dip coating process and with the probe depth of the CLS. The results are consistent with the observation of a Cu-deficient layer near the surface of the film, especially if the defect states associated with the transitions are due to $V_{Cu}$ defects. These are acceptors and their formation would be favored in an n-type region. Furthermore, the epitaxial layers show a higher concentration of deep acceptor defects than do the polycrystals, consistent with possible transitions to these states. Therefore, we propose that the subgap luminescence near the surface results from the region of modified composition and that the transitions are band-to-acceptor defect states with enhanced density resulting from the surface type inversion. However, with the exception of the depth dependence of the signal, the result could also be consistent with the TPC results discussed next.

4.3 Bulk states and band tails

Polycrystalline samples from IEC and epitaxial layers from UIUC were examined by TPC as discussed in detail in Refs. [9,13]. The results show the presence of two hole traps, 0.7 and 0.9 eV above the valence band edge as well as at least one band tail with a width of $\sim0.022$ eV, and varying from sample to sample somewhat. The hole trap energies did not vary significantly as the band gap energy was changed in the polycrystals. The band tail width refers to the dominant band tail. If one of the band edges is sharper than the other, the sharper edge will be undetectable. The epitaxial layers showed nearly identical behavior to the polycrystals for the deeper (0.7 eV) defect state but a somewhat higher density of the 0.9 eV state. The epitaxial layer had a somewhat wider band tail. There was a correlation between the band tail width and device performance, especially in the short-circuit current, although other aspects of the device certainly also influence the performance. The TPC results for devices based on an IEC layer and a UIUC epitaxial layer are shown in Fig. 3. The energies of the defect states are similar to the range of energies found in CLS results. However, an analysis of the TPC data shows that these states (and the band tails) are not located in a near surface layer, but are distributed throughout the film. TPC data are not sensitive to states in the lower portion of the energy gap.
while CLS data do not determine in which part of the gap the detected states are located.

Comparison of the TPC and CLS results suggest the possibility that the CLS data reflect radiative emission from the conduction band to acceptor defects [5] near the valence band edge, while TPC data reflect defect states nearer the conduction band edge. This interpretation is consistent with Hall effect [14] and time-resolved photoluminescence [15] data on similar samples. Such an interpretation would imply that defect states in the upper portion of the energy gap and the dominant band tail are very similar for very dissimilar deposition processes. The CLS data imply that there is a higher density of acceptor states in the epitaxial layers than in the NREL samples, consistent with carrier concentrations measured by Hall effect and from interpretation of device results. A note of caution however. Doubtless, the CLS data also include defect-to-defect and valence-band-to-defect emissions and it is certainly possible that both the CLS and TPC results reflect the same defect at 0.9 eV depth. The 0.7 eV deep state was not evident in the CLS data but is very clear in the TPC results. If the 0.9 eV defect is the same in both measurements, then it must be in the top portion of the energy gap.

4.4. Modeling with AMPS

The defect states suggested by the CLS, TPC and other measurements, along with values from the literature were used as input to models of various devices using the AMPS computer code. No satisfactory fits to the device results could be obtained without strong inversion of the surface of the absorber layer. In the fits, a 2-nm thick layer with a shallow donor concentration of 10^{13}/cm^3 was assumed, as suggested by the Cd results in Section 4.1. IEC devices based on materials similar to those measured by TPC were simulated in detail. Good agreement between the device performances and the model results were found, suggesting that the values obtained experimentally are consistent with the device results [10]. It was then possible to vary the simulation parameters to test the resulting device behaviors. The minority carrier lifetime in the epitaxial layers has been found to be much shorter than in most polycrystalline CIGS samples [15]. Simulations increasing the defect state interactions with minority carriers and especially increasing the impact of the band tails results in shortening the carrier lifetime over a range similar to that observed experimentally. This shorter lifetime correlated with a significant loss in the red-photon response of the solar cells, as observed in the epitaxial devices. Furthermore, correlations between band tail widths and device performances, observed by TPC, were reproduced by AMPS, although the magnitude of the current loss in the device was not as severe in the model as in the real device. This is not surprising as many other changes in the real devices occurred in addition to increases in the band tail widths. Once a set of parameters had been established for the IEC device, several other device results from Shell Solar and Global Solar Energy were modeled, changing only the density of defects and the band edges (based on measurements of the composition depth profiles for these devices). The fits were good for the other devices [10].

5. Conclusions

The results suggest the presence of a range of defects in the energy gap of CIGS. In the upper half of the energy gap, these defects are probably located ~0.7 and 0.9 eV above the valence band edge and relatively independent of sample preparation process or composition. Likewise, the dominant band tail in the material appears to have a typical width of ~0.022 ± 0.005 eV. A near-surface region with enhanced defect density probably also occurs. We suggest that the primary defects giving rise to these states, which are enhanced near the surface due to the type inversion there, are near the valence band edge. These defects presumably contribute to recombination in the space-charge region of the device. Finally, we suggest that direct observation of a near surface Cd layer accounts for the surface inversion, which is necessary to obtain good fits to the device results.

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