Optical, Structural, and Electrical Characterization of Colloidal Nanocrystalline Silicon

by

Junho Jeong

A thesis submitted in conformity with the requirements for the degree of Master of Applied Science Graduate Department of the Edward S. Rogers Sr. Electrical and Computer Engineering University of Toronto

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Master of Applied Science

The Edwards S. Rogers Sr. Department of Electrical and Computer Engineering

University of Toronto

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Abstract

In this thesis, colloidal nanocrystalline silicon (ncSi) capped with allylbenzene (AB) groups, is created using a sol-gel method. This novel material, AB-ncSi, is size separated and its optical, structural, and electrical characteristics are investigated in detail. For optical characterization, the photoluminescence (PL) peak is located for each fraction of the nanoparticles to determine its diameter. The AB-ncSi samples have diameters ranging from 2.89 nm to 7.65 nm. Ellipsometry and scanning electron microscopy (SEM) are used to estimate the film thickness and average distance between the particles, respectively, for structural characterization. No correlation was found between AB-ncSi size and film thickness however the estimated average distance between the particles decreased with decreasing diameter. Finally, for electrical characterization, conductivity of size-separated samples is measured and the temperature dependent conductance is analyzed. The results emerging from these analyses suggest that the charge transport mechanism for AB-ncSi is nearest-neighbor hopping (NNH) albeit VRH is also a potential contributor.
Acknowledgments

First of all, I would like to thank my supervisor, Professor Kherani, for his encouragement, guidance, and support throughout this journey. It has been my privilege to take part in research at the APD Labs in the Advanced Photovoltaics and Devices Research group. Furthermore, I would like to extend my gratitude to Professor Ozin for facilitating access to the Materials Chemistry Research group, where the colloidal nanocrystalline silicon samples were synthesized.

I would like to thank the many whose generous input and assistance provided from our group made this research possible. I would like to thank Dr. Davit Yeghikyan and Dr. Tome Kosteski for their technical assistance. I would like to thank John Zhu, for fruitful discussions and his guidance in the cleanroom. I would like to thank Keith Leong, for his technical input in designing the experiments. I would like to thank Joel Loh for his help with the SEM. I would like to thank Zahidur Chowdhury, Paul O’Brien, and Pratish Mahtani for answering any questions I had about the thesis.

A special thanks goes to Melanie Mastronardi for sharing her expertise on the subject of nanocrystals and the synthesis of all the nanocrystal samples. Many thanks also go to Dr. Eric Henderson and Dr. Danny Puzzo for discussions relating the chemistry of the nanocrystals.

I would like to thank Dohyoung, Issac, James, Jay, and Min for their companionship.

Finally, I would like to thank my parents, sister, and fiancée Moon, for their love, support and motivation that makes me strive toward my goals despite any obstacles.
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<th>Description</th>
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<tbody>
<tr>
<td>AB</td>
<td>Allylbenzene</td>
</tr>
<tr>
<td>AFM</td>
<td>Atomic Force Microscopy</td>
</tr>
<tr>
<td>Ag</td>
<td>Silver</td>
</tr>
<tr>
<td>AOM</td>
<td>Acoustic-Optic Modulator</td>
</tr>
<tr>
<td>Ar</td>
<td>Argon</td>
</tr>
<tr>
<td>ASCII</td>
<td>American Standard Code for Information Interchange</td>
</tr>
<tr>
<td>a-Si:H</td>
<td>Hydrogenated Amorphous Silicon</td>
</tr>
<tr>
<td>BNC</td>
<td>Bayonet Neill-Concelman</td>
</tr>
<tr>
<td>BSE</td>
<td>Back Scattered Electron</td>
</tr>
<tr>
<td>c-Si</td>
<td>Crystalline Silicon</td>
</tr>
<tr>
<td>C10</td>
<td>Decyl</td>
</tr>
<tr>
<td>CdS</td>
<td>Cadmium Sulfide</td>
</tr>
<tr>
<td>CdSe</td>
<td>Cadmium Selenide</td>
</tr>
<tr>
<td>CdTe</td>
<td>Cadmium Telluride</td>
</tr>
<tr>
<td>CH\textsubscript{3}CH\textsubscript{2}OH</td>
<td>Ethanol</td>
</tr>
<tr>
<td>CQDs</td>
<td>Colloidal Quantum Dots</td>
</tr>
<tr>
<td>Cr</td>
<td>Chromium</td>
</tr>
<tr>
<td>CVD</td>
<td>Chemical Vapor Deposition</td>
</tr>
<tr>
<td>CXA</td>
<td>Computer X-ray Analyzer</td>
</tr>
<tr>
<td>e-beam</td>
<td>Electron Beam</td>
</tr>
<tr>
<td>E-T</td>
<td>Everhart-Thornley</td>
</tr>
<tr>
<td>EDS</td>
<td>Energy Dispersive X-ray Spectroscopy</td>
</tr>
<tr>
<td>Acronym</td>
<td>Term</td>
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<tr>
<td>---------</td>
<td>------</td>
</tr>
<tr>
<td>EM</td>
<td>Electromagnetic</td>
</tr>
<tr>
<td>FET</td>
<td>Field Effect Transistor</td>
</tr>
<tr>
<td>GaAs</td>
<td>Gallium Arsenide</td>
</tr>
<tr>
<td>GPIB</td>
<td>General Purpose Interface Bus</td>
</tr>
<tr>
<td>H₂</td>
<td>Hydrogen</td>
</tr>
<tr>
<td>H₂O</td>
<td>Water</td>
</tr>
<tr>
<td>HF</td>
<td>Hydrogen Fluoride</td>
</tr>
<tr>
<td>HSiCl₃</td>
<td>Trichlorosilane</td>
</tr>
<tr>
<td>InP</td>
<td>Indium Phosphide</td>
</tr>
<tr>
<td>IV</td>
<td>Current-Voltage</td>
</tr>
<tr>
<td>LEDs</td>
<td>Light Emitting Diodes</td>
</tr>
<tr>
<td>LMS</td>
<td>Laser Micromachining System</td>
</tr>
<tr>
<td>MATLAB</td>
<td>Matrix Laboratory</td>
</tr>
<tr>
<td>N₂</td>
<td>Nitrogen</td>
</tr>
<tr>
<td>NaCl</td>
<td>Sodium Chloride</td>
</tr>
<tr>
<td>NCs</td>
<td>Nanocrystals</td>
</tr>
<tr>
<td>ncSi</td>
<td>Nanocrystalline Silicon</td>
</tr>
<tr>
<td>Nd:YVO₄</td>
<td>Neodymium-doped Yttrium Orthovanadate</td>
</tr>
<tr>
<td>Nd³⁺</td>
<td>Triply Ionized Neodymium Ions</td>
</tr>
<tr>
<td>NNH</td>
<td>Nearest-Neighbor Hopping</td>
</tr>
<tr>
<td>PbS</td>
<td>Lead Sulfide</td>
</tr>
<tr>
<td>PbSe</td>
<td>Lead Selenide</td>
</tr>
<tr>
<td>PL</td>
<td>Photoluminescence</td>
</tr>
<tr>
<td>PMT</td>
<td>Photomultiplier Tube</td>
</tr>
<tr>
<td>PV</td>
<td>Photovoltaics</td>
</tr>
<tr>
<td>Acronym</td>
<td>Description</td>
</tr>
<tr>
<td>---------</td>
<td>-------------</td>
</tr>
<tr>
<td>PVD</td>
<td>Physical Vapor Deposition</td>
</tr>
<tr>
<td>QY</td>
<td>Quantum Yield</td>
</tr>
<tr>
<td>RAE</td>
<td>Rotating Analyzer Ellipsometer</td>
</tr>
<tr>
<td>RPE</td>
<td>Rotating Polarizer Ellipsometer</td>
</tr>
<tr>
<td>SE</td>
<td>Secondary Electron</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning Electron Microscopy</td>
</tr>
<tr>
<td>SET</td>
<td>Single-Electron Transistor</td>
</tr>
<tr>
<td>Si</td>
<td>Silicon</td>
</tr>
<tr>
<td>Si(Li)</td>
<td>Lithium-drifted silicon</td>
</tr>
<tr>
<td>SiO₂</td>
<td>Silicon Oxide</td>
</tr>
<tr>
<td>SWI</td>
<td>Semiconductor Wafer, Inc.</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission Electron Microscopy</td>
</tr>
<tr>
<td>TEM₀₀</td>
<td>Transverse Electo-Magnetic</td>
</tr>
<tr>
<td>TLM</td>
<td>Transmission Line Method</td>
</tr>
<tr>
<td>TOF</td>
<td>Time Of Flight</td>
</tr>
<tr>
<td>VI</td>
<td>Virtual Instrument</td>
</tr>
</tbody>
</table>
## List of Symbols

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>A, B, and C</td>
<td>Fitting Parameters for Ellipsometry</td>
</tr>
<tr>
<td>$A_{EP}$</td>
<td>Constant relating Electron-Phonon interaction</td>
</tr>
<tr>
<td>$A_s$</td>
<td>Surface area which charge passes through</td>
</tr>
<tr>
<td>$b$</td>
<td>Radius of the Particle</td>
</tr>
<tr>
<td>$c$</td>
<td>Speed of Light</td>
</tr>
<tr>
<td>$C_0$</td>
<td>Capacitance of the individual particle in its surrounding</td>
</tr>
<tr>
<td>$d$</td>
<td>Diameter of ncSi</td>
</tr>
<tr>
<td>$E_0$</td>
<td>Bandgap of Bulk Silicon</td>
</tr>
<tr>
<td>$E_{CB}$</td>
<td>Coulomb Blockade Energy</td>
</tr>
<tr>
<td>$E_g$</td>
<td>Energy of Photon</td>
</tr>
<tr>
<td>$E_{PL}$</td>
<td>Energy of PL Light</td>
</tr>
<tr>
<td>$f$</td>
<td>Frequency of the rotating element</td>
</tr>
<tr>
<td>$G$</td>
<td>Exponential Decay of Local Tunneling</td>
</tr>
<tr>
<td>$G_0$</td>
<td>Constant that accounts for charge carrier concentration and local particle environment around the centre</td>
</tr>
<tr>
<td>$h$</td>
<td>Plank’s Constant</td>
</tr>
<tr>
<td>$k_B$</td>
<td>Boltzmann constant</td>
</tr>
<tr>
<td>$\ell$</td>
<td>Gap Distance</td>
</tr>
<tr>
<td>$L_T$</td>
<td>Transfer Length</td>
</tr>
<tr>
<td>$M^2$</td>
<td>Beam parameter product to ideal Gaussian beam ratio</td>
</tr>
<tr>
<td>$P$</td>
<td>Polarizer azimuth in the RAE/RPE</td>
</tr>
<tr>
<td>$q$</td>
<td>Elementary Charge, $1.602 \times 10^{-19}$ C</td>
</tr>
</tbody>
</table>
$r$  Core-to-core Length of the Particles

$R$  Electrical Resistance (V/I)

$r'$  inter-(surface)-distance

$R^2$  Coefficient of Determination

$r_s$ and $r_p$  Normalized Reflection Ratio of s- and p- polarized components

$R_{SH}$  Sheet resistance not covered by the contacts

$R_{SK}$  Sheet resistance of the semiconductor under the contacts

$R_T$  Total Resistance between adjacent metal pads

$S_0$  Ground Singlet Level

$S_n$  Excited Singlet Level

$T_0$  Temperature constant

$T_1, T_2, ...$  Triplet Levels

$\chi$  Tunneling Decay Length

$\alpha$ and $\beta$  Parameters measured from the RAE/RPE

$\alpha_r$  Reciprocal of the radius of the states

$\gamma$  Factor that varies in the interval $\frac{1}{4} < \gamma < 1$

$\varepsilon_3$  Energy required to jump to the next state

$\lambda$  Wavelength of Light

$\nu_{ph}$  Constant relating the strength of interaction with phonons

$\rho_c$  Specific Contact Resistivity

$\sigma$  Conductivity

$\Psi$ and $\Delta$  Stokes Parameters
1 Introduction

1.1 Motivation

The motivation of this research is to enable the application of colloidal nanocrystalline silicon (ncSi) based optoelectronic devices, such as photovoltaics, light emitting diodes (LEDs), and charge coupled devices (CCD). The field of semiconductor nanocrystals (nc), including colloidal quantum dots (CQDs), has gained much attention over the past decade because they display unique properties (chemical, electrical, optical, etc.) when compared to their bulk counterparts. II-VI and III-V compounds such as CdSe, CdS, InP, GaAs, and PbSe have already been investigated extensively. There are many reports that describe the synthesis processes and develop an understanding of the quantum confinement effects in these direct bandgap semiconductors owing to the fact that these materials can be prepared with well-defined size, shape, and surface chemistry [1]. With this knowledge of these materials, a number of applications have been demonstrated such as single-electron transistors (SET) [2], light emitting diodes (LED) [3], photovoltaics (PV) [4], and fluorescent labeling [5]. However, these compound semiconductors are found to be toxic in nature.

Silicon (Si), on the other hand, is a bio-inert semiconductor and non-toxic [6]. Hence, researchers have begun to investigate nanocrystalline silicon (ncSi) given its unique chemical and optical characteristics. When the length scale of silicon is reduced to sub-100 nm, the bandgap energy increases and the pseudo-continuous bands become discrete energy levels with direct-like bandgap semiconductor behavior. As the particle dimensions are further decreased to the Bohr exciton radius, 5 nm in the case with silicon, quantum confinement effects appear shifting the photoluminescent response into the visible light spectrum as shown in Figure 1.1 [7]. There has been minimal investigation on the electrical properties of ncSi. Investigation of the charge transport mechanism is considered to be one of the most fundamental studies required to best guide future application studies. Further, it will serve as a basis for subsequent research on key electrical parameters such as carrier mobility.
1.2 Colloidal Nanocrystalline Silicon

Nanocrystalline silicon (ncSi) created from chemical vapor deposition (CVD) has been around since the mid 80’s and has traditionally been referred to as microcrystalline silicon [8]. The ncSi is typically embedded in a thin film of SiO₂ [8] or hydrogenated amorphous silicon (a-Si:H) [9]. This approach has posed limitations on the control over particle size and surface chemistry given that once the ncSi film was created the ncSi particles were fixed in the film. There has been significant research into the electrical [10] and optical [9] properties of this type of ncSi but little with colloidal ncSi. Colloidal ncSi first sparked interest in the early 90’s when Brus et al. published there studies on ethylene glycol ncSi colloids in Science [11].

The significance of colloidal ncSi in this study is that it is synthesized by a sol-gel method developed by Henderson et al [12-13]. The simplified version of the synthesis procedure is as follows. First, the sol-gel polymers are synthesized by rapidly adding deionized water into trichlorosilane (HSiCl₃) at 0 °C under an Argon (Ar) atmosphere. The resulting polymers are heat-treated at 1100 °C in a slightly reducing atmosphere of 5%H₂/95%Ar for 1 hour. This produces silicon nanocrystals embedded in a matrix of silicon oxides. This mixture is grounded
into fine powder and the salt is removed by washing it repeatedly. The resulting powder is then added to an etching solution which consists of a 1:1:1 mixture of 49% HF(aq) : H₂O : CH₃CH₂OH. The resulting freestanding hydrophobic, hydride-terminated silicon nanocrystals are extracted using hexanes. In this study, which utilizes this synthesis technique, our nanocrystals are capped with allylbenzene (AB) groups instead of decyl (C₁₀) groups by hydrosilylation. The end product is a solution of extremely stable orange colloidal suspensions of AB-ncSi in toluene [14].

The AB-ncSi samples used in this study are shown below in Figure 1.2.

![Figure 1.2: Size separated AB-ncSi samples used in this study](image)

### 1.3 Thesis Objective & Overview

In this research the optical, structural, and electrical characteristics of size separated colloidal AB-ncSi samples are thoroughly investigated. For the optical characterization, photoluminescence (PL) of the samples are investigated to estimate the diameter of the AB-ncSi samples. Using ellipsometry and scanning electron microscopy (SEM), the structural properties are studied. Ellipsometry is used to measure the thickness of the AB-ncSi thin films and SEM
images are used to observe the average distance between the AB-ncSi particles in the film. Finally for electrical characterization, size and temperature dependent conductivity values are measured using the transmission line method (TLM) test structure. This structure is selected to measure the resistance of the film while factoring out the contact resistance between the film and the contact pads. Each characterization is deemed to correspond to a piece of the puzzle comprising this overall study such that when all the results are brought together we expect to be able to determine the charge transport mechanism in AB-ncSi.

The thesis is structured as follows: (with each chapter consisting of the optical, structural, and electrical subsections) Chapter 2 presents all the theory involved in the thesis. Chapter 3 describes the sample preparation and experimental setup for the characterizations. Chapter 4 contains all the significant data obtained from the various experiments. Chapter 5 undertakes key discussions and analyses for each of the experiments and draws the big picture by connecting the pieces together. Chapter 6 concludes with a summary of key results emerging from each characterization and thus the determination of the charge transport mechanism, and discusses the challenges and the potential future direction of this study.
2 Theory

2.1 Photoluminescence (PL)

Photoluminescence (PL), as implied by the word, is emission of optical radiation resulting from non-thermal excitation of energy states of atoms with photons or light. More specifically, PL involves creating an electron-hole pair by the absorption of an energetic incident electromagnetic wave, and subsequently recombining the electron-hole pair radiatively that results in photon emission. PL has high-energy resolution that makes it a reliable measurement tool in applications such as identifying impurities in semiconductors [15].

Both radiative transitions and non-radiative transitions take place in PL. These transitions and its principal pathways are shown below in the schematic energy-level diagram Figure 2.1. The radiative transitions could be further sub-divided into fluorescence and phosphorescence. This depends on whether the transition is a spin-allowed transition between equal multiplicity (singlet to singlet or triplet to triplet) or a spin-forbidden transition between two states with different multiplicity (triplet to singlet) [16].

![Figure 2.1: Principal transition pathways of PL. Radiative transition (---) and Nonradiative transition (-----). S₀, S₁, ...: singlet levels; T₁, T₂, ...: triplet levels. A: absorption, IC: internal conversion, IS: intersystem crossing, F: fluorescence, P: phosphorescence [16]
When a photon strikes the molecule, the energy of the photon is absorbed and the molecule’s electron is raised from its ground state ($S_0$) to an excited singlet state ($S_n$). The excited electron then selects the de-excitation pathway which minimizes the lifetime of the excited state. In most cases, the excited electron first quickly drops to the lowest levels ($S_1$ or $T_1$) through a nonradiative process. The excited electron further jumps down states through radiative transitions, most commonly, fluorescence ($S_1$ to $S_0$) and phosphorescence ($T_1$ to $S_0$). [16]

For semiconductors, the energy gap between $S_0$ and $S_1$ is considered to be its bandgap energy. This means one is able to calculate the bandgap energy of a semiconductor by measuring the wavelength of the photoluminescence from the following equation,

$$E_g = hf = h \frac{c}{\lambda}$$

where $h$ is the Plank’s constant, $c$ is the speed of light, and $\lambda$ is the wavelength of the photon detected from photoluminescence.

The quantum yield (QY) of a PL material is determined by the following equation [16],

$$QY = \frac{\text{number of photons emitted}}{\text{number of photons absorbed}}$$

It is a representation of how efficiently energy from the excitation light source is transferred to the PL for a particular sample. QY is also another way of quantitatively expressing the intensity of the PL for the purpose of comparing with other samples.

For nanoparticles, quantum confinement plays a significant role in the PL spectrum. Consequently, using the PL data the diameter of the nanoparticles could be calculated. Ledoux et al. [17] empirically formulated an equation to use the photoluminescence data to determine the diameter of the ncSi. The equation is formulated using the data from atomic force microscopy (AFM) and PL measurements and is given as,

$$E_{PL} = E_0 + \frac{3.73}{d^{1.39}} + \frac{0.881}{d} - 0.245$$
where $E_{PL}$ is measured in eV, $E_0$ is the bandgap of bulk silicon ($E_0=1.12$ eV), and $d$ is the diameter of the ncSi measured in nanometers. As observed in Equation 3, the PL energy of ncSi is blueshifted with respect to the bandgap of bulk silicon from the infrared range to the visible range, which is due to quantum size effects. The bandgap widens as a result of quantum confinement that comes into effect when crystallites become smaller than 5 nm.

### 2.2 Ellipsometry

The ellipsometric technique is optically powerful and versatile. It can be used to successfully measure thin films with thicknesses of up to 5 µm and at the same time the optical properties of the film (refractive index and extinction coefficient) can be obtained. Another advantage of this technique is that it is non-destructive, not involving any contact with the film, and this is why ellipsometry is widely used in electronics and in general with semiconductor and metallic substrates [18].

The basic principle of ellipsometry is measuring the change of polarization of light upon reflection of the material of interest. The exact change in the polarization is determined by the samples’ thickness, and complex refractive index or dielectric function tensor. However there is a very important assumption that must be made in order to correctly interpret the measurements made. The sample is considered to be composed of small number of discrete, well-defined layers that are optically homogeneous and isotropic. If these assumptions are violated, this invalidates the standard ellipsometric modeling procedure and more advanced variants of techniques must be applied [19].

![Figure 2.2: Schematic setup of an ellipsometer. Note that the light source and detector are at the same angle with respect to the normal plane.](image)
The schematic setup of an ellipsometry experiment is shown above in Figure 2.2. Electromagnetic (EM) radiation is emitted from the light source and linearly polarized by the polarizer. This EM radiation then passes through an optional compensator (retarder or quarter wave plate) and reflects off the surface of the sample. The reflected EM radiation then passes through an optional compensator, a second polarizer, which is called an analyzer, and enters into the detector. In some ellipsometers there is a phase-modulator in the path of the incident light instead of the compensator. The incident and reflected light span the plane of incidence. EM radiation that is polarized parallel to this plane is called p-polarized and when polarized perpendicular to this plane it is called s-polarized [19].

In ellipsometry, we measure two of the four Stokes parameters, which are conventionally denoted by $\Psi$ and $\Delta$. The EM radiation incident on the sample can be decomposed into the s- and p-polarized components. The s-component is oscillating perpendicular to the plane of incidence and parallel to the sample surface while the p-component is oscillating parallel to the plane on incidence. The amplitude of the s- and p-components after reflection are normalized with respect to their initial values and are denoted $r_s$ and $r_p$, respectively. The ellipsometer measures the ratio of $r_s$ and $r_p$ which is in relation with $\Psi$ and $\Delta$ as follows,

$$p = \frac{r_p}{r_s} = \tan(\Psi)e^{i\Delta}$$

(4)

As shown from the above equation, $\tan(\Psi)$ is the amplitude ratio upon reflection, and $\Delta$ is the phase shift difference. Because the ellipsometer only measures the ratio of $\Psi$ and $\Delta$ rather than the absolute values, ellipsometry is very robust, accurate, and reproducible. For example, there is little concern about light scattering and fluctuations and requires no standard sample or reference beam [19].

The ellipsometer only measures the ratio of $\Psi$ and $\Delta$, therefore it cannot be converted directly into optical constants of the sample. The analysis requires creating a model that well describes the sample that is measured. Direct inversion of $\Psi$ and $\Delta$ is only possible in cases of isotropic, homogeneous, and infinitely thick films. In all of the other cases a layer model must be established, which considers the complex refractive index and thickness parameters of all individual layers of the sample in the correct layer sequence. Then using an iterative procedure,
such as the least-squares minimization, unknown optical constants and/or thickness parameters are varied, and values of $\Psi$ and $\Delta$ are calculated using the Fresnel Equations. The calculated $\Psi$ and $\Delta$ values that best match the experimental data provides the optical constants and thickness parameters of the sample [19].

One of the most commonly used ellipsometry measurement configuration is the rotating analyzer ellipsometer (RAE) or the rotating polarizer ellipsometer (RPE). It is the first photometric ellipsometer and functions by measuring the 1st and 2nd harmonics in the reflected light. The time dependent signal collected here can be stated as follows,

$$I(t) = I_0 \{1 + \alpha \cos(2ft) + \beta \sin(2ft)\}$$

(6)

where $\alpha$ and $\beta$ are parameters measured from the RAE/RPE, and $f$ is the frequency of the rotating element. Furthermore, the relationship between the terms $\alpha$ and $\beta$, and $\Psi$ and $\Delta$ can be expressed as,

$$\tan \Psi = \tan P \left(\frac{1+\alpha}{1-\alpha}\right)^{1/2}$$

(7)

$$\cos \Delta = \frac{\beta}{(1-\alpha^2)^{1/2}}$$

(8)

where $P$ is the polarizer azimuth in the RAE/RPE.

### 2.3 Scanning Electron Microscopy (SEM)

As the name implies, the SEM is a microscope that uses electrons rather than light to form an image. The SEM has a large depth of field that allows a large surface area of the sample to be focused at the same time. In addition, it produces high-resolution images, which means that closely spaced features can be examined at high magnification [20].

The basic principles of SEM is scanning through the sample while firing a beam of electrons that interact with the atoms that make up the sample, producing signals that contain information about the sample's surface topography, composition and other properties such as electrical conductivity. More specifically, these signals are secondary electrons (SE), back-scattered
electrons (BSE), characteristic X-rays, specimen current, transmitted electrons, etc. In most SEMs, SE detectors and BSE detectors are common. Depending on what the customer requires the manufacturer usually attaches additional signal detectors on the SEM [20].

![Schematic drawing of the electron beam of the SEM showing the electron gun, lenses, the deflection system, the electron detector, and the user display](image)

**Figure 2.3**: Schematic drawing of the electron beam of the SEM showing the electron gun, lenses, the deflection system, the electron detector, and the user display [20]

The schematic drawing of the SEM is shown above in **Figure 2.3**. The vacuum pumps must pump the chamber such that it is at high vacuum conditions, typically about $10^{-4}$ Pa (roughly one billionth of atmospheric pressure). The electron gun generates electrons and accelerates them to energies in the range of 0.1-30 keV. Usually this initial beam of electrons has a large spot size and therefore must be de-magnified by a series of electron lenses. For most SEMs, the electron beam at the sample has a spot size less than 10 nm that contains sufficient probe current to form an acceptable image [20].

The SEM scans a sample such that it creates an image point by point. The deflection system (Scan Coils in **Figure 2.3**) causes the beam to move to a series of discrete locations along a line
and then along another line below the first, and so on, until a rectangular 'raster' is generated on the specimen. Concurrently, the same scan generator creates a similar raster on the viewing screen [20].

The contrast in an image is created from the difference in electron beam-specimen interaction from point to point. As the electron beam impinges on the specimen there are a variety of signals generated and one could choose a certain signal to create an image. The electronics of the detector system converts the signals to point-by-point intensity changes on the viewing screen and produces an image. As mentioned earlier, SE and BSE are the two signals most often used to create SEM images. The standard Everhart-Thornley (E-T) detector collects both SE and BSE as shown in Figure 2.4.

![Figure 2.4: Signals from SE and BSE collected by the E-T detector [20]](image)

When a positive voltage is applied to the collector screen, which is placed in front of the detector, both SE and BSE signals are collected. However, when a negative voltage is applied, pure BSE signals are captured because the low energy SEs are repelled. The electrons captured by the scintillator create pulses of light which are converted into electronic signals by the photomultiplier tube (PMT). This signal is further amplified and created into an image seen on the display [20].
Using SEM it is possible to perform energy dispersive X-ray spectroscopy (EDS) with an appropriate detector in the system. EDS is an analytical technique used for elemental analysis or chemical characterization of the specimen. X-ray is another signal produced from the specimen when the electron-beam of the SEM impinges on it. The X-ray photons enter the detector, which is made of lithium-drifted silicon (Si(Li)), and creates a photoelectron. The photoelectron is then converted into a voltage pulse by a preamplifier and then the computer x-ray analyzer (CXA) collects the data to create a histogram of intensity by voltage. The schematics diagram of the EDS is shown in Figure 2.5.

![Figure 2.5: Schematic representation of an EDS and associated electronics [20]](image)

### 2.4 Hopping Conduction Mechanisms

Quantum tunneling is a quantum mechanical phenomenon where a particle, given its property of wave-particle duality, tunnels through a potential barrier with a thickness of around 1-3 nm. In general, this process is thermally activated. Charge particles can tunnel between two localized states and this is known as local tunneling. The exponential decay of local tunneling is given by [21],

$$G = G_0 \exp[-X(r - 2b)]$$

(9)
where $G_0$ is the constant that accounts for charge carrier concentration and local particle environment around the centre, $\mathcal{X}$ is the tunneling decay length of the corresponding charge carrier, $r$ is the core-to-core length of the particles, and $b$ is radius of the particle. The term $(r - 2b)$ is also known as the inter-(surface)-distance $(r')$ and is depicted as given in Figure 2.6.

![Figure 2.6: Schematic diagram of inter-(surface)-distance, $r' = r - 2b$](image)

As an electron is transferred from one neutral particle to an adjacent neutral particle, the first particle becomes one elementary charge ($q$) negative and the second one positive. This process is called “electron-hole” transfer by tunneling and the energy required is known as the Coulomb blockade energy ($E_{CB}$) and is given by [22],

$$E_{CB} = q^2 / C_0$$  

where $C_0$ is the capacitance of the individual particle in its surrounding.

Hopping conduction mechanism is defined when a series of such tunneling transpires to yield a global conduction. This only happens if wave functions are localized. Each time the electron moves, it tunnels (or hops) from one localized state to another, whose wave function overlaps with the first state. The electron must exchange energy with a phonon each time it moves since the two states have quantized energies. The probability of hopping is in the form [23],

$$P \sim v_{ph} \exp \left(-2ar - \frac{E_3}{k_BT}\right)$$
where $\nu_{ph}$ depends on the strength of the interaction with phonons, $\alpha$ is the reciprocal of the radius of the states, and $\varepsilon_3$ is the energy required to jump to the next state. Furthermore, calculations from **Equation 11** lead to the formula for conductivity ($\sigma$) given as [23],

$$
\sigma = A_{EP} \exp \left[ - \left( \frac{T_0}{T} \right)^{\gamma} \right]
$$

where $A_{EP}$ is a constant that depends on the electron-phonon interaction, $T_0$ is a constant, $T$ is the temperature, and $\gamma$ is a factor that varies in the interval $\frac{1}{4} < \gamma < 1$. At sufficiently low temperatures and neglecting the interactions between the electrons, $\gamma$ in **Equation 12** is equal to $\frac{1}{4}$ and the hopping conduction mechanism is known as variable range hopping (VRH). In VRH, the preferred optimized conduction path is determined by the competing requirements, minimum $\varepsilon_3$ and minimum tunneling distance ($= r$). This concept is illustrated in **Figure 2.7**. Additionally, when taking into account the electrostatic interaction involved, or the energy to overcome $E_{CB}$, the term $\gamma$ is increased to $\frac{1}{2}$.

![Figure 2.7: Schematic diagram of hopping condition mechanism.](image)

Another commonly known hopping conduction mechanism is the nearest-neighbor hopping (NNH). This usually takes place at higher temperatures or for small $\varepsilon_3$, when the interparticle tunneling route prefers the nearest neighbors that correspond to the lowest average tunneling resistance that enables continuous hopping. For NNH, $\gamma$ is equal to 1. Therefore, by plotting the natural log of resistivity against $T^{-1/4}$ and $T^{-1}$ of a material of interest then comparing its linear fit, one can predict which hopping mechanism takes place in the material.
2.5 Transmission Line Model (TLM)

The transmission line model (TLM), or transfer length method, is the most commonly used method for measuring contact and channel resistances, using a test structure that resembles a transmission line for electricity. It involves fabrication of a series of rectangular metal pads on a strip of semiconductor, which is the material of interest. The metal pads are distributed by varying the gap distances and the thin strip of semiconductor is electrically isolated from the surrounding area. An example of a TLM pattern is shown in Figure 2.8.

![Figure 2.8: TLM test structure](image)

**Figure 2.8**: Typical TLM test structure, showing rectangular metal contacts (grey) at varied gap distances and the rectangular semiconductor strip (orange) that the metal contacts are fabricated on. Note that the semiconductor strip must be electrically isolated close to the edge of the metal pads from the surrounding region (white). Z represents the width of metal pads (grey) and W represents the width of the semiconductor strip (orange).

As seen in Figure 2.8, the TLM usually utilizes a four-point probe measurement technique. Four-point probe measurements prevent errors caused by parasitic resistance between probes and contacts. One pair of probes is placed on the two most outer contacts supplying the current, and the second pair of probes measures the voltage between adjacent contacts. Assuming that the metal contact’s resistivity is negligible, and the semiconductor strip’s boundary is very close to the edge of the contacts, the total resistance \( R_T \) between adjacent pads can be represented as [24],

\[
R_T = \frac{2R_{SK}kT}{W} + \frac{R_{SH}\ell}{W}
\] (13)
where $R_{SK}$ is the sheet resistance of the semiconductor under the contacts, $R_{SH}$ is the semiconductor sheet resistance not covered by the contacts, $L_T$ is the transfer length, and $\ell$ is the distance between the gap. Transfer length ($L_T$) is the characteristic length extending from the edge of contacts, inside which the majority of the current transfer takes place. The transfer length can be represented as [24],

$$L_T = \sqrt{\rho_c / R_{SK}}$$  \hspace{1cm} (14)

where $\rho_c$ is the specific contact resistivity. Figure 2.9 shows how the electrical current crowds into a region of length $L_T$ as the charge is transferred from the semiconductor into the metal contacts.

![Diagram](image)

**Figure 2.9:** Crowding of current into a length of $L_T$ from the edge of a metal contact. At $L_T$ from the contact edge, the voltage drops off to $1/e$ of its initial value at the edge. A very small fraction of current transfers into the metal contact outside this transfer length region [25].

A linear plot of $R_T$ as a function of gap distance ($\ell$) allows the extraction of contact resistance $R_C$ (y-intercept), semiconductor sheet resistance $R_{SH}$ (slope), and transfer length $L_T$ (x-intercept). If no intermixing or chemical reaction occurs between contacting metal and semiconductor, i.e. $R_{SK}$
= R_{SH}, the transfer length is simply half of L_T. Such plot will look something like Figure 2.10.

**Figure 2.10:** General plot of $R_T$ as a function of gap distance $\ell$ for TLM test structure [25].
3 Experiments

3.1 Integrating Sphere Method (PL)

3.1.1 Introduction

The PL data is measured using the setup in Prof. Ozin’s lab which uses the integrating sphere method. In this method the sample is placed inside a hollow sphere that has its inner surface coated with reflecting material. For an ideal integrating sphere, regardless of the angle of the beam of light entering the sphere, the light is redistributed isotropically over the sphere interior surface [26]. The schematic of the integrating sphere is given in Figure 3.1.

Figure 3.1: Schematic diagram of integrating sphere with the incident light directed to the sample that is in the middle of the sphere [26]
3.1.2 Apparatus

The integrating sphere used in this experiment is custom made from Gighertz Optik, the light source is a 365 nm LED from Thorlabs (M365L2), the optical fiber that collects the light is 1 mm in diameter from Ocean Optics, and this light is fed to the spectrometer from Ocean Optics (Maya2000). The spectrometer is then connected to the computer making the data analysis convenient. The actual setup with all the components measured above is given in Figure 3.2.

Figure 3.2: Apparatus for integrating sphere used in the experiment

3.1.3 Sample Preparation

The PL measurement of AB-ncSi is made in solution form before it is drop casted into a thin film. Experiments are done in solution because we were uncertain if the thin film of AB-ncSi would be able to absorb the 365 nm light. This is because there is insufficient understanding of the material, specifically the absorption coefficient, and we are unable to create thick films in the micron range.
All the AB-ncSi samples (P1 to P19) are all individually poured into separate test tubes and measured one at a time. There is no special treatment done to the samples, just directly distributed from the main batch of samples. For the measurement, the test tube with the cap attached is placed in the sample holder and then lowered into the integrating sphere. The sample holder is then screwed tightly on to the integrating sphere. During this process, one must be careful such that the test tube does not fall off the sample holder. The test tube with the cap, on the sample holder is shown in Figure 3.3.

Figure 3.3: Test tube and sample holder for PL experiment

3.1.4 Measurement using LabVIEW

Once the sample holder is secure in the integrating sphere, the 365 nm LED light is turned on, and the virtual instrument (VI) programed in LabVIEW is started. The user interface of this VI is given in Figure 3.4.
Figure 3.4: User interface of LabVIEW virtual instrument (VI) for PL measurements

This VI not only takes the data from the spectrometer and graphically displays the data but also performs the absolute quantum yield calculations, which will be further explained in the Analysis/Discussion section. The PL data is stored as an ASCII (American Standard Code for Information Interchange) text file, where the first column is the wavelength in nm and the second is the intensity with arbitrary units.

There is a limited spectral range over which intensity measurements can be made. This limit is set by the Maya2000 spectrometer. It has a spectral range from approximately 300 nm to around 1100 nm.

3.1.5 Challenges

There is a limited spectral range over which intensity measurements can be made. This limit is set by the Maya2000 spectrometer. It has a spectral range from approximately 300 nm to around
1100 nm. Due to this limitation, it was difficult to measure the PL data for P15, P17, and P19 samples.

### 3.2 Ellipsometer SOPRA GE-5E

#### 3.2.1 Introduction

The model name of the ellipsometer used in this study is SOPRA GES-5E. The actual model is shown in Figure 3.5.

![SOPRA GES-5E used in the experiment](image)

**Figure 3.5:** SOPRA GES-5E used in the experiment

The SOPRA GES-5E is interfaced with the software WinSE, which is shown below in Figure 3.6, to take measurements. Here one could adjust the angle of the incident beam, analyzer angle, integration time, position of the stage, etc. A critical step before taking actual measurements is checking the signal. At this step, the height of the stage is adjusted to get the optimal signal with maximum counts and a symmetry value in the range of ±2%.
Data collected from WinSE is then analyzed using the program Winelli II (shown below in Figure 3.7). Using this software, the film properties such as thickness, refractive index, etc. could be determined. First the data is transferred into a spreadsheet and a structure, which is to simulate the sample, is created. It is important that the user has an idea of what the film is consist of and what properties the film(s) have. The user could select different layers of this structure and also define its properties. Then the software characterizes the film using either an n&k model or a dispersion model, which includes laws such as Cauchy, Tauc Lorentz, etc. After the structure is complete, a data fit for the defined structure is carried out using a regression process. Through a number of iterations the program alters the film properties that the user selects to be adjustable (in our case the film thickness) to find the best fit. The fit of the data is represented by the coefficient of determination, the $R^2$ value.
3.2.2 Sample Preparation

To minimize the time required preparing for the experiments, one set of samples are fabricated for ellipsometry measurements and conductivity measurements. From a range of size separated mono-disperse AB-ncSi samples (AB73- P1, P3, P5, P7, P9, P11, P13, P15, P17, P19), as shown in Figure 1.2 (in Section 1.2) the PL graph was well-defined with only samples P5, P7, P9, P11, and P13. Only these samples were further investigated by creating test samples with them. The substrate for the test sample is fused silica, which is purchased from Semiconductor Wafer, Inc. (SWI) has a thickness of 1 mm, a surface roughness less than 15 Å, and a resistivity of $7 \times 10^{17}$ Ω-m. On to this fused silica substrate metal is deposited using electron beam deposition of chromium (Cr-5 nm) and then silver (Ag-1 um). The details describing the metal contacts are related to the characterization of electrical properties, and will be further discussed later in
**Section 3.5.** Once the metallization is complete, AB-ncSi samples are drop casted on to the fused silica approximately at a 10 ° angle. Then the test sample is post-treated on a hotplate at around 110 °C under purging nitrogen (N\(^2\)) gas for 2 hours. This post-treatment is intended to evaporate the solvent, toluene (boiling point = 110.6 °C), of the AB-ncSi film. The schematic and the actual test sample are shown below in **Figure 3.8.** Because the thin film of AB-ncSi does appear to be transparent, in the schematic the AB-ncSi film is illustrated in red.

![Figure 3.8](image-url)  
**Figure 3.8:** (a) Top and (b) side view of schematic (*not to scale), and (c) the actual test sample

### 3.2.3 Measuring Film Thickness using SE

An additional step required in the signal checking process is adjusting the spot size of the incident light. Turning the pin located above the tip of the light source does this. As indicated in **Figure 3.8 (a)**, the bottom section of the test sample is where the ellipsometry measurements will take place. The spot size of the incident light is fine-tuned to approximately 3 mm in diameter to ensure that the light is exposed only to AB-ncSi film and not on the metal pads.

The recipe used for all the measurements is shown below in **Figure 3.9.** The incident angle is chosen to be 55.5 ° because this is the Brewster's angle for fused silica. Other than this, the recipe follows the standard recipe for common ellipsometry measurements.
3.2.4 Challenges

The ncSi film under investigation is not a solid uniform film. Furthermore, the variation in surface roughness at different locations of the film makes it difficult to measure the exact film thickness. This is observed when comparing ellipsometry measurements made at different locations on the same film.

3.3 Hitachi S-5200

3.3.1 Introduction
The model name of the SEM used in this study is Hitachi S-5200. The actual model is shown in Figure 3.10.

![Figure 3.10: Hitachi S-5200 used in the experiment](image)

The Hitachi S-5200 is capable of looking at the topography or the cross-section of the sample. Depending on which option is chosen, the corresponding sample holder must be used. This sample folder would fit inside the slot at the tip of the probe, as shown in Figure 3.11. Depending on whether performing topography or cross-section SEM, the corresponding sample holder must be chosen. For both cases the sample size cannot exceed approximately 5 mm x 7 mm x 1 mm. To secure the sample in place carbon paste or double-sided carbon tape is used. Carbon based adhesive is used to ensure no charge is built up on the sample.

![Figure 3.11: Probe used for both topography and cross-section SEM](image)

### 3.3.2 Sample Preparation

If the sample for SEM is not conductive enough, the sample can experience charge build up because of the electron beam. This makes it difficult to visualize the sample using the SEM. To
resolve this problem, a thin layer of carbon could be coated on to the sample. Carbon is commonly used because it has a low atomic number making it electron transparent and is a good conductor (another commonly used material is gold).

The initially plan was to use the fused silica sample and have it coated with carbon to eliminate charge build up. However, the fused silica sample is actually too thick (>1 mm) and scribing it into the required dimensions, 5 mm x 7 mm, is impossible. Therefore, a new set of samples was created using a substrate that is conductive and easy to scribe. The substrate chosen is highly doped (antimony) crystalline silicon (c-Si) from Okmetic, which has a resistivity value in the range of 0.005 Ω-cm to 0.025 Ω-cm, and thickness of (200 ± 25) µm. The entire wafer is metalized with 1 µm of Ag using electron beam sputtering, AB-ncSi directly deposited on c-Si will be very challenging to observe on the SEM since they have the same atomic number, Z. This sample wafer is then scribed into squares with 2 cm sides. The samples chosen for SEM are AB-ncSi P1, P5, P9, and P13. P1 is included in the list since we wanted to see large contrasts in the AB-ncSi particle size. Using the same method mentioned in Section 3.2.2, AB-ncSi is drop casted onto the square sample. The square piece is spilt in half, and only one half is post-treated on a hotplate at around 110 °C under purging N₂ for 2 hours. The other half is left untreated for comparison. Each of the half square samples is further scribed to dimensions roughly 5 mm x 7 mm, as shown in Figure 3.12. One more sample is scribed with no AB-ncSi on it to see just the Ag on the c-Si wafer.

![Figure 3.12: SEM sample, AB-ncSi P1 drop casted on 1 µm Ag deposited on 200 µm c-Si](image)

### 3.3.3 Taking Measurements

Once the sample preparation is complete and secured to the probe, it is inserted into the chamber. A software interface for taking measurements on the Hitachi S-5200 is displayed in Figure 3.13. Here the various parameters of the electron beam, stage, aperture, etc. is controlled.
After adjusting the voltage and current value to a desired value, the electron beam is turned on. The voltage and current values are set to 1.0 kV to 5.0 kV and 25 µA to 40 µA, respectively. Once the electron beam is on, it has to be properly aligned. Then at low magnification the sample is located and a significant feature is selected. This feature will be used as a reference point when moving onto the high magnification. At high magnification, a focusing process takes place, then the x- and y-stigmatism is adjusted. This process is the most delicate step in taking SEM images and requires patience. After all the required preliminary steps are taken to get a clear image using the SEM, the sample is navigated to find regions of significance, alter the magnification, adjust the brightness and contrast, and then capture images onto the computer.

3.3.4 Challenges

Sample preparation is the most challenging component in SEM measurements. It is difficult to create a close-packed ncSi film using the drop-cast technique and even if such film is created the
orientation of the ncSi particles become dispersed after post-treatment (annealing at 110 °C under purging N₂).

The ncSi film is not very conductive and supports charge build up on the surface causing difficulties when examining the samples under the SEM.

3.4 Laser Micromachining System (LMS)

3.4.1 Introduction

The laser system used for micromachining is the Spectra Physics BL6S 106Q, diode pumped, Q-switched, Nd:YVO₄ laser, emitting at 1064 nm with an option of frequency doubling. The laser operates by an end pumped resonator providing a Gaussian TEM₀₀ mode output. The resonator is pumped by 40 W diode bar which is fiber coupled. The lasing medium is Nd:YVO₄ and is comprised of neodymium doped yttrium orthovanadate crystal. For this medium, the triply ionized neodymium ions (Nd³⁺) replace yttrium atoms. With an acoustic-optic modulator (AOM) the quality factor of the resonator is modified, supporting pulse repetition rates from 5 kHz to 200 kHz. Including the facts mentioned above, further detail about the laser is summarized in Table 3.1.

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<thead>
<tr>
<th>Parameters</th>
<th>Parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>Max Power [W]</td>
<td>5</td>
</tr>
<tr>
<td>Repetition rate [kHz]</td>
<td>5 – 200</td>
</tr>
<tr>
<td>Max. Pulse Energy [mJ]</td>
<td>0.165</td>
</tr>
<tr>
<td>Pulse Width [ns]</td>
<td>6 – 14</td>
</tr>
<tr>
<td>Mode</td>
<td>TEM₀₀</td>
</tr>
<tr>
<td>Standard Deviation of pulse-to-pulse variation @ 35 kHz</td>
<td>&lt; 3%</td>
</tr>
<tr>
<td>Beam Diameter [mm]</td>
<td>0.5</td>
</tr>
<tr>
<td>Full Angle Beam Divergence [mrad]</td>
<td>3</td>
</tr>
<tr>
<td>M²</td>
<td>&lt; 1.2</td>
</tr>
</tbody>
</table>

The LMS used in this study is custom built from OpTek Systems for our lab and is shown in Figure 3.14 (a). The output of the laser head is delivered to the working surface by one of two optional paths depending on the wavelength selection, 1064 nm or 532 nm. Then the beam is
directed onto a vertical optical breadboard, with a certain configuration of optically selective mirrors, allowing for real time monitoring via a camera as shown in Figure 3.14 (b). The final objective, a 50 mm achromatic doublet, is mounted on a vertically oriented linear stage with a 0.5 µm resolution, providing focusing functionality.

Figure 3.14: (a) Laser micromachining system from OpTek and (b) the internal overview of the machine

Operation on the Optek LSM is done through a software program, Toronto V1. A screenshot of this program is shown in Figure 3.15. The video feed is directly shown on the video display screen (sub-screen with a large black cross inside) and the laser could be controlled in 3 axes x, y, and z. One could directly insert commands in the ‘MDI line’ area or run pre-designed codes in the ‘Program’ section. These codes are written in A3200 NView commands using the NView HMI software. Here not only the movement of the laser controlled but also the laser properties such as trigger pulse, frequency, etc.
3.4.2 Creating a Shadow mask

Using the LMS, the shadow mask for the TLM metal contacts are made. The material for the shadow mask is non-polished 200 µm thick Si wafer. A thin wafer is chosen to ensure the laser can cut through the wafer. The pattern designed is 5 rows of six 2 mm x 2.5 mm holes with the first gap between holes to be 200 µm with increments of 100 µm. The schematic diagram of this design for a single row and the actual shadow mask is shown in Figure 3.16. This pattern design is the final version chosen after a series of trial-and-errors. When the metal pad is too small, it did not fit the IV measuring apparatus and when the gaps were below 200 µm, the metal vapors seeped through the narrow spacing between the shadow mask and diffused on the substrate. The 532 nm laser used to create the shadow mask had the following setting; diode current is set to 28
A, trigger pulse width is 3 ns, and the frequency to 3 kHz. The NView command code for this design, ‘DM_5ROW_2000X2500_100UM INC.PGM’ is in Appendix A.

![Schematic diagram of shadow mask](image)

**Figure 3.16**: (a) Single row schematic diagram of shadow mask (*Not to scale) and (b) the actual 200 µm thick Si shadow mask

### 3.4.3 Challenges

The laser milling melts the Si wafer creating rough edges and limiting the resolution of the gap spacing. Furthermore, the cutout Si wafer pieces did not come off easily because the Si pieces adhered on the stainless steal substrate underneath. Often in the process of removing them the shadow mask broke.
3.5 Electron beam deposition

3.5.1 Introduction

Electron beam (e-beam) deposition, also known as e-beam evaporation, is one of the most commonly used physical vapor deposition (PVD) techniques for metallization, thin film metal depositions. As the name implies, the e-beam is used to heat the metal source producing metal vapors, which impinge and adhere to the substrate and thus creates a film. The metal source is usually in the form of pellets and is held in a crucible inside a high vacuum chamber (as seen in Figure 3.17), in the range of $10^{-7}$ Pa to $10^{-9}$ Pa. Using magnets the e-beam is accelerated and focused onto the crucible that contains the metal pellets. When these hot electrons with high kinetic energy strike the metal, it rapidly absorbs the energy of the electrons which thus heats the metal. As the metal heats up to a vaporization point, metal atoms evaporate into the vacuum, traversing to and impinging on the substrate, and the film starts to grow [27].

![E-beam deposition chamber](image)

**Figure 3.17**: E-beam deposition chamber used in the study
In this study, the K. J. Lesker e-beam evaporation system is used for metallization and is shown in Figure 3.18.

Figure 3.18: K. J. Lesker e-beam evaporation system. On the left shows the control system where the user could adjust settings of the deposition. On the right shows the actual chamber where the metal deposition takes place.

3.5.2 Metallization

The metallization is composed of a stack of chromium (Cr) and silver (Ag). First a 5 nm layer of Cr is deposited to improve the adhesion of Ag, with a thickness of 1 µm. Using the K Operation Vacuum user interface program, displayed in Figure 3.19 (a), one could control the deposition rate by adjusting the voltage supplied to the e-beam. The thickness is monitored using the
program SQM sensor, given in Figure 3.19 (b). It is important to use the correct density, tooling, and z-factor values for different metals.

Figure 3.19: (a) K Operation Vacuum software for operating the e-beam deposition and (b) metal film thickness monitoring program SQM sensor (the parameter values are for Sensor 1 and 2 are for Ag and Cr, respectively)

The AB-ncSi is expected to have a very low conductivity values. Therefore to ensure that the current is actually flowing through the film and not the substrate underneath, 1 mm thick fused
silica is used as the substrate. The fused silica substrate is cut to approximately 2.5 cm x 2.5 cm (Figure 3.20 (a)). Then the 200 µm thick Si shadow mask is centered (Figure 3.20 (b)) and secured onto the fused silica piece with nonconductive adhesive tape. After metallization, the tape is carefully removed (Figure 3.20 (c)) and the shadow mask is removed. The final product is shown in Figure 3.20 (d).

![Figure 3.20](image)

**Figure 3.20**: (a) bare fused silica piece 2.5 cm x 2.5 cm and 1 mm thick, (b) Si shadow mask is centered on the fused silica piece, (c) after deposition the adhesive taped is removed, and (d) the final product is metal pads (5 nm Cr & 1 um Ag) spaced with different gaps.

The details related to drop casting and the post-treatment procedures are already mentioned in Section 3.2.2, hence, will not be discussed again here. However, one of the key points to highlight is the fact that the metal deposition is done before creating the thin film of AB-ncSi.
This is because of 1) the risk of damaging the AB-ncSi film while placing the shadow mask on top of the film and 2) the nonconductive adhesive tape does not adhere on top of the AB-ncSi film.

3.5.3 Challenges

It is crucial that the shadow mask and substrate are in hard contact. If there is any gap between the two, the metal vapors can seep through making the gap between the metal pads smaller than designed.

3.6 Measuring Conductivity

3.6.1 Introduction

For conductivity measurements, the Keithley 6517 programmable electrometer was the key component in the apparatus, which is shown in Figure 3.21. Other components of the setup include the computer, metal shielding box, and the stage temperature controller. Using a GPIB cable the computer, through LabVIEW, controls the electrometer to apply a voltage and measure the current by adjusting the following settings: settling time (time where the voltage is applied but no measurements are made), averaging time (time where voltage is applied and the data is recorded then averaged), voltage range, and voltage interval. The front panel of the LabVIEW virtual instrument (VI) is given in Figure 3.22.
The metal shielding box is a crucial component because the current measurements are expected to be lower than the pico-ampere range. The particular electrometer model used in the experiment, the Keithley 6517, could measure down to the femto-ampere range. Without the shielding, a simple waving of the hand around it will easily interrupt the measurements. The box not only blocks out electric field but also light. With this box the sample can be completely measured in dark and this is important since the AB-ncSi can react to light. Furthermore, to protect the signal between components, triaxial cables are used to make connections between the metal shielding box to the electrometer. The interior of the box is shown in Figure 3.23. While securing the probe to the 2 metal pads around a particular gap, a third probe is connected to the metal pad on the edges of the sample to ground any static surface charge on the sample.

**Figure 3.22:** Front panel of LabVIEW VI used for measuring conductivity
3.6.2 Taking the Measurement

The IV parameter settings used for all the conductivity measurement is given below in Table 3.2.

Table 3.2: Parameter values used in VI for all measurements

<table>
<thead>
<tr>
<th>Parameters</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Settling time [sec]</td>
<td>110</td>
</tr>
<tr>
<td>Average [# of values]</td>
<td>100</td>
</tr>
<tr>
<td>Voltage range [V]</td>
<td>from -10 to 10</td>
</tr>
<tr>
<td>Voltage interval [V]</td>
<td>0.5</td>
</tr>
</tbody>
</table>

Before each measurement there is a waiting period of 100 sec. This time is given for the grounding of the static surface charge. The recorded data is saved as a ‘.txt’ file which makes it easy to transfer and analyze.
3.6.3 Challenges

The current measurements are very low, in the tens and hundreds of femto amperes, and sensitive to the point that the slightest movement in the lab will throw off the measurements. Multiple samples had to be measured in order to take into account that the film thickness varied with location.
4 Data Results

4.1 PL Data

When first looking at the data of the different samples, it may seem they all have the same peak. This is actually the peak from the 365 nm LED light source. The spectrometer picks up all the signals from the integrating sphere and it is unavoidable that the light source, which is exciting the AB-ncSi particles, is the most dominant signal. Figure 4.1 shows a measurement of sample AB-ncSi P5, and one can see a sharp peak around 365 nm and a small broad peak around 695 nm.

![Figure 4.1: Intensity vs. Wavelength of AB-ncSi P5](image)

Drawing together all the measurements of the samples results in a graph shown in Figure 4.2. As seen in Figure 4.2, the PL data becomes very noise near the spectral limit of the spectrometer, around 1100 nm, for samples P1 and P3. In addition, the PL signal for samples P15, P17, and P19 is too low such that it is indistinguishable from the background signal. The PL graphs are
most clear for samples P5 to P13 and further experiments (film morphology and conductivity studies) will be focused on these samples.

Figure 4.2: Intensity vs. Wavelength of all AB-ncSi samples

4.2 Ellipsometry Data

The film under investigation is not a solid film and is created from drop casting. As a result, the AB-ncSi film is rough and not completely even. This is reflected in the ellipsometry measurements. However, taking one measurement takes less than 2 minutes. Thus, multiple measurements are taken from each test sample by slightly moving the position of the test sample. After a series of measurements, the most noise-free measurement is selected for each test sample. In selecting the least noisiest test sample data, the series of data was roughly analyzed using the software Winelli II to find the coefficient of determination, $R^2$ value. The sample data that had
the highest $R^2$ value was chosen for further analysis in calculating its film thickness. Displayed below in Figure 4.3 is an example of one selected and one noisy data with its $R^2$ values.

![Figure 4.3: Alpha vs. Energy of AB-ncSi P7 (a) selected ($R^2 = 0.758533$) and (b) noisy sample ($R^2 = 0.582652$)](image)

4.3 SEM Data

The samples are observed in the following order: the 1 µm Ag coated c-Si sample (blank sample), the AB-ncSi coated sample without the post-treatment, and the post-treated AB-ncSi sample, as shown in Figure 4.4. The blank sample is only measured once and is for reference since the AB-ncSi films are so thin the Ag layer underneath should be visible. It is necessary for differentiating grain boundaries of the AB-ncSi film and the grain boundaries of the Ag layer.
As seen in Figure 4.4 (a), the grain boundaries of the Ag are clearly seen. This gives reference for making observation of AB-ncSi film samples. The relatively large grey spots seen in Figure 4.4 (b) to (d) are the grain boundaries of Ag and looks blurry because the SEM is focused on the AB-ncSi film on top. There are no other boundaries visible in the AB-ncSi films that have not been post-treated. However, for the post-treated samples at lower magnification, as seen in Figure 4.4 (d), the boundaries in the films are observed. These cracks are most likely caused by the tension created in the AB-ncSi film during the annealing process, as the solvent is evaporated. Such observation is present in all the AB-ncSi films investigated (AB-ncSi P1, P5, P9, and P13).
From comparing Figure 4.4 (a) to the rest, it can be deduced that the small white dots observed in Figure 4.4 (b) to (d) are the AB-ncSi particles. Furthermore, when taking a closer look at Figure 4.4 (b) and (c), it is observed that the AB-ncSi comes closer together after the post-treatment. The average distance between the AB-ncSi is further investigated and discussed in detail in the next section. Such trend is found in all the rest of the samples, AB-ncSi P5, P9, and P13. Figure 4.5 illustrates the SEM image of the post-treated of all the AB-ncSi samples along with the image of the solution form of the AB-ncSi sample as the inset.

![SEM images of post-treated AB-ncSi samples](image)

**Figure 4.5:** SEM images of post-treated AB-ncSi (a) P1 sample, (b) P5 sample, (c) P9 sample, and (d) P13 sample with the image of the samples in solution as the inset.

The diameter of all the AB-ncSi samples is expected to be in the range of 2 nm to 4 nm. The P1 sample is expected to have the largest particle size and the P13 sample to be the smallest. From Figure 4.5, it is difficult to state such difference since the magnification is not high enough. However, a significant difference in colour is observed when looking at the solution form of the
samples from the insets of Figure 4.5. It was extremely challenging to zoom in on one of these AB-ncSi particles due to the limited resolution of the SEM, 1.8 nm at 1.0 kV. To visibly compare the size of the AB-ncSi particles an instrument with higher resolution must be used, such as transmission electron microscopy (TEM).

4.4 Conductivity Data

For our experiment, it is important to know what the background noise is for the measurements because the current being measured is around $10^{-14}$ A to $10^{-13}$ A range. The I-V curve measured for background noise is given in Figure 4.6. Here the probes are hovering/suspended in air while the measurement took place. We are mainly interested in the slope of the I-V curve when calculating the conductivity. Any I-V curve with a slope below $2.34 \times 10^{-16}$ will be considered incorrect.

![Figure 4.6: Background noise of conductivity measurement](image)

There are five sets of metal pads with the same gap distance on each sample. Considering that the AB-ncSi film may not be uniform, the average slope of three values is used to represent a particular gap. A sample raw data for AB-ncSi P5 gap 1 for three sets (s01, s03, s05) are shown in Figure 4.7. It is observed that there is a stabilizing period in the -10 V to -8 V range. The linear fit takes into consideration this behavior.
4.4.1 Size dependent Data

As mentioned before in Section 4.1, the conductivity is measured only for samples AB-ncSi P5, P7, P9, P11, and P13. This is because only these samples show clear PL data for calculating the diameter size of the samples. All the measurements are made at room temperature for this section.

4.4.2 Temperature Dependent Data

For this section only one sample (AB-ncSi P5) and one gap (gap 1) is examined. This is because we are not concerned in calculating the exact conductivity value, which is already done in size dependent measurements, but interested in finding the trend of conductance as the stage temperature is raised. The temperatures explored are from 25 °C to 85 °C with 15 °C increments and the data measured is organized and presented in Table 4.1.
Table 4.1: Conductance value of AB-ncsi P5 gap 1 for different sets and temperatures

<table>
<thead>
<tr>
<th>Temp.</th>
<th>Set s01 [S]</th>
<th>Set s03 [S]</th>
<th>Set s05 [S]</th>
<th>Average</th>
</tr>
</thead>
<tbody>
<tr>
<td>25 °C / 298 K</td>
<td>9.09E-16</td>
<td>7.28E-16</td>
<td>8.70E-16</td>
<td>8.36E-16</td>
</tr>
<tr>
<td>40 °C / 313 K</td>
<td>8.42E-16</td>
<td>9.15E-16</td>
<td>9.55E-16</td>
<td>9.04E-16</td>
</tr>
<tr>
<td>55 °C / 328 K</td>
<td>9.26E-16</td>
<td>9.39E-16</td>
<td>1.06E-15</td>
<td>9.75E-16</td>
</tr>
<tr>
<td>70 °C / 343 K</td>
<td>1.05E-15</td>
<td>1.04E-15</td>
<td>1.04E-15</td>
<td>1.04E-15</td>
</tr>
<tr>
<td>85 °C / 358 K</td>
<td>1.02E-15</td>
<td>1.05E-15</td>
<td>1.14E-15</td>
<td>1.07E-15</td>
</tr>
</tbody>
</table>
5 Analysis & Discussion

5.1 Quantum Yield (QY) and AB-ncSi Diameter from PL

The wavelength, which corresponds to the peak intensity of each sample, the calculated bandgap energy from Equation 1, and its QY values, which is calculated using Equation 2, is given in Table 5.1. The QY is calculated with the IV, by inputting the ‘Excitation Range’, which is the range for the 365 nm LED light, and the ‘Emission Range’, which is the range of the PL (refer to Figure 3.4). As mentioned in Section 4.1, the PL peaks for samples P15, P17, and P19 were difficult to determine because their peak intensities were very low and located close to the 365 nm LED light source. In turn, the bandgap energy and the QY of these samples cannot be calculated and therefore is omitted from Table 5.1. Finally, the estimated diameters of the AB-ncSi particles are calculated by using Equation 3 and included in Table 5.1.

<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>P1</td>
<td>983.712</td>
<td>1.26</td>
<td>0.252</td>
<td>7.65</td>
</tr>
<tr>
<td>P3</td>
<td>855.724</td>
<td>1.45</td>
<td>0.278</td>
<td>5.37</td>
</tr>
<tr>
<td>P5</td>
<td>694.647</td>
<td>1.79</td>
<td>0.313</td>
<td>3.64</td>
</tr>
<tr>
<td>P7</td>
<td>649.296</td>
<td>1.91</td>
<td>0.177</td>
<td>3.28</td>
</tr>
<tr>
<td>P9</td>
<td>620.709</td>
<td>2.00</td>
<td>0.076</td>
<td>3.07</td>
</tr>
<tr>
<td>P11</td>
<td>608.171</td>
<td>2.04</td>
<td>0.030</td>
<td>2.98</td>
</tr>
<tr>
<td>P13</td>
<td>595.164</td>
<td>2.08</td>
<td>0.010</td>
<td>2.89</td>
</tr>
</tbody>
</table>

To graphically represent the data in Table 5.1, plotting the QY and bandgap energy with its respective sample numbers are shown in Figure 5.1. The bandgap energy is increasing with the sample number, but the QY does not show a consistent trend. It increases until sample P5 then
decreases afterwards. This is because when calculating the QY the range for samples P1 and P3 is cut off by the spectral limit of the spectrometer as shown in Figure 4.2.

![Figure 4.2](image)

**Figure 4.2:** Sample number vs. Bandgap energy and QY for AB-ncSi

The graph of Figure 5.1 is then re-plotted (Figure 5.2) with the following two modifications: 1) the samples P1 and P3 are omitted and 2) the x-axis is replaced with the estimated diameter of the AB-ncSi particle. As the diameters of the particles are included in the plot it is seen that the slopes become the opposite when compared with Figure 5.1. This is because the particle diameter decreases with increasing sample number. The trend of the bandgap energy decreasing with the diameter increasing is a general trend observed in various semiconductor nanocrystals, such as CdSe [28], CdTe [28], PbSe [30], and PbS [31].

![Figure 5.2](image)

**Figure 5.2:** Re-plot of Fig. 5.1 with two modifications: 1) the samples P1 and P3 are omitted and 2) the x-axis is replaced with the estimated diameter of the AB-ncSi particle
In Figure 4.5, the SEM images of the AB-ncSi film shows the distribution of the nanocrystals, however due to the limitations of the SEM the diameter of these particles could not be measured. From this study, the estimated diameters of the AB-ncSi samples are the best estimates and of direct interest in this study. This information will be helpful in understanding the transport mechanism after the conductivity study is completed.

5.2 AB-ncSi film thickness from Ellipsometry

As mentioned in Section 3.2.1, the data measured in ellipsometry gives the user less meaningful information until it is analyzed with Winelli II. It is also essential to know some properties of the film under investigation. In our case, the substrate is fused silica and this film is defined using the n&k file available from the library in the program. The tricky part is defining the AB-ncSi film. Here, I received advice from Dr. Danny Puzzo (PDF with Prof. Lu and Kherani’s groups in MSE and MSE-ECE). The AB-ncSi film is defined using the standard dielectric function and the Cauchy model with a thickness value of 0.05 µm (50 nm), which is a rough estimate. One key value/parameter in this model is ‘A’, which is assigned as 1.85 (1.70 for C10-ncSi). After the structure is set, the data is fitted to the Alpha-Energy and Beta-Energy (refer to Section 2.2 Equations 7 and 8) plots in the regression process. When setting the conditions for the regression, it is important to set the range for the energy values as 1.4 eV to 2.0 eV and ensuring the thickness is checked as a non-fixed value. Winelli II runs multiple iterations altering the film thickness, A, B, and C values to find the best fit for both Alpha-Energy and Beta-Energy plots as displayed in Figure 5.3, where the green line represents the best fit (alpha and beta here are values referring to Equations 7 and 8 from Section 2.2).
Along with the graphical representation of the data, Winelli II outputs the parameter values (film thickness, A, B, C, etc.) that produce such best-fit line. This is a crucial part in understanding the property of the film and in deciding whether or not to accept the data values. One of the key
things to check is the polarity of the film value, ensuring it is a positive value, and the other is whether the ‘A’ value within error is 1.85, which is the initial value assigned for the regression. In general, when performing analysis for ellipsometry, we accept the film parameters when the $R^2$ value is above 0.990. However, in our case, since the film is not a solid film, we accept the film parameters if the $R^2$ value is above 0.600. The parameter values for the line of best fit in **Figure 5.3** are given in **Figure 5.4**.

**Figure 5.4**: Fitted parameters of AB-ncSi P5 from line of best fit in Figure 5.3

Figure 5.4 shows that the film thickness of AB-ncSi P5 is calculated to be $(52.147 \pm 43.060)$ nm. The error is quite large but this is once again due to the fact that the film is not a uniform, solid film. This trend was seen in all the film thickness measurements as given in **Table 5.2**.

**Table 5.2**: Film thickness, ‘A’ parameter, and $R^2$ of all AB-ncSi samples measured

<table>
<thead>
<tr>
<th>AB-ncSi sample</th>
<th>film thickness [nm]</th>
<th>parameter ‘A’ [unitless]</th>
<th>$R^2$ [unitless]</th>
</tr>
</thead>
<tbody>
<tr>
<td>P5</td>
<td>52.147 ± 43.060</td>
<td>1.6817 ± 0.18044</td>
<td>0.870820</td>
</tr>
<tr>
<td>P7</td>
<td>54.739 ± 42.892</td>
<td>1.6638 ± 0.16185</td>
<td>0.758533</td>
</tr>
<tr>
<td>P9</td>
<td>82.539 ± 34.089</td>
<td>1.6861 ± 0.17251</td>
<td>0.672681</td>
</tr>
<tr>
<td>P11</td>
<td>78.822 ± 15.866</td>
<td>1.6239 ± 0.19402</td>
<td>0.682652</td>
</tr>
<tr>
<td>P13</td>
<td>76.246 ± 14.368</td>
<td>1.6403 ± 0.17429</td>
<td>0.638764</td>
</tr>
</tbody>
</table>
5.3 Distance between AB-ncSi from SEM

The focus of the SEM image analysis is on the change in distance between the AB-ncSi particles before and after the annealing post-treatment process in each set of samples (AB-ncSi P1, P5, P9, and P13). Additionally, we want to see if there is any correlation between AB-ncSi particle size and distance between particles in an annealed film. This will provide vital information in understanding the charge transport mechanism in the AB-ncSi film. This is discussed much in-depth with the conductivity measurements in Section 5.4.

Using Matrix Laboratory (MATLAB), a tool to measure the average distance between the AB-ncSi particles is created. Creating a fully automated program was challenging since the SEM figures had different brightness and contrast level it was difficult to set a certain value for finding the white dots, the AB-ncSi particle, and differentiating it from the grain boundaries created from the Ag layer underneath. Therefore the process of selecting the AB-ncSi particles to be examined is manually chosen. In turn, using the whole SEM image did not make sense because not all the AB-ncSi particles are to be highlighted for measurements. A section of the SEM image is cropped (the size is kept constant around 240 x 235 pixels) and is imported to the MATLAB program for analysis, as indicated in Figure 5.5 (a) and (b) as a red box. The “ginput” function is used to set the number of points, which the x- and y-coordinates in pixels are returned, for calculations. In our case 20 points are selected and each of the points’ x- and y-coordinates are used to calculate the distance between two points \(d_{12} = \sqrt{(x_2 - x_1)^2 + (y_2 - y_1)^2}\). The code is then designed to compare these distances and find the shortest distance between two points. The average of these distances, 19 in our case, is calculated to find the average distance between the ncSi particles. The 20 points that are specified for each images is depicted as a white cross in Figure 5.5 (c) and (d). In this particular sample (P1), the average distance between AB-ncSi particles before and after post-treatment is 46.15 pixels and 30.31 pixels, respectively. At 150k magnifications, each pixel is calculated to be approximately 0.809 nm. After annealing, the distance between the AB-ncSi particles in the P1 film decreased by 33%. The full m-code for this MATLAB program is given in the Appendix B.
Figure 5.5: SEM images of AB-ncSi P1 film (a) before and (b) after post-treatment with section that is cropped shown in the red box. These sections of the images ran through MATLAB for calculating the distance between AB-ncSi particles (c) before and (d) after post-treatment with each AB-ncSi particle used in calculation specified with a white cross.

Using the same method, the distance between the AB-ncSi particles in each sample before and after post treatment is calculated. These values are given in Table 5.3, which includes the percentage drop of the distance. From Table 5.3, it can be stated that all the film samples decreased over 32% and there is a correlation found between the AB-ncSi particle size and the distance between the particles after post-treatment. As the particle size increases, the average distance between the particles also increases as shown in Figure 5.6.
Table 5.3: Distance between AB-ncSi particles, $r$, for each sample before and after post-treatment.

<table>
<thead>
<tr>
<th>AB-ncSi sample</th>
<th>Not treated [pixels]</th>
<th>[nm]</th>
<th>Post-treated [pixels]</th>
<th>[nm]</th>
<th>Percentage drop</th>
</tr>
</thead>
<tbody>
<tr>
<td>P1</td>
<td>46.15</td>
<td>37.33</td>
<td>30.31</td>
<td>24.52</td>
<td>35%</td>
</tr>
<tr>
<td>P5</td>
<td>36.03</td>
<td>29.15</td>
<td>23.06</td>
<td>18.66</td>
<td>36%</td>
</tr>
<tr>
<td>P9</td>
<td>28.32</td>
<td>22.91</td>
<td>19.26</td>
<td>15.58</td>
<td>32%</td>
</tr>
<tr>
<td>P13</td>
<td>17.12</td>
<td>13.85</td>
<td>11.47</td>
<td>9.28</td>
<td>33%</td>
</tr>
</tbody>
</table>

Figure 5.6: Diameter from PL measurements vs. Average distance between particles from SEM for AB-ncSi samples P1, P5, P9, and P13.

The measured distance between the ncSi particles are not entirely accurate. The distance is calculated using the SEM images where the estimated length is based on the number of pixel. The MATLAB script accurately calculates the distance in pixels and this value is converted to the nm length scale. Hence, the distance measured/calculated in nm are systematically representative. However, the positions of the AB-ncSi particles in the MATLAB script contain errors because they are chosen manually. Often it is difficult to pinpoint the nanocrystals since the resolution of the SEM is of the same order as its diameter, approximately 2 nm. It is highly likely some AB-ncSi particles did not show up as clearly as other neighboring nanocrystals, making it a source of error. Furthermore, implicit in this calculation is the assumption that the nanocrystals are dispersed on a 2 dimensional plane. Nevertheless, comparison of the
average relative distance between the nanoparticles with respect to the diameter of the particles does provide a useful systematic measure albeit not an absolute measure.

5.4 Transport mechanism in AB-ncSi

5.4.1 Size dependent Conductivity

With the ellipsometry measurements in Section 5.2, the surface area \( A_s \) through which the charge is traversing in the film can be calculated (thickness x length of metal pad). Conductivity can be determined by rearranging the equation below

\[
R = \frac{\rho}{A_s} \ell
\]  

(15)

where \( R \) is resistance (V/I) and \( \ell \) is the length/gap between the metal pads.

To get a graph like Figure 2.10, \( R_T \) is the inverse of \( 1/R \), which is basically the slope value of the I-V curve mentioned in Section 4.4. Bringing all these values together for a particular fraction size, for instance AB-ncSi P11, we get something like Table 5.4. Then graphing \( R_T \) versus \( \ell \) will give Figure 5.7. From this graph the contact resistance (\( R_C \)) is calculated by halving the y-intercept value, which in this case is \( 5.75 \times 10^{13} \) \( \Omega \). Furthermore, it is deduced from Equation 15, that slope \( R_{SH}/W \) is equal to \( \rho/A \). In turn the resistivity and conductivity of the film are calculated to be \( 2.29 \times 10^{10} \) \( \Omega \)m and \( 4.36 \times 10^{10} \) S/m, respectfully.

Table 5.3: Parameters for calculating conductivity of AB-ncSi P11 thin film

<table>
<thead>
<tr>
<th>gap number</th>
<th>length [m]</th>
<th>1/R [1/ohm]</th>
<th>( R_T ) [ohm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>2.00E-04</td>
<td>8.32E-16</td>
<td>1.20E+15</td>
</tr>
<tr>
<td>2</td>
<td>3.00E-04</td>
<td>8.17E-16</td>
<td>1.22E+15</td>
</tr>
<tr>
<td>3</td>
<td>4.00E-04</td>
<td>8.25E-16</td>
<td>1.21E+15</td>
</tr>
<tr>
<td>4</td>
<td>5.00E-04</td>
<td>7.92E-16</td>
<td>1.26E+15</td>
</tr>
<tr>
<td>5</td>
<td>6.00E-04</td>
<td>7.69E-16</td>
<td>1.30E+15</td>
</tr>
</tbody>
</table>
Similarly, the conductivity of all the other AB-ncSi samples is calculated and plotted with respect to its diameter (calculated from PL measurement) in Figure 5.8.

Figure 5.7: $R_T$ vs. $\ell$ for AB-ncSi P11

Figure 5.8: Conductivity vs. Diameter of all AB-ncSi samples
The result in Figure 5.8 indicates that the conductivity is decreasing with increasing bandgap energy. This is actually the opposite of what is expected with bulk semiconductor. With bulk, having a smaller bandgap energy level gives a higher chance for the electron to jump from the valence band to the conduction band. In turn, higher chance of jumping the gap leads to more electrons in the conduction band, which means higher conductivity.

Analyzed SEM images (from the Section 5.3) show that the smaller AB-ncSi particles are closer to each other than larger particles. This fact can be related to the result in this section if the charge transport mechanism is nearest-neighbor hopping (NNH). To confirm this, a temperature dependent study is required.

### 5.4.2 Temperature dependent Conductance

Once again, it is noted that the conductance is measured for the temperature dependent study not conductivity. Only a single gap length is examined (meaning the TLM does not apply), not allowing the calculation independent of the contact resistance.

In order to distinguish between variable range hopping (VRH) and NNH, as mentioned in Section 2.4, the natural log of conductivity against $T^{-1/4}$ and $T^{-1}$ to find which dependence has a better fit. However, in our case, instead of conductivity values the conductance can be used since the only variation in the experiment is temperature, within the range of not altering the AB-ncSi film. Conductance is basically conductivity multiplied by the surface area, and divided by the length that the charge travels. Because the film is not changing, the surface area and length are constants, permitting the use of conductance as a replacement for conductivity.

Using the average conductance for different temperatures in Table 4.1, for graphing convenience the negative of the natural log value is plotted against $T^{-1/4}$ and $T^{-1}$ and is given in Figure 5.9 and Figure 5.10, respectively.
Figure 5.9: $-\ln(dI/dV)$ vs. $T^{1/4}$ for AB-ncSi P5

Figure 5.10: $-\ln(dI/dV)$ vs. $T^{-1}$ for AB-ncSi P5

The $R^2$ value for $T^{-1}$ fit is slightly higher than the $T^{1/4}$ fit, but only by 0.4%. Therefore it could be said that the charge transport mechanism is NNH but is indistinguishable from VRH. In order to
confidently state which hopping mechanism ncSi follows, we will have to extend the temperature range of study, for example, starting from 77 K up to 373 K.

5.5 Discussion

The conductivity value of the ncSi film is very low, varying in the range of $10^{-12}$ S/m to $10^{-10}$ S/m. However, when comparing to other conductivity studies of semiconductor NCs in the past, the results of this thesis appear reasonable. Talapin and Murray reported that the oleic acid capped PbSe had conductivity values less than $10^{-9}$ S/m with an interparticle spacing of 1.5 nm [32]. As the native capping was removed, the interparticle spacing reduced to 1.1 nm and the conductivity increased to $3 \times 10^{-8}$ S/m [32]. Drndic et al. studied CdSe NCs capped with trioctyphosphine oxide (TOPO) and showed that the resistance of the film decreased from $7 \times 10^{20} \Omega$ to $1 \times 10^{20} \Omega$, as the film was annealed and the surface-to-surface separation decreased from 1.1 nm to 0.5 nm [33]. Similarly, in our study, as the size of the ncSi decreased the separation between the particles also decreased and the conductivity increased.

From the temperature dependent conductance studies, the charge transport mechanism of the ncSi does not show a completely clear distinction of VRH and NNH, but the experimental results appear to lean towards NNH. Romero and Drndic reported that their PbSe NCs capped with oleic acid followed the NNH model for high temperatures (above 200 K) but switched to Efros-Shklovskii VRH (ES-VRH) in the low temperature region (below 200 K) [34]. The ES-VRH (where $\gamma$, a factor in Equation 12, is closer to $\frac{1}{2}$) is similar to VRH but taking into consideration the Coulomb blockade present between the particles [22]. In addition, Kastner et al. have reported similar results with PbSe nanocrystals with oleic acid caps [35]. They did a thorough temperature dependence study, from 4 K to 295 K, and stated that the charge transport mechanism is NNH but can alternatively be explained by VRH with the hopping distance comparable to the distance between the nanoparticles. Furthermore, Oda et. Al. examined plasma deposited ncSi encapsulated with 1.5 nm SiO$_2$ shell in the temperature range of 40 K to 200 K and discovered that the charge transported through ES-VRH [36]. The temperature range investigated in this thesis is from 298 K to 358 K. Considering this range, the conclusion of this
study appears to be in accord with the other studies mentioned above that the charge transport is NNH.

The novelty of this study comes from the fact that the charge transport mechanism is investigated through size dependent conductivity and temperature dependent conductance of colloidal ncSi (drop casted from its colloidal form) utilizing the TLM test structure which allows direct measurement of the conductivity of the film while factoring out the effect of contact resistances.
6 Conclusion

6.1 Thesis Summary

In this study, we thoughtfully designed experiments to explore the optical, structural, and electrical properties of colloidal ncSi so as to better understand its potential application in optoelectronic devices, such as photovoltaics, LEDs, etc. The nanoparticles are prepared using a solution-based method involving HF etching to free the ncSi from the thermally treated silicon-rich oxide precursor and subsequently capping it with allylsilane (AB) groups. In addition, the AB-ncSi samples are size separated into 10 different groups to examine the size effect on the different properties mentioned above.

For optical characterization, the integrating sphere method is utilized to study the PL. Here the AB-ncSi is in solution form, poured into a cuvette and lowered into the sphere where the sample is excited with a 365 nm LED. Any light signal generated in the integrating sphere is transferred to the spectrometer by optical fibers. The PL peak is found for the different fractions and the diameter of the AB-ncSi is calculated. Our samples’ diameters ranged from 2.89 nm to 7.65 nm.

For structural characterization, the thin films created from drop casting are examined using ellipsometry and SEM. The main purpose of ellipsometry is to measure the thickness of the film for different nanoparticle sizes. The film thickness showed no correlation with the size of the AB-ncSi, nevertheless this data is important in calculating the conductivity of AB-ncSi films. Using SEM, images of the films were taken before and after annealing in order to measure the change in the average distance between the particles. On average all the nanoparticles came 33% closer to each other after annealing at 110 °C under purging N₂. In addition, SEM images indicated that particles with shorter distance between them correlated with the smaller quantum dots. For instance, the AB-ncSi samples with the diameter of 7.65 nm is on average 24.52 nm (centre-to-centre) apart, while samples with diameter of 2.89 nm were only 9.28 nm away from each other. These calculated distances between ncSi particles while not entirely representative do provide a useful measure to first order.
For electrical characterization, TLM test structures were fabricated using a shadow mask made from laser micromachining. With these test structures, the conductivity of size-separated samples and the temperature dependent conductance are measured. The advantage of using TLM is the ability to measure the conductivity of only the film - being able to factor out the contact resistance between the AB-ncSi film and the metal pads. The conductivity values of the samples are in the range from $10^{-12}$ S/m to $10^{-10}$ S/m, with the conductivity increasing as the diameter of the particles is decreasing. The charge carrier transport is explained by NNH. To confirm this, temperature dependent conductance is measured for AB-ncSi P5 fraction with a channel length of 200 µm (gap 1). For VRH and NNH, conductance has a $T^{-1/4}$ and $T^{-1}$ dependence, respectively. The linear fit shows that $T^{-1}$ has a higher $R^2$ correlation value albeit only by 0.4%. The results suggest that the charge transport mechanism is NNH however the presence of VRH cannot be ruled out.

The research reported herein is a first step towards experimental characterization of colloidal ncSi samples and accordingly set the stage for future investigation of this novel material.

### 6.2 Future Work

The ultimate goal is to use ncSi for optoelectronic devices. For this to happen further studies on the optical, structural, and electrical characterizations need to be carried out, some of which include:

i) Studying the absorption, transmittance, and reflectance will be a key milestone in optical characterization of ncSi films. In this study the optical characterization of ncSi is only done in solution form. However, in all optoelectronic devices the ncSi will be utilized as thin film.

ii) Developing a technique to deposit a thicker, uniformly distributed, and crack-free film. The thickest ncSi thin film created in this study is around 100 nm and non-uniform. Depositing thicker films is not only important for device applications but also for higher-level characterization.
iii) Exploring different ligands and post-treatment techniques to create a close packed ncSi film. In this study, the only ligand used was AB and post-treatment performed is annealing at 110 °C under purging N₂. Shorter molecules than AB could be experimented and annealing can be done at higher temperatures with different gases or even in vacuum. Other possible post treatments include, hydrogen plasma treatment, etc. The objective will be decreasing the interparticle spacing.

iv) Utilization of TEM to take a closer look at the individual nanoparticles in the film. The biggest limitation in the SEM is that even at the maximum resolution, it is difficult to differentiate the nanocrystals. With TEM, measuring the distance between the ncSi more accurately and even observe the difference in structure for the surface and the core.

v) Extend the temperature range for the dependent conductance study. For measurements in the low temperatures, below 77 K, a new system to hold the sample under vacuum during the measurements will be required due to condensation at lower temperatures. This will give a clear distinction between NNH and VRH.

vi) Designing a system to investigate the electron and hole mobility of ncSi will be the next crucial step in electrical characterization. Charge mobility is one of the most important parameters when creating a device, because it indicates how fast or slow charge carriers will travel in the device. The two most common techniques are the field effect transistor (FET) method (refer to Appendix C) and the time-of-flight (TOF) method.
References


[23] N. F. Mott, Metal-Insulator Transitions, Taylor & Francis, Bristol (1990)


Appendix A

NView command program code for shadow mask

```
000 | ;start a
001   move left for each successive pad
002   move downward for each successive row
003
004   'TIM Mask Pattern
005
006   '10/05/2010
007
008
009
010
011   'TIM Pattern variables
012   DVAR Smirror
013   DVAR Spad_L
014   DVAR Spad_W
015   DVAR Spads
016   DVAR Space_seed
017   DVAR Sinc_gap
018
019   'Laser Machining Variables
020   DVAR Spasses
021   DVAR $SPEED
022   DVAR $ERF
023   DVAR $PULSEWIDTH
024   DVAR $REPWIDTH
025   DVAR $FREQ
026   DVAR $tone
027
028   'Dynamic Variables
029   DVAR $inc
030   DVAR $gap
031   DVAR $brown
032
033   'Write Variables to Laser Power Supply
034   $DOS.1 = 1  ; Switch Laser Gating Off
035   $PULSEWIDTH=3  ; SET WIDTH OF TRIGGER PULSE
036   $REP=30000  ; SET LASER FREQUENCY in Hz
037   $SPEED=5.1
038   Spasses=20
039
040
041
042   'Pad Sequence 1: Set TIM VARIABLES
043   Smirror = -1  ; direction to write TIM pattern ("1"-starts in the upper right corner of the
044   Spad_L = 2.0  ; metal pad length
045   Spad_W = 2.5  ; metal pad width
046   Spads = 6  ; number of pads in pattern
047   Space_seed = 0.2  ; width between first and second pad
048   Sinc_gap = 0.1  ; rate of increase of width between consecutive pads
049
050
051
052   $PULSEWIDTH=INT((1/$SPEED)*1000000)
053   $FREQ=INT($PULSEWIDTH/$2)
054
055   $G71  ; Ensure system is in Metric mode ($G70 = inches)
056   $G91  ; Ensure system is in incremental mode ($G90 = absolute)
057
058   ENABLE X Y Z  ; Enable all three axes
059
060   G92 XY0
061
062   'Configure Laser PSO Pulses
063
064   PSOCONTROL X RESET
065   PSOCURSE $PULSEWIDTH $REPWIDTH $FREQ  ; Define pulse output.
066   PSOCURSE $PULSE $FREQ  ; PSO output is PULSE.
```
G69
G70 RPT 5
G71
G72 $DO2.X = 1 ;Open Laser Shutter
G73
G74
G75
G76 G4 F0.2
G77 G188 ;velocity profiling in stages do not slow to zero between passes
G78 $DO8.Z = 0 ;Switch Laser Gating On- Laser Gate should be open from R6232
G79 G4 F1
G80 PSOCNTROL X FIRE CONTINUOUS ; Repeatedly fire pulses
G81
G82 $Inc=0
G83
G84 RPT $Spds
G85
G86 $DO8.Z = 0 ;Switch Laser Gating On- Laser Gate should be open from R6232
G87 G4 F.1
G88 PSOCNTROL X FIRE CONTINUOUS ; Repeatedly fire pulses
G89
G90 'Cut Pad
G91 RPT $passes
G92 G1 X($Spd_L*$Mirr) F$Spd
G93 G1 X($Spd_N*$Mirr) F$Spd
G94 G1 Y-($Spd_L*$Mirr) F$Spd
G95 G1 Y-($Spd_N*$Mirr) F$Spd
G96 ENDRT
G97 PSOCNTROL X OFF ;Turn Laser Off
G98 G4 F0.1
G99 $DO8.Z = 1 ;Switch Laser Gating Off
G100 G4 F0.2
G101 'Calculate gap
G102 $gap = $Space_seed*$Inc
G103 $Inc = $Inc*$Inc_gap
G104
G105 'Move gap distance
G106 Dwell 0.1
G107 G1 X-($Spd_W*$gap)*$Mirr) F16
G108 Dwell 0.2
G109 ENDRT
G110
G111 G90 X0
G112 G91 Y(2.7)
G113 $DO2.X = 0 ;Close Laser Shutter
G114 ENDRT
G115
G116
G117
G118
G119
G120
G121
G122
G123
G124
G125 M2
Appendix B

MATLAB m-code for calculating the average distance between AB-ncSi particle

```
% CalcPnts.m calculates the average distance between points

% Load image onto MATLAB
H = imread('semP1.jpeg');
I = imread('semP5.jpeg');
J = imread('semP9.jpeg');
K = imread('semP13.jpeg');

% Display image
image(J);

% number of points = n
n = 10;
[x, y] = ginput(n);

% Calculate total average distance
temp2 = [];
d = [];
i = 1;
h = 1;
%m = n*(n-1)/2;

% Find the shortest distance for two points
for x = 1:n
    temp = 200;
    for j = x+1:n
        temp2(i) = ((x(k)-x(j))^2 + (y(k)-y(j))^2)^0.5;
        if temp > temp2(i)
            temp = temp2(i);
            i = i+1;
        end
    end
    d(h) = temp;
    h = h+1;
end

% Calculate the average distance
d(n) = [];
davg = mean(d);
```
Appendix C

Field Effect Transistor (FET) Method to measure mobility

In the FET method, the FET is first fabricated such that the material of interest, in this case CQDs, is deposited in the channel between the source (S) and drain (D) as shown in Figure A-1.

![Figure A-1](image)

Figure A-1. Schematic diagram of thin-film transistor (TFT) where the source and drain is 2 µm of Ag on 5 nm of Cr, the thin red layer is the ncSi, and p++-Si is the gate.

For the particular example shown in Figure A-1., the thin film of ncSi is deposited using drop casting onto the p++-Si/SiO₂ chip with the Cr/Ag contacts (5 nm/ 2 µm) e-beam evaporated. As seen in this particular example, the film thickness of the material of interest could be very thin, in the sub 100 nm range.

Once the TFT is fabricated the mobility measurement is relatively simple. The carrier mobility is calculated from the I-V (current-voltage) curve measured. Based on the regime in which the I-V curve lies, linear or saturated, the expression for I_{SD} varies as such,

\[
I_{SD} = \frac{W}{L} \mu C (V_G - V_T) V_{SD}
\]

Linear regime: \( I_{SD} = \frac{W}{L} \mu C (V_G - V_T) V_{SD} \) (1)

Saturated regime: \( I_{SD} = \frac{W}{2L} \mu C (V_G - V_T)^2 \) (2)
where $I_{SD}$ and $V_{SD}$ are the current and voltage bias between source and drain, respectively, $V_G$ is the gate (G) voltage, $V_T$ is the threshold voltage, $C$ is the capacitance of the gate dielectric, and $W$ and $L$ are the width and length of the conducting channel.

Here the carrier transport is affected by structural defects within the thin film layer, the surface topology and polarity of the dielectric, and the contact resistance at source and drain metal/thin film interface.