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# Cu(In,Ga)Se<sub>2</sub> mesa diodes for the study of edge recombination

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#### ABSTRACT

The concentrating approach was applied on Cu(In,Ga)Se<sub>2</sub> to develop photovoltaic devices with increased efficiency using less rare materials. To withstand the operating conditions, Cu(In,Ga)Se<sub>2</sub> devices are miniaturized. Compared to previous generations of microcells, with only window layer structuration, microcells with a mesa design are fabricated. These microcells are created by etching ZnO, CdS and Cu(In,Ga)Se<sub>2</sub> layers. The crucial issue addressed in this study is the electrical behavior of the device edges, to determine if microcells suffer from perimeter recombination.

We analyze the influence of different etching techniques on the edge recombination signal. It is found that bromine etch result in well passivated surfaces, and devices as small as  $50 \times 50 \,\mu\text{m}$  do not experience edge recombination efficiency limitations. This behavior is remarkable compared to that of the microcells made of crystalline materials. For devices where the edges are deteriorated by a chemical post-treatment, a quasi-shunting signal coming from the edges is seen. We tested these microcells under concentrated illumination and important open-circuit voltage and efficiency gains are seen.

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# 1. Introduction

Cu(In,Ga)Se<sub>2</sub> has proven to be very efficient as a solar cell absorber, with over 20% efficiency reached recently [1,2]. By creating pixels on a Cu(In,Ga)Se<sub>2</sub> substrate, we were able to test electrically different locations, and have a feedback on the spatial homogeneity of the Cu(In, Ga)Se<sub>2</sub> cells [3]. Moreover due to the reduced size of the cells, (5 to 500 µm wide), the heat and spreading resistance losses are made negligible, making high flux characterizations available [4,5]. We analyze the current-voltage curve under high concentrations to gain insight in the physical properties of Cu(In,Ga)Se<sub>2</sub> cells. By using mesa architecture we can also access elements concerning the electrical behavior of etched sidewall surfaces, and see the influence of different chemical treatments on the surface on the recombination velocity. Cu(In,Ga) Se<sub>2</sub> mesa cells have already been used in previous studies, either by top contact etching [6] or etching of the whole stack [7], but the edge recombination was not studied in details. This information is very important in the perspective of device development of Cu(In. Ga)Se<sub>2</sub> microcells, to determine if mesa microcells suffer from perimeter recombination, which are known to be limiting for III-V crystalline microcells.

#### 2. Fabrication of mesa diode

#### 2.1. Overview of the process

In order to create mesa Cu(In,Ga)Se<sub>2</sub> solar cells, the process is as follows. A standard Cu(In,Ga)Se<sub>2</sub> solar cell is created. For this study we use solely co-evaporated substrates. We proceed to a first photolithographic step (AZ® 5214 photoresist, AZ Electronics Materials). An array of photoresist blocks is thus created on the cell surface. Then the front window is etched with a hydrochloric acidic solution. Both ZnO and CdS are etched due to the low pH of the solution. Then the Cu(In,Ga)Se<sub>2</sub> layer is chemically etched. Two different solutions are studied for wet etching. Then the photoresist is dissolved in acetone. As such the micro-block solar cells can be tested with a probe on the top of the cell, and a contact on the Mo back substrate. However it can be interesting to contact the micromesa by a peripheral metallic contact, and a contacting procedure has been developed (Fig. 2).

# 2.2. Chemical etching

The first solution used for chemical etching is a KBr/Br<sub>2</sub> aqueous solution, with 4  $10^{-2}$  mol.L<sup>-1</sup> of Br<sub>2</sub> and 1 mol.L<sup>-1</sup> of KBr. As we are processing on complete solar cells, the pH of the solution has to be quasi-neutral to prevent the etch of both ZnO and CdS layers, during







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Fig. 1. (a) Scanning electron microscope (SEM) image of a microcell edge after etch: the edge is not vertical and the incline sidewalls are 1 to 2 µm wide. (b) SEM image of a microcell where CIGS has been sufficiently etched to have a ZnO overhang.

the etch of the 2 to 3  $\mu$ m Cu(In,Ga)Se<sub>2</sub> layer. The pH is thus adjusted around 7 with the addition of KOH. The solution preparation was done in collaboration with the Institut Lavoisier de Versailles.

The second solution, used for comparison is a KBr/H<sub>2</sub>SO<sub>4</sub>/H<sub>2</sub>O<sub>2</sub>/KOH aqueous solution. An acidic KBr solution is oxidated by hydrogen peroxide, in order to form  $Br_2$  in-situ. Then the pH is adjusted around 7 by the addition of KOH.

The etching of Cu(In,Ga)Se<sub>2</sub> is not isotropic, thus we have sidewalls that are inclined, with a slope over 1  $\mu$ m in length (Fig. 1a). Depending on the respective etching time of Cu(In,Ga)Se<sub>2</sub> and of the window layer, we can obtain two types of samples: samples with bare Cu(In,Ga)Se<sub>2</sub> at the edge (Fig. 1a), and mesas with a ZnO:Al overhang (Fig. 1b). If not mentioned, the studied mesas are of the first type.

#### 2.3. Contacting microcells

With the two etching procedures we can create mesa diode solar cells. We can measure them by contacting the Mo back contact and ZnO:Al window layers with micro-probes. If this technique is satisfactory for dark characterization, we need to have a better connection if we want to measure the devices under illumination. Indeed the probe placed on the ZnO:Al will cause an important shading, especially for the smallest devices.

We developed procedures for contacting the mesa diodes. The simplest one, noted  $(a \rightarrow b \rightarrow c)$  contacts all the cells through an insulation with a polymer (an epoxy based photoresist) that lets the top of the

micro-block unprotected and a subsequent ZnO:Al deposition on the whole substrate that connects all the micro-block surfaces. If a metallic peripheral contact is needed, lithography is done to protect the top of the micro-blocks from the deposition of a metallic layer. Then ZnO:Al is deposited on the whole substrate.

# 3. Characterization of mesa diodes

#### 3.1. Theory

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 [8]:

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

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



**Fig. 2.** (Left) contacting process. Two different processes ( $a \rightarrow b \rightarrow c$  and  $a \rightarrow b \rightarrow d \rightarrow e \rightarrow f$ ) can be done depending on the need for a metallic layer. In step b a polymer is deposited to planarize the sample after etching and prevent shunts. In step c a ZnO layer is sputtered to contact the cells. In step d the mesas are protected for metal deposition in step e before ZnO:Al sputtering in step f. (Right) optical images of a sample at the end of the two processes. The squares are  $1 \times 1 \text{ mm}^2$ .



Fig. 3. (Upper)  $J_{01}$  and  $J_{02}$  as a function of micromesa area, on contacted mesa diodes, etched in KBr/Br<sub>2</sub>. (Lower) the series and the shunt resistance as a function of micromesa area.

#### 3.2. Dark measurements

We measure the mesa diodes obtained from a KBr/Br<sub>2</sub> etching solution. We can see that the saturation current  $J_{02}$  of ideality 2 is predominant. It is comprised between  $10^{-5}$  and  $10^{-6}$  mA/cm<sup>2</sup>. The saturation current  $J_{02}$  is comprised between  $10^{-10}$  and  $10^{-15}$  mA/cm<sup>2</sup> (Fig. 3). If we look at the series and shunt resistances, we can see that they are roughly proportional to the cell surface, i.e. the value in ohm cm<sup>2</sup> is roughly constant. The area/perimeter ratio at which edge recombination equals bulk recombination is less than 10 µm, which is much less

than that for crystalline Si or GaAs microcells [9,10]. In other words, no edge signal can be measured down to devices of  $10^{-5}$  cm<sup>2</sup>. This means that mesa diode sidewalls have a low recombination velocity, and they influence poorly the overall devices.

The mesa diodes obtained from  $KBr/H_2O_2$  solution have poor electrical response, which may be due to the effect of hydrogen peroxide on  $Cu(In,Ga)Se_2$  surfaces [11]. In order to gain more information, we proceed to a hydrogen peroxide treatment after a  $KBr/Br_2$  etch, by immersion of a sample for 1 min in a hydrogen peroxide solution.

As expected we can see an edge effect at low voltage (Fig. 4). A leakage component is seen at low bias. For the smaller cells, 50  $\mu$ m diameter, this leakage current coming from the edge becomes predominant over the diode current over a large voltage range. Thus we can confirm the degradation of Cu(In,Ga)Se<sub>2</sub> surfaces with the use of hydrogen peroxide. It should be noted that the  $J_{02}$  current density, measurable at higher bias is unchanged by the surface treatment. This observation was earlier mentioned in the literature [11]. Thus mesa microdiodes are a useful tool to probe the behavior of Cu(In,Ga)Se<sub>2</sub> surfaces electrically and see the influence of sidewall surface on a mesa device.

#### 3.3. Behavior under concentration

With an adapted metallic electrical contact, the microscale mesa diodes can also be tested under concentrated illumination, using a laser. The values of efficiencies take into account the spectral mismatch between a laser probe and a normal solar spectrum [12]. In (Fig. 5), we can see a classical behavior under concentration, with an increase of the Voc with respect to the logarithm of the concentration ratio, which is the reason for the increase of the efficiencies [13]. These efficiencies have a maximum at a relatively high concentration ratio, which shows the low resistivity of our samples, and the good quality of the contacts. For the bigger mesa however (250 µm diameter), the efficiency saturates earlier due to higher spreading resistance losses [4,5]. A maximum open-circuit voltage (Voc) of 953 mV under concentration is obtained at 1650 suns on a 25 µm mesa microcell. It should be noted that the saturation of Voc at high concentration is due to an increase in the device temperature [13]. It can also been seen that for shunted device the concentration help the recovery of normal Voc and efficiency values (140 µm mesa in Fig. 5).

We can thus see that mesa microdiodes can be good devices for concentrator cells. The electric characterization of the global mesa diodes shows that edges do not have a strong influence on the device. In order to gain more insight on the sidewall influence, we proceed to the local characterization of the edge by light beam induced current (LBIC), photoluminescence (PL) or electron beam induced current (EBIC).



Fig. 4. (Upper) IV curve before and after peroxide treatment for a square microcell with 300 µm edge. (Lower) Same for a square microcell with 50 µm edge.



Fig. 5. (Left) Voc as a function of concentration of test under 532 nm laser, the dimensions given correspond to the diameter of the mesa diodes. (Right) efficiency as a function of concentration for the same mesa diodes.

#### 4. Local characterization

# 4.1. LBIC measurement

A LBIC measurement is performed with a 532 nm laser beam. The laser spot is around 1 µm in diameter. The mesadiodes tested are diodes that are not contacted, but they are individually microwelded for the measure. Thus we can measure the behavior of the edge just after the wet etch, prior to any post-treatments, or further process steps. In Fig. 6 we can observe that the slope of the LBIC at the edge of the sample is very steep, indicating low recombination. We can fit the signal by a simple model to estimate both the diffusion length *L* and the product of surface recombination *S* by the lifetime  $\tau$  [9]. We find a diffusion length of 0.9  $\mu$ m and,  $S \times \tau$  of 0.83  $\mu$ m. The value of  $S \times \tau$  is maximum, indeed the slope of the signal is convoluted with the laser spot diameter, thus the actual slope could be even steeper, and thus  $S \times \tau$  is smaller. If we estimate  $\tau$  to be around 6 ns, than we have  $S < 1.3 \ 10^4 \text{ cm/s}$ , which is rather low, and in the order of what is found for grain boundary recombination velocity [14]. It should be noted that the LBIC signal is near zero in the first 5 µm of the mesa, where the ZnO:Al was etched (see Fig. 1a). Preliminary EBIC measurements, realized on the edge of these mesa diodes (in the portion where ZnO was etched away) also show a steep slope, with a maximum collection reached at 1 µm from the edge, confirming this good passivation of the surfaces.

In order to complete these measurements we recorded photoluminescence cartographies measurements.



Fig. 6. LBIC measurements with 532 nm laser. The orange points are the experimental data and the dotted lines correspond to the fit. Fit with L = 900 nm,  $S \times \tau = 8.3 \cdot 10^{-1}$  µm.

#### 4.2. Luminescence cartographies

PL spectra cartographies of mesa diodes are measured. We are using a confocal microscope with a 532 nm laser. In Fig. 7a and b we have respectively the PL intensity and optical image of a mesa diode, which is 100 µm wide. The PL intensity cartography is obtained by integrating at each position the PL spectrum between 900 and 1100 nm. We can see that the PL intensity on the mesa is high but negligible on the ZnO overhang.

In Fig. 7c, we plot the PL intensity profile integrated between x = 0 and  $x = 20 \mu m$ . We can see a steep increase of the signal at the device edge. The signal goes from minimum to maximum at about 3  $\mu m$ , confirming the good passivation of the edges (indeed this slope is convoluted with the laser spot diameter which is around 2  $\mu m$  in this



**Fig. 7.** (a) PL intensity cartography using a confocal microscope and a 532 nm laser. Intensity is determined by integration of the signal between 900 and 1100 nm. (b) In inset an image from optical microscope of the device. The ZnO overhand is visible. (c) A profile of the PL intensity of graph (a) integrated between x = 0 and  $x = 20 \,\mu\text{m}$ .

setup). The slope of the PL intensity at the device edge is very similar with samples having bare Cu(In,Ga)Se<sub>2</sub> at the edge. Indeed, we detect on those samples nearly no PL emission on bare Cu(In,Ga)Se<sub>2</sub> and a strong signal on the Cu(In,Ga)Se<sub>2</sub>/CdS/ZnO regions. This fact is often reported in the literature and indicates that the surface of Cu(In,Ga)Se<sub>2</sub> is passivated by the CdS layer.

### 5. Discussion

We can see either from global electrical measurements or local characterization that the different Cu(In,Ga)Se<sub>2</sub> mesa diodes fabricated have very passivated surfaces.

With current voltage measurements on the device we have seen that we cannot detect a recombination current proportional with the mesa perimeter down to devices of  $5 \ 10^{-5} \text{ cm}^2$ . The light measurement confirms this fact as the open-circuit voltage is found independent of the mesa area. Tests under concentration showed that the mesa diodes have a standard concentrator cell behavior with open-circuit voltage and efficiency increase over up to three concentration decades.

The devices studied for global current voltage measurement presented a narrow region of bare  $Cu(In,Ga)Se_2$  absorber at the edges due to the ZnO under etch. Thus we could wonder if this bare  $Cu(In,Ga)Se_2$ region does not act as a passivation layer. Thus we proceed to PL measurement on both type of devices and the PL signal at the edges show comparable increase, indicated a similar recombination behavior of the edges.

Thus the KBr/Br<sub>2</sub> bromine etch seems an appropriate microstructuration solution for  $Cu(In,Ga)Se_2$  mesa. This is coherent with previous studies that show  $Cu(In,Ga)Se_2$  cells with absorber thinned in this bromine solution showed good efficiencies [15,16]. Indeed this chemical etch keeps the surface stoichiometry intact during etching, avoiding the formation of highly defective compound on the surface. On the contrary we have seen that a hydrogen peroxyde treatment has a strong influence on the surface, leading a shunting behavior.

In summary, we can see that only a region at 1 to 2  $\mu$ m from the device edges is influenced by the sidewall surfaces. Thus Cu(In,Ga)Se<sub>2</sub> microdevices can be equivalent to their large area counterparts in terms of efficiency, which is not the case for III–V microcells [10,17]. This may arise from the fact that the relatively low diffusion lengths in Cu(In,Ga)Se<sub>2</sub> (around 1  $\mu$ m) prevents the edges from deteriorating much the microdevices performance.

# 6. Conclusions

We fabricated Cu(In,Ga)Se<sub>2</sub> mesa microdiodes by chemical etching. We have shown that these devices can be good concentrator cells, with on average an absolute 2% efficiency increase per concentration decade up to around 1000 suns, and record open circuit voltages obtained over 950 mV. Our study shows that Cu(In,Ga)Se<sub>2</sub> sidewall surfaces are naturally well passivated by the chemical etch in KBr/Br<sub>2</sub> bromine solution. Further studies will look more closely on the transport properties at the Cu(In,Ga)Se<sub>2</sub> surfaces to determine more precisely the recombination velocity.

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