ABSTRACT

Light dependent current transport mechanisms are the main reason for the failure of the superposition principle of dark and light IV curves of most chalcogenide solar cells. While the photocurrent collection is nearly constant, a significant variation of the forward bias characteristics of these devices takes place as effect of illumination. Different behaviours can be seen in different cells but the physical phenomenon underlying all these observations is the ‘electronic doping’ of the CdS window layer. A high density of deep trap centres with strongly asymmetrical Capture Cross-Section (CCS) changes radically the conductivity and type behaviour of this layer under illumination. The consequent bending and rearrangement of the energy bands modifies the current transport across the device. Different transport mechanism are analysed and modelled in the discussion.

1. INTRODUCTION

The IV Characteristics of thin film chalcogenide solar cells present several non-idealities with respect to the predicted behaviour of photovoltaic p-n junctions. Although this is a well-known fact since the very first appearance of these devices more than thirty years ago, researchers do not seem to have found and shared yet a convincing explanation of the observed phenomena.

In the last years, parallel to the expansion of R&D following the creation of the first pilot lines aimed to the industrial production of CdTe and CI(G)S PV modules, a growing interest in the investigation on these devices has led to a renewed, increased effort in their characterisation and modelling. Recent works [1-4] have identified, for several classes of solar cells, different light dependent current transport mechanisms that consistently describe the features of the observed IV curves. It is possible, from these models, to formulate important hypothesis on the inherent power losses and technological problems of thin film chalcogenide solar cells. The intent of this paper is to review, extend, classify and harmonise these models –in as much as it is possible– in a single, general picture.

2. ELECTRONIC DOPING

The underlying physical phenomenon that links the transport mechanisms that we are going to analyse is the so-called ‘electronic doping’ [5]. For clarity of discussion we will briefly recall its working principle. Electronic doping occurs when a high density of deep level defect changes conductivity and type behaviour of a semiconductor under illumination. This can happen when the defect level has strongly asymmetrical CCS and behaves like a trap in the dark but as a recombination centre under illumination.

We can describe this process in an n-type CdS layer (Fig. 1) as follows. If deep acceptor impurities are introduced in a quantity comparable to the shallow donor levels, in equilibrium conditions and at room temperature they will all be ionised (occupied by an electron) and the number of free carriers will be given by \( n \approx N_D - N_A \). The CdS is compensated; the effective doping will be strongly reduced or even converted to p-type. Ionised acceptors will be negatively charged; therefore it is reasonable to assume that they will have a larger CCS for holes than the subsequent CCS for electrons in the neutral state. Under illumination, the population of the defect level will be determined strongly by the CCS for electrons and holes.

Fig. 1 ‘electronic doping’ of CdS. Deep acceptor impurities are present in a quantity comparable to the shallow donor levels. In equilibrium conditions the number of free carriers will be given by \( n = N_D - N_A \). Under light injection levels such that the hole demarcation level lies below the defect level (right), most of the defect centres will become unoccupied. As a result, the total fixed charge (or the effective doping, if preferred) in the layer will increase. This will cause rearrangement of the energy bands across the junction and affect the current transport through the cell.
For the simplified case of a defect state at mid gap, the occupation $f$ of the level will in fact be given by

$$f \approx \frac{\sigma_n n + \sigma_p p}{\sigma_n n + \sigma_p p}$$  \hspace{1cm} (1)

where $\sigma_n, \sigma_p$ are the capture cross sections for electrons and holes respectively. Normally the term $\sigma_n n_0$ can be neglected in any case for high injection conditions the expression reduces to $\sigma_n n (\sigma_n n + \sigma_p p)$. Since $\sigma_p \gg \sigma_n$, most of the trap levels will be unoccupied under steady state illumination conditions. As a result, the total fixed charge (or the effective doping, if preferred) in the layer will increase, and the CdS layer will regain its original n-type behaviour. Clearly such a semiconductor as a partner in a p-n junction will have a major effect on the cell’s energy bands under illumination. It is worth noting that deep acceptor levels are a peculiar characteristics of II-VI compounds (~1.0 eV for sulphides, 0.6 eV for selenides and a ‘modest’ 0.3 eV for tellurides) [6]. Restricting our analysis to CdS, donor compensation is likely to be negligible during CdCl$_2$ treatments in Oxygen atmosphere, promoted during the cell processing steps, and in analysis to CdS, donor compensation is likely to be a ‘modest’ 0.3 eV for tellurides) [6].

### 3. CURRENT TRANSPORT ANALYSIS

Two characterisation techniques offer a suitable analysis tool that can separate and identify each of the transport mechanism occurring in the cell, and at the same time provided evidence for the discussed photoactivity of the CdS layer in chalcogenide solar cells: Apparent Quantum Efficiency (AQE) measurements and cell photocurrent gain ($g$) analysis. AQE measurements [9,1,10] have shown how secondary photocurrents can rise under blue light photoexcitation i.e. by generation of excess carriers in the first hundreds of nanometers of the device. They have the same spectral responsivity as CdS, and result in the apparent change of the device’s forward bias characteristics of the device, which results in the apparent change of the device’s photocurrent, which in turn, as a matter of fact, remains substantially constant. As far as the analysis is limited to the photovoltaic junction, we can identify two classes of light dependent current transport phenomena: light-modulated majority carrier barriers and light-dependent recombination currents.

#### 4.1 Modulated Conduction Band Spike Majority Carrier Barrier

This type of majority carrier barrier limits the diffusion component of the current at forward bias voltages above 400-600 mV, in dependence of the height of the Conduction Band (CB) spike. It is likely to form in CIS-CIGS devices [14]. It is effective as soon as the top of the CdS conduction band lies above the level of the Absorber conduction band maximum (Fig. 2). The light-modulation of the CdS decreases the barrier height, increasing the forward bias current. Given that the dominant component of the forward current in this voltage range is still given by recombination/tunnelling paths, the effect of modulation of the CB spike can be detected only at higher bias voltages (700 mV and above), and results in an apparent decrease of the series resistance under illumination. This type of barrier requires either charged interface states or that the work function of the Absorber is higher than the work function of CdS.

#### 4.2 Modulated Bulk Majority Carrier Barrier

It is a specific model that applies to CdTe solar cells, apparently after strong activation treatment. A barrier forms due to the (debated) presence of a buried homojunction and heavy compensation of the CdS layer. A Modulated Barrier Photodiode (MBP) –like barrier forms in the front region of the device and control the transport mechanism through the device, as heavily suggested by the power law dependence of the photocurrent gain of the cell [3]. The whole cell can be in first approximation described by an MBP in series with the main photovoltaic junction. When a voltage is applied to the cell only majority carriers with sufficient energy to be transported over the barrier can contribute to the forward current. The emitter of the photovoltaic junction
is floating and the potential distribution through the cell will adjust itself so that a constant current will flow through the device. As the CdS bulk barrier is lowered by light there will be an intensified thermonic emission over it, the potential will re-distribute across the device and the forward current will increase. In these conditions the superposition principle does not hold anymore and there will be crossover between dark and light IV characteristics. The internal resistance due to this majority carrier barrier, which depends on the irradiance level, is an important limiting factor for cell efficiency, inherent to the cell structure.

So far we have not yet considered the effects of recombination currents, whose magnitude is strongly affected by the photoactivity of the CdS window layer. Theory predicts, for a single level recombination at midgap in the space charge region (SCR), a total junction forward current given by

\[ J_F = J_{diode} + J_{rec} \approx \]

\[ \approx J_{o1} \left( e^{\frac{Q}{kT}} - 1 \right) + J_{o2} \left( e^{\frac{Q}{kT}} - 1 \right) \]

(2)

where in first approximation we may write the simplified expression of proportionality

\[ J_{o2} \propto q \exp \left( \frac{\phi_{off}}{kT} \right) U_{MAX} W_{mr} \]

(3)

here \( \phi_{off} \) is the effective barrier height that electrons injected form CdS need to cross before recombination, \( U_{MAX} \) is the highest recombination rate in the SCR, \( W_{mr} \) is the equivalent width of the zone of maximum recombination, which is a monotonically growing function of the depletion layer width on the absorber side \( W_{Absorber} \) and is given by \( W_{mr}=\pi k T / E_{acc} \) being the electric field at the recombination rate maximum. Expression (3) takes into account the fact that electrons can recombine only once that they are injected from the CdS window layer into the absorber (injected hole current is negligible).

Current transport through an heterojunction is generally dominated by recombination currents. Significant changes in its value would have a significant effect on the IV characteristics in the fourth and even first quadrant. This is exactly what happens under illumination. The light modulation of CdS from intrinsic to n-type has the effect of generally lowering \( \phi_{off} \) and is always increasing the extension of \( W_{Absorber} \) (Fig. 4); from equation (3) it is possible to see that both these facts increase the value of \( J_{o2} \). The ratio of \( J_{o2} / J_{o1} \) in the dark in typical chalcogenide devices is at least 10⁷. It is experimentally found that \( J_{o2} \) may vary as much as 5 orders of magnitude from 0.01 to 1 sun for CdTe [15]. This dramatic increase of \( J_{o2} \) is sufficient, in the worst cases, to induce crossover between light and dark IV characteristics. A similar behaviour can be predicted for tunnelling-recombination currents in presence of a deep donor defect level in the Absorber [13].

Fig. 3 Modulated barrier action under illumination. In forward bias, the light induced lowering of the barrier leads to an increased forward current

4.3 Light Dependent Space Charge Region Recombination

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Fig. 4 Light dependent SCR recombination. \( J_{o2} \) increases under illumination due to a) lowering of the mean effective barrier that electrons need to cross before recombination and b) extension of the depletion layer width.

4.4 Light Dependent Interface Recombination Current

In contrast to what observed so far for other current transport mechanisms, where the forward bias current increases under illumination, short wavelength radiation has the effect of reducing the interface recombination current, when present. This phenomenon can be understood with the help of Fig. 5. For any given Voltage, the following relation holds

\[ \phi_{CdS} + \phi_{Absorber} \approx \text{constant} \]

(4)

where \( \phi_{CdS} \) is the distance between the electron quasi-fermi level and the CdS conduction band maximum and \( \phi_{Absorber} \) is the distance between the hole quasi-fermi level and the Absorber valence band minimum. The largest between \( \phi_{CdS} \) and \( \phi_{Absorber} \) determines the magnitude of the interface recombination current –through its prefactor–. For small applied voltages the largest of the two is \( \phi_{Absorber} \). Because of equation (4), if \( \phi_{CdS} \) decreased the \( \phi_{Absorber} \) barrier would automatically increase and the interface recombination current would become smaller. This is what actually happens due to the electronic doping of CdS, and results in an apparent increase of the photocurrent at moderate forward bias. For larger voltages
\(\phi_{\text{Absorber}}\) will get smaller and smaller and eventually the situation reverts. The extent to which this variation of the interface recombination current influences the IV characteristics depends on the dominant recombination transport mechanism in the cell. This is the only model amongst the ones considered that is able to describe the apparent increase of the light generated photocurrent for moderate forward bias. A similar behaviour can be predicted for tunnelling-recombination currents in presence of a deep donor defect level in CdS [13].

These diverse current transport mechanisms determine the general dark-light IV characteristics pattern shown in Fig. 6. In addition to resistive effects and possible variations of the collection efficiency with applied bias voltage, the cell’s apparent photocurrent \(I_{ph}\) is affected by the light induced variations of \(J_{01}\) and \(J_{02}\). These light dependent current transport mechanisms provide a description of the general features of the dark-light IV such as their crossover, semilog behaviour and the \(\Gamma(V)\) function and its dependence on wavelength. It can be shown that processing conditions are critical in determining the dominant current transport in a cell [13].

5. CONCLUSIONS

Dark-light IV characteristics of chalcogenide solar cells are governed by electronic doping, which affects their photovoltaic performance and ultimately cell efficiency. The modulation of the CdS window layer introduces apparent gain/loss mechanisms (e.g. increase of recombination currents, decrease of series resistance) that need to be taken into account. It is the dark characteristics in the first place which result modified by the introduction of acceptors, while the 1-sun characteristics revert almost completely to that of an equal cell, but with a n-type CdS layer. Nevertheless, excessive formation of compensating acceptors in the window layer is always accompanied by (and is an indication of) indiffusion of impurities and defect formation [2,11] with the consequent degradation of cell’s performance. The interdependence between cell processing steps which are beneficial for the absorber but may degrade the window layer rises the issues of ‘protecting’ the CdS layer, searching for alternative windows layers and/or employing buffer layers. Discussing the impact of the introduction of acceptors in CdS per se is controversial, in that on one hand it is expected that it would strongly reduce minority carriers lifetime, on the other the drift field in the window layer may well compensate for the expected reduction in collection efficiency. As a ‘side’ effect, it has been experimentally observed that the acceptor states increase extrinsic photoexcitation well below the CdS band edge [12]. Direct or thermally assisted photoexcitation from/to a broad distribution of defects is the most likely explanation for a response tail that can extend more than 1 eV below the band edge of pure CdS. If indeed this were proven to be depending on impurity photovoltaic effect, II-VI materials may reveal to be a low cost alternative for ultrasensitive high efficiency photovoltaic conversion.

REFERENCES