FABRICATION AND OPTIMIZATION OF LIGHT CARRIER COLLECTION
MANAGEMENT STRUCTURE USING LEAD SULFIDE QUANTUM DOTS AS
LIGHT ABSORBER

A Dissertation in
Engineering Science and Mechanics
by
Nghia Dai Nguyen

© 2014 Nghia Dai Nguyen

Submitted in Partial Fulfillment
of the Requirements
for the Degree of

Doctor of Philosophy

December 2014
The dissertation of Nghia Dai Nguyen was reviewed and approved* by the following:

Stephen J. Fonash  
Kunkle Chair Professor of Engineering Science and Mechanics  
Dissertation Advisor  
Co-chair of Committee

Wook Jun Nam  
Assistant Professor of Engineering Science and Mechanics  
Research Associate, CNEU  
Co-chair of Committee

Osama O. Awaldelkarim  
Professor of Engineering Science of Mathematics

Jeffrey R. S. Brownson  
Associate Professor of Energy and Mineral Engineering

Judith A. Todd  
P. B. Breneman Department Head  
Head of the Department of Engineering Science and Mechanics

*Signatures are on file in the Graduate School
ABSTRACT

Light and carrier collection management (LCCM) architecture for thin film photovoltaic and detector is among the latest attempts to enhance light absorption while maintaining the collection of charge carriers. Exciting progress has already been made with amorphous Si (a-Si) solar cells where short circuit current ($J_{sc}$) is greatly enhanced while no other sacrifice is made for other performances. Effective light trapping phenomena inside the structure are considered the main contributors. This work explores and studies the known phenomena such as radiation, traveling waveguided, traveling Bloch, Mie, and plasmonic modes.

Lead sulfide (PbS) colloidal quantum dots (CQDs) is a novel light absorber that is categorized in the third generation of solar cells where it shows potential to be highly efficient (more than Shockley-Queisser efficiency limit) yet still very affordable to made. They exhibit quantum mechanical properties that may improve the photovoltage and photocurrent beyond their classical limits. However, its use mainly limits in conventional planar architectures. These architectures suffer major drawbacks in terms of efficiency due to the compromise between light and carrier collection.

This study explores the incorporation of PbS CQDs into the LCCM structures that remove the compromise and boost efficiency. Using three-dimensional Maxwell’s equations solver presents an accurate and time/resource-saving method to optimize the LCCM structures. Based on design criteria that consider fabrication of these cells, optimized structures are found with more than 30% improvement over their planar counterparts. Proof-of-concept cells are also manufactured successfully in methods that
have great potential for scale-up. This makes the pursuit of cheap and clean energy one step closer to reality.
# TABLE OF CONTENTS

List of Figures ................................................................................................................... vi
List of Tables ...................................................................................................................... xii
Acknowledgements ............................................................................................................ xiii

Chapter 1 Why PbS Quantum Dots and Light Carrier Collection Management .......... 1
  1.1 Light and Carrier Collection Management ............................................................. 2
  1.2 Lead Sulfide Quantum Dots as Light Absorber ..................................................... 5
  1.3 Numerical Modeling and Optimization ................................................................. 10

Chapter 2 Understanding Light Trapping Phenomena Present in LCCM Structures .. 14
  2.1 How light enters medium ..................................................................................... 14
  2.2 Possible trapped modes of light inside a structure of media ................................ 16
  2.3 Radiation (Fabry-Perot) mode ............................................................................. 17
  2.4 Traveling waveguided and Bloch modes ............................................................. 22
    2.4.1 Waveguided mode ..................................................................................... 22
    2.4.2 Bloch mode ............................................................................................. 27
  2.5 Mie mode ............................................................................................................ 28
  2.6 Plasmonic mode .................................................................................................. 31
  2.7 Trapped modes in 1D grating – 2D structures ..................................................... 32
  2.8 2D gratings – 3D structures ............................................................................... 37

Chapter 3 Structure Design and Optimization of PbS QDs LCCM Cells with
  Optical Numerical Modeling .......................................................................................... 42
  3.1 First LCCM model – LCCM1 ............................................................................. 45
  3.2 Second LCCM model – LCCM2 ......................................................................... 52

Chapter 4 Fabrication Process Design and Trial Cells ................................................. 59
  4.1 Nanomold fabrication .......................................................................................... 60
  4.2 First LCCM cell – Sol-gel process flow ............................................................... 63
  4.3 Second LCCM cell – ALD process flow ............................................................... 67
  4.4 Manufacturability and comparison with existing fabrication methods .......... 72

Chapter 5 Conclusion and Future Work ...................................................................... 76

Appendix A HFSS Input Format and Material Data...................................................... 78
Appendix B Transfer Matrix Method (TMM) ................................................................. 84

References ....................................................................................................................... 87
LIST OF FIGURES

Figure 1-1: The solar cell on the left depicts an absorber layer that has been designed to absorb all wavelengths with energies above its band gap. The planar design on the right uses the same absorber but has now been designed with the material’s charge carrier collection length in mind. Adapted from [7]. Courtesy of Charles A. Smith. .................................................................3

Figure 1-2: (A) Nanodome array from Zhu et al. fabricated from Langmuir-Blodgett assembly substrate. The scale bar is 500nm (Reprinted (adapted) with permission from [11]. Copyright © 2010 by American Chemical Society). (B) Cross-section SEM image of the nanodome array from Nam et al. fabricated glass superstrate. (Reprinted (adapted) with permission from [6]. Copyright © 2011, AIP Publishing LLC) .........................................................5

Figure 1-3: (A) AM1.5G solar spectrum from ASTM G173–03 reference spectra. The bandgaps for some common bulk semiconductors are: TiO$_2$ 3.3 eV; CdS 2.5 eV; CdSe 1.7 eV; CuInS$_2$ 2.154 eV; CdTe 1.5 eV; InP 1.34 eV; Cu$_2$S 1.21 eV; Si 1.12 eV; CuInSe$_2$ 2 1.0 eV; InN 0.8 eV; Ge 0.66 eV; CuFeS$_2$ 2 0.6 eV; PbS 0.41 eV; InAs 0.35 eV and PbSe 0.28 eV. (B) Concept of using PbS CQDs with different sizes to build a triple-junction tandem solar cell [4]. Copyright © 2011 by WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim) .........................................................6

Figure 1-4: Single-junction CQD solar cell architectures. (a) Schottky CQD solar cell. (b) Depleted heterojunction CQD solar cell. (c) Depleted bulk heterojunction CQD solar cell. (d) CQD-sensitized solar cell. Also shown are the electron band diagrams of each architecture as indicated. Note that the depleted heterojunction and depleted bulk heterojunction solar cells share the same band diagram, with the only difference being the larger volume of CQDs within the depletion region due to the interfacial higher surface area between the TiO$_2$ and CQD film (Reprinted (adapted) with permission from [2]. Copyright © 2011 by American Chemical Society) .........................................................9

Figure 1-5: (A) LCCM cell from process flow 1 drawn with HFSS: Green is ZnO, purple is PbS CQDs film, yellow is Au. (B) A “vacuum box” is used to encapsulate the cell and placeholder for Floquet ports and Master/Slave boundary conditions.........................................................................................................................12

Figure 1-6: Band diagram of the anticipated depleted heterojunction photovoltaic cell from AMPS-1D..................................................................................................................................................13

Figure 2-1: The three possible interactions for light when it travels from a less-dense medium to a more-dense medium. (a) Reflection. (b) Refraction. (c) Diffraction........................................................................................................................................................14
Figure 2-2: Schematic shows the existence of radiation (Fabry-Perot) mode in a single slab of material. ................................................................. 17

Figure 2-3: Schematic of how anti-reflective coating (ARC) works. .................. 18

Figure 2-4: Reflection spectra of planarly-stacked ZnO, PbS QDs and Au layers. ZnO thickness is chosen to be an effective ARC for wavelength 576 nm (peak in the solar spectrum). (a) Reflection spectra calculated analytically with transfer matrix method (TMM). (b) Reflection spectra obtained by HFSS simulation. Courtesy of Ozgur Cakmak. .................................................. 19

Figure 2-5: Reflection spectra of planarly-stacked ZnO, PbS QDs and Au layers. (a) 500 nm thick ZnO layer and varying PbS QDs thickness. (b) 100 nm PbS QDs and varying ZnO thickness. Courtesy of Ozgur Cakmak. .............................. 21

Figure 2-6: Dispersion diagram of a uniform waveguide. The dispersion line for air is red. The gray shaded area is for the radiation modes that only propagate in air. Discrete guided bands are labeled even and odd. Expansion picture of the uniform waveguide. (Reprinted (adapted) with permission from [25]. Copyright © 2008 by Princeton University Press) ........................................ 23

Figure 2-7: Dispersion diagram of a uniform waveguide. (a) Position of the random plane wave propagating in \( k \) direction on the dispersion diagram. (b) Position of the plane wave on the dispersion diagram when its angle of incident increases to the maximum. (Reprinted (adapted) with permission from [25]. Copyright © 2008 by Princeton University Press) ......................... 24

Figure 2-8: Dispersion diagram of the waveguided modes. Schematic of the waveguided modes inside the uniform waveguide. (Reprinted (adapted) with permission from [25]. Copyright © 2008 by Princeton University Press) ......... 25

Figure 2-9: Dispersion plot of the waveguide modes. A different perspective on FP modes. (Reprinted (adapted) with permission from [25]. Copyright © 2008 by Princeton University Press) ......................................................... 26

Figure 2-10: Dispersion diagram of waveguided modes. Representation of diffraction aided waveguided modes. (Reprinted (adapted) with permission from [25]. Copyright © 2008 by Princeton University Press) ........................................ 27

Figure 2-11: Dispersion diagram of periodic waveguide. Periodicity is a. (Reprinted (adapted) with permission from [25]. Copyright © 2008 by Princeton University Press) .................................................................................. 28

Figure 2-12: Dispersion diagram of periodic waveguide. Guided Bloch resonances. (Reprinted (adapted) with permission from [25]. Copyright © 2008 by Princeton University Press) .......................................................... 29
Figure 2-13: Schematic of Rayleigh scattering and Mie scattering. ..........................30

Figure 2-14: Schematic of Mie scattering versus Mie resonance. ..............................30

Figure 2-15: Schematic of surface plasmon resonance. ........................................31

Figure 2-16: (a) Schematic of the 2D structure studied by Brongersma et al. in [27]. (b) Schematic of the unit cell of the 2D structure studied by Vasudev et al. in [28]. .................................................................31

Figure 2-17: Intensity plot of radiation Fabry-Perot mode and the schematic of how it occurs in [27]. Adapted by permission from Macmillan Publishers Ltd: Nature Materials [27], copyright © 2014. .................................................................32

Figure 2-18: (a) Structure schematic and waveguided mode. (b) Intensity plot of the waveguided mode. (c) Dispersion plot of the structure and where the waveguided mode is found. This paper was published in Optics Express and is made available as an electronic reprint with the permission of OSA. The paper can be found at the following URL on the OSA website: http://dx.doi.org/10.1364/OE.20.00A385. Systematic or multiple reproduction or distribution to multiple locations via electronic or other means is prohibited and is subject to penalties under law. ........................................33

Figure 2-19: Intensity plot and structure schematic of waveguided mode found in [27]. Adapted by permission from Macmillan Publishers Ltd: Nature Materials [27], copyright © 2014. .................................................................34

Figure 2-20: (a) Structure schematic of hybridized Bloch mode. (b) Intensity plot of the hybridized Bloch mode. (c) Dispersion plot of the structure and where this hybridized Bloch mode is found. This paper was published in Optics Express and is made available as an electronic reprint with the permission of OSA. The paper can be found at the following URL on the OSA website: http://dx.doi.org/10.1364/OE.20.00A385. Systematic or multiple reproduction or distribution to multiple locations via electronic or other means is prohibited and is subject to penalties under law. ........................................35

Figure 2-21: Intensity plot and structure schematic of guided Bloch resonances found in [27]. Adapted by permission from Macmillan Publishers Ltd: Nature Materials [27], copyright © 2014. .................................................................36

Figure 2-22: (a) Structure schematic of Mie mode. (b) Intensity plot of the Mie mode. (c) Dispersion plot of the structure and where this Mie mode is found. This paper was published in Optics Express and is made available as an electronic reprint with the permission of OSA. The paper can be found at the following URL on the OSA website: http://dx.doi.org/10.1364/OE.20.00A385. Systematic or multiple
reproduction or distribution to multiple locations via electronic or other means is prohibited and is subject to penalties under law.

Figure 2-23: Intensity plot and structure schematic of hybridized Mie mode found in [27]. Adapted by permission from Macmillan Publishers Ltd: Nature Materials [27], copyright © 2014.

Figure 2-24: (a) 3D perspective of our LCCM structure. (b) Cross-sectional perspective of our LCCM structure.

Figure 2-25: Absorber absorption spectra of thick TCO planar cell, LCCM cell, and thin TCO planar cell. Simulation results are obtained by HFSS.

Figure 2-26: Calculated absorption coefficients of PbS QDs, nc-Si, and a-Si. [29] [30] [31]

Figure 2-27: Schematic explains how dome nanostructure allows for more gradual change in refractive indices, therefore reducing reflection and enhancing light absorption over planar cell.

Figure 3-1: Compilation of simulated J_{sc} results where PbS QDs layer thickness is gradually increased with four different AZO thicknesses: 50nm, 100nm, 200nm, and 500nm.

Figure 3-2: (A) 3D hexagonal lattice unit cell of the first LCCM model. (B) Cross-sectional area of this cell with variables—L, dia, and t—to be optimized. AZO is green. PbS QDs is purple. Gold is yellow.

Figure 3-3: Reflection spectra of the first LCCM model. t = 100nm. L and dia are varied (a-d). Red spectra are for L^{touch}, and blue spectra are for L = L^{touch} + 200nm.

Figure 3-4: Reflection spectra of the first LCCM models. L=600nm, dia=400nm. t is varied.

Figure 3-5: 3D compilation of J_{sc} results of the first LCCM models. X-axis is L spacing; y-axis is effective thickness; z-axis is J_{sc}. The wired surface shows the J_{sc} performance of the shown planar cell for comparison. The sphere represents the optimum spot to aim for best J_{sc}, longest L, and lowest effective thickness.

Figure 3-6: Compilation plot of the first LCCM cells at the L^{touch} condition color-highlighted.

Figure 3-7: Compilation plot of the first LCCM cells with the most optimized cells color-highlighted.
Figure 3-8: (A) 3D hexagonal unit cell of the second model. (B) Cross-sectional area of this cell with variables—\(L, \text{dia}\), and \(t\)—to be optimized.

Figure 3-9: Reflection spectra of the second LCCM models. \(t=100\)nm. \(L\) and \(\text{dia}\) are varied.

Figure 3-10: Reflection spectra of 4 second LCCM models. \(L=600\)nm; \(\text{dia}=400\)nm; \(t\) is varied.

Figure 3-11: 3D compilation of \(J_{sc}\) results of the second LCCM models. X-axis is \(L\) spacing; y-axis is effective thickness; z-axis is \(J_{sc}\). The wired surface shows the \(J_{sc}\) performance of the shown planar cell for comparison. The sphere represents the optimum spot to aim for best \(J_{sc}\), longest \(L\), and lowest effective thickness.

Figure 3-12: Consolidation plot of simulated LCCM2 cells with the \(L_{\text{touch}}\) condition color-highlighted.

Figure 3-13: Consolidation plot of simulated LCCM2 cells with the most optimized cells highlighted.

Figure 4-1: (a) 3D perspective schematic of the nano mold fabrication process to replicate nanodomes. (b) Side-view schematic of the same process steps in a. Step1: Have a master mold. Step 2: Dispense liquid resin. Step3: Secure glass slide on top and expose to UV to cure the liquid resin. Step 4: Separate the glass from the master mold.

Figure 4-2: (a) Top down FESEM images of the Si master mold where the nanodome are spaced 1 m apart. (b) The cross-sectional images of the nanodomes seen in a. (c) Side-view schematic showing the nanodome area of the nano mold process using the Si master mold.

Figure 4-3: FESEM images of the positive PUA mold. (a) Top-down with spacing \(L=1000\)nm. (b) Top-down with spacing \(L=500\)nm. (c) At 45° angle view with spacing \(L=500\)nm.

Figure 4-4: (a) Cross-sectional FESEM of a positive Si mold. (b) Top-down FESEM image of the negative PUA mold. (c) Side-view schematic showing the nanodome area of replicating negative PUA mold from positive mold. Courtesy of Professor Wook Jun Nam.

Figure 4-5: (a) 3D perspective of the process step to fabricate AZO sol-gel. (b) Side view of the same process steps. (c) Top-down FESEM image of the resulting AZO film. (d) Contact AFM image of the same film.
Figure 4-6: XRD results of the fabricated AZO sol-gel film. (b) XRD results of different sol stabilizers from [35].

Figure 4-7: (a) 3D perspective schematic of the process steps to fabricate the second LCCM cell. (b) Side-view schematic showing the nanodome area of the same process flow.

Figure 4-8: (a) Cross-sectional FESEM image of the LCCM2 made from negative PUA mold L=500nm. (b) Cross-sectional FESEM image of control flat cell. (c) Cross-sectional FESEM image shows conformal coating of AZO.

Figure 4-9: UV-VIS measurement light transmission through glass slide, and PUA on glass.

Figure 4-10: (a) Cross-sectional FESEM image Adachi et al. [34] cell fabricated with layer-by-layer dip-coating. (b) Cross-sectional FESEM images Kim et al. [20] cell fabricated with layer-by-layer dip-coating.

Figure 4-11: (a) Schematic of the standard layer-by-layer spin-coating process with active materials usage yield and required total material indicated. (b) Photograph of the as-synthesized long-ligand-capped PbS CQD solution before the solution exchange (left) and the exchanged short-ligand-capped CQD solution in a non-polar solvent (right). [38]

Figure 5-1: Real and imaginary relative permittivity data of colloidal PbS QDs in solvent. [29]

Figure 5-2: n and k data for ZnO used for all simulations in previous chapters. [41]

Figure 5-3: n and k data of AZO grown by ALD. VASE Measurement. Courtesy of Rona Banai.

Figure 5-4: Real and imaginary relative permittivity of nanocrystalline Si (nc-Si). [30]

Figure 5-5: Real and imaginary relative permittivity data of Au.

Figure 5-6: Real and imaginary relative permittivity data of Ag.
LIST OF TABLES

Table 2-1: List of the possible trapped modes of light inside a structure of media. ........................ 16

Table 3-1: Optimization criteria........................................................................................................ 44

Table 3-2: Compilation of results of all simulated first LCCM cells. Separated by
3 different waveguide thickness $t$. Increasing $dia$ are labeled by gradient from
white to purple. Increasing $L$ is labeled by gradient from white to bronze.
Increasing \textit{effective thickness} is labeled by gradient from white to blue.
Increasing $J_{sc}$ is labeled by gradient from green to yellow to red. ......................... 51

Table 3-3: Compilation of results of all simulated second LCCM cells. Separated
by 3 different waveguide thickness $t$. Increasing $dia$ are labeled by gradient
from white to purple. Increasing $L$ is labeled by gradient from white to
bronze. Increasing \textit{effective thickness} is labeled by gradient from white to
blue. Increasing $J_{sc}$ is labeled by gradient from green to yellow to red............... 58
I’d like to dedicate this thesis to my parents, my sister, my brother-in-law, my nieces, and all my friends. Without their unconditional love and support, this would not be a reality.

I’d like to express a very special thanks to Professor Stephen J. Fonash and Professor Wook Jun Nam for their intellectual guidance, and financial support.

I’d like to thank Professor Brownson, and Professor Awadelkarim for their feedback, support, and valuable time.

Many sincere thanks should go to my friends and colleagues, Ozgur Cakmak, Charles A. Smith, and Zack Gray, for their inputs, feedback, and support.

I also appreciate all the help from CNEU staffs.
Chapter 1

Why PbS Quantum Dots and Light Carrier Collection Management

In recent years, quantum dots (QDs) photovoltaic (PV) cells have gained tremendous interest due to their low-cost solution processability and quantum effect tunability to specific light spectrum [1][2][3]. Being a part of the third-generation PV cell, these cells, besides from affordability, have the very high potential to exceed the Shockley-Queisser efficiency limit because of enhanced collection of hot carriers or carriers from impact ionization [4]. Lead sulfide (PbS) QDs, in particular, emerge as one of the best candidates as light absorber for PV application. In terms of device performance, recent progress has been every exciting with 7% power conversion efficiency (PCE) PbS QDs based cell from Ip et al. [5] However, their accomplishment was a good ligand passivation method which is to improve the transport behavior of the QDs film. Cell architecture plays an equally important role in maximizing PCE while reducing the usage of the materials. Sub-wavelength nanostructure is found to significantly enhance photon absorption many times over the planar design. The so-called Light and Carrier Collection Management (LCCM) previously developed by the Fonash research group at the Pennsylvania State University [6] presented a good example. Combining this with PbS QDs as light absorber promises to unleash the competitive potential of this kind PV cell with current first and second-generation PV technologies. In turn, the success of this project could mean the reality of cheap and clean energy is one step closer.
Humanity also is living in a middle of another revolution, the revolution of numerical computing. Computers penetrate every aspect of life and almost all corners of the modern world. Engineers are taking full advantage of a new tool in designing, numerical modeling or computer simulation. With expanding computing resources, more and more sophisticated physical phenomena such as photovoltaic action become possible to simulate. Most significantly, simulation helps bypassing the costly and time-consuming prototyping step, and offers excellent optimized designs without much resources and testing. Using simulation tools to optimize the LCCM PbS QDs solar cell is another main goal of this thesis work.

1.1 Light and Carrier Collection Management

It is a common practice that a new absorber material is tested with the most simplistic architecture, the “planar architecture.” Designating any structure that has material layers stacked planarly on top of one another, this architecture allows PV experts to focus more on the characteristics of the layer. However, planar cells are severely inefficient. There are 2 competing design criteria in the planar architecture: light absorption length and carrier collection length. For example, amorphous Si (a-Si:H) has collection length approximately 300nm while having absorption length of 1 μm [7]. Figure 1-1 illustrates two scenarios in which only one criterion is satisfied. Both do not have the best PCE because they maximize either photocurrent or photovoltage separately, not at the same time. Alternative architectures need to be explored, so that maximum
amount light can still absorb while absorber layer remains minimum for the best carrier collection.

Figure 1-1: The solar cell on the left depicts an absorber layer that has been designed to absorb all wavelengths with energies above its band gap. The planar design on the right uses the same absorber but has now been designed with the material’s charge carrier collection length in mind. Adapted from [7]. Courtesy of Charles A. Smith.

The notion of “light trapping” feature has been explored very early on with single-crystal silicon cell. By taking advantage of the anisotropic etching property of silicon [8], [9], manufacturers can create multiple random-sized pyramid structure on the outer surface of the light absorber. These can be quite effective in reducing external light reflectivity, and increasing internal light scattering. This idea has naturally spread to the second-generation by starting the cell fabrication process with pre-textured transparent conducting oxide (TCO) superstrate [10], then the deposited light absorber subsequently achieves texturing from it. Nevertheless, the randomness in this technique does not
always guarantee improvement. Additionally, wet etching means waste of materials. This is one conscious point that also makes the third-generation cell superior to the other two.

Recent works of Zhu et al. [11], and Nam et al. [6] have demonstrated excellent light trapping property of sub-wavelength periodic nanodome arrays in Figure 1-2. Both publications investigated this new structure with single junction p-i-n a-Si:H as the main light absorber. Zhu et al. showed a significant 25% enhancement in power conversion efficiency (PCE) of the nanodome cell over the flat film one of the absorber nominal thickness of 280 nm. Interestingly, they also showed that the nanodomes can create the “lotus-leaf” effect of self-cleaning that is valuable for solar panels. Unlike Zhu’s work, utilizing superstrate configuration, Nam et al. exhibited a high PCE 8.17% using a-Si:H of nominal thickness of 400 nm. They also numerically emphasized the importance of the dome spacing in trapping light that Zhu et al. did not cover. Overall, both works implicitly agree that the performance enhancement originates from the sub-wavelength nanodome structures. While cleverly lengthening the traveling path of light, these LCCM structures still allow the absorber to remain thin, thereby satisfying the charge carrier collection length criterion at the same time. This is the ultimate goal of PV cell architects.
1.2 Lead Sulfide Quantum Dots as Light Absorber

QDs gain their recognition as the next generation light absorber due to the quantum physics that outreaches the scope of Shockley-Queisser efficiency limit. These nano-sized—smaller than or comparable to the deBroglie wavelength of carriers—compound semiconductors can exhibit radically different relaxation dynamics compared to their bulk counterparts [3]. This phenomenon, in turn, gives rise to an excellent chance to improve photovoltage by collection of hot carriers or photocurrent by impact ionization [12]. Moreover, the quantum confinement in these QDs leads to the widening in band gap. The smaller the dimension of the dots is; the larger their band gaps become [13]. This band gap tuning ability makes QDs enormously versatile for spectrum-specific PV cells as well as multijunction cell.
PbS is a direct band gap compound semiconductor belonging to the larger family of lead chalcogenide along with lead selenide (PbSe), and lead telluride (PbTe). In bulk, PbS is not suitable for PV application due to its small band gap of 0.41 eV [4]. The optimal choice for AM1.5G spectrum lies between the range of 1.1 – 1.4 eV. In this range, most of the available photons can be absorbed while photovoltage—dictated by the value of the band gap—can also be high enough for useful applications. This is where band gaps of bulk silicon, CIGS, and CdTe fulfill. However, thanks to quantum confinement, PbS can be made into QDs whose band gap fit in that optimal range. At the same time, the excitons in PbS have the Bohr radius of 18 nm, and that helps PbS QDs enjoying a unique ability to produce a single material triple-junction solar cell as seen in Figure 2-3.

Figure 1-3: (A) AM1.5G solar spectrum from ASTM G173–03 reference spectra. The bandgaps for some common bulk semiconductors are: TiO 2 3.3 eV; CdS 2.5 eV; CdSe 1.7 eV; CuInS 2 1.54 eV; CdTe 1.5 eV; InP 1.34 eV; Cu 2 S 1.21 eV; Si 1.12 eV; CuInSe 2 1.0 eV; InN 0.8 eV; Ge 0.66 eV; CuFeS 2 0.6 eV; PbS 0.41 eV; InAs 0.35 eV and PbSe 0.28 eV. (B) Concept of using PbS CQDs with different sizes to build a triple-junction tandem solar cell [4]. Copyright © 2011 by WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim)

PbS QDs may be synthesized as colloidal solution at very low cost and high control. This can then be processed into thin film at or near room temperature on both
hard and soft substrates. Along with the already exceptional optical absorption, these colloidal quantum dots (CQDs) would be the most ideal PV absorber except for one shortcoming: very poor carrier transport. While extensive mechanistic understanding of transport and recombination still needs work, Tang et al. [4] presented three main arguments. The first argument is that the organic ligands encapsulating the QDs effectively confine charge carriers within. The main transport possible here is tunneling to other CQDs or variable range hopping. Although these mechanisms work on different principles and models, they both agree on one thing: electrical conductivity improves when the inter-particle spacing decreases. This is confirmed experimentally by Liu et al. [14]. Exchanging original long ligands for shorter ones on these QDs in device fabrication has become such a practice. In fact, there has been an ongoing search for the best ligand-exchange method to enhance the mobility of electrons and holes in these films. Secondly, the level of passivation of the QDs affects the midgap defect states. These states are responsible for increased recombination of free carriers, thereby lowering the internal quantum efficiency and short circuit current ($J_{sc}$). Besides that, they also suppress the quasi Fermi level splitting under illumination, thus decreasing open circuit voltage ($V_{oc}$). Sufficient passivation of the dots is a prerequisite of a good PV cell. Unlike the first point, the length of the ligands does not matter here. The importance is in how strongly they can passivate the dots. The last discussion is about QDs doping. PV performance crucially depends on doping type and doping density of the absorber. Self-purification—wherein dopants segregate out from the core—creates difficulty in introducing impurity into the QDs. However, many researchers have found that ligand
treatments can alter the net doping type and density by passivating the QDs surface defects. In general, lead chalcogenide CQD films are p-type.

For single-junction CQD—such as PbS CQDs—solar cell, PV experts are currently exploring 4 basic architectures: Schottky, depleted heterojunction (DH), depleted bulk heterojunction (DBH), and CQD-sensitized cells (CQD-SSC) [2]. Figure 1-4 schematically shows these along with their corresponding band diagrams. We can easily spot the planar design in both Schottky and DH cells where LCCM architecture has the potential to improve. Both DBH and CQD-SSC are not new ideas. Originating from organic bulk heterojunction solar cell, DBH architecture strives to overcome the trade-off between exciton diffusion length and light absorption length by interlacing the two materials making up the heterojunction. The current CQD-SSC cell [15] simply replaces the molecular dye by monolayer CQDs. This means that thick electrode still has to be used to absorb light, thus requiring the liquid electrolyte. Johnston et al. [16] published an excellent example of Schottky PbS QDs solar cell. Pattantyus-Abraham et al. [17] also did representative work on PbS QDs DH cell. PbS QDs DBH cell was lately attempted by Leschkies et al. [18] and Barkhouse et al. [19] with great promises. Arguably, Kim et al. [20] explicitly stated that their cell was a DH, but a more careful eye would state that their cell is more DBH. It would be very worthwhile to see if our LCCM PbS cell would be able to compete with these works.
In order to combine the strengths of PbS CQDs and LCCM architecture, I propose the utility of material layers as that of the DH CQD solar cell as seen in fig. 1-4B. The main reason is that the nanodome array can be created on the ZnO/TiO$_2$ layer using the method that I will present in the next section. The PbS CQDs will then be deposited next to take the shapes of the nanodomnes. Gold (Au) electrode is then covered the PbS QDs film to finish the device.

The three stages—optical generation, carrier separation, and carrier collection—of photovoltaic action may be simulated individually by optical simulation and by transport simulation. The former models how light interact with structure and material layers in terms of optical absorption. The ladder simulates how these absorbed photons affect the
charge carriers and how those, in turn, may behave. Software programs dedicating to PV have been developed quite early on. AMPS-1D [21] and PC1D [22] are well-known examples which perform the two simulation tasks in one package. Nonetheless, the 1D in their names states that they can simulate only one-dimensional structures such planar PV cells. The LCCM nanodome array is three-dimensional (3D) thus requires more sophisticated code. Recent work from Isabella et al. [23] presents the one of the latest attempt at simulating 3D PV structure that offers great agreement and insights to PV experts.

The combination of PbS CQDs and LCCM architecture can potentially accomplish many aspects of third-generation solar cells that researchers strive for. In addition to that, optimization using numerical simulation will realize the best design that hopefully will provide a big impact to PV community in small and the world in large. The next chapter describes in details the methods that I plan to use in this project.

1.3 Numerical Modeling and Optimization

HFSS™ stands for High Frequency Structure Simulation. Originally designed for microwave applications, it has long established great reception from both industry and academia sectors. In short, it is a 3D Maxwell’s equations solver employing finite element method (FEM) as the main structure discretization. Light is treated as electromagnetic waves instead of rays as in geometric optics. This feature is critical for our LCCM design because the dimensions of the LCCM are sub-wavelength of visible
light. In other words, light behaves more wave-like within our structure rather than ray-like.

It is possible to draw the nanodome array with the HFSS\textsuperscript{TM}, but simulating it would be very expensive in terms of computing power and time. Modeling a unit cell of that array with periodic boundary conditions would be more logical. Figure 1-5 shows an example of the LCCM unit cell sketched with HFSS\textsuperscript{TM}. The transparent extruded hexagonal shape in B serves as the placeholders for boundary conditions (BCs). In simpler words, it acts as the space the light travels before entering the LCCM cell. In HFSS\textsuperscript{TM}, I chose it to be air for simplicity sake. However, as observed in Figure 3-1, light has to go through glass first. I clearly assume light can go through glass without significant loss. This is not so far from life with available high-transparency glass substrates. In detail, the top and bottom faces of the “vacuum box” are where special BCs called Floquet ports are placed. The top Floquet simulates propagating plane waves of light toward the LCCM and absorbs any reflected waves; the bottom one similarly absorbs any transmitted waves. At this stage of designing, we only look at normal incident plane waves. On the parallel side faces of the vacuum box, paired periodic BCs—called Master and Slave in HFSS\textsuperscript{TM}—are placed to match the optical electric/magnetic field on both faces\textsuperscript{1}. For our hexagonal LCCM, there will be 3 pairs of these BCs. This setup is run and solved in frequency domain because we are currently interested only in steady-state effects. A frequency sweep from 200-1000 tHz, corresponding to 300-1500 nm in light wavelength, shall be done for most cases here.

\textsuperscript{1} A phase delay value has to be entered to the corresponding master and slave pair in case the plane wave enters the LCCM at an angle other than normal.
Figure 1-5: (A) LCCM cell from process flow 1 drawn with HFSS: Green is ZnO, purple is PbS CQDs film, yellow is Au. (B) A “vacuum box” is used to encapsulate the cell and placeholder for Floquet ports and Master/Slave boundary conditions.

The main input that I need to provide to run these simulations is frequency-dependent complex relative permittivity/refractive index. These data are usually accessible from literature in terms of experimental measurements. Appendix A contains the values I used for each layer in the ladder chapters, and HFSS input format. The simulation settings can be found in appendix B in Charles A. Smith’s Master of Science thesis [24].
The anticipated device has the band diagram as seen in Fig. 1-6. In this we can see that the photovoltaic action comes from two sources: effective force at the ZnO and PbS QDs interface, and electrostatic force by PbS QDs and Au junction. From this band diagram, excitons created within the PbS QDs will be separated by the heterojunction, and then electrons will flow to the left while holes will exit to the right. The electrostatic force from the Schottky barrier between Au and PbS QDs layer will constructively add this behavior. This affirms that this device will surely work as a photovoltaic cell.
Chapter 2

Understanding Light Trapping Phenomena Present in LCCM Structures

This chapter is dedicated to understanding the light trapping phenomena that is crucial to solar cell architects. Only by comprehending these, the appropriate architecture can be chosen to maximize light absorption.

2.1 How light enters medium

There are three possible scattering interactions for light, as electromagnetic wave, as it travels from one medium to another medium.

![Figure 2-1: The three possible interactions for light when it travels from a less-dense medium to a more-dense medium.](a) Reflection. (b) Refraction. (c) Diffraction)

From figure 2-1, light travels from medium 1 denoted with refractive index $n_1$ to medium 2 with refractive index $n_2$. Refractive index is the relative measure of how much
denser a material is optically compared to free space. Specifically for solar cells, medium is usually air where $n_1$ is approximately 1, medium 2 is the solar cell material layer where $n_2$ is greater than 1. The first interaction is reflection where the incident light is reflected at the interfaces of the two media. The law of reflection dictates that the incident angle—measured from a normal line at the point of incident—has to be equal to the reflected angle as seen in figure 2-1a, i.e. $\theta_{inc} = \theta_{rfl}$. Besides from the change in propagation direction, the reflected light remains the same as the incident light in terms of wavelength. If medium 2 is considered to be semi-transparent (not fully reflective), the second phenomenon called refraction can also happen at the interface of the two media as seen in figure 2-1b. Refraction follows Snell’s law which can be summarized by the following formula,

$$n_1 \sin \theta_{inc} = n_2 \sin \theta_{rfr} \quad [2.1]$$

This formula shows how much the direction of the propagation of the refracted light will change compared to the incident direction. The exact amount depends on the refractive indices of the two media. In addition, if the assumption that medium 2 is denser than medium 1 stands, the wavelength or group velocity of the light will be reduced. Refraction is the first way that light can get inside a solid. The third possible route is by the so-called diffraction. Diffraction happens when light sees a finite obstacle in its direction of propagation. The obstacle will scatter the light in multiple other directions. Commonly, diffraction can be seen clearly in the slit experiment (figure 2-1c) where the size of the slit is comparable to the wavelength of the incident light. Interference pattern of the scattered light can be captured, and indicate the existence of diffraction. Diffraction is of interest to solar cell architects because of its ability to change the
incident direction of light. Reflection, refraction and diffraction are three possible pathways that light can take when it travels from a semi-transparent medium to another semi-transparent medium. However, in order for the light to exist or be captured inside a medium, allowed states or modes need to be present inside the medium. The next section categories and discusses these possible states.

2.2 Possible trapped modes of light inside a structure of media

When light travels into a structure of media, it may be trapped in several modes or states. Table 2-1 lists the names and characteristics of these modes.

Table 2-1: List of the possible trapped modes of light inside a structure of media.

<table>
<thead>
<tr>
<th>Mode name</th>
<th>Characteristics</th>
</tr>
</thead>
<tbody>
<tr>
<td>Radiation</td>
<td>Fabry-Perot (F-B) resonance present in multilayer thin film planar structure. Strong dependency on layer thickness.</td>
</tr>
<tr>
<td>Traveling waveguided</td>
<td>Light propagating into the open direction of the waveguide. Diffraction can couple into waveguided mode. Dependency on periodicity of the scatterers whose size is small compared to the waveguide thickness.</td>
</tr>
<tr>
<td>Traveling Bloch</td>
<td>Requirement of a photonic crystal structure. Dependency on the aspect ratio and periodicity of the structure.</td>
</tr>
<tr>
<td>Localized Mie resonance</td>
<td>Localized in the nano-scale structure existing in the medium. Dependency on the size of the nano-structure.</td>
</tr>
<tr>
<td>Plasmonic</td>
<td>Present with thin layer structure of dielectrics and metals that have the plasma frequency comparable to that of the incoming light. (e.g. gold or silver with visible light)</td>
</tr>
<tr>
<td>Hybrid</td>
<td>Complex combination of the mentioned-above modes.</td>
</tr>
</tbody>
</table>
2.3 Radiation (Fabry-Perot) mode

Figure 2-2: Schematic shows the existence of radiation (Fabry-Perot) mode in a single slab of material.

Considering a simple case a single slab of material $n_2$ inside a less dense material $n_1$ as seen in figure 2-2, a plane wave (pw) number 1 travels normally from $n_1$ to $n_2$. At the interface of the two media, pw 1 partially reflects into pw 2, and refracts into pw 3. Assuming that pw 3 can propagate within $n_2$ without any significant loss, pw 3’ at the back interface only differs from pw 3 in phase depending on the thickness of the slab. Pw 3’ then reflects into pw 4 and refracts into pw 5. Pw 4 then turn into pw 4’ at the front interface with a change in phase. Pw 6 and pw 7 are respectively the reflection and refraction of pw 4’. This can repeat indefinitely until all the power of the pw 1 dissipates toward zero. Radiation or Fabry-Perot (FP)—named after two French physicists, Charles
Fabry and Alfred Perot—mode is the varying degrees of interference of all the pw traveling outward from \( n_2 \) at the front and back interfaces. The example of anti-reflective coating is a great application of radiation/FP mode.

If the thickness of the slab is \( \frac{\lambda}{4n_2} \) (where \( \lambda \) is the wavelength of interest), pw 3’ will phase shift \( \frac{\pi}{4} \) compared to pw 3 which share the phase value with pw 1 and 2. In turn, pw 4’ would phase shift \( \frac{\pi}{4} \) compared to pw 4. Pw 7 shares its phase value with pw 4’. This makes pw 2 and pw 7 exactly \( \frac{\pi}{2} \) out of phase. This is the condition for destructive interference. In other words, the slab effectively minimizes the reflection of wavelength \( \lambda \) when it impinges on it. One can expect of dip in reflection spectrum of this slab right at wavelength \( \lambda \).

Figure 2-3: Schematic of how anti-reflective coating (ARC) works.
Figure 2-4: Reflection spectra of planarly-stacked ZnO, PbS QDs and Au layers. ZnO thickness is chosen to be an effective ARC for wavelength 576 nm (peak in the solar spectrum). (a) Reflection spectra calculated analytically with transfer matrix method (TMM). (b) Reflection spectra obtained by HFSS simulation. Courtesy of Ozgur Cakmak.

Figure 2-4 is shown here as the main validation for my HFSS simulation. For planarly-stacked layers, the total reflection spectra of the device can be calculated analytically using transfer matrix method (TMM) which is discussed in detail in appendix B. Figure 2-4a and b show significant agreement. This indicates the finite element meshing and HFSS simulation analysis are adequate for accuracy. The further simulation results can be trusted if the same conditions are satisfied.

The ZnO layer thickness is chosen specifically to be 60 nm to effectively suppress the reflection of wavelength 576 nm. The refraction index of ZnO is 2.4 at this
wavelength. The addition of the light absorber PbS QDs is meant to stay closer to reality of solar cell devices which consists of multiple thin films layers. The three-layer planar structure here should be a working device as explained earlier in chapter 1. It is easy to see that the 60nm ZnO layer effectively suppresses reflection at wavelength 576 nm regardless of the PbS QDs layer thickness. However, solar architects are interested in utilizing the whole solar spectrum. Interestingly, when the PbS QDs layer is thicker, the reflection of the device is better especially in the long wavelength region where absorption is weak. This is logical not only because of the light absorption length concept, but also that fact that the FP mode is less pronounced in a thicker layer. If the goal is to maximize the light absorption while keeping the absorber thin, this is obviously a detrimental effect.
It is not surprising to see that, when only the PbS QDs thickness layer is varied, the reflection in the long wavelength region (region 2) changes. This is because those wavelengths of light are weakly absorbed with PbS QDs compared to higher wavelength. This allows them to form significant FP modes inside the PbS QDs and be altered when the thickness is changed. Compared to PbS QDs, ZnO is less absorptive throughout the wavelength spectrum, and thus varying the ZnO layer thickness affects the FP modes throughout the spectrum. In fact, the thicker the ZnO layer gets, the more peaks and
valleys are present because more wavelengths of light are being reflected of the ZnO and PbS QDs interface. The valleys are good indication of light trapping, but they are always accompanied by the peaks. For this reason, avoiding the peaks and valleys altogether is the best solution.

2.4 Traveling waveguided and Bloch modes

This section explores further on the concepts of traveling waveguided and Bloch modes. The common coupling method for both of these modes is the utility of periodic structures, and, thus, it is a good idea to distinguish them.

2.4.1 Waveguided mode

Waveguided, or shortly guided, mode can exist is the open direction of a uniform waveguide as seen in figure 2-6. This is a similar picture seen from previous section. This means that radiation modes exist here particularly within the light cone region of the dispersion diagram.
Figure 2-6: Dispersion diagram of a uniform waveguide. The dispersion line for air is red. The gray shaded area is for the radiation modes that only propagate in air. Discrete guided bands are labeled even and odd. Expansion picture of the uniform waveguide. (Reprinted (adapted) with permission from [25]. Copyright © 2008 by Princeton University Press)

The light cone region is separated from the guided region by the dispersion line. In this particular case, \( n_1 \) is approximately 1 for air. With \( c \) as the absolute speed of light in free space, and \( \omega \) as the angular frequency, the air dispersion line may be constructed according to this,

\[
k_\parallel = \frac{\omega}{c}
\]

[2.2]

\( k_\parallel \) (called \( k \) parallel) is the parallel component of a random wave propagating in the direction of \( k_\circ \) as seen in figure 2-7a. This wave has an angle of incident, \( \theta_1 \), with respect to the normal direction. As this angle increases, the \( k_\parallel \) component also increases. However, if this wave resides in air, it will eventually hit the maximum \( k_\parallel \) value right on the dispersion line. Without any other means, this wave will never couple into the waveguided region of the dispersion diagram.
Figure 2-7: Dispersion diagram of a uniform waveguide. (a) Position of the random plane wave propagating in $k_o$ direction on the dispersion diagram. (b) Position of the plane wave on the dispersion diagram when its angle of incident increases to the maximum. (Reprinted (adapted) with permission from [25]. Copyright © 2008 by Princeton University Press)
Waveguided modes can only exist in bands as seen in the dispersion diagram. The characteristic of these modes is that they experience total internal reflection inside the waveguide. As a result, they are guided in the open direction of the waveguide as seen in figure 2-8. The odd and even are labeled for the parity nature of the wavefunction that exist in these bands.

![Dispersion diagram of the waveguided modes. Schematic of the waveguided modes inside the uniform waveguide.](image)

If light from air can be coupled into these waveguide modes, they are trapped and can be collected. Nevertheless, as mentioned earlier, without any special means, there is no way a light exist within the light cone can be coupled into the waveguided modes. We already called these radiation FP modes as seen again in a different perspective in figure 2-9. Since Maxwell’s equations require that the tangential components of the wave vectors be continuous at the interfaces, the transmitted light $k_{\parallel}$ is always equal to that of
the incident light. The light cone region may also be called the continuum of radiation modes. In other words, refraction fails to couple light in air into waveguided modes.

Figure 2-9: Dispersion plot of the waveguide modes. A different perspective on FP modes. (Reprinted (adapted) with permission from [25]. Copyright © 2008 by Princeton University Press)

Where refraction fails, diffraction succeeds. In figure 2-10, small obstacles or finite discontinuities are placed on the waveguide. If they are arranged periodically, diffraction order lines may be constructed on the dispersion plot as followed,

\[ k_\parallel = \frac{m2\pi}{L} \]  \[ 2.3 \]

where m is integer indicating the diffraction order, and L is the periodicity of the obstacles. The intersections between these diffraction lines and the waveguided bands are the particular frequencies and \( k_\parallel \) of the light that are coupled into the waveguided modes. This is the essence of diffraction aided waveguide modes.
2.4.2 Bloch mode

Periodic structure also means the existence of Bloch mode. Bloch mode or wave is named after the Swiss physicist, Felix Bloch, for his work on the expression of the wavefunction of a particle in a periodic potential environment such as a crystal. When one divides the uniform waveguide seen earlier into a periodic one as in figure 2-11, the dispersion diagram changes drastically. Besides from unchanged the light cone region and the dispersion line, the dispersion diagram now exhibits the appearances of Brillouin zone and band gap regions. This is analogous to the case of electrons in a crystal.
The Brillouin zone is where all the distinct Bloch modes occur. Any other mode happens outside of the Brillouin zone can be reduced to its equivalent inside the Brillouin zone by taking the appropriate reciprocal lattice vector. The white region can be called the guided Bloch mode region. These specific waves can propagate along the periodic waveguide without any loss. What is not being shown here is the extension of these mode lines into the light cone zone (redrawn in figure 2-12). The light that resides on these lines are called guided resonances by Fan et al. in [26]. The term guided is because they relate to waveguided mode in the uniform waveguide. However, instead of being able to exist inside the periodic waveguide indefinitely like the guided Bloch modes, they have finite lifetime. Their E-M power in the dielectric waveguide is quite significant, but it can leak out to air, and diminish in time. They still retain their periodicity of the Bloch
wave, and can be coupled into from air to form resonances. In order to make a clearer distinction, this thesis refers to these modes as *guided Bloch resonances*.

Our initial LCCM design seen in previous chapter is a combination of uniform and period waveguide. This is why it is important for us to understand both waveguided and Bloch mode.

2.5 Mie mode

The fourth mode takes its name from the German physicist, Gustav Mie, whose main contribution is the phenomenon called Mie scattering. Differing from Rayleigh scattering, Mie scattering happens when the incident light wavelength is comparable to
the size of the scatterers. Figure 2-13 shows schematically the difference between Rayleigh scattering and Mie scattering for spheres.

Another distinction for Mie scattering is the appearance of resonance condition. At right frequency and angle, instead of being scattered, the incident light experiences total internal reflection and forms resonance with itself. The nanostructures in the LCCM structure provide spaces for these resonances to happen.

Figure 2-13: Schematic of Rayleigh scattering and Mie scattering.

Figure 2-14: Schematic of Mie scattering versus Mie resonance.
### 2.6 Plasmonic mode

Plasmonic mode is widely explored for thin films of gold, silver, and platinum because their plasmonic frequencies lie within the visible spectrum. Another familiar name for plasmonic mode is surface plasmon resonance. As figure 2-15 schematically displays, a light source can excite the surface plasmon polariton—traveling in the open direction of the metallic film—when it impinges through the prism at the right angle. Refraction through the prism helps trapping the light in the metallic film. Metallic grating thin films can also achieve similar effects.

![Figure 2-15: Schematic of surface plasmon resonance.](image-url)
2.7 Trapped modes in 1D grating – 2D structures

One-dimensional grating or two-dimensional structures have been studied extensively in literature. This section attempts to go through two typical of such structures seen in figure 2-16.

Both of these structures are assumed to extend infinitely out of the page, and their unit cells are repeated indefinitely in the lateral direction. The following images are full-wave simulation results that these two groups reported in their respective publications. Radiation FP mode intensity plot can be seen in figure 2-17.
The distinct standing wave pattern seen in the intensity plot above signifies the existence of FP mode inside the structure. This is the result of the combination of all the waves bouncing of the interfaces between the waveguide layer and others.

Figure 2-18: (a) Structure schematic and waveguided mode. (b) Intensity plot of the waveguided mode. (c) Dispersion plot of the structure and where the waveguided mode is found. This paper was published in Optics Express and is made available as an electronic reprint with the permission of OSA. The paper can be found at the following URL on the OSA website: http://dx.doi.org/10.1364/OE.20.00A385. Systematic or multiple reproduction or distribution to multiple locations via electronic or other means is prohibited and is subject to penalties under law.

Figure 2-18 shows what one can expect to see in the intensity plot of waveguided mode. There is very distinct resonance pattern that only localizes in the uniform waveguide part of the whole structure. Most importantly, the dispersion plot seen in 2-18c (with $E - G$ instead of $\omega - k$) points where this waveguided mode is found. It apparently resides on the waveguided band that can be constructed by varying the pitch.
length or periodicity of the nanostructures. As a result of varying pitch length, the
diffraction order lines move and map out the waveguided band according to equation [2.3]. Similarly, waveguided mode can also be seen with the other structure as in figure 2-19.

![Waveguided mode schematic and intensity plot](image)

Figure 2-19: Intensity plot and structure schematic of waveguided mode found in [27]. Adapted by permission from Macmillan Publishers Ltd: Nature Materials [27], copyright © 2014.

Again, the lack of field enhancement outside of the waveguide and distinct resonant pattern indicate this as waveguided mode.

The following image show what guided Bloch resonances may look like in terms of field intensity.
First, the intensity plot (seen in 2-20b) shows field periodicity that is a sign for Bloch mode. Secondly, field intensity displaying in air is another characteristic of this mode. The absorption enhancement line (2-20c) also points toward dependency on pitch length for these resonances.
Figure 2.21: Intensity plot and structure schematic of guided Bloch resonances found in [27]. Adapted by permission from Macmillan Publishers Ltd: Nature Materials [27], copyright © 2014.

Guided Bloch resonance is also on display here. There is a high possibility that hybridization have occurred with waveguided mode due to the field intensity pattern.

Figure 2.22: (a) Structure schematic of Mie mode. (b) Intensity plot of the Mie mode. (c) Dispersion plot of the structure and where this Mie mode is found. This paper was published in Optics Express and is made available as an electronic reprint with the permission of OSA. The paper can be found at the following URL on the OSA website: http://dx.doi.org/10.1364/OE.20.00A385. Systematic or multiple reproduction or distribution to multiple locations via electronic or other means is prohibited and is subject to penalties under law.
Unlike the waveguided and Bloch modes seen earlier, the Mie mode here only depends on the presence of the nanostructure. It can be seen in 2-22c that this mode resides within a band of light energy, and it is independent of the pitch length. Although this aspect was not explored here in both publications, Mie mode would only change with the size of the nanostructure. Noticeably, the field intensity leaks into the waveguide and the layer below. This really opens channels for Mie mode to hybridize with other available modes in the waveguide.

![Figure 2-23: Intensity plot and structure schematic of hybridized Mie mode found in [27]. Adapted by permission from Macmillan Publishers Ltd: Nature Materials [27], copyright © 2014.](image)

The possible hybridization seen above may have occurred between Mie and waveguided mode or guided Bloch resonance.

### 2.8 2D gratings – 3D structures

Two-dimensional gratings are very important structures to be studied with light trapping. 1D gratings are limited in one dimension. Our LCCM is such a structure as seen in figure 2-24.
Figure 2-24: (a) 3D perspective of our LCCM structure. (b) Cross-sectional perspective of our LCCM structure.

Preliminary simulation results are obtained to gauge the performance enhancement of LCCM structure over its planar counterparts. Since we are interested in these cells as PV devices, the absorber light absorption plays a crucial role in device performance. The following formula is used to calculate the absorption specifically for the active layer.

\[
A(\lambda) = \int_V \pi \frac{c}{\lambda} \varepsilon''(\lambda) |E(\lambda)|^2 dV
\]  

[2.4]
where $E(\lambda)$ is the wavelength/frequency specific electric field, $\varepsilon''(\lambda)$ is the wavelength/frequency-specific imaginary relative permittivity, $\lambda$ is the wavelength of light, $c$ is the speed of light in free space, and $V$ is the volume of the layer of interest.

![Absorption Spectra](image)

Figure 2-25: Absorber absorption spectra of thick TCO planar cell, LCCM cell, and thin TCO planar cell. Simulation results are obtained by HFSS.

The thick TCO planar cell is used here as lower limit to the LCCM1 cell, and the thin TCO planar is the upper limit in terms of volume of absorber. It is logical to consider that more absorber means more light absorption. However, the LCCM structure appears to defy that logic. It outperforms the thin TCO planar cell in various regions. One can say that the LCCM makes better use of the absorber. It is critical to mention that the light trapping phenomena discussed extensively above did not show themselves throughout the absorption spectra. The first likely reason for this is that PbS QDs are such strong light absorber.
Figure 2-26: Calculated absorption coefficients of PbS QDs, nc-Si, and a-Si. [29] [30] [31]
Figure 2-26 confirms the strength of PbS QDs as light absorber over other common absorber materials such as nanocrystalline silicon (nc-Si) and amorphous silicon (a-Si). The second explanation can be understood by examining figure 2-27. As pw travels down to the multilayer structure, it experiences change in refractive indices. For a planar cell (figure 2-27a), it is an abrupt change from $n_1$ to $n_2$. This results in much reflection seen earlier in the discussion of FP modes. On the other hand, for the dome nanostructure, it undergoes a much more gradual change in refractive indices; $n_3$ and $n_4$ can be thought of as average refractive indices which depend on the amount of volume of each material in each slab. Reflection becomes less, and absorption is improved.

Figure 2-27: Schematic explains how dome nanostructure allows for more gradual change in refractive indices, therefore reducing reflection and enhancing light absorption over planar cell.
Chapter 3
Structure Design and Optimization of PbS QDs LCCM Cells with Optical Numerical Modeling

This chapter is dedicated to the discussion of structure design and optimization of different LCCM structures using optical numerical modeling. Cost and efficiency are the most important concerns of cell manufacturing, but, unfortunately, they do not always agree. There always has to be a certain compromise, and that is why optimization is a crucial design step. As introduced in the previous chapter, active layer absorption matters the most in cell design. In fact, if we assumed internal quantum efficiency (IQE) of 1, the device absorption spectrum should coincide with external quantum efficiency (EQE) plot of the device. For this convenience, I will use this assumption throughout this chapter.

With the assumption IQE=1 (all absorbed photons create free electron-hole pairs), this spectrum can be turned into the maximum short circuit current density that these particular cells are capable of in the ideal world.

\[
J_{sc} = e \int_{300nm}^{Bandgap\ wavelength} A(\lambda)\Phi(\lambda)d\lambda
\]  \[3.2\]

where \(\Phi(\lambda)\) = wavelength/frequency-specific photon flux of AM1.5G standardized spectrum
$J_{sc}$ provides one performance metric for optimization. However, the presence of the nanostructure in LCCM also poses another challenge in fairness with the planar cells in terms of absorber volume. Effective thickness of LCCM is taken into account when comparing with planar cells. To calculate the effective thickness of an LCCM,

$$\text{effective thickness (nm)} = \frac{\text{total absorber volume (nm}^3\text{)}}{\text{unit cell planar coverage area (nm}^2\text{)}}$$

[3.3]

These metrics along with the chosen design parameters are adequate to evaluate performance of LCCM cells. Figure 3-2 displays the simulated results of $J_{sc}$ of planar cells.

![Figure 3-1: Compilation of simulated $J_{sc}$ results where PbS QDs layer thickness is gradually increased with four different AZO thicknesses: 50nm, 100nm, 200nm, and 500nm.](image-url)
The increasing PbS QDs layer thickness gradually increases the $J_{sc}$ values to a saturating point. Also logically, the thicker the AZO layer gets, the more light loss is introduced to these planar structure, thereby reducing the $J_{sc}$. Unusually, some cells having absorber thickness around 275 nm take a dive in performance. In the long wavelength region, these cells have a prominent FP reflection peak in the photon rich region. This means these photons do not get absorbed, and be turned into short-circuit current.

*Effective thickness* is used as the metric to gauge how much material is used for the absorber. An optimized cell used the least material while producing the most current. Another important criterion is the dome spacing L (or pitch length, or nanostructure periodicity). In regard of fabrication of the 2D grating, larger L often means less material waste, and less time-consuming processes. Table 3-1 summarizes the design criteria that are considered simultaneously in the optimization process.

Table 3-1: Optimization criteria.

<table>
<thead>
<tr>
<th>Name</th>
<th>Short hand (unit)</th>
<th>Justification</th>
</tr>
</thead>
<tbody>
<tr>
<td>Short circuit current</td>
<td>$J_{sc}$ (mA/cm²)</td>
<td>Maximization. It relates directly to the amount of light absorption the cell can do.</td>
</tr>
<tr>
<td>Dome spacing (Pitch)</td>
<td>L (nm)</td>
<td>Maximization. It makes fabrication of these cells easier.</td>
</tr>
<tr>
<td>Effective thickness</td>
<td>Eff t (nm)</td>
<td>Minimization. It means that less absorber material is needed, and thinner cells have less bulk recombination.</td>
</tr>
</tbody>
</table>
3.1 First LCCM model – LCCM1

Figure 3-3A displays the unit cell (UC) of the first model inspired from the 1D grating structure by Brongersma et al. [27]. This model is a 2D grating arranged in hexagonal lattice which can allow for the most tight-packed array. 3-3B shows the cross-sectional area of the same UC and the design parameters to be optimized.

Light is simulated to enter through the top AZO layer through the PbS QDs layer, and then reflected back because of the Au layer. As mentioned in the previous chapter, PbS QDs is a strong light absorber. The strong signs of most light trapping resonances are largely obscure in these simulation results. The dome structure acts more like a light concentrator, therefore enhancing the light absorption over broad range of wavelength. This is exactly what solar architects aim for.
Figure 3-3: Reflection spectra of the first LCCM model. \( t = 100\)nm. \( L \) and \( \text{dia} \) are varied (a-d). Red spectra are for \( L^{\text{touch}} \), and blue spectra are for \( L = L^{\text{touch}} + 200\)nm.

FP modes dominate these LCCM structures according to these reflection spectra. At the \( L^{\text{touch}} \) condition (\( L = \text{dia} \)), the peaks and valleys in region 1 are effectively suppressed. However, more interestingly, at \( L = L^{\text{touch}} + 200\)nm, the last two reflection
peaks are minimized. This remains true regardless of what \( dia \) value is.

![Figure 3-4](image-url): Reflection spectra of the first LCCM models. \( L=600\text{nm}, \ dia=400\text{nm}. \  t \) is varied.

Increasing the waveguide thickness \( t \) leads to shifting effect of the peaks in region 2. This could be used advantageously when one desires to move these reflection peaks. It can be seen that increasing \( t \) redshifts the peaks, but, at some point, the peak blueshifts. This provides a limit on the \( t \) design parameter. Thicker waveguide does allow for more coupling, but this raises concerns for transport. Thicker waveguide has much larger bulk recombination which reduces the open circuit voltage \( V_{oc} \) of the device. Quantum dots are also known for their limited exciton diffusion length which deters the collection of free charge carriers. Using less material for the absorber is economically beneficial.
Figure 3-5: 3D compilation of $J_{sc}$ results of the first LCCM models. X-axis is $L$ spacing; y-axis is effective thickness; z-axis is $J_{sc}$. The wired surface shows the $J_{sc}$ performance of the shown planar cell for comparison. The sphere represents the optimum spot to aim for best $J_{sc}$, longest $L$, and lowest effective thickness.

The above plot collectively shows the performance of the all the first LCCM models that I have simulated. The z-axis is for the $J_{sc}$ values obtained with IQE assumed to be 1; the y-axis is the effective thickness to fairly compare with planar cells; the x-axis is for $L$ spacing for larger $L$ cells are easier to be manufactured. The performance of planar cells that have 200nm thick AZO and varying absorber thickness is shown as the wired surface. The concept of $L$ spacing does not apply for planar cells, so it just forms a constant-surface like shown.

In general, the entire LCCM models outperform the planar cells. According to the color code, increasing the waveguide thickness $t$ shows a saturating trend in terms of
They improve an average of 6 mA/cm² (around 18% increase) on the $J_{sc}$ while keeping comparable effective thickness with the corresponding planar cells.

It is interesting to see that the cells at the L$^{touch}$ condition is consistent in terms of $J_{sc}$. Increasing $dia$ also allows for larger $L$ cells, but slightly compromises Eff $t$. Figure 3-7 shows the most optimized cells with respect to the set criteria.
Figure 3-7: Compilation plot of the first LCCM cells with the most optimized cells color-highlighted.

Table 3-2 numerically shows the simulated cells with respect to the optimization criteria. The most optimized LCCM1 cells are concentrated within the red circle. Since the dome height is kept constant at 300nm, changing dia also means changing the aspect ratio (AR) of the dome. Starting from a 1:1 AR to 1:2 AR, it is worthy to notice that the better cells have smaller AR value than 1:1.
Table 3-2: Compilation of results of all simulated first LCCM cells. Separated by 3 different waveguide thickness $t$. Increasing $dia$ are labeled by gradient from white to purple. Increasing $L$ is labeled by gradient from white to bronze. Increasing effective thickness is labeled by gradient from white to blue. Increasing $J_{sc}$ is labeled by gradient from green to yellow to red.

<table>
<thead>
<tr>
<th>L (nm)</th>
<th>Eff t (nm)</th>
<th>Jsc (mA/cm$^2$)</th>
<th>L (nm)</th>
<th>Eff t (nm)</th>
<th>Jsc (mA/cm$^2$)</th>
<th>L (nm)</th>
<th>Eff t (nm)</th>
<th>Jsc (mA/cm$^2$)</th>
<th>L (nm)</th>
<th>Eff t (nm)</th>
<th>Jsc (mA/cm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>200</td>
<td>359.1</td>
<td>36.94</td>
<td>300</td>
<td>346.4</td>
<td>36.97</td>
<td>400</td>
<td>337.4</td>
<td>37.57</td>
<td>500</td>
<td>330.6</td>
<td>37.35</td>
</tr>
<tr>
<td>300</td>
<td>281.4</td>
<td>37.31</td>
<td>400</td>
<td>281.4</td>
<td>37.48</td>
<td>500</td>
<td>281.4</td>
<td>37.86</td>
<td>600</td>
<td>281.4</td>
<td>37.78</td>
</tr>
<tr>
<td>400</td>
<td>202.0</td>
<td>36.35</td>
<td>500</td>
<td>216.1</td>
<td>38.11</td>
<td>600</td>
<td>226.0</td>
<td>37.81</td>
<td>700</td>
<td>233.3</td>
<td>37.67</td>
</tr>
<tr>
<td>500</td>
<td>165.3</td>
<td>36.85</td>
<td>600</td>
<td>180.6</td>
<td>37.73</td>
<td>700</td>
<td>192.5</td>
<td>36.94</td>
<td>800</td>
<td>202.0</td>
<td>36.96</td>
</tr>
<tr>
<td>600</td>
<td>145.3</td>
<td>35.87</td>
<td>700</td>
<td>159.2</td>
<td>35.64</td>
<td>800</td>
<td>170.8</td>
<td>35.54</td>
<td>900</td>
<td>180.6</td>
<td>36.12</td>
</tr>
<tr>
<td>700</td>
<td>133.3</td>
<td>33.91</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>800</td>
<td>125.5</td>
<td>31.94</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>200</td>
<td>459.1</td>
<td>37.89</td>
<td>300</td>
<td>446.4</td>
<td>38.17</td>
<td>400</td>
<td>437.4</td>
<td>38.41</td>
<td>500</td>
<td>430.6</td>
<td>38.8</td>
</tr>
<tr>
<td>300</td>
<td>381.4</td>
<td>39.6</td>
<td>400</td>
<td>381.4</td>
<td>39.97</td>
<td>500</td>
<td>381.4</td>
<td>39.91</td>
<td>600</td>
<td>381.4</td>
<td>39.59</td>
</tr>
<tr>
<td>400</td>
<td>302.0</td>
<td>39.19</td>
<td>500</td>
<td>316.1</td>
<td>39.18</td>
<td>600</td>
<td>326.0</td>
<td>39.81</td>
<td>700</td>
<td>333.3</td>
<td>39.74</td>
</tr>
<tr>
<td>500</td>
<td>265.3</td>
<td>37.89</td>
<td>600</td>
<td>280.6</td>
<td>39.22</td>
<td>700</td>
<td>292.5</td>
<td>39.3</td>
<td>800</td>
<td>302.0</td>
<td>39.1</td>
</tr>
<tr>
<td>600</td>
<td>245.3</td>
<td>37.52</td>
<td>700</td>
<td>259.2</td>
<td>38.32</td>
<td>800</td>
<td>270.8</td>
<td>38.17</td>
<td>900</td>
<td>280.6</td>
<td>38.03</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>200</td>
<td>559.1</td>
<td>39.41</td>
<td>300</td>
<td>546.4</td>
<td>39.66</td>
<td>400</td>
<td>537.4</td>
<td>39.82</td>
<td>500</td>
<td>530.6</td>
<td>39.95</td>
</tr>
<tr>
<td>300</td>
<td>481.4</td>
<td>39.92</td>
<td>400</td>
<td>481.4</td>
<td>40.2</td>
<td>500</td>
<td>481.4</td>
<td>40.13</td>
<td>600</td>
<td>481.4</td>
<td>39.94</td>
</tr>
<tr>
<td>400</td>
<td>402.0</td>
<td>39.54</td>
<td>500</td>
<td>416.1</td>
<td>39.44</td>
<td>600</td>
<td>426.0</td>
<td>39.39</td>
<td>700</td>
<td>433.3</td>
<td>39.66</td>
</tr>
<tr>
<td>500</td>
<td>365.3</td>
<td>38.38</td>
<td>600</td>
<td>380.6</td>
<td>38.91</td>
<td>700</td>
<td>392.5</td>
<td>39.05</td>
<td>800</td>
<td>402.0</td>
<td>39.38</td>
</tr>
<tr>
<td>600</td>
<td>345.3</td>
<td>37.6</td>
<td>700</td>
<td>359.2</td>
<td>37.94</td>
<td>800</td>
<td>370.8</td>
<td>38.45</td>
<td>900</td>
<td>380.6</td>
<td>38.33</td>
</tr>
</tbody>
</table>

Cell engineers can use a table such as table 3-1 to make a much more informed decision on cell manufacturing. More criteria can always be added on to make the optimization even more rigorous, but this presents one way to do that.
3.2 Second LCCM model – LCCM2

Figure 3-8: (A) 3D hexagonal unit cell of the second model. (B) Cross-sectional area of this cell with variables—\( L \), \( \text{dia} \), and \( t \)—to be optimized.

It is unsurprising that the thick TCO layer of LCCM1 allows for much FP ringing. Naturally, a thinner TCO layer should be better in terms of reducing these. Hence the second LCCM model is designed as shown in 3-8. The design parameters remain the same except the diameter \( \text{dia} \). This is chosen according to the demand of fabrication that is slightly different from LCCM1 which will be discussed in chapter 4.
Figure 3-9: Reflection spectra of the second LCCM models. \( t = 100 \text{nm} \). \( L \) and \( dia \) are varied.

The conformal coating of the TCO layer indeed improves the reflection spectra. Compared to figure 3-3, there is virtually no reflection in region 1 of higher energy photon. Another reason, as stated the previous chapter, is that the dome nanostructure allows for much more gradual change in refractive indices. In this case, it reduces reflection as \( pw \) travels from air to the TCO layer. Again, very interestingly, for cells at \( L = L^{touch} + 200 \text{nm} \), the reflection in the longer wavelength region is suppressed. Especially when \( dia \) is increased, there is an elongation of the low reflection region over
This time, changing the waveguide thickness $t$ does not show the shifting as before with LCCM1. Still, increasing it does help the reflection to certain extent.
Figure 3-11: 3D compilation of $J_{sc}$ results of the second LCCM models. X-axis is $L$ spacing; y-axis is effective thickness; z-axis is $J_{sc}$. The wired surface shows the $J_{sc}$ performance of the shown planar cell for comparison. The sphere represents the optimum spot to aim for best $J_{sc}$, longest $L$, and lowest effective thickness.

The wire-frame surface is meant to show the performance of the corresponding planar cells with 100nm TCO on the light facing side. From figure 3-1, the performance of these planar cells is better than that of the ones seen earlier with LCCM1. Yet the LCCM2 cells are still better. The upper right image in the above figure shows a much more dramatic effect of changing $dia$ on $J_{sc}$ performance. The lower left image exhibits a favorable trend in increasing spacing $L$ and $dia$. Incrementing the waveguide thickness $t$ has the same saturating effect. Much attribution should go into the conformal coating of AZO layer because LCCM2 models outperform even the LCCM1. At the highest point,
LCCM2 improves 12 mA/cm² (over 30% increase) in $J_{sc}$ over the corresponding planar cell.

Figure 3-12: Consolidation plot of simulated LCCM2 cells with the $L^{touch}$ condition color-highlighted.

Figure 3-12 shows much more pronounced effect of changing $dia$. At the $L^{touch}$ condition, changing $dia$ really helps improving $J_{sc}$ and $L$. It emphasizes the fact that having a high AR for these cells is not the best. The most optimized cells for LCCM2 are highlighted in figure 3-13 and table 3-3.
Figure 3-13: Consolidation plot of simulated LCCM2 cells with the most optimized cells highlighted.

Once again, the most optimized cells have small waveguide thickness, small dome AR value, and reasonably large $L$. Whether this trend continues this way is another matter of future work.
Table 3-3: Compilation of results of all simulated second LCCM cells. Separated by 3 different waveguide thickness $t$. Increasing $\text{dia}$ are labeled by gradient from white to purple. Increasing $L$ is labeled by gradient from white to bronze. Increasing effective thickness is labeled by gradient from white to blue. Increasing $J_{sc}$ is labeled by gradient from green to yellow to red.

<table>
<thead>
<tr>
<th>t=100nm</th>
<th>L</th>
<th>Eff $t$</th>
<th>Jsc</th>
<th>L</th>
<th>Eff $t$</th>
<th>Jsc</th>
<th>L</th>
<th>Eff $t$</th>
<th>Jsc</th>
</tr>
</thead>
<tbody>
<tr>
<td>dia=300nm</td>
<td>nm</td>
<td>nm</td>
<td>mA/cm²</td>
<td>nm</td>
<td>nm</td>
<td>mA/cm²</td>
<td>nm</td>
<td>nm</td>
<td>mA/cm²</td>
</tr>
<tr>
<td>200</td>
<td>352.9</td>
<td>40.06</td>
<td>43.46</td>
<td>400</td>
<td>320.9</td>
<td>43.72</td>
<td>400</td>
<td>317.3</td>
<td>45.16</td>
</tr>
<tr>
<td>300</td>
<td>328.5</td>
<td>42.53</td>
<td>45.19</td>
<td>500</td>
<td>305.9</td>
<td>45.16</td>
<td>500</td>
<td>302.9</td>
<td>47.56</td>
</tr>
<tr>
<td>400</td>
<td>313.2</td>
<td>42.80</td>
<td>45.37</td>
<td>600</td>
<td>305.9</td>
<td>42.53</td>
<td>600</td>
<td>302.9</td>
<td>47.79</td>
</tr>
<tr>
<td>500</td>
<td>308.5</td>
<td>42.93</td>
<td>45.19</td>
<td>700</td>
<td>317.3</td>
<td>45.16</td>
<td>700</td>
<td>314.1</td>
<td>47.79</td>
</tr>
<tr>
<td>600</td>
<td>305.9</td>
<td>42.53</td>
<td>45.16</td>
<td>800</td>
<td>317.3</td>
<td>45.16</td>
<td>800</td>
<td>314.1</td>
<td>47.79</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>t=200nm</th>
<th>L</th>
<th>Eff $t$</th>
<th>Jsc</th>
<th>L</th>
<th>Eff $t$</th>
<th>Jsc</th>
<th>L</th>
<th>Eff $t$</th>
<th>Jsc</th>
</tr>
</thead>
<tbody>
<tr>
<td>dia=300nm</td>
<td>nm</td>
<td>nm</td>
<td>mA/cm²</td>
<td>nm</td>
<td>nm</td>
<td>mA/cm²</td>
<td>nm</td>
<td>nm</td>
<td>mA/cm²</td>
</tr>
<tr>
<td>200</td>
<td>352.9</td>
<td>40.06</td>
<td>43.46</td>
<td>400</td>
<td>320.9</td>
<td>43.72</td>
<td>400</td>
<td>317.3</td>
<td>45.16</td>
</tr>
<tr>
<td>300</td>
<td>328.5</td>
<td>42.53</td>
<td>45.19</td>
<td>500</td>
<td>305.9</td>
<td>45.16</td>
<td>500</td>
<td>302.9</td>
<td>47.56</td>
</tr>
<tr>
<td>400</td>
<td>313.2</td>
<td>42.80</td>
<td>45.37</td>
<td>600</td>
<td>305.9</td>
<td>42.53</td>
<td>600</td>
<td>302.9</td>
<td>47.79</td>
</tr>
<tr>
<td>500</td>
<td>308.5</td>
<td>42.93</td>
<td>45.19</td>
<td>700</td>
<td>317.3</td>
<td>45.16</td>
<td>700</td>
<td>314.1</td>
<td>47.79</td>
</tr>
<tr>
<td>600</td>
<td>305.9</td>
<td>42.53</td>
<td>45.16</td>
<td>800</td>
<td>317.3</td>
<td>45.16</td>
<td>800</td>
<td>314.1</td>
<td>47.79</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>t=300nm</th>
<th>L</th>
<th>Eff $t$</th>
<th>Jsc</th>
<th>L</th>
<th>Eff $t$</th>
<th>Jsc</th>
<th>L</th>
<th>Eff $t$</th>
<th>Jsc</th>
</tr>
</thead>
<tbody>
<tr>
<td>dia=300nm</td>
<td>nm</td>
<td>nm</td>
<td>mA/cm²</td>
<td>nm</td>
<td>nm</td>
<td>mA/cm²</td>
<td>nm</td>
<td>nm</td>
<td>mA/cm²</td>
</tr>
<tr>
<td>200</td>
<td>352.9</td>
<td>40.06</td>
<td>43.46</td>
<td>400</td>
<td>320.9</td>
<td>43.72</td>
<td>400</td>
<td>317.3</td>
<td>45.16</td>
</tr>
<tr>
<td>300</td>
<td>328.5</td>
<td>42.53</td>
<td>45.19</td>
<td>500</td>
<td>305.9</td>
<td>45.16</td>
<td>500</td>
<td>302.9</td>
<td>47.56</td>
</tr>
<tr>
<td>400</td>
<td>313.2</td>
<td>42.80</td>
<td>45.37</td>
<td>600</td>
<td>305.9</td>
<td>42.53</td>
<td>600</td>
<td>302.9</td>
<td>47.79</td>
</tr>
<tr>
<td>500</td>
<td>308.5</td>
<td>42.93</td>
<td>45.19</td>
<td>700</td>
<td>317.3</td>
<td>45.16</td>
<td>700</td>
<td>314.1</td>
<td>47.79</td>
</tr>
<tr>
<td>600</td>
<td>305.9</td>
<td>42.53</td>
<td>45.16</td>
<td>800</td>
<td>317.3</td>
<td>45.16</td>
<td>800</td>
<td>314.1</td>
<td>47.79</td>
</tr>
</tbody>
</table>
Chapter 4

Fabrication Process Design and Trial Cells

The fabrication of the nanodomes can be made possible with nano molding technology. Like its predecessor for larger size parts, this technology has the advantage for scale-up operation. This is attractive for photovoltaic manufacturing to reduce cost and increase throughput which usually translates to more affordable product. First, it requires a master mold that carries the exact shape of the part. Secondly, it needs a liquid resin (usually polymer) that can be cured or hardened to take the shape of the master mold. Separation of the hardened part from the master mold is the last step of the process. The next subsection discusses how I fabricated the nanodomes with nano molding technology.
4.1 Nanomold fabrication

Figure 4-1: (a) 3D perspective schematic of the nano mold fabrication process to replicate nanodomes. (b) Side-view schematic of the same process steps in a. Step 1: Have a master mold. Step 2: Dispense liquid resin. Step 3: Secure glass slide on top and expose to UV to cure the liquid resin. Step 4: Separate the glass from the master mold.

The schematic above shows the general steps to fabricate the nanodomes from a master mold which, in this case, is a silicon (Si) substrate. Figure 4-2a shows an example of the structure that can be etched into the Si master mold by using electron beam lithography and reactive ion etch with oxygen (O₂) and sulfur hexafluoride (SF₆) (Courtesy of Professor Wook Jun Nam).
Figure 4-2: (a) Top down FESEM images of the Si master mold where the nanodome are spaced 1 m apart. (b) The cross-sectional images of the nanodomes seen in a. (c) Side-view schematic showing the nanodome area of the nano mold process using the Si master mold.

The Si master mold\(^2\) seen in 4-2a, b may be referred to as a negative mold because it contain the etched away structure. The nanodome array area (seen in 4-1a) of this Si master mold is a 3x3 mm square. The dimensions of the nanodomes seen in figure 4-2b is the starting points of all the simulated models done chapter 3. The replicated mold dimensions are initially assumed to be very close to these. Following the process schematic seen in 4-2c produces a positive mold (positive picture of the mold). The liquid resin used is called polyurethane acrylate (PUA) oligomer which contains a few monomer units. It can be cured robustly by exposure to ultraviolet (UV) light. The UV-cured PUA is a hard and transparent plastic [32] that can take shape down to 100nm.

---

\(^2\) To help the release of the PUA mold from the master mold, self-assembled monolayers are coated on the master mold to increase its surface energy.
range in dimension [33]. Figure 4-3 shows the positive PUA mold replicated from a negative Si master mold. Liquid phase PUA is cured under UV lamp (300-400nm wavelength).

![FESEM images of the positive PUA mold. (a) Top-down with spacing L=1000nm. (b) Top-down with spacing L=500nm. (c) At 45° angle view with spacing L=500nm.](image)

Using this positive mold as the master mold, one can also prepare another negative mold just like the master mold following the schematic in 4-4c. On the other
hand, a positive Si mold can be used in place of the positive PUA mold to minimize the change in dimensions (figure 4-4a).

Figure 4-4: (a) Cross-sectional FESEM of a positive Si mold. (b) Top-down FESEM image of the negative PUA mold. (c) Side-view schematic showing the nanodome area of replicating negative PUA mold from positive mold. Courtesy of Professor Wook Jun Nam.

The next fabrication process will utilize these negative and positive molds as the starting point for the LCCM cells.

4.2 First LCCM cell – Sol-gel process flow

The following fabrication steps attempt to create a PV cell that resembles the first LCCM model simulated in chapter 3. One approach involves using zinc oxide (ZnO) sol-gel to replicate the nanodomes.
ZnO sol-gel is prepared by magnetically stirring zinc acetate 2-hydrate (Zn(CH$_3$COO)$_2$·2H$_2$O) into 2-methoxyethanol on a hot plate at 65°C (concentration is 0.5mol). The sol stabilizer, diethanolamine (HN(CH$_2$CH$_2$OH)$_2$, DEA), is then added to this drop by drop until the solution becomes clear. The solution is then let cool and added with 2-nitrobenzaldehyde as the UV-sensitive agent and aluminum nitrate nonahydrate (Al(NO$_3$)$_3$·9H$_2$O) as a dopant. The ratio of Al:Zn is kept at 2% at. The solution is aged for 24 hours before use.

The process steps to make nanodomes with AZO sol-gel is shown in figure 4-5a,b. First step is to spin-coat the mixed sol-gel solution onto a standard-cleaned glass slide at 2000 rpm for 30 seconds. Each spin step typically provides a 100nm film. The film can be made thicker by alternately spinning and heating the film on a hot plate at 110°C for 1 minute. A 500 nm film of AZO is aimed here to match with simulation models. In the second step, the positive PUA mold made in the first section is then pressed firmly on top of the film. The whole setup is loaded into the CNI compact thermal nanoimprinter, and pressed at 3-4 bar. The third step is to remove the setup from the nanoimprinter, and placed under UV lamp (300-400nm wavelength) to activate the hardening of the film for 30 minutes. Once the film is hardened, the PUA mold can be removed from the AZO film. This final film is then annealed at 550°C in a furnace to completely cure the sol-gel. This concludes the last step of the process.
Figure 4-5: (a) 3D perspective of the process step to fabricate AZO sol-gel. (b) Side view of the same process steps. (c) Top-down FESEM image of the resulting AZO film. (d) Contact AFM image of the same film.

The nanodomes widen after the final annealing step according to the FESEM image (from roughly 250 nm to 442.1 nm). The AFM image only shows a 71nm depth. This means that the film thickness also shrinks considerably. Most of all, the measured resistivity of the film is around 10 Ω.cm. While other groups reported much lower resistivity values [34], they all used as slightly different chemistries from my mixture and had the film crystal growth strongly in the (002) direction. Hosseini Vajargah et al. [35]
confirms the role of sol stabilizer as the main ingredient to have a preferred crystal growth in the (002) direction.

![XRD results](image)

Figure 4-6 shows the x-ray diffraction (XRD) result of the fabricated AZO sol-gel film. It agrees well with the results found in [35]. Moreover, it also shows that only sol-gel solutions made with either monoethanolamine (MEA) or triethylamine (TeA) are capable of having the preferred crystal growth in the (002) direction. Simulation results and this setback obligate me to move on to the fabrication of the second LCCM cell.
4.3 Second LCCM cell – ALD process flow

The second LCCM model requires a conformal coating of the AZO. There are only a few thin film deposition techniques that are capable of that. Atomic layer deposition (ALD) is one of those. In principle, gas precursors of certain oxides and metals can react with surface species in a self-limiting manner one molecule layer at a time. This can be repeated multiple times to make the thin film slowly grow with great control on the thickness. ALD thin film requires a binary (AB) reaction sequence. For example, reactions to deposit Al₂O₃ are [36]

\[
\text{AlOH}^* + \text{Al(CH}_3)_3 \rightarrow \text{AlOAl(CH}_3)_2^* + \text{CH}_4
\]

\[
\text{AlCH}_3^* + \text{H}_2\text{O} \rightarrow \text{AlOH}^* + \text{CH}_4
\]

and for ZnO as

\[
\text{ZnOH}^* + \text{Zn(CH}_2\text{CH}_3)_2 \rightarrow \text{ZnOZn(CH}_2\text{CH}_3)^* + \text{CH}_3\text{CH}_3
\]

\[
\text{ZnOZn(CH}_2\text{CH}_3)^* + \text{H}_2\text{O} \rightarrow \text{ZnOH}^* + \text{CH}_3\text{CH}_3
\]

The asterisk denotes surface species. By alternating depositing ZnO and Al₂O₃, AZO alloy film can form with great control on the thickness and a conformal coating for the nanodomes. In my particular case, 10 AB sequences of ZnO follows by 1 AB sequence, and then by another 10 AB sequences of ZnO. This supercycle is repeated for up to 43 times at 200°C to achieve 100nm of AZO thin film. The measured resistivity is 1.83×10⁻³Ωcm which is suitable to be a transparent conductive oxide (TCO). The ALD equipment used is Cambridge Nanotech ALD 200 System.
Figure 4-7: (a) 3D perspective schematic of the process steps to fabricate the second LCCM cell. (b) Side-view schematic showing the nanodome area of the same process flow.

The 7-step process flow in figure is how I design to fabricate the LCCM2 cells. The first step starts with obtaining the negative PUA mold fabricated from either the positive Si master mold or positive PUA mold. The second step is to deposit of 100 nm conformal AZO on the negative PUA mold with ALD. In the third step, colloidal oleic acid (OA) capped PbS QDs in toluene is drop-casted onto the nanodome area and let dry with a light downdraft of nitrogen to promote uniform spreading. A polydimethylsiloxane (PDMS) stamp is placed on top of the QDs layer and loaded into
the nanoimprinter. A pressure of 3-4 bar is used while substrate temperature ramps slowly to 120°C to evaporate solvent. Removing the whole setup from the imprinter and create openings through the PDMS to the nanodomes area is step five. Gold is then subsequently DC sputtered on top of the whole area using Denton Desktop Pro sputtering tool. The final step is to remove the sample from the sputtering chamber, and slowly peel the PDMS stamp away.
The cross-sectional FESEM images show that drop-casting and nanoimprinting is a good method to fill the nanodomes. ALD is definitely able to produce conformal coating of AZO. This is a viable process to create the LCCM2 structure. To compare with simulation results, optical loss in glass and PUA should be taken into account. Figure 4-9 shows the UV-VIS measurement of the transmission of glass slide, and that of PUA on glass for comparison.

In this particular spectrum, the estimated light loss through glass alone is 10%, or 90% transparent compared to air. Adding PUA accounts for about 5% more in loss. This makes PUA very attractive for such application.
4.4 Manufacturability and comparison with existing fabrication methods

This subsection is dedicated to the discussion of how manufacturable my fabrication process can be and comparison with fabrication methods that are popularly employed.

Manufacturability of a product is defined as the extent to which that product may be manufactured with relative ease at minimum cost and maximum reliability. Manufacturability at the nanoscale adds extra complexity because of dimensions. Most of the techniques and equipment used to fabricate the cells in this chapter are abundantly proven with integrated circuit (IC) industry. For example, the Si master molds are fabricated with e-beam lithography and reactive ion etching (RIE). The PUA molds are then fabricated with nanomolding which can be scaled up quite easily. For the deposition of AZO and TiO$_2$, ALD is another method that IC industry is utilizing extensively. The combination of drop-casting and nanoimprinting presents a new and unique way to deposit CQDs that promises lower cost and higher throughput comparing to other popular methods utilized by other research groups. Adachi et al. [37] and Kim et al. [20] has good success filling the nanofeatures using layer-by-layer dip-coating method seen in figure 4-10.
Dip-coating is a very precise method which allows for good control over the final film thickness and good uniformity. Ligand exchange can also be performed in between the layer to help with transport performance. However, dip-coating is known to be very time-consuming, therefore whether high throughput can be achieved with this method is
questionable. Spin-coating is the last common method to create thin film of CQDs. Like dip-coating, it offers great control on uniformity and film thickness. Still, Fischer et al. [38] shows the benefit of drop-casting CQDs film over spin-coated one in terms of material usage seen in figure 4-11.

For drop-casting, the controllability of the thickness is low, but it can be improved with a systematic study. Drop-casting also requires the high wettability of the surface which could be a limiting factor. However, surface treatments are common, and can mitigate this. The film uniformity is another difficulty. However, using nanoimprinting can remedy this as seen in figure 4-8a. Another interesting potential that this method could have is that the high pressure used in nanoimprinting could render the short ligand exchange step obsolete. This requires in-depth study in the future. If it is proven to be true, it will impact tremendously the future of PbS CQDs PV cells. Table 4-1 summarizes the common techniques used for depositing PbS CQDs film.
Table 4-1: Summary of the common techniques to deposit PbS CQDs film and their features.

<table>
<thead>
<tr>
<th>Method</th>
<th>Uniformity</th>
<th>Material Use</th>
<th>Ligand Exchange</th>
<th>Time cost</th>
</tr>
</thead>
<tbody>
<tr>
<td>Layer-by-layer spin-coating</td>
<td>Good</td>
<td>Much</td>
<td>Yes, for each layer</td>
<td>Much</td>
</tr>
<tr>
<td>Layer-by-layer dip-coating</td>
<td>Good</td>
<td>Minimal</td>
<td>Yes, for each layer</td>
<td>Most</td>
</tr>
<tr>
<td>Drop-casting</td>
<td>Poor</td>
<td>Minimal</td>
<td>Yes, but it has to be done to the whole solution</td>
<td>Minimal</td>
</tr>
<tr>
<td>Drop-casting with nanoimprinting</td>
<td>Good</td>
<td>Minimal</td>
<td>Potentially no</td>
<td>Minimal</td>
</tr>
</tbody>
</table>
Chapter 5
Conclusion and Future Work

This thesis has attempted to understand how light may interact with structure of media, including the LCCM. Reflection, refraction, and diffraction are different possible pathways that light can take when it comes from one medium to another. Once inside, radiation (FP), traveling waveguided, traveling Bloch, Mie, and plasmonic modes are the possible light trapping phenomena that can help enhancing the light absorption. However, for strong absorber like PbS QDs, some of these phenomena do not play significant roles. Especially in LCCM architecture, the domes also allow for gradual change in refractive indices that minimizes reflection and improves absorption. For the same reason, the cells with thin conformal TCO coating outperform the thicker and non-conformal ones. Another important point is the aspect ratio (AR) of the dome. Through optimization, both LCCM1 and LCCM2 agree that the lower AR value can really enhance light absorption. The design criteria stops at 1:2 AR, but further study may be needed to see if this trend continues.

Fabrication process design emphasizes the feasibility to manufacture both LCCM1 and LCCM2 structures. Using ALD to deposit the conformal coating of AZO over the nanostructure is also unique for this thesis. Additionally, the utility of both drop-casting and nanoimprinting presents a new and promising technique for depositing the QDs film. This could potentially be very cost-effective and robust way in filling the nanodomes while eliminating the time-consuming ligand-exchange step. Nevertheless, it
requires great control on solution dispensing to manage the final thickness. A systematic study can really help improving this.

For future work, poly-3-hexyl thiophene (P3HT) is a popular polymer used in organic solar cell as the main absorber and an electron donor. It has been used in conjunction with devices with PbS QDs [39] [40] to enhance performance due to its beneficial band formation. With electron affinity of 3.3 eV, it acts as an efficient electron blocker layer. I propose the fabrication and simulation of the LCCM structure device using PbS QDs and P3HT where P3HT can replace the planar part of the device. I believe this device will perform even better than the ones seen in this thesis.

It is this thesis goal to display the importance of LCCM architectures for PV applications in specific, and other optoelectronics in general. The combined strength of the light trapping LCCM architecture with strong absorber such as PbS CQDs promises the future of highly efficient and yet highly affordable PV cells that the solar electric industry yearns for.
Appendix A

HFSS input format and material data

In order to run an HFSS simulation, beside setting up the simulation parameters and drawing the structure with graphical tools, material data has to be inputted. Since this is an E-M simulation, the only material property of interest is permittivity. Particularly, the dimensionless frequency dependent relative permittivity and dielectric loss tangent are used. Absolute permittivity is a measure of how much resistance encounters when electric field is formed inside a medium. For free space, it is \( \varepsilon_0 = 8.8541878176 \times 10^{-12} \) F/m. All other materials is compared relatively to this value, so their absolute permittivities can be calculated as,

\[
\varepsilon = \varepsilon_r \varepsilon_0
\]  

[A.1]

where \( \varepsilon_r \) is called the relative permittivity or dielectric constant. For free space, it is unity.

There are many kinds of materials. If a material is linear, homogeneous, lossless, and isotropic, \( \varepsilon \) is a scalar. If the material is anisotropic, \( \varepsilon \) turns into a tensor of rank 2. The most common materials are lossy, homogeneous, and isotropic. Their \( \varepsilon \) are typically frequency dependent and complex with the real and imaginary part. This also translates that their relative permittivity \( \varepsilon_r \) is also frequency dependent and complex as shown in figure A-1 for PbS QDs in solvent. Dielectric loss tangent for HFSS can be calculated as
\[ \delta = \frac{\varepsilon_I}{\varepsilon_R} \]  

For conductive materials, it may be better to use frequency dependent conductivity instead of dielectric loss tangent which can be calculated from

\[ \sigma = \omega \varepsilon_0 \varepsilon_I \]  

where \( \omega \) is angular frequency.

Complex relative permittivity also relates closely to complex index of refraction \( \tilde{n} \) which is regarded in the following form,

\[ \tilde{n} = n + ik \]  

where \( n \) is called the refractive index indicating the phase velocity of E-M wave in the medium, and \( k \) is called extinction coefficient indicating the absorption loss of E-M wave.

Figure 5.1: Real and imaginary relative permittivity data of colloidal PbS QDs in solvent. [29]
inside the medium. The relation between complex relative permittivity and complex index of refraction is

\[ \tilde{n} = \sqrt{\varepsilon_r \mu_r} \]  \hspace{1cm} [A.5]

where \( \mu_r \) is complex relative permeability. In this particular thesis, it is assumed to be 1 for all materials because they are not ferromagnetic materials. From this, the dimensionless values of \( n, k, \varepsilon_R, \) and \( \varepsilon_I \) can be transformed by the following

\[ \varepsilon_R = n^2 - k^2 \]  \hspace{1cm} [A.6a]

\[ \varepsilon_I = 2nk \]  \hspace{1cm} [A.6b]

\[ n = \sqrt{\varepsilon_R^2 + \varepsilon_I^2 + \varepsilon_R} \]  \hspace{1cm} [A.6c]

\[ k = \sqrt{\varepsilon_R^2 + \varepsilon_I^2 - \varepsilon_R} \]  \hspace{1cm} [A.6d]
Figure A-2 shows the n and k data of AZO layer used in all simulations of the previous chapters. However, the method of deposition for this kind of AZO is not ALD. A more rigorous approach is to perform a variable angle spectroscopic ellipsometric (VASE) measurement on the AZO film grown by ALD.

![Graph showing n and k data of AZO grown by ALD](image)

Figure 5-3: n and k data of AZO grown by ALD. VASE Measurement. Courtesy of Rona Banai.

The difference in data is apparent. Other material data used are displayed in figure A-4 and A-5.
Figure 5-4: Real and imaginary relative permittivity of nanocrystalline Si (nc-Si). [30]

Figure 5-5: Real and imaginary relative permittivity data of Au.

Because Au is a metal, its real relative permittivity can become negative in certain range of wavelengths.
Figure 5-6: Real and imaginary relative permittivity data of Ag.

With these data, I have to convert them into the format compatible to HFSS. The first is the real relative permittivity as frequency-dependent data. The second is the dielectric loss tangent as frequency-dependent data.
Appendix B

Transfer Matrix Method (TMM)

If we examine Fig. B-1 and try to come up with the Transfer Matrix Method (TMM) parameters of the simple transmission line (TL),

\[
E_{1+} = E_{2+} e^{jl}, \quad E_{1-} = E_{2-} e^{-jl}
\]  

[B.1]

where \( l \) is the length of the TL. Then, the propagation matrix becomes

\[
\begin{bmatrix}
E_{1+} \\
E_{1-}
\end{bmatrix} =
\begin{bmatrix}
e^{jl} & 0 \\
0 & e^{-jl}
\end{bmatrix}
\begin{bmatrix}
E_{2+} \\
E_{2-}
\end{bmatrix}
\]  

[B.2]

The total electric and magnetic fields at the ports can be expressed in the following way,

\[
E_{i} = E_{i+} e^{-jkz} + E_{i-} e^{jkz}
\]  

[B.3]

\[
H_{i} = \frac{1}{\eta} \left[ E_{i+} e^{-jkz} - E_{i-} e^{jkz} \right]
\]  

[B.4]

where \( \eta = E/H \) is again the wave impedance that we had defined previously.

Accordingly, the following relation can be established

\[
\begin{bmatrix}
E_{i} \\
H_{i}
\end{bmatrix} =
\begin{bmatrix}
1 & 1 \\
1/\eta & -1/\eta
\end{bmatrix}
\begin{bmatrix}
E_{i+} \\
E_{i-}
\end{bmatrix}
\]  

[B.5]
Figure B-1: The TMM adaption of the simple TL.

Hence, by making use of the following equation

\[
\begin{bmatrix}
E_1 \\
H_1
\end{bmatrix} = \begin{bmatrix}
1 & 1 \\
1/\eta & -1/\eta
\end{bmatrix} \begin{bmatrix}
e^{jkl} & 0 \\
0 & e^{-jkl}
\end{bmatrix} \begin{bmatrix}
1 & 1 \\
1/\eta & -1/\eta
\end{bmatrix}^{-1} \begin{bmatrix}
E_2 \\
H_2
\end{bmatrix}
\]

[B.6]

which is equal to

\[
\begin{bmatrix}
E_1 \\
H_1
\end{bmatrix} = \begin{bmatrix}
cos kl & j\eta \sin kl \\
j\sin kl/\eta & \cos kl
\end{bmatrix} \begin{bmatrix}
E_2 \\
H_2
\end{bmatrix}, \quad \begin{bmatrix}
E_1 \\
H_1
\end{bmatrix} = \begin{bmatrix}
A & B \\
C & D
\end{bmatrix} \begin{bmatrix}
E_2 \\
H_2
\end{bmatrix}
\]

[B.7]

Actually, TMM method comes handy for the cascaded systems and it works with the ABCD parameters of the system that the microwave engineers are already accustomed with. Thus, a conversion from the ABCD to S parameters yields the total transmission and reflection of the cascaded configuration.

\[
T = S_{21} = \frac{2(R_{01}R_{02})^{1/2}}{AZ_{02} + B + CZ_{01}Z_{02} + DZ_{01}}, \quad [B.8]
\]

\[
R = S_{11} = \frac{AZ_{02} + B - CZ_{01}Z_{02} - DZ_{01}}{AZ_{02} + B + CZ_{01}Z_{02} + DZ_{01}}, \quad [B.9]
\]

where \(R_{01}\) and \(R_{02}\) are the real parts of the seen impedances at the input and output terminals, respectively, likewise \(Z_{01}\) and \(Z_{02}\) are the impedance values at the corresponding terminals. These equations are for the most general case. If we assume
that the cascaded network is inserted in between two dielectrics of the same kind, i.e.,

\[ R_{01} = R_{02} = Z_{01} = Z_{02} = Z \]

Eq. [B.8] and [B.9] turns into a simplified version.
References


Ngia Dai Nguyen
107 Avon Court
Malvern, PA 19355
Cellular: (484) (885-3870)
Email: nguyennd114@gmail.com
www.linkedin.com/pub/ngia-dai-nguyen/4b/647/a4a/

Education
2008-2014
Candidate for Ph.D. in Engineering Science and Mechanics
The Pennsylvania State University, University Park, PA (GPA: 3.40)
Expected graduation: December 2014

2004-2008
B.S. with Honors in Engineering Science and Mechanics
The Pennsylvania State University, University Park, PA (GPA: 3.44)

Research Experience
2010-2014
Research Assistant, Ph.D. Thesis Research
The Pennsylvania State University, Engineering Science and Mechanics
Description: I design, optimize, and fabricate proof-of-concept light trapping solar cell architectures with PbS quantum dots as the main absorber.
- Simulate optical phenomenon in PbS quantum dots photovoltaic cells using ANSYS HFSS
- Optimize light trapping architecture for device performance and in-depth study of electromagnetic interactions. More than 30% improvement.
- Use AMPS-1D to simulate charge carrier transport within the designed cells
- Successfully fabricate the proof-of-concept cells using techniques including UV nanoimprinting lithography, atomic layer deposition, spray-coating, sputtering, etc.
- Characterize the fabricated cell with techniques including solar simulator, UV-VIS spectroscopy, FESEM

2008-2010
Research Assistant, Master Thesis Research
The Pennsylvania State University, Engineering Science and Mechanics
Description: I investigated the effects of ultra-thin metallic layer on thermal crystallization of amorphous silicon.
- Investigated effects of ultra-thin Pt seeding layer on amorphous silicon thin films upon annealing for applications of thin film transistors, liquid crystal display, and photovoltaic
- Engaged with developing equipment such as chemical vapor deposition, atomic layer deposition, physical vapor deposition, rapid thermal annealing
- Analyzed and characterized results from equipment such as optical microscope, Raman Spectroscopy, X-Ray Diffraction (by staff), UV-VIS spectroscopy, FESEM

Teaching Experience
2010-2014
Teaching Assistant, Solar Cell Device Physics
The Pennsylvania State University
- Help students with concepts from lectures, homework, and exams
- Evaluate all homework and exams
- Organize and contribute to course materials such as figures, concepts, questions, and discussion

2007-2014
Teaching Assistant, Nanofabrication Manufacturing & Technology
Center of Nanotechnology Education and Utilization
- Demonstrate various labs of vacuum system simulation, and photolithography, microfluidics, sputtering, plasma reactive ion etching, etc.
- Train students to work with lab equipment and cleanroom procedures
- Evaluate corresponding lab reports and homework
- Participate in gauging students’ skills in communication, lab equipment, and teamwork
- Consistently achieve 9/10 ratings as a TA in terms of knowledge and communication

Professional Qualifications
Semiconductor Process: Lithography, RIE, PECVD, sputtering, evaporation, ALD, wet chemistry, oxidation furnace, nanoimprinting
Characterization: Optical microscope, ellipsometry, profilometer, AFM, FESEM, JV measurement, UV-VIS spectroscopy
Basic Programs: Microsoft Office (Word, Excel, Powerpoint)
Programming Language: Matlab, C++, Scilab
Markup Language: Latex, HTML, XHTML
CAD: ANSYS HFSS, AMPS-1D, SolidWorks

Awards and Honors
Outstanding Academic Achievement in the College of Engineering
The Lawrence E. Hallstrom Memorial Scholarship
The Thomas McKelvey Engineering Award
Outstanding Summer Research Completion
Dean’s list – Fall 2017 and Spring 2008

Presentations and Publications
“Paving the way for High-performance Quantum Dots Solar Cells” – Photovoltaic Specialist Conference (2013)

Professional Affiliations
U.S. Green Building Council, LEED Green Associate
Institute of Electrical and Electronic Engineers, Member
American Solar Engineers Society, Member

Leadership Positions
Vietnamese Student Association – President
Engineering Graduate Student Council – Engineer Representative
Penn State Chapter of American Solar Engineers Society – Social chair

Languages
Professionally fluent in American English and natively in Vietnamese

References available upon request