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Electrical characterization of thin film nanostructure templates

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Electrical Characterization of Thin Film Nanostructure Templates

Christopher James Garman

Thesis Submitted to
The College of Engineering and Mineral Resources
At
West Virginia University
In partial fulfillment of the requirements for the degree of

Master of Science
In
Electrical Engineering

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The Lane Department of Computer Science and Electrical Engineering

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2001

An improved apparatus for anodizing aluminum films on Si substrates is presented. In addition, an explanation is given for adapting the system to SiC and glass substrates. The system presented is optimized for throughput and safety to focus on volume production. MOS capacitors created with the system are analyzed with capacitance-voltage measurement techniques to provide insight into device operation. Ni is deposited into porous alumina templates to create Ni nanostructures.

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Finally, I would like to dedicate this work to my fiancée, Mary Jean Masters, and to my parents, James and Paula Garman, all of whom assisted in countless ways. I gratefully acknowledge the remainder of my family for their constant support and encouragement.

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1.0 Introduction

The Nanostructures Research Group (NRG) at West Virginia University has developed a thin film porous alumina template-based nanostructure synthesis technique that has the potential for fabricating high-performance photonic and electronic devices [1,2, 10]. The fabrication technique is based on anodization, or electrolytic oxidation, of an aluminum thin film into porous alumina that contains a periodic array of nanoscale pores. The nanostructure material is then synthesized inside these pores. When aluminum is anodized in an appropriate acidic electrolyte under controlled conditions, it oxidizes to form a hydrated aluminum oxide (alumina) containing a two dimensional hexagonal array of cylindrical pores as schematically shown in Figure 1.1.

Figure 1.1 – Schematic Top and Cross-Sectional Views of Pores Formed in Anodized Alumina

Anodization of aluminum is a well-established industrial process and is widely used for coloring and anticorrosion applications. The reaction is performed in a simple wet chemistry apparatus where the aluminum layer is polarized as the anode (positive), and a platinum electrode is used as the cathode (negative). Anodization can be performed under constant current (galvanostatic) or constant voltage (potentiostatic) conditions. Sulfuric acid and oxalic acids are typically used for the anodization of aluminum. The pore diameter and the inter-pore spacing depend on the anodization conditions such as electrolyte pH, temperature and the anodization current density, and the aluminum microstructure features, such as grain size. The anodization parameters can be precisely controlled to form pore diameters between 4 and 100 nm with less than 10% variance in the pore size distribution in bulk aluminum (Figure 1.2) [24].

Figure 1.2 – SEM Top View of Bulk Porous Alumina Showing Highly-Ordered Pores

Pores can be up to several microns deep. Since anodized alumina is electrically insulating and transparent over a wide visible spectrum, it can be an ideal embedding material for nanoscale electronic and photonic devices. In fact, during the past fifteen

years, porous alumina fabricated on *bulk* aluminum substrates has been used to synthesize various semiconductor and magnetic materials [3-6]. Nanostructures are created in the pores by electrochemical synthesis or colloidal deposition inside the pores [3,7]. Some of the species introduced into the bulk nanoporous alumina include: gold, nickel, iron, CdS, ZnS, CdSe, GaAs and ternary semiconductor compounds ($\text{Cd}_x\text{Zn}_{1-x}\text{S}$). However, the use of bulk alumina precludes most photonic and electronic device applications due to the opaque nature of the unconverted aluminum substrate, and the inability to integrate the nanostructure arrays with other devices. To overcome this barrier, the NRG and the University of Notre Dame extended this fabrication technique by using an aluminum thin film deposited on a silicon substrate as the basis for template fabrication, and have since extended it to other substrates including glass and ITO coated glass [2]. NRG and Notre Dame are currently working on the implementation of a variety of photonic and electronic devices based on this thin film template based synthesis technique.

The overall objective of this thesis is to advance the preceding fabrication technique towards the realization of high-performance nanoscale devices. The specific contributions of this thesis are: (i) the development of an improved anodization apparatus that significantly increases wafer throughput and safety, (ii) the development of electrical characterization tools for the alumina templates, and (iii) process development for the synthesis of nickel nanostructures. The remainder of the thesis is organized as follows. Chapter 2 discusses the evolution of several versions of anodization equipment that are consistently used throughout the remainder of the research. In Chapter 3,

electrical characterization techniques, which provide information regarding the template and template-substrate interface, are explained. In Chapter 4, a method for creating nickel nanostructures using electrochemical deposition is described. Finally, Chapter 5 presents a summary and conclusions of this thesis.

2.0 Development of an Improved Anodization

Apparatus

Anodization is the primary process step in the template-based nanostructure fabrication technique. Anodization is also an important process step for the formation of porous silicon, which has been a topic of significant interest because of its ability to emit visible light [9-11]. This chapter describes the contributions of this thesis towards the development of an improved anodization apparatus and its impact on the template-based nanofabrication technology research.

2.1 *Earlier Anodization Apparatus*

Although the anodization process has been around for many decades, the anodization apparatus and procedure have remained relatively unchanged. Anodization is typically performed in an apparatus similar to the one shown in Figure 2.1, which is the first improved version developed by the NRG. This is an improvement over typical cells, where the sidewalls are vertical and the wafer is mounted at the bottom or sidewall of the cell. The slanted mounting area on the sidewall was a design improvement to increase heat removal by preventing eddy currents near the wafer surface. The bottom of the cell has a removable cover, where the substrate is placed on an O-ring. When the cover is fixed securely to the bottom of the tank, the O-ring forms a seal that prevents leakage of the electrolyte from the cell. Electrical contact to the substrate is achieved by a metallic spring or strip on the metallized back of the substrate. Anodization is performed using a

few simple steps. First, the substrate is placed on the O-ring and the cover is replaced. Second, the electrolytic solution is transferred to the container. Next, anodization is performed by inducing a constant current between the substrate and the platinum cathode immersed in the electrolyte. The electrolyte is circulated during anodization to remove the heat generated by the electrochemical reactions. After the anodization is completed, the solution is transferred out of the container, and the cover is removed to retrieve the anodized substrate, which is then rinsed and dried.

Figure 2.1 – First Anodization Apparatus Developed by NRG

Although the anodization apparatus described above is fairly straightforward to implement, it has many limitations as listed below.

(i) The procedure is slow due to the time required to safely mount the sample and transfer the electrolyte before and after anodization.

(ii) The hazardous electrolytic solution has to be transferred before and after each anodization; this excessive acid handling is not only wasteful, but also poses a safety concern.

(iii) The equipment is not very versatile in terms of wafer size and shape, which is determined by the O-ring and the cover. Thus, to anodize wafers of different sizes, different anodization cells are required.

(iv) The equipment and the process are not suitable for economic volume production.

In order to overcome these drawbacks, two different versions of the apparatus were developed as a part of this thesis [14]. The improved apparatus are efficient, safe, flexible regarding wafer size, and are appropriate for commercial volume production.

2.2 Vacuum Immersion Apparatus

The first improvement on the anodization process developed as part of this thesis is the vacuum immersion apparatus shown in Figure 2.2. The apparatus consists of four main components: an aluminum structural frame, an aluminum Y-direction carriage, a Teflon Z-direction immersion assembly, and a user control panel. Currently, wafers are fed into – and taken from – the process manually. However, this system is fully compatible with a belt-driven wafer delivery and extradition system, allowing for integration into a fully automated semiconductor manufacturing facility. An important difference between this apparatus and the traditional one described above is the way the substrate is mounted on the Teflon immersion assembly. In this apparatus, the substrate is not used as a seal for the hazardous electrolytic solution; it is secured to the Teflon sample holder by means of a small vacuum port surrounding the gold spring contact, as shown in Figure 2.3. Thus, O-rings are not necessary in this setup and substrates of any size and shape can be used.

Figure 2.2 – Vacuum Immersion Apparatus

The vacuum immersion apparatus is based upon a Y-Z robotic manipulator that moves the silicon wafer through the various stages of the anodization process (Figure 2.2). Horizontal motion is realized through a unipolar stepper motor fitted with a 32-pitch gear. This gear mates with a 32-pitch rack secured to the top of the apparatus framework. The four phases of the motor are driven by the PIC16F84 microcontroller and buffered through power transistors. By varying the order and rates of phase firing, the overall horizontal motion of the carriage assembly may be controlled. Friction is reduced through the use of Nylon bearing strips placed in parallel with the toothed rack. No feedback for horizontal motion is required because travel throughout the processing cycle of each wafer is limited to the negative Y direction. Vertical motion is realized through a 12 VDC motor also fitted with a 32-pitch gear. This gear mates with an identical idling

gear secured to the carriage. These two gears mate with vertically mounted 32 pitch racks that are fastened to Teflon rods, which in turn support the solid Teflon immersion assembly. The motor is driven using an integrated circuit that is responsible for speed, direction and braking throughout vertical motion. Speed feedback is realized by an infrared transmitter-detector pair, mounted across the teeth in the rack. By taking this information into account, the PIC processor may calculate the proper depth to immerse a wafer, given the depth of the acid bath.

Figure 2.3 – Vacuum Immersion Assembly

The operator interface is realized through a control panel located remotely from the anodization system. This remote interface provides a high degree of safety not currently available in other anodization systems. The entire mechanical processing system may be enclosed in a fume hood or behind splashguards to protect the user from the process

chemicals. Only a single control cable is required to tether the operator to the reaction equipment. The anodization process may be controlled in either the Manual or Automatic mode, by properly setting the Manual / Automatic switch on the control panel. This allows a precise human interface for delicate experimental work, while maintaining full automation capabilities for large-scale production runs. In Manual mode, the operator is fully responsible for all process motion and timing. Horizontal and vertical movements are controlled by large toggle switches on the control panel. In this mode, the operator may intervene in an erroneous cycle, or perform experiments that do not follow the traditional anodization process. In Automatic mode, the user programs the time constraint for the anodization and rinse portions of the cycle through a numeric keypad on the control panel. Time constraints are entered for both the anodization and rinse cycles. The user may also enter the number of substrates that the system should process under these specifications. Once the operator confirms these settings, the system automatically performs the anodization cycle(s) according to the input specifications.

2.3 Aperture Exposure Immersion Apparatus

Although the Vacuum Immersion system outlined in section 2.2 provided several considerable advantages over the Standard Anodization Technique of 2.1, it was replaced by the more elegant process of Aperture Exposure Immersion (AEI), also developed as a part of this thesis. AEI provides a means of anodizing a select region of the sample, as opposed to its entire surface. This style of anodization allows exposure of several areas on a single wafer to varying electrolytic reactions, at a very high throughput.

AEI is similar to the previous apparatus in that the sample is vertically immersed into the electrolyte bath. However, in AEI, the sample is held in place not by vacuum, but by an aperture assembly constructed of Teflon (Figure 2.4.) This mask protects the bulk of the sample while template formation occurs in an insulated area.

Figure 2.4 – Aperture Exposure Immersion Assembly

A sample wafer is loaded by placing it on a 3.8 mm thick Cu anode contact table located inside a Teflon O-ring. The height of this table may be raised or lowered for substrates of varying thickness by adjusting the three screws that it rests upon. Next, a Teflon mask is placed on top of the sample, ensuring that the appropriate area is exposed through the

aperture. Another Teflon O-ring provides a liquid-tight seal that also holds the wafer sample in place. Four hinged arms that fold up from two opposite sides then secure this mask. On each arm is a threaded Teflon wing nut that is tightened until the mask and sample are held firmly in place.

On the first AEI constructed, a shallow relief was carved around the aperture to reduce the effects of shadowing and to increase the electrolyte circulation. It was later found that this relief compromises the strength of the mask and allows it to flex quite easily. In several cases, the electrolytic solution leaked into the chamber and caused corrosion. To correct this problem, a second mask was created using a vertical hole with no relief area. Experimentation has proven that aperture shape has little effect on shadowing.

Once the sample is firmly fixed in the AEI, the entire assembly is lowered into a 2 liter Teflon beaker containing the electrolytic solution. Connections are made as shown in Figure 2.5.

Figure 2.5 – Anodization Setup

2.4 Anodization Process

Regardless of the apparatus used, the actual anodization procedure remains essentially the same. The back of the sample to be anodized is sputtered with a layer of Al alloy at least 100 nm thick to provide a back electrical contact. This contact constitutes the anode of the electrolytic reaction. To anodize templates on insulating substrates, a small piece of conductive foil is wrapped around the edge of the sample so that contact is made between the top of the sample and the copper plate below. A Pt wire immersed in the electrolytic solution opposite the material to be anodized provides the cathode. It is important to ensure that this wire is as far from the sample as possible to produce uniform current fields and to reduce the effects of fringing. A distance of 5 cm or more is recommended.

Using the AEI technique, the sample is placed on the 3.8 mm thick copper plate electrode, creating an electrical contact. A Teflon-insulated 22AWG Al wire provides connection to this plate. The sample is fixed in place by the Teflon aperture mask and lowered into a 2 liter Pyrex beaker containing the electrolytic solution. For Al_2O_3 templates, 200 ml of H_2SO_4 and 800 ml of H_2O are mixed to create this electrolyte. The electrolyte is chilled to 1° C and circulated for the duration of the process.

Once the anode and cathode contacts are connected to the power supply, a constant current is passed through the solution and sample. Current densities in the range of 5 to 70 mA/cm^2 have been successfully used to create Al_2O_3 templates. The voltage is

recorded as a function of time by a multimeter that interfaces to a PC. Once anodization is complete, the sample is removed and rinsed in deionized H₂O, then dried with N₂.

It has been shown [21] that pore formation geometries in the alumina layer are proportional to the anodization voltage. Pore spacing (center to center of nearest neighbors) obeys a constant of 2.5 nm/V, and pore diameters are governed by a constant of 1.29 nm/V.

3.0 Capacitance Voltage Characterization of Templates

Capacitance-voltage measurement (CV) is a widely accepted means of testing metal oxide semiconductor (MOS) capacitor samples and determining device parameters such as carrier density, Fermi level, flatband voltage and threshold voltage. These values not only serve as the basis for other calculations, but also provide valuable data regarding device performance. Since anodized alumina is an insulator, CV characterization could potentially be used to characterize the templates as well as the template/silicon interface. Towards this goal, this thesis investigated MOS capacitors formed by aluminum/porous-alumina/silicon structures, as shown in Figure 3.1.

Figure 3.1 – Cross Section of a MOS Capacitor Formed by a Porous Alumina Insulator

3.1 Theoretical Background

The capacitance of an MOS structure depends on whether the semiconductor is in accumulation, depletion, or inversion, and thus is a function of the bias voltage. These regions (for a P-type wafer) are shown in Figure 3.2. CV characteristics are obtained by measuring the capacitance of a device at different bias voltages using a small superimposed AC signal.

Figure 3.2 - Typical Capacitance Voltage Scan of a P-type MOS device

Accumulation occurs when the majority carriers are attracted to the oxide-semiconductor interface by an external DC bias, which for the P-type wafers used in this research, takes place with a negative bias. During accumulation, device capacitance is independent of the bias voltage. The highly doped silicon is a good conductor, therefore the addition of majority carriers has little or no effect on the capacitance. In this region, the capacitance (C_o) may be described by:

$$C_o = \frac{\epsilon_{ox} \cdot A}{t_{ox}}$$

where t_{ox} represents the oxide thickness, ϵ_{ox} is the oxide permittivity, and A is the area of the top contact. During accumulation, the device has a capacitance that is approximately equal to the capacitance under no bias.

In the depletion region, small forward-bias voltages begin to repel holes from the interface. This repulsion creates a depletion layer in the semiconductor, just below the oxide layer. As the magnitude of this bias grows, so does the thickness of the depletion layer. This activity makes the capacitor respond as if its conducting plates were being pulled apart, thereby resulting in a smaller device capacitance. The capacitance continues to diminish as a function of bias, until a threshold voltage is reached, where inversion occurs.

Once the gate voltage reaches the threshold voltage, the device enters the inversion region, where a thin layer of negative charge is collected at the oxide/semiconductor interface. The capacitance under this condition depends upon the frequency of measurement. At low frequencies (< 100 Hz) thermally generated minority carriers (electrons in this case) approach the interface. As the forward voltage is increased, more electrons are generated, and an equilibrium condition is reached. At this point, device capacitance is once again independent of the applied voltage, and approximately equal to C_{ox} . At higher frequencies (>100 Hz) the presence of majority carriers (holes) overshadows the small numbers of electrons being thermally generated. Since the electrons cannot respond to the high frequency signal, their effects are negligible. In this case, device capacitance is lowered, as determined by the sum of the thickness of the oxide and the depletion layers attained at the onset of inversion.

The energy band diagrams of these regions are given in Figure 3.3 below.

Figure 3.3 – Energy Band Diagrams of a P-MOS Capacitor

3.2 Device Fabrication

A number of aluminum/porous alumina/P-Si MOS capacitors were fabricated using the following technique. P-type silicon substrates were first summa-cleaned, then immersed in a 1% HF bath, rinsed, and dried with N₂. Then, a 100 nm layer of Al was sputter deposited on the back of the wafer, followed by annealing at 450° C for 30 minutes. Next, a 100 nm layer of Al was deposited on the top of the wafer, which was then annealed at 400° C for 30 minutes to ensure good adhesion. The wafers were then anodized in 20% sulfuric acid at current densities of 15, 20 and 30 mA/cm². Some of these wafers were then pore widened in 5% phosphoric acid for either 3 or 6 minute durations. The purpose of pore widening is to remove any remaining barrier layer (alumina) at the alumina/silicon interface, as well as to remove impurity ions remaining from the anodization process. Finally, a number of Al contacts, each 1.59 mm in diameter, were sputtered through a shadow mask on top of the template to create the capacitors (Figure 3.4). A schematic cross section is provided in Figure 3.5. Table 3.1 lists the various samples that were used in this experiment.

Figure 3.4 - MOS Capacitors with Porous Oxide Layer

Figure 3.5 – Schematic Representation of a Single MOS Capacitor

Anodization Current Density	Not Pore Widened (number of wafers)	Pore Widened 3 min (number of wafers)	Pore Widened 6 min (number of wafers)
15 mA/cm ²	2	1	1
20 mA/cm ²	2	1	1
30 mA/cm ²	2	1	1

Table 3.1 - List of Samples Used for CV Measurement

3.3 CV Measurements

CV and IV measurements were performed on the samples by using an HP 4275 LCR meter and a probe station. Before any measurements were taken, the LCR meter was turned on and allowed to stabilize for at least 2 hours. Each wafer to be characterized was placed on a probe station and each of the individual Al pads was contacted using a needle probe, as shown in Figure 3.6. Once the sample was connected to the instrumentation cables, the microscope light was turned off, and the cover to the probe station was closed. A heavy black cloth was placed over the station to block ambient light and guard against any photocurrent effects.

Figure 3.6 - Probe Station Setup

Capacitance measurements were performed at a frequency of 1.0 MHz. The bias voltage was varied from -15 VDC to +15 VDC, using the HP 4140A DC voltage source, controlled by Lab View software. For the pore widened samples, a DC bias range of -5 VDC to +5 VDC was used to avoid excessive leakage currents. At each bias point, the capacitance was recorded by a PC connected to the HP LCR meter.

3.4 Results and Analysis

First, current-voltage (IV) measurements were performed on each capacitor sample to determine the range of bias voltages to be used for CV measurements. Typical current-voltage results for pore-widened and non-widened samples are shown in Figures 3.7 and 3.8, respectively. On each wafer, the 5 devices with the lowest leakage currents were selected for CV measurements. For each of these selected devices, three CV scans were taken.

Figure 3.7 - Typical Current-Voltage Data for Pore-Widened Samples

Figure 3.8 - Typical Current-Voltage Data for Samples With No Pore Widening

To correct for noise, these three measurements were averaged to provide a characteristic profile for a single device. This process was repeated across the 5 selected devices on each of the 12 samples, for a total of 180 measurements. The results of CV measurements on the different samples are shown in Figures 3.9 through 3.23. A Matlab program was written to analyze the resulting data and calculate device parameters such as theoretical carrier density, threshold voltage, and flatband voltage.

Figure 3.9 - 15 mA/cm², Not Pore Widened, $C_0 = 174$ pF

Figure 3.10 - 15 mA/cm², Pore Widened 3 min, $C_0 = 300$ pF

Figure 3.11 – Pad Layout, 15 mA/cm², Pore Widened 3 min

Figure 3.12 - 15 mA/cm², Pore Widened 6 min, Co = 300 pF

Figure 3.13 – Pad Layout, 15 mA/cm², Pore Widened 6 min

Figure 3.14 - 20 mA/cm², Not Pore Widened, $C_o = 143$ pF

Figure 3.15 - 20 mA/cm², Pore Widened 3 min, Co = 260 pF

Figure 3.16 – Pad Layout, 20 mA/cm², Pore Widened 3 min

Figure 3.17 - 20 mA/cm², Pore Widened 6 min, Co = 300 pF

Figure 3.18 – Pad Layout, 20 mA/cm², Pore Widened 6 min

Figure 3.19 - 30 mA/cm², Not Pore Widened, Co = 178 pF

Figure 3.20 - 30 mA/cm², Pore Widened 3 min, Co = 70 pF

Figure 3.21 – Pad Layout, 30 mA/cm², Pore Widened 3 min

Figure 3.22 - 30 mA/cm², Pore Widened 6 min, $C_0 = 320$ pF

Figure 3.23 – Pad Layout, 30 mA/cm², Pore Widened 6 min

3.5 Discussion

The CV data presented in the previous section were analyzed using a Matlab program developed for this project (Appendix A) to obtain the threshold voltage and flatband voltage of the devices. The carrier density of the substrate was also calculated and compared with the known substrate density for verification, which matched very well.

The threshold voltages obtained from the CV data are shown in Figure 3.24. In this research, threshold voltage (V_{TH}) is defined as:

$$V_{TH} = V (C_{inv} + (C_o - C_{inv}) \cdot 0.05)$$

This is the voltage at which the capacitance drops to 5% of the difference between its maximum and minimum values.

For each anodization current density, the threshold voltages are plotted for different capacitor pad of the various samples: those not pore widened, those widened for 3 minutes, and those widened for 6 minutes. It may be noted that pore widening has a significant effect on threshold voltage distribution for samples anodized at 15 mA/cm². This is an important observation since lower current densities are typically used to obtain smaller pore diameters. For samples anodized at 20 mA/cm² and 30 mA/cm², the effect

of pore widening on the threshold voltage distribution is not as obvious. However, pore widening of 3 minutes appears to produce lower variations in threshold voltages.

Figure 3.24 - Distribution of Threshold Voltage as a Function of Current Density

The CV data also show a distribution of the flatband voltage as shown in Figure 3.25.

Here, flatband voltage (V_{FB}) was calculated using the expression:

$$V_{FB} = V (C_o - (C_o - C_{inv}) \cdot 0.05)$$

This is the voltage at which the capacitance drops to 95% of the difference between its maximum and minimum values.

Although the flatband voltage shows a large distribution, an average value for the pore-widened samples was calculated to be -3.29 V. It can be seen from Figure 3.25 that the flatband voltage distribution is significantly reduced for the pore-widened samples. The improvement in V_{FB} for the pore-widened samples is believed to be due to the removal of the impurity ions left by the anodization process. This is currently being verified by photoluminescent (PL) measurements on samples with and without pore-widening. The presence of impurities is expected to create a series of peaks on PL scans. Pore-widened samples should show a lower intensity at each of these peaks indicating the removal of these impurities.

Figure 3.25 – Distribution of Flatband Voltage as a Function of Current Density

It is encouraging to note that similar characteristics have also been observed in capacitors formed on AlO:N insulators created by the oxidation of AlN thin films on silicon [25]. The AlO:N insulators, which are non porous, are being investigated as alternatives for SiO₂. A flatband voltage of $V_{FB} = -2.723$ V was obtained in [25], as shown in Figure 3.26.

Figure 3.26 - C-V Curve of a Al_2O_3 Capacitor Created by the Oxidation of AlN [25]

It is, however, important to note that the devices investigated in this thesis use *porous* alumina structures created by electrochemical means, rather than crystalline arrangements grown by epitaxial methods.

After considering C_o of each capacitor, it is simple to calculate the dielectric constant for each sample using the following relationship:

$$\epsilon_r = \frac{C_o \cdot t_{ox}}{\epsilon_o \cdot A}$$

where C_o is the oxide capacitance (F), t_{ox} is the oxide thickness (m), and A is the area of the top contact (m²). The results are given in Table 3.2 below.

Current Density (mA/cm ²)	Not Pore Widened	Pore Widened 3 min	Pore Widened 6 min
15	$C_o = 174$ pF $\epsilon_r = 1.98$	$C_o = 300$ pF $\epsilon_r = 3.42$	$C_o = 300$ pF $\epsilon_r = 3.42$
20	$C_o = 143$ pF $\epsilon_r = 1.63$	$C_o = 260$ pF $\epsilon_r = 2.96$	$C_o = 300$ pF $\epsilon_r = 3.42$
30	$C_o = 178$ pF $\epsilon_r = 2.02$	$C_o = 70$ pF $\epsilon_r = 0.80$	$C_o = 320$ pF $\epsilon_r = 3.65$

Table 3.2 - Calculated Dielectric Constants of Capacitors

It is interesting to note in Table 3.2 that the relative dielectric constant increases after pore-widening has been performed. The only instance where this does not occur is for the sample that was anodized at 30 mA/cm², and pore-widened for 3 minutes. It is important to note that this sample was damaged before measurement, and is included for the purposes of completion, and thus it may be disregarded.

The change of dielectric constant exhibited by the templates after pore-widening indicates a change in pore geometry due to the process. Although pore-widening slowly increases the diameter of the template pores, the increase in oxide capacitance (and therefore the relative dielectric constant) may at first seem contradictory. The explanation for this phenomenon is that the plates of the capacitor (the Si substrate and the Al top contact) are closer together in pore-widened samples. The reason for this is that when the Al top contact is sputtered onto unwidened samples, it creates a semi-uniform covering across the pores. In pore-widened samples, however, impurities inside

the pores are drastically reduced, and the Al top contact deposits partially inside the pore during the sputtering process (Figure 3.27).

Figure 3.27 - Effects of Pore Widening on Geometry

Although the oxide is a complex porous structure, the total capacitance, C_o , may be approximated as two capacitances in parallel. Therefore,

$$C_o = C_{air} + C_{al}$$

where C_o (F) is the total capacitance, C_{air} (F) is the capacitance due to the air-filled pores, and C_{al} (F) is the capacitance due to the alumina pore walls. Since the walls are constructed of alumina, with a dielectric constant of approximately $\epsilon_{al} = 9.7$, and the pores are filled with air, with a dielectric constant $\epsilon_{air} = 1.0$:

$$C_o = \frac{\epsilon_{air} \cdot \epsilon_o \cdot A_{air}}{t_{air}} + \frac{\epsilon_{al} \cdot \epsilon_o \cdot A_{al}}{t_{al}}$$

By microscopic inspection of devices, it is noted that the porosity, P (ratio of pores to total area), is quite high. It is also known that the thickness of alumina (t_{al}) existing after anodization is at least 200 nm. And finally, it is known that the thickness of the air layer is less than that of the alumina layer.

If these three quantities are considered across a short range, viable measurements of pore dimensions may be estimated using the relationship above. This was performed using Matlab code, shown in Appendix B. The resulting plots for samples anodized at 15, 20, and 30 mA/cm² appear in Figures 3.28, 3.29, and 3.30, respectively.

Figure 3.28 - Pore Geometry Estimation for 15 mA/cm² Sample

Figure 3.29 - Pore Geometry Estimation for 20 mA/cm² Sample

Figure 3.30 - Pore Geometry Estimation for 30 mA/cm² Sample

It can be seen from Figures 3.28 through 3.30 that for a selected thickness of the alumina and air layers, the porosity of the template increases with an increase in anodization current density, as expected. Porosity is expected to increase linearly as a function of anodization potential, as indicated by other studies [21].

Since the alumina layer is known to be between 200 and 300 nm, and the air layer is known to be thinner than the alumina layer in these pore-widened samples, we may place boundary conditions upon these relations. These conditions are shown in Figures 3.31 through 3.33. The region of valid estimation is contained in the trapezoid bounded by the conditions $x > 200\text{E-}9$, $x < 300\text{E-}9$, $y < x$, and of course $y > 0$; where x is the thickness of the alumina layer in meters, and y is the thickness of the air layer in meters.

Figure 3.31 - Viable Dimensions of Pores of 15 mA/cm² Sample

Figure 3.32 - Viable Dimensions of Pores of 20 mA/cm² Sample

Figure 3.33 - Viable Dimensions of Pores of 30 mA/cm² Sample

By examining these graphs, we can see that the porosity in each of the pore-widened samples is at least 77%. If the thickness of the alumina layer is fixed at 200 nm (as is expected to be the case) we see that the porosity of the nanostructures is even higher.

It is also interesting to note that in each case, as the thickness of the alumina is increased, the thickness of the air layer approaches an asymptote near 100 nm. Therefore, regardless of the actual porosity, the air layer is at least 100 nm thick. It may be thus inferred that the aluminum top contact, which is sputter deposited on top of the pores, enters the pores by no more than 100 nm. This number seems reasonable from prior experience, although verification for these particular samples was not performed because of imaging limitations.

4.0 Fabrication of Nickel Nanostructures

The Nanostructures Research Group has recently established collaboration with the NASA Glenn Research Center to investigate the use of nickel nanostructures for preferential synthesis of carbon nanotubes on Silicon Carbide (SiC) substrates. The nickel nanostructures will be synthesized *electrochemically* on silicon carbide substrates using the template-based fabrication technique. The objective of this thesis was to develop the process steps for the synthesis of nickel nanostructures. Due to the high cost of SiC substrates, silicon wafers were used as substrates in this thesis. The technique will be transferred to SiC substrates once the process steps are finalized.

Electrochemical synthesis was considered the preferred technique for the deposition of the nickel nanostructures since the electric current flow would be concentrated through the pores. The fabrication process development involves two steps: (i) experimental determination of nickel deposition rate, and (ii) the deposition of nickel inside the template pores. They are described in the following sections.

4.1 Electrochemical Deposition of Nickel

Electrochemical deposition of nickel was performed in an apparatus similar to the anodization apparatus, with the platinum cathode replaced by a nickel anode. A dedicated apparatus similar to the ‘Aperture Exposure Immersion’ system described in

section 2.3 was developed for this purpose to avoid contamination. The ion bath used is a solution of 800 ml of de-ionized H₂O containing 240 g of NiSO₄, 36 g of NiCl₂, and 24 g of H₃BO₃. The powdered chemicals were carefully dissolved in DI water and heated to a temperature of 60 C on a hot plate. A magnetic stirrer was used to maintain a uniform temperature. Silicon substrates coated with 100 nm thick top films of aluminum were used for the experimental determination of nickel deposition rate. An aluminum back contact on the silicon substrate acted as the cathode. The samples were mounted on the apparatus, which was then immersed in the solution. Electrodeposition was performed by exciting a constant current. The samples were then thoroughly rinsed in DI H₂O and dried with N₂ gas.

4.2 Deposition Rate Characterization

For varying deposition current densities and durations, the supply of electrons, N_e (mol), to the reaction can be calculated by the relation

$$N_e = \frac{A \cdot J \cdot t}{N_a \cdot e_c} \quad (mol)$$

where A is the deposition area (m²), J is the deposition current density (A/cm²), t is the reaction duration (s), N_a is Avogadro's number (mol⁻¹), and e_c is the charge on a single electron (C). Since each Ni⁺² ion requires 2 electrons to create Ni:

the number of Ni atoms, N_{ni} , that deposit will be one half of the number of available electrons, N_e :

$$N_{Ni} = \frac{N_e}{2} \quad (mol)$$

The expected number of deposited atoms and corresponding deposited mass is given for several reactions in Table 4.1 below.

Current Density (mA/cm ²)	Deposition Time (s)	Ni Ions Deposited (μmol)	Deposition Mass (μg)
7	300	14.0	822
14	90	8.4	493
20	90	11.7	687

Table 4.1 - Expected Depositions of Various Reactions

From these masses, and given the density of Ni ($D_{Ni} = 8.908 \times 10^6 \text{ g/m}^3$) and the deposition area ($1.28 \times 10^{-4} \text{ m}^2$), it is straightforward to calculate the thickness, T (m), of the Ni film:

$$T = \frac{M}{A \cdot D_{Ni}} \quad (m)$$

where M is the deposited mass (g), and A is the deposition area (m²).

The calculated thickness for each reaction is given in Table 4.2 below.

Current Density (mA/cm ²)	Deposition Time (s)	Deposited Thickness (nm)	Deposition Rate (nm/s)
7	300	721	2.39
14	90	432	4.81
20	90	603	6.70

Table 4.2 - Expected Thickness of Various Deposition Reactions

Electrodeposition of nickel was then performed as demonstrated by each of the reactions outlined above. Deposition times were varied from 90 s to 300 s. The thickness of the deposited nickel film was measured using an Alpha Step. The results are summarized in Table 4.3 shown below.

Sample Number	Current Density (mA/cm ²)	Deposition Time (sec)	Ni Thickness (nm)	Deposition Rate (nm/s)
041701C	20	90	110	1.222
041701D	14	90	70	0.777
041701E	7	300	40	0.133

Table 4.3 - Results of Electroplating Experimentation

The deposition rate of nickel calculated from Table 4.3 is plotted as a function of current density in Figure 4.1.

The experimental growth rate, R (nm/s), of electrodeposited nickel film on an area of 1.28 cm^2 can be determined from the following relationship:

$$R = 0.084 \cdot J - 0.453$$

where J is the current density in mA/cm^2 .

Figure 4.1 - Electroplating Deposition Rate of Ni

Photographs of the samples used to perform this analysis are shown in Figures 4.2 through 4.5.

Figure 4.2 – Sample 041701B

14 mA/cm², 90 s, 85 nm film, 125 x magnification

Displays nonuniformity with impurities, regions of localized clumping and areas where plating does not occur.

Figure 4.3 – Sample 041701C

20 mA/cm², 90 s, 110 nm film, 125 x magnification

Displays regular coverage with slight variations in grain size.

Figure 4.4 – Sample 041701D

14 mA /cm², 90 s, 70 nm film, 125 x magnification

Displays highly regular grain size with few impurities and very few regions of low coverage.

Figure 4.5 – Sample 041701E

7 mA/cm², 300 s, 40 nm film, 125 x magnification

Displays uneven coverage with localized clumping.

4.3 Discussion

Although the expected and actual deposition rates of Ni do not agree exactly, they do show that a linear relation exists. Several factors may explain these differences. The empirical equations used for estimation do not account for the losses due to electrode potentials or impurities in the solution. This fact helps to explain the offset of the current density displayed by the experimental data, which suggests the existence of a small activation energy required to overcome these potentials.

4.4 Synthesis of Nickel Nanostructures

Once several processes were performed on bare Si wafers and an approximate deposition rate was obtained, nickel nanostructures were created in anodized alumina templates. Since each pore has a lower resistance than the surrounding alumina structure, the flow of Ni^{+2} ions is localized to these areas. The ions enter each of the pores and deposit when they encounter the Si interface at the bottoms.

Samples were deposited at a current density of 10 mA/cm^2 to provide the best results, as indicated by preliminary experiments. All samples exhibited visual indications that deposition was successful – a Ni film was easily seen on each by the unaided eye. The samples are currently awaiting further imaging.

5.0 Summary and Conclusions

At the beginning of this project, a great deal of time was spent in designing an improved apparatus to facilitate faster processing of samples for the work ahead. An inexpensive system was devised that is easy to use and produces dependable samples. As a result, device throughput of the Nanostructures Research Lab has increased more than tenfold, along with an increase in safety and a decrease in chemical usage.

Preliminary electrical characterization by capacitance-voltage measurement predicted that device parameters could be obtained to complement other characterizations. It was also demonstrated that alumina-based MOS devices created in this project are comparable to those designed in other facilities, with more established techniques.

Once the quality of the oxide templates was proven, the ability to synthesize semiconductor nanostructures within the pores was demonstrated by the electrochemical deposition of nickel. This simple procedure shows the possibilities that exist for creating complex devices in nanoscale dimensions.

6.0 Future Work

To expand upon the research presented here, it is suggested to explore several areas in future work. First, it would be useful to correlate the CV measurement data with photoluminescent measurements on pore-widened templates. This would give a better understanding of the effect of pore-widening and help to support the hypothesis that the process removes or reduces impurity ions in the pores. Second, the CV measurements could be extended to devices fabricated on SiC substrates. By closely examining the data presented herein, it would be elementary to migrate to this new substrate type. Third, the Ni deposited inside pores should be characterized by microscopy to validate the predictions made in this thesis. Once this is complete, it would be incremental to fabricate Ni nanostructures on SiC substrates.

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8.0 Appendices

These appendices contain information that is supplemental to the research conducted herein. Details of the equipment, source code, and procedures are given to facilitate further work in these areas.

8.1 Appendix A – Capacitance Voltage Data Evaluation Software

% Must use Excel to convert the data file to MS-DOS CSV file type prior to use.

```
clc;
file = input('Enter the data file to evaluate (*.csv):', 's');
```

```
% read in the file
cv = csvread(file, 0, 0);
plot(cv(:,1), cv(:,2));
title('Capacitance vs. Voltage');
xlabel('Voltage (V)');
ylabel('Capacitance (F)');
```

```
% Find the slope
slope = min(diff(cv(:,2))) / min(diff(cv(:,1)));
```

```
% Find the capacitance center of the dropoff
cmid = (max(cv(:,2)) + min(cv(:,2))) / 2;
```

```
% Find the voltage center of the dropoff
for i = 1:1:size(cv, 1)
    if (cv(i,2) > cmid) & (cv(i+1,2) < cmid)
        vmid = cv(i,1);
        vmidindex = i;
    end
end
```

```
%Calculate line ends and plot regression line
vmark1 = cv(vmidindex - 10, 1);
vmark2 = cv(vmidindex + 10, 1);
cmark1 = cmid + slope * (vmark1 - vmid);
```

```

cmark2 = cmid + slope * (vmark2 - vmid);
line([vmark1, vmark2], [cmark1, cmark2], 'color', 'red');

% Evaluate 1/c^2
c2 = cv(:,2).^2;
figure(2);
plot(cv(:,1), 1./c2);
title('1/C2 vs Voltage');
xlabel('Voltage (V)');
ylabel('1/C2 (F^-2)');

% Find the slope
slope2 = max(diff(1./c2)) / max(diff(cv(:,1)));

% Find the capacitance center of the dropoff
cmid2 = (max(1./c2) + min(1./c2)) / 2;

% Find the voltage center of the dropoff
for i = 1:1:size(c2, 1)-1
    if (1./c2(i) < cmid2) & (1./c2(i+1) > cmid2)
        vmid2 = cv(i,1);
        vmidindex2 = i;
    end
end

%Calculate line ends and plot regression line
v2mark1 = cv(vmidindex2 - 10);
v2mark2 = cv(vmidindex2 + 10);
c2mark1 = cmid2 + slope2 * (v2mark1 - vmid2);
c2mark2 = cmid2 + slope2 * (v2mark2 - vmid2);
line([v2mark1, v2mark2], [c2mark1, c2mark2], 'color',
'red');

% Establish constants for calculations
es = 11.9; % Relative dielectric constant for Si
e0 = 8.854187e-14; % F/cm
q = 1.602177e-19; % C
A = 1.98e-6; % m^2 Cross sectional area of top capacitor
plate
ni = 1.02e+10; % /cm^3 Density of intrinsic Si
phi_m = 5.17; % eV Work Function of P+ Si
xs = 4.05; % eV e- affinity of P+ Si
tox = 100e-9; % m Oxide Thickness
noc = 1e10; % / cm2
Eg = 1.12; % eV

% Acceptor Density
na = 2 / (-q * es * e0) * (-1 / slope2 / A);
ndtext = sprintf('Na = %0.5g /cm3', na);
disp(ndtext);

% Find Capacitance at Flatband and Threshold Points

```

```

cdiff = max(cv(:,2)) - min(cv(:,2));
cfb = min(cv(:,2)) + 0.95 * cdiff;
cth = min(cv(:,2)) + 0.05 * cdiff;

% Find the Voltages that Correspond to the Capacitances
for i = 1:1:size(cv,1)
    if cv(i,2) > cfb
        vfb = cv(i,1);
    end
end

vfbtext = sprintf('Vfb = %.05g V', vfb);
disp(vfbtext);

for i = size(cv,1):-1:1
    if cv(i,2) < cth
        vth = cv(i,1);
    end
end

vthtext = sprintf('Vth = %0.5g V', vth);
disp(vthtext);

```

8.2 Appendix B – Pore Geometry Estimation Software

```
c15 = 174e-12;
c20 = 143e-12;
c30 = 178e-12;

e = 8.85e-12;

Pair = 0.5:0.1:0.9;
Pal = 1-Pair;
Aair = 2e-6.*Pair;
Aal = 2e-6.*Pal;

tal = 10e-9:10e-9:1000e-9;

figure(1);

for i = 1:size(Aair,2)
    tair15 = (e*Aair(i)) ./ (c15 - (9.7*e*Aal(i)./tal));

    for j = 1:size(tair15,2)
        if (tair15(j)>0)
            plot(tal(j:size(tal,2)),tair15(j:size(tair15,2)))
            hold on;
            break;
        end
    end
end

axis([0 1000e-9 0 600e-9]);

xlabel('Thickness of Alumina Layer (m)');
ylabel('Thickness of Air Layer (m)');
title('Allowable Dimensions of 15 mA/cm2 Sample Calculated
at Various Porosities');

figure(2);

for i = 1:size(Aair,2)
    tair20 = (e*Aair(i)) ./ (c20 - (9.7*e*Aal(i)./tal));

    for j = 1:size(tair20,2)
        if (tair20(j)>0)
            plot(tal(j:size(tal,2)),tair20(j:size(tair20,2)))
            hold on;
            break;
        end
    end
end
```



```

end

axis([0 1000e-9 0 600e-9]);

xlabel('Thickness of Alumina Layer (m)');
ylabel('Thickness of Air Layer (m)');
title('Allowable Dimensions of 20 mA/cm2 Sample Calculated
at Various Porosities');

figure(3);

for i = 1:size(Aair,2)
    tair30 = (e*Aair(i)) ./ (c30 - (9.7*e*Aal(i)./tal));

    for j = 1:size(tair30,2)
        if (tair30(j)>0)
            plot(tal(j:size(tal,2)),tair30(j:size(tair30,2)))
            hold on;
            break;
        end
    end
end

axis([0 1000e-9 0 600e-9]);

xlabel('Thickness of Alumina Layer (m)');
ylabel('Thickness of Air Layer (m)');
title('Allowable Dimensions of 30 mA/cm2 Sample Calculated
at Various Porosities');

```

8.3 Appendix C – Aperture Exposure Immersion Apparatus

The AEI apparatus was designed and built for use in electrolytic deposition and synthesis of semiconductor nanostructures. Because of the acidic nature of most anodization solutions, Teflon (PTFE) was selected as the material for construction.

Each AEI apparatus consists of two main components – the faceplate and the base. Bases and faceplates may be interchanged to provide more versatility in experiment design. For example, a single base may be used with several faceplates with varying aperture sizes to provide control over the size of the anodized area.

8.3.1 Base Construction

The base is constructed from 2” Teflon stock. All cuts are made with a band saw using a 0.250” thick 6 TPI blade. All holes normal to the plane of the stock are drilled with a Craftsman drill press. The angled back contact access hole is drilled with a 1/8” x 6” long bit in a right angle power drill. To create the recessed area for the back contact table, use a 2 3/8” hole saw in a drill press to rough the outline. Remove the excess material by hand with a chisel. Refer to Figure 8.1 for detailed plans.

Figure 8.1 – Detailed Construction Plans for AEI Base

8.3.2 Faceplate Construction

Faceplates are constructed from 0.500" Teflon stock. All cuts were made with a band saw using a 1/4" thick 6 TPI blade. The bevel on the edge of the faceplate provides clearance for the wing nuts when they are hinged into position. These cuts are made by tilting the table to 45°. Refer to Figure 8.2 for details.

Figure 8.2 – Detailed Construction Plans for AEI Faceplate

Once all cuts are made, the face opposite the bevel is polished to a mirror finish. Fasten well-moistened 220 grit wet/dry sandpaper to a flat surface and polish in a random orbital manner. Rinse the sandpaper and repeat several times until smooth. Repeat the process with 600 grit wet/dry sandpaper until a reflection can be seen.

When polished, dry thoroughly and select a Viton O-ring that is slightly larger than the aperture of the faceplate. Secure the O-ring to the polished side with marine-grade silicone sealant. Use only a small amount of silicone so that it does not cover the O-ring where it will contact the sample wafer. See Figure 8.3 for details.

Figure 8.3 – Detail of O-Ring Seating on Faceplate