Elucidation of homojunction formation in CuInS₂ with impedance spectroscopy

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Type transformation in CuInSe\textsubscript{2} and CuInS\textsubscript{2} solar cells is an important issue with far reaching consequences. In the present study, the presence of a p-n homojunction inside CuInS\textsubscript{2} in a TiO\textsubscript{2}/CuInS\textsubscript{2} device is revealed with a detailed impedance spectroscopy and capacitance study. A n-type CuInS\textsubscript{2} film with a thickness of 40 nm is found at the TiO\textsubscript{2} (n-type)/CuInS\textsubscript{2} (p-type) interface. The effective donor density of this n-type film is \(2 \times 10^{17} \text{cm}^{-3}\) at 400 K and is higher than the effective acceptor density in the remaining p-type CuInS\textsubscript{2}, being \(4 \times 10^{16} \text{cm}^{-3}\) at 400 K. Both densities decrease upon increasing the temperature. This is explained by the activation of a Cu\textsuperscript{p} acceptor state in n-type CuInS\textsubscript{2} and a thermally activated hole trap in p-type CuInS\textsubscript{2}.

I. INTRODUCTION

Chalcopyrite semiconductors have attracted widespread attention for use in thin-film solar cells.\textsuperscript{1-4} CuInS\textsubscript{2} has a high absorption coefficient of \(1 \times 10^{5} \text{cm}^{-1}\) at 500 nm,\textsuperscript{5} and a direct band gap of 1.5 eV, which matches well with the solar spectrum.\textsuperscript{6} To date, efficiencies up to 19\% are obtained with chalcopyrite-based solar cells.\textsuperscript{7} Unfortunately, the most efficient chalcopyrite-based solar cell configurations contain the toxic components Cd and Se. In our configuration, instead of the use of ZnO buffer has been introduced. However, in the spray pyrolysis deposition method, which is used to prepare the samples, the application of TiO\textsubscript{2} instead of ZnO gives better results. TiO\textsubscript{2} and ZnO have approximately the same valence and conduction band positions, which allow the use of TiO\textsubscript{2} as electron accepting material.\textsuperscript{8} Furthermore, an In\textsubscript{2}(S,Se)\textsubscript{3} buffer layer can be used instead of CdS(S,Se). Nanu et al. reported efficiencies up to 4\% for TiO\textsubscript{2}/CuInS\textsubscript{2} solar cells, without buffer layer.\textsuperscript{9} Furthermore, these cells can be produced on a large scale, using low-cost deposition techniques, with efficiencies up to 7\%.\textsuperscript{10} Nevertheless, the efficiency still needs to be improved, which is a strong incentive to investigate the defect chemistry of CuInS\textsubscript{2} in depth. Charge carrier densities between \(10^{17}\) and \(10^{18} \text{cm}^{-3}\) have been found with capacitance studies on chalcopyrite-based solar cells.\textsuperscript{11-13} In this paper, the defect chemistry of CuInS\textsubscript{2} is studied by measuring the temperature dependence of the space-charge capacitance in TiO\textsubscript{2}/CuInS\textsubscript{2} devices.\textsuperscript{9,14,15} With this approach, we are able to elucidate the effective carrier densities and the widths of the depletion regions in n-type TiO\textsubscript{2} and p-type CuInS\textsubscript{2}. Furthermore, we provide evidence for the presence of a 40 nm thin interfacial n-type region in CuInS\textsubscript{2} between n-type TiO\textsubscript{2} and p-type CuInS\textsubscript{2}, i.e., homojunction formation. The presence of this n-type layer is expected to be independent of the metal oxide layer used. Furthermore, when the mechanism of the formation of the n-type layer can be controlled, the need of a CdS or In\textsubscript{2}S\textsubscript{3} buffer layer may disappear.

The study of homojunction formation in chalcopyrite crystals dates back to the 1970s. In these studies, semiconductor-type transformation at the interface of CuInSe\textsubscript{2} crystals have been stimulated by applying specific annealing conditions. n- to p-type transformation is observed when annealing CuInS\textsubscript{2} or CuInSe\textsubscript{2} at high temperatures (>650 °C) in S or Se vapor, respectively. p to n transformations are observed after annealing the Zn, Cd, In, or Cu plated p-type samples at T> 200 °C, and after annealing in Cd vapor at 400 °C or Cd-ion implantation.\textsuperscript{16-22}

In 1974, Wagner et al. introduced the first CdS/CuInSe\textsubscript{2} photovoltaic detector\textsuperscript{23} and the first chalcopyrite-based solar cells are obtained in 1975 and 1977.\textsuperscript{24,25} Type transformation of CuInSe\textsubscript{2} also occurs in CdS/CuInSe\textsubscript{2} solar cells after CdS deposition on both single crystal and thin-film CuInSe\textsubscript{2}. Type transformation in single crystals is probably caused by Cd diffusion in CuInSe\textsubscript{2}, leading to a homojunction in CuInSe\textsubscript{2} instead of the expected heterojunction.\textsuperscript{26-30} In thin-film devices, the origin of this phenomenon is assigned to the presence of a Cu-poor surface defect layer at the CdS interface.\textsuperscript{31-34} In 1992, Cahen et al. showed that it is also possible to create a homojunction in CuInSe\textsubscript{2} by applying a...
strong electric field on the samples at room temperature. In the studies described above, the presence of a homojunction in CuInSe₂ has been detected with electron-beam-induced current (EBIC) and secondary ion-mass spectroscopy (SIMS). With these techniques only thick type-converted CuInSe₂ layers (several micrometers) can be observed.

Less is known about this phenomenon in CuInS₂, especially not for the CuInS₂/TiO₂ combination of the present investigation. By using impedance spectroscopy, we have been able to monitor the presence of a n-type region in CuInS₂ with unprecedented accuracy. The thickness, as well as the effective donor and acceptor densities, has been determined. Furthermore, by measuring the temperature dependence of the interface capacitance, the energy positions of the involved deep acceptor state and deep hole trap have been found.

II. EXPERIMENTAL ASPECTS

Flat anatase n-type TiO₂ and Cu-rich p-type CuInS₂ films are subsequently deposited by spray pyrolysis on transparent conductive oxide (TCO) glass substrates (SnO₂: F, Libbey Owens Ford, TEC-18). More information about the spray deposition of CuInS₂ and TiO₂ has been published previously. Circular carbon spots (diameter of 2.3 mm) are applied onto CuInS₂ as back contact (graphite conductive adhesive, aqueous based, Alfa Aesar). TiO₂ without CuInS₂ layers are analyzed in 0.1M KOH electrolyte, with a Ag/AgCl reference electrode. Current-voltage (J-φ) measurements are recorded with a Princeton Applied Research potentiotstat (PAR283). For impedance spectroscopy (IS) and capacitance-voltage (C-φ) measurements, a frequency response analyzer (Schlumberger FRA 1255) is added. For IS measurements, an ac voltage of 10 mV is applied in a frequency range of 100 Hz–1 MHz in addition to a dc bias. The TiO₂/CuInS₂ samples are mounted in a nitrogen atmosphere in a N₂ cryostat (Oxford Instruments Optistat DN). J-φ, IS, and C-φ data are measured in the temperature range of 300–500 K. All experiments are performed in the dark. A Veeco Dektak 8 surface profiler is used for layer thickness determination.

III. RESULTS AND DISCUSSION

J-φ measurements in the dark show good diode behavior at all temperatures, as shown in Fig. 1. Impedance spectra at different potentials and temperatures are presented in Fig. 2. The equivalent circuit, shown in Fig. 3, represents the frequency response between 100 Hz and 1 MHz adequately. Nonlinear least squares fitting of the equivalent circuit elements to the impedance spectra gives excellent results for all temperatures. At frequencies above 10 kHz, the fits have a relative error of less than 4%. In the equivalent circuit, R1 represents the series resistance, R2 the shunt resistance, C₁ the space-charge capacitance, and the R₃-CPE₁ branch the trapping of charge carriers in deep states. For frequencies above 100 kHz, the R₁C₁ branch dominates over the others, i.e., \( \tau_{R₁C₁} \ll \tau_{R₃-CPE₁} \). Accordingly, at 1 MHz C₁, being the space-charge capacitance, can be calculated directly from the imaginary part of the impedance Z". Comparing the C₁ values obtained from fitting and that from Z" at 1 MHz indeed shows good agreement. For instance, at T=400 K and φ =0 V C₁=2.4 nF obtained from fitting and 2.7 nF when calculating from Z" at 1 MHz. Upon constructing a Mott-Schottky plot of C₁² vs φ, the obtained slopes and transition voltages (to be discussed below) are not affected by the small overestimation of the space-charge capacitance at 1 MHz.

Figure 4 shows Mott-Schottky C⁻²-φ plots recorded at 1 MHz at different temperatures. All transition voltages and slopes are summarized in the supplemental material. At high temperatures (T>340 K) three slopes are observed, while at low temperatures (T<340 K) only two slopes are found. To distinguish between the different regions (i.e., slopes) in the C⁻²-φ plots, the TiO₂ and TCO films. Impedance analysis and C-φ profiling on TCO/TiO₂ samples is performed in a KOH electrolyte to ensure a well-defined Schottky contact. Figure 5 shows the results of a C-φ measurement on a TCO/TiO₂ sample recorded at 10 kHz. Donor densities of 2×10¹⁷ and 2×10²⁰ cm⁻³ are found for TiO₂ and TCO, respectively. TiO₂ has a film thickness of 140 nm, which is in excellent agreement with surface profiler measurements. Upon combining these results with the C⁻²-φ plots of TiO₂/CuInS₂ devices with solid contacts, the slope at φ<−0.5 V corresponds well with that of TiO₂. The situation where TCO is dominant is never found, which implies that between 300 and 500 K at −1 V, TiO₂ is not in full depletion.

First, the C⁻²-φ behavior at high temperatures is discussed. For φ>−0.5 V two slopes are left unassigned, which means that in addition to TiO₂, at least two other space-charge regions must be present, both located in the CuInS₂ film. It is known that due to copper diffusion the conductivity of CuInS₂ can change from p-type to n-type.40,41 We also have taken into account the possibility of Cu migration into TiO₂, although it is rather unlikely that the positively charged Cu ions will migrate against the electric field toward the TiO₂. Cu diffusion into TiO₂ yields Cu⁺ donor states, which leads to an increase of the donor density at the TiO₂ surface region. However, a TiO₂ region with N_D>2×10¹⁷ cm⁻³ is not observed. Therefore, we conclude that between p-type CuInS₂ (p-CuInS₂) and n-type TiO₂ (n-TiO₂) a n-type CuInS₂ (n-CuInS₂) layer is formed during
the deposition and annealing. With a p-n homojunction inside the CuInS₂ film, the device is now modeled as a p-n-n system (p-CuInS₂/n-CuInS₂/n-TiO₂). Both CuInS₂ layers are in full depletion at \( \phi < -0.5 \) V, as shown in Fig. 6-I. The situation at \( 0 \) V close to the flatband situation, is presented in Fig 7. Now, the sample is described by a p-n homojunction inside CuInS₂ with no electric field present in TiO₂ because this is the junction where p-type and n-type materials meet. At the intermediate voltage region \(-0.5 \) V \(< \phi < 0 \) V, only one of the CuInS₂ regions (n or p) has reached full depletion. Model A (II-A) considers a fully depleted n-CuInS₂ layer, while model B (II-B) considers a fully depleted p-CuInS₂ layer. Both possibilities are modeled with the mathematical analysis given in the supplemental information.\(^{39}\)

The local electric field \( E \) is calculated by integration of the Gauss equation. We assume homogeneous donor and acceptor concentrations in the n-type and p-type CuInS₂ regions, respectively. The potential drop over the layers is calculated from integrating the electric field. When a potential \( \phi \) falls across the depletion region in the sample, the capacitance \( C \) of the sample is given by

\[
C = \frac{dQ_n}{d\phi} = \frac{dQ_p}{d\phi}.
\]

Here, \( Q \) is the charge in the depletion layer. Interface and surface states are not included in our model. The complete

FIG. 2. Impedance spectra of TiO₂/CuInS₂ devices at different potentials and temperatures. At \( \phi = 0.5 \) V the high-frequency regime is magnified in the inset.

FIG. 3. Equivalent circuit for a TiO₂/CuInS₂ device. \( R_1 \) represents the series resistance, \( R_2 \) the shunt resistance, and \( C_1 \) the space-charge capacitance. The low frequency \( R_1\)-CPE₁ branch represents charge trapping in deep states.
mathematical analysis can be found in the supplemental material and the final results are summarized here. The situation of Fig. 6-I, in which both CuInS$_2$ layers are in full depletion, leads to

$$\frac{1}{C^2} = \left(1 + \frac{\varepsilon_{\text{CIS}} N_{\text{D,p-CIS}}}{\varepsilon_{\text{TiO}_2} N_{\text{D,TiO}_2}}\right) \left(1 - \frac{\varepsilon_{\text{CIS}} N_{\text{P,n-CIS}}}{\varepsilon_{\text{TiO}_2} N_{\text{D,TiO}_2}}\right) + \frac{2(\varepsilon_{\text{CIS}} N_{\text{D,p-CIS}} + \varepsilon_{\text{TiO}_2} N_{\text{D,TiO}_2})}{q\varepsilon_{\text{TiO}_2} N_{\text{D,TiO}_2} N_{\text{A,p-CIS}}} \phi. \quad (3)$$

Here, $\varepsilon$ is the dielectric constant, $q$ is the electron charge, $N$ is the ionized donor or acceptor density, and $w$ is the layer thickness.

When $n$-CuInS$_2$ is fully depleted, model A (Fig. 6-II-A) holds, leading to the following equation:

$$\frac{1}{C^2} = \left(1 + \frac{\varepsilon_{\text{CIS}} N_{\text{A,p-CIS}}}{\varepsilon_{\text{TiO}_2} N_{\text{D,TiO}_2}}\right) \left(1 - \frac{\varepsilon_{\text{CIS}} N_{\text{D,p-CIS}}}{\varepsilon_{\text{TiO}_2} N_{\text{D,TiO}_2}}\right) + \frac{2(\varepsilon_{\text{CIS}} N_{\text{D,p-CIS}} + \varepsilon_{\text{TiO}_2} N_{\text{D,TiO}_2})}{q\varepsilon_{\text{TiO}_2} N_{\text{D,TiO}_2} N_{\text{A,p-CIS}}} \phi. \quad (2)$$

When $p$-CuInS$_2$ is fully depleted, model B (Fig. 6-II-B) holds, i.e.,
be the dominant donor in this Cu-poor region. We conclude that model B holds, meaning that the acceptor density of 4 \times 10^{17} \text{ cm}^{-3} at 400 K is found for model A. Model B leads to a 40 nm n-CuInS\textsubscript{2} film with a donor density of 2 \times 10^{17} \text{ cm}^{-3} and a 90 nm p-CuInS\textsubscript{2} layer with an acceptor density of 4 \times 10^{16} \text{ cm}^{-3} at 400 K. Because we initially deposited Cu-rich p-type CuInS\textsubscript{2}, we are drawn to conclude that model B holds, meaning that the p-CuInS\textsubscript{2} film reaches full depletion before the n-CuInS\textsubscript{2} film does. A film thickness of 40 nm for the n-type region is in excellent agreement with the findings of Kötschau and Schock\textsuperscript{32} who observed a Cu-depleted surface layer of 5–60 nm in CuInSe\textsubscript{2} with grazing incidence x-ray diffraction. However, they did not report the presence of a homojunction in CuInSe\textsubscript{2}. Although we have indications that the n-type region formed at the TiO\textsubscript{2}/CuInS\textsubscript{2} interface is Cu poor as well, further investigations are in progress. Most likely, In\textsubscript{Cu} will be the dominant donor in this Cu-poor n-type region.

Since in CuInS\textsubscript{2} both donor and acceptor states are rather deep, their ionization probability is strongly related to the temperature. Accordingly, the properties of the homo- and heterojunction change upon varying the temperature. At temperatures below 500 K, the effective donor density in TiO\textsubscript{2} is constant; only a small increase of the donor density around 500 K is observed. At temperatures below 400 K, the flatband situation is not reached within the applied potential range. Below 340 K, only two slopes are found, and the p-CuInS\textsubscript{2} film is always in full depletion within the applied potential range. A clear temperature dependence is found for donor and acceptor densities in n-CuInS\textsubscript{2} and p-CuInS\textsubscript{2}, respectively, as shown in Fig. 7. It is remarkable that both acceptor and donor densities decrease with increasing temperature, opposite to our expectations. Assuming Boltzmann statistics, an activation energy of 146 meV for n-CuInS\textsubscript{2} is found, which is in excellent agreement with the presence of Cu\textsuperscript{in} acceptors\textsuperscript{42,43}. The fact that an acceptor is activated in n-type CuInS\textsubscript{2} explains the decrease in effective donor density upon increasing the temperature. In p-CuInS\textsubscript{2}, an activation energy of 244 meV is found. For CuInS\textsubscript{2}, this activation energy has not been reported yet. Hole traps with activation energies of 260–280 meV have been found for CuInSe\textsubscript{2}\textsuperscript{44–46}. Therefore, we postulate the presence of a thermally activated hole trap located 244 meV below the valence band. Hole traps are neutral when empty and positively charged when a hole is captured.

Although the chemical nature of these hole traps cannot be inferred from our experiments, it is plausible that the oxidation of Cu\textsuperscript{2+} to Cu\textsuperscript{2+} is involved. Thermal activation of a hole trap in p-CuInS\textsubscript{2} explains the decrease of the effective acceptor density. From the derived acceptor and donor densities, in combination with the transition points of the C\textsuperscript{2}\phi plots, the n-type and p-type CuInS\textsubscript{2} film thicknesses are found to be independent of the temperature, as expected.

When heating up the samples to 500 K in nitrogen, irreversible changes may occur. To evaluate the extent of such relaxation, the experiments are repeated at room temperature after cooling down the samples from 500 K. Only small differences are observed. Figure 8 shows a shift of the capacitance in the C\textsuperscript{2}\phi plot at 300 K before and after heating to 500 K. Despite the small decrease of the capacitance, no significant differences are observed in the slopes and the transition voltages of the plots. Nevertheless, the capacitance shift indicates a minor change in the defect structure at 500 K, which is now under investigation.

IV. CONCLUSIONS

With a detailed C\textsuperscript{2}\phi study, we provide evidence for the presence of a p-n homojunction in CuInS\textsubscript{2} spatially sepa-
rated from the TiO$_2$/CuInS$_2$ interface. A n-type CuInS$_2$ layer of 40 nm with a donor density of $2 \times 10^{17}$ cm$^{-3}$ at 400 K is present at the TiO$_2$/CuInS$_2$ interface. The remaining p-CuInS$_2$ layer has a thickness of 90 nm and an acceptor density of $4 \times 10^{16}$ cm$^{-3}$ at 400 K. Both acceptor and donor densities decrease with increasing temperature, due to the presence of a Cu$_{in}$ acceptor level in n-CuInS$_2$ and a yet unidentified thermally activated hole trap in p-CuInS$_2$. Activation energies of 1.46 and 244 meV are found, respectively.

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39. See EPAPS Document No. E-IAPAU-102-120714 for a table with all transition voltages and slopes of the C$^{-2}$-C measurements and the mathematical analysis of the capacitance of the four situations shown in Fig. 6. This document can be reached through a direct link in the online article’s HTML reference section or via the EPAPS homepage (http://www.aip.org/pubservs/epaps.html).