

Keysight Technologies

Applications of KFM and CSAFM/STM in Characterizations of Photovoltaic Materials

Application Note

Overview

Photovoltaic (PV) devices are made from various types of semiconductor materials, which are deposited or arranged in a variety of structures. About 90% of the current PV systems are from Si based cells, however, non-silicon based thin-film technologies hold significant growth potential. The three main types of materials used for solar cells are i) silicon, including single-crystalline, multicrystalline, and amorphous Si; ii) polycrystalline thin films, including copper indium diselenide (CIS) and cadmium telluride (CdTe); and iii) single-crystalline thin film of gallium arsenide. There is also research in the areas of organic PV cells and dye-sensitized solar cells (DSC) [1, 2].

The driving force for PV research is to increase the cell efficiency, to lower the cost of PV production, thus to reduce the energy payback time. This leads to a continuing search for new materials of higher light absorption coefficient, better photovoltaic conversion efficiency, and longer time stability. The efficiency of light absorption and photovoltaic conversion depends highly on the electronic and structural properties of the material, particularly on the proper alignment of the electronic band structures at the various interfaces in a multi-junction PV device [1, 3]. Therefore, the examination of electronic and structural properties of the solar cell components in model geometries and in working structures is essential for the improvement of these devices. Scanning probe techniques (STM, AFM, etc), including ones that provide an access to local electric properties, are important techniques for characterization of surfaces, bulk structures, and cross-sections of cells and their components with high spatial resolution. The AFM-based studies of local electric properties are performed either by sensing of the electrostatic force interactions between a sample and a sharp metallic probe, or by direct measurements of the sample property (tip-sample current, capacitance, local sample impedance, etc) while a probe is profiling the sample topography.

The measurement of the electrostatic tip-sample forces is the basis of Kelvin Force Microscopy (KFM) which provides quantitative mapping of surface potential. The latter can be interpreted in terms of

local variations of electron work function, doping profiles, orientation and strength of molecular dipoles, etc. Kelvin Force Microscopy has been used in a variety of studies to investigate the electronic properties of chalcopyrite solar cell materials [4, 6]. KFM has been used to study the work function differences between different facets of crystal orientation on single grains of CuGaSe₂, to characterize the grain boundary structures within polycrystalline absorber materials, and to study the cross-section of the junction region through a complete solar cell device. KFM has also been used to study organic solar cells (OPV). The investigation of a classical organic solar cell system consisting of MDMO-PPV/PCBM is well suited to analysis using KFM, together with high resolution SEM data, resulting in identification of a barrier for electron transmission from the electron-rich PCBM nanoclusters toward the extracting cathode, and correlation of the power conversion efficiency to the nano-scale morphology in the bulk heterojunction [7]. A recent study demonstrated that acid washed MWNTs (multi-walled nanotube) can be easily dispersed in a poly(3-hexylthiophene) (P3HT) polymer matrix, and can be used to enhance light absorption and carrier transport of P3HT [8]. In this study, KFM was used to differentiate the work function of the dopants from the polymer matrix, which further implied that hole transport was from the MWNTs within the system. The device shows an increase of 29% power conversion efficiency due to faster carrier transport.

Current sensing AFM (CSAFM), also known as conducting AFM, is another powerful technique for the characterization of photovoltaic materials [9-11]. In this method a biased conducting probe scans the sample surface in the contact mode and the current is detected when the probe encounters conducting locations. As the result the image of current variations is recorded simultaneously with the sample topography. CSAFM complements STM because due to the control of the tip-sample force it can be applied to heterogeneous conducting samples which could not be examined with STM. This method has been used to study the electron transport properties of domains and grain boundaries in polycrystalline thin films and to distinguish between different component domains in polymer blends. Particularly, when combined with an external optical excitation, CSAFM can be used to study the localized photocurrent effect and its correlation to the local electronic structure of the material. As illustrated in Figure 1, the optical excitation can be applied either from above the sample, or below the sample. In the later case, the AFM platform is usually coupled to a commercial ILM (inverted optical microscope) station. For example, the Keysight 5500ILM system combines the 5500 AFM system from Keysight to an ILM from commercial manufacturers such as Zeiss, Nikon, and Olympus, providing exceptional high resolution AFM imaging and optical capabilities.

In this application note STM, CSAFM, and KFM capabilities of the Keysight SPM systems and its applicability in solar cell

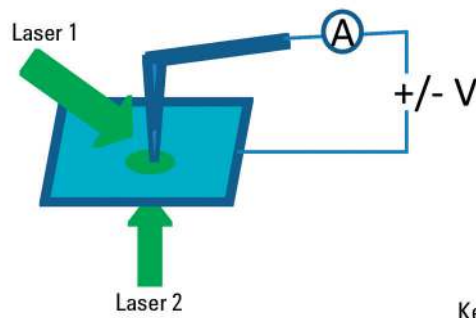


Figure 1. Illustration of Current sensing AFM combined with external illumination for the characterization of photovoltaic materials. Laser illumination could be applied from above the sample as indicated by laser 1, or from below the sample (laser 2) when combined with an inverted optical microscope (as shown by the picture of the Keysight 5500ILM system).

research will be demonstrated using a number of samples including one electrically active multi-junction solar device.

Single Molecule Conductivity Measurements Using CSAFM and STM for Organic Photovoltaic Materials

Both current sensing AFM as well as STM can be utilized to perform single molecule conductivity measurements for organic photovoltaic materials and devices. As organic photovoltaic accrue more interest in terms of creating cheaper solar cell devices, basic research into the conductive properties of the molecular components will become more crucial to synthesis and design. Scanning probe microscopy is an excellent platform for performing these types of measurements, as the sharp probes are able to provide good contacts to single molecules.

One method of performing these types of measurements is referred to as the single molecule “break junction” method. This method has been pioneered on the scanning probe microscope by Xu and Tao [12]. In this method, molecules are either in solution or they are fixed onto a conductive substrate and subsequently either the current sensing AFM probe, or the STM tip, approaches the substrate and is withdrawn at a fixed speed while measuring the decay of the current. When a molecule attaches to both the substrate and the tip, steps or plateaus form

in the current decay curves. The position of these steps represent the molecular conductance of the molecules being probed, and can be easily represented on histograms produced by combining many of these curves that contain steps.

CSAFM has already been utilized to examine the conductance of single alkane molecules attached to Indium Tin Oxide (ITO) surfaces [13]. By applying conducting AFM, it is also possible to examine the force required to break the bonds between individual molecules and the ITO surface. Although the molecules were simple alkane chains, the connection to photovoltaic research is apparent in the choice of substrate and this initial work on simple molecular system can pave the way for more complex systems involving photoactive molecules.

The single molecule “telegraph” method is another way to study single molecule conductivity on molecules of photovoltaic relevance. In this method, the gap between the surface and the tip is kept fixed by monitoring the conductivity of the gap. If molecules are affixed to the surface and have a binding group that will attach to the tip, then periodically the molecule will connect to the tip, spanning the tunnel gap. The connection will quickly break and reform for a short duration, in which the conductance of the gap will increase and decrease in a two level fashion, with the lower level indicating the conductance of the gap without the linking molecule, and the higher level indicating the conductance after bond forming. Both levels can be utilized to determine the conductivity of the molecule in question. An example measurement of a conducting organic

film on ITO is shown in Figure 2. This technique has been utilized to examine the conductivity through DNA base pairs and could be utilized to understand the conductivity through potentially light absorbing molecules [14].

CSAFM Characterization of nc-Si:H Films and TCO Substrates

Hydrogenated nanocrystalline silicon (nc-Si:H) has recently been considered as a low-cost replacement for a-SiGe:H. The superior long wavelength response of this material offers the possibility of reaching higher efficiencies. However, many issues regarding its electronic and optical properties are not completely understood. nc-Si:H film growth depends strongly on the growth conditions and the substrate. nc-Si:H has a complicated heterogeneous microstructure that consists of a mixture of crystalline silicon (c-Si) grains, grain boundaries and/or a-Si:H “tissue”. The heterogeneous microstructure of nc-Si:H leads to complicated transport properties. The main question concerning electrical conduction of nc-Si:H is about the carrier pathway in the film. Conducting AFM was used intensively to investigate this problem by measuring localized electron transport properties of the nc-Si:H film. Early analysis of conducting AFM data by Rezek et al [9] concluded that currents flow through the columnar Si crystallites within the material, while data from Azulay et al [10] indicate transport mainly occurs in the disordered material surrounding the crystallites. Cavallini et al [11] proposed a different

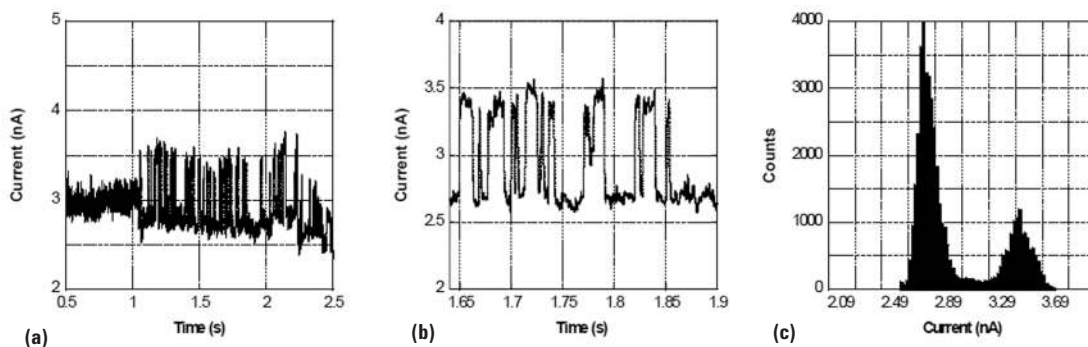


Figure 2. Telegraph measurement of a conducting organic film on ITO: (a) current signal going into a telegraph “switching mode”, (b) zoom-in window showing the two level switching, (c) histogram of current trace with the lower peak showing the baseline conductance and the higher peak showing the switching level.

mechanism based on their conducting AFM measurement, stating that current flows mainly through the nanocrystalline aggregates which constitute the electrical network. Machida et al [15] have recently studied the effect of hydrogenation on the electron transport property of poly-Si films using conducting AFM. Simultaneously obtained surface topography and current images of the poly-Si films both before and after hydrogen termination are compared. Detailed analysis of the I/V characteristics of the poly-Si film before and after hydrogen termination indicates that the conduction mechanism of grains in the hydrogenated poly-Si film resembles that of the conduction mechanism in semiconductors. On the other hand the conduction mechanism of grain boundaries is similar to metallic conduction mechanism, and is governed by hopping conduction mediated by electrical defects in grain boundaries.

Transparent conductive oxides (TCO) such as SnO₂ and ITO play a very important role in PV cells. Particularly, ITO is widely used in organic solar devices as the supporting substrate. The structure and conductivity of these TCO films will certainly affect the performance of the device. Kim et al [16] studied the conductivity and electronic structure of ITO with a variety of techniques including CSAFM, KFM, and X-ray photoelectron spectroscopy (XPS). The current voltage measurement revealed that fresh ITO surfaces show ohmic behavior with patches of nonconductive regions, and adsorption of strong electronegative ions such as F⁻ cause the depletion of electrons from the surface thus the reduction of in-plane conductivity. Even though ITO is widely used in today's research and development of organic PV cells, there is an increasing concern over its availability due to the limited natural supply of indium. Consequently, continuing efforts have been made in finding effective replacements for ITO. For example, Fluorine tin oxide (FTO) is one interesting material among many possible candidates. The topography and current images of FTO from a CSAFM experiment are compared with ITO in Figure 3. It is clear that FTO shows a rougher surface with larger grain size and less uniform conductivity.

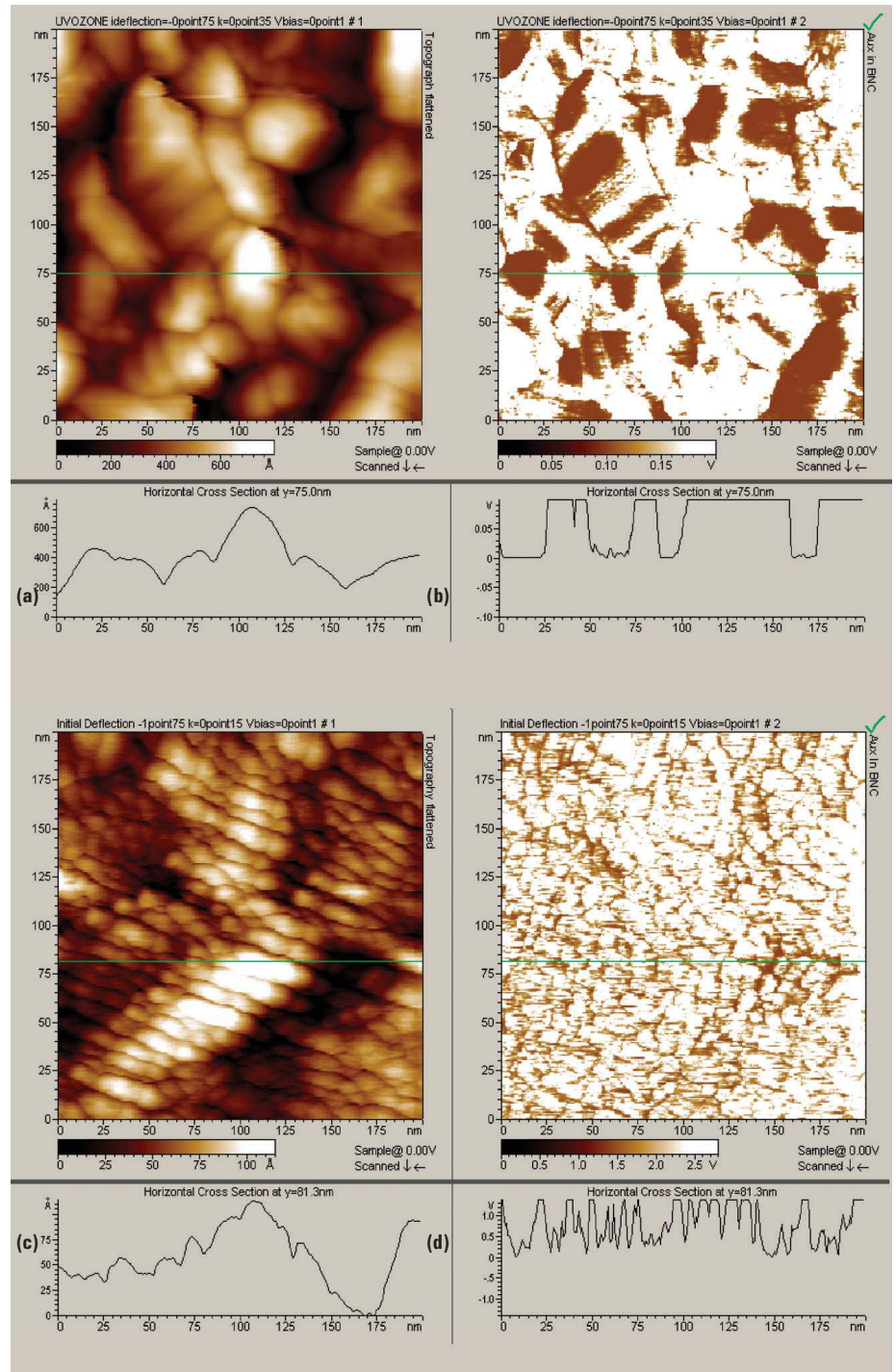


Figure 3. Simultaneous topography (a) and current (b) images of Fluorine tin oxide (FTO) and topography (c) and current (d) images of indium tin oxide (ITO) obtained using CSAFM. FTO shows larger grain size on the surface than ITO. The current image also shows some of the large grains on FTO have very low conductivity.

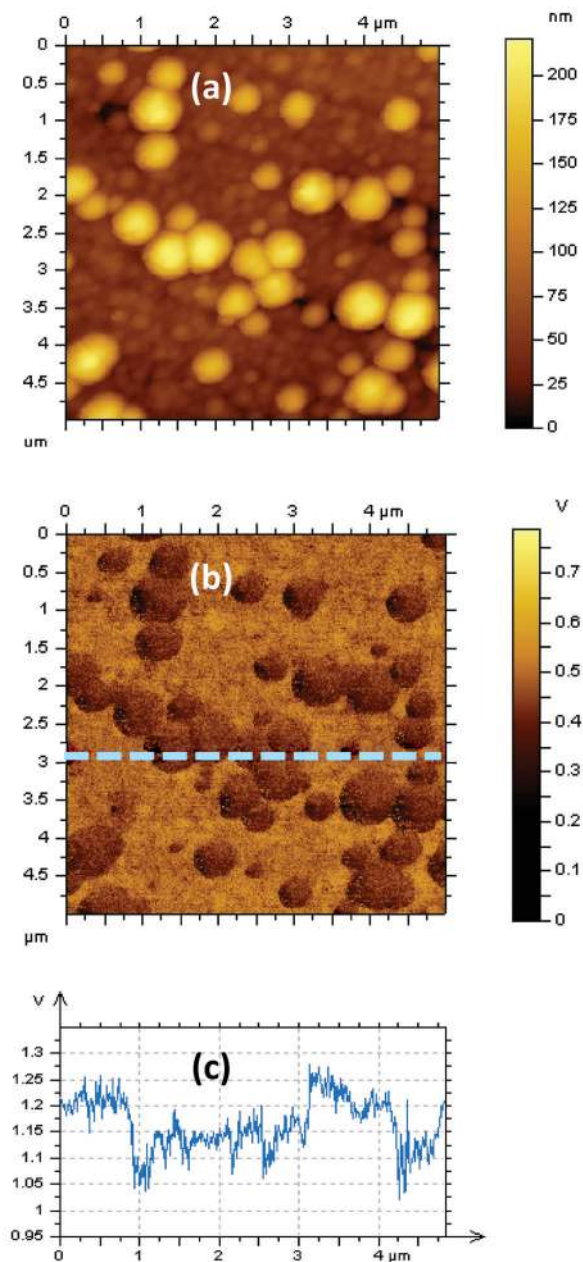


Figure 4. Topography (a) and surface potential images of Si crystalline clusters deposited on amorphous Si. The potential profile along the dotted line is presented in (c).

Advanced Single-Pass KFM Measurements

A Keysight 5500 AFM system equipped with the MAC III controller is especially useful for making multi-frequency measurements, including EFM and KFM. The MAC III has three dual phase lock-in amplifiers (LIA) converting the AC inputs to amplitude and phase. These digitally-controlled analog LIA have a broad bandwidth (up to 6 MHz) that covers the operation bandwidth of the

photodetector employed in the microscope. KFM measurement is performed using two LIAs simultaneously, with the first LIA tracking the mechanical oscillation of the cantilever for topography imaging, and the second LIA tracking the electric modulation for electrostatic force measurement. The surface potential is measured by nullifying the electrostatic force with a servo-loop that supplies a dc offset to the tip. The electrostatic force is nullified when the tip voltage equals the local surface potential of the sample. Because the

electrostatic force is nullified constantly during the measurement, the topography image obtained is truly deconvoluted from electrostatic effects. Figure 4 shows an example of topography and KFM images obtained simultaneously on a sample of hydrogenated nanocrystalline (nc-Si:H) and amorphous (a-Si:H) mixed-phase Si thin film. On this sample, clusters of nc-Si:H phase were embedded in the surrounding a-Si:H tissues. By comparing the topography image to the KFM image, it is evident that the nc-Si:H clusters exhibit a much lower surface potential, ~ 200 mV, than the surrounding amorphous phase.

KFM measurements can be done either by amplitude modulation (AM-AM) or frequency modulation (AM-FM) of the electrostatic signal. In AM-AM, the changes of the electrostatic tip-sample force are detected and nullified for getting surface potential difference between the tip and the sample. In the AM-FM mode, the electrostatic force gradient is used for the same purpose. More details about the KFM measurements can be found in the recent Keysight application note [17].

KFM Study of Potential Barrier Associated with Grain Boundaries in Polycrystalline Thin Films

The interfacial states in the band-gap and potential barrier associated with grain boundaries in polycrystalline silicon can exert detrimental influence on electrical conductivity and therefore overall device performance. However, not all grain boundaries are potential sites for electrical activity because individual grain boundaries have their own character depending on the orientation relation between two adjoining grains. A simultaneous topography and surface potential imaging of a polycrystalline Si film is shown in Figure 5(a) and 5(b), revealing potential variations across different domains and grain boundaries on the surface. As seen from the line profile presented in Figure 5(c), the potential variations is approximately 50-100 mV between domains and GBs. One needs to realize that, however, the measured potential variations in this sample can be smaller than reality due to the existence of thick oxide layers on the

sample surface. Consequently, for accurate surface potential measurements in the study of Si materials and devices, it is necessary to address the issue of the oxide layers carefully. Polycrystalline semiconductors generally exhibit poor optoelectronic properties compared to their single-crystal counterparts due to the existence of grain boundaries containing dislocation cores, which typically create deep levels and act as effective recombination centers. Thus, for polycrystalline solar cells, GB (grain boundary) passivation is extremely important to suppress the harmful effects of GBs. Surprisingly, however, without special GB passivation, the efficiency of polycrystalline Cu(In, Ga)Se₂ (CIGS)-based solar cells are surpassing their single-crystal counterparts. Therefore, understanding the GB behavior in CuInSe₂ (CIS) chalcopyrite films has attracted great attention for many years. Yanfa Yan et al reported studies of GB structures in CIS based on first-principles density-functional theory and potential measurements over GBs in CIGS films grown on Na-free and Na-containing substrates with KFM [6]. These results provide direct evidence revealing that GBs in pure CIGS are electrically benign and Na segregation into GBs in CIS is responsible for the measured electrical potentials. The interstitial Na atoms in GBs and perfect regions in CIS are shallow donors and not recombination centers. The electrical potentials created by Na segregation at GBs repel holes and attract electrons, thus help carrier separation. As a result, Na-segregated GBs could be beneficial to performance in CIS-based solar cells, explaining the fact that CIS-based solar cells must be grown on soda-lime glass substrates to achieve superior efficiency.

KFM Cross-section Measurement over the Junction of a III-V Tandem Device

Built-in electrical potential is a critical element in solar cells. KFM provides a direct measurement of the potential, and the electric field that is related to the defect states in the junctions can be further deduced. Figure 6(a) and (b) simultaneously recorded AFM and KFM images of the cross-section of a III-V tandem junction cell. The tandem cell consists of two

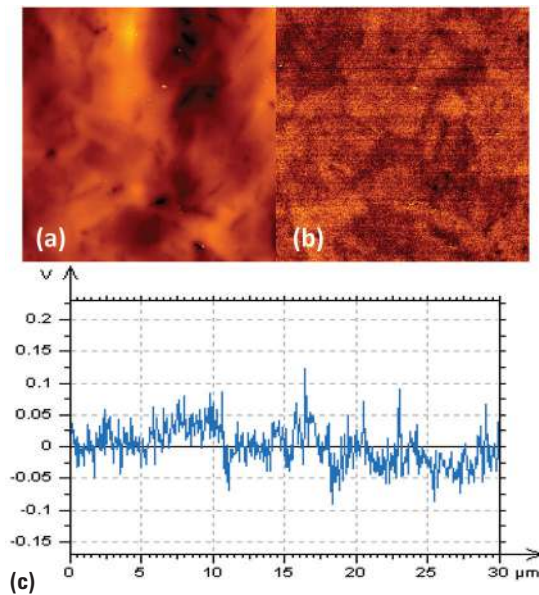


Figure 5. Simultaneous topography (a) and KFM-FM imaging (b) revealed the presence of potential difference between domains and at grain boundaries of a polycrystalline Si film. A line profile from the potential image is shown in (c).

individual cells with the top cell having a larger band gap than the bottom cell. The potential profile in Figure 7(a) shows two potentials on the top and the tunneling junctions. The potential on the bottom junction is affected (flattened) by the laser used in AFM, which is primarily absorbed by the bottom cell because of the smaller band gap than the photon energy. When the tandem cell is set to a short circuit condition, the charges separated at the bottom cell are accumulated at the top cell, i.e., the flattened potential at the bottom cell is applied to the top cell. Therefore, the potential on the top cell increased significantly as shown in Figure 7(c), and the increased amount is identical with the potential decrease in the bottom cell as induced by the AFM laser.

When the cell is intentionally illuminated with a strong white light, absorption of

the light mainly occurred in the top cell, and this induced a significant potential decrease in the top cell, as shown in Figure 7(b). With both the white light and laser illuminations, the potentials at both top and bottom cells are flattened, and subsequently the potential on the tunneling junction contributes significantly to the observed data. Interestingly, if the cell is changed from open circuit to short circuit under the white light illumination, the charges separated at the top cell are accumulated at the bottom cell, and this induced a large potential increase in the bottom cell, as shown in Figure 7(d). These changes in the potential configurations are useful in understanding the underlying device physics in solar cells.

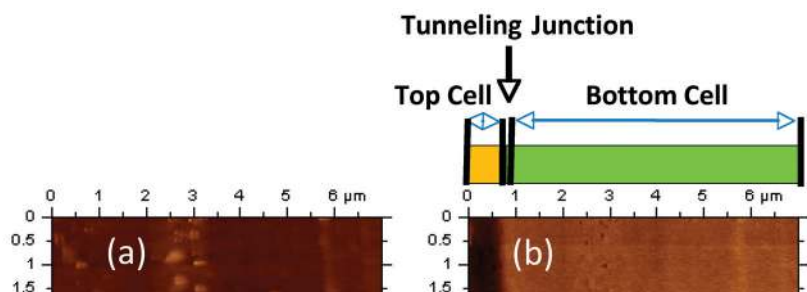


Figure 6. Topography(a) and potential (b) images along the cross-section of III-V Tandem cell.

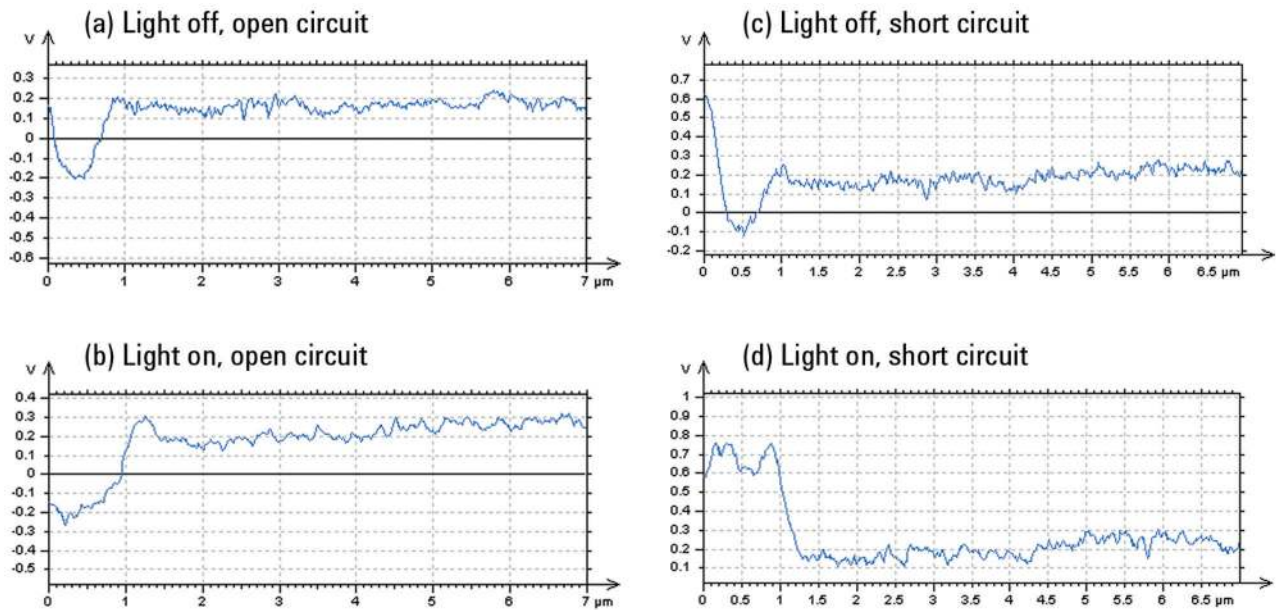


Figure 7. Potential profile across the junctions of a III-V Tandem cell as shown in Figure 5. These profiles are recorded at conditions where (a) the cell is at open circuit with no illumination, (b) the cell is at open circuit with illumination on, (c) the cell is at short circuit with no illumination, and (d) the cell is at short circuit with illumination on.

Summary

In summary, scanning probe techniques are vital tools for green energy research due to their capability to characterize structural and electronic properties of PV materials at the nanometer and single molecule scale. These studies can be performed either on surfaces of model samples and devices as well as on bulk sample structures, which can be “opened” for observation by ultramicrotomy with diamond knives

or FIB. STM and CSAFM can be used to study the conductivity of single molecules. CSAFM is particularly powerful in measuring localized conductivity in polycrystalline materials, and studying the transport mechanism of charge carriers in different domains and grain boundaries. Kelvin probe force microscopy measures the surface potential with fine spatial resolution of few nm and voltage resolution of (~10 mV) by

probing the coulomb force between AFM tip and sample. KFM applications in the characterization of solar cell materials and devices are demonstrated in measurements of electrical potential in junctions of devices and band bending on grain boundaries of polycrystalline materials.

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