A Novel nonlithographic method to fabricate nanoparticles and its application in crystallization of amorphous silicon thin films

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A NOVEL NONLITHOGRAPHIC METHOD TO FABRICATE NANOPARTICLES
AND ITS APPLICATION IN CRYSTALLIZATION OF
AMORPHOUS SILICON THIN FILMS

by

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ABSTRACT

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In recent years nanoparticles fabricated by nonlithographic techniques have shown a very promising alternative implementation to make novel electronic and photonic devices. However, the size control of these nanoparticles has been a great challenge. In this dissertation we used a custom designed ultrahigh vacuum nanocluster deposition system to investigate the size control of nanoparticles by varying different process parameters. The experimental values are compared with existing models and results are found to be in good agreement.

Silicon thin films are very important for the fabrication of a variety of devices including flat panel displays and solar cells. However, the Si thin films used in most of these devices today are amorphous in nature, which limits their performances and functionalities. In this dissertation we investigated the crystallization of amorphous Si thin films using aluminum and other metals as a seed layer. We achieved a temperature of 500 °C to crystallize the amorphous Si thin films, which is much below softening point of glass. In addition, we also investigated the crystallization of amorphous Si thin films using Al nanofilms. Our results show an average 70% increase of transmission coefficient in visible spectrum after Si is crystallized by Al nanofilms.
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CHAPTER 1
INTRODUCTION

In recent years nanoparticles have become to more and more promising for the implementation of a variety of novel electronic and photonic devices with outstanding functionalities and performances. A few examples of these devices are quantum dot LEDs and lasers; nanoparticle based high efficiency solar cells, single electron devices, and plasmonic devices. For most of them it is typically required for the nanoparticle dimensions to be in the range of 1 to 20 nm with a size variation of 10% or less. The current lithographic techniques are not suitable for the implementation of such nanoparticles. Nonlithographic techniques therefore are being increasingly used for their fabrication [1, 2]. However, most current nonlithographic techniques are based on self-organization process, so they suffer from lack of flexibility or lack of engineering control. Among them, chemical solution based techniques are predominant [3, 4]. While such solution based techniques are capable of producing nanoparticles with the required dimensions, they require complex passivations which involve organic capping molecules to prevent aggregation. These capping molecules further modify the electrical surface properties of the nanoparticles, making charge injection/extraction difficult.

We investigated a novel nonlithographic method [5] to fabricate nanoparticles which overcomes the above problems. One of applications of this method is fabricate aluminum nanoparticles which can further be used to crystallize amorphous silicon (a-Si) thin films. The crystallization of a-Si thin films is increasingly gaining interest for fabricate devices such as thin film transistor (TFT) and thin film solar cells [6, 7, and 8]. However, in this dissertation we only investigated aluminum nanofilm induced
crystallization which is a necessary step for the further investigation of aluminum nanoparticle induced crystallization.

1.1 A Novel Method to Fabricate Nonlithographic Nanoparticles

Our method is based on an ultra high vacuum (UHV) nanoparticle deposition system (NanoSys-1) which is custom build for the implementation of nonlithographic nanoparticles to solve the above issues. This system utilizes a combination of inert gas condensation technique and sputtering evaporation to generate nanoparticles [9]. The unique part of this system is the nanoparticle sized control which is implemented by varying the flow rate of inert condensation gases, and parameters of a quadruple mass filter (QMF). In such a way, there are two different methods to implement nanocluster size control. The first method involves magnetron sputtering vaporization of target materials followed by an inert gas condensation in an aggregation region to form nanoclusters with different sizes. The second method involves a quadruple mass filter which is located between the aggregation region and the deposition chamber. The QMF used in this dissertation is designed for analyzing, electrostatically manipulating and filtering charged nanoparticles. Nanoclusters with wide size variation coming out of the nanoparticle sputtering source passing through aggregation region are filtered by the QMF to allow clusters of a preselected specific size with an adjustable distribution. Our experimental results are in good agreement with the existing theoretical models [10-13].

We also investigated the second nanoparticle deposition system (NanoSys-2) which is an improved version of NanoSys-1. For this system besides the nanoparticle size control we investigated the nanoparticle deposition rate control as well. Comprehensive
data were obtained for gold nanoparticle. These data showed how the deposition rate is controlled by varying the flow rate of magnetron sputtering gas (argon was used in this work), the flow rate of aggregation gas (helium was used in this work), the aggregation length, and the magnetron sputtering power.

1.2 Metal Induced Crystallization of Silicon

Silicon thin films are very important for the fabrication of a variety of electronic and photonic devices. However, the silicon thin films used in most of these devices today are amorphous in nature, which limits their performances and functionalities. In recent years the crystallization of amorphous silicon (a-Si) is increasingly gaining interest for fabricating polycrystalline silicon devices such as thin film transistors (TFTs) and thin-film solar cells [14]. Most attention in the field of crystallization has been given to solid phase crystallization (SPC) and laser crystallization [15]. But SPC suffers from long annealing times and rather high temperature while laser crystallization remains an expensive and complex process. Due to these problems, metal-induced crystallization (MIC) has been investigated as an alternative crystallization process for thin-film device fabrication [16, 17], although the interaction of metal and a-Si has been studied for many years.

Aluminum-induced crystallization is one of the most used techniques because it has the following advantages: simple processing, process temperature normally below 600 °C (glass softening point), standard industrial fabrication techniques, and short time of crystallization (less than one hour). It is also due to the fact that Al has a low resistivity and a good adhesion to a-Si. In this dissertation, we first investigated both bulk aluminum
and bulk silver induced crystallization of a-Si in a wide range of annealing temperatures (from 200 °C to 1,000 °C). The deposition of silicon on these two metals was done by electron beam evaporation. The silicon of 400-nm thickness was deposited onto the aluminum with a thickness of 100 nm. After the deposition the thin films were then annealed at different temperatures under a nitrogen filled furnace. Under annealing the metal was induced into a-Si, and making it to crystallize. The crystallization then was investigated by two different techniques, X-ray diffraction (XRD), and Raman spectroscopy. The lowest crystallization temperature we achieved was 500 °C which is much below the glass softening point. The silver induced crystallization was done in the same procedure, but with two different thicknesses of silicon layers. They were 400 nm and 250 nm. The silver induced crystallizations were also observed. There was not much difference in annealing temperature for difference thicknesses. But the lowest temperature needed for silver was 700 °C.

In this dissertation three low-melting-point metals (lead, tin, and indium) with different thicknesses in a total of 18 samples were also investigated for the crystallization of silicon thin film with an annealing temperature range of 140 °C to 580 °C. However, there were no crystallizations observed for the temperature range we used.

1.3 Aluminum Nanofilm Induced Crystallization of Silicon

After bulk aluminum induced crystallizations of Si thin films were confirmed we investigated aluminum nanofilm induced crystallization of silicon thin film which is the preparation for aluminum nanoparticle induced crystallization. The thicknesses of aluminum nanofilm we used were 2 nm, 6 nm, and 10 nm which were also deposited by
electron beam evaporation. The thicknesses deposited onto the aluminum nanofilms were 3 nm, 8 nm, and 13 nm. We investigated nine samples in total. The annealing temperature was kept at 500 °C for all samples which were maintained in a high vacuum chamber during the annealing process. After the annealing the results were examined by X-ray diffraction and Raman spectroscopy. The crystallization of 13-nm Si deposited on 10-nm aluminum nanofilm and 8-nm Si deposited on 10-nm aluminum were detected by the X-ray diffraction. Raman spectroscopy didn’t detect any crystallization of all nine samples. We then used a spectrophotometer to investigate the optical property of the annealed samples. Our results showed an average 70% increase of transmission coefficient in visible light spectrum compared to the ones before the annealing. From this fact we believe all the nine samples of a-Si thin films were crystallized by aluminum nanofilms.

1.4 Organization of the Dissertation

This dissertation is divided into three parts. Part one covers the structure, functionalities and performances of a nanocluster deposition system. This system was used to fabricate nonlithographic nanoparticles for the investigation of deposition rate control. The nanoparticle size control is also covered in part one which including the control by gas aggregation, and by a quadruple mass filter. Part two covers metal induced crystallization of silicon thin films at low temperatures. Five different kinds of metals were used to do this investigation. Based on the work done in part two, part three covers aluminum nanofilm based metal crystallization of silicon thin films. At the end of this dissertation a detailed recommendation of future work for aluminum nanoparticle based metal crystallization of silicon thin films is included.
CHAPTER 2
NONLITHOGRAPHIC FABRICATION OF NANOPARTICLES

2.1 Introduction

Nanoparticles of metals and semiconductors are getting more and more interests in recent years for their superior functionalities and performances to fabricate electronic, photonic, and plasmonic devices. The dimensions of these nanoparticles are required to be in the range of 1 to 20 nm. In this dissertation we utilized a novel nonlithographic method to fabricate nanoparticles within such a range. The method was implemented using an ultra high vacuum system (NanoSys-1) which was custom built by Oxford Applied Research, UK [18] (figures 2.01 and 2.02 show the front view and the rear view [19]). We investigated the parameters controlling the size of nanoparticles, and the parameters controlling nanoparticle deposition rate.

![Figure 2.01 Front view of NanoSys-1](image)

Figure 2.01 Front view of NanoSys-1
2.2 Nanoparticle Deposition System

This system has a nanoparticle unit which includes nanocluster source housed in an aggregation tube, and a quadruple mass filter (QMF) to implement size-controlled nanoparticle deposition (figure 2.03). NanoSys-1 also includes a mini e-beam evaporator with 4 pockets mainly to implement metal contacts on a nano device (figure 2.04).

Figure 2.02 Rear view of NanoSys-1

Figure 2.03 Deposition chamber, QMF, and nanocluster source
To implement nanoparticle-based devices such as single electron transistors, quantum dot lasers a system should be able to fabricate three components. They are (a) nanoparticles, (b) metal contacts, and (c) isolation dielectrics. NanoSys-1 also equipped with a torus 2” magnetron type sputtering source (made by Lesker [20], figure 2.05) to deposit isolation dielectrics.
The ultra high vacuum of NanoSys-1 is achieved by five pumps (figure 2.06). Pump 1 and 2 are dry mechanical pumps while pumps 3 through 5 are turbo pumps [19].

Figure 2.06 Schematic diagram showing the location of all pumps

Figure 2.07 shows the vacuum level maintained in the deposition chamber during this dissertation work.

Figure 2.07 Vacuum level maintained in the deposition chamber
2.2.1 Components and Functions

In this dissertation we only investigated the nanoparticle unit (figure 2.08) which includes the nanocluster source, and the quadruple mass filter (QMF).

![Image](image1.png)

Figure 2.08 Nanoparticle unit

2.2.1.1 Nanocluster Source

From figure 2.09 it can be seen the nanocluster source is housed in aggregation tube [19]. A magnetron discharge is used to generate nanoclusters.

![Image](image2.png)

Figure 2.09 Schematics of nanocluster source and aggregation tube
Figure 2.10 Outer view of the magnetron sputtering source

The magnetron (figures 2.10 and 2.11) is specially designed for high pressure (up to several Torr) operation and a high sputtering rate. Rare earth magnets are installed behind the magnetron targets which are standard 2 inches in diameter. The whole magnetron assembly is water cooled, and its distance to the aperture can be adjusted by linear motion drive. By varying this distance the residence time of nanocluster in the aggregation region is varied, and hence the nanocluster size.

Figure 2.11 Inner view of the magnetron (sputtering gun)
The nanocluster growth process can be explained by assuming the growth of embryos into larger clusters by a two-body collision. This is a vapor condensation process where clusters grow by accepting atoms arriving on their surface. According to several related theories the growth of cluster in the nanocluster source is a function of traveling distance, i.e. the aggregation length, z. The equation [21] can be expressed as

\[
\frac{d\phi}{dz} = K_1 \phi^{2/3} \left[ 1 - \exp \left( K_2 \left( \frac{1}{\phi_0^{1/3} - \phi^{1/3}} \right) \right) \right] \quad \text{.................. (1)}
\]

where

\[
K_1 = \frac{\pi r_a^2 Q v_a}{v_d} \left( \frac{8 k_B T}{m_a} \right)^{1/2} \quad \text{.................. (2)}
\]

and

\[
K_2 = \frac{2 \sigma V_a}{k_B T r_a} \quad \text{.................. (3)}
\]

In the above equation \( \phi \) is the cluster radius at any time during growth, \( \phi_0 \) is the initial cluster size, \( r_a \) is the radius of an incoming vapor atom, \( Q \) is the number density of vaporized atoms, \( v_d \) is the drift velocity of materials, \( m_a \) is the mass of vaporized atom, \( \sigma \) is the surface tension, \( V_a \) is the atomic volume, \( k_B \) is the Boltzmann constant, and \( T \) is the temperature in Kelvin. Besides the magnetron power, practically the cluster size and deposition rate can be varied by adjusting aggregation length, rate of the gas flow, the type of the gas, the temperature of the aggregation region, and the aperture size.

The aggregation tube is cooled by water or liquid nitrogen; and it is sealed by a co-axial outer tube with a T-piece (aggregation cooling tube). In such a structure a differential pump can be installed to maintain a high vacuum (up \( 10^5 \) Torr) in the deposition chamber, meanwhile a high aggregation gas pressure (up to several Torr). There are three gas inlets, one for sputtering (normally Ar), one for aggregation (can be Ar or He), and the other is connected to a vacuum gauge to monitor the pressure inside of the aggregation tube. This gas outlet is also can be used as a secondary aggregation gas to provide a combined aggregation gases.
2.2.1.2 Quadruple Mass Filter

The function of a quadruple mass filter (QMF) can be seen in figure 2.12 [5]. Mechanically the core of QMF assembly consists of four metal rods (made of aluminum in most cases, figure 2.13) and a nanocluster detector plate on which the cluster ion current (in a magnitude of nano amperes) can be measured.

Figure 2.12 Schematics of the function of QMF

Figure 2.13 Structure of quadruple mass filter
The opposite rods are electrically connected to each other. A voltage with a DC and AC component is applied to two pairs of poles in a polarity of \((U + V \cos 2\pi ft)\) and \(-(U + V \cos 2\pi ft)\) where \(U\) is the DC voltage, \(V\) is the AC voltage, and \(f\) is the AC frequency (figure 2.14) [22]. The cluster ions entering along the axis of the quadruple will oscillate due to the electric filed. They can be selected according their mass to charge ratio by the voltage applied so that only ions of a defined mass will be pass through these four rods and reach the ion detector plate. The quadruple mass filter acts as a band-pass filter. The DC component \(U\), the AC component \(V\), and the AC frequency \(f\) are the parameters to select the desired mass, hence the nanoparticle size.

![Schematics of working principle of QMF](image)

Figure 2.14 Schematics of working principle of QMF

From the related theories the cluster mass to be selection is directly proportional to the amplitude of the AC voltage and inversely proportion to the square of the AC frequency applied to the poles. The following equation can be expressed this selection:
\[ M = 7 \times 10^7 \frac{kV}{f^2d^2} \]

In the above equation [23] \( M \) is the mass to be selected in atomic mass unit, \( k \) is a correction factor with a range between 1 and 2, \( V \) is the AC voltage applied in a unit of volts, \( f \) is the AC frequency applied, and \( d \) is the diameter of the poles in unit of meters. The current generated on the cluster ion detector plate can be used to monitor this mass selection. By varying (scanning) \( V \) a mass spectrum of the passing cluster beam then can be acquired. During the scanning the ratio of \( U/V \) must be kept constant. This is done automatically by the QMF controller. The reason to keep the ratio of \( U/V \) constant is that this ratio determines the resolution of QMF, i.e. the width of the cluster mass band transmitted through the filter. The theoretical resolution according to Mathieu equation [24] can be expressed as:

\[ \Delta M/M = 7.936 \times \left(0.16784 - \frac{U}{V}\right) \]

From the above equation we can see as the ratio of \( U/V \) increases, the ratio of \( \Delta M/M \) decreases which implies the mass band transmitted through the filter will be narrower.

In reality the ratio of \( \Delta M/M \) is also affected by some other factors, such as the length of the quadruple rod, the initial energy of cluster ions, the frequency of applied AC voltage, and intensity of cluster flux. The variation of the selected mass \( \Delta M \) can be expressed [23] as the following equation:

\[ \Delta M = 4 \times 10^9 \frac{V_Z}{f^2L^2} \]

where \( V_Z \) is the energy of the ions, \( f \) is applied AC frequency, and \( L \) is the length of quadruple rods.
2.2.2 Results and Discussion

We investigated both techniques to control nanoparticle sizes: by varying flow rate of aggregation gas, and by using the QMF. Before deposition a substrate must be loaded in the main (deposition) chamber. Cu was used as the target material. Figure 2.15 shows the substrate control unit. Figure 2.16 shows a substrate is on the way to be mounted on the sample holder (the red color is due to the illumination of heating lamps).

Figure 2.15  Substrate control unit for loading, rotating, and heating

Figure 2.16  Substrate on the way to be mounted on the sample holder
There is a movable quartz crystal thickness monitor (QCM) in the main chamber. Once a desirable ion beam flux (deposition rate) reached is will be moved away, and then a substrate will be mounted (figure 2.17).

2.2.2.1 Size Control by Gas Aggregation

The parameters were set as follows:

- Argon flow rate: 70 SCCM
- Magnetron sputtering power: 50 W (335 volts and 0.15 amps)
- Aggregation length: 100 mm
- Deposition time: 20 min

The vacuum levels were observed as follows:

- Deposition chamber: $1.40 \times 10^{-7}$ Torr (before the argon and helium fed in)
- Deposition chamber: $1.66 \times 10^{-5}$ Torr (after argon and helium fed in)
- Sputtering source: $2.67 \times 10^{-1}$ Torr (argon pressure in aggregation tube)
Without aggregation gas (helium flow rate = 0) the sputtering gas Ar acts as the aggregation gas. From figure 2.18 it can be seen the average size of the Cu nanoparticles is about 20 nm. With the helium fed in it can be seen the average size is reduced to about 10 nm. This size is in a good agreement with the calculation of equation (1).
2.2.2.2 Size Control by Quadruple Mass Filter (QMF)

The parameters for deposition rate were set as follows:

- Argon flow rate: 50 SCCM
- Helium flow rate: 20 SCCM
- Aggregation length: 100 mm
- Magnetron sputtering power: 70 W (278 volts and 0.25 amps)
- Deposition time: 20 min

The parameters of size selection on the QMF as follows:

- AC voltage: 248 V, and AC Frequency: 3 kHz (figure 2.20)
- Mass of nanoparticles: 2,973,547 amu (equivalent to 10 nm in diameter)

The vacuum levels were observed as follows:

- Deposition chamber: 1.50 x 10^{-7} Torr (before the argon and helium fed in)
- Deposition chamber: 3.21 x 10^{-5} Torr (after argon and helium fed in)
- Sputtering source: 4.85 x 10^{-1} Torr (argon pressure in aggregation tube)

![Image of QMF control unit](image)

Figure 2.20 Parameters selected for Cu nanoparticles with size of 10 nm
Figure 2.21 Cu nanoparticles with QMF = OFF

Figure 2.21 shows the deposition with the QMF turned off. Thus the sized selection was only determined by the gas flow rate. The average size of the nanoparticles is about 20 nm which is in agreement with the calculation. Figure 2.22 shows the deposition with QMF turned on with the related parameters set for diameter = 10 nm.

Figure 2.22 Cu nanoparticles with QMF = 10 nm
2.3 Dual Nanoparticle Deposition System

This versatile multi deposition system built by Oxford Applied Researches [25] basically consists of two units, one nanoparticle unit, similar to the Nanosys-1 and the other part is a CVD unit built by DCA Instruments (figure 2.23).

![Figure 2.23 Front view of NanoSys-2](image)

2.3.1 Components and functions

The nanoparticle unit consists of a nanocluster source, a quadruple mass filter (QMF), a 4-pocket electron-beam evaporator, and a UHV pulsed DC sputter source, descriptions of which are similar to that of Nanosys-1. There are two major improvements. (1) It has much higher deposition efficiency due a new design of the aggregation tube (figure 2.24). (2) The substrate holder has some special features which are not provided in the Nanosys-1. The substrate manipulator has freedom of movement in all three directions (figure 2.25). Therefore the charge nanoclusters can be selectively deposited from the incoming cluster beam to avoid the deposition of neutral particles,
which will not be affected by the QMF. Thus size-distribution of the nanoparticles will be very uniform. Along with the substrate rotation and substrate heating capabilities, substrate biasing is also provided to make the system versatile enough for the fabrication of nanoparticle-based photonic and electronic devices.

Figure 2.24  Exit apperture of aggregation tube

Figure 2.25  Sample to be loaded in the deposition chamber
2.3.2 Results and Discussion

2.3.2.1 Deposition Rate Control

There are four parameters controlling the nanoparticles deposition rate in NanoSys-2. They are argon flow rate, helium flow rate, aggregation length, and the magnetron sputtering power. The deposition rates were recorded by a quartz crystal thickness monitor (QCM) made by Sigma Instruments [26] with a model number of SQM-160 (figure 2.26).

![Quartz crystal thickness monitor](image)

Figure 2.26 Quartz crystal thickness monitor used to determine deposition rates

The first parameter we varied was magnetron sputtering power by adjusting voltage and current. The other parameters were preset as follows:

- Argon flow rate: 70 SCCM
- Helium flow rate: 25 SCCM
- Aggregation length: 100 mm

Three vacuum levels (there were small variations during the experiment) in the deposition system were observed as follows:

- Deposition chamber: $1.24 \times 10^{-7}$ Torr (before the argon and helium fed in)
• Deposition chamber: $1.08 \times 10^{-4}$ Torr (after the argon and helium fed in)

• Magnetron sputtering source: $8.03 \times 10^{-1}$ Torr (the argon pressure)

We found the lowest deposition rate can be $0.05 \, \text{Å/sec}$, or $3 \, \text{nm/min}$. This may be very suitable for a thin layer nanoparticle deposition. We also found the deposition rate is proportional to the magnetron sputtering power below 100 W. Once the power is larger than 100W the deposition rate has not much increase which stays around $1.28 \, \text{Å/sec}$, or 77 nm/min (figures 2.19, and 2.20).

<table>
<thead>
<tr>
<th>Voltage (volts)</th>
<th>Current (amp)</th>
<th>Power (watt)</th>
<th>Rate (Å/sec)</th>
<th>Rate (nm/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>276</td>
<td>0.06</td>
<td>17</td>
<td>0.05</td>
<td>3.0</td>
</tr>
<tr>
<td>284</td>
<td>0.10</td>
<td>28</td>
<td>0.07</td>
<td>4.2</td>
</tr>
<tr>
<td>292</td>
<td>0.15</td>
<td>44</td>
<td>0.24</td>
<td>14</td>
</tr>
<tr>
<td>299</td>
<td>0.20</td>
<td>60</td>
<td>0.44</td>
<td>26</td>
</tr>
<tr>
<td>305</td>
<td>0.25</td>
<td>76</td>
<td>0.57</td>
<td>34</td>
</tr>
<tr>
<td>312</td>
<td>0.34</td>
<td>106</td>
<td>1.16</td>
<td>70</td>
</tr>
<tr>
<td>320</td>
<td>0.42</td>
<td>134</td>
<td>1.24</td>
<td>74</td>
</tr>
<tr>
<td>327</td>
<td>0.50</td>
<td>163</td>
<td>1.28</td>
<td>77</td>
</tr>
</tbody>
</table>

Figure 2.27 Chart of deposition rate vs. magnetron sputtering power
The second parameter we varied was the aggregation length (Figure 2.29). The other parameters were set as follows:

- Argon flow rate: 70 SCCM
- Helium flow rate: 25 SCCM
- Magnetron power: 65 W (296 volts and 0.22 amps)

Three vacuum levels of the deposition system were observed about the same as the first part. They were:

- Deposition chamber: $1.32 \times 10^{-7}$ Torr (before the argon and helium fed in)
- Deposition chamber: $9.2 \times 10^{-5}$ Torr (after argon and helium fed in)
- Magnetron sputtering source: $6.4 \times 10^{-1}$ Torr (argon pressure)
We found varying of the aggregation length (figure 2.29) has a very strong control over the nanoparticle deposition rate. A few-centimeter change will make the deposition rate change more than 10 times. We also found the peak value of the deposition rate is at the aggregation length of 50 mm (Figure 2.30). After the aggregation length is larger than 50 mm the deposition rate will decrease.

<table>
<thead>
<tr>
<th>Aggregation Length (mm)</th>
<th>10</th>
<th>20</th>
<th>30</th>
<th>40</th>
<th>50</th>
<th>60</th>
<th>70</th>
<th>80</th>
<th>90</th>
<th>100</th>
</tr>
</thead>
<tbody>
<tr>
<td>Deposition Rate (Å/s)</td>
<td>0.05</td>
<td>0.18</td>
<td>0.36</td>
<td>0.65</td>
<td>0.75</td>
<td>0.71</td>
<td>0.68</td>
<td>0.66</td>
<td>0.63</td>
<td>0.61</td>
</tr>
<tr>
<td>Deposition Rate (nm/min)</td>
<td>3.00</td>
<td>10.8</td>
<td>21.6</td>
<td>39.0</td>
<td>45.0</td>
<td>42.6</td>
<td>40.8</td>
<td>39.6</td>
<td>37.8</td>
<td>36.6</td>
</tr>
</tbody>
</table>

Figure 2.30  Chart of deposition rate vs. aggregation length
The third parameter we varied was argon flow rate. We found the deposition rate is directly proportional to the argon flow rate. There is a minimum Ag flow rate needed for the plasma occur in magnetron sputtering source. The parameters were set as:

- Helium flow rate: 25 SCCM
- Aggregation Length: 100 mm
- Magnetron power: 110 W (313 volts and 0.35 amps)

There vacuum levels during the deposition process were observed as follows:

- Deposition chamber: $1.24 \times 10^{-7}$ Torr (before the argon and helium fed in)
- Deposition chamber: $(3.2$ to $9.8) \times 10^{-5}$ Torr (after argon and helium fed in)
- Magnetron sputtering source: $(1.2$ to $11.6) \times 10^{-1}$ Torr (argon pressure)
We found the minimum argon flow rate is about 30 SCCM (Figure 2.32) to make a useful deposition which is about 0.04 Å/sec, or 2.4 nm/min. We also found the argon flow has the strongest control over the deposition rate. Three times of argon increase (from 30 SCCM to 100 SCCM) could cause about 30 times of increase of the deposition rate (figure 2.33)
The fourth parameter we varied was helium flow rate. The range we varied was from 2 sccm to 40 sccm. We found there is big increase of deposition rate between 20 sccm to 30 sccm. The other parameters were set as follows:

- Argon flow rate: 80 SCCM
- Aggregation Length: 100 mm
- Magnetron power: 110 W (313 volts and 0.35 amps)

Three vacuum levels during the deposition process were observed as follows (there were small variations):

- Deposition chamber: $1.24 \times 10^{-7}$ Torr (before the argon and helium fed in)
- Deposition chamber: $1.08 \times 10^{-4}$ Torr (after argon and helium fed in)
- Magnetron sputtering source: $8.03 \times 10^{-1}$ Torr (argon pressure)

The result for how helium flow rates controls the nanoparticle deposition rate is shown in figure 2.34; a plot of such control is shown in figure 2.35.

<table>
<thead>
<tr>
<th>Helium Flow Rate (sccm)</th>
<th>2</th>
<th>5</th>
<th>10</th>
<th>15</th>
<th>20</th>
<th>25</th>
<th>30</th>
<th>35</th>
<th>40</th>
</tr>
</thead>
<tbody>
<tr>
<td>Deposition Rate (Å/s)</td>
<td>0.36</td>
<td>0.37</td>
<td>0.47</td>
<td>0.50</td>
<td>0.56</td>
<td>0.60</td>
<td>0.90</td>
<td>0.88</td>
<td>0.86</td>
</tr>
<tr>
<td>Deposition Rate (nm/min)</td>
<td>21.6</td>
<td>22.2</td>
<td>28.2</td>
<td>30.0</td>
<td>33.6</td>
<td>36.0</td>
<td>54.0</td>
<td>52.8</td>
<td>51.6</td>
</tr>
</tbody>
</table>

Figure 2.34 Chart of deposition rate vs. helium
2.3.2.2 Size control by Gas Aggregation

Comparing to NanoSys-1 we found NanoSys-2 has a much more efficient deposition performance. A smaller sputtering power and a shorter deposition time can produce the same amount of deposition as NanoSys-1 does. The parameters were set as follows:

- Argon flow rate: 50 SCCM
- Aggregation length: 100 mm
- Magnetron sputtering source Power: 52 W (305 volts and 0.17 amps)
- Deposition time: 7 min

The vacuum levels were observed as follows:

- Deposition chamber: \(2.32 \times 10^{-8}\) Torr (before the argon and helium fed in)
- Deposition chamber: \(3.2 \times 10^{-5}\) Torr (after argon and helium fed in)
- Magnetron sputtering source: \(5.38 \times 10^{-1}\) Torr

Figure 2.35  Plot of deposition rate as a function of helium flow rate
Without aggregation gas (helium flow rate = 0) the sputtering gas argon acts as the aggregation gas. From figure 2.36 it can be seen the average size of the Au nanoparticles is about 40 nm. With the helium fed in it can be seen the average size is reduced to about 20 nm. This size is in a good agreement with the calculation of equation (1).
It is obvious to see from figures 2.38 and 2.39 the function of nanoparticle size selection by varying the aggregation gas flow. With no He gas the average size of Au particles is around 40 nm while with the gas flow = 40 sccm the average size is 10 nm.
CHAPTER 3
METAL INDUCED CRYSTALLIZATION

3.1 Introduction

Metal-induced crystallization (MIC) is a method by which amorphous silicon (a-Si) can be converted into polycrystalline silicon at relatively low temperatures. In MIC the metal is deposited on to a substrate (normally is glass), and then deposit a-Si thin film on to the metal. The structure is then annealed at temperatures between 200 °C and 1000 °C which transforms the a-Si film into polycrystalline silicon.

The process of MIC starts with the interaction between the metal and Si atoms. The difference in the electric negativity between the metal and the silicon leads to redistribution of the electric charge of the metal-Si bonds closer to the metal atoms, which changes the position of the electrons around the neighboring Si-Si bonds. The electron pairs from electrons belonging to two neighboring Si atoms transform to electrons belonging to more than two neighboring Si atoms, i.e., the electrons in a-Si are no longer localized and they occupy delocalized orbital’s. It changes the distance between the silicon atoms because the Si-Si bonds are loosen now. The metal phase being responsible for loosening the covalent bonding in silicon makes the amorphous phase unstable. The interface boundary between the metal and the a-Si layer is appropriate for a metal-Si interaction leading to the process of a-Si crystallization because of amorphous silicon imperfections - vacancies, dislocations and dangling bonds. During the isothermal heat treatment, the metal film is dissolved into the semiconductor film where it diffuses and precipitates [27].
The crystallization of amorphous silicon (a-Si) is increasingly gaining interest for polycrystalline silicon devices such as thin film transistors (TFTs) and thin-film solar cells. In relation to solar cell devices [28], the crystallization of a-Si offers the opportunity for using low temperature, and therefore low-cost substrates which is vitally important for the reduction of the overall costs of solar cells. Most attention in the field of crystallization has been given to solid phase crystallization (SPC) and laser crystallization (LC). But SPC suffers from long annealing times and rather high temperature while laser crystallization remains an expensive and complex process. Due to these problems, metal-induced crystallization (MIC) has been investigated extensively in recent years.

The main difference between aluminum induced crystallization and other metal induced crystallization is due to the different reaction behavior. Al or other metals form a eutectic with silicon. A eutectic is the melting point of a mixture of two or more solids depends on the relative proportions of its ingredients. The initial step during the annealing of the Al/a-Si interface is dissolution of a-Si in Al (figure 3.01 a), followed by diffusion of the Si solute through the metal (figure 3.01 b). Due to weakening of covalent bonds of the a-Si, the diffusion of Si atoms into metal film takes place. Because of the continuous supply of Si atoms, the Si grains will continue to grow at these sites until they contact each other and form a continuous film. This results in layer inversion. For Al, this process can start immediately because of the solubility of Si in the metal film. But, for Ag this solubility is negligible even at high temperatures. This explains why Al is much more efficient in lowering the crystallization temperature than silver (Ag). The metal film is saturated with Si, the dissolved semiconductor becomes supersaturated and the super saturation can be relieved by crystallite growth. The mechanism of crystallization
involves intermixing of Al and Si atoms (figure 3.01 c) and the formation of an alloy of high metal concentration in the amorphous Crystalline interface. The Al layer with its crystal structure induces in the newly formed Si phase, a structural conformity with the crystalline phase. As a result, polycrystalline Si grains are formed. The Al atoms diffuse along the grain boundaries and segregate between them and outside of the poly-Si layer. The process of crystallization will stop when all of Al is repulsed at the a-Si and poly-Si interfaces. This process is known as the aluminum-induced layer exchange process.

Figure 3.01 Process of metal induced crystallization of Al
3.2 Experiments

To process metal induced crystallization we need first deposit a layer of metal (aluminum or other metals) to a substrate (glass or quartz). There are two sets of metals we used in this work. The first set is aluminum and silver, and the second set is lead, tin, and indium which all have a very low melting point. The substrates we used are made of quartz. Second, we need deposit a layer of silicon on the top of it. Finally, the samples will be annealed at a certain temperature for a certain amount of time. The annealed sample will further be characterized using X-ray diffraction technique and Raman spectroscopy to confirm the crystallization.

3.2.1 Equipment Used

In this experiment we used four pieces of equipment: an e-beam evaporator, an annealing furnace, an X-ray diffractometer, and a Raman spectroscope.

3.2.1.1 E-Beam Evaporator

Figure 3.02 shows the e-beam evaporator used in this work which was custom built by Sharon Vacuum. It has a 24”x24”x18” chamber with four pocket 6-kW electron beam gun. Electrons are emitted from a heated filament and are accelerated to a high energy of several kilo eV. Electron current can be adjustable from typically 10 mA to 200 mA. A permanent, horseshoe magnet bends and guides the e-beam in a circular path from the filament to the source. The materials in the crucible should be at least 1/3 full, but not more than 3/4 full. If there is not enough material, it is possible to burn a hole through the bottom of the crucible and supporting copper hearth. For a clean deposition, the beam current should be adjusted to just melt a spot in the middle of the material. As power is increased and more material is melted, the deposition rate increases, but also the amount
of spitting of droplets of material increases. A proper power therefore should be carefully chosen to suit desirable deposition rate.

Figure 3.02 The e-beam evaporator from Sharon Vacuum

Figure 3.03 shows the schematic diagram of electron beam evaporator [29]. When the electron beam from electron gun focused by magnetic plates falls onto the source material, the kinetic energy of the beam is transformed to thermal energy and creates high temperature on source material. This in turn vaporizes the material and the vaporized material condenses on the substrate forming a thin layer. The crucible in which the target is placed, acts as the anode. A magnetic field is also applied to bend the electron trajectory. The electron beam is generated by an electron gun, which uses the thermionic emission of electrons produced by a tantalum cathode. The crucible in which the target is placed, acts as the anode. A magnetic field is also applied to bend the electron trajectory. The electron beam makes the target material to vaporize; this vapor is then condensed on the substrates forming a thin film.
There are other methods that can be used to form thin films, namely filament evaporation and sputter deposition. But e-beam evaporation method has an advantage in this work. The following chart shows a comprehensive comparison.

<table>
<thead>
<tr>
<th>Methods</th>
<th>Pros</th>
<th>Cons</th>
</tr>
</thead>
</table>
| **E-Beam Evaporation** | 1. High temperature materials  
2. Good for liftoff  
3. Highest purity | 1. Some CMOS processes sensitive to radiation  
2. Alloys difficult  
3. Poor step coverage |
| **Filament Evaporation** | 1. Simple to implement  
2. Good for liftoff | 1. Limited source material (no high temperature)  
2. Alloys difficult  
3. Poor step coverage |
| **Sputter Deposition** | 1. Better step coverage  
2. Alloys  
3. High temperature materials  
4. Less radiation damage | 1. Possible grainy films  
2. Porous films  
3. Plasma damage/contamination |
3.2.1.2 Annealing Furnace

Lindberg/Blue M 1100°C box furnace is used for annealing of the samples (figure 3.04). This furnace features a choice of microprocessor-based single set point or programmable control instrumentation. It includes special insulation and heating element to minimize outer surface temperatures while maintaining uniform heat distribution within the chamber. Controlled heat-up rate eliminates thermal shock to materials. It has quick heat-up and cool-down rates which can be programmed by the user.

Figure 3.04 Lindberg/Blue M furnace used for annealing

The unique double wall construction minimizes exterior surface temperatures for operator safety and energy efficiency. Long life Type "K" thermocouple is used. This furnace has air vent and air inlet for inert gas. In order to avoid oxidization we used nitrogen gas which is from a liquid nitrogen tank. The main power on/off switch is located on control panel. There is a safety door switch to interrupt power to heating
element when door is opened. This protects heating element and minimizes exposure to the user. Microprocessor-based control with advanced self-tuning feature automatically sets best control parameters for the thermal process. PID control (proportional, integral, derivative) prevents overshoot.

There is a LED display of actual temperature vs. set point. It may be configured to display temperature in either °C or °F. A stand alone AC power supply is needed since this furnace works at 208/240V and 50/60Hz. The heat-up/cool-down graph for the furnace is shown in figure 3.05. This graph shows the minimum time needed for the furnace to heat up and to cool down. If a longer time (slower heating rate) to heat up or a longer time to cool down is desired, then the program function must be set first.

![Heat-Up/Cool-Down Graph](image)

Figure 3.05  Graph showing heat-up and cool-down dates
3.2.1.3 X-ray Diffractometer

X'Pert PRO Diffractometer made by PANalytical [30] is used to study the crystallization of metal induced silicon thin films. Figure 3.06 shows the actual machine used in this dissertation. The X-Ray sources present in this diffractometer are 3 kW Copper tube and 2 kW Cobalt tube. The optic components used are focusing and parallel PreFix optics, programmable slits, and tunable diffracted beam monochromator. Detectors used are Xe proportional counter and solid state X'cellerator. The software used for analysis is Hi-Score search-match type, X'Pert Plus crystallographic analysis software with riveted capability and ProFit line profile analysis software. X-Ray Diffraction analysis is performed with an automated diffractometer and the data analyzed with a computerized least squares technique. An X'Pert PRO x-ray diffractometer, equipped with a graphite monochromator and a copper tube is used to collect the thin films data. The data is collected on a PC and analyzed using a computerized search and match procedure.

Figure 3.06 X’Pert PRO X-Ray Diffractometer
Solid matters can be categorized into amorphous and crystalline. In Amorphous materials the atoms are arranged in a random way. For example, glasses are amorphous materials, also silicon films formed e-bema evaporation in this work. In Crystalline materials, the atoms are arranged in a regular pattern, and there are smallest elements that by repetition in three dimensions describe the crystal. About 95% of all solids are described as crystalline. X-Ray diffraction (XRD) is one of the most powerful techniques for qualitative and quantitative analysis of crystalline elements and compounds. The information obtained includes degree of crystallinity, types and nature of crystalline phases present, amount of amorphous content & size and orientation of crystallites.

An electron in an electromagnetic field will oscillate with the same frequency as the field. When an X-ray beam hits an atom, the electrons around the atom start to oscillate with the same frequency as the incoming beam. In almost all directions we will have destructive interference. In crystals the atoms are arranged in a regular pattern, and in a very few directions we will have constructive interference. The waves will be in phase and there will be well defined X-ray beams leaving the sample at various directions. Hence, a diffracted beam may be described as a beam composed of a large number of scattered rays mutually reinforcing one another.

X-ray diffraction employs electromagnetic waves with a wavelength on the order of 1 angstrom. Since wave diffraction occurs when the dimensions of the diffracting object are of the same order of magnitude as the wavelength of the incident wave. X-ray diffraction of semiconductor thin films is generally carried out in a diffractometer. The
source of the X-rays is called an X-ray tube. It consists of a water-cooled copper target onto which an accelerated electron beam is impinging inside a vacuum tube (figure 3.07).

![Figure 3.07 LabRAM HR Raman spectrometer](image)

From the Bremsstrahlung effect, X-rays are emitted with wavelengths that are characteristic of the copper element. Through these inelastic interactions, X-rays are emitted which can have energies as high as the beam energy. These X-rays are then filtered and collimated into a beam through the use of a monochromator consisting of nearly perfect silicon crystals placed at specifically chosen angles to permit reflection of the X-rays. Diffracted waves from different atoms can interfere with each other and the resultant intensity distribution is strongly modulated by this interaction. If the atoms are arranged in a periodic fashion, as in crystals, the diffracted waves will consist of sharp interference maxima (peaks) with the same symmetry as in the distribution of atoms.
Measuring the diffraction pattern therefore allows us to deduce the distribution of atoms in a material.

3.2.1.4 Raman Spectroscope

A Raman spectrometer LabRAM HR system from the Horiba Scientific was used to study the crystallization of our samples. This system provides ultra high spectroscopic resolution. It also provides unique wavelength range capability. Due to these kinds of functionalities this system provides both great flexibility and high performance. Figure 3.08 shows the actual machine used in this dissertation. It is an integrated, simple to use, and high stability instrument designed to undertake reproducible Raman measurements. Its high resolution mode is uniquely ideal for subtle band analysis such as that for phase (crystalline/amorphous), or hydrogen and weak bonding forces and semiconductor stress measurements. Band analysis in the order of 0.3 cm\(^{-1}\) to 1 cm\(^{-1}\) is particularly suited to the HR mode. It is suitable for Raman, fluorescence and luminescence measurements. Multiple laser capability provides wavelength from visible to near IR [31].

![LabRAM HR Raman spectrometer](image)

Figure 3.08  LabRAM HR Raman spectrometer
When photons are incident upon a medium, they get scattered either elastically (Rayleigh scattering) or inelastically (Raman scattering). The scattering process without a change of frequency is called Rayleigh scattering, and this process is described by Lord Rayleigh. In Rayleigh scattering, the energy of the emitted photon is the same as the incident photon. On the other hand, in Raman scattering, the energies of the scattered and incident photons are different.

A change in the frequency of the light is called Raman scattering. Raman shifted photons of light can be either of higher or lower energy, depending upon the vibrational state of the molecule. The inelastically scattered light can be collected, and information about the energy levels within the medium can be deduced from the energy change in the light. Most of the molecules are initially in the ground state but because of thermal agitation, some of the molecules will be in excited state. The scattering process can be explained as the incoming photon raises the molecule to a virtual (non-existent) excited state. But since the molecule cannot remain in this virtual level, it must immediately come back to a lower level with the emission of a photon. If the molecule falls into the same level as it started from, there is no frequency shift in emitted photon and this is called as Raleigh scattering. If the molecule falls into a different level, the energy of the emitted photon must differ from that of incoming photon in order to conserve total energy, the emitted photon has a different frequency. This process is called Raman scattering. The frequency can decrease giving rise to Stokes lines in the spectrum or increase giving anti-Stokes lines.

This depends on whether the molecule starts in the ground state or an excited state. The larger the Raman shift, the higher the excited state, and the less likely it is to be
thermally populated. Therefore, anti-Stokes lines with small Raman shifts are likely to be observed.

Raman spectroscopy has become an important analytical and research tool. It can be used for applications as wide ranging as thin films, semiconductors, pharmaceuticals, polymers and carbon nano-materials. Raman spectroscopy is a light scattering technique, and can be explained as a process where a photon of light interacts with a sample to produce scattered radiation of different wavelengths. Raman spectroscopy is extremely rich in information. This information may be useful for chemical identification, characterization of molecular structures and effects of bonding.

Comparing to other spectroscopy Raman Spectroscopy has the following advantages:

- It is nondestructive and can quickly determine structural characterization of crystalline, non-crystalline, and amorphous materials.
- The sample preparation is much simpler.
- It can provide higher sensitivity with comparable selectivity and chemical speciation.
- It is equally useful to identify any type of organic, inorganic and biochemical species in solid, liquid or gas form.
3.2.2 Crystallization with Aluminum/Silver

The first set of experiments we did was used aluminum and silver to crystallize silicon thin films. The aluminum target material was from Kamis Incorporated. It has a purity of 99.999%. The silver target material was from Kurt J. Lesker; and it has a purity of 99.99% (figure 3.09). The other metals (tin, lead, and indium) for the second of experiment were also from Kurt J. Lesker.

![Image of Metals](image_url)

Figure 3.09  Metals used for induced crystallization of silicon

The substrates we used were 2-in sapphire (Al₂O₃) wafers with a thickness of 330 microns which were first deposited a layer of Al with a thickness of 100 nm using the e-beam evaporator. A layer of Si with a thickness of 400 nm was then immediately deposited in an in situ way, namely without breaking the vacuum in the deposition chamber. The detailed deposition parameters are list in figure 3.10.
<table>
<thead>
<tr>
<th>Deposition Materials</th>
<th>Crucibles Used</th>
<th>Pressure (Torr)</th>
<th>Current (mA)</th>
<th>Voltage (kV)</th>
<th>Rate (Å/sec)</th>
<th>Thickness (nm)</th>
<th>Time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>BN</td>
<td>$1.4 \times 10^6$</td>
<td>52</td>
<td>7.17</td>
<td>0.33</td>
<td>100</td>
<td>50</td>
</tr>
<tr>
<td>Ag</td>
<td>Mo</td>
<td>$3.2 \times 10^6$</td>
<td>18</td>
<td>7.51</td>
<td>2.7</td>
<td>100</td>
<td>6</td>
</tr>
<tr>
<td>Si</td>
<td>Mo</td>
<td>$1.8 \times 10^6$</td>
<td>76</td>
<td>7.74</td>
<td>1.5</td>
<td>400</td>
<td>45</td>
</tr>
<tr>
<td>Si</td>
<td>Mo</td>
<td>$1.8 \times 10^6$</td>
<td>76</td>
<td>7.74</td>
<td>1.5</td>
<td>250</td>
<td>28</td>
</tr>
</tbody>
</table>

Figure 3.10  E-beam evaporator deposition conditions and results

The second sample was to be used to investigate silver induced crystallization of amorphous aluminum thin films. A layer of 100-nm silver was first deposited on sapphire substrate followed by 400-nm Si deposition in the same way as the first sample. It would be very informative to get a result for crystallization with a thinner Si layer and the same thickness of silver. Thus, we made the third sample with 100-nm of Ag and 250-nm of Si deposited on the top of it. All detailed deposition parameters are also listed in figure 3.10.

3.2.3 Crystallization with Indium/Lead/Tin

The second set of experiments we did was using three metals with a low-temperature melting point. They are indium with a melting point of 157 °C, tin with a melting point of 232 °C, and lead with a melting point of 327 °C. They were first deposited on glass and quartz substrates with a thickness of 70 nm respectively. Then a layer of Si with a thickness of 150 nm was immediately deposited on the top of it. All the depositions were done by the e-bam evaporator from Sharon Vacuum. It should be pointed out the crucibles used for these three metals are made of alumina ($\text{Al}_2\text{O}_3$) which is an insulator. A special attention must be paid when conducting the evaporation. Figure 3.11 shows the details of all parameters applied to the evaporation.
<table>
<thead>
<tr>
<th>Deposition Materials</th>
<th>Crucibles Used</th>
<th>Pressure (Torr)</th>
<th>Current (mA)</th>
<th>Voltage (kV)</th>
<th>Rate (Å/sec)</th>
<th>Thickness (nm)</th>
<th>Time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>In</td>
<td>Al₂O₃</td>
<td>2.4 x 10⁻⁶</td>
<td>30</td>
<td>7.26</td>
<td>1.0</td>
<td>70</td>
<td>12</td>
</tr>
<tr>
<td>Pd</td>
<td>Al₂O₃</td>
<td>2.9 x 10⁻⁶</td>
<td>17</td>
<td>7.51</td>
<td>1.0</td>
<td>70</td>
<td>12</td>
</tr>
<tr>
<td>Sn</td>
<td>Al₂O₃</td>
<td>2.6 x 10⁻⁶</td>
<td>28</td>
<td>7.64</td>
<td>1.0</td>
<td>70</td>
<td>12</td>
</tr>
<tr>
<td>Si</td>
<td>Mo</td>
<td>1.6 x 10⁻⁶</td>
<td>120</td>
<td>7.21</td>
<td>1.3</td>
<td>150</td>
<td>20</td>
</tr>
</tbody>
</table>

Figure 3.11 Summary of the deposition conditions and results

After the depositions were done the samples were annealed at the different temperatures. They were 140 °C, 220 °C, 310 °C, 450 °C, and 580 °C (figure 3.12). We did not anneal the metals at temperature of 750 °C (they were deposited on quartz instead of glass). The annealing processes were done in the Lindberg/Blue furnace with nitrogen venting. The annealing time was 60 minutes.

Figure 3.12 Annealed Indium/Lead/Tin to be tested by XRD
3.3 Results and Discussion

From the results of X-ray diffraction technique and Raman spectroscopy we can conclude that the amorphous silicon thin films were successfully crystallized by aluminum and silver. The lowest temperature for aluminum is 500 °C, while for silver the lowest temperature is 700 °C. However, we found the other three metals did not crystallized the a-Si thin films under the temperature range we applied (the highest temperature was 580 °C) though all of these three metals have a melting point much lower than the aluminum’s which implies the eutectic points for these metals and silicon are higher than the one for aluminum induced crystallization of Si thin films.

3.3.1 Results from X-Ray Diffraction

The results of crystallizations were investigated using the X’Pert PRO Diffractometer. All samples were checked before they were annealed. Figure 3.13 shows the crystalline of a sample only from the substrates (Al₂O₃), not from Al (2θ = 28.3°).

![XRD plot of 400-nm Si on 100-nm Al before annealing](image-url)
Figure 3.14 shows the results of crystallizations from samples deposited with 100-nm aluminum and then 400-nm silicon on a sapphire substrate (melting point of 2030 °C). There were six samples; they were annealed at the different temperatures.

From the $2\theta = 28.3\degree$ on the XRD plots it can be clearly seen the Si layers were crystallized. The lowest temperature to crystallize amorphous silicon is 500 °C. It also can be seen from the plots the high temperature the more a-Si atoms will be crystallized. Figures 3.15 and 3.16 show Ag induced crystallization. The lowest temperature needed for a detectable Si crystallization is about 700 °C which is much higher than aluminum (500 °C). This temperature is also above the glass softening point (660 °C).
Figure 3.15  XRD plots of 400-nm Si on 100-nm Ag after annealing

Figure 3.16  XRD plots of 250-nm Si on 100-nm Ag after annealing
Figure 3.17 shows the result of crystallizations from a sample deposited with 70-nm indium and then 150-nm silicon on a glass substrate. The XRD scanning angle of 2θ was from 10 degrees to 40 degrees. A peak at 28.3° was not present which means a-Si was not crystallized at the annealing temperature of 580 °C. This implies the eutectic point of Indium and silicon is higher than 580 °C. A peak at 33.9 °C is contributed from crystalline indium.

Figure 3.17 XRD plot of 150-nm Si on 70-nm indium after annealing at 580 °C

Figure 3.17 shows the result of crystallizations from a sample deposited with 70-nm lead and then 150-nm silicon on a glass substrate. Figure 3.18 shows the result of crystallizations from a sample deposited with 70-nm tin and then 150-nm silicon. No peaks at 28.3° were shown which means Si was not crystallized at the temperature of 580 °C. This implies the eutectic points of lead and Si, tin and Si are higher than 580 °C. The peaks at 31.2° and 30.8° are contributed from crystalline lead and tin.
Figure 3.18 XRD plot of 150-nm Si on 70-nm lead after annealing at 580 °C

Figure 3.19 XRD plot of 150-nm Si on 70-nm tin after annealing at 580 °C
3.3.2 Results from Raman Spectroscopy

The samples with aluminum induced crystallization, and silver induced crystallization were also investigated using Raman spectroscopy. The Raman spectrometer LabRAM HR system from the Horiba Scientific was used for this work. Figure 3.20 shows the results. This confirmed the lowest temperature to crystallize Si is 500 °C. The plot also shows the higher annealing temperature the more silicon will be crystallized. Figures 3.21 and 3.22 show the results form silver induced crystallization of Si thin films. These results match the ones from X-ray diffraction technique very well.

![Raman plots of 400-nm on 100-nm Al after annealing](image)

Figure 3.20  Raman plots of 400-nm on 100-nm Al after annealing
Figure 3.21 Raman plots of 400-nm Si on 100-nm Ag after annealing

Figure 3.22 Raman plots of 250-nm Si on 100-nm Ag after annealing
CHAPTER 4
NANOFILM INDUCED CRYSTALLIZATION

4.1 Introduction

Currently the silicon used to fabricate thin film transistors (TFT) is most amorphous which limits the performance and functionality of Flat Panel Display and other photonic devices, like solar cells (figure 4.01).

![Diagram of flat panel display](image)

**Figure 4.01** Structure of flat pane display

Using aluminum induced crystallization to convert the amorphous silicon to polycrystalline silicon is a very promising technique (figures 4.02 to 4.05) [32]. However, the most researches done so far are using bulk aluminum with a thickness of several hundred nanometers which will significantly block the light from the LED. Therefore the performance of a Flat Panel Display made in such a way will be greatly reduced. In this dissertation we deposited a layer of aluminum nanofilm with a thickness of 2 nm to 10 nm on glass prior to depositing a layer of amorphous Si.
Figure 4.02 Amorphous Si on Al before annealing

Figure 4.03 Si atoms diffusing into Al after annealing starts

Figure 4.04 Si crystallized gains start growing and replacing Al

Figure 4.05 Crystallized Si substituted Al layer
The procedure for this work is quite different in many ways comparing to the bulk aluminum induced crystallization.

- The glass substrates were cleaned supersonically besides the regular alcohol/methanol cleaning due to the scale of a nanofilm to be deposited.
- The chamber of the e-beam evaporator was cleaned thoroughly to eliminate any possible contaminations.
- The deposition thickness indicator (QCM) was re-calibrated, and compared to a standard.
- The vacuum level of the deposition chamber was kept at 10^{-7} Torr instead of 10^{-6} Torr which was used for the previous bulk metal induced crystallization.
- The Al deposition rate was kept at 0.1 Å/sec instead of 1Å/sec used in the previous bulk aluminum deposition.
- The annealing process was kept in a high vacuum chamber (NanoSys-1) instead of a nitrogen filled furnace.

In order to determine the improvement of the optical property for crystallized Si versus a-Si we measured the transmission coefficient in visible spectrum before and after the annealing. An average of increase of transmission coefficient of 70% was found. The characterization of crystallization of a-Si was done by using X-ray diffraction technique and Roman spectroscopy. Due to the nano-scale (3 to 13 nm) deposition of a-Si XDR only detected two samples out of nine while Roman technique didn’t detect any crystallization. The crystallization was confirmed by a spectrophotometer in term of transmission coefficient.
4.2 Experiments

Due to the scale (a few nanometers) of aluminum and silicon to be deposited the experiments for crystallizing amorphous silicon was performed in a much careful way comparing the previous ones, and more equipment were used.

4.2.1 Additional Equipment Used

Besides the e-beam evaporator, X-ray diffractometer, and Raman spectroscopy the following additional equipment were used.

4.2.1.1 Ultrasonic Cleaning Unit

This cleaning unit is made by Elma GmbH & Co KG, Germany. The model number is Transsonic T1-H (figure 4.06). It provides an effective ultrasonic power of 200 watts with a frequency selection of 25 kHz and 45 kHz. The unit has a sweep function for a continuous shifting of sound pressure maxima. It also has a degas function for efficient degassing of the cleaning liquid.

Figure 4.06 Elma T1-H15 Ultrasonic cleaning unit
4.2.1.2 Surface Profiler

This surface profilometer (figure 4.07) delivers a unique combination of precise, reliable, simple and easy-to-use measurements. This Dektak 6M Stylus Profilometer [33] provides the flexibility to perform precise step height measurements for thin films down to less than 100 angstroms, as well as thick-film measurements up to several hundred microns thick. The system includes a Low Inertia Sensor 3 (LIS 3), an innovative head that incorporates key technology advances to deliver extremely repeatable measurements with unprecedented sensitivity and vastly increased flexibility.

This system has capability of long scans up to 30 mm with extremely stable baseline and up to 60,000 data points per scan. It measures step heights on any surface with programmable stylus force down to 1 mg and Z-height capability to 1 mm. The instrument has vertical resolution in nanometers and horizontal resolution as small as about twenty nanometers.

Figure 4.07 Dektak 6M stylus surface profilometer
Our samples were first measured by a built-in quartz crystal monitor inside chamber of the e-beam evaporator. The samples then measured by the above surface profilometer which was calibrated by a standard (figure 4.08) from Tenco Instruments.

![Figure 4.08 Thickness Calibrator from Tenco Instruments](image)

4.2.1.3 Scanning Electron Microscope

A scanning electron microscope (SEM) with a model number of JSM-7500F from JEOL [34] was used in this work (figure 4.09). It is a field emission scanning electron microscope (FESEM) capable of SEI resolutions down to 1 nm and magnification of 25 to 1,000,000. The JSM-7500F FESEM incorporates a cold cathode field emission gun, ultra high vacuum, and sophisticated digital technologies for high resolution high quality imaging of nanostructures. Featuring a conical FE gun and a semi-in-lens objective lens, the system is capable of high resolution imaging as well as high quality real time image
display at all scan speeds, enabling observation and recording of superior images even in a bright room.

![JEOL 7500F Scanning Electron Microscope](image)

**Figure 4.09** JEOL 7500F Scanning Electron Microscope

The JSM-7500F is able to handle samples up to 8 inches in diameter. The JSM-7500F is a super intelligent PC SEM assuring compatibility with future computer technologies. Its unique graphical user interface controls condition setup, motor stage drive, imaging, and data filing, assuring stable and reliable operation.

### 4.2.1.4 Spectrophotometer

A spectrophotometer [35] with a model of V670 from the Jasco Analytical Instruments (figure 4.10) was used in this dissertation. It detects a wavelength range from 190 to 2700 nm with an auto switching function between two detectors, a photomultiplier tube, and a PbS photoconductive cell. It has two light sources, Deuterium lamp (190 nm to 350 nm) and a halogen lamp (330 nm to 2700 nm), with an auto switching between the two lamps. The optical system consists of a single monochromator with a plane grating of
1200 lines/mm in UV/VIS region, and a second plane grating of 300 lines/mm in NIR region.

Figure 4.10  Spectrophotometer

4.2.2 Procedures

In order to get the high-quality samples with just a few nanometer thickness a great deal of care were taken to do this experiment.

4.2.2.1 Substrate Cleaning

The first stage of cleaning was that the glass substrates were rinsed in alcohol (electronic grade) for 3 minutes, followed by rinsing in de-ionized water (DI water) for 1 minute. Then they were rinsed in methanol (electronic grade) for 3 minutes, followed by rinsing in DI water for 1 minute. Finally the substrates were rinsed in 35% of H₂O₂ for another 3 minutes followed by rinsing in DI water for 1 minute. The second stage of the cleaning was to use a Sonicator. The glass substrates were supersonically cleaned for 20 minutes using a power of 100 watts and a frequency of 25 kHz (figure 4.11).
4.2.2.2 Nanofilm Deposition

The aluminum nanofilms were deposited using the same e-beam evaporator. But before the deposition the chamber was cleaned thoroughly using alcohol to eliminate any possible contaminations (figure 4.12).

Figure 4.11 Substrate is under supersonic cleaning

Figure 4.12 Aluminum in a crucible inside of the e-beam evaporator
The built-in deposition thickness indicator (QCM) was re-calibrated using the surface profilometer which was first calibrated with a standard. The vacuum level of the deposition chamber [36] was kept at $10^{-7}$ Torr instead of $10^{-6}$ Torr which was used for the previous bulk metal induced crystallization (figure 4.13).

![Image of vacuum control panel](image)

**Figure 4.13** High vacuum level was maintained during the deposition

The Al deposition rate was kept at 0.1 Å/sec instead of 1Å/sec used in the previous bulk aluminum deposition to keep the highest deposition uniformity. The Al thicknesses of 2 nm, 6 nm, and 10 nm were deposited. Following the Al nanofilm deposition Si nanofilms were immediately *in situ* deposited. The deposition rate was also kept at 0.1Å/sec. The Si thicknesses of 3 nm, 8 nm, and 13 nm were deposited. The silicon target used was from Kurt J. Lesker Company (figure 4.14). The 0.25-inch thick Si target was first broken into small chunks before loading into the crucibles. After the Si evaporates it will become amorphous.
Figure 4.14  Silicon target used in the e-beam evaporator

Figure 4.15 shows a few Si wafers after the deposition. These wafers were immediately stored in a decicator after removed from the e-beam evaporator.

Figure 4.15  Si wafers with depositions from the e-beam evaporator
4.2.2.3 Sample Annealing

The annealing process was done in a high vacuum chamber (NanoSys-1). The temperature was kept at 500 °C. The annealing time was 60 minutes (figure 4.16).

4.3 Results and Discussion

Our samples were observed using the SEM during the different stages of the experiment. The samples were characterized by X-ray diffraction technique and the spectrophotometry before and after annealing.

4.3.1 Images from SEM

Aluminum nanofilms were first observed using the SEM with a magnification of 160,000 for 2-nm film, and a magnification of 100,000 for both 6-nm and 10-nm films. Figure 4.17 shows the samples were mounted on the sample holders of the SEM in positions of both top view and cross-sectional view.
From figures 4.18, 4.19, and 4.20 it can be seen Al nanofilm actually are formed by nanoclusters. There are gaps among these nanoclusters.
The thickness of nanofilms from the QCM were determined by the equivalency of the mass from the nanoclusters. There are voids among the nanoclusters. The thinner the nanofilms indicated from the QCM, the more voids.

Figure 4.19  Aluminum nanofilm with a thickness of 6 nm

Figure 4.20  Aluminum nanofilm with a thickness of 10 nm
Figure 4.21 Cross sectional view of Al nanofilm with thickness of 2 nm

Top view of Si nanofilms can be seen in figures 4.21 and 4.22. It is clear to see that after the annealing Si nanofilms were fused by Al nanofilms.

Figure 4.22 Si nanofilm of 3 nm on 2-nm Al before annealing
With a magnification of 200,000 the cross-sectional view of thickness of a 2-nm Al nanofilm can be seen in figure 4.23.

4.3.2 Plots from X-Ray Diffraction

After the annealing all nine samples (figure 4.24) were characterized using an X-ray diffractometer (figure 4.25).
Out of nine samples only two samples showed the crystal Si character angle of 28.5°. They are 13-nm Si with 10-nm Al deposited underneath (figure 4.26), and 8-nm Si with 10-nm Al deposited (figure 4.27).

Figure 4.25 The sample holder of X’Pert PRO X-Ray Diffractometer

Figure 4.26 XRD plot for Si of 13 nm deposited on 10-nm Al after annealing
X-ray diffraction technique failed to detect crystalline Si in all other samples with plots similar to figure 4.28 since the thickness of Si is too thin.
4.3.3 Graphs from Spectrophotometry

One of the performance improvements for crystalline Si versus amorphous Si is the optical property, namely the transmission coefficient in visible spectrum. From our results the transparency of Si is increased about 70% after the annealing. We believe this increment is due to the crystallization of amorphous silicon which implies we successfully crystallized amorphous Si thin films using Al nanofilms.

The transmission coefficients were measured using a Jasco spectrophotometer. In order to eliminate the effect of the glass substrate a second identical substrate is needed (figure 4.29).

Figure 4.29  Samples loaded in the chamber of the spectrophotometer

In that way the transmission coefficients measured are solely contributed to the silicon and the aluminum. It can clearly be seen from the following graphs the transmission coefficients are greatly improved.
Comparing figure 4.31 to figure 4.30 the increase of transmission coefficient is about 180% though the net values are relatively low (17% and 6%) due to the thickness of Si and Al film (the vertical scales are different for these two graphs).

Figure 4.30 Si of 13 nm deposited on 10-nm Al before annealing

Figure 4.31 Si of 13 nm deposited on 10-nm Al after annealing
Comparing figure 4.33 to figure 4.32 the increase of transmission coefficient is about 50%. It is noticed the net values of transmission coefficients are increased (24% and 16%) due to the reduction of the thickness of Si and Al film.
Comparing figure 4.35 to figure 4.34 the increase of transmission coefficient is about 50%. The net values of transmission coefficients are further increased (32% and 21%) due to the more reduction of the thickness of Si and Al film.
Comparing figure 4.37 to figure 4.36 the increase of transmission coefficient is about 38%. The net values of transmission coefficients are decreased (11% and 8%) due to the increase of the thickness of Si and Al film.
Figure 4.38  Si of 8 nm deposited on 6-nm Al before annealing

Comparing figure 4.38 to figure 4.37 the increase of transmission coefficient is about 56%. The net values of transmission coefficients are increased (25% and 16%) due to the decrease of the thickness, mainly in aluminum film.

Figure 4.39  Si of 8 nm deposited on 6-nm Al before annealing
Figure 4.40  Si of 8 nm deposited on 2-nm Al before and after annealing

Figures 4.40 and 4.41 are showing the increase of transmission coefficient after annealing (dotted lines). The vertical axis is the transmission coefficient.

Figure 4.41  Si of 3 nm deposited on 6-nm Al before and after annealing
Comparing figure 4.43 to figure 4.42 the increase of transmission coefficient is about 56%. The net values of transmission coefficients are decreased (11% and 8%) due to the increase of the thickness of Si and Al film.
We also measured the transmission coefficient changes extending the spectrum into infrared. Figure 4.45 shows one of the samples. The increase of coefficient (dash line) is consistent with the visible spectrum.
Figures 4.46 and 4.47 are showing another sample with the spectrum extended to infrared. There is an 55% increase of transmission coefficient. The discontinuity in the graphs at 900 nm is due to the switching the detectors in the spectrophotometer.
CHAPTER 5

CONCLUSIONS AND RECOMMENDATION

5.1 Conclusions

In this dissertation we studied a novel nanocluster deposition system (NanoSys-1) that fabricates nonlithographic nanoparticles under an ultra high vacuum environment. We achieved a vacuum of $8.42 \times 10^{-10}$ Torr (Figure 2.06) in the deposition chamber. We investigated two different techniques to control the size of nanoparticles, and found they are in good agreement with the existing theories. We also studied an improved version of nanocluster deposition system (NanoSys-2). With this system we investigated four parameters (sputtering source power, aggregation length, argon flow rate of sputtering source, and helium flow rate of aggregation gas) controlling the deposition rate, and found they have better control ability than ones from NanoSys-1.

As a preparation for nanoparticle induced crystallization we first investigated bulk metal induced crystallization of amorphous silicon thin films. We used five metals: aluminum, silver, indium, lead, and tin. We achieved a temperature of 500 °C for aluminum, and a temperature of 700 °C for silver to crystallize amorphous silicon. We found the temperature needed to crystallize amorphous silicon using indium, lead, or tin is higher than 580 °C, which is above the softening point of glass.

After successfully crystallized a-Si thin film we investigated amorphous silicon crystallization using aluminum nanofilm which is a preparation for the future investigation of using aluminum nanoparticles. The thicknesses of the Al nanofilms we used were 2 nm, 6 nm and 10 nm. We examined the transmission coefficient before and after the annealing of our samples using a spectrophotometer. Our results show an
average of 70% increase of transmission coefficient in visible spectrum. We conclude the a-Si films were successfully crystallized by Al nanofilms.

5.1.1 Nanoparticle Size Control

We investigated two different techniques to control the size of nanoparticles. Cu and Au nanoparticles were used to investigate this function. The results are as follows.

- **Size control by gas aggregation.** Both NanoSys-1 and NanoSys-2 were used to do this investigation. Helium was used as the condensation gas. For NanoSys-1 we applied a helium flow rate of 20 SCCM (achieved a size of 20 nm in diameter); for NanoSys-2 we applied two helium flow rates: 20 SCCM (achieved a size of 20 nm in diameter) and 40 SCCM (achieved a size of 15 nm in diameter). Our results are reasonably well comparing the theoretical calculation. We also found for the same deposition parameters NanoSys-2 only needs 1/3 of the time to finish the deposition.

- **Size control by QMF.** NanoSys-1 was used to do this investigation. The parameters on QMF were set for 10 nm. Our result shows great agreement with the theory.

5.1.2 Nanoparticle Deposition Rate Control

The parameters to control deposition rate of nanoparticles for NanoSys-1 are available from the acceptance data provided by the manufacturer. We examined these parameters and found they are in fair agreement. Since NanoSys-2 has only finished the first deposition unit. There are no data from the manufacturer yet. We did extensive work and investigated how the parameters controlling the deposition rate. These parameters
are: power of magnetron sputtering source, aggregation length, argon flow rate, and helium flow rate. The results are as follows.

- **Power of magnetron sputtering source.** We found the minimum power needed is from 15 to 30 watts under which the deposition rate is almost constant which is around 0.05 Å/sec or 3 nm/min. When the power is increased from 30 to 110 watts the deposition rate is increased linearly from 15 to 70 nm/min. Above 110 watts the deposition rate is not much increased. It stays around 75 nm/min.

- **Aggregation length.** We found the minimum aggregation length needed for a useful deposition is 10 mm under which the deposition rate is 0.05 Å/sec, 3 nm/min. As the aggregation length increases the deposition rate increases linearly. When the aggregation length increases to 50 mm the deposition rate reaches a maximum value (0.75 Å/sec, or 45 nm/min). The deposition rate will start decreasing slowly as the aggregation length is larger than 50 mm until to 100 mm which is the maximum for NanoSys-2.

- **Argon flow rate.** We found the minimum argon flow rate is about 30 SCCM under which a deposition rate of 0.04 Å/sec, or 2.4 nm/min was recorded. As the argon flow rate increases from 40 to 100 SCCM the deposition rate increases linearly. A deposition rate of 1.2 Å/sec, or 73 nm/min was recorded.

- **Helium flow rate.** We found there is no minimum value for helium flow rate. A deposition rate of 0.35 Å/sec, or 20 nm/min, was observed under a
condition of no helium flow. We found helium flow rate does not control
the deposition rate as much as the previous three parameters.

5.1.3 Metal Induced Crystallization

We used five different metals to investigate bulk metal induced crystallization
(MIC). We used both X-ray Diffraction and Raman spectroscopy to characterize our data.

The results are as follows.

- **Aluminum, melting point: 660 °C.** We found the lowest annealing temperature to
crystallize a-Si is 500 °C. This is a temperature much below the softening point of
glass (630 °C)

- **Silver, melting point: 961 °C.** The lowest annealing temperature to crystallize a-
Si is 700 °C was observed. We found for thinner a-Si layer (250 nm) a higher
percentage of crystallization will be achieved. We also found the same annealing
temperature aluminum crystallizes high percentage of a-Si.

- **Indium, melting point: 157 °C.** The highest annealing temperature we applied was
580 °C which is close to the softening point of glass. We did not find any
crystallization of a-Si.

- **Lead, melting point: 327 °C.** The highest annealing temperature we applied was
580 °C which is close to the softening point of glass. We did not find any
crystallization of a-Si.

- **Tin, melting point: 232 °C.** The highest annealing temperature we applied was
580 °C which is close to the softening point of glass. We did not find any
crystallization of a-Si.
5.1.4 Nanofilm Induced Crystallization

We used 9 samples with combinations of different thicknesses of aluminum nanofilms and a-Si thin films (Figure 5.01). We used both XRD and Raman spectroscopy to characterize our data. The XRD only detected Si crystallization of two samples with highest thickness combination: 8-nm a-Si deposited on 10-nm aluminum, and 13-nm a-Si deposited on 10-nm aluminum. The Raman spectroscopy technique did not detect any crystallization of our samples.

<table>
<thead>
<tr>
<th>Thickness Al nanofilms</th>
<th>2 nm</th>
<th>2 nm</th>
<th>2 nm</th>
<th>6 nm</th>
<th>6 nm</th>
<th>6 nm</th>
<th>10 nm</th>
<th>10 nm</th>
<th>10 nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thickness a-Si Film</td>
<td>3 nm</td>
<td>8 nm</td>
<td>13 nm</td>
<td>3 nm</td>
<td>8 nm</td>
<td>13 nm</td>
<td>3 nm</td>
<td>8 nm</td>
<td>13 nm</td>
</tr>
<tr>
<td>T. C. Before Annealing</td>
<td>55%</td>
<td>30%</td>
<td>21%</td>
<td>25%</td>
<td>16%</td>
<td>16%</td>
<td>9%</td>
<td>8%</td>
<td>6%</td>
</tr>
<tr>
<td>T.C. After Annealing</td>
<td>75%</td>
<td>42%</td>
<td>32%</td>
<td>54%</td>
<td>25%</td>
<td>24%</td>
<td>12%</td>
<td>11%</td>
<td>17%</td>
</tr>
<tr>
<td>Percentage Increase</td>
<td>36%</td>
<td>40%</td>
<td>50%</td>
<td>116%</td>
<td>56%</td>
<td>50%</td>
<td>33%</td>
<td>38%</td>
<td>180%</td>
</tr>
</tbody>
</table>

Figure 5.01 Chart of comparison of transmission coefficients

However, we believe all samples are crystallized after we characterized the data using a spectrophotometer. From the above chart it can be seen the transmission coefficient (T.C.) is significantly increased (with an average of 70%) after annealing. The only explanation for the increase of transmission coefficient we can make is the a-Si thin film has been crystallized.
The following are conclusions for our investigation of Al nanofilm induced amorphous silicon thin film crystallization:

- Si thin films using Al nanofilms were crystallized at a temperature of 500 °C.
- The transmission coefficient for visible spectrum increased about 70%.
- A new technique found to determine the crystallization of silicon thin film.

5.2 Recommendation

Based on the investigation we have done there are several recommendations we like to propose for the future work on the nanoparticle deposition system and use it to do nanoparticle induced crystallization of Si thin film.

5.2.1 Nanoparticle Deposition System

5.2.1.1 Deposition rate control

The deposition rate of nanoparticles from both NanoSys-1 and NanoSys-2 are controlled by four parameters. They are: power of magnetron sputtering source, aggregation length, argon flow rate, and helium flow rate. We investigated all of these four parameters, and made four individual plots indicating how the deposition rate is controlled by these parameters. The more informative way to show how the deposition rate is controlled is to plot a three dimensional graph. We propose to plot two graphs instead of four in the future work. 1) Deposition rate (Z-axis) vs. magnetron power (X-axis), and the aggregation length (Y-axis). 2) Deposition rate (Z-axis) vs. argon flow rate (X-axis), and helium flow rate (Y-axis).
5.2.1.2 Size control by gas aggregation

There are three recommendations we would make here. First, we suggest investigating how the variation of aggregation length would control the size of nanoparticles. From the existing theories [37, 38,] we know the time nanoparticles stay in the aggregation tube (residence time) has an important effect on the control of the size. The quantitative result will give more flexibility to control the size of nanoparticles.

Second, also from the existing theories [39, 40] the temperature of the aggregation tube is a parameter to control the size; the lower temperature, the faster condensation. When a smaller size (1 to 2 nm) of nanoparticles is needed a liquid nitrogen cooling system should be used instead of cold water cooling from a chiller. Currently there are no work has done for this study. It would be very helpful to get the results of this as a reference to do future deposition of nanoparticles with smaller sizes.

Last, but not least we noticed the size control can also be obtained by varying argon flow rate (the argon is originally intended for the magnetron sputtering source). But to do so, the deposition rate will be changed too as we stated in early part of this dissertation. Also, the change of argon flow rate (it determines the argon pressure) will change the magnetron power which is controlled by the applied voltage, the current produced under that voltage, and the argon pressure. As a result, it will make the predictability of size control more difficulty. By changing argon flow rate to control the size of nanoparticles should be avoided.
5.2.1.3 Size control by quadruple mass filter (QMF)

The quadruple mass filter (QMF) used in this dissertation is only capable to filter charged particles (ions). But a small percentage of particles from the magnetron sputtering source are neutrals. These neutral particles with different sizes will be deposited on the samples which will reduce the quality of size controlled deposition. In order to solve this problem the manufacturer of the QMF has installed two pairs of deflection plates on the exit aperture of the QMF. So far no study has done to investigate how effect these plates will work. For a high quality sized controlled deposition these neutrals must be eliminated. We would recommend this as the future work.

5.2.2 Nanoparticle Induced Crystallization

We deposited 2 nm, 6 nm and 10 nm of aluminum nanofilms on amorphous silicon (a-Si) thin film. The thickness of our nanofilms is from the conversion of the mass deposited which is done automatically by a QCM. The nanofilm we deposited to crystallize amorphous silicon actually is a layer of nanoparticles with different sizes. Therefore, the uniformity of the crystallized silicon will be difficult to control. Here we recommend using NanoSys-2 to deposit aluminum nanoparticles with a preselected size to improve the uniformity.

Here is the detailed procedure we are suggesting. First, eliminate all neutrals from the QMF by applying appropriate deflecting voltages.

- Deposit the different sizes (from 1 to 5 nm) of Al nanoparticles by using the combination of both QMF and gas aggregation size control with a highest distribution of desired size.
Figure 5.02  Mini e-beam evaporator installed on NanoSys-2

- Deposit a layer of a-Si with different thickness (from 2 to 20 nm) using the mini e-beam evaporator installed in the deposition chamber (Figure 5.02, the arrow pointer). This will yield two advantages. First, the deposition will be in situ (Figure 5.03, the arrow pointer). Second, the mini e-beam evaporator yields more uniform particles than a regular e-beam evaporator.

- Characterize the transmission coefficient in visible spectrum.

- Anneal these samples near 500 °C by using the built-in heater in the main chamber at different amount of time. Characterize the transmission coefficient of each sample in visible spectrum after annealing.
Figure 5.03 Mini e-beam evaporator in deposition chamber of NanoSys-2

- Determine the minimum size of Al nanoparticles needed to achieve the desired transmission coefficient.
- Determine the minimum amount time needed to achieve the desired transmission coefficient.

Since both X-ray diffraction technique and Raman spectroscopy failed to exam crystallization of thin films with a thickness of a few nanometers. We used the significant increase of transmission coefficient after annealing to determine the crystallization of the a-Si films. So far as we know there is no existing theory related to this technique. We recommend doing some theoretical study to confirm the validity of this technique. We also recommend finding an alternative technique to exam the crystallization of thin films with a thickness of a few nanometers.
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