Fabrication of Composite Nanomaterials For Thin Film Amorphous Silicon Solar Cells

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FABRICATION OF COMPOSITE NANOMATERIAL FOR THIN FILM AMORPHOUS SILICON SOLAR CELLS
FABRICATION OF COMPOSITE NANOMATERIALS FOR THIN FILM AMORPHOUS SILICON SOLAR CELLS

A thesis submitted in partial fulfillment of the requirements for the degree of Master of Science in Microelectronics-Photonics

By

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University of Arkansas Pine Bluff
Bachelor of Science in Physics, 2009

December 2011
University of Arkansas
Abstract

A material with the precise combination of amorphous silicon and polycrystalline silicon would be able to take advantage of the high absorption capabilities of amorphous silicon and the electron transport capabilities of polycrystalline silicon. Polycrystalline nanostructures in the form of wires can also take advantage of other properties of light absorption, trapping and scattering inherent in nanowire structures. These properties of high absorption and electron transport in one device would lead to advances in the search for highly efficient low cost solar cells and sensors. In this work a thin film material composed of an array of polycrystalline silicon nanostructures imbedded in amorphous silicon is fabricated. The crystallization of the amorphous silicon in nanometer select areas was achieved through aluminum induced crystallization. The precise control of crystallization was achieved through a focused ion beam created template of SiO$_2$. The film was characterized utilizing SEM and TEM.
This thesis is approved for recommendation to the Graduate Council.

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<table>
<thead>
<tr>
<th>Chapter</th>
<th>Title</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Introduction</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>1.1 Background</td>
<td>1</td>
</tr>
<tr>
<td></td>
<td>1.2 Why Aluminum Induced Crystallization?</td>
<td>4</td>
</tr>
<tr>
<td></td>
<td>1.3 Plasma Enhanced Chemical Vapor Deposition</td>
<td>5</td>
</tr>
<tr>
<td></td>
<td>1.4 RF Sputtering</td>
<td>9</td>
</tr>
<tr>
<td></td>
<td>1.5 Research Purpose and Objective</td>
<td>11</td>
</tr>
<tr>
<td></td>
<td>1.6 Organization</td>
<td>13</td>
</tr>
<tr>
<td>2</td>
<td>Characterization Methods and Tools</td>
<td>14</td>
</tr>
<tr>
<td></td>
<td>2.1 Overview of Characterization Equipment</td>
<td>14</td>
</tr>
<tr>
<td></td>
<td>2.2 Scanning Electron Microscope</td>
<td>14</td>
</tr>
<tr>
<td></td>
<td>2.3 Transmission electron microscope</td>
<td>21</td>
</tr>
<tr>
<td></td>
<td>2.4 Focused Ion Beam Processes</td>
<td>24</td>
</tr>
<tr>
<td>3</td>
<td>Preliminary Investigations</td>
<td>32</td>
</tr>
<tr>
<td></td>
<td>3.1 Methods of Creating Aluminum Nanodots</td>
<td>32</td>
</tr>
<tr>
<td></td>
<td>3.2 Polycarbonate Track Etch/ Anodized Aluminum Membranes</td>
<td>32</td>
</tr>
<tr>
<td></td>
<td>3.3 Diblock Copolymers</td>
<td>34</td>
</tr>
<tr>
<td></td>
<td>3.4 Molecular Beam Epitaxy</td>
<td>35</td>
</tr>
<tr>
<td>4</td>
<td>Experimental Procedure</td>
<td>38</td>
</tr>
<tr>
<td></td>
<td>4.1 Substrate Cleaning Procedures</td>
<td>38</td>
</tr>
<tr>
<td></td>
<td>4.2 Deposition Procedures</td>
<td>39</td>
</tr>
<tr>
<td></td>
<td>4.3 Experimental Procedure for Track Etch Membranes/Anodized Aluminum Anodisc</td>
<td>40</td>
</tr>
<tr>
<td></td>
<td>4.4 Experimental Procedure for Diblock Copolymers Template</td>
<td>41</td>
</tr>
<tr>
<td></td>
<td>4.5 Experimental Procedure for Molecular Beam Droplet Epitaxy</td>
<td>42</td>
</tr>
<tr>
<td></td>
<td>4.6 Focused Ion Beam Pattern Creation</td>
<td>43</td>
</tr>
<tr>
<td></td>
<td>4.7 Deposition/Annealing/Removal of Aluminum</td>
<td>44</td>
</tr>
<tr>
<td></td>
<td>4.8 Transmission Electron Microscope Sample Preparation</td>
<td>44</td>
</tr>
<tr>
<td>5</td>
<td>Results and Discussion</td>
<td>50</td>
</tr>
</tbody>
</table>
5.1 Results from Anodized Aluminum Anodisc .......................................................... 50
5.2 Results of Polycarbonate Track Etch Membrane ............................................ 53
5.3 Results from Diblock Copolymer Templates .................................................... 57
5.4 Results from Molecular Beam Droplet Epitaxy ................................................. 65
5.5 Results from SiO₂ Template .............................................................................. 68
Chapter 6: Conclusion and Future Work ................................................................... 81
References .................................................................................................................. 83
Appendix A: Description of Research for Popular Publication .................................. 87
Appendix B: Executive Summary of Newly Created Intellectual Property ................. 90
Appendix C: Potential Patent and Commercialization Aspects of listed Intellectual Property
Items ............................................................................................................................. 91
  C.1 Patentability of Intellectual Property (Could Each Item be Patented) .................... 91
  C.2 Commercialization Prospects (Should Each Item Be Patented) ............................ 91
  C.3 Possible Prior Disclosure of IP .......................................................................... 91
Appendix D: Broader Impact of Research ................................................................... 93
  D.1 Applicability of Research Methods to Other Problems ....................................... 93
  D.2 Impact of Research Results on U.S. and Global Society .................................... 93
  D.3 Impact of Research Results on the Environment ............................................... 94
Appendix E: Microsoft Project for MS MicroEP Degree Plan ...................................... 95
Appendix F: Identification of All Software Used in Research and Thesis/Dissertation Generation ............................................................................................................. 96
List of Figures

Figure 1.3.1: Steps of CVD process.................................................................................................................. 6
Figure 1.3.2: MVSystems PECVD chamber .................................................................................................... 7
Figure 1.4.1 MVSystems sputtering chamber schematic .................................................................................. 11
Figure 1.5.1: Array of polycrystalline nanodots and roots embedded in amorphous silicon on a silicon substrate.................................................................................................................................................. 12
Figure 1.5.2: Single crystalline silicon nanopit with crystalline dendrites growing from the nanopit.......................................................... 13
Figure 2.2.1: Signals generated from electron beam and sample interaction [17] .................................... 17
Figure 2.2.2: Image scanning electron microscope components [26] ......................................................... 21
Figure 2.3.1: Image of Transmission Electron Microscope[29] .................................................................. 22
Figure 2.3.2: Bragg diagram of beam interaction with crystalline sample[33] ........................................... 23
Figure 2.4.1: Schematic example of Focused Ion Beam deposition............................................................. 26
Figure 2.4.2: Schematic of Focused Ion Beam system [41] ........................................................................ 27
Figure 2.4.3: Image of Liquid Metal Ion Source[43] .................................................................................... 28
Figure 2.4.4: Schematic of gas field ion source[44] .................................................................................... 29
Figure 3.2.1: Left: image of Aluminum anodisc/ Right is image of honeycomb structure of Anodisc[47] .................................................................................................................................................... 33
Figure 3.2.2: Image of polycarbonate track etch membrane[48] ................................................................. 33
Figure 3.3.1: a) lamellae form b) cylinder form c) spheres[50] ..................................................................... 35
Figure 3.2.28: III-V Molecular beam epitaxy system[52] ....................................................................... 37
Figure 4.1.1: Deposition Tray ...................................................................................................................... 38
Figure 4.2.1: MVSystems Cluster Tool ................................................................. 39

Figure 4.2.2: MVSystems Cluster tool Schematic .................................................. 40

Figure 4.6.1: Bitmap Focused Ion Beam Pattern ...................................................... 43

Figure 4.8.1: Probe and Platinum source are placed near the surface for TEM sample preparation ................................................................. 45

Figure 4.8.2: Protective Platinum strip is deposited upon intended area for TEM sample preparation ................................................................. 46

Figure 4.8.3: Rectangular trenches are etched above and below the platinum strip. Stage is then tilted and thin sample under protective strip is etched away from surface. ................. 46

Figure 4.8.4: Probe is brought close enough to touch the sample in preparation to deposit platinum ................................................................................................. 47

Figure 4.8.5: Platinum is deposited to attach the probe to the sample and then the ion beam is used to completely detach the sample from the surface ......................................................... 48

Figure 4.8.6: Stage is lowered away from the probe before retracting the probe ................. 48

Figure 4.8.7: Probe with sample is gentle brought into contact with TEM grid prong in preparation to attach with platinum ................................................................................................. 49

Figure 4.8.8: TEM sample is attached with platinum and detached from the probe by etching with the ion beam ................................................................................................. 49

Figure 5.1.1: Anodisc with deposited aluminum deposited onto the surface ..................... 51

Figure 5.1.2: SEM image of substrate from Anodisc aluminum deposition ..................... 51

Figure 5.1.3 SEM image of sporadic aluminum deposition on surface under Anodisc ....... 52

Figure 5.1.4: SEM image of random aluminum deposition through Anodisc template ........ 52

Figure 5.2.1: SEM Image of polycarbonate track etch membrane after aluminum deposition .... 54
Figure 5.2.2: SEM image of aluminum dots deposited through polycarbonate track etch membrane with 80nm diameter holes ................................................................. 55

Figure 5.2.3: SEM image of aluminum dots deposited through polycarbonate track etch membranes with 100nm diameter holes ................................................................. 55

Figure 5.2.4: SEM image of aluminum dots deposited through polycarbonate track etch membranes with 200nm diameter holes ........................................................................ 56

Figure 5.2.5: SEM image of aluminum dots deposited through polycarbonate track etch membranes with 400 nm diameter holes ........................................................................ 56

Figure 5.2.6 Nanodot Diameter (nm) vs. Template diameter (nm) with 15% error ............... 57

Figure 5.3.1: SEM image of 2000 rpm spincoated PS-b-P4VP after solvent anneal and development .................................................................................................................. 59

Figure 5.3.2: SEM image of 3000 rpm spin coated PS-b-P4VP after solvent anneal and development .................................................................................................................. 59

Figure 5.3.4 Higher magnification SEM image of 3000 rpm spin coated PS-b-P4VP after solvent anneal and development .................................................................................................. 60

Figure 5.3.4: HRSEM image of 3000 rpm spin coated PS-b-P4VP after solvent anneal and development showing phase separation .................................................................................. 60

Figure 5.3.5: SEM image of 500 rpm spin coated PS-b-P4VP after solvent anneal and development .................................................................................................................. 61

Figure 5.3.6 Higher magnification of SEM image of 500 rpm spin coated PS-b-P4VP after solvent anneal and development .................................................................................. 61

Figure 5.3.7: SEM image of 1500 rpm spin coated PS-b-P4VP after solvent anneal and development .................................................................................................................. 62
Figure 5.3.8: Higher magnification SEM image of 1500 rpm spin coated PS-b-P4VP after solvent anneal and development ............................................................. 62

Figure 5.3.9: SEM image of 2500 rpm spin coated PS-b-P4VP after solvent anneal and development ........................................................................................................... 63

Figure 5.3.10: Higher magnification SEM image of 2500 rpm spin coated PS-b-P4VP after solvent anneal and development ........................................................................................................... 63

Figure 5.3.11: SEM image of 3500 rpm spin coated PS-b-P4VP after solvent anneal and development ........................................................................................................... 64

Figure 5.3.12: Higher magnification of 3500 rpm spin coated PS-b-P4VP after solvent and development ........................................................................................................... 64

Figure 5.3.13: 2000 rpm spincoated PS-b-P4VP /18 hr solvent anneal and development ........ 65

Figure 5.3.14: 2000 rpm spin coated PS-b-P4VP/ 24 hr solvent anneal and development .... 65

Figure 5.4.1: HRSEM image of aluminum nanodots from 2 2nm MBE deposition ................. 66

Figure 5.4.2: Higher magnification HRSEM image of aluminum nanodots from 2nm MBE deposition ........................................................................................................... 67

Figure 5.4.3: HRSEM image of aluminum nanodots from 6nm MBE deposition ................. 67

Figure 5.4.4: Higher magnification image of aluminum nanodots from 6nm MBE deposition... 68

Figure 5.5.1: TEM sample with measured sample thickness.................................................... 70

Figure 5.5.2: HRSEM image of array of holes in SiO₂ ................................................................. 70

Figure 5.5.3: Higher resolution image of HRSEM Focused Ion Beam hole in SiO₂ ............... 71

Figure 5.5.4: Schematic of cross-section of TEM sample array of holes ............................... 71

Figure 5.5.5: Crosssection TEM sample of array of highlighted holes ................................. 72
Figure 5.5.6: Higher magnification image of one of the TEM crosssection of Focused Ion Beam holes ........................................................................................................................................72

Figure 5.5.7: Selected Area Diffraction Image of area A from figure 5.1.5 directly under the hole ........................................................................................................................................73

Figure 5.5.8: HRSEM image of array of holes in silicon after deposition/annealing/and etching of aluminum for substrate ........................................................................................................................................74

Figure 5.5.9: Higher magnification HRSEM image of array of holes from figure 5.1.7 ........74

Figure 5.5.10: HRSEM image of one of the holes with morphological changes in the surface... 75

Figure 5.5.11: Schematic representation of TEM cross-section after deposition/annealing/and etching of aluminum ........................................................................................................................................76

Figure 5.5.12: TEM cross-section image of the array of holes from figure 5.1.7 .................76

Figure 5.5.13: Higher magnification image of TEM crosssection image of array of holes ....77

Figure 5.5.14: SAED image of Area C Figure 5.1.10.................................................................77

Figure 5.5.15: SAED image of Area B on Figure 5.1.10..........................................................78

Figure 5.5.16: Highlighted atomic planes of crystallized region Figure 5.1.13 ......................80
List of Tables

Table 2.2.1: Comparison of Optical and Electron Microscopes [14] ........................................ 16

Table 2.4.1: Ion Beam Process Characteristics[36]................................................................. 25

Table 2.4.2: Energy Requirements Associated with Various Physical Processes [39] .......... 26

Table 5.4.1: Surface Characteristics of MBE Nanodot Growth ............................................. 68

Table 5.5.1: Orientation and atomic lattice distance of Aluminum and Silicon ....................... 79
Chapter 1: Introduction

1.1 Background

Silicon is the second most abundant element in the earth’s crust. Not only is it crucial to the construction industry as a constituent of stone, glass, concrete and cement but it has also been the dominant material of choice for the semiconductor and solar cell industries. Silicon solar cells throughout the semiconductor and solar cell industry can be found with three different forms of silicon 1) crystalline silicon 2) amorphous silicon or 3) polycrystalline silicon.

About eighty percent of these solar cells are composed of monocrystalline silicon; the other eighteen to twenty percent are comprised of different thin film solar cells. The industry standard process for producing monocrystalline silicon is the Czochralski process. The Czochralski process involves slowly pulling a seed crystal from molten SeG polycrystalline silicon. The resultant monocrystalline silicon crystal is usually greater than 12.5 cm in diameter and has a length of 1 to 2 m. Up to half the ingot is lost in cutting waste. The monocrystalline silicon crystal is then cut into 300 to 350 μm thick wafers. The high temperature involved with the Czochralski process, the cutting waste, and the thickness of the monocrystalline silicon needed to absorb a usable amount of light all add to the cost of solar cells. These factors are what help fuel the research in thin film solar cell technology.

The materials most commonly used for thin film silicon solar cells are amorphous silicon and polycrystalline materials. The polycrystalline materials most used are polycrystalline silicon, cadmium telluride or cadmium indium (gallium) deselenide. All of these are amenable to large area deposition, with amorphous silicon being the more developed of the thin film processes. These materials can also be deposited at much lower temperatures than the Czochralski process and they use less than 1% of the amount of material than wafer based silicon processes. Common
methods for thin film deposition include physical vapor deposition (PVD), chemical vapor deposition (CVD), electrochemical vapor deposition or a mixture of PVD and CVD.

The wafer based monocrystalline silicon retains its dominance because of its well developed manufacturing process and its ability to provide stable solar cell yields of 11% to 16%. Thin film solar cells solve several major issues associated with the high cost of the manufacturing involved with the wafer based technology and provide yields of 10% commercially. In the end the process with a reasonable yield at a low manufacturing cost will become the dominant process in the solar cell industry.

Monocrystalline silicon has a highly periodic structure which aids in the charge carrier mobility. It being an indirect bandgap semiconductor means that a vast majority of the recombination that occurs within crystalline silicon will be due to impurities or lattice defects. These defects and impurities cause trap sites that reduce the electron transport capabilities of a semiconductor. Having a highly periodic structure throughout the material in contrast to polycrystalline silicon or amorphous silicon allows mono- crystalline silicon to have the advantage in charge carrier transport over the other two states of silicon.

Monocrystalline silicon being an indirect band gap semiconductor also comes with drawbacks, such as having poor absorption properties. In an indirect bandgap semiconductor the \( k \) vectors of the maximum energy in the valence band and the minimum energy in the conduction band occur at different values in the crystal momentum.\[1\] The direct bandgap semiconductors such as Gallium Arsenide have their \( K \) vectors at the same value of crystal momentum. Direct band gap semiconductors when exposed to photons need energy equivalent to the bandgap energy to directly transition electrons from the valence band to the conduction band. On the other hand indirect band gap semiconductors need much larger photon energies to get direct transitions.
from the valence band to the conduction band. The indirect band gap energy of monocrystalline silicon is 1.1 eV and the direct band gap energy is 3.4 eV. In order for the electron to make the full transition to the valence band in the indirect bandgap semiconductors it needs a photon and a phonon. A phonon is a quantized unit of lattice vibration.[2] The probability of the indirect bandgap semiconductor obtaining a photon of the right energy and a phonon is lower than the probability of a direct bandgap semiconductor obtaining only a photon. This causes a lowering of the absorption coefficient and the light must travel further into the monocrystalline material before it is absorbed. This makes it necessary to have more indirect bandgap material for comparable absorption to direct bandgap material.

Amorphous silicon is an allotropic noncrystalline form of silicon. It is a direct band gap semiconductor. Its bandgap energy ranges from 1.4 ev to 1.8 ev. Needless to say its absorption properties are much greater than that of crystalline silicon and are one of the reasons this material is a staple material in the thin film photovoltaic industry.

Amorphous material also has its drawbacks. Being an amorphous material means that it has no long or short term periodic structure. There will be more defects and dangling unterminated silicon atoms present in this state of silicon. The high level of defects and dangling bonds causes there to be a greater probability that charge carriers will be trapped at these sites and never collected. The high amount of defects present in amorphous silicon prevented it from being practical for the fabrication of electronic devices in the beginning. It was later found by accident that when amorphous silicon is deposited from silane (SiH₄) it reduces the defect sites by several orders of magnitude. This material is known as hydrogenated amorphous silicon (a-Si:H). It was also discovered that hydrogen reduces the defect sites in the material by bonding to
terminated silicon atoms.[3] This discovery made amorphous silicon a contender as a usable semiconductor material.

Polycrystalline silicon is a form of silicon that is a collection of monocrystalline crystallites connected through grain boundaries. These grain boundaries are composed of disordered atoms of silicon and serve as recombination sites for photogenerated carriers. Inside these grain boundaries the crystalline silicon may have different crystal orientation than its neighbors and it is assumed that charge carriers act the same as if in bulk silicon material.

Polycrystalline silicon can be formed by utilizing a seed crystal and allowing molten silicon to cool or deposit at 625°C. It can also be formed by depositing amorphous silicon onto a substrate and crystallizing it at high temperatures during solid phase crystallization or at lower temperatures during metal induced crystallization. The metal induced crystallization process involves a thin film of metal being deposited onto a thin film of amorphous silicon and then annealed. It has been found that crystallization of amorphous silicon by this method can be performed at temperatures as low as 150°C.

Polycrystalline silicon is an indirect bandgap semiconductor with the same bandgap as crystalline silicon but its carrier transport properties suffer because of the grain boundaries surrounding the numerous crystallites. Polycrystalline silicon’s absorption capabilities are greater than that of monocrystalline silicon because of its light scattering from lattice imperfections.[4]

1.2 Why Aluminum Induced Crystallization?

The question must be asked why use aluminum as the crystallizing catalyst for the metal induced crystallization of a thin film of amorphous silicon. There are at least twenty known metals that can be used to crystallize amorphous silicon. These metals include Ti, Hf, Zr, Nb, V, Ta, Cr, Mo, W, Mn, Re, Fe, Ru, Co, Rh, Ir, Ni, Pd, Pt, Cu, Ag, Au, and Al.[5] Out of these
metals only seven of these metals reduce the crystallization temperature of amorphous silicon. These metals are Ni, Pt, Cu, Pd, Au, Al, and Ag.[5] Of these metals, the metals which provide the lowest crystallization temperatures are Au and Al. Not only is aluminum less expensive than gold but it is one of the most abundant elements on earth thus making a prime candidate in the areas of cost effective manufacturing of solar cells. There is another factor that makes aluminum a better candidate than gold. When a metal is used to crystallize amorphous silicon it also dopes the amorphous silicon becoming an impurity within the new polycrystalline silicon material. The energy level of gold as an impurity within silicon is near the middle of silicon energy band. These near midband energy levels provide readily available recombination centers of electrons and holes before they can be collected.[6] This will decrease device performance. If these recombination centers are too numerous then the improvements made by doping of the amorphous silicon with that metal will be negated and the closer that metals energy level is to silicon’s midband energy level worse the effect.[6]

1.3 Plasma Enhanced Chemical Vapor Deposition

The thin film depositions of amorphous silicon involved in this research were fabricated utilizing a process known as plasma enhanced chemical vapor deposition (PECVD). In traditional chemical vapor deposition (CVD) a gas or a mixture of gases are introduced into the deposition chamber and the substrate is heated to cause a chemical reaction in the gases near the surface of the substrate.[7] An illustrative figure and steps of the chemical vapor deposition process is shown in Figure 1.3.1.
Steps of CVD Process [7]

1. Transport of reactants into deposition chamber
2. Transport of reactants by diffusion from the main stream of gas through boundary layer to the surface of substrate
3. Adsorption of reactants to surface
4. Chemical reaction or decomposition at the surface
5. Desorption of byproducts from the surface
6. Transport of byproducts by diffusion through the boundary layer and back to gas stream
7. Transport of byproducts away from deposition region

A plasma enhanced chemical vapor deposition process utilizes thermal energy and plasma energy to create the reactions needed for thin film deposition. Many different films may be created with PECVD, but for the purpose of this research the deposition process will be the
deposition of amorphous silicon. In the deposition of amorphous silicon the reactant gas silane (SiH₄) is introduced into a chamber with the substrate. Heat, usually between 200 -350°C, is provided by a heater installed in the chamber. Plasma is then contained between two electrodes. These electrodes could be two plate electrodes for a direct current discharge or the conductive walls of the chamber and a plate electrode for an alternating current discharge. An illustrative figure of the plasma enhance chemical vapor deposition chamber utilized in this research can be seen below in Figure 1.3.2.

Figure 1.3.2: MVSystems PECVD chamber
The forming of the plasma occurs by applying an electric field at 13.56 Mhz to a low pressure gas. High frequency electric fields are used in the alternating current discharge because it allows lower voltages to be used to obtain plasma discharge and it produces approximate time independent discharges that will not repeatedly initiate and extinguish. Once the plasma has been initiated it sustains itself by high energy electrons bombarding and ionizing atoms and molecules.

There are many interactions occurring in the plasma that aid in producing a thin film. The main three factors are plasma induced fragmentation, free radical generation, and ion bombardment of the surface. In the plasma, the bombardment of SiH₄ with high energy electrons causes the gas to dissociate and create ionized, neutral, or fragmented molecules and free radicals such as SiH, SiH₂, and SiH₃. The free radicals have unpaired electrons and are highly reactive. These highly reactive free radicals formed from inelastic collisions, along with the other species present, are absorbed into the surface and interact with each other and the surface to form a thin film. The mass difference between the gas molecules and the accelerated electrons cause the electrons not to lose much energy during elastic collisions in the plasma.[8] The inelastic collisions between electrons and gas molecules will also not release much energy unless the electron is above the threshold energy. During deposition there is a potential between the wafer surface and the plasma. The wafer surface is the negative end of this potential difference. This will attract the positive ions to the surface of the wafer at accelerated speed causing bombardment of the surface by positive ions. Some high energy electrons may also be able to strike the surface. This bombardment of the surface transfers energy to the surface which enhances reactions that are occurring at the surface of the substrate. The end result of the plasma
induced fragmentation, free radical generation and ion bombardment of the surface is a thin film of hydrogenated amorphous silicon.

1.4 RF Sputtering

The MVSystems deposition tool used in this research has the capability of depositing amorphous silicon and aluminum through PECVD or sputtering. Sputtering is a physical vapor deposition method that does not require thermal energy. This deposition process occurs by ejecting surface atoms from a target through momentum transfer from energetic ions supplied through plasma.[9, 10] The PECVD system and the sputtering system used in this work were quite similar. There are many different types of sputter deposition techniques, but for this research RF sputter deposition will be discussed in detail. In order to understand the radio frequency sputtering technique a basic understanding of DC sputtering is necessary. In DC sputtering, similar to DC PECVD, a voltage is applied across two electrodes and it creates plasma. Argon is used in both DC and RF sputtering most frequently because the mass of argon is large enough to make the interaction between the ion and the electric field negligible at 13.56 Mhz.[11] Other lighter gases such as He which are affected by the RF field at these frequencies will cause a change in the arrival energies of the ions [11]. The plasma created will be composed of neutral argon atoms, positive argon ions, and electrons. The cathode is the material to be deposited and it is also known as the target. The anode, which is usually grounded, will be where the substrate will be located. The positive ions located within the plasma are accelerated toward the cathode because of the voltage bias applied. These energetic ions striking the surface sputter atoms from the surface that then travel to through the plasma to the surface of the substrate where they condense and form a film. An important fact for DC sputtering is that the target must be conductive since it acts as an electrode. Radio Frequency sputtering was developed as a
useful technique to deposit insulating materials. DC sputtering was inadequate for sputtering of insulating materials because when a negative DC voltage is applied the target positive ions are attracted to the target and a positive charge accumulates. This causes the negative voltage at the surface to become less than the amount needed to sustain the plasma.

The answer to this problem came in the form of RF voltages being capacitively coupled to the plasma through the insulating target. This would negate the charge buildup on the surface by continuous striking of electrons. This occurs because of the mass difference between electrons and ions. Electrons can respond much faster to the changes in the electric field than the ions. As a result, a buildup of electrons occurs at the electrodes causing a DC potential to be created and maintained between the electrodes and the plasma.\[12\] This negative self bias has to meet the requirements of the net current being zero averaged over each cycle. \[12\]The heavier ions, although slow to react to the rapidly changing electric field, will be effected by the DC potential between the plasma and the electrodes. The negative self bias will accelerate these positive ions toward the electrodes. This brings about the issue of both electrodes being bombarded with ions, and both electrodes being sputtered would cause difficulties in film deposition. The voltage drop between electrode one and two are related to the electrode areas as shown in Equation 1.1.

\[
\frac{V_1}{V_2} = \frac{A_2}{A_1^{m}}
\]

Equation 1.1

Because RF current must remain equal for both electrodes if the area of one of the electrodes is changed then the current density must also change to keep the current of electrode one and two equal. In essence the smaller electrode will require higher current density to keep the current equal with electrode two. This will cause the electric fields to higher around the smaller electrode. This in turn will cause the voltage drop to be much higher for the smaller electrode causing almost all sputtering to occur at the smaller electrode and mimicking the
voltage distribution of the DC sputtering but without the conductive target electrode. Another method of making the target electrode smaller is to increase the size of the other wafer electrode. This can be done by connecting the wafer electrode to the chamber or making the chamber and the wafer electrode electrically the same by connecting them both to ground. This method is shown in the MVsystems sputtering chamber shown in Figure 1.4.1.

![Figure 1.4.1 MVSystems sputtering chamber schematic](image)

1.5 Research Purpose and Objective

Polycrystalline and amorphous silicon as mentioned earlier are staples in the semiconductor thin film industry. Their properties, strengths and weaknesses have been
extensively researched. In the past when forming polycrystalline silicon thin films the method was to either deposit as a polycrystalline silicon film at high temperatures or to deposit amorphous silicon and crystallize it at a low temperature by annealing with a thin film metal catalyst. This method of crystallizing is highly efficient for complete conversion of materials but it could also be used for hybrid materials.

The goal of this research is to produce a composite material. This material could be composed of nanometer size nanocrystalline crystallites embedded in matrix of amorphous silicon as shown below. The crystallites are expected to have dendritic nanoroots that extend into the amorphous material to aid in light trapping and carrier transport. In this research work the focused will be the fabrication of this new material and the characterization of this new material. It is the hypothesis of this research that the new composite material composed of amorphous silicon and polycrystalline silicon will exhibit the best properties of both of its subsequent parts.

Figure 1.5.1: Array of polycrystalline nanodots and roots embedded in amorphous silicon on a silicon substrate
Figure 1.5.2: Single crystalline silicon nanopit with crystalline dendrites growing from the nanopit

1.6 Organization

This thesis is divided into six chapters. Chapter one will consist of a small background summary, research purpose and organizational guide to the thesis. Chapter two will divulge information on methods to create metal nanoparticles on a silicon surface. Chapter three presents experimental procedure with brief review of deposition methods used. Chapter four will introduce the characterization methods used with brief sections on each characterization tool. Chapter five will contain results and discussion and Chapter six will contain conclusions and future work.
Chapter 2: Characterization Methods and Tools

2.1 Overview of Characterization Equipment

The equipment utilized for characterization included an environmental scanning electron microscope, transmission electron microscope and the focused ion beam. The scanning electron microscope was utilized for investigating morphological changes in the sample. The transmission electron microscope was used to investigate internal structure changes of the substrate before and after processing. The focused ion beam was used to create thin samples from the substrate to be investigated using the transmission electron microscope. The characterization equipments used in this work were a FEI Titan 80-300 transmission electron microscope, a FEI Environmental Scanning Electron Microscope XL 30, and a FEI XT Nova Nanofab (high resolution SEM with focused ion beam).

2.2 Scanning Electron Microscope

The scanning electron microscope is a microscope that utilizes electrons instead of light to create an image from a sample. Its development is based on De Broglie’s discovery that electrons have an assigned wavelength.\[13\] The wavelength of electrons is very small when compared with visible light and at an accelerating voltage of 100kv the electrons wavelength will be .004 nm.\[13\] These extremely small wavelengths of the electrons allow greater resolution of a sample than an optical microscope.\[13\] Why is the wavelength of the electron so important to the resolution of an electron microscope? It is important because of an equation known as Abbe’s equation as shown in Equation 2.1.
\[
d = \frac{0.612 \lambda}{n \sin \alpha}
\]

- \(d\) = resolution
- \(\lambda\) = wavelength of imaging radiation
- \(n\) = index of refraction of the medium between the light emitting point and the lens, relative to free space
- \(\alpha\) = aperture angle or half angle of cone of light from the specimen to the front lens of the objective
- \(n \sin \alpha\) = N.A. numerical aperture (represents the light gathering power of the numerical lens)

To obtain the best possible resolution the wavelength of the imaging must be small and the numerical aperture needs to be as large as possible. The smallest wavelength for visible light is around 400 nm but the wavelength of electrons is as mentioned earlier dependent upon the particle velocity. It can be calculated using Equation 2.2 widely known as the De Broglie Equation.

\[
\lambda = \frac{h}{mv}
\]

- \(\lambda\) = wavelength of particle
- \(h\) = Plank’s constant
- \(m\) = mass of the particle
- \(v\) = velocity of the particle

A comparison of two different types of electron microscopes and an optical microscope can be seen in Table 2.2.1.
### Table 2.2.1: Comparison of Optical and Electron Microscopes [14]

<table>
<thead>
<tr>
<th></th>
<th>Optical Microscope</th>
<th>Scanning Electron Microscope</th>
<th>Transmission Electron Microscope</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Objective</strong></td>
<td>Surface Morphology in sections of 1-40 μm</td>
<td>Surface morphology</td>
<td>Internal structure of a material in sections of 40-150 nm</td>
</tr>
<tr>
<td><strong>Source of Illumination</strong></td>
<td>Visible Light</td>
<td>High Speed electrons</td>
<td>High Speed electrons</td>
</tr>
<tr>
<td><strong>Resolution limits</strong></td>
<td>Ca. 200 nm</td>
<td>Ca. 3-6 nm</td>
<td>Ca. 3-6nm</td>
</tr>
<tr>
<td><strong>Magnification</strong></td>
<td>10-1000x</td>
<td>20-150,000x</td>
<td>500-500,000x</td>
</tr>
<tr>
<td><strong>Depth of Field</strong></td>
<td>.002-.05 nm (N.A. 1.5)</td>
<td>.003-1mm</td>
<td>.004-.006mm (N.A. 10⁻³)</td>
</tr>
<tr>
<td><strong>Lens type</strong></td>
<td>Glass</td>
<td>Electromagnetic</td>
<td>Electromagnetic</td>
</tr>
<tr>
<td><strong>Image formation</strong></td>
<td>On eye by lens</td>
<td>Cathode ray tube</td>
<td>Phosphorescent plate by lenses</td>
</tr>
<tr>
<td><strong>Minimum Resolution</strong></td>
<td>0.22 μm (with average wavelength of 550 nm and a numerical aperture of 1.4[15])</td>
<td>1 nm to 20 nm dependent upon instrument[16]</td>
<td>0.2-0.5 nm[17]</td>
</tr>
</tbody>
</table>

A focused beam of electrons scans linearly across the surface with electrons striking in different areas. The impinging electrons cause interactions with the surface of the sample in the form of elastic and inelastic scattering. This elastic and inelastic scattering can result in the release of backscattered electrons, auger electrons, secondary electrons, transmitted electrons and x-rays from the sample.[18] These can be seen in Figure 2.2.1.

The backscattered electrons, transmitted electrons and secondary electrons can all be collected by electron detectors and displayed. Composition information can be gathered from the analysis of auger electrons and excited x rays. Backscattered electrons are caused by single or multiple scattering of an incident electron with the atomic nucleus or outer shell electron of the sample.[19] These electrons are characterized by low energy loss and a scattering angle of 90° or more and many times leaving the surface with energy greater and 50 eV. Elements with high atomic numbers have more protons and thus cause large number electrons to be backscattered.
The large amount of energy associated with backscattered electrons makes it difficult for them to be absorbed. This causes the region where backscattered electrons are produced to be larger than that of secondary electrons. This in turn causes lateral resolution problems but also allows for information about the sample from beneath the surface. They can be collected for morphology or compositional data.

The inelastic collisions which are characterized by a large transfer of energy from the electron beam to atoms in the sample produces the secondary electrons. When the electron beam strikes the sample it ionizes atoms and loosely bound electrons within the sample are released. These released electrons are the secondary electrons. Secondary electrons are characterized as low energy, usually between 3-5 eV, which means they could only have escaped from a few
nanometers below the surface.[21] This attribute allows secondary electrons to be utilized as reliable indicators of beam position and surface morphology.

Auger electrons are produced when an atom in the substrate is ionized and an electron from an inner shell escapes and then an outer shell electron falls back to fill the vacancy left in the inner shell.[22] The auger electron will carry away this energy after the electron fills this vacancy. Different elements have different energies characteristic to them so chemical information can be gathered from the amount of energy released.

Characteristic x-rays can be produced when an inner shell electron is displaced by an electron from the electron beam and an outer shell electron falls back to fill the vacancy and to reestablish charge balance.[22] When this occurs an x-ray photon is released and the energy of this x-ray can be used to obtain chemical information about the sample.

The basic components of a scanning electron microscope include electron gun, magnetic lenses, scanning coil, vacuum system with chamber, detectors (scintillation or solid state) and an image recorder. A triode electron gun is composed of three components a filament which is the cathode, a Wehnelt cylinder, and an anode.[23] The cathode material is usually tungsten but other materials can also be used such as lanthanum hexaboride, field emission guns or Schottky. The operation of the electron gun consists of a voltage being applied to the tungsten loop causing it to heat to above 727°C. Accelerating voltages for scanning electron microscopes are usually between 5kV to 30kV. The anode with respect to the cathode is positive and it attracts the electrons. The electrons accelerate from the filament to the anode and past the anode down the column of the scanning electron microscope. One of the biggest parameters for the electron gun is its brightness ($\beta$). Improving the brightness improves the scanning electron microscopes
imaging abilities. Filament material, temperature of filament and voltage are factors that affect the brightness.

\[ \beta = \frac{\text{current}}{\text{area} \times \text{solid angle}} \]  

Equation 2.3

The magnetic lenses job is to focused the electrons from the electron gun on to the sample to provide optimal images.[24] The magnetic lenses are similar to solenoids in that they are composed of copper wire wound round an iron fixture in a particular geometry to Focused the beam. The focal length of the lens in the scanning electron microscope depends on the gun voltage and the current within the copper coil.

\[ f_c = \frac{k \nu}{Lc^2} \]  

Equation 2.4

- \( f_c \) = focal length of the condenser
- \( k \) = a number that depends on the geometry of the pole pieces and the number of turns in the coil
- \( \nu \) = the accelerating voltage
- \( Lc \) = the lens current

There are two coils located in the bore of the objective lens that cause the beam to scan over a designated area. This process is also known as rastering.

The typical vacuum for a scanning electron microscope is \( 10^{-6} \) torr. When the scanning electron microscope is in operation the electron gun, column, columns and detectors are kept in vacuum. Suitable vacuum is usually provided through the joint use of two types of pumps. The first pump is a mechanical pump which will bring the vacuum to \( 10^{-2} \) torr. The most commonly used pump would be a rotary mechanical pump. The second pump starts once the
vacuum has reached $10^{-2}$ torr. These types of pumps are used to reach $10^{-4}$ to $10^{-6}$ torr. Some examples of the types of pumps used for these high vacuum processes are vapor diffusion pumps, turbomolecular pumps, gettering pumps, sputter ion pumps and cryoadsorption pumps. Without the vacuum there would be large amounts of scattering of electrons by gas atoms present in the chamber.

Detectors for backscattered electrons and secondary electrons are usually either scintillation or solid state detector. With the scintillation detector electrons that pass through the screen are accelerated into photomultiplier tube.[25] In this process electrons strike a fluorescent screen which emits photons upon contact.[26] These photons then make contact with a photocathode which converts the photon back into an electron. The electrons are then magnified though a series of increasing potential anodes. [27]Then they are collected at the final anode as an electrical signal.

The solid state detectors perform the same operation but instead of using a photocathode a photodiode is used. When the photon makes contact with the photodiode an electrical signal is produced.[28] The basic schematic for scanning electron microscope is represented by Figure 2.2.2.
2.3 Transmission electron microscope

Another type of electron microscope is the transmission electron microscope. It is used to study the internal structure of sample that is only 200-40 nanometers thick. There are several methods for preparing these thin samples. A small sample is taken from the larger sample utilizing electron discharge or ion milling. Then this sample is milled and polished to the desired thickness dependent upon the accelerating voltage of the transmission electron microscope. The transmission electron microscope works similar to the scanning electron microscope in the beginning. The basic components of a transmission electron microscope include source of illumination, (triode electron gun) condenser lenses, objective lenses, objective lens aperture and projector lens as can be seen in Figure 4.2.1.
A voltage of 200kV or higher is applied to a tungsten filament with transmission electron microscopes. In transmission electron microscopes this is between the ranges of 100 to 300kV. Electromagnetic coils also known as condenser lenses Focused the beam onto the sample. The electrons then pass through the sample. If the sample is too thick then there will be an excessive amount of absorption and diffraction and no transmitted electrons for imaging. While the electrons are passing through the sample there are several interactions that aid in the forming of an image. As electrons are traveling through the inner structure of the sample they are absorbed, transmitted or scattered because of differences in the atomic arrangement within the sample. The elastically scattered electrons will have a high scattering angle, and the inelastically scattered will have a low scattering angle. There is an objective aperture placed at the back focal plane of the objective lens. It allows contrast by allowing unscattered electrons and most
inelastically scattered electrons to continue down the column.[34] The elastically scattered electrons which have a higher scattering angle are absorbed by the aperture. This process will form a bright field image. Another type of image that can be formed is a dark field image. A dark field image is created by doing the exact opposite of the bright field image process. Instead of blocking the elastically scattered electrons they are allowed to pass through the aperture and the unscattered and inelastically scattered electrons are absorbed.[35] Another option that is available on some transmission electron microscopes is the selected area diffraction image. As mentioned earlier diffraction is one of the interactions that occur between the electron beam and the sample. In crystalline samples scattering may occur in specified directions as defined by the Bragg equation.

\[ n\lambda = 2dsin\theta \]

**Equation 2.5**

- \( n \) = integer
- \( \lambda \) = wavelength
- \( d \) = crystal lattice spacing
- \( \theta \) = angle of diffraction

![Bragg diagram of beam interaction with crystalline sample](image)
These scattered electrons, if they pass through the objective aperture, will produce a bright spot. If they are absorbed, they will produce a dark spot. This diffraction, along with dark field imaging mentioned earlier, can be used to locate crystalline structures within the sample.[37, 38] This process is known as selected area diffraction. Once the electrons have passed through the sample they are focused again utilizing the magnetic lens and then amplified onto a fluorescent screen.

2.4 Focused Ion Beam Processes

The focused ion beam can be utilized for many applications such as micromilling, doping of material, and analyzing structure and composition of a material.[39] In this work the beam was mostly utilized for milling and deposition in the preparation of TEM samples. Different ion beam process characteristics can be seen in Table 2.4.1.

Although there are numerous and various applications for the ion beam and focused ion beam, the ones focused on in this section include beam interaction with the sample during ion beam milling and the ion beam deposition. These two techniques are the techniques utilized in the fabrication of TEM samples.

During ion beam milling, also known as ion etching or ion sputtering, an ion or ions bombard a surface. When performing an ion milling process it is important to know the amount of time it will take to create the pattern or to mill a section of the surface. This can be calculated by utilizing Equations 2.6 and 2.7.[40]
If the energy of the incoming particles is large enough then there will be momentum transfer creating bond breakage and ballistic material ejection at the surface.\cite{41} If the energy is not within this range then other processes will take over, such as physical adsorption and ion implantation, as shown in Table 2.4.2.
Table 2.4.2: Energy Requirements Associated with Various Physical Processes [42]

<table>
<thead>
<tr>
<th>Ion energy (eV)</th>
<th>Reaction</th>
</tr>
</thead>
<tbody>
<tr>
<td>&lt;3</td>
<td>Physical adsorption</td>
</tr>
<tr>
<td>4-10</td>
<td>Some surface sputtering</td>
</tr>
<tr>
<td>10-5000</td>
<td>Sputtering</td>
</tr>
<tr>
<td>10K-20K</td>
<td>Implantation</td>
</tr>
</tbody>
</table>

Not only can ions be used to remove material but they can also be used to deposit material. This process is known as ion deposition and usually requires a precursor gas, many of which are organometallics. During this process the precursor gas adsorbs to the surface and the ion beam is used to dissociate the gas molecules on the surface leaving behind the metal.[43] The ions will also sputter the film just deposited if the gas flow has been stopped or the supply fully exhausted. In focused ion beam deposition this gas is provided from a long capillary tube directly to the area scanned by the focused ion beam. This process can be viewed in Figure 2.4.1.

Figure 2.4.1: Schematic example of Focused Ion Beam deposition
The ion beam is primarily used as a micromachining tool. Focused ion beams can also be used similar to the scanning electron microscope as a characterization tool. When an energetic ion strikes a surface a few electrons are usually emitted. These emitted electrons are collected and used in a similar manner to the way secondary electrons with the scanning electron microscope is used.[43]

The basic components of a focused ion beam microscope consist of ion source, suppressor, extractor, lens, aperture, objective lens, detector, and gas injector. These can be seen in Figure 2.4.2.

![Figure 2.4.2: Schematic of Focused Ion Beam system](image)

[44]
The focused ion beam system begins with the source of ions. The point source of ions for the focused ion beam systems can be provided by either liquid metal ion sources or gaseous field ion source. The liquid metal ion source is the most popular commercially and it has the ability to produce an optically bright focused ion beam. It consists of a Ga$^+$ ion source with a coiled reservoir and a sharpened tungsten tip. An electric field is applied to the tungsten needle in order to obtain the ions. The tungsten tip coil and wire loop are all welded to each other. The tungsten coil which has current passing through it keeps the ion source molten. The tungsten needle provides a path for the molten metal while the electric field is being applied and when it reaches the tip it forms a cusp and emits ions. This cusp is popularly known as a Taylor cone. An image of the liquid metal ion source can be seen in Figure 2.4.3.

Figure 2.4.3: Image of Liquid Metal Ion Source [46]
There other less popular metals and metallic alloys that are capable of being used as liquid metal ion sources. These sources include In, Au/Si, Au/Si/Bi, Pd/As/B. The other source available to focused ion beam systems is the gas field ion source. It consists of a tungsten needle that has been cooled to cryogenic temperatures. On the tip of this needle are condensed gases that may include H, He, Ne, Ar. A voltage is applied between tip and an electrode as before with the liquid metal ion source to extract the ions. A schematic of the gas field ion source may be seen in Figure 2.4.4.

![Figure 2.4.4: Schematic of gas field ion source](image)

When gauging the quality of a focused ion beam there are two characteristics that are examined. These characteristics include the brightness and energy spread of the focused ion beam. The brightness of the focused ion beam is measured in A/cm²sr. Ideally what is
desired is a large current of ions emitted from a small area (the tip of tungsten needle) into a small angle. Containing these like charges takes extreme conditions such as high electric field and the sharp tungsten tip. The formula for brightness is shown in Equation 4.8.

\[ \beta = \frac{I}{\Omega AV} \]  

Equation 2.8

- \( \beta \) = Brightness (A/cm\(^2\) steradian)
- \( I \) = current
- \( A \) = area from which the current is emitted
- \( \Omega \) = the solid angle in which the current is emitted
- \( V \) = the potential through which the ions have been accelerarted

The second factor of importance in a focused ion beam system is the beam spread. Ions when passed through an ion lens have a focal length dependent upon their initial ion energy when emitted from the ion source. The difference in energies from the ions will lead to a blurring of the image. Needless to say the smaller the energy spread the less the blurring.

After the ions have been created then they will go through the column. The column of a focused ion beam system is very similar to that of the electron beam system with a few differences. The extractor is the concentric electrode that is the electrode mentioned when applying the high voltage between the needle and the electrode. The suppressor also known as a Wehnelt cylinder surrounds the liquid metal ion source. Its job involves focusing the ions coming from the ion sources’ Taylor cone to a point between the suppressor and the extractor.[49] At this point another voltage is applied between the extractor and the first lens to accelerate the ions down the column. Next is the first lens. The first lens’ responsibility is to
align the ions with the beam defining aperture. The beam defining aperture is the spotsize. It determines the amount of ions that will reach the second lens to be focused onto the sample thus controlling the ion beam current. After this there are other devices involved with the beams movement and alignment, these are known as quadropoles and octupoles. Some of the responsibilities of this point are aligning the beam along optical axis, deflection of the beam for scanning the beam across the surface as in focused ion beam pattern writing and astigmatism correction.[49]
Chapter 3: Preliminary Investigations

3.1 Methods of Creating Aluminum Nanodots

The process of creating the final sample presented in Figure 1.5.1 and taking advantage of the metal induced crystallization process is actually a three step process. The first step is to be able to deposit amorphous silicon onto the surface. This process is readily available through the MVSystems deposition system. The second step is to be able to create aluminum nanodots over a large enough area to be characterized. The third is to be able to place these dots in contact with the amorphous silicon surface without an Al\textsubscript{2}O\textsubscript{3} layer inhibiting the metal induced crystallization process.

3.2 Polycarbonate Track Etch/ Anodized Aluminum Membranes

There were several methods preliminarily investigated for their usefulness in being able to create aluminum nanodots on the surface of a substrate. The first area of investigation included commercially available templates such as Whatman Anodized Aluminum Anodisc and Polycarbonate track membranes. The anodized aluminum disk is a porous disk composed of a high purity alumina matrix.[50] It is created electrochemically. Its original purpose was filtration of chemical and biological agents. Its dimensions include 60 μm thicknesses with an entire disc radius of 13mm, 25mm, or 47 mm. The pore sizes available ranged from .02 μm to .2 μm and the porosity for all of these size ranges was from 25-50%. The membrane was also flat and had support ring around the edges of the material. This made it much easier to attach the membrane to the substrate while covering a minimum amount of pores. Images of the anodized aluminum disc and surface structure can be seen in Figure 3.2.1.
Polycarbonate track etch membranes were another choice for a commercially available template with nanometer sized holes already fabricated. These membranes are also originally suited for biological and chemical agent filtration. These filters came in 13mm, 25mm, and 47mm filter diameters. There pore sizes ranged from .01μm to 30 μm. The advantage that these filters had over the anodisc was the fact there was no set thickness. The thickness of these filters ranged from 6μm to 10μm. These filters however did not have support rings around the edges and were readily pliable which caused difficulty in attaching membrane to a substrate surface. The porosity of these membranes was in the range of 1.2% to 15%. An image of the surface of a polycarbonate track etch membrane can be seen in Figure 3.2.2.

Figure 3.2.1: Left: image of Aluminum anodisc/ Right is image of honeycomb structure of Anodisc[50]

Figure 3.2.2: Image of polycarbonate track etch membrane[51]
3.3 Diblock Copolymers

The second area investigated was a chemically formed polymer based template known as linear Diblock Copolymers. A block is a sequence of the same monomers covalently bonded together. A monomer can be an atom or molecule, but it has the ability to link itself chemically to other monomers. A polymer is a chain of these monomers covalently linked together. Linear diblock copolymers are two different sets of blocks covalently linked to form a chain like molecule. Diblock copolymers have an interesting capability. The two blocks that form the diblock copolymer can self assemble under the right conditions into microdomains or nanodomains of different block material. [52] The size of these sections is determined by the molecules size which can range from 10 to 100 nm typically. Diblock copolymers can separate into three different morphological forms. These forms are lamellar, cylindrical, and spherical [52]. The morphological change that takes dominance is the dependent upon the ratio between the two blocks. For example, a ratio of 1:1 between block A and block B by volume typically leads to lamellar morphology. [53] A ratio of 3:1 leads to cylinders of B block formed in a hexagonal matrix of block A.[53] A ratio of 6:1 and above leads to spheres of B form in a body cubic centered form of A.[53] The idea with this method was to take advantage of the property of the separation of the copolymers with different molecular weights remove one of the copolymers and use the remainder as a template. Examples of these morphological forms can be seen in Figure 3.3.1.
3.4 Molecular Beam Epitaxy

The third area investigated was the process of creating aluminum nanodots on the surface of a substrate utilizing molecular beam epitaxy or more specifically droplet epitaxy. Molecular beam epitaxy is an extensive subject and cannot be fully explained in one section of a thesis, but a summary of the overall process will be provided with emphasis toward the specific process used in these experiments. In molecular beam epitaxy a flux of compound or elemental material such as Ga, As, In or Al is directed at a substrate surface. On the surface of the substrate during this process it is possible to either grow an atomic layer or produce nanostructures. What event occurs in each case is dependent upon the type of material being deposited and the type of substrate chosen. These elemental or compound materials can be introduced in a solid, liquid or gaseous state. If introduced in a solid or liquid state they are heated to the vapor phase. If already in the gaseous state it is introduced like the other states from the flux generator to the substrate. To maintain a high state of purity with the epitaxial layers during epitaxial growth stringent vacuum requirements are usually around $1 \times 10^{-10}$ torr before introducing the substrate into the chamber and deposition procedures. Molecular beam epitaxy is a line of sight process. The pressure within the growth chamber must be low enough so that the distance between the
substrate and source is shorter than the mean free path of the flux. The walls of the chamber are cryogenically controlled so that particles or molecules that may collide in the chamber are trapped on the chambers walls and this happens normally at pressures of $10^{-5}$ torr or less. The deposition rate of material can be controlled one of two ways 1) alter the evaporation conditions or 2) interrupt the flux with a high speed mechanical shutter. The ability of molecular beam epitaxy is that it provides the ability to control the composition of a structure to one atomic layer (monolayer). It is very difficult to find a generic molecular beam epitaxy system because the systems are very dependent upon the type of material being grown but a schematic of a III-V molecular beam epitaxy system is shown in Figure 3.2.8.

There are three types of sources available for conventional molecular beam epitaxy. They are Knudsen effusion cells, which we use in this research, gaseous source, and high temperature evaporators. The Knudsen effusion cell will be discussed here. It is used as a low partial pressure source in evaporators for materials such as As, Ga, Al, Hg. Typical Knudsen cell is composed of a crucible, heating element, cooling system, heat shields and a shutter. The crucible could be composed of pyrolytic, quartz, graphite, tungsten, or boron nitride.

Droplet epitaxy, the technique used to create the aluminum nanodots, is a type of molecular beam epitaxy introduced by Chickyow and Koguichi which involved introducing a flux of material to the surface of a substrate and annealing during the process.
Figure 3.2.28: III-V Molecular beam epitaxy system[55]
Chapter 4: Experimental Procedure

4.1 Substrate Cleaning Procedures

The N-type (Sb doped) silicon substrates were rinsed with 100% acetone and dried with pressurized nitrogen. This process was repeated with 100% isopropyl alcohol (IPA). The samples were then immersed in a solution of 10:1 deionized water and hydrofluoric acid for 5 seconds and dried with pressurized nitrogen. The samples were then loaded into the deposition tray as shown in the Figure 4.1.1 below and placed in the MVSystems loading chamber for delivery to the deposition chamber.

![Deposition Tray](image_url)

Figure 4.1.1: Deposition Tray
3.2 Deposition Procedures

Depositions were performed utilizing the MVSystems cluster tool. This tool had five deposition chambers (MPZ’s) and one loading zone (ITZ). Its deposition chambers capabilities included RF Magnetron sputtering of amorphous silicon and aluminum thin films and plasma enhanced chemical vapor deposition of hydrogenated amorphous silicon thin films at pressures below $10^{-7}$ torr. Its annealing chamber had temperature range 25°C to above 400°C at pressures of $10^{-3}$ torr. Chambers 1 and 2 (MPZ 1&2) were used for plasma enhanced chemical vapor deposition with chamber one designated for undoped a-Si:H and chamber 2 for doped a-Si:H, chamber 3 (MPZ3) was used for amorphous silicon sputtering and chamber 4 (MPZ 4) is used for aluminum sputtering. Chamber 5 (MPZ 5) was the annealing chamber. The digital image and schematic of the MVSystems cluster tool are included in Figures 4.2.1 and 3.2.2.

Figure 4.2.1: MVSystems Cluster Tool
The deposition of 500 nm of amorphous silicon onto the substrate was performed in MPZ1. The flow rate of SiH$_4$ was 20 sccm with a chamber pressure of 5 mtorr and a substrate temperature of 250°C. The sample was then transferred under vacuum to MPZ3 for SiO$_2$ deposition of 50 nm. This occurred at 250°C with an argon flow rate of 20 sccm and an oxygen flow rate of 4 sccm. The chamber pressure was maintained at 10 mtorr.

4.3 Experimental Procedure for Track Etch Membranes/Anodized Aluminum Anodisc

The experimental procedure for the two commercial templates was the same. The templates would be attached to the surface of the substrate with Kapton tape around the edges.
and the process for deposition of aluminum was started. The samples were then removed and the substrate was examined utilizing scanning electron microscope. The anodized aluminum template had minimum thickness available of 60 μm and its pore diameter was 0.1 μm. The nominal pore diameters that are available for these sizes is .01, .1, and .2 μm. The polycarbonate track etch membranes for the pore diameters utilized in these experiments had a thickness of 7 μm. The pore sizes utilized ranged from .08 to .4 μm.

4.4 Experimental Procedure for Diblock Copolymers Template

This information was obtained from several papers authored by Dr. Thomas P. Russell et al from the University of Massachusetts Amherst and personal correspondence with another of the authors Dr. Soojin Park. The experimental procedure for the diblock copolymers is completed in two sections. The first section is the creation of the polymer solution the other section is the spin coating and vapor annealing. In our experiment a 4 mL polymer solution of .5% wt solution polystyrene-b-vinyl pyridine (PS-b-P4VP) was created. The solution is can normally be between .5% to .8% wt solution in a 3-4 mL solution. The diblock copolymer PS-b-P4VP was obtained commercially from Polymer Source Inc. The number average molecular weight (Mn) for the polystyrene (PS) was 57.5 kg/mol. The number average molecular weight for vinyl pyridine was 18.5 kg/mol. This ratio of 3:1 between the polymers is the ratio necessary to bring about the phase separation into vertical cylinders.

To create the polymer solution, 20 mg of PS-b-P4VP is dissolved in a 4 mL solution composed of a 70:30 ratio of toluene to tetrahydrofuran. This is dissolved at 70°C for two hours and then allowed to cool to room temperature. This process has better results if performed in amber bottles with Teflon lined caps. The solution is then spincoated onto the surface of a substrate at 2000 rpm for 60 seconds. Next the substrate is sealed within an amber bottle with a
cap that has Teflon lining. The Teflon lining is to keep the vapor from the solvents from causing
damage the caps. This is known as solvent annealing and must be left for 12 hours. The solution
within the amber bottle is composed of an 80:20 ratio of toluene and tetrahydrofuran and it must
not be allowed to touch the thin film of polymer on the surface of the substrate. Only the vapors
of the solution should be allowed in contact with the polymer for 12 hours.

After the twelve hour solvent annealing, the samples should be submerged in pure
ethanol for 20 minutes for surface restructuring. The ethanol removes the polymer that forms the
cylinder region after the phase separation during solvent annealing. The next step if there is a
pronounced difference in the morphological structure would be to plasma etch to the bottom of
the polymer or transfer the pattern to a harder template such as silicon dioxide and then prepare
for metallization.

4.5 Experimental Procedure for Molecular Beam Droplet Epitaxy

Silicon substrates were (100) diced into 1 cm squares after being degreased with acetone
and methanol respectively. They were then dried in atmosphere by spinning at 1000 rpm until
dry. The sample was then loaded into a Veeco Gen 2 molecular beam epitaxy chamber with a
pressure of $10^{-10}$ torr. The substrates were then ramped to 1000°C at a rate of 25°C/min for 60
min to remove any oxides from the surface. In situ, reflection high energy electron diffraction
(RHEED) was used to indicate if the surface was atomically flat or contained large scale
contamination. The Al was deposited onto the surface of the substrates for 30 sec at a substrate
temperature of 550°C. The effusion cell temperature was kept at 1055°C for sample 1 (2nm
sample) whereas the beam equivalent pressure was $1.05 \times 10^{-7}$ torr. Sample 2 (6nm sample) was
deposited at 1105°C with a beam equivalent pressure of $3.85 \times 10^{-8}$ torr. The fluxes provided a
calibrated growth of 2nm and 6nm assuming a 2 dimensional thin film growth.
4.6 Focused Ion Beam Pattern Creation

After the depositions of amorphous silicon and silicon dioxide, there needed to be holes created in an array though the silicon dioxide film to the amorphous silicon surface. This was achieved utilizing the focused ion beam and its pattern software. Patterns created using the focused ion beam need to be in a bitmap format. The beam was programmed to respond to certain colors present in the bitmap. The beam unblanked on certain colors and dwelled at that spot depending on the color. This design was very simple without a need for varied dwell times. Thus, only two colors were needed one color for blanking the beam and the other for unblanking the beam. This can be seen in Figure 4.6.1.

![Figure 4.6.1: Bitmap Focused Ion Beam Pattern](image)

The size of the blue section was the size of the dots. The blue sections made up of pixels but the software of the focused ion beam only allowed a maximum of 4096 pixels X 4096 pixels in the loaded bit map. When uploading the bitmap image to the focused ion beam software the
dimensions of the blue circles were controlled by controlling the area of the entire square. For example the image in Figure 4.6.1 was 4096 X 4096 pixels and it was uploaded with the dimensions in the x and y direction as 40.96 μm and each pixel effectively became .01 microns. The last step was to decide the size of the circles dependent upon the pixel size. These holes were created with a beam of Ga$^{3+}$ ions at a current of 50 pA and accelerating voltage of 30kV.

4.7 Deposition/Annealing/Removal of Aluminum

After the pattern was created through the silicon dioxide film to the amorphous silicon the sample was immediately taken to the MVsystems chamber MPZ4 for sputtering a layer of aluminum 50nm thick. The sputtering was performed at a pressure of 5 mtorr using a flow rate of the argon gas of 20 sccm. The substrate was kept at room temperature for the deposition. After the aluminum deposition the sample was held in vacuum and annealed for 30 minutes at 350°C. The unreacted aluminum was then chemically etched from the surface by dipping for 5 min in an aluminum etchant solution (85% phosphoric acid, 5% nitric acid, 5% acetic acid, and 5% DI water at 25 °C) and then rinsed with de-ionized water to remove any traces of the etchant solution.

4.8 Transmission Electron Microscope Sample Preparation

Once a substrate was prepared it had a section milled by focused ion beam so that it could be characterized inside the transmission electron microscope. Although the steps for this process were numerous and could change from one focused ion beam system to the next, a general overview is deemed necessary for thorough disclosure of the research subject.
TEM Sample Preparation:

1. Bring probe and source of platinum close to designated spot after substrate has been brought to eucentric height. Setting the stage at the eucentric height allows the stage to be tilted without the point of interest being moved. (Figure 4.8.1)

![Probe and Platinum source are placed near the surface for TEM sample preparation](image)

**Figure 4.8.1: Probe and Platinum source are placed near the surface for TEM sample preparation**

2. Deposit platinum strip with electron beam with a length of 10 μm, width of 1.5 μm, and a thickness of .5 to 1 μm. (Figure 4.8.2)

3. Etch Trenches on each side of the platinum strip with a length of 10 μm, width of 5 μm, with a depth of 4 μm using a beam current of 3-5 nA. (Figure 4.8.3)
Figure 4.8.2: Protective Platinum strip is deposited upon intended area for TEM sample preparation

4. Perform a U cut with the focused ion beam using 30 to 50 pA beam current at a depth of 1 μm. (Figure 4.8.3)

Figure 4.8.3: Rectangular trenches are etched above and below the platinum strip. Stage is then tilted and thin sample under protective strip is etched away from surface.
5. Bring in probe and attach to sample by depositing a square patch half on the sample and half on the tip. The dimensions of the square vary with needle and sample size but should be at least 400 nm in thickness. (Figures 4.8.4 and 4.8.5)

Figure 4.8.4: Probe is brought close enough to touch the sample in preparation to deposit platinum
Figure 4.8.5: Platinum is deposited to attach the probe to the sample and then the ion beam is used to completely detach the sample from the surface.

6. Separate the sample from the substrate using a beam current of 3-5 nA. (Figure 4.8.6)

Figure 4.8.6: Stage is lowered away from the probe before retracting the probe

7. Bring Probe with TEM sample and platinum source to TEM grid and attach with square that is at least 300 to 500 nm thick with half of square on grid and sample.(Figure 4.8.7)
8. Detach the probe from sample with focused ion beam current of 3 to 5 nA current and then polish the sample by about 1 μm at a beam current of about 0.1 nm until the thickness is around 200 nm. (Figure 4.8.8)

Figure 4.8.7: Probe with sample is gentle brought into contact with TEM grid prong in preparation to attach with platinum

Figure 4.8.8: TEM sample is attached with platinum and detached from the probe by etching with the ion beam
Chapter 5: Results and Discussion

5.1 Results from Anodized Aluminum Anodisc

Deposition through the anodisc template was sporadic at best. Figure 5.1.1 is an image of the surface of a piece of anodisc after deposition of aluminum. Figure 5.1.2 is an SEM image of an area where some of the sputtered aluminum made it to the surface. It was thought that since this did not occur everywhere on the surface there may have been an opening in the Kapton tape or a crack in the template. The SEM images in Figures 5.1.3 and 5.1.4 show two different areas on the surface of the substrate of crystalline silicon. As can be seen there were different nanostructures and these did not occur all over the surface only sporadically which leads us to believe the sputtered aluminum may have found a way under the tape or a crack in the material. The shapes in the Figure 5.1.4 are slightly indicative of the shapes found on Figure 5.1.1. Although this method created aluminum nanostructures on to the surface of the substrate, this method was not reliable due to the sporadic nature of the aluminum structures and there may be difficulty in reproducibility. The sporadic nature of this method will also lead to problems after crystallization when a focused ion beam TEM sample is to be created.
Figure 5.1.1: Anodisc with deposited aluminum deposited onto the surface

Figure 5.1.2: SEM image of substrate from Anodisc aluminum deposition
Figure 5.1.3 SEM image of sporadic aluminum deposition on surface under Anodisc

Figure 5.1.4: SEM image of random aluminum deposition through Anodisc template
5.2 Results of Polycarbonate Track Etch Membrane

Figure 5.2.1 is an SEM image of a polycarbonate track etch membranes surface. These commercial membranes were available with holes ranging from 80 nm to 1 μm or more with a hole diameter variance of 15%. In our test we used track membranes with size ranges that were available from 80 nm to 400 nm. As can be seen in by Figure 5.2.1 the holes do not appear to be periodic. Figure 5.2.2 shows the surface of a substrate after aluminum sputtering deposition. These show a different range of dot sizes. The track etch membrane hole diameter for these depositions was 80 nm. What is interesting is that in Figure 5.2.2, there are dots at least two or three times the size of 80 nm. This phenomenon is repeated with the other track etch membranes with holes of a different diameter. We believe this is because there were some points on the membrane that were not in full contact with the surface even though the track etch membrane was attached with kapton tape around the edges. This membrane is not rigid and is also not supported around the edges like the anodized aluminum anodisc. This membrane is pliable which would allow situations in which the entire membrane is not in contact with the substrate simultaneously. We believe that this was the cause of the dots of different size ranges. A plot of the variation of known hole diameters to experimental dot diameters is shown in Figure 5.2.6. If the membrane is not touching the surface then the aluminum deposited through the holes is not confined by the edge of the hole of the membrane. If the aluminum is not confined it may be free to move along the surface of the substrate. There were trials to attach the membrane to the surface with adhesives and then etch out the holes these were not successful in keeping the membrane attached to the surface and providing holes that were open to the surface of the substrate. Figures 5.2.3 through 5.2.5 are SEM images of the surface after deposition through a template with holes of an average diameter of 100, 200, and 400 nm respectively. The better
success at the creating dots using this template as compared to the anodisc template is due to the thicknesses available in the templates. The Anodisc ratio of hole diameter to membrane thickness was an order of magnitude larger than the ratio of the polycarbonate track etch membranes ratio. The anodisc template had a minimum thickness of 60 μm. The polycarbonate track etch membranes had a range of 7 μm to 20 μm.

![SEM Image of polycarbonate track etch membrane after aluminum deposition](image)

**Figure 5.2.1: SEM Image of polycarbonate track etch membrane after aluminum deposition**
Figure 5.2.2: SEM image of aluminum dots deposited through polycarbonate track etch membrane with 80nm diameter holes

Figure 5.2.3: SEM image of aluminum dots deposited through polycarbonate track etch membranes with 100nm diameter holes
Figure 5.2.4: SEM image of aluminum dots deposited through polycarbonate track etch membranes with 200nm diameter holes

Figure 5.2.5: SEM image of aluminum dots deposited through polycarbonate track etch membranes with 400 nm diameter holes
5.3 Results from Diblock Copolymer Templates

Figure 5.3.1 through Figure 5.3.4 were our best results from the diblock copolymer trials. Figure 2.2.1 is an SEM image of the diblock copolymers after it has been spin coated at 2000 rpm, solvent annealed and undergone surface restructuring. As is seen in the image there appear to be indentations into the surface of the diblock copolymer material. There also appears to be blank spaces where these indentations did not occur. This would be cause difficulties if a periodic array of nandots is needed. Figure 5.3.3 is an SEM image of another sample with the same procedure as Figure 5.3.2 except it was spin coated at 3000 rpm. There was an improvement in that the blank spaces that was plainly evident in Figure 5.3.2 in that they no longer exist in the latter images. One issue that persisted was the fact that these were not actually holes but indentations into the polymer. Figure 5.3.4 is a high resolution SEM image of the
surface of Figure 5.3.3. It has a higher resolution image of the surface indentations and part of the polymer peeled away to show the phase separations beneath the surface. At this point the papers suggested plasma ashing or etching of the polymer surface to transfer the pattern. The issue we faced was that 2000 rpm gave a more defined indentation which may be better for the plasma ashing but the indentations had blank spaces. The 3000 rpm samples that had all the indentations completely covering the substrate were clearly shallower. Figures 5.3.5 through 5.3.14 were experiments with the diblock copolymer process. The parameters of spincoating speed and solvent anneal time was varied in an attempt to obtain more defined indentations that completely covered the surface of the substrate.

In Figures 5.3.5 to 5.3.12, the spin coating speeds were varied from 500 to 3500 rpm with intervals of 1000. This change away from the process obtained from the Russell et al caused a similar reaction on the surfaces of all of the surfaces. Instead of the polymers self assembling into a equally spaced template of nanodomains the surfaces self assembled into microdomains. This result was repeated with all of the spin speeds except for 2000 and 3000 rpm. Figures 5.3.12 and 5.3.13 were SEM images of the surface of the substrates after altering the solvent anneal times to 18 and 24 hours respectively. These anneal times were used with the 2000 rpm process parameter because it had the most defined indentations of all of the trials. The longer solvent anneal times as can be seen from the images stripped the surfaces and made the indentations less defined. In this research there was found other techniques that may be used in conjunction with this technique shown. This technique consisted of heat treatment near the glass transition temperature of the polymers for better separation. Although attempts to create a template were unsuccessful from the polymer itself, it is believed the patterned of the indentations may be able to be transferred onto another material by utilizing reactive ion etching.
Figure 5.3.1: SEM image of 2000 rpm spin coated PS-b-P4VP after solvent anneal and development

Figure 5.3.2: SEM image of 3000 rpm spin coated PS-b-P4VP after solvent anneal and development
Figure 5.3.4 Higher magnification SEM image of 3000 rpm spin coated PS-b-P4VP after solvent anneal and development.

Figure 5.3.4: HRSEM image of 3000 rpm spin coated PS-b-P4VP after solvent anneal and development showing phase separation.
Figure 5.3.5: SEM image of 500 rpm spin coated PS-b-P4VP after solvent anneal and development

Figure 5.3.6: Higher magnification of SEM image of 500 rpm spin coated PS-b-P4VP after solvent anneal and development
Figure 5.3.7: SEM image of 1500 rpm spin coated PS-b-P4VP after solvent anneal and development

Figure 5.3.8: Higher magnification SEM image of 1500 rpm spin coated PS-b-P4VP after solvent anneal and development
Figure 5.3.9: SEM image of 2500 rpm spin coated PS-b-P4VP after solvent anneal and development

Figure 5.3.10: Higher magnification SEM image of 2500 rpm spin coated PS-b-P4VP after solvent anneal and development
Figure 5.3.11: SEM image of 3500 rpm spin coated PS-b-P4VP after solvent anneal and development

Figure 5.3.12 Higher magnification of 3500 rpm spin coated PS-b-P4VP after solvent and development
Figure 5.3.13: 2000 rpm spincoated PS-b-P4VP /18 hr solvent anneal and development

Figure 5.3.14: 2000 rpm spin coated PS-b-P4VP/ 24 hr solvent anneal and development

5.4 Results from Molecular Beam Droplet Epitaxy

Figure 5.4.1 and Figure 5.4.2 show images of the surface of the flux calibrated 2nm growth. The aluminum spheres presented in these two figures show a range of approximate
diameters of 15nm to 70nm. Some of the nanostructures on the surface are not spherical but oblong in shape. It was not known if the nanostructure formed this way or is the effect of two of the spherical nanostructures joining during deposition.

Figures 5.4.3 and 5.4.4 show images of the flux calibrated 6nm deposition. The range of sizes has not changed but the appearance of many more of the oblong structures is readily apparent. It was also apparent that patches of spherical nanostructures dispersed around the spherical nanostructures and oblong nanostructures on the surface. These patches seemed to be composed of spherical shaped nanostructures themselves.

![Image of aluminum nanodots from 2 2nm MBE deposition](image)

**Figure 5.4.1:** HRSEM image of aluminum nanodots from 2 2nm MBE deposition
Figure 5.4.2 Higher magnification HRSEM image of aluminum nanodots from 2nm MBE deposition

Figure 5.4.3 HRSEM image of aluminum nanodots from 6nm MBE deposition
Figure 5.4.4: Higher magnification image of aluminum nanodots from 6nm MBE deposition

Table 5.4.1: Surface Characteristics of MBE Nanodot Growth

<table>
<thead>
<tr>
<th></th>
<th>2 nm MBE deposition</th>
<th>6 nm MBE deposition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total Area</td>
<td>46629 nm$^2$</td>
<td>39653 nm$^2$</td>
</tr>
<tr>
<td>Total # of dots</td>
<td>123</td>
<td>639</td>
</tr>
<tr>
<td>Average dot area</td>
<td>379.10 nm$^2$</td>
<td>62.09</td>
</tr>
<tr>
<td>Fraction of surface</td>
<td>30%</td>
<td>39%</td>
</tr>
</tbody>
</table>

5.5 Results from SiO$_2$ Template

Figure 5.5.1 is an example of the typical thickness of the samples taken from the arrays of crystalline structures found in the surface of the substrate. The experiments were broken into two categories. The first category involved taking a sample from an array created from the substrate that had not had aluminum deposited onto the surface. This was done to remove the focused ion beam as one of the causes for crystallization that may be found in the material. Figures 5.5.2 and
5.5.3 show the effect that the focused ion beam had on the surface of the substrate through the SiO$_2$. The scale bar in Figure 5.5.3 showed the hole to be less than 500 nm in diameter in both the x and y direction. Figure 5.5.4 is a schematic of the cross-section focused ion beam TEM sample. Platinum was placed at the top of the sample as a protective layer while the sample was prepared. Figure 5.5.5, the actual sample, shows the highlighted holes in the SiO$_2$ through to the amorphous silicon in a linear periodic fashion that coincided with the dimensions of the array. Figure 5.5.4 is not drawn to scale. The white line between the platinum and the amorphous silicon was the SiO$_2$. Figure 5.5.6 is an image directly beneath one of the holes. This image was taken in order to check for morphological damage that may have been caused during the creation of the SiO$_2$ template. The highlighted area A was the area that was checked for crystallization utilizing selected area electron diffraction. The aperture through which the diffraction was collected had a diameter of 150 nm. Figure 5.5.7 is the selected area electron diffraction measurement. The broad flat rings and absence of periodic bright spots within the rings was indicative of a powdered material or an amorphous material.
Figure 5.5.1: TEM sample with measured sample thickness

Figure 5.5.2: HRSEM image of array of holes in SiO₂
Figure 5.5.3: Higher resolution image of HRSEM Focused Ion Beam hole in SiO$_2$

Figure 5.5.4: Illustrative schematic of cross-section of TEM sample array of holes (not drawn to scale)
Figure 5.5.5: Crosssection TEM sample of array of highlighted holes

Figure 5.5.6: Higher magnification image of one of the TEM crosssection the bottom of Focused Ion Beam holes
Figure 5.5.7: Selected Area Diffraction Image of area A from figure 5.1.5 directly under the hole

Figure 5.5.8 was the same experimental setup of an array of holes created with the focused ion beam through an oxide layer to the amorphous silicon layer beneath. This is an image of the surface after the aluminum was deposited, the sample was annealed for 30 minutes, and the aluminum was etched from the surface. Figure 5.5.9 shows the diameter of several of the holes and the spacing. It also shows a slight color difference directly surrounding the holes in comparison with the space between the holes. This can also be seen in Figure 5.5.8 but is more prevalent in the latter. Figure 5.5.10 is a higher magnification image of one of the holes that the process of depositing, annealing and etching had a definite effect on the surface and inside the hole. This pitting effect is quite common in aluminum induced crystallization when the aluminum and amorphous silicon diffuse into each other. The aluminum was also etched and it may have caused some of the other material to be taken with it. As for the effect on the silicon dioxide, the dioxide was deposited onto the surface utilizing sputtering while flowing oxygen
into the sputtering chamber so the SiO₂ may be silicon rich and the aluminum would have had no problem reacting with this silicon also.

**Figure 5.5.8:** HRSEM image of array of holes in silicon after deposition/annealing/and etching of aluminum for substrate

**Figure 5.5.9:** Higher magnification HRSEM image of array of holes from figure 5.1.7
Figure 5.5.10: HRSEM image of one of the holes with morphological changes in the surface.

Figure 5.5.11, although not drawn to scale, is a schematic drawing TEM cross section of the layout of the thin film layers that will be shown by later figures. Figure 5.5.12 is the TEM image of a cross section of the array of holes shown in Figure 5.5.2 and 5.5.3. In this image there was a definite morphological change beneath the hole. In Figure 5.5.13, a higher magnification TEM image of one the holes, two areas were highlighted that were analyzed using selected area electron diffraction. Figure 5.5.14 is a selected area electron diffraction image of area C that was taken through an aperture with a diameter of 150 nm. The images broad flat concentric rings were indicative of amorphous material. Figure 5.1.15 is a selected area electron diffraction image of area B that has also been taken with an aperture diameter of 150 nm. This diffraction image with its thin lines of concentric bright spots was indicative of polycrystalline material. Each ring represented a different orientation of crystal within the circumference of the aperture in which the image was taken. There are at least seven visible lines of concentric bright spots within image and each line of concentric circles is a different orientation of crystal.
Figure 5.5.11: Illustrative schematic representation of TEM cross-section after deposition/annealing/and etching of aluminum (not drawn to scale)

Figure 5.5.12: TEM cross-section image of the array of holes from figure 5.1.7
Figure 5.5.13: Higher magnification image of TEM crosssection image of array of holes

Figure 5.5.14: SAED image of Area C Figure 5.1.10
The next step after establishing that there were nanocrystalline regions underneath the holes that were created by the focused ion beam was to establish whether the crystalline material was actually crystalline silicon or traces of aluminum that had not been fully etched away. To determine whether the crystalline material was aluminum or polycrystalline silicon the diameter of the three of the concentric rings of bright spots were measured. The diameters of these rings were converted to real space units and they corresponded to the distance between atomic planes for the orientation that corresponded to that ring. Table 5.5.1 is an example of what the rings diameter should measure depending on the crystalline material being measured and that materials orientation. There was a 10% error in the measurements but the atomic planes’ distances of aluminum and silicon were outside this range of error in the first ring. Table 5.5.1 show the measurements of rings 1 through 3 and their equivalent diameters in real space. These
measurements correlated within the error range of 10% with that of crystalline silicon unlike that of aluminum.

**Table 5.5.1: Orientation and atomic lattice distance of Aluminum and Silicon**

<table>
<thead>
<tr>
<th></th>
<th>Orientation</th>
<th>Calculated Distance</th>
<th>Measured Distance</th>
</tr>
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<tbody>
<tr>
<td>Silicon</td>
<td>Ring 1</td>
<td>111</td>
<td>.3135 nm</td>
</tr>
<tr>
<td></td>
<td>Ring 2</td>
<td>220</td>
<td>.1920nm</td>
</tr>
<tr>
<td></td>
<td>Ring 3</td>
<td>220</td>
<td>.1637 nm</td>
</tr>
<tr>
<td>Aluminum</td>
<td>Ring 1</td>
<td>111</td>
<td>.2338 nm</td>
</tr>
<tr>
<td></td>
<td>Ring 2</td>
<td>200</td>
<td>.2025 nm</td>
</tr>
<tr>
<td></td>
<td>Ring 3</td>
<td>311</td>
<td>.1432 nm</td>
</tr>
</tbody>
</table>

It was not conclusive whether the crystalline area was in the exact structure of a nanowire. What was known was that an array of nanocrystalline regions had been created in a 500 nm thick film of amorphous silicon and that these regions were nanocrystalline silicon as shown in the measurement of the distance between the atomic planes of the material in three different orientations. It was known that the nanocrystalline region as shown through SAED Figure 5.5.15 is polycrystalline in nature. The regions from Figure 5.5.15 had grain boundaries that can be seen in Figure 5.5.16. Although this provided further proof of the polycrystalline nature of the material, it was not totally conclusive that the material is surrounded in this area by amorphous silicon. The areas that appear amorphous in the surroundings may have had a different orientation. The diameter of at least seven different orientations of crystals in the x and
y direction are no more than 150 diameters in either the x or the y direction and in the z direction it has to be less than 300 nm because the thickness of the sample is no more than 300 nm. If it was assumed that all the crystals were the same size and the volume of the area of a cylinder with the height of 300 nm and the radius of 75 nm then the cylinder like shape had a volume of 5.3014 X 10^6 nm. If the volume was divided by 7 assuming all of the volumes were equal for each crystal, then the volume of each crystal was 7.5 X 10^5 nm. With this information and the 7 different crystals having the same height of 300 nm then the radius of each crystal could be no more than 26.24 nm. Even though this was a thought experiment and there may be more than seven orientations due to some of the orientations not being visible due to structure factors, it was known that there are at least 7 orientations and there dimensions in the x and y direction are less than 150 and the z direction is less than 300 nm. There may yet be nanowires in the material. The process of taking a focused ion beam sample etches the sides of the holes away and it is clearly evident from Figure 5.5.13 that the crystallization occurs in all directions. There is no evidence to suggest that the crystallization did not also occurred in the direction within the amorphous material that was cut away. This section of material that was cut away may yet shed light on the structure of the material and yield the nanowires.

![Highlight atomic planes of crystallized region](image)

**Figure 5.5.16: Highlighted atomic planes of crystallized region Figure 5.1.1**
Chapter 6: Conclusion and Future Work

In this work, as a proof of concept several methods were investigated for their effectiveness in producing a composite nanomaterial that was composed of amorphous silicon with nanometer crystalline nanostructures embedded within the amorphous material. The template based methods were ineffective in being able to produce nanometer aluminum structures on the sample in a repeatable fashion. The ability to create nanometer aluminum structures on the surface in contact with the amorphous silicon was a vital step in the creation of the nanomaterial.

The diblock copolymer method was a strong candidate for template creation because of the ease with which the template could be attached to the surface. It also had the ability to create nanometer sections of the two polymers over the entire surface with ease. The difficulty and what will need to be optimized is the removal of one of the polymers during the surface restructuring so that this template procedure can be taken advantage of in the future.

The molecular beam epitaxy option only had one weakness. It was the temperatures that were used to heat and remove oxides from the surface and the processing temperature. These temperatures were well above the temperatures needed to crystallize amorphous silicon. In order to take advantage of the aluminum induced crystallization procedure the amorphous silicon must not be crystallized before the aluminum is deposited. In the future the molecular beam epitaxy process may be used to create the dots first by covering the surface of the substrate with the amorphous silicon where the growth of the crystalline regions may be up instead of down. Lastly the oxide template was created with the focused ion beam. This method was perfect for a proof of concept but the entire surface will need to be covered in order to usable for optical and
electrical characterization measurements. Another thing that can be addressed in future experiments is to vary the anneal times to see the effect on the amount of crystallization that occurs. In the end a better template may need to be created utilizing e beam lithography or x-ray photolithography to cover an area large enough for optical and electrical characteristics that will allow this investigation to move forward to device creation.
References


[27] B. Zemel, "Tracers in the Oil Field," pp. 52, .


Appendix A: Description of Research for Popular Publication
A recent breakthrough has been found at the University of Arkansas in the labs of Dr. Hameed Naseem, a tenured professor and senior scientist at the University of Arkansas Solid State Laboratory. The leader on this project is Benjamin Newton. He is a graduate student at the University of Arkansas Fayetteville in the Microelectronics Photonics Graduate Program.

Benjamin Newton excitedly exclaims “This could revolutionize the solar cell industry and bring about a whole new field for research in composite materials”

This new material is a combination of polycrystalline silicon crystals within the nanometer size range that are embedded in a matrix of amorphous silicon film. These crystalline sites are arranged in a rectangular array.

What is so special about this material you may ask? It involves taking advantage of two properties that are inherent in polycrystalline and amorphous silicon. To fully understand the importance of these devices a brief glimpse of the solar cell industry must be given.

The most efficient of commercial solar cells is the monocrystalline silicon solar cell. It is also the most expensive which makes it cost prohibitive for much of the middle class. The reason for this high cost is the high temperatures involved with producing the crystal, the amount of material needed for light absorption, and the amount of material wasted due to cutting the wafer. Thin film solar cells do not suffer from these setbacks and can be deposited onto flexible substrate which broadens the ability of placement of the thin film solar cells.

The issue faced with thin film solar cells is the efficiency is not comparable to that of monocrystalline silicon which means more cells are needed to produce the same amount of energy produced from the already cost prohibitive solar cells.

The path taken by the research team to address this was to take an in depth look at the two materials most thin film solar cells are composed of amorphous silicon or polycrystalline silicon. Amorphous silicon is great at absorbing light and polycrystalline silicon is great at electron conduction, but neither one of them does both of them well.

If a material could be found or created that was a combination of both of these types of silicon then the logic followed by this research group is that it may be a material with both properties of high light absorption and electron conduction.
With this goal in mind, Benjamin Newton started researching a way to create this material and recently solved this issue through the use of a technique known as aluminum induced crystallization. He accomplished this task by creating a template with nanometer sized features and depositing aluminum. These nanometer sized regions of contact between aluminum and the amorphous silicon surface when annealed will crystallize into polycrystalline silicon.

The future work of this research will include a thorough investigation into the light absorption and electron conduction properties of this new material.
Appendix B: Executive Summary of Newly Created Intellectual Property

The following list of new intellectual property items were created in the course of this research project and should be considered from both a patent and commercialization perspective.

1. A process for creating a composite nanomaterial composed of amorphous silicon matrix embedded with polycrystalline silicon nanocrystals

2. A second process for creating aluminum nanodots on the surface of crystalline silicon utilizing the molecular beam droplet epitaxy.
Appendix C: Potential Patent and Commercialization Aspects of listed Intellectual Property Items

C.1 Patentability of Intellectual Property (Could Each Item be Patented)

1. Due to prior disclosure of intellectual property this process cannot be patented. If the process were to be patented, there would need to be a licensing of the general patent for aluminum induced crystallization.

2. The second process can be patented.

C.2 Commercialization Prospects (Should Each Item Be Patented)

The two items listed were then considered from the perspective of whether or not the item should be patented.

1. The method for creating a new material should not be patented because of prior disclosure. If prior disclosure had not occurred then a patent should not be obtained without obtaining a general license of the aluminum induced crystallization process.

2. The second process should not be patented because it may be considered the next logical step for a person knowledgeable in the art of molecular beam epitaxy.

C.3 Possible Prior Disclosure of IP

The following items were discussed in a public forum or have published information that could impact the patentability of the listed IP.
1. This newly created process of isolated nanometer crystallization of amorphous silicon was presented publicly at The International Conference of Metallic Coatings and Thin Films (April 27-30, 2010) in San Diego California.
Appendix D: Broader Impact of Research

D.1 Applicability of Research Methods to Other Problems

The process of fabricating hybrid thin film materials will open many other fields. Thin films are used throughout industry. They are used in solar cells, light emitting diodes, and optical detectors. This process will revolutionize these fields and many more as this process is used to create other hybrid materials that may be used in future fields to come. Amorphous silicon is not the only material that can be crystallized while in contact with metal. These new materials will need thorough testing but the new properties discovered from these materials can be used to mitigate scientific problems of the future.

D.2 Impact of Research Results on U.S. and Global Society

It has already been shown throughout the solar cell industry that it is more cost effective to produce thin film solar cells that it is to produce crystalline solar cells. The problem lies in the gap between efficiencies of the thin film solar cells and the crystalline solar cells. This process could close that gap and allow the United States and Global Society to invest in this more environmentally healthy and cost effective method of relieving their energy needs. This would allow each country to sustain a large majority of its own energy needs and reduce conflict between nations.
D.3 Impact of Research Results on the Environment

Solar cells themselves do not have any adverse effects on the environment but the process to make solar cells does produce some chemical waste. These chemical waste and their processes are well understood throughout industry and can be properly disposed. The process contained within this research uses standard techniques that are thoroughly understood throughout industry in an innovative but thoroughly understood method that will not create any new waste that does not already have a safe method of disposal.
Appendix E: Microsoft Project for MS MicroEP Degree Plan
Appendix F: Identification of All Software Used in Research and Thesis/Dissertation Generation

Computer #1:
   Model Number: Toshiba: Satellite L505D-S5965
   Serial Number: 69042120Q
   Location: 209 N. Lapis Lane Apt #4
   Owner: Benjamin Newton

Software #1:
   Name: Microsoft Office 2007
   Purchased by: Benjamin Newton

Software #2:
   Name: Microsoft Project
   Purchased by: University of Arkansas Site License