Imaging EQE in CIGS solar cells with high spatial resolution

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\textbf{Abstract} — We use sub-micron scanning photocurrent microscopy to spatially resolve variations in the collection properties of CIGS thin-film solar cells made from a quaternary target. Spectrally dependent photocurrent measurements show remarkable variations in the current collection properties of the grain boundaries and grain cores. We combine EQE maps with Raman and EBSD scans to infer a direct correlation between the electrical and structural properties of the material comprising these polycrystalline devices.

\textbf{Index Terms} — solar energy, thin-film, CIGS, scanning probe microscopy, optoelectronic properties.

I. INTRODUCTION

CIGS-based solar cells have recently attracted a lot of interest as a marketable PV technology: they have high optical absorption (active layers \(\approx 2\ \mu m\)), potential low cost/W installation [1], compatible with flexible substrates, and respond well under concentrated illumination [2]. Further, the bandgap of the CIGS layer depends on the Ga content, and varies between 1.02 and 1.68 eV, allowing for bandgap engineering for multijunction designs [3]. To date, the best CIGS single-junction solar cells are formed by a three-stage co-evaporation process with an In-rich surface termination, with efficiency of 21.7 \(\pm\) 0.7 \% and \(V_{oc}\) = 0.796 V [4].

Here, we probe the collection properties of CIGS solar cells fabricated using a quaternary target to deposit the active layer, which consistently produces polycrystalline, highly oriented grains with controlled stoichiometry, and bandgap of 1.10-1.20 eV [5], [6]. This one-step method has the following advantages: the CIGS layer is obtained without requiring a post-deposition selenization [7], and it permits uniform deposition over large areas (modules), representing a potential cost reduction of the technology. Briefly, soda lime glass coated with 500 nm of Mo is used as the substrate. CIGS films with 2 \(\mu m\) in thickness are deposited by radio frequency (RF) magnetron sputtering. A 50 nm thick CdS \(n\)-layer is deposited by chemical bath deposition, 50 nm ZnO is added to increase shunt resistance, and 200 nm of Al\(_2\)O\(_3\)-ZnO (transparent conductive oxide - TCO) can be easily deposited with sputtering depending on the type of measurements we would perform (Fig 1(a)). The grains comprising the CIGS solar cells are \(\approx 1\ \mu m\) in size (Fig 1(b)), and the fabricated CIGS devices have an average efficiency of 10\% (Fig 1(c)). The external quantum efficiency (EQE), Fig 1(d), is greater than 80\%, but decreases rapidly for wavelengths (\(\lambda\)) < 600 nm. Although it is well known that a thinner CdS layer can improve the EQE of the devices [8], it is still unclear how the different interfaces within the material layer affect the collection of the carriers within the device.

Fig. 1 (a) Schematic of CIGS/CdS device. (b) SEM of CIGS grains. (c) Light J-V under AM 1.5 global illumination for the best device fabricated. \(V_{oc}\) = 489 mV, \(J_{sc}\) = 33.8 mA/cm\(^2\), \(FF\) = 64.3\%, and \(\eta\) = 10.6\%. (d) EQE of the same device.
Several characterization techniques have been combined to investigate the structural, optical, and electrical properties of polycrystalline materials [9], [10], [11]. In particular, scanning probe microscopy techniques have been used to aid explaining the potential beneficial role of the grain boundaries in polycrystalline PV materials [12], [13], [14]. Despite the remarkable progress achieved in the field, measurements of the local electrical properties of in operando CIGS devices are still missing. Here, we spatially resolve and quantify the charge collection characteristics of the CIGS grains by resolving the EQE of the device with sub-micron spatial resolution through spectrally dependent scanning photocurrent microscopy. Further, we correlate these measurements with the local structural properties of the different grains composing the absorber layer of thin-film solar cells, through Raman and electron back scattering diffraction (EBSD) measurements.

II. MEASURING LOCAL EQE BY SCANNING PHOTOCURRENT MICROSCOPY WITH SUB-MICRON SPATIAL RESOLUTION

The photocurrent scans were performed on the CIGS solar cells using 50x objective and a piezo scanning stage with 100 x 100 µm² range. The measurements were performed using a supercontinuum laser as the excitation source, with tunable wavelength, at room temperature. Confocal images were acquired in the same area for comparison between the morphology and the photocurrent signal. All measurements were performed at the same distance from the top contact of the device, to ensure comparable photocurrent maps.

By selecting the wavelength of the local source of illumination we build a ‘photocurrent tomography’ of the device, with sub-micron spatial resolution. By combining the photocurrent scans with Raman maps on the same region of the sample we can determine possible variations in composition within the interfaces and between the grains, which is extremely useful for characterizing the material under investigation here.

III. RESULTS AND DISCUSSION

Fig 2 shows the distribution of grain orientation in a representative CIGS device and a series of spectrally dependent photocurrent scans, where different CIGS grains are partially resolved. At short wavelengths (λ = 450 nm) the CIGS grains and interfaces behave similarly, and the photocurrent values are approximately the same. Surprisingly, significant variations in photocurrent are observed for λ = 550 nm for the different grains, only revealed by the sub-micron resolved scans presented here. This result strongly indicates that the distinct types of interfaces (formed by the different grains’ orientation) affect the transport of carriers between the grains in a different manner.

From the precise knowledge of the power density we inferred local variations in the EQE of the device with high spatial resolution (Fig 3), defined as: \( (hc/\lambda q)(I/P) \), where \( h \) is Planck’s constant, \( c \) is the speed of light in vacuum, \( q \) is the electronic charge, \( \lambda \) is the excitation wavelength, \( I \) is the generated photocurrent, and \( P \) is the incident power. The generated current and the incident power are determined directly from the photocurrent measurements and the power source calibration, respectively. The EQE scan shown in Fig 3(a) reveals variations in the collection characteristics of the material [15], most likely related to variations in the transport barrier of the different interfaces. Fig 3(b) displays the EQE enhancement, defined here as the local EQE divided by the
average EQE for the scanned area. We find that certain CIGS grains reduce the overall collection efficiency of the device, see grey circles, while other grains have an enhancement of up to 20% (navy circles). A direct relationship between the crystal orientation of the different grains and the EQE of each particular grain will be determined by combining EBSD and photocurrent microscopy on the same region of the sample. The spatial resolution of our measurements can be improved by 1000x by using near-field scanning optical microscope (NSOM) probes [15,16].

We established a direct correlation between the local electrical and structural characteristics of the interfaces on the carrier transport properties by combining Raman maps with the EQE measurements. A representative Raman spectrum is shown in Fig 4(a), which presents peak shifts at 175, 300, and 600 cm\(^{-1}\), corresponding to the CIGS and Cu\(_2\)Se vibrations, respectively [17]. Figs 4(b)-(d) display Raman and EQE scans for the very same region of the CIGS device. For the Raman maps, each pixel corresponds to one spectrum, where we also use a piezo scanner to spatially resolve the signal. We built the maps in (b) and (c) by selecting the Raman shifts indicated in Fig 4(a), where the color scale corresponds to the intensity of the selected peak shift. We find that the peak referring to 175 cm\(^{-1}\) shows a very uniform distribution over the CIGS layer (Fig 4(b)), while the shift corresponding to 300 cm\(^{-1}\) is closely related to the photocurrent signal (compare (c) and (d)). This result strongly suggests that the grains comprising the CIGS layer varies in composition, which results in significant variations in the local collection characteristics of the device, only revealed by the EQE high spatial resolution maps presented here.

IV. CONCLUSIONS

The collection characteristics of CIGS grains and interfaces were probed by spectrally and spatially scanning photocurrent microscopy measurements. Moreover, an effective EQE map showed remarkable variations in the collection properties of the different grain orientations within the device. A direct correlation between the various interfaces and the transport properties of solar cell can be established by measuring photocurrent and Raman on the same region of the sample.

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REFERENCES


