DEVELOPING AND APPLYING THE SCANNING PROBE MICROSCOPY TECHNIQUE FOR SOLAR CELL MATERIALS

by

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A thesis submitted to the Faculty and the Board of Trustees of the Colorado School of Mines in partial fulfillment of the requirements for the degree of Doctor of Philosophy (Materials Science).

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The study of electrical properties of solar cells at the nanometer (nm) scale has benefited greatly from characterization techniques using scanning probe microscopy (SPM), a unique and powerful tool. These characterization techniques help scientists understand the fundamental physics of materials properties and device operation and provide vital information in photovoltaic research. This work focuses on developing and applying SPM, which includes atomic force microscopy (AFM) and scanning electron microscopy (SEM)-based characterizations, to solar cell materials and devices. We include extensive studies of current and emerging photovoltaic materials and devices, such as silicon, copper indium gallium diselenide (CIGS), copper zinc tin diselenide (CZTS), III-V, and perovskite materials and devices.

The subjects covered in my research concern the following: 1) understanding fundamental physics of device operation of CIGS and CZTS solar cells, and the nature of their p-n junction; 2) developing an in-situ characterization capability on an AFM platform to study photovoltaic reliability; 3) studying the fundamental mechanism of potential-induced degradation; 4) developing the near-field transport imaging (TI) technique, combining SEM and near-field optical microscopy primarily to study defects associated with carrier transport; 5) applying TI on GaAs hillock defects to investigate how hillock defects affect carrier transport; 6) investigating the electron-beam-induced damage on novel perovskite materials; and 7) using Kelvin probe force microscopy (KPFM) to examine the p-n junction quality of SnO$_2$-based solar cells.
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ACKNOWLEDGMENTS

One quiet afternoon four years ago, my advisor, Dr. Yanfa Yan at The University of Toledo, asked me where I wanted to pursue an internship. Of course, I said NREL. And thus begun my long and wonderful journey at this world-renowned laboratory. Three years ago, my NREL advisor, Dr. Mowafak Al-Jassim, directed me to the Colorado School of Mines (CSM) for Ph.D. study.

A special thanks goes to Dr. Yan, who guided me into the world of photovoltaics and offered me many opportunities while always being so helpful. I also thank Dr. Naba Paudel, who helped me put my hands on cadmium telluride solar cells and taught me how to do research in my early days. I’m thankful for the Yan group, realizing that it is unusual that we contact each other frequently and continue to work together on projects even after having left four years ago.

My four-year adventure at NREL has produced a lifetime of wealth for me. I thank Mowafak for providing a great platform for my growth from a young student to an independent researcher. I always remember the very first lesson from Mowafak: “You will not be trained to be a scientist, but will be a salesman that sells science.” It turns out that I did learn science and technology here, but also, the art of writing, presentation, and communication. I thank Dr. Chun-Sheng Jiang and Dr. Helio Moutinho for being my supervisors and training me to do cutting-edge science. They are knowledgeable and patient; their doors are always open to me whenever I have questions. I thank Dr. Nancy Haegel for her inspiration and being a great mentor, as well as the many NRELians who gave me abundant help and who I cannot adequately thank them here. I thank my CSM advisor, Dr. Brian Gorman, for his kindness in offering me the freedom to work on a topic of my own interest. Over these years, I have worked on many projects and experiments, and with the experience and skills learned at NREL, I feel ready to embrace any challenge in the future. I also thank Don Gwinner for his help with editing and formatting.

I have made many friends at NREL, especially through wonderful times over lunch, which included much fun and laughter, but also sparked new ideas through the intersection of disciplines. I thank Drs. Zhen Li and Ye Yang for inspiring me, both as nice roommates and friends. I also thank Ms. Yinong Sun for her companion and encouragement; it is difficult to imagine life without you around. And finally, I thank my family—my parents and sister—for their emotional support during some difficult times of living in a foreign country.
And I thank my department for arranging mandatory teaching assistant assignments for me, even though I was very busy with research projects, I learnt a lot.
CHAPTER 1

INTRODUCTION

My research area is scanning probe microscopy (SPM), which includes techniques based on atomic force microscopy (AFM) and scanning electron microscopy (SEM)—with a focus on solar cell materials and devices. I developed novel techniques or used cutting-edge microscopy techniques to study current and emerging photovoltaic (PV) materials and devices such as silicon (Si), copper indium gallium diselenide (CIGS), copper zinc tin diselenide (CZTS), cadmium telluride (CdTe), III-Vs, and perovskites. The characterization techniques help to understand the fundamental physics involved in device operation and can provide useful information in PV research. This dissertation includes papers primarily from three projects during my Ph.D. study.

1. In a “From Modules to Atoms” project, increase the reliability/stability of commercially relevant PV technologies.” My role was to use AFM-based techniques (e.g., Kelvin probe force microscopy (KPFM), scanning capacitance microscopy (SCM), and scanning spreading resistivity microscopy (SSRM)) to study reliability issues of solar panels, including potential-induced degradation (PID), defect metastability, and impurity diffusion and reverse-bias breakdown problems—down to the nanometer scale. These degradations last for long times and become worse toward the end of a module’s lifetime. Currently, an in-depth understanding of material science issues that pertain to solar module reliability is in its infancy. A permanent solution, rather than mitigation of these issues, requires an in-depth understanding of the fundamental material science properties that drive the degradation mechanism. AFM-based techniques are powerful tools for investigating these reliability issues and providing insights within this field.

2. Develop and apply the transport imaging (TI) technique. This technique combines scanning electron microscopy (SEM) and near-field scanning optical microscopy (NSOM) techniques by imaging light associated with local recombination. This “transport imaging” is related to, but different from, standard cathodoluminescence (CL), because it maintains the spatial information in the emitted light. One can “see” the transport of carriers and determine minority carrier or exciton diffusion lengths from a single image and map spatial variations in drift and diffusion behavior properties. Carrier
transport has traditionally been considered a limit to the spatial resolution of CL imaging. However, dual-probe transport imaging allows us to exploit that behavior to visualize directly the combined influences of diffusion, drift, surface recombination, and photon recycling on energy transport in luminescent materials—from the nano scale to the micron scale.

3. Develop or use cutting-edge microscopy techniques to study some important properties of PV materials and devices, such as CIGS, CZTS, and perovskite. The organic-inorganic halide perovskite solar cells have especially demonstrated a rapid increase in power conversion efficiency in the past five years, with a record efficiency of 22.1% that is comparable to “mature” thin-film techniques such as CdTe and CIGS. However, some fundamental questions about the electronic properties of perovskite remain unanswered. Microscopic study is required for a deeper understanding that will help to optimize device performance.

Chapter 2 focuses on developing and applying a novel technique—scanning capacitance spectroscopy (SCS)—to determine the exact junction locations in CIGS and CZTS solar cells. Multiple nm-scale polycrystalline layers and lateral μm-scale inhomogeneity raise many questions in thin-film PV. One question is the nature of the junction in CIGS and whether it is at the heterointerface or is a buried homojunction. In CIGS- and CZTS-based devices, the p-n junction is formed by different materials, and defects at the heterointerface can significantly alter the cell performance, especially open-circuit voltage ($V_{oc}$), by changing the carrier transport across the junction. Because of the complexity of the junction interface, the assumption that a metallurgical heterointerface is the electrical junction may be inaccurate because there can be interdiffusion of elements and dopant impurities. Addressing these controversial issues is critical for advancing thin-film PV technologies. For example, determining the junction location in CIGS devices will provide crucial guidance for developing new window layers for increased device short-circuit current density ($J_{sc}$). In this work, I report on determining junction locations in CIGS and CZTS and on using high-resolution SCS measurements to understand the large $V_{oc}$ difference between CIGS and CZTS solar cells.

Chapter 3 describes the technique development of an in-situ accelerated life stressing capability on an AFM platform to study potential-induced degradation (PID). In step with the
global PV market and installed capacity, PV performance reliability has become increasingly important. And PID has attracted extensive attention because it can massively degrade cell performance. However, microscopy characterization in this area is limited and the fundamental mechanism of PID is unclear. Furthermore, analytical tools can only examine a certain stage of the degradation, and PID has been reported to be reversible and metastable. The in-situ AFM-based microscopy technique we have developed allows direct observation of PID kinetics and reveals transitions of reliability-related metastable states; thus, we can monitor structural, electrical, and opto-electrical changes of the sample under stresses. Such experiments may be impossible in ex-situ studies. By designing a sample holder, we can apply a high voltage and high temperature to a sample with the same structure as the solar panel. In this work, KPFM measurements are shown as an example of characterization and analysis. The capability developed is easy to adapt to all other AFM-based techniques.

Chapter 4 concerns the investigation on the fundamental mechanism of PID. PID has been reported to be related to sodium ions diffusing into stacking faults that exist in the Si p-n junction, which cause local electrical shunting. PID can cause a massive decrease in module performance, and it becomes more severe as the system voltage of an array increases. It is questionable whether local shunting in the modules is the only major degradation mechanism associated with the massive decay or even failure in a module. In this chapter, I report on a large area (at millimeter scale) of p-n junction change caused by PID, and this phenomenon is different from the previous knowledge of stacking-fault pinpoint defects. We used KPFM and electron-beam induced current (EBIC) to study the electrical properties across the p-n junction of a heavily degraded lab-stressed multicrystalline silicon cell. Sodium is suspected to correlate with PID, so elemental distribution mapping was acquired by secondary-ion mass spectrometry (SIMS). The transition region of a functional and malfunctional junction is very sharp, in about the 1-µm range. KPFM also observed a recovery of the junction by heat treatment. All results are consistent and indicate a new PID behavior that has never been reported previously.

Chapter 5 focuses on the development of the transport imaging (TI) technique. To improve solar cell device performance, it is vital to measure minority-carrier diffusion length $L_d$, which is the average length that a minority carrier diffuses before recombining. Several techniques exist for measuring minority-carrier lifetime, but techniques that do not require a sample to have electrical contacts—thus, “contactless” techniques—are useful for evaluating
lifetime prior to device completion. An important example is time-resolved photoluminescence (TRPL), which is often used to determine the effects of various processing treatments on lifetime. In most cases, existing techniques are adequate for characterizing the aggregate, large-area lifetime of solar cell materials. However, techniques are needed that allow researchers to probe the effects of microscopic defects on carrier lifetime and diffusion length; such techniques would allow for a more in-depth understanding of processing treatments and would accelerate device development. We have developed a novel technique for the contactless measurement of $L_d$—called near-field transport imaging—that allows one to “image” carrier transport on the microscopic scale. In this technique, the electron beam of an SEM generates excess carriers within a micro- to nano-sized volume of subsurface material while the beam is fixed at a point or a line on the sample surface. Carrier diffusion from the generation volume is tracked by scanning an optical fiber with a nano-sized aperture above the surface and detecting the local light emission due to carrier radiative recombination.

Chapter 6 concerns the application of the TI technique; specifically, we investigated the carrier transport affected by hillock defects in gallium arsenide (GaAs). Hydride vapor-phase epitaxy (HVPE) is proven to produce high-quality GaAs materials comparable with other expensive techniques; however, it is difficult to avoid the formation of hillock defects on the sample surface. The defects act as nonradiative recombination centers and hinder further improvement of solar cell performance. The study the defect-associated charge-carrier transport properties is important, but, to date, no work reports on the quantitative measurement and direct mapping of carrier transport around these defects. With the TI technique, one can directly visualize the combined influences of diffusion, drift, surface recombination, and photon recycling on energy transport. In our work, the same hillock was examined by TI, near-field CL, standard CL, energy-dispersive X-ray spectroscopy (EDS), and electron backscattered diffraction (EBSD). The area around hillocks has a much higher non-radiative recombination rate, which significantly affects the carrier-transport process.

Chapters 7 and 8 focus on novel technique application for perovskite materials and devices. Chapter 7 concerns the non-stability issue of novel perovskite materials under an electron beam. Organic-inorganic halide perovskite solar cells have recently demonstrated a rapid increase in power conversion efficiency. However, the uncertainty about the stability of perovskite solar cells may be a potential obstacle hindering their large-scale application, and
stability still needs to be fully examined. Perovskite materials, as soft matter, could be affected by high-energy irradiation during SEM-based characterization. Investigating the possible changes of perovskite materials during characterization is critical to understanding the properties of perovskites because the interactions of perovskite with different probes could cause artifacts that complicate results and lead to unreliable information. CL is very sensitive to material opto-electronic properties (e.g., charge-carrier recombination and defect luminescence) and can provide a much higher spatial resolution than conventional PL techniques. CL has been widely used to characterize conventional thin-film photovoltaic materials (e.g., CdTe and CIGS). Therefore, CL is expected to be a suitable characterization technique to quantitatively study the potential impact of a high-energy electron beam on perovskite properties (e.g., composition, crystal structure, and defect properties). In this research, the in-situ interaction of perovskite materials with the high-energy electron beam was monitored by the change of CL signals.

Chapter 8 describes the use of KPFM potential profiling to determine the junction quality of SnO$_2$-based perovskite solar cells, which are continually showing great potential and have achieved high efficiencies to date of up to 22%. Ideally, the better optical and electrical properties of SnO$_2$ provide the possibility of achieving better performance than that of the most common TiO$_2$-based cells; however, the champion cell still uses TiO$_2$ as an electron-selective layer (ESL). The inferior performance of cells made of SnO$_2$ ESL may not be due to its intrinsic material properties. Rather, subpar performance is likely due to issues of processing optimization, which cause poor material quality, junction quality, and interface defect states. Therefore, a better understanding of the interface electronic properties between the ESL and perovskite is required to optimize alternative ESL materials. This work concerns a procedure to assess the quality of the ESL/perovskite junction by measuring potential distribution on the cross-section of SnO$_2$-based perovskite solar cells using KPFM. The results provide critical guidance for improving perovskite devices and deepen our understanding of related device physics. This work clearly shows the difference of the junction from the perspective of nm-resolution potential distribution across the junction and back contact.

Chapter 9 includes the list of publications during my Ph.D. study and a short summary of these papers.
CHAPTER 2

LOCATING THE ELECTRICAL JUNCTIONS IN Cu(In,Ga)Se$_2$ AND Cu$_2$ZnSnSe$_4$ SOLAR CELLS BY SCANNING CAPACITANCE SPECTROSCOPY

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2.1 Abstract

We determined the electrical junction (EJ) locations in Cu(In,Ga)Se$_2$ (CIGS) and Cu$_2$ZnSnSe$_4$ (CZTS) solar cells with ~20-nm accuracy by developing scanning capacitance spectroscopy (SCS) applicable to the thin-film devices. Cross-sectional sample preparation for the SCS measurement was developed by high-energy ion milling at room temperature for polishing the cross section to make it flat, followed by low-energy ion milling at liquid nitrogen temperature for removing the damaged layer and subsequent annealing for growing a native oxide layer. The SCS shows distinct p-type, transitional, and n-type spectra across the devices, and the spectral features change rapidly with location in the depletion region, which results in determining the EJ with ~20-nm resolution. We found an n-type CIGS in the region next to the CIGS/CdS interface; thus, the cell is a homojunction. The EJ is ~40 nm from the interface on the CIGS side. In contrast, such an n-type CZTS was not found in the CZTS/CdS cells. The EJ is ~20 nm from the CZTS/CdS interface, which is consistent with asymmetrical carrier concentrations of the p-CZTS and n-CdS in a heterojunction cell. Our results of unambiguously

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determination of the junction locations contribute significantly to understanding the large open-circuit voltage difference between CIGS and CZTS.

2.2 Introduction

Junction location in solar cells is a critical factor for conversion efficiency, especially in thin-film photovoltaics (PV). In these cells, the junction is formed by different material partners and the defects at the heterointerface can significantly affect open-circuit voltage ($V_{oc}$) by changing the carrier transport over the junction. Junction location is often conveniently assigned to the chemical heterointerface. However, because of the complexity at the interfaces—where interdiffusion of the main component elements and dopant impurities readily occur [1,2]—the assumption of junction location at the metallurgical heterointerface may be inaccurate. In fact, the junction location can depend on the detailed processing method and parameters related to junction formation [3,4]. For example, in high-performance CdS/Cu(In,Ga)Se$_2$ (CIGS) devices made by the 3-stage coevaporation of the absorber and chemical bath deposition (CBD) of the CdS window layer, the junction was proposed on the CIGS side, 10s of nm away from the CdS/CIGS interface [3], which is supposed to benefit the $V_{oc}$ of the device by avoiding interface recombination. However, solid direct evidence for this assumption has not been reported. The junction location in Si homojunction and III-V homo- and heterojunction devices are well defined and known. However, in the leading polycrystalline thin-film devices of CIGS, CdTe, and Cu$_2$ZnSnSe$_4$ (CZTS), knowledge of the exact junction location has been lacking, although the state-of-the-art CIGS and CdTe devices have achieved conversion efficiencies greater than 21% [5]. It is believed that to further improve the efficiency toward the Shockley-Queisser limit, research and development (R&D) based on better understanding is necessary. Therefore, determining the exact junction location in thin-film devices would not only improve the material/device understanding, but is also expected to guide future device R&D.

In this work, we report on the determination of junction locations in CIGS and CZTS by developing scanning capacitance spectroscopy (SCS). CIGS and CZTS have similar crystal and electronic structures and have similar bandgaps. However, the conversion efficiency ($E$) for these two types of solar cells is very different—($E_{CIGS}$-$E_{CZTS}$)/$E_{CIGS}$~ 40%—which is mainly the result of the $V_{oc}$ difference (31%) and fill factor difference (12%) [5]. The junction quality can be a
main factor for the inferior $V_{oc}$ of CZTS versus CIGS. Indeed, our SCS results show significantly different junction locations in the two devices.

Scanning capacitance microscopy is a technique based on atomic force microscopy (AFM) that images the majority-carrier density by measuring $dC/dV$ at each (x,y) point with a fixed DC bias voltage [6]. However, the results can be inaccurately converted to carrier concentration if the surface charge and band bending are not uniform in the imaged area [7]. However, in SCS, the $dC/dV$ signal in this work was acquired as a function of DC bias at every target point, which would compensate for the effects of surface band bending [6, 7]. This is especially necessary for thin-film PV because the surface band bending is expected to be inhomogeneous among the multiple layers and within a polycrystalline layer. Because of its high resolution, SCM/SCS measurements would provide vital information for junction determination and carrier characteristics in the junction/depletion area [8–10].

2.3 Experiment

The CIGS and CZTS devices were fabricated by the co-evaporation method. Details of the processing procedures and parameters, as well as the device performances are described in Refs. [11–13]. Briefly, the CIGS and CZTS absorber films were deposited on Mo-coated soda-lime glass substrates by co-evaporation of elements, then followed by CBD deposition of CdS and magnetron-sputtering of ZnO transparent conductive oxide (TCO) layers. Finally, a front contact of Ni/Al metal grids was evaporated using masks.

For the SCS measurement, a metal-insulator-semiconductor (MIS) structure is required. By sweeping DC bias (1 Hz) and an AC voltage (~90 kHz) between the SCM tip and the sample, the $dC/dV$ signal is measured with a lock-in amplifier as a function of the DC voltage. SCS has not been applied to materials other than silicon [6–10], mainly because of the challenge in creating a high-quality insulating layer, which is critical for the probe/sample capacitance measurement to be unaffected by the conductance through the probe/sample. We have developed a sample preparation procedure to make a high-quality thin insulating layer on the cross-sectional surfaces of CIGS/CdS and CZTS/CdS devices. We expended a significant amount of time exploring how to grow a high-quality insulating layer between the metal probe and the semiconductor samples. This process included atomic layer deposition (ALD) of Al$_2$O$_3$ layers on the sample, chemical vapor deposition (CVD) of diamond-like carbon (DLC) on the probe, and thermal oxidation of the sample surface to grow native oxide [14]. We have screened out the
former two approaches because the thin layer (~10 nm) was not adequately insulating, possibly due to defects in the layer. Electrical conductance probably flows by hopping through the defects. We were able to grow a high-quality insulating layer by thermal oxidation, which yielded high-quality SCS data. It is worth noting that growing an ALD layer on a cross-section flattened by ion-milling or mechanical polishing can be much different from growth on a plan-view of a film, because ALD depends critically on the ordering of the substrate surface.

For sample preparation, the device was cleaved and encapsulated by gluing a ~0.1-mm-thin layer of glass on the device side. The glass protects the film from polishing damage later in the process and from the SCM probe drop-off when using the probe to scan around the device edge (the TCO side). The cross-section was mechanically polished to make a relatively flat area for later fine polishing; we used diamond pads with a particle size down to 3 µm. The sample was then ion milled by a JEOL cross polisher (IB-09101CP) at 4 kV for 12 hours to make a flat crater in which the cross-sectional surface of the device is adequately flat (overall corrugation spanning the cross section is less than 20 nm) for the SCS measurement. A flat surface is critical for avoiding topographic effects and for the subsequent growth of a high-quality oxide layer.

Following the room-temperature cross-sectional ion milling, an important step is low-temperature (~140 K) and glancing-angle (6°) ion milling by a Fischione M1010 system, using 2 kV and 3 mA for 2 hours. This milling removed the damaged surface layer created by the room-temperature and high-energy ion milling. In growing the thermal oxide layer, the samples were heated in a homemade furnace with pure oxygen flow. The optimized condition is 200 °C for 30 min with 80 sccm oxygen flow for CIGS/CdS, and 225 °C for 15 min with 80 sccm oxygen flow for CZTS/CdS.

The SCM/SCS data were obtained by using a Vecco D3100 AFM system with a Nanoscope V controller. A Pt-Ir tip with a spring constant of ~18 N/m (Rocky Mountain Nanotechnology, 25Pt300B) was employed because of its excellent conductance for the capacitance-probing microwave (~1 GHz). The tip was virtually grounded, and the DC and AC voltages were applied to the sample. In the SCM measurement, \( V_{dc} \) and \( V_{ac} \) were set at 0 V and 3V. In SCS, \( V_{dc} \) was swept from -2 V to 2 V with a frequency of 1 Hz. The SCS or the dC/dV-\( V_{dc} \) curves were taken along a line ~280 nm long across the depletion region with a step size of 5 or 10 nm. No thermal drift was observed during the measurement, as verified by taking AFM/SCM images before and after the SCS measurement. Because neither AFM nor SCM
provide chemical information, we performed scanning electron microscopy (SEM) imaging on the same sample area on which we performed the AFM/SCM/SCS imaging to identify the chemical interfaces of CIGS/CdS and CZTS/CdS, i.e., the metallurgical junction (MJ) of the devices. SEM images were taken in an FEI Nova 630 Nano field-emission SEM system with both secondary electron (SE) and backscattering electron (BSE) modes.

2.4 Results and Discussions

Figure 2.1 shows an SCM/SCS measurement across the CIGS junction; Figure 2.1(a) is an SCM image in a scan size of 1 μm x 125 nm, 2.1(b) is an example of a line profile of the SCM image, and 2.1(c) is an example of SCS spectra at three typical locations of p-type, n-type, and depletion region. The SCM results show typical MIS dC/dV characteristics: positive in p-type, negative in n-type, and transitional in the depletion regions. The dC/dV-V_{dc} curves have a peak or valley shape, which corresponds to the change from depletion to nearly flat band, and to accumulation [6]. The SCM data taken at V_{dc}=0 V are positive and negative at the p- and n-regions, which is consistent with the SCS results. The SCS spectra in the depletion region exhibit a mixture of positive and negative, details of which depend on the specific location in the depletion region due to degrees of carrier flows from both p- and n-sides [6–10].

We have measured X-ray photoelectron spectroscopy (XPS) on bare CIGS film that underwent the same annealing processes. The results show that the surface layer contains O, In, Ga, Cu, Se, C, and Na, as expected. Although the chemical composition and structure of the insulating layer are not clear at the current stage, the SCS spectral characteristics allow for assessing whether the insulating layer quality is adequate for the SCS measurement. If the capacitance measurement was significantly affected by the probe/sample conductance, the dC/dV-V_{dc} curve would show a largely asymmetrical shape such as Figure 2.1(d) because of the interference of the DC current with the capacitance sensor when changing V_{dc}. The relatively symmetrical SCS shape illustrates that the measurement is dominated by the MIS capacitance [6]. The SCS peak and valley shapes due to the change in space-charge region from depletion to accumulation elucidate that the measured capacitance is dominated by the semiconductor capacitance but not by that of the insulating layer, i.e., the insulating layer is adequately thin. Therefore, we could judge the data quality by examining the data appearance, which is critical for the subsequent determination of junction location.
2.4.1 CIGS junction determination

Because detailed spectra could depend sensitively on the specific location in the depletion region, we expect to determine the junction location in fine resolution/accuracy of nanometers [7–10]. However, the location of the CIGS/CdS interface or MJ cannot be determined directly from the corresponding SCM and AFM images. High-resolution SEM images were taken on the same area; such images are sensitive to the chemistry of the layers in the sample.

The cross-sectional surface after annealing is mixed, with flat regions covered with a uniform insulating layer and regions covered with particle-like surface features. Figures 2.2(c) and 2.2(d) show a typical pair of SCM and AFM images. One sees from the AFM image the uniform regions in the upper part of the image, where the SCM image clearly exhibits a p-n junction. However, the lower part of the AFM image shows particle-like surface features, and we believe these features are oxide aggregations caused by the annealing. On these features, the SCM does not show well-defined p and n characteristics. In fact, these surface features are needed for later determination of the CdS/CIGS interface by aligning SEM and AFM images. Therefore, we take SCS spectra on the uniform regions that are close to the easily recognizable features.
We take SCS spectra and determine the MJ relative to the SCS locations in the following experimental procedures: (1) taking SCS along a line right after SCM/AFM images were taken [Figures 2.2(a) and 2.2(b)]; (2) enlarging the SCM/AFM area to include more features for later comparison with SEM imaging [Figures 2.2(c) and (d)]; and (3) taking SEM images on the same area and determining the SCS location in the SEM image by comparing the AFM and SEM

Figure 2.2 (a) SCM image and (b) the corresponding error-mode AFM image taken on a cross-section of a CIGS/CdS device; the horizontal bars in the figures indicate the location where SCS data were taken. (c) and (d) are larger-area images; the black frames indicate the positions of (a) and (b). (e) SEM and (f) AFM images taken on the same area; the blue lines indicate the same features on the images; the blue bars indicate the position of the SCS measurement. (g) shows the geometry relations of images.
images [Figures 2.2(e) and 2.2(f)]. Figure 2.2(g) shows the geometry relations of the AFM and SCM images. By this alignment procedure, the SCS location relative to the MJ is determined with 10-nm accuracy, which is critical for determining junction location.

Figure 2.3 (a) An SEM image showing the locations where SCS data were taken; (b) SCS spectra in the near-junction region; and (c) C-V curves numerically integrated from the SCS data in (b). The positions, indicated by the prefix #, are counted from left to right, and the distances are from the MJ. The spectra at locations as indicated in (a) are discussed in this paper.

Figure 2.3(a) shows the SEM image with the locations where the SCS spectra were taken. In this particular data set, a total of 28 spectra were taken with a step size of 10 nm, and the MJ was identified at position #26. Figure 2.3(b) shows the spectra on positions from #21 to #27, where the junction is located. One sees that spectra #25 to #27 are similar and exhibit an n-type signature with negative dC/dV values over the applied V_{dc} range. However, spectra #25 is in the CIGS side, 10 nm away from the MJ, which indicates the existence of an n-type CIGS layer—i.e., the CIGS device has a buried homojunction. However, this 10-nm distance from the MJ is in the same order of the SCS step size and the SEM/AFM alignment accuracy. The appearance of
n-type SCS varies 10~30 nm from the MJ, depending on specific locations, possibly because of the nonuniform nature of polycrystalline devices. Figure 2.4 shows another spectra set across the junction, with the appearance of n-type SCS from 30 nm away from the MJ. Therefore, the SCS results provide an unambiguous demonstration of a buried homojunction of the high-performance 3-stage CIGS device with efficiency of 17.3%, open-circuit voltage of 0.648 V, short-circuit current of 34.27 mA/cm$^2$, and fill factor of 77.86%.

Moving toward the CIGS side, the spectra change rapidly (#21–#25 in Figure 2.3b), as expected in the depletion region. The carrier density in this region is low, and the spectra are largely determined by receiving carriers from both side of the junction; therefore, the spectra change sensitively with the location. Changes in the SCS spectra between neighboring points can be distinguished clearly in the junction region, indicating a possible resolution within 10 nm in locating the electrical junction (EJ). This was not a surprise with a probe diameter of ~40 nm, because 5-nm resolution has been reported for SCM imaging using a 50-nm diameter probe due to the probe-sample contact area being smaller than the probe diameter [15]. With the location changes toward the p-side from #25 to #21, the spectra changes from an n-like signature (negative SCM dC/dV) toward p-like (positive dC/dV). Whether the SCM is p-like (positive) or n-like (negative) and the flection point of the SCM dC/dV signal depends sensitively on the specific location of the probe and the bias voltage ($V_s$) applied—or, in other words, how much the carrier is extracted/repulsed by the probe from both sides. Quantitative understanding requires three-dimensional device modeling that takes into account the carrier flows in the device p-n junction and in the MIS structure on the cross-section. We note that $V_s$ in the graphs are DC bias voltage applied between the probe and sample. No bias voltage is applied between the front and back contacts of the solar cell (short circuit). These spectra in Fig. 2.3(b) are highly asymmetrical due to the uneven carrier flow from the p- and n-sides, which were taken on a high-quality MIS area and inside the depletion region. These spectra are different from the asymmetrical ones taken on the p-side of a low-quality MIS area outside the depletion region such as the one shown in Fig. 2.1(d).

To further examine the spectra, we numerically integrated the SCS spectra and obtained C-V curves, as shown in Fig. 2.3(c). Curves #25 to #27 are similar, with an n-type signature where the capacitance decreases monotonously and then saturates with further increasing $V_{dc}$ due to the transition from near flat band to depletion [6–10]. Curves #21 to #24 show a decrease in
the capacitance and then an increase with an inflection at different V_{dc}. At position #22, 40 nm away from the MJ, the inflection point is at V_{dc}=0 V. This characteristic indicates the EJ location. At the EJ, where the carrier concentration is the minimum across the junction, the capacitance should have its minimum at V_{dc}=0 V, assuming no fixed charges in the insulating layer, and hence, no lateral shift of the C-V curve. This assumption is supported by the SCS spectra at the p- and n-sides [Fig. 2.1(c)], where the symmetric SCS around V_{dc}=0 V demonstrates the absence of a significant amount of fixed charges in the insulating layer. Because of the significant change in the C-V curve and the clear distinction between the neighboring pixels around the EJ, we estimate that the resolution of EJ identification from the SCS measurement is within 10 nm. In our case of SCS spectra around the EJ, where carrier concentration is extremely low and carrier flow is contributed from both sides of the junction, the SCS spectra are very sensitive to the specific location. Also, at the local area, the surface is adequately flat at less than a few nm, and the insulating layer is uniform and thin. All these factors and the much smaller probe/sample contact area than the probe size result in the fine resolution of SCS in determining the EJ location. However, because our resolution in determining the MJ is about 10 nm, the uncertainty in locating the EJ is \( \sigma_{EJ} = \sqrt{\sigma_{S}^2 + \sigma_{a}^2} \approx 15 \) nm, where \( \sigma_{EJ} \), \( \sigma_{S} \), and \( \sigma_{a} \) are standard deviations of the EJ, SCS, and SEM/AFM alignment, respectively.

Finally, we show the change in SCS spectra around the edge of the depletion region. The SCS spectra at position #0 (260 nm from the MJ) exhibit a typical p-type signature, with a relatively symmetrical shape (Fig. 2.5), whereas the spectra at position #2 (240 nm from the MJ, 200 nm from the EJ) already show distortion or transition. The spectra begin to change rapidly around this area, indicating the location of the edge of the depletion region. This results in a depletion width of about 200 nm, and a consequent CIGS doping in the low \( 10^{16} \text{ cm}^{-3} \) range, which is consistent with the expected value of \( \approx 2 \times 10^{16} \text{ cm}^{-3} \).

A buried homojunction in the CIGS layer indicates that the CdS and ZnO layers are inactive in collecting photo-excited carriers for high-efficiency CIGS solar cells. During CdS deposition, Cd\(^{2+}\) could diffuse into CIGS. The Cd\(^{2+}\) ions could occupy Cu\(^{1+}\) sites and act as donors [2–4], leading to the formation of shallow n-type CIGS. On the other hand, a nanometer-thin layer of ordered vacancy compound (OVC) formed on the CIGS subsurface region could
Figure 2.4 An SEM image showing the locations where SCS data were taken and the SCS spectra in the near-junction region; #37 is an all-negative SCS signal, which represents n-type CIGS, and it is 30 nm away from the MJ.

Figure 2.5 SCS spectra taken at locations #0, #2, and #4 in Fig. 2.3(a), which are 260, 240, and 220 nm away from the MJ.
facilitate a homojunction. This junction determination also provides the insight that CdS is not the ultimate interfacial material and illustrates the potential to achieve high-efficiency Cd-free devices. Indeed, CIGS cells using zinc oxide-sulfide as a buffer layer have achieved over 21% efficiency [16].

2.4.2 CZTS junction

The junction determination procedure was also applied to CZTS, where we observed rapid transition of SCS spectra in the depletion region similar to that in CIGS. Figure 2.6 shows a spectra set with a total of 64 spectra and a step size of 5 nm. The MJ is at position #52 in Fig. 2.6(a). The EJ (#48), where the C-V curve shows its minimum at $V_{dc}=0$ [Fig. 2.6(b)], is 20 nm away from the MJ. Similar to CIGS, the spectra change rapidly around the junction, indicating a comparable resolution in determining the EJ to the step size (5 nm). The uncertainty in determining the MJ from the alignment of AFM and SEM is ~20 nm, which is similar to the distance from EJ to MJ. Therefore, we cannot determine whether or not the EJ is located exactly at the MJ. However, the asymmetrical doping at both sides of the junction suggests a deviation of the EJ location from the p-n junction. If the p-n junction is exactly at the MJ, then a 20-nm deviation of the EJ is consistent with the carrier concentrations of $\sim5\times10^{16}/\text{cm}^3$ in CZTS and $2\times10^{17}/\text{cm}^3$ in CdS. The spectra at the MJ show transit features in a p-n junction, which is different from the entire n-signature in the CIGS junction. Therefore, the SCS measurement demonstrates a heterointerface junction, rather than a homojunction.

CZTS and CIGS have similar crystalline structure and similar direct bandgaps. However, the $V_{oc}$ values of the two devices differ by 240 mV, which is the most important factor affecting the difference in power output of the state-of-the-art devices. Our results of the junction locations indicate the possibility of different transport mechanisms over the junction between the two devices. Recombination-dominated transport can significantly degrade $V_{oc}$ by losing energy at the interface. Conversely, a homojunction can significantly mitigate the interface recombination by facilitating diffusion transport across the junction, which suggests a plausible route for improving CZTS devices.
2.5 Conclusions

We have developed an SCS technique that is applicable to leading thin-film CIGS and CZTS solar cells. We accomplished this by developing a procedure to prepare cross-sectional samples and grow high-quality insulating layers, which is critical for SCS measurements. The spectra show distinct p-, transitional, and n-signatures across the devices. By comparing the SCS data with AFM and SEM images, we found that CIGS has a buried homojunction, and the EJ is located ~ 40 nm inside the CIGS absorber. An n-type CIGS was found in the region adjacent to the interface. We also determined that the CZTS/CdS cells have a heterointerface junction with a shallower EJ (~20 nm) than in CIGS. Our results, which unambiguously determine junction locations, contribute significantly to understanding the $V_{oc}$ difference between the two devices. The results also indicate a plausible route for improving the devices by avoiding the interface recombination of carrier transport across the junction.

Acknowledgments

The authors thank Bobby To for taking the SEM images, Drs. Lorelle Mansfield and Ingrid Repins for providing CIGS and CZTS samples, and Dr. Arrelaine Dameron for growing the Al2O3 layers by ALD, and Dr. Craig Perkins for XPS measurements. This work was
supported by the U.S. Department of Energy under Contract No. DE-AC36-08GO28308 with the National Renewable Energy Laboratory.

2.6 References


CHAPTER 3

DEVELOPMENT OF IN-SITU HIGH-VOLTAGE AND HIGH-TEMPERATURE STRESSING CAPABILITY ON ATOMIC FORCE MICROSCOPY PLATFORM

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3.1 Abstract

Reliability has become an increasingly important issue as photovoltaic technologies mature. However, researching reliability at the nanometer scale is in its infancy; in particular, in-situ studies have not been reported to date. Here, to investigate potential-induced degradation (PID) of solar cell modules, we have developed an in-situ stressing capability with applied high voltage (HV) and high temperature (HT) on an atomic force microscopy (AFM) platform. We designed a sample holder to simultaneously accommodate 1000-V HV and 200°C HT stressing. Three technical challenges have been overcome along with the development: thermal drift at HT, HV interference with measurement, and arc discharge caused by HV. We demonstrated no observable measurement artifact under the stress conditions. Based on our in-situ stressing AFM, Kelvin probe force microscopy potential imaging revealed the evolution of electrical potential

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across the junction along with the PID stressing time, which provides vital information to further study the PID mechanism.

3.2 Introduction

The global photovoltaics (PV) market and installed PV capacity have grown rapidly over the past decade through a combination of PV technology advances and policy initiatives [1]. In step with this growth, PV performance reliability has become increasingly important. Among all the reliability issues, potential-induced degradation (PID) has received extensive attention because it can lead to a massive decrease of module performance [2,3,4,5,6]. PID is due to the potential difference between the module frame/glass and solar cell. This effect occurs in all major types of solar modules and becomes more severe with an increase of solar array system voltage. Currently, extensive study of PID is at the panel/cell scale [3,4,5,6,7,8]; however, this effect has only been studied by limited microscopy characterization methods [9,10,11,12], such as secondary-ion mass spectrometry and transmission electron microscopy. These measurements can provide a deeper understanding of PID-related defect chemistry and structure, and electrical properties of the p-n junction. However, these powerful analytical tools only examine a certain degree of degradation, and the PID mechanism remains unclear. Questions related to the fundamental mechanism such as sodium contamination and partial recovery have yet to be answered [2]. It is has been well reported that Na diffuse into stacking faults and cause the local shunting of p-n junction. However, it is not clear whether the stacking faults existed before the PID or were induced by the PID. Moreover, it is questionable whether the local shunting is the only PID mechanism. PID can be reversible and metastable, so in-situ monitoring of microscopic structural, electrical, and opto-electrical changes under stresses allows direct observation of degradation kinetics and reveals transitions of reliability-related metastable states. Such observation may be impossible in ex-situ studies, and the in-situ monitoring provides the possibility to gain a deeper understanding the PID mechanism.

AFM-based characterizations have been unique and powerful tools to study nanometer (nm)-scale electrical properties of solar cells [13,14,15,16,17,18,19,20,21]. Here, we have developed an in-situ stressing capability based on our AFM platform: a sample holder is designed to stress a small piece of solar module (1 cm × 1 cm) at high voltage (HV) up to 1000 V and simultaneously at high temperature (HT) up to 200°C. The accelerated life test (ALT)
standard condition for PID is 1000 V at 85°C [2,9]. This experimental design and setup allowed us to do ALT and measure the change in nm-scale electrical properties with degradation in real time. Specifically, we apply Kelvin probe force microscopy (KPFM) measurements on cross-sections of the devices, with direct imaging of the evolution of the electrical potential across the junction with nm resolution during the degradation process. In this paper, we will show thermal-drift suppression under different high temperatures, KPFM test results with and without the HV and HT stresses, as well as preliminary in-situ HV stressing results of potential images across a multicrystalline silicon (c-Si) junction along with the degradation process. In addition to KPFM, the in-situ stressing capability on the AFM platform can also be used for other nanoelectrical probes such as scanning capacitance microscopy (SCM) [17], scanning capacitance spectroscopy (SCS) [18], scanning spreading resistance microscopy (SSRM) [19], and conductive AFM [20].

3.3 Experimental Design and Technical Barrier

We designed and tested a sample holder based on our existing AFM platforms, to accommodate two stressing capabilities of 0–1000-V HV and 25–200°C HT. The design SOLIDWORKS files are shown in supporting materials (Figure 3.9–3.17). Figure 3.1 shows a photo of the designed sample holder that is capable of simultaneous HV and HT stressing and is

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Figure 3.1 A photograph of the in-situ stressing sample holder based on the AFM platforms.
compatible with all the electrical imaging of KPFM, SCM, SCS, SSRM, and conductive AFM. Figure 3.2 schematically shows functions of the sample holder. A piece of sample of a c-Si solar cell module is subjected to the HV and HT stressing, while the nm-scale electrical imaging on cross-sections of the sample is being performed with a bias voltage applied to the cell, in order to image the electrical change across the junction. Three key challenges that our development confronted and has overcome are the following: thermal drift, HV interference with the electrical measurement, and HV arc discharge. Thermal drift is detrimental for high-resolution microscopy study, and the drift becomes more serious as temperature increases. As HV is applied across the solar module glass, electric field leakage can substantially interfere with the small potential (~1 V) measurement across the solar cell junction. Because the AFM-based techniques use small (centimeter-size) samples, the HV can cause arc discharge that may damage the sample and apparatus.

3.4 Cross-Sectional Sample Preparation

To simulate the PID process, the sample structure is made to be identical to a silicon module: a piece of multicrystalline silicon (mc-Si) cell is covered by pre-polymerized ethylene vinyl acetate (EVA) and a tempered solar glass. The silicon solar cell studied in this work is the conventional Boron-doped p-type Si, with a single front junction (Phosphor-doped emitter) and
SiN\textsubscript{x} on top. The working solar cell (shunt resistance larger than 500 ohm-cm\textsuperscript{2}) was partially covered by the glass (as shown in Figure 3.2) to expose the cell’s front contact so that a bias voltage can be applied across the cell; this procedure is needed for the KPFM measurements to avoid the effect of the fixed surface charge [21]. In other electrical measurements of SCM and SSRM, a bias voltage is applied to the whole cell through either the front or back contacts but not across the cell, so the cell is not required to be alive (sufficiently large shunt resistance). Because the AFM-based imaging technique requires a flat surface, the sample was fine-polished to make the overall corrugation of the cross-section surface less than 20 nm. The polishing procedure was chemical-mechanically polishing with deionized water using a set of different diamond pads with particle size down to 100 nm, and followed by a polishing using silica colloids with a soft cloth [21]. Note that the tempered glass, EVA, and silicon cross-sectional surface need to be in the same plane for cross-sections of the different materials to be polished to the same height. As a result, the polishing needs to be for more than ~2 hours and must be constantly checked to make sure the soft EVA material will not cover the front side of the silicon solar cell.

3.5 Thermal Drift Suppression

Thermal drift occurs when there is heat exchange with the surrounding environment. The sample holder and the sample are made of different materials and have complicated geometries. So any small mismatch of thermal expansions can cause huge thermal drift in the nm to µm scales. In practice, it takes a very long time to reach a true thermal equilibrium state when there is a significant temperature difference between the material and surrounding environment. Even though the temperature measured by a thermocouple stabilizes within a fraction of a degree, a small thermal change can still cause significant thermal drift at elevated temperatures. We designed the sample holder with two approaches to suppress thermal drift of the sample: 1) make the thermal nonuniformity/gradient inside the sample holder small by making a ceramic cover of the sample holder (ceramic material has a lower thermal conductivity than metals) and tighten the sample firmly to the holder; and 2) make a symmetrical design and locate the sample at the center of the symmetrical geometry. The thermal drift is well within acceptable levels: 6 nm/min at 85°C (the standard accelerating stress condition), and 13 nm/min at 200°C. Figure 3.3 shows two AFM images taken consecutively over a time interval of 5 min. Line profile analysis across
a particle feature illustrates a thermal drift rate of 5.7 nm/min in both the X and Y directions. The ability to follow the same sample area is important. If the thermal drift is less than 10 nm/min (10 µm/16 h), it is easy to follow the same area overnight, and thus, it is acceptable. If it is >100 nm/min (100 µm/16 h), it will be difficult to follow the same area. Figures S3.10 and S3.11 show the AFM images and line profiles taken at 125°C and 200°C.

3.6 Eliminating High-Voltage Interferences

HV interference with the electrical measurement, which had been the most challenging problem, was resolved by three electrical wirings and shielding. The 1000-V HV significantly affected the potential measurement on the silicon sample. Figure 3.4 shows potential profiles across a Si junction under a forward bias voltage $V_b = +0.5$ V applied to the device. With a 1000-V HV applied to the glass (simulating the system voltage in a solar array), the potential profile changed significantly—decreasing ~500 mV in the emitter and ~200 mV in the absorber—which should not occur in the potential inside a solar cell but is likely an artifact of the HV affecting the potential measurement in the AFM system. The three electrical cases were: 1) four sidewalls of module glass out of its six faces (except for the side applied with the HV and the side adjacent to the Si cell) must be shielded with conductive materials (silver paint);

![Image 1](image1.png)

Figure 3.3 (a) and (b) are consecutive AFM images taken on the cross-section of a Si solar cell with a time interval of 5 minutes, at a temperature of 85°C. The particle on the surface was used to identify the imaging area. 3(c) and 3(d) show line profiles along the lines in (a) and (b) in both X and Y directions, for examining the thermal drift rate.
2) the glass shielding must be grounded together with one side of the solar cell to the grounding line of the voltage source for applying the bias voltage ($V_b$) across the solar cell, and $V_b$ is applied to the other side of the cell; and 3) the HV source (including its grounding line) must be isolated from all the other power sources for the $V_b$, AFM, and electrical AFM. This discovery of the combination of all the factors required considerable effort because there are many ways to combine these factors. The glass shielding is effective to screen out the large HV leaking from the glass sidewalls. The separation of HV power electronics and its grounding lines effectively isolated its interference through the power lines. The glass shielding paired with the $V_b$ source grounding line (for bias applied across the solar cell) prevented possible interference through grounding loops.

Figure 3.5 shows the potential imaging results with and without 1000-V HV. The images and profiles showed no observable changes in the potential imaging by the HV. Figures 3.5a–d show the results with no HV: Figure 3.5a shows AFM topography of the solar cell cross section, and Figures 3.5b–d show the potential image at $V_b = 0$, -1, and -1.5 V (reverse bias), respectively. Figures 3.5e–h) show the corresponding images with 1000-V HV applied to the glass. Figure 3.6a shows the potential profiles under various bias voltages without a HV, and Figure 3.6b is the potential difference subtracted by the 0-V profile; Figure 3.6c shows the

![Figure 3.4](image.png)  
**Figure 3.4** Potential profiles measured by KPFM with no high voltage and 1000-V voltage applied to the module glass, showing a significant change in the potential profile by the high voltage.
electrical field difference by taking the first derivative of the potential differences in Figure 3.6b. The peaks of the electric field indicate that the p-n junction location is ~300 nm from the cell surface. The depletion width is estimated to be 500 nm, which is consistent with the doping concentration in a conventional silicon solar cell. Similarly, Figures 3.6e–f showed the potential profiles, potential difference, and the electrical field difference across the junction with the 1000-V HV applied to the glass. The measurements with and without HV are identical, demonstrating that the HV has not interference and cause the measurement artifact.

The arc discharge under 1000-V HV was resolved by the following experimental improvements: 1) make the sharp edges and corners of all the parts of the sample holder (~15 parts) rounded to avoid local extreme electric field; and 2) ground the metal brackets in the sample holder (Figure 3.1) to the HV source ground line that is isolated from the glass shielding and solar cell grounding lines. The mechanism of the latter is not clear, likely because of the need to locate the HV grounding (and also its negative electrode connected to ground) close to the HV line so that a faint charge loop can be formed to prevent high-energy charge accumulated in the electrical lines and in the power source.

![Figure 3.5 KPFM potential and the corresponding AFM images taken in the junction area of a c-Si solar cell under reverse bias voltages of $V_b = 0$ V, $V_b = -1$ V, and $V_b = -1.5$ V; 5a–d without a HV and 5e–h under a HV of 1000-V applied to the module glass. These KPFM potential imaging results illustrate no observable change by the HV applied to the module glass.](image-url)
We have successfully designed and developed the \textit{in-situ} HV and HT stressing capability on the AFM platform, and we have used it to study \textit{in-situ} PID of conventional p-type c-Si solar cells.

\subsection*{3.7 Application of \textit{In-Situ} Stressing Capability}

To investigate the evolution of potential profiles under ALT conditions, we made a fresh sample and examined it by KPFM imaging along with the HV stressing. We tracked the change over a long period of time and observed the degradation process. Figure 3.7 shows the \textit{in-situ} measured results during HV stress in 40 days at room temperature (RT). Note that this stress time is prolonged compared to normal laboratory PID time. This is necessary in our case because PID causes randomly defective areas, and we have to stress a longer time and keep monitoring the change in the potential image until an area close to the cross-sectional surface is degraded and can be observed in the potential images.
Figure 3.7 a–b) AFM taken in the junction area and the corresponding potential image at reverse bias of -1.5 V; c–d) after 20 days of HV stress, the AFM and potential images on the same location; e–f) after 40 days HV stress, the AFM and potential images on the same location. Significant change is observed in potential images during HV stress.

Figure 3.7a shows the initial AFM image of the cross-section; we used the amplitude-error image to clearly show the interface between silicon cell and EVA, the Si/EVA interface is indicated by the black dash line; Figure 3.7b shows the KPFM potential image at reverse bias voltage of -1.5 V. At the p-n junction (~0.5 µm from the Si/EVA interface), the applied voltage drops the most (the interface between bright and dark areas), and the emitter width is
approximately uniform. With HV stress 20 days, the potential profiles start to appear significantly different. Figure 3.7c shows an AFM image taken on the same area as Figure 3.7a. However, the potential image of Figure 3.7d with reverse bias voltage of -1.5 V shows that the emitter width or the junction depth becomes significantly smaller than the initial state and the junction depth appears less uniform, indicating an electrical degradation of the junction. As the area starts to degrade, we usually observed development of electrical potential degradation with PID-stressing time, as observed in Figures 3.7e and 3.7f after 40 days of PID at RT. Figure 3.7e shows an AFM image in the same location as Figures 3.7a and 3.7c; however, the KPFM image in Figure 3.7f shows large differences from the initial state in Figure 3.7b and the state after 20 days stressing in Figure 3.7d. Note that Figures 3.7e and 3.7f were both combined by two scans, as we scan a very large area of ~350-µm total length along the junction and every image is 5 µm × 5 µm. As shown in Figure 3.7f, the location or area over which the applied voltage drops becomes broad and smeared out. Meanwhile, the potential amplitude (~0.5 V) across the junction area becomes smaller than Figures 3.7b and 3.7d, and much smaller than the applied voltage amplitude (1.5 V).

Figure 3.8 shows a transition area between a normal and an abnormal potential drops across the junction, as highlighted by the red circle, and the Si/EVA interface is indicated by the black dash line. The results were collected after 20 days stressing. Potential imaging on the

Figure 3.8 a) AFM taken in the junction area; b) the corresponding potential image at reverse bias of -1.5 V, the red circle highlighted the sharp transition between degraded and good area.
pristine cell showed normal potential drop such as Figure 3.7b everywhere in the cell, as confirmed by random sampling of the KPFM imaging. When the sample starts to degrade by PID, we tried to take as much data as possible to capture the transition region. The AFM of the cross section is showed in Figure 3.8a, and the corresponding potential image taken at reverse bias of -1.5 V is showed in Figure 3.8b. In the normal junction area, the potential drop was observed at the location of p-n junction, similar to the result in Figure 3.7b; in a degraded junction area, the potential drop is close to the Si/EVA interface, similar to the one in Figure 3.7d. As indicated by the red circle, the transition from the normal to abnormal potential areas is within a short distance of ~1 µm.

The transition between the areas with the normal and abnormal potentials suggests a new PID mechanism rather than the well-reported local shunting caused by Na diffusion into stacking faults. A local shunt can also cause the potential drop deficit around the shunt over a large area, depending on resistance of the local shunt and sheet resistance of emitter, which leads the apparent junction collapse as appeared on the junction potential imaging. However, if the local shunting was the reason for our abnormal potential imaging, the potential drop must gradually change from the location of local shunting to the normal potential area in a much longer range of ~100 µm, because the ~100 ohm sheet resistance would increase resistance of the electrical current path through the local shunts and the emitter gradually. Because of the short transition distance of ~1 µm, the PID we observed should not be caused by a local shunting, but is likely dominated by an actual large-area junction damage, which has not been reported so far. Although the detailed mechanism of this PID degradation is not clear at present, this in-situ change of potential distribution across the junction indicates a degradation of junction—or, in other words, deviation from a good/normal junction of c-Si solar cell. Detailed study and analysis of the potential evolution will be published in the near future.

3.8 Conclusions

We have designed and developed a sample holder to accommodate an in-situ stressing capability with HT and HV on the AFM platform: 1) By designing the symmetrical sample holder and using a heat shield, the thermal drift was largely suppressed; 2) We overcame the challenges of HV interference with measurements by separating the HV power electronics and effectively shielding and grounding; 3) The HV-caused arc discharge was eliminated by grounding the sample holder and sample and by removing high-curvature areas. The results
under stress conditions demonstrated no measurement artifacts. Furthermore, we used the developed capability to study in-situ PID of a silicon cell by KPFM potential imaging, and we observed significant change in the potential images along with the degradation process. We also observed that the transition between normal and abnormal junction areas is sharp (~1 µm). Currently, it has not been reported with a paralleled characterization tool like this KPFM with in-situ stressing capability. Further investigation of PID issues using this capability is expected to provide new insights in understanding the PID mechanism(s). In addition to KPFM potential imaging, this stressing capability is also compatible with other AFM-based nm-scale electrical characterizations such as SCM, SCS, SSRM and conductive AFM.

Acknowledgements

This work was supported by the U.S. Department of Energy under Contract No. DE-AC36-08GO28308 with Alliance for Sustainable Energy, LLC, the Manager and Operator of the National Renewable Energy Laboratory.

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3.9 References


### 3.10 Supporting Materials

![Figure 3.9 SOLIDWORKS screen capture of the designed sample holder part 1, macor chuck.](image)
Figure 3.10 SOLIDWORKS screen capture of the designed sample holder part 2, base frame.

Figure 3.11 SOLIDWORKS screen capture of the designed sample holder part 3, base plate.
Figure 3.12 SOLIDWORKS screen capture of the designed sample holder part 4, left holder.

Figure 3.13 SOLIDWORKS screen capture of the designed sample holder part 5, right holder.
Figure 3.14 SOLIDWORKS screen capture of the designed sample holder part 6, insulating tube.

Figure 3.15 SOLIDWORKS screen capture of the designed sample holder part 7, macor insulating block.
Figure 3.16 SOLIDWORKS screen capture of the designed sample holder part 8, high voltage contact.

Figure 3.17 SOLIDWORKS screen capture of the designed sample holder part 9, heater cover.
Figure 3.18 (a) and (b) are consecutive AFM images taken on the cross-section of a Si solar cell with a time interval of 5 minutes, at a temperature of 125°C. The particle on the surface was used to identify the imaging area. 18(c) and 18(d) show line profiles along the lines in (a) and (b) in both X and Y directions, for examining the thermal drift rate.

Figure 3.19 (a) and (b) are consecutive AFM images taken on the cross-section of a Si solar cell with a time interval of 5 minutes, at a temperature of 200°C. The particle on the surface was used to identify the imaging area. (c) and (d) show line profiles along the lines in (a) and (b) in both X and Y directions, for examining the thermal drift rate.
CHAPTER 4

LARGE-AREA JUNCTION DAMAGE IN POTENTIAL-INDUCED DEGRADATION OF c-Si SOLAR MODULES

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4.1 Abstract

We report a large area of millimeter-scale p-n junction damage caused by potential-induced degradation (PID) of lab-stressed crystalline-Si modules. Kelvin probe force microscopy results show electrical potential change across the junction, and a recovery was observed after heat treatment. Electron-beam induced current results support the large-area damage instead of local shunts and a much lower collected current for the affected junction area. Furthermore, secondary-ion mass spectrometry indicates that the large-area damage correlates with sodium contamination. The consistent results shed new light on PID mechanisms to investigate that are essentially different than the widely reported local junction shunts.

Index Terms — potential-induced degradation, junction damage, large area, recovery, microscopy.

4.2 Introduction

Potential-induced degradation (PID) has been an important degradation component in all types of major solar modules, and it gets more severe as the system voltage of a solar array increases. PID could cause a massive decrease of module performance [1][2][3]. For crystalline-silicon (c-Si)-based modules, PID has been reported to be related to sodium ions diffusing into extended defects that exist in the Si p-n junction, causing local electrical shunting [4][5][6]. However, a nanoscale understanding of PID is still in its infancy. PID is a complicated material

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and device issue, with many different degradation kinetics and mechanisms among the different solar modules. It is questionable whether local shunting in c-Si modules is the only major degradation mechanism associated with massive degradation or even module failure.

In this paper, we report a large area of p-n junction change by PID that occurred at the millimeter scale. We imaged the electrical potential across the junction of a multicrystalline silicon (mc-Si) cell using Kelvin probe force microscopy (KPFM), current collection using electron-beam induced current (EBIC), and elemental distribution using secondary-ion mass spectrometry (SIMS). We found movement of the apparent electrical field from the p-n junction location to the front surface of the cell. We also observed a recovery of the movement by heat treatment via tracking the potential change in the same location. Characterization of the electric field in heavily PID-shunted regions shows that there is a broad reduction in the junction potential instead of localized perturbations of the electric field at defects. In EBIC measurements of the cross section, a much lower current was collected and the affected area is large instead of just being local shunts. SIMS results indicate a large area of sodium contamination around the damaged junction area. These consistent results suggest a PID behavior, which has not been reported in the literature.

4.3 Experiment Details

KPFM measurements require a working cell so that external bias voltage can be applied to the junction (i.e., a sufficiently large shunt resistance). We have performed the KPFM imaging on an in-house mini-module without edge damage, instead of on commercial field-stressed modules that have damage after being cored at selected PID areas in the module. In making the mini-module, a conventional front-junction (n⁺/p) mc-Si cell was sandwiched with glass substrate and superstrate and with pre-polymerized ethylene vinyl acetate (EVA) as encapsulant. All the layer materials were held together with clamps without melting the EVA. After laboratory PID stressing, the cell was removed from the mini-module without mechanical damage.

A constant bias voltage of -1,000 V was applied to the shorted mini-module in an environmental chamber at a temperature of 25°C and 10% relative humidity for two weeks. Significant PID was observed by the development of dark current-voltage (I-V) curves captured periodically over the course of the stress. The mini-module was then delaminated to extract the cell. A piece of the cell with heavy PID degradation, as identified by photoluminescence (PL)
imaging, was cut out of the cell. The sample contains the most-degraded area in the cell according to the PL image as shown in Fig. 1 (no PL contrast in the same area before the PID). We cleaved the sample across the darkest PL area and used silver epoxy to glue the cell emitter (n+) face to another piece of silicon. This sandwich sample preparation prevents probe drop-off when scanning the probe close to the front side of the cell or across the junction. The sample was chemical-mechanically polished with deionized water using a set of different diamond pads and finally using silica colloids with a soft cloth. The polishing process must be well controlled to ensure: 1) a flat surface necessary for atomic force microscope (AFM)-based imaging; 2) that the cell has to be alive for the KPFM measurement; and 3) that the heavily PID-stressed area is not polished away.

![Image of sample preparation](image)

Figure 4.1 PL mapping of a PID-shunted area. The sample was cleaved to expose the cross section, indicated by the red dash line. The KPFM analyzed region is between two metal grids with most serious PID-affected area.

KPFM is an AFM-based technique that measures electrostatic potential on the sample surface at a spatial resolution of ~30 nm and a potential resolution of ~10 mV [7]. To avoid the effect of surface charges, we applied a bias voltage to a working device and measured the corresponding changes of surface potential. Because the surface-charge configuration should not change with a small bias voltage $V_b$ of 0–2 V, the measured change of the surface potential is about the same as the potential change in the bulk. In this way, we determined the potential change in the bulk by measuring the surface potential change across the p-n junction [8].

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EBIC was performed on fresh and heavily degraded samples using identical conditions of an electron-beam voltage of 15 kV and a current of 0.8 nA. SIMS data were acquired from degraded and non-degraded areas on one sample.

**4.4 Results and Discussion**

We investigated the electrical potential across the p-n junction on the cross section around the darkest PL area between the two silver grids over a total length of ~2 mm (Fig. 4.1). We found three significantly different kinds of areas, labeled as “No PID,” “PID-affected area,” and “transition area,” where the electric-field peak or the potential drop is, respectively, at the normal junction location, at the cell front surface, and between them; details of the KPFM results will be shown later. In contrast to the current knowledge of PID—that is, junction shunts in highly localized spots within a few micrometers range—we observed a large, continuous PID-affected area (~1.5 mm), with the abnormal electrical potential in the junction area (indicated in Fig. 4.1). We also observed normal electrical potential across the junction in the regions under the metal grids and nearby areas. In the transition region, transitional potential behaviors were observed in some local areas, and mixtures of normal and abnormal potentials were observed in some other areas. The large PID-affected area with the abnormal potential is identified by random measurement of the whole area (~1.5 mm) by adequately dense sampling.

![Diagram](image)

**Figure 4.2** a) AFM of a good area with normal junction; b) the KPFM image at -1.5 V corresponding to a); c) potential profiles of an area in b); d) potential difference curves; e) electric-field difference curves showing a good p-n junction characteristic.

We next show the typical KPFM results on the three regions of “No PID,” “PID-affected,” and “transition area.” Figure 4.2a shows an AFM image on the “No-PID” region, and Fig. 4.2b shows the corresponding potential image at a reverse bias voltage $V_b$ of 1.5 V. The three black dashed lines from top to bottom in Fig. 4.2 were drawn following the Si/Ag-epoxy interface, p-n junction location, and depletion edge of the p-type Si, respectively. Figure 4.2c
shows the line profiles of potential averaged from the potential images and aligned with their corresponding AFM line profile. We took the potential images with varying $V_b$ applied to the device to derive the potential change in the bulk by measuring the surface potential changes. The 0-V potential profile was subtracted from the 0.5-V and 1.5-V potential profiles (Fig. 4.2c) to get the profiles of potential differences (Fig. 4.2d). The $V_b$-induced change in the electrical field was obtained by taking the first derivative of the potential difference. The peak of the electric field indicates the p-n junction location (Fig. 4.2e), which is ~400 nm from the cell surface or epoxy/cell interface, consistent with the junction depth. The junction depletion width is ~500 nm as estimated from the electric-field profile at 0.5 V, which is also consistent with that of a conventional industrial solar cell. Therefore, the p-n junction in this region behaves normally from the perspective of electrical potential.

Figure 4.3 shows typical KPFM images across the junction in the “PID-affected” region. The potential image (Fig. 4.3b) and the electric-field peak (Fig. 4.3c) all show the potential drop at the cell/Ag-epoxy interface. The $V_b$ applied to the Si cell should drop at the p-n junction if the local cell area is functioning normally. The appearance of the electric-field peak at the cell/epoxy interface suggests a significantly damaged junction; external reverse-bias voltage applied to the cell does not drop at the junction. In this case, because the Ag-epoxy/cell contact resistance should not be very small, the $V_b$ drop at the interface—instead of at the junction—is consistent with the shunted junction if the equivalent resistance of the shunted junction is much smaller than the contact resistance at the epoxy/cell interface. Another possibility is that the real p-n junction moved due to PID. A junction movement by Ag metallization was reported, where local recrystallization of the emitter at high temperature was responsible for the junction movement and junction damage [3]. However, we do not have a clear picture of how high voltage can cause the junction movement. On the other hand, one may speculate that a highly insulating local epoxy/cell contact can cause the abnormal voltage drop at the interface. This mechanism can be excluded because if the junction were normal, then $V_b$ would drop at the normal junction location through an emitter path, as in the case of an isolated cell itself. Therefore, the abnormal electric potential/field is likely caused by junction damage or shunting.
Figure 4.3 a) AFM of a PID-affected area; b) the KPFM image potential image at -1.5 V corresponding to a); c) electric-field difference curves showing an abnormal p-n junction characteristic, there is no change in the potential from the cell base to the cell surface at the epoxy interface.

Figure 4.4 shows potential imaging in the transition region. Two types of transitions between the normal and abnormal junctions were observed. The first is shown in Figs. 4.4a and 4.4b, where the transition occurs in ~1 µm, which is about or slightly larger than the “depletion range” generated by a $V_b$ of -1.5 V applied to the junction. This type should have a relatively abrupt transition between the normal and damaged junctions. The second type is shown in Figs. 4.4c and 4.4d, where the location of the electric-field peak is at a location significantly shallower than the normal junction depth. The green circle in Fig. 4.4d indicates such an area adjacent to two junction-damaged areas. Because we lack a picture of the kinetics for the real junction movement by high voltage, we prefer an explanation that this apparent movement of electric-field peak is caused by a moderately damaged junction, an equivalent resistance of which is comparable to that at the epoxy/cell interface. The equivalent resistance depends on the quality of the junction, e.g., the gap state density and recombination velocity. In this case, $V_b$ would drop at both the junction and interface. If KPFM measurements cannot resolve the two voltage drops, then the electric-field peak would appear at a location between the junction and interface. Therefore, this type of transition may indicate a moderately damaged junction.

We also investigated the thermal annealing effect on damaged junctions. Interestingly, the PID-affected areas can be recovered by heat treatment, similar to the macroscale I-V recovery reported in the literature [9][10]. The sample was heated on a hot plate at 300°C for 30 minutes. After the heat treatment, most of the PID-affected area was gone and behaves as the normal area, according to the identical KPFM measurement. Figure 4.5 shows the change of a PID-affected area to a normal area on the same location. Figures 4.5a and 4.5b show the AFM
images in the same location, with the black dashed lines indicating the Si/epoxy interface. It is clear that before heat treatment, the voltage drops at the epoxy/cell interface (Fig. 4.5c); but after treatment, the voltage drop moved deeper into the Si to a normal junction depth (Fig. 4.5d). Further investigation is needed and in-situ stressing of the Si solar cell on the AFM platform is in progress.

![Figure 4.4](image1.png)

Figure 4.4 a) AFM of a transition area; b) the KPFM potential image at 1.5 V corresponding to a); c) AFM of another transition area; d) the potential image at 1.5 V corresponding to c).

![Figure 4.5](image2.png)

Figure 4.5 a) AFM of a PID-affected area; b) potential image at 1.5 V corresponding to a); c) after heat treatment, the AFM image of the same location; d) after heat treatment, the potential at 1.5 V.
EBIC imaging was performed on similar pieces of fresh and heavily degraded areas as the KPFM measurement. Figure 4.6 shows that the EBIC images are much different between the fresh and degraded samples. Figures 4.6a and 4.6b show an SEM and an EBIC image taken on the fresh sample. The wide bright region (~10 μm) around the cell front face is consistent with a normal junction, which can collect current widely and operates as a regular solar cell. However, in a heavily degraded area (Figs. 4.6c and 4.6d), the EBIC image shows much smaller current collections with a current intensity two orders of magnitude smaller than that of the normal junction. The vertical stripe-like pattern is likely caused by the cross-sectional sample polishing, which causes the small current-collection contrast. Therefore, the EBIC imaging suggests no
significant minority-carrier collection in the heavily degraded area, which is consistent with the large-area junction collapse as observed by the KPFM measurement.

On the same degraded sample as imaged by KPFM, we use SIMS to examine the normal junction area and abnormal area. Figure 4.7a shows the SIMS image of Si, and Fig. 4.7b shows the sodium image on the same area. The sodium line profiles across the junction are shown in Fig. 4.7c. A large amount of sodium was detected from the abnormal junction areas, especially close to the edge of silicon, where the p-n junction was located; in contrast, the sodium concentration of the normal junction area is just at a background level. These results indicate that the large-area junction damage may correlate with sodium diffusion into the area. Further investigation is required for a deeper understanding of this observed large-area junction damage in PID.

Figure 4.7 a) SIMS image of Si on one degraded area; b) SIMS image of Na corresponding to a); c) Na line profiles of four different areas on the cross section, showing high concentration of Na on abnormal areas, but background level of Na on normal areas.

4.5 Conclusions

We studied the PID of a silicon mini-module by measuring the potential profiling across the p-n junction. We found that the PID-affected region has junction damage in large and continuous areas; this observation is different from the current knowledge that PID shunts are localized in small and separate spots. The KPFM results show that the potential drops at the p-n junction location in a normal junction area, whereas the potential drop is right at the Si/epoxy interface in the PID-affected abnormal area. In the transition region, two types of transition behavior were observed. Furthermore, we observed a recovery of PID after heat treatment, which is consistent with other macroscale recovery studies. EBIC results are consistent with the large-
area junction damage by showing a faint current collection in the damaged junction area. SIMS results show high sodium contamination around the abnormal junction area. These findings are essentially different from the widely reported local junction shunts.

Acknowledgements

C. X. thanks Dr. Harvey Guthrey (NREL) for EBIC training, Dr. Yuanyue Liu (Caltech) for fruitful discussion on theoretical calculation. This work was supported by the U.S. Department of Energy under Contract No. DE-AC36-08GO28308 with the National Renewable Energy Laboratory. The U.S. Government retains and the publisher, by accepting the article for publication, acknowledges that the U.S. Government retains a nonexclusive, paid up, irrevocable, worldwide license to publish or reproduce the published form of this work, or allow others to do so, for U.S. Government purposes.

4.6 References


CHAPTER 5

NEAR-FIELD TRANSPORT IMAGING APPLIED TO PHOTOVOLTAIC MATERIALS

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5.1 Abstract

We developed and applied a new analytical technique—near-field transport imaging (NF-TI or simply TI)—to photovoltaic materials. Charge-carrier transport is an important factor in solar cell performance, and TI is an innovative approach that integrates a scanning electron microscope with a near-field scanning optical microscope, providing the possibility to study luminescence associated with recombination and transport with high spatial resolution. In this paper, we describe in detail the technical barriers we had to overcome to develop the technique for routine application and the data-fitting procedure used to calculate minority-carrier diffusion length values. The diffusion length measured by TI agrees well with the results calculated by time-resolved photoluminescence on well-controlled gallium arsenide (GaAs) thin-film samples. We report for the first time on measurements on thin-film cadmium telluride using this technique, including the determination of effective carrier diffusion length, as well as the first near-field imaging of the effect of a single localized defect on carrier transport and recombination in a GaAs heterostructure. Furthermore, by changing the scanning setup, we were able to demonstrate near-field cathodoluminescence (CL), and correlated the results with

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standard CL measurements. The TI technique shows great potential for mapping transport properties in solar cell materials with high spatial resolution.

5.2 Introduction

The study of charge-carrier transport, including the determination of minority-carrier diffusion length ($L_d$), is a key requirement to a better understanding of solar-cell performance and to provide guidance on improvements. Many powerful techniques, such as electron-beam induced current (EBIC) and time-resolved photoluminescence (TRPL), have been used to study this phenomenon in photovoltaic (PV) materials [1–6]. However, there is no characterization tool like transport imaging (TI) that provides contactless and quantitative $L_d$ measurement with sub-micron spatial resolution [7–9]. In TI, contrary to EBIC, there is no need for a p-n junction for the measurements, so single materials can be studied without the need of any type of electrical contact. TI is an innovative approach that integrates near-field scanning optical microscopy (NSOM) with the imaging and highly localized excitation capabilities provided by incident electrons in a scanning electron microscope (SEM); it thus enables “seeing” carrier transport by imaging light associated with local recombination [10–13]. This technique has the potential to investigate carrier-transport properties in individual grains and near grain boundaries, and it can be applied to nanostructures or solar cells in cross section, which will help improve the understanding of critical processing factors that cause inhomogeneous carrier transport in thin-film PV material, and could ultimately provide guidance to passivate associated defects.

Here, we describe the development of near-field TI and apply it to two important solar cell materials: single-crystal gallium arsenide (GaAs) and cadmium telluride (CdTe) thin films. In a TI measurement, the electron beam is either fixed in spot or in a linescan mode and used to generate charge carriers as a steady-state point or line source. Some fraction of generated carriers will recombine as they diffuse away from the generation point, producing luminescence. The luminescence is detected by the probe of an NSOM system scanning over the surface of the sample. The magnitude and distribution of the luminescence signal are a signature of the diffusion/recombination process and provide information on the effective diffusion length of carriers in the material. The latter can be calculated by fitting the diffusion equation to the intensity distribution mapped by the NSOM probe. Using NSOM is a main requirement for near-field (high-resolution) analysis, because it is not affected by the diffraction limit that exists in optical microscopes [10]. To validate the technique, we first worked on well-controlled single-
crystal GaAs samples and established a fitting procedure, using Matlab, to extract $L_d$ values from the TI measurements. Then, we compared these measurements with $L_d$ values calculated from TRPL data, and the results agree well with each other. Using the same setup, we collected the first-ever near-field TI signal from CdTe thin films and calculated values of diffusion length. Furthermore, using a slightly different scanning geometry, we acquired near-field cathodoluminescence (CL) data. In this setup, instead of scanning the NSOM probe relative to the sample, we keep the probe fixed relative to the electron beam, while the sample is scanned. We analyzed CdTe thin films and obtained data showing grains and grain boundaries, which were correlated with conventional CL images. This is an additional mode of imaging and analysis that makes TI even more versatile. Most importantly, the strength of the TI technique is to examine the nanometer-scale transport properties rather than the macroscale. We studied a defective area on a GaAs sample and compared with a neighboring good area, showing that the luminescence distribution of TI and near-field CL imaging are significantly affected by the local defect, enabling high-resolution imaging of the effect of the defect on local transport, which can provide important guidance for material growth and device fabrication.

5.3 Experiment

The TI technique as described here combines two microscopes—a Hitachi S4000-N SEM
and an NSOM/atomic force microscope (AFM) Nanonics Multiview 2000. See Figure 5.1 for a simple drawing of the analysis setup. The SEM operates in spot mode or linescan mode, using the electron beam to generate electron-hole pairs at the areas of interest with very small dimensions (i.e., a 20-keV electron beam generated carriers in CdTe is indicated by Monte Carlo simulation of electron trajectory using the CASINO software [14], see Figure 5.10). The AFM allows the system to acquire data in the near-field; the NSOM probe scans the sample surface and collects light via an optical fiber (which also acts as an AFM probe), with aperture size ranging from 150 to 500 nm. The larger the aperture size, the higher the intensity of the collected TI signal. The luminescence signal varies as \((d/\lambda)^4[10]\), where \(d\) is the diameter of the probe and \(\lambda\) is the wavelength of the emitted radiation. Consequently, the intensity of the signal drops rapidly as the diameter of the probe decreases. However, the spatial resolution is inversely proportional to the diameter of the probe, and there is an ongoing compromise between signal intensity and resolution. For near-field CL, the electron beam and NSOM probe are fixed relative to one another, while the sample moves during analysis. In this case, the signal is collected at a given distance from the generation point, after part of the generated carrier population has already recombined. By changing the distance between the electron beam and the NSOM probe it is possible to obtain additional information on the charge recombination process.

The optical fiber is made of SiO\(_2\), which emits light in the 300–600-nm range under direct electron-beam excitation. To eliminate possible artifacts due to light emitted from the optical fiber from either incident or scattered electrons, we used long-wavelength pass filters to suppress luminescence below 800 nm, while allowing all luminescence from the sample to be measured (the solar cell absorber materials of interest here have a bandgap of < 2 eV, which means the emission wavelength is > 620 nm). Figure 5.2 shows the CL spectrum of two different types of optical fibers that we are currently using and the transmission curve of the filter. It clearly shows that the filter cuts the light from the fiber, while the luminescence from the samples can go through. The CL spectra to determine fiber emission were collected under beam conditions of 20 kV and 18 nA, with and acquisition time of 1 second. A similar experiment can be found in ref. [15].

Because the TI technique involves an electron beam, one main technical challenge that can affect the results is sample/probe charging during the measurements, which was resolved by carefully grounding the SEM equipment and NSOM probe. Another critical issue is optimizing
the TI signal, because the luminescence can be weak. The steps necessary to accomplish this task are: optimization of the process for stripping/cleaving the optical fibers; keeping the opening of the fiber clean and carefully aligning it with the photodetector systems; and fine tuning the multiple gain scan parameters in the AFM system. By doing these, we were able to optimize the TI signal and increase the signal-to-noise ratio. Finally, because the probe needs to be maintained in near-field position, very close to the sample surface, sample/probe charging and imperfect feedback control parameters may lead to probe crash and sample scratching. This issue was resolved by slowing down the probe approaching speed, constantly checking the probe resonant frequency, and using a high-feedback gain during approach, and using amplitude-feedback mode instead of phase-feedback mode. Figure 5.2 shows an example of probe/CdTe sample damage due to inappropriate approach procedure and non-optimal feedback parameters.

Figure 5.2 CL spectra of different SiO$_2$ optical fibers showing that the blocking filter can remove any fiber-related signal.

5.4 Results and Discussions

5.4.1 Transport imaging of GaAs

We used TI to investigate the transport properties of a GaAs sample grown by hydride vapor phase epitaxy. The structure consists of an InGaP/GaAs/InGaP double-heterostructure on GaAs substrate. The GaAs layer is 400 nm thick, doped p-type, with carrier concentration of
$3 \times 10^{16}$ cm$^{-3}$; the InGaP layers on top and below are 30 nm thick, doped in the high $10^{18}$ cm$^{-3}$. The function of the cap layer is to reduce surface recombination. For this structure, most of the TI signal comes from the GaAs film (the 30-nm InGaP layer is too thin to produce significant luminescence, and the GaAs substrate has a negligible luminescence). The TI measurement is shown in Figure 5.3a, for a scan area of 30 $\mu$m $\times$ 30 $\mu$m with 512 points $\times$ 512 points. No drifting was observed during data acquisition, judging by the SEM images of the sample and the NSOM probe before and after scanning. To acquire the image, the electron beam is fixed at the center of the lower edge of the image, with the SEM set in spot mode, while the optical fiber is scanned to collect the spatial distribution of the luminescence. The probe aperture size is 300 nm, with the electron beam set at 20 kV. The TI image has a symmetric luminescence shape around the point of generation, which is expected with this isotropic GaAs sample. Clear decay of the intensity as a function of distance from the excitation source was observed in the image due to the diffusion and recombination of the excess minority carriers; on the lower edge of the image, the dark spot is due to the shading of the electron beam by the NSOM probe. Figure 5.3b shows the intensity variation marked by a green line in Figure 5.3a, from the point of excess carrier generation to a distance where there is no more measurable luminescence. By fitting this line to the proper diffusion equation, the value of $L_d$ can be obtained. In this case, the solution of the diffusion equation is a Bessel function, for the geometry of a point source on a thin film (point source in quasi 2-D film) [10]. We developed a data-fitting procedure for extracting reliable diffusion-length values using the curve-fitting tool in Matlab software. We used the equation

$$y = k \cdot \text{Besselk} \left(0, \frac{x}{L_d}\right) + b,$$

where Besselk is a modified Bessel function of second kind, and $k$, $L_d$, and $b$ are fitting parameters: $k$ is the scaling magnitude, and $b$ is the offset of background. By varying the values and range of $k$ and $b$, and optimizing the data processing, we established a reproducible procedure for calculating $L_d$ values. The raw data and fitted curve are shown in Figure 5.4a; the fitted equation and fitting parameters are shown in the inset. The signal-to-noise ratio of the TI signal is high and the fitting curve agrees well with the raw data, resulting in a small fitting error. We calculated $L_d = 5.2 \pm 0.1 \mu$m.

To validate our results, we compared the value of $L_d$ measured by TI with the one indirectly obtained from TRPL measurements of the minority-carrier lifetime, $\tau$. The relation between $L_d$ and $\tau$ is:
\[ L_d = \sqrt{D \cdot \tau} \]

The result from TRPL measurements for this sample is shown in Figure 5.4b. The measured value of \( \tau \) is 15.7 ns, and the value of the diffusion coefficient, \( D \), is estimated from the doping \( (= 3 \times 10^{16} \text{ cm}^{-3}) \) and the majority-carrier electron mobility in GaAs \( (= 5,000 \text{ cm}^2/\text{Vs}) \). The calculated value for \( L_d \) is 4.9 \( \mu \text{m} \). This value is very close to the one found by extracting \( L_d \) \( (5.2 \text{ \mu m}) \) and validates our TI measurements to within \( \sim 7\% \). However, the estimate from TRPL also includes uncertainty associated with majority- versus minority-carrier mobility estimates.

We assume here that surface recombination at the heterostructure interface is low. It is important to remember that the TI measurement provides a direct image of where the carriers go—including all factors such as bulk behavior, surface recombination, and the extent to which ambipolar diffusion plays a role. Thus, it shows the actual behavior of interest in a given structure.

For further verification, we analyzed another GaAs sample, and the values of \( L_d \) measured by TI and TRPL were 4.4 and 4.5 \( \mu \text{m} \), respectively. The results are shown in Figures S5.3 and S5.4. Again, the agreement between the values of \( L_d \) measured by both techniques was very good. This was the first time results from near-field TI measurements were validated by comparison with another well-established analytical technique.

Figure 5.3 a) TI image of a GaAs single crystal sample with a 30-nm InGaP cap layer, the blue dot indicates the position of the electron beam (not to scale); b) Light intensity decay taken on the green line shown on a).
Figure 5.4 a) Matlab fitting of the light intensity decay from Fig. 5.3b); b) TRPL data of the same GaAs sample.

5.4.2 Transport imaging of CdTe

CdTe has been one of the leading commercial solar cell materials. However, the champion cell efficiency (22.1%) is still well below its theoretical limit (~33%) [16][17]. A major limitation is the low open-circuit voltage ($V_{oc}$) obtained in this polycrystalline solar cell, and the charge-transport property difference between grains, and between grain interiors and grain boundaries, may play an important role hindering $V_{oc}$. Local values and variations of $L_d$ will provide valuable insight into mechanisms that limit recombination and provide a feedback mechanism for engineering optimized materials and grain structures. However, very limited work has been done for direct observation of carrier-transport properties in different areas of the cell, mainly due to the limitation of the current analytical techniques. For this work, we used CdTe samples grown by close-spaced sublimation, with grain size larger than 10 µm; see Figure 5.5 for electron backscattered diffraction (EBSD) mapping of the sample.

Figure 5.5a shows the TI image of the CdTe thin film. The position of the electron beam was fixed at the center of the lower edge of the image, while a 300-nm aperture-size optical fiber was scanned to collect the spatial distribution of the luminescence. Prior to analysis, the sample was ion milled at a low beam energy of 3 kV to get a flat surface without altering material properties; similar treatments have been used for sample preparations at NREL for microscopy measurements [18–21]. The NSOM image shows the transport of charge carriers in a symmetrical geometry, because CdTe is expected to be an isotropic material. The dark spot at the lower edge is due to probe shading of the electron beam, and, we use filters to screen out the
luminescence from the NSOM probe. As for the GaAs case, excess carriers are constantly
generated at the electron-beam position, and diffuse away, and luminescence caused by their
recombination was captured by the NSOM probe scanning over the surface. The scan area is $8 \times
8 \, \text{m}$, with 256 points $\times$ 256 points, and no drifting was observed during data acquisition. It is
important to mention that CdTe generally has much weaker luminescence than GaAs, which
makes it more challenging to work with. Although the signal intensity is much smaller than for
GaAs, it is still high enough to be detected by the optical detector, and the decay from the
electron-beam position to the upper edge of the image is clear. The probe aperture size is 300
nm, with the electron beam set at 20 kV. The intensity profile in Figure 5.5b shows quantitative
recombination of charge carriers as a function of distance from the electron-beam position (green
line in Figure 5.5a). As indicated in Figure 5.5a, the line is from the electron-beam generation
point toward an area with no luminescence, and it follows the decay in the TI signal. We used the
same data-fitting procedure in Matlab for extracting diffusion length of the material. Figure 5.6
shows the fitting of the light intensity decay shown in Figure 5.5b. For this sample, we find a
value for $L_d$ equal to 0.70 $\mu$m, which is much smaller than the one obtained for the high-quality
GaAs film, and it is within the range generally expected for similar CdTe samples. The fitting
curve agrees well with the raw data, and $L_d = 0.70 \pm 0.07 \mu m$. Due to the lower luminescence,
the spreading of the TI data and the uncertainty in the calculated $L_d$ value are higher than for the
GaAs sample. In Figure 5.5a, different directions of light intensity decay on the same image were
also examined, and $L_d$ values are similar. The values of $L_d$ calculated at the positions marked by
white lines are 0.65 and 0.72 $\mu$m, respectively; the average value of the three $L_d$ is 0.69 $\mu m$,
with a standard deviation of 0.03 $\mu m$. Note that, due to the shorter diffusion length in this
material, the shape of the probe itself is more directly reflected in the TI distribution.

To the best of our knowledge, this is the first time that measurements of near-field TI
data, including calculation of $L_d$ values, have been reported for a polycrystalline thin film.

For a more rigorous treatment of the diffusion/recombination process, several factors
need to be considered, such as surface recombination velocity, excess carrier injection level, and
three-dimensional transport. Currently, we are taking these parameters into consideration,
including modeling of the TI data. This work will be presented in a future publication.
Figure 5.5 a) TI data of a CdTe thin film. The blue dot in 5a is the approximate position of the electron beam (not to scale) and the dark area is the shade of the optical fiber over the beam; b) Light intensity decay of the TI signal on the position marked by the green line on the TI data.

Figure 5.6 Fitting light intensity decay of Fig. 5b) in Matlab to determine diffusion length.

However, as noted earlier, the image reflects the actual carrier transport in the structure, which is the value of interest. If surface passivation techniques can be developed, it should be possible to observe direct transport between contact layers in thin-film solar cells with this technique, seeing the various effects of grain boundaries, interfaces, and spatial material variation.
5.4.3 Near-field CL vs. conventional CL of CdTe

Another potential application of the TI setup is for near-field CL analysis [22–25]. As mentioned before, in this mode, instead of scanning the NSOM probe, we kept it and the electron beam stationary, about 1 µm away from each other, and physically scanned the CdTe sample. To compare near-field CL and conventional CL done on the same location, we placed focused ion beam (FIB) marks on the surface of the sample. Both the conventional CL and near-field CL were done under similar electron-beam conditions and at room temperature. The conventional CL was acquired in a JEOL 7600 field-emission SEM; the mapping was collected in a 300 × 300 pixel SEM image by synchronizing a cryogenic silicon charge-coupled device with the electron-beam scanning [21]. It shows the total far-field luminescence mapped to the point of excess carrier generation. The near-field CL was acquired in a 512 × 512 pixel image with the sample scanning point by point. Figure 5.7a shows the conventional CL map, and Figure 5.7b shows the near-field CL map, with the SEM backscattered image in the background to show the grains and the grain boundaries structures. The correspondence between the conventional and near-field CL images is clear—all the same grains and same grain boundaries can be identified in the image, as “A” and “B” in the images indicate the same grains. The images are very similar because with the proximity between the electron beam and NSOM probe in TI, we probe the recombination events more closely.

Figure 5.7 Comparison between conventional CL a) and near-field CL b) analyses on the previous TI-analyzed CdTe thin film. To be able to analyze the same area, FIB marks were put on the sample, as seen on the top left of the images. Same grains on both images are marked A and B.
signal close to the generation point. The main advantage of near-field CL over conventional CL is that the latter attributes the total luminescence to the point of generation, including any excess carrier diffusion, or photon recycling. Hence, the signal from carriers recombining far away from the generation point can affect the CL signal at that point. In the case of near-field CL, we can control this effect, by placing the electron beam and the NSOM probe close to each other. So, ideally the measured luminescent area of near-field CL can be more restricted, and it has a higher possibility to detect localized defects. Also, by changing the distance between the electron beam and the NSOM probe, it is possible to obtain additional information on the charge recombination process. Note that this is an additional mode of analysis that makes the TI technique more versatile.

5.4.4 Transport and near-field CL imaging of a defective area on GaAs

The TI technique can be very powerful for analyzing localized material transport properties at the submicron scale. We examined a GaAs sample with a high density of defects; the structure consists of an InGaP/GaAs/InGaP double-heterostructure on GaAs substrate. The GaAs layer is 2 μm thick, doped n-type, with carrier concentration of $2 \times 10^{15}$ cm$^{-3}$. Similar to the previous GaAs sample, the InGaP layers on top and below are 30 nm thick, doped in the high $10^{18}$ cm$^{-3}$. The function of the cap layer is to reduce surface recombination while being too thin to produce significant luminescence, and the light from the substrate is negligible.

Near-field CL was first performed in a region with a clear defect as indicated by the SEM image; the experimental condition is the same as the one described in Section 3.3. The SEM image in Figure 5.15 shows that the defect size is $\sim 4 \mu$m. However, a much larger area with weaker near-field CL luminescence was observed in the CL image in Figure 5.8a. The full width at half maximum (FWHM) of the dark region seen in Figure 5.15 is $\sim 10 \mu$m, and the defective area has a more symmetrical shape when comparing with the morphology image. This is not a surprise because the material around the physically observed defective area may not have as high quality as material far from the defect. Also, the defect probably affects recombination in an area far beyond the defect itself.

The TI imaging was conducted with the electron beam operating in linescan mode. It is easier to observe the net effect of the defect on local transport by using a line source for carrier generation, which results in a net 2-D carrier diffusion perpendicular to the line source, rather than diffusion in every direction in a fixed point source condition. The location and geometry of
two different scans are shown in Figure 5.8b: one scan is in the vicinity of the defect, and one is in a control area away from the defect. Significant nonuniformity luminescence was observed in Figure 5.8c, where the defective area clearly affects carrier transportation. In Figure 5.8c, the carrier generation source is indicated by the green line on the bottom and the contours show the decay rate—the denser the contour lines, the smaller the effective diffusion length in the region; the orange color indicates highest luminescence intensity, and as it decays, the color turns to blue or black at lower luminescence. As carriers diffuse, non-radiative recombination increases at the defect region, and, consequently, luminescence decreases. In the mapping, we observed diffusion-length variations around the defect and the neighboring good area. Because the SEM is operated in linescan mode in this study, the geometry is a line source on a thin film (quasi 2-D film), and the solution for the net diffusion behavior is an exponential function [10]:

\[ y = k \cdot \exp\left(-\frac{x}{L_d}\right) + b, \]

where \( k, L_d, \) and \( b \) are fitting parameters: \( k \) is the scaling magnitude, and \( b \) is the offset of background. The fitted curves of line 1 of Figure 5.8c are showed in Figure 5.9a, and the fitted diffusion length is \( 5.6 \, \mu m \). A neighboring area with no observable defects was also examined by TI in linescan mode, where the luminescence is uniform (see Figure 5.8d). Similarly, we use Matlab to fit line 2 of Figure 5.8d, the diffusion length is \( 12 \, \mu m \) (see Figure 5.9b), which is significantly longer than the fitted diffusion length of line 1. The TI mapping results image the local carrier-diffusion process, rather than giving a single averaged value of diffusion length, as would be the case for values obtained from TRPL measurements. The TI technique allows us to “see” the behavior of the carrier when there is a defect on its diffusion path. Figures 5.9c and 5.9d show the 3-D views of the TI images in Figures 5.8c and 5.8d, which provides a clear visual comparison of carrier transportation between the defective area and good area. From this data is clear that the investigation of various defects affecting carrier transportation process can provide important guidance for material growth and device fabrication.

This was the first time that the influence of a single defect on the charge-carrier diffusion/recombination process has been observed by TI, and shows the potential of this technique to study the transport properties in semiconductor materials.
5.5 Conclusions

We have applied a newly developed near-field transport imaging technique to study the diffusion of charge carriers in solar cell materials, including single-crystal and defective GaAs and polycrystalline CdTe thin films, and established a fitting procedure in Matlab curve-fitting tool to calculate values of diffusion length. The comparison of diffusion-length values calculated by TRPL and TI agree well with each other, which validates our measurements, and it shows that TI is a powerful tool for characterizing solar cell materials.
is a new and powerful tool to measure transport properties in solar cell materials. The first-ever near-field TI analysis of CdTe was performed, including calculation of diffusion-length values.

![Graphs and 3-D views of transport imaging](image)

**Figure 5.9** a) Raw data of line 1 shown in Fig. 5.8c and fitted curve; b) Raw data of line 2 shown in Fig. 5.8d and fitted curve; c) 3-D view of the transport imaging of the defective area in Fig. 5.8c; d) 3-D view of the transport imaging of the good area in Fig. 5.8d.

This technique has great potential to investigate individual grains and grain boundaries because the analyzed area can be on the order of a few micrometers. With the electron beam and NSOM probe fixed, we were able to acquire near-field CL and correlate the results with conventional CL on the same CdTe sample. The study of a defective GaAs sample shows the strength of the TI technique, with a unique capability to investigate transport in a localized area and “see” the carrier diffusion process. We observed clear nonuniformity of the transport image around the defective location, whereas the luminescence is uniform on a good region. TI will be a powerful tool.
addition to CL, EBIC, and the suite of optical techniques to investigate localized transport properties with high spatial resolution.

Acknowledgments

The authors thank Dr. David Albin (National Renewable Energy Laboratory) for providing the CdTe sample. C. X. thanks Dr. Xianguang Yang (Jinan University, P. R. China) for fruitful discussion on NSOM scanning, and Dr. Mingjian Cui and Yuanzhi Liu (The University of Texas at Dallas, USA) for helpful discussion of Matlab fitting. This work was supported by the U.S. Department of Energy under Contract No. DE-AC36-08GO28308 with the National Renewable Energy Laboratory.

5.6 References

5.7 Supplemental Materials

Figure 5.10 Monte Carlo simulation of 20-kV electron trajectory in CdTe using the CASINO software.
Figure 5.11 Probe/sample damage due to non-optimized approaching and feedback parameters.

Figure 5.12 a) TI image of a GaAs single-crystal sample with a 30-nm InGaP cap layer; the blue dot indicates the position of the electron beam (not to scale); b) Light intensity decay taken on the green line shown on a).
Figure 5.13 a) Matlab fitting of the light intensity decay from Fig. 12 b); b) TRPL data of the same GaAs sample.

Figure 5.14 EBSD of the large-grain CdTe thin film analyzed in this work.
Figure 5.15 SEM image of the defective area studied in Section 5.4.3.

Figure 5.16 a) Near-field CL image of the defective area studied in Section 5.4.3; b) Light intensity of the black line in near-field CL image showed in a).
CHAPTER 6
CARRIER TRANSPORT STUDY OF GALLIUM ARSENIDE HILLOCK DEFECTS

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A paper to be submitted to Solar Energy Materials and Solar Cells.

6.1 Abstract
Gallium Arsenide (GaAs) grown by hydride vapor phase epitaxy often has hillock defects on the surface. The defects act as nonradiative recombination centers and hinder further improvement of solar cell performance. In this paper, we applied a newly-developed technique, near-field Transport Imaging (NF-TI or simply TI) to GaAs thin-film with high density of hillocks. On the same defects, we also performed near-field cathodoluminescence (NF-CL), standard CL, electron backscattered diffraction (EBSD) and energy-dispersive X-ray spectroscopy (EDS). We found that the luminescence intensity around the hillock area is two orders of magnitude lower than on the good area, and the fitted diffusion length can be over five times smaller. Also, the transition region between good and hillock-affected area shows a gradual change in diffusion length values.

6.2 Introduction
Hydride vapor phase epitaxy (HVPE) is a fast growth technique for thin-film III-V materials deposition, which has the potential to significantly lower manufacturing costs [1]. Although HVPE is proven to produce high-quality GaAs materials comparable with other expensive techniques [2,3], it is difficult to avoid the formation of hillock defects on the surface [4], which in general have an oval shape. The hillocks are defects formed at the GaAs film and propagate through the deposited layer. The formation of hillocks depends on the growth rate, film thickness, and substrate contamination. The size of hillocks can be up to tens of microns and they can significantly alter the electrical and optical properties of Gallium Arsenide (GaAs) thin film [5–10]. In few studies on molecular-beam epitaxial (MBE) growth, it has been reported that the hillocks are often due to Ga spitting and/or the formation of Ga₂O₃. It is believed that excess

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condensation of Ga from the orifice of the crucible can drip back into the cell, resulting in Ga droplets on the substrate; if there is Ga oxide, the oxide will land on the growth surface and act as Ga nuclei [11-13]. These hillocks will act as nonradiative recombination centers and hinder solar cell performance. To further understand the role of these hillocks in HVPE-grown samples, it is important to study the defect associated charge-carrier transport properties. However, to date there are no reports on quantitative measurement and direct mapping of carrier transport around these defects.

With near-field transport imaging (TI) technique, one can directly visualize the combined influences of diffusion, drift, surface recombination and photon recycling on energy transport [14–18]. In a TI measurement, the excitation is either fixed on a spot or on a line, and generates charge carriers as a steady-state point or line source, respectively. Some fraction of generated carriers will recombine as they diffuse away from the generation point, producing luminescence. The luminescence is detected by the probe of a near-field scanning optical microscope (NSOM) scanning over the surface of the sample. NSOM has a high spatial resolution that beats the diffraction limit, allowing direct mapping of the carrier transport process in the vicinity of individual defects, single interfaces or grain boundaries[14,19].

In this paper, we use the newly-developed TI [19] for direct mapping of the transport properties of the hillocks. We observed over 5 times shorter diffusion length near the hillock area and the affected range is much larger than the morphology. The transition between good and hillock area was examined by standard cathodoluminescence (CL), near-field CL (NF-CL) and TI, and the results showed a gradual change in the luminescence and carrier diffusion process. Energy-dispersive X-ray spectroscopy (EDS) and electron backscattered diffraction (EBSD) were performed on the same hillocks, and the results were correlated, where we found irregular crystalline structure and non-stoichiometry area were comparable to the hillock morphology, but the size is smaller than the TI-affected region.

6.3 Experimental Procedure

The HVPE-grown sample consists of an InGaP/GaAs/InGaP double-heterostructure deposited on GaAs substrate. The GaAs layer is 2-μm thick, and n-type doped, with carrier concentration of \(2 \times 10^{15} \text{ cm}^{-3}\). The GaAs film has a high density of hillocks on the surface (~\(10^3\) cm\(^2\)), as indicated by SEM. The encapsulated InGaP layers on top and bottom are 30-nm thick, doped in the high \(10^{18}\) cm\(^{-3}\), and are designed to reduce surface recombination. The top cladding
layer is too thin to produce significant luminescence, and the light from the substrate is negligible, meaning that the TI signal comes from the GaAs film. To avoid charging during the TI measurements, the sample was well grounded. Finally, a light ion milling was performed to improve the EBSD signal after the TI and EDS scans.

We first used TI to investigate the carrier diffusion around the hillock area; and found that the hillock affects a large area, leading to a weak signal compared to the reference area (> 100 μm). We then performed standard CL to confirm these results. Furthermore, NF-CL measurement was also done on the same location and further confirmed the weak CL signal around the hillock area, and scanned across the transition region between bright and dark CL area. The TI and CL signals were also collected from the transition region. Finally, in order to understand the chemical composition and crystal structure, EDS and EBSD signal were acquired from the same hillock area.

The TI set up uses an NSOM (Nanonics Multiview 2000), installed in the chamber of a field-emission Nova 630 scanning electron microscope (FE-SEM). The FE-SEM provides a highly focused electron beam for carrier generation; while the AFM allows the NSOM probe to collect the sample luminescence in the near-field, this combination make it possible for high spatial resolution mapping of charge-carrier transport. We used an NSOM probe with aperture diameter of 300-nm to acquire the signal; this is a good compromise between getting sufficient amount of light intensity and maintaining high resolution. In TI mode, we set the electron beam in linescan mode, and scanned the NSOM probe to map the carrier diffusion. In this mode, the electron beam is fixed in a line rather than a point, and the decay of the TI signal is perpendicular to the electron-beam line. In another mode, NF-CL scans can be performed. In NF-CL, the electron beam and the NSOM probe are fixed in relation to each other - the distance between the probe and electron beam used in this work was 1 μm – while the sample is scanned. Although NF-CL is similar to standard CL, it has a fundamental difference: in NF-CL the luminescence collecting NSOM probe is positioned at a fixed distance from the electron beam generation point, while in CL the whole luminescence is collected and attributed to the point of carrier generation. Only a portion of light emission underneath the NSOM probe can be collected, while all other portions are lost, therefore the CL intensity is weaker than conventional CL in similar e-beam conditions.
EDS and EBSD were done on the same SEM under the same beam condition. The standard CL measurement was done on a JEOL JSM-5800 system; the mapping was collected with one spectrum for each pixel in a 256 × 256 pixel SEM image, by a silicon charge-coupled device synchronized with electron-beam movement [20]. The electron beam in all measurements is 20 kV, ~1.5 nA.

6.4 Results and Discussions

The SEM image in Fig. 6.1a shows that the GaAs sample has a high density of hillocks; there are usually stacking faults/dislocations at the center of them [8]. Based on the surface morphology, the size of a hillock is less than 40 × 40 μm². Surprisingly, the signal intensity of TI around the hillock is about two orders of magnitude lower than that of the area with no observable defects by SEM. Also, the area affected by the hillock is tens of microns away from its center. This unexpected large hillock-affected area is confirmed by standard CL mapping, as observed in Fig. 6.1b – the luminescence intensity around the hillocks acquired by standard CL is also weak, indicating a strong nonradiative recombination in this area. Furthermore, because the hillocks are close to each other so the whole region may be defective, the affected area, with much lower luminescence, can reach few hundreds of micrometers.

Figure 6.1 a) SEM on the TI-analyzed area, showing a high density of hillocks, the hillock analyzed by TI (shown in Fig. 6.2) is highlighted by the red circle; b) standard CL mapping on the same area, showing a large area of weak luminescence around the hillocks, the transition area between bright and dark area is highlighted by the orange rectangle is studied by TI (Fig. 6.3).
Figure 6.2a shows the schematic of the TI scan, with the electron beam operating in linescan mode. The carriers diffuse in random path but the average decay is in the direction perpendicular to the carrier generation line. Part of the carriers recombine and produce luminescence, which is collected by the NSOM probe. The TI scan area is indicated by the purple rectangle. The carrier diffusion is in quasi 2-D because the GaAs film is thinner than the diffusion length and the signal generation from the GaAs substrate is low enough to ignore. Fig. 6.2b shows the carrier diffusion map of a reference area with no observable surface defect in 3-D, and the TI map of the hillock area is shown in Fig. 6.2c - an SEM image of the hillock is showed in the inset. Although both TI maps show uniform luminescence decay, the decay in Fig. 6.2c is much more dramatic than the one in Fig. 6.2b. Fig. 6.2d shows the light intensity decay for the two cases, the reference good area has an initial intensity about two orders of magnitude higher than the hillock area; and the signal of the good area decays slowly for more than 20 $\mu$m, while the signal on the hillock area decays in about 10 $\mu$m. We used the curve-fitting tool in the Matlab software to fit the two curves in Fig. 6.2d to extract the effective diffusion lengths. As the geometry of the experiment is a line carrier generation source on a thin film (quasi 2-D film), the solution fits to an exponential function [14]:
\[
y = A \cdot \exp(-x/L_d) + B,
\]
where $A$, $L_d$, and $B$ are fitting parameters: $A$ is the scaling magnitude, $L_d$ is the diffusion length, and $B$ is the offset of the background. The fitted curves agree well with the experimental data points. For the good area, the fitted $L_d$ is $9.6 \pm 0.1 \mu$m; while the hillock area has a significantly lower diffusion length of $1.9 \pm 0.2 \mu$m. These results demonstrate that TI can measure the local carrier-diffusion process precisely, and provide the effective diffusion length of specific localized areas, rather than an averaged diffusion length value of a large area of the sample, as given by techniques such as standard time-resolved photoluminescence (TRPL).
Figure 6.2 a) The schematic of TI scanning with electron beam in linescan mode; b) The TI mapping of a good area without any visible defects, showing a long decay, the green line indicates the electron beam generation; c) The TI mapping of a hillock area, the green line indicates the electron beam generation, the inset is a higher magnification SEM image of the hillock; d) solid lines are the Matlab fitted decay of the two TI signal in b) and c), the points are raw data.

Furthermore, we used TI to probe the transition area observed in standard CL in Fig. 6.1b. NF-CL is done to confirm the transitional features between bright and dark regions. Fig. 6.3a shows the NF-CL mapping results, where we observed distinguishable luminescence contrast in one scan. The bright region indicates higher material quality: the darker area suggests lower material quality or enhanced non-radiative recombination. The NF-CL image is very helpful to identify the exact location for doing TI mapping, as the SEM (Fig. 6.1a) only shows a smooth surface with no features. We performed similar TI experiment on the NF-CL scanned
area; again the electron beam is in linescan mode, allowing a net 2-D carrier diffusion perpendicular to the line source and easily resolving the non-uniform carrier transport in such region. In Fig. 6.3a, the dash green line indicates the electron beam line for carrier generation, and the TI-scan area is 40 x 40 \( \mu m^2 \) below in the image. A 2-D contour TI mapping of the transition area is shown in Fig. 6.3b, the decay is faster on the left side than on the right side, which is consistent with the results in Fig. 6.3a. The image contains 256 x 256 pixels. Fig. 6.3c shows the fitting of the 256 lines in Fig. 6.3b, the decay is from the top of the image of carrier generation to the bottom of the image, where there is no detectable luminescence. The fitting procedure is the same as described above. The fitted diffusion length value increases from the left side (~3.3 \( \mu m \)) to the right side (~5.7 \( \mu m \)), in agreement with the decay trend in Fig. 6.3b. Also, as expected, the \( L_d \) values in the transition area are larger than the ones around the hillock, but smaller than the ones in the reference good region.

Figure 6.3 a) NF-CL mapping in the transition area between good and hillock region, the green dash line indicates electron beam excitation; b) TI mapping of the purple rectangle area in the transition area, the green dash line indicates electron beam excitation, the red arrow shows the luminescence decay direction; c) Matlab fitting of diffusion length value of every line in 3b).

The EBSD results on the hillock area are observed in Fig. 6.4, and show a single crystalline material, close to the (001) direction. Fig. 6.4a is the SEM image of the hillock, and Fig. 6.4b shows an inversion pole figure map of the overall image, indicating that the area around the hillock does not have EBSD-detectable poor crystallinity. Only the small dark area looks really damaged and cannot be indexed. Notice that the size of the small dark area is much smaller than the TI-affected area. This suggests the hillock-affected recombination area that is far beyond the EBSD-observed structural defect size. Fig. 6.4c is the data quality image, and the grey region around the hillock indicates higher strain than in the brighter area. Still, this area only involves
the large physical defect, and is much smaller than the low-luminescence area observed in TI and CL. Similar results were obtained from another hillock. The EBSD results indicate that the effect of hillocks in the TI data is not related to the observed structural defects, at least at the sensitivity of the EBSD technique. The whole region may have a high density of extended defects or point defects that lower the luminescence but not detectable by EBSD.

Figure 6.4 a) SEM image of the hillock; b) EBSD inverse pole figure image; c) EBSD data quality image.

Figure 6.5 shows EDS mapping performed on the same hillock area analyzed by TI. Differently than the results in Ref. 5, where the composition of the oval defects of GaAs films deposited by water-mediated close-spaced vapor transport is identical as the rest of the epitaxial film, significant non-stoichiometry is observed in the hillock area as compared as to the defect-free area. On the hillock, there are areas that are rich in oxygen, and areas rich in phosphor and indium, while some areas are poor in gallium and arsenic. Outside the physical location of the hillocks, the composition is uniform. Similar results were obtained from another hillock. Notice that, as in the EBSD case, the EDS data is only affected in the physical area of the hillocks, as observed in the SEM images, which is much smaller than the area with lower luminescence, as observed in TI and CL analysis. This observation indicates a complex influence of the hillocks on the transport properties of the material, affecting an area much larger than their physical size. It is possible that the area has a high density of extended defects or point defects but not observed by EBSD and EDS.
Figure 6.5 EDS mapping around the hillock area studied by TI.

6.5 Summary

We studied the carrier transport properties of HVPE-grown GaAs hillock defects by near-field transport imaging technique. The area around hillocks have higher non-radiative recombination rate, which significantly affects the carrier transport process. The CL intensity is two orders of magnitude lower in the defective area, and five-times shorter diffusion length is observed at the hillock. Furthermore, the diffusion length value gradually increases as we transition from the hillocks to the defect-free area. Finally, SEM, EBSD, and EDS analyses showed that the hillocks affect the transport properties on an area much larger than the observed physical dimensions.

6.6 References


CHAPTER 7

MECHANISMS OF ELECTRON-BEAM-INDUCED DAMAGE IN PEROVSKITE THIN FILMS REVEALED BY CATHODOLUMINESCEENCE SPECTROSCOPY

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7.1 Abstract

Electron-beam-induced damages in methylammonium lead triiodide (MAPbI₃) perovskite thin films were studied by cathodoluminescence (CL) spectroscopy. We find that high energy electron beam could significantly alter perovskite properties through two distinct mechanisms: (1) defect formation caused by irradiation damage; and (2) phase transformation induced by electron-beam heating. The former causes quenching and broadening of the excitonic peaks in CL spectra, whereas the latter results in new peaks with higher emission photon energy. The electron beam damage strongly depends on the electron beam irradiation conditions. Although CL is a powerful technique to investigate the electronic properties of perovskite materials, irradiation condition should be carefully controlled to avoid any significant beam damage. In general, reducing acceleration voltage and probing current coupled with low temperature cooling

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is more favorable for CL characterization and potentially for other scanning electron beam based techniques as well. It is also shown that the stability of perovskite materials under electron beam irradiation can be improved by reducing defects in the original thin films. Effects of electron beam irradiation on formamidinium lead triiodide (FAPbI$_3$) and CsPbI$_3$ thin films were also investigated. FAPbI$_3$ shows similar behavior as MAPbI$_3$, whereas CsPbI$_3$ displays higher resistance to electron beam damage than its organic-inorganic hybrid counterparts. Using CsPbI$_3$ as a model material, we observed non-uniform luminescence in different grains of perovskite thin films. It is also discovered that black-to-yellow phase transformation of CsPbI$_3$ tends to start from the junctions at grain boundaries.

Keywords: defect formation, phase transformation, stability, non-uniform

7.2 Introduction

Over the past few years, perovskite materials have attracted great research interest because of their enormous potential for low-cost and high-efficiency solar cells. Although the certified power conversion efficiency has surged beyond 20%,$^1$ the stability of the perovskite solar cell could be a potential obstacle hindering its large-scale applications and still remains to be fully examined. It is well known that moisture could attack the organic-inorganic hybrid perovskite due to the hygroscopic nature of the alkylammonium cation. Simulations and experiments also suggested that these materials tend to decompose at elevated temperature even in an inert atmosphere.$^{2,3}$ For some specific compounds, such as formamidinium lead iodide, phase transformation happens at a relatively low temperature with low energy cost.$^{2,4}$ The competition of perovskite and non-perovskite phases could also lead to instability of the solar cells. So far most of the stability studies have focused on the change of material properties under solar cell working conditions or accelerated testing conditions.$^{5-9}$ But to our knowledge, no research has been done to study the potential property change of perovskite materials during various characterization processes. Theoretically, the organic-inorganic hybrid perovskite materials, as a soft matter,$^{10}$ could be affected by the high-energy irradiation probes such as an electron-beam, X-ray, and high-intensity laser beam. Investigating the plausible change of the perovskite materials during characterization is critical to understanding the properties of perovskite because the interactions of perovskite with different probes could cause artifacts that are expected to complicate the results and lead to unreliable information.
The electron microscopy is a common and powerful tool that provides valuable information on the microstructure, composition, and nanoscale properties of materials. Scanning electron microscopy (SEM) has been widely used to study the morphologies and compositions of perovskite solar cells. There are only a few studies using transmission electron microscopy to study this material, probably because of the perovskite property change under high-energy electron beam. Ideally, electron microscopy can also be used to investigate the crystallinity and transport properties of the perovskite materials in-situ, using signals of backscattering electrons, X-ray, and cathodoluminescence (CL). However, such studies were rarely reported, which is presumably due to the difficulty in maintaining the material integrity during electron-beam irradiation.

One of the unique features that lead to high efficiencies of perovskite solar cells is perovskite’s low trapping state and long carrier transport length, which had been intensively characterized and manifested by time-resolved photoluminescence (TRPL). CL is an SEM-based technique that characterizes the luminescence of a material under the excitation of a high-energy electron beam. CL is very sensitive to material opto-electronic properties (e.g., charge-carrier recombination and defect luminescence) and can provide a much higher spatial resolution than conventional PL techniques. CL has been widely used to characterize conventional thin-film photovoltaic materials (e.g., CdTe and CIGS). Therefore, CL is expected to be a suitable characterization technique to quantitatively study the potential impact of a high-energy electron beam on perovskite properties (e.g., composition, crystal structure, and defect properties).

In this research, we investigated the in situ interaction of perovskite materials with the high-energy electron beam by monitoring the change of CL signals. We studied the electron-beam damage of the often-studied perovskite material (methylammonium lead iodide or MAPbI₃) during SEM characterization. We found that the properties of MAPbI₃ changed permanently during CL characterization, showing excitonic peak broadening with fast decay of intensity, and new peaks forming at higher photon energy range.

We propose two damage mechanisms to explain the behaviors of CL signal changes. The CL peak broadening and decreased intensity is resulting from the formation of non-radiative defects caused by irradiation damage. The appearance of new CL peaks at relatively high photon energy can be attributed to partial decomposition of the perovskite materials induced by electron-beam heating, which leads to the formation of intermediate phases at levels higher than the
bandgap. CL characterization at a lower temperature eliminates the intermediate phase formation caused by electron-beam-induced high temperature, but the irradiation-damage-induced CL broadening effect can still be observed. Heat treatment of MAPbI$_3$ films generated new CL peaks at higher photon energy similar to the intermediate phase caused by electron-beam heating. Both experiments further confirm the proposed two mechanisms independently. Time-resolved PL and transient absorption spectra measurements from the electron-beam-irradiated areas confirm the permanent change of the material’s optoelectronic properties after electron beam-damage. As-deposited and degraded perovskite films showed different CL stability, which suggests that CL spectroscopy can serve as a tool to probe film quality. Finally, other perovskite materials, such as formamidinium lead iodide (FAPbI$_3$) and cesium lead iodide (CsPbI$_3$), were also examined by CL spectroscopy. The inorganic perovskite CsPbI$_3$ showed a more stable CL emission under the electron beam, enabling CL mapping of CsPbI$_3$ films. With the advantage of high spatial resolution in SEM, we found that our CsPbI$_3$ film has different defect chemistry in grains and its yellow-to-black phase transformation tends to start from grain boundaries. Possible directions for acquisition of stable CL information from perovskite materials are also discussed.

### 7.3 Materials and Methods

Methylammonium iodide (MAI) and Formamidinium iodide (FAI) were purchased from Dyesol. PbI$_2$ (99.9985%) and CsI were purchased from Alfa Aesar. The precursor materials were used as purchased. All perovskite materials were deposited as thin films on FTO glass with a solvent engineering technique. Typically, equal molar quantities of precursors were dissolved in a solvent mixture of dimethylformamide and dimethyl sulfoxide (volume ratio of 7:3) with a concentration of 1 M. The precursor solutions were dispensed on FTO glass and spun coated at 5000 rpm. Excess toluene was applied during spin coating, which promoted fast nucleation and crystal growth of the perovskite materials. After spin coating, the MAPbI$_3$ films were annealed at 100°C for 5 min. The FAPbI$_3$ films were annealed at 170°C for 10 min to achieve black $\alpha$-phase. The CsPbI$_3$ films were dried at 100°C for 10 min and remained in the yellow phase (orthorhombic phase). Before CL characterization, the CsPbI$_3$ films were annealed at 350°C for 10 min in a nitrogen atmosphere to achieve the desirable black (cubic) phase. The CsPbI$_3$ films were quickly transferred to the SEM vacuum chamber after annealing to avoid phase transition. The cubic phase of CsPbI$_3$ was stable under vacuum during SEM and CL characterization.
MAPbI$_3$ single crystals were grown using a reported anti solvent vapor-assisted crystallization method.$^{19}$ Quantities of 0.5 M PbI$_2$ and 1.5 M MAI were dissolved in gamma-butyrolactone (GBA) and kept in an open vial to allow slow diffusion of dichloromethane vapor into the solution. MAPbI$_3$ crystals nucleated from the supersaturated solution and grew to millimeter size in 1-3 days.

CL measurements were performed on a JEOL JSM-5800 system (see Figure 7.7 for the schematic of the CL system). We investigated CL spectra of perovskite materials with different beam voltages and currents as a function of time. The magnification was fixed at 3000X, with an area of $\sim$1000 $\mu$m$^2$ exposed to the electron beam; CL spectra acquiring time was 1 second. All measurements were done at room temperature unless otherwise stated. The samples were transferred to the CL vacuum chamber for characterization to avoid extra material degradation. The CL signal generation volume (the 5 kV case shown in Figure 7.8) was simulated by the Monte Carlo method of electron trajectory using the CASINO software.$^{28}$ CL mapping was done with an acquiring time of 15 milliseconds. We collected one spectrum for each pixel in a 256 $\times$ 256 pixel SEM image using a silicon charge-coupled device synchronized with electron-beam movement.

### 7.4 Results and Discussions

We first systematically examined the effect of varying the electron-beam conditions (beam voltage, beam current, and irradiation time) on the change of CL signals of the MAPbI$_3$ perovskites. The voltage was varied from 2 to 10 kV, and the current varied from 0.2 to 14 nA. The results are shown in Figure 7.1. All the spectra were normalized to compare the emission profiles clearly, because the CL signal can drop two orders of magnitude from the original one within 30 seconds of exposure under the high-energy electron beam. CL data (5 kV, 2nA condition) without normalization were shown in supporting materials as an example (Figure 7.9a). The initial CL emission at 1 second had a single excitonic peak at the photon energy level of $\sim$1.6 eV. As the electron beam bombarded the material, the peak became broader and shifted to higher energy, while the excitonic peak intensity decreased. A higher voltage or current electron beam yields a CL signal with higher intensity but faster decay rates (see Figure 7.9b). For 2 kV, 0.2 nA, we did not observe a significant change of the CL signal but the intensities were low at $\sim$60 counts; signal-to-noise ratio was high. For 2 kV, 2 nA, there is no obvious photon energy shift during 30 seconds of irradiation time. The full width at half maximum

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(FWHM) slightly increased from 0.109 to 0.122 eV within 3 minutes, and the peak intensity was ~120 counts and dropped to ~50 counts. It is worth mentioning that we also observed significant spectrum blue shift after a longer irradiation time of 5 minutes at 2 kV. For higher accelerated voltages and a low current of 0.2 nA, the CL spectra behavior is similar: the initial perovskite peak shifted to slightly higher photon energy and the FWHM became larger. As the voltage increased to 8 and 10 kV, the emission photon energy captured at 1 second had already shifted to ~1.62 eV. As the beam current increased to 2 nA, the excitonic peak started to decrease faster and a CL signal at 1.7-2.3 eV was detected. For higher current, such as 14 nA, the films were seriously damaged after 30 seconds, the CL signal intensities were low, and new peaks appeared and decreased faster. The property change of the perovskite materials under electron-beam irradiation increased with an increase in acceleration voltage, electron-beam current, and exposure duration. In general, a combination of low voltage, low current, and short exposure time was needed to reduce the impact of electron-beam irradiation on the electro-optical

Figure 7.1 Systematical examination of damage effect as a function of beam voltage, beam current, and irradiation time (spectra intensity were normalized).
properties of perovskites. These results provide the rationale for choosing the appropriate parameters to unveil the degradation mechanisms.

The above-mentioned trend may be interpreted by using two damage mechanisms: defect formation caused by irradiation damage and phase transformation induced by electron-beam heating. No donor-acceptor (D-A) bands were observed (see Figure 7.10 for the larger energy range), which is consistent with theoretical results: most intrinsic defects are created in shallow levels.\(^{29}\) The broadening and quenching of the excitonic peaks (the main 1.6 eV CL peak for MAPbI\(_3\)) is possibly due to the formation of defects caused by electron beam. The formation of defects could be due to high-energy irradiation damage mechanism, i.e., atoms within the perovskite lattice are displaced by the high-energy electrons. The knock-on process is expected to cause the formation of point defects and point defect pairs and clusters.\(^{30}\) Frenkel-type defects could be generated, which involves an ionized atom by excess electrons moving to interstitial site in the lattice. Recent theoretical calculations indicate that I migration barrier can be as low as 0.6 eV.\(^ {31}\) The electron beam can pass energy to ions and displace them through knock-on or Frenkel defect mechanism. Defects with deep levels could introduce non-radiation recombination centers, leading to the drop of excitonic CL peak intensity after electron-beam irradiation. On the other hand, displaced atoms distort the perovskite crystal structure that broadens the excitonic peak. However, the electron beam induced defects cannot explain the new peaks appearing at higher photon energy. In general, defects would only introduce peaks at energies lower than the excitonic peaks. The new high-energy peaks could be attributed to the formation of an intermediate phase during the decomposition of perovskite, which was likely caused by the electron-beam heating effect, especially with higher voltage, beam current and longer duration. With a 10 nm spot size, the 5 kV and 2 nA electron beam would result in a irradiation power density of \(1.3\times10^{11}\) W/m\(^2\), which is potentially high enough to induce local heating. Despite the appearance of these high-energy peaks, the excitonic peak was still detected, suggesting that the perovskite material is not completely damaged. The rapid change (both intensity and peak location) of the new peaks suggests that the new-formed intermediate material is also not stable. There is no appearance of a PbI\(_2\) peak (~2.4 eV) in the CL spectra, which indicates that there is very little or no material fully decomposed to PbI\(_2\). The heating effect could also be seen in the low voltage and current condition, but with a slower changing rate. For example, when using 2 kV and 2 nA electron beam, it would take several minutes to show
significant blue shift in the CL spectra. In contrast, when using the lowest power (2 kV and 0.2 nA) in this study, the CL spectra was stable for long enough time to acquire CL images. The low luminescence intensity made signal detection difficult in the current system; however, it points out the direction of using low-power electron beams coupled with more a sensitive system to attain CL images for future studies.

To verify our interpretation, we have further conducted the following two experiments: (1) CL measurement of samples at low temperature to reduce the electron-beam-induced heating effect; and (2) CL measurement of samples with different heat treatment prior to the electron-beam irradiation. CL spectra of MAPbI$_3$ were taken at room temperature (RT) and low temperature with liquid nitrogen cooling (LT) and shown in Figure 7.2a. For spectra at LT, the signal intensity dropped quickly and peak broadening could still be seen. This confirmed that the peak broadening is due to the knock-on mechanism, which cannot be avoided even at low temperature. The knock-on damage would depend on the energy of the electron beam, but is not sensitive to sample temperature. In comparison to the CL spectra taken at RT, no high-energy peaks are observed when the measurement is done at LT. This suggests that the mechanism for generating high-energy peaks is different from the knock-on mechanism. Perovskites are not good electrical or thermal conductors. Hence, a focused electron beam can generate localized heating and partially decompose the material. The electron-beam heating effect could be reduced by the forced cooling of liquid nitrogen, inhibiting the formation of a higher energy peak in the CL spectra. Figure 7.2b shows the normalized CL spectra of MAPbI$_3$ films with different heat treatments prior to the electron-beam irradiation. The MAPbI$_3$ films were heated in dry nitrogen atmosphere, either at 100°C for 40 or 140 minutes or at 150°C for 40 minutes. All three samples were then examined by CL with 2 kV, 2 nA for 30 seconds, which is a relatively mild condition that should not create the high-energy peaks (Figure 7.1). For the film treated at 100°C for 40 minutes, no photon at 1.8-2.3 eV could be detected, but a small offset and asymmetric shape of the peak towards the higher photon energy was observed. For the sample treated at 100°C for 140 minutes, the CL spectrum showed a shoulder at higher energy of 1.8-2.0 eV without a noticeable PbI$_2$ peak. For the 150°C treatment, the shoulder was further extended to 2.1 eV. A PbI$_2$ peak at ~2.4 eV was also detected due to MAPbI$_3$ decomposition after such high-temperature treatment. Unlike the perovskite CL signal, the PbI$_2$ peak was stable and slightly increased under electron-beam irradiation. Thus, the observed peaks at energies higher than the excitonic peaks are caused
by the thermal annealing rather than the knock-on effect (as discussed above). The blue shifting of CL peaks of the annealed samples resemble the spectra features measured under high voltage and current conditions as shown in Figure 7.1. This together with Figure 7.2a confirms that the higher energy peaks are caused by electron-beam heating induced phase transformation (the formation of an intermediate phase associated with perovskite decomposition). EDS results show a slight decrease of I/Pb ratio (Figure 7.14 and Table 7.1), which likely results from partial loss of MAI during electron-beam irradiation. This observation is consistent with the previously discussed electron-beam heating effect that could cause the film decomposition and formation of an intermediate phase during CL characterization.

Figure 7.2 (a) CL spectra of MAPbI$_3$ under 5 kV, 12 nA at room temperature (RT) and low temperature with liquid nitrogen cooling (LT); and (b) CL spectra of MAPbI$_3$ films with different heat treatment (irradiation condition was set to 2 kV, 2 nA for 30 seconds), original, and heated at 100°C for 40 and 140 minutes, and at 150°C for 40 minutes.

To further investigate the degradation effect of the electron beam, more characterizations were done on the beam-influenced area. A sequence of CL spectra was taken at different voltages and shown in Figure 7.3a. First, a low voltage of 1 kV was applied to attain the initial spectrum of the area without causing significant beam degradation. Then a voltage of 5 kV was applied at the same area for 30 seconds to introduce electron-beam degradation. The degradation can be clearly seen from the CL spectrum change as the excitonic peak broadened and a shoulder appeared at higher energy. The beam was then blocked for 30 minutes to allow enough time for potential recovery of the radiated area. Subsequently, another spectrum was taken under 1 kV at the same spot. The attained spectrum showed a broad excitonic peak and a similar shoulder at 1.7-2.1 eV of the 5 kV spectrum, which indicates that the damage effect of a high-energy
electron beam to MAPbI$_3$ is permanent and irreversible. We tried to further annealed the sample under dry nitrogen environment at 70 °C for 10 minutes and use 1 kV to take the spectrum in the same area. But the CL signal showed a similar peak at high-energy range and annealing cannot reverse the phase transformation (Figure 7.12). The electron-beam-affected area was further characterized by transient absorption (TA) spectroscopy (Figure 7.3c and 7.3d). The photon energy of pump is 2.48 eV, and the probe is white light continuum. The unaffected and electron-beam-affected areas from the same sample were examined under the same conditions. As shown in Figure 7.3c and 7.3d, the TA spectra for both areas show sharp bleach centered at 1.66 eV and the broad photo-induced absorption band extending to higher energy, which is consistent with previous TA studies of MAPbI$_3$ perovskites. The similar spectral shape suggests that the light-absorbing component is still from the perovskite material. However, the magnitude of the TA signal for the electron beam affected area is ~50% of that for the unaffected area, indicating that the perovskite is partially damaged after electron-beam irradiation. The kinetics of the TA

![Figure 7.3](image)

Figure 7.3 (a) CL spectra of a 5-kV, 12-nA electron-beam damaged area, with 1 kV, 1 nA CL measurement for initial and final spectra, (b) Carrier lifetime of fresh and unaffected area derived from TA measurements, (c) TA spectroscopy for fresh area, and (d) TA spectroscopy for electron-beam affected area.
bleach reflects the lifetime of the photo-induced carriers. As shown in Figure 7.3b, the carrier lifetime for the beam-affected area is significantly shorter than the unaffected area, suggesting increased defects in the affected area, which is consistent with the decrease of the TA intensity.

For MAPbI₃, both intensity and shape of CL spectra were changed significantly even under a mild electron-beam condition, such as 2-5 kV, which is a commonly used condition in SEM-based characterization techniques. The change in CL spectra indicates a potential change of the electro-optical properties of the material, although the surface morphologies can still remain the same under similar electron-beam conditions (5 kV, 3.6 nA) (Figure 7.13). To avoid significant electron-beam damage to the MAPbI₃ and acquire a stable CL emission profile, it is important to keep the electron-beam energy low with low voltage and low current. Thus, it is necessary to take caution that the material may have been changed from the pristine state and the electron beam could introduce side effects like ones observed in this study when doing SEM-based in situ analyses and measurements.

![Figure 7.4 CL spectra of MAPbI₃ fresh film, and single crystal chunk and degraded film (irradiation condition was set to 5 kV, 12 nA for 30 seconds).](image.png)

Although the electron-beam damage hindered the requisition of a stable CL spectrum from MAPbI₃ thin films, we found that the change of CL spectra can be used as a tool to investigate the quality of the films. Freshly deposited, air-exposed degraded MAPbI₃ films and MAPbI₃ single crystal chunk have different density of defects. Figure 7.4 compares the CL spectra of three samples (i.e., as-deposited, aged-in-air, and single-crystal MAPbI₃ perovskite) measured under 5kV, 12 nA condition. After 30 seconds of electron beam-irradiation, the as-deposited film shows a slight blue shift of the original perovskite peak, and a broad shoulder is
observed. The degraded (aged-in-air) sample has the same signature as fresh thin film but with an apparent high-energy shoulder and a new peak from PbI₂, which is consistent with its XRD pattern (Figure 7.14). In contrast, the CL spectrum of the single-crystal MAPbI₃ sample remains unchanged with the same photon energy and only a 50% decrease of intensity during 4 minutes, which is much slower than the thin-film polycrystalline sample (the CL signal peak intensity decreased to 50% of the initial value in seconds with same electron-beam condition). These results suggest that eliminating defects is critical for improving the stability of perovskites, because polycrystalline thin films have more defects than single-crystal chunk.

Perovskite materials with different cations were also investigated by CL, with the spectra shown in Figure 7.5. The electron-beam energy was set to 5 kV and 12 nA, the same condition as in Figure 7.4. Similar to MAPbI₃, formamidinium lead iodide (FAPbI₃) also displays decreasing excitonic peak (1.53 eV) intensity and new peaks at high energy up to 2.1 eV (Figure 7.5a). Thus, FAPbI₃ is not much more stable than MAPbI₃ under electron-beam irradiation. The behavior is very different for all the inorganic perovskite material CsPbI₃, which shows a CL signal peaked at 1.76 eV that remains unchanged with a strong intensity of ~10,000 counts even after 5 minutes of electron-beam irradiation (Figure 7.5b). More importantly, the CL spectra of CsPbI₃ do not have any high-energy peaks, even after long-time electron-beam irradiation. But CsPbI₃ still has knock-on damage showing an excitonic peak broadening and decrease, but the FWHM reached maximum value after 3 minutes and the CL signal became stable because the number of shallow levels is limited.

Figure 7.5 CL spectra of other perovskite materials; (a) FAPbI₃ under 5kV, 12 nA within 30 seconds, (b) CsPbI₃ under 5kV, 12 nA within 5 minutes.
It is worth noting that for MAPbI$_3$, a low-voltage and low-current electron beam shows less influence at a short time (30 seconds), but the attained CL signal is too low to complete a clear CL image. Moreover, the material tends to degrade during the relatively long mapping time (~10 minutes), which makes it more difficult to achieve a reliable CL image. This in principle could be improved by using higher quality MAPbI$_3$ material with fewer defects, conducting CL measurements at low temperature, and carefully selecting the electron-beam parameters such as acceleration voltage and probe current. On the other hand, the inorganic perovskite CsPbI$_3$ with a more stable signal under electron-beam irradiation can serve as a model material for electron-beam-related microscopic study of perovskite materials. Figure 7.6 shows the SEM and CL images of CsPbI$_3$ measured with 5 kV, 1 nA. The CL intensity was high enough to acquire clear CL mapping. Unfortunately, the heat treatment of CsPbI$_3$ before CL characterization generated some cracks at the grain boundaries because of the significant grain growth during high-temperature annealing, which made it difficult to compare the CL signals at grain interiors versus that at grain boundaries. The color in the CL image is divided into red, green, and blue regions by different energy windows of 1.69-1.73, 1.73-1.77 and 1.77-1.81 eV, respectively. In the CL mapping, emission photon energy and intensity varies from grain to grain, and even within a single grain. The variation could arise from the inhomogeneity of composition or non-radiative defect states. The CL spectra of three representative points (1, 2, and 3 on the CL image) are shown in Figure 7.6c. On points 1 and 3, the spectra are slightly different, which may be due to compositional differences. Some grains are obviously brighter, while some are darker, indicating that the non-radiative recombination rate is different from grain to grain. Detailed defect chemistry and distribution analysis requires more intense study. On point 2, no CL signal was detected around 1.77 eV (bandgap of CsPbI$_3$ black phase), although no obvious void is observed at the same spot from the SEM image (Figure 7.6a). The reason for the low CL emission could be a phase transition of CsPbI$_3$ from black phase to yellow phase at this particular spot. It is interesting that similar dark spots (indicated by arrows) in the CL mapping are all located at the crossings of grain boundaries, which indicates that the phase transition may tend to start from the grain boundaries and then spread into the grain interiors. Further investigation is ongoing to understand the preferable phase transition at grain boundaries and the possible means to restrain the phase transition and consequently improve the material stability.
Figure 7.6 (a) SEM image, (b) CL image of CsPbI$_3$ under 5 kV, 1 nA, and (c) CL spectra of points 1, 2 and 3 in (a).

7.5 Conclusions

We systematically studied the CL spectra of MAPbI$_3$ perovskite under different electron-beam conditions at room temperature. Under the low-energy electron beam, excitonic peak broadening and a decrease in CL signal intensity was observed within a short time period of 30 seconds. A higher energy beam resulted in the appearance of new peaks at higher photon energies. These results indicate that the electron-beam-induced damage involves two mechanisms: (1) defect formation caused by irradiation damage and (2) intermediate phase induced by electron-beam heating. The irradiation damage caused excitonic peak changes, whereas the electron-beam heating effect led to a new CL peak at higher energy. The CL spectrum attained at a lower temperature with liquid nitrogen cooling showed no higher energy
peak, but excitonic peak broadening with decrease in intensity was still observed. Heat treatment to MAPbI$_3$ films generated higher energy CL peaks, which confirmed the electron-beam heating mechanism. Transient PL and absorption study indicates that the electron-beam-affected area partially degrades perovskite material, with a significantly lower carrier lifetime and 50% less transient absorption. The electron-beam degradation is permanent and irreversible. CL characterization was applied to investigate perovskite samples with different qualities. It is found that less-defective material is more stable under the electron beam irradiation. Perovskite materials containing different cations (e.g., FAPbI$_3$ and CsPbI$_3$) were also studied by CL technique. FAPbI$_3$ showed behavior similar to MAPbI$_3$, with a reduced intensity and a blue shift in photon energy. In contrast, CsPbI$_3$ appears more stable, which is consistent with its better thermal stability. CL images of CsPbI$_3$ suggest that the defect distribution can vary in different grains and black-to-yellow phase transformation tends to start from the junctions of grain boundaries. Our study suggests that the high energy electron beam could introduce extra side effects during SEM-based characterizations. Therefore, caution should be exercised to avoid significant change of material properties from its pristine state during measurement. In general, low acceleration voltage, small probing current, and sample cooling are favorable for reducing the electron beam damages.

Acknowledgement

This work was supported by the U.S. Department of Energy under Contract No. DE-AC36-08GO28308 with the National Renewable Energy Laboratory.

Supporting Information

This information is available free of charge via the Internet at http://pubs.acs.org.

7.6 References


(16) C. G. Bischak, E. M. Sanehira, J. T. Precht, J. M. Luther, N. S. Ginsberg, Heterogeneous Charge Carrier Dynamics in Organic-Inorganic Hybrid Materials: Nanoscale Lateral and Depth-


7.7 Supporting Materials

The femtosecond transient absorption (TA) spectrometer used for this study is based on a regeneratively amplified Ti:sapphire laser system. Briefly, the 800 nm output pulse (150 fs, 3 mJ/pulse, and 1 kHz repetition rate) from the regenerative amplifier was split in two parts with a 10% beam splitter. The reflected light, with about 25 µJ/pulse, was directed to a delay stage. After that, the power of the beam was attenuated by a neutral density filter (~3 µJ) and focused into a 2 mm thick sapphire window to generate a white light continuum (WLC) probe (430 nm - 800nm). After collimation with a concave mirror, the white light was divided into a signal and a reference beam. While the signal beam measures the absorption of the sample, the reference beam is used to correct the laser intensity fluctuation. The signal was focused into the sample with a second concave mirror. After the sample, the probe beam was collimated and then focused into a fiber-coupled visible spectrometer. The transmitted fundamental beam was further split into two equivalent beams to pump two TOPAS OPAs for generating visible pump and mid-IR probe. The visible pump was also attenuated by neutral density filter and chopped at 500 Hz. The pump was focused on the sample overlapping with the probe. The TA experiments were performed at room temperature.

Energy dispersive spectroscopy (EDS) was done in an FEI Nova 630 Nano field-emission SEM system under 10 kV, 2 nA, which is the lowest voltage can be applied in balance of acquiring good signal and mimic the condition under CL measurement without much sample damage.
Figure 7.7 System schematic of CL microscope\textsuperscript{[1]}.

Figure 7.8 CL signal generation volume simulated by CASINO software.
Figure 7.9 Peak intensities change as a function of time in different electron beam conditions.

Figure 7.10 CL spectra of MAPbI$_3$ under 5 kV, 2nA electron beam with a wider photon energy range than shown in Figure 7.1, showing no Donor-Acceptor type bands.
Figure 7.11 EDS mapping and composition peaks.

Table 7.1 Averaged atomic percentage of Iodine and Lead in three areas and I/Pb ratio.

<table>
<thead>
<tr>
<th>Condition</th>
<th>Avg. Atom % I</th>
<th>Avg. Atom % Pb</th>
<th>Atomic ratio I/Pb</th>
</tr>
</thead>
<tbody>
<tr>
<td>Initial</td>
<td>16.5</td>
<td>5.4</td>
<td>3.1</td>
</tr>
<tr>
<td>Irradiated</td>
<td>15.0</td>
<td>5.6</td>
<td>2.7</td>
</tr>
</tbody>
</table>
Figure 7.12 CL spectra of a 5-kV, 12-nA electron-beam damaged area, with 1 kV, 1 nA CL measurement for initial, damaged, and annealed spectra.

Figure 7.13 SEM images of same area before and after 10 min electron beam radiation (5kV, 3.6 nA).
Figure 7.14 Comparison of XRD patterns of degraded and fresh MAPbI$_3$ thin films.

References

CHAPTER 8
JUNCTION QUALITY OF SnO\textsubscript{2}-BASED PEROVSKITE SOLAR CELLS INVESTIGATED BY NANOMETER-SCALE ELECTRICAL POTENTIAL PROFILING

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8.1 Abstract

Electron-selective layers (ESLs) and hole-selective layers (HSLs) are critical in high-efficiency organic-inorganic lead halide perovskite (PS) solar cells for charge-carrier transport, separation, and collection. We developed a procedure to assess the quality of the ESL/PS junction by measuring potential distribution on cross-section of SnO\textsubscript{2}-based perovskite solar cells using Kelvin probe force microscopy. Using the potential profiling, we compared three types of cells made of different ESLs but otherwise having identical device structure: 1) cells with PS deposited directly on bare fluorine-doped SnO\textsubscript{2} (FTO)-coated glass; 2) cells with an intrinsic SnO\textsubscript{2} thin layer on the top of FTO as an effective ESL; and 3) cells with the SnO\textsubscript{2} ESL and adding a self-assembled monolayer (SAM) of fullerene. The results reveal two major potential drops or electric fields at the ESL/PS and PS/HSL interfaces. The electric-field ratio between the ESL/PS and PS/HSL interfaces increased in devices as follows: FTO < SnO\textsubscript{2}-ESL < SnO\textsubscript{2}+SAM; this sequence explains the improvements of fill factor (FF) and open-circuit voltage.

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(V_{oc}). The improvement of FF from the FTO to SnO$_2$-ESL cells may result from the reduction in voltage lose at the PS/HSL back interface and the improvement of V$_{oc}$ from the prevention of hole recombination at the ESL/PS front interface. The further improvements with adding a SAM is caused by the defect passivation at the ESL/PS interface, and hence, improvement of the junction quality. These nanoelectrical findings suggest possibilities for improving the device performance by further optimizing the SnO$_2$-based ESL material quality and the ESL/PS interface.

8.2 Introduction

Organic-inorganic hybrid lead halide perovskite (PS) solar cells have developed rapidly, now reaching a conversion efficiency of 22.1%.[1] In the solar cell structure, electron-selective layers (ESLs) and hole-selective layers (HSLs) are critical for the transport, separation, and collection of charge carriers. The most common device architecture uses titanium dioxide (TiO$_2$) as the ESL.[2–6] However, it has been argued that TiO$_2$ may not be the ultimate ESL material because of band misalignment with PS and relatively low electron mobility.[7–9] In fact, other oxides, such as ZnO and SnO$_2$, have similar or ever better optical and electrical properties than TiO$_2$.[9–12] In particular, SnO$_2$-based solar cells are continually showing great potential and have achieved high efficiencies up to 21% to date.[12–21] Ideally, the better band alignment of SnO$_2$ and PS[9] and higher electron mobility provide the possibility of achieving better performance than that of TiO$_2$-based cells; however, the champion cell still uses TiO$_2$ as ESL. The inferior performance of cells made of SnO$_2$ ESL may not be due to its intrinsic material properties. Indeed, steady-state photoluminescence showed a quenching effect, and time-resolved photoluminescence showed additional reduced lifetime with PS deposited on SnO$_2$ rather than on TiO$_2$—indicating more efficient electron transfer from PS to SnO$_2$ layer than PS to TiO$_2$, and thus, great potential for future improvement.[17,21,22] Rather, subpar performance is likely due to issues of processing optimization, which causes poor material quality, junction quality, and interface defect states. A deeper understanding of the interface electronic properties between the ESL and PS is therefore required to optimize alternative ESL materials.

This paper describes a procedure we developed to investigate the interface between a SnO$_2$-based ESL and PS absorber, where we do potential profiling across the interface using Kelvin probe force microscopy (KPFM).[23–26] The applied bias voltage to the devices drops at
both sides of the front interface of ESL/PS and back interface of PS/HSL. By comparing the
electric-field distribution at both the front and back interfaces with changes to the SnO$_2$-based
ESL structure, we observed improvements of the front-junction quality by adding an intrinsic
SnO$_2$ ESL and further improvement by adding a self-assembled monolayer (SAM) layer. These
results explain the gains in cell performance from the perspective of junction quality.

8.3 Experiment

Three types of PS cells[12–16] (Figure 8.1) were subjected to potential profiling: 1) Cells
without an ESL, where the PS layer was deposited directly on a bare TEC15 substrate, a soda-
lime glass coated with fluorine-doped SnO$_2$ (FTO). FTO is a highly conductive n-type
semiconductor that serves as the ESL. Because photo-generated holes in the PS active layer can
diffuse to the ESL/PS interface and recombine with the high concentration of electrons in the
FTO right at the FTO/PS interface, this device has no effective ESL or hole-blocking effect [12].
2) Cells with an extra layer of intrinsic SnO$_2$ as an alternative ESL with effects of both electron-
transport and hole-blocking.[13,14] Because of the low density of electrons in this layer,
recombination of holes diffused to the SnO$_2$/PS interface can effectively be prevented. 3) Cells
with a self-assembled monolayer of fullerene deposited on the top of intrinsic SnO$_2$.[15,16]

The intrinsic SnO$_2$ layer was made by two processes of either solution or atomic layer
deposition (ALD). Solution-based SnO$_2$ was prepared by a low temperature solution process; the
solution of 0.1 mol L$^{-1}$ SnCl$_2$ (Alfa, anhydrous 99.9985%) dissolved in ethanol was spin-coated
on clean FTO substrates (Pilkington, NSG TEC-15) with a spin rate of 2000 rpm for 30 s,
followed by annealing at 185 °C for 1 h. These substrates were cleaned using plasma etching for
15 min before PS deposition. The plasma-enhanced ALD processed SnO$_2$ layer was deposited on
the FTO substrates using an equipment of Ensure Scientific Group AutoALD-PE V2.0 equipped
with a plasma generator. Tetrakis(dimethylamino)-tin(IV) (99%, TDMA-Sn, Strem Chemicals
Inc.) was used as the Sn precursor. Oxygen and argon are used as oxidizer and carrier gases,
respectively. The temperature of the reaction is fixed at 100 °C during the deposition process.
The SnO$_2$ films are annealed on a 100 °C hot plate for 1 hour. C60-SAM was spin-coated by
dissolving C60-SAM solution in chlorobenzene with concentration of 4 mg/mL at 3000 rpm for
30 s. Lead iodide (Pbl$_2$, Alfa Aesar, 99.9985%), methylammonium iodide (MAI, Dyesol),
formamidinium iodide (FAI, Dyesol), lead thiocyanate (Pb(SCN)$_2$, Sigma-Aldrich, 99.5%),
dimethyl sulfoxide (DMSO, Sigma-Aldrich, 99.8%) and N,N-dimethylformamide (DMF, Sigma-Aldrich, 99.8%) were used without further purification. The perovskite precursor solution was prepared using a Lewis acid-base adduct approach with the mixture of MAI, FAI, PbI\(_2\), and DMSO in DMF, where the molar ratio of DMSO and PbI\(_2\) is 1:1. A 45% by weight precursor solution of MA\(_{0.7}\)FA\(_{0.3}\)PbI\(_3\) was prepared with PbI\(_2\), MAI, FAI, Pb(SCN)\(_2\) and DMSO (molar ratio=1:0.7:0.3:0.02:1) in DMF. The solution was stirred for 12 h on a 60 °C hot plate before deposition. The PS precursor solution was spin-coated on the ESL first at 500 rpm for 3 s, and then at 4000 rpm for 60 s using a fast deposition-crystallization technique with diethyl ether as the anti-solvent agent. After spin coating, the PS film was annealed at 65 °C for 2 min and then 100 °C for 5 min. All of these processes were carried out in a N\(_2\) filled glove box. 2,2',7,7'-tetrakis(N,N'-di-p-methoxyphenylamine)-9,9'-spirobifluorene (Spiro-OMeTAD) was used as the hole transport material and deposited on the PS film at 2000 rpm for 60 s. The Spiro-OMeTAD was co-doped using Li-bis-(trifluoromethanesulfonyl) imide (Li-TFSI) and Co-TFSI. The Spiro-OMeTAD solution was prepared by dissolving 72.3 mg Spiro-OMeTAD (Shenzhen Feiming Science and Technology Co., Ltd., 99.0%) in 1 mL chlorobenzene with 28 µL 4-tert-butylpyridine (Sigma-Aldrich, 96%), 18 µL Li-TFSI (Sigma-Aldrich, 99.95%) (520 mg/mL in acetonitrile) and 18 µL Co(II)–TFSI salt (FK102, Dyesol) (300 mg/mL in acetonitrile). A layer of 80 nm gold (Au) was then deposited on the top using thermal evaporation.

The devices were cleaved from the film side to expose the cross section, and no further treatment (e.g., polishing, ion milling) was applied to the cross-sectional sample so as to avoid complications and artifacts from the treatment (See Fig. 8.6 for details of cleaving method and the description in supplemental materials). In the KPFM measurement, the FTO side or front side
of the device was grounded, and bias voltage was applied from the back contact of the devices. The measurements were performed in an Ar-filled glove box with water and oxygen content < 0.1 ppm to mitigate possible degradation of the devices.

KPFM is based on the noncontact mode of an atomic force microscope (AFM). By probing and nullifying the Coulomb force between the probe (Nanosensor PPP-EFM) and the sample, KPFM measures the contact potential difference between the probe and sample. The workfunction of the probe remains unchanged, and the electrostatic potential on the sample’s surface is mapped at a spatial resolution of ~30 nm and a potential resolution of ~10 mV.[23] Topographic and electrical images were collected simultaneously during the probe scanning. In KPFM measurements, the surface potential is often dominated by electrical charges trapped on the cross-sectional surface, which is nonuniform across the surface and depends on the cleaving of the sample. To avoid the effect of surface charge and to “see” the potential distribution in the device bulk, we applied a bias voltage to a working device and measured the changes of surface potential with the bias voltage. Because the surface charge configuration should not change with the small bias voltage of 0–2 V, the measured change of the surface potential is about identical with the potential change in the bulk. In this way, we determined the potential change in the bulk by measuring the surface potential change,[23–26] which is the device characteristic we aim to investigate in this paper.

KPFM measurements were performed with varying bias voltage from -1.5 V (reverse bias) to +0.5 V (forward bias) on the same area. The quality of the p-n junction can be assessed by the current leak or equivalent shunt resistance under reverse bias voltages through measuring voltage drop at the junction. All KPFM data were collected in dark, no photo-induced current during the measurements. For every set of data, we find an area with a relatively flat surface (<50-nm corrugation) on the cross section to eliminate the cross-talk of topography and potential signals. We examined two different locations on two samples for each type of cells to ensure reliable results. The line potential profiles were averaged from 64 scan lines of potential images. The relatively slow scan—each image takes about 3 min—is to ensure data quality, and no plausible ion migration was observed in the small bias voltages. To minimize the effect of ion migration, if any, we altered the forward and reverse voltages for data acquisition by taking images in the order of 0 V, -0.5 V, +0.5 V, -1 V, and so on. We also used a much faster scan rate (30 s per image) and found no significant difference except for the data noise level or quality.
Scanning electron microscopy (SEM) images identified the multiple layers in the device and their interfaces.

8.4 Results and Discussion

Photocurrent density-voltage (J-V) curves and device performance parameters of the solar cells used in this work are shown in Figure 8.2 and Table 8.1, respectively. The three types of cells—made on the bare FTO (also noted as ESL-free cell), intrinsic SnO$_2$ ESL, and SnO$_2$ adding a SAM—all have state-of-the-art efficiencies. The PS active layer and PS/Spiro back interface should be identical among the cells; the only variation is the ESL and ESL/PS interface. The cell with intrinsic SnO$_2$ is significantly improved and shows less hysteresis, compared with the HBL-free cell. In reverse scan (i.e., from $V_{oc}$ to $J_{sc}$), the two devices have an ~20% difference in conversion efficiencies (SnO$_2$: 17.78% and ESL-free: 13.91%), which results from differences of ~8% in fill factor (FF) (73.85% and 68.10%), 12% in $V_{oc}$ (1.07 and 0.94 V), and 3% in $J_{sc}$ (22.40 and 21.64 mA/cm$^2$). In forward scan (i.e., from $J_{sc}$ to $V_{oc}$), the two devices have an ~40% difference in conversion efficiencies (SnO$_2$: 16.33% and ESL-free: 9.85%), which results from differences of ~18% in FF (70.68% and 58.08%), 24% in $V_{oc}$ (1.03 and 0.78 V), and 3% in $J_{sc}$ (22.4 and 21.62 mA/cm$^2$).

The SnO$_2$ layer was deposited by either solution-based spin coating or atomic layer

Figure 8.2 J-V curves of the three types of ESL cells subjected to the potential profiling study.
deposition (ALD). We did not observe a significant difference in the best devices between these two methods. However, ALD has better reproducibility than spin coating, because ALD is well controllable when depositing such a thin film (~15 nm).[9,16,24] The ALD SnO₂ adding SAM has the best efficiency of 19.28% (19.25%) among the three cells, with a $V_{oc}$ of 1.09 V (1.09 V), a $J_{sc}$ of 23.20 mA/cm² (23.20 mA/cm²), and a FF of 76.39% (76.35%) measured under reverse (forward) voltage scan. Adding the SAM layer mainly improved FF (from 73.85% to 76.39% under reverse scan, and from 70.68% to 76.35% under forward scan); the $V_{oc}$ and $J_{sc}$ values are similar to the cell with intrinsic SnO₂ ESL. SAM is expected to passivate interface trap states and enhance charge transfer.[15,22,25,26] Recent publications[27–31] found that PS and metal oxides can react and form an unwanted MAI- or PbI₂-rich interface, which is an electron extraction barrier. It is possible that the SAM can suppress or minimize such reactions to form a cleaner interface. The statistical results of 94 PS cells performance are shown in Fig. 8.7 and Table 8.3. And the stable output of typical cells of each type is shown in Fig. 8.8, indicating significant different performance for these cells. Fig. 8.9 showed the representative external quantum efficiency (EQE) curves of the three types of cells, and the calculated $J_{sc}$ under a 100 mW cm⁻² AM1.5 spectrum. The EQE results clearly showed change at 600-800 nm, which suggests higher recombination of the device without SnO₂ ESL. In general, this recombination loss is introduced by less-than-ideal collection efficiencies of photo-generated carriers. The longer the wavelength has the deeper the generation of carriers, hence the higher the possibility of recombination.[32] The light dependence of $V_{oc}$ curves are shown in Fig. 8.10, indicating a reduced trap-assist recombination by the reduction of ideality factor from 1.76 (ESL-free), 1.54 (SnO₂ ESL) to 1.38 (SnO₂+SAM). The dark I-V curves in Fig. 8.11 showed large decrease in current from the ESL-free to SnO₂ ESL cells and further slight decrease in the SnO₂+SAM cell. These performance parameters suggest a difference in junction quality and a large difference in carrier transport across the device, including barriers in the front junction and back interface. The superior $V_{oc}$ of the low-temperature, solution-processed SnO₂ device is not surprising because SnO₂ has a barrier-free conduction-band alignment, whereas the device with the most commonly used TiO₂ ESL has an ~80-meV band misalignment. The hysteresis effect is also decreased substantially by adding SnO₂ and SAM, which will not be discussed in this paper, as the focus here is p-n junction quality.
Table 8.1 Photovoltaic Performance Parameters of the Three Types of Cells

<table>
<thead>
<tr>
<th>Cell Type</th>
<th>Scan Direction</th>
<th>Voc (V)</th>
<th>Jsc (mA/cm²)</th>
<th>FF (%)</th>
<th>Eff. (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ESL-free</td>
<td>Reverse</td>
<td>0.94</td>
<td>21.64</td>
<td>68.10</td>
<td>13.91</td>
</tr>
<tr>
<td></td>
<td>Forward</td>
<td>0.78</td>
<td>21.62</td>
<td>58.08</td>
<td>9.85</td>
</tr>
<tr>
<td>SnO₂ ESL</td>
<td>Reverse</td>
<td>1.07</td>
<td>22.40</td>
<td>73.85</td>
<td>17.78</td>
</tr>
<tr>
<td></td>
<td>Forward</td>
<td>1.03</td>
<td>22.40</td>
<td>70.68</td>
<td>16.33</td>
</tr>
<tr>
<td>SnO₂ + SAM</td>
<td>Reverse</td>
<td>1.09</td>
<td>23.20</td>
<td>76.39</td>
<td>19.28</td>
</tr>
<tr>
<td></td>
<td>Forward</td>
<td>1.09</td>
<td>23.20</td>
<td>76.35</td>
<td>19.25</td>
</tr>
</tbody>
</table>

Figure 8.3 shows potential-profiling results across the FTO ESL-free cell. Figure 8.3(a) is an SEM image of the device with an FTO layer thickness of 380 nm, PS layer of 630 nm, HSL of 200 nm. The potential line profiles [Fig. 8.3(b)] were averaged from 64 scan lines of potential images (Supplemental Fig. 8.12) along the device lateral direction to enhance the signal/noise ratio. The 0-V potential profile was subtracted from the potential profiles taken at the various bias voltages, and the results are potential changes from the 0-V profile [Fig. 8.3(c)]. First derivatives of the potential profiles are taken to get electric field differences [Fig. 8.3(d)]. On the ESL-free device, two large electric fields on both the ESL/PS and PS/Spiro interfaces were observed, but not in the middle of the PS layer. These electric-field profiles indicate a p-n junction-like cell with the main junction at the ESL/PS interface and a significant potential barrier at the PS/Spiro interface; but they are not favorable to the widely discussed p-i-n-like junction or excitonic device. If it was a p-i-n junction or an excitonic device, the electric field would mainly be located across the PS layer.

The large electric-field peak at the PS/HSL back interface suggests a poor main junction at the ESL/PS interface. With a bias voltage applied to the device—because the electric current through the device or through the front junction and back barrier must be the same—if there is a significant voltage drop at the back side, the voltage drop at the front junction must be reduced. This indicates a reduced equivalent shunt resistance in the front junction, resulting from poor junction quality or increased reverse saturation current $J_0$ and/or diode ideality factor. Therefore, the front junction can be assessed using the ratio of voltage drop between the front and back sides as identified from the electric-field profile. The back PS/HSL barrier should be identical in the three types of cells, so we use this procedure to compare their front-junction quality.

In our previous work, we found that all of the voltage drop in TiO₂ ESL-based PS devices occurred on the front junction, but neither on the back PS/Spiro interface nor in the PS
active layer. We concluded that the PS device is a normal p-n junction cell similar to the polycrystalline inorganic solar cells such as CdTe and Cu(In,Ga)Se₂, and the free p-type carrier in the PS absorber was in $\sim 10^{16}$/cm$^3$ order. Differing from the previous work,[23] we found a large electric peak or voltage drop at the PS/Spiro back interface in the SnO₂ ESL-based devices. This indicates a poorer SnO₂-based junction quality, and thus, a great opportunity for further improving the SnO₂-based junction or interface. Further, we developed a novel characterization for the front junction diode quality by comparing the electric field peaks between the front ESL/PS junction and PS/Spiro back interface with varying the ESL layer material and processing, which provides an unparalleled junction evaluation, as detailed later.

On the potential profiles (Fig. 8.3b), one sees a change in the potential at TCO with varying the bias voltage, while TCO of the device was grounded during the KPFM measurement. Two reasons can be responsible for the potential at TCO. (1) Because cleaving the sample cross-section would create shunts and decrease the shunt resistance, current under a $V_b$ is larger than an actual device with the same bias voltage. This changes the potential at TCO because of the series resistance of TCO and contact resistance. (2) The other is the contribution of interaction of probe cantilever with the sample regions other than under the probe tip. When a bias is applied to the back contact and the tip is on TCO, cantilever can “sense” the voltage at the device stack in some degree.

The same experiment procedure was applied to the SnO₂-ESL cells and the results are shown in Figure 8.4, the corresponding potential images are showed in Supplemental Fig. 8.13. Figure 8.4(a) shows an SEM image of the SnO₂-ESL cell; the structure is similar to the ESL-free layer except for the ~15-nm additional intrinsic SnO₂ layer. The SnO₂-ESL and ESL-free cells were fabricated in the same batch so that all the layer structures other than the intrinsic SnO₂ should be identical. Figure 8.4(b) shows the potential profiles across the device under the various bias voltages. Figures 8.4(c) and 8.4(d) show the electrical potential and field differences from the 0-V ones, respectively. Similarly, there are two electric-field peaks at the SnO₂/PS and PS/Spiro interfaces [Fig. 8.4(d)]. However, the main potential drop or the electric field occurs over the interface between n-type SnO₂ ESL and the p-type PS absorber layer. There is still a peak at the PS/Spiro interface, but it is significantly smaller when compared with the ESL-free cell.
The degree of voltage drop at the ESL/PS junction relative to that at PS/Spiro is significantly larger in the SnO$_2$ device than in the ESL-free device. This result indicates a better diode quality factor of the ESL/PS junction and/or a smaller $J_0$ of the SnO$_2$ device than the ESL-free device, which is consistent with the $V_{oc}$ difference of the two devices. In other words, if the front junction is better formed and the reverse current flowing through the junction is reduced, then the potential/voltage drop at the backside interface will decrease. In this case, the two junctions will compete less, which leads to better performance. This highlights that SnO$_2$ can work as an effective hole-blocking layer because it prevents photo-generated hole recombination at the FTO/PS interface. The $J_{sc}$ values of the two devices are similar, which indicates that FTO and FTO/SnO$_2$ can both work as good electron-transport layers.

Figure 8.3 (a) An SEM image showing layer structure of the ESL-free cell; (b) Potential profilings across the ESL-free cell under different bias voltages; (c) Potential differences across
the ESL-free cell subtracted by the 0-V curve; and (d) Electric-field difference across the ESL-free cell, taken by the first derivative in (c).

Figure 8.4 (a) An SEM image showing layer structure of the SnO$_2$-ESL cell; (b) Potential profilings across the SnO$_2$-ESL cell under different bias voltages; (c) Potential differences across the SnO$_2$-ESL cell subtracted by the 0-V curve; and (d) Electric-field difference across the SnO$_2$-ESL cell, taken by the first derivative in (c).

On the other hand, the smaller voltage drop at the PS/Spiro interface of the SnO$_2$ device is consistent with the pronounced FF and $V_{oc}$ gain. In fact, FF should be a significantly affected parameter by this “back-contact” voltage drop. This is because voltage loss at the back side of the device greatly affects the voltage at the maximum power output point of a J-V curve, and hence, greatly affects FF. It is worth mentioning that we examined the cells with both solution-based spin-coating and ALD SnO$_2$ layers. ALD SnO$_2$ is expected to be better crystallized and
less defective material, but we observed no significant difference of KPFM results on the cells with similar performances. This indicates that the SnO₂ ESL cells in this study are representative and independent from the deposition methods. However, this does not necessarily mean that cells with intrinsic SnO₂ could not be improved; with a better SnO₂/PS interface, we would expect a higher performance device.

SAM is reported to improve the cell performance by promoting charge extraction of ESL, passivating the ESL/PS interface defect states,[15,22,25,26] or making a cleaner interface of ESL/PS.[27–31] The reduction in defective sites at the SnO₂/PS interface is expected to lead to a lower nonradiative recombination rate and thus improve the junction quality. Figure 8.5 shows the potential-profiling results across a cell with SnO₂ and SAM. The corresponding potential images are showed in Supplemental Fig. 8.14. The SEM image [Fig. 8.5(a)] is similar to that without the SAM layer [Fig. 8.4(a)] because the SAM layer is too thin to be resolved in the SEM image. Similar to the two cells above, Fig. 8.5(b) shows the potential profiles under the various bias voltages; Figure 8.5(c) shows the potential change with bias voltages; and Fig. 8.5(d) shows the electric-field changes. As expected, the KPFM results show the largest peak ratio of ESL/PS versus PS/HSL among the three types of SnO₂-based cells. The main potential drop is at the p-n junction formed by SnO₂/SAM/PS, but the peak at PS/Spiro (relative scale) is smaller than the SnO₂ cell without SAM. As discussed above, because the electrical current flowing through all the regions must be the same in the steady state, the voltage drop at the PS/Spiro interface is determined by the ratio between the equivalent shunt resistance at the interface and the sum of all other equivalence resistance in the circuit loop including the front junction, the series resistance, and contact resistance etc. Although the back contact materials are the same among the three devices, the voltage drop at the backside is different, because the total equivalent shunt resistance and the shunt resistance of the front junction are different among the three devices. This is how we can assess the front-junction quality by comparing the voltage drop ratio among the devices. The smaller peak at the PS/Spiro side indicates a smaller $J_0$ and a better interface quality of SnO₂/SAM/PS than SnO₂/PS. We did same experiments on two different locations of two samples for each type of cells to ensure reliable results, another set of representative potential-profiling results are showed in Supplemental Fig. 8.15–8.17.
Figure 8.5 (a) An SEM image showing layer structure of the SnO$_2$+SAM cell; (b) Potential profilings across the SnO$_2$+SAM cell under different bias voltages; (c) Potential differences across the SnO$_2$+SAM cell subtracted by the 0-V curve; and (d) Electric-field difference across the SnO$_2$+SAM cell, taken by the first derivative in (c).

Table 8.2 lists the ratios of the two peak heights or electric field strength under reverse bias of -1.5 V for the three types of cells. The ESL/PS interface is noted as “Peak 1” and the PS/Spiro interface as “Peak 2.” For the four sets of data we examined on each type of cells, the ESL-free cell has an average Peak 1/Peak 2 ratio of 0.39; the SnO$_2$ cell has an average ratio of 1.65; and the SnO$_2$+SAM cell a ratio of 3.25. We examine the electric field peak ratio under a reverse bias voltage rather than under a forward bias, because the data under reverse are more reliable. Electric current under forward bias is relatively large, which generally leads to bad data quality and the potential profiling is not stable for a time period during the measurement with a
large current. These KPFM results are consistent with cell performances; the larger the peak1/peak2 ratio, the better the front-junction quality, the lower the voltage loss at the back side, and the better the FF and \( V_{oc} \). Most likely, the improvement by adding the SAM layer is because of defect-state passivation at the SnO\(_2\)/PS interface. The SAM layer may also promote charge extraction.[25,26,33] However, its effect may be minor because the layer is very thin and carriers can tunnel through it.

The junction quality assessment results (Table 8.2) as evaluated by the equivalent shunt resistance through the measurement of voltage drop are consistent with the device performance parameters (Table 8.1) by changing the SnO\(_2\)-based ESL processing. This consistency also showed up with the I-V hysteresis as shown in Fig. 8.2, the larger the Peak 1/Peak 2 ratio, the smaller the hysteresis. In another note, however, this voltage drop measured by potential profiling cannot deduce detailed mechanisms of the junction improvement by changing the SnO\(_2\)-based ESL processing, such as interface passivation, band alignment, or prevention of interface reaction etc.

Table 8.2 Peak Ratios of KPFM Electric Field at the ESL/PS and PS/HSL Interfaces

<table>
<thead>
<tr>
<th>Cell Structure</th>
<th>Experiment set #</th>
<th>Peak1 Intensity (a.u.)</th>
<th>Peak2 Intensity (a.u.)</th>
<th>Peak1/Peak2 Ratio</th>
<th>Peak1/Peak2 Ratio average</th>
</tr>
</thead>
<tbody>
<tr>
<td>ESL-free</td>
<td>1</td>
<td>310</td>
<td>600</td>
<td>0.52</td>
<td>0.39</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>574</td>
<td>1438</td>
<td>0.40</td>
<td></td>
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<tr>
<td></td>
<td>3</td>
<td>135</td>
<td>418</td>
<td>0.32</td>
<td></td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>39</td>
<td>122</td>
<td>0.32</td>
<td></td>
</tr>
<tr>
<td>SnO(_2) ESL</td>
<td>1</td>
<td>476</td>
<td>284</td>
<td>1.68</td>
<td>1.65</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>324</td>
<td>194</td>
<td>1.67</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>131</td>
<td>77</td>
<td>1.70</td>
<td></td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>382</td>
<td>245</td>
<td>1.56</td>
<td></td>
</tr>
<tr>
<td>SnO(_2) + SAM</td>
<td>1</td>
<td>254</td>
<td>110</td>
<td>2.31</td>
<td>3.25</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>398</td>
<td>104</td>
<td>3.83</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>278</td>
<td>55</td>
<td>5.05</td>
<td></td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>207</td>
<td>114</td>
<td>1.82</td>
<td></td>
</tr>
</tbody>
</table>

8.5 Conclusions

We investigated the junction electrical property of SnO\(_2\)-based PS solar cells by profiling the electrical potential across the devices in nm resolutions using the nanoelectrical probe of
KPFM. We further developed a procedure to assess the ESL/PS junction quality by comparing the electric-field ratio at the front ESL/PS and back PS/HSL interfaces between the cells with changing only the ESL. We found significant differences in the electric-field ratio in the increasing order of ESL-free < SnO$_2$-ESL < SnO$_2$ + SAM, which is consistent with the FF and $V_{oc}$ gains and I-V hysteresis reductions resulting from the ESL improvements. The correlation of these KPFM results with cell performance is understood in terms of ESL/PS front-junction quality and voltage loss at the PS/HSL back interface. The ESL-free cell has the largest relative potential drop at the PS/Spiro interface among the three cells, suggesting a relatively poor p-n junction at the FTO/PS interface, which leads to a poor $V_{oc}$, and a large voltage loss at the back side, which leads to a poor FF. The increase of the electric-field ratio by adding the SnO$_2$-ESL proposes, on one hand, improved junction quality by preventing photo-generated hole recombination, and, on another hand, a significant reduction in voltage loss at the back interface. The further increase of electric-field ratio between the front and back interfaces by adding a SAM agrees with effectively passivating defect states at the ESL/PS interface. The procedure of potential profiling and comparing the electric-field ratio provides novel nanoelectrical characterization related directly to cell performance. This characterization also has a broad implication for an unparalleled junction quality evaluation for wide photodiode-based optoelectronic devices. The results of PS devices highlight possible further improvement of the ESL material and interface/junction quality.

Acknowledgements

The authors thank Bobby To for taking SEM images. C.X thanks Dr. Zhen Li (National Renewable Energy Laboratory, USA) for fruitful discussion. This work was supported by the U.S. Department of Energy under Contract No. DE-AC36-08GO28308 with the National Renewable Energy Laboratory.

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Supporting Information

Method to cleave the sample, sketch of how to cleave the sample to expose cross section, statistical performance of the three types of cells, table of statistical results of performance,
stable output of the three types of cells, EQE, light dependence of Voc, dark I-V, KPFM mapping of the cells, extra potential profiling of the three types of cells.

8.6 References


8.7 Supporting Materials

How we cleaved the sample to expose the cross-section:

The substrate was scribed on film side, but out of the device region, then we cleave the glass from the film side, without touching the device. We found it is better than cleaving from the backside, because cleaving from the backside would put a compressing force to the device films and damage the device cross-section we worked on. The samples were fresh cleaved and measured by KPFM in glovebox.

![Diagram](image)

First scribe from the film side:
- Device with masked Au back contact
- Films, unfinished device, no Au

Cleave the glass and get x-section for KPFM:
- Device with masked Au back contact
- Films, unfinished device, no Au
- X-section examined by KPFM

Figure 8.6 Sketch of how to cleave the sample to expose the cross-section.

J-V and EQE

J-V curves were measured using a Keithley2400 sourcemeter under standard AM1.5 illumination using a solar simulator (PV Measurements Inc.) with an output intensity of 100 mW/cm². For light intensity dependence test, the light intensity was later adjusted between 0.794 and 100...
mW/cm\(^2\) using neutral density filters. External quantum efficiency (EQE) measurement was carried out with a spectral response system (PV Measurements Inc.) using 100 Hz chopped monochromatic light ranging from 300 nm to 900 nm under relatively near-dark test conditions.

Table 8.3 Statistical results of photovoltaic parameters of 94 cells made using SnO\(_2\) ESLs, error values represent the standard deviation.

<table>
<thead>
<tr>
<th>samples</th>
<th>Scan directions</th>
<th>(V_{\text{OC}}) (V)</th>
<th>(J_{\text{SC}}) (mA/cm(^2))</th>
<th>FF (%)</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ESL-free</td>
<td>Reverse</td>
<td>0.98±0.03</td>
<td>21.00±0.57</td>
<td>63.35±2.80</td>
<td>13.02±0.80</td>
</tr>
<tr>
<td></td>
<td>Forward</td>
<td>0.70±0.01</td>
<td>21.01±0.53</td>
<td>53.38±4.03</td>
<td>7.84±0.92</td>
</tr>
<tr>
<td>SnO(_2) ESL</td>
<td>Reverse</td>
<td>1.07±0.01</td>
<td>21.76±0.32</td>
<td>74.59±1.35</td>
<td>17.35±0.43</td>
</tr>
</tbody>
</table>

Figure 8.7 Statistical performance of the three types of ESL cells, a) open-circuit voltage, b) short-circuit current, c) fill factor and d) efficiency.
<table>
<thead>
<tr>
<th></th>
<th>Forward</th>
<th>Reverse</th>
<th>SnO₂+ SAM</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Efficiency (%)</strong></td>
<td>1.05±0.01</td>
<td>1.11±0.01</td>
<td>21.76±0.33</td>
<td>22.00±0.26</td>
</tr>
<tr>
<td></td>
<td>70.83±1.91</td>
<td>77.83±2.19</td>
<td>16.20±0.52</td>
<td>18.97±0.61</td>
</tr>
<tr>
<td><strong>Time (s)</strong></td>
<td>1.09±0.01</td>
<td>1.09±0.01</td>
<td>21.98±0.27</td>
<td>21.98±0.27</td>
</tr>
<tr>
<td></td>
<td>74.61±2.48</td>
<td>77.83±2.19</td>
<td>17.93±0.80</td>
<td>18.97±0.61</td>
</tr>
</tbody>
</table>

Figure 8.8 Typical stable output of the three types of ESL cells.

![Graph showing efficiency over time for SnO₂+ SAM, SnO₂ ESL, and ESL-free cells.](image-url)
Figure 8.9 Typical EQE of the three types of ESL cells.

Figure 8.10 Typical light dependence of Voc of the three types of ESL cells.
Figure 8.11 Typical dark I-V curves of the three types of ESL cells.

Figure 8.12 An SEM image showing layer structure of the ESL-free cell, AFM image of the cross-section; and potential imaging across the cell under different bias voltages under $V_b=0, +0.5, -0.5, -1, -1.5 \text{ V}$. 
Figure 8.13 An SEM image showing layer structure of the SnO$_2$ ESL cell, AFM image of the cross-section; and potential imaging across the cell under different bias voltages under $V_b$=0, +0.5, -0.5, -1, -1.5 V.
Figure 8.14 An SEM image showing layer structure of the SnO$_2$ + SAM cell, AFM image of the cross-section; and potential imaging across the cell under different bias voltages under $V_b$=0, +0.5, -0.5, -1, -1.5 V.
Figure 8.15 Potential profiling of ESL-free cell similar to Figure 8.8.
Figure 8.16 Potential profiling of SnO$_2$ ESL cell similar to Figure 8.9.
Figure 8.17 Potential profiling of SnO$_2$ + SAM cell similar to Figure 8.10.
CHAPTER 9
CONCLUSIONS

The document presented the results of seven studies in the development and application of cutting-edge scanning probe microscopy techniques to investigate current and emerging PV materials and devices. These novel applications help us understand the fundamental physics in device operation and provide vital information in PV research.

9.1 Summary of Work

By developing the scanning capacitance spectroscopy technique, I was able to study leading thin-film CIGS and CZTS solar cells and determine their electrical junction locations at ~20-nm accuracy. I found an n-type CIGS region next to the CIGS/CdS interface, which indicates a homojunction. In contrast, there is no such n-type layer found in CZTS cells. This unambiguous determination of electrical junction locations contributes significantly to understanding the open-circuit voltage difference between the two devices, but it also provides a plausible route for improving the device performance by avoiding recombination at the metallurgical interface. In the CIGS cell fabrication process, the CdS layer is often deposited by chemical bath deposition. The reaction occurs in an alkaline environment and may slightly change the CIGS surface and Cd\textsuperscript{2+} could diffuse into CIGS. It is possible that the Cd\textsuperscript{2+} ions occupy the Cu\textsuperscript{1+} sites and act as donors, making a shallow n-type CIGS. However, the case can be different in CZTS cells. Researchers may need to look for an alternative approach to treat the CZTS top surface to tune the electrical junction to a homojunction, thus making CZTS devices with better performance.

To investigate solar cell reliability issues, scanning probe microscopy techniques such as KPFM, SCM, and C-AFM provide a unique approach to study fundamental failure mechanisms. More importantly, \textit{in-situ} characterization is an ideal tool for studying the evolution of electrical properties at different degradation stages. A well-reported PID mechanism is sodium diffusion into stacking faults and its penetration of the p-n junction, thus causing local shunting. In Chapters 3 and 4, I describe my discovery of a new fundamental PID mechanism that has never been reported. Sodium, more than just diffusing through stacking faults, is more likely to diffuse
everywhere and cause large-area material and junction degradation with point defects. I reported a large area of millimeter-scale material and p-n junction damage caused by PID, and the transition between good and damaged areas is abrupt. Furthermore, time-of-flight secondary-ion mass spectrometry indicates that the large-area damage correlates with sodium contamination. The consistent results shed new light on PID mechanisms, showing that they are essentially different than the widely reported local junction shunts. These results could lead to new guidance in the industrial process of fabricating PID-resistant modules. Currently, the PID mechanism remains unclear and industry players have different “PID-resistant” approaches; but it is uncertain whether these approaches would solve the PID issue or simply mitigate the performance decay. Because the fundamental mechanism is different, the approaches may need to change accordingly.

Using the developed transport imaging technique, one can “see” the transport of carriers and determine minority carrier or exciton diffusion lengths from a single image and map spatial variations in drift and diffusion behavior properties. Although carrier transport has traditionally been considered a limit to the spatial resolution of CL imaging, dual-probe transport imaging allows us to exploit that behavior to directly visualize the combined influences of diffusion, drift, surface recombination, and photon recycling on energy transport in luminescent materials—from the nano to the micron scale. It is widely believed that the efficiency gap between lab champion cells and commercial modules is largely caused by point and extended defects in the absorber materials. However, despite previous efforts to identify and quantify the properties and the impact of these defects in polycrystalline PV materials, no definitive understanding has emerged that can be tied directly to increases in efficiency or other performance measures. Minority-carrier diffusion and drift are fundamental factors important to all solar cell performance parameters of open-circuit voltage, short-circuit current, and fill factor. The transport imaging technique can provide advantages superior to the related techniques by: a) direct (not deduced) imaging of minority-carrier diffusion/drift; b) generating and monitoring recombination at any specific locations of interest; and c) investigating carrier kinetics in a wide range of inhomogeneous media involving extended defects, grain boundaries, and interfaces without limitation. In the case of GaAs hillock defects, the area around a hillock has a higher non-radiative recombination rate, and the low luminescence significantly affects the carrier-transport process. The significantly shorter diffusion length area may act as a sink to the carriers, and the
overall carrier diffusion is affected. The smaller diffusion length could be due to a high intensity of extended defects around the hillock area, and the affected area is larger than the hillock’s physical size. The presence of a hillock can lead to lower open-circuit voltage and be harmful for device performance; hence, eliminating hillock defects by changing film growth condition is critical.

In perovskite work, novel scanning probe microscopy techniques were applied to this exciting new material family. However, the study of microscopic properties in these materials by electron-based microscopy is very limited due to low thresholds for damage caused by the electron beam. CL spectroscopy revealed the electron-beam damage mechanisms, which include irradiation damage that causes shallow defects, and beam heating that induces an intermediate phase. The degradation occurs in seconds, which means it is difficult to study perovskite materials by applying electron-beam-based microscopy techniques such as CL mapping and electron-beam induced current. Several options may allow these techniques to work: 1) scan at low temperature, 2) coat a thin protective layer on the sample surface, and 3) use much lower beam energy, or combine all these approaches. Because an electron beam is still able to damage the sample in the characterization process, AFM-based techniques can be ideal for microscopy studies. In Chapter 8, I developed a procedure to assess the quality of the electron-selective layer (ESL)/perovskite junction by measuring potential distribution on a cross-section of SnO$_2$-based perovskite solar cells using Kelvin probe force microscopy. Using the potential profiling, I compared three types of cells made of different ESLs but otherwise having identical device structure. The results reveal two major potential drops or electric fields at the ESL/perovskite and perovskite/Spiro interfaces. The electric-field ratio at the ESL/PS and PS/Spiro interfaces explains the improvements of fill factor and open-circuit voltage. The improved FF from the FTO to SnO$_2$-ESL cells results from the reduced voltage lose at the perovskite/Spiro back interface, and the improved open-circuit voltage results from preventing hole recombination at the ESL/perovskite front interface. The further improvements by adding a SAM can be caused by defect passivation at the ESL/perovskite interface, and hence, improved junction quality. The results provide vital information about alternative ESL in perovskite solar cells and the interface quality.
9.2 Future Work

During my Ph.D. study, I developed and applied many novel microscopy techniques to investigate solar cell materials and devices. The most important lesson learned is that no one technique is perfect for measuring a particular parameter. But I know the advantages, disadvantages, and limitations of each technique: what is the best case for applying a certain technique, and/or what one should not try to do with some particular technique.

In chapter 2, I described the SCS technique. In the future, it will be ideal to apply this technique to new CIGS cell architectures, such as the CIGS/Zn(O,S) structure, or to study the influence of potassium fluoride (KF) post-deposition treatment. The results would provide vital information for these modern high-efficiency CIGS-based cells. Using the SCS technique to locate the junction with a resolution of 20 nm can help determine whether the device is a homojunction like the CIGS described in chapter 2, or a hetero-interface similar to previous CZTS cells. The homojunction is preferred because it can prevent the carrier from recombining right at the absorber and window layer interface; hence, the homojunction is beneficial for higher open-circuit voltage. If it is a hetero-interface, is there a way to deposit the window layer and turn the CIGS surface into n-type? Also, the SCS technique is applicable to CdTe-based solar cells. Currently, the Cd(Se,Te) buffer layer is the focus as an important means to improve short-circuit current. Knowing the exact junction location determined by SCS can guide further improvement of cell performance. The SCS technique can also be applied to silicon-based cells; however, it is not necessary to make such an effort to locate the exact junction location. The doping profile can be sufficiently collected by scanning capacitance microscopy, which is a simpler version of the SCS technique (SCM only takes images, whereas SCS requires SCM mapping, plus doing spectroscopy on every point). Finally, measuring the junction locations in multijunction devices would be the ultimate goal of technique development; but this requires more rigorous simulation to gain a deeper understanding of what signal to expect because of the measurement.

The issues of PV reliability and bankability become increasingly important as technologies mature and deployment increases rapidly. Degradation has significant economic implications in both cost of delivered electricity and of module replacement. Some electronic reliability issues are not fully understood, which can lead to module power losses that develop from mechanisms such as potential-induced degradation (PID), light-induced degradation (LID),
metastabilities of materials, impurity diffusion, and reverse-bias breakdown due to partial shading. The AFM-based technique is uniquely powerful to further investigate the detailed failure mechanisms, especially with its in-situ stressing capability. In particular, within the PV market, the most common back-surface field (BSF) cells are being replaced by high-efficiency passivated emitter rear cell (PERC) architectures. Among the PERC devices, LID has attracted more attention and the failure mechanism is unclear at this point. I will be able to use the novel AFM-based techniques to study the physics and monitor the evolution of micro- and nanometer electrical properties in real time. Other types of high-efficiency Si cells, such as the heterojunction with intrinsic thin-layer (HIT) structure, also have similar issues with degradation of their passivation layers. The Kelvin probe force microscope will be a powerful tool to study such issues. Although AFM-based techniques are useful for studying electrical properties at very high spatial resolution, other imaging techniques are needed to fully characterize the degradation and obtain a more complete picture of the underlying physics. For example, photoluminescence or electroluminescence would help to approximately locate the target location, and secondary-ion mass spectrometry could then be used to study the related chemistry.

Because of its high spatial resolution, the transport imaging technique is uniquely suited to study carrier transport in polycrystalline thin-film solar cell materials and the transport properties in a cross section for carrier movement in a real device. I hope to continue studying CdTe materials and their inter- and intra-grain carrier transport. CdTe has had many interesting developments in recent years, such as alumina passivation, Cd(Se,Te) as a buffer layer, and doping the material at a higher level with group V elements (phosphorous, arsenic). How would these changes affect the carrier transport compared to the current state-of-the-art CdTe? Also, the same experiments can be conducted on CIGS materials, for example, to determine the influence of KF treatment. In cross-sectional samples, absorber materials often are graded—e.g., CIGS has different gallium ratios, and CdTe has smaller grain sizes in the junction but larger grains on the back side—so how would carriers diffuse and drift in a real device? And if there is some passivation or back-surface electric field, would the carrier be reflected back? The technique can also be applied to multijunction III-V cells to study carrier transport in a more complex structure. More importantly, the transport imaging technique can be used to study reliability issues. How do carrier transport properties change in a degraded area? And if Si-based materials and devices need to be investigated—at the moment, most reliability studies focus on Si and CdTe—then it
would be better to switch to an InGaAs detector instead of the current Si detector; this is because of the higher signal conversion efficiency at longer wavelengths in the InGaAs detector. The current experimental setup is probably not suitable for perovskite materials. According to work described in Chapter 7, defects can be induced in perovskite materials by the high-energy electron beam. The same is true for quantum dot solar cells and organic PV devices. Material damage may cause measurement artifacts and lead to unreliable information.

Applying cutting-edge scanning probe microscopy techniques can substantially impact research advances in solar cell materials and devices.

During my Ph.D. study, I actively collaborated with researchers from many groups, and the following list represents publications that I was involved in with them.


N. R. Paudel, Corey R. Grice, C. Xiao, and Y. Yan, The effects of high temperature process...

\textbf{PATENT}

\textit{A Graded Catalytic-Protective Layer For An Efficient And Stable Water-Splitting Photocathode, Record of Invention (ROI) No. 17-27 No. 62/444,215. NREL, J. Gu, J. A. Aguiar, K. X. Steirer, Y. Yan, C. Xiao, J.A. Turner, etc.}

\textbf{CONFERENCE PAPERS}


N. R. Paudel, \textbf{C. Xiao,} Y. Yan, Study of close space sublimation (CSS) grown SnS thin-films for solar cell applications, \textit{2015 IEEE PVSC conference.}