Investigation of capacitance transients in CuInS$_2$ due to ionic migration

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ABSTRACT

Transport of mobile ions in n-TiO$_2$/n-CuInS$_2$/p-CuInS$_2$ thin-film devices is studied with the transient ion-drift (TID) method. In contrast to the normal TID method, a mobile ion profile is created in the CuInS$_2$ layer, which can be described by the Gouy–Chapman theory. Activation energies for diffusion of 0.5 and 1.0 eV are found. We postulate that these activation energies are related to the associated defect, $(Cu_{In}'' \ In_{Cu}^{\bullet\bullet})^x$, which introduces a deep electronic state inside the bandgap of CuInS$_2$. This defect can accept or release an electron and drift out of the depletion region. This will lower the concentration of recombination centers in the depletion region, which explains the self-healing property of CuInS$_2$.

1. Introduction

Chalcopyrite semiconductors are promising candidates to be used in thin-film solar cells [1–4]. Although impressive efficiencies up to 19% are reached for Cu(In,Ga)Se$_2$ [5] and 12.5% for CuInS$_2$ [3], further improvement of the device performance can be accomplished. The mobility of copper (Cu) ions in chalcopyrites is a well-known issue in these solar cells [6–11], but also indium (In) mobility has been reported [12]. Although ion-mobility can give chalcopyrite-based solar cells self-healing properties, and probably plays a role in the light soaking effect [13], it is also shown that under certain conditions Cu can physically segregate from the chalcopyrite layer [7]. Under specific circumstances Cu-transport can be used to change the semiconductor type. In this way p–n homojunctions or nano-scaled transistors are created in chalcopyrites [14–20]. Furthermore, it has been shown that Cu(In,Ga)Se$_2$-based solar cells also recover after a decrease in efficiency caused by electron or proton irradiation [21–23]. The nature of the instability of p-type CIGS, on long and short range, is nicely reviewed and discussed by Guillemoles et al. [24]. Long-range effects are assigned to Cu mobility. Short-range effects are ascribed to donor defects that capture electrons or are transformed to acceptors via defect chemical reactions. In the latter case, both isolated single defects and defect complexes can be involved.

Here, we present a detailed transient ion-drift (TID) study of TiO$_2$/CuInS$_2$ heterojunctions. With this method the mobile ion transport in thin-film TiO$_2$/CuInS$_2$ devices can be determined, leading to better understanding of the chemical stability. In previous investigations we have shown that a p–n homojunction is present in CuInS$_2$ in TiO$_2$/CuInS$_2$ heterojunctions [25]. Fig. 1 shows the band diagrams of these devices at three potentials.

A brief description of the TID method is given below. In the past, this method has been applied on single-crystalline CuInSe$_2$, but never on thin films. Diffusion coefficients of 10^{-12}–10^{-13} cm^2/s have been found, which were assigned to Cu-migration [26]. Much larger diffusion coefficients in single crystalline and polycrystalline CuInSe$_2$ and CuInS$_2$ are reported using electron beam-induced current (EBIC) and point electrode techniques, i.e., 10^{-5}–10^{-10} and 10^{-6}–10^{-9} cm^2/s, respectively [6,7,10,11]. The origin of the Cu-transport in chalcopyrites is not well understood but is believed to be related to mobile copper interstitials ($Cu_i^{\bullet}$) or copper vacancies (V_{Cu}''). In the present TID measurements smaller diffusion coefficients are found, and are probably related to the migration of In instead of Cu. Moreover, we postulate a relation between this In-related defect and the earlier reported, but yet unassigned, defect around 1 eV above the valence band [27–29].

2. TID theory

The first application of the TID method has been reported by Heiser and Mesli in 1993 [30,31]. Later, Lyubomirsky et al. [26] applied this method on single-crystalline CuInSe$_2$. The TID method is similar to deep-level transient spectroscopy (DLTS)

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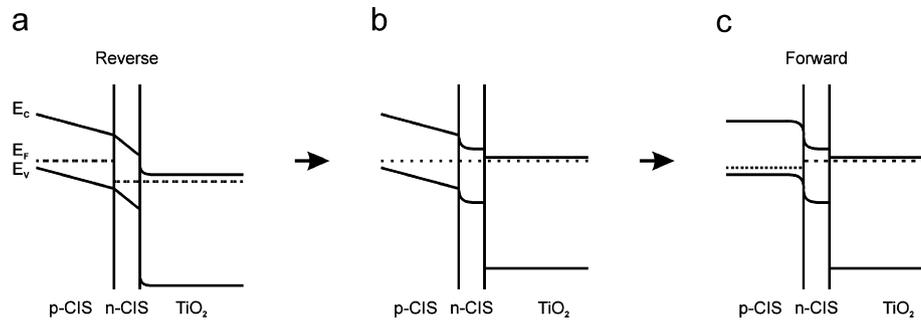
Fig. 1. Band diagrams for p-CuInS$_2$/n-CuInS$_2$/TiO$_2$ heterojunctions at the three potential regions as concluded in our previous study [25]. (I) The band diagram at reverse potentials, when n- and p-type CuInS$_2$ are both in full depletion. (II) The band diagram around 0 V when only p-CuInS$_2$ is in full depletion. (III) The situation close to the flat band potential when neither the n-type nor p-type CuInS$_2$ is in full depletion.

[32], although in TID the observed transients are caused by ionic transport instead of trapping of electrons. Mobile ions drift under the influence of the electric field in the depletion layer. After applying a potential step in reverse direction, the mobile ions move in the same direction as the electronic charges, i.e., mobile acceptors are negatively charged and follow the electrons, and mobile donors are positively charged and follow the holes. After some time all mobile ions are removed from the depletion layer and accumulate at the depletion layer edge. Subsequently, the concentration profile of mobile ions will flatten due to thermal diffusion to the bulk. The following assumptions are made: (i) drift of mobile ions is much faster than thermal diffusion, (ii) the mobile ion concentration is much lower than the doping level (i.e., non-mobile donors and acceptors), which implies that the space-charge region is not affected noticeably by the redistribution of the mobile ions, and (iii) the background doping is uniform. Under these conditions a capacitance transient,

$$\Delta C(t) = [C(0) - C(\infty)][1 - e^{-t/\tau}] \tag{1}$$

can be expected. In general, the transient time τ is longer for TID than those obtained with DLTS, because ionic diffusion is usually a slower process than trapping and detrapping of electrons.

Similar to DLTS, there are basically two transient times. The equivalent of the trap filling time is the ion 'flattening time'

$$\tau_f \approx \frac{w^2}{D} \tag{2}$$

and the equivalent of the carrier emission time, after the reverse voltage step, the ion 'accumulation time'

$$\tau_a = \frac{kT\varepsilon}{q^2 DN} \approx \frac{w^2 kT}{qD\phi_r} \tag{3}$$

Here, w is the depletion width, q is the elementary charge, D is the ion-diffusion coefficient, N is the non-mobile donor or acceptor concentration, k is Boltzmann constant, ε is the dielectric constant, and ϕ_r is the reverse potential. Although TID and DLTS are almost similar, there is an important difference. For DLTS the filling time of traps is much shorter than the carrier emission time, while the opposite is true for their TID equivalents, i.e., $\tau_f/\tau_a > 1$. The ion-diffusion coefficient from Eq. (3) can be written as

$$D = D_0 e^{-E_A/kT} \tag{4}$$

in which D_0 is the pre-exponential factor and E_A the activation energy. The activation energy can be calculated from the slope of a $\ln(\tau_a/T)$ vs. $1/T$ plot.

3. Experimental aspects

Flat films of TiO$_2$ and CuInS$_2$ are obtained from Advanced Surface Technologies in Bleiswijk. The samples are made with spray deposition on transparent conductive oxide (TCO) glass (SnO$_2$:F) as described elsewhere [33–35]. Carbon spots (diameter 2.3 mm) are used as back contact (Graphite conductive adhesive, aqueous-based, Alfa Aesar). Impedance and CV measurements are described in our previous work [25]. Both are recorded with a potentiostat (PAR283) in combination with a frequency response analyzer (Schlumberger FRA 1255). A dc voltage is aplied over the samples with the potentiostat. An ac voltage of 10 mV with a frequency of 1 MHz is superimposed on this voltage by the FRA. The CV measurements are recorded at a scan rate of 50 mV/s. TID measurements are obtained with the same set-up. First, the samples are brought to a reverse potential of −1 V for 100 s. Subsequently, the potential is stepped to the flattening potential of 0 V for 300 s and finally back to the accumulation potential of −1 V. The capacitance response is monitored on a computer using Labview with a rate of 2 points/s. The TiO$_2$/CuInS$_2$ samples are mounted in a cryostat (Oxford Instruments Optistat DN). TID and impedance spectra are recorded in the temperature range of 300–500 K under nitrogen atmosphere to prevent oxidation of CuInS$_2$. All measurements are duplicated on another sample from another deposition with the same parameters. Similar results are found for both samples.

Raman measurements are performed using a home-built set-up. A Nd:YVO$_4$ laser, operating at a wavelength of 532 nm, is used as the excitation source (SpectraPhysics Millennia). Neutral density filters are used to adjust the power of the laser. Light detection occurs with a liquid-nitrogen-cooled CCD camera (Princeton Instruments LN/CCD-1100-PB) connected to an Acton Spectra Pro 2500i monochromator.

4. Results and discussion

4.1. Impedance and Mott–Schottky measurements

In a previous paper, we have discussed the impedance and Mott–Schottky behavior of the samples in detail [25]. The main results and conclusions of that work are necessary to clarify the present TID results and are summarized here. The impedance spectra in Fig. 2 show that, at frequencies above 1 MHz, a resistor and capacitor in series describe the equivalent circuit for the samples at both flattening (0 V) and accumulation (−1 V) potential for all applied temperatures. The capacitance represents the capacitance of the depletion region, which can be obtained from