CRYSTALLIZATION OF AMORPHOUS SILICON THIN FILMS INDUCED BY NANOPARTICLE SEEDS

By
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A DISSERTATION PRESENTED TO THE GRADUATE SCHOOL OF THE UNIVERSITY OF FLORIDA IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

UNIVERSITY OF FLORIDA

2009
To my parents and brother
ACKNOWLEDGEMENTS

I would like to acknowledge the many individuals that have made this work possible. First, I would like to thank my advisor, Dr. Rajiv K. Singh, for his guidance, support and encouragement for my research. The open environment that he has provided over the years that I have worked with him has made for a very dynamic and rewarding graduate school experience. I would also like to thank Dr. David Norton, Dr. Stephen Pearton, Dr. Brent Gila, and Dr. Fan Ren for kindly participating on my dissertation committee.

I would like to also acknowledge all my friends and coworkers who made graduate school such a memorable time. Seoungyong Son, Jaeseok Lee, Myunghwan Oh, Purushotam Kumar, Sushant Gupta, Aniruddh Khanna, Junghoon Jang, Kerry Siebein and others provided the social perspective that is always necessary in life.

I would also like to thank the administrative and support staff of the Department of Materials Science and Engineering for their efforts in making success possible.

Finally, I would like to thank my parents, my brother and the rest of my family for the endless love and support they have provided over the many years of my extended education.
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Abstract of Dissertation Presented to the Graduate School of the University of Florida in Partial Fulfillment of the Requirements for the Degree of Doctor of Philosophy

CRYSTALLIZATION AND CHARACTERIZATION OF AMORPHOUS SILICON THIN FILMS INDUCED BY NANOPARTICLES SEED

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May 2009

Chair: Rajiv. K. Singh
Major: Materials Science and Engineering

Crystallization of amorphous Si (a-Si) thin film has received extensive interest for their attractive applications into Si thin film transistors and Si based solar cells. Among various crystallization techniques, Solid phase crystallization (SPC) and Excimer laser crystallization (ELC) were investigated. Firstly, Solid phase crystallization (SPC) of amorphous silicon thin films deposited by the DC magnetron sputtering system with a modification in nucleation step was investigated at low temperature. The thin film consists of polycrystalline nanoparticles embedded in an amorphous matrix which can act as nuclei during crystallization, resulting in a lower thermal energy for the nucleation. The lowering energy barrier for nucleation would shorten the transition time from amorphous into polycrystalline silicon resulting from the reduction of incubation time and also lower the processing temperature spontaneously. In addition, a comprehensive study of the growth mechanism of the sputtered amorphous silicon thin films is presented during annealing. Samples were prepared with various substrate temperatures and RF power in order to optimize the crystallization of a-Si after the deposition. Also, the effects of annealing condition were examined. Low pressure N₂ ambient during SPC promoted crystallization of a-Si thin films and the crystallinity. The low pressure annealing had a large impact on the crystallinity and growth behavior of subsequent films. In addition, the
crystallinity, incubation time, the crystallized volume fraction and growth rate of the films annealed in a conventional furnace have been extensively studied by XRD and HRTEM. It was believed that crystalline Si nanoparticles would act as nuclei for growth of crystalline Si thin films, thus removing the high temperature requirement for nucleation, resulted in the improvement of the crystallization of a-Si.

Secondly, the controlled Super Lateral Growth (SLG) can be obtained by nanoparticle induced crystallization (NIC) technique during laser annealing, which led to enhance the random super lateral growth (SLG) of Si thin films for the excimer laser crystallization (ELC). The crystallinity and surface information of the films irradiated by excimer laser have been studied by Raman spectroscopy, FESEM and AFM. Also, Transmission electron microscopy (TEM) was employed in order to obtain structural information. Polycrystalline Si nanoparticles, which have higher melting point than those of amorphous phase, would survive at high energy density of laser. In general, super lateral growth (SLG) occurs at vary narrow laser energy density region. Thus, it tends to be sensitive to laser energy density, which means not easy to control because of the characteristics of the mechanism of the SLG. In this study, poly-Si nanoparticles would act as nucleation seeds for the growth of the films during the solidification. Those nanoparticle seeds provided more probability to survive at higher density of energy compared to that without nanoparticle seeds, resulted in the large grain size distribution and the controlled super lateral growth (SLG), relatively independent of laser energy density.
CHAPTER 1
INTRODUCTION

1.1 Silicon Based Photovoltaic

Photovoltaic has the huge potential for future energy supply system. Recently, a considerable amount of money has been widely invested in the research, development and demonstration. Table 1-1 shows the technical and the theoretical potentials of several renewable energy sources such as biomass, wind and solar energy.[1] Both potentials of PV electricity is high enough to contribute considerably to the abatement of the global CO₂ problem.

Photovoltaic (PV) is an important energy technology for many reasons such as environmental benefits. As a domestic source of electricity, it contributes to the nation's energy security. As a relatively young, high-tech industry, it helps to create jobs and strengthen the economy. As it costs increasingly less to produce and use, it becomes more affordable and available. Furthermore, few power-generation technologies have as little impact on the environment as photovoltaics. As it quietly generates electricity from light, PV produces no air pollution or hazardous waste. It doesn't require liquid or gaseous fuels to be transported or combusted. And because its energy source - sunlight - is free and abundant, PV systems can guarantee access to electric power. PV frees us from the cost and uncertainties surrounding energy supplies from politically volatile regions. Table 1-2 lists some of advantages and disadvantages of photovoltaics. Therefore, Photovoltaics is an excellently suitable solution for low power electricity supply in rural and remote areas in developing countries. Photovoltaics have a similar but smaller market in industrialized countries as well. All these solar energy technologies put the sun's energy to work for us in our homes, schools, businesses, and government buildings. They are being developed because they are reliable, they have very few environmental impacts, and they make use of an abundant domestic energy resource: sunlight.
Semiconductor solar cells fundamentally quite simply devices. Semiconductors have the capacity to absorb light and to deliver a portion of the energy of the absorbed photons to carriers of electrical current – electrons and holes. A semiconductor diode separates and collects the carriers and conducts the generated electrical current preferentially in a specific direction. Thus, a solar cell is simply a semiconductor diode that has been carefully designed and constructed to efficiently absorb and convert light energy from the sun into electrical energy. A simple conventional solar cell structure is depicted in Figure 1-1.

All electromagnetic radiation, including sunlight, is composed of particles called photons, which carry specific amounts of energy determined by the spectral properties of their source. Photons also exhibit a wavelike character with the wavelength, $\lambda$, being related to the photon energy, $E_\lambda$, by

$$E_\lambda = \frac{hc}{\lambda} \tag{1.1}$$

Where $h$ is Plank’s constant and $c$ is the speed of light. Only photon with sufficient energy to create an electron-hole pair, that is, those with energy greater than the semiconductor bandgap ($E_g$), will contribute to the energy conversion process. Thus, the spectral nature of sunlight is an important consideration in the design of efficient solar cells.

Solar cell are made of materials called semiconductors, which have weakly bonded electrons occupying a band of energy called the valence band. When energy exceeding a certain threshold, called the band gap energy, is applied to a valence electron, the bonds are broken and the electron is somewhat “free” move around in a new energy band called the conduction band where it can “conduct” electricity through the material. Thus the free electrons in the conduction band are separated from the valence band by the band gap (measured in units of electron volts or eV). This energy need to free the electron can be supplied by photons, which are particles of
light. Figure 1-2 shows the idealized relation between energy (vertical axis) and the spatial boundaries (horizontal axis).

When the solar cell is exposed to sunlight, photons hit valence electrons, breaking the bonds and exciting them to the conduction band. There, a specially made selective contact that collects conduction-band electrons drives such electrons to the external circuit. The electrons lose their energy by doing work in the external circuit such as pumping water, spinning a fan, powering a sewing machine motor, a light bulb, or a computer. They are restored to the solar cell by the return loop of the circuit via a second selective contact, which returns them to the valence band with the same energy that they started with. The movement of these electrons in the external circuit and contacts is called the electric current. The potential at which the electrons are delivered to the external world is slightly less than the threshold energy that excited the electrons; that is, the band gap. Thus, in a material with a 1 eV band gap, electrons excited by a 2 eV photon or by a 3 eV photon will both still have a potential of slightly less than 1 eV (i.e. the electrons are delivered with an energy of 1 eV). The electric power produced is the product of the current times the voltage; that is, power is the number of free electrons times their potential.

Since only photon with $h\nu > E_g$ can create electron-hole pairs and contribute to the output of the solar cell, it is obvious that the band gap determines how well the solar cell is coupled to the solar spectrum. A simple analysis can be performed to predict the maximum solar cell efficiency. More complete analyses of the theoretical limits of solar cells are given elsewhere.[2-4] Assuming the maximum energy that can be extracted from an absorbed photon is $E_{gs}$, the maximum efficiency can be expressed as

$$
\eta_{\text{max}}(E_g) = \frac{1}{q} \frac{E_G I_{\text{inc}}}{P_{in}} = \frac{E_G}{(P_{in} / A)} \int_{\lambda < \lambda_g} f(\lambda) d\lambda
$$

(1-2)
This is plotted in Figure 1-3 for an AM1.5 global spectrum and shows a maximum efficiency of 48% at about $E_g=1.1$ eV, close to the band gap of silicon. Of course, this is only a simple estimate and assumes that $V_{oc}=1/qE_g$ and $FF=1$, which are obvious exaggerations. Perfect light trapping was also assumed so that $I_{sc}=I_{inc}$, but that is a more realistic prospect. Under non-concentrated solar illumination, the actual maximum theoretical efficiency for a silicon solar cell is approximately 30%. However, this simple approach does serve to demonstrate the important role the semiconductor band gap plays in determining solar cell performance and shows that band gaps between 1.0 and 1.6 eV have nearly equivalent maximum theoretical efficiencies.

Figure 1-4 shows the efficiency for PV materials with band gap energy between 1.0 and 1.6 eV. From solid state physics we know that silicon is not the ideal material for photovoltaic conversion. It is a material with relatively low absorption of solar radiation, and, therefore, a thick layer of silicon is required for efficient absorption. Theoretically, light absorption is impeded because it requires a change of momentum. Thus, materials with a direct band structure which gives very strong light absorption are more suitable for solar cell technology. They belong to the class of compound semiconductors like GaAs or InP, which are III-V compounds according to their position in the periodic table. Other important groups are II-VI and I-III-VII compounds, which, just like the elemental semiconductors, have four bonds per atom. However, there are problems with low efficiency and insufficient stability prevented further penetration of Copper Indium Diselenide (CIS), and Cadmium Telluride (CdTe).

The new technology is based on the ternary compound semiconductors CuInSe$_2$, CuGaSe, CuInS$_2$ and their multinary alloy Cu(In,Ga)(S,Se)$_2$ (CIGS). The first results of single crystal work on CuInSe$_2$ were extremely promising, but the complexity of the material looked complicated as a thin film technology.
In spite of the complicated manufacture and the high cost, crystalline silicon still dominates the market today and probably will continue to do so in the immediate future. This is mostly due to the fact that there is an abundant supply of silicon as raw material, high efficiencies are feasible, the ecological impact is low, and silicon in its crystalline form has practically no degradation. Furthermore, detailed models that take into account surface characteristics and the multi-reflections within the wafer show that absorption can be greatly enhanced.[5, 6] Therefore, a very thin layer of Si can offer a high degree of absorption of the solar spectrum—nearly as much as a thick wafer and direct band gap materials.

Besides, such a thin-film Si (TF-Si) solar cell offers many advantages that can lower the cost of generating solar electricity. A TF-Si cell offers bellows:

1. Reduced bulk recombination leading to lower dark current, higher \( V_{oc} \) and higher FF of the device. Compared to a thick cell, a thin cell of the same material quality can yield higher device performance. Likewise, for a comparable performance, TF-Si solar cell requires lower material quality than a thick cell.

2. Potential for low cost cells/module

3. Potential for lightweight photovoltaics,

4. Lower energy consumption for device fabrication

5. Potential for flexible solar cells.

These advantages of TF-Si solar cells, in concurrence with the performance advantage, make the very attractive for the future. Practical realization of solar cells with the above advantages poses many challenges in both the design and device fabrication. These challenges include an efficient method for light-trapping to compensate for reduced thickness, and a low-cost substrate to support the thin film. Low-cost substrates generally imply materials that may not be compatible with the high temperature required for formation and processing of Si film. This incompatibility can arise because of impurities in the substrate that can diffuse into the Si...
film, softening of the substrate, thermal mismatch, and less desirable electronic properties of the interface.

1.2 Synthesis of Polycrystalline Si Film

Many researches have been performed to lower processing temperature in order to reduce the cost. Generally, there are two methods to obtain polycrystalline silicon thin films on insulators. One is a direct deposition method with the use of disilane (Si$_2$H$_6$) as a precursor or plasma enhanced chemical vapor deposition (PECVD).[7, 8] In this method, the grain sizes are very small which is deleterious for electrical performance. Also, the surface is very rough, thus further hampering the properties of the devices. To engineer the poly-Si morphology a number of approaches are followed based manipulation of the poly-Si chemical vapor deposition (CVD) process,[9, 10] on excimer laser crystallization (ELC), of a-Si films,[11, 12] or on solid phase crystallization (SPC) of a-Si.[13-20] Of these techniques, SPC is one of the most promising methods to obtain poly-Si films from the amorphous phase. Compared to CVD poly-Si films, poly-Si films obtained by SPC of a-Si films are characterized by a larger grain size, i.e., by a reduced density of grain boundaries, and indeed, some of the electrical characteristics have been improved by using SPC poly-Si films.[13, 14] Unfortunately, the SPC technique significantly increases the crystallization temperature and process time which are deleterious for manufacturing. SPC of a-Si has recently met with renewed interest since the discovery that the presence of metal impurities strongly modifies the crystal grain nucleation and growth kinetics, allowing considerable improvement of the electrical characteristic.[19, 20]

For excimer laser crystallization, in contrast to solid-phase crystallization (SPC), the silicon film is melted for very short time by laser annealing. This technique provides a low thermal budget and low defect density in grains due to melting and rapid regrowth, resulted in very fine grain distribution in the range of 0.1–0.2 μm.[21] However, the low defect density
inside the grains have led to give rise to high carrier mobilities (100–300 cm²/V·sec).[22] Despite the large mobilities produced by this method, there are several drawbacks. The formation of very small grains gives rise to surface non-uniformity which leads to non-uniform oxide growth. In addition, uniformity in processing is difficult due to small size of the laser beam and due to very sensitive to laser energy density for the super lateral growth (SLG).

1.3 Present Approach

In order to fabricate very large grain sized polycrystalline Si thin films on insulators at low temperatures and with short processing times, we have investigated a new technique in this study. This technique is based on the application of a nanoparticle seeds to induce the solid phase crystallization (SPC) of amorphous Si thin films. The application of a nanoparticle seed leads to improvement of the growth of the silicon film, resulting in the formation of large grains. Grains larger than 2 μm have been obtained. Studies to understand the nature of the growth process have been investigated in this dissertation. Also, low pressure N₂ annealing promoted the crystallization of a-Si thin films during SPC.

In addition, excimer laser crystallization (ELC) was carried out to control the super lateral growth ((SLG) when nanoparticles were embedded in amorphous Si matrix. Nanoparticle embedded samples irradiated by excimer laser showed large grain size distribution, relatively not sensitive to laser energy density.
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<td>640</td>
<td>6000</td>
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Units: exajoule per year
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<th>Disadvantages of photovoltaics</th>
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<td>Fuel source is vast and essentially infinite</td>
<td>Fuel source is diffuse (sunlight is a relatively low-density energy)</td>
</tr>
<tr>
<td>No emissions, no combustion or radiative fuel for disposal (does not contribute perceptibly to global climate change or pollution)</td>
<td>High installation costs</td>
</tr>
<tr>
<td>No moving parts (no wear)</td>
<td>Poorer reliability of auxiliary (balance of system) elements including storage</td>
</tr>
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<td>Ambient temperature operation (no high temperature corrosion or safety issues)</td>
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<tr>
<td>High reliability in modules (&gt;20 years)</td>
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<td>Modular (small or large increments)</td>
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<td>Quick installation</td>
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<td>Can be integrated into new or existing building structure</td>
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<td>Can be installed at nearly any point of use</td>
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<td>Daily output peak may match local demand</td>
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<tr>
<td>High public acceptance</td>
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<tr>
<td>Excellent safety record</td>
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Figure 1-1 Schematic of a simple conventional solar cell. Creation of electron-hole pairs, $e^-$ and $h^+$, respectively, is depicted.
Figure 1-2 Schematic of a solar cell. Electrons are pumped by photons from the valence band to the conduction band. There they are extracted by a contact selective to the conduction band (an n-doped semiconductor) at a higher (free) energy and delivered to the outside world via wires, where they do some useful work, then are returned to the valence band at a lower (free) energy by a contact selective to the valence band (a p-type semiconductor).
Figure 1-3 Theoretical maximum efficiency as a function of semiconductor band gap for an AM1.5 global spectrum
Figure 1-4 Best small area (0.5-5cm²) efficiency for various technologies measured under standard laboratory test conditions. MJ concentrators are double junctions before 1995, and triple junctions after. a-Si represents stabilized efficiency after extended light soaking and are MJ after 1990.
CHAPTER 2
LITERATURE REVIEW

In general, the formation of polycrystalline Si films from the amorphous phase is controlled by nucleation and growth processes. The pre-existing nucleation seeds would affect the growth behavior which is important in controlling the microstructure of the films for solid phase crystallization (SPC). In addition, laser annealing of amorphous Si films has been widely investigated due to the excellent electrical properties. The nanoparticles embedded in amorphous matrix also would act as nucleation seeds for excimer laser crystallization (ELC), resulted in the controlled super lateral growth (SLG).

In this chapter, the literature for nucleation and growth mechanisms in solid phase crystallization (SPC) is reviewed. This is followed by a discussion of seed-based crystallization related to my research. Also, literature pertaining to excimer laser crystallization (ELC) and laser-solid interactions of Si films are introduced. The rest of the chapter is devoted to mechanisms of laser crystallization of thin films.

2.1 Solid Phase Crystallization (SPC) of a-Si

Solid phase crystallization of a-Si on insulators such as glass has been widely investigated.[23-29] The thermodynamics and kinetics of solid phase crystallization of Si films from amorphous phase has been explained by classical nucleation and growth theory. When amorphous Si films are annealed to a certain temperature, the film is transformed into thermodynamically stable crystalline phase through four steps, including incubation, nucleation, growth and steady state.[30-32] In this process, small crystallites as nucleation site are formed and then grow with time in amorphous matrix. In case of a-Si films with a crystalline layer, this transition occurs at the crystalline and amorphous interface referred to as solid-phase epitaxy (SPE). The growth rate of the crystallization is strongly dependent of temperature. It follows an
Arrhenius behavior with an activation energy of 2.68±0.05eV over a growth rate range of more than 10 orders of magnitude.[30, 32] as shown in Figure 2-1 which reported by Olson and Roth for a-Si on top of <100> oriented c-Si are shown.[30] Also, it is presented that the impurity content strongly affects the kinetics of SPE, indicating dopants such as B, P, and As can promote the growth rate by more than one order of magnitude.[30, 33, 34] while contaminants such as C, O, F, or noble gases strongly decelerate the growth rate of films.[30, 35, 36] Moreover, the presence of n-type and p-type dopants also produces a compensating effect in the growth rate.[30, 37, 38] Another important result is the dependence of interface velocity on substrate orientation.[30, 39] Also, Spaepen and Turnbull have reported a structural model of thermal annealing in which the crystalline and amorphous interface resolved into a free energy minimum by the formation of terraces with a <111> orientation.[40] Thus, some defects in the amorphous phase strongly affect for the crystallization process.

Figure 2-2 shows the free energy diagram of a-Si (in both the relaxed and unrelaxed states) and of liquid Si with respect to crystalline Si.[41, 42] It is clear the a-Si has higher free energy than c-Si, and thus it exists as a kinetically meta-stable phase. The melting temperature of a-Si is predicted to be smaller than that of c-Si and to depend on the relaxation state. These last properties have indeed experimentally verified by ultra-short pulsed laser annealing.[42, 43]

2.1.1 Nucleation Theory for Solid Phase Crystallization

The crystallization of amorphous Si films generally occurs through a nucleation and growth process.[29] These phenomena have been explained by the classical nucleation and growth theory as mentioned previously.[23-29] According to the classical theory, the nucleation of the films occurs because of the reduction of the total free energy of the system. The Gibbs free energy change for this nucleation process, \( \Delta G_n \), is determined by the difference in volume free energy change for atoms in the crystalline phase relative to that of the amorphous phase and the
amount of interface energy which is generated by the a-Si/c-Si interface, if the strain energy is small enough to be neglected. The energy change due to formation of an n-mer of a nucleating phase is given by[44]

$$\Delta G_n = \Delta G_v \cdot V + \gamma \cdot S + \Delta G_\varepsilon \cdot V$$  \hspace{1cm} (2-1)

where $\Delta G_v$ is the free energy difference per unit volume due to the phase transformation, $V$ is the volume of an n-mer of the nucleating phase, $\gamma$ is the interfacial free energy between the cluster and the parent phase, $S$ is the surface area of the cluster, $\Delta G_\varepsilon$ is the strain energy per unit volume associated with the formation of the cluster. In order to describe the cluster of arbitrary shape and configuration, atomic volume, $\Omega$, and the shape factor, $g(\theta) = (2+ \cos \theta)(1-\cos^2 \theta)/4$, are introduced. The volume of an n-mer cluster and surface area can be expressed by $V = n \cdot \Omega$ and $S = g(\theta) \cdot \Omega^{2/3} \cdot n^{2/3}$. Equation (2-1) can be simplified as follows:

$$\Delta G = \Delta G_v \cdot \Omega \cdot n + \gamma \cdot g(\theta) \cdot \Omega^{2/3} \cdot n^{2/3}$$  \hspace{1cm} (2-2)

When the first derivative of Equation (2-2) equals to zero, the cluster reaches the critical size which can be a nuclei. From this, we can derive the critical free energy, $\Delta G^* k$, and the number of atoms in the critical cluster, $k$.

$$k = -(8/27) \cdot (1/\Omega) \cdot [\gamma \cdot g(\theta)/G_v]^3$$  \hspace{1cm} (2-3)

$$\Delta G^* k = -1/2 \cdot k \cdot \Omega \cdot \Delta G_v$$  \hspace{1cm} (2-4)

For time dependent nucleation rate it was reported by Turnbull[45] as

$$J^* (t) = J^* k \cdot \exp(-\tau / t)$$  \hspace{1cm} (2-5)

where $t$ is the time and $\tau$ is an incubation time.

The incubation time can be derived by the assumption of random walk model in the critical region.[44] In this approximation, $\tau$, the incubation time, is defined as the time for a cluster to
move from the subcritical size, $k - \delta/2$, to a supercritical size, $k + \delta/2$ along the Gibbs free energy barrier with the random walk distance, $\delta$. The value of $\delta$ is computed from the Gibbs free energy change equation by setting

$$\Delta G_k^+ - \Delta G_n^* = k_T$$

(2-6)

$$k - n = \delta / 2$$

(2-7)

Thus,

$$\delta = \left[-8k_T/(\partial^2 \Delta G_n^* / \partial n^2)\right]^{1/2}$$

(2-8)

In the random walk theory, the time which is necessary for a particle to displace the distance, $\delta$, in one dimension is given by

$$\tau = \delta^2 / \beta_k$$

(2-9)

Therefore, the incubation time, $\tau$, can be expressed as follows:

$$\tau = -8k_T/\left[\beta_k(\partial^2 \Delta G_n^* / \partial n^2)\right]$$

(2-10)

2.1.1 Growth Theory for Solid Phase Crystallization

The grain growth mechanism in solid phase crystallization of amorphous Si is the same as that of solid phase epitaxial growth (SPE). However, this crystallization needs a nucleation step before the growth process occurs. Due to this complication, an accurate measurement of the growth rate becomes very difficult. The growth rate is determined by fitting the crystallized volume and nucleation rate into the Avrami’s equation.[23] Another method to measure the growth rate is a direct observation of grains to grow with the TEM.[24] The reported activation energies for the grain growth, (2.4~3.3eV), are similar to those for epitaxial regrowth, (2.4~2.9eV).[23-25]
Grain growth mechanisms have been studied by many researchers. [26-28] Nakamura et al. found that the grains of (110) surface plane have a preferential growth in the <112> direction along twin boundaries. It results in the formation of dendrite shaped grains. Noma et al. had investigated the grain growth process for differently oriented grains. The growth rates for the grains have the same trend as those of the epitaxial regrowth (v(110)>v(110)>v(111)). The nucleated grains are bounded by the slowest growing plane, (111), during the crystallization process. Therefore, the growth rate of grains is determined by the rate of forming the (111) plane. As mentioned in previous reviews of epitaxial growth, the (111) plane is difficult to grow due to more incorporated atoms for migration of the a-Si/c-Si interface than other planes. In (111) growth, micro-twins are formed on the interface to enhance the growth. An end point of twin plane provides atomic steps as nucleation sites for the growth. [28]

According to Noma’s model, the shapes of variously oriented grains are decided by a location of (111) twin planes with respect to film surface. For example, the <110> oriented surface grains have a preferential growth in the <211> direction and branch in other coplanar <221> directions. This results in a dendrite shape. On the other hand, when (111) twin planes are parallel to the film surface in <111> oriented grains, the shapes become disc type. [27] Based on the work by others, we know that the randomly nucleated grains usually form micro-twins during the grain growth. From reviews in this section, it is known that the mechanism and the trend of solid phase growth of crystalline Si particle in a-Si thin films is the same as those of the epitaxial growth.

2.2 Excimer Laser Crystallization (ELC) of a-Si

Since the first results related to laser annealing of ion-implanted semiconductors were obtained, many of papers in the field has been reported enormously. [46-48] As mentioned previously, laser crystallization of poly-Si films results in the highest carrier mobility compared
to those attained by any technique. However, although researches on this technique have been actively performed,[12] the transformation mechanisms are not yet well understood. Also, attempts at quantitative estimates of the effects of high-power laser irradiation have been limited due to the lack of precise temperature and phase-dependent optical and thermophysical parameters.[49] Literature reviews related to this topic follow.

2.2.1 Laser-Solid Interaction

Electromagnetic radiation with wavelength ranging from ultraviolet to infrared interacts exclusively with electrons, as atoms are too heavy to respond significantly to the high frequencies ($\nu > 10^{13}$ Hz).[50] Therefore, the optical properties of matter are determined by the energy states of its valence electrons (bound or free). Bond electrons generally only weakly respond to the external electromagnetic wave and affect only its phase velocity. Free electrons, however, can be accelerated and therefore extract energy from the field. Since the field is periodically changing, the oscillating electrons reradiate their kinetic energy (cause of reflection) or collide with the atoms, giving their energy to the lattice.

Absorption of incident energy fundamentally dictates the resultant thermal state of the material and therefore is a suitable point to begin an analysis of laser-solid interactions. The complex refractive index, $n^*$, defines two quantities which describe the degree of coupling of the incident radiation with the material, namely reflectivity $R$ and absorption coefficient $\alpha$. It is defined as[51]:

$$n^* = n - ik \quad (2.1)$$

Where $n$, the real part, is the ratio of the phase velocities in vacuum and the material. The extinction coefficient $k$ describes the damping of the light wave. For normal incidence, reflectivity and absorption are related to $n$ and $k$ by, respectively:
\[ R = \frac{(n-1)^2 + k^2}{(n+1)^2 + k^2} \] (2.2)

and

\[ \alpha = \frac{4\pi k}{\lambda} \] (2.3)

where \( \lambda \) is the wavelength of the radiation.

As mentioned previously, the mechanisms involved in absorption of incident radiation in materials are defined by the electronic structure of the material, and therefore it is useful to discuss exclusively semiconductors. In semiconductors, five distinct mechanisms for the absorption of light can be identified.[48]

1) Photons with energy (\( h\nu \)) much less than the band-gap energy (\( E_g \)) can excite lattice vibrations directly.

2) Free or nearly free carriers can be excited by absorption of light with \( h\nu < E_g \); such carriers will always be present as a result of finite temperature and doping.

3) An induced metallic-like absorption due to free carriers generated by the laser radiation itself can occur.

4) For photon energies \( > E_g \) absorption will take place by direct and indirect (photon-assisted) excitation of electron-hole pairs.

5) Absorption induced by broken symmetry of the crystalline lattice is possible.

The largest contributions to absorption of laser radiation with \( h\nu > E_g \) by crystalline or amorphous silicon are found in mechanisms (4) and (5), respectively. Mechanism (3), however, may be the cause of discrepancies of actual as compared to calculated absorption coefficient value.[52] Through the focus here is on absorption of ultra-violet radiation (KrF excimer laser operating at 248nm) by amorphous or fine-grained polycrystalline silicon, the state of the material is not particularly critical in this instance because \( \alpha \) is saturated at \( \sim 106 \text{ cm}^{-1} \) for this wavelength in silicon. This value is more characteristic of metals, and is virtually independent of
both temperatures[49] and state of the material, i.e., it is approximately the same for crystalline, 
amorphous, and liquid silicon. An analysis of absorption coefficient reported by Jellison, et 
al.[53] reinforces this as no change in \( \alpha \) was observed over the temperature range 300-1000K for 
355nm Nd:YAG radiation.

Reflectivity value for silicon depends on wavelength as well as crystalline state. 
Absorption coefficient and reflectivity values for crystalline silicon at room temperature as a 
function of wavelength are shown in Figure 2-3. From this figure it can be seen that the 
reflectivity demonstrates relatively high values in the UV regime and represent \( R \sim 65\% \) for 
248nm radiation. Through the reflectivity is relatively high in the UV regime, the absorption 
coefficient is at this maximum values.

Silicon is an indirect band-gap material.[54] This means that the maximum of the valence 
band do not occur at the same point as the minimum of the conduction band in k-space, where \( k \) 
is the wave vector. As mentioned previously, absorption of radiation with \( h\nu \geq E_g \) predominantly 
occurs by inter-band transitions, this case including those of an indirect nature. An indirect 
transition requires a change in both energy and momentum (the quantity \( k \) is proportional to the 
momentum). A two-step process is therefore required because the photon can provide a change 
in energy but not (significantly) in momentum. Momentum is conserved thorugh phonon 
interaction as illustrated in Figure 2-4. Through a phonon can only absorb very small energies, it 
is able to absorb a large momentum when compared to an electron.[51] Also, although a broad 
spectrum of phonons is available, only those with the required momentum change are usable. 
Direct transitions are also possible in an indirect gab material, if the photon energy is sufficient 
(\( h\nu > 3.4 \) eV for Si). This explains in the high absorption coefficient values observed for UV 
radiation (\( h\nu \sim 5\)eV).
When a beam of photons of energy $h\nu > E_g$ is absorbed in a semiconductor, excited carriers, which results in lattice heating.[55], is a complicated process and an field of active research.[56] Excited carrier relaxation times on the order of picoseconds have been derived and confirmed using time-resolved investigation of the absorption coefficient. As incident radiation is converted to increasing lattice temperatures, the thermophysical properties of the material dictate temperature distribution and phase changes. This aspect of laser annealing area has been actively investigated.[57-61]

2.2.2 Mechanisms of Eximer Laser Crystallization

The basic mechanism of laser heating proceeds through photon absorption and the subsequent rapid transfer of energy (within picoseconds) from the electrons to the lattice.[62-64] During laser crystallization of amorphous silicon thin films, the incident radiation leads to surface melting when sufficient energy employed. This liquid phase becomes unstable as rapid cooling takes place after the pulse is over. The mechanisms (nucleation and solidification) that then take place and lead to the resultant microstructure have been widely investigated.[12, 22, 47, 65, 66] Nucleation and solidification processes in pulsed laser crystallization of silicon thin films can be divided into three regimes, differentiated by whether complete melting of the film occurs.

First, the energy density is not high enough to melt the surface film completely in partial-melting regime. After melting, there exists an unmelted crystalline layer at the bottom of the film. The final microstructure in this regime results in a fine-grained c-Si

In near-complete-melting regime, the SLG regime, where the ratio of grain size to film thickness can exceed a factor of $\sim 10$ is due to significant lateral regrowth from unmelted and discontinuous solid seeds at the bottom oxide interface. This is evident at the higher end of the partial-melting regime, where a small increase in the energy density produces an extremely sharp
increase in the grain size. To date, these laterally grown poly-Si films correspond to the largest average grain sized poly-Si films produced by a single-pulse ELC process.[12, 21]

Finally, in complete-melting regime, a sharp and sudden increase in the melt duration is strong indication of a transition to complete melting followed by super-cooling and transformation of the film. Before the onset of the solidification, substantial super-cooling followed by either transition or steady-state nucleation, and then growth of solids occurs. Typically, the microstructure in this regime is fine-grained Si. This regime can be compared with recent investigation on super-cooling of a liquid Si film by S. Stiffler et al.[67-70] It was found that when the cooling rate of the liquid Si exceeds about $3 \times 10^{10}$ K/s, homogeneous nucleation of the solid takes place, resulting in a fine-grained Si microstructure.

Based on three regimes, there are two mechanisms for excimer laser crystallization of a-Si; the explosive crystallization and the super lateral growth (SLG).

In the first case, where complete melting of the film does not occur, several potential theories have been proposed. Thompson et al.[71] and Lowndes et al.[72] support the following dynamic. At low energy densities the laser energy only melts a portion of the film, creating a thin liquid layer near the surface. As the liquid begins to solidify as relatively large-grain polycrystalline silicon, the latent heat released raises the temperature of the resolidified poly-Si above the temperature of the first order phase transition of a-Si to the metallic liquid, $T_{\alpha-1}$. The underlying a-Si material then begins to melt. This new liquid is severely under-cooled compared to the poly-Si layer and therefore resolidifies as fine-grained poly-Si. Thus a thin liquid layer is presumed to propagate through the a-Si material as a result of the released latent energy. This is the explosive recrystallization process. It is self-sustaining until eventually it is quenched by the energy required to raise the temperature of the a-Si solid in front of the liquid to $T_{\alpha-1}$. The final
The other proposed mechanism for non-complete melting of Si films is by Im et al.\[12\] Im argues that in his films explosive crystallization of a-Si occurs at the onset of the transformation, implying that partial melting of explosively crystallized fine-grained Si is occurring rather than partial melting of an amorphous film. It is suggested that early triggering of explosive crystallization may be attributed either to (i) the presence of microcrystalline clusters in the LPCVD samples, which was confirmed by analyzing solid-phase crystallization behavior and is absent in high-dose ion irradiated amorphized samples which called the Super Lateral Growth (SLG) regime and (ii) the possible presence of impurities, such as hydrogen. In this regime, almost complete melting of the film occurs to the extent that there is a discontinuous Si film composed of discrete islands. Growth from these clusters proceeds, resulting in an unusually large (300-400nm) grain size. If greater laser energy is used the resultant grain size returns to smaller values (~50-100nm), typical of lower-energy density irradiation as shown in Figure 2-6.\[12\]
Figure 2-1 Temperature dependence of the thermal epitaxial crystallization rate for ion implanted a-Si layers on (100) silicon substrate[30]

\[ E_a = 2.7 \text{ eV} \]
Figure 2-2 Free energy diagram of amorphous and liquid Si with respect to crystal Si. Diagrams for both relaxed (continuous line) and unrelaxed (dashed line) a-Si are shown. Note that the melting temperature of a-Si is different from that of crystal silicon and it depend on the relaxation state[41, 42]
Figure 2-3 Reflectivity and absorption coefficient values as a function of wavelength for crystalline silicon at room temperature[50]
Figure 2-4 Schematic of indirect interband transition in silicon including phonon momentum exchange[51]
Figure 2-5 Schematic of explosive crystallization process

FP-Si – Fine poly-Si
LP-Si – Large poly-Si
I-Si – liquid silicon
a-Si – amorphous silicon
Figure 2-6 Schematic of the super lateral growth (SLG)[12]
CHAPTER 3
EXPERIMENTAL TECHNIQUES

This chapter will cover the experimental methods for thin film deposition, annealing techniques and characterization of the Si films. The first sections will describe the deposition systems for the thin films, and the procedures used to prepare the samples. All films used in this work were grown with the DC magnetron sputtering system and Plasma Enhanced Chemical Vapor Deposition (PECVD) system. In addition, annealing systems were introduced for solid phase crystallization and excimer laser crystallization. The following section will explain the techniques used to measure the properties of the thin films. Various analyzing tools were employed to investigate the structural, electrical properties of the films. These techniques include X-ray diffraction (XRD), Raman Spectroscopy, Scanning electron microscopy (SEM), and Transmission electron microscopy (TEM).

3.1 Growth Techniques

3.1.1 DC Magnetron Sputtering System

Sputter deposition is one of the most widely used techniques for the fabrication of thin-film devices on the desired substrate. It is used primarily for the deposition of metal thin films, as well as the various related thin films which function as diffusion barriers, adhesion or orientation layers, or seed layers. Sputter deposition is usually carried out in diode plasma systems known as magnetrons, in which the cathode is sputtered by ion bombardment, and emits the atoms, which are then deposited on the desired substrate in the form of a thin film.

The most widely used technology for sputter deposition is based on the magnetron cathode. Originally, physical sputter deposition utilized dc diodes, which were simply parallel plates powered by a power supply of several kilovolts in a working pressure of several tens to several hundreds of mTorr. The negative plate, also known as the cathode, was bombarded by ions from the plasma set up between these two plates, and cathode atoms were dislodged from the metal surface. These atoms could then deposit on other surfaces inside the vacuum system, forming films.
The principal type of system currently used for high-rate deposition of metals, alloys, and compounds is known as the magnetron cathode system. This type of tool uses magnetic confinement of electrons in the plasma, which results in a higher plasma density than in either the RF or DC diode systems. The higher plasma density reduces the discharge impedance and results in a much higher-current, lower-voltage discharge.

The electron confinement on a magnetron is due to the presence of orthogonal $E$ and $B$ fields at the cathode surface. This results in a classic $E \times B$ drift for electrons (the Hall effect), which gives rise to a sequence of cycloidal hopping steps parallel to the cathode face as shown in Figure 3-1. As a result, the secondary electrons which are emitted from the cathode because of ion bombardment are confined to the near vicinity of the cathode. In a magnetron, the electric field is always oriented normal to the surface of the cathode. The transverse magnetic field is configured so that the $E \times B$ drift paths form closed loops, in which the trapped, drifting electrons are constrained to circulate many times around the cathode face.

A schematic of the DC magnetron sputtering deposition of Si used for this research is shown in Figure 3-2. A DC power source was used to sputter the Cz-Si target, which was place 10cm below the substrate. A gas of Ar was supplied to the main chamber during deposition. Ar atoms were ionized by the electric field into $\text{Ar}^+$ ions. Electrons from Ar ionization were accelerated and impacted other Ar atoms to form self-sustaining $\text{Ar}^+$ plasma in the chamber. $\text{Ar}^+$ ions bombarded the un-doped Cz-Si target to knock off atoms of Si from the target by momentum transfer. Finally, these Si atoms were deposited on the substrate.

3.1.2 Plasma Enhanced Chemical Vapor Deposition (PECVD)

The STS310PC PECVD system was used for the deposition of silicon dioxide and amorphous Si films for excimer laser crystallization (ELC). The system was equipped with 13.56 MHz and 187.5 kHz frequencies and was capable of mixed frequency recipes. The temperature of the system was normally kept at 300 °C. 2% silane gas was used for the deposition of a-Si.
3.2 Thin Film Annealing

3.2.1 In-situ low pressure N₂ Annealing

Amorphous Si films deposited on SiO₂/Si substrate were in-situ annealed in vacuum ambient with N₂. A base pressure was 1.3x10⁻³ torr and working pressure was 1.2x10⁻¹ torr with gas. A tungsten wire heater was placed under the substrate which was located in the center of the quartz tube as shown in Figure 3-3. Maximum temperature up to 1000°C could be reached for this in-situ annealing with the ramping rate of 10°C/min. Figure 3-4 shows the diagram of heat cycle of Si thin films during annealing in a conventional furnace.

3.2.2 Excimer Laser Annealing (ELA) System

Laser annealing was performed with a Lambda Physik LPX 305 excimer laser operating with KrF (248nm) and pulse width ~25 ns (FWHM). The beam was collimated using a long focal length (200cm) lens. The beam was then focused using a spherical lens with a 25cm focal length. Distance from the lens to the sample holder was varied to control the energy density at the sample surface. Discharge voltage was also varied in the laser control system to alter the beam energy and hence energy density at the sample. Total energy was measured immediately after the focusing lens to incorporate energy loss through the lenses. Schematic diagrams of the laser setup are given for each experiment illustrated in Figure 3-5.

3.3 Analytical Techniques

3.3.1 X-ray Diffraction (XRD)

X-ray diffraction (XRD) is a non-destructive tool for analyzing material properties such as crystallinity, strain and grain size. Also, the phase identification and orientation can be easily analyzed with this technique.

The incident X-ray interact with the periodic crystal planes and results in constructive and destructive interface. Only the condition satisfying the Bragg’s Law gives the constructive interference.
Bragg’s Law: \( n\lambda = 2dsin\theta \)

Where \( n \) is the order of diffraction, \( \lambda \) is the x-ray wavelength, \( d \) is the interplanar spacing of crystal planes, and \( \theta \) is the incident angle of x-ray.

In this research Philips APD 3720 X-ray and Philips X’pert MRD high resolution diffractometers were used. The Philips APD 3720 system using Cu K\( \alpha \)(\( \lambda = 1.5405\text{Å} \)) was employed for 0-20 scans to check for preferred orientation of crystalline and identify polycrystalline Si nanoparticles. The domain size can be obtained by using Scherrer’s formula from 0-20 scans:

\[
\text{Scherrer’s formula: } t = \frac{0.89\lambda}{B \cos \theta_B}
\]

where \( t \) is thickness of crystallite, \( \lambda \) is the wavelength, \( B \) is FWHM (full width at half maximum), and \( \theta_B \) is the Bragg angle. However, the APD 3720 uses theta-2theta Bragg-rentano setup and this hinders a geometric freedom. Thus, the Philips X’pert was used to get further information from crystallized Si thin films. The Philips X’pert high resolution diffractometer uses 4-circle goniometer and gives various setting like omega, phi and Chi scan (Figure 3-4). The glazing incident x-ray diffraction (GIXD) was used to investigate the crystallinity of the surface of Si thin films

3.3.2 Raman Spectroscopy

Raman spectroscopy is a spectroscopic technique used in condensed matter physic and chemistry to study vibrational, rotational, and other low-frequency modes in a system. It relies on inelastic scattering, or Raman scattering, of monochromatic light, usually from a laser in the visible, near infrared, or near ultraviolet range. The laser light interacts with phonons or other excitations in the system resulting in the energy of the laser photons being shifted up or down. The shift in energy gives information about the phonon modes in the system. The Raman effect occurs when light impinges upon a molecule and interacts with the electron cloud of the bonds of that molecule. The incident photon excites the molecule into a virtual state. For the spontaneous Raman effect, the
molecule will be excited from the ground state to a virtual energy state, and relax into a vibrational excited state, which generates Stokes Raman scattering. If the molecule was already in an elevated vibrational energy state, the Raman scattering is then called anti-Stokes Raman scattering as shown Figure 3-6. A change in the molecule polarization potential or amount of deformation of the electron cloud with respect to the vibrational coordinate is required for the molecule to exhibit the Raman effect. The amount of the polarizability change will determine the Raman scattering intensity, whereas the Raman shift is equal to the vibrational level that is involved.

3.3.3 Scanning Electron Microscopy (SEM)

Field Emission Scanning Electron Microscopy (FESEM) was used to examine the surface structure of the poly-Si thin films annealed by a conventional furnace and excimer laser. A JEOL JSM 6400 operating at 15kV and a working distance of 15mm was used to obtain the surface information.

3.3.4 Transmission Electron Microscopy (TEM)

High Resolution Transmission Electron Microscopy (HRTEM) was dominantly carried out in order to study the microstructure of the crystallized Si thin films in this work. A JEOL 2010F tungsten filament 200kV TEM with point to point resolution of 2.3Å was used to obtain the structural properties of the films. The preparation of the samples for TEM analysis depended on the desired geometry of sample observation. In general, there are two methods: plan view and cross-sectional view. In this dissertation, both methods were carried out to examine the structure information.

For TEM sample preparation, the sample was cut into 3mm diameter discs. And then plan-view sample preparation began with mechanical polishing of the back of the sample with Alumina powder (size of ~100 μm) until it was ~50 μm thick with two types of sand papers after glued with anti-etching wax to a circle holder. The sample was carefully removed from the circle holder, and mounted onto Teflon flame cylinder with paraffin on edge of backside of the sample in order to make a sample electron transparent. The sample was then slowly etched with mixture of 25 % Hydrofluoric
acid (HF) and 75% Nitric acid (HNO$_3$) until a small hole appeared. After etching the sample was soaked into Heptane solution for a few hours in order to completely remove the residue of the protecting wax.
Figure 3-1 Schematic of motions of electrons in crossed E and B fields. The vertical electric field $E$ is consistent with the presence of a cathode located at the bottom of the figure. The magnetic field is oriented perpendicularly to the page.
Figure 3-2 DC magnetron sputtering system
Figure 3-3 Schematic of in-situ vacuum annealing system

Figure 3-4 Heat cycle in a conventional furnace during annealing
Figure 3-5 Schematic of setup for laser anneal of samples in seeded nucleation experiments
Figure 3-6 Energy level diagram showing the states involved in Raman signal
CHAPTER 4
NANOPARTICLE INDUCED CRYSTALLIZATION OF AMORPHOUS SILICON THIN FILMS BY THE DC MAGNETRON SPUTTERING SYSTEM

4.1 Introduction

Polycrystalline silicon has been widely investigated for their applications in the fabrication of thin film transistors (TFTs) and solar cell devices.[73] For this application, large grain size and the high quality of polycrystalline silicon are required to achieve high electron-hole mobility, which is critical for better performance.[74] Furthermore, low temperature processing, less than 600°C, is highly desirable for compatibility with low cost substrate such as glass. In general, high quality polycrystalline silicon thin films can be obtained by the crystallization of amorphous silicon using PECVD or sputtering system followed by low temperature thermal annealing. Alternatively, poly-Si thin films can be deposited directly at below 600°C, provided that low deposition rates are sufficiently employed.[75] However, the grain size of as-deposited polycrystalline silicon films is much smaller than that of the crystallized silicon films. Moreover, the surface roughness associated with as-deposited polycrystalline Si films is generally higher than that of recrystallized silicon films.[76]

Solid phase crystallization (SPC) is a widely used method because of not only its simplicity and low cost but also its ability to produce a smooth interface and excellent uniformity with a high reproducibility.[77] SPC process at 600°C, however, usually requires a long annealing time of over 20-60hrs to complete the transformation to poly-Si films with large grain size, making it difficult for manufacturing.[77, 78] In addition, poly-Si films made in this process have a high density of in-grain defects due to low crystallization temperatures, which may deteriorate the electrical properties.[77-79] Thus, various methods have been employed to shorten the crystallization time as well as improve the performance for the poly-Si based devices.[66, 79-81]
Recently, various kinds of methods using seed templates have been employed to enhance the crystallization of amorphous silicon thin film. Crystallites embedded in a-Si layer,[82] metal nanocrystals embedded in a-Si layers,[83] and nanowires embedded in a-Si layers.[84] In fact, these synthetic methods have produced the large grains of poly-Si at low temperature below 600°C, and reported the improved electron mobility and the controlled orientation of silicon films. Nevertheless they sometimes induced some drawbacks such as mechanical damages induced by stress, randomly oriented grains, and metal contaminations. High quality nanoparticles, in this respect, can act as interesting nucleation seeds when imbedded in a-Si matrix during solid-phase crystallization.

In this work, a new modification in the nucleation step, which can lead to enhance the crystallization of amorphous silicon thin film, is proposed for the fabrication of photovoltaic silicon based devices.

4.2 Experimental

The high crystalline silicon nanoparticles in a-Si matrix were in situ synthesized using a two-step scheme. First, polycrystalline Si nanoparticles were dispersed with ethanol using ultrasonication at a power of 220W for 1hr. LFSiO₂ (low frequency silicon dioxide) layer was deposited on Si substrate by PECVD under the condition of 2% silane gas (SiH₄, 400sccm) and nitrus (N₂O, 1420sccm). The working pressure in the chamber was 550mTorr and the substrate temperature was maintained at 300°C. The dispersed nanoparticle solution was uniformly spin-coated on SiO₂/Si substrate at 2000rpm for a few seconds. And then Reactive Ion Etching (RIE) was carried out in order to remove native oxide from the surface of nanoparticles under the condition of CHF₃ (40sccm), O₂ (10sccm) gas flow for few seconds. DC power of 100W whereas RF power of 200W was used.
Subsequently, amorphous silicon thin films were deposited by the DC magnetron sputtering system. The base pressure obtained in deposition chamber was 6.8x10^{-8} Pa. Non-doped Cz-Si target and the mixture of Ar and H₂ gases were used for the deposition. A number of sets of samples were prepared with various substrate temperatures in the rage of 200-400°C, for two RF powers 150 (low power) and 200W (high power) in order to optimize the condition for the deposition of a-Si. The sputtering pressure was 3x10^{-1} Pa. An 800nm thick amorphous Si was deposited on the spin-coated substrate (Nanoparticles/SiO₂/Si).

Finally, the Solid-phase crystallization (SPC) at different temperatures for 1-20hrs was carried out in a conventional furnace under an air condition.

4.3 Results and Discussion

Figure 4-1 shows the deposition rate as a function of substrate temperature for the two RF power conditions 150 and 200W, respectively. Two main parameters, which are the substrate temperature and RF power, can change directly the film growth mechanism. They control precursor mobility and surface reactions. Furthermore, the RF power also changes the energy of species impinging the substrate. In the low temperature region, the deposition rate increased with the substrate temperature, while the deposition rate decreased with the substrate temperature in the high temperature region. As shown in Fig. 4-1, the deposition rate is larger for films deposited with higher RF power in the low temperature region presumably due to an increase in electrons and energetic ions, which enhance both the ionization rate of argon atoms and the sputtering yield, and the subsequent Si flux at the growing surface. The films growth rate is governed by the flux of adatoms arriving at the substrate. This explains the increase in the deposition rate with increasing deposition RF power as shown in Fig. 4-1 and 4-2. In the high temperature region, however, the deposition rate became larger in films deposited with lower RF power. The temperature corresponding to the maximum value of the deposition rate depends on
the RF power. At 150W, the deposition rate reached its maximum value at 350 °C. However, at 200W, the temperature for the maximum deposition rate was lowered to 300 °C. The reactivity at the growing surface is related to the hydrogen surface coverage. An increase of the substrate temperature leads to the reduction of the hydrogen surface coverage. Thermally stimulated hydrogen desorption has been observed by infrared absorption spectroscopy (IRAS) in a temperature range up to 350 °C.[85] Therefore, as shown in Figure 4-1, the substrate temperature $T_{\text{max}}$ corresponding to maximal deposition rates are 350 and 300 °C for two used RF powers of 150 and 200W, respectively. Above these temperatures, the deposition rate becomes controlled by the surface reaction rather than by the incoming flux of adatoms. In this high temperature region two features may take place: the hydrogen desorption from the bulk and therefore a change of the surface reaction probability. At 350 °C or above, hydrogen starts to diffuse from the a-Si:H bulk outward, which induces an increase in the hydrogen surface coverage of the growing film and a reduction of the deposition rate.

Figure 4-2 shows the average deposition rate as a function of RF power. The average deposition rate gradually increased as RF power increased. Also, deposition rate for each sample with the average value and standard deviation is summarized in Table 1. This result is in good agreement to the work of Webb[84] and Savvides’s[86] where an increase in deposition rate is attributed to an increase in the density of Ar ions when the power is increased.

For analysis, X-ray diffraction (XRD) was employed after annealing the deposited films to measure the crystallinity of silicon films depending on different temperature and annealing time.

Figure 4-3 shows the variation of XRD intensity with substrate temperature for two different RF power conditions 150 and 200W after annealing at 700°C for 10hrs. As the substrate temperature increased, the intensity gradually increased. As can be seen in Fig 4-3,
intensity reached its maximum value at a substrate temperature equal to 300°C for each RF power 150 and 200W, while decreased at 400°C. Thus, the optimized conditions of substrate temperature of 300°C and RF power of 200W was obtained to produce high quality of poly-Si thin films in our study.

Figure 4-4 shows the grazing incident X-ray diffraction (GIXD) profiles of the silicon thin films before and after annealing in air at different temperatures for 10hrs. No obvious diffraction peaks were observed before annealing in both samples implying the as-deposited silicon thin films to be amorphous. Also, nanoparticles embedded in amorphous matrix before annealing don’t affect the intensity of XRD. Nanoparticles embedded samples, however, had significantly higher crystallinity under the same annealing condition compared with those crystallized conventionally illustrated in Fig 4-4. (b). Those figures show diffraction peaks at 28.44° and 47.30° representing (111) and (220) orientations of the crystallized Si thin film for both samples, with and without the nanoparticle seeds, respectively, indicating the crystallization of the thin films has initiated. These peaks show that crystalline silicon has been formed during solid phase crystallization (SPC) and that the films are of polycrystalline phase.

Figure 4-5 indicates the full-width at half-maximum (FWHM) of the diffraction peaks at (111) as a function of annealing temperature. This shows the effect of nanoparticle seeds on the film’s crystallinity for various annealing temperatures. It can be also observed from Fig. 4-5 that the nanoparticles embedded in a-Si matrix affected the crystallinity of the poly-Si film. As the annealing temperatures increased, FWHM decreased and the peak intensity of the films increased gradually. It also shows that FWHM was effectively minimized in the sample with nanoparticle seeds after annealing. Poly-Si thin films can be fabricated with relatively good crystallinity by the nanoparticle induced crystallization (NIC) technique.
The comparison between the thin films with and without the nanoparticles after solid phase crystallization (SPC) at 530°C and 700°C for 10hrs is shown in Fig. 4-6(a) and (b), respectively. Annealing temperature was increased from 450°C with 20°C intervals to confirm the effect of nanoparticles for the crystallization as nuclei in amorphous matrix. The sample with nanoparticles embedded in amorphous Si matrix has initiated the crystallization at 530°C whereas the other showed no peaks at (111) and (220) orientations as evident from Fig. 4-6(a). This shows the transition from amorphous to polycrystalline Si in samples with nanoparticle seeds occurred at lower temperature in our process. Also, the difference in intensity when annealed at 700°C for 10hrs was maximized compared to that of the plain sample illustrated in Fig. 4-5(b).

Figure 4-7 shows cross sectional TEM images of the crystallized Si thin film after annealing for 3hrs at 700°C. The thickness of the film was about 800nm. Crystallites in the film were observed. Also, SAD patterns of the films indicate the film was of polycrystalline phase as shown in Fig 4-7 (d).

Figure 4-8 shows the typical grain size in films which were annealed at 700°C for 10hrs in air. In previous result, the difference of intensity between samples was maximized at 700°C for 10hrs. In this condition, the average grain size of the nanoparticle induced sample (~300nm) was about 3 times larger than that of plain sample (~100nm). This indicates the importance of our technique in terms of not only the processing time reduction but also the fabrication of high quality thin films with large grains. Thus, great improvement in both of the crystallization temperature and transition time can be simultaneously achieved by this seed based approach.

4.4 Summary

We investigated the SPC growth behavior of un-doped a-Si thin films prepared by the DC sputtering system after annealing in air when crystalline nanoparticles were directly employed as
the seed nuclei. For the growth mechanism of a-Si:H films, the influence of substrate
temperature is divided into two main processes. At first, in low temperature region the deposition
rate is controlled by the flux of arriving adatoms from the plasma. Secondly, at high temperature
region the deposition rate is controlled by the surface reactions where the hydrogen surface
coverage plays a key role. The optimum substrate temperature and RF power to produce the a-Si
thin film for the crystallization were obtained. High quality polycrystalline Si thin films were
fabricated by the nanoparticle-induced crystallization at relatively low temperature and short
time. XRD and HRTEM analysis showed that our modification in the nucleation step promoted
the crystal growth process by reducing the nucleation time, and then enhanced the crystallinity of
the thin films. The measured grain size in the nanoparticle embedded sample was relatively
higher compared to that of the crystallized Si films without nanoparticle seeds. Based on our
observations, we suggest that the uniformly dispersed layer of high quality Si nanoparticles can
be promising seed nuclei for the SPC process to achieve a high quality poly-Si thin film for
photovoltaic Si based devices.
Table 4-1 Deposition rate of all the samples with average value and standard deviation with different RF powers

<table>
<thead>
<tr>
<th>RF power (W)</th>
<th>Deposition rate (Å/min)</th>
<th>Average deposition rate (Å/min)</th>
<th>Standard deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Sample 1</td>
<td>Sample 2</td>
<td>Sample 3</td>
</tr>
<tr>
<td>100</td>
<td>24.5</td>
<td>24.9</td>
<td>25.1</td>
</tr>
<tr>
<td>150</td>
<td>26.9</td>
<td>26.1</td>
<td>26.5</td>
</tr>
<tr>
<td>200</td>
<td>30.1</td>
<td>29.4</td>
<td>30.5</td>
</tr>
<tr>
<td>250</td>
<td>34.9</td>
<td>34.8</td>
<td>35.9</td>
</tr>
</tbody>
</table>
Figure 4-1 Variation of the deposition rate as a function of substrate temperature for two RF powers of 150 and 200W
Figure 4-2 Average deposition rate as a function of RF power at substrate temperature of 300 °C
Figure 4-3 XRD intensity as a function of substrate temperature for two RF powers of 150 and 200W after annealing
Figure 4-4 GIXD patterns of silicon thin films: (a) samples without and (b) with nanoparticle seeds before and after annealing for 10hrs at different temperature in air.
Figure 4-5 The full-width at half-maximum (FWHM) of the diffraction peaks at (111) orientation between samples with and without nanoparticle seeds after annealing in air.
Figure 4-6 GIXD pattern of a-Si thin films crystallized at (a) 530°C, and (b) 700°C for 10hrs on a plain and nanoparticle embedded substrate annealed in air.
Figure 4-7 Cross section TEM images and SAD patterns of Si thin films after annealing in air for 10hrs at 700° C
Figure 4-8 Plan-view TEM micrographs of samples (a) without and (b) with nanoparticle seeds after annealing in air at 700°C for 10hrs.
CHAPTER 5
POST ANNEALING EFFECTS OF AMORPHOUS SILICON THIN FILMS BY
NANOPARTICLE INDUCED CRYSTALLIZATION

5.1 Introduction

Recently, the crystallization of amorphous silicon (a-Si) has been widely investigated for its application in the Si-based microelectronic devices.[87-89] However, for these applications, large-grained poly-Si is required to achieve high electron-hole mobility, which is critical for increased performance.[74] Low temperature processing (<600°C) is highly desirable for compatibility with low cost substrates such as glass. In general, high quality polycrystalline silicon thin films can be simply obtained by the crystallization of amorphous silicon (a-Si) deposited using plasma-enhanced chemical vapor deposition (PECVD) or sputtering followed by low temperature thermal annealing. Alternatively, poly-Si thin films can be also deposited directly below 600°C, provided that deposition rates are sufficiently low.[75] However, the grain size of this as-deposited polycrystalline silicon films is typically much smaller than that of the crystallized silicon films. Moreover, the surface roughness associated with as-deposited polycrystalline Si films is generally higher than that of crystallized silicon films.[76]

Various methods for crystallization of amorphous Si have been widely employed.[22, 78, 79, 90-94] Solid phase crystallization (SPC) is widely used method of fabricating poly-Si films because of simplicity and low cost as well as the ability to produce a smooth interface with the substrate, excellent uniformity, and high reproducibility.[80] However, SPC process at 600°C usually requires a long annealing time of 20-60 hrs to complete the transformation to poly-Si films with large grain size.[80, 82] In addition, poly-Si films made in this process have a high density of defects in grains which may deteriorate the electrical properties.[82, 83] Thus, various methods should be employed to shorten the crystallization time and enhance the film quality as well as improve the performance of poly-Si based devices.[20, 83, 95, 96]
Recently, various kinds of processing techniques using seed templates have been employed to enhance the crystallization of a-Si thin films. Specifically crystallites embedded in a-Si layer,[97] metal nanocrystals embedded in a-Si layers,[98] and nanowires embedded in a-Si layers[99] have been used to enhance the crystallization. In fact, these methods have produced large-grained poly-Si at temperatures below 600°C with and reported improved electron mobility. Therefore, high quality nanoparticles, in this respect, can presumably act as nucleation seeds during solid-phase crystallization (SPC) when directly imbedded in an a-Si matrix. Also, for the poly-Si films by SPC, the surface oxygen suppresses the migration of Si atoms on the a-Si surface.[100] Thus, low pressure N₂ annealing was carried out to examine the effect of oxygen atoms at the surface and crystallization mechanism.

In this work, a new modification in the nucleation step to enhance the crystallization of an a-Si thin film before annealing in low pressure N₂ ambient is proposed for the fabrication of high-quality poly-Si films for photovoltaic devices.

5.2 Experimental

Poly-Si nanoparticles in amorphous Si matrix were synthesized in situ using a two-step scheme. First, polycrystalline Si nanoparticles were dispersed in ethanol using ultra-sonication at a power of 220W for 1hr. Next, a low frequency silicon dioxide (SiO₂) layer was deposited on crystalline Si substrate by PECVD using 2% silane (SiH₄) and nitrus gases (N₂O) flowing at 400 and 1420 sccm, respectively. The working pressure in the chamber was 550 mTorr and the substrate temperature was maintained at 300°C. The dispersed nanoparticle solution was spin-coated on SiO₂/Si substrate at 2000rpm for a few seconds. Subsequently, reactive ion etching (RIE) for 10s using CHF₃ and O₂ gases flowing at 40 and 10sccm, respectively, was carried out to remove native oxide from the surface of nanoparticles. DC power of 100W whereas Rf power of 200W was used for the etching.
Subsequently, a-Si thin films were deposited by the direct current (DC) magnetron sputtering system. The base pressure obtained in deposition chamber was 6.8x10^-8 Pa, whereas sputtering pressure was 3x10^-1 Pa. A non-doped Cz-Si target and the mixture of Ar and H2 gases were used for the deposition. RF power and DC voltage were 200W and 125V, respectively. An 800nm thick amorphous Si was deposited on the spin-coated substrate at 300°C.

Finally, SPC process at different temperatures for 1-20hrs was carried out in a conventional furnace with low pressure (1.2x10^-1 Torr) N2 after wet-etching of native oxide on the surface with HF solution.

For analysis, X-ray diffraction (XRD) was used after annealing to measure the crystallinity and grain size of silicon films depending on various temperature and time. Also, the samples were analyzed by means of high resolution transmission electron microscopy (HRTEM) in order to determine the structure, the crystallized volume fraction and growth rate of the films.

**5.3 Results and Discussion**

Figure 5-1 shows the grazing incident x-ray diffraction (GIXD) profiles of the silicon thin films before and after annealing in low pressure (1.2x10^-1 Torr) N2 ambient at different temperatures for 10hrs. No obvious diffraction peaks were observed before annealing in both samples which means the as-deposited silicon thin films to be amorphous and nanoparticles embedded in a-Si matrix didn’t affect the crystalline phase as shown in Fig. 5-1(b). Nanoparticles embedded samples, however, had significantly higher crystallinity after annealing compared with those crystallized conventionally. Those figures show diffraction peaks at 28.44° and 47.30° representing (111) and (220) preferred orientations of the crystallized Si thin film for both samples with and without the nanoparticles, respectively, indicating the crystallization of the thin films has initiated.
Figure 5-2 shows the full-width at half-maximum (FWHM) of the (111) reflection in samples with and without spin-coated nanoparticles after annealing for different temperatures in low pressure (1.3×10⁻³ Torr) N₂ ambient for 10h. Samples with nanoparticles showed smaller FWHM (higher crystallinity) than those without nanoparticles. Comparison of the FHMW of the diffraction peaks at (111) orientation between with and without nanoparticles when annealed in air or low-pressure N₂ ambient is summarized in Table 5-1. From this data the nanoparticle embedded samples annealed in low pressure N₂ ambient show the lowest FMHW intensity indicating the highest quality film. Based on this result, the optimization of annealing conditions was determined. Also, this allows investigating the seed effect on the film’s crystallinity for the various annealing temperatures. It was believed that the nanoparticles embedded in a-Si matrix and annealing in low pressure N₂ ambient affected the crystallinity of the poly-Si films. As the annealing temperature increased, FWHM decreased and the peak intensity of the films increased. Thus, this means that poly-Si thin films can be fabricated with relatively good crystallinity by this nanoparticle induced crystallization (NIC) technique in low pressure N₂ ambient.

In general, the average grain size can be evaluated from the breadth of the X-ray Bragg diffraction peaks with Scherrer’s formula.[101]

\[
G_{\text{SIZE}} = \frac{7.94}{\text{FWHM} \cdot \cos \theta},
\]

where \(G_{\text{SIZE}}\) is the grain size (nm), FWHM (degree) is the full-width at half-maximum of diffraction peaks, \(\theta\) is the diffraction Bragg angle. And Figure 5-3 shows the annealing time dependence of the average grain size for the thin films after SPC with and without the nanoparticle seeds. It can be seen that the average grain size increases fast first and then slow as the annealing time prolongs, and the average grain size for the films with the nanoparticle seeds increases much faster than those without the pretreatment for the same SPC annealing time,
which indicates that the nanoparticle seeds can promote the crystallization of the a-Si thin films during the SPC process.

The structure of both nanoparticles and crystallized silicon thin films with and without nanoparticle seeds was extensively studied by high resolution transmission electron microscopy (HRTEM). All samples were examined in a JEOL 2010F electron microscope, operating at the accelerating voltage of 200kV.

Figure 5-4 and 5-5 show plan-view TEM images, XRD and SAD patterns of polycrystalline Si nanoparticles, respectively. The size of nanoparticles was in the range of 15~20nm as shown in Figure 5-4. Also, the diffraction peaks at 28.44° and 44.30° representing (111) and (002) reflection of the poly-Si nanoparticle were evident illustrated in Figure 5-5(a). From the selected area diffraction (SAD) patterns, the silicon nanoparticles were of polycrystalline phase as shown in Figure 5-5(b). Also, spots in SAD patterns show the high quality of poly-Si nanoparticles. The crystallized sample with nanoparticle seeds showed similar SAD patterns compared to those of polycrystalline nanoparticles illustrated in Figure 5-15, indicating the crystallization was induced by nanoparticle seeds.

Figure 5-6, 5-7 and 5-8 show the plan-view TEM images of polycrystalline Si thin films without nanoparticle seeds after annealing in low pressure N₂ ambient for 3, 10, and 20hrs at 700°C, respectively. From the Fig. 5-6, some crystallites, of which the size was less than ~20nm, were observed indicating the random nucleation was initiated. Also, the random growth of the films has occurred during the crystallization depending on annealing time. The average grain size was in the range of 150~1000nm as shown in Fig. 5-7 and 5-8, respectively.

Figure 5-9 shows the SAD patterns of poly-Si samples without nanoparticles after annealing for 10, 20h at 700°C, respectively. As the annealing time increased, the ring shape of
SAD patterns became much clear, indicating the improvement of the crystallinity of the films depending on annealing time.

Figure 5-10, 5-11, 5-12, 5-13 and 5-14 show the plan-view TEM images of poly-Si thin films after annealing in low pressure N\textsubscript{2} at 550, 600, 650, 700 and 800 °C for 10hrs, respectively. As annealing temperature increased, the grain size of samples with nanoparticle seeds increased. In general, the grain size of polycrystalline silicon thin films fabricated by SPC is finally decided by the competition between nucleation rate and growth rate of crystallites,[102] in high temperature region, it will produce a lot of nuclei in the a-Si thin films which will inhibit the further grain growth process in the growth stage and reduce the grain size in the steady state. However, nanoparticle seeded samples weren’t affected due to the pre-existing nuclei.

Figure 5-16 shows the experimental incubation time as a function of temperature. As the thickness of the amorphous Si layer increases, the incubation time becomes longer. Also, the incubation time decreases when the annealing temperature increases. The incubation times depends on nucleation and growth processes. If the annealing temperature increases, the nucleation and growth process becomes fast. The temperature dependency can be expressed by an Arrhenius relationship:

$$\tau = \tau_0 \cdot \exp\left(\frac{Q_T}{kT}\right)$$

(5-2)

Where $\tau_0$ is a pre-exponential factor and $Q_T$ is the activation energy for the incubation time. From the slope of the Arrhenius curve in Fig. 5-16, the activation energy of 2.9 eV can be calculated. The activation energy is also useful thermodynamic parameter which can be used to estimate the interface energy and the Gibbs free energy for forming a critical nucleus.

In this study, the crystalline fraction was defined as the ratio of crystallized parts to the whole area in the observed TEM images. Crystallized volume fraction was obtained though
several TEM images. Since the sizes of the observed grains were larger than the film thickness, the crystalline area fraction could be assumed to be the crystalline volume fraction. Generally, the annealing time dependence of the crystalline fraction is expressed by Avrami’s equation[103, 104]

\[
\chi = 1 - \exp\left(\frac{t - \tau_0}{\tau_c}\right)^{m+1},
\]

(5-3)

Where \(\chi\) is the crystalline volume fraction, \(t\) is transformation duration and \(\tau_0\) is a lag time for nucleation and \(\tau_c\) is a characteristic time.

\[
\tau_c = \left(\frac{3}{\pi r_g^2 r_{ns} d}\right)^{1/3},
\]

(5-4)

where \(r_g\) is the growth rate and \(r_{ns}\) is the steady-state nucleation rate.

As discussed above, nanoparticles embedded in a-Si matrix can promote the nucleation and growth during solid phase crystallization (SPC). In other words, the activation energy for nucleation is lowered. From the equation (5-3) as transformation time (t) increases, the crystalline volume fraction (\(\chi\)) increases. In our study, nucleation time is not required which results in the reduction of incubation time since nanoparticles can act as nuclei for the crystallization of a-Si thin films. Crystallization from the surface would be due to the poly-Si surface having no oxygen atoms and Si atoms on surface having bigger free energies while in the case of samples annealed in air, the surface oxygen suppresses the migration of Si atoms on the a-Si surface. This indicates that the migration of Si atoms is controlled by the surface oxide and pushes Ar atoms out of the films from the surface. Thus crystals grow on the surface and the diffusion of Ar is important.[100]

Figure 5-17 shows the annealing time dependence of the crystallized volume fraction of the Si thin films at various annealing temperatures. From the figure, it can be seen that
crystallization began after a certain incubation time, and a longer annealing time was required for the film to be completely crystallized as annealing temperature decreased. It was found that the time to be fully crystallized was significantly reduced and the measured crystallized volume fraction of the Si films was relatively enhanced in the crystallized films induced by nanoparticles illustrated in Fig. 5-17(b). This indicates that nucleation for the crystallization was successively modified by our approach, which effectively led to the reduction of the transition time from amorphous to polycrystalline phase.

Figure 5-18 shows the behavior of the growth rate of poly-Si thin film depending on temperatures indicated. The lower growth rate in our experiments can arise from the small size of poly-Si nanoparticles and crystalline phase used as the seed nuclei for the crystallization of a-Si. According to the thermally activated growth theory,[105] the solid-phase growth velocity (ν) is given by

\[
\nu = \frac{kT}{h \cdot \delta} \exp\left(-\frac{E_a}{kT}\right)[1 - \exp\left(-\frac{\Delta g_{ca}}{kT}\right)],
\]

\[
\approx \frac{\Delta g_{ca}}{h \cdot \delta} \exp\left(-\frac{E_a}{kT}\right), \quad \text{when } \Delta g_{ca} = kT,
\]  \hspace{1cm} (5-5)

Where δ is the distance across the interface of crystalline and amorphous phases, Eₐ is the activation energy for the crystallization, and Δgₖa is the free energy difference between crystalline and amorphous phases. Here, Eₐ is usually interpreted as the energy involved in bond breaking or bond arrangement responsible for SPE growth and it can be obtained from the slope of the plot in Fig. 5-18. Thus, Eₐ = 3.2 eV which is close to the value reported by R. Iverson for epitaxial crystallization.[23] Equation (5-4) also indicates that the SPE growth velocity is proportional to the free energy difference between the crystalline and amorphous phase Δgₖa.

According to Gibb-Thomson effects,[106] the free energy of nanosized particle of phase α faced with phase β is raised by amount of \(2\gamma V_m/r\), where \(\gamma\) is \(\alpha/\beta\) the interfacial energy, \(V_m\) is the
molar volume of $\beta$, and the $r$ is the radius of the nanosized particle. This size effect can be applied to our study where the poly-Si nanoparticles have average size of 15~20nm, leading to a larger free energy than that of a flat Si substrate. In addition to, grain defects in the polycrystalline phase of nanoparticle increases the free energy, resulted in the reduction of the growth rate. As a result, the free energy difference between the crystalline and amorphous phase $\Delta g_{ca}$ become smaller when c-Si nanoparticles are employed as the seed for the crystallization of a-Si, and the SPE growth velocity is decelerated according to Equation (5-5) compared to SPE with the single crystalline template.

The crystallization is a combination of nucleation and growth. Therefore, the median crystallization time, $t_{50}$, in which 50% of a-Si has crystallized, was determined from the fitted volume fraction curve. The temperature dependence of $t_{50}$ is shown in Figure 5-19. The activation energy for the crystallization of samples with nanoparticle seeds was relatively lower than those without nanoparticle seeds. The activation energy for the crystallization of the nanoparticle seeded sample is 2.6 eV. It is very close to the activation energy for the incubation time, $\tau$, which is 2.9 eV. Actually, the incubation time is related not only to the nucleation process, but also to the growth process. Therefore, both activation energies are supposed to be very close in value.

In general, the solid phase crystallization (SPC) of the amorphous Si thin films proceeds through four steps, including incubation, nucleation, growth and steady state.[107, 108] Nanoparticle seeds can reduce the incubation time, the a-Si thin films with nanoparticle seeds start nucleation for short time, and fewer annealing time is needed for the crystals to achieve the same average grain size for the thin films with nanoparticle seeds than those without nanoparticles. In this study, crystalline nanoparticles can act as nuclei which led to the reduction
of the nucleation time and lower crystallization temperature due to lower activation energy after annealing in low pressure N2 ambient.

Consequently, the crystallites induced by nanoparticles grew much faster than those crystallized conventionally under the same annealing conditions, resulting in the higher crystallized volume fraction and growth rate.

5.4 Summary

We investigated the SPC growth behavior of un-doped a-Si thin films prepared by the DC sputtering system when crystalline nanoparticles were directly employed as the seed nuclei after annealing with low pressure (1.2×10⁻¹ Torr) N₂ ambient. Relatively higher quality polycrystalline Si thin films were fabricated by the nanoparticle-induced crystallization (NIC) with low pressure N₂ at relatively lower temperature and shorter time compared to those annealed in air. This indicates that crystallization from the surface would be due to the poly-Si surface having no oxygen atoms and Si atoms on surface having bigger free energies while in the case of samples annealed in air, the surface oxygen suppresses the migration of Si atoms on the a-Si surface. XRD and HRTEM analysis showed that our modification in the nucleation step promotes the crystal growth process by reducing the incubation time, and then improves the crystallinity of the thin films. The activation energy for incubation was lower, while the measured crystallized volume fraction and growth rate in the nanoparticle embedded sample were relatively higher compared to those of the crystallized Si films without nanoparticle seeds. Based on our observations, we suggest that the uniformly dispersed layer of high quality Si nanoparticles can be promising seed nuclei for the SPC process to achieve a high quality poly-Si thin film for photovoltaic Si based devices.
Table 5-1 Comparison of the full-width at half-maximum (FWHM) of the diffraction peaks at (111) orientation between the plain and nanoparticle-induced samples when annealed in air or low pressure N\textsubscript{2} ambient

<table>
<thead>
<tr>
<th>Temp. (°C)</th>
<th>Plain sample</th>
<th>Annealed with N\textsubscript{2}</th>
<th>Nanoparticle sample</th>
<th>Annealed with N\textsubscript{2}</th>
</tr>
</thead>
<tbody>
<tr>
<td>600</td>
<td>2.39</td>
<td>1.81</td>
<td>1.36</td>
<td>1.02</td>
</tr>
<tr>
<td>700</td>
<td>1.42</td>
<td>1.19</td>
<td>1.19</td>
<td>0.98</td>
</tr>
<tr>
<td>800</td>
<td>1.26</td>
<td>1.01</td>
<td>1.06</td>
<td>0.82</td>
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CHAPTER 6
EXIMER LASER CRYSTALLIZATION OF THE AMORPHOUS SILICON THIN FILMS
INDUCED BY NANOPARTICLES

6.1 Introduction

Recently, excimer laser crystallization (ELC) has widely investigated to fabricate high performance polycrystalline silicon thin film transistor.[109-111] Excimer lasers typically operate in the ultraviolet and hence photons are absorbed by the silicon thin films within a few nanometers of the surface. Melting and solidifying occur on a nanosecond time scale, often without affecting the underlying substrate. This technique enables the use of inexpensive substrates, such as glass, which are highly preferable for low cost, large-area electronics devices. Excimer laser crystallization (ELC) of amorphous silicon films is a well-established method for producing large grain polycrystalline silicon films on glass substrates. Although the application has primarily been focused on TFTs, its adaptability for photovoltaics (PV) has attracted considerable interest.[112-114] However, due to the random location of the grain boundaries thin film transistors (TFTs) made in these films show poor device-to-device uniformity.[93, 115] The necessity of sufficiently large mono-crystalline islands, the fabrication of such devices, however, would require a method to control their location.[116, 117] With ELC, grains having a diameter exceeding the film thickness can be obtained due to the super-lateral growth (SLG) phenomenon.[12] SLG occurs very sensitively depending on laser power density which means difficult to control. This refers to the process in which the film is nearly completely melted such grains grow laterally from the few isolated solid portions remaining at the interface.

In this study, by artificially controlling SLG from these solid seeds, nanoparticles embedded in a-Si matrix, the large grains is also easily obtained without the sensitivity of laser power density.
6.2 Experimental

The poly-Si nanoparticles in a-Si matrix were in situ synthesized using a two-step scheme. First, polycrystalline Si nanoparticles were dispersed with ethanol using ultra-sonication at a power of 220W for 1hr. LFSiO₂ (low frequency silicon dioxide) layer was deposited on glass substrate by the plasma enhanced chemical vapor deposition (PECVD) under the condition of 2% silane gas (SiH₄, 400sccm) and nitrous (N₂O, 1420sccm). The working pressure in the chamber was 550mTorr and the substrate temperature was maintained at 300 °C. The dispersed nanoparticle solution was uniformly spin-coated on SiO₂/Si substrate at 2000rpm for a few seconds. And then Reactive Ion Etching (RIE) was carried out to remove native oxide from the surface of nanoparticles under the condition of CHF₃ (40sccm), O₂ (10sccm) gas flow for 10seconds. DC power of 100W whereas Rf power of 200W was used.

Subsequently, amorphous silicon thin films were deposited by PECVD. The base pressure obtained in deposition chamber was 8.4x10⁻¹ mTorr. 2% silane (SiH₄, 2000sccm) and Ar (390sccm) gases were used for the deposition. RF power (13.56 MHz) was 30W. The working pressure was 800 mTorr. A 200nm thick a-Si was deposited on the spin-coated substrate at 300°C.

For excimer laser crystallization (ELC), we have performed single shot irradiation of a-Si thin film (200 nm thick) deposited by PECVD. And the samples were dehydrated at 500°C for few hours in a vacuum condition (1.3x10⁻³ Torr).

Subsequently, laser annealing was performed with a Lambda Physik LPX 305 excimer laser operating with KrF (248nm) and pulse width ~25ns (FWHM). The beam was collimated using a long focal length (200cm) lens. The beam was then focused using a spherical lens with a 25cm focal length. Distance from the lens to the sample holder was varied to control the energy density at the sample surface. Laser processing of the seeds embedded samples was done. All
samples were irradiated in air with a single pulse for each sample. As mentioned previously, the laser beam impinges on the surface of the sample so the nanoparticle seeds in contact with the film interface may affect nucleation during the solidification. Given this arrangement, it is worthy to note that complete melting of the film is necessary from the seeds to potentially affect nucleation in the molten film. Laser energy densities used for this set of samples ranged from 100 to 450mJ/cm². Though higher energy densities were initially examined, it was found that values exceeding 500mJ/cm² caused ablative loss of the film.

6.3 Results and Discussion

Figure 6-1 shows Raman spectra of the deposited films as a function of laser energy density. No Raman peak is observed in the case of the as-deposited sample. Evidence of a crystalline phase started to show after an energy density of 200mJ/cm². Only above 200mJ/cm², a peak around 520cm⁻¹ started to appear that indicates the initiation of crystallinity in the film. The crystalline peak became sharp after 320mJ/cm². However, the peak occurred at 518cm⁻¹, which was lower by a few wave numbers than the number observed for monocrystalline silicon. This observation has been attributed to phonon confinement,[118] possibly due to the presence of nanocrystals embedded in a-Si:H environment. Stress-induced effects are also reported to cause this behavior.[118] The Raman peak intensity increases up to 320mJ/cm² and decreases at 350mJ/cm². This decrease could be due to the induced surface damage by high energy laser beam. Similar results of decreasing Raman intensity peak due to higher-energy ion implantation in semiconducting films were reported by many workers.[119] Also, amorphous phase was characterized by shoulder around the Raman shift of 480cm⁻¹.[120] We could not observe shoulders for more than that of 200mJ/cm².

We studied the laser crystallization of a-Si thin films having nanoparticles as seed layer on glass as a function of the laser energy density. Figure 6-2 illustrates the Raman spectrum of the
samples as a function of laser energy. As the laser energy increased from 200 to 380mJ/cm², Raman intensity also increased. Similar results were observed in samples without nanoparticle seeds. But, in the samples with nanoparticle seeds, the amorphous phase could be observed around 480cm⁻¹ in all samples. It indicates that the crystallization in samples with nanoparticle seeds did not fully complete at the lower energy. At same time, it is also observed that in theses samples the crystallization was possible at the energy levels as low as 200mJ/cm² in contrast to the samples having no nanoparticle seeds, where higher energy is needed to initiate crystallization. Although the samples of (c) and (d) were irradiated with the laser of different energy densities, both of them had the similar crystalline volume fraction of 72% could be concluded that the laser energy of 290mJ/cm² is the optimized laser crystallization energy for α-Si with nanoparticle seeds.

The crystalline volume fractions of samples were calculated from the integrated intensities of the Raman peaks, with Gaussian fits for the amorphous peak (Iₐ) and Lorentzian fits for the crystalline peaks (Iₐ). The calculation was done as proposed by Tsu et al. with crystalline volume fraction (Xₐ) given by Eq. (6-1), where γ is the ratio of the backscattering cross-sections amorphous and crystalline phases,[120]

$$X_c = \frac{I_c}{I_c + (\gamma)I_a} \quad (6-1)$$

The selection of a value for γ is complex due to its dependency on absorption coefficient of amorphous and crystalline silicon.[121] Different energy densities result in different grain sizes, which further complicates the analysis, since the absorption coefficient changes too.[122] γ has been calculated to be between 0.8 and 0.9, the most widely used value being 0.8 for mixed phase silicon, especially for excimer laser crystallized silicon.[121, 123, 124] For this analysis too, γ was taken to be 0.8.
Figure 6-3 shows the crystalline volume fraction of poly-Si films for different laser energy density. The crystalline volume fraction increased as the laser energy density increased. Moreover, the crystalline volume fraction was maximized in samples with nanoparticle seeds. In case of the samples without nanoparticles, the crystalline volume fraction was 66% at laser energy density of 320mJ/cm². This means that only 66% region had the electrical-band structure of crystalline silicon and the residual 34% region had a band structure associated with disordered bonding states. The crystalline volume fraction increased to 72% in samples with nanoparticle seeds. An important reason of the high crystalline volume fraction close to 72% was the increase in the grain size.

Figure 6-4, 6-5, 6-6 and 6-7 show the field emission scanning electron microscopy (FESEM) images of nanoparticles dispersed on the SiO₂/glass and samples without nanoparticle seeds after Secco etching. A selective wet chemical etch method was used to examine the surface information. The solution is the so called Secco etchant, which is widely used to investigate defects in the semiconductor industry. The composition of the solution is as follows:

\[ \text{HF} + \text{K}_2\text{Cr}_2\text{O}_7 + \text{H}_2\text{O} \text{ in a ratio of } \text{HF} : \text{H}_2\text{O} = 2 : 1 \text{ with } 44\text{g K}_2\text{Cr}_2\text{O}_7 \text{ dissolved in 1l of the of } \text{H}_2\text{O}. \]

It etches defect on all surfaces. From Fig. 6-5 and 6-6 as laser energy density increased, the grain size of the films slightly increased. Also, the super lateral growth (SLG) can be observed and the maximum grain size was 1~4μm as shown in Figure 6-7.

Figure 6-8 and 6-9 show the FESEM images of nanoparticle seeded samples after Secco etching. As laser energy density increases, average grain size of films increases. Moreover, grains induced from nanoparticles were relatively larger than those with no nanoparticle seeds.

In addition to, Figure 6-10 shows the grains induced by nanoparticle seeds at energy densities of 290 and 320mJ/cm², respectively. The grain size of films didn’t decrease in sample
with nanoparticle seeds, while the grain size of plain samples rapidly decreased after SLG region due to the complete melting. This result indicates that the SLG can be easily controlled, even at the high energy density which led to the complete melting of the films, since poly-Si nanoparticles, which has higher melting point than that of amorphous Si phase, in amorphous matrix can act as nucleation seeds.

Figure 6-11 and 6-12 show the AFM images of samples with and without nanoparticles after laser annealing at various laser energy densities. Substantial mass transport occurs during the growth of the disk structures induced by the lateral solidification.[125] This suggests that lateral growth plays a major role in the formation of poly-Si grains even in the partial melting regime, as already reported for SP irradiated samples.[126]

RMS comparison as a function of laser energy density in samples with and without nanoparticle seeds is shown in Figure 6-13. Maximum values of RMS were observed at the laser energy density where SLG occurred in both samples. Moreover, nanoparticle seeded samples have higher roughness compared to that of non-seeded samples which mean more applicable for photovoltaic device due to the capability of light trapping.

Figure 6-14 shows average maximum grain size as a function of laser energy density for samples without and with nanoparticle seeds crystallized by excimer laser irradiation. The grain size changes significantly in the range of energy density between 250 and 320mJ/cm², and has the maximum value at 290mJ/cm² for both films, whereas the grain sizes are slightly different, being 800nm and 650nm for the plain and nanoparticle seeded films, respectively.

Figure 6-15 and 6-16 show TEM images and SAD patterns of samples with nanoparticle seeds annealed at laser energy density of 290 and 320mJ/cm², respectively. Single crystalline phase was observed at laser energy density of 290mJ/cm² as shown in Figure 16(a).
6.4 Summary

In this study, the investigation of the ELC of a-Si films by PECVD was carried out to prepare large grains at a low process temperature for a glass substrate. We reported the excimer laser crystallization of a-Si films deposited on glass with or without nanoparticle seeds. Nanoparticles can act as nucleation seeds led to SLG. Laser with energy density starting from 200mJ/cm² was employed to bring crystallization in a-Si films with or without nanoparticle seeds. Films did not fully crystallize at energy density of laser less than 260mJ/cm². The value of maximum crystal volume fraction in samples with nanoparticles seeds was calculated as 72% at the high energy density of 290mJ/cm². The presence of SLG in poly-Si thin films was confined to a very narrow energy density range, thus explaining the difficulties to reveal SLG in such a material. However, nanoparticle induced poly-Si films was not relatively sensitive to the narrow range of laser energy density for SLG, and also showed the larger grain size of the films compared those of samples without nanoparticle seeds.

High quality poly-Si thin films were successively obtained by the nanoparticle induced crystallization technique. This result shows low temperature poly-Si is promising for fabricating large grains on a glass substrate for large-area microelectronic applications.
Figure 6-1 Raman spectroscopy of plain samples at various laser energy densities indicated
Figure 6-2 Raman spectroscopy of nanoparticle embedded samples at different laser energy densities: (a) 200mJ/cm² (b) 260mJ/cm² (c) 290mJ/cm² (d) 320mJ/cm²
Figure 6-3 Volume fraction as a function of various laser energy densities with and without nanoparticle seeds
Figure 6-4 SEM images of dispersed nanoparticles on the SiO$_2$/glass substrate
Figure 6-5 SEM images of plain samples annealed at laser energy density of 230mJ/cm²
Figure 6-6 SEM images of plain samples annealed at laser energy density of 320mJ/cm²
Figure 6-7 SEM image of the super lateral growth (SLG) annealed at laser energy density of 350mJ/cm²
Figure 6-8 SEM images of nanoparticle embedded samples annealed at laser energy density of 200mJ/cm².
Figure 6-9 SEM images of nanoparticle embedded samples annealed at laser energy density of 260mJ/cm²
Figure 6-10 SEM images of Si thin films irradiated by excimer laser at 290 and 320 mJ/cm², respectively.
Figure 6-11 AFM images of samples without nanoparticle seeds annealed at laser energy density of 230 and 350mJ/cm²
Figure 6-12 AFM images of nanoparticle embedded samples annealed at laser energy density of 200 and 290mJ/cm²
Figure 6-13 RMS as a function of laser energy density in samples with and without nanoparticle seeds
Figure 6-14 Grain size distribution as a function of various laser energy densities with and without nanoparticle seeds
Figure 6-15 TEM images of nanoparticle seeded samples annealed at laser energy density of 290 and 320mJ/cm²
Figure 6-16 SAD patterns of nanoparticle seeded samples annealed at laser energy density of 290 and 320 mJ/cm²
CHAPTER 7
CONCLUSION

The research presented in this dissertation focused on the crystallization of amorphous silicon thin film embedded with nanoparticle seeds. Two different types of crystallization techniques, which are solid phase crystallization (SPC) and excimer laser crystallization (ELC), were carried out to produce high quality poly-Si thin films. Firstly, a-Si films deposited by the DC magnetron sputtering system were investigated for solid phase crystallization (SPC). Nanoparticle seeded Si thin films were annealed in a conventional furnace to understand the behavior of the crystallization and obtain a high quality films. For excimer laser crystallization (ELC), a-Si thin films with nanoparticle seeds were deposited by PECVD followed by the dehydration process in order to remove the native oxide on the surface of nanoparticles. Film properties were examined by various characterization tools. Relatively large improvement of the crystallization of a-Si films was observed.

7.1 Solid Phase Crystallization (SPC) of the Seeded Films

We investigated the SPC growth behavior of undoped a-Si thin films prepared by the DC sputtering system when crystalline nanoparticles were directly employed as the seed nuclei. High quality polycrystalline Si thin films were fabricated by the nanoparticle-induced crystallization at relatively low temperature and short time. XRD and HRTEM analysis showed that our modification in the nucleation step promotes the crystal growth process by reducing the nucleation time, and then improves the crystallinity of the thin films. The measured crystallized volume fraction in the nanoparticle-induced sample is relatively higher compared to that of the crystallized Si films without nanoparticles.

Based on our observations, we suggest that the uniformly dispersed layer of high quality Si nanoparticles can be promising seed nuclei for the SPC process to achieve a high quality poly-Si
thin film for photovoltaic Si based devices. Also, nanoparticle seeds influences the formation of nucleation at the interface between a-Si matrix and nanoparticle. The interfacial energy of a nucleus at the contacted interface with the seed is reduced by forming a low energy boundary with the seed like a special grain boundary between two grains. Some special misorientation between two contacted crystals can reduce the interfacial energy dramatically compared to random misorientation between them because the result is two crystals matched very well without dangling bonds. According to our results, the preferred texture of grains resulting from the crystallization is \( <111> \). Compared to this crystallization, nanoparticle seed induced crystallization has a much shorter lag time for the crystallization. Furthermore, its crystallinity is much better than that of the plain sample, as shown in the results.

Therefore, this technique to crystallize amorphous Si thin films on insulators can meet simultaneously the demands which the LCD (Liquid Crystal Display) industries are desperately asking to improve the performance of thin film transistors (TFT) and to make a process compatible with a low melting temperature glass substrate. It can reduce the thermal budget of the process by inducing crystallization at lower annealing temperature for a much shorter period. In addition to that, it can provide much better crystallinity, which improves the electrical properties of TFT, such as high driving current, low leakage current, and better oxide integrity.

### 7.2 Excimer Laser Crystallization (ELC) of the Seeded Films

We reported the excimer laser crystallization (ELC) of a-Si films deposited on glass with or without nanoparticle seeds. Nanoparticles can act as nucleation seeds led to SLG. Laser with energy density starting from 200mJ/cm\(^2\) was employed to bring crystallization in a-Si films with or without nanoparticle seeds. Films did not fully crystallize at energy density of laser less than 260mJ/cm\(^2\). The value of maximum crystal volume fraction in samples with nanoparticles seeds was calculated as 72% at the high energy density of 290mJ/cm\(^2\). The presence of SLG in poly-Si
thin films was confined to a very narrow energy density range, thus explaining the difficulties to reveal SLG in such a material. However, nanoparticle induced poly-Si films was not relatively sensitive to the narrow range of laser energy density for SLG. Thus, the controlled the super lateral growth (SLG) can be obtained by excimer laser crystallization with nanoparticle seeds.

Subsequently, high quality poly-Si thin films were successively obtained by the nanoparticle induced crystallization technique. This result shows low temperature poly-Si is promising for fabricating large grains on a glass substrate for large-area microelectronic applications
REFERENCES


BIOGRAPHICAL SKETCH

Taekon Kim was born on February 23, 1977, in Seoul, South Korea. After graduating from high school in 1995, he attended Hong-ik University and earned a bachelor’s degree in materials science and engineering in February 2002.

In August 2004, he enrolled at the University of Florida in the Department of Materials Science and Engineering to pursue Ph.D under the advisement of Dr. Rajiv K. Singh. His main research involved crystallization and characterization of amorphous Si thin films for solar cell. He is co-author of more than 10 journal and conference papers.