$Cu(In,Ga)Se_2$ mesa microdiodes: study of edge recombination and behaviour under concentrated sunlight

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ABSTRACT

In order to develop photovoltaic devices with increased efficiency using less rare semiconductor materials, the concentrating approach is applied on Cu(In,Ga)Se2 thin film devices. For this purpose, Cu(In,Ga)Se2 microcells with a mesa design are fabricated. The influence of the edge recombination signal is analyzed. It is found that with an appropriate etching procedure, devices as small as 50x50 µm do not experience edge recombination efficiency limitations. Under concentration, significant Voc gains are seen, leading to an absolute efficiency increase of two points per decade.

Keywords: $Cu(In,Ga)Se_2$, thin film, mesa diodes, microcell, concentration, edge recombination

1. INTRODUCTION

In order to limit the consumption of rare material, $Cu(In,Ga)Se_2$ concentrator cell are studied. It has been shown previously that diminishing the size of $Cu(In,Ga)Se_2$ solar cells enables the use of concentrated illumination[1,2]. A specific point is studied in this paper: the role of edge recombination. Indeed if edge recombination velocity is too high, microscale CIGS devices may encounter high recombination current densities, and thus their performances could be hindered. It is known that for mono-crystalline GaAs solar cells, the device size should not be decreased under 0.1 mm²[3]. The goal of the present study is to evaluate the importance of edge recombination on $Cu(In,Ga)Se_2$ mesa diodes, and thus determine if $Cu(In,Ga)Se_2$ mesa diodes with perimeters in the tens of microns, or hundreds of micron range, have good electrical performances.

2. FABRICATION OF $CU(IN,GA)SE_2$ MESA DIODES

2.1 Fabrication of the $Cu(In,Ga)Se_2$ cells

The fabrication of $Cu(In,Ga)Se_2$ mesa diodes begins with the realization of a standard $Cu(In,Ga)Se_2$ thin film solar cell. A molybdenum layer of thickness 500 nm is deposited on a soda-lime glass substrate. Then a 2 µm thick $Cu(In,Ga)Se_2$ layer is deposited by a three-stage co-evaporation process [4,5]. A 50 nm thick CdS layer is deposited by chemical bath deposition [6], and finally a ZnO:i/ ZnO:Al bilayer is deposited by sputtering (thickness 300 nm).
Once this $Cu(In,Ga)Se_2$ substrate is completed, we process to the realization of the mesa.

2.2 Etching procedure

The mesa are obtained from the $Cu(In,Ga)Se_2$ solar cell by successive etching (Figure 1). First a lithographic step is performed to protect areas on the substrate by photoresist (step b). Then the ZnO window layer and CdS buffer layer are etched in an aqueous hydrochloric acidic solution (step c and d). The $Cu(In,Ga)Se_2$ is etched by a bromine solution (step e) [7,8]. Finally the photoresist is rinsed in acetone (step f), and the mesa can be measured directly. To ease electrical measurements, a planarization and then contacting procedure can be used (step g and h) [9].

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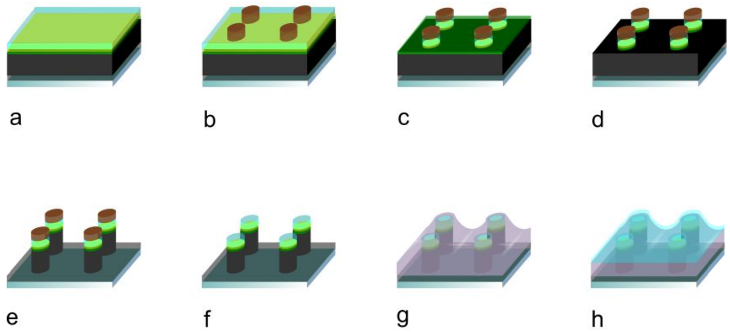

Figure 1. Fabrication process of $Cu(In,Ga)Se_2$ mesa diodes

2.3 Electrical characterization

The current-voltage characteristics of the mesas are measured both in the dark in a four point-probe configuration, and under illumination (AM1.5G illumination, Newport class AAA solar simulator) in a two point-probe configuration. We seek to determine an electrical signal coming from the edges. Indeed, we model the total recombination current $I_{01/02}$ as composed of a bulk and a perimeter component [10] :

$$I_{01/02} = J_{01/02,bulk} \times A + J_{01/02,perimeter} \times P$$

And thus

$$J_{01/02} = J_{01/02,bulk} + J_{01/02,perimeter} \times \frac{P}{A}$$

Where $J_{01/02,bulk}$ and $J_{01/02,perimeter}$ are the saturationcurrent density associated to volume recombination and to perimeter recombination respectively, A the mesa area and P its perimeter. Thus we expect to see a dependence of the diode current density with respect to the mesa geometry.

3. EFFECT OF THE MESA EDGE ON ELECTRICAL PERFORMANCES OF THE DIODES

3.1 Measurement of an electrical signal form the edges

We measure the current-voltage characteristics of the $Cu(In,Ga)Se_2$ mesa diodes, and fit the curves by a two-diode model (Figure 2 left). Then we plot the current saturation density, corresponding to an ideality factor of 2, as a function of the microcells area (Figure 2 right), as well as the open-circuit voltage under AM1.5 illumination.

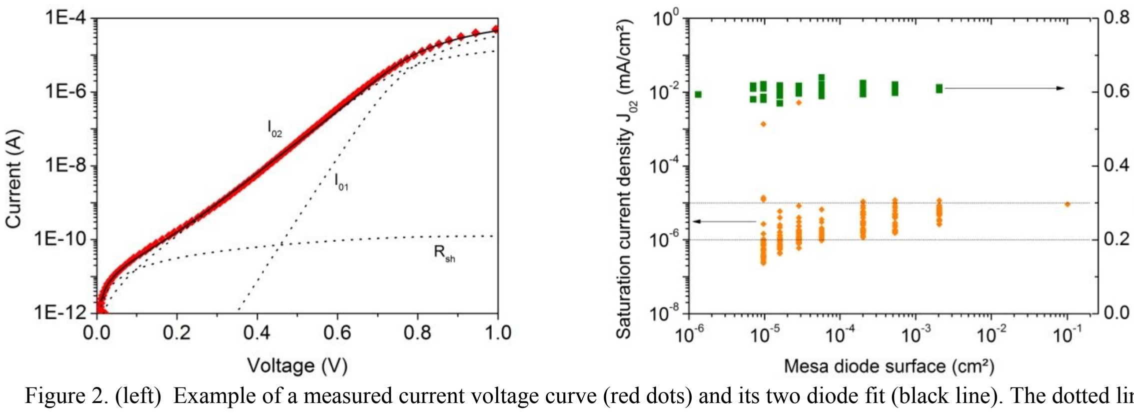

Figure 2. (left) Example of a measured current voltage curve (red dots) and its two diode fit (black line). The dotted lines correspond to the different components of the fitting equation (right) Saturation current density J02 and Open circuit voltage under AM1.5G illumination as a function of the $Cu(In,Ga)Se_2$ mesa diode area.

We can see that the saturation current densities, evaluated from dark measurements, are almost constant for mesa between 10^{-5} and 10^{-1} cm². It could be seen that the value even tends to decrease slightly for very small devices. The opposite behavior would be expected if a significant contribution to the recombination current was given by the edges, as the ratio perimeter/area is bigger for smaller devices. Thus, we can conclude that edge recombination effect is negligible on our devices. This indicates that bromine etches result in well passivated surfaces. As a consequence of this independence of dark currents on the mesa area, the open-circuit voltage is also constant (Figure 2).

3.2 Degradation of the surface

In complement to the experiment described before, we intentionally degraded the Cu(In,Ga)Se_2 surfaces by proceeding to a peroxide treatment, to see if the edge current become measurable. The sample is immersed in a aqueous peroxide solution for 1 mn and measured again afterwards. We observed a signal coming from the perimeter, as it is more intense of the smallest mesa. This signal is mainly a shunt current, as can be observed in Si microdiodes [11]. This behavior is logical as peroxide etches are known to degrade Cu(In,Ga)Se_2 surface and form some metallic phases (indium and selenium for example), which could explain the apparition of shunt current [12].

4. CONCLUSION

We have fabricated Cu(In,Ga)Se2 microcells with a mesa design. The influence of the edge recombination was studied and is found very weak for Cu(In,Ga)Se_2 solar cells. Indeed it is found that with an appropriate etching procedure, devices as small as 50x50 µm do not experience edge recombination efficiency limitations. Under concentration, significant Voc gains are seen, leading to an absolute efficiency increase of two points per decade.

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