Band bending independent of surface passivation in ZnO/CdS/Cu(In,Ga)(S,Se)$_2$ heterojunctions and Cr/Cu(In,Ga)(S,Se)$_2$ Schottky contacts

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We have employed admittance spectroscopy and deep-level transient spectroscopy in order to investigate the electronic properties of ZnO/CdS/Cu(In,Ga)(S,Se)$_2$ heterojunctions and Cr/Cu(In,Ga)(S,Se)$_2$ Schottky contacts. Our work concentrates on the origin of an energy-distributed defect state commonly found in these systems. The activation energy of the defect state addressed continuously shifts upon air annealing or damp-heat treatment and is a valuable measure of the degree of band bending in Cu(In,Ga)(S,Se)$_2$-based junctions. We demonstrate that the band bending within the Cu(In,Ga)(S,Se)$_2$ layer, reported in the literature to become minimal after air exposure, returns after the formation of either a Schottky contact or a heterojunction. The earlier phenomenon turns out to be independent of a surface passivation due to the CdS bath deposition. © *2003 American Institute of Physics.* [DOI: 10.1063/1.1576500]

Thin-film solar cells based on polycrystalline Cu(In,Ga)(S,Se)$_2$ chalcopyrite absorbers yield a relatively high energy conversion efficienciy of 18.8% on laboratory scale devices[1] and up to 12.5% on large area modules.[2,3] Still, some fundamental characteristics of the earlier material system are not understood completely, one of them being the diverse processes influencing the band bending of the heterojunction. A model proposed by Rau *et al.*[4] explains the comparatively strong band bending of heterojunction devices by an absorber surface passivation due to the subsequent CdS bath deposition. In this letter, we present admittance spectroscopy and deep-level transient spectroscopy (DLTS) measurements on ZnO/CdS/Cu(In,Ga)(S,Se)$_2$ heterojunctions and Cr/Cu(In,Ga)(S,Se)$_2$ Schottky contacts, showing that the strong band bending derives from the process of contact formation at the Cu(In,Ga)(S,Se)$_2$-based junction independent of a CdS induced passivation.

The samples investigated were nonencapsulated ZnO/CdS/Cu(In,Ga)(S,Se)$_2$ solar cells and Cr/Cu(In,Ga) $\times$(S,Se)$_2$ Schottky diodes. The fabrication of the chalcopyrite absorber layers is based on rapid thermal processing of stacked elemental layers.[5] The Schottky devices have been fabricated by thermal deposition of a 50-nm-thick Cr film on top of the uncleaned Cu(In,Ga)(S,Se)$_2$ surface, followed by a 200-nm-thick Au layer for mechanical protection.[6] Accelerated lifetime tests under standardized damp-heat (DH) conditions at 85 °C ambient temperature and 85% relative humidity were performed for various time spans ranging from 6 to 438 h.[7] A subset of the Schottky devices was subject to the DH test as well, depositing the metal front contacts only after DH treatment of the absorber layer. The electrical characterization of the test cells was done with the help of current–voltage characteristics, admittance spectroscopy (using a Solartron 1260 impedance analyzer) and DLTS (using a Semitrap 82E spectrometer). Temperature-dependent measurements in the range of 20–350 K were carried out in a liquid helium closed-cycle cryostat.

Upon applying capacitance spectroscopy, we disclose several different bulk traps and a defect state, further on called β, in the ZnO/CdS/Cu(In,Ga)(S,Se)$_2$ solar cells. The latter is commonly interpreted as an interface defect state being located at the CdS/Cu(In,Ga)(S,Se)$_2$ heterojunction.[8,9] We were able to identify this defect state in our samples with admittance spectroscopy as well as minority, majority, and reverse DLTS, respectively. Preliminary results have been reported elsewhere.[6,7,9] The corresponding admittance spectra (measured at 0 V bias) of as-grown and DH-treated samples are shown in Fig. 1. The temperature-dependent

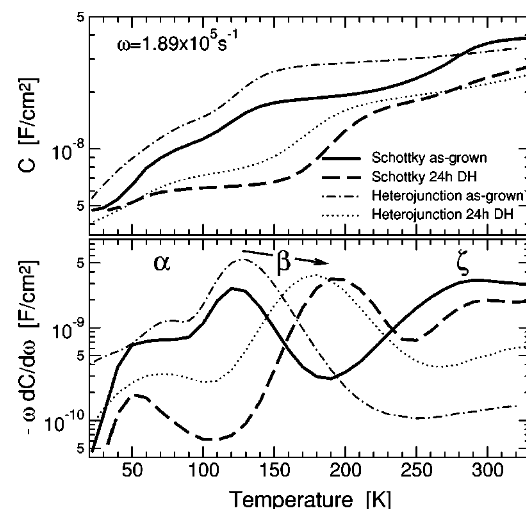

FIG. 1. Capacitance and differentiated capacitance (with respect to frequency) spectra vs temperature of the as-grown and 24 h DH-treated Cr/Cu(In,Ga)(S,Se)$_2$ Schottky diodes. The corresponding admittance spectra of ZnO/CdS/Cu(In,Ga)(S,Se)$_2$ solar cells are juxtaposed for comparison. α can be attributed to the activation of the absorber layer. The deep trap ζ was discussed elsewhere (see Ref. 6).

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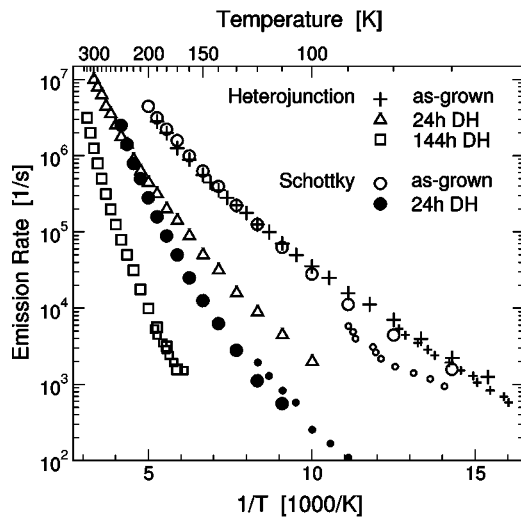

FIG. 2. Arrhenius plot of the emission rates of the defect state β, detected with admittance spectroscopy (larger symbols) as well as DLTS (smaller symbols) on both as-grown and 24 h DH-treated $Cr/Cu(In,Ga)(S,Se)_2$ Schottky diodes and $ZnO/CdS/Cu(In,Ga)(S,Se)_2$ solar cells (as-grown and 24 h/144 h DH treated), respectively. In both sample configurations, β shows almost identical emission rates in the as-grown state and clearly shifts due to the DH treatment. The emission rates were extracted from differentiated capacitance spectra and from DLTS spectra recorded with a quiescent bias of 0 V, applying filling pulses of 0.5 V height and 20 μs width.

emission rates of the charge carriers from the defect state β are summarized in an Arrhenius representation (see Fig. 2). In DLTS, β is extracted from a minority-carrier signal which can be measured regardless of applying injection pulses or not. The activation energy of the defect state β increases continuously with time elapsed under DH conditions from about 80 meV in as-grown samples to about 340 meV after 438 h exposure to DH conditions.[9] We have discovered the defect state β in the $Cr/Cu(In,Ga)(S,Se)_2$ Schottky junctions as well, for both, as-grown and DH-treated absorbers. The corresponding admittance spectra are displayed in Fig. 1, the Arrhenius plots in Fig. 2. In the Schottky junctions, the typical shift of the defect state β with DH treatment to higher activation energies is clearly recognized again.

Note that the state β can be commonly observed in $ZnO/CdS/Cu(In,Ga)(S,Se)_2$ solar cells. Herberholz *et al.*[8] reported β (referred to as N1 therein) in $ZnO/InS_x/Cu(In,Ga)Se_2$ heterostructures, we previously detected it in $ZnO/ZnSe/Cu(In,Ga)(S,Se)_2$ heterojunctions and $Cr/Cu(In,Ga)(S,Se)_2$ Schottky diodes.[6] In the latter case, it is remarkable that the emission rate of β nearly coincides for as-grown heterostructure samples and as-grown Schottky diodes (see Fig. 2). Our experimental results provide evidence that the defect state β is not affected by the ZnO front contact (including the CdS or ZnSe buffer layer) and, hence, located in the absorber layer.

The common interpretation of β as energetical distribution of interface defect states[8,9] implies that the activation energy equals the difference of conduction band minimum and electron quasi-Fermi level at the $CdS/Cu(In,Ga)\times(S,Se)_2$ interface. The assumed origin of this activation energy is depicted in a blow-up of the corresponding band diagram in Fig. 3. Igalson *et al.*[10] propose another explanation for the origin of the defect state β. They hold four discrete donor-like defect states in the absorber bulk (with activation energies of 80, 150, 350, and 570 meV) responsible for the different instances of β. They also report on an additional influence of the junction electric field on the emission rates of those traps.

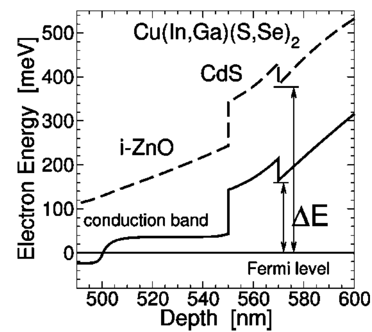

FIG. 3. A detail of the band diagram of a $ZnO/CdS/Cu(In,Ga)(S,Se)_2$ heterojunction solar cell. The assumed origin of the activation energy ΔE of the interface defect state β is sketched before (solid line) and after DH exposure (dashed line).

We emphasize two experimental findings indicating an energy distribution of states rather than the existence of discrete ones. First, the good agreement of our different measurements with one distinct Meyer–Neldel rule points to a common origin of the different instances of the defect state β.[7] Second, the height of the capacitance step changes continuously and is proportional to the activation energy,[7] which would not be expected for the case of several discrete defect states.

With the help of DLTS, we clearly identify β as a minority-carrier signal,[6] i.e., the width of the space charge region diminishes directly after having applied the filling pulse. If β were a bulk trap, it would probably be a donor-like defect state. A prerequisite to detect such a shallow bulk minority-carrier trap—the activation energy of β for as-grown samples amounts to about 80 meV—is a large band bending close to the interface between the front contact and the absorber, confining the possible spatial location of the detection of the defect state to the $Cu(In,Ga)(S,Se)_2$ surface. The crucial question remains why the above minority-carrier defect state can be detected using DLTS without the intentional injection of minority carriers (either by optical injection or, in case of the heterojunction, by injection pulses). For Schottky junctions based on n-Si, the observation of minority-carrier traps with DLTS has been reported in case of relatively large barrier heights.[11] Comparable conditions are given in $Cu(In,Ga)(S,Se)_2$-based heterojunctions, because the observation of a type inversion at the (*in vacuo*) $Cu(In,Ga)Se_2$ surface[12] indicates a high band bending. Thus, bulk minority-carrier defect states can be detected in $Cu(In,Ga)(S,Se)_2$ heterojunctions and Schottky contacts even without minority-carrier injection.

We consider the interpretation of β as energy-distributed defect state in the $Cu(In,Ga)(S,Se)_2$ surface region to be more likely than the proposition of Igalson *et al.*[10] However, we can draw conclusions about the band bending of the junction using either model. With the common interpretation of β as an interface defect state, the information on the band bending is directly obtained by the activation energy measured. In the Igalson model, the detection of a minority-carrier defect state located in the absorber layer with activa-

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tion energies as low as 80 meV is only possible for the electron quasi-Fermi level being very close to the conduction band. We conclude that the detection of β in as-grown $Cu(In,Ga)(S,Se)_2$-based heterojunctions and Schottky contacts signifies a strong band bending.

$Cu(In,Ga)(S,Se)_2$ films exposed to ambient air display a relatively small band bending, as reported by Weinhardt *et al.*[13] who measured a Fermi-level position (relative to the conduction band minimum) of 0.5 eV via applying inverse photoemission spectroscopy. *In vacuo* as-grown $Cu(In,Ga)Se_2$ surfaces, however, show a type inversion,[12] i.e., the Fermi level is located very close to the conduction band.[14] The impact of ambient air on the band bending of $Cu(In,Ga)Se_2$ films has been measured directly by Rau *et al.*[4] They observed a 200 meV decrease of the band bending using *in situ* ultraviolet photoelectron spectroscopy after contact with ambient air compared to the *in vacuo* result. Devices finished after an air exposure of the absorber layer, however, show a strong band bending again.[7] In order to explain such a nontrivial phenomenon, Rau *et al.*[4] proposed that the CdS bath deposition is responsible for a reintroduction of positive surface charges and a restauration of the band bending to the state before the air exposure.

Our capacitance measurements demonstrate a strong band bending for both, $ZnO/CdS/Cu(In,Ga)(S,Se)_2$ heterojunctions and $Cr/Cu(In,Ga)(S,Se)_2$ Schottky contacts, even though the respective absorber layers were exposed to ambient air during processing. Thus, the restauration of the band bending does not depend on the subsequent CdS bath deposition, dissenting the previous model by Rau *et al.*[4] The concrete mechanism being responsible for such behavior is still unknown. One possible explanation would be a Fermi-level pinning by a high concentration of interface defect states developing only after contact formation, independent of the contact layer applied, i.e., a reorganization of the chalcopyrite surface due to the junction built-in electric field. Such an effect could result from the field-induced migration of Cu.[4]

In summary, we have presented admittance spectroscopy and DLTS measurements on $ZnO/CdS/Cu(In,Ga)(S,Se)_2$ heterojunctions and $Cr/Cu(In,Ga)(S,Se)_2$ Schottky contacts. A commonly reported defect state with a continuously shifting activation energy depending on the sample treatment presumably originates from an energy distribution of defect states located at the $Cu(In,Ga)(S,Se)_2$ surface. The activation energy of this energy distribution indicates the prevailing degree of band bending, which is relatively small after air exposure, but increases considerably after the formation of a Schottky contact or a heterojunction. The increase of the band bending after the contact formation does not depend on the existence of the CdS buffer layer.

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