Fabrication and Characterization of Amorphous/Nanocrystalline Thin Film Composite

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Fabrication and Characterization of Amorphous/Nanocrystalline Thin Film Composite
Fabrication and Characterization of Amorphous/Nanocrystalline Thin Film Composite

A dissertation submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy in Microelectronics-Photonics

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Abstract

Combining the absorption abilities of amorphous silicon and the electron transport capabilities of crystalline silicon would be a great advantage to not only solar cells but other semiconductor devices. In this work composite films were created using molecular beam epitaxy and electron beam deposition interchangeably as a method to create metallic precursors. Aluminum induced crystallization techniques were used to convert an amorphous silicon film with a capping layer of aluminum nanodots into a film composed of a mixture of amorphous silicon and nanocrystalline silicon. This layer was grown into the amorphous layer by cannibalizing a portion of the amorphous silicon material during the aluminum induced crystallization. Characterization was performed on films and metallic precursors utilizing SEM, TEM, ellipsometry and spectrophotometer.
Acknowledgements

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Lastly and most important of all my wife who was my lab buddy many times so that I could stay late and was not angry when I had to work on the weekends to finish this degree.
Dedication

This dissertation is dedicated to my wife, my son Bennett Earl Newton, my siblings and my parents.

If the sky is the limit how did we get to the moon?

Benjamin Newton
# Table of Contents

Abstract ......................................................................................................................................... vii
Acknowledgements ...................................................................................................................... viii
Dedication ....................................................................................................................................... x
Table of Contents ........................................................................................................................... xi
List of Figures .............................................................................................................................. xiv
List of Tables ................................................................................................................................ xx

Chapter 1: Introduction ................................................................................................................... 1

1.1 Background ........................................................................................................................... 1
1.2 Reaction between Amorphous Silicon and Crystalline Aluminum ...................................... 3
1.3 Al Metallic Nanodot Formation ............................................................................................ 6
1.4 Surface Energy and the Capillarity Theory ........................................................................ 10
1.5 Amorphous Silicon Solar Cell ............................................................................................ 12
  1.5.1 Introduction .................................................................................................................. 12
  1.5.2 Optoelectronic Properties of Amorphous Silicon ........................................................ 13
  1.5.3 Physics of Operation of P-I-N Solar Cells ................................................................... 17
1.6 Organization ........................................................................................................................ 22

Chapter 2: Aluminum Nanodots Calculations .............................................................................. 23

Chapter 3: Experimental Procedures ............................................................................................ 27

3.1 Substrate Cleaning Procedures ........................................................................................... 27
3.2 Thin Film Deposition Procedures ....................................................................................... 27
3.3 Experimental Procedure for Molecular Beam Epitaxy ....................................................... 28
3.4 Experimental Procedure for Electron Beam Evaporation ................................................... 30
3.6 Plasma Enhanced Chemical Vapor Deposition .................................................................. 32
3.7 Molecular Beam Epitaxy .................................................................................................... 33
3.8 Electron Beam Evaporation ................................................................................................ 34

Chapter 4: Results and Discussion ............................................................................................... 36

4.1 Results from MBE deposition on Crystalline Silicon .......................................................... 36
4.2 Results from MBE deposition on Amorphous Silicon ....................................................... 38
4.3 Results from E-beam Evaporation on Crystalline Silicon .................................................. 39
4.4 AFM Results of Electron beam Evaporation on Glass ....................................................... 41
4.5 SEM Results from 150/250/350 Annealed MBE Deposited Aluminum ......................... 42
4.6 SEM Results from Annealed 150/250/350 and Aluminum Etched Samples .................. 45
4.7 TEM Results from Unannealed and 150/250/350 Annealed MBE Deposited Aluminum. 49
4.8 Optical Results from MBE 4nm Unannealed and 150/250/350 Annealed Samples ........ 56
4.9 SEM Results from Electron Beam Evaporation on Amorphous Silicon ....................... 61
   SEM Results for 2nm Unannealed and 150/250/350 Annealed Samples ......................... 61
   SEM Results for Etched 2nm Unannealed/150/250/350 Samples ................................... 64
   SEM Results for 4nm Unannealed/150/250/350 Samples .............................................. 68
   SEM Results for Etched 4nm Unannealed/150/250/350 Samples ................................... 72
4.10: TEM Results of Electron Beam Evaporation on Amorphous Silicon ....................... 76
4.11 Optical Characterization Results of Electron Beam Evaporation on Amorphous Silicon 80
4.12 Electrical Characterization Results of Electron Beam Evaporation on Amorphous Silicon Unetched ..................................................................................................................... 91

Chapter 5: Conclusions and Future Work .................................................................................. 95

5.1 Conclusions ......................................................................................................................... 95

References ..................................................................................................................................... 98

Appendix A: Description of Research for Popular Publication .............................................. 105

Appendix B: Executive Summary of Newly Created Intellectual Property ......................... 107

Appendix C: Potential Patent and Commercialization Aspects of listed Intellectual Property

Items ............................................................................................................................................. 108

C.1 Patentability of Intellectual Property (Could Each Item be Patented) ......................... 108
C.2 Commercialization Prospects (Should Each Item Be Patented) ................................ 108
C.3 Possible Prior Disclosure of IP ..................................................................................... 109

Appendix D: Broader Impact of Research ............................................................................. 110

D.1 Applicability of Research Methods to Other Problems .............................................. 110
D.2 Impact of Research Results on U.S. and Global Society ............................................. 110
D.3 Impact of Research Results on the Environment ......................................................... 111
Appendix E: Microsoft Project for PhD MicroEP Degree Plan ................................................. 112

Appendix F: Identification of All Software Used in Research and Thesis/Dissertation Generation ..................................................................................................................................................... 113

Appendix G: All Publications Published, Submitted and Planned ............................................. 114

Appendix H: Plagiarism Check .................................................................................................. 115
List of Figures

Figure 1.1.1: 3 dimensional image cross sectional image of intended nanoroot growth.............. 1
Figure 1.1.2: Image representing 3 types of silicon........................................................................ 2
Figure 1.2.1: Image representing aluminum induced crystallization process............................. 3
Figure 1.3.1: 2.5 nm thin film annealed at 350°C for 30 min on C-Si substrate ......................... 6
Figure 1.3.2: Heteroepitaxial growth modes [14]...................................................................... 9
Figure 1.4.1: Vapor deposition process on the surface of substrate [14]................................. 11
Figure 1.5.1: Schematic representation of density of states distribution for a-Si:H showing conduction band edge (Ec), valence band edge (Ev), tail states, extended states and defect states [40].......................................................................................................................... 15
Figure 1.5.2: Energy band diagram of an a-Si p-i-n solar cell in thermodynamic equilibrium in the dark/ Ev (valence band)/ Ec (conduction band)/ EF (Fermi level)/ Vbi (built in potential) [40].......................................................................................................................... 18
Figure 1.5.3: Electric field profile generated from numerical simulation for 400 nm thick single junction a-Si solar cell under thermodynamic equilibrium and 1 sun conditions at open circuit conditions [40].......................................................................................................................... 20
Figure: 3.2.1: Cross section view of samples prepared with Al nanostructures.................. 28
Figure 4.1.1: High resolution SEM image of 2 nm MBE deposition [66].............................. 36
Figure 4.1.2: High resolution image of 6 nm deposition 6nm MBE deposition [66].................. 37
Figure 4.2.1: High resolution image of 4 nm of aluminum on amorphous silicon.................. 38
Figure 4.3.1: High Resolution image of 4 nm of aluminum on crystalline silicon.................. 39
Figure 4.3.2: X ray spectroscopy measurements of Al nanodots deposited by electron beam evaporation [67] .................................................................................................................... 40

Figure 4.4.1: Left image: AFM measurement of aluminum nanostructures on glass substrate/ Right: image AFM measurement of bare glass substrate [67] .............................................. 41

Figure 4.5.1: SEM images of MBE deposited aluminum annealed at 150˚C with increasing magnification ........................................................................................................................ 42

Figure 4.5.2: SEM images of MBE deposited aluminum annealed at 250˚C with increasing magnification ........................................................................................................................ 43

Figure 4.5.3: SEM images of MBE deposited aluminum annealed at 350˚C with increasing magnification ........................................................................................................................ 44

Figure 4.6.1: Etched images of MBE deposited aluminum annealed at 150˚C with increasing magnification ........................................................................................................................ 45

Figure 4.6.2: Etched Images of MBE deposited aluminum annealed at 250˚C with increasing magnification ........................................................................................................................ 47

Figure 4.6.3: Etched Images of MBE deposited aluminum annealed at 350˚C with increasing magnification ........................................................................................................................ 48

Figure 4.6.4: Images of the surfaces of 150˚C, 250˚C and 350˚C etched MBE samples .......... 49

Figure 4.7.1: TEM image of unannealed MBE deposited aluminum on amorphous silicon....... 49

Figure 4.7.2: Higher resolution TEM image of unannealed sample with SAED image of blue highlighted area ........................................................................................................................................ 50

Figure 4.7.3: Higher resolution TEM image of unannealed sample showing atomic planes ...... 51

Figure 4.7.4: TEM image of 150˚C annealed MBE deposited aluminum on amorphous silicon. 52

Figure 4.7.5: TEM image of 250˚C annealed MBE deposited aluminum on amorphous silicon. 53
Figure 4.7.6: TEM image of 350˚C annealed MBE deposited aluminum on amorphous silicon. 54

Figure 4.7.7: TEM images of 350˚C sample with changing angle of diffraction....................... 55

Figure 4.8.1: Normalized reflection data for A-Si, annealed and unannealed samples.............. 57

Figure 4.8.2: Etched normalized reflection data for A-Si annealed and unannealed samples..... 58

Figure 4.8.3: Graph of average reflection data from 450 nm to 590 with reference to annealing temperature for etched and nonetched samples ................................................................. 59

Figure 4.9.1: SEM images of 2 nm unannealed sample with electron beam evaporated aluminum on amorphous silicon ............................................................... 61

Figure 4.9.2: SEM images of 2 nm 150˚C sample with electron beam deposited aluminum on amorphous silicon ........................................................................................................... 62

Figure 4.9.3: SEM images of 2 nm 250˚C sample electron beam deposited aluminum on amorphous silicon ........................................................................................................... 62

Figure 4.9.4: SEM images of 2 nm 350˚C sample electron beam deposited upon amorphous silicon surface ................................................................................................................. 63

Figure 4.9.10: SEM images of etched unannealed 2 nm sample of electron beam deposited on amorphous silicon ........................................................................................................... 64

Figure 4.9.11: SEM images of etched 2 nm 150˚C sample of electron beam deposited aluminum on amorphous silicon ........................................................................................................... 65

Figure 4.9.12: SEM images of etched 250˚C sample of electron beam deposited aluminum on amorphous silicon ........................................................................................................... 66

Figure 4.9.13 SEM images of etched 350˚C sample of electron beam deposited aluminum on amorphous silicon ........................................................................................................... 67

Figure 4.9.14 SEM images of etched 150˚C, 250˚C and 350˚C for comparison.......................... 67
Figure 4.9.14: SEM images of 4 nm unannealed sample of electron beam deposited aluminum on amorphous silicon surface ................................................................. 68

Figure 4.9.15: SEM images of 4 nm 150˚C sample of electron beam deposited aluminum on amorphous silicon surface .................................................................................. 69

Figure 4.9.16: SEM images of 4 nm 250˚C sample of electron beam deposited aluminum on amorphous silicon surface .................................................................................. 70

Figure 4.9.18: SEM images of unetched 150˚C, 250˚C and 350˚C for comparison .................. 71

Figure 4.9.17: SEM image of 4 nm 350˚C sample of electron beam deposited aluminum on amorphous silicon surface .................................................................................. 71

Figure 4.9.19: SEM images of etched unannealed sample of electron beam deposited aluminum on amorphous silicon surface ................................................................................. 72

Figure 4.9.20: SEM images of etched 4 nm 150˚C sample of electron beam deposited aluminum on amorphous silicon surface .................................................................................. 73

Figure 4.9.21: SEM images of etched 4 nm 250˚C sample of electron beam deposited aluminum on amorphous silicon surface .................................................................................. 74

Figure 4.9.22: SEM images of etched 4 nm 350˚C sample of electron beam deposited aluminum on amorphous silicon surface .................................................................................. 75

Figure 4.9.23: SEM Images of etched 4 nm 150˚C, 250˚C and 350˚C samples ...................... 75

Figure 4.10.1: TEM cross section of 2 nm 350˚C sample ..................................................... 76

Figure 4.10.2: TEM cross section of 4 nm 350˚C sample ..................................................... 77

Figure 4.10.3: Higher resolution TEM cross section of 4 nm 350˚C sample with SAED images of highlighted areas ......................................................................................... 78

Figure 4.10.4: TEM cross section of 4 nm 350˚C sample showing atomic planes ............... 79
Figure 4.11.1: Graph of transmission results from 2 nm samples compared with A-Si ............... 80
Figure 4.11.2: Graph of reflection results of 2 nm samples compared with A-Si ..................... 82
Figure 4.11.3: Graph of absorption results of 2 nm samples compared with A-Si ................. 83
Figure 4.11.4: Graph of transmission results of 4 nm samples compared with A-Si ........... 84
Figure 4.11.5: Graph of reflection results of 4 nm samples compared with amorphous silicon .. 85
Figure 4.11.6: Graph of absorption of results of 4 nm samples compared with amorphous silicon ................................................................. 86
Figure 4.11.7: Graph of average transmission results of 2 nm and 4 nm samples with respect to increasing annealing temperature ...................................................... 87
Figure 4.11.8: Graph of average reflection results from 2 nm and 4 nm samples with respect to increasing annealing temperature ............................................................. 88
Figure 4.11.9: Graph of average absorption results from 2 nm and 4 nm samples with respect to increasing annealing temperature ............................................................. 89
Figure 4.11.10: Graph of average absorption results from 2 nm and 4 nm samples with respect to increasing annealing temperature ......................................................... 90

Figure 4.12.1: Current vs. voltage measurement for 150 C sample testing 4 points of Van der Pauw measurement ................................................................. 91
Figure 4.12.2: Current vs. voltage measurements for 250 C sample testing 4 points Van der Pauw measurement ....................................................................................... 92
Figure 4.12.3: Current vs. voltage measurements for 350 C sample testing 4 points Van der Pauw measurements ................................................................. 92
Figure 4.12.4: Current vs. voltage measurements for no anneal sample testing 4 points Van der Pauw measurements ................................................................. 93
Figure 4.12.5 Graph of resistivity measurements for 4nm unetched samples .............................. 94

Figure 4.12.6 Graph of resistivity measurements for 4 nm etched samples ................................. 94
List of Tables

Table 3.3.1: MBE Preliminary Depositions................................................................. 30
Table 3.3.2 MBE Deposition on Amorphous Silicon Thin Film................................. 30
Table 3.4.1 Electron Beam Evaporator Deposits on Amorphous Silicon Thin Film........ 32
Chapter 1: Introduction

1.1 Background

The background section of this research project is not one background, but rather three separate background sections that must be combined in order for the goal of the project to be self-evident. The goal of this project was to create a composite nanomaterial that could be inserted into the intrinsic region of a n/i/p solar cell with the intention of improving light absorption and collection probability of minority carriers in comparison to the standard intrinsic amorphous silicon layer that is currently being utilized. An example of this type of material can be seen in Figure 1.1.1.

The nanoroots which extend into the amorphous matrix would be doped p type. They would form a radial pn junction with the amorphous matrix. The thin film would be composed of two of the three forms of silicon. Silicon can be in a crystalline, polycrystalline or amorphous form. Each form has its strengths and weaknesses. Crystalline silicon has a very ordered structure
which makes it great for minority carrier lifetime but it is a poor absorber in comparison to amorphous silicon. Polycrystalline silicon has a semi ordered structure made up of smaller regions composed of crystalline silicon connected by grain boundaries. It is better at minority carrier transport than amorphous silicon but shares crystalline silicon’s weakness of poor absorption. Amorphous silicon has no ordered structure and has great absorption capabilities but the high amount of disorder leads to a poor electron transport. A representative image of the three types can be seen in Figure 1.1.2.

![Figure 1.1.2: Image representing 3 types of silicon.](image)

This task was interesting in that the method chosen to accomplish this task incorporated three separate research areas that must be combined into one process method. The three separate areas included aluminum nanodots that could be self-assembled over large surface area, the aluminum induced crystallization method for converting amorphous silicon to polycrystalline silicon and lastly the n/i/p solar structure and operation. With that in mind there was no one section of background material and no papers with previous work with all of these methods combined. The next question is why use amorphous silicon. It was not the only type of thin film solar cell. The
answer to this question lay with the societal push for more environmentally friendly renewable energy sources. In the arena of photovoltaic devices silicon based devices have been researched the most and have the most infrastructure involved in their manufacture. As the demand grows for silicon then that will also affect the price of silicon material. It must be noted that the solar cell industry demand for silicon is not as large as the semiconductor industry. This is where thin film silicon solar cells save the day. The amorphous silicon solar cell can absorb as much light in 1-2 µm that a crystalline silicon solar can absorb in 300 µm. The only drawback of the amorphous silicon is the high amount of defects that decrease carrier collection. Whoever can find a way to take advantage of the amorphous silicon high absorption and lower its defect density issues will lead the photovoltaic renewable energy race. Whoever can achieve this with already existent scalable equipment will be the future of solar cell production.

1.2 Reaction between Amorphous Silicon and Crystalline Aluminum

Aluminum induced crystallization is a process by which a thin film of amorphous silicon is subsequently crystallized by being in close contact with an aluminum layer and the two layers are annealed. This can be seen in Figure 1.2.1.
This process has a profound effect on the amorphous silicon layer. It not only changes the amorphous silicon to crystalline silicon but it also changes the amorphous silicon layer from intrinsic to p-type. This new found order in its crystalline lattice of the former amorphous silicon improves its minority carrier collection probability but it lowers its absorption coefficient. This process is important to the microelectronics industry because of its use in the production of thin film transistors and thin film solar cells.

Aluminum and silicon have a eutectic temperature at 577°C. Below this temperature the Aluminum induced crystallization process is thought to be a solid state process. [1] It is accepted that the crystallization of amorphous silicon is in response to the reduction of its Gibbs free energy. [2, 3, 4, 5] This fact however does not explain how aluminum aids in this Gibbs free energy reduction. It must also be stated that there are many conflicting theories as to the mechanism of aluminum induced crystallization. One theory suggests that inside the aluminum layer is where crystallization of amorphous silicon crystallization begins. [6, 7, 8] In these works it is believed that the silicon nuclei are formed at the interface between the amorphous silicon and aluminum within the metal layer. These nuclei then grow deeper into the aluminum layer aided in the growth by the other silicon atoms that are diffusing from the amorphous silicon and aluminum layer interface. Once the silicon grain growth has reached the other side of the aluminum layer the crystalline growth stops in the vertical direction but continues laterally until met by the boundary of another silicon crystallite. A contrasting theory suggests that the diffusion of aluminum atoms into the amorphous silicon layer is what initiates crystallization. [9]

In this work electron transfer from aluminum to amorphous silicon was observed. This brought about a proposed diffusion mechanism in which metal atoms move into the amorphous silicon being deposited at the substitutional sites. This in turn further enhances the diffusion of
the silicon, hydrogen and more metal atoms into the amorphous silicon layer. This diffusion creates a continuous internal electric field until the metal and silicon atoms mix entirely. Another proposed mechanism is the formation of a metastable aluminum silicide layer that forms at the interface of the silicon aluminum layer that then initiates crystallization. [10, 11] In this mechanism it is believed that in order to initiate crystallization the silicide that is formed at the interface of the amorphous silicon and aluminum must be of high metallic concentration. If there is not enough aluminum for a formation of the alloy then the crystallization will not start or it will stop if it had started crystallizing. Lastly is a proposed mechanism where the aluminum and silicon interface and the aluminum grain boundaries are the initial sites of crystallization [2, 3, 5, 12] In this work it was suggested that mobile electrons in the aluminum had a screening effect on the covalent bonds of the silicon layer that are closest to these mobile electrons. These now weakly bonded silicon atoms had the ability to migrate. This ability to migrate made itself evident in the diffusion of silicon atoms into the grain boundaries of the aluminum layer and along the aluminum sub layer grain boundaries to where the crystallization begins.

As can be inferred from the aforementioned mechanisms, the aluminum induced crystallization process is neither completely understood nor agreed upon. What is known is the effect that crystallizing amorphous silicon has on its properties. Not only does it bring some short range order to its lattice structure essentially changing it to polycrystalline but also the aluminum is a p-type dopant in the new polycrystalline thin film. The crystallization process allows the formerly amorphous silicon thin film to gain advantages of a polycrystalline film. These advantages include longer minority carrier diffusion lengths and lower defect density but it loses amorphous silicon’s high absorption coefficient. A material composed of a mixture of both materials may be able to take advantage of the positive attributes of both states of silicon.
1.3 Al Metallic Nanodot Formation

Nanostructures, in particular metallic nanodots, are being extensively investigated for potential applications in solid state devices. [13] Information processing, [14] localized plasmon effects, [15] and enhanced light absorption. [16] They have been an integral part in creating other nanostructures such as silicon nanowires. [17] A bulk of the investigations with metallic nanodots have been done with metals that aggregate into metallic nanodot easily when exposed to high temperatures such as Ag and Au. [18, 19] Other metals such as Al that cannot create nanodots simply by annealing have to use template methods to create nanodots. These methods include but are not limited to anodized alumina template, [20] electron beam lithography, [21] and diblock copolymers embedded with metallic salts. [22] There is little research available on aluminum nanodots and even less research on self-organized aluminum nanodots. Much of the research done on self-organized aluminum nanodots has been done on GaAs substrates. [13] This was achieved through droplet epitaxy. Metallic nanodots, for metals that do not have a high reactivity with oxygen, are remarkably simple to create. For example if a thin film of Au was deposited onto a silicon substrate annealed at or above the eutectic. This will cause the thin film of gold to break up into nanostructures of gold as seen in Figure 1.3.1.

Figure 1.3.1: 2.5 nm thin film annealed at 350°C for 30 min on C-Si
Other metals such as Al are not as accommodating as Au because Al is highly reactive with oxygen. Therefore when the thin film is brought into atmosphere and placed into the annealing chamber an Al₂O₃ layer has already formed. This layer restricts Al ability to create nanostructures on the surface of a crystalline silicon substrate. It might be asked why use Al when it is shown that Au readily forms nanostructures on the surface. There are other drawbacks to using Au instead of Al. Au produces deep level traps in silicon. These traps may be thought of as defects that are at an energy level near the middle of the bandgap of the semiconductor where the probability of recombination of electrons and holes increases tremendously. All of these being very deleterious to solar cell operation.

Another setback of both of the thin films is the fact that creating the nanostructures is not the only parameter that must be taken into consideration. With that in mind the process is not as simple as creating a thin film of aluminum on the surface of an amorphous silicon layer and annealing in an oxygen free atmosphere because if the aluminum is in contact with the amorphous silicon all over the surface then it will crystallize it everywhere instead of separate regions.

Taking these constraints into consideration led to the investigation of creating nanodots while depositing instead of creating a thin film first. The key to this type of deposition was found in the processing techniques in the fabrication and growth of quantum dots.

The growth of quantum dots is a self-assembled growth. In order to understand what occurs in this process a basic understanding of epitaxial growth of films is needed. Epitaxial growth can go through different stages. The early stage is known a nucleation. During the nucleation stage vapor atoms or molecules from the depositing material condenses on the surface of the substrate. Once the surface has come into contact with this vapor small islands which are
uniform in distribution and mobile are formed. At this time during the growth the islands are 3D in nature and separate from each other. As the growth continues the original atoms or molecules impinging the surface absorb the new atoms or molecules to grow in size. This process continues to occur until the prior mobile islands merge with each other to form a liquid like material. This is especially prevalent if the substrate is kept at a high temperature. As the merging of islands increases the number of islands decreases. Additional deposition causes the islands to disappear forming unfilled trenches eventually leading to thin film formation. What is wanted in quantum dot growth and metallic dot growth for this research is to stop the growth at the island stage before it coalesces into a thin film.

The three modes of heteroepitaxial growth are the Volmer Weber growth, Frank van der Merwe and the Stranski Krastanov growth. [13, 14] The Volmer Weber growth mode is also known as island growth because of the three dimensional islands that form on the surface during this type of growth. These islands are stable nucleation clusters that form on the surface because the molecules or atoms of the material being deposited is more strongly attracted to itself than the substrate. An example of this type of growth is the growth of quantum dots.

The Frank van de Merwe growth mode is also known as the layer mode. This mode has the opposite effect of the Volmer Weber growth mode. Its nucleation clusters grow and coalesce in two dimensions. This forms a planar layer. This occurs because the atoms or molecules of this deposit are more attracted to the substrate than each other. An example of this type of growth would be epitaxial growth of single crystal semiconductor thin films.

The third example is the Stranski Krastanov also known as the layer plus island growth. Early in the deposition process the atoms and molecules that are being deposited create the nucleation clusters in two dimensions. After one to two monolayers have been grown the layer
no longer supports two dimensional growth and then three dimensional growth begins and the islands form. Those first two monolayers are known as the wetting layers. Although the two dimensional to three dimensional transition is not well understood, it is known that changes in the binding energy in a Frank Van de Merwe (layer) growth can cause two dimensional to three dimensional growth. An example of this is the strain induced self-assembled growth of InAs quantum dots on GaAs substrate. With knowledge of these three growths the goal was to achieve Volmer-Weber growth of the aluminum on the surface of amorphous silicon before the amorphous silicon has the opportunity to fully crystallize. An example of all three heteroepitaxial growth modes can be seen below in Figure 1.3.2.

Figure 1.3.2: Heteroepitaxial growth modes [14]
1.4 Surface Energy and the Capillarity Theory

According to the capillarity theory (droplet theory), a solid nucleates from its liquid or vapor phase by creating a solid liquid (s-l) or solid vapor (s-v) interface with the substrate. [15] These interfaces or surfaces have energies that are associated with them. The atoms of the surface are less constrained than the atoms in the bulk. This causes the atoms on the surface to have more energy than the bulk atoms. Surface energy is the difference between the energy of the surface atoms and the bulk atoms. [15] In homogeneous nucleation systems there is a thermodynamic driving force to reduce the number of dangling bonds of atoms at the surface by them rebonding to each other. The surface energy has units of J/m² and is usually represented by γ.

The capillarity allows a qualitative look at film nucleation [16, 17]. It is a broad general theory that does not take into consideration atomistic assumptions. It does, however, provide a way to deduce connections between variables such as substrate temperature, deposition rate and critical nucleus size. In this research the capillarity theory was used as a way to predetermine whether it was possible to create aluminum nanodots on the surface of crystalline or amorphous silicon. Although this theory can be used to calculate critical film nucleus size and nucleation rate, in reference to this work it was used to determine whether the Volmer Weber growth on crystalline or amorphous silicon was possible. The explanation of the capillarity theory will be restricted to this function. With the capillarity theory, the atoms or molecules from the vapor impinging the surface is assumed to create nuclei (islands) that have a mean dimension of r. The free energy change associated with the creation of the islands is represented by Equation 1.1. An example can be seen in Figure 1.4.1.
\[ \Delta G = \alpha_3 r^3 \Delta G_v + \alpha_1 r^2 \gamma_{fv} + \alpha_2 r^2 \gamma_{fs} - \alpha_2 r^2 \gamma_{sv} \]  

Equation 1.1

- \( \Delta G_v \) = chemical free energy change that drives condensation reaction
- \( \alpha_1 \) = geometric constant \( 2\pi(1-\cos\theta) \)
- \( \alpha_2 \) = geometric constant \( \pi \sin^2\theta \)
- \( \alpha_3 \) = geometric constant \( \pi (2 - 3\cos\theta + \cos^3\theta)/3 \)
- \( \gamma_{vf} \) = interfacial tension between vapor and film
- \( \gamma_{fs} \) = interfacial tension between film and substrate
- \( \gamma_{sv} \) = interfacial tension between substrate and vapor
- \( \alpha_1 r^2 \) = curved surface area of nucleus
- \( \alpha_2 r^2 \) = projected circular area on substrate of nucleus
- \( \alpha_3 r^3 \) = volume of nucleus

Figure 1.4.1: Vapor deposition process on the surface of substrate [14]
Figure 1.4.1 is a representation of the vapor deposition process and the angle \( \theta \) is dependent on the properties of the substrate and the properties of the material that is being deposited. This angle and Young’s equation (Equation 1.2) for interfacial tensions can be used to predict the type of growth from the three growth modes.

\[
\gamma_{sv} = \gamma_{fs} + \gamma_{vf} \cos \theta \tag{Equation 1.2}
\]

In order for a Volmer Weber growth to occur the angle \( \theta \) must be greater than zero. This in turn yields the relation of Equation 1.3.

\[
\gamma_{sv} < \gamma_{fs} + \gamma_{vf} \tag{Equation 1.3}
\]

For Frank Van de Merwe growth the \( \theta \) is equal to zero and yields Equation 1.4.

\[
\gamma_{sv} = \gamma_{fs} + \gamma_{vf} \tag{Equation 1.4}
\]

The Stranski Krastanov growth is opposite of the Volmer Weber growth and yields Equation 1.5

\[
\gamma_{sv} > \gamma_{fs} + \gamma_{vf} \tag{Equation 1.5}
\]

These equations gained from the capillarity theory were used to determine whether surface energy between the aluminum nanodots and the amorphous silicon substrate are favorable for nandot formation.

1.5 Amorphous Silicon Solar Cell

1.5.1 Introduction

Amorphous silicon was first deposited from silane gas in 1969 by Chittik et al. [18] Amorphous silicon films that were deposited from evaporation and sputtering techniques were already in existence at this time. It was found that the technique using silane gas to deposit amorphous films created films that were superior to films from sputtering or evaporation due to
the lower defect density of the silane gas films. The next stage in the evolution of the amorphous thin film was the ability to dope the film. This was found independently by Carlson [19], Spear and Le Comber [20]. The first conversion efficiency of 2% was reported by Carlson and Wronski in 1976. [21] It was found during the early investigations of amorphous silicon that the amorphous silicon that was deposited from silane was actually an alloy of hydrogen and amorphous silicon known as hydrogenated amorphous silicon. In these investigations it was discovered that hydrogen had a definite effect on the optoelectronic properties of the amorphous silicon. [22] In 1977 it was discovered that these thin films suffered changes to the photoconductivity and the dark conductivity when exposed to sunlight. [23] This was later known as the Staebler Wronski effect. These changes in the conductivities were later found to be completely reversible once the films were annealed at 150°C for several hours. [23] The discovery of the Staebler Wronski effect led to the development of amorphous silicon solar cells that have very thin active layers. The reduction in the thickness of the junctions was not all positive. It led to a decrease in the absorption of sunlight, and an increase in shorts and shunts. The low light absorption issue was addressed by incorporating textured optical reflectors into the design. [24, 25] The shorts and shunts issue was solved by a curing process developed by RCA laboratories in which they applied a reverse bias to the solar cell. [26] Further investigations into hydrogenated amorphous silicon led to a number of discoveries and advancements.

1.5.2 Optoelectronic Properties of Amorphous Silicon

Amorphous silicon has a lack of long range order in comparison with crystalline silicon. This extremely short range order creates band tails and a continued distribution of localized states in the bandgap of amorphous silicon. These states are a result of the randomness and defects in the amorphous silicon material. [23, 27] These localized states in the bandgap
determine electronic properties by acting as recombination centers. [28] Amorphous silicon and amorphous silicon alloys have a high absorption coefficient because of this lack of long range order which also helps amorphous silicon to act as a pseudo direct bandgap semiconductor. [29] The electron density of states in amorphous silicon is a function of energy. The randomness of the amorphous silicon structure creates a continuous distribution of localized gap states. The region of extended states is where the electrons and holes can move as free carriers. The properties of high absorption and the bandgap of amorphous silicon can be adjusted by the incorporation of hydrogen, germanium, or carbon into the thin film. [30, 31, 32] Incorporating hydrogen into the amorphous silicon can widen the bandgap and remove defects (dangling bonds). Bandgaps as high as 2 eV can be obtained in an amorphous silicon film with the use of hydrogen. [33, 34] Incorporating very high amounts of hydrogen into the deposition process can also create very thin layers of protocrystalline silicon. These protocrystalline layers are not useful as intrinsic absorber layers. Carbon and germanium alloyed with amorphous silicon can also be used to change the bandgap of amorphous silicon. These alloys have a higher defect density than that of amorphous silicon. There is a tradeoff with how much germanium or carbon can be added before the efficiency of the cell decreases. [35, 36, 37] A typical density of band defects in amorphous silicon deposited from plasma enhanced chemical vapor deposition is less than $10^{16}$ cm$^{-1}$ of the hydrogen content is at 10 at %. There is a decline in defect density near the tail states. Optical absorption between $10^3$ cm$^{-1}$ and 10 cm$^{-1}$ are the result of the absorption in both the valence and conduction band tail states. The valence band tail states are also due to defects in the bandgap that are introduced due to the randomness of amorphous silicon. [38] In amorphous silicon the densities of the bandgap states near the valence band are higher than those near the conduction band. [39] The upper limit of the available bandgap of amorphous silicon is set at
1.9 eV due to the phase change of amorphous silicon to protocrystalline silicon when the silane is over diluted with hydrogen. The lower limit of the bandgap of amorphous silicon is set at 1.3 eV due to the deleterious effects on efficiency that occur when incorporating too large an amount of germanium. These lower and upper limits provide a large enough range to construct single or multijunction solar cells from amorphous silicon and its alloys.

Amorphous silicon’s metastable nature causes the determination of a complete model of its density of states to be difficult. There are many models available and all of these models include conduction and valence band tails. The different models do not agree however on the distribution of states near the bandgap. A schematic example of one of the distribution of states models is shown in Figure 1.5.1.

![Figure 1.5.1: Schematic representation of density of states distribution for a-Si:H showing conduction band edge (Ec), valence band edge (Ev), tail states, extended states and defect states [40]](image-url)
The gap states consist of three types. There are neutral dangling bond states \( (D^0) \) located in the middle of the gap, negative defect states \( (D^-) \) located below the middle of the gap and positively charged defect states \( (D^+) \) located above the middle of the gap. \([41, 42, 43]\) The gap states are critical to the collection probability of amorphous silicon solar cells. Amorphous silicon and germanium alloys have a higher density of deep lying states than that of intrinsic amorphous silicon but the germanium has little to no effect on the tail states. Low level impurities such as oxygen, nitrogen or carbon at levels below several times \( 10^{18} \text{ cm}^{-3} \) have miniscule effects on the electronic properties. \([44]\) With that being said, growth procedures that have an effect on the microstructure which may include the amount of hydrogen dilution of the silane do have an effect on electronic properties. \([45, 46, 47]\) It can be conceived then that an optimization of growth procedures is of extreme importance in the fabrication of commercial level amorphous silicon solar cells. In intrinsic amorphous silicon free carriers travel in the extended states at mobilities of \( 10 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1} \) and \( 1 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1} \) for electrons and holes respectively. \([39]\) To achieve commercially efficient amorphous silicon solar cell operation the densities of the deep lying states should be approximately \( 10^{15} \text{ cm}^{-3} \) to \( 10^{16} \text{ cm}^{-3} \) or lower. This level of deep lying gap states in turn causes the lifetime to be between \( 10^{-8} \text{ s} \) to \( 10^{-6} \text{ s} \). \([28]\) The low level of deep lying gap states lowers the space charge, density which in turn lowers the electric field within the intrinsic region. This allows the electric field created from the p and n section of the amorphous silicon solar cell to extend across the entire cell with minimal to no significant interference from electric fields that may be created within the intrinsic region. \([28]\) The amorphous silicon germanium alloys retain their low midgap state densities around \( 10^{16} \text{ cm}^{-3} \) even with the germanium being as high as 60 at. %. The same cannot be said of carbon. Carbon has a much
more deleterious effect on the structure of the amorphous silicon and it causes a higher density of defects at less than 10 at % which disqualifies it as an absorber layer.

The intrinsic layers used in the amorphous silicon solar cells, although it has a Fermi level near the midgap, were typically slightly n-type. Amorphous silicon’s low amount of midgap defects is what allows amorphous silicon to be doped p type or n type. The addition of dopants such as phosphorous or boron increases the level of defects in the midgap states. This in turn drastically reduces the lifetime of the amorphous silicon material. This is the reason that the doped amorphous silicon thin films are not used as absorber layers in the amorphous silicon solar cells. The p doped layers of a-SiC:H [48] or p-type protocrystalline silicon [49] to create a p/i junction. The n doped layers of amorphous silicon or the n type microcrystalline silicon are used as ohmic contacts. The p doped sides are used as window. The Fermi levels of the p type amorphous silicon and the p type protocrystalline are 0.4 eV and 50 meV from the valence band respectively. The Fermi levels of the n doped ohmic contacts of n type amorphous silicon and microcrystalline silicon are 0.2 eV and 50 meV from the conduction band respectively. These p doped, n doped and i layers are combined into p-i-n and n-i-p cells and have been found to obtain built in voltages over 1 volt. [50]

1.5.3 Physics of Operation of P-I-N Solar Cells

In amorphous silicon solar cells a p-i-n or n-i-p structure is utilized. This structure allows the properties of a-SiGe:H and intrinsic amorphous silicon to be utilized as an absorber layer. An energy band diagram p-i-n structure is shown in Figure 1.5.2.
The p and n layers are used to provide potential difference across the device. Because the p and n doped layers have a high defect density and have short lifetimes [51] the photocarriers generated in this area do not contribute to the overall photocurrent. In the fabrication of single junction p-i-n solar cells, the layer known as the window layer is deposited onto transparent conducting oxide. Next the intrinsic layer is deposited upon the p layer. It is used as an absorber layer. Lastly, the n layer is deposited and used as an ohmic contact. There are certain properties that make a particular transparent conducting oxide optimal for its use in a p-i-n solar cell. These optical qualities include low sheet resistance, high optical transparency between 400-1000 nm, and ideally no potential barrier at the interface between the p layer and the transparent conducting oxide. Any band bending at the interface between the p layer and the transparent conducting oxide is due to bandgap, doping, thickness and density of defects of the p layer. The

Figure 1.5.2: Energy band diagram of an a-Si p-i-n solar cell in thermodynamic equilibrium in the dark/ Ev (valence band)/ Ec (conduction band)/ EF (Fermi level)/Vbi (built in potential) [40]
p layer typically has a thickness of approximately 10 nm. This minimizes optical absorption in the p layer allowing as much light as possible to reach the absorber i layer. The thin p layer also helps achieve a high open circuit voltage. The large density of defect states in the bandgap of the amorphous silicon is responsible for the different operation of the p-i-n solar cell in comparison to the crystalline silicon solar cell. In amorphous silicon solar cells the light is absorbed in the i layer and electrons and holes are generated are swept out of the cell due to the electric field across the cell provided by the n and p layers. In crystalline silicon solar cells photogenerated carriers are primarily collected due to diffusion current but in amorphous silicon solar cells due to their high defect density the primary collection mechanism is due to the drift current. The defects in the material whether native or light induced act as recombination centers and they shield the effect of the electric field across the solar cell. During 1 sun illumination of the amorphous silicon solar cell the photocarrier generation, recombination rates and the electric field become non-uniform across the solar cell. The density of midgap defects, normally around $10^{16}$ cm$^3$, under 1 sun illumination causes the built in electric to decrease across the amorphous silicon solar cell. This can be seen in Figure 1.5.3.
This effect seen in Figure 1.5.3 is caused by the large number of trapped carriers in the localized states shielding the influence of the electric field causing a significant reduction near the center of the i layer. The interface between the p and i layers also has a strong effect on the solar cell properties. [52, 53, 54, 55] Buffer layer between the p and i layers are used to decrease the amount of interface defects. Buffer layers composed of protocrystalline Si:H have proven to be highly effective. [56, 57] The open circuit voltage of an amorphous silicon solar cell is strongly affected by quasi Fermi level splitting. The quasi Fermi level splitting is dependent upon the bandgap and density of photocarriers produced in the i layer. Therefore the open circuit voltage is dependent upon the bandgap. [58] Large values of built in potential are desired for two reasons. They limit the quasi Fermi splitting and they control the electric field present across the device. Typically the D⁰, D' and D⁺ gap states determine recombination and lifetime of the
amorphous silicon solar cell but as the illumination reaches 1 sun conditions quasi Fermi level splitting increases to the point where band tail effects must be taken into consideration [59] P layer and i layer interface regions, under 1 sun illumination, can increase recombination to the point where it has a greater effect on open circuit voltage from that of the bulk recombination. This is particularly evident after light induced defects. [60]

Short circuit current is a result of the collection of carriers produced in the i layer. The collection of those carriers depends on the optical absorption and thickness of the i layer. One must also be able to extract these carriers before recombination. The amount of light absorbed by the i layer can be increased simply by increasing the thickness of the i layer. However, there is a trade off because of the defect density of amorphous materials. The farther the photogenerated carriers have to travel the less the probability of collection. This in turn effects the short circuit current and the fill factor. The challenge remains to maximize the optical absorption but to keep carrier collection at high enough values not to decrease the fill factor. One approach that was used to solve this problem was the use of textured substrates and reflectors. [24, 25] The fill factor is strongly affected by the i layer thickness. The p/i layer interface strongly affects carrier collection and electric field distribution. This in turn affects open circuit voltage and fill factor. These effects are major factors behind why amorphous silicon solar cells are fabricated as thin as possible. These factors also led to the development of tandem a-Si:H/ a-SiGe:H and triple junction a-Si:H/ a-SiGe:H/a-SiGe:H solar cell designs. These designs allow increased absorption even though the layers are thin by having more than one layer. They avoid the deleterious effects of having a thicker i layer. Each i layer of the tandem and multijunction design must have its thickness and optical absorption adjusted to generate the same amount of photocurrent during 1 sun illumination.
1.6 Organization

This dissertation is divided into 5 chapters. Chapter One consists of a background section that includes sections on the purpose of the research, interactions between amorphous silicon and aluminum, aluminum nanodot growth, and amorphous silicon solar cells. Chapter Two is composed of the theoretical calculations on aluminum nanodot growth on amorphous silicon surfaces. Chapter Three presents the experimental procedures. Chapter Four contains of results and discussion. Chapter Five consists of conclusions and future work.
Volmer Weber growth is the growth that is associated with creating the islands of deposited material (nanodots) on a specified substrate. It is represented by Equation 1.3. This equation involves calculating the interfacial energy between the substrate and the vapor ($\gamma_{sv}$). For this research it was represented by the interfacial energy between the amorphous silicon layer and air. The next variable to be calculated was represented by $\gamma_{vf}$, the interfacial energy between the vapor and the film. This was calculated as the interfacial energy between the aluminum and air. Lastly, there was the interfacial energy between the film and the substrate ($\gamma_{fs}$). This was composed of the interfacial energy between the aluminum and the amorphous silicon. The calculations for this work were borrowed heavily from the theoretical work of Zhao et al. [2] The methods for these calculations were taken from a larger model with calculations for the driving forces behind a layer exchange reaction between an amorphous silicon layer and an aluminum layer.

The surface energy ($\gamma_{sv}$) of an amorphous material was considered for a very slow moving liquid for the purposes of these calculations and it was related to temperature through this equation. [61]

\[
(\gamma V^{2/3})_T = (\gamma V^{2/3})_0 + bT
\]  

Equation 2.1

- $V$ = molar volume at temperature T
- $T$ = temperature (K)
- $(\gamma V^{2/3})_0$ = surface enthalpy at 0K
  - liquid (amorphous) silicon 0.480 mJ/mol [61]
- $b$ = measure of entropy
\[ b = \frac{(\gamma V^{2/3})_{T_m} - (\gamma V^{2/3})_0}{T_m} \]  

Equation 2.2

- \( T_m \) = melting point of c-Si (1685 K)

The surface energy of the crystal aluminum was represented by \( \gamma_{vf} \) in Equation 1.3. The surface energy of crystalline aluminum at an arbitrary temperature was estimated utilizing: [61]

\[ \gamma^T = \gamma^o + \frac{dy}{dT} T \]  

Equation 2.3

- \( \gamma^o \) = surface energy at 0K
  
  - crystalline aluminum = 1.169 J/m² [61]

- \( \frac{dy}{dT} = -0.18 \text{ mJ/m}^2 \) [62]

- \( T \) = temperature (K)

The interfacial energy between the crystalline aluminum and the amorphous silicon was represented by the \( \gamma_{fs} \) from Equation 1.3. It was represented by a combination of the enthalpy of c-Al phase, the entropy of a-Si phase and the chemical energy between a-Si and c-Al.

\[ \gamma_{Al-aSi}^{\text{interfacial}} = \gamma_{Al-aSi}^{\text{enthalpy}} + \gamma_{Al-aSi}^{\text{entropy}} + \gamma_{Al-aSi}^{\text{interaction}} \]  

Equation 2.4

\[ \gamma_{Al-aSi}^{\text{enthalpy}} = 2.5 \times 10^{-9} \left( \frac{\Delta H_m^{Al}}{V_{Al}^{2/3}} \right) \]  

Equation 2.5

- \( \Delta H_m^{Al} \) = aluminum melting enthalpy (10.79 kJ/mol) [64]

- \( V_{Al} \) = molar volume of aluminum at melting point (10.50 X 10^{-6} m³/mol) [61, 62]
The entropy was estimated using the equation 2.6 [65]

\[ \gamma_{Al-aSi}^{entropy} = 0.52 \times 10^{-7} \frac{T}{V_{a-Si}^{2/3}} \]  

Equation 2.6

- \( T \) = temperature (K)
- \( V_{a-Si} \) = molar volume of (liquid) a-Si at melting point (11.01 X 10^{-6} m^3/mol) [61, 62]

The chemical interaction energy between amorphous silicon can be represented by:

\[ \gamma_{Al-aSi}^{interaction} = \frac{\Delta H_{Al in Si}^{interface}}{C_0 V_{Al}^{2/3}} \]  

Equation 2.7

- \( \Delta H_{Al in Si}^{interface} \) = enthalpy increase due to addition of one mole of Al atoms to an infinitely large reservoir of silicon
- \( C_0 \) = constant depending on shape Wigner Seitz cell 4.5 X 10^8 [61, 62]
- \( V_{Al} \) = molar volume of Al

Calculations were also performed for creating aluminum nanodots on a crystalline silicon surface. The calculation of \( \gamma_{sv} \) for crystalline silicon was identical to that of crystalline aluminum in Equation 2.3. The \( \gamma^* \) for crystalline silicon was 1.25 mJ/mol [61] and the \( \frac{dy}{dt} \) for crystalline silicon was 0.15 mJ/m^2. [62] The \( \gamma_{sv} \) for the crystalline silicon was identical to that of the amorphous silicon calculations because the deposition material remained aluminum. The interfacial energy between the crystalline silicon substrate and the crystalline aluminum (\( \gamma_{fs} \)) was represented by:

\[ \gamma_{Al-cSi} = \gamma^{interaction} + \gamma^{mismatch} \]  

Equation 2.8

\( \gamma^{interaction} \) = the same as Equation 2.7
\[
\gamma_{\text{mismatch}} = \frac{1}{6} \left( \gamma_{\text{surface energy}}^{\text{cAl}} + \gamma_{\text{surface energy}}^{\text{cSi}} \right)
\]

Equation 2.9

- \( \gamma_{\text{surface energy}}^{\text{cAl or cSi}} = \) was found using Equation 2.3 for Al or cSi

The \( \gamma_{\text{mismatch}} \) was equivalent to the strain caused by the mismatch of lattices at the interface of the crystalline silicon and the crystalline aluminum.
Chapter 3: Experimental Procedures

3.1 Substrate Cleaning Procedures

There were two substrates used in the research experiments, N doped silicon wafers and Corning alkaline earth boro-aluminosilicate glass. Both substrates were rinsed in acetone and dried with nitrogen. Next the substrates were immersed into isopropyl alcohol and dried with nitrogen. The samples were then immersed into a mixture of 1:1 hydrochloric acid and hydrogen peroxide to clean any incidental oils or organics from the surface of the substrates. Lastly before placing substrates into the deposition chamber they were dipped into a 10:1 mixture of deionized water and hydrofluoric acid for 5 seconds. For silicon, this process hydrogen terminated the surface and helped prevent a native oxide for several hours. The glass samples were not subjected to this last HF dip process. If the samples cannot be placed into the deposition chamber within 5 hours of the HF dip then the samples were immersed again into the hydrogen fluoride mixture. After a layer of amorphous silicon was deposited onto the glass sample it was subjected to immersion into the hydrofluoric mixture.

3.2 Thin Film Deposition Procedures

There were two films deposited onto the surface of the substrates using a Plasma Thermo SLR730. There was a 400 nm film of silicon dioxide film (SiO$_2$) deposited first on the substrate, followed by a 300 nm layer of amorphous silicon (a-Si). It was found through experimental results that a layer of silicon dioxide was needed to relieve the stress that occurred between the substrate and the film when heated above 300°C. This layer stopped the amorphous silicon layer from cracking and peeling from the surface of the substrate. The parameters for the silicon
dioxide deposition included a substrate temperature of 250°C, a power of 25 watts and a pressure of 900 mtorr. The flow rates of SiH₄, N₂O, N₂ were 32 sccm, 900 sccm, and 400 sccm respectively. This resulted in a deposition rate was 40 nm/min. The parameters for the amorphous silicon deposition included a substrate temperature of 250°C, a flow rate of 240 sccm of SiH₄, a power of 50 watts and a chamber pressure of 900 mtorr. This resulted in a deposition rate of 30 nm/min. A schematic of the sample can be seen in Figure 3.2.1 which also identifies the area where Al nanostructures were still to be formed.

![Figure: 3.2.1: Cross section view of samples prepared with Al nanostructures](image)

3.3 Experimental Procedure for Molecular Beam Epitaxy

There were several experiments performed in the molecular beam epitaxy chamber. Aluminum nanodots were first deposited on crystalline silicon substrates and then the procedure was modified to deposit them on the surface of amorphous silicon. The parameters for the crystalline silicon substrate deposition were as follows. Silicon substrates were diced into 1 cm squares and then subjected to the substrate cleaning procedure. These substrates were then placed into a Veeco Gen 2 molecular beam epitaxy chamber. This chamber was brought to 10⁻¹⁰ torr before the samples were loaded through a load lock chamber. The substrates were brought to a
temperature of 1000˚C at a ramp rate of 25˚C/min. This process was carried out for a time period of 60 min. In situ reflection high energy electron diffraction (RHEED) was used to determine whether the surface of the substrate was atomically flat or contaminated.

The next step involved the deposition of aluminum. During the deposition of aluminum the substrate was kept at 550˚C. The deposition time was 30 seconds. There were two samples deposited during this preliminary deposition. Sample 1 had the equivalent of 2 nm of aluminum deposited and the sample 2 had the equivalent of 6 nm of aluminum. Sample 1 had an effusion cell temperature of 1055˚C and a beam equivalent pressure of 1.07 X 10^-7 torr during deposition. Sample 2 had an effusion cell temperature of 1105˚C and a beam equivalent pressure of 3.85 X 10^-8 torr. After the deposition these samples were investigated for nanodot growth utilizing the scanning electron microscope.

There was another experimental run involving the molecular beam epitaxy chamber. In the second experiment the substrates were subjected to the same cleaning process. Then there was a 300 nm layer of silicon dioxide and a 400 nm layer of amorphous silicon deposited onto the surface of the crystalline silicon substrate before deposition. In this experiment, because of the crystallization temperature of amorphous silicon, the substrate was only heated to 550˚C before transferring the sample to the deposition chamber. There was a 60 minute ramp up to the desired 550˚C temperature. The effusion cell temperature was 1080˚C and the beam equivalent pressure was 6.32 X 10^-8 torr. The growth time was 30 seconds and the amount of aluminum deposited was equivalent to a 4 nm layer of aluminum. After deposition the sample was characterized utilizing a scanning electron microscope and then diced into 4 separate pieces. Then three of the 4 samples were annealed at 150, 250 and 350˚C for 30 minutes each and characterized utilizing a scanning electron beam microscope. After annealing the samples were
optically characterized utilizing an ellipsometer. Then the aluminum was stripped from the surface utilizing Aluminum Etchant Type D Transene. The surfaces of the samples were examined again in the scanning electron microscope and then they were optically characterized on the ellipsometer. Descriptions of the depositions performed in MBE chamber can be seen in Tables 3.3.1 and 3.3.2.

### Table 3.3.1: MBE Preliminary Depositions

<table>
<thead>
<tr>
<th>Run</th>
<th>Substrate</th>
<th>Aluminum Deposited</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>C-Si</td>
<td>2 nm</td>
</tr>
<tr>
<td>2</td>
<td>C-Si</td>
<td>6 nm</td>
</tr>
</tbody>
</table>

### Table 3.3.2: MBE Deposition on Amorphous Silicon Thin Film

<table>
<thead>
<tr>
<th>Run</th>
<th>Substrate</th>
<th>Anneal Temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>A-Si/SiO₂/C-Si</td>
<td>0°C</td>
</tr>
<tr>
<td>2</td>
<td>A-Si/SiO₂/C-Si</td>
<td>150°C</td>
</tr>
<tr>
<td>3</td>
<td>A-Si/SiO₂/C-Si</td>
<td>250°C</td>
</tr>
<tr>
<td>4</td>
<td>A-Si/SiO₂/C-Si</td>
<td>350°C</td>
</tr>
</tbody>
</table>

### 3.4 Experimental Procedure for Electron Beam Evaporation

This set of experiments was performed after success with the creation of aluminum nanodots on the surface of crystalline silicon in an effort to repeat the process in an electron beam evaporator. There was a preliminary deposition in which crystalline silicon substrates and Corning 1737 glass substrates that had been subjected to the cleaning process were loaded into
the electron beam evaporator. The glass substrates were not immersed in 10:1 HF and Deionized water solution because of the etching that would occur on the glass substrate in that solution. The deposition time was 30 seconds and the amount of aluminum deposited was 4 nm. The substrate temperature was approximately 550°C and the pressure was in the range of $10^{-6}$ torr. This deposition was performed on a custom built electron beam evaporator by MDC.

The next attempt of e beam evaporation was performed on a set of crystalline silicon substrates that were processed through the cleaning procedure followed by deposition of a 300 nm layer of SiO$_2$ and a 400 nm layer of a-Si. This deposition was carried out in a BJD 1800 Temescal electron beam evaporator. The temperature of the substrate was 500°C during deposition. The substrates were rotated at 15 revolutions per minute for uniform deposition. The amount of aluminum deposited on the surface was 4 nm for the first trial and 2 nm for the second trial. Before the aluminum was deposited the substrate was heated at 24% power for 20 seconds, 15% power for 15 seconds and 12% power for 20 seconds. The pressure before deposition was $2.7 \times 10^{-7}$ torr and during deposition it was $3 \times 10^{-5}$ torr. A table of the depositions performed in the electron beam evaporator can be seen in tables 3.4.1. All samples used a 30 second deposition time at 550°C followed by a 30 minute anneal time at 150°C, 250°C or 350°C.
3.6 Plasma Enhanced Chemical Vapor Deposition

The amorphous silicon and the silicon dioxide films deposited in these experiments were deposited utilizing a process known as plasma enhanced chemical vapor deposition. In the traditional chemical vapor deposition gases are introduced to a heated substrate inside the deposition chamber. [76] This gas contains the reactants that recombine to form the film. Gases are used to both transport and supply reactants to the deposition chamber. The reactants diffuse through the boundary layer, come into contact with the surface of the heated substrate and are adsorbed. The chemical reaction occurs separating the gas from the reactant to be deposited onto
the surface of the substrate. The byproduct of the reactants are desorbed from the surface and boundary layer and carried from the deposition chamber in the same gas stream.

In the plasma enhanced process thermal energy from the heated substrate and plasma energy cause the chemical reaction. The amorphous silicon film and the silicon dioxide film were both created from plasma enhanced chemical vapor deposition. The creation of the plasma occurred by applying an electric field to the reactant filled gas. For the purposes of this research this gas was silane (SiH₄). A typical frequency used for this electric field is 13.56 Mhz. The use of high frequency electric fields allowed the use of lower voltages to initiate the plasma. The plasma then sustained itself with the high energy electrons ionizing atoms and molecules in the reactant gas.

The thin film was produced from three interactions that occurred in the deposition chamber. The first interaction was plasma induced fragmentation. The high energy electrons caused the SiH₄ to disassociate into SiH, SiH₂, SiH₃. These free radicals had unpaired electrons which allowed them to react with each other and the substrate to form a thin film. The reaction between the free radicals and the surface was in response to the potential difference between the plasma and the substrate. The plasma acted as the positive end of the potential. The negative end (substrate) attracted the free radicals causing an ion bombardment of the surface. The end result of these three processes was the production of a thin film of amorphous silicon.

3.7 Molecular Beam Epitaxy

Molecular beam epitaxy is a deposition process that involves directing a flux of compound or elemental material at a substrate surface. For the purpose of this research the element deposited was Al but the MBE can be used to deposit elements such as Ga, As and In.
This method of deposition can be used for atomic layer deposition or to produce nanostructures. The materials to be deposited can be introduced to the surface in a solid, liquid or gaseous state. The solid or liquid state of the material is usually heated to vapor phase to introduce it to the substrate surface. If the material is already in a gaseous state then flux generator is used. Molecular beam epitaxy systems have very high vacuum requirements, typically around $10^{-10}$ torr. This is done to achieve high purity in the deposited layers. In molecular beam epitaxy the substrate must been line with the source of the material to be deposited. The high vacuum also allows the mean free path of the flux of the material to be higher than the distance between the source and the substrate. [77] The rate of deposition during this process is typically controlled through altering the evaporation conditions or a high speed mechanical shutter [78]. Molecular beam epitaxy systems are usually built with a specific set of material to be deposited. The source of deposition material for molecular beam epitaxy can come from Knudsen effusion cells, gaseous source, or high temperature evaporator. The Knudsen effusion cell was used in this research. It was composed of crucible, heating element, cooling system, heat shields and a shutter. The technique that was used to create the aluminum nanodots was technique known as droplet epitaxy. It involved depositing a material onto the surface of a substrate and annealing during the deposition process. This process was created by Chickyow and Koguichi. [79]

3.8 Electron Beam Evaporation

Electron beam evaporation is a type of physical vapor deposition. In this process a beam of electrons produced typically from tungsten filament bombard the deposition material. The deposition material acts as an anode attracting the electrons while the tungsten filament acts as the cathode. This process occurs at a minimum pressure of $7.5 \times 10^{-5}$ torr. [80] The electrons
heat the material to its vaporization point of the deposition material from solid to gaseous form. These gaseous atoms after leaving the target material in the crucible precipitate and coat the substrate and everything else in the chamber within line of sight.
4.1 Results from MBE deposition on Crystalline Silicon

The first deposition performed in the molecular beam epitaxy was deposited on crystalline silicon. The two samples created had 2 nm and 6 nm of aluminum deposited on the surface. The surface of these two samples can be seen in Figures 4.1.1 and 4.1.2. These samples were characterized utilizing the scanning electron microscope.

![Figure 4.1.1: High resolution SEM image of 2 nm MBE deposition [66]](image-url)
These first two depositions were preliminary depositions to prove whether aluminum would form nanostructures on the surface of crystalline silicon in a nonoxidizing environment. The 2 nm deposition shown in Figure 4.1.1 showed more separation between the nanostructures. All other parameters besides the amount of aluminum was kept constant. It was accepted that in the 6 nm deposition shown in Figure 4.1.2 that the lack of total separation of all nanostructures was primarily due to the excess amount of aluminum deposited in contrast to the 2 nm deposition. The average diameter of the more spherical nanostructures in Figure 4.1.1 was 38 nm and, although not shown in this figure, there were also oblong shaped nanostructures in this figure with an average length of 100 nm. The average diameter of the larger spherical nanostructures in the 6 nm deposition was 53 nm in Figure 4.1.2 and the smaller spherical nanostructures had an average diameter of 13 nm. The oblong shaped nanostructures in Figure 4.1.2 had an average diameter of 100 nm.

Figure 4.1.2: High resolution image of 6 nm deposition 6nm MBE deposition [66]
4.2 Results from MBE deposition on Amorphous Silicon

The second deposition performed in the MBE chamber was performed on a substrate that was constructed of three layers. A 400 nm layer of silicon dioxide was deposited on the surface of the crystalline silicon and a 300 nm layer of amorphous silicon was deposited onto the silicon dioxide layer. The 4 nm aluminum was deposited onto the layer of amorphous silicon at a substrate temperature of 550°C. Figure 4.2.1 is a high resolution SEM image of the surface of the amorphous silicon layer after aluminum deposition.

![Figure 4.2.1: High resolution image of 4 nm of aluminum on amorphous silicon](image)

The average dot diameter was 10 nm. The nanostructures were smaller in size than the aluminum nanostructures deposited onto the crystalline silicon substrate. The nanostructures appear to be denser than the nanostructures in Figure 4.1.1 and on sections of 4.1.2. There appeared to be clear separation between each nanostructure in Figure 4.2.1. Also in Figure 4.2.1 there appeared to be no oblong nanostructures. The nanostructures in this sample appear to be confined to more
spherical like dimensions. These differences may be due to the difference in the surfaces that were deposited upon. Amorphous silicon surface is much less uniform than a crystalline silicon surface. This lack of uniformity would restrict the movement of the aluminum atoms on the amorphous silicon in comparison with that of the crystalline silicon surface. This restricted movement would not allow as many of the nanodots to combine to form larger nanodots.

4.3 Results from E-beam Evaporation on Crystalline Silicon

The use of the molecular beam epitaxy chamber was never considered as a final solution. It was used in the beginning because of the measure of control that was allowed when using the chamber. The encouraging results from the MBE chamber led to this deposition in a custom built MDC electron beam evaporator. In this deposition the substrate was crystalline silicon. The interesting change in this deposition was that the chamber was only brought to $10^{-6}$ torr before deposition began. Figure 4.3.1 is a higher resolution image of the crystalline silicon surface after 4 nm of aluminum was evaporated onto the surface of the substrate.

![Figure 4.3.1: High Resolution image of 4 nm of aluminum on crystalline silicon](image)
The average diameter of the aluminum nanostructures was 10 nm. The fact that the chamber was only at $10^{-6}$ torr when deposition began to take place caused some ambiguity as to whether the aluminum nanodots were indeed aluminum nanodots covered in a layer of aluminum oxide or whether the aluminum nanodots were actually completely composed of aluminum oxide. Figure 4.3.2 was composed of data taken from x-ray spectroscopy measurement confirming the presence of aluminum and aluminum oxide. This helped confirm that aluminum nanostructures created in a more stringent oxygen depleted environment were also safe from total oxidation.

Figure 4.3.2: X-ray spectroscopy measurements of Al nanodots deposited by electron beam evaporation [67]
4.4 AFM Results of Electron beam Evaporation on Glass

Corning 1737 glass substrates were subjected to the exact same experimental parameters as those of the crystalline silicon substrates. The thought process behind these growths of nanostructures on substrates other than amorphous silicon was to see if the nanostructures could be formed and the amorphous silicon deposited on top of the nanodots, allowing crystallization from the bottom up instead of from the top down. Figure 4.4.1 is composed of two AFM measurement images comparing the surface of a clear glass substrate and a substrate with dots on the surface. The dot sizes were larger in size than the dots found on the crystalline silicon substrates. The main difference in the nanostructures on the glass surface was that they appeared to not have any separation between the dots.

![Figure 4.4.1: Left image: AFM measurement of aluminum nanostructures on glass substrate/ Right: image AFM measurement of bare glass substrate [67] ](image-url)
4.5 SEM Results from 150/250/350 Annealed MBE Deposited Aluminum

The sample shown in Figure 4.2.1 was created in the molecular beam epitaxy chamber. It was also diced into four pieces and three of the pieces were annealed at 150, 250 and 350°C respectively for 30 minutes each and then characterized by SEM before and after etching the aluminum from the surface. Figure 4.5.1 is a group SEM images of the surface of section of the MBE deposited sample that was annealed at 150°C.

Figure 4.5.1: SEM images of MBE deposited aluminum annealed at 150°C with increasing magnification
In image C the aluminum nanostructures have been shown as deposited onto the surface of an amorphous silicon layer. In all three images morphology changes in the surface were seen when compared to the unannealed image in Figure 4.2.1. There were dark spots in all three image scales. These dark areas were similar to nucleation sites seen in conventional aluminum induced crystallization and were believed to be nucleation sites for crystallization in these samples also. Figure 4.5.2 show SEM images of the surface of the sample that was annealed at 250°C for 30 minutes.

Figure 4.5.2: SEM images of MBE deposited aluminum annealed at 250°C with increasing magnification
There were noticeable changes from the morphology of the 150°C sample and the unannealed sample. The dark nucleation sites for crystallization viewed in the 150°C sample also appear in the 250°C sample but with 2 times the amount of nucleation spots. There was not an extreme shift in the size of the nucleation sites. The aluminum nanostructures are also still present after annealing in both the 150°C sample and the 250°C sample. Figure 4.5.3 shows that increasing the temperature caused an increase in the nucleation sites but there was a reduction in size of the nucleation sites in Image G in reference to Image A and Image D. The aluminum nanostructures continued to be visible on the surface in Image I.

Figure 4.5.3: SEM images of MBE deposited aluminum annealed at 350°C with increasing magnification
It must be mentioned that although the figures in Section 4.5 show a number of morphology changes these changes were only on the surface. The crystal sizes can be grown below the visible surface to a maximum of 0.25 cm, 0.25 cm and 300 nm in the x, y and z direction respectively due to the maximum dimensions of the amorphous silicon film. This is due to the maximum dimensions of the film. There was also a noticeable change in the interaction of the aluminum and the amorphous silicon as the annealing temperature increased.

4.6 SEM Results from Annealed 150/250/350 and Aluminum Etched Samples

In this section the surfaces of the samples shown in section 4.5 were etched in Transene Aluminum Etchant Type D. Figure 4.6.1 shows the SEM of the etched surface of the 150°C annealed sample.

![Etched images of MBE deposited aluminum annealed at 150°C with increasing magnification](image)

Figure 4.6.1: Etched images of MBE deposited aluminum annealed at 150°C with increasing magnification
There were greater than a ten times the amount of visible nucleation sites clearly discernable on the surface Image A in comparison with its nonetched counterpart. This indicated that a large amount of nucleation occurred below the initial aluminum layer. Image B showed that the nucleation sites are did not remain separate but grew into each other. In Image C remnants of the aluminum nanostructures were still visible. It must also be noted that although there was much activity at the surface of this film, it does not necessarily constitute a change directly underneath the film or deep into the film. The etching procedure could have taken some of the crystalline regions from the surface if there was an excess of aluminum in that particular area. There was no foreseeable way to control this found at that time.

Figure 4.6.2 showed a change in the 250°C sample from the unetched sample. The nucleation sites that appeared to be separated in the unetched sample were actually connected into several networks of crystals some spanning more than 50 micron in length. The aluminum nanostructures are also gone from the surface. This could have been due to the aluminum etchant or the increased temperature would have provided the increased energy for more aluminum to be diffused into the surface to increase crystal growth. The nanodots were also close enough to where the grain boundaries could connect if there was enough aluminum nearby.
Figures 4.6.3 represented the etched surface of the 350°C annealed sample. In image G a network of crystalline material longer than 200 µm was achieved. Another interesting thing noticed was the network of white fractal like structure also covering the surface as seen in image H. Upon closer inspection in Image I these white sections were composed of small crystalline nucleation sites that were not fully connected with each other. There was also an absence of the remnants of any of the aluminum dots that were noticeable in the other samples. It was also noted that even though the network spanned over 200 µm, there were branches of the network that clearly had nanometer dimensions.
Figure 4.6.4 represents an image of the three annealed samples with the etched surfaces. It showed how dramatically the surface of the samples changed as the annealing temperature increased. The figure also showed the increase in nucleation size from nanometer to tens of micrometers to hundreds of micrometers.
4.7 TEM Results from Unannealed and 150/250/350 Annealed MBE Deposited Aluminum

Figure 4.7.1 is a bright field TEM image of an unannealed sample of the MBE deposited aluminum. This sample was prepared using the focused ion beam TEM preparation technique. In this technique a platinum strip is deposited to protect the sample area and the sample is dug from the surface using a focused ion beam of Ga\(^{3+}\). It is then attached to a sample holder and thinned.
down to 250 nm or less. Although this sample was not annealed it was seen that there was a nanocrystalline composite that formed before the annealing process.

Figure 4.7.2 is a higher resolution image of the same unannealed sample as shown in Figure 4.7.1. Along with this image is shown two highlighted blue areas that were subjected to a selected area electron diffraction (SAED). The two areas subjected to this characterization showed that there were areas of crystalline and amorphous material and only amorphous material. The SAED image with the broad diffuse rings indicated a purely amorphous silicon area. The SAED image with the bright spots and broad diffuse rings indicated an area with both amorphous material and crystalline material.
All other samples that were annealed at 150, 250 and 350˚C had this layer of nanocomposite material because all other samples were taken from this sample. In essence all the other samples started with a layer of crystalline material that was formed during the initial deposition of aluminum upon the surface of the sample.

Figure 4.7.3 shows the atomic planes of the unannealed sample. The plane could be the \( <111> \) plane of aluminum or silicon. The distance between atomic planes for aluminum and silicon are 2.338 Å and 3.138Å respectively. The distance between the lines was calculated by counting the number of repeating atomic plane lines within the 5 nm resolution line to calculate the atomic plane spacing. Sixteen lines were counted revealing a distance between the spacing of 3.125 Å, indicating an approximate crystalline silicon lattice. The area that was used for
calculation is marked by a black rectangle. The atomic planes that were measured seem to have a ripple effect going across the planes. This was caused by another set of planes of a different orientation located behind the first set of planes. The ripple effect is a result of the planes interference with each other as electrons are passing through the sample.

Figure 4.7.4 is an image of the TEM sample that was created from standard TEM sample preparation. Standard TEM sample preparation involves cutting a sample into a 2.5 mm X 2.5 mm square and attaching them to each other with a heat treated epoxy. Then the attached pieces are thinned perpendicular from the surface first by utilizing sand paper and later by ion beam. A layer of nanocrystalline composite was expected because all of the annealed samples were taken from the unannealed sample. One interesting effect, or lack of, was that the nanocomposite region made no change in the amount of amorphous silicon material that was crystallized. The nanocomposite layer confined to less a 50 ± 5 nm layer at the top of the amorphous silicon layer.

Figure 4.7.4: TEM image of 150°C annealed MBE deposited aluminum on amorphous silicon
Figure 4.7.5 is a TEM image of the 250°C annealed sample. It was also prepared utilizing the standard preparation method. It was seen in the image that the crystallized regions near the epoxy had not gone further into the amorphous silicon, even though this sample was annealed at a higher temperature. It was noted that in the surface SEM images the samples had distinct morphology changes but in the TEM images the crystallized sections were not growing further into the surface with an increase in temperature. This could be because of the small amount of aluminum used.

Figure 4.7.5: TEM image of 250°C annealed MBE deposited aluminum on amorphous silicon

Figure 4.7.6 is an image of a TEM sample that was prepared using the focused ion beam method of TEM sample preparation. It was a dark field single area electron diffraction image. In this type of image the crystallized regions are shown as bright areas in the nanocrystalline composite. It was noted that the crystallized regions did not extend further into the amorphous region than did the unannealed sample.
Figure 4.7.7 shows images of the 350˚C sample in which the incident electron beam angle was changed. The images of the different crystalline orientations were taken and numbered while tilting the sample between -10 and 10 degrees. This angle change caused the angle of diffraction to change and highlighted crystallites that had different orientations than the previous angle. During rotation some bright spots disappeared and others appeared. This technique did not reveal if the structure was root like but it did reveal that the orientation of growth was not all in one direction. It was noted that images 1 and 5 had similar bright areas in that were illuminated. This could have been caused by either two crystals with very close orientations or the incident angle of the electron beam of Image 1 could have been at 10˚ and the incident angle of Image 5 at 350˚ or an angle close to that angle.
Figure 4.7.7: TEM images of 350°C sample with changing angle of diffraction
4.8 Optical Results from MBE 4nm Unannealed and 150/250/350 Annealed Samples

Reflection measurements were taken of the samples on Woollam variable angle spectroscopic ellipsometer (V.A.S.E.). First a baseline reflection was taken to establish the value of the ambient light. The baseline reflection was taken from a sample of silicon with a 25 nm layer of silicon dioxide on its surface. The angle of reflection was at 15˚ as was the minimum angle of reflection for the instrument. Next the samples’ reflection was measured. Once the reflection of the ambient and the baseline sample and sample to be characterized was known then the ambient was subtracted by the ellipsometer. The reflection measurements for the baseline sample and the sample to be characterized were both taken at the same angle of reflection and wavelength range. The data being presented was therefore normalized.

Figure 4.8.1 is a normalized graph of the reflection data taken from an amorphous silicon sample, the annealed and unannealed samples for comparison. In the earlier figures a change of only 50 nm was seen in the width of the crystallized region growing into the amorphous silicon regions. These reflectivity samples were not etched before this data was taken so the aluminum nanodots were on the surface of these samples. Therefore aluminum nanodots could have increased the amount of reflection by scattering some of the incident light. Reflection decreased as the annealing temperature was raised until the wavelength 680 nm and then the nanodot samples reflect more than the amorphous sample. The purpose of taking this data was to see if there would be an effect on the reflection of the nonetched samples as the annealing temperature increased. With an increased annealing temperature there is an expectation of an increase in crystallization. It was expected that this increase in crystallization would also cause a change in optical properties. There was expected to be a decrease in reflection between the samples due to scattering and light trapping from nanowires grown into the surface of the sample.
It was also expected for there to be a linear relationship between the increase in annealing temperature and a decrease in reflection. This was not found. The 350˚C sample was never more than 45% less reflection than the other samples. The no anneal, 150˚C and 250˚C sample are never more than 5% in difference in reflection from 450 to 590. The shifting of the peaks and troughs of the reflection data is never more than 30 nm in difference. The peaks in the reflection data are due to the light interacting with several thin films on the surface of a substrate. The width between peak to peak of one of the reflection plots can be used to calculate the thickness of the amorphous silicon layer. The shifting of these peaks could be due to the varying thickness of the nanocomposite film due to crystallization at different temperatures.

Figure 4.8.2 is a graph of the samples after they have been subjected to an etching process. There was a 43% increase in reflection in the 350˚C etched samples form 450 nm to 590. The 150˚C and the no anneal sample reflectivity dropped by 50% from 450nm to 590 nm.
There was less than 2% change from 450 nm to 590 nm from nonetched to etched 250°C reflectivity sample. The peaks and troughs remain within at least 30 nm of each other as in the nonetched samples. This may be due to the aluminum being etched from the surface. Much of the aluminum in the higher temperature annealed sample may have been absorbed within the sample for crystallization. The nonannealing and lower temperature annealed sample may have used less of the aluminum that was deposited onto the surface due to lower amount of energy being provided to the system. Figure 4.8.1 and 4.8.2 show that the aluminum nanodots have some effect on the reflectivity of the samples. The reflectivity data was not conclusive enough to make a connection between the reflectivity and the annealing temperature.

![Reflection of Nanodots Etched](image)

**Figure 4.8.2: Etched normalized reflection data for A-Si annealed and unannealed samples**
Figure 4.8.3 is a graph of the average reflection values of the etched and non-etched samples from 450 nm to 590 nm. This data was taken to ascertain whether the annealing temperature would have an effect on the reflectivity of these samples.

At the onset it was believed that an increase in annealing temperature would have a linear trend with respect to the reflection. This assumption was based on the fact that a greater annealing temperature at a constant annealing time typically produces more crystallization when attempting to crystallize an entire film. It must be noted that when attempting to crystallize an entire film there is typically no aluminum restriction as with these samples. The assumption about a linear relationship with time was wrong as the data etched were not linear with respect to annealing temperature. The etched was more linear than the non-etched but more data points to be would be needed conclusive. The reflection was higher for the non-etched at the 0°C annealing temperature.
This was expected because the aluminum would add to the reflection from the surface. The interaction when the sample was annealed would have an affect on the other samples average reflection. The non etched samples decreased as the temperature became higher. This could have been due to the aluminum being consumed by the aluminum induced crystallization process. The etched samples were not decreasing in reflectivity as the temperature rose. This could be due to the different structures that were formed on the surface during annealing. More investigation will be required to be certain as to why the reflectivity is not decreasing.
4.9 SEM Results from Electron Beam Evaporation on Amorphous Silicon

SEM Results for 2nm Unannealed and 150/250/350 Annealed Samples

The experimental parameters that were used on the MBE machine for the fabrication of the nanocomposite film were repeated on an electron beam evaporator. In these experiments there were two different amounts of aluminum deposited onto the surface of amorphous silicon. The aluminum was deposited on the samples in either a 2 nm or 4 nm film. After the deposition the samples were annealed at 150˚C, 250˚C and 350˚C. Figure 4.9.1 shows an SEM image of the surface of the unannealed sample that had 2 nm of aluminum deposited onto the surface. The aluminum nanostructures shown were in the size range of 3-5 nm.

Figure 4.9.1: SEM images of 2 nm unannealed sample with electron beam evaporated aluminum on amorphous silicon

Figure 4.9.2 shows the image of the sample that had 2 nm of aluminum deposited onto the surface of amorphous silicon after it was annealed at 150˚C. The size of the aluminum dots showed no change but there were large areas of contrast change. This could have been due to roughness of the surface of the sample where in some are higher or lower than the surrounding
area or some of the aluminum coalesced in the surrounding area. There also seemed to be tiny pits in the brighter areas of the 100 nm scale image along with what appeared to be nucleation areas.

Figure 4.9.3 is an image of the 2 nm aluminum 250°C annealed sample. In these images there were dark nanometer sized areas on the surface of the sample. In this image it is difficult to observe certain aluminum nanostructures.

Figure 4.9.3 is an image of the 2 nm aluminum 250°C annealed sample. In these images there were dark nanometer sized areas on the surface of the sample. In this image it is difficult to observe certain aluminum nanostructures.
Figure 4.9.4 is an image of the 2 nm 350°C sample. Images were taken over larger areas in this sample because areas had apparent delamination in the form of bubbling. This instability in the layers may have been due to the different thermal expansion rates of the several thin layers of material. It is also very difficult in this image to observe the absence or existence of aluminum nanoparticles.

Figure 4.9.4: SEM images of 2 nm 350°C sample electron beam deposited upon amorphous silicon surface
SEM Results for Etched 2nm Unannealed/150/250/350 Samples

Figure 4.9.10 was an SEM image of the unannealed sample after deposition and etching. It was seen that all of the aluminum had not been totally removed. This was due to the intermixing of aluminum and amorphous silicon due to the high temperature the sample was exposed to during deposition. Another difference that was noted was the lack of dark nucleation areas in this sample once the aluminum was removed. This was a difference in behavior of the material than that of the MBE samples.

Figure 4.9.11 is an SEM image of the surface of the 150°C sample after it was etched of aluminum. The etching process etched micrometer sized circles into the surface of the film. It also left some of the aluminum particles behind on the surface of the substrate. There were micrometer sized dark areas that appeared to be areas where nucleation was occurring.
Figure 4.9.12 are SEM images of the surface of the 250˚C sample after etching of aluminum. The etched 250˚C sample was very similar in surface morphology to the 150˚C etched sample. There were nanometer pieces of aluminum that were not etched from the surface and the dark areas that appeared to be nucleation were no longer visible on the surface.

Figure 4.9.11: SEM images of etched 2 nm 150˚C sample of electron beam deposited aluminum on amorphous silicon
Figure 4.9.13 is an SEM image of the 350°C sample after etching that showed a large change in its surface compared to unetched 350°C sample. The large dark areas from the nonetched 350°C sample appeared to have nanometer sized nucleation sites hidden beneath the aluminum layer. Although it was not conclusive with prior samples, as an example the nucleation areas typically meant there was crystallization below those areas. The more conclusive evidence would have to come from the TEM cross section of the samples. In the MBE samples all of the samples that showed nucleation sites also showed crystallization below the surface. After etching the 350°C sample it showed that these large areas could have been made of many smaller crystallized regions closely packed together. These regions may have been connected with small amounts of residual aluminum that when etched away separated these sites.
Figure 4.19.14 is an image comparing the surfaces of the 2 nm etched thin films showing the change in the surface with the change in annealing temperature. Nucleation areas are not visible in the 150°C and 250°C samples but the 350°C surface showed a large amount of interaction between aluminum and the amorphous silicon.
SEM Results for 4nm Unannealed/150/250/350 Samples

Figure 4.9.14 are images of the surface of the unannealed sample that had 4 nm of aluminum deposited onto the surface of amorphous silicon. These aluminum nanostructures were closely packed together with diameter ranges from 10 nm to 30 nm. The aluminum nanostructures also appeared to have little to no separation between them and in some areas were overlapping. There were also small dark areas above the aluminum nanostructures.

![Figure 4.9.14: SEM images of 4 nm unannealed sample of electron beam deposited aluminum on amorphous silicon surface](image)

Figure 4.9.15 are images of the surface of the 150°C sample that 4 nm of aluminum deposited onto the surface of amorphous silicon. This sample after annealing appeared the same as the unannealed sample on the surface.
Figure 4.9.15: SEM images of 4 nm 150°C sample of electron beam deposited aluminum on amorphous silicon surface

Figure 4.9.16 are images of the 250°C sample with 4 nm of aluminum on the surface of amorphous silicon. The diameter and the presence of dark areas on top of the nanostructures is unchanged. The dark nucleation sites are showing on the surface of the thin film. This may not necessarily mean an increase in crystallite size. It was anticipated that there was more interaction just below the surface that may become visible after etching the aluminum.
Figure 4.9.16: SEM images of 4 nm 250°C sample of electron beam deposited aluminum on amorphous silicon surface

Figure 4.9.17 are SEM images of the 350°C sample which had the 4 nm of aluminum deposited onto an amorphous silicon film. The dimensions and spacing of the nanostructures remained the same as the lower temperature samples. The dark contrast areas have doubled in size. The images also showed that structures were beginning to grow out of the surface of the amorphous silicon. Figure 4.19.18 is an image comparing the surfaces of the 2 nm unetched thin films showing the change in the surface with the change in annealing temperature.
Figure 4.9.17: SEM image of 4 nm 350°C sample of electron beam deposited aluminum on amorphous silicon surface

Figure 4.19.18 SEM images of unetched 150°C, 250°C and 350°C for
SEM Results for Etched 4nm Unannealed/150/250/350 Samples

Figure 4.9.19 are SEM images of the 4 nm unannealed sample after etching the aluminum. The aluminum nanostructures diminished in size by 50% and there was larger spacing between the nanostructures was quadrupled. The dark areas that were above the unetched nanostructures are now no longer evident. The surface did not appear to have more than two on nucleation sites on the surface of Figure 4.19.19. There is a possibility that these samples have a completely crystallized layer of polycrystalline underneath the aluminum because of the proximity of the nanodots during deposition.

Figure 4.9.19: SEM images of etched unanneal sample of electron beam deposited aluminum on amorphous silicon surface

Figure 4.9.20 showed the surface of the etched 4 nm 150°C sample which had similar results to that of 4.9.19. That is the nanostructures had decreased in size by and the space between nanostructures has increased by the same percentage of the unannealed sample. It might also have had a thin layer of totally crystalline material. Evidence of at least one nucleation site was found.
Figure 4.9.21 showed images of the etched 4 nm 250°C sample surface. There was at least a 10X increase in nucleation sites found on this sample with an increase in annealing temperature. The small rock like features remain evident on the surface and their size and spacing remain constant.
Figure 4.9.22 showed the surface of the etched 4nm 350°C sample. Nucleation sites are also visible on this sample. The nanosized rocklike features originally seen on the surface of 4.9.19 continued to remain on this sample also. The size of the rocklike features also do not change in size even with higher annealing temperature.
Figure 4.9.22: SEM images of etched 4 nm 350°C sample of electron beam deposited aluminum on amorphous silicon surface

Figure 4.9.23 showed the images of the 150°C, 250°C and 350°C sample for comparison with one another. The 250°C sample was the only sample to show signs of nucleation on the surface.

Figure 4.9.23: SEM Images of etched 4 nm 150°C, 250°C and 350°C samples
4.10: TEM Results of Electron Beam Evaporation on Amorphous Silicon

TEM results were taken from the 2 nm 350°C sample. The results are shown in Figure 4.10.1. No areas of crystallization were found in the cross section sample. It was thought because of the earlier success with the crystalline regions on the surface also appearing in the cross section of the MBE samples that this would be the case in the electron beam evaporation 2nm 350°C sample. This assumption was not correct. Several areas near the surface of the amorphous silicon were characterized utilizing SAED. None of the areas showed any crystallization as indicated by bright spots. It must be mentioned that this does not necessarily mean that there were no spots of crystallization but that none were found in the TEM sample that was taken.

Figure 4.10.1: TEM cross section of 2 nm 350°C sample

TEM results were also taken from the 4 nm 350°C sample. This was done in order to ascertain whether the samples would show any root formation or just show a homogenous thin film of crystalline material below the platinum surface. With this goal in mind the TEM sample was taken from the sample that would have the highest probability of showing the largest amount of
crystallinity. The results from the 4nm 350˚C sample can be seen in Figures 4.10.2 to 4.10.4. In Figure 4.10.2 the layer composed of amorphous and nanocrystalline silicon is marked.

![Figure: 4.10.2: TEM cross section of 4 nm 350˚C sample]

This sample also proved the earlier assumption wrong. Its surface after etching did not show small dark crystallization sites, yet there was crystallization below the surface. Several discolorations of varying sizes were seen. These were the crystalline areas. Area C was singled out and magnified as shown in Figure 4.10.3. In this image the length at which the crystalline area extended into the amorphous area was 70 nm. The SAED area is marked by this blue circle were the areas where the SAED was performed. This was the largest crystalline area found on this sample. In area A there were broad diffuse rings showing that it was amorphous material. In Area B there are bright spots but they are not intense. The smaller the crystal the less intense the bright spot. The nanocrystalline area was wider at the surface and tapered off as it extended into the amorphous material, which was promising for the root formation but not conclusive. Not all the crystalline areas extended the same distance into the material.

There was also an overlapping of crystalline material. This can be seen in figure 4.10.4. In this figure there was an area that had ripples like that found in water, (below and right of
region B). This effect was created by two different crystal orientations overlapping. It was very
difficult to determine whether it is a root structure because of the limitations at that time of how
the crystallization is characterized. Figure 4.10.4 is a magnified image of the region to the right
of region B that showed the ripple effect caused by the overlapping crystals.

Figure 4.10.3: Higher resolution TEM cross section of 4 nm 350°C sample with SAED images of highlighted areas
Figure 4.10.4: TEM cross section of 4nm 350°C sample showing atomic planes
4.11 Optical Characterization Results of Electron Beam Evaporation on Amorphous Silicon

Optical characterization was performed on the 2 nm and 4 nm samples and then compared to a nonannealed amorphous silicon film of the same thickness. The reflection measurements were taken in reference to an aluminum mirror and at a 5° angle of incidence. The absorption measurements were taken utilizing an integrating sphere. This technique allowed the measurement to distinguish the effect of scattering from the surface with that of actual absorption. In Figure 4.11.1 from 450 nm to 550 nm the transmission for all samples appears to be equal.

![2 nm Transmission Graph](image)

**Figure 4.11.1: Graph of transmission results from 2 nm samples compared with A-Si**

From 550 nm to 591 the A-Si thin film had the highest transmission starting from 10% at 550 nm and moving to 18.5% at 591 nm. The other films were all below these values at this wavelength range. The other films from highest to lowest transmission values in this wavelength range were
150 C, 250 C, no anneal and 350 C. It must be noted that 250 C and the no anneal sample had less than 2% difference in transmission at this wavelength range. From 594 nm to 617 nm the 250 C and the no anneal sample had the largest transmission starting at 19% and continuing to 36%. The other films from highest to lowest transmission are α-Si, 150 C and 350 C. From 617 nm to 665 nm α-Si had the largest transmission ranging from 36% to 54%. The other films from highest to lowest in this range are 150 C, 350 C, 250 C and no anneal. No anneal sample and 250C sample had negligible differences in this range also. From 672 nm to 723 nm the no anneal and the 250C had the highest transmission ranging from 36% to 79% transmission. The other films from highest to lowest transmission in this range were α-Si, 150 C and 350 C. Lastly from 723 nm to 750 nm α- si has the highest transmission ranging from 80% to 84%. The other films from highest to lowest transmission in this wavelength range were 350 C, 150 C, 250 C and no anneal. The 350 C and the 150 C differences in absorption were negligible just as with the 250 C and the no anneal differences were at this wavelength range. In These transmission measurements were taken in order to establish first if there is a difference in transmission of the amorphous films with the nanocomposite films and then if there was some difference between the nanocomposite films. Figure 4.11.2 reflection measurements for the 2 nm samples in comparison with amorphous silicon sample are shown.
The reflection measurements were taken at a 5° angle of incidence and they were taken in reference to an aluminum mirror. Reflection measurements were taken on the Shimadzu UV 3600 Spectrophotometer. The reflection measurements of 4.11.2 showed that the highest reflection from 450 nm to 556 nm was the 150°C sample ranging from 42% reflection to 50% reflection. The other films from highest to lowest reflection are the 250°C, no anneal, amorphous silicon and the 350°C sample. It must be noted that in this wavelength range the 350°C reflection percentage is more than 30% lower than the other reflection measurements. The 250°C, no anneal and amorphous silicon on glass sample had reflection values that have a less than 7% difference the entire shown spectrum range. The 350°C sample continued to have the lowest reflection values except from 604 nm to 620 nm and 706 nm to 736 nm. The 150°C sample
continued to have the highest reflection values except at 560 nm to 579 nm, 625 nm to 668 nm and 729 nm to 749 nm. In figure 4.11.3 the measurements for the absorption measurements of the 2 nm samples in comparison to the amorphous silicon sample are shown.

![2 nm Absorption](image)

**Figure 4.11.3: Graph of absorption results of 2 nm samples compared with A-Si**

These measurements were taken using an integrating sphere. This process entails enclosing the sample inside the integrating sphere. This sphere is hollow with a white diffuse reflective coating. The sphere also has entrance and exit points for the incident light and measurement. Light scattered from the surface of the sample is evenly distributed inside the sphere and measured. This allows the total power of the light within the sphere to be measured before and after the sample is introduced. The ratio of power within the sphere before and after the sample is introduced can be used to find the absorption of the film.

The absorption data showed a at least a 50% drop in absorption between the amorphous silicon no anneal film and all of the nanodot films from 450 nm to 620 nm. This absorption
difference tapers off from 650 to 750. It must be noted that the pseudo direct bandgap of amorphous silicon hovers around 1.8 eV which correlates to 688 nm. All 2 nm nandot samples absorption stayed lower than 35%. The highest absorption of the amorphous silicon sample was at 68%. The 2 nm samples also showed that all of the 2 nm samples stopped absorbing around 688 nm which is the bandap of an amorphous film.

Figure 4.11.4 shows that all samples with nanodot structures transmission measurements were all within 10% of each other through the entire 450 nm to 750 nm range. The amorphous silicon transmission measurements increased above those of the nanostructures samples starting at 509 nm and continued to 750 nm. Figure 4.11.5 showed that the reflection measurements of amorphous silicon was lower than all of the nanostructure thin films except at 577 nm to 596 nm and 649 nm to 697 nm.

Figure 4.11.4: Graph of transmission results of 4 nm samples compared with A-Si
The reflection measurements from highest to lowest of the nanostructured thin films were no anneal, 150 C, 250 C and 350 C. The order of highest reflection reverses starting at 680 nm and continues to 750 nm. The reflection measurements of all nanostructures became approximately equivalent during the range of 566 nm to 588 nm. Figure 4.11.6 showed that the absorption of the amorphous silicon was higher than all of the 4 nm nanostructures until 650 nm.

Figure 4.11.5: Graph of reflection results of 4 nm samples compared with amorphous silicon
The nanostructure films became higher than the amorphous silicon film from 650 nm to 750 nm. The 4 nm samples have a higher absorption than the 2 nm in the range of 650 nm to 750 nm. The nanostructured films in order of highest absorption to lowest absorption were 150 C, 250 C, no anneal and 350 C. The interesting part about the 4 nm samples is that the absorption data reinforces the crosssectional TEM images of the nanocomposite material. The bandgap of amorphous silicon is 1.8 eV which means that it should stop absorbing around 688 nm. The bandgap of crystalline silicon is 1.2 eV so it should not stop absorbing until 1033 nm. In Figure 4.11.6 the nanocomposite films are still absorbing past the bandgap of amorphous silicon. This increased the evidence of the existence of the nanocomposite film.

Figure 4.11.7 is a graph of the average transmission measurements from 450 nm to 590 nm of the 2 nm and 4 nm samples. This was done to ascertain if there was a linear tread that developed when the annealing temperature was increased, if there was any effect at all.
Figure 4.11.7 did not show a linear trend for either the 2 nm or the 4 nm sample but it did show that the transmission for the 4 nm samples was lower. This was interesting in that the 4 nm samples had more crystalline material in them than the 2 nm sample.

This was confirmed by the absorption data of both samples. The 2 nm samples absorption stopped around 688 nm along with the amorphous silicon sample. The 4 nm sample continued to absorb past the bandgap of amorphous silicon. Amorphous silicon had a higher absorption coefficient in the nanometer range that the average transmissions were taken from. The 2 nm sample, which had a larger amount of amorphous silicon than the 4 nm samples, had higher transmission. This was counter to what was known about amorphous silicon being the better absorber. Although this information was promising it could not be taken as conclusive until it was compared with the reflection data because the light could be being reflected or scattered instead of absorbed.
Figure 4.11.8 is a graph of an average of reflection measurements from 450 nm to 590 nm of both the 2 nm and the 4 nm films.

![Graph of average reflection measurements](image)

**Figure 4.11.8: Graph of average reflection results from 2nm and 4nm samples with respect to increasing annealing temperature**

Figure 4.11.8 showed that the 4 nm average reflection measurements were below those of the 2 nm sample. This was promising because the transmission measurements for the 2 nm sample were also lower. The only pathways left for the incident light were scattering or absorption. If the absorption was higher for the 4 nm sample then it would prove that the thin film with the nanocomposite layer was actually absorbing more light than the layer with more amorphous silicon inside and outside the bandgap of amorphous silicon. The absorption graphs already showed that the bandgap was extended. Figure 4.11.9 is a graph of the average of absorption measurements from 450 nm to 590 nm of the 2 nm and the 4 nm samples. There is a trend with
the 2 nm samples that show a decrease in reflection with an increase annealing temperature. The 4 nm samples continued to not be linear with respect to the annealing temperature.

Figure 4.11.9 provides conclusive evidence that the 4 nm nanocomposite thin film was better at absorption than the 2 film inside and outside the bandgap of amorphous silicon. The only difference between the two films was the nanocomposite layer. This better absorption could be due to the many different orientations of crystals providing light trapping within the amorphous material.

Figure 4.11.9 provides conclusive evidence that the 4 nm nanocomposite thin film was better at absorption than the 2 film inside and outside the bandgap of amorphous silicon. The only difference between the two films was the nanocomposite layer. This better absorption could be due to the many different orientations of crystals providing light trapping within the amorphous material.

Figure 4.11.10 is a graph of the average absorption of the 2 nm and 4 nm samples from 670 nm to 720 nm in reference to the annealing temperature. It showed that there was no linear relationship between the annealing temperature in either the 2 nm or 4 nm samples.
The 4 nm absorption was higher than the 2 nm samples at all annealing temperatures by at least 133%. The 2 nm average absorption values being so near to 0 with a range across the bandgap of amorphous silicon adds more evidence that this material is amorphous.

Figure 4.11.10: Graph of average absorption results from 2nm and 4nm samples with respect to increasing annealing temperature
4.12 Electrical Characterization Results of Electron Beam Evaporation on Amorphous Silicon Unetched

The 2 nm and 4 nm samples had room temperature IV and sheet resistance measurements taken utilizing the Van der Pauw method. The 2 nm samples resistivity was exceedingly high due to leakage current and could not be presented with any expectation of accuracy. The 4 nm sample room temperature measurements were successful. The 4 nm resistivity measurements are shown in Figures 4.12.5 and 4.12.6. Figures 4.12.1 through 4.12.4 show the linear relationship of current and voltage for the 4 nm samples between the point metal contacts placed at the 4 corners of the film.

![Graph showing current vs. voltage measurement for 150 C sample testing 4 points of Van der Pauw measurement](image)

**Figure 4.12.1: Current vs. voltage measurement for 150 C sample testing 4 points of Van der Pauw measurement**
Figure 4.12.2: Current vs. voltage measurements for 250 C sample testing 4 points Van der Pauw measurement

Figure 4.12.3: Current vs. voltage measurements for 350 C sample testing 4 points Van der Pauw measurements
After the current voltage measurement the sheet resistance was measured at room temperature on the samples and the resistivity were calculated. Each sample was measured 4 times before they were etched and measured another 4 times after etch. The resistivity increased as expected by the etching of the aluminum but the trend remained the same with the samples. The resistivity decreased as the annealing temperature increased most apparent in the 350˚C samples. This resistivity change was due to the increase in crystalline material resulting from the aluminum induced crystallization process. These measurements are shown in Figure 4.12.5 and Figure 4.12.6.

Figure 4.12.4: Current vs. voltage measurements for no anneal sample testing 4 points Van der Pauw measurements
Figure 4.12.5 Graph of resistivity measurements for 4nm unetched samples

Figure 4.12.6 Graph of resistivity measurements for 4 nm etched samples
Chapter 5: Conclusions and Future Work

5.1 Conclusions

In this work a thin film of composite material was grown utilizing the aluminum induced crystallization process. This thin film was created using deposition techniques of the molecular beam epitaxy, electron beam evaporation, and plasma enhanced chemical vapor deposition. It was found that the 2 nm sample did not create a composite film even at the highest annealing temperature. It can be supposed that the TEM sample that was created missed a crystalline section and that there were crystalline regions in the film. The problem with this hypothesis is that the absorption data for the 2 nm films showed that the bandgap (1.2 eV) of all of the 2 nm films was the same as that of a completely amorphous film. This lent credibility that either there was no crystallization or that the crystallization was in such small amounts it was not enough to shift the bandgap in all of the samples. If this hypothesis is to be believed then it was concluded that a minimum amount of aluminum needs to be deposited in order to illicit a physical response when the film is annealed. This provides a crucial piece of information for future runs when a standard recipe for producing the nanocomposite layer would be constructed.

In contrast to the 2 nm films, the 4 nm films showed a bandgap shift in its absorption data in which the films kept absorbing past the bandgap of amorphous silicon thin films. This was also done with only a maximum of 70 nm of the amorphous silicon film being converted to the composite material. Another interesting piece of information is that there is less than a 30% difference in absorption for all nanocomposite films at different temperatures. This led to the conclusion that all the crystallization occurred as soon as the aluminum was deposited on the surface. The resistivity measurements showed a difference in the film electrically when the film was annealed. So although it was not visible by an increase in crystal growth down into the
amorphous film, there was a definite change occurring within the amorphous film during annealing.

The etched and non-etched 4 nm samples showed that sheet resistance was lowered as the annealing temperature increased. This trend continued after the aluminum was etched from the surface. This provided evidence that the resistivity was not lowered because of aluminum but due to a change in the film. In essence this work provided evidence that a way has been created to shift the band gap of a thin film and to lower the resistivity of the film. Several other material aspects were found.

The creation of the nanodots on the film was possible but it may not be necessary. The 4 nm samples did not have totally separated nanostructures but did give a composite film. It was originally thought that the entire film would crystallize unless the aluminum was completely separated. There must be a minimum amount of aluminum for the composite film to occur. There may only need to be a restrictive amount of aluminum to produce the composite film but not so little as to not crystallize at all.

The growth of aluminum nanostructures on readily available equipment. Aluminum nanostructures are not new they are just typically made with template because of the difficulty of producing the nanodots thermally because of aluminum’s restrictive oxide layer once exposed to atmosphere. Aluminum nanostructures along with other metallic nanostructures are also used in batteries, nanowire growth and bioluminescence research. Another important fact is that the nanostructures were created in at least one set of experiments using readily available equipment and techniques.

The films were also created on glass substrates which allowed them to be optically and electrically characterized without the need for specialized equipment. The thin films were also
able to cover large areas which in the future will allow for easier characterization and creation of new devices. In the future it may be found that amorphous silicon is not the only material in which a composite material may be useful.

Amorphous germanium films are can also be crystalized by aluminum thin films. Although this work is a proof of concept the importance of a hand tailored thin film with chosen crystalline areas will be invaluable in the future not just in the solar cell industry. This work has laid the ground work for future developments with this technique.
References


Appendix A: Description of Research for Popular Publication

New Research Field May Have Been Found

By: Benjamin Newton

Four years ago Dr. Hameed Naseem a professor at the University of Arkansas Fayetteville had asked himself a question. Can amorphous silicon thin film solar cells be improved by creating electron highways within the solar cell? These avenues would provide a route in the material that has fewer defects allowing for a higher probability of collecting minority carriers.

Amorphous silicon solar cells are great at absorbing energy but the electron transport is very poor because of defects. These defects can be thought of as potholes in a road large enough to stop a car. Dr. Naseem’s idea was to create a better highway in the material. The better highway in this case would be a nanocrystalline wire.

With this idea in hand he put Benjamin Newton one of his best Microelectronics Photonics doctoral candidates on the task. This student used nanosized aluminum to create these pathways in the amorphous material utilizing a technique known as aluminum induced crystallization. He then crystallized certain regions while keeping the rest of the material amorphous.

With his technique he was able to widen the band gap of the amorphous silicon thin film and decrease the resistivity of the material. In an interview with this magazine Benjamin Newton was quoted as saying “This opens the door for not just amorphous silicon thin films but any amorphous film that can be crystallized using a metal. It is like discovering a whole new field of research.”
Benjamin Newton went on to explain that the difference in their technology is that it does not seek to crystallize the entire film which either gives you only the properties of a polycrystalline film. He also mentioned that incidentally they also found a way to create aluminum nanodots without a template, which is usually difficult because aluminum is easily oxidized. A 3 dimensional image of this revolutionary film can be seen in Figure 1 below.

The University has filed a patent on this research as they move forward to protect all the intellectual property that may come from discovering a material that could revitalize the amorphous thin film silicon industry.

Figure 1: 3 dimensional cross section of nanocomposite film for next generation solar cells
Appendix B: Executive Summary of Newly Created Intellectual Property

1. A process for creating aluminum nanostructures on the surface of crystalline and amorphous semiconductor material and glass.

2. A method of creating a film composed of nanocrystalline silicon and amorphous silicon layers grown into each other
Appendix C: Potential Patent and Commercialization Aspects of listed Intellectual Property

Items

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

1. The process for creating aluminum nanostructures on the surface of crystalline and amorphous silicon and glass surfaces cannot be patented because it would be considered obvious to a person skilled in the art.

2. There has been a provisional patent application filed for the material created through the University of Arkansas. The patent number is 61641596.

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

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

1. This process of creating aluminum nanostructures is not worth the patent the information is out there. It is not new of itself but a method used to achieve something else. Its commercialization value is minimal.

2. The method should be patented. This may be a new field a way to create not only better solar cells but sensors as well.
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.


D.1 Applicability of Research Methods to Other Problems

The research of combining different phases of the same material through selective crystallization is not only applicable to amorphous and nanocrystalline silicon. Amorphous silicon and aluminum are also not the only metal and semiconductor that have a crystallizing effect when in close proximity while being annealed. This method of creating these other materials to ascertain if there is a combined effect hitherto unknown will be the future. One day we may be able instead of just looking for the material that has the right properties for the job in the very narrow window to tailor making the material for the device from its combined abilities.

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

This research will have no impact on the U.S. and Global Society as of yet. This is because it is in the infancy of its research phase. The material that was created during this research needs to go through several iterations and characterized before it can leave the lab. This aspect significantly reduces the impact it will have on the everyday citizen. The material may in the future if knowledge of its capabilities become more widespread will increase research and cause frustration among many graduate students thus causing an uptick in alcohol sales.
D.3 Impact of Research Results on the Environment

This research method involved in this research will not impose any further impact on the environment that does not already exist from the creation of molecular beam epitaxy, plasma enhanced chemical vapor deposition or electron beam evaporation equipment or gases. The research was performed with only these equipments mentioned above.
Appendix E: Microsoft Project for PhD MicroEP Degree Plan

1. Writing background for dissertation
2. Take candidacy test
3. Optimize pill solar deposition
4. Help install and learn e-beam lithography
5. Run experiments for nanoroot growth
6. Start putting results in dissertation
7. Write up PhD proposal
8. Nanoroot experiments
9. Prepare pill solar cell with nanoroots
10. Characterize pill solar cell with roots
11. Start putting results into dissertation
12. Bring rough draft to professor and thesis committee
13. Discuss thesis improvements with committee
14. Begin Powerpoint
15. Bring rough draft of power point to research professor
16. Incorporate changes into rough draft
17. Gather all final necessary forms for thesis turn in and defense
18. Practice for thesis defense
19. Send all abstract title and scheduling information to microprep
20. Last day of public presentation
21. Last day to defend
22. Dead day
23. Graduate with masters degree
Appendix F: Identification of All Software Used in Research and Thesis/Dissertation Generation

Computer #1:
   Model Number: ASUS Q500
   Serial Number: D1N0AS08375901C
   Location: 1648 N. Linda Jo Place Fayetteville Arkansas 72703
   Owner: Benjamin Newton

Software #1:
   Name: Microsoft Office 2007
   Purchased by: Benjamin Newton
Appendix G: All Publications Published, Submitted and Planned


5. B. Newton, H. Abu-Safe, M. Benemara, S.Yu and H. Naseem.“Fabrication of Site Specific Amorphous/NanoCrystalline Silicon Composite Thin Film for Solar Cells”, 38th IEEE PVSC Conference, Austin, TX, June 2012.


Appendix H: Plagiarism Check

This dissertation/thesis was submitted by {your name} to http://www.turnitin.com for plagiarism reviewed by the TurnItIn company’s software. I examined the report on this dissertation that was returned by that plagiarism review site and attest that in my opinion the items highlighted by the software are incidental to common usage and are not plagiarized material.

_______________________

Ken Vickers
Director, MicroEP Graduate Program

_______________________

Dr. Hameed Naseem
Dissertation Director