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Light-induced current mapping in oxide based solar cells with nanoscale resolution

Shrabani Panigrahi*, Tomás Calmeiro, Rodrigo Martins, Elvira Fortunato*

Departamento de Ciência dos Materiais, CENIMAT/i3N, Faculdade de Ciências e Tecnologia–Universidade Nova de Lisboa and CEMOP/Uninova, 2829-516 Caparica, Portugal

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ABSTRACT

Transport properties of photo-induced charge carriers through different grains in the polycrystalline photovoltaic devices strongly depend on the microstructural pattern of the active layers. Therefore, photocurrent mapping with nanoscale resolution is important to know about the electrical responses of the different grains in the polycrystalline photovoltaic devices. Here, we have used photoconductive atomic force microscopy for mapping the photocurrent with nanoscale resolution of two types of ZnO nanorods/Cu_2O based solar cells. The morphology and current have been measured simultaneously with nanoscale resolution from the top surfaces of the devices at different applied voltages. It is demonstrated that the nanostructure of the active layers is one of the most important variables determining device performances. Different local photovoltaic performances have been observed from these two devices due to various microstructural and electrical phenomena of their seed layers. On the other hand, significant variations in short-circuit current have been observed from different grains of the devices which appeared more alike in the micrograph owing to various transport properties of photocarriers. It is observed that the grain boundaries are more preferable for charge collection over the grain interiors. It shows a higher short circuit current close to the boundary than the grain inside. This study illustrates an important area for future fundamental research to enhance the performances of the polycrystalline photovoltaic devices through better control of morphology and improving the inherent properties of the active layers.

1. Introduction

Utilizing solar power through converting electrical energy by a solar cell or photovoltaic cell is a suitable way to provide the world's consistently growing energy needs [1–4]. The improvement in solar cell technology from silicon based solar cells to further developments in thin films solar cells, dye sensitized solar cells, organic solar cells and perovskite solar cells show an enhancement in cell efficiency day by day [5–9]. The conversion efficiency of a solar cell depends on the spectrum and intensity of the incident light as well as the microstructure and inherent properties of the active layers [10–12]. The research to optimize the manufacturing process to improve the microstructural and intrinsic properties of the active layers has a vital significance in the performance of a solar cell. In case of thin film solar cells, active layers are composed of nano-sized crystalline grains and their interfaces, *i.e.* boundaries which induce microscopic dislocations, vacancies, and indistinct bonds [13]. Therefore, the properties in the nanoscale range are different for different grain interiors (GI) and grain boundaries (GB). According to these points, the local photovoltaic performances would be different from one grain to another. In a macro-scopic scale, the obtained efficiency of the bulk heterojunction solar cell is the whole combination of the local photovoltaic performances of the different grains. Hence, to improve the performances of the bulk heterojunction solar cells, it is important to know the local photovoltaic performances of the different grains. There are some reports on the large scale imaging techniques like laser beam induced current (LBIC) mapping, light beam induced current (LBIC) mapping used to characterize the photovoltaic performances of the different cells [14–16]. Alternatively, different microscopic techniques such as transmission electron microscopy (TEM), atomic force microscopy (AFM), and scanning transmission X-ray microscopy (STXM) have been used to study the morphology of the nanostructured materials [17–19]. However, these systems can only provide the information about the microstructure of the film not about the photovoltaic performances of the individual grain in the micrographs. In this context, photoconductive atomic force microscopy (pc-AFM), a nanoscale imaging method, allows to establish the direct correlations between the morphology and the electrical responses of the different grains. It is used to map the local photocurrent and the

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* Corresponding authors.
E-mail addresses: spqdot@gmail.com (S. Panigrahi), emf@fct.unl.pt (E. Fortunato).

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microstructure of the film simultaneously [20–22]. Furthermore, it has been used to record the electronic information with nanoscale resolution from photovoltaic materials by applying some voltages between the conductive tip and the sample. By measuring the photocurrent as a function of applied voltages, we are able to obtain the photovoltaic parameters such as short-circuit current (I_{SC}), open-circuit voltage (V_{OC}) and fill factor (FF) for different grains in the nanoscale range. Recently, it has been implemented for analyzing the photovoltaic performances of different solar cells in nanoscale range [23–28]. Due to the small radius of the tip (≈ 25 nm) used in the pc-AFM measurement system, photovoltaic performances can be studied with nanoscale resolution (better than 100 nm). The results are connected with the bulk device photovoltaic performances and also provide a complete picture on the charge carrier transport mechanism within different grains and boundaries in the polycrystalline photovoltaic devices.

In this report, pc-AFM has been used for mapping the local photocurrent of two oxide based solar cells with two different seed layers at various applied voltages including under short-circuit condition. By solution process technique, we have developed two different types of ZnO nanorods (NRs)/Cu_2O based solar cells on un-doped ZnO and Al doped ZnO (AZO) seed layers, respectively. In oxide based solar cells, ZnO/Cu_2O hetero-junction has the most constructive conduction band edge alignment for solar cell applications [29,30]. We have observed the variation in the local photovoltaic performances between two devices due to different microstructural and electrical properties of their seed layers. On the other hand, a surprising range of photocurrents has been detected from different grains of the devices, which are appearing more similar in the topography image. In macroscopic scale, we have always studied the photovoltaic performances for bulk heterojunction solar cells having different seed layers. Here, the observation of local photoresponses in solar cells is significant to know the basic photovoltaic mechanism inside the cells depending on the microstructure and other features of the active layers.

2. Experimental details

2.1. Materials

ITO coated glass substrate, zinc acetate di-hydrate [$Zn(CH_3COO)_2 \cdot 2H_2O$], Aluminium chloride ($AlCl_3 \cdot 6H_2O$), methanol (solvent), acetic acid (catalyst), hexamethylenetetramine [$(CH_2)_6N_4$], copper(II) acetate monohydrate ($Cu(CH_3COO)_2 \cdot H_2O$), glucose (reducing agent), and isopropanol (solvent). All used chemicals (reagent grade) were purchased from Aldrich. No further purification was done; the chemicals have been used for making the cell materials. De-ionized water from Millipore equipment was used.

2.2. Device fabrication

ITO coated glass substrates were thoroughly washed by soap solution and then rinsed by de-ionized water, acetone and iso-propanol, respectively, and finally these were dried in a dry air stream. At first, very thin (~ 40 nm) seed layer was deposited on the substrate by spray pyrolysis technique using a commercial spraying system (SONOTEK Exacta Coat). The substrate of ITO glass was kept at 340 °C and the precursor solution of zinc acetate di-hydrate (0.05 M) with methanol and acetic acid (mixing ratio 49:1) was sprayed on the substrate for the deposition of un-doped ZnO seed layer with a pneumatic spray nozzle (Spraying Systems Co.) at a flow rate of 1 mL/min. For Al doping, hexahydrate aluminum chloride ($AlCl_3 \cdot 6H_2O$) was added in the parent solution. The Al/Zn ratio in the solution was varied from 1 at% to 4 at %. The doped seed layer (3 at%) which showed the best electrical properties was used for the next step for making the device structure.

At the next step, ZnO NRs were fabricated on the seed layer (undoped and doped) assisted substrate by a chemical solution deposition process with an aqueous solution of zinc acetate di-hydrate and hexamethylenetetramine. The seed layer assisted substrates were immersed in that solution for 3 h at 90 °C to grow the ZnO NRs. The samples were then washed by de-ionized water and annealed under vacuum by using rapid thermal annealing (RTA) treatment at 500 °C for 1 min.

After the growth of ZnO NRs, Cu_2O layer was deposited on the ZnO layer by the spray pyrolysis technique. A precursor solution of copper (II) acetate monohydrate (0.02 M) and glucose (0.03 M) dissolved in water and isopropanol (mixing ratio 4:1) was sprayed by the ultrasonic nozzle on the ZnO layer at 275 °C using a hot plate. The solution flow rate and the airflow pressure were the same at the time of seed layer deposition. Before the deposition of the contact layer, finally the heterojunction was annealed in vacuum at 500 °C for 30 s using RTA. For the bulk device measurement, Au back contacts (thickness ~ 150 nm) were deposited by thermal evaporation (Vinci Technologies) technique onto the Cu_2O layer using a shadow mask where each contact patch had a diameter of 1.75 mm, corresponding to an area of 0.0237 cm^2.

2.3. Measurement details

All pc-AFM measurements were performed using an MFP-3D AFM (Asylum Research, SantaBarbara, CA) using an ORCA-2 current preamplifier holder operated in air. All current measurements were performed using conductive PtIr-coated silicon AFM tip (Nanoworld, CONTPt) with a resonant frequency of ~ 13 kHz and force constant of ~ 0.2 $N\,m^{-1}$. The scan speed was 1 Hz and the images were acquired with a resolution of 1024 × 1024 pixels. We have illuminated the device with a Fiber-Lite MI-150R light source.

To know about the surface potential, Kelvin Probe Force Microscopy (KPFM) was used with Olympus AC240TM probes (spring constant: 2 N/m, resonant frequency: 70 kHz) system in a double pass mode. We have illuminated the device by the same light source.

For electrical characterization, a digital source meter (Keithley Model 2400) was used to apply the voltages to the cell while the current was recorded. Illumination was provided through AM 1.5 illumination conditions with a Sciencetech SS1.6kW-A-2-Q system consisting of a Xe lamp with a light intensity of 100 $mW\,cm^{-2}$. The morphological characterizations of the seed layers, ZnO NRs and ITO/ZnO/Cu_2O/Au devices were performed by SEM measurements using a Carl Zeiss AURIGA Cross Beam workstation. For focused ion beam (FIB) experiments, Ga^+ ions were accelerated to 30 kV at 10 pA and the etching depth was kept around 1000 nm. The structural characterization of the seed layers and NRs were performed by X ray diffraction (XRD) analysis using the computer-controlled Panalytical Xpert PRO system (Cu Kα radiation; $\lambda = 1.5405$ Å) and X´Celerator 1D detector. The electrical properties were determined from resistivity and Hall coefficient measurement at room temperature. The electrical resistivity, carrier concentration and mobility measurement of the seed layers were done using a Hall Effect measurement system (BiO-RAD). Optical transmittance was obtained by using UV–vis–NIR spectrometer (Perkin Elmer; Lambda 950).

3. Results and discussion

Local photocurrent measurement was performed on the same devices which were used for bulk device photovoltaic measurement previously to correlate the performances of the devices in microscopic scale. In the beginning, current density-voltage (*J-V*) measurements for the bulk devices have been performed under simulated AM1.5G illumination at ambient environment using a solar simulator (Fig. S1a). The details of the photovoltaic performances for the bulk devices are in Supporting information. To know the local photocurrent responses of the solar cells, a pc-AFM measurement set-up with a sample holder and light source was used. Fig. 1 shows the schematic diagram of the planar NR based oxide solar cell mounted in a pc-AFM configuration for measuring the local photocurrent. This system is based on conductive