Local Photocurrent Mapping and Cell Performance Behavior in a nm-Scale for Monolithically Interconnected Cu(In,Ga)Se$_2$ Solar Cells

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Summary

The local efficiency of lamellar shaped Cu(In,Ga)Se$_2$ solar cells has been investigated using scanning near-field optical microscopy (SNOM). Topographic and photocurrent measurements have been performed simultaneously with a 100nm tip aperture. The lamellar shaped solar cell with monolithic interconnects (P-scribe) has been investigated in a nanometer scale for the first time at different regions using SNOM. It was found that, the cell region between P1 and P2 significantly contribute to the solar cells overall photocurrent generation. The photocurrent produced depends locally on the sample topography and it is concluded that it is mainly due to roughness changes of the ZnO:Al/i-ZnO top electrode. Regions lying under large grains of ZnO produce significantly less current than regions under small granules. The observed photocurrent features were allocated primarily to the ZnO:Al/i-ZnO top electrode. They were found to be independent of the wavelength of the light used (532nm and 633nm).

Introduction

The world need for energy is greatly increasing. Therefore, finding new alternatives to break dependence on fossil fuels is indispensable. Due to its potential as a clean and renewable energy, solar energy is considered as a valuable substitute. The design and fabrication of highly efficient photovoltaic devices has an increasing importance.

With a 22,6% conversion efficiency (Press release, Centre for Solar Energy and Hydrogen Research Baden-Württemberg, Germany) Cu(In,Ga)Se_2 (CIGSe) solar cells are promising and inexpensive devices. Nevertheless, there are basic questions related to CIGSe research that are intensely debated such as grain boundaries (Rau *et al*, 2009) and presence of defects (Igalson *et al*, 2009) in correspondence to the general function and efficiency of CIGSe solar cells and devices.

Various surface-analysis techniques including transmission electron microscopy (Wada *et al*, 1996), atomic force microscopy and X-ray microscopy (Lim *et al*, 2012) have been used to study the morphology of solar cells. However, these methods suffer from a lack of direct information about the effect of the nanoscale features of the device. Modified techniques have been also used to characterize the efficiency and the morphological and topographic properties of solar cells, e.g. Photoluminescence and electroluminescence (Lavrenko *et al*, 2012), scanning Kelvin-probe microscopy to measuring the local open circuit voltages with sub 100nm resolution (Li *et al*, 2012), photocondutive AFM to mapping the local photocurrent in organic solar cells (Li *et al*, 2012; Coffey *et al*, 2007). Whereas in near-field cathodoluminescence, electron beam microscopy is combined with optical microscopy (Yoon *et al*, 2013). Another method for mapping the local photocurrent is scanning near-field optical microscopy (SNOM) (Neil *et al*, 2004; Gu *et al,* 2005; Gu *et al*, 2006; Mueller *et al*, 2009).

SNOM is a powerful technique (Hecht *et al*, 2000) that combines the potentials of both, scanning probe microscopy and optical microscopy. SNOM implies scanning of a probe, usually a tapered optical fiber, across a sample leading to the illumination of a sub-wavelength area lying under the probe aperture. The sample is always illuminated in the region of the evanescent field by keeping the tip at less than 10nm distance from the surface. This allows the investigation of optical properties of the surface with an optical resolution better than the diffraction limit of the incident light. Thus, two dimensional maps of optical and topographic properties can be simultaneously obtained. Other properties of the surface, such as absorption, fluorescence and reflection, can be studied by operating SNOM in different detection configurations (Girard, 2005; Andrae *et al*, 2015). In the case of solar cells, SNOM can be similarly used to map the local distribution of photocurrent (Rouis *et al*, 2016). The evanescent field at the fiber tip apex is coupled to the top electrode and converted to a propagating optical field. Thus the light can reach the buried active layer and locally produces photocurrent. This technique is called scanning near-field photocurrent microscopy (SNPM).

Experiment

A home-built SNPM was used to measure the topography and the photocurrent of the samples. Modulated monochromatic light (λ=532nm or 633nm) is injected into a single-mode optical fiber, which is tapered at the extremity to form a cone-like shaped tip (tips from LovaLite, Besançon, France). Tips are coated with aluminum, leaving a nanometric aperture at the end playing the role of a "nanosource" of light (100 nm aperture). The tip is firmly glued onto a tuning-fork. The local photocurrent generated by the sample when illuminated through the tip aperture is detected with a lock-in amplifier (Princeton Applied Research, Oak Ridge, TN, USA). The topographic information is measured with a second lock-in amplifier (Signal Recovery, Oak Ridge, TN, USA) by detecting the shear-forces, resulting from the interactions between the tip and the sample surface, *via* a tuning-fork feedback system.

The sample is based on a monolithic interconnected Cu(In,Ga)Se_2 solar cell (P-scribe technique (Hermann *et al*, 2006)). The layer-structure of a typical sample is ZnO:Al/i-ZnO/CdS/CIGSe/Mo/Glass. An intrinsic *p*-type CIGSe layer (2µm) was deposited onto a molybdenum coated soda-lime glass in a multi-stage co-evaporation process with a Cu-rich phase during film growth (Kaufmann *et al*, 2005), followed by deposition of two buffer layers of cadmium sulfide (CdS) (50 nm) and intrinsic zinc oxide (i-ZnO) (100nm). Finally, a layer (*n*-type) of ZnO:Al (800nm) was deposited as front contact. The cell performance was analyzed before SNPM measurements with a sun simulator (WACOM sun simulator, standard test conditions, AM 1.5). The CIGSe material used for the experiments shows an averaged active area based efficiency of 14.5±0.1% when using the monolithical contacts. The monolithic interconnect was established by structuring single cells with a P1, P2 and P3 scribe-based patterning technique. The lateral cell dimension was reduced stepwise from 1900 to 200 µm (Reinhold *et al*, 2015). The geometry of the sample is shown in Figure 1(a). The interconnection zone includes three patterning structures, named as P1-scribe, P2-scribe and P3-scribe, by first dividing the molybdenum back contact with a P1-scribe, followed by a P2-scribe into the Cu(In,Ga)Se2 layer and finally a P3-scribe, that separates the front-contact between two cells (Reinhold *et al*, 2015). The different regions investigated are marked on Figure 1(a) by "micro-cell" and by the numbers "1, 2, 3, 4 and 5".

Results and discussion

Investigation of the P-scribes

In order to define the spatial resolution of our SNPM, we made a comparison between topographic images obtained by SNPM and by scanning electron microscopy (SEM) (Figure 2). The topographic image in Figure 1(a) shows that the surface of the sample is constituted of small granules of sizes~100–150nm which defines the limit of resolution of our SNPM. Deep crevices are observable between the large grains of the ZnO:Al top layer. In some regions, the small granules form large conglomerates of ~2µm size. The same topographic feature is observed in the SEM micrograph [Figure 2(b)]. However, the SEM picture reveals that the grain size varies from ~50 to 200nm. The difference observed between both topographic analyses is explained by the well-known convolution of sample features with the tip geometry inherently present when performing SNOM (Klapetek *et al*, 2011).

To track changes in the micro-cell performance through the different patterning regions P1, P2 and P3, we performed spatial resolved photocurrent measurements (@ λ=532 nm) in different positions of the monolithic interconnected solar cell from the cell center to the structuring zone, as shown in Figure 1(a). The cell center (micro-cell) will be discussed below in Figure 4. The photocurrent maps (Figure 3) reveal that the average photocurrent value decreases as we get far from the micro cell toward the P3-scribe. Figure 3(a) & (f) correspond to the position 1 from Figure 1(a) (middle of the P1-scribe). They show the same behavior of the local photocurrent as observed on the micro-cell [Figure 4, position "micro-cell" in Figure 1(a)] despite the absence of the Mo back contact underneath, i.e. the photocurrent is higher in regions containing small aggregates than in regions containing large aggregates. However, the highest value of the photocurrent (~35 nA) is lower than that in Figure 4. This can be explained by the fact that the distance travelled by the charge carriers becomes longer. In fact the photocurrent, in this geometry, is collected by the part of Mo-back contact situated to the left of P1-scribe. Thus some are lost before being collected. At the edge of the P1-scribe [position 2, Figure 1(a)], the behavior of the photocurrent appears to be the same at both sides of the edge [Figure 3(b) & (g)]. The highest value of photocurrent (~50 nA) is slightly higher than that obtained at position 1. In addition, at the very edge of the P1-scribe, the photocurrent is unexpectedly higher. This might be due to local increase of the amount of scattered light at the edge, leading to local enhancement of light absorption by the solar cell. Moving to the position 3, edge of the P2-scribe, the value of the photocurrent drops drastically and becomes negligible in comparison to the micro-cell [Figure 3(c) & (h)] because this position is laterally far from the back contact and the charge carriers are probably mostly lost before they could be collected. The right side of Figure 3(h) (limit of P2-scribe) exhibits higher current (~0.4 nA) than the left side (~0.2 nA). The ZnO:Al/i-ZnO layer at this zone is relatively thinner due to curvature induced by the absence of CIGSe underneath. Hence, a higher amount of light can reach the (buried) p-n junction leading to more photo-generated current. The photocurrent behavior in the middle of P2-scribe [Position 4, Figure 1(a)] becomes totally different from that observed on the micro-cell. Figure 3(d) & (i) show that regions containing large aggregates contribute to the photocurrent more than regions containing small aggregates. At this area from the sample (P2-scribe), no CIGSe is beneath the ZnO:Al/i-ZnO top electrode. The light passing through the small aggregates does not contribute to producing current and is “wasted”. However, big aggregates can scatter the light into different directions [Figure 1(b)]. The scattered light can then reach the active area, which can lead to an augmentation of the photocurrent. Finally at the edge of P3-scribe [Position 5, Figure 1(a)], we observe photocurrent on the part where the solar cell is, while the part of the scribe where no other materials exist than molybdenum produces no current [Figure 3(e) & (j)].

The P1-scribe separates the Mo back contact in two parts. This means that the charge carriers are generated, at the part of the cell to the left of the P1-scribe in Figure 1(a), and one would assume in a first idea that no current would be collected by the back electrode situated to the right. The measurements depicted in Figure 3 show that the photocurrent at the different positions of the patterned sample (P1, P2, P3 scribes) is lower than the photocurrent produced by the micro-cell, but not zero. This proofs that this part of cell still contributes also to the overall photocurrent.

Investigation of the micro-cell

In Figure 4, an example of topography (a) and photocurrent (b) of a 5×5μm^2 region is shown. A clear variation of the generated photocurrent can be noticed. The regions of the active layer, that are lying under large grains of ZnO:Al, on the left and bottom of the topography image, appear to produce less current than other regions. This is confirmed by the line-scan analysis [Figure 4(c)] taken from topography and photocurrent maps (horizontal white line), respectively. The photocurrent profile indicates a variation in the local photo-response of the device that can be attributed in the topography to grains of different size and height. From the topographic profile, a height of the large grains of ZnO:Al of about 50-60nm can be derived while the size of the small grains amounts to about 10-20nm. The regions under largest particles contribute, with 70 nA, significantly less to the photo-response than the regions under the small ones, with 100-120nA.

These observations may be attributed to local variation of the electrical properties (conductivity, resistivity) of the top electrode that might happen due to the local variation of its thickness. However, we consider that the lateral resistivity of ZnO:Al films does not locally depend on the thickness. We can assume that the total lateral resistance is R+R1 (R1 corresponds to the illumination area and R to the distance from the illumination area to the electrode), R will be far larger than R1 (R>>R1), therefore the local resistance of ZnO:Al will not influence the total resistance.

These observations may also be attributed to a local variation of the optical properties (absorption, transmission) of the ZnO:Al layer that might happen due to the local variation of its thickness. According to McDaniel et *al*. (1997), our observation could be explained by the fact that light coming from the SNOM aperture diffracts somewhat before it reaches the active area, i.e. the buried p-n junction. Also, the reduction in the photo-response could be due to higher recombination velocities at the grain boundaries. Because SNPM is a surface sensitive technique, the observed topographic features are mainly attributed to the surface of the device, which is the ZnO:Al top electrode. It is sufficiently thick (~800nm) to completely equalize the topographic details of the CIGSe/CdS layer. The topography images show the morphology of the ZnO:Al surface. The observed behavior of the photocurrent could be due to local changes of the ZnO:Al optical properties. Shi et *al*. (2010) studied the influence of the film thickness, among other parameters, on the electrical and optical properties of layered films of ZnO:Al/i-ZnO for the application of CIGSe solar cells. They showed that a variation of the thickness of the ZnO:Al/i-ZnO results in a variation of the transmission, which can translate to a variation in generated photocurrent.

The topography images show that the surface is not uniform, but contains topography changes due to the presence of grains of different sizes and heights. This means that the thickness of the ZnO:Al/i-ZnO layer changes locally, leading to local variations of its optical properties. After Shi et *al*. (2010), a variation of the thickness of the ZnO:Al/i-ZnO with $\Delta t \sim 50$nm involves a variation of the transmission $\Delta T \sim 10\%$. This analysis is in accordance with Shi et *al*. (2010) and might explain the observed behavior of the photocurrent in this experiment (Figure 4).

The photocurrent features appear to be independent of a slight variation in wavelength of the light used. We show in the Figure 5 two measurements made on the same region with two different wavelengths, 532nm in (a)-(b) and 633nm in (c)-(d). Note that the second measurement, Figure 5(c)-(d), is slightly shifted to the left in comparison to the first measurement. The photocurrent value is higher for the 633 nm wavelength. This can be attributed to change of the intensity of light at the tip aperture when changing the laser wavelength. The photocurrent maps highlight generally the same features as compared, for example, between the zones marked 1-to-4 and 1'-to-4'. Less photocurrent is generated in the regions under large grains while it increases considerably in regions under small particles.

Conclusion

In conclusion, we have used SNPM to investigate the local photocurrent of monolithically interconnected Cu(In,Ga)Se_2 solar cells with a tip aperture 100 nm under monochromatic light illumination. Simultaneous measurements of the topography and the photocurrent produced by the sample have been performed. The investigation of different regions of the P-scribe based interconnection zone showed diverse properties in the photocurrent generation that is investigated in a nanometer scale for the first time. It was found that, the cell region between P1 and P2 significantly contributes to the solar cells photocurrent generation. We showed that the different positions of the patterned sample (P1, P2, P3 scribes) contribute also to the overall photocurrent. The photo-response of the device is significantly lower under the regions that contain large grains of ZnO:Al/i-ZnO, while the regions containing smaller particles exhibit larger photo-response. The behavior of the photo-response was the same for the two different wavelengths (532nm and 633nm) used in this experiment. This work is complementary with the work of McDaniel et al (1997). We linked the observed photocurrent local behavior to the change of the local optical properties of the top electrode, as we attribute the observed topography mainly to the sample surface. In addition, we introduced for the first time spatial resolved measurements of the photocurrent of micro-structured (P-scribe technique) CIGSe solar cells.

This spatially resolved photocurrent measurements revealed the different activity at the boundary areas. Future optimizations of such type of solar cells should take it into account.

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