Nickel-Induced Crystallization of Amorphous Silicon
Nickel-Induced Crystallization of Amorphous Silicon

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Honors Program

By

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Abstract

One- and two-dimensional silicon nanostructures, such as nanodots, nanowires, and surface topography, have potential uses in a variety of fields, including microelectronics, photonics, and tribology. In this thesis research, nickel-induced crystallization (NIC) of amorphous silicon (a-Si) was investigated to determine the suitability of NIC of a-Si to produce silicon nanostructures on silicon substrates. The results show that formation of both surface topography and nanowires is possible with NIC of a-Si. In addition, the formation of nanostructures is very sensitive to Ni thickness, and the resulting nanostructures and films display a high degree of repeatability. The results obtained from this research provide a solid foundation for future studies in NIC of a-Si.
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Chapter 1

Introduction

1.1 Background

1.1.1 Silicon Nanostructures

Silicon nanostructures, such as nanodots and nanowires, have garnered much interest recently for potential application in electronic and photonic devices. Silicon surface topography has been successfully used to alter the tribological properties of silicon surfaces. In addition, surface topography has been shown to exhibit, with the appropriate chemical modification, both hydrophobic and hydrophilic properties. Due to the usefulness of these nanostructures, methods of fabrication warrant more investigation.

1.1.2 Amorphous Silicon

Crystalline silicon (c-Si) has favorable electrical and optical properties that make it an ideal material for use in electronic and photonic applications. Amorphous silicon (a-Si) is a non-crystalline allotrope of silicon that does not display the long-range order that is inherent in c-Si. This break-down in the crystal structure results in dangling bonds, with a subsequent degradation of electrical and optical properties. However, a-Si is much cheaper to produce than c-Si. Because of this, a-Si has become the material of choice for large-area electronics applications, such as thin film transistors (TFTs) and photovoltaic devices. Therefore, it is desirable to find methods to produce polycrystalline silicon films from a-Si at a low cost.

1.1.3 Metal-Induced Crystallization of a-Si

Metal-induced crystallization (MIC) is one method of producing polycrystalline silicon films at a low cost. In MIC, when a-Si comes into contact with the metal, the
activation energy of crystallization is lowered and the a-Si crystallizes at a much lower
temperature than without the metal. Notably, a-Si crystallizes below the eutectic
temperature during MIC. Common metals used in MIC are Al, Ni, Au, and Ag.

Aluminum and Ni are the two most widely used metals for MIC. Production of
silicon nanostructures via aluminum-induced crystallization (AIC) of a-Si has been
widely investigated, but nanostructure production via nickel-induced crystallization
(NIC) has not been as extensively studied. Much of the research in NIC is actually in the
field of nickel-induced lateral crystallization (NILC). During NILC, only islands of Ni
are deposited on an a-Si film, as opposed to the blanket Ni deposition used in NIC. Upon
annealing, crystallization begins at the metal island and proceeds laterally along the a-Si
film. NILC prevents the relatively high level of Ni contamination that is inherent in
polycrystalline silicon films produced by NIC and is capable of producing large lateral
grains that are desired for electronic applications.

1.1.4 Mechanisms of Crystallization

The actual mechanism that governs MIC is not well understood. Several physical
mechanisms have been proposed. The first, which occurs for eutectic metals, is based on
electron screening and silicon diffusion. The electron screening weakens the covalent
bonds of a-Si and allows diffusion of Si atoms into the metal film. These Si atoms then
find preferred nucleation sites and continue to grow until they contact each other,
resulting in continuous films. Near the eutectic temperature of the metal-Si binary
system, the diffusion and crystallization rate increases, likely due to the presence of
liquid eutectic material. Another mechanism, which occurs for compound-forming
metals, is based on the diffusion of metal silicide. Crystallization only begins when a
metal silicide film forms at the interface of the metal layer and a-Si. Metal silicide nodules then diffuse down through the a-Si film, leaving a trail of poly-Si. The diffusion of metal silicide nodules through the a-Si film is the result of a difference in chemical potential between the metal silicide/a-Si interface and the metal silicide/poly-Si interface. The final mechanism, termed Vapor-Liquid-Solid (VLS), is based on vapor saturation of a liquid catalyst. Crystal growth through unassisted direct adsorption of a gas is typically very slow. The rate of crystallization can be increased by introducing a liquid alloy catalyst that can absorb the source material carrier gas. When the liquid catalyst becomes saturated with source material, crystallization proceeds from nucleation sites at the solid-liquid interface.

1.1.5 NIC of a-Si

The basic process steps of NIC of a-Si are shown in Figure 1.1. The main parameters that effect NIC of a-Si are: 1) a-Si thickness, 2) Ni thickness, and 3) the annealing conditions and etching process.
1.2 Motivation

Silicon nanostructures have a wide variety of uses, and as such, methods of fabrication warrant more study. Nanostructures have been produced with other types of MIC, notably AIC\textsuperscript{2,3}, yet nanostructure production via NIC of a-Si has not been extensively studied. Nanodots and nanowires have potential applications in the area of electronics, while surface topography has shown to be useful in tribological applications. As such, the primary focus of this research is to investigate the suitability of NIC of a-Si to produce silicon nanostructures. Once the production of nanostructures by NIC of a-Si is established, the uses of these nanostructures can be further investigated. The specific goals of this research are to demonstrate the production of nanostructures using NIC of a-Si and characterize these nanostructures in terms of geometry and chemical composition.
1.3 Organization of the Thesis

This thesis is divided into five chapters. The present chapter has introduced metal-induced crystallization and proposed mechanisms of crystallization. Chapter two is a review of current literature in the area of nickel-induced crystallization of a-Si. Chapter three details the experimental techniques and characterization methods used. Chapter four presents a discussion of the results of this research. Finally, chapter five contains the conclusion and recommendations for future work.
2.1 Research in NIC and NILC of a-Si

Much of the research in metal-induced crystallization of a-Si using nickel as the crystallization-inducing metal has been in the area of NILC. Y.-D. Lin and Y.S. Wu studied the effect of oxygen in the nickel films used in NILC at various temperatures. Wet oxide films of 500 nm thickness were grown at a substrate temperature of 1,050 °C, followed by a 100-nm-thick layer of a-Si. A photo-resist patterning technique was employed to produce islands of a-Si. Then, a 10-nm-thick layer of nickel was deposited on some samples using DC sputtering at room temperature. On the other samples, a 10 nm thick layer of nickel-oxide was deposited using DC sputtering in air. These samples were then annealed in a nitrogen atmosphere at temperatures between 500 and 600 °C. Scanning electron microscopy (SEM) revealed the presence of needle-like morphology at the NILC front. The results showed that the presence of oxygen in the nickel films reduced the NILC length, but did not adversely affect the crystal morphology. The NILC rates for both the Ni and NiO samples increased with increasing annealing temperature. The only adverse effect of oxygen in the nickel films was retardation in the nucleation of poly-Si. This was a caused by the incubation time needed for reduction of NiO to Ni for crystallization mediation. This incubation time increased with decreasing temperature, and the reduction rate becomes too low to accommodate crystallization below 500 °C.

L.K. Lam et al. studied the kinetics of NILC used in the production of TFTs. The major objective of this study was to determine the activation energies of NILC for both rapid thermal annealing (RTA) and conventional furnace annealing (CFA). First,
120-nm-thick a-Si was deposited on Corning 1737 substrate. After patterning, wet oxide of 120 nm thickness was deposited, followed by 240 nm of a-Si at the gate region. After patterning of the a-Si gate layer, the wafers were ion-implanted with $5 \times 10^{-15}$ cm$^{-2}$ phosphorus at 100 keV. Finally, a 10-20 nm layer of Ni was blanket evaporated onto the source, drain, and gate regions. Recrystallization was attained by RTA at temperatures from 520 to 640 °C in a nitrogen environment and by CFA in nitrogen at 500-600 °C. The NILC velocity was measured using optical microscopy. According to the results, the NILC velocity of the RTA samples proceeded at a rate three times faster than the CFA samples. Activation energies were determined from the slopes of plots of NILC velocity vs. inverse temperature. The activation energy was determined to be 1.75 eV for RTA and 1.86 eV for CFA. Although the activation energies are comparable, the NILC velocity is faster for RTA by a factor of 3. In addition, the electrical properties of TFTs fabricated using both annealing methods were similar.

L.F. Li et al. studied the effect of an applied electric field on NILC of a-Si thin films, a process known as field-aided lateral crystallization (FALC). A 90-nm-thick a-Si film was deposited on a 500 nm layer of thermally grown oxide. Nickel films were electron-beam evaporated onto the a-Si layer and patterned into strips using a shadow mask. The samples were annealed in a 500 °C, 0.04 Torr argon environment for 5 hours. To test for FALC effects, the specimen was clamped into an insulating boron nitride holder, with two carbon electrodes each in contact with a Ni strip. A DC voltage was applied between the electrodes, resulting in an induced electric field of 600 V/cm. Atomic force microscopy (AFM) of the crystallization front shows dendritic lateral growth. AFM imaging also reveals that large NILC grains are actually a mosaic of
needle-like subgrains. The orientation of these subgrains deviate slightly from each other, as shown by the AFM imaging. FALC specimens also showed dendritic growth, but the diffusion rate was accelerated by the applied electric field. In addition, the growth orientation of the FALC subgrains was normalized by the electric field. The NILC and FALC growth fronts are distinctive, due to electric field enhancement on the lateral crystallization.

M. Qin et al. investigated the effect of annealing temperature on NILC rate. Initially, 100 nm of a-Si was deposited on 300 nm of wet oxide, followed by 400 nm of low temperature oxide (LTO). Then, windows were patterned into the LTO and 5 nm of Ni was electron beam evaporated onto the a-Si layer. The samples were annealed by CFA in nitrogen at 500-680 °C for 2 to 18 hours. Some samples were annealed again at 1000 °C for 2 hours to study second grain growth at high temperatures. Samples were characterized by optical microscopy, Raman spectroscopy, AFM, and transmission electron microscopy (TEM). The NILC growth rate depends strongly on annealing temperature, with a maximum growth rate at 625 °C. The films formed are a mixture of large and small grains and contain many defects. However, a second high-temperature anneal promotes secondary crystallization that results in improvement of the NILC films. TEM imaging reveals that the samples that were annealed again at 1000 °C have clear grain structures.

C.F. Cheng et al. studied the effect of nickel thickness on NILC. First, 700 nm of wet oxide was deposited on silicon substrates, followed by 100 nm of a-Si and 400 nm of LTO. Seed windows were opened in the LTO, and Ni thin films were evaporated onto the exposed a-Si. Nickel thicknesses were 5, 10, and 50 nm. The wafers were subjected
to 550 °C annealing in a nitrogen environment for 50 hours to induce crystallization, followed by a second anneal for 1 hour at 900 °C to enlarge the grain sizes. After the annealing, a CMOS process was performed to fabricate n-channel TFTs. The performance of the TFTs was used as a rubric for the quality of poly-Si. The results show that thicker nickel films resulted in better TFT performance, particularly the mobility of the poly-Si layer.

K.H. Park et al. investigated the microstructural evolution of Ni during crystallization of a-Si by NILC. An oxide layer of 200 nm was grown on glass substrates, onto which 200 nm a-Si films were deposited by PECVD. A very thin Ni layer was coated on the a-Si films by dc magnetron sputtering. The samples were annealed at temperatures between 400-470 °C for durations of 2 minutes. Microstructure characterization was performed by planar TEM. Their results showed that octahedral NiSi$_2$ precipitates formed at low annealing temperatures. At higher temperatures, the precipitate shape changed due to crystal nucleation on the {111} planes of NiSi$_2$. Crystalline silicon growth was developed by the migration of NiSi$_2$ precipitates. In addition, collisions between stationary precipitate particles and migrating precipitate particles produced additional c-Si growth in variants of the <111> direction.

In the area of conventional NIC, Z. Jin et al. developed a physical mechanism for NIC based on redistribution of Ni in the a-Si film. Thin nickel films, ranging from 70 nm to 1 µm, were deposited on oxidized silicon substrates, followed by Ni films of 5-10 nm thicknesses. Heat treatment was performed for 1 to 90 hours in a conventional furnace at 500 °C. During heat treatment, nitrogen gas was delivered to the furnace at a flowrate of 5 L/min. The c-Si films produced were studied by Raman spectroscopy,
optical microscopy, and TEM. Based on the results, they proposed a 3-step mechanism for NIC: Silicide formation, breakup of silicide layer into nodules, and nodule transport. This model accounts for the inversion of Ni and Si during crystallization, as well as provides a viable explanation for long-range Ni transport through the entire film.

J.-D. Hwang et al. proposed a two-step annealing process, designed to reduce the long annealing times used in conventional NIC and to improve the electrical and structural properties of poly-Si films. Amorphous silicon films of 100 nm thickness were deposited on oxidized Si wafer substrates, followed by 5 nm Ni films. The two-step annealing process consisted of 10 minutes of rapid thermal annealing RTA and CFA for 5 to 20 hours. They quantified the crystalline grain size versus annealing time. The largest grains were produced after 5 hours of CFA, with a steady decrease in grain size with increasing annealing time. XRD analysis of the poly-Si films shows the presence of (111), (220), and (322) crystals in the crystallized region.

Using a method similar to NIC, Huntagalung et al. produced a “nanowhisker” using nickel as a catalyst. In their method, very thin Ni films were deposited on Si substrates by spin-coating. A silicon powder was then thermally evaporated onto the Ni films. Heat treatment parameters were 1 hour at 1,050 °C. During spin-coating, the Ni films separated into discrete islands instead of a continuous film. During heat treatment, these islands served as nucleation sites for crystal growth. SEM and TEM imaging confirm the production of a one-dimensional silicon nanostructure with a spherical Ni tip. The authors contend that this structure is similar to those that would be produced by the VLS mechanism, and thus the production of silicon nanowires can be explained by VLS.
Despite all of the research in NIC and NILC of a-Si, the production of nanostructures by NIC of a-Si has not been well investigated. The focus of this research is to determine the suitability of traditional NIC of a-Si to reliably produce silicon nanostructures, including surface topography and nanowires.
Chapter 3
Experimental Techniques

3.1 Process Steps of NIC of a-Si

The relevant processing steps in NIC of a-Si are plasma enhanced chemical vapor deposition (PECVD), native oxide growth, thermal evaporation, annealing, and wet selective etching. Characterization techniques employed include optical microscopy, scanning electron microscopy (SEM), and energy dispersive X-ray spectroscopy (EDS).

Figure 3.1 shows a flow chart of the relevant processes used in this study. Single crystal silicon (111) wafers were chosen as substrates due to availability and the relative ease in which they may be cut into small samples. Amorphous silicon films were deposited on the substrates by means of PECVD. After a-Si deposition, the wafers were allowed to sit in air in order for a native oxide film to develop. Nickel was then deposited on the native oxide layer with a thermal evaporator. After evaporation, the wafers were diced into small samples. These samples were then annealed in a furnace in air in order to provide the activation energy required for crystallization of a-Si. Unreacted Ni was removed by wet selective etching.

The processes used in this study are similar to those used in the literature, yet there are differences. As stated in chapter 2, much of the literature on NIC is actually on NILC, which has different objectives, namely the production of large lateral grains. The studies in the literature typically use relatively low annealing temperatures and very long annealing times (up to 90 hours). However, this study uses higher annealing temperatures with shorter annealing times. In addition, the formation of silicon nanostructures has been well documented with other forms of MIC, namely AIC.
However, the results from AIC cannot be extended to NIC, mainly due to differences in chemical reactions present during annealing and characteristic activation energies.

![Process Flow Chart for NIC of a-Si](image)

**Figure 3.1: Process Flow Chart for NIC of a-Si**

### 3.1.1 Amorphous Silicon Deposition

PECVD is a common method of thin film deposition. During PECVD, the deposition of thin films through chemical reactions of the gas phase of the source material is assisted by a plasma produced by an electric field. The electrons generated
by this plasma create free radicals during collisions with source gas atoms in the reaction chamber. These radicals migrate to the substrate surface and interact with surface atoms and other nearby radicals to produce solid thin films at relatively low ambient temperatures.

The properties of thin films deposited by PECVD can be controlled by adjusting process parameters. These parameters include substrate temperature, chamber pressure, radio frequency (RF) power, and source gas flow rate. Notable advantages of PECVD include good film adhesion, uniform film deposition, and low deposition temperatures due to the energy provided by the plasma.

In this study, PECVD was used to deposit a-Si thin films on silicon substrates. The substrate temperature, chamber pressure, RF power, and silane flow rate were controlled at 250 °C, 1 Torr, 20 W, and 85 sccm, respectively. These conditions produced a 100 nm thick a-Si thin film.

3.1.2 Native Oxide Growth

When exposed to air, silicon oxidizes to form silicon dioxide films. This native oxide layer has been shown to have an impact on AIC of a-Si, so the a-Si films were also allowed to oxidize for this study. Native oxide growth proceeds quickly after first exposure to air, but the native oxide thickness levels off after approximately two days. Thus, the a-Si layers were allowed to sit in air for at least two days after deposition to allow growth of a consistent SiO₂ layer.

3.1.3 Nickel Evaporation

Thermal evaporation is an effective method of film deposition for materials that have manageable melting and vaporization temperatures and high degrees of adhesion.
with the target material. In this study, an Edwards Auto-306 thermal evaporator was used to evaporate Ni films onto the native oxide films. The advantages of thermal evaporation are smooth, uniform films and little risk of substrate contamination. In addition, the low chamber pressures used during thermal evaporation prevent reactions between the vapor and atmosphere and also lower the melting and vaporization temperatures of the source material.

Figure 3.2 shows the relevant components of a thermal evaporator. Source material is loaded into the evaporation boat, which is connected to an electrode. The electric current supplied by the electrode provides the energy to vaporize the source material. When the source material evaporates, it migrates upward and deposits on the target and the evaporator walls. A crystal resonator is used to measure deposited film thickness. The mass deposited on the crystal is sensed as a change in resonance frequency. A user-supplied density value is used by the internal computer to convert changes in mass to deposited film thickness.

In this study, Ni films of 5 nm, 10 nm, 20 nm, and 95 nm were deposited on the native oxide films. Nickel wire was used as source material, and tungsten boats were used as the evaporation vessel. Base pressures used for evaporation were on the order of $2 \times 10^{-6}$ mbar, while the base current used to initiate evaporation was 4 amps. The current was adjusted \textit{in situ} to normalize the deposition rate to 0.4 nm/s.
3.1.4 Annealing

Annealing is a heat treatment that is generally used to refine the microstructure, relieve internal stresses, and alter the material properties of a sample. In this study, annealing is used to provide the energy required to initiate the crystallization of a-Si. Annealing was accomplished with an electric furnace with an alumina-based interior. Instead of placing the sample in a room-temperature furnace and allowing the sample to be heated up along with the furnace, as in the literature, the samples were placed in the furnace only after it had reached a pre-set steady-state temperature. After the sample was annealed, it was allowed to cool in air. The most important parameters in the annealing process are annealing time and annealing temperature. Figure 3.3 shows the annealing matrix that was used for all Ni thicknesses.
<table>
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</table>

Figure 3.3: Matrix of Annealing Conditions Used for All Ni Thicknesses

3.1.5 Selective Etching

Oftentimes, after annealing, unreacted metal source will be left on the sample surface. In general, this unreacted metal is undesirable and must be removed. Wet selective etching is a process in which this unreacted metal is removed by a chemical solution. It is important, though, to make sure that the chemical used as an etchant will not etch the target material, remove the developed microstructure, or adversely damage the substrate. For some applications, complete removal of the materials to be etched is not desired, and so the etch rate of the etchant is an important parameter. If complete removal is desired, careful monitoring of the etchant is not required.

For these experiments, TNT Copper Etch, which contains sulfuric acid, copper sulfate, and hydrogen peroxide, was used for complete nickel removal. This etchant does not damage either crystalline or amorphous silicon, so it is appropriate for this study. The etch rate is very fast. For copper, it is 0.25 microns per second at room temperature; an etch rate for Ni is not available, but should be similar. The samples were immersed in the etchant bath for approximately 5 minutes at room temperature, to insure that all unreacted Ni would be removed. After etching, characterization of the developed films can begin.
3.2 Sample Characterization

3.2.1 Optical Microscopy

Optical microscopy is useful for qualitatively assessing the quality of films on the etched samples. Optical microscopes use the light reflected off a sample, along with a series of lenses, to magnify sample images. Magnification capabilities of 1000x are common for optical microscopes. The optical microscope used in this study has a maximum magnification of 100x.

3.2.2 Scanning Electron Microscopy

Scanning electron microscopy (SEM) imaging is a useful technique for producing highly-magnified, three dimensional surface topography images with high resolution. During SEM imaging, a beam of electrons is scanned across the surface of a sample. These electrons interact with atoms on or near the sample surface and create secondary electrons that are collected by a detector. The signals that reach this detector are then used to produce a real-time image of the surface topography via a beam from a cathode-ray tube.

3.2.3 Energy Dispersive X-Ray Spectroscopy

EDS is used to determine the elemental composition of a sample surface. The EDS detector is integrated into the scanning electron microscope and operates in conjunction with SEM imaging. In addition to the secondary electrons that are liberated during electron beam scanning, X-rays that are characteristic of the atomic species that make up the surface are also produced. Since each element in the periodic table has a unique electron structure, the X-rays that are produced are also unique, and thus the
spectra produced by EDS can be used to determine which chemical elements are present in a surface.
Chapter 4

Results and Discussion

4.1 Summary of Experiments Performed

Since producing silicon nanostructures by NIC of a-Si has not been well investigated, a systematic study has been performed to establish the process and characterize the silicon nanostructures that were produced. In this study, four different nickel thicknesses were used to assess the viability of NIC of a-Si to produce silicon nanostructures. The relevant results that will be discussed include: 1) types of nanostructures produced, 2) the sensitivity of nanostructure production to Ni thickness, 3) result repeatability, 4) characterization of the chemical composition of nanostructures, and 5) a discussion of a probable crystallization mechanism.

4.2 Fabrication and Characterization of Processed Samples

The primary objective of this study is to evaluate the suitability of NIC of a-Si to produce silicon nanostructures and surface topography and to characterize the resulting structures with optical microscopy, SEM imaging, and EDS.

A 100-nm-thick film of a-Si was deposited on single crystalline silicon (111) wafers by means of PECVD. The substrate temperature, chamber pressure, RF power, and silane flow rate were controlled at 250 °C, 1 Torr, 20 W, and 85 sccm, respectively. After a-Si deposition, the wafers were allowed to sit in air for at least two days for native oxide growth. Then, nickel films of 5 nm, 95 nm, 10 nm, and 20 nm were deposited by thermal evaporation. The base pressure used during evaporation was on the order of 2x10^{-6} mbar and the evaporation rate was 0.4 nm/s. After a-Si and Ni deposition, the wafers were diced into small 1.5 cm x 1.5 cm pieces for further processing.
These small samples were then chosen randomly to be annealed for a certain time and temperature. After annealing, the samples were etched using TNT Copper Etch to remove any unreacted Ni from the sample surface. During etching, the samples are submerged in the etchant for approximately 5 minutes, and then rinsed in de-ionized water to remove any residual etchant from the surface. Finally, the samples were blown dry with a nitrogen gun.

The finished samples were characterized with optical microscopy, SEM, and EDS. Optical microscopy was used to qualitatively determine the quality of the processed films. The microscope used in this study is capable of magnifications of 10x, 20x, 40x, and 100x. At 100x magnification, it is possible to discern the presence of microstructure, but further determination of microstructure size and geometry is not possible. SEM imaging provided high-magnification images of the sample surfaces. At these magnifications, sub-micron details are apparent, and it is possible to determine the size and geometry of the structures produced. In addition, SEM imaging provided excellent depth of field, resulting in discernment of three-dimensional details of the sample surfaces. EDS characterization provided information on the chemical composition of the produced structures and surfaces. In this study, EDS was used to assess the Ni concentration remaining in the samples after etching. Since all unreacted Ni was removed during etching, EDS signatures that correspond to Ni could be a result of Ni atoms that have diffused into the a-Si films, or, more likely, indicates the presence of nickel silicides.
4.3 Discussion of Nickel Thicknesses

In this experiment, four different Ni thicknesses were used to perform NIC of a-Si: 5 nm, 95 nm, 10 nm, and 20 nm. A discussion of the rationale behind the specific Ni thickness, relevant SEM images, and an interpretation of the results for each Ni thickness is presented below.

4.3.1 5 Nanometers

The first Ni thickness used was 5 nm. This thickness was inspired by the literature, which cited crystallization results for 5 nm samples at 550 °C for 30 min and 800 °C for 10 s. Additionally, these two conditions were used as the limiting cases for the annealing matrix that was used across all Ni thickness. Figure 4.1 shows a results matrix for post-etch 5 nm samples.

The SEM magnification for the images in Figure 4.1 is 10,000x. For this Ni thickness, most of the conditions produced spider-like growths, which are not desirable as silicon nanostructures. Notable exceptions include 700 °C for 10s, which displays much more robust growth, and 800 °C for 30 min and 10 min, both of which produced surface texture. The occurrence of nanostructures represents an early experimental success, as structures such as these have applications for surface wetting. However, the population density of these structures is too low for practical applications, so further experimentation is required to produce more useful structures.
4.3.2 95 Nanometers

The next nickel thickness used was 95 nm. This thickness was inspired by the desire to form silicon nanowires via NIC of a-Si in a method that is similar to the method used to produce silicon nanowires via AIC of a-Si. Since very little research has been done in nanostructure production using traditional NIC, much less on the formation of nanowires, the methods and results from AIC were extended to this study. Formation of silicon nanowires by AIC of a-Si has been confirmed using 800 nm of Al on 100 nm of a-
Si\(^2\). Because of this, the original intent was to evaporate as much Ni as possible onto the 100 nm a-Si film. However, a boat failure resulted in deposition of only 95 nm of Ni. Figure 4.2 shows a pre-etch results matrix for 95 nm samples, and Figure 4.3 shows a post-etch results matrix for 95 nm samples.

The SEM magnification used in Figures 4.2 and 4.3 is 10,000x. Contrary to the results from the 5 nm samples, these samples are completely covered with a continuous film with a very fine microstructure. In addition, for some samples, notably 800 °C for 30 min and 10 min, an underlying structure is apparent, yet is completely covered by the continuous film. Furthermore, a comparison between the pre-etch and post-etch SEM images shows that there is very little change in the appearance of the film. Since the copper etchant does indeed etch unreacted Ni, these films must be composed of some Ni-containing compound that cannot be etched. Therefore, 95 nm Ni films are ineffective at producing silicon nanostructures, because any structures that are produced are buried beneath a continuous film that cannot be removed by conventional etching.
<table>
<thead>
<tr>
<th>Time</th>
<th>550 °C</th>
<th>600 °C</th>
<th>700 °C</th>
<th>800 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>30 min</td>
<td><img src="image1.png" alt="Image" /></td>
<td><img src="image2.png" alt="Image" /></td>
<td><img src="image3.png" alt="Image" /></td>
<td><img src="image4.png" alt="Image" /></td>
</tr>
<tr>
<td>10 min</td>
<td><img src="image5.png" alt="Image" /></td>
<td><img src="image6.png" alt="Image" /></td>
<td><img src="image7.png" alt="Image" /></td>
<td><img src="image8.png" alt="Image" /></td>
</tr>
<tr>
<td>30 s</td>
<td><img src="image9.png" alt="Image" /></td>
<td><img src="image10.png" alt="Image" /></td>
<td><img src="image11.png" alt="Image" /></td>
<td><img src="image12.png" alt="Image" /></td>
</tr>
<tr>
<td>10 s</td>
<td><img src="image13.png" alt="Image" /></td>
<td><img src="image14.png" alt="Image" /></td>
<td><img src="image15.png" alt="Image" /></td>
<td><img src="image16.png" alt="Image" /></td>
</tr>
</tbody>
</table>

Figure 4.2: Pre-Etch Results Matrix for 95 nm Samples
The results from the 95 nm samples show that Ni films that are roughly the same thickness as the a-Si films are undesirable for creating nanostructures. For this reason, the next Ni thickness chosen was 10 nm, with the expectation that this would build on the results of the 5 nm samples. Figure 4.4 shows the results matrix for post-etch 10 nm samples.

<table>
<thead>
<tr>
<th></th>
<th>550 °C</th>
<th>600 °C</th>
<th>700 °C</th>
<th>800 °C</th>
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<tr>
<td>30 min</td>
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<td>10 s</td>
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</tbody>
</table>

Figure 4.3: Post-Etch Results Matrix for 95 nm Samples

### 4.3.3 10 Nanometers

The results from the 95 nm samples show that Ni films that are roughly the same thickness as the a-Si films are undesirable for creating nanostructures. For this reason, the next Ni thickness chosen was 10 nm, with the expectation that this would build on the results of the 5 nm samples. Figure 4.4 shows the results matrix for post-etch 10 nm samples.
The SEM magnification used in Figure 4.4 is 20,000x. Most of the 10 nm samples also produced spider-like growths, much like the 5 nm samples. However, there are differences. First, the surface growth on the 700 °C for 10 s sample has evolved into a continuous film, as opposed to the same conditions on the 5 nm sample which produced more robust growth. In addition, the results for the 800 °C for 30 min and 10 min
samples, which produced surface topography for the 5 nm samples, now appear to be surface deposits instead of three-dimensional protrusions. Not all of the results were discouraging, however. Nanowire formation was confirmed on the 550 °C for 30 min, but not uniformly across the entire sample. This result will be detailed in Section 4.4.

4.3.4 20 Nanometers

The 20 nm thickness was chosen at the same time as 10 nm thickness to provide a decent resolution of utilized Ni thicknesses. The samples were processed immediately after the 10 nm samples without regard to the results of the 10 nm samples. Figure 4.5 shows the results matrix for post-etch 20 nm samples.

The SEM magnification used in Figure 4.5 is 20,000x. The 20 nm samples show signs of film formation and have more in common with the continuous films from the 95 nm samples than the spider-like growths from the 5 nm and 10 nm samples. Notably, all evidence of surface topography is gone. Ostensibly, 20 nm is the lower limit for undesirable continuous film growth. However, the 550 °C for 30 min sample produced evidence of nanowires, but not uniformly across the entire sample. These nanowires are of poorer quality than those formed with a 10 nm Ni thickness. This result will also be detailed in Section 4.4.
4.4 Nanostructures Produced

4.4.1 Surface Topography

Surface topography was produced for 5 nm Ni thickness using conditions of 800 °C for 30 min and 10 min. The sizes of the islands range from about 1 micron to sub-micro lengths. Furthermore, these structures were produced uniformly across the sample. However, the population density of the structures is too low for most practical applications. An increase in Ni thickness from 5 nm to 10 nm did not produce the
expected increase in population density, but instead degraded the quality of the topography. More investigation is needed to produce topography with a higher population density.

4.4.2 Nanowires

Small areas containing nanowire-like growths were formed on both 10-nm- and 20-nm-thick Ni samples at 550 °C for 30 min. These nanowire-like growths have a diameter of approximately 50 nm. This result is a significant accomplishment, as it proves that nanowire formation is possible using NIC of a-Si. Figure 4.6 shows 20,000x magnification SEM images of the nanowire growths for both the samples with 10 nm and 20 nm Ni thicknesses.

![Figure 4.6: SEM Imaging of Nanowire Growths for (a) 10 nm and (b) 20 nm Ni](image)

As can be seen from Figure 4.6, the 10 nm growths are very well ordered and propagate in roughly parallel lines. The 20 nm growths, however, are not as continuous and display degradation in quality. The fact that nanowire-like growths were obtained using identical annealing conditions is likely not a coincidence; something special occurs during that condition to initiate nanowire formation. Now that the formation of
nanowires by NIC of a-Si is confirmed, more investigation is needed in order to
determine how to reliably produce these results across entire samples.

4.5 Sensitivity of Nanostructure Production to Ni Thickness

Clearly, the formation of nanostructures by NIC of a-Si is very sensitive to Ni
thickness. This is most apparent by examination of the SEM images of the 800 °C for 30
min and 10 min samples for both 5 nm and 10 nm Ni thicknesses, which can be found in
Figures 4.1 and 4.4, respectively. In addition, as can be seen in Figure 4.6, the formation
of nanowires is sensitive to a change in Ni thickness from 10 nm to 20 nm. This
sensitivity to Ni thickness is in stark contrast to AIC of a-Si, which is not as sensitive to 5
or 10 nm changes in Al thickness, but may be more sensitive to annealing time.

4.6 Repeatability of Results

Repeatability of results is important for any experimental study. To this end, the
results from multiple samples processed with the same conditions have been compared to
determine the degree of repeatability that is possible with NIC of a-Si. The first set of
conditions is 800 °C for 30 minutes with 5 nm Ni thickness. These samples were
annealed at the same time. The other set of conditions is 800 °C for 30 min with 95 nm
Ni thickness. These samples were annealed on different dates. Figure 4.7 shows two
samples from the first set of conditions, while Figure 4.8 shows two samples from the
second set of conditions.
The SEM magnification used in Figure 4.7 is 10,000x. The SEM magnifications used in Figure 4.8 are 10,000x and 5,000x. As can be seen from Figures 4.7 and 4.8, the results are reasonably repeatable regardless of whether the samples are annealed at the same time or at different times, as long as the same annealing conditions are used. Visual inspection shows that the structures present in Figure 4.7 are roughly the same size. For Figure 4.8, note that two different magnifications are used. This makes visual inspection of repeatability more difficult. However, inspection of the sizes of the buried structures using the included length scales confirms that the buried structures are indeed the same size, with a similar population density.
4.7 Discussion of Chemical Composition of Films and Nanostructures

4.7.1 Surface Topography

EDS signatures from 800 °C for 30 min with 5 nm Ni thickness are shown in Figure 4.9. The signature for the island includes two small Ni peaks, which represents the expected Ni contamination that is inherent in NIC. The signature for the “off-island” portion of the sample has a much less pronounced Ni peak. This result indicates that most of the Ni contamination is imbedded in the microstructure. Further investigation of both the structures and the “off-island” surfaces is needed to determine the crystalline structure of the sample.

![Figure 4.9: EDS Signatures for (a) On-Island and (b) Off-Island](image)

4.7.2 Nanowires

An EDS signature for the nanowires produced from 500°C for 30 min with 10 nm Ni thickness is shown in Figure 4.10. Like the islands that are were also produced, there is some Ni contamination present. More investigation is needed to determine if this Ni contamination will adversely affect the supposed usefulness of these nanowires.
4.7.3 Continuous Films

The continuous films that were produced from the 95 nm Ni thickness samples were especially confounding in that no visual changes in film structure were apparent after etching. A post-etch EDS signature for a continuous films formed by 800 °C for 30 min with 95 nm Ni thickness is shown in Figure 4.11. A large Ni peak indicates that a large amount of Ni is still present in the film. EDS analysis of an unannealed Ni film confirms that the etchant used does indeed etch Ni, so the prominent Ni peak is the result of the presence of a Ni-containing compound or compounds, likely nickel silicides. Since these films cannot be etched, Ni films that are roughly the same thickness as the a-Si films cannot produce desirable results, at least with the present procedure. More investigation with a different methodology is needed.
4.8 Discussion of Crystallization Mechanism

The actual physical mechanism behind metal-induced crystallization, including NIC of a-Si, is not well understood. Three proposed crystallization mechanisms were detailed in Chapter 1. All three mechanisms are based on a layer exchange mechanism, which is facilitated by diffusion of particles through the a-Si layer. The VLS mechanism requires the source material to be provided by a carrier gas, so it is not a likely model to describe NIC. The Ni-Si binary system exhibits eutectic behavior, so the eutectic mechanism is plausible. However, eutectic behavior was not evident in this study because of the relatively low activation energies for nickel silicide formation. Because of the affinity for nickel silicide formation during annealing, the metal silicide diffusion mechanism is a likely crystallization mechanism for NIC.
Chapter 5

Conclusions and Recommendation for Future Work

5.1 Conclusions

Nickel-induced crystallization of amorphous silicon has been systematically studied to determine its suitability for producing nanostructures. The nanostructures and films produced were characterized using optical microscopy, scanning electron microscopy, and energy dispersive X-ray spectroscopy.

This study has confirmed that the formation of both surface topography and nanowires is possible with NIC of a-Si. However, the population density of the surface topography is currently too low for practical applications, and nanowire growth is restricted to finite areas on a sample surface, as opposed to uniform growth across a sample. The formation of nanostructures seems to be very sensitive to Ni thickness, as 5-10 nm changes in Ni thickness result in drastic changes in the types and conditions in which nanostructures are formed. In addition, the results display a high degree of repeatability.

EDS analysis confirms that Ni contamination is a result of the annealing process, as all EDS signatures have at least a small Ni peak. It remains to be seen if this Ni contamination has an adverse effect on the usefulness of the nanostructures. In addition, the presence of Ni contamination implies that the activation energies for formation of Ni silicides are relatively low. Since the etching procedure removes all unreacted Ni, any remaining Ni must be the in the form of Ni silicides. Since Ni silicides cannot be etched with the present method, any condition that produces continuous Ni silicide films is inappropriate for forming nanostructures. Finally, due to the relative ease of Ni silicide
formation, the likely crystallization mechanism for NIC of a-Si is based on the diffusion of Ni silicide particles to facilitate layer exchange.

5.2 Recommendations for Future Work

The results of this study provide a solid foundation for future studies in NIC of a-Si. Notably, the formation of both surface topography and nanowires has been confirmed, which provides opportunities for future studies to improve the quality of the nanostructures produced by NIC of a-Si. A few of these future research directions are discussed below.

5.2.1 Effects of Native Oxide Layer Removal on NIC of a-Si

When a-Si is exposed to air, a native oxide layer will grow spontaneously. Usually, these films are left on the a-Si layer during NIC to insure that removal of the layer will not add any experimental irregularities. In addition, the native oxide layer is used to prevent the crystalline structure of a silicon substrate from interfering with the crystallization of a-Si. However, it has been shown through studies of NILC that crystallization of a-Si can propagate along these exposed grain boundaries if the native oxide layer is removed. Crystallization along grain boundaries may be a crucial step in producing uniform nanowire production across entire samples surfaces, so more investigation is warranted.

5.2.2 Exchange of Ni and a-Si Layers for Moderately Thick Ni Films

Moderately thick Ni films which are the order of 0.5 to 1.5 times the thickness of the a-Si layer have been shown to be inappropriate for producing nanostructures due to the continuous nickel silicide films that they form. However, if the metal silicide diffusion mechanism correctly describes NIC of a-Si, then transposing the Ni and a-Si
layers could produce more compelling results. Under these circumstances, Ni silicide particles would diffuse upward into the a-Si film instead of remaining buried by the continuous Ni silicide film. This could provide one way of “unburying” the nanostructures that are visibly buried during traditional NIC of a-Si with moderately thick Ni layers.

5.2.3 The Effect of Very Thick Ni Films on NIC of a-Si

Under the experimental conditions used in the current study, the amount of Ni present was the limiting reagent for Ni silicide formation. However, if the Ni layer is so thick that not all of the Ni can react to form Ni silicide, again more compelling results may be produced. For this study, the very thick nickel films should be on the order of at least four times the thickness of the a-Si films. This ratio could be achieved by simple evaporating more Ni onto the native oxide layer, using a thinner a-Si layer, or both.

5.2.4 The Effect of Magnetic Fields on NIC of a-Si

Nickel is a magnetic element and thus responds differently to electromagnetic fields compared to aluminum. Literature has shown the application of an electric field improves the results of NILC by normalizing the crystallization direction and growth rate. Application of a magnetic field during MIC should have similar results. The use of a transverse magnetic field during annealing could be key to producing vertically standing nanostructures from NIC of a-Si.

5.2.5 Combined NIC and AIC of a-Si

Formation of nanostructures by AIC has long been established. Now that formation of nanostructures by NIC of a-Si is established, the possibility for combined NIC and AIC can be realized through the use of a mixed Ni and AL layer. Although
crystallization is based on exchange of metal and a-Si layers for both methods, the way this layer exchange is facilitated is likely different for each method. Combination of AIC and NIC could provide novel nanostructure shapes. The activation energies for crystallization of a-Si via AIC and NIC are different, so crystallization would begin at random locations, and at random times, on the sample surface based on the local metal concentration. Difficulties in this approach include simultaneous evaporation of Ni and Al, as each have characteristic melting and vaporization temperatures, and the reproduction of Ni-Al films in a controllable way. Another method of combined AIC and NIC would involve stacked continuous Ni and Al films, as opposed to a single, mixed layer. More investigation of the physical plausibility of both of these methods is required.
References


