Charge carrier transport in $CuInS_2$-based nanostructured solar cells

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1. Introduction

The eta-solar cell has been investigated with increasing interest during the past six years due to its potential as a low cost concept [1,2]. This inorganic solid state version of the dye-sensitized solar cell (DSSC) consists of a nano-structured *n*-type metal oxide, an extremely thin absorber, and a hole conductor. Here, we study a variant of the eta-cell, the so called 3D-cell, in which the light absorbing material is absorber and hole conductor at the same time [3]. Although efficiencies of 4% already have been obtained in a 3D TiO_2–Al_2O_3–In_2S_3–$CuInS_2$ system [4], there are still questions concerning the low V_{oc} and fill factor of these cells, in particular when compared to liquid junction cells.

Therefore, intensity modulated photocurrent spectroscopy (IMPS) is performed to study the photogenerated charge transport in the 3D-cell. First order analysis in terms of the characteristic time constants shows that the photocurrent response of the 3D-cell is 4 orders of magnitude faster than the response of DSSCs. Furthermore, a decrease of the photocurrent time constant is observed with increasing background illumination intensity as well as a dependence on bias voltage.

2. Experimental

Our 3D-cell is built on a SnO_2:F coated glass substrate on which a 100 nm dense TiO_2 layer is sprayed before a 3 •m nanostructured n-type TiO_2 layer is deposited by doctor blade; the TiO_2 particle size is 50 nm. Then a 15 nm In_2S_3 buffer layer is deposited with ALD, as well as a *p*-type $CuInS_2$ layer. The $CuInS_2$ absorber first fills up the pores of the nanostructured electrode and then 'tops' the whole structure with a layer of about 200 nm. At last, a Au contact is evaporated, defining a cell size of 0.04 cm^2. The efficiency of the cell is 3.5%. More details are to be found in [4].

During the IMPS measurements, the cell is illuminated through the glass substrate with light of 635 nm from a 15 mW diode laser, and white bias light. About 45% of the laser light intensity (68 W/m^2) is modulated by an opto-acoustic modulator thus creating a modulated photonflux $e\bullet\bullet(\bullet)$. The modulated photocurrent $\bullet j(\bullet)$ was detected as the voltage drop over a 50 • resistance, connected parallel to the cell.

3. Results and discussion

The opto-electrical transfer function $T(\bullet)$ is defined as $T(\bullet) = \bullet j(\bullet) / e\bullet\bullet(\bullet)$. The characteristic time constant $\bullet_{IMPS}$ is determined from the minimum of the imaginary part of $T(\bullet)$ as $\bullet_{IMPS} = (\bullet_{min})^{-1} = (2\bullet f_{min})^{-1}$. Since the hole mobility in the $CuInS_2$ turns out to be very high [5], we assume that $\bullet_{IMPS}$ reflects the electron transport through the nanostructured TiO_2 film. On the other hand, [6] and preliminary intensity modulated photovoltage data show that the electron life time may not be so much longer than the transport time, which implies that our assumption regarding the interpretation of $\bullet_{IMPS}$ might not be exactly correct.
In Fig. 1 we see that $\bullet_{IMPS}$ is in the order of 10 • s, whereas for the DSSC values in the range of 100 ms were reported [7]. Fig. 1 also shows

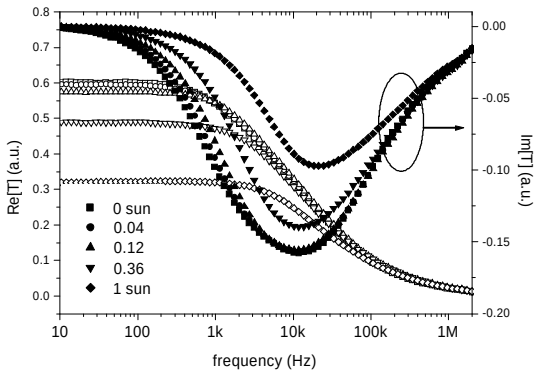

Fig. 1. Real and imaginary parts of opto-electrical transfer function of 3D-cell as a function of background illumination intensity, bias voltage 0 V, room temperature.

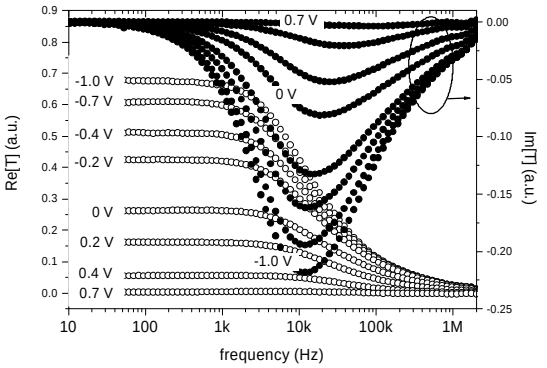

Fig. 2. Real and imaginary parts of opto-electrical transfer function of 3D-cell as a function of bias voltage, background illumination intensity 1 sun, room temperature.

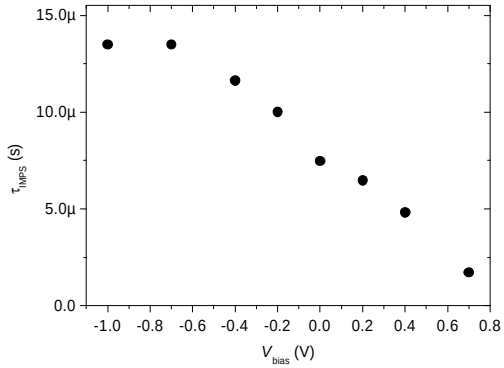

Fig. 3. Characteristic time constant $\bullet_{IMPS}$ as a function of bias voltage, background illumination intensity 1 sun, room temperature.

a significant light sensitivity of the time constant. This suggests that next to band transport, also hopping transport takes place which benefits from the increased trap filling above some critical illumination intensity $I_{0,crit}$. For the 3D-cell, an increase of the photocurrent response times up to a factor 10 is observed for 1 sun illumination with respect to 0 sun.

The strikingly fast photocurrent response can possibly be ascribed to a lower charge accumulation at the interface. One of the possible reasons for this is showed in Fig. 2, namely an observed voltage dependence of the time constant; $\bullet_{IMPS}$ decreases with a factor 10 upon increasing the bias voltage towards higher forward bias. If we assume total depletion of the TiO_2 nanoparticle as well as the pores that are filled with $CuInS_2$, this can not be interpreted as the existence of an electric field, which could have caused very fast band and hopping transport with respect to the field free DSSC. Moreover, Fig. 3 shows that the time constant decreases for higher forward voltage which is just the opposite of what could be expected in case of an electric field.

An other interpretation seems therefore more reasonable and explains the voltage dependence with the same mechanism as the one that we used to explain the illumination dependence. That is, higher forward voltage as well as high illumination intensity, causes a flat band situation due to an increase of mobile charge carriers. Since more traps can thus be filled, trapping and detrapping times become faster.

Together with another distribution or density of interface states at the $TiO_2 – In_2S_3$ or $In_2S_3 – CuInS_2$ interface with respect to that at the TiO_2 – dye interface, this could account for the observed voltage dependence as well as the observed fast time constants.

Alternatively, the influence of the positive holes in the $CuInS_2$ due to their high mobility [5] can speed up the electron transport through the TiO_2.

4. Conclusion

In the 3D-cell, both band transport and hopping transport occurs. The current that flows due to these transport mechanisms is diffusion driven.

5. Acknowledgements

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