Time-of-Flight studies on TiO_2 – $CuInS_2$ heterojunctions

Joris Hofhuis, Joop Schoonman, Albert Goossens

Opto-Electronic Materials, Faculty of Applied Sciences, Delft University of Technology, Julianalaan 136, 2628 BL Delft, the Netherlands. email: J.P.T.Hofhuis@tudelft.nl

Introduction

$TiO_2/CuInS_2$ heterojunctions show a remarkable photovoltaic activity. Spray pyrolysis can be used to deposit both materials in ambient atmosphere, which opens up a low cost route for large-scale production of thin film solar cells. However, spray pyrolysis may induce defects in the materials, which limits the overall solar cell performance. An important aspect is the charge carrier mobility, which can be measured with the Time of Flight (ToF) technique. In ToF, a short laser pulse creates charge carriers at the TiO_2/CIS junction, which drift away from the junction region by the internal electric field. The moving charges are detected using two (non-blocking) electrodes in a DC circuit. In this way, the samples under investigation are active solar cells and the outcome of the ToF measurements are of direct relevance to optimizing $TiO_2/CuInS_2$ PV devices.

The cells subject to ToF studies are carefully prepared to fulfil the requirement of having an RC response time less than the transit time. The applied electric field, the film thicknesses, and the temperature have been varied in the investigations. In addition, the impedance of the cells has been measured to derive the internal potential distribution. Three cells have been investigated, all having a CIS layer thickness of about 500 nm. The TiO_2 thickness has been varied. i.e. 200 nm, 300 nm and 400 nm.

Results

In Figure 1, the capacitance of the 200 nm sample as a function of reverse bias is shown, derived from impedance measurements. At reverse bias the capacity is bias independent, which indicates a uniform distribution of interface states. The value of the capacitance is $2\cdot10^{-6}$ F/cm^2 from which a surface state density of $N_i = 1.2\cdot10^{13}$ cm^{-2}V^{-1} can be derived.

In ToF measurements, first an electric field is established by applying a reverse bias pulse over the sample. The inset of Figure 2 shows the current response, which is the result of emptying interface states upon applying the bias. The decay time is 1 μs and is independent on the applied bias. In Figure 2 the extracted charge as a function of applied bias pulse is shown, which is linear with the applied bias voltage in accord with a uniform interface state distribution. The surface state density can be derived from the slope in Figure 2 and amounts to $N_i = 5.2\cdot10^{12}$ cm^{-2}V^{-1}, which differs a factor 2 from the value derived from capacitance data.

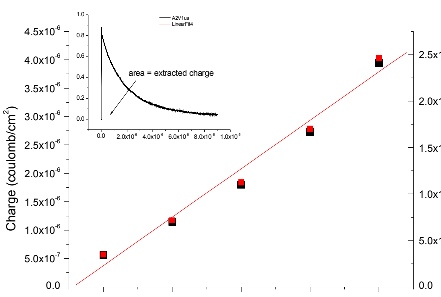

Figure 2: extracted charge as a function of applied bias. Inset: current response

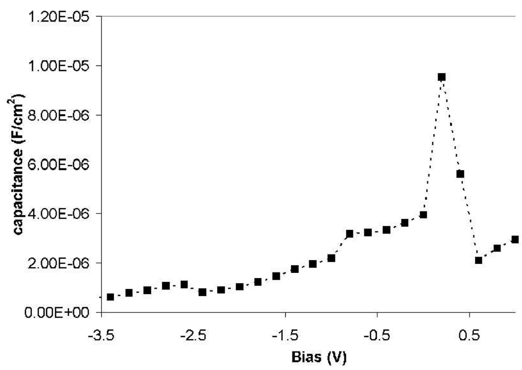

Figure 1: Impedance measurements

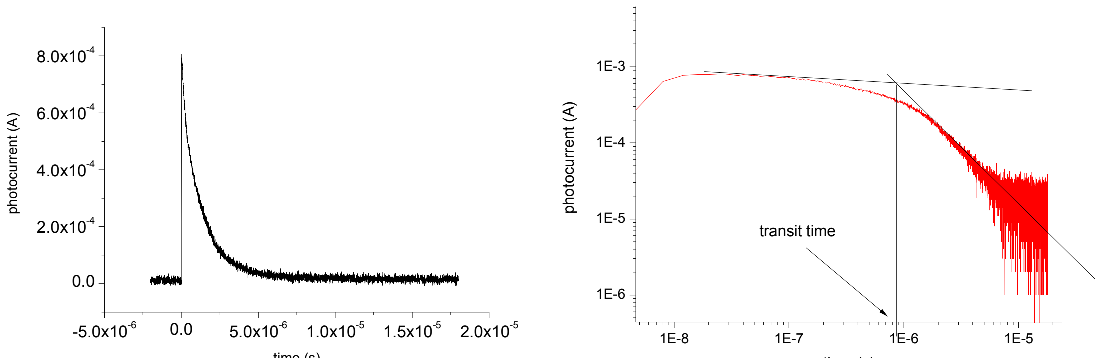

Figure 3a(left): Time of Flight photocurrent on a linear scale Figure 3b(right): Time of Flight photocurrent on a log-log scale. The lines illustrate the determination of the transit time

180 μs after the bias pulse, a short laser pulse (7 ns) is applied by which conduction band electrons are generated almost instantaneously at the TiO_2/CIS interface. This transient, shown in Figure 3a for 2.5V applied bias, can only be measured if the response time of the electrical system is fast enough. Figure 3b shows a log-log plot of the transient current at 2.5 V applied bias. The transit time (τ) is defined as indicated in the figure.

Figure 4 shows the inverse of the transit time as a function of applied bias for the TiO_2 layer thicknesses. At an applied bias below 1V, the transit time is independent of the voltage, while above 1V a linear relation between 1/τ and V is observed. From the slope the mobility can be determined, if the field strength in TiO_2 is known. A correction is needed to account for the distribution of the applied bias over the TiO_2 and CIS components. After this correction is made the found mobilities are
$0.7\cdot10^{-2}$ cm²/Vs (200 nm), $1.7\cdot10^{-2}$ cm²/Vs (300 nm) and $1.8\cdot10^{-2}$ cm²/Vs (400 nm).

Figure 5 shows the band-diagram of the TiO_2/$CuInS_2$ heterojunction. We assume that TiO_2 is in full depletion, CIS is heavily doped ($N_a=10^{18}/cm^3$), and the Fermi-level in the TiO_2 determines the surface state occupancy. When we use an interface state density of $1\cdot10^{13}cm^{-2}V^{-1}$, a reverse electric field in the TiO_2 at low applied voltages (V<1) is predicted which shifts to normal when the Fermi-level in the TiO_2 moves to the bottom of the interface states at V>1. If the electric field in the TiO_2 is reverse, migration of the electrons in TiO_2 is governed by diffusion instead of drift.

We can calculate the mobility using the transit time below 1V using $D=\frac{\mu kT}{e}=\frac{l^2}{2\tau}$
$=2\cdot10^{-2}$ cm²/Vs (200 nm), $1.4\cdot10^{-2}$ cm²/Vs (300 nm)
and $1.5\cdot10^{-2}$ cm²/Vs (400 nm). The 300 and 400 nm samples are in excellent agreement with the values calculated from the normal ToF-situation.

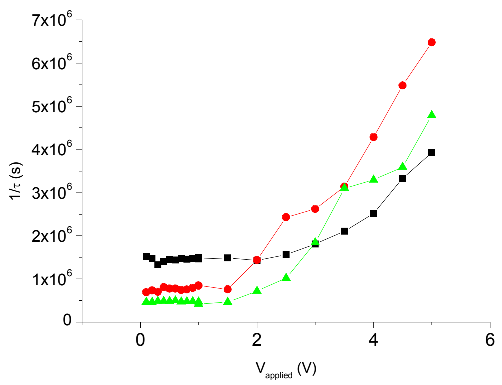

Figure 4: 1/t versus applied bias

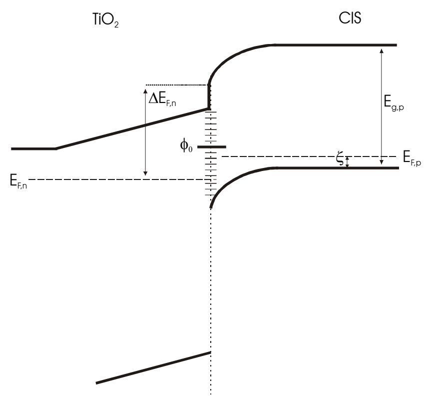

Figure 5: Band diagram of the TiO_2/CIS heterojunction