

Assessing Local Voltage in CIGS Solar Cells by Nanoscale Resolved Kelvin Probe Force Microscopy and Sub-Micron Photoluminescence

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Abstract — Here we use nanoscale resolved Kelvin Probe Force Microscopy (KPFM) to locally probe the open circuit voltage in CIGS thin film solar cells. Illumination-dependent KPFM shows that the grain boundaries and grain cores present variations in surface photovoltage, as a consequence of the local variation of the open circuit voltage. Additionally, room temperature sub-micron PL scans were used to map the recombination centers in the polycrystalline CIGS films.

Index Terms — solar energy, thin-film, scanning probe microscopy, CIGS.

I. INTRODUCTION

The remarkable progress recently observed for thin film copper indium gallium diselenide (CIGS) solar cells has demonstrated its promising application as an alternative photovoltaic material. CIGS combines the advantage of thin-film technologies, which uses reduced amount of material, and rapid/low-cost deposition methods – key factors for successful and marketable technologies. To date, the best CIGS solar cells fabricated have efficiency of 19.8% under 1-sun illumination^[1].

Despite the rapid improvement observed in the performance of CIGS solar cells, the open circuit voltage (V_{oc}) is still the primary limiting factor for producing high-efficiency devices. Today, the best laboratory cells and mini-modules have V_{oc} approximately equal to 0.7 V^[1]. Therefore, in order to boost the performance of the devices, it is imperative to understand the origin of the difference between the theoretical and experimental values of the V_{oc} . It is known that the grain cores (GCs) and the grain boundaries (GBs) in CIGS present distinct electrical properties; however, the mechanisms for carrier transport between grains with different structures are still not well understood. The significant improvement of CIGS solar cells strongly depends on boosting the V_{oc} of the devices, which is primarily related to (a) defects and interfaces between grains, (b) recombination, (c) doping level, and (d) contacts. Therefore, measuring the V_{oc} and resolving the recombination centers with nanoscale resolution can lead to new device designs with enhanced performance.

Scanning probe microscopy techniques have been extensively used to characterize the electrical and optical properties of thin film solar cells^[2,3,4,5,6,7]. In particular, photo-assisted Kelvin Probe Force Microscopy (KPFM)^[8] using a scanning tunneling microscope has been used to determine the band profile of the GBs, which was found to help the carrier separation^[9]. Moreover, KPFM has been implemented to map the nanoscale distribution of surface potential in CIGS solar cells^[10,11]. Here, we combine nanoscale KPFM with sub-micron photoluminescence to spatially assess the local voltage and recombination centers in CIGS solar cells.

II. MEASURING LOCAL VARIATIONS IN V_{oc} BY ILLUMINATION DEPENDENT KELVIN PROBE FORCE MICROSCOPY

We use sputtering from a quaternary target to deposit the CIGS layer, which consistently produces polycrystalline, highly oriented grains with controlled stoichiometry, and a bandgap of 1.1 eV. All the details concerning the deposition method and the overall characteristics of the resulting thin films were previously presented at PVSC^[12]. Briefly, soda lime glass coated with 500 nm of Mo was used as the substrate. CIGS films with 2 μ m in thickness were deposited by RF magnetron sputtering. A 50 nm thick CdS layer was

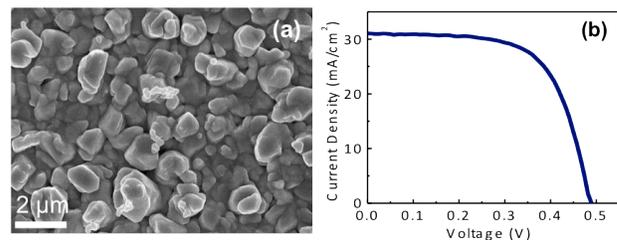


Fig. 1 CIGS solar cells. (a) SEM image of CIGS grains obtained by deposition from a quaternary target using RF magnetron sputtering. (b) Light J-V curve under AM1.5 global illumination showing best photovoltaic device performance, with $\eta = 10.5\%$.

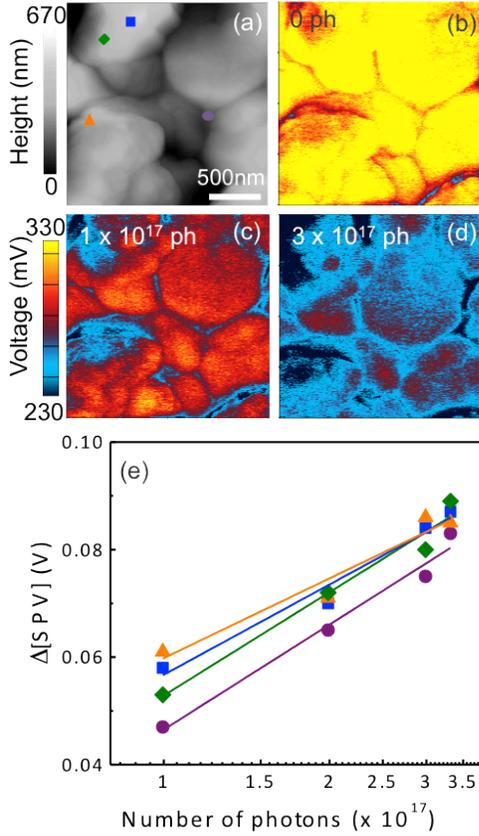


Fig. 2 Intensity dependent KPFM. (a) AFM topography for CIGS solar cell. KPFM under illumination: (b) 0, (c) 1×10^{17} , and (d) 3×10^{17} photons. (e) Difference in surface photovoltage ($\Delta[SPV]$) as a function of number of photons for selected points (as signed in image (a)) obtained from KPFM under illumination at 660 nm.

deposited by chemical bath deposition. The ZnO anti-reflection coating was not added, in order to allow for the CIGS/CdS grains to be measured. Fig. 1(a) shows a representative SEM image of the grains composing the CIGS solar cells used in the experiments presented here. The best fabricated CIGS devices showed efficiency $\sim 10\%$, as shown in the light J-V curve of Fig. 1(b), very suitable for the spectrally resolved KPFM and sub-micron photoluminescence (PL) measurements.

KPFM was used to locally probe the voltage of the CIGS devices with nanoscale resolution. All measurements were performed using a platinum-coated Si probes with <40 nm in radius, at ambient environment, and room temperature. The sample was uniformly illuminated by a monochromatic light source (660 nm) to provide varying number of photons. This technique also allows for spectrally resolved KPFM, i.e., wavelength-dependent measurements of the V_{oc} of GCs and GBs (in progress).

Sub-micron PL scans were performed on the CIGS solar cells using a 100x objective (NA 0.9) and a piezo scanning stage of $100 \times 100 \mu\text{m}^2$ range. The measurements were performed using an excitation source at 532 nm, at room

temperature. Confocal images were acquired in the same area for comparison between the morphology and the PL signal, as shown in the next session.

III. RESULTS AND DISCUSSION

Fig. 2(a-d) show images of the surface voltage of the CIGS grains as a function of the number of red photons (660 nm) illuminating the solar cell. Fig. 2(b) shows the dark surface voltage. Most GCs have a constant distribution of voltage (~ 330 mV), indicating that the CIGS film is uniform in composition. Nevertheless, the high resolution KPFM image also shows that most of the GBs present a lower voltage, which corresponds to a higher V_{oc} . Moreover, some regions of the GCs present surface voltage similar to the GBs, as displayed in Fig. 2(c).

In order to investigate the effect of the illumination on the local voltage of the GCs, the CIGS solar cell was illuminated with a controlled number of photons. As shown in Fig. 2(c), we could resolve variations in surface voltage in regions as small as 20 nm. The change in the surface photovoltage ($\Delta[SPV]$) increases with the photon flux. This result is a direct consequence of the increase in the $V_{oc}^{[11]}$. As shown by the orange triangle region in Fig. 2(a), the voltage of the GCs that originally behave similar to the GBs is kept constant by increasing the photon flux. The increase in the photovoltage varies from GCs to GBs, suggesting a variation of the V_{oc} for the GBs, as shown in Fig. 2(e).

By illuminating the sample with a continuum laser with controlled power density we were able to resolve variations in surface photovoltage as a function of selected wavelengths, as shown in Fig. 3. In other words, we mapped relative variations in V_{oc} with nanoscale resolution for both GCs and GBs. Here, the holes (positive charges) are collected, and the dark color on the KPFM images actually corresponds to a larger SPV. As expected, the SPV signal increases for longer wavelength, independent of the grains' interfaces. This result suggests that the recombination at GBs and GCs are similar and, therefore, the difference in the optoelectronic properties of the GBs could be associated to the collection characteristics of the polycrystal interfaces.

The imaging of local variations in photovoltage by KPFM is a non-destructive measurement technique that can be expanded to other PV materials, and only requires a bottom contact. To quantify and minimize the contribution of topography to the surface photovoltage measurements, the morphology of the surface of the samples can be modified by polishing, plasma etching, or Ga-ion beam milling processes^[7]. Alternatively, depending on the morphology of the sample to be analyzed, heterodyne KPFM might be implemented instead, which allows for the analysis of very rough surfaces^[13]. Further, by calibrating the KPFM setup with respect to the transmission of the sample and of the optical beam path, the angle of incidence of light, the IQE of the solar

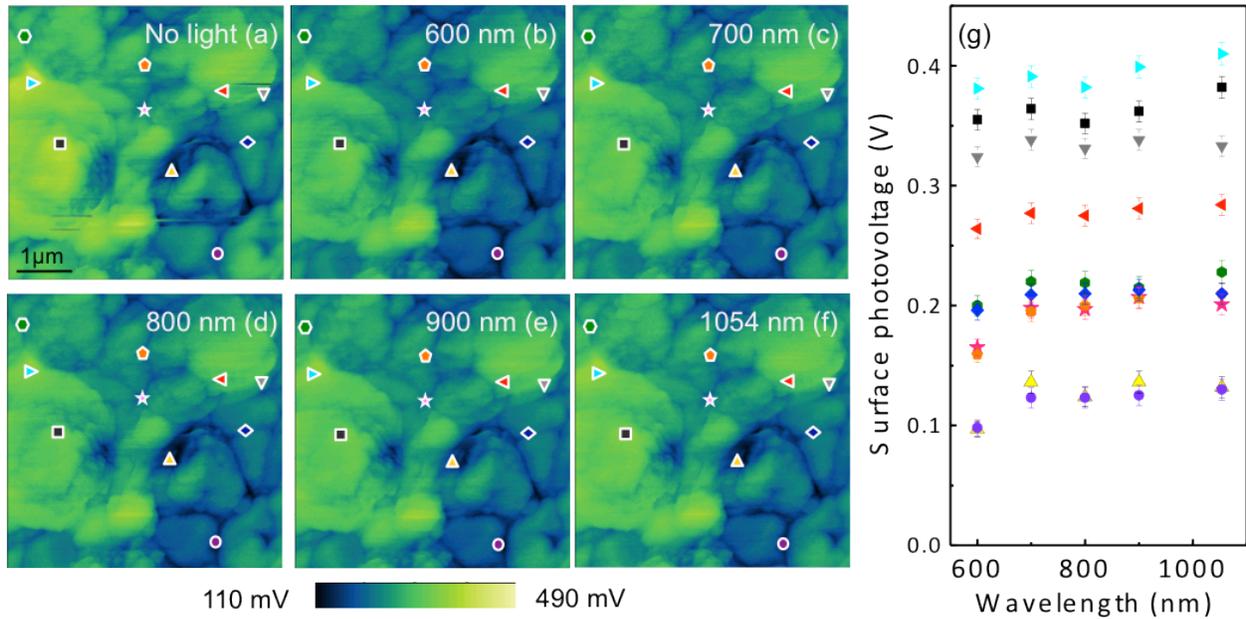


Fig. 3 Spectral-dependent KPFM. Scans under (a) dark and (b-f) single wavelength illumination conditions. (g) Surface photovoltage as a function of wavelength for selected points of the scan.

cell, and the area illuminated, one can infer absolute values for the open circuit voltage.

The luminescence of the polycrystalline grains was measured with sub-micron resolution by PL. Fig. 4(a-b) show a confocal microscopy image and a sub-micron PL map of the CIGS grains. The intensity scale of the PL signal is

normalized by the peak at 1080 nm, characteristic of CIGS material. The PL signal contrast is not necessarily correlated to the grains morphology and is a direct result of the spatial variation in the recombination statistics. Moreover, this variation is mostly caused by defect structures, which can be resolved by nanoscale PL measurements using a near field

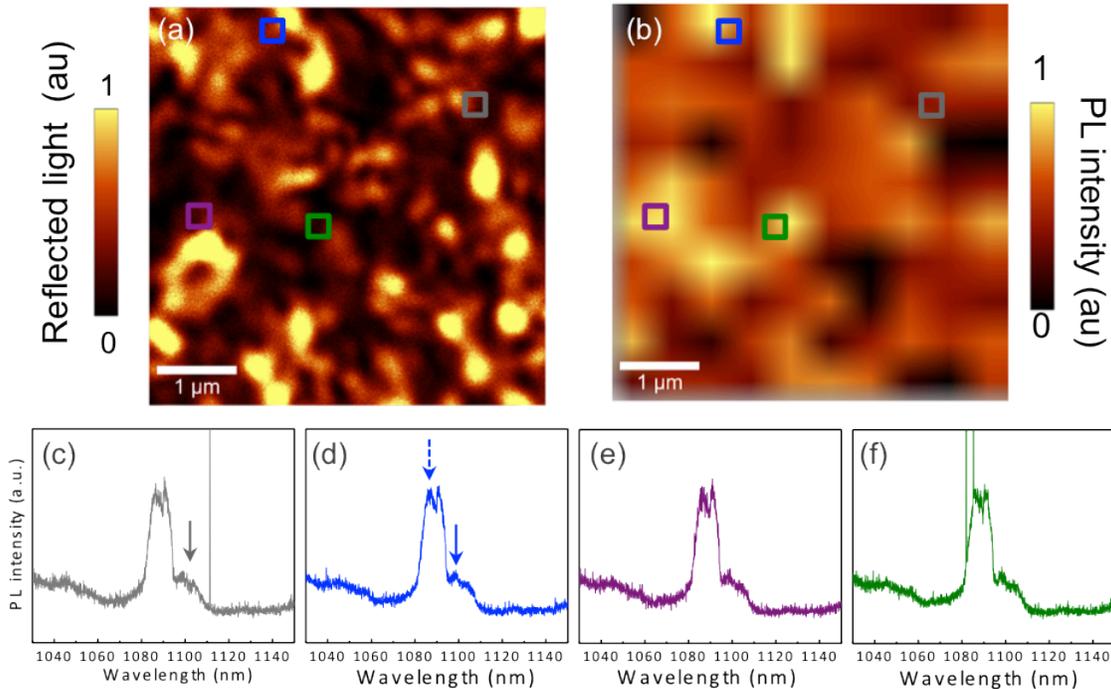


Fig. 4 Sub-micron PL imaging. (a) Confocal microscopy image of the reflection signal showing non-uniform CIGS grains. (b) Sub-micron photoluminescence scan showing intensity variation at 1080 nm. (c) – (f) PL spectra measured at the positions in (b). Light source: 532 nm.

scanning microscopy probe with <100 nm in diameter. The single spectrum shown in Fig. 4(c-f) strongly indicates that the CIGS material emission varies from grain to grain. KPFM and sub-micron PL measurements on the same region of the solar cell sample for a quantitative evaluation of the V_{oc} variation and the emission properties of different grains can be studied by the approach presented here.

IV. CONCLUSIONS

Illuminated KPFM is used to locally map the surface photovoltage and, therefore, the V_{oc} of polycrystalline CIGS solar cells. Further, spectrally resolved measurements can give a direct correlation between GC and GB morphology and the optoelectronic properties of the material. Further, sub-micron PL is used to map recombination centers in CIGS material. Combined, these measurements can be implemented to locally assess V_{oc} in any inhomogeneous PV device.

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