INTERFACE ENGINEERING IN INORGANIC-ABSORBER NANOSTRUCTURED SOLAR CELLS

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KATHERINE ELIZABETH ROELOFS

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Stacey Bent, Primary Adviser

I certify that I have read this dissertation and that, in my opinion, it is fully adequate in scope and quality as a dissertation for the degree of Doctor of Philosophy.

Michael McGehee

I certify that I have read this dissertation and that, in my opinion, it is fully adequate in scope and quality as a dissertation for the degree of Doctor of Philosophy.

Friedrich Prinz

Approved for the Stanford University Committee on Graduate Studies.

Patricia J. Gumport, Vice Provost for Graduate Education

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Abstract

The focus of this work is variants on the dye-sensitized solar cell (DSSC) that employ inorganic materials as the light absorber, replacing the organic dye molecules used in DSSCs. Such DSSC-inspired devices are emerging technologies in the broader class of thin film solar cells, and include quantum-dot sensitized solar cells (QDSSCs) and perovskites solar cells (PSCs). Quantum-dot sensitized solar cells employ semiconductor nanocrystals, or quantum dots, as the light absorber. The band gap of quantum dots varies with size, allowing for a tunable absorption onset in these devices, among other benefits. PSCs, in which the absorber is $CH_3NH_3PbI_3$, or variants thereof, with the perovskites crystal structure, first attracted attention in 2012 and have shown an unprecedented rise in efficiency to current record values of 20.1%. QDSSCs and PSCs can be fabricated completely from solution processed materials that can be low-purity, contrasting favorably with the industrial standard, silicon solar cells, which require expensively-processed, high-purity silicon. This tolerance to defects is partially due to the nanostructured design of some PSCs and all QDSSCs, in which a nanostructured bulk heterojunction is formed between the electron-transport material, the absorber, and the hole-transport material. However, the high interfacial areas involved in such designs leads to high rates of interfacial recombination, causing losses in photocurrent, and limiting device efficiency.

In this work, I will present methods to reduce interfacial recombination in these inorganic-absorber nanostructured solar cells though surface modifications. In QDSSCs, these include growing ultra-thin insulating metal oxide films by atomic layer deposition (ALD) at the interface and controlling of the nucleation and growth of the inorganic absorber. These studies provide insight into the working mechanisms of QDSSCs, through a combination of the highly-controlled nature of ALD, where films can be grown a single atomic layer at a time and an interface can be atomically engineered, X-ray absorption measurements of interfacial geometric and electronic structure, and detailed studies of the resulting solar cell performance. I will also detail the use of ALD to grow entire material layers in perovskites solar cells, both ALD TiO_2 as the electron-transport material, and ALD NiO_x as the hole-transport material. Despite their high efficiencies,

PSCs are unstable and rapidly degrade when exposed to moisture or excessive heat. The use of ultra-conformal inorganic layers grown by ALD to cap the perovskites absorber, instead of the currently-employed organic layers, has the potential to improve the stability, and thus efficiency, of perovskites solar cells.

Acknowledgements

As the culmination of my formal education, completing my doctorate could not have been completed without the help of many people along the way – advisors, mentors, colleagues, family, and friends. I am greatly indebted to everyone who has taught, trained and supported me, and I hope I have already begun to pass along this mentoring to the next generation as part of a lifetime goal of mine. As they say, it takes a village, and I think I have had at least three villages worth of help!

First, I would like to thank my family – my aunts, uncles and cousins, my siblings, and particularly my parents. I would not be here without my parents' help. As chemists, my parents encouraged me from an early age in the sciences, and particularly when I entered college it was with their encouragement that I pursued engineering. I think from my father I learned a lot about experimental design, such as the "on or off" experimental method – before you do any close testing, double a variable and see if it makes any difference. From my mother, I undoubtedly learned multi-tasking, organization, and of particular use has been the advice to always have at least two projects running at once. Having my sister Becca close by in Berkeley for the last few years of my time here has been a great moral support and source of fun weekends in the city. My older brother Kevin continues to provide a guide in navigating the paths of upper education, and my younger brother Sean has excelled at being my favorite younger brother. My aunt Libby and uncle Mark have served as a second family during my time at Stanford, with Mark organizing expeditions and weekend morning Frisbee and Libby teaching me to surf (and making me coffee that knocks my teeth off!); a great benefit of going to Stanford has been getting to spend more time with them. And of course, my cousins Kimmy, Emily, and Chelsea have brought a lot of fun and joy into my life out here. My aunt Margie and uncle Bruce have encouraged me throughout my degree, with

Margie's great advice on life and science (as an early example of a materials scientist!), and Bruce's reminders to take some time to play music and have fun. I hope to be seeing more of my favorite Florida cousins Jen, Cynthia, and Annette now that I'm moving back east. Finally, I'd like to thank my grandparents, Dawn and Gene, who have connected and grounded my life from an early age. Dawn has always nurtured my right brain, while Gene has given me an interest in history and heritage.

The second village that continued my scientific education was my undergraduate experience in Chemical Engineering at Princeton University. A number of professors were influential in giving me the tools and groundwork to tackle any research project in the sciences. Early on, Robert Prudhomme guided my interests in the Bioengineering certificate branch off of Chemical Engineering, as well as guiding my choice of summer internships. It was in Athanassios Panagiotopoulos's class that I first fell in love with thermodynamics, and it is in his script from the handwritten class notes that I still see the thermodynamic relations in my mind. My interest in materials science began in Richard Register's polymer class, and continued and expanded to inorganic materials in George Scherer's class on ceramics. Throughout my undergrad career, it was a pleasure to interact with Lynn Loo, who has since shown her continued availability for help and advice. My heartfelt thanks go always to Nan Yao, the advisor of my senior research project, who opened my eyes to the field of microscopy and gave me a lasting love for nanoscale imaging. I was extremely lucky that my senior project also brought me into contact with Jerry Poirier formerly of the Imaging Analysis Center (IAC) at Princeton, a scientist and environmentalist who drove me an hour each way from my hometown in Delaware to Princeton over the summer for my senior research project.

At Stanford, my education was continued with a third group of mentors guiding my graduate career. It is with deep gratitude that I thank my advisor Stacey Bent. I have learned a lot from her these past five years. I am incredibly grateful for her organized, responsive, and thoughtful management of the group and of my projects here. I am also grateful that Stacey has always supported my long-term goals, both personal and professional. Through the many courses I have taken, Stacey stands out as an incredible teacher and lecture, in her organization and clarity of explanation. My knowledge of

surface science and materials characterization has really been formed through these past five years of research with Stacey. In group meetings, I still do not know how she manages to maintain razor focus on our experimental details and the implications of various results of each of her students through four hours of meetings on Wednesdays, with only a cup of tea for caffeine. I also feel I have learned a great deal from Stacey about how to write scientific proposals; sometimes it seems as if Stacey possesses a 'magic wand' which transforms long-winded flat paragraphs into compelling statements. Finally, I have learned about group management, lab safety, and a general approach to making progress in scientific research. Stacey has even welcomed the group into her home each year for a summer get-together, which has been a great pleasure. I could not have asked for a better advisor.

I am lucky to have such an outstanding defense committee. Mike McGehee has welcomed me into his lab and his help and that of his group has been instrumental in the success of my projects. Moreover, I was able to take Mike's solar cells course early on in my graduate career, which gave me a strong grounding in the fundamentals and a broader picture of the industrial aspects of solar cells. I still remember my first meeting with Mike, where I was so nervous I read from pre-written questions from my notebook! I had the fortune of seeking Chris Chidsey's input on my research projects early on. Chris's questions cut down to the core of your project and get to what you are really trying to learn and accomplish. I have benefited from his advice to inter-relate my various hypotheses to create a full assessment of the system, and in mathematical terms if possible, so that contradictions or issues of scale will be clear. I have only had the pleasure of interacting with Fritz Prinz in the last two years of my time here, though I have worked with his group closely throughout. It has been very fun to see another ALD lab in action, and to learn tips and techniques on everything from ALD to TEM. I am grateful for the interest he has taken in my projects, in providing career advice, and serving as a member of my reading committee. Alberto Salleo has always brightened up the materials science department, and I had an early interest in his research. Moreover, his thermodynamics course was one of my favorite (and hardest!) core courses, and I think I particularly benefitted both from his theoretical rigor and practical, everyday examples. Moreover, I have had learned a lot from members of his group, on

synchrotron methods and characterizing the electrical properties of organic materials. It was a true pleasure that Alberto agreed to be a member of my defense committee, and I would like to thank him.

I would like to thank Tom Brennan, who mentored me closely in the Bent group for the first three years of my PhD and completed several projects with me. Tom is both a strategic researcher and a deep thinker; I remember our brainstorming sessions very fondly. As a side-note, I have yet to come across a better file organization system than Tom's. I developed my writing style for scientific papers from reading Tom's previous work and seeing his editing process in our co-written papers. On a more technical side, Tom modified the transient photovoltage and photocurrent systems, as well as passed on Matlab and Python scripts which were a great help in getting me started on mass-analyzing my data.

Tom helped begin an incredibly fruitful collaboration with Orlando Trejo and John Xu from Fritz Prinz's research group, which has produced great results over the past years. I got to spend a lot of time with Orlando on campus and down and the synchrotron and I greatly respect his thorough approach to studies. For example, in our last project analyzing XANES data, from the raw spectra at least five different levels of analysis were required, each with a different software to correctly calibrate, normalize, analyze, and pair with simulation results. Through this Orlando jumped in to learn each new software, and in the end we were able to really dig into the physical meaning behind the results.

I am grateful to all the previous students in the Bent group; I would like to name them here with a few details that come to mind. From Han-Bo-Ram Lee I learned to make beautiful posters, presentations, and figures, and how to design robust experiments. From Jon Bakke, I learned how to write personal statements and represent myself well scientifically. From Marja Mullings I learned many tips about professional work environment and presentation, and even ergonomics. Han Zhou was an inspiration for making dedicated and consistent progress in experiments. Speaking of persistence, I don't think I could have seen a better example of working through experimental equipment troubleshooting than Nid Methaapanon's year-long struggle with the *in-situ*

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Figure 2-8. Interfacial band structure depicting the potential impacts of inorganic surface treatments in QDSSCs. Here, a nanocrystal of the nanoporous anode (i.e., a TiO_2 nanocrystal) is depicted in navy, the inorganic coating layer in magenta, and the light-absorbing quantum dot (QD) in yellow. The hole-transport material (HTM) is shown in light blue. (a) The interfacial band structure prior to deposition of the metal oxide layer. Only recombination pathways from the photoanode to the QD are shown, from (α) the anode conduction band and (β) the anode density of states (DOS), although recombination can also occur with the HTM. (b) Recombination barrier layers will reduce both (α) and (β) recombination processes due to the tunneling effect. (c) Recombination barriers may also alter the DOS of the anode, by passivating trap states, leading to further reductions in the (β) recombination path. (d) The recombination barrier layer may also act as a surface dipole, shifting the anode conduction band upward. (e) Due to the difficulties of conformally growing Ångstrom-thick inorganic layers on a nanoporous anode, it is possible that multiple geometric configurations of the anode/inorganic coating/QD exist within the same device. 37

Figure 2-9. The role of $TiCl_4$ treatment in QDSSCs (n-TiO_2/CdS QDs/electrolyte). (a) *J-V* curves as a function of TiO_2 CBD time; inset shows dark *J-V* curves. The highest efficiency is achieved at 30 min. (b) Open circuit voltage decay curves under AM 1.5 illumination, show that the highest electron lifetimes (slowest rate of V_{OC} decay) are achieved for the 30 min samples. (c) Schematic of the authors' proposed mechanism. With increasing TiO_2 CBD times, the resulting TiO_2 coating is believed to decrease

interfacial recombination, an effect which dominates at the 30 min CBD time point. For thicker TiO_2 coatings, though, it is believed that the detrimental effects of transport resistance lead ultimately to the lower observed electron lifetimes at 60 min. Reprinted from Ref. 81, Copyright 2012, with permission from Elsevier. 38

Figure 2-10. (a) Inorganic layers of Al_2O_3, $BaTiO_3$, and MgO deposited at the interface in ETASCs. (b) All three metal oxide layers served to improve the V_{OC}, a good indication of decreased interfacial recombination, though only in the MgO case did J_{SC} values improve as well. (c) A double layer treatment of $BaTiO_3$ followed by MgO, provided even better improvements in performance than either treatment alone. The device parameters of the J-V curves are included, and have the following units: J_{SC} (mA/cm^2), V_{OC} (V), FF (unitless), and η (%). Reprinted from reference 75. 40

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