

**OPTICAL PROPERTIES AND APPLICATION OF TEMPLATE
ASSISTED ELECTRODEPOSITED NANOWIRES AND
NANOSTRUCTURES**

by

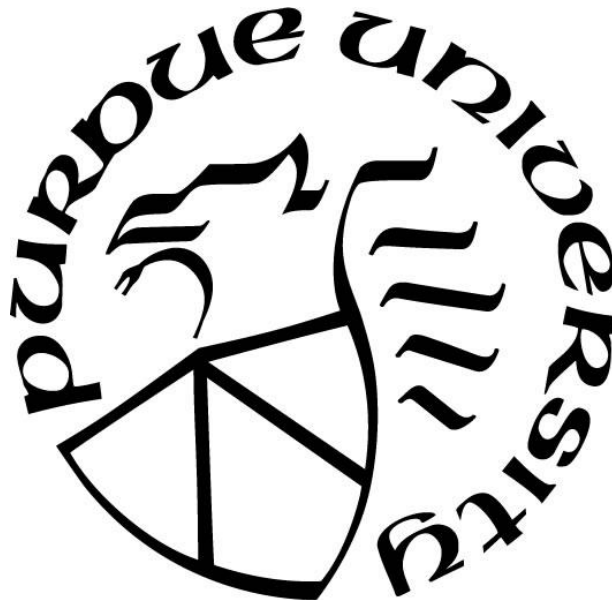
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Dedicated to
my parents Mr. Md. Badiuzzaman & Mrs. Rokeya Begum,
and my loving wife Musbiha Binte Wali.

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LIST OF ABBREVIATIONS

AAO	Anodic alumina oxide
AFF	Areal Fill Fraction
AR	Antireflective
BNW	Branched nanowire
BPAA	Branched Porous Anodic Alumina
CVD	Chemical vapor deposition
EDX	Energy Dispersive X-ray
FESEM	Field Emission Scanning Electron Microscope
HBPAA	Hierarchically Branched Porous Anodic Alumina
IO	Inverse Opal
ITO	Indium tin oxide
IR	Infrared
MWIR	Mid-infrared
NH	Nanohole
NIR	Near infrared
NW	Nanowire
PAA	Porous Anodic Alumina
PIO	Photomodified Inverse Opal
pR	p-polarized Reflectance
RBNW	Randomly Branched Nanowire
SAED	Selective area electron diffraction
SLG	Single layer graphene
SPR	Surface Plasmon Resonance
sR	s-polarized Reflectance
UV-vis	Ultraviolet-visible
VLS	Vapor-liquid-solid

ABSTRACT

Self-assembled templates allow the creation of many complex arrays of nanostructures, which would be extremely difficult and expensive, if not impossible, to realize using any of the other available fabrication techniques. The complexity of these advanced nanostructures, synthesized using the various template assisted electrodeposition techniques, can be controlled to nanometer scale range by tuning the structural properties of the template, which is achieved by adjusting its various growth parameters during the self-assembly process.

Electrodeposition allows the creation of arrays of various metallic and semiconducting nanostructures. Monitoring the electrodeposition conditions permit the creation of single crystalline nanostructures of a particular material, or the formation of heterostructures using multiple electrodeposition steps. This work demonstrates the template assisted electrodeposition of vertically aligned nanowire arrays, both straight and branched, of metals, and a direct bandgap, III-V semiconductor, indium antimonide (InSb), which has one of the smallest known bandgap of any material. The template assisted electrodeposition of metallic, and InSb inverse opal (IO) structures is also shown, and the fabrication of a novel zipper shaped nanostructure by laser photomodification of a Ni IO structure is reported.

The optical characterization of the various nanostructures realized in this work have been examined. The results from this work confirm the ability to tune the optical spectra of nanostructures of the same material with similar volume fill fractions by structural modulation, where the different optical responses can be attributed to the structural differences of the actual structure as opposed to the material properties of the solid.

1. INTRODUCTION

1.1 Motivation

The ability to fabricate and synthesize nanostructures is a crucial factor that is required to create nano-scale devices. Quantum devices have generated a considerable amount of interest that arises from the possibility of confining the movement of electrons in more than one direction in semiconductors. The prospect of multidirectional confinement in nanostructures has been made possible by the various techniques of nanofabrication.

Nanowires are nanostructures that have diameters in the nanometer range and have length, which may span several hundreds of microns. In a one-dimensional (1D) nanowires the movement of electrons is spatially constrained in the lateral (radial) direction, but is not constrained along the (axial direction) length. In recent years, the synthesis, characterization and applications of nanowires have become active areas of research. Template assisted fabrication of semiconducting and metallic nanowires open an exciting new frontier where complex nanowire morphologies may be realized by controlling the structural parameters of the template. This would grant the ability to control and tune the diameter, pitch, aspect ratio, length and the composition of the nanowires. While several methods of nanowire growth have been reported in literature, template assisted electrodeposition has provided the greatest range of flexibility in growing nanowires of various structural parameters. Moreover, the capability to synthesize nanowire arrays offer great advantages by growing them in arrays of ordered porous structures.

One of the most common templates used for the synthesis of nanowire arrays are Porous Anodic Alumina (PAA) templates. The PAA templates, made of porous aluminum oxide, have several advantages that include their rigidity and ability to withstand relatively high temperatures, an aspect that allows annealing of nanowires within the PAA template to improve their crystallinity. The PAA templates are also very well suited for the electrodeposition process, since aluminum oxide (the material composition of PAA) is an insulator and therefore does not interfere with the electrochemical process. The nanowire arrays grown in the PAA templates are fairly free-standing and all align in a unidirectional fashion.

1.2 Indium Antimonide (InSb)

Among the various semiconducting materials, Indium Antimonide (InSb) has gained a significant amount of interest and recognition for many of its impressive intrinsic qualities. It is a III-V semiconductor material with a direct energy band gap of 0.17 eV at 300 K, which rises to about 0.23 eV when the temperature drops to 80 K. It has one of the lowest (direct) bandgap energy of any material. Since the bandgap (E_g) of a material is related to the corresponding cut-off wavelength ($\lambda_{\text{cut-off}}$) for photon generation (due to electron-hole recombination), through the following equation:

$$\lambda_{\text{cut-off}} [\text{nm}] \approx \frac{1240 [\text{eV} \cdot \text{nm}]}{E_g [\text{eV}]} \quad (1.1)$$

Therefore, bulk InSb with $E_g \approx 0.17$ eV at room temperature, will have an approximate cut-off wavelength ($\lambda_{\text{cut-off}}$) of:

$$\lambda_{\text{cut-off, InSb}} \approx \frac{1240}{0.17} \approx 7294 \text{ nm} = 7.294 \mu\text{m} \quad (1.2)$$

With a cut-off wavelength of around $\sim 7 \mu\text{m}$, InSb is a popular and an ideal material for detection of light in the infrared (IR) region of the spectrum. InSb is also known to possess one of the highest ambient-temperature electron mobility ($\mu_e \sim 80000 \text{ cm}^2/\text{Vs}$), and have a ballistic length of up to 700 nm at room temperature, which makes it a potential candidate for high speed electronic devices, and magnetoresistive sensors. Considering the properties of bulk InSb, it has become an active area of research to understand their effects in InSb based nanostructures and implement these qualities in various applications.

InSb nanowires (NWs) are being studied extensively to overcome the disadvantages and setbacks of working in cryogenic temperature and the generation of high dark current, which are demonstrated by photodetectors made up of narrow bandgap materials. The degradation of the detection capability in narrow band-gap materials, such as InSb, in the larger frequency range stems from the higher dark current due to the electron-hole pair generation-recombination, and

minority carrier diffusion. Planar photodetectors usually subdue the dark current generation by decreasing the absorption volume, which to some extent compromises the responsiveness of the device. Nanowire and nanostructure based photodetectors have the advantage of having an extremely small absorption volume that allows the suppression of dark current, and at the same time their optical coupling properties and shorter response time increases their responsiveness. Furthermore, NW or nanostructure based detectors provide an increased lifetime of the photo-generated carriers as well as a low transit time that allows these nano-sized detectors to demonstrate a higher gain than their bulk counterparts [1].

The motivation behind these studies is driven by the idea of quantum confinement in InSb NWs and nanostructures with sizes smaller than its Bohr exciton radius, which is about ~65 nm for InSb. As explained earlier, it is believed that in nanowire based photodetectors, due to their size shrinkage, will cause suppression of dark currents. Furthermore, the suppression of phonon scattering in nanostructures allows NW based photodetectors to work at an elevated temperature condition. The nanowires that are considered as one-dimensional structures with high surface to volume ratios having shortened carrier transit time and prolonged photocarrier life time, are suitable for photodetectors having a high signal to noise ratio. These qualities of InSb NWs make them a potential building block for interesting optoelectronic devices.

1.3 Template Assisted Electrodeposition

This thesis discusses in detail about the growth and fabrication of InSb NW arrays, both straight and branched, and nanostructures inside the pores and voids of intricately structured, highly regular- hexagonally close packed (hcp), self-assembled templates with complex morphologies, using electrodeposition techniques. The allure of using these template assisted electrodeposition method is that this bottom-up approach to fabricate complex advanced nanostructures can be controlled down to the nanometer scale range by controlling and tuning the structural parameters of the template through the regulation of the various growth parameters during the self-assembly process.

A major advantage of the electrodeposition approach for the fabrication of nanostructures is the ability to grow many elements and compounds, including InSb, at or near room temperature under atmospheric conditions [2-4]. As reported and demonstrated in this work, template assisted electrodeposition of InSb nanostructures at room temperature produced nanocrystalline structures,

which upon annealing transforms the entire structure to single crystalline, without any visible dislocations, twin defects or stacking faults. It was also discovered that the electrodeposition of crystalline InSb nanostructures, even without annealing, is possible in templates with very small structural dimensions that is caused by the confinement of the crystal planes in the reduced dimensional channels [5].

Furthermore, electrodeposition allows the creation of arrays of various other metallic nanostructures, and semiconductor-metal heterostructures. Apart from NW arrays, this work also discusses and reports the template assisted electrodeposition of metallic nickel (Ni), and novel InSb based inverse opal (IO) structures, using opal templates of self-assembled monodispersed polystyrene microbeads. The fabrication of a novel metallic zipper shaped nanostructure was also demonstrated by a laser photomodification technique on a Ni IO structure that transforms a highly symmetric hcp structure of the IO to a controlled asymmetric (unidirectional zipper shaped) structure without the use of any lithographic techniques.

1.4 Optical Characterization of Nanostructures

Even though the term ‘Nanotechnology’, the study and science of manipulating matter in nanometer scale, has been coined and used since the middle of the 20th century, it has been discovered in recent times that nanoparticles have been inadvertently used in artifacts by human beings for nearly two millennia or possibly more. The Lycurgus cup, for instance, has been around since Roman time, is a classic example of the use of metallic nanoparticles to change the appearance of the object, Figure 1.1 [6]. This dichroic cup appears green when observed using reflected light, and red when light is transmitted through the cup from a light source behind it. Scientists have discovered that the presence of metallic nanoparticles in the cup, causes this phenomena. In the reflectance mode the metallic nanoparticles in the cup are coarse enough to reflect light without eliminating transmittance, while in transmission mode the same particles while scattering the blue end of the spectrum allows the passing of red light.

Similarly, nanoparticles have been discovered in the beautiful stained glass windows of many medieval churches and mosques. While our ancestors, discovered that adjusting gold in molten glass resulted in a beautiful reddish tint, whereas addition silver colored the glass brilliantly yellow, they did not understand the reason behind these optical characteristics. It was not until the

advent of many of the technologies that are available now, that scientists have only started understanding the physics behind the optical characteristics of materials in their nanostructures.



Figure 1.1. 4th century, Roman-era Lycurgus cup, a dichroic cup that contains metallic nanoparticles in the glass that causes the change in color of the cup when viewed in reflectance mode or transmittance mode. Figure from [6].

Tailoring the structural properties and dimensions of a nanostructure allows the control and manipulation of the optical and photonic properties of a material. This increasingly important area of research has piqued the curiosity of scientists to explore various methods of tuning the optical properties of a material. Various nanostructures have been researched for applications ranging from antireflective (AR) coatings, to photovoltaics and photodetectors, to photonic crystals for allowing efficient coupling of light. Nanotechnology allows the controlled structural modulation of a material to tune the optical characteristics by adjusting and controlling the geometry of the nanostructure. The optical characterization of the various structures realized in this work have been examined, and their results confirm the ability to tune the optical spectra of nanostructures of the same material with similar volume fill fractions by structural modulation alone. The different optical responses are attributed to the structural differences of the actual structure as opposed to the bulk property of the material.

1.5 Outline

This work has been segmented into several chapters, with each of them giving a broad idea of the various concepts and experimental procedures. Since the template assisted nanowire growth plays a major role in this work, the properties and growth mechanism of porous anodic alumina (PAA) templates has been discussed in detail in Chapter 2. It also discusses about the various methods of tuning the structural properties of the PAA to create a template for the desired nanowire parameter. The chapter also discusses about the ways of creating a hierarchically branched PAA for use in fabricating possible branched nanowire arrays.

The third chapter, Chapter 3, focusses on the various fabrication techniques used to grow semiconducting, specifically InSb, and metallic nanowires. The effect of crystallinity as a function of nanowire diameter has also been studied prior to, and post annealing [5]. The various NWs grown have been analyzed by observing them under a field effect scanning electron microscope (FESEM), high resolution transmission electron microscope (HRTEM) and x-ray diffraction (XRD) to confirm their crystallinity and composition. Chapters 4 and 5, discusses about the wavelength dependent absorption of vertically aligned NW arrays. Chapter 4 focusses on randomly branched hierarchical NW arrays, while Chapter 5 focusses on straight NW arrays, both of which have interesting wavelength dependent optical characteristics that has been explained as a result of the waveguiding modes present in the nanowires [7].

In Chapters 6 template assisted electrodeposition of IO structures have been discussed in great detail, while reporting the fabrication of a novel zipper shaped nanostructure using a laser based photomodification technique on the fabricated IO structure. The final chapter, Chapter 7, presents the concluding remarks of this thesis.

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2. POROUS ANODIC ALUMINA MEMBRANES

2.1 Introduction

Porous Anodic Alumina (PAA) has been, and is being used as a template for the growth and fabrication of nanowires (NW) and nanostructures of materials for a wide variety of applications ranging from optoelectronic to magnetic to biological sensing. PAA templates have also been used for filtration and microfluidic applications. Thin PAA templates can be fabricated by anodizing layers of aluminum (Al) deposited on a hard and rigid substrate, such as a Si wafer or a transparent glass surface [1, 2]. This chapter, and the next two, primarily focuses on the template assisted fabrication of NWs in free standing PAA membranes, which are created by anodizing thin sheets of ultra-pure aluminum (Al). The first part of this chapter discusses about the physics and chemistry of the formation of hexagonal close packed (hcp) structures on a PAA membrane. The middle section, discusses about the methods for improving the regularity of pores on such a structure, and the final section describes about the methodology for structural modulation of a PAA template to create branched structures. A portion of the work presented in this chapter has been published by the author in the Proceedings of the *IEEE* 18th Biennial University/Government/Industry Micro-Nano Symposium (UGIM), 2010 [2].

Under atmospheric conditions, aluminum (Al) has a natural tendency to oxidize and form a very thin layer of alumina (aluminum oxide- Al_2O_3) which protects the metal from further oxidation. If the Al is anodized in an electric field in a neutral or an alkaline solution, with a pH greater than 5, the self-limiting alumina is further oxidized to form a planar barrier type oxide, whereas a porous oxide is formed when anodized in certain acidic conditions. This type of porous oxide is known as anodic aluminum oxide (AAO) or porous anodic alumina (PAA), which have been studied for more than six decades [3]. This work will focus on the structure and application of these PAA membranes.

2.2 Structure of Porous Anodic Alumina (PAA) Membranes and Overview

Long term anodization of Al in certain acidic solution (electrolyte) results in the formation of highly ordered nano-pores, also known as alumites, which form an orderly arrangement of closed packed hexagonal cells. The pores propagate into the Al surface due to an electric field

enhanced dissolution of alumina at the oxide/electrolyte front and the oxidation at the alumina/aluminum interface. Each ordered hexagonal cell contains a central cylindrical pore that projects in the direction normal to the surface of the Al underneath the oxide layer. The diameter of the pores depends strongly on the anodization conditions, and can range from one third to about half of the cell size. A self-organizational process dominates during the formation of PAA membranes, where the repulsive forces between the neighboring aluminum/alumina interfaces causes the formation of ordered and regular hexagonal close packed (hcp) pore arrays. The pores are terminated at the oxide/Al interface in the form of a hemispherical oxide barrier layer, which will be discussed later in detail.

Initially the pores form randomly on the planar Al surface with preferences on spots with the highest electric field concentrations such as any microscopic cracks, crevices and depressions on the Al surface. As anodization progresses these randomly formed pores reorganize themselves, by merging and splitting, to form very regular hexagonal pore packed arrangement at the bottom of the PAA membranes. Therefore, it is quite common to see pores on a PAA membrane to be distributed in a very disorderly manner at the top surface, but the cross section reveals very straight pores at the bottom of the PAA membrane at the end of a relatively long anodization step.

At the end of the, afore mentioned, relatively long anodization step or process, the removal of the PAA membrane from the Al surface reveals a highly ordered concave pattern on the surface of the Al left behind by the hemispherical oxide barrier layer at the pore bottoms. Repeating the anodization process on the now pre-textured Al surface results in the nucleation of pores on the concave impressions, which results in pore arrays that are much more regular than the PAA membranes formed after the first step of anodization. This replication of a honey-comb structure in Al by repeating the anodization process in multiple steps has been pioneered by Masuda *et al.* [4], and has been used extensively in this work. Figure 2.1 shows the schematic of a very regular hcp pore arrays of a PAA membrane depicting the central pore in each hexagonal cell terminating in a hemispherical barrier at the pore bottom with a thin (relative to the cell wall thickness) barrier layer.

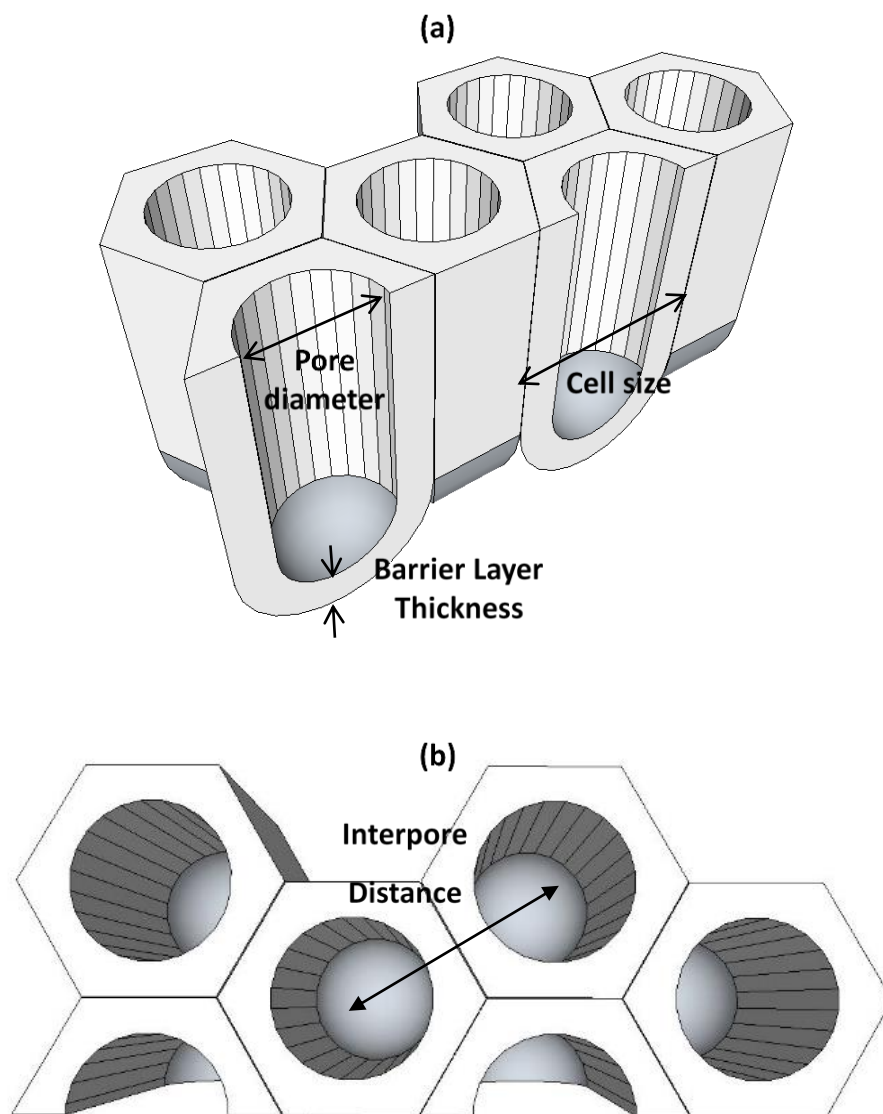


Figure 2.1. Schematic of the pores in a Porous Anodic Alumina (PAA) membrane. (a) Cross-sectional view of a PAA membrane illustrating the hexagonal close packed (hcp) structure showing the cell size, individual pore diameters, and the terminating hemispherical barrier layer in each cell. (b) Top view of a PAA membrane highlighting the Interpore distance (center to center distance between two adjacent pores). Image taken from [1].

2.3 Pore formation and growth in PAA membranes

It must be noted that the formation of PAA (Al_2O_3) occurs during the anodization of Al in an acidic electrolyte under certain conditions. The barrier type of Al_2O_3 on the other hand forms in the presence of a neutral or alkaline solution (pH greater than 5) due to the very high Faradaic current efficiency, close to a 100% [5], which causes the formation of a plain non-porous layer of oxide that extends throughout the exposed surface of Al to form an insulating barrier oxide layer. In the case of barrier anodic alumina, any protons or hydrogen ions generated as the byproduct of the hydrolysis process, get locally neutralized by the base, and as a result this greatly thwarts growth and propagation of the alumites (pores) into the aluminum substrate.



Due to the neutralization of hydrogen ion, when anodizing Al at higher pH, the electric field enhanced alumina dissolution at the electrolyte/oxide interface is absent. Therefore, this keeps the barrier type alumina formation uniform.

The formation of porous aluminum oxide membrane or film is possible when the exposed surface of Al is anodized in the presence of an acidic electrolyte. Some of the more common acidic electrolytes used for anodization are sulfuric acid (H_2SO_4), oxalic acid ($\text{H}_2\text{C}_2\text{O}_4$) and phosphoric acid (H_3PO_4). The Faradaic efficiency in the formation of PAA is about 70% or lower than the efficiency of forming barrier type alumina layer [5]. The progression of pores into the surface of Al attributed due to the balanced dissolution of oxide and formation of oxide reaction taking place at the electrolyte/oxide, and oxide/Al interfaces respectively at the hemispherical pore bottoms. The diameters of the pores, which depend on the type of acid used in the anodization, can range anywhere from about 10 nm to more than 150nm. Furthermore, the diameter and pitch of the pores in a PAA film also depend on the anodization voltage, type of acid and the pH value of the electrolyte, as explained in Figure 2.2.

Pores formed during the anodization process are found to be the smallest when anodized in a sulfuric acid (H_2SO_4) solution with pore diameters ranging from ~15nm to ~55nm, depending on the anodization voltage, temperature and concentration of electrolyte. Medium sized pores, with diameters ranging from ~30nm to ~80nm, are obtained by anodizing Al in an oxalic acid ($\text{H}_2\text{C}_2\text{O}_4$)

solution., while phosphoric acid (H_3PO_4) based electrolyte solutions are reserved for creating PAA films with the largest diameters of above 100nm [6].

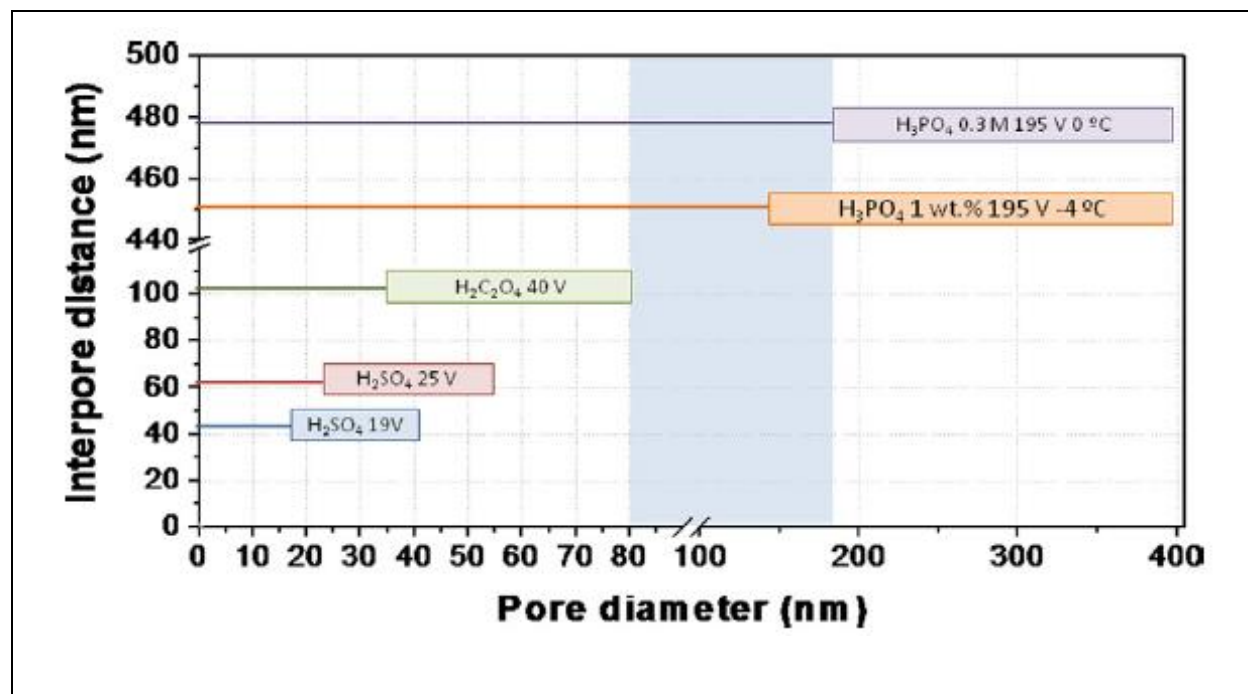


Figure 2.2. Plot showing the pore diameter, and the corresponding inter-pore distance, in a PAA template that can be controlled by the concentration and the type of the acid used in the electrolyte, anodization voltage, and temperature of the electrolytic cell. Figure from [6].

An ability to tune the structural properties of the PAA membranes by varying the diameter, pitch, and thickness (pore length) of the porous oxide, can be achieved by adjusting the anodization voltage, type of acid and anodization time. The pore fraction (fraction of the porous oxide surface covered in pores) on the surface of the PAA membrane may also be controlled by a technique known as ‘pore-widening’, where the porous membrane’s pore diameter may be increased by widening the pore, using a H_3PO_4 solution. This causes the pores to get bigger, but maintain the original pitch, which provides additional leverage for controlling the areal fill fraction (AFF) of pores on the surface of the PAA membrane.

Figure 2.3a shows the FESEM images of a PAA surface that has a surface pore diameter of ~50 nm with a center to center distance between two adjacent pores, pitch, of ~110 nm. The PAA template was then treated to a pore widening solution of 5% H_3PO_4 solution, heated to 30°C, for ~40 minutes. The PAA template was then found to have a widened pore diameter of ~65 nm,

while maintaining the same pitch of ~ 110 nm, Figure 2.3b. The SEM images were taken, in both instances, after the templates were deposited with a ~ 10 nm thick film of Au. Figure 2.3c shows the plot of pore diameter vs. widening time for a similar study done by another group [7].

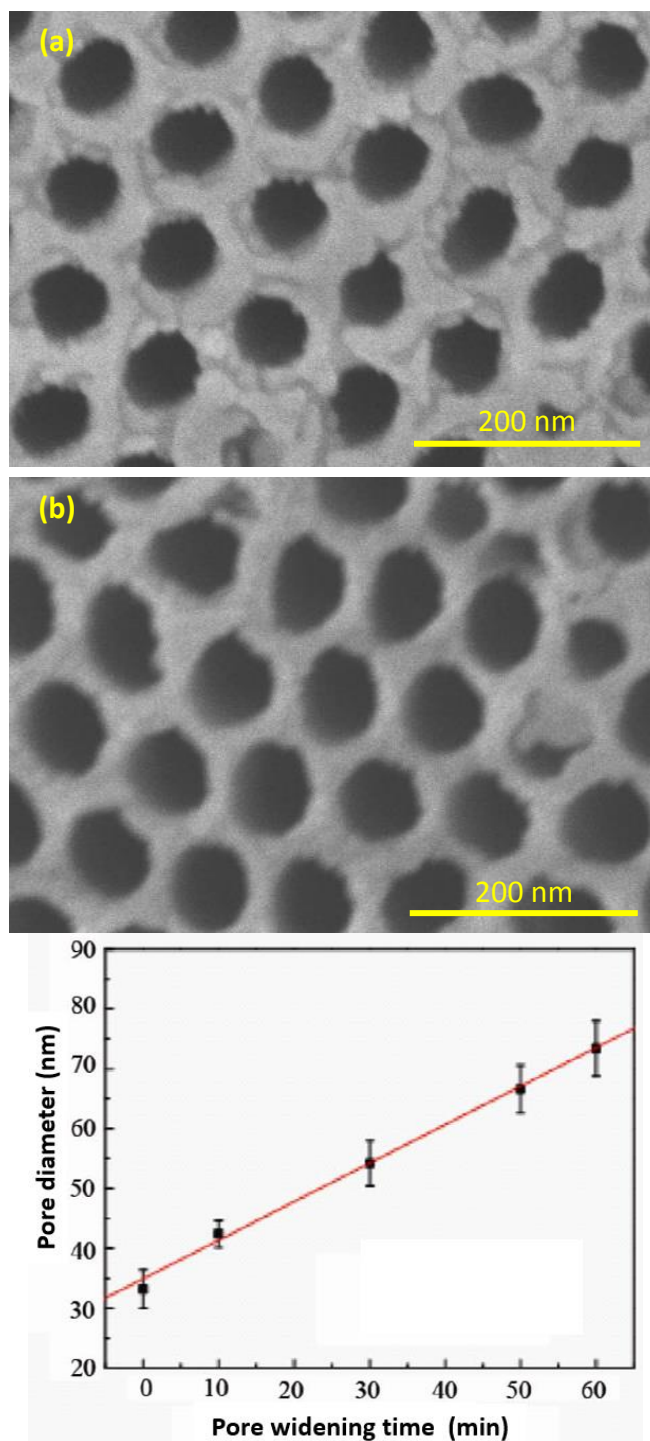


Figure 2.3. SEM images of PAA membranes before and after the pore widening process. (a) SEM image of PAA membrane prior to pore widening (diameter ~ 50 nm, pitch ~ 110 nm). (b) SEM image of the PAA membrane after pore widening (diameter ~ 65 nm, pitch ~ 110 nm). In each case, the PAA membranes have been evaporated with a ~ 10 nm thick layer of Au prior to taking the SEM image. (c) Plot of pore diameter vs. pore widening time, Figure 2.3c from [7].

The terminating hemispherical barrier layers that forms at the interface between the alumina and the unanodized Al, at the pore bottoms, have a thickness that can range from 10 nm to over 100nm. The hemispherical barrier layer maintains a constant thickness throughout the anodization process as the barrier layer dissolves (at the electrolyte/oxide front) and regenerates (at the oxide/Al interface) at a constant rate. This balance in the rates allows the formation and further propagation of pores into the Al with a constant barrier layer thickness. Figure 2.4a shows the cross-sectional FESEM image of a hemispherical barrier layer at the pore bottom, whereas Figure 2.4b shows the bottom surface of the unopened barrier layers of the PAA membrane.

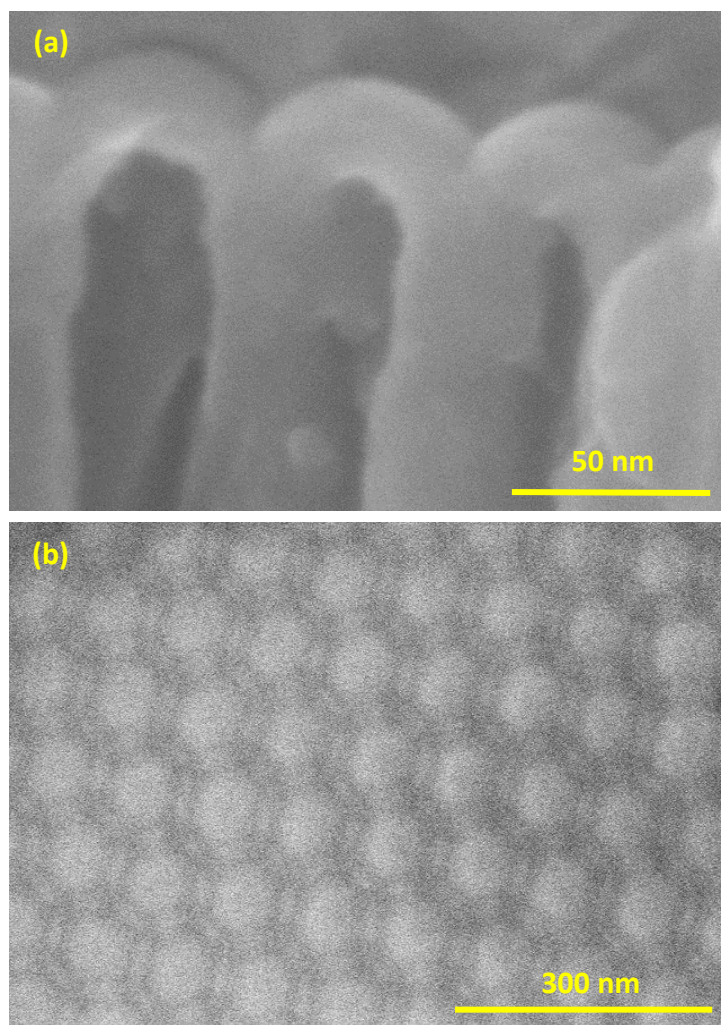


Figure 2.4. SEM images of a PAA membrane. (a) FESEM image of the cross-section of a PAA membrane focusing on the thin hemispherical pore bottom oxide barrier layers. Figure from [2]. (b) FESEM image of the bottom surface of a PAA membrane with the unopened pore bottom surface of the hemispherical barrier layers.

It is difficult to obtain a highly ordered hcp structure of PAA in relatively large areas (range of mm^2), but with pre-texturing of Al, with highly ordered hexagonal close packed dimples or dents, prior to the anodization, have yielded long range ordered cell structures [8]. This calculated pre-texturing process can be achieved by using lithographic techniques or by multiple step anodization, where the depressions left by the first step of anodization (as shown in the schematic of the cross-sectional view of the PAA layer in Figure 2.5) would act as future pore initiation sites.

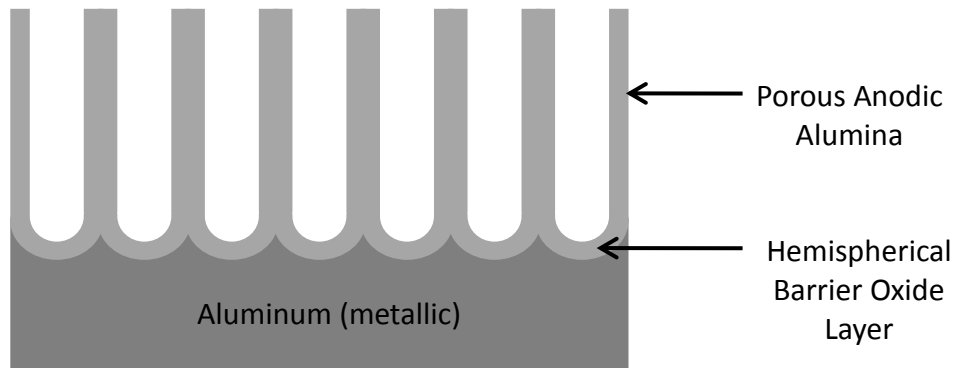


Figure 2.5. Schematic of the cross-sectional view of the formation of a Porous Anodic Alumina (PAA) membrane. The hcp arrangement of the hemispherical barrier layer at the bottom leaves behind depressions on the Al that would act as future pore initiation sites for multiple step anodization process.

During the anodization process of PAA membranes, two distinct types of oxides are observed. The cell walls are made of the first type of oxide that are made of pure and compressed aluminum oxide (alumina), which is formed as a result of the expansion and rearrangement of pores during PAA formation. The other, less dense amorphous oxide that surrounds each of the pores forms the second type of oxide. Regardless of the electrolyte type and the anodization voltage, the ratio of the dense inner oxide thickness to the outer portion is a constant 0.2 ± 0.02 for well-ordered hexagonally arranged pores [9]. Therefore, the outer oxide is roughly five times as thick as the inner cell walls. The FESEM image, Figure 2.6, shows the clear distinction between the two types of oxides. The lighter colored walls of the circular pores (alumites), and the hexagonal cells are the oxides with higher packing density, whereas the darker regions in between the two are the less dense amorphous oxide regions of the PAA structure.

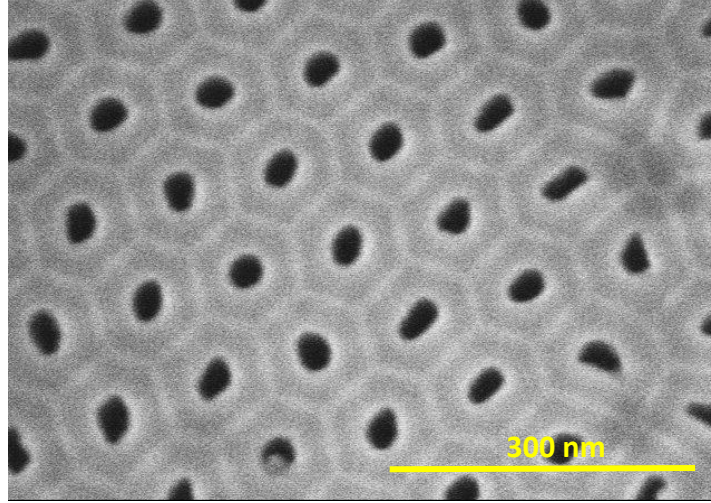


Figure 2.6. FESEM image of a PAA membrane showing the two distinct densities of the aluminum oxide in each hexagonal porous cell. The brighter hexagonal pore walls are the compressed alumina pore walls with higher packing density as opposed to the darker regions.

2.4 Electrochemical and mechanical process of pore formation

Thin layers of native, self-limiting oxides that are formed on the surface of Al, on exposure to atmospheric oxygen, have the capability to support a huge electric field gradient (in the order of several MV/cm) across it. Even the most planar Al surfaces will display a large number of pits and deformities at a nanoscopic scales. These pits and surface indentations acts as pore nuclei sites during the anodization process. Aluminum ions, formed at the oxide-Al interface in the very beginning of anodization process, get distributed in the oxide layer.



At the electrolyte-alumina front, at the bottom of each porous oxide, the electrolysis of water splits water molecule to form oxygen (O^{2-}) and hydrogen ions (H^+).



The O^{2-} ions migrate through the oxide barrier layer and reaches the oxide-Al interface due to the electric field. On reaching the Al interface, the O^{2-} reacts with Al^{3+} ions to form aluminum oxide (Al_2O_3), which allows the propagation of the porous oxide barrier layer into the Al surface.



Majority of the oxide goes into the formation of the sidewalls of the alumites, therefore the activity, such as the hydrolysis of water, at the circle of intersection between the pores cylindrical walls, and hemispherical segment of the pore bottom, are the primary cause for the propagation of pore into the Al surface [5]. The schematic of the process has been shown in Figure 2.7.

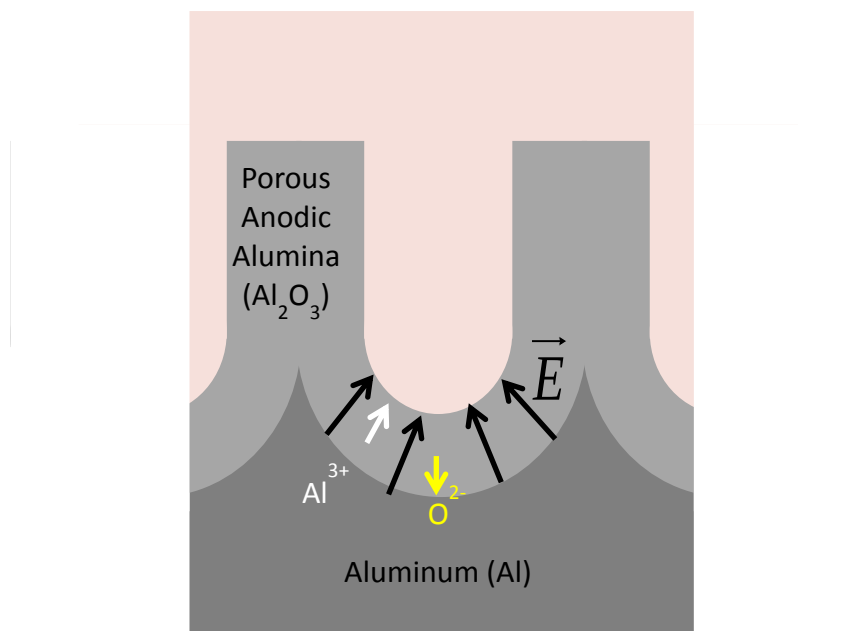
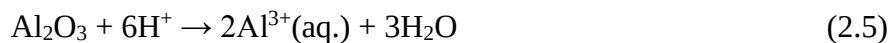


Figure 2.7. The direction of electric field $\vec{E}$ at the bottom of the pore during anodization. Image taken from [1].

Meanwhile, at the electrolyte/alumina front there is an electric-field enhanced alumina dissolution at the pore bottom, which causes the pore to deepen further in the direction of the pore formation. The migration of Al^{3+} ions from Al across the oxide-Al interface to the alumina pore bottom, and the O^{2-} ions formed during the electrolysis of water, crosses into the alumina through the electrolyte-oxide interface, causing the propagation of pores further into the Al surface. About 30% of the Al^{3+} ions in the oxide dissolves into the electrolyte and releases heat, whereas the other 70% of the current is responsible for the production of the solid oxide [5].



Some of the protons or the hydrogen ions (H^+) that are produced may migrate towards the cathode, and leave the electrolysis cell as hydrogen gas.



A sort of a competition exists between the formations of conjugate anions by the dissociation of the electrolytic acids and the hydrolysis of water taking place near the sides of the pore bottoms. The dissociation reactions for the three types of the most commonly used acids for aluminum anodization are listed below:

Sulfuric Acid (H_2SO_4):



Oxalic Acid ($H_2C_2O_4$):



Phosphoric Acid (H_3PO_4):



In all of the reactions (Equations 2.6-2.8), the conjugate anions have the ability to replace the oxygen ions (O^{2-}) in the oxide, and thereby have the capability of showing up in the pore walls as impurities [5, 10]. The formation of the pores during the initial stages of the anodization process triggers a self-catalyzing pore growth process with the help of the acid and the electric potential that penetrates into the pores, as shown in the schematic in Figure 2.8. It has been observed that the initially formed disordered pores reorder themselves, due to a horizontal mobility of the ions in the barrier layer, to an equilibrium state once they form hexagonal close packed (hcp) arrays [5].

For specific anodization conditions (*i.e.* anodization voltage, type and pH of the acid in the electrolyte, and temperature), the diameter of the pores remain uniform, while the thickness of the PAA membrane (height of the porous channels) can be controlled by regulating the anodization time. Depending on the acid of the electrolyte, the applied potential or the anodization voltage ranges from 10V to nearly 200V (see Figure 2.2), which generates highly localized Joule heating,

which along with high current density, and the exothermic acid-catalyzed oxide dissolution causes a local temperature spike at the oxide-electrolyte interface.

The heat generated may cause thermal expansion of the alumina, which along with the change in the volume due to the formation of aluminum oxide (Al_2O_3), may introduce a considerable amount of stress within the barrier layer, as shown in the schematic of Figure 2.8. It has been observed, that with long anodization time, a flat and free standing Al foil begins curve and buckle due to the volume expansion as anodization progresses. With the progression of anodization, the pore sizes increase due to the merger of adjacent pores, until the cells have rearranged to form a hexagonal pore packed structure. The attack of field assisted hydrogen ion on the oxide layer causes the penetration of the pores deep into the Al surface. In a more alkaline electrolyte, the concentration of hydrogen ion is diminished, which reduces the possibility of field assisted hydrogen ion attack on the oxide, as a result forms a more planar barrier type oxide layer.

During the first few seconds of anodization, the domain size is indeed small due to the random distribution of pores on the newly formed anodic alumina. As the anodization time progresses the domain sizes grow due to the gradual merger and alignment of random pores along the boundaries [5]. Therefore it makes it extremely hard to achieve highly ordered hexagonal pores, without pre-texturing, for thinner layers of Al. Thicker layers of Al that can support longer time anodization, which can provide a better chance of forming an ordered array during the anodization process [8]. Lengthier anodization time allows for alumite adjustment that forces shallower pores to merge with deeper ones, and that rearrangement is caused by repulsive forces experienced by adjacent pores.

Past studies in PAA membranes have shown that the pore regularity in PAA membranes from untreated (without pre-texturing) Al is extremely poor in films of thicknesses below $1\mu\text{m}$. The regularity starts to improve in anodized Al films of thicknesses greater than $1\mu\text{m}$ and reaches a good hexagonal pore packed structure when anodized up to a thickness of $20\mu\text{m}$ [8]. As a result, it is not possible to achieve a good pore ordering even with multiple step anodization without a lengthy first step anodization (of around $\sim 20\mu\text{m}$), and therefore rules out the possibility of conducting a two or more step anodization in thinner Al films (thicknesses less than $10\mu\text{m}$) to achieve regular pore ordering.

The structural properties and self-organizational capabilities in PAA depend on the anodization conditions [11]. With the atomic density of Al in aluminum oxide (Al_2O_3) lower than

that of metallic aluminum (Al), the origin of forces between neighboring pores rises as a result of the mechanical stress that occurs due to the expansion at the alumina-Al interface. Since the oxidation only takes place near the hemispherical pore barrier layer, the volume expansion occurs in the vertical direction, causing the pore walls to be pushed upwards. Volume expansion has been found to be directly proportional to the anodization voltage, and conditions that lead to a moderate volume expansion has been identified to be the most suitable for obtaining hexagonal ordered pore cells [11]. Large volume expansion (for higher anodization voltage) leads to the formation of structural defects in the alumina with reduced interaction with neighboring pores, whereas in cases of volume contraction (associated with lower anodization voltage), the absence of repulsive forces between the pores prevents the formation of any ordered porous structures [11]. A previous study has detailed the volume change of alumina with respect to the original thickness of Al at different anodization voltages in a 20 wt. % H_2SO_4 based electrolyte, as detailed in Table 2.1 [11].

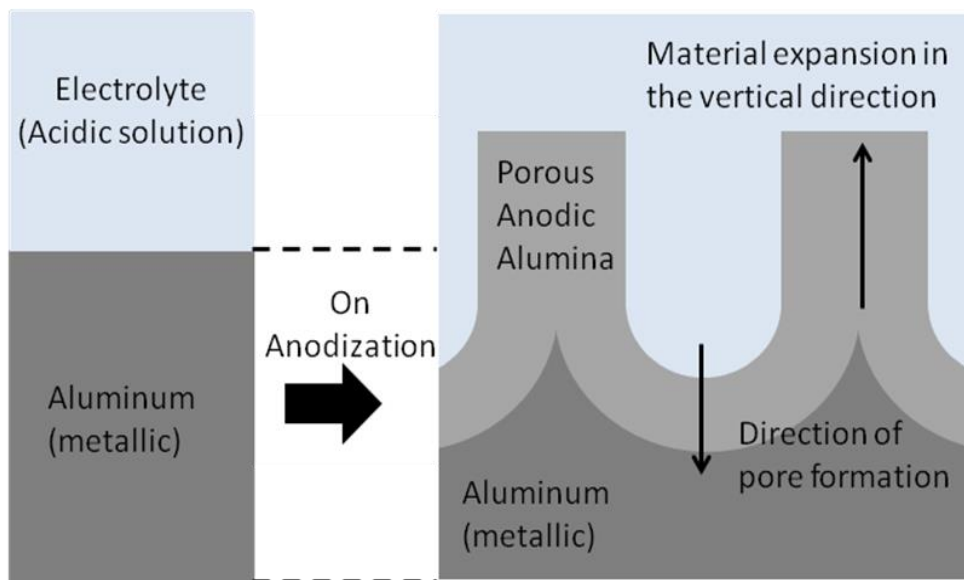


Figure 2.8. Schematic of volume expansion during the anodization of aluminum to form a Porous Anodic Alumina (PAA) membrane. Figure from [1].

The alumina film growth rate is found to be approximately a constant and does not depend on the curvature of the pore bottom. It has also been noted that a decrease in the curvature of the pore radius increases the film dissolution rate, which increases the pore size, on the other hand, as the pore gets wider the oxide dissolution rate slows down. These two constant competing processes keep the alumina pore radius fairly constant during the anodization procedure [9, 10].

Table 2.1. Volume expansion or contraction of alumina (Al_2O_3) with respect to the original thickness of the aluminum (Al) layer at different anodization voltages. Anodization performed using 20 wt. % sulfuric acid (H_2SO_4) at 1°C , [11].

Anodization Voltage	Percentage of original Al layer thickness
18 V	86%
18.7 V	122%
19 V	141%
20 V	134%
25 V	162%

2.5 Anodization

As discussed earlier, multiple steps of anodization of Al yields PAA membranes with regular hexagonal pore packed structure without the requirement of expensive pre-texturing of Al surface using lithographic techniques. For many of the PAA templates fabricated in this work, a two-step anodization method has been implemented to get porous arrays in very regular hexagonal pore packed structure using different anodization conditions.

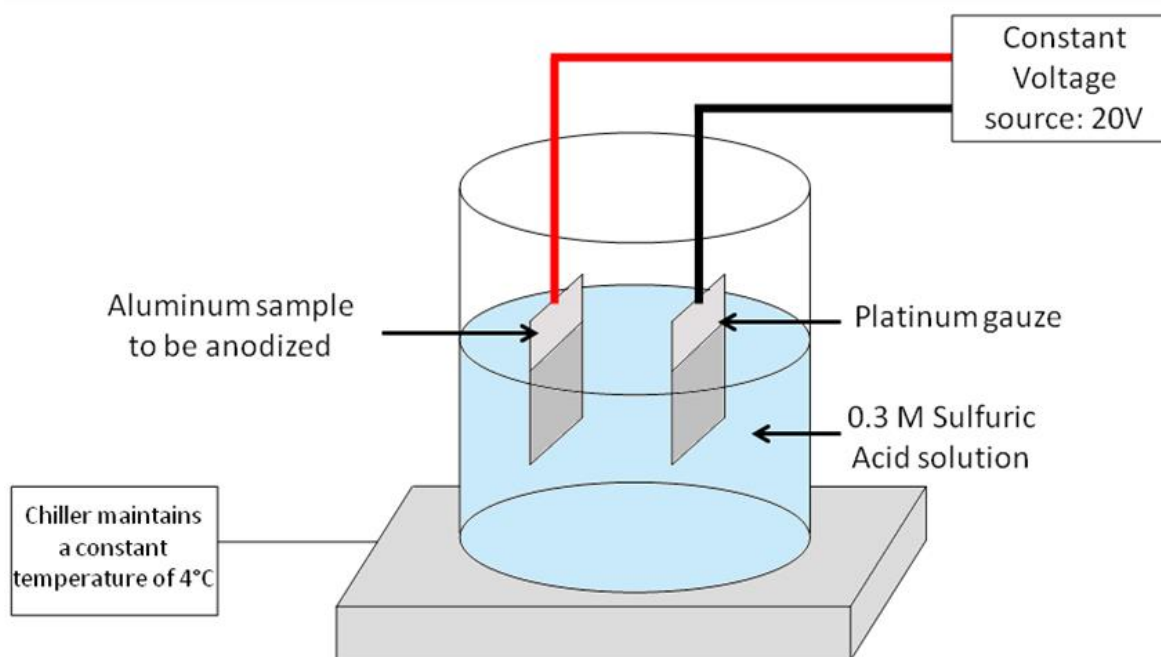


Figure 2.9. Schematic of the electrolytic bath set-up for the anodization of the aluminum (Al) sample to create PAA templates. Figure from [1].

Anodization, which is an electrolytic oxidation of Al, in this case, is conducted in a two electrode electrochemical cell, as shown in Figure 2.9. Two types of electrolyte has been used for anodization of Al foil in this work. For the smaller diameter pores, Al surface was anodized in 0.3 M sulfuric acid (H_2SO_4), whereas for larger pore PAA membranes the Al surface was anodized in 0.3 M oxalic acid ($\text{H}_2\text{C}_2\text{O}_4$) solutions. The electrolytes were always chilled to 4°C (or lower depending on the various anodization conditions and requirements) using a (Thermo Fisher Scientific) chiller that allowed the anodization to be conducted at a constant temperature. For a two-step anodization process, the first step of anodization must be conducted long enough to achieve a hexagonal pore packed structure at the pore bottoms to leave an impression on the remaining layer of Al. As explained earlier, the regularity greatly improves once the thickness of anodized Al reaches 20µm or more. Therefore for most of the anodization done for this work, ultra-pure (99.999%) and thick (250 µm) Al foil has been used for anodization, which are thick enough to support two lengthy steps of anodization to form very regular hexagonal pore packed PAA membranes which would be used as a template for nanowire and nanohole growth.

The pure Al foil was the anode of the electrolytic set up, and a pure platinum (Pt) gauze was used as the cathode. The Al foil was cleaned using an acetone, methanol followed by an isopropanol (IPA) rinse. The inactive area of the Al foil, the regions not to be anodized, were coated with a thick layer of electrically insulating and transparent lacquer coating to prevent the exposure of those region to the electrolytes and therefore prevent anodization. The electrodes were connected to a constant DC voltage supplier, and the Al foil was anodized using different anodization voltages based on the diameter and structural requirements of the PAA templates being made.

Figure 2.10, shows a series of SEM images of the surface of a ~2 µm thick Al thin film (Figure 2.10 (a) and (b)) deposited on a Si wafer after anodization, and the surface of a free standing, thick anodized Al surface (Figure 2.10c). Figure 2.10a shows the anodized surface of the thin film of Al after a brief anodization step, the image reveals the pore formation in small grain sizes. As expected, the pore regularity is poor. Removing the top anodized layer, and using the indentations left behind by the hemispherical barrier layers of the first step of anodization, the sample was re-anodized, as seen in Figure 2.10b.

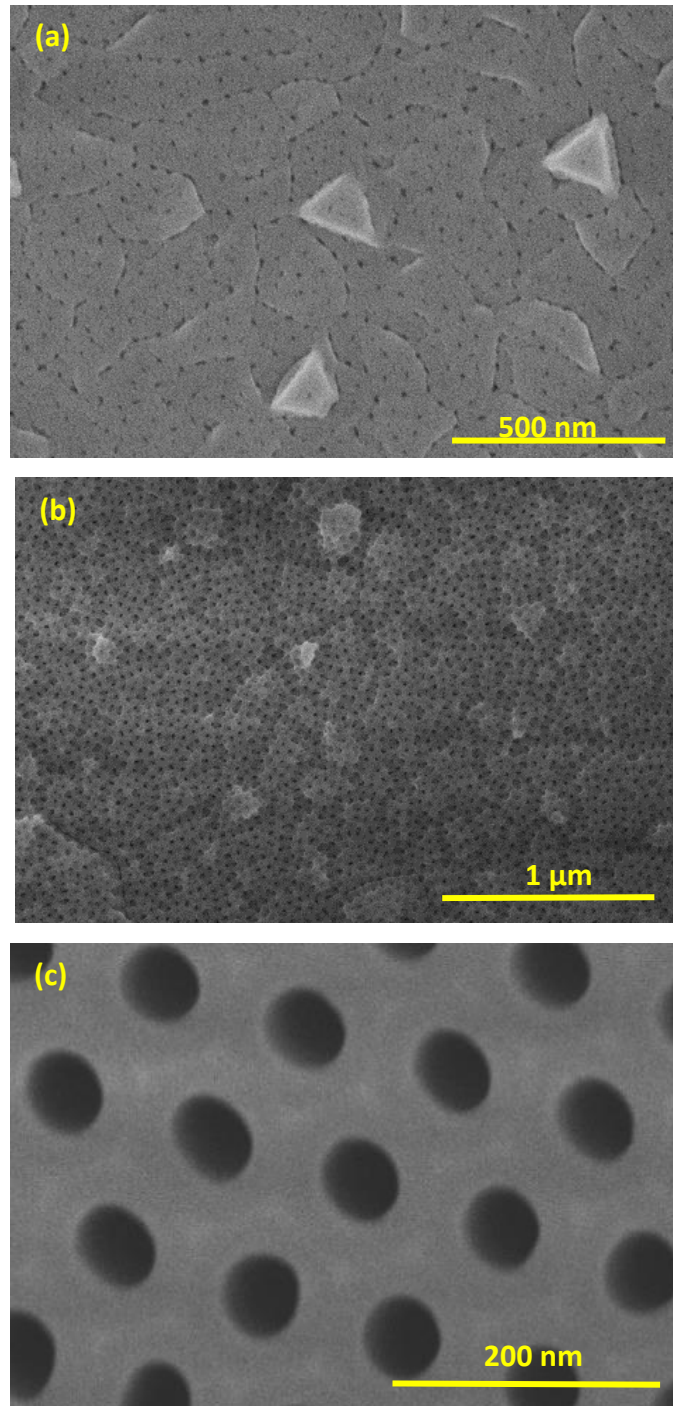


Figure 2.10. FESEM images of PAA membranes showing improvement of pore regularity with two step anodization and a longer anodization time. a) FESEM image of a PAA membrane surface after the first step of anodization. Figure from [1]. b) FESEM image of a PAA membrane surface after a short first step of anodization (~10 minutes) followed by a second step of anodization in a thin Al film (~2μm). Figure from [1]. (c) FESEM image of a PAA membrane after a lengthy first step of anodization (~12 hours) followed by a second step of anodization in a thick Al foil (~250 μm).

The ordering appears to have improved, when compared with Figure 2.10a, but due the relatively short anodization period, the pores (alumites) are still in the process of rearranging themselves to form regular hexagonal arrays. Such regularity, as explained previously, can only be achieved by anodizing through at least 15-20 μm thick layer of Al, or through pre-texturing the surface using lithographic techniques.

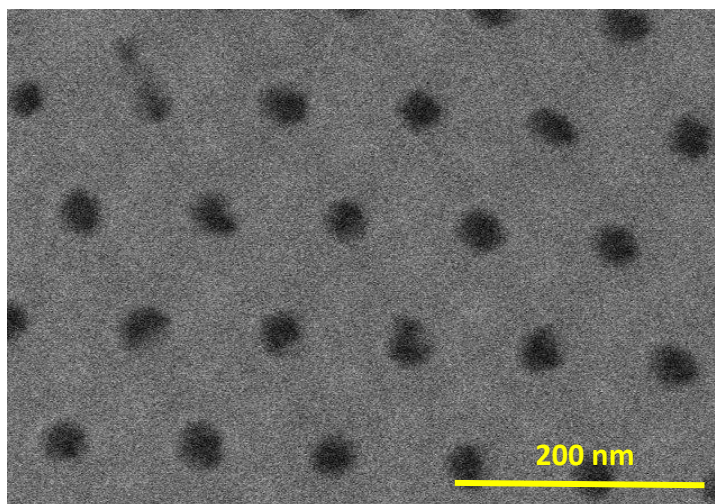


Figure 2.11. FESEM image of the surface of a very thin layer of a very regular, hexagonally close packed, PAA membrane on an Al substrate fabricated using a two-step anodization method. The Al foil was very briefly (4 min) anodized at 40 V in a 0.3M oxalic acid solution, after a very lengthy first anodization step. The image captures the initial stages of pore nucleation on the dimples left behind by the pore bottoms after the first step of anodization.

After the first step of anodization, which usually ran anywhere from 10 hours to 20 hours to anodize Al thicknesses of well over 20 μm in order to get regular hexagonal pore packed arrangement at the pore bottoms, the PAA membrane was etched away. An alumina etchant, a mixture of DI water (48.25 ml), phosphoric acid (H_3PO_4) (1.75 ml) and chromic oxide (Cr_2O_3) (2.3 g), was used at $\sim 65^\circ\text{C}$ is used to etch the porous Al_2O_3 film from the Al foil. The long first anodization step ensures the hemispherical pore bottoms to leave behind a very regular hexagonal pore packed impression on the Al substrate, which would act as future nucleation site of pores during the next anodization (as seen in Figure 2.11), and hence getting the same effect as pre-texturing the Al surface prior to anodization. The image (Figure 2.11) captures the very initial stages of pore nucleation on the pre-dimpled Al during the second step of anodization with pore sizes still expanding. Figure 2.10c, shows the SEM image of a PAA surface obtained from a two-

step anodization process, after a lengthy second-step of anodization with the pores reaching their final sizes. The SEM images (Figures 2.10c and 2.11) show a very regular array of hcp pores on the PAA surface, which was possible due to the multiple step anodization process undertaken in both cases.

The anodization current during the first and second steps of anodization have a similar profile, but differ in magnitude during the initial phase of anodization. The anodization current during the second step of anodization is usually higher than the first step, during the initial phase, due to the difference in the thickness of the oxide, as observed in Figure 2.12. The planar oxide of an Al foil during the first step of anodization has a slightly thicker native oxide, when compared with the oxide at the center of each depression on the Al surface right before the second anodization step. A slightly thinner oxide results in a lower resistance, which results in the anodization current during the second step of anodization to be higher than the first step in the initial phase of PAA growth.

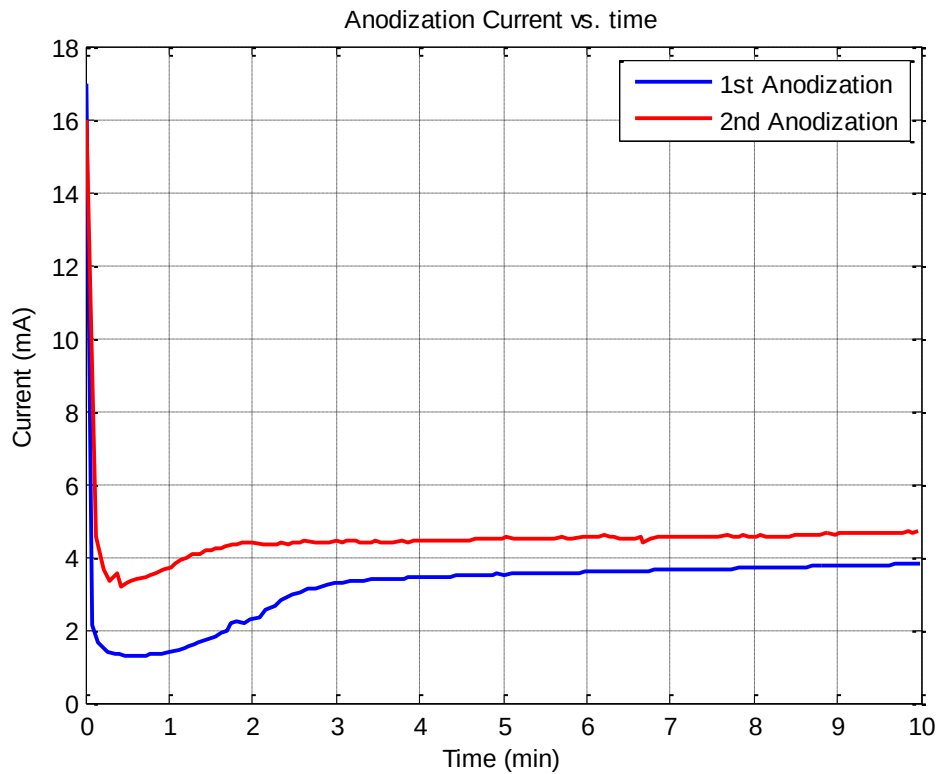


Figure 2.12. Anodization current plot of the first and second step of anodization for a very thin film (2 μm) of aluminum (Al). Figure from [2].

The anodization current versus the pore growth stage, explained in Figure 2.13, shows the plot of current versus time for the anodization of a thin layer of evaporated Al on a Si substrate with an adhesion layer of titanium [2]. During the initial stage of PAA formation, the current is very high due to the low resistance of anodizing pure Al with a very thin layer (in the order of a very few atomic layers) of native oxide. As the anodization progresses the formation of a barrier oxide, leads to an increase in resistance that causes a drop in the current. During the pore growth step, the current is fairly constant and finally drops once most of the Al supply has been anodized.

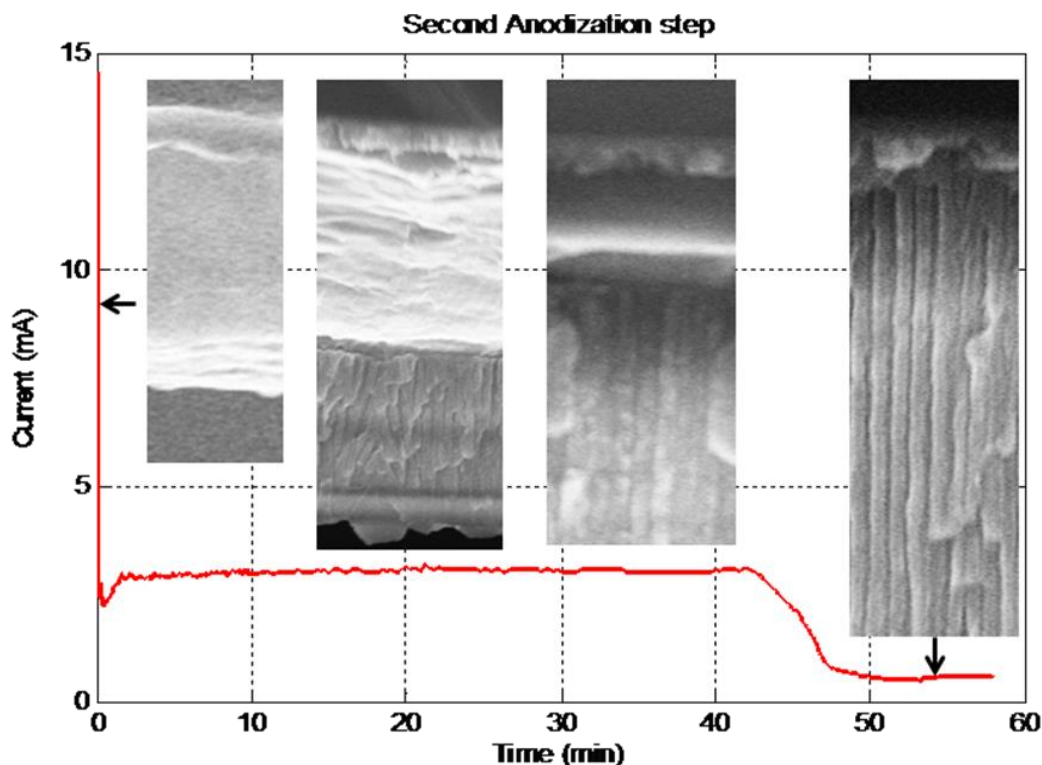


Figure 2.13. The anodization current (mA) versus anodization time (min) plot for a two-step anodization process of an Al foil to create a PAA template. The inset pictures (FESEM images) indicate the various stages of PAA formations as the anodization time progresses. Figure from [2].

2.6 Hierarchically Branched Porous Anodic Alumina (HBPA) template

A unique method of creating hierarchically branched nanopores inside PAA templates has been presented by Meng *et al.* [12]. To create these branched PAA (BPAA) templates, the process starts with a two-step anodization process of thick Al foil, with the first step of anodization conducted at 0.3 M oxalic acid solution at 8-10 °C under a constant voltage, in the range of 40-72

V for 8 hours. After the removal of the PAA membrane from the first anodization process, the Al undergoes a second step of anodization where the voltage is reduced in steps to create branched pores. To create ‘Y-branched’ pores, the anodization is initially carried out under similar condition as the first step of anodization followed by reduction of anodization voltage by a factor of $\frac{1}{\sqrt{n}} = \frac{1}{\sqrt{2}}$, where n is the number of branches desired at each junction. This process has been demonstrated for generating multiple branching by changing the factor of voltage reduction, by updating the value of n . It has been stated that for anodization voltages less than 25 V, the PAA template is washed in DI water for around 30 minutes to purge any traces of oxalic acid and continue the subsequent anodization in 0.3 M sulfuric acid [12].

Hierarchically branched PAA (HBPAAs) templates have been fabricated by the process outlined above, and it was found that the hexagonal distribution of pores improved when starting the first step of anodization with a smaller voltage, and then during the second step of anodization, increasing the voltage by a factor of $\sqrt{n}$, where n is the number of branching desired. This would cause n number of smaller branches to merge together to form the larger pores. To demonstrate this effect the following experiment was designed and executed. Two thick ultra-pure Al foils were cleaned in acetone, methanol, and IPA, and prepared for anodization. The first sample for the Hierarchically Branched Porous Anodic Alumina (HBPAAs) template was anodized for ~18 hours in a 0.3 M oxalic acid solution at 40V with the electrolyte constantly kept at 4°C. The long hours of anodization ensures the formation of regularly distributed surface indentations on the Al, after the removal of the PAA formed in the first step, using the previously mentioned alumina etching technique. The second step of anodization was also conducted under the same condition, 0.3 M oxalic acid (4°C) solution at 40V for ~21 hours, which was followed by the branching technique described by Meng *et al.* to create two ($n = 2$) branches from the central trunk at each pore, using the following formula [12]:

$$\left(\text{New Anodization Voltage for} \right) = \left(\text{Anodization Voltage} \right) \times \left(\frac{1}{\sqrt{n}} \right) \quad (2.10)$$

Here, n is the number of branches desired from the central trunk of each of the larger pore of the PAA membrane. Therefore, the anodization voltage after ~21 hours of anodization was

immediately reduced by a factor of $\frac{1}{\sqrt{n}} = \frac{1}{\sqrt{2}}$, and the new anodization voltage was set at

$40 \text{ V} \times \left(\frac{1}{\sqrt{2}}\right) \approx 28.28 \text{ V}$. The HBPAA1 sample was anodized at this new voltage for a further ~3

hours. The cross-sectional SEM image of the HBPAA1 template is presented in Figure 2.14a, which captures the depth at which the branching of the central pore takes place. The thinner pores at the branches was observed to be relatively less ordered when compared with the trunks of the thicker pores prior to branching. This is also evident from the SEM image of the bottom surface of the HBPAA1 membrane, after etching away the un-anodized Al in a saturated HgCl_2 solution at room temperature for ~1 hour. Although, the unopened pore bottom surface, Figure 2.14b, shows mostly hcp arrays of the hemispherical pore barriers, there seems to be a few structural deformities.

For the second set of experiment, to create a HBPAA template (HBPAA2), the PAA template starts off with the formation of smaller pores (with thinner channels), and by voltage regulation the pores are merged together to form larger pores (with thicker channels). Therefore, structurally HBPAA2 that starts off with cylindrical pores of smaller radius that eventually merge to form pores with larger radius, which is structurally opposite to that of HBPAA1.

HBPAA2 template was initially anodized in 0.3M oxalic acid (4°C) at 25 V for several hours, followed by an alumina etching process. The template was further anodized at the same condition for nearly ~11 hours before ramping up the voltage by a factor of $\sqrt{n}$, where n is the number of pores that are to be merged to create a thicker pore. The equation set for merging n number of smaller pores to form thicker pores was set as follows:

$$\left(\begin{array}{c} \text{New Anodization Voltage for} \\ \text{merging } n \text{ smaller branches} \end{array} \right) = \left(\begin{array}{c} \text{Anodization} \\ \text{Voltage} \end{array} \right) \times (\sqrt{n}) \quad (2.11)$$

After ~11 hours of anodization, the anodization voltage was increased by a factor of $\sqrt{2}$, to merge every 2 smaller pores to form a larger pore, and anodized for several more hours.

This process of ramping up the voltage by a factor of $\sqrt{n}$ to merge pores, as opposed to decreasing voltage by a factor of $\frac{1}{\sqrt{n}}$ to split pores, was found to increase the regularity of the

hexagonal distribution of pores, as observed from comparing the regularity of the SEM images of the hemispherical pore barrier layer of HBPAA1 (Figure 2.14b) and HBPAA2 (Figure 2.14d). Figure 2.14c shows the merging of smaller pores on the bottom of the SEM image (cross-sectional image of HBPAA2) to form the larger pores on the top of the image, which is opposite to the structure of HBPAA1 (Figure 2.14a).

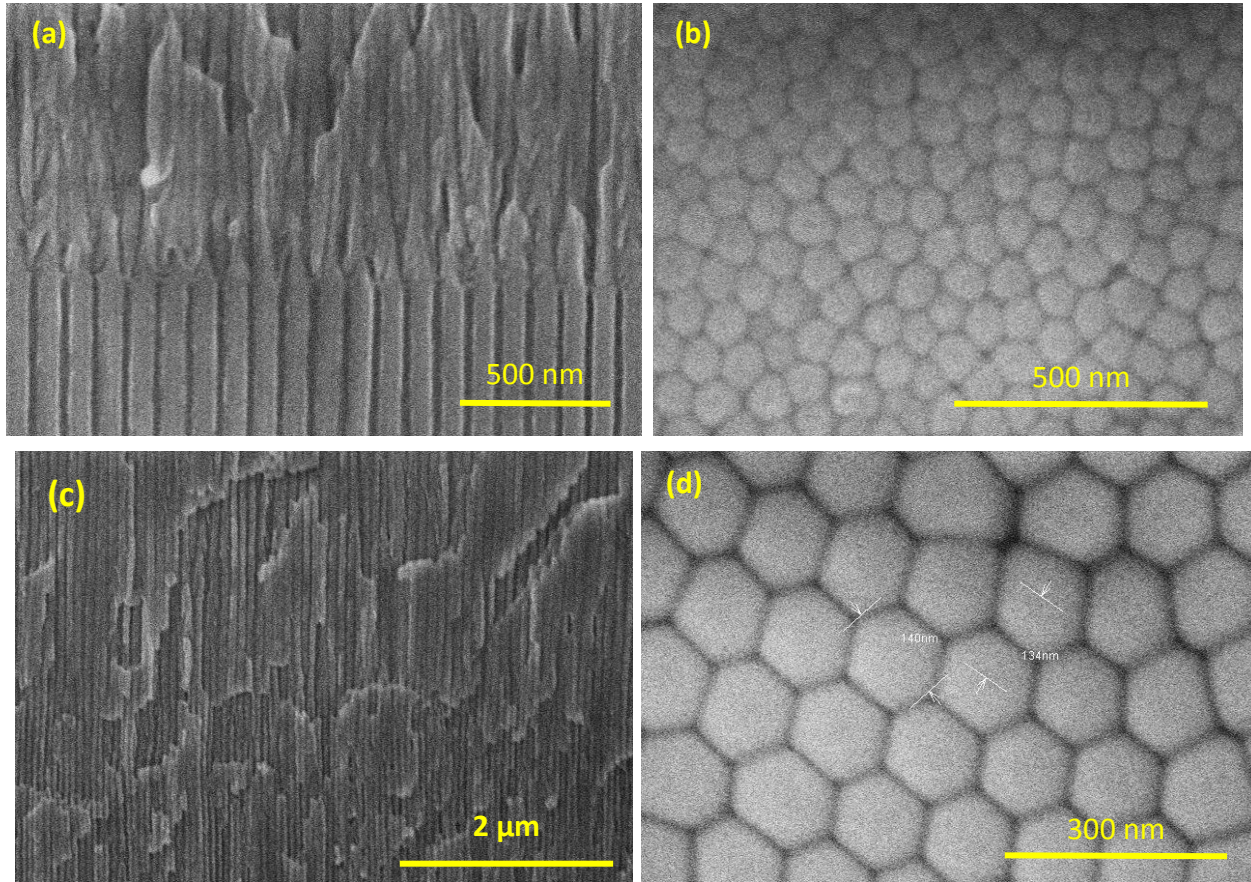


Figure 2.14. FESEM images of hierarchically branched PAA templates (HBPAA). (a) Cross-sectional FESEM image of the HBPAA1 template created by reducing the voltage by a factor of $\frac{1}{\sqrt{2}}$ to create a ‘y-branching’ in the PAA membrane. (b) FESEM image of the bottom surface of the unopened hemispherical barrier layers of the smaller pores of HBPAA1, formed by splitting larger pores, showing a lesser degree of pore regularity than the initially grown larger pores. (c) FESEM of the cross-sectional image of the HBPAA2 template created by starting with smaller pores, followed by merging smaller pores to form larger pores by increasing the voltage factor by $\sqrt{2}$, and therefore creating the same branching effect. (d) FESEM image of the bottom surface of the unopened larger pores HBPAA2 showing a greater hexagonal regularity in the distribution of the hemispherical pore barrier layers, than that of (b).

2.7 Concluding remarks

PAA membranes offer an exciting prospect for being used as a template for the growth and fabrication of various nanostructures such as nanowires (NWs) and nanoholes (NHs) of semiconducting materials and metals. The tunability of PAA templates by controlling the anodization voltage and time, type and pH of acid in the electrolyte, and pore widening techniques provide exciting opportunities to fabricate and explore the physical, electronic and optical properties of nanomaterials with different structural properties, as will be discussed in the upcoming chapters. A bottom up approach of creating a hierarchically branched PAA membrane has also been discussed, which provides a powerful approach to produce nanostructures of greater morphological complexity that could have far-reaching implications in future design of complex nanostructured materials.

2.8 References

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3. TEMPLATE ASSISTED ELECTRODEPOSITION

3.1 Introduction

Due to the tunable physical properties of nanowires, metallic and semiconductor nanowires are of great interest for new generations of nanoelectronic, photonic, optoelectronic, thermoelectric and bio-electronic applications, which have very unique properties when compared with their bulk material counterparts [1-5]. Nanowires (NWs) have been successfully grown using various techniques such as chemical vapor deposition (CVD), which uses a vapor-liquid-solid (VLS) mechanism to grow NWs whose diameter is dictated by the catalyst particle size and growth conditions [6]. Although a widely used method for NW growth, the CVD method has certain limitations such as the inability to grow hierarchically branched NWs, which has the potential for some very interesting optical properties, and limited prospect of a catalyst free growth of NWs.

Electrochemical deposition, or electrodeposition, is another widely used method for growing semiconductor based and metallic nanowires using a structurally engineered template to obtain arrays of vertically aligned NWs, whose structural properties may be tailored by pre-designing the template [7, 8]. A major advantage of the electrodeposition approach for the growth of NWs is the ability for many elements and materials to be grown at or near room temperature under atmospheric conditions [9-11].

There has been a recent rise in interest in exploring the technological implications and fundamental issues of optical interaction with nanostructured material (such as NWs) in areas ranging from size quantization to dielectric confinement as a function of size, shape and periodicity that have been applied in NW based photodetectors and photovoltaics [12-18]. There are several interesting properties, such as enhanced light trapping and absorption that has been demonstrated using NWs of different structures such as conical nano-needle shaped NWs, and dual diameter NWs. Therefore, there is a lot of interest in growing NWs of phase pure materials with complex morphologies as they have a lot of potential for devices with novel applications. A portion of the work presented in this chapter has been published by the author in the Proceedings of the IEEE (Nano) International Conference on Nanotechnology, 2014 [19], and another part of the work has been published in the Journal of Applied Physics (J. App. Phys. 116, 083506 (2014)) [20].

3.2 Indium Antimonide

Indium Antimonide (InSb) is a very interesting III-V semiconducting, direct bandgap material that has a low electron effective mass. Among any of the known semiconductors, other than carbon nanotubes, InSb has the highest electron mobility of $78000 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$, electron drift velocity, and ballistic length of up to 700 nm in room temperature. This makes it a promising candidate for high speed and low power nanoelectronic devices. It also has the smallest bandgap of any known III-V material with a bandgap of around 0.17 eV at room temperature. The bandgap (E_g) of a material is related to the corresponding cut-off wavelength ($\lambda_{\text{cut-off}}$) for photon generation (due to electron-hole recombination), through the following equation:

$$\lambda_{\text{cut-off}} [\text{nm}] \approx \frac{1240 [\text{eV} \cdot \text{nm}]}{E_g [\text{eV}]} \quad (3.1)$$

Therefore, InSb with $E_g \approx 0.17 \text{ eV}$ at room temperature, will have an approximate cut-off wavelength ($\lambda_{\text{cut-off}}$) of:

$$\lambda_{\text{cut-off, InSb}} \approx \frac{1240}{0.17} \approx 7294 \text{ nm} = 7.294 \mu\text{m} \quad (3.2)$$

As a result, bulk InSb with a cut-off wavelength of around $\sim 7 \mu\text{m}$, is an ideal material for detecting wavelengths into the middle infrared (mIR) region of the wavelength spectrum, which makes it an ideal for IR detectors.

A prior work, by another research group, on the tunable bandgap of InSb NWs has been reported to be dependent on the structural parameter, mainly diameter, of the NWs along with the operating temperature [21]. For photonic confinement in a NW, the diameter (d_{NW}) of the NW should be equal to or less than the Bohr exciton radius (a_{Exciton}), which is the composite bound-state of electron and hole. InSb has a large Bohr exciton radius of $\sim 65 \text{ nm}$ (compared to Si that has a radius of 4.9 nm), and as a result its bandgap can be tuned when the diameter of the NW is less than 65 nm. The bandgap of an InSb NW has been reported to change with the diameter as follows:

$$E_{g,NW} = E_{g,Bulk} + \frac{h^2}{8d^2} \left(\frac{1}{m_h^*} + \frac{1}{m_e^*} \right) - \frac{1.8q^2}{\epsilon d} \quad (3.3)$$

Where, $E_{g,NW}$ is the bandgap of an InSb NW as a function of the diameter, $E_{g,Bulk}$ is the bandgap of bulk InSb, m_h^* is the effective mass of a hole, m_e^* is the effective mass of an electron, q is the charge of an electron, ϵ is the dielectric constant, d is the diameter of the NW, and h is the Planck's constant.

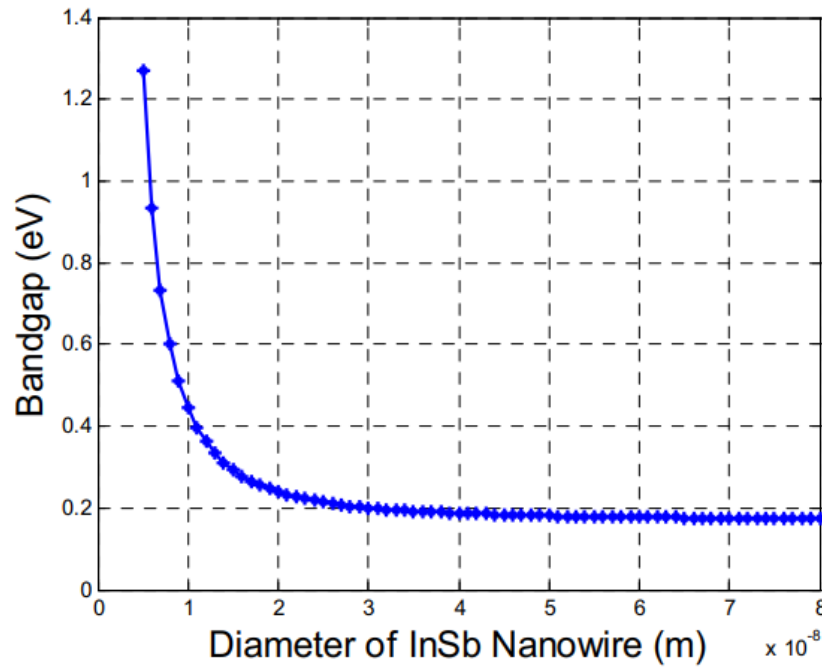


Figure 3.1. The relationship between the diameters of an InSb NW as a function of its diameter. Figure from [21].

The relationship between the bandgap of an InSb NW and its diameter is shown in Figure 3.1. It can be observed from the plot that for the diameter of the NW, $d_{NW, InSb} > 65$ nm, greater than 65 nm, the InSb NW has the same bandgap as it's bulk counterpart, $E_{g, InSb NW, d_{NW} > 65 \text{ nm}} = E_{g, Bulk InSb}$. As the $d_{NW, InSb} < 65$ nm, the bandgap starts increasing from 0.17 eV to 0.6 eV at diameter of ~ 8 nm, which reduces the cut-off wavelength from $\sim 7 \mu\text{m}$ to $\sim 2 \mu\text{m}$ and lower. Therefore, it is possible to tune the photonic absorption in InSb NWs by modulating their diameter. Hence, the optical

properties of the NWs can be controlled by structural modification of the same material, which makes the study of nanowires and nanostructures, especially of InSb, so interesting.

3.2.1 Electrodeposition of Indium Antimonide Nanowires using PAA templates

To study the crystallinity and quality of electrodeposited InSb NWs of different dimensions, branched NWs (BNWs) is a good option as the crystallinity and material quality of the NWs of different diameters can be studied by analyzing the various branches of the same BNW. Branched nanowires (BNWs) also have many unique optical properties like, an anti-reflecting surface that encourages light trapping by varying the dielectric constant of the material, and wavelength dependent absorption, which will be discussed in a later chapter.

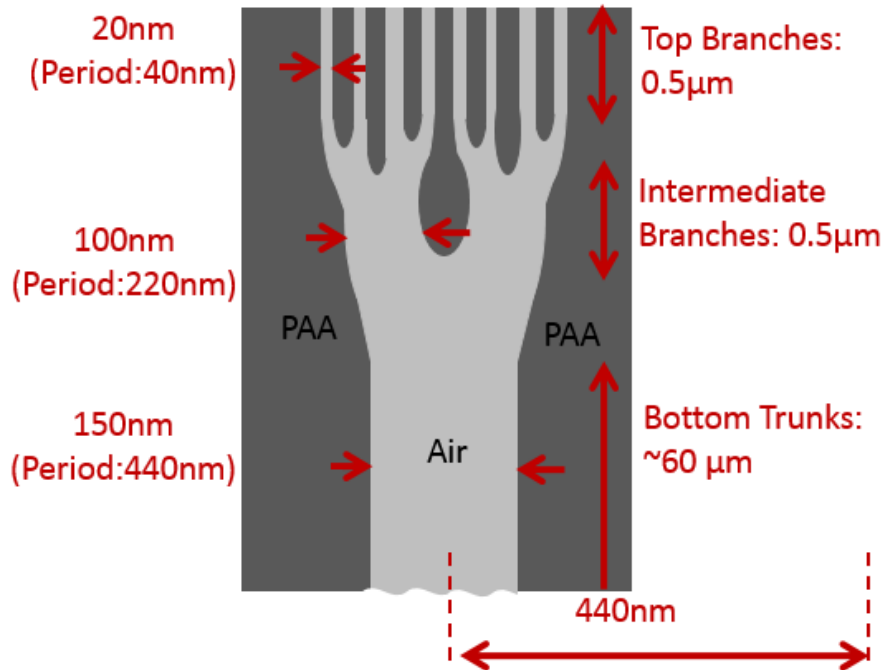


Figure 3.2. An ideal schematic diagram of the cross-section of a single branched pore in the commercially available branched porous anodic alumina (BPAA) template, showing the three distinct layers or regions of branching with the approximate diameter and period of each branch listed in the diagram.

A 60 μm thick commercially available PAA template (Anodisc 13 from Whatman) was used for the growth of vertical arrays of InSb BNWs. Unlike the traditionally lab grown PAA template that requires the removal of the hemispherical pore barrier layer at the pore bottom to

make tubular templates for NW growth, the commercially available branched porous anodic alumina (BPAA) templates have open pores on both ends. The BPAA template has straight pores of diameter ~ 150 nm with a pitch of ~ 440 nm for most of the template, all the way to the bottom surface of the template. The actual branching of the nano-pores occurs in the top ~ 1.5 μm of the template. Within this randomly branched region of the template, the branching appears to be hierarchical with the intermediate branches having a diameter of ~ 100 nm, and the branches closest to the top surfaces of the BPAA template appeared to have an average diameter of ~ 20 nm, as shown in Figure 3.2. This hierarchical branching in the BPAA template is an ideal template for the growth of a hierarchical, randomly branched NW (RBNW) array of InSb.

The top surface of the BPAA template with the smallest pore branches was evaporated with a 100 nm layer of gold (Au) in an e-beam evaporator system. The Au, at the bottom of the smallest pores, would act as the active electrode during the InSb electrodeposition. The electrodeposition was conducted in a three-electrode electrochemical cell, as shown in Figure 3.3, using a platinum (Pt) gauze as the counter electrode, and a silver/silver chloride (Ag/AgCl) (saturated 3M NaCl) reference electrode (0.175V versus the Normal Hydrogen Electrode (NHE)). All the potentials reported here, are in reference to this electrode (Ag/AgCl). The electrolyte for the electrodeposition of InSb consisted of an aqueous solution of 0.15 M indium chloride (InCl_3), 0.1 M antimony chloride (SbCl_3) along with complexing agents 0.36 M citric acid, and 0.17 M potassium citrate, at pH of 1.8 [9]. The potassium citrate is used in the electrolyte to shift the reduction potential of both the indium ions (In^{3+}) and the antimony ions (Sb^{3+}) to a common deposition potential that facilitates InSb co-deposition [20]. The order of mixing the electrolyte, *i.e.* mixing citric acid and potassium citrate to water prior to adding the SbCl_3 and InCl_3 , was found to be crucial, otherwise SbCl_3 reacts with water (if added first to water) to form an insoluble white precipitate, making the electrolyte useless.

The electrolyte of indium trichloride (InCl_3) forms ions of indium (In^{3+}) and chlorine (Cl^-). The electrode reaction and the standard electrode potentials for indium (In) deposition are as follows:





Overall, the reaction can be written as:

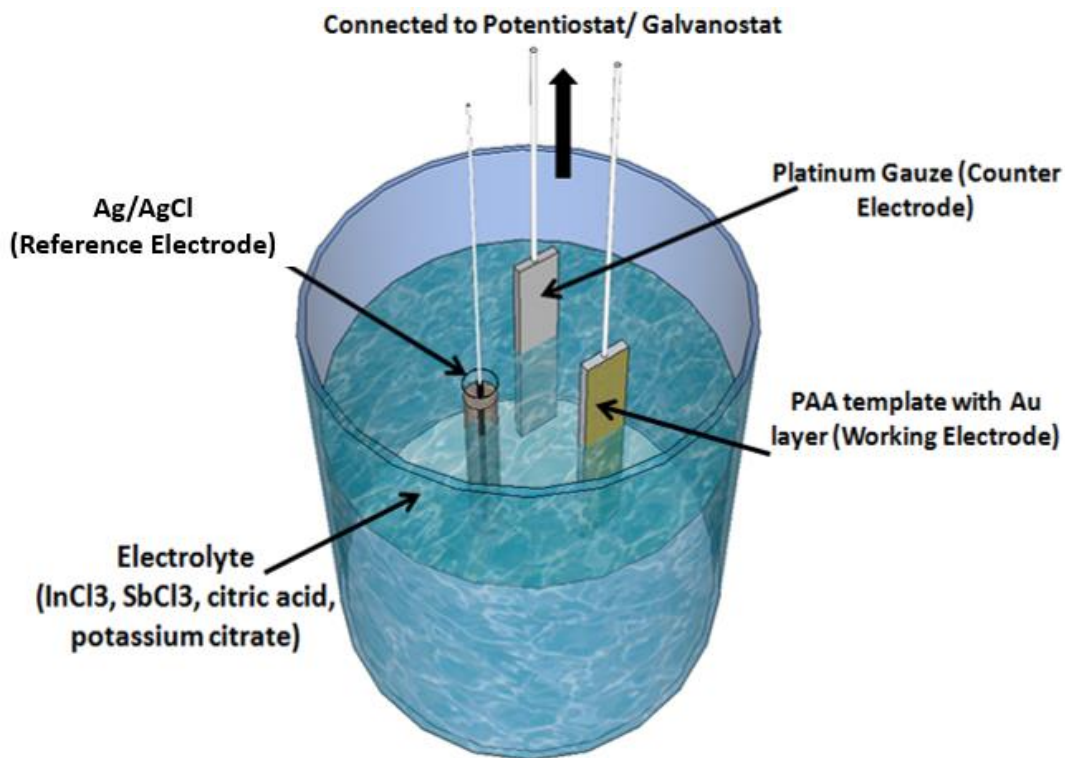


Figure 3.3. Schematic of the electrochemical cell for the electrodeposition of InSb BNWs.

On contact with water, antimony trichloride (SbCl_3) undergoes a hydrolysis process forming antimony oxychloride (SbOCl) and hydrogen chloride (HCl), which further dissociates into their ionic form of (SbO^+ , H^+ , Cl^-) in the electrolyte. The electrode reaction and the standard electrode potentials for antimony (Sb) deposition are as follows:



The large potential difference (~ 0.84 V) in the electrode potential of In and Sb ions/atoms can be brought down to 100 mV or less by the potassium citrate complexing agent, and therefore a favorable deposition potential can be attained close to the In electrode potential. This is caused by the acetate ions of the complexing agent to bind with the Sb ions from the electrolyte, which results in a change in the electrochemical activity of the Sb ion and hence bringing down the potential to a lower value. Thus, the overall chemical reaction in the cathode can be summarized as [22]:



The reaction at the anode consists of a water decomposition process to form hydrogen (H^+) ions, and the release of gaseous oxygen (O_2) as bubbles.

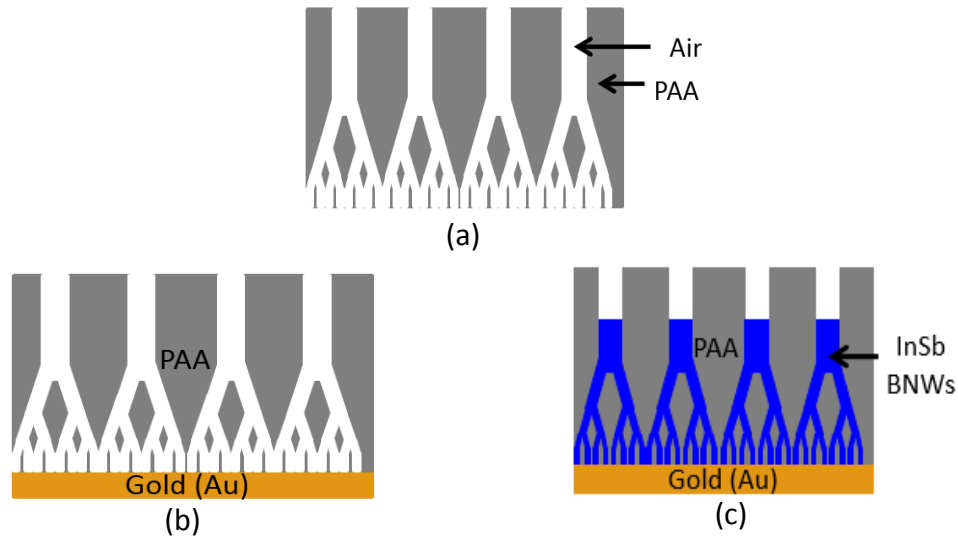


Figure 3.4. Schematic diagrams of the cross-section of the BPAA before and during the InSb electrodeposition process. (a) Empty branches of the BPAA template, (b) thin layer of Au (100 nm) evaporated on the branched, smaller pore side of the BPAA template, (c) schematic of the InSb RBNW deposited in the nano-pores of the BPAA.

A Princeton Applied Research (PAR) potentiostat/galvanostat (model 273) was used for the electrochemical studies of the ionic species. Using cyclic voltammetry, an equilibrium deposition potential for the electrodeposition of InSb was found to be between -1.0 V and -1.5 V, with a reduction peak at around -1.5 V potential [20]. The electrodeposition time, which correlates to the average length of the InSb RBNWs, was controlled by closely monitoring the deposition current (I) versus the deposition time (t) at a particular deposition voltage (V). Since the deposition rate (or the NW growth rate) depends on the deposition potential, the RBNWs were deposited at a deposition potentials ranging from -1 V to -1.5 V (vs. the Ag/AgCl reference electrode). A schematic of the electrodeposition process of InSb RBNW is shown in Figure 3.4.

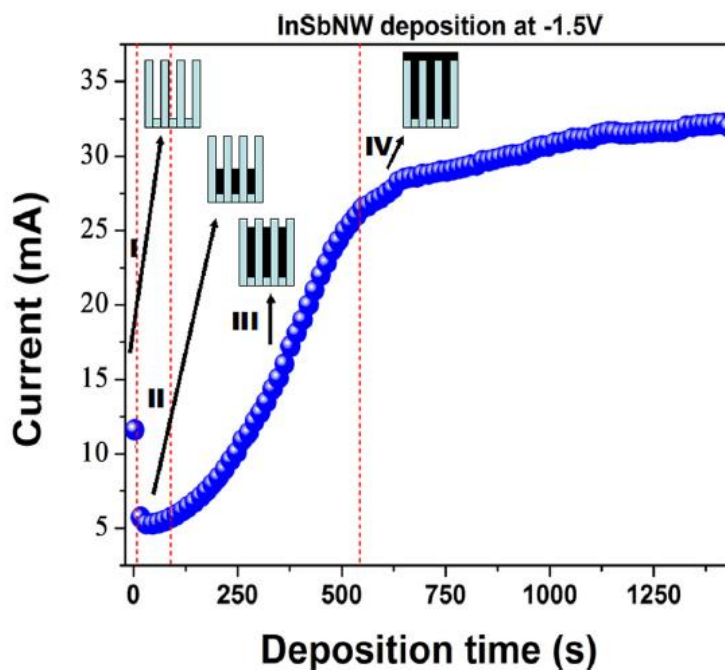


Figure 3.5. Plot of the electrodeposition current of InSb NWs at room temperature during the four stages of NW growth. Figure from [20].

The length of the InSb RBNWs in the arrays were controlled by keeping track of the integrated electrodeposition current during the nanowire growth. The integrated current $\int Idt$ represents the total charge Q_{Total} transferred during the process.

$$\text{Therefore, } \int I \, dt = Q_{\text{Total}} = zN_A N_M \quad (3.12)$$

Where, z is the atomic number, N_A is Avogadro's number, N_M is the number of moles of the material deposited. The actual lengths of the electrodeposited InSb RBNWs were measured using the SEM images of the wires.

The InSb NW growth may be classified into four distinct stages during the growth or electrodeposition process, as explained in Figure 3.5. In the first stage (region I) the relatively large and sudden drop in the electrodeposition current is the result of diffusion related ion transport down the very narrow channels of the nano-pores for the initiation of the growth process, or the nucleation of the molecular seed layer at the bottom of the Au covered pores. In region II, due to the relatively small number of ions at the bottom of each pore, the deposition current remains relatively small and more-or-less constant. In region III, a dramatic rise in the deposition current is observed, where the linear increase in the current versus the electrodeposition time signals the pore getting deposited with InSb. The increase in current can be attributed to the rise in InSb RBNW height, which means a decrease in the distance ions need to travel down the pore to reach the deposition site, in other words a reduction in the resistance.

As the NWs grow in length they eventually outgrow the entire length of the BPAA template and overgrow by forming small caps (the bend in the deposition current between regions III and IV), which eventually coalesced to form a continuous thin film of InSb. This causes a saturation in the deposition current (a linear rise in current is still observed, but with a much more gradual slope) [20].

3.2.2 Characterization of Indium Antimonide RBNWs

As explained in the earlier section, InSb may be electrodeposited using the aforementioned recipe at a growth potential between -1.0 and -1.5V. The growth is slower for the deposition potential of -1.0V than -1.5V. To get NWs of various lengths, in region III of their growth process, the duration of InSb RBNWs depositions were varied for different templates from 10 minutes to 45 minutes. The density of NWs in the template were confirmed by looking at SEM images of the cross-section, Figure 3.6a, of the PAA template and by looking at the surface of the template, Figure 3.6b, after partially dissolving the PAA with a 1 M potassium hydroxide (KOH) solution.

The fill factor of the templates was found to be around 80%, with nanowires of varying lengths as a function of anodization time. The growth rate of the RBNWs in region III was found to be $\sim 0.34 \mu\text{m}/\text{min}$, as seen in Figure 3.6c [20].

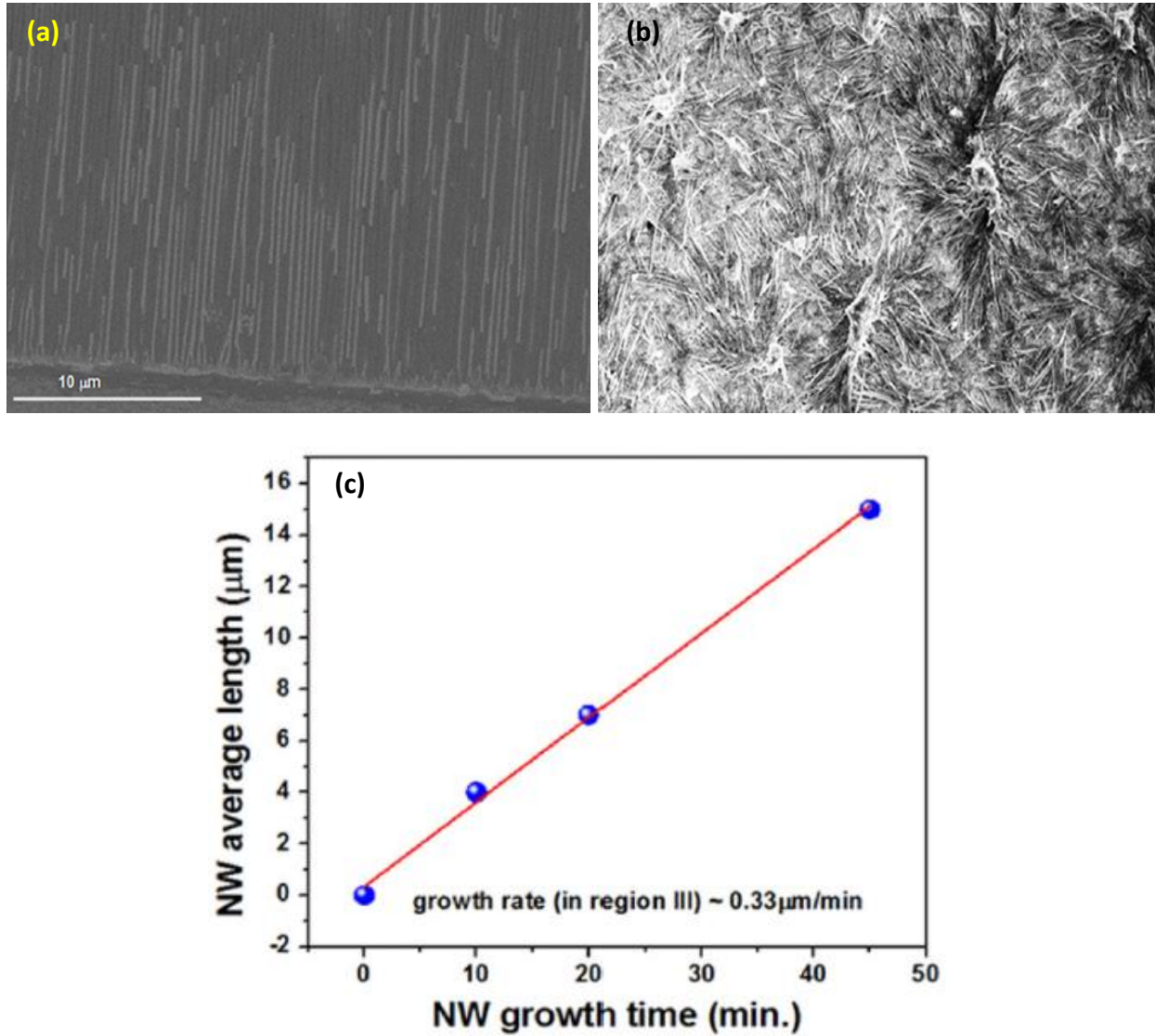


Figure 3.6. (a) FESEM image of the cross section on the BPAA after InSb RBNW deposition for 45 min at -1.5V, (b) FESEM image of the surface of the BPAA after a partial etch with 1M KOH reveals the InSb RBNWs, (c) plot of the InSb RBNW growth rate in region III at a deposition voltage of -1.0 V. Figure from [20].

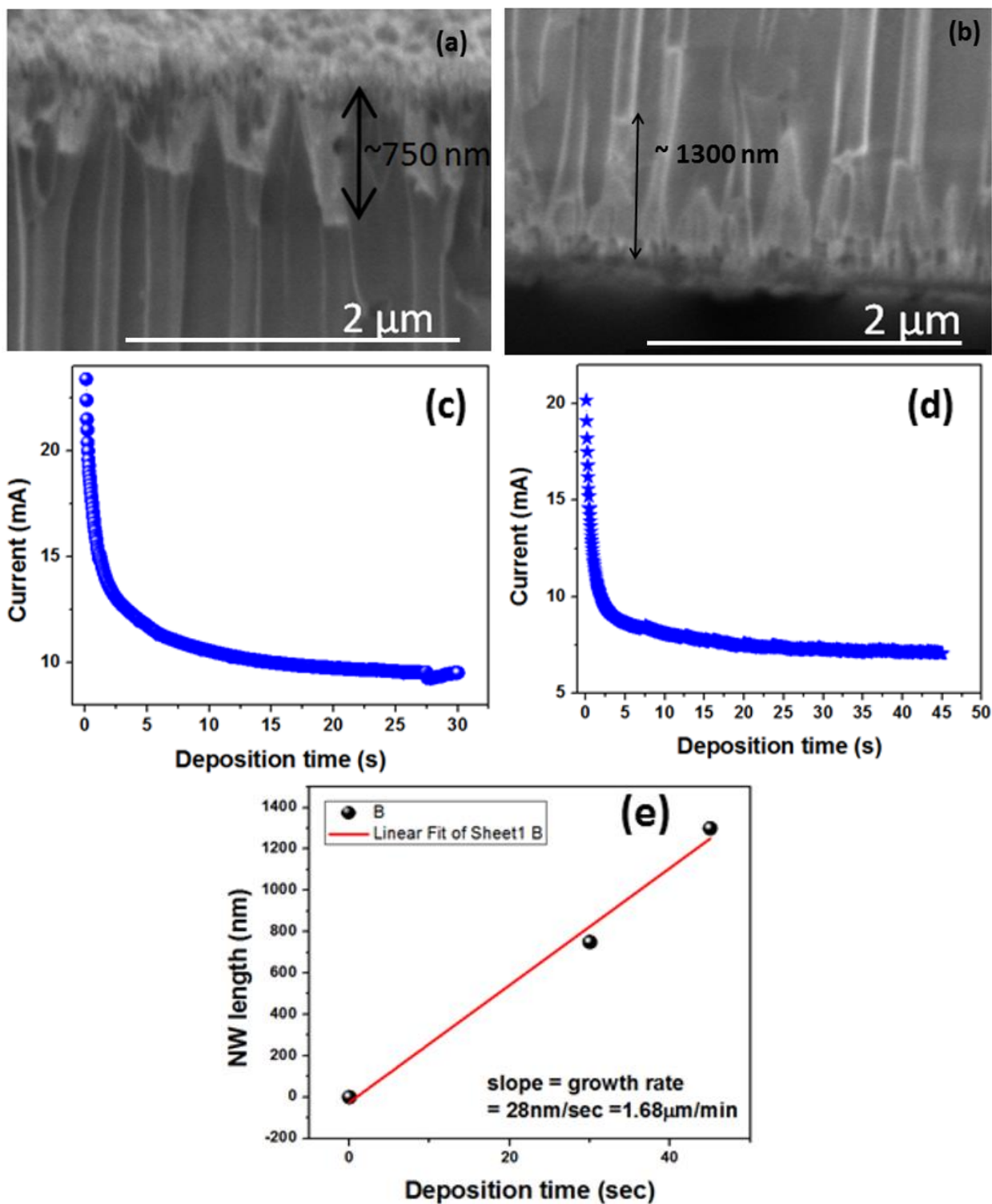


Figure 3.7. FESEM images of InSb RBNWs electrodeposited for (a) 30 sec and (b) 45 sec. The electrodeposition current during the growth of the InSb RBNWs ((c) deposition time- 30 sec, (d) deposition time- 45 sec) in region II of the electrodeposition. (e) The plot showing the growth rate of InSb RBNWs during region II of the RBNW growth. Figure from [20].

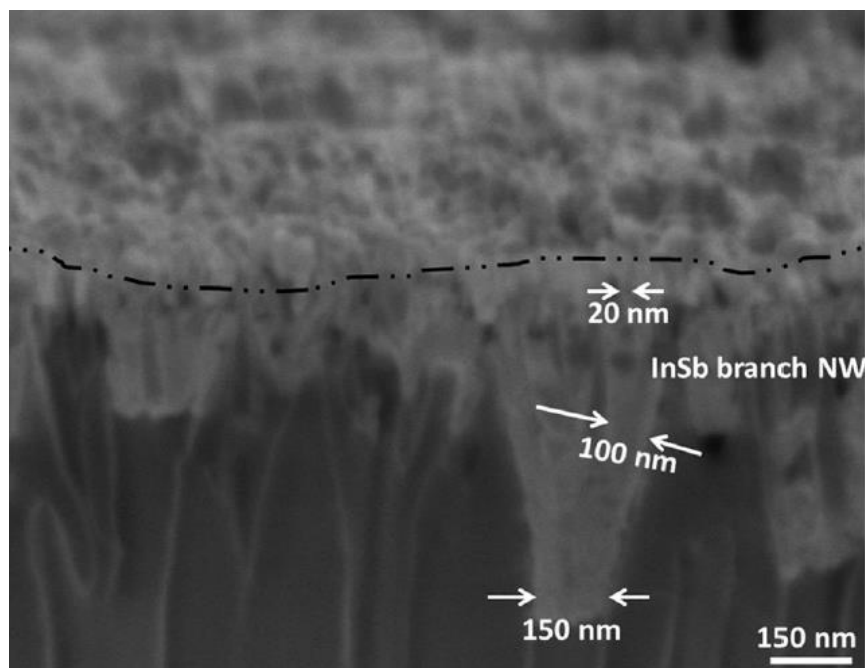


Figure 3.8. High resolution FESEM showing the heirarchical regions of InSb RBNWs. Figure from [20].

By regulating and decreasing the time of electrodeposition, shorter InSb RBNWs were grown to estimate the growth rate for region II of the electrodeposition process. The growth rate was estimated to be $\sim 1.68 \mu\text{m}/\text{min}$ for an electrodeposition voltage of -1.0 V , Figure 3.7. The branched NWs were closely inspected by observing the top branched regions, and using FESEM images the top most branches were found to have NWs of branches $\sim 20\text{nm}$ diameter, which eventually merged to form intermediate branches of diameter 100nm . The intermediate branches finally merged together to form the main trunks of the InSb RBNWs with a diameter of $\sim 150 \text{ nm}$, as seen in Figure 3.8. Large area deposition (in circular BPAA templates of diameter $\sim 1 \text{ cm}$) have been demonstrated [20].

3.2.3 Crystallinity of Indium Antimonide RBNWs

To probe the details of the branched structure of the InSb RBNWs, their crystal and lattice structure and orientation, and surface roughness, a high resolution transmission electron microscopy (HRTEM), EDX analysis, and Raman spectroscopy on the samples were performed before and after annealing.

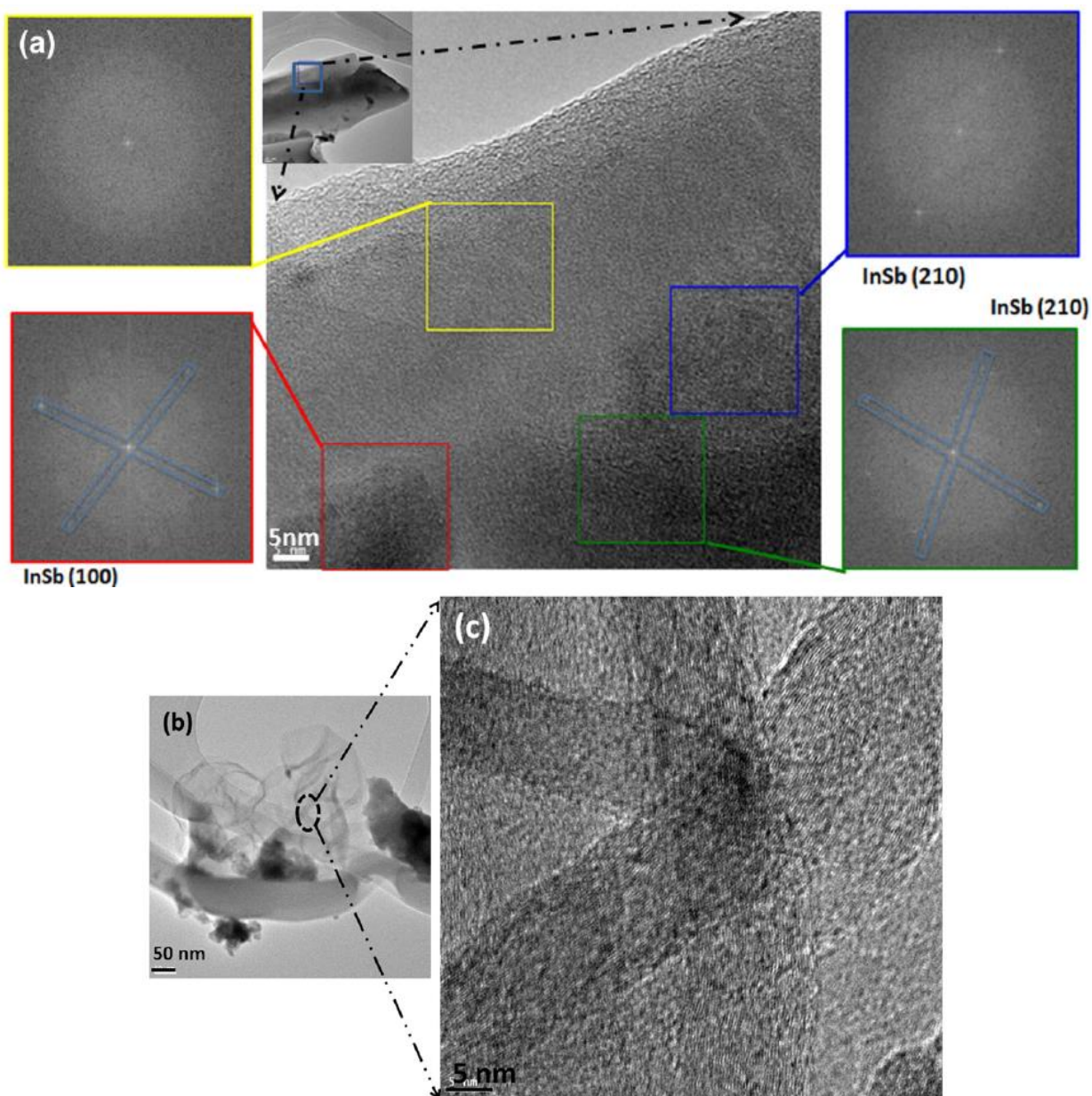


Figure 3.9. (a) HRTEM image of the trunk region (diameter ~ 150 nm) of the InSb RBNWs grown at room temperature at an electrodeposition voltage of -1.5 V, prior to annealing. The colored inset shows the HRTEM images of the different regions of the RBNW showing both amorphous and nanocrystalline regions of InSb phase with different crystallographic orientations identified by the SAED patterns. (b) Low resolution TEM image of the InSb RBNWs following PAA removal, with a (c) HRTEM zoomed-in portion showing the smaller diameter branches. These regions are highly crystalline prior to any annealing treatment. Figure from [20].

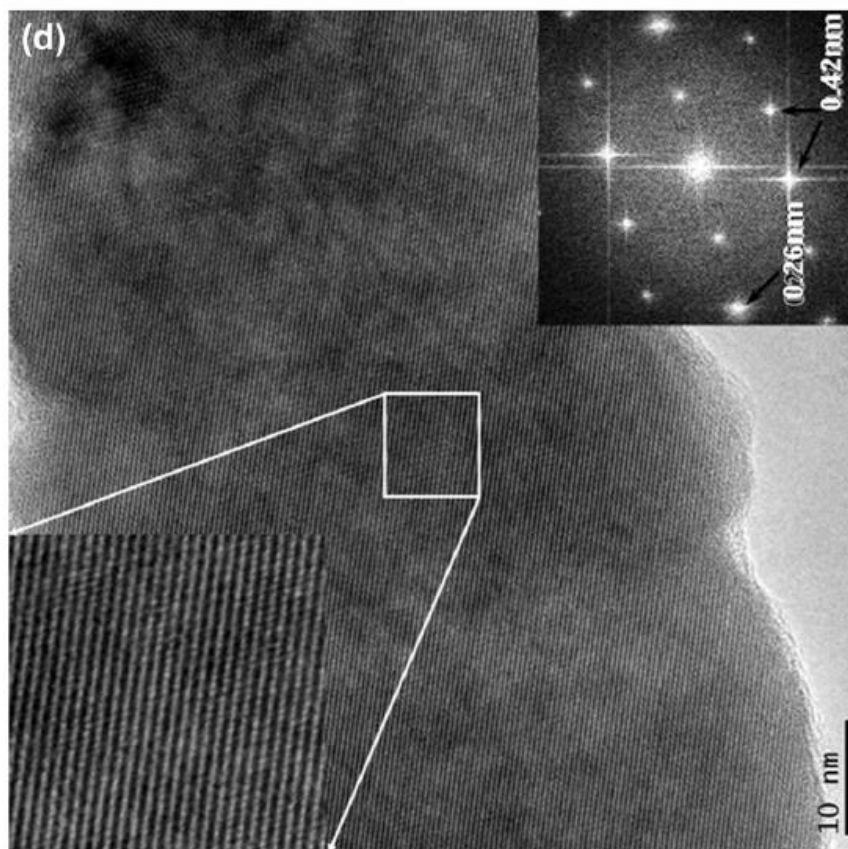


Figure 3.9. (d) HRTEM image of the InSb RBNW trunk after thermal annealing, displaying parallel lattice planes along $\langle 111 \rangle$ direction. Figure from [20].

Annealing was performed in two steps, first at 125°C for 6 hours followed by a 4 hour anneal at 420°C in argon with a flow rate of 30 sccm. The HRTEM images of the InSb RBNW branches show an amorphous outer edge with nanocrystalline regions present in the interior of the nanowire body. Selective area electron diffraction (SAED) patterns were recorded from different locations of the RBNW body, Figure 3.9a. Certain regions on the thickest regions of the NW (trunk) indicated a featureless diffraction pattern suggesting a non-crystalline nature, while other regions displayed diffraction patterns as indicated by the lattice indices of InSb. It was therefore concluded that the room temperature growth of the InSb RBNWs produced nanocrystalline structures with randomly oriented nanocrystals. The HRTEM images of the smallest, upper branches of the InSb RBNWs prior to annealing, some of which had diameters of 10-15 nm, were crystalline and had parallel lattice planes, Figure 3.9 (b and c) [20].

The nucleation and crystallization of the RBNWs in the smallest diameter branches were due to the confinement of the crystal planes in the reduced dimensional channels. This was suggested based on a work by Jiang *et al.* [23], who reviewed the crystallization of organic compounds in nanoporous materials and correlated the preferred orientation of nanocrystal growth in PAA template with competitive nucleation (kinetics of crystallization vs. the thermodynamics of nucleation) in confined pores.

Post annealing of the InSb RBNWs transform the entire structure to become single crystalline, without any visible dislocations, twin defects or stacking faults. The HRTEM of the trunk region of the InSb RBNW post annealing displayed a crystalline growth along $\langle 111 \rangle$ direction in the NW, Figure 3.9d. The surface of the RBNW has also been observed to have a roughness that varies between 5 and 7 nm. The compositional uniformity of the constituent elements in the RBNW was confirmed by an EDX analysis.

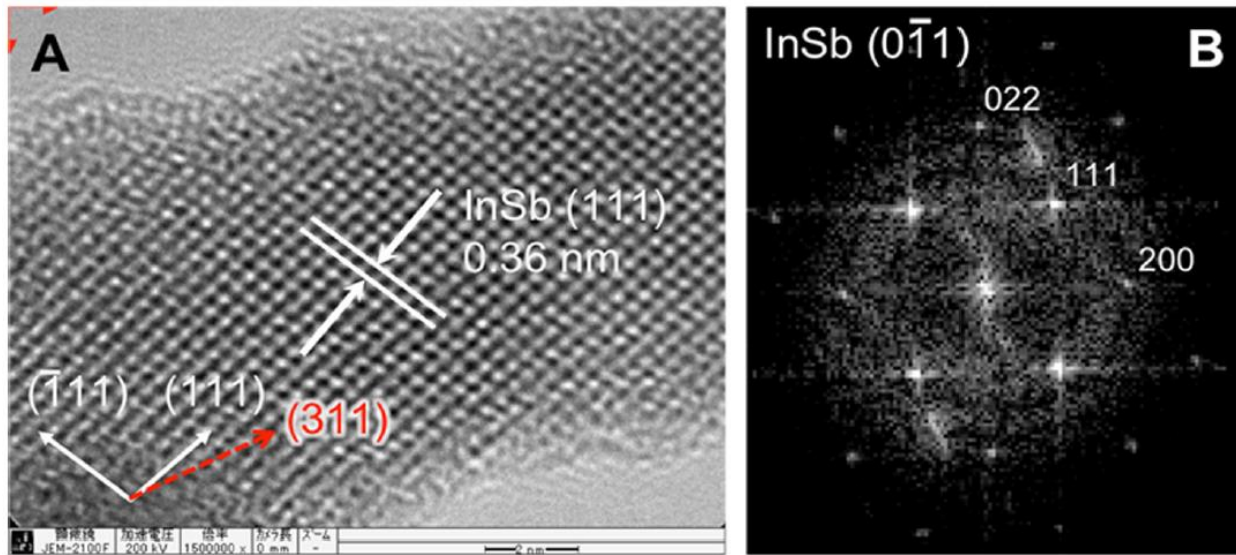


Figure 3.10. (a) STEM image of a sub-10 nm diameter ultra-thin InSb RBNW grown at -1.5V showing an InSb zinc blende structure. After annealing the ultrathin wire grows along the $\langle 311 \rangle$ direction. (b) SAED pattern showing the diffraction points of the InSb RBNW. Figure from [20].

Scanning transmission electron microscopy (STEM) image of the smallest branches of the InSb RBNW was analyzed by looking at an ultra-thin ~ 10 nm diameter wire. The wire was found to be highly crystalline with a growth direction determined, by comparing the SAED pattern with the theoretical diffraction pattern of InSb (ICSD code: 640411), to be along $\langle 311 \rangle$ direction,

Figure 3.10. The parallel lattice planes along $\langle 111 \rangle$ direction were well resolved the inter-planar spacing was measured to be ~ 0.36 nm, which corresponds to InSb crystal. A 9% lattice relaxation was found in the RBNWs when the measured inter-planar spacing was compared with the theoretical one [20].

3.3 Template Assisted Electrodeposition of Metallic Nanowires

Nanostructures of metals and semiconductors have generated significant interest in the scientific community and have been scrutinized for their interesting material, electrical and optical properties. Metallic nanostructures in particular show interesting properties, such as selective photoabsorption, when embedded in matrices of transparent dielectrics [24]. The selective absorption at a particular frequency by metallic nanoparticles has been attributed to Surface Plasmon Resonance (SPR) [25]. The structure, shape, size, and crystallinity of the nanostructures are crucial factors that ultimately determine their characteristics.

3.3.1 Template Assisted Electrodeposition of Branched Silver Nanowires

Silver nanowires (Ag NWs) and nanostructures are of particular importance as they have very interesting optical, electrical, and plasmonic properties. For instance, Ag NW mesh that forms a percolating network may be prepared by coating a solution to flexible substrates. These structures are known to have high transmittance and low sheet resistance that rival the optical and conducting properties of well-established transparent conductors such as indium tin oxide (ITO) [26]. Also, branched or nanodendritic structures of Ag have great potential as plasmonic routers or for chemical sensing purposes [27-30].

Fabrication and deposition of Ag nanoparticles and nanostructures have been achieved by various methods including, but not limited to, thermal evaporation, electron beam lithography etc. [24, 25]. On the other hand, template assisted growth and fabrication of NWs are quite popular because of the variety of NWs realized with various materials, such as metals and semiconductors. Compared to the vapor-liquid-solid (VLS) growth process, the template assisted growth provides good control over the structure of the NWs. The templates allow the growth of the NWs to be anisotropic with a fixed size, distribution and geometry. Among the various types of templates that are available, PAA templates, whose pore sizes, pitch, regularity and template thicknesses can be

controlled during the anodization of aluminum, have been used extensively to fabricate NWs. PAA templates have very low absorption in the visible (vis) and near-infrared (nIR) spectrum of light, and therefore these templates form an excellent matrix for analyzing and studying the optical properties of vertically aligned NWs. The actual diameter and length of the NWs depend on the pore sizes of the templates, and the time of deposition in the nano-channels of these PAA membranes.

Vertically aligned, randomly branched Ag RBNWs were electrodeposited within the pores of a branched porous BPAA template, described previously in Figure 3.2. A nano-structure made of thin metallic nanowires, like the Ag RBNWs, in a matrix of an isolating dielectric material, such as the alumina in a BPAA template, is of interest as it is expected to have an extremely low plasma frequency [31]. The samples were inspected by scanning electron microscopy (SEM) and x-ray diffraction (XRD).

Ag RBNWs were deposited within the pores of the BPAA template by potentiostatic electrodeposition of Ag. The electrodeposition was performed in a three-electrode setup using a PAR (Princeton Applied Research) 273A potentiostat. Using an e-beam evaporator, the working electrode was formed by evaporating a 100 nm thick gold (Au) film on the “top” branched side of the BPAA template (containing the smallest diameter pores). Platinum (Pt) gauze was used as the counter electrode. Ag/AgCl (3 M NaCl) reference electrode was used, and all electrodeposition potentials are in reference to this electrode. The Ag RBNW deposition was carried out in an electrolyte containing a solution of 0.05 M silver nitrate (AgNO_3) and 0.57 M boric acid (B(OH)_3) without agitation, and at room temperature [19, 32]. Prior to the deposition, the solution was purged with nitrogen to reduce the amount of dissolved oxygen. The exposed Au film, on the back of the working electrode, and the edges were carefully covered with a layer of an insulating material (clear lacquer coating) to facilitate the deposition of Ag only within the confines of the nano-channels of the BPAA template. The DC electrodeposition was conducted at a constant deposition potential of +0.04V [19]. This method avoids the use of extremely poisonous cyanide based electrolytes that are usually used for the electrodeposition or electroplating of Ag.

In order to study the optical properties of the Ag RBNWs in the alumina matrix, it is crucial to remove the highly reflective, and opaque Au layer. Due to the higher reactivity of Ag in comparison to Au, any wet chemical etching would preferentially attack the Ag BNWs at a rate faster than the Au film, thereby destroying the sample. Therefore, a dry plasma etching technique

was employed in this work. The Au layer was etched using argon (Ar) plasma (Plasma Tech Reactive Ion Etching (RIE) system) at 200 W with a flow rate of 50 sccm and a pressure of 100 mtorr for 9 minutes. Only the surface with the Au layer was exposed to the plasma. The sample was later inspected to ensure the removal of Au by visual observation and by analysis of the sample surface in SEM. The regions containing Ag BNWs were visibly distinct from the regions devoid of them.

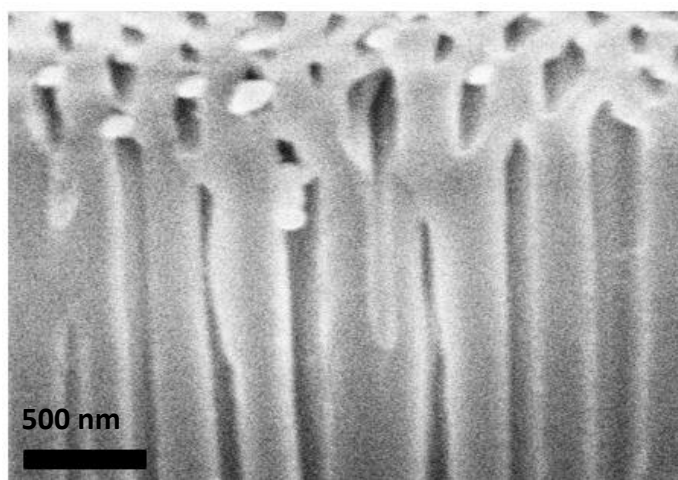


Figure 3.11. Cross-sectional FESEM image of vertically aligned randomly branched silver (Ag) RBNW arrays. Figure from [19].

The material composition of the RBNWs was confirmed to be Ag by XRD measurements. Field Emission Scanning Electron Microscopy (FESEM) was used to observe the branching of the Ag RBNWs. From the cross section of the BPAA matrix containing Ag RBNWs, as seen in Figure 3.11, the RBNWs appear to be vertically aligned and hierarchically stacked with relatively clear distinctions between the regions with different diameters of the Ag RBNWs. The FESEM image also confirms that the Ag RBNWs are independently branched, nominally parallel to each other, and continuous.

3.3.2 Template Assisted Electrodeposition of Branched Copper Nanowires

Copper (Cu) is one of the most important metals for the micro- and nanoelectronics industry for their extensive use in electronic circuits as interconnects. Having excellent electrical conductivity and being mechanically flexible, nanostructures of Cu, particularly Cu NWs have

been researched in recent years for their potential application as flexible transparent electrodes in optoelectronic devices, and as flexible and stretchable electrodes for wearable devices.

Various methods have been used for the fabrication of Cu NWs, which include vapor-liquid-solid (VLS) growth techniques, pulsed-laser deposition (PLD), chemical vapor deposition (CVD), and template assisted synthesis. Due to the tunable properties of templates such as PAA, template assisted growth techniques are preferred and can be used to grow many types of high aspect ratio complex nanostructures, like the branched NWs discussed earlier.

Hierarchical, randomly branched arrays of vertically aligned Cu RBNWs were fabricated using a template assisted electrodeposition of Cu within the branched nano-pores of a commercially available BPAA template, as described in Figure 3.2. The electrodeposition was conducted in a three-electrode electrochemical cell using a gold, Au, covered BPAA template as the active electrode. A ~100 nm thick Au layer was evaporated on the open pore side of the thinner branches of the BPAA template. A Pt gauze was used as the counter electrode, and a Ag/AgCl electrode (3 M NaCl) being used as the reference electrode. The electrodeposition was carried out at room temperature in an electrolyte containing an aqueous solution of 0.5M sulfuric acid (H_2SO_4) and 0.05M copper sulfate ($\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$), at a constant deposition voltage of -0.08 V.

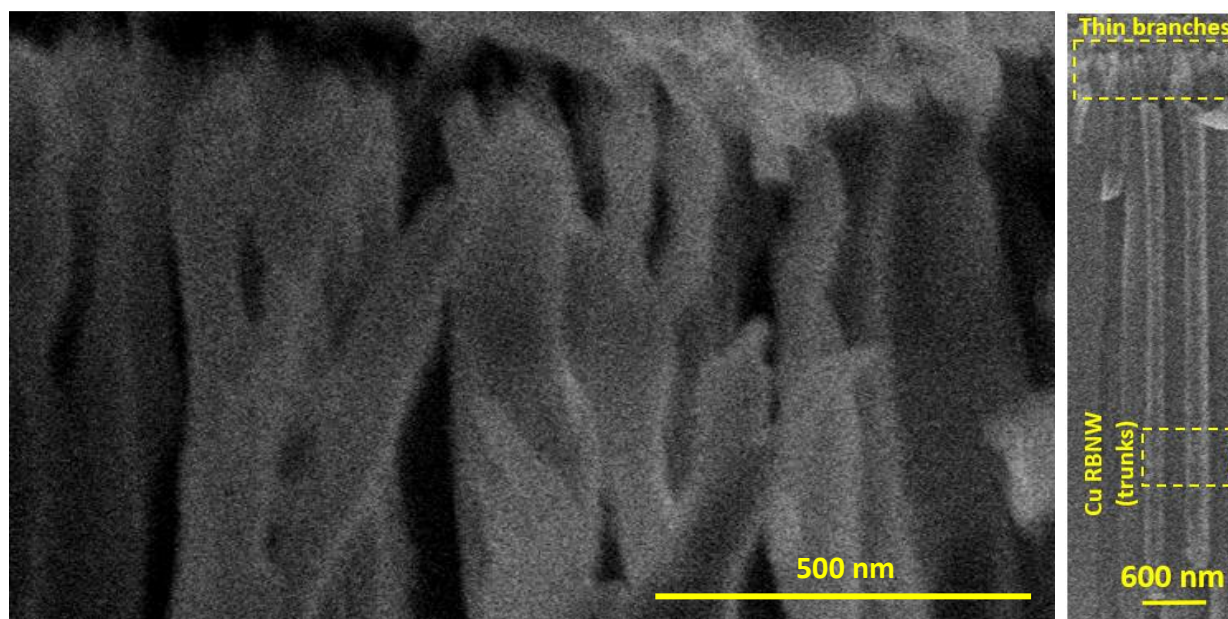


Figure 3.12. (Right) Cross-sectional FESEM image of the top branches of the vertically aligned Cu RBNW arrays in a BPAA matrix. (Left) FESEM image showing the high aspect ratio of the ($\sim 5 \mu\text{m}$ long) Cu RBNWs with the thin branches on the top, and the thicker trunks on the bottom highlighted.

The material composition of the Cu RBNWs were confirmed by an XRD measurement of the samples. The branched Cu NWs were found to have a wavelength dependent absorption, which was measured using a PerkinElmer UV-vis-NIR spectrophotometer (Model Lambda 950) with an integrating sphere arrangement. Field Emission Scanning Electron Microscopy (FESEM) was used to observe the branching of the Cu RBNWs. The cross-section of the Cu RBNWs were observed using FESEM images, Figure 3.12, where the RBNWs appear to be vertically aligned and hierarchically stacked with relatively clear distinctions between the regions of different diameters. The FESEM images confirm the successful fabrication of vertical arrays Cu RBNWs with diameters ranging from 150 nm to sub-20 nm by electrodeposition in a mesoporous, hierarchical BPAA template.

3.4 Template Assisted Electrodeposition of Heterostructures

There is a growing interest in one-dimensional (1-D) nanostructures with functional electronic characteristics. The motivations for these studies are due to the changes in properties that arise from quantum confinement, and the potential application of nanowires in very high

density logic, memory, optoelectronic, and sensing devices [33]. A lot of interest has been generated in the past decade for the preparation of these 1-D materials such as nanowires, nanotubes or nanorods for nano-scale device applications. Homogeneous NWs have already been used and demonstrated in many nanoscale devices, which further piques interest in the fabrication of single NW or arrays of NW based devices, as their small sizes permit highly dense packing of devices. In order to realize NW based devices, there is a great research interest in fabricating NW based heterostructures that can be used for different purposes, such as a p-n junctions or metal-semiconductor contact. Stable metal-semiconductor heterojunctions with well-defined interfaces are crucial for the functioning of NW based devices as they depend on metal-semiconductor junctions for contacts with low resistance and good thermal stability. Template assisted electrodeposition allows for the synthesis of structurally complex NW based heterostructures, by selectively electrodepositing metal on vertically aligned semiconductor NWs that can be used for fabrication of NW based devices.

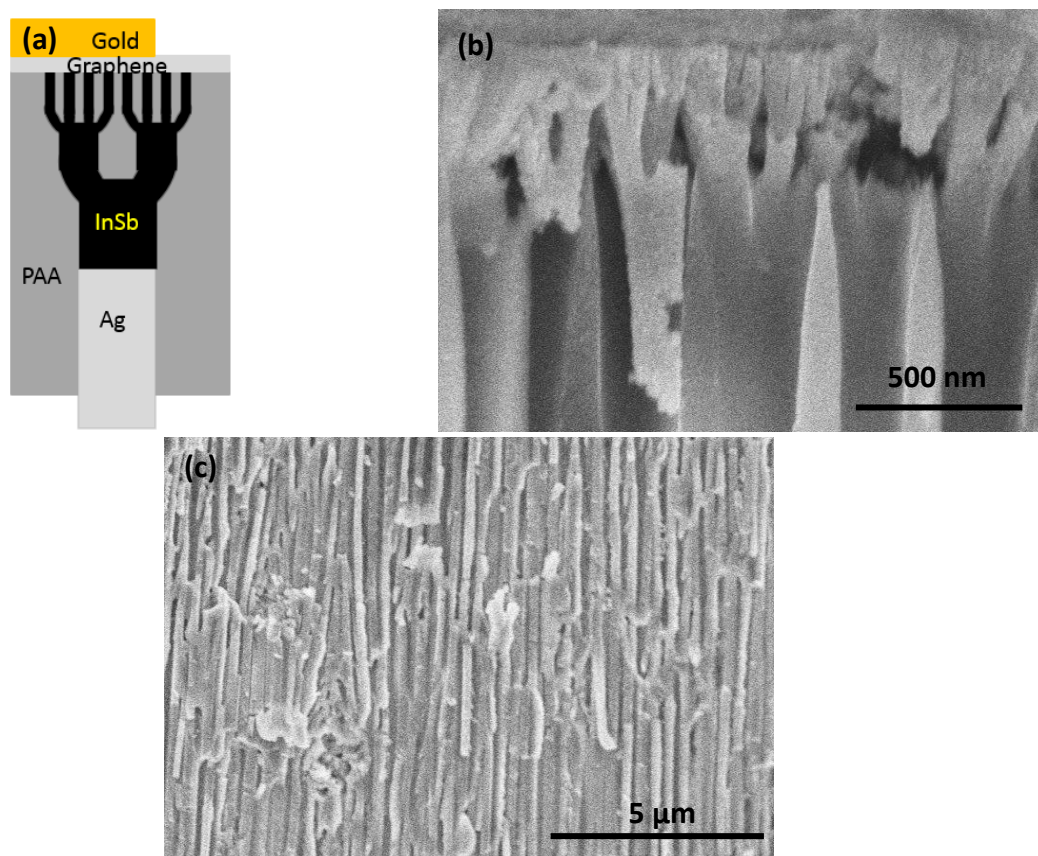


Figure 3.13. (a) Schematic diagram of the electrodeposited InSb/Ag heterostructure RBNW. (b) FESEM cross-sectional image of the InSb grown branches on the top regions of the InSb/Ag RBNW array. (c) FESEM cross-sectional image of the Ag NWs grown in the trunk region of the of the InSb/Ag RBNW array in a BPAA matrix.

A novel vertically aligned array of InSb/Ag heterostructure has been synthesized in a BPAA template, see schematic in Figure 3.13a. A commercially available BPAA template (see Figure 3.2 for schematic of the template) has been used for this experiment. Part of the NW heterostructure was fabricated in a three-electrode electrochemical cell. The surface of the BPAA containing the smaller pores was metalized to make it the active electrode. A layer of commercially available graphene (will be discussed in detail in Chapter 5, Section 5.4) was transferred on the small porous surface of the BPAA template prior to evaporating a very thin (~5 nm) layer of titanium (Ti) as an adhesion layer, followed by a ~200 nm thick layer of Au. The exposed metal surface was covered with an insulating clear lacquer coating to prevent the deposition on the outside surface. Pt gauze was used as a counter electrode, and a Ag/AgCl (3 M NaCl) was used as the reference electrode for the first step of InSb electrodeposition.

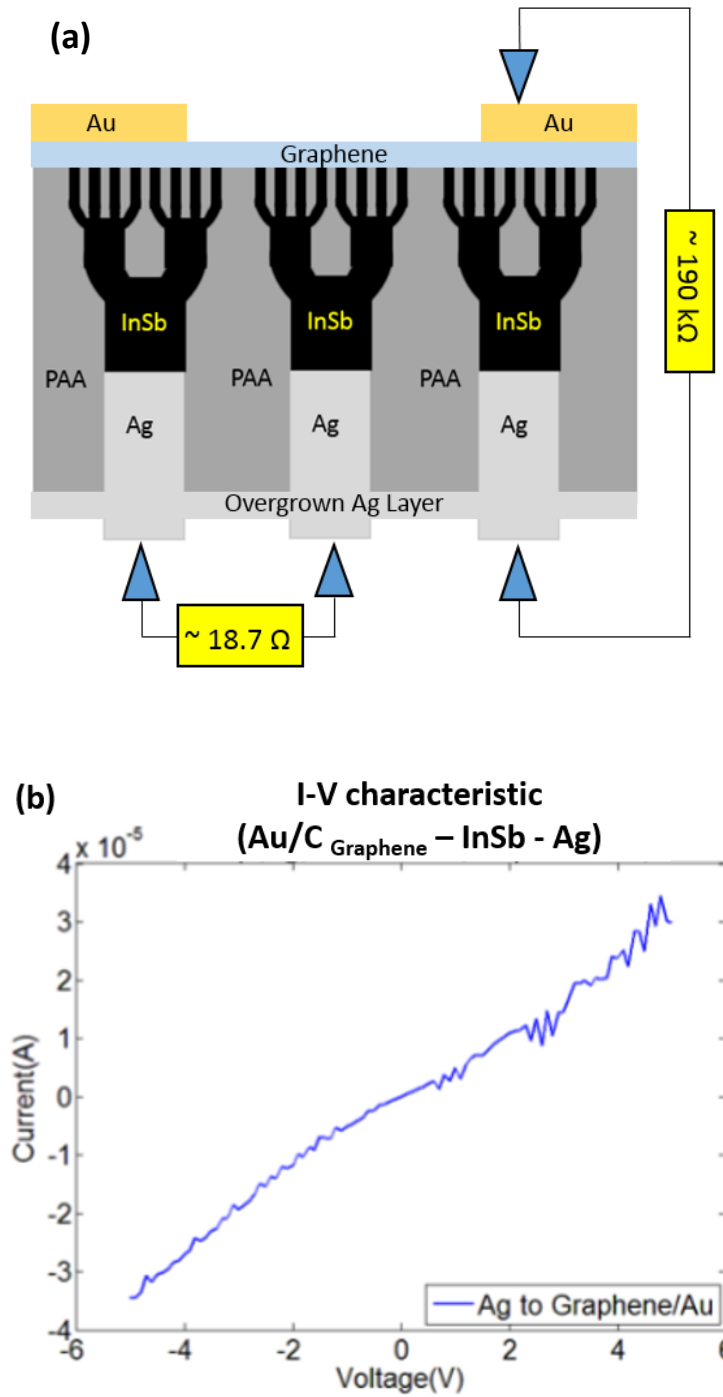


Figure 3.14. (a) Schematic diagram showing the resistance between the contacts. (b) Current versus voltage plot between gold and silver contact of the Au/graphene-InSb-Ag heterostructure.

The electrolyte for the electrodeposition of InSb consisted of an aqueous solution of 0.15 M indium chloride (InCl_3), 0.1 M antimony chloride (SbCl_3) along with complexing agents 0.36 M citric acid, and 0.17 M potassium citrate, at pH of 1.8. Using cyclic voltammetry, an equilibrium deposition potential for the electrodeposition of InSb on the BPAA template surface covered in $\text{C}_{\text{graphene}}/\text{Ti}/\text{Au}$ was found to be -1.78 V. InSb RBNWs were electrodeposited in the porous branches of the BPAA template using the aforementioned process for 2700 seconds. The InSb deposited template was washed in DI water several times before the Ag electrodeposition step.

Silver was electrodeposited on the InSb RBNWs to fill up the remaining portion of the pores, and allow the Ag to overgrow from the other side (larger pore side of the BPAA template) to form a metallic (Ag) contact. As the control of the length of Ag was not critical in this case, the Ag NWs were deposited, in room temperature, using a two-electrode electrochemical cell. The active electrode was the BPAA template consisting of $\text{InSb}/\text{C}_{\text{graphene}}/\text{Ti}/\text{Au}$, and the counter electrode was a pure Ag rod. The 50 ml electrolyte for the electrodeposition consisted of an aqueous solution containing 0.9 g AgNO_3 , 3 g Na_2SO_3 , 6.62 g $\text{K}_3\text{C}_6\text{H}_5\text{O}_7 \cdot \text{H}_2\text{O}$, and $\text{B}(\text{OH})_3$ added to make the final solution have a pH of ~ 7.2 . The electrodeposition was conducted at a constant voltage of -0.2 V for ~ 2 hours. The array of InSb/Ag heterostructure RBNW's cross-section was observed using scanning electron microscopy, Figures 3.13 (b and c).

The physical connection between the InSb and the Ag interface, see schematic in Figure 3.14a, was tested by measuring the I-V characteristics of the InSb/Ag RBNW array, Figure 3.14b. The resistance between two points on the overgrown Ag film was measured to be $\sim 18.7 \Omega$, whereas the resistance of the InSb RBNW between the Au and the Ag contact was observed to be $\sim 190 \text{ k}\Omega$. This demonstrates the template assisted electrodeposition of a continuous semiconductor-metal heterostructure based NW, which further opens up an exciting avenue to create structurally complex nanostructures that can be used to create NW based devices, like an array of NW based detector or a sensor.

3.5 References

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4. WAVELENGTH-DEPENDENT REFLECTANCE AND ABSORPTION IN VERTICAL ARRAYS OF BRANCHED NANOWIRES

In the previous chapters, the author discusses about various PAA based template fabrication technologies, and the various types of structures of several materials that can be realized by template assisted electrodeposition of semiconducting and metallic nanowires. This chapter will focus on the optical characteristics of both a III-V semiconductor (InSb) based, and a metallic (Ag) randomly branched, vertically aligned nanowire array using the template assisted electrodeposition technique. Part of this work has been published by the author in the journal Nano Letters (Nano Lett. 2012, 12, 6112-6118.) [1], and another part of the work has been published in the Proceedings of the IEEE (Nano) International Conference on Nanotechnology, 2014 [2].

4.1 Introduction

The interaction of light with periodically modulated solid state nanosystems constitutes the platform for many interesting phenomena in modern optics and metamaterials [3, 4]. One system of particular interest for photovoltaic and detector/ imager devices involves semiconductor nanostructures (nanowires/ nanoclusters), which can effectively absorb light with energies above the local bandgap and yield a photocurrent associated with separating the generated electron-hole pairs. Several groups have investigated aligned arrays of semiconductor nanowires as potential structures of interest for these applications [4-6]. There are several physical effects that can be attributed to the use of aligned nanowires. Within a vertically aligned array of nanowires, it is possible to decouple the two fundamental length scales for photovoltaic devices, namely the absorption length (axial in a nanowire array) and the minority carrier diffusion length (radial) [7]. At very small diameters, it is also possible to increase the bandgap energy (with respect to the bulk value) via electronic size quantization [8]. While the interface between air and an array of nanowires provides lower optical reflectance than an air/bulk interface of the same semiconductor, several groups have further reduced surface reflection in structures with tapered or stepped transitions along the length of the nanowire, as shown in Figure 4.1, with reported structures include dual-diameter nanopillars (DNPLs) [9], nanoneedles (NNs) [10], and nanoholes (NHs) [11]. A DNPL array provides a stepped change between a low-fill factor top layer and a high-fill

factor bottom layer, which provides broadband absorption close to unity in 300–900 nm regime [9]. Conical nanoneedles (NN) provide a tapered change in the fill factor, resulting in a very low reflectance [10]. The lower reflectance is typically attributed to the graded dielectric transition and paves the way for allowing a higher fraction of the incident light to be absorbed. Many prior nanowire array studies have considered dielectric properties associated with the non-unity filling ratio and/or graded/stepped transition, which can generally be understood in terms of an effective media analysis [4, 10]. However, one would expect photonic effects, e.g., the coupling between photons and the nanowires to depend on the ratio between the photon wavelength and the local nanowire diameter.

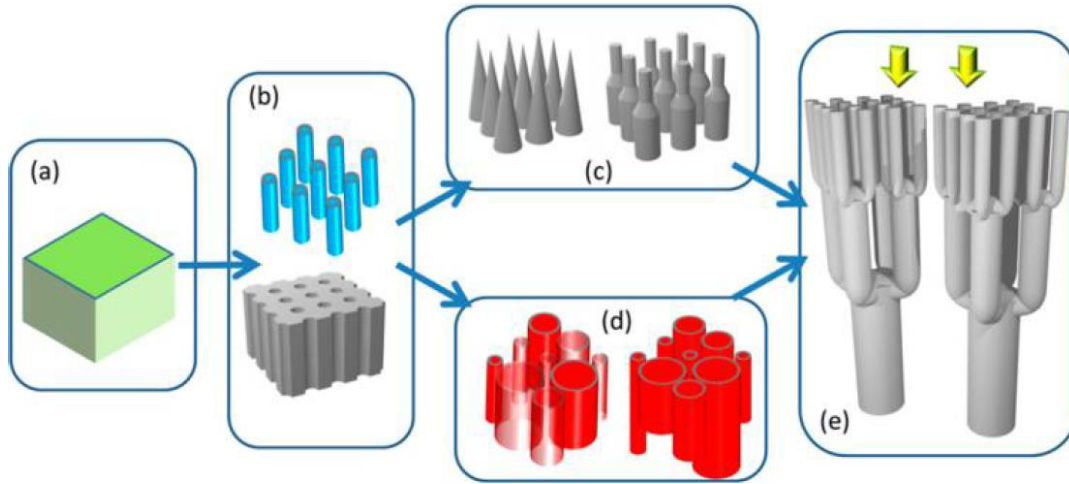


Figure 4.1. Schematic of various nanostructure arrays being studied for photonic or photovoltaic applications. In contrast to bulk films (a), arrays of nanopores or nanowires (uniform (b) and tapered/dual diameter (c)) can provide wavelength properties associated with size-dependent photonic coupling, resulting in reduced reflection and enhanced absorption. Randomness in diameter within the arrays allows tailoring of the absorption (d) with wavelength. This study investigates hierarchical, branched nanowire structures (e), which can allow tuning of the wavelength-dependent absorption within the various regions. Figure from [1].

Hu *et al.* [4], theoretically analyzed the reflectance and absorption of a silicon nanowire array as a function of the diameter, length, and filling ratio of individual nanowire arrays. This study concluded that in the short wavelength regime (<413 nm) the overall fraction of incident light absorbed within the array is much higher than that of a thin film structure, due to decreased reflection. The absorption in the longer wavelength region (413–1127 nm) is suppressed but can be improved with NW length, filling ratio, and/or by introducing light trapping mechanisms [4].

A second trend in vertically oriented NW involves increasing the diameter distribution, so that a broadband absorption is possible. While highly ordered structures can provide relatively sharp resonances, structures with disorder such as distributions in diameters or lengths, can yield high broadband absorption or wide-angle collection of light [12]. Random NW arrays can provide significant diffused reflectance (in contrast to the specular reflectance in case of a periodic array) arising from strong multiple optical scattering events and can lead to additional light trapping [12-17]. Unfortunately, while the randomness in diameter allows broadband absorption, it is counterbalanced by reduced absorption due to high reflectance of larger diameter NWs. In this chapter, we offer a third possibility to show that a hierarchical, vertical stacking of NWs with random diameter distribution can simultaneously maximize absorption and minimize reflection and thereby combine the advantages of the approaches discussed above. To validate the concept, a coupled experimental and modeling study is presented on vertically aligned, branched nanowire arrays. In contrast to most prior branched nanowire studies, the current arrays exhibit hierarchical stacking, i.e., the average diameter changing monotonically from layer to layer. The study demonstrates low reflectance (significantly different from that expected for a thin film of comparable thickness) and a unique wavelength-dependent absorption that can be explained on the basis of structurally dependent photonic effects. The experimental results are well fit by a model considering the wavelength-dependent coupling to a given diameter nanowire and the random distribution of diameters within the various regions of the structure.

4.2 BPAA template assisted growth of vertically aligned randomly branched InSb nanowires (InSb RBNWs)

Vertically aligned arrays of randomly branched, hierarchical nanowires (RBNW) of indium antimonide (InSb) were electrodeposited in the confines of the commercially available branched porous anodic alumina (BPAA) templates. The structure and parameters of the branched pores of the BPAA have been discussed previously, see Figure 3.2. A statistical analysis from the FESEM of the cross section of the BPAA template was performed to find the diameter and pitch of the NWs, and as explained previously, the BPAA can be distinguished into three distinctive hierarchical regions. The smallest and the topmost branches of the template has the thinnest pores of diameter $\sim 20\text{nm}$ with a pore-to-pore spacing (pitch) of 40nm . The intermediate branches were found to have diameters of $\sim 100\text{nm}$ with a pitch $\sim 220\text{nm}$, while the largest branches, which formed

the trunks, were found to be of diameter $\sim 150\text{nm}$ and having a pitch of $\sim 440\text{nm}$, Figure 4.2a. It was observed that the BPAA template for the RBNW structure exhibited randomness in both diameter and segment length in each region. This randomness was found to play a significant role in defining the optical properties of the branched InSb NWs [1].

InSb RBNWs of different lengths were deposited in the BPAA templates (smallest pores covered with a gold (electrode) layer) using the electrodeposition method discussed in detail in Chapter 3 (Section 3.2), which formed highly crystalline structures post annealing, Figure 4.2 (b and c).

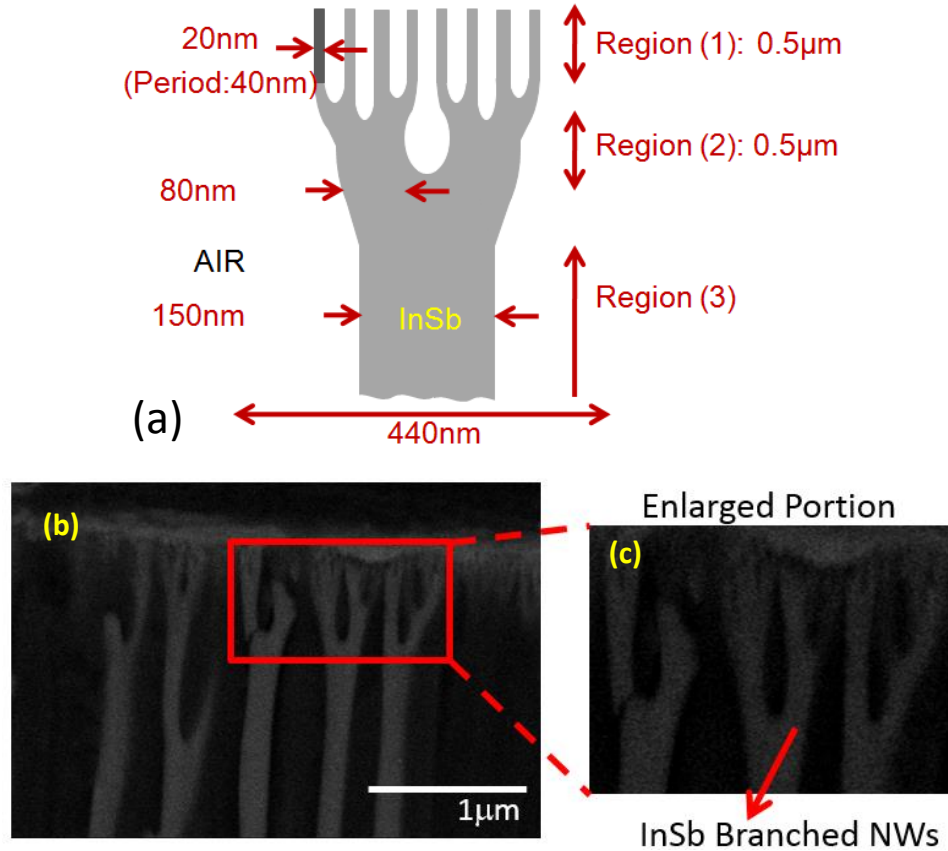


Figure 4.2. (a) An ideal schematic diagram of a single InSb RBNW showing the vertically stacked regions with their respective diameters and period (or pitch) , (b) cross-sectional FESEM image of a representative InSb RBNW showing the three layers of branching, (c) zoomed-in section of the array near the top surface, close to the NW branches. Figure from [1].

In general, the number of stacks in the multilayer stack can be extended to any number for light manipulation. To decouple the effects and properties associated with various layers in the

hierarchical RBNW structure, four types of structures were characterized. The reference structure (RBNW-ref) consists of a BPAA membrane that is not backfilled with InSb. This structure (RBNW-ref) shows negligible absorption in the spectrum of interest (less than 1% for wavelengths 850 nm and beyond). The second structure (RBNW0) consists of a BPAA membrane backfilled with $\sim 20\ \mu\text{m}$ of InSb followed by a $\sim 10\ \mu\text{m}$ etch-back of the alumina to form a free-standing array with a thickness larger than typical absorption lengths (effectively eliminating reflections from alumina surface during reflectance measurements).

Finally, InSb RBNW1 (wire length $\sim 800\ \text{nm}$, consisting primarily of regions 1 and 2 (see Figure 4.3a) and InSb RBNW2 (wire length $\sim 1400\ \text{nm}$, including all three regions) consist of shorter nanowire structures. The alumina membrane was not etched back in these samples as they were required for structural support. The sample shown in Figure 4.2b is representative of type RBNW0, prior to back-etching of the alumina.

4.3 Optical Measurements

For the optical measurements, the RBNW samples were thoroughly cleaned with ultrapure DI water, dried with N_2 gas, and prebaked at $\sim 90\ ^\circ\text{C}$ to thoroughly dry the samples. The gold electrode was etched away using gold etchant (Transene Co.). For reflectance and transmittance measurements, a PerkinElmer UV-vis-NIR spectrophotometer (Model Lambda 950) with an integrating sphere arrangement was used. Prior to each set of measurements, the system was calibrated with the white standard reflector from PerkinElmer. Also with identical experimental conditions, the reflectance and transmittance spectra of a blank BPAA were recorded, and the absorbance was found to be less than 1% for wavelengths larger than 850 nm (our spectrum of interest). After all instrumental calibration, data of RBNW1 and RBNW2 were taken.

The reflectance (R) and transmittance (T) of the samples were measured, and the absorbance (A) was calculated from these characteristics. About $1\ \text{mm}^2$ of the “top” surface of each sample (i.e., containing smallest diameter pores/wires) was illuminated at normal incidence ($\theta = 0^\circ$), arranged inside an integrating sphere setup, with the wavelength of the incident light ranging from 300 nm (UV) to $2\ \mu\text{m}$ (NIR to mid-IR). Figure 4.3b shows the measured R versus wavelength for the free-standing NW array (RBNW0). For comparison, we plot the R calculated from effective medium approximation using the bulk material parameters of InSb and the fill factors for the different regions (inferred from FESEM) [18]. The R of a thin film of equivalent thickness (~ 800 and ~ 1400

nm) would be approximately $\sim 47\%$ (UV-vis) and $\sim 37\%$ (near-IR). While the measured reflectance appears to be well approximated by the effective media approach, we will see later that the approach cannot describe local absorption within and transmission through the photonic nanostructure.

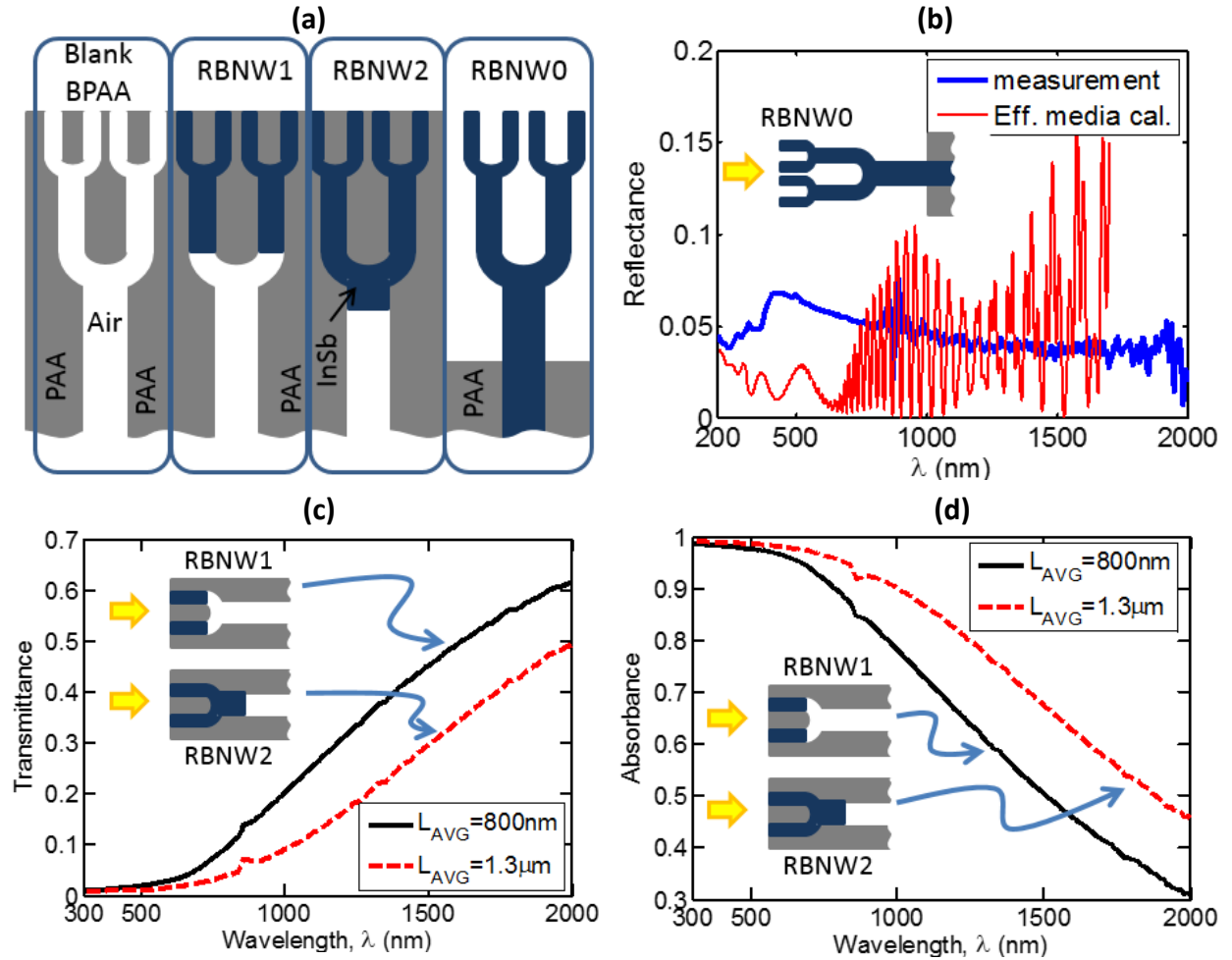


Figure 4.3. Reflectance, transmittance, and normalized absorbance of vertically aligned InSb RBNWs. (a) simplified cross-sectional schematic of a blank BPAA, BPAA with ~ 800 nm long InSb RBNWs (RBNW1), BPAA with ~ 1.4 μm long InSb RBNWs (RBNW2), and a schematic of the etched back sample (RBNW0); (b) measured reflectance of RBNW0 and reflectance calculated for same nominal structure from effective media theory; (c) measured transmittance of RBNW1 (black) and RBNW2 (red); (d) the normalized absorbance of RBNW1 (black) and RBNW2 (red) calculated from the measured reflectance and transmittance. Figure from [1].

Figure 4.3c shows the measured T of RBNW1 and RBNW2 in the 300–2000 nm range. The T is small in the lower wavelength range (< 700 nm), and it rises linearly for wavelengths > 700 nm.

nm (RBNW1) and >850 nm (RBNW2), indicating that a broader range of wavelengths is absorbed for samples with significant filling in region 3.

In order to differentiate the effects of absorption and reflection and to allow direct comparison among samples with different R, we define a normalized absorption (A^*), given by:

$$\text{Normalized Absorption } (A^*) = \frac{1 - R - T}{1 - R} \quad (4.1)$$

The measured A^* of RBNW1 and RBNW2 (Figure 4.3d) shows nearly complete absorption for wavelengths up to ~ 700 nm (RBNW1) and ~ 850 nm (RBNW2). The absorbance decreases linearly in the NIR regime, with the rate being somewhat faster for the shorter arrays of RBNW. The absorption band can be tuned by designing the RBNW layers with specific average diameters. This broadband and wavelength-dependent absorption along with its tunability in branched NW structure is unique and the key results of this particular work.

4.4 Analysis of the wavelength dependent absorption in InSb RBNWs

To understand the origin of the wavelength-dependent absorption in such a complex hierarchical RBNW structure and its implication of depth-resolved absorption, we theoretically interpret the T and A^* spectra associated with the different configurations. The numerical analysis was implemented using the electromagnetic simulator COMSOL RF-module [19]. To replicate the experiments, the optical properties of InSb and alumina were used and a normal incidence of the plane wave was assumed [20].

As we will see below, the characteristic randomness in diameter of RBNW has a significant effect on the broadening of the absorption spectrum, which can be explained neither by a periodic structure nor exclusively by the variation in the lengths of the NWs. In order to understand the effects of this randomness, a model assuming that the diameter has a Gaussian distribution characterized by a mean diameter ($\bar{d}$) and standard deviation (σ) was assumed. The structures associated with samples RBNW1 and RBNW2 were modeled using two-layer random nanowire (RNW) arrays corresponding to regions 2 and 3 in Figure 4.2a. Since NWs with diameters of ~ 20 nm do not significantly couple to wavelengths over the measurement range (300–2000 nm), region 1 was omitted in the optical modeling. This approximation reduces computational burden and

simplifies conceptual interpretation of the results. This approach is justified because as we will see later that we can consistently interpret the salient features of the experiments using with the simplified structure. Analysis of the FESEM images show that the two-step RBNW array structure has $(\bar{d}_a, \sigma_a) \sim (100, 25)$ nm in region 2 and $(\bar{d}_b, \sigma_b) \sim (150, 25)$ nm in region 3. The length of the top region is kept fixed at 700 nm, and the length of the bottom layer is chosen to achieve the same overall length as either RBNW1 or RBNW2. In this model, the NWs are embedded within a thick layer of alumina, to be consistent with the experimental measurements.

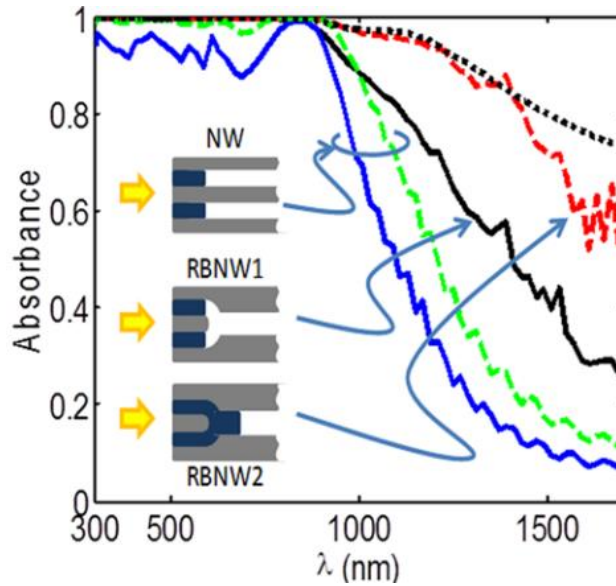


Figure 4.4. Comparison of numerically determined normalized absorbance for vertically aligned InSb NWs and thin film. Normalized absorbance calculated from model for single-layer NW array with uniform diameter (100 nm) and thickness of 800 and 1400 nm (solid blue and dashed green lines respectively) and for random diameters for single layer (RBNW1, solid black line) and bilayer (RBNW2, red dashed line). The calculated normalized absorbance for a thin film with bulk properties and thickness of 800 nm (black dotted line) is shown for comparison. Structures with uniform diameters have steep decrease in absorbance, corresponding to cutoff wavelength, while structures with randomness in diameter exhibit a more gradual roll-off. Figure from [1].

Figure 4.4 shows the calculated A^* versus wavelength for various structures. The A^* calculated for a spatially uniform thin film with bulk material properties and thickness of 800 nm is also shown for reference (black dotted line). To decouple the effects of fluctuation in NW length vs randomness of diameter, a single layer, uniform-diameter (100 nm) NW array is modeled for two different lengths (800 and 1400 nm, solid blue and dashed green curves, respectively). The

curves show a relatively sharp cutoff at ~ 1000 nm, well below that expected for the bulk thin-film (dotted line) as well those for RBNWs. The fluctuation in NW length therefore cannot explain the broadband absorption observed in experiment.

Next the responses of the experimental structures RBNW1 (length = 800 nm) and RBNW2 (length = 1400 nm) was modeled, not as a uniform periodic array but as structures with random diameter distribution in region 2 (for RBNW1) and regions 2 and 3 (for RBNW2). Remarkably, the introduction randomness in diameter immediately broadens the absorption profile. For structures of the same length, the random structures exhibit significant absorption over much broader band, with a more gradual roll-off in the absorption spectrum, in comparison to the uniform array with same length and same mean diameter(s). Consistent with experiments in Figure 4.3, the structure representing RBNW2 has a more gradual roll-off (in comparison to that of RBNW1), indicative of the two different diameters in the two regions and randomness in both layers. The higher absorption is predominantly due to the bottom layer with higher mean diameter of NWs, which more efficiently couple the longer wavelengths. Based on these simulations, our experimental results are best explained in terms of the wavelength-dependent photonic coupling to the randomly sized nanowires within regions 2 and 3. The roll-off in A^* reflects the average diameters and characteristic randomness in the branched NW structures. Electronic size quantization effects cannot explain the observed A spectra; even for diameters of 20 nm, the bandgap would be expected to broaden by ~ 100 meV (using bulk effective mass for InSb), corresponding to a cutoff wavelength of ~ 4.6 μm .

The close agreement between theory and experiment allows us to establish a remarkable feature of the RBNW arrays, namely, the depth specific wavelength-dependent absorption. As we will show in the following discussion, the RBNW arrays have the ability to differentiate the three distinct regions for filtering and absorbing UV, Vis, and IR waves in the same structure. This effect arises from the geometry of the stacked NW and not from the electronic properties of the NWs.

To understand the wavelength-dependent absorption in various regions of the stacked NW, let us begin with a simple argument. If the individual branches of the RBNW array are approximated as isolated, non-interacting waveguides, then the cutoff wavelength ($\lambda_{\text{cutoff}}/n_{\text{InSb}}$) of the InSb waveguide is given by:

$$\frac{\lambda_{\text{cutoff}}}{2} / n_{\text{InSb}} = d, \quad (4.2)$$

where d is the diameter of the NW. Assuming, the average refractive index of InSb n_{InSb} in the 300–1000 nm range is ~ 4.25 [20], the λ_{cutoff} for region 2 ($d = 100$ nm) is ~ 850 nm, while that of region 3 ($d = 150$ nm) is ~ 1275 nm. Incident wavelengths shorter than these cutoffs would efficiently couple to the nanowires and be absorbed within the respective region.

Longer wavelengths would pass through the respective layers, with significantly reduced absorption and reflection. Note that the calculated cutoff for region 1 ($d = 20$ nm) is less than 300 nm, so the nanowires in this region are not expected to absorb significantly within the measured wavelength range. In short, the wavelength range absorbed within each region can be independently controlled by controlling the average diameter (and randomness) within the respective region. While such effects can be achieved by employing layers with different bandgaps or through electronic size quantization, the effect in this study arises from the structure itself, rather than the electronic properties of the material.

This elementary argument is supported by detailed numerical simulation result in Figure 4.5a (for RBNW2). The wavelength resolved solution shows that nearly 95% of the coupled light with $\lambda < 680$ nm is absorbed by the top portion (~ 800 nm) of the BNW array. Only a small fraction of the longer wavelength photons are absorbed in this region. As we move deeper into the structure (region with $d \sim 150$ nm), the normalized absorbance exceeds 90% for $\lambda < 1000$ nm and approaches 80% for $\lambda \sim 1000$ –1300 nm. If the NWs within each region were spatially uniform, sharp cutoff in the absorption spectra of UV, vis-, and IR regions of the incident waves could be assigned to unique spatial regions. The gradual cutoff (linear decrease of absorption vs wavelength) in the absorption spectrum is caused by the randomness of the diameter distribution. Figure 4.5b shows a much simpler picture of this analysis. The normalized absorption is subdivided into three wavelength bands. As we see, $\lambda \sim 201$ –800 nm rapidly reaches high normalized absorption (top 800 nm of the NW). The longer wavelengths are not strongly absorbed in the top 800 nm but are absorbed in the underlying region, containing larger diameter NWs ($d \sim 150$ nm). As noted earlier, the wavelength-dependent absorption does not arise from size quantization effects. Therefore, our tailored broadband absorption in UV–vis and the wavelength-dependent absorption in the IR region are attributed to structural effects.

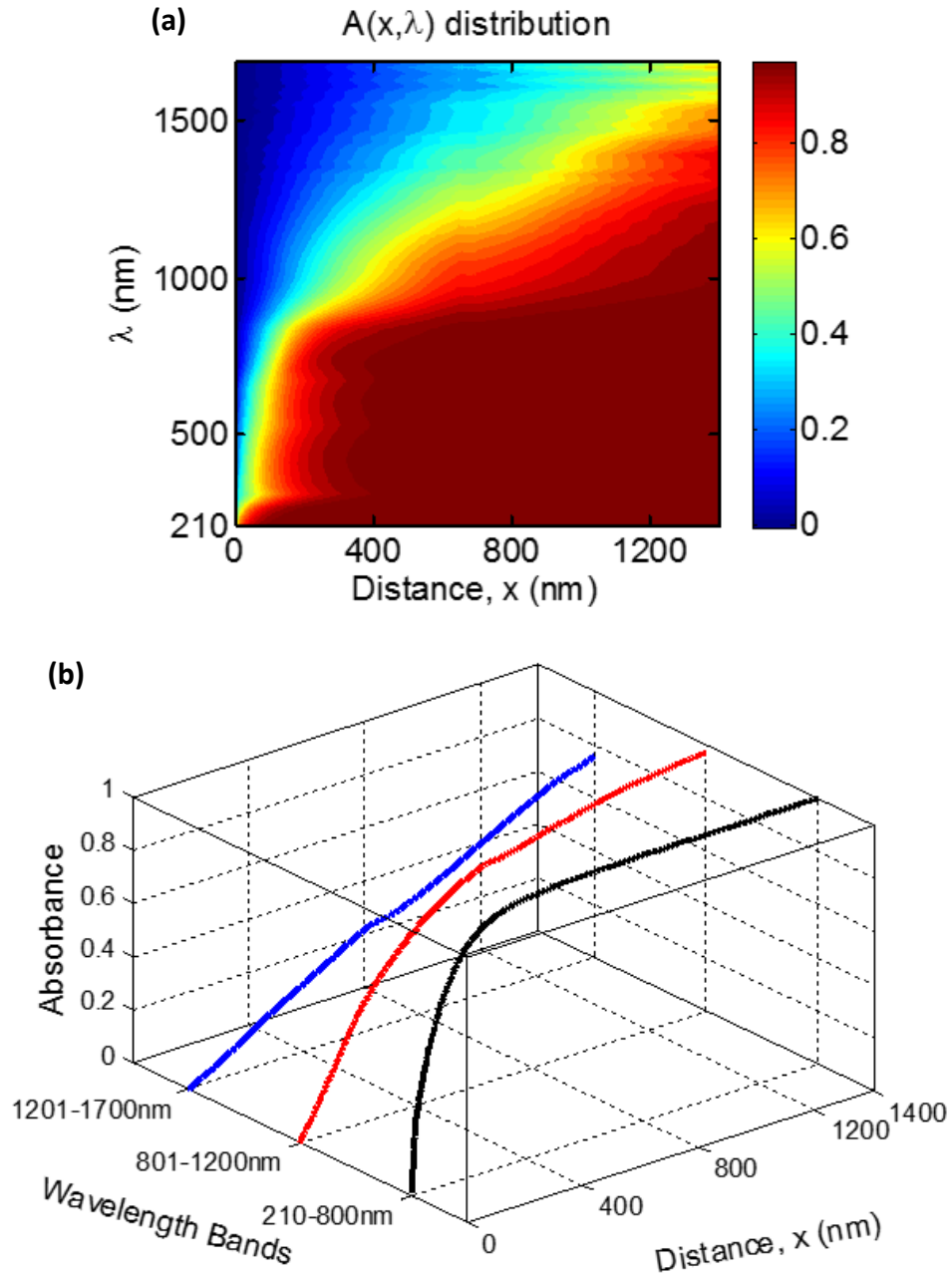


Figure 4.5. Numerically determined cumulative normalized absorbance of vertically aligned branched InSb NWs. (a) The cumulative normalized absorption for three separate bands of wavelengths. The shortest wavelength band (210-800 nm) is absorbed very quickly at smaller depths ($x < 800$ nm), which contain nanowires with relatively small diameter (~ 100 nm). The higher bands are absorbed relatively weakly within the first 800 nm and more strongly within the region with larger diameter nanowires ($x > 800$ nm). Image taken from [1].

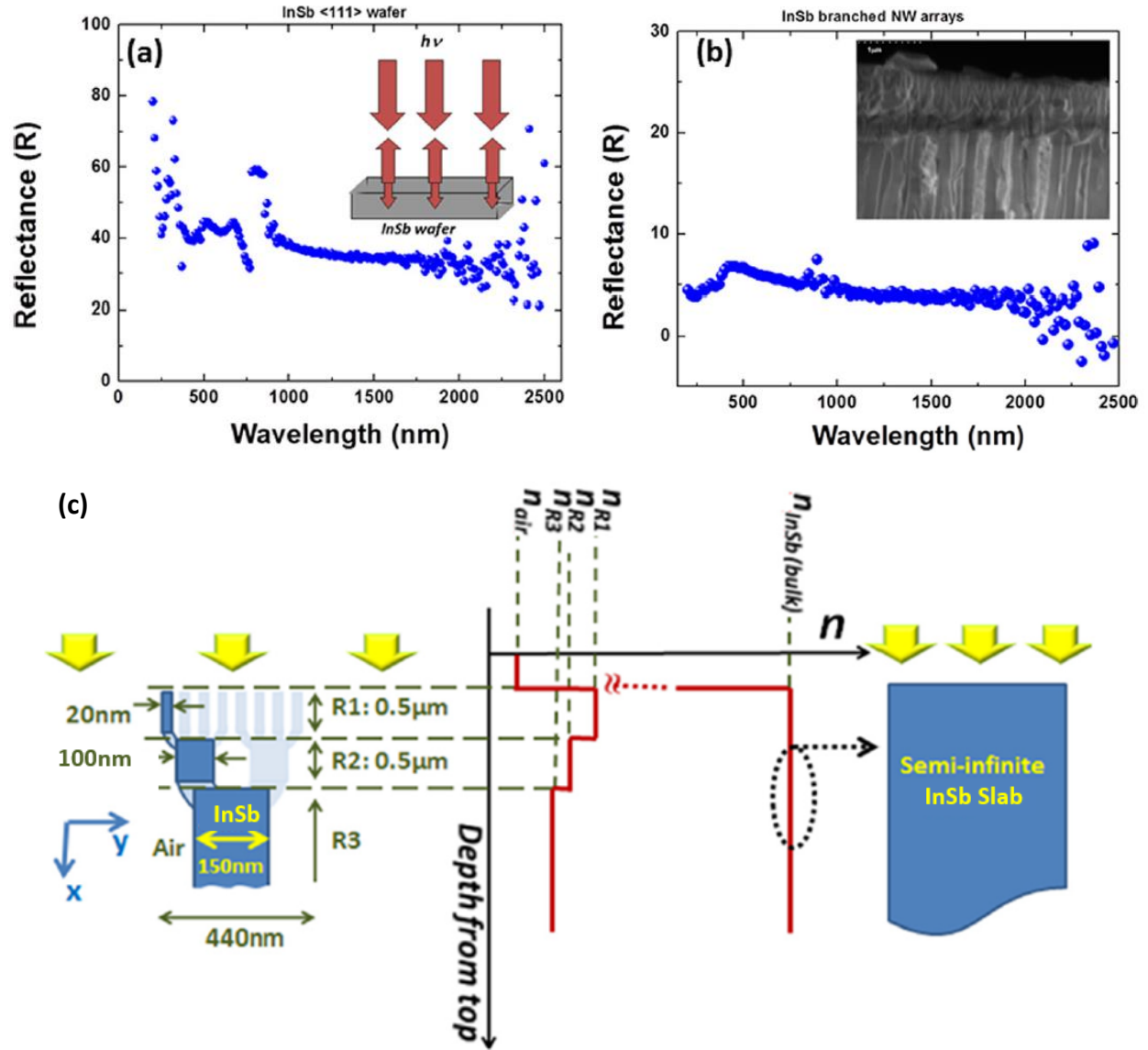


Figure 4.6. UV-vis-IR reflectance spectrum of (a) bulk InSb (wafer) and (b) InSb RBNW array. Inset shows a cross sectional FESEM image of an array with PAA etched back from the top surface. (c) Schematic shows the change in refractive index of the medium as seen by light as it approaches and passes through the branched nanowires. For comparison of impedance mismatch, a bulk InSb picture is included in the figure. Figure from [21].

An interesting corollary to the discussion above is that the observed absorbance and reflectance properties of such hierarchical structures cannot be reproduced by effective media approximation. Since photonic coupling effects are typically not included, wavelength-dependent absorption effects within the various regions are not accurately modeled using effective media. In order to achieve low reflectance, typical impedance matching approaches based on effective media approximations would employ a structure with a monotonic change in the volume fraction from air to the dielectric medium (InSb), corresponding to a gradual change in the refractive index.

In the case of the RBNW arrays, the volume filling fractions inferred from SEM imaging ($\sim 19.6\%$, $\sim 16.2\%$, and $\sim 9.1\%$ in the top, intermediate, and bottom regions, respectively) decrease with increasing depth, indicating that the lower reflectance compared to bulk InSb does not arise from this impedance matching, Figure 4.6. The low reflectance of our RBNW arrays compared to bulk InSb is attributed to the photonic coupling and random size distributions within the arrays.

In summary, hierarchical InSb RBNW array was developed, and the reflectance and absorbance spectra for these arrays was measured. The nominal size distribution within each of the three regions has been determined by FESEM. The samples exhibit a very low broadband reflectance with near unity normalized absorbance in UV–vis range and a wavelength selective absorbance in the NIR range. A model considering the diameter-dependent photonic coupling and random distribution of diameters has been used to analyze structures representing the various RBNW samples. The low reflectance and wavelength-dependent absorbance are both explained in terms of cutoff frequencies for photonic coupling into the nanowires in a given region (specific diameter). The randomness in the structure broadens the absorption spectra and can in principle be used to achieve tailored photonic properties, including specific absorbance profiles. This ability to tailor photonic properties through structure, both average diameters and randomness, could enable novel future optoelectronics devices, including wavelength-selective IR detectors/imagers and photovoltaic devices.

4.5 Optical Characteristics of Vertically Aligned Arrays of Branched Ag NWs

There has been some study about optical properties of straight Ag NW arrays [22, 23]. While bulk Ag has higher reflectance (lower absorbance) in the visible range of the spectrum, straight Ag NW arrays have lower reflectance (higher absorbance) in the same wavelength range. This interesting result has been attributed to the plasmonic effect of the Ag NW arrays. On the

other hand, the optical properties of vertically branched Ag NWs (Ag BNWs) has not been reported. Therefore, in this section the optical characteristics of branched Ag NWs (Ag RBNWs) will be discussed. The electrodeposition process and the structure, Figure 4.7, of Ag RBNWs have been discussed in detail in Chapter 3 (Section 3.3).

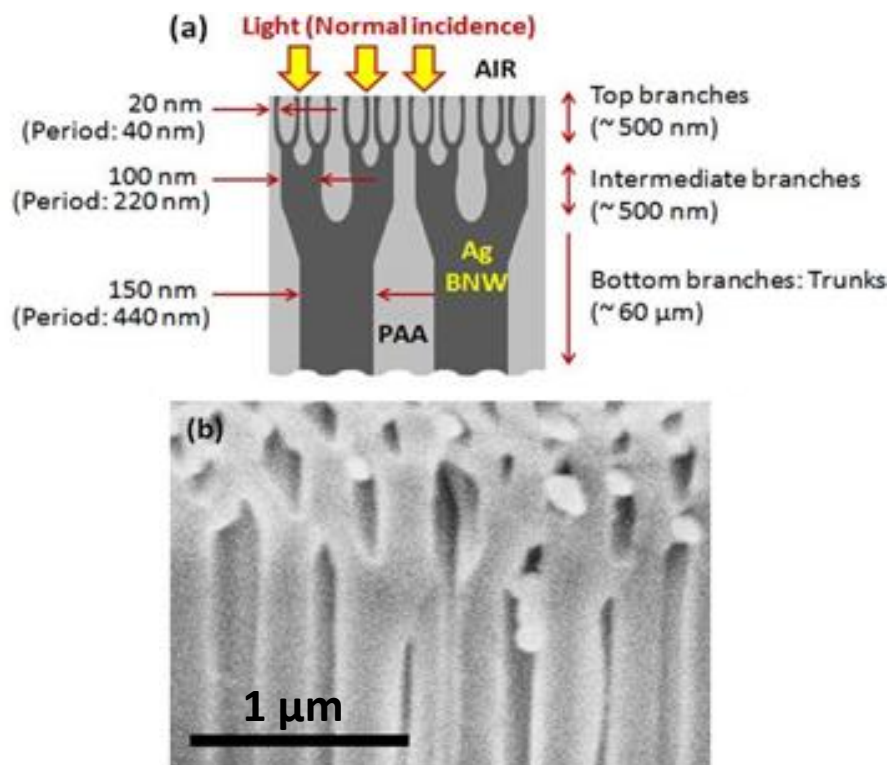


Figure 4.7. Schematic of the Ag RBNWs in the Branched Anodic Alumina (BPAA) template; (b) cross-sectional FESEM image of vertically aligned randomly branched Ag RBNW arrays. Figure from [2].

The Ag RBNW were electrodeposited in a BPAA template, and the Au electrode layer was etched away from the top layer, using a dry plasma etching technique, discussed in Chapter 3 (Section 3.3), exposing the branched Ag RBNW in a very low absorbing BPAA template. The reflectance (R) and transmittance (T) of the Ag BNWs in the BPAA matrix were measured using a PerkinElmer UV-vis-NIR spectrophotometer (Model Lambda 950) with an integrating sphere arrangement. The R and T were measured by illuminating a region of about 1 mm² of the bare branched BPAA surface containing the BNWs, without the Au layer, Figure 4.7a. The measurements were performed at normal incidence, with the wavelength range from 320 nm to 2000 nm (UV to NIR range). A standard white reflector from Perkin Elmer was used to calibrate

before each set of measurements. The absorbance by the Ag BNWs in the BPAA matrix was calculated from the R and T spectra of the sample. The absorbance for a blank BPAA template, without Ag BNWs, were also measured for comparison, Figure 4.7b.

The average packing density on the branched side of the BPAA template was found to be ~33 %. The actual filling factor may be higher, as the possibility remains that some of the topmost branches of the Ag BNWs may have been removed during the Ar plasma etch process required for the removal of Au layer. There can be many factors that can negatively affect the filling factor of the pores, such as the presence of microscopic cracks in the BPAA template. Packing density may also be influenced by the existence of contaminants or debris inside the nano channels or on the surface of the templates that could effectively block the deposition path. Non-uniformity of the electrical resistance channels in each pore may also contribute to varying growth rates of BNWs in different regions of the template. On the bottom side (trunk section), most of the nano channels of the BPAA template appeared to be empty. A small percentage of the BNWs filled the entire cross-sectional length (~60 μm) of the template and subsequently served as nucleation sites for Ag nanostructures on the other surface. The length of the Ag BNWs ranged from a few microns to ~60 μm .

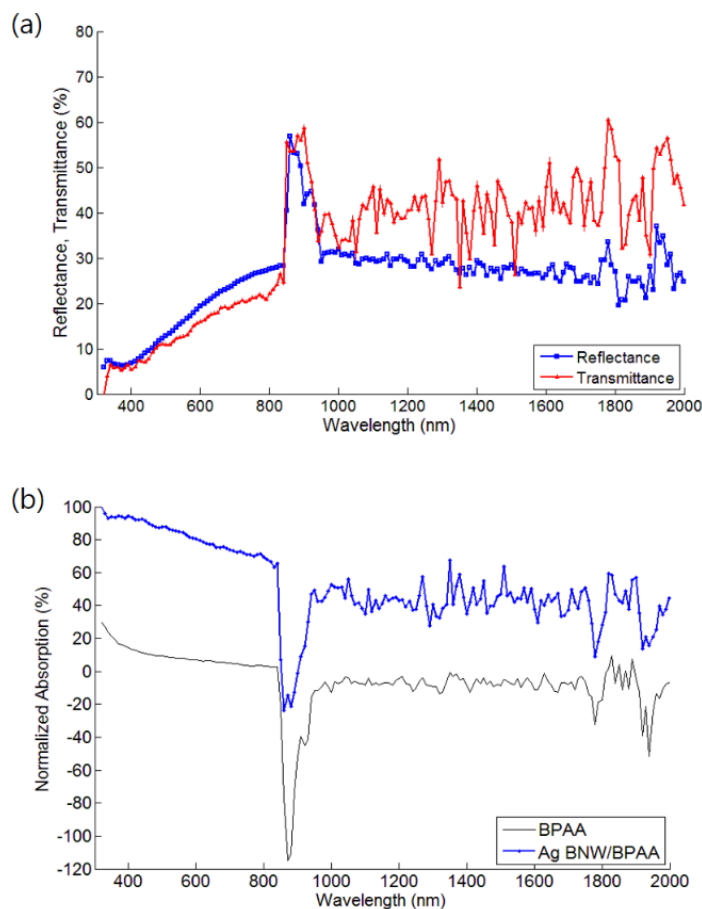


Figure 4.8. Reflectance and transmittance of Ag RBNWs with normal incidence on the branched side; (b) Normalized absorption of Ag BNWs and blank BPAA with respect to wavelength. Artifacts around 850 nm arise from detector change and should be ignored. Figure from [2].

The measured R and T spectra of the Ag BNWs, with light incident on the top branched surface of the sample, are shown in Figure 4.8a. As observed in the figure, the R increases sharply, from 5% to about 25%, as the wavelength of the incident light increases from 320 nm to 800 nm. The minimum value of R is observed near $\lambda \sim 300$ nm. The R of the Ag BNWs stabilizes at around 25-30%, as the wavelength of the incident light reaches the NIR range of the spectrum. The spike in the plots that are observed in Figure 4.8a, at wavelengths of around 850 nm, arise due to the switching of detectors in the spectrometer. Therefore these artifacts should be ignored when considering the measured R and T spectra, along with the resulting absorbance, of the sample.

The measured R and T spectra exhibit the same general trend which was observed in straight Ag nanowire structures when incident light was perpendicular to the surface of the templates containing the NWs [23]. In bulk Ag, a sharp reflectance minimum at around 320 nm is

attributed to plasmonic effects in Ag. In a prior study [23], silver-alumina composite material also showed a clear dip in the reflectance spectra of the sample at around 320 nm. While the decreases in R and T at the lowest measurement wavelengths in the current study may correspond to plasmonic effects, it is difficult to draw strong conclusions from this region due to the lack of data below 300 nm.

As demonstrated by Lee *et al.* [24], the T of Ag thin film drops rapidly as the film thickness increases from 3 nm to 30 nm. The T is less than ~5% for Ag films of thickness 30 nm in the wavelength range of 900 nm - 2 μ m. On the other hand, the Ag RBNWs which have more amount of Ag along the light pathway than the thin film Ag (30nm) has, display higher T than the Ag thin film. The T of the Ag BNWs increases steadily from about 4% to 27%, as the incident wavelength rises from 320 nm to 800 nm. For NIR range of the spectrum, the T stays in the vicinity of 40%, which is higher than the T of thin films of Ag of thickness as low as 9 nm [24].

The absorbance of the Ag BNWs in the BPAA template was calculated from the measured R and T spectra. To investigate the amount of absorption taking place in the BPAA template, R and T measurements of an empty BPAA template were performed. While the actual absorption taking place in the empty template was 15-30% in the UV region, the absorption almost reaches zero in the vis- and NIR spectrum range, as can be seen from the plot in Figure 4.8b. Negative absorption of BPAA after the switching of detectors in the spectrophotometer may be attributed to the uncertainty of measurement. To better understand the fraction of light absorbed in the sample versus that reflected from the sample, a normalized absorbance (A^*) was defined by Equation 4.1 in Section 4.3:

$$\text{Normalized Absorption } (A^*) = \frac{1 - R - T}{1 - R} \quad (4.1)$$

As observed in Figure 4.8b, the normalized absorbance was calculated and found to be very high (100-70%) in the UV-visible range. While a plasmonic peak is observed at 350-400 nm for Ag nanowire arrays, the peak is hidden in our branched structure because of the shift of plasmonic peak depending on diameter of nanowires. As the diameter increases, the plasmonic peak is shifted toward longer wavelength (redshift) [22]. It should be noted that direct comparison

of absorbance between BPAA and Ag BNW/BPAA must be avoided as plasmonic resonance and wave-guiding modes are subject to the change of surroundings [25].

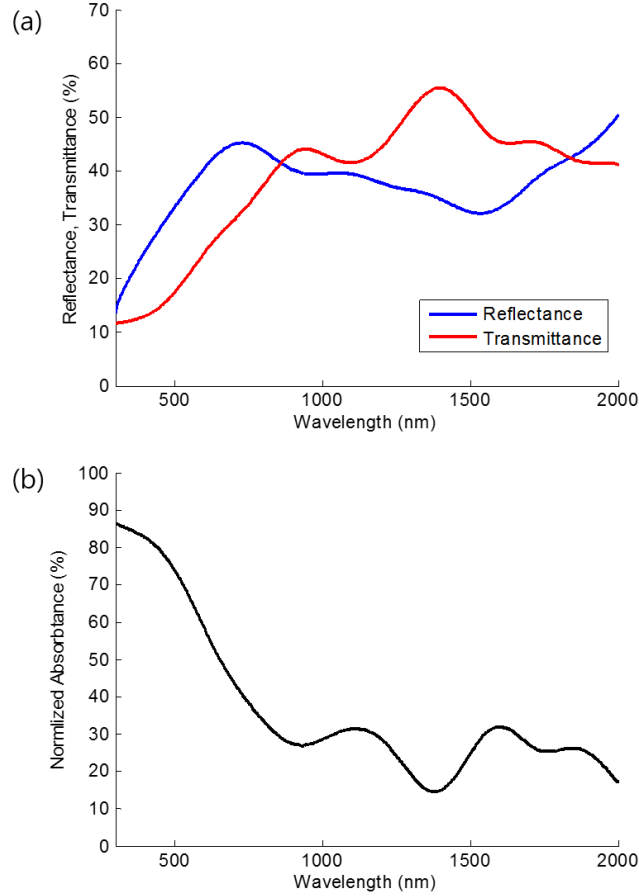


Figure 4.9. Numerically calculated (a) reflectance, transmittance, and (b) absorption of Ag RBNWs and PAA composite when incident light is perpendicular to the surface of Ag RBNWs/BPAA structure. Figure from [2].

In contrast to Ag thin films of thickness as low as 9 nm which exhibit significant decreases in absorbance for wavelengths above 1 μm [24], the normalized absorbance of Ag BNWs remains at approximately 40% over this wavelength range. Thus the light that does not get absorbed in the top branches of the Ag BNWs with the smallest diameters, reaches the regions with larger diameters and gets absorbed in the lower branches having higher diameters.

It is interesting to note that the volume filling fractions of the pores in these BPAA templates were determined to be $\sim 19.6\%$ for the top most branches, $\sim 16.2\%$ for the middle and $\sim 9.1\%$ for the bottom trunk regions of the template [1, 21]. This is opposite to the typical tapered

transition one would employ to achieve low R. The relatively small reflectance in the UV-visible range and the amount of transmittance despite the high impedance mismatch indicates the presence of wave-guiding effect in the structure.

The optical properties of Ag BNWs and BPAA composite were numerically calculated using the spectral averaging of the FDTD data from indiscriminately selected frames. Simulations are done for a number of frames until a convergent set of averaged spectra is obtained [26]. For simplicity, the BNWs were split into three layers whose diameters (length) are 20 nm (500 nm), 100 nm (500 nm), and 150 nm (4 μ m) respectively. Packing density of Ag BNWs is considered in this calculation as well. As shown in Figure 4.9, the R, T, and absorbance are all in general agreement with our experimental data quantitatively. R and T are slightly higher in numerical calculation by 15-20% and as a result, absorbance in the wavelength range of 900 nm – 2 μ m remains at 30%. Considering that the experimental data showed 40% of absorption, more absorption on the experiment is because the actual length of Ag BNWs varies up to 60 μ m. It is also another indication that the packing density of Ag BNWs may be higher than our estimation (33%).

In this work, vertically aligned, hierarchically stacked, randomly branched Ag NWs were grown in a template assisted process by electrodeposition. The BNWs were found to be independently branched, continuous and parallel to each other. The low reflectance and transmittance of the sample appears to be due to the presence of the vertical arrays of Ag BNWs. The normalized absorbance of the Ag BNWs is higher (100-70%) in the UV-visible part of the spectrum and reduces to around ~40% for the wavelengths in the NIR range. The appreciable amount of transmittance in the structure along with the lower reflectance (UV-visible) is thought to be due to a wave-guiding effect in the structure.

4.6 References

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5. WAVELENGTH DEPENDENT ABSORPTION IN VERTICALLY ALIGNED STRAIGHT INDIUM ANTIMONIDE NANOWIRE ARRAYS

The previous chapters have discussed extensively about the growth and fabrication of porous anodic alumina (PAA) templates, and how the structural parameters and the physical complexity of such templates can be controlled by adjusting the various anodization conditions while fabricating them. The synthesis of nanowires within the intricate pores of these templates depend on certain conditions for successfully growing them. This chapter will discuss about some of the issues faced during the process of template assisted electrodeposition, and will provide the solution to some of these issues. Template assisted electrodeposited straight InSb NWs will be discussed, and the optical characterization of these vertically aligned NW arrays has also been reported. Part of the contents of this chapter has been taken from a current manuscript written by the author for consideration of a future publication.

5.1 Introduction

Vertically aligned NW arrays have a lot of potential applications ranging from photovoltaics to light detection to sensing [1-3]. There are several techniques that have been utilized to grow arrays of NWs, which include the vapor-liquid-solid (VLS) method or the chemical vapor deposition (CVD) method, which have their advantages but also some limitations, for instance it would also be extremely difficult and expensive, if not impossible, to grow arrays of complex nanostructures, such as hexagonal close packed arrays of branched NWs or other three-dimensional nanostructures using these techniques. Electrodeposition, on the other hand, provides a relatively cost effective way to grow nanostructures using a bottom-up approach that can be used to fill the shape of any mold or matrix when proper electrical connections (electrode) are laid. Therefore, template assisted electrodeposition allows the growth of intricate, regularly spaced, hexagonal close packed (hcp) nanostructure arrays by filling by the voids in the pre-structured template, which allows the creation of complex structures with relative ease. While there are some limitations of the electrodeposition technique, namely the inability to grow nanostructures of insulating and/or non-conducting organic materials, many of the materials used in the electronics

or semiconductor industry are either semiconducting or metallic, both of which can be potentially electrodeposited using the right deposition parameters and conditions.

5.2 Converting PAA Templates to Active Electrodes

5.2.1 Growth of Straight Porous Anodic Alumina (PAA) Templates

A 250 μ m thick pure aluminum (Al) foil was anodized using a two-step anodization technique to yield a regular hcp array of straight porous PAA template [4, 5]. Both the first and second steps of anodization were conducted in a 0.3 M oxalic acid solution in a two-electrode electrochemical cell at 4°C. The first step of anodization was conducted for nearly 19 hours at 40 V using a platinum (Pt) gauze as the counter electrode, and a pure Al foil as the working electrode. The long hours of anodization ensures the pores arrange themselves in a regular hexagonal pore packed (hcp) structure, as discussed in Chapter 2 (Section 2.4). The first layer of alumina (Al_2O_3) was subsequently removed by submerging the PAA grown on the Al foil, in a heated (65°C) chromic acid solution for an hour. The removal of the porous alumina layer from the Al surface, leaves behind a very regular, hcp dimpled impressions on the Al foil, created by the self-assembled hemispherical pore barriers of the intermediate alumina layer. These self-assembled hcp dimples pre-texture the surface of the Al that act as the future nucleation sites for the pores formed in the next step of anodization, thereby ensuring a regular hcp array.

The second step of anodization was conducted in the same acidic electrolyte for about 24 hours. The remaining Al was etched away from the sample by submerging the PAA membrane covered Al foil in a saturated mercury chloride solution (HgCl_2) for about an hour in room temperature. The clear translucent PAA template was then submerged in a pore barrier removal solution, 5wt% phosphoric acid (H_3PO_4) solution, at $\sim 30^\circ\text{C}$ for about 70 minutes. The pores were inspected using a field effect scanning electron microscope (FESEM) to find the pore diameter to be approximately 70nm with a center-to-center pitch of about 110 nm, as seen in Figure 5.1. The PAA matrix is then used as a template for electrodepositing InSb NWs.

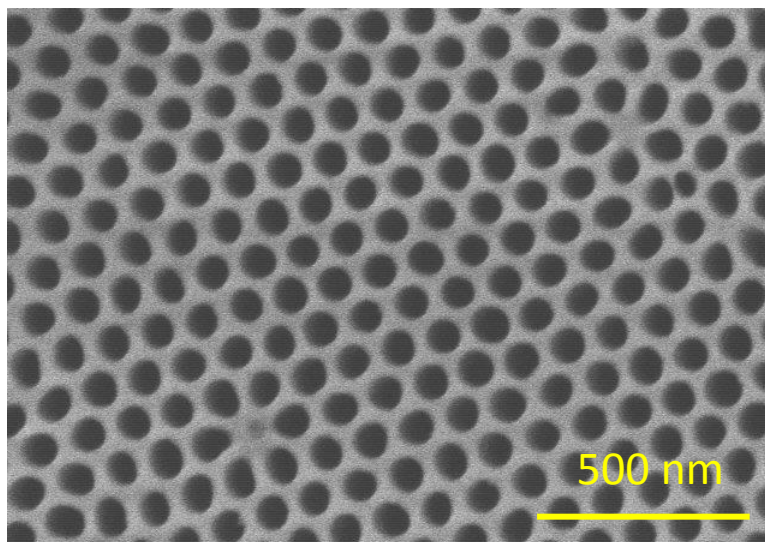


Figure 5.1. FESEM image of the PAA surface, with pore diameter ~ 70 nm and pitch ~ 110 nm. The pores exhibit hcp arrangement.

5.2.2 Metallization of PAA template to make an Active Electrode

The chemical composition of PAA is aluminum oxide (Al_2O_3), an insulating material, which by itself cannot act as an electrode in the electrodeposition process. Once the pores of the PAA template are opened, on both ends, usually one of the end is covered in a conducting material, which would act as the active electrode in the electrochemical cell. The electrodeposition of many materials, including InSb, utilize gold (Au) as the active electrode [6-8]. For this experiment, a ~ 100 nm thick Au layer was evaporated on the PAA template, to convert it into an active electrode for InSb electrodeposition. Unfortunately, it was found that the InSb failed to deposit in most of the pores. To investigate the potential problem, the Au covered PAA template was observed under a scanning electron microscope (FESEM), to analyze the surface of the PAA template, and it was discovered that the improper contact formation caused the failure of the active electrode. The FESEM images, Figure 5.2a, revealed that the ~ 100 nm thick Au layer evaporated on the PAA surface failed to seal off the pores completely. Furthermore, the application of an insulating clear lacquer coating on the Au surface, to prevent the electrodeposition on the unwanted surfaces and sides, can cause the lacquer seep into the open pores and physically obstruct the electrolyte from coming into contact with the active electrode. As a result, the absence of a metallic electrode (Au), at the pore bottom, during the electrodeposition process disrupts the anions and cations in the electrolyte from nucleating and forming an InSb seed layer essential for the NW growth, thus

leaving the pores empty. As observed from the cross-sectional image, Figure 5.2b, of the PAA template with ~ 100 nm thick Au layer, the Au tends to stick on top of the cell walls or form trails of deposit within the pores of the PAA template.

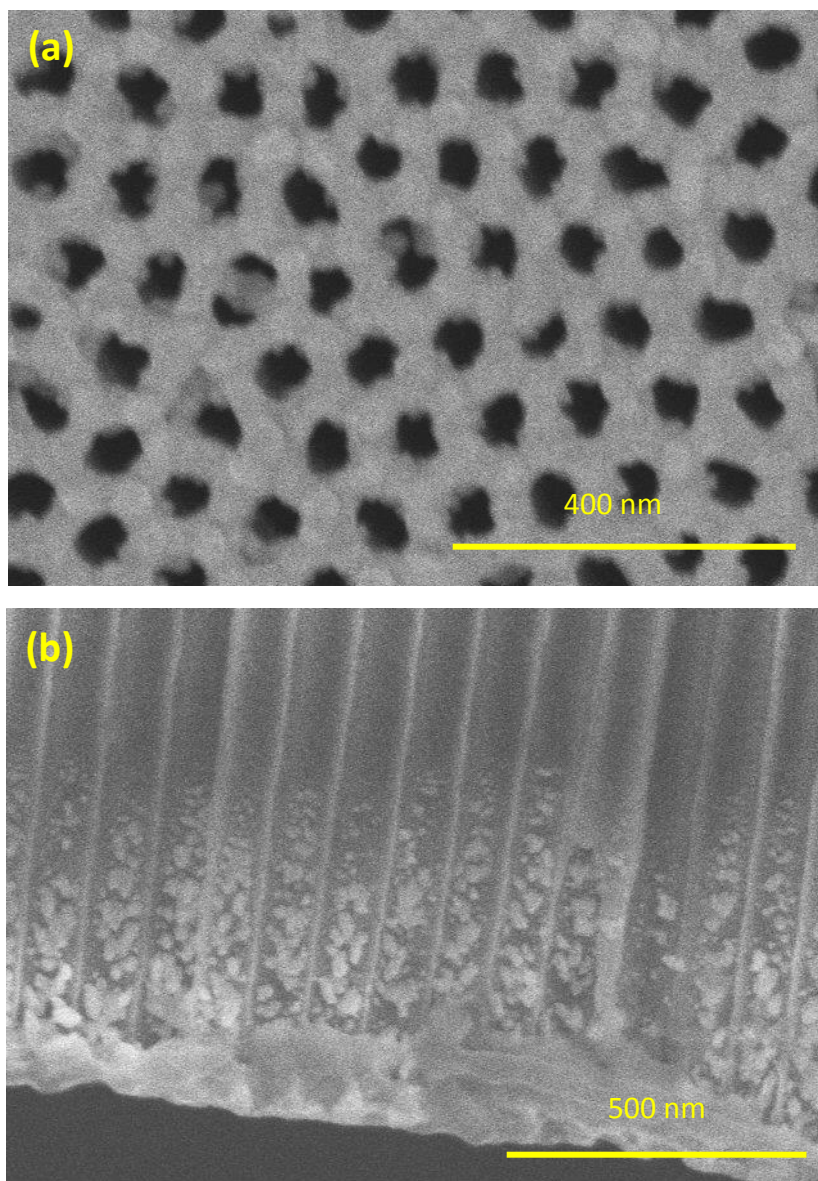


Figure 5.2. (a) FESEM image of the PAA surface (diameter ~ 80 nm, pitch ~ 120 nm) after a 100 nm Au evaporation fails to seal the pores. (b) FESEM image of the cross-section of a PAA template showing trails of evaporated gold along the pore walls, without the Au completely sealing the pores.

5.2.3 Metallic Films and Nanoparticles on PAA Templates

To further investigate the contact issue in a PAA template, a set of experiments were performed to study the effect of metal deposition on PAA templates. Two identical PAA templates were anodized using the conditions mentioned in Section 5.3, with their transparent, hemispherical pore barrier layer left intact by covering the back side with a clear, transparent protective layer. For the porous side of the templates, the bottom half of each of these templates were treated with 5wt% phosphoric acid (H_3PO_4) solution, at $\sim 30^\circ\text{C}$, to widen the pores. This would result in each of the template having two different pore diameters (d_1, d_2) while maintaining the same center-to-center pitch. Therefore the top half (d_1 , smaller pore region) of the template would have a higher surface area (alumina to hole ratio) than the lower half (d_2 , larger pore region). The surface of the first template was evaporated with a thin layer, ~ 10 nm, of Au, whereas the second template was evaporated with a thin layer, ~ 10 nm, of Ag, see schematic in Figure 5.3. A thin film of metal covering the surface of an hcp array of pores of a PAA surface can be considered as an hcp arrangement of holes on a thin metallic surface, and can be called a nanohole (NH) array.

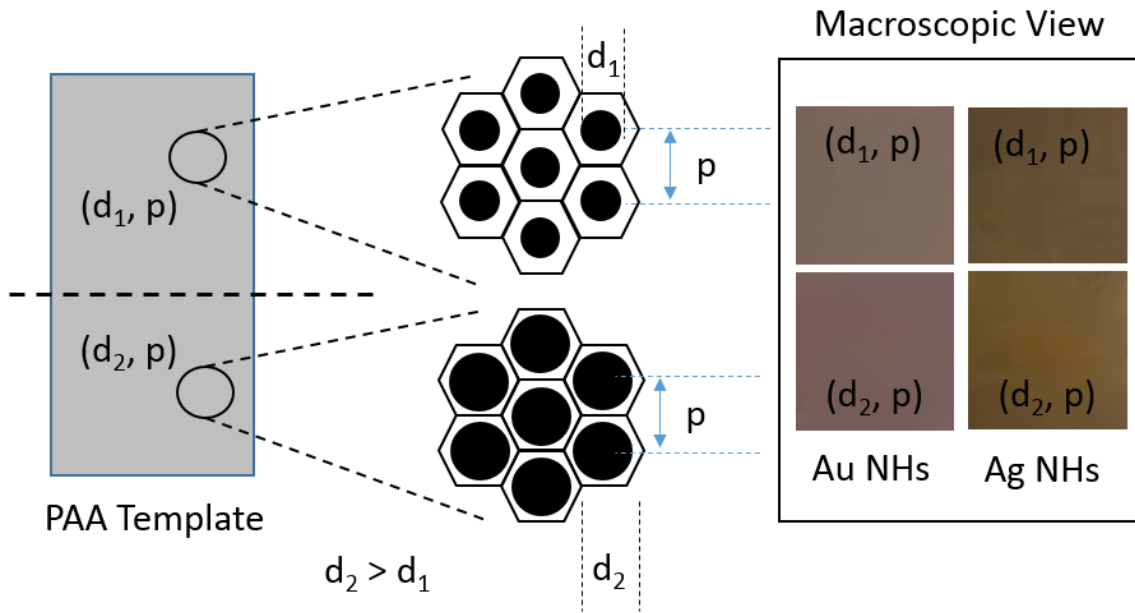


Figure 5.3. Schematic of the PAA template with the pore sizes in the bottom half widened. Thus, pore diameter on the lower half (d_2) is greater than the diameter on the upper half (d_1), $d_2 > d_1$.

As it is known, the observed color of nanoparticles are different from the colors of their bulk material. For instance, due to the surface plasmon resonance (SPR) phenomenon, smaller nanoparticles, ~ 30 nm, of Au in colloidal solutions are known to absorb in the blue-green portion of the optical spectrum while reflecting red light. As the size of the Au nanoparticle increases, the wavelength of absorption due to the surface plasmon resonance shifts to the red end of the visible spectrum, which causes the solution to reflect light in the blue-violet end of the spectrum. As the size of the nanoparticle approaches the bulk limit, the absorption band shifts to the IR region of the optical spectrum that causes the nanoparticles to reflect most of the light in the visible range of the spectrum causing the suspended nanoparticles to appear clear or translucent. Similarly, the color of silver nanoparticles appear yellowish, as they tend to reflect yellow light of the optical spectrum. Therefore, due to the plasmonic properties of Au and Ag nanoparticles, on a first order basis, it is possible to distinguish surfaces laden with nanoparticles of two different sizes by visually inspecting them.

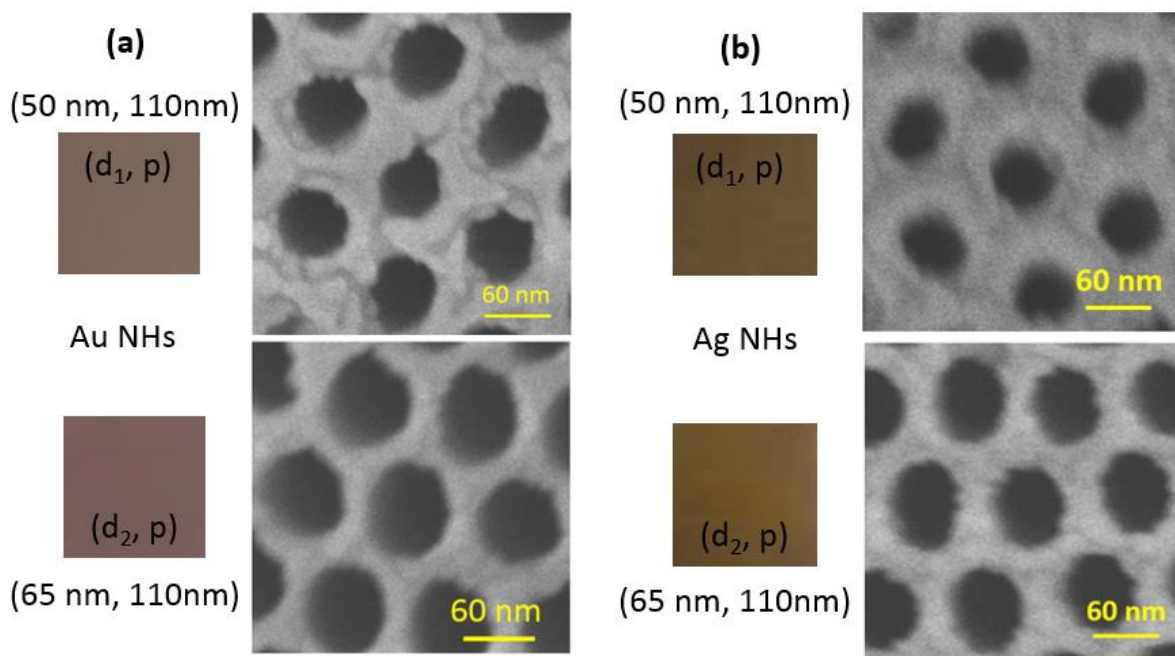


Figure 5.4. FESEM images of the ~ 10 nm thick metallized (a) Au NH, and (b) Ag NH arrays. The diameter and pitch, (d, p) of the metallized NH surfaces are noted beside the respective macroscopic images.

Macroscopic view of the templates containing the Au NH and Ag NH arrays, although still translucent, now exhibit a purplish and a yellowish appearance, respectively, as seen in Figure 5.3.

It is interesting to note that the color of the bottom half of the NH arrays appear more prominent than that of the top, as the surface area of the top-half is greater, and appears more translucent like the underlying PAA template. The color of the NH arrays appear the same when visually observed from the other side of the PAA template (side containing the transparent hemispherical barrier layer). The surface of the Au and Ag NH arrays were further inspected using a scanning electron microscope, Figure 5.4. In all four of the metallized surfaces, the Au and Ag deposits appeared as nanoparticles of the metals try to clump together to form bigger particles, as a precursor to forming continuous metallic films. The NH arrays with ~ 10 nm thick metal clearly exhibit open pores.

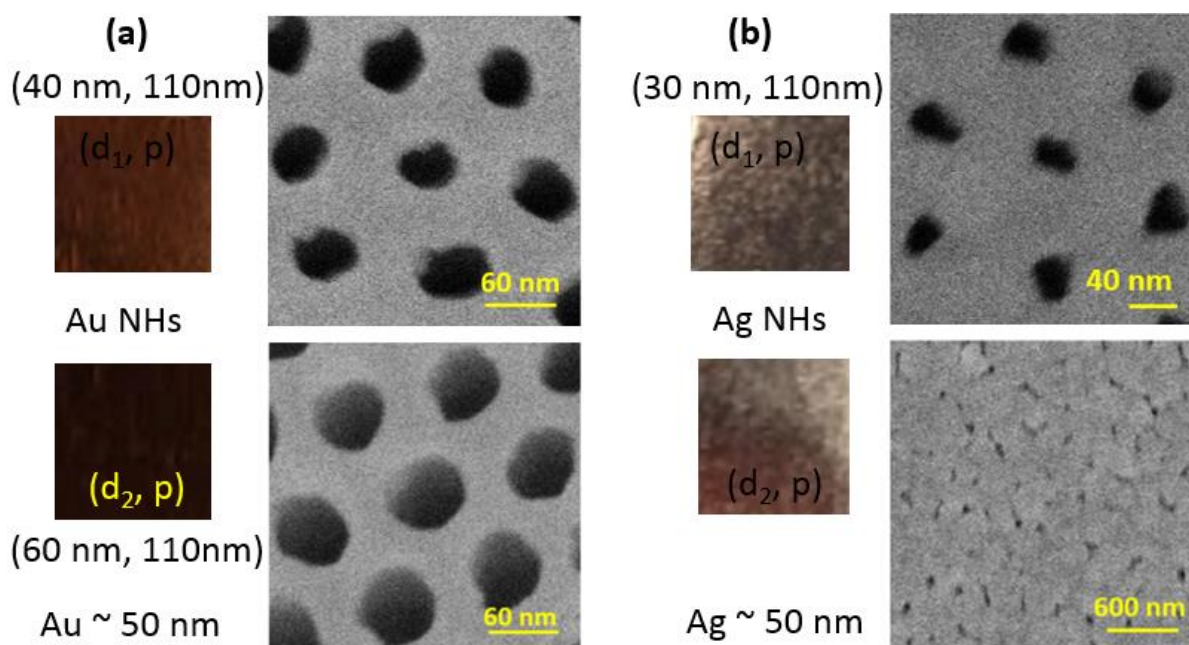


Figure 5.5. FESEM images of the ~ 50 nm thick metallized (a) Au NH, and (b) Ag NH arrays. The diameter and pitch, (d, p) of the metallized NH surfaces are noted, where possible, beside the respective macroscopic images. The macroscopic image of the ~ 50 nm thick Ag NH array appear similar visually, while it was still possible to distinguish the ~ 50 nm Au NH arrays based on visual inspection.

The Au and Ag NH arrays were deposited with an additional ~ 40 nm of Au and Ag, respectively, thereby increasing the thickness of each metal to a total of ~ 50 nm. The Au and Ag NH arrays were once again observed from the open pore side. The appearance of the Au NH array, especially the top half of the PAA, was closer to that of the bulk metal. The lower half of the Au NH array also appeared golden, albeit darker than the top half. As for the Ag NH array, both the top and bottom half had the silvery appearance of bulk Ag. On inspecting the FESEM images of

the metallic surfaces, it appears that for the Au NH array, although still visible, the pore diameter appeared to be smaller than before. This indicated that the Au particles were coalescing to form a continuous film on the PAA surface, and was slowly covering the edges of the pores, Figure 5.5a. The FESEM surface images of the Ag NH arrays exhibited a more continuous film formation on the PAA surface than the Au NH array. Although pores were still visible in the bottom half (region previously with larger diameter) of the Ag NH template, Ag appears to cover the edges of the pores more aggressively than Au, which assists in forming a more continuous, pore-free, metallic film on a PAA surface using smaller amount/thickness of evaporated metal, Figure 5.5b.

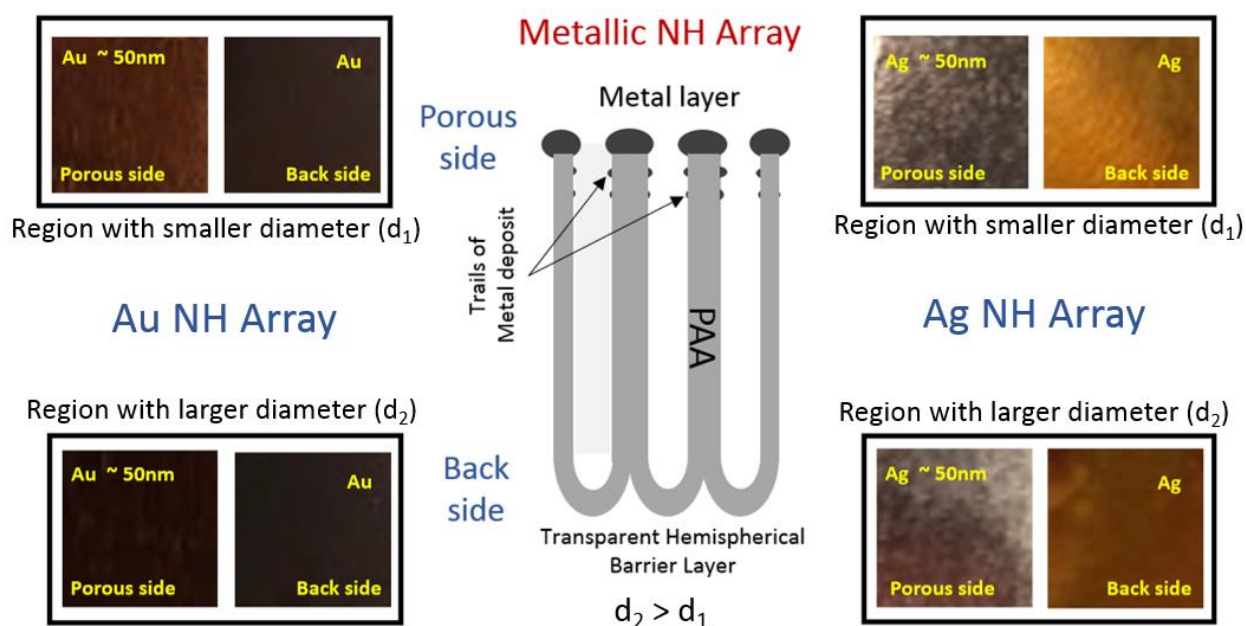


Figure 5.6. Schematic of the metallized PAA surface forming metallic NH array. The metal is evaporated on the porous side of the PAA template with the transparent hemispherical barrier layer still intact. The schematic depicts the trail of metal deposited in the porous channels of the PAA template during the metallization of the surface. The four insets show the actual colors of the template observed from either end (porous or the back side) of the template surface.

It was interesting to note that unlike the ~10 nm thick NH arrays, the thicker metallic (~50 nm thick) NH arrays had different colors depending on which side the template was observed from, Figure 5.6. The Au NH array when observed from the back side (side containing the hemispherical barrier layer) appeared darker and more reddish than when it was observed from the porous side. Similarly, the Ag NH array appeared yellowish golden when observed from the back side of the template. The few tens of nanometer thick hemispherical pore barrier layer is not thought to be the

cause of this perceived difference in color, rather the trail of metallic deposits that cover the walls of the porous side, as seen in Figure 5.2b, is suspected to be the reason. These trails contain minute nanoparticles of metal, and thus, as explained earlier, when one observes the template from the back side, one sees the light reflected from these nanoparticles first, rather than the metallic layer. Therefore, this difference in coloration can be attributed to the structural properties of the nanostructure or nano-droplets as opposed to the material properties of the solid.

To summarize this sub-section, to effectively convert a PAA template to an active electrode for electrodeposition, it is crucial to deposit a continuous metallic/conducting film to completely seal the pores on the porous surface of the template. The amount (volume and /or thickness) of metal evaporated on PAA template should be adjusted to the size of the pores (and their pitch) on its surface. Templates with larger pores require a thicker metallization, as opposed to surfaces with smaller pores. Moreover, the type of metal deposited on the surface can also be a deciding factor in the thickness of the metal required. As seen in this section, Ag tends to form a continuous film and seal the pores on a nano-porous surface for a smaller metallization thickness than Au, on a surface with similar diameter-to-pitch ratio. Finally, it was concluded that visual inspection can be effective in determining the presence of nanoparticles or nanostructures (NH array) on the PAA surface.

5.3 Template Assisted Electrodeposition of Vertically Aligned, Straight InSb NW Arrays

Wavelength dependent optical response of the vertically aligned InSb NW arrays depend on the fill factor of the NWs in the PAA pores, as a result it is essential to increase the number of NW filled pores in the PAA template. One of the primary reasons, as discussed in the previous section, NWs fail to nucleate at the pore bottom, during a PAA template assisted electrodeposition process, is the failure of the pores to be sealed and metallized properly during the metallic evaporation step to form an active electrode. As explained in the previous sub-section the appropriate thickness of evaporated metal would effectively seal and metallize the pore bottoms of a PAA template and convert it to an electrode that can be used during electrodeposition.

A PAA template with straight pores was anodized using the process described in Section 5.2, having diameter of ~ 70 nm with a center-to-center pitch of ~ 110 nm. As described in Figure 5.2, a ~ 100 nm thick Au layer would not be able to sufficiently seal the pores of a porous template

with ~70 nm diameter. Therefore, a relatively thick layer of Au, ~400 nm, was deposited on the PAA template using an electron beam evaporator. The deposited Au thickness was more than five times the diameter of the pores on the PAA template, and at such thickness the pores are completely sealed and metallized, which effectively forms the active electrode for the electrodeposition.

The InSb electrodeposition was conducted in a three-electrode system, as described in Chapter 3, using a Pt gauze as a counter electrode and an Ag/AgCl electrode used as a reference electrode. The Au deposited PAA sample was used as the active electrode in the electrodeposition process. The electrolyte used for the electrodeposition consisted of a mixture of 0.1 M antimony trichloride (SbCl_3), 0.15M indium trichloride (InCl_3), 0.36M citric acid, and 0.17M potassium citrate. The active electrode was briefly pre-soaked to wet the nano-channels of the pores and better facilitate the electrolyte to reach the pore bottom for the NW deposition. The electrodeposition was conducted at -1.5 V with respect to the reference electrode for 90 minutes. The InSb deposited sample was submerged in a commercially available iodine based gold etchant for 5 minutes to etch away the Au layer. The InSb deposited regions were observed to be very dark. The structural characteristics were analyzed by observing the vertically aligned, straight InSb NW filled template, using a FESEM.

The FESEM image, Figure 5.7a, of the surface of the Au etched template showed nearly all the pores were successfully electrodeposited with InSb. This proves that the ~400 nm thick Au layer on the PAA template successfully seals and metallizes the pores of diameter ~ 70 nm, which in turn helps in increasing the fill-factor of the NW array. The cross-sectional FESEM image of the sample was observed, and the InSb NWs were found to have an average length of ~5.5 μm in the porous channels of the template, Figure 5.7b. Growing the NWs in PAA template has an additional benefit of providing structural support to these high aspect ratio nanostructures, and keeping them all vertically aligned, which would otherwise clump together if the matrix were removed. Moreover, the insulating PAA matrix prevents the physical contact between any two NWs in the array. Finally, the optically transparent PAA matrix has low absorption (high transmittance) in the vis- and NIR wavelength spectrum, and does not optically interfere and pose a major problem during the optical characterization of such vertical arrays of NWs.

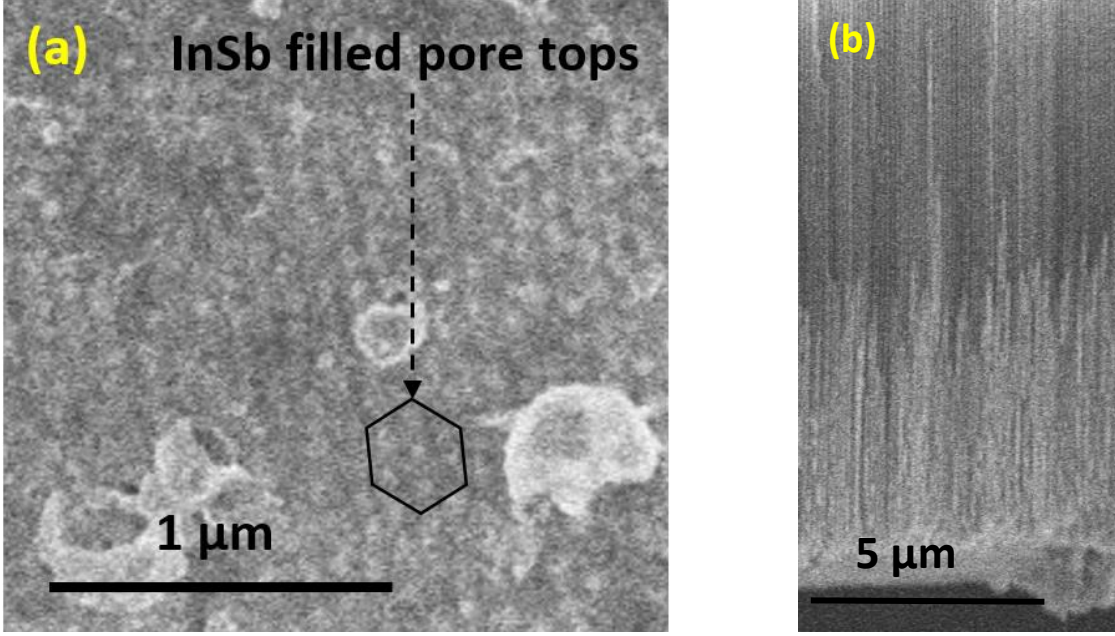


Figure 5.7. FESEM images of a PAA template assisted electrodeposited array of vertically aligned, straight InSb NWs of diameter ~ 70 nm. (a) FESEM image of the Au etched PAA template surface with the inset showing hexagonal close packed arrangement of InSb filled pores. (b) Cross-sectional FESEM image of the vertically aligned, straight InSb NW arrays in the straight PAA matrix.

5.3.1 Optical Characterization of a vertically aligned, straight InSb NW array

Optical measurements of the vertically aligned, straight InSb NW array was recorded in the integrating sphere of a Perkin-Elmer Lambda 950 spectrophotometer at near normal angle of incidence in the wavelength range of 300 nm to 2 μ m. To better understand the amount of incident light actually getting absorbed into the InSb NW-PAA matrix, a normalized absorbance (A^*) has been defined as:

$$A^* = \frac{1 - R - T}{1 - R} = \frac{A}{1 - R} \quad (5.1)$$

The normalized absorption normalizes the absorbed light with respect to the light that actually enters the NW-template matrix, *i.e.* the incident light minus the reflected light. The measured reflectance (R), transmittance (T), and the corresponding absorption (A^*) of the ~ 5.5 μ m long InSb NWs were found to be wavelength dependent, Figure 5.8.

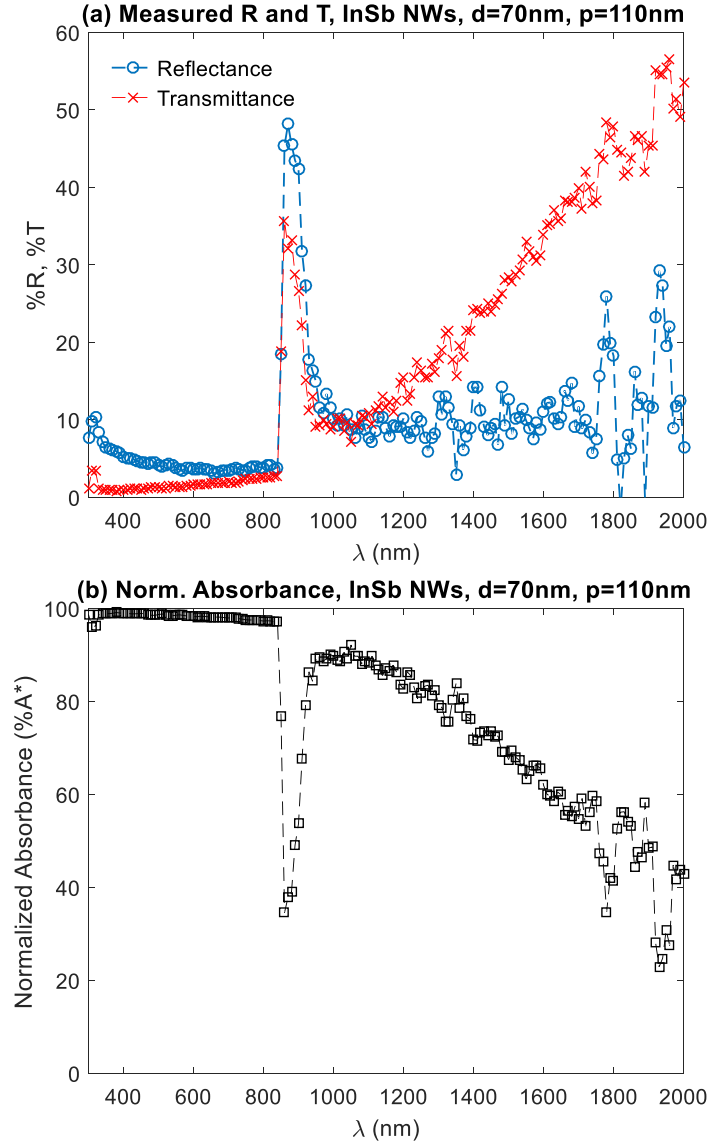


Figure 5.8. (a) Measured reflectance (R) and transmittance (T), as a function of wavelength (λ), of a $\sim 5.5 \mu\text{m}$ long array of straight InSb NWs in PAA matrix. (b) Normalized absorbance of the straight InSb NW array in PAA matrix. The artifact peak observed at $\lambda \sim 850 \text{ nm}$ is due to a detector change in the optical spectrophotometer and should be ignored.

The transmittance is observed to be well below 10% in the UV-vis range of the spectrum, but starts to increase in the near infrared (NIR) end of the spectra and reaches a reflectance of $\sim 50\%$ at a $\lambda \sim 2000 \text{ nm}$. The reflectance on the other hand remains low throughout the UV-vis-NIR spectrum, and starts to fluctuate beyond 1700nm, but the average reflectance remains at around $\sim 10\%$ or lower. The normalized absorption was calculated, using Equation 5.1, using the reflectance and transmittance measurement data, and a strong wavelength dependence was

observed in the InSb-PAA sample. The normalized absorption was observed to be very high (> 95%) in the UV-visible wavelengths of light, as expected by visually inspecting the very dark InSb deposited regions of the PAA template. There is a gradual decline in the normalized absorption in the NIR range of the spectrum, where the InSb NW array starts becoming more and more transparent to NIR wavelengths of light. The roll off in the absorption spectra in the vertically aligned InSb NWs in PAA matrix begins at a wavelength much smaller than the cut-off wavelength of bulk InSb, $\sim 7 \mu\text{m}$, and as such the optical spectra is attributed to the nano-structuring of InSb, as opposed to the material property of bulk InSb. The artifact peak observed at $\lambda \sim 850 \text{ nm}$ is due to a detector change in the optical spectrophotometer and should be ignored.

5.3.2 Numerical Modeling of a vertically aligned, straight InSb NW array

To analyze the wavelength dependent absorption in a vertically aligned straight InSb NW array in a PAA matrix, and its implication of depth-resolved absorption, a mathematical model of the optical spectra associated with the various configurations of the NWs was implemented. The numerical model considered the optical characteristics of the straight nanowire arrays with NW diameter of 70 nm with a pitch of 110 nm, both with and without the PAA matrix, for different lengths of the NWs. Figure 5.9, compares the simulated normalized absorbance (A^*) in an InSb NW array within a PAA matrix for NW lengths of 5 μm and 7 μm , with the A^* calculated from the measured data in the InSb NW array with NW lengths of $\sim 5.5 \mu\text{m}$, as seen in the FESEM images, Figure 5.7b.

As expected the simulated normalized absorbance profile of the 5 μm long NW arrays matches more closely with the measured data for wavelengths in the UV-vis- and NIR range of the optical spectrum. The slightly broader roll-off observed in the measurement, when compared with the simulated absorbance graph, may be attributed to inhomogeneous broadening due to fabrication imperfections, surface roughness, and deviation in the periodicity and dimensions of the actual NW array from the ideal unit cell in the numerical model.

(Measured and Simulated) A^* of InSb NWs in PAA matrix, $d=70\text{nm}$

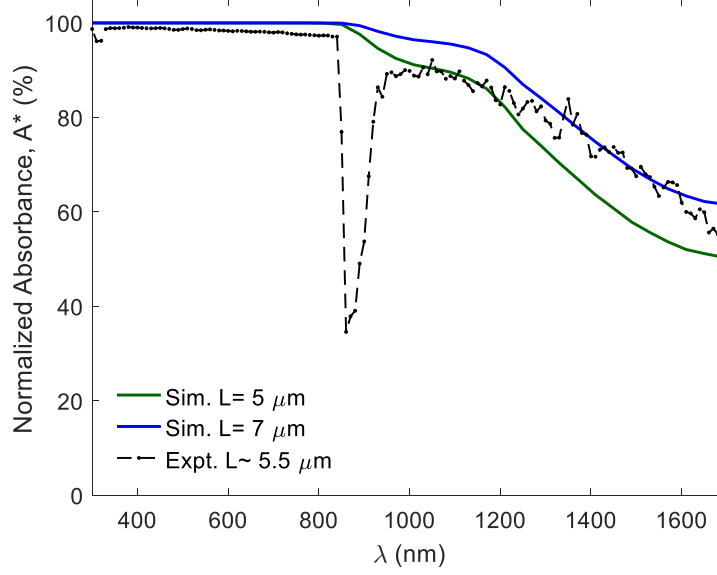


Figure 5.9. Comparison between the simulated (normalized) absorbance, A , in the straight InSb NW array with NW lengths of, $L=5\text{ }\mu\text{m}$ and $7\text{ }\mu\text{m}$, and the A^* from optical measurements from an array with $L\sim 5.5\text{ }\mu\text{m}$ long NWs. The artifact peak observed at $\lambda\sim 850\text{ nm}$ is due to a detector change in the optical spectrophotometer and should be ignored.

It is worth noting that, as explained in Chapter 4 (Section 4.4), the wavelength dependent absorption observed in the NW arrays is not due to size quantization effects, but is attributed to the waveguiding effects of the NW array. To illustrate this point, let the cut-off wavelength of the NW array be at the wavelength when the absorption falls to $\sim 90\%$. As observed in Figure 5.9, the normalized absorbance of $\sim 90\%$ in the InSb NW arrays is measured at a wavelength of 990 nm . Size quantization would have required InSb NWs to have a diameter of $\sim 5\text{ nm}$ to achieve a cut-off wavelength $\lambda_{\text{cut-off}}\sim 990\text{ nm}$, as explained below:

$$E_g [\text{eV}] \approx \frac{1240 [\text{eV} \cdot \text{nm}]}{\lambda_{\text{cut-off}} [\text{nm}]} = \frac{1240}{990} \approx 1.25 [\text{eV}], \quad (5.1)$$

Based on size quantization effect, the bandgap of InSb NWs is $\sim 1.25\text{ eV}$ when the diameter of the NW is shrunk to $\sim 5\text{ nm}$, see graph in Figure 3.1.

The numerical model also predicted that the absorbance profile can be regulated by controlling the length of NWs electrodeposited in the template. Figure 5.10, plots the absorbance in the InSb NW array as a function of the NW length, within a PAA matrix.

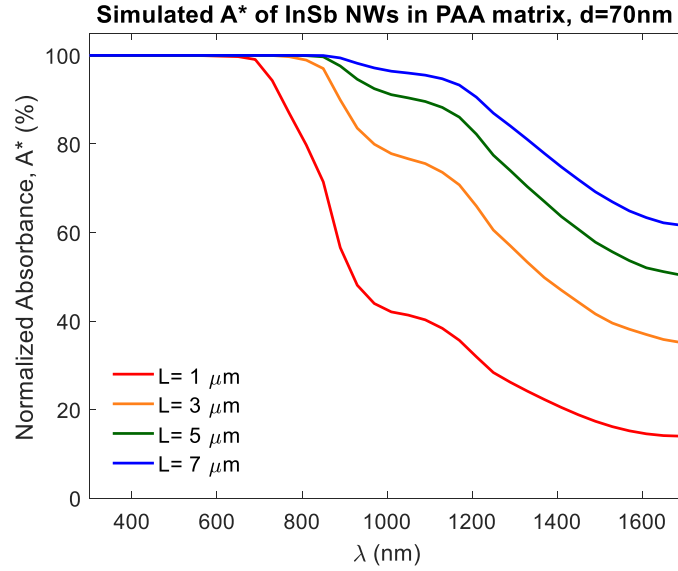


Figure 5.10. Plot of the simulated (normalized) absorbance with respect to the wavelength (λ) of InSb NW arrays (diameter, $d = 70$ nm) of various lengths.

Table 5.1. Wavelength at different absorbance cut-offs as predicted by a numerical model for an array of vertically aligned, straight InSb NW ($d = 70$ nm, $p = 110$ nm) arrays in a PAA matrix.

Length of the NW in array	Absorbance ~80%	Absorbance ~60%
1 μm	$\lambda \sim 810$ nm	$\lambda \sim 881$ nm
3 μm	$\lambda \sim 970$ nm	$\lambda \sim 1250$ nm
5 μm	$\lambda \sim 1200$ nm	$\lambda \sim 1450$ nm
7 μm	$\lambda \sim 1300$ nm	$\lambda \sim 1690$ nm

It is noted that the plot predicts the fall in absorbance to be more gradual with increasing length of the NWs in the array. For instance, the measured absorbance falls to ~80% (at $\lambda \sim 1240$ nm), and ~60% (at $\lambda \sim 1600$ nm), which are similar to the simulated absorbance cut-offs, for ~80% (at $\lambda \sim 1240$ nm), and ~60% (at $\lambda \sim 1450$ nm), for the 5 μm long NW arrays, Figure 5.9. The same model predicts that the absorbance drop from ~100% to ~60%, at $\lambda \sim 881$ nm for NWs of $L = 1$ μm , as opposed to the same drop in absorbance at wavelengths of ~1450 nm for NWs of $L = 5$ μm , Table 5.1.

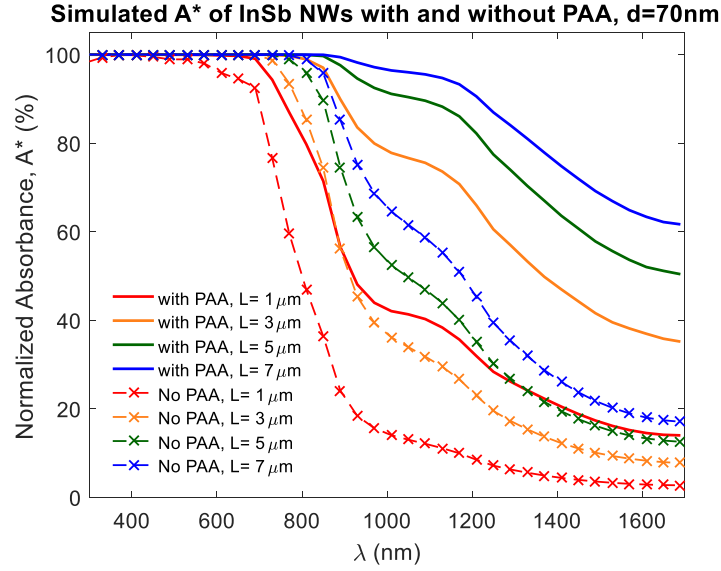


Figure 5.11. Plot of the simulated (normalized) absorbance with respect to the wavelength (λ) for InSb NW arrays (diameter, $d = 70$ nm) of various lengths. The plot predicts the shift in the absorbance profile for vertically aligned InSb NW arrays, with and without the surrounding PAA matrix.

The simulation also predicts a sharper absorbance profile for the InSb NW arrays of the same dimension ($d = 70$ nm, $p = 110$ nm), for the model without the surrounding PAA matrix. Therefore, the simulation predicts that by etching back the surrounding PAA matrix, the InSb NW arrays can act as an optical filter more efficiently.

To summarize, aligned arrays of semiconductor nanowires are of interest for various applications, including photovoltaics, imagers and biological interfaces. While bandgap changes due to quantization effects [9] and the potential to decouple the optical absorption direction (vertical) from the charge extraction direction (horizontal) are well recognized, it is also possible to tune the absorption spectra via structure, e.g. the nanowire diameter and pitch. In particular, wavelengths shorter than the nanowire diameter will not efficiently couple into the nanowires, resulting in low absorption even at photon energies well above the bandgap. Infrared detectors/imagers with various cutoff wavelengths could be realized by employing narrow bandgap nanowires with various diameters, and the effect could be extended into the UV-vis range for photovoltaic or imager applications. In this study, the absorbance of vertical arrays of uniform diameter InSb nanowires is presented. Optical absorbance is found to be a function of the structural properties of the nanowires, such as the diameter, pitch and length. The nanowires were fabricated using a template assisted electrochemical deposition technique. The pore diameter and pitch of the

PAA templates were controlled by the anodization conditions of the template. The length of the nanowires was determined by the duration of electrodeposition within the nanochannels of the PAA template [6]. The nanowires exhibited a diameter of around 70 nm with a pitch of ~ 110 nm and an average length of ~ 5.5 μm . A wavelength dependent absorbance is observed in the nanowire arrays, with very high absorption (near 100%) in the UV and visible range of the spectrum and a steadily declining rate of absorption in the IR range (around 40% at $\lambda \sim 2$ μm), with the cut-off wavelength at around ~ 990 nm (absorbance falls to $\sim 90\%$). Based on the bulk bandgap of InSb (0.17 eV), the cut-off wavelength of bulk material is ~ 7 μm . The lower cutoff wavelength for nanowire arrays can be explained by waveguiding effects as opposed to size quantization effects, which would have required the InSb nanowires to have a diameter of ~ 5 nm to achieve such a cut-off wavelength. The experimental results were verified using mathematical models which also predicted a shift in the absorption cut-off for nanowire arrays of different length. These structures have potential use as *in-situ* wavelength dependent optical filters or for InSb based IR detectors with controlled cut-off wavelengths.

5.4 Using graphene to effectively convert a PAA template to an Active Electrode

Since the wavelength dependent optical response of the vertically aligned InSb NWs depend on the fill factor of the NWs in the PAA pores, it is essential to increase the number of NW filled pores in the PAA template. One of the primary reasons the InSb NWs fail to nucleate at the pore bottom, during the electrodeposition process, is the failure of the pores to be sealed properly during the Au evaporation process. It has been observed in Section 5.2 that the pores sometimes fail to completely seal even for deposited Au film thicknesses of 100nm (for pore diameters of $\sim 70\text{nm}$). The absence of a metallic electrode (Au), at the pore bottom, during the electrodeposition process prevents the anions and cations in the electrolyte to nucleate and form InSb seeds for NW growth, thus leaving the pore empty.

One solution of this problem is to evaporate thicker layers of metal, as explained in Section 5.3, to ensure the pores are effectively sealed and metallized. However, this solution could have a potential disadvantage, especially when using PAA templates with larger pores, as it would require thicker layers of metal to completely seal and metallize the pore bottoms of the template to effectively form an active electrode. With noble metals being the common choice for electrode layer for many of the electrodeposition techniques, and these metals being very expensive, the cost

of evaporating thick layers can become prohibitively expensive, especially for PAA templates with larger pores.

This sub-section will report and discuss about another way to circumvent the low fill factor issue faced during PAA assisted NW growth, by utilizing a layer of graphene along with the metallic (or conducting) layer to effectively form a contact for the active electrode during the electrodeposition process. The continuous film of graphene intimately envelopes and seals the pore bottoms, and therefore has the potential to provide a good contact for the electrodeposition process. A metallic layer should be deposited on the graphene, which acts as an additional protection for the graphene from peeling away or floating off during the electrodeposition step. This evaporated metallic layer, along with the graphene, can effectively seal off the pore bottoms and form an effective electrode, with relatively smaller thicknesses of metal.

5.4.1 Graphene as a transparent conductor

Graphene (C_g , C_{graphene} , or just C) is a form of crystalline carbon, which is made up of a sheet of C of a single atomic thickness. Due to its linear band structure, C_g has exhibited unprecedented physical properties, such as extremely high electron mobility in room temperature, very low resistivity, and very high optical transparency, which makes it an ideal transparent conductor.

The graphene used in this work, is a commercially available CVD grown, single layer graphene (SLG) (ACS Co., MA) grown on both sides of a Cu foil. To remove the graphene layer from one side of the Cu foil, PMMA- poly-(methyl methacrylate), a photoresist is spin coated on one side of the C_g covered Cu foil. The uncovered, sacrificial, C_g layer is etched away using a reactive-ion etching (RIE) technique using O_2 plasma. The Cu foil is then etched away, by gently floating the (PMMA coated) C_g covered Cu foil in an iron nitrate solution. After the Cu is etched away, the PMMA covered C_g layer is rinsed in DI water and dilute HCl solution repeatedly to remove traces of Cu. The PMMA covered C_g is then transferred onto the porous surface of the PAA template, and left to dry completely. Once the C_g intimately covers the pores of the PAA template, the PMMA coating is removed using a hot acetone technique [10].

The PAA template used in this experiment used the same anodization condition as reported in Section 5.2, yielding a PAA template of diameter ~ 70 nm and pitch of ~ 110 nm. The C_g was transferred on the porous surface of the PAA template. A ~ 100 nm thick layer of Au was

evaporated on the C_g covered PAA template. As explained in Section 5.2.3, trails of gold nanoparticles get deposited in the porous channels of the PAA template before, the metallic particles on the surface coalesce to form a continuous film thereby sealing the pores to form an effective electrode for the electrodeposition. Figure 5.12, shows the photograph of the C_g covered PAA template after evaporating it with a Au layer, viewed from the pore barrier side of the PAA template.

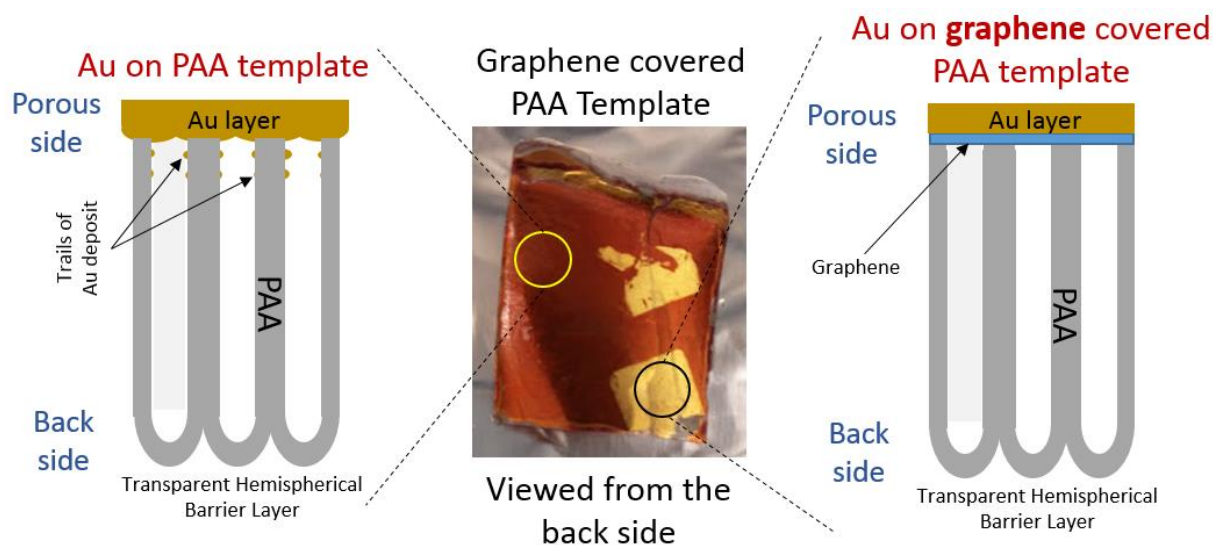


Figure 5.12. Photograph of a graphene covered PAA template metallized with a layer of Au. The picture shows a clear color difference between regions that are covered in graphene (appears golden due to the color of the Au film that forms on top of it), and the regions not covered in graphene (appears reddish due to the plasmonic properties of Au nanoparticles that coat the walls of the pores). The schematic of the two scenarios are shown on either side of the photograph.

There is a clear and visible color distinction between the porous region covered with C_g , and the region not having any C_g layer. The reason for this color difference is that the highly conducting C_g prevents any of the metallic nanoparticle from entering and sticking to the side walls of the pores during the metal evaporation step, while still effectively sealing the pore with a conducting layer. The absence of any of the aforementioned nanoparticles in the pore walls of the C_g covered region, gives the appearance of those regions the same color as that of the bulk metal (Au in this case), whereas the regions not containing C_g , has the reddish color associated with the nanoparticles of the Au that stick to the pore walls.

The metallized graphene covered PAA template can be used to electrodeposit both metallic, and InSb NW arrays and other nanostructures. Since graphene has very low absorption (very high

transmittance), on a PAA template it can act as an *in-situ* transparent conductor. The growth of randomly branched NW array of InSb/Ag heterostructure has been reported in Chapter 3 (Section 3.4), using a metallized graphene covered PAA template assisted electrodeposition technique, Figure 3.13.

5.5 Summary

PAA templates have been regularly used for electrodepositing highly crystalline NWs and nanostructures with advanced structural complexities. This chapter discusses about the template assisted electrodeposition of highly regular, hcp arrays of vertically aligned straight InSb NWs, which have wavelength dependent optical response. The optical characterization of such NW arrays require a high fill factor in the pores of the PAA template. Failing to effectively seal the pores of a PAA template with a conducting material, has been shown as one of the primary reason for poor NW fill factor. This problem can be solved, either by using thicker metallic films on the PAA template, or by using a layer of transparent and highly conducting graphene layer to effectively form a contact layer for the formation of the electrode for electrodeposition.

Finally, the absorbance in a vertical array of template assisted electrodeposited, uniform diameter, InSb nanowires is reported, where the absorbance is found to be a function of the structural properties of the nanowires, such as the diameter, pitch and length. A wavelength dependent absorbance is observed in the nanowire arrays, with very high absorption in the UV and visible range of the spectrum, and a steadily declining rate of absorption in the IR range, which allows these structures to have potential use as *in-situ* wavelength dependent optical filters or for InSb based IR detectors with controlled cut-off wavelengths. The cutoff wavelength of the nanowire arrays can be explained by waveguiding effects as opposed to size quantization effects. The experimental results were verified using mathematical models which also predicted a shift in the absorption cut-off for nanowire arrays of different length.

5.6 References

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6. ARTIFICIAL OPAL TEMPLATES FOR THE ELECTRODEPOSITION OF INVERSE OPAL (IO) STRUCTURES

The opalescence in naturally occurring opals have captured the minds of people for millennia. The price and gem quality of opals depend greatly on the size and periodic arrangement of silica spheres, which in turn determines the colors of the stone. This natural phenomena in opals have provided an inspiration to the scientific community to synthetically produce opal structures by self-assembly of hexagonally close packed (hcp) arrangements of monodisperse spherical microbeads of different sizes and materials, including polystyrene. The interstitial voids between the three dimensionally arranged arrays of microbeads of the regular and periodic opal templates can be filled by using various techniques, and then the microbeads can be removed to create very interesting inverse opal (IO) structures. These structures have been studied for more than two decades and have been demonstrated to show fascinating mechanical, fluidic, magnetic and optical properties, with applications ranging from aesthetics to catalysis to photovoltaics to membrane filtration [1-14]. Numerous methods, such as chemical bath deposition, chemical vapor deposition, ionic spraying, and surface self-assembly, have been employed to fabricate IO structures [1, 12-18]. Electroplating or electrodeposition on the other hand provides a relatively less expensive and a quick approach to creating metallic and semiconducting IO structures [6, 19-25]. Metallic inverse opal (IO) structures are of interest for their various applications and have unique optical characteristics. The optical response of these structures may be tuned by controlling the structural properties, such as the material, the periodicity and the diameter of the spherical air voids in them. In this work the reflectance properties of IO structures of nickel (Ni) and InSb have been studied. Part of the contents of this chapter has been taken from a current manuscript written by the author for consideration of a future publication.

6.1 Introduction

The optical response of metallic inverse opal (IO) structures may be tuned by controlling the structural properties, such as the material, the periodicity, and the diameter of the spherical air voids within them. This work involves the synthesis and characterization of a Ni and an InSb based IO structure. The measured reflectance for the IO nanostructures, due to its symmetry, is found to

be independent of the angle of rotation between the surface and the polarization of the incident light. A full wave numerical simulation of a representative structure was used to model the reflectance spectra, which generally agrees with the measured data, and indicates the optical tuning capability of such structures as a function of their structural characteristics.

6.2 Artificial Opal Template using an hcp Array of Polystyrene Microbeads

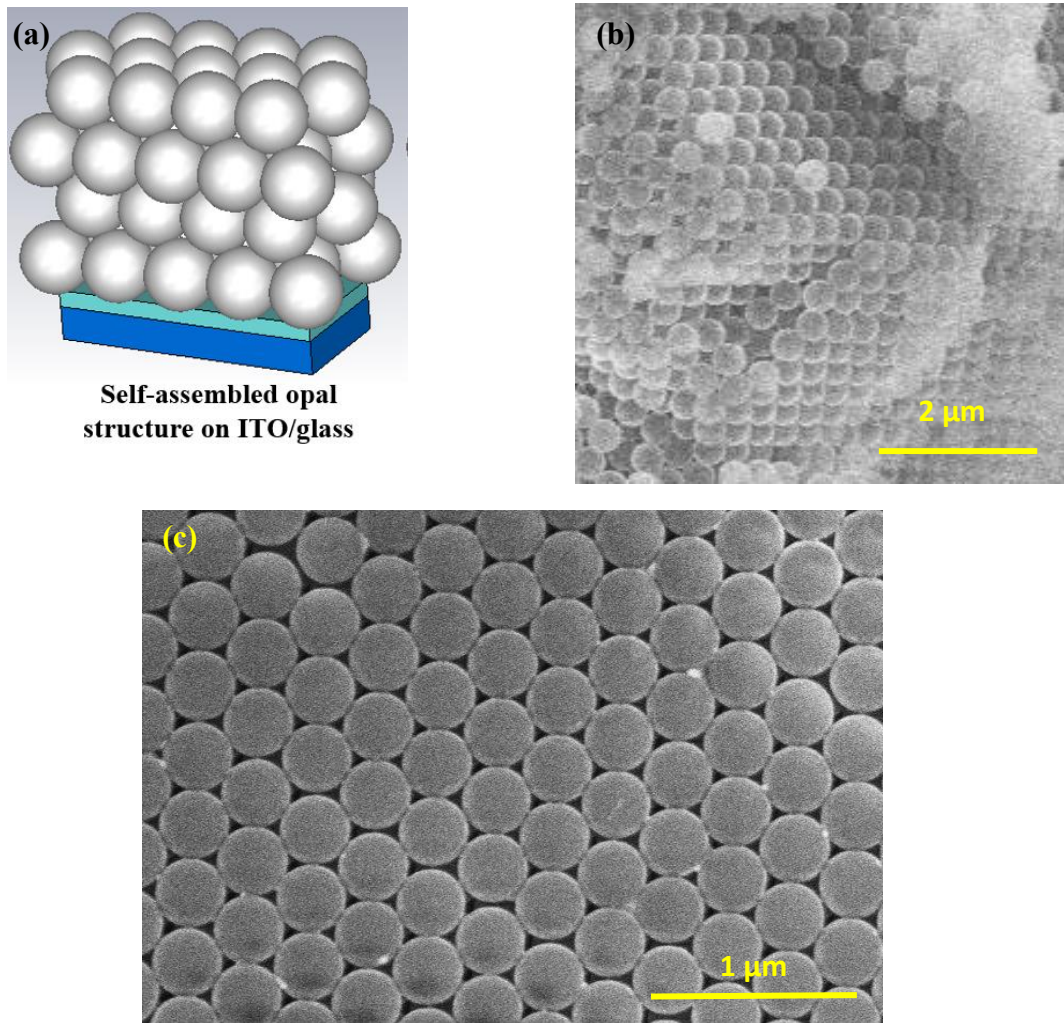


Figure 6.1. (a) Schematic of an opal template using four layers (for illustration purposes) of hexagonal close packed arrays of polystyrene microbeads on an ITO coated glass substrate. (b) FESEM image (slightly tilted view) of the cross-section of the array of polystyrene microbeads structure. (c) FESEM image of the top surface of the opal template containing the arrays of polystyrene microbeads.

To create an Inverse Opal (IO), a synthetically created opal template must be created first. The opal structure, in this case, are made of commercially available, single diameter (~ 400 nm), polystyrene microbeads (Bangs Laboratories Inc.) that are self-assembled to a regular, three-dimensional hexagonal close packed (hcp) array, Figure 6.1a. The polystyrene microbeads were assembled on a transparent glass substrate (University Wafer Inc.) coated with a ~ 180 - 200 nm thick layer of transparent and conducting indium tin oxide (ITO). The glass/ITO substrate was cleaned in acetone, methanol, and isopropyl alcohol (IPA) to remove any organic residue from the substrate. The substrate was then vertically suspended in a colloidal solution containing 0.1 wt% monodispersed polystyrene beads, diameter ~ 400 nm, in a furnace at 60 °C for over 36 hours. With the gradual evaporation of the liquid, a self-assembled opal structure forms on the substrate. The opal templates are then annealed at 95 °C for five hours to increase the area of contact between adjacent microbeads, which furthermore enhances the structural stability of the self-assembled opals. The size, shape, and structural characteristics of the array of polystyrene microbeads (opal template) was analyzed by field emission scanning electron microscopy (FESEM) imaging, Figure 6.1 (b and c). A three-dimensional hcp arrangement with long range order was observed.

6.3 Nickel (Ni) Inverse Opal (IO) Structure

6.3.1 Template Assisted Electrodeposition of Ni IO structure

This template would be used to create the Inverse opal (IO) structure by filling the void within the polystyrene microbeads by electrodeposition. The voids within the structure are filled with Ni, using a slightly modified electrochemical deposition technique described previously in literature, in a three-electrode electrochemical cell [6, 15]. The electrically conducting ITO layer on the glass substrate would act as the active electrode in the electrochemical cell. A Pt mesh was used as the counter electrode, and a Ag/AgCl (3M NaCl) electrode (BASi Inc.) was used as the reference electrode. The electrolyte used for the Ni deposition contained a solution of 0.5 M nickel sulfate (NiSO_4), 0.12 M nickel chloride (NiCl_2), and 0.3 M boric acid (H_3BO_3). The electrodeposition voltage was set at -1 V with respect to the reference electrode. The thickness of the deposited Ni layer can be controlled by regulating the time of electrodeposition. The IO structure is formed, once the opal template or the arrays of polystyrene microbeads are etched away completely, see schematic in Figure 6.2a. This is achieved by submerging the

electrodeposited opal template in tetrahydrofuran [(CH₂)₄O, (THF)] at 40 °C for an hour, followed by a fresh treatment in THF for an additional hour to remove any remaining traces of polystyrene in the template, which leaves behind a skeletal Ni IO structure, which visually appears green at this stage.

The surface images of the Ni IO structure was taken with a Hitachi S-4800 Field Emission Scanning Electron Microscope (FESEM). The size, shape, and structural characteristics of the Ni IO structures were analyzed by the FESEM images, Figure 6.2 (b and c).

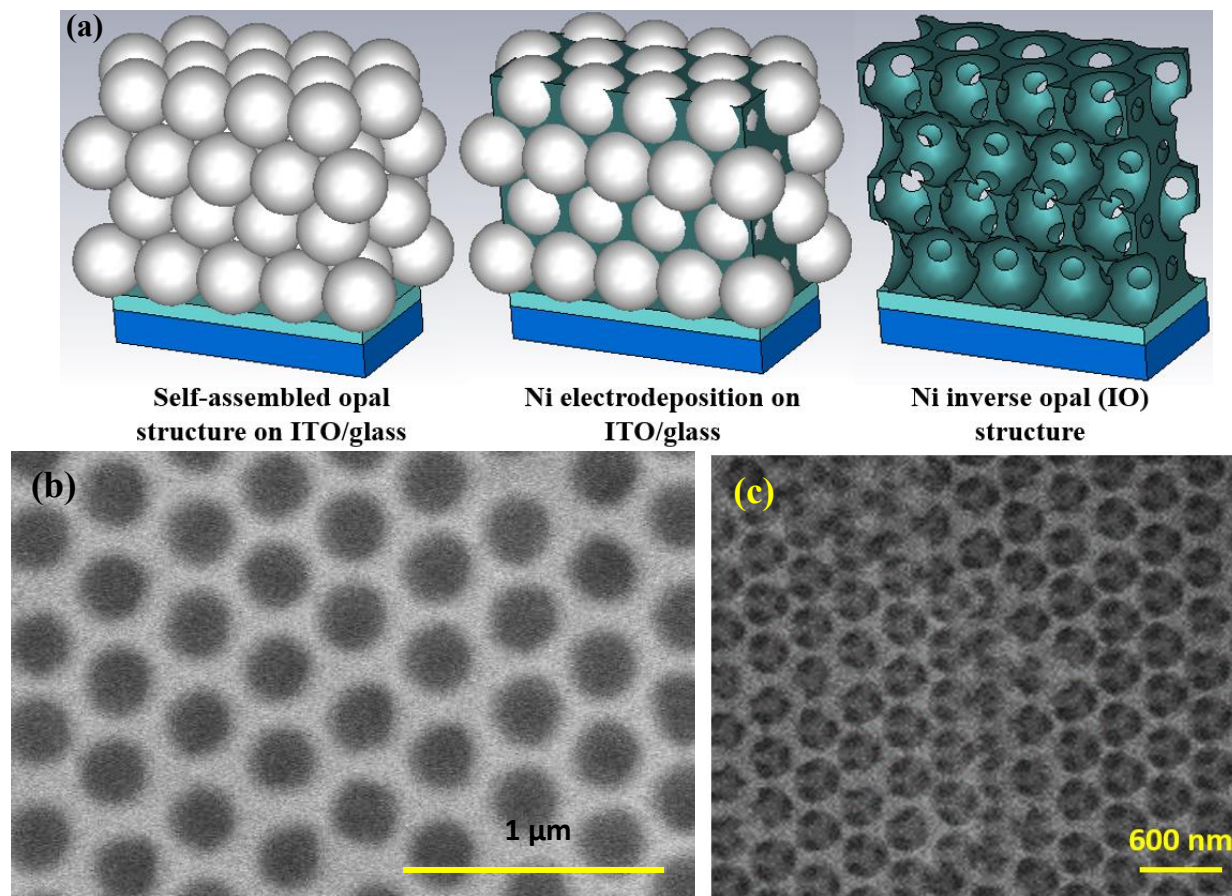


Figure 6.2. (a) Schematic of the steps involved in a template assisted electrodeposition of Ni IO structure. Ni is electrodeposited, on the ITO surface, in the voids of the hcp arrays of polystyrene microbeads (opal template). The microbeads are then etched away to reveal the skeletal frame of the Ni IO structure. (b) FESEM image of the Ni IO surface showing long range ordering in the IO structure, in a region of the template where Ni covers a little more than half the thickness of the terminal polystyrene microbeads layer (*i.e.* off the central plane), similar to the central figure in the schematic in part (a). The center-to-center distance, inter-cavity pitch, between two adjacent cavities is ~ 400 nm. (c) Another FESEM image of the Ni IO surface clearly showing the circular channels in the underlying inter-cavity walls.

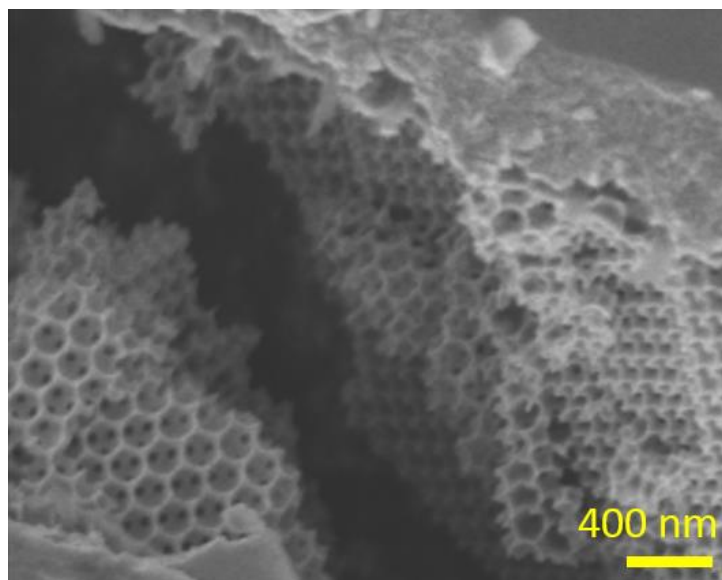


Figure 6.3. FESEM image of the cross-section of a Ni IO structure, a slightly tilted view. The number of layers in the IO structure appears to be >11 layers (thickness > $\sim 4\mu\text{m}$).

A three-dimensional hcp arrangement with long range order was observed. The diameter of the air voids, and the center-to-center distance between adjacent cavities (inter-cavity pitch) in the Ni IO structure is consistent with that of the polystyrene beads ($\sim 400\text{ nm}$), Figure 6.2c. As expected, the thermal annealing of the opal structure increases the contact area between adjacent beads. This contact area, in turn, creates the circular channels in the inter-cavity walls of the IO structures, which are evident in the FESEM images, Figure 6.2c. These channels allow the effective etching of the beads by forming *in situ* interconnected pathways for the etchant. The cross-sectional FESEM image, Figure 6.3, of the Ni inverse opal (IO) sample shows the structure to be at least 11 layers deep. The typical thickness of the IO structure in this study was at least $\sim 4\mu\text{m}$ (or ≥ 11 layers), as observed from the cross-sectional FESEM image. The IO thickness can be varied up to the thickness of the initial opal structure by regulating the electrodeposition time. In this study, the final thickness of the electrodeposited Ni was less than that of the initial stack of polystyrene beads.

6.3.2 Reflectance Measurement of the Ni IO structure

The total reflectance measurements, specular and diffuse, were recorded in the integrating sphere of a Perkin-Elmer Lambda 950 spectrophotometer at a near normal ($\theta = 8^\circ$, smallest angle allowed by the spectrophotometer) angle of incidence in the wavelength range of 300 nm to $2\mu\text{m}$.

The reflectance spectra for the Ni IO structure is also compared with the theoretical reflectance spectra of bulk Ni at normal incidence, Figure 6.4. Bulk Ni has a reflectance that ranges from ~46-67% throughout the visible range of light, which increases to about ~83% at a wavelength (λ) of 2 μm in the near-infrared (NIR) range [26]. In an hcp structure, the total volume fill fraction of the spherical air cavities is ~74%, which translates to ~26% metallic Ni content in the IO structure. A ~1 μm thick bulk Ni film contains the same volume of Ni per unit area as the ~4 μm thick IO structure, so the reflectance spectra of the two may be compared. The measured reflectance of the Ni IO structure is considerably smaller than that of the bulk Ni layer in the wavelength (λ) range of 300 nm to 2 μm , and generally rises with wavelength in the range from 800 nm to 2 μm . A broad but clear resonance peak is observed at around 580 nm, which is consistent with the greenish color of the sample on visual inspection. Furthermore, the measured reflectance of the Ni IO structure was also compared with that of a calculated reflectance, using the effective media approximation, of a structure containing 24% Ni and 76% air. The effective media approximation also over predicts the reflectance in the measured wavelength range, and is unable to account for the resonance peak observed in the reflectance spectra of the Ni IO structure, which is formed as a result of the periodic structural property of the surface as opposed to the material property.

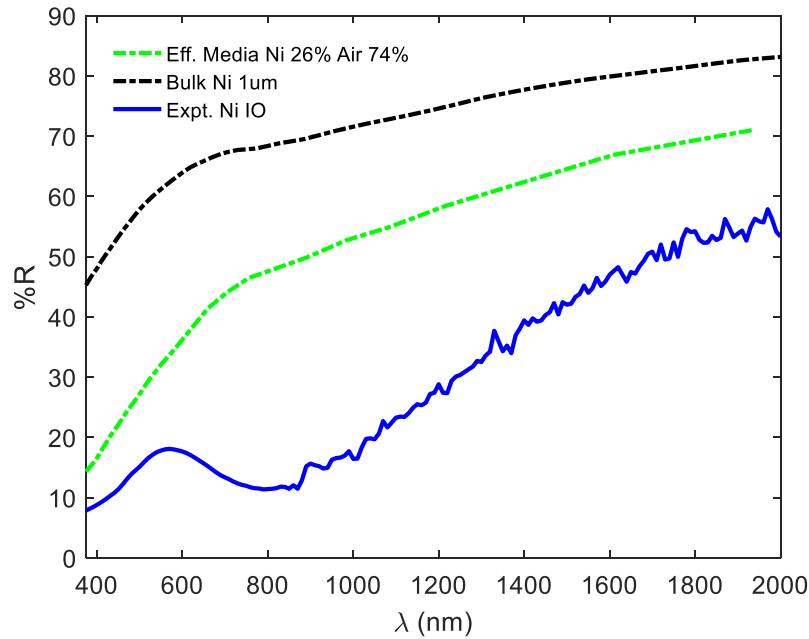


Figure 6.4. Reflectance (non-polarized) measured from the Ni IO surface compared with the theoretical reflectance of a 1 μm thick Ni film, and the calculated reflectance using effective media approximation of a structure containing Ni (24%):air (76%).

Due to the symmetric nature of the nanostructure, the reflectance from Ni IO surface is expected to be independent of the angle of rotation, ϕ , about the surface normal. This was confirmed by taking a linearly-polarized reflectance measurement with an ellipsometer. Note that Figure 6.5 shows the relationships between the various coordinate systems: rectangular coordinates (xyz) are most convenient for describing the structure, while polar coordinates with angles of incidence (θ) and rotation (ϕ), where $\phi = 0^\circ$ along the yz-plane and $\phi = 90^\circ$ along the xz-plane, are used to describe the incident light for reflectance studies. Schematic of the unit cell, Figure 6.5b, shows the top view of a representative IO structure with the Ni filling up to half the height of the terminating spherical cavity layer (*i.e.* up to the central plane of the terminating layer), along with the circular channels visible in each of the topmost hemispherical voids.

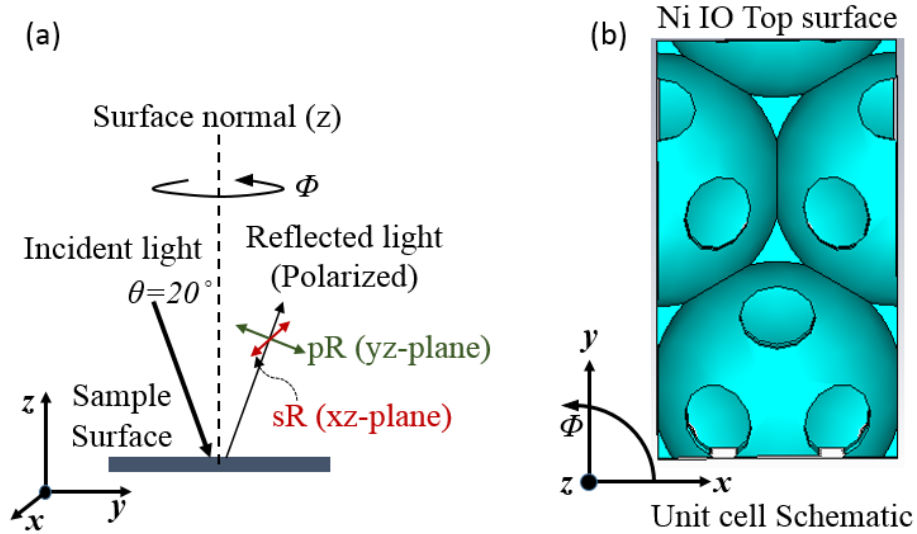


Figure 6.5. Directional vectors with the p-polarized reflectance (pR), along yz-plane ($\phi = 0^\circ$) and the s-polarized reflectance (sR), along xz-plane ($\phi = 90^\circ$). (b) Schematic of the unit cells of an unmodified Ni IO surface (left), and a laser annealed Ni PIO surface (right).

The out-of-plane s-polarized (sR) and in-plane p-polarized (pR) reflectance were measured, at room temperature, using a J.A. Woollam V-VASE UV-VIS-NIR spectroscopic ellipsometer. The incident beam was set at a small angle of $\theta = 20^\circ$, as shown in Figure 6.5a, which is as close to normal incidence as permitted by the ellipsometer. At normal incidence ($\theta = 0^\circ$, and $\phi = 0^\circ$, *i.e.*, parallel to the yz-plane), the sR (parallel to the xz-plane, $\phi = 90^\circ$) and pR (parallel to the yz-plane, $\phi = 0^\circ$) represent polarization along x- and y- axes, respectively; measurements at $\theta = 20^\circ$ provide reasonable approximations of these polarizations for the Ni IO structures. The reflectance for the

Ni IO structure is expected to be the same for x- and y-polarized light at $\theta = 0^\circ$, and similar at $\theta = 20^\circ$ due to the symmetric and periodic nature of the structure in the xy-plane.

As seen in Figure 6.6, the previously measured non-polarized reflectance measured at a near-normal ($\theta = 8^\circ$) incidence using the integrating sphere of a spectrophotometer is compared with the polarized (in-plane, p-polarized (pR) and out-of-plane, s-polarized (sR)) reflectance measured at a small angle of incidence ($\theta = 20^\circ$, smallest angle permitted by the equipment) using an ellipsometer. The reflectance spectra all appear to be similar to one another, with all of them having the resonance peak at ~ 580 nm. The slight difference in the reflectance spectra arise due to the measurements being recorded at non-zero small angles of incidence due to equipment limitations, as opposed to reflectance at normal incidence, and due to slight structural deviations in the actual nanostructure.

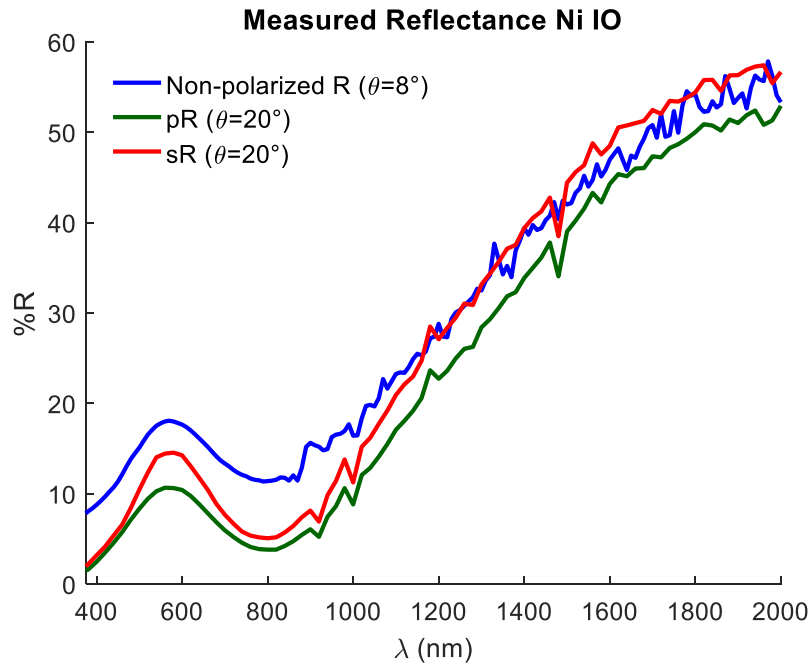


Figure 6.6. The measured non-polarized reflectance (near-normal incidence $\theta = 8^\circ$) of the Ni IO structure is compared with its polarized reflectance measured using an ellipsometer at the smallest angle of incidence ($\theta = 20^\circ$) as permitted by the equipment. The measured s-polarized (along xz-plane, $\phi = 90^\circ$), sR, and p-polarized (along yz-plane, $\phi = 0^\circ$), pR, reflectance, for a linearly polarized incident ($\theta = 20^\circ$) beam are plotted in the graph.

6.3.3 Numerical Modeling of the Ni IO structure

A representative Ni inverse opal (IO) structure, Figure 6.7, was modeled using a full wave numerical simulation employing the finite element method (FEM) with CST Studio Suite, a commercially available electromagnetic field simulation software, using four and a half stacks of regular arrays of hcp spherical cavities arranged in a matrix, or frame, of Ni, representing the cavities left behind by the polystyrene microbeads in the IO sample. It was found that the reflectance response for a thicker IO structure was exactly the same in the wavelength range of calculation, from 375-2000 nm. Thus a smaller stack of Ni IO structure was used for the simulation, as this approximation reduces computational burden and simplifies conceptual interpretation of the results. Although the unmodified Ni IO structure emulated in this model was thick enough to ignore the transmittance and reflectance at the Ni-ITO-glass interfaces, a 100 nm thick ITO layer was sandwiched between the Ni IO structure, and a 200nm thick glass layer, for consistency with the actual IO structure. The center to center distance between two adjacent air cavities was set as 400 nm, but the radius of the spherical cavities was set as $200 + 10 = 210$ nm. This would simulate the circular channels seen in the SEM images, Figure 6.2c, of the Ni IO structure.

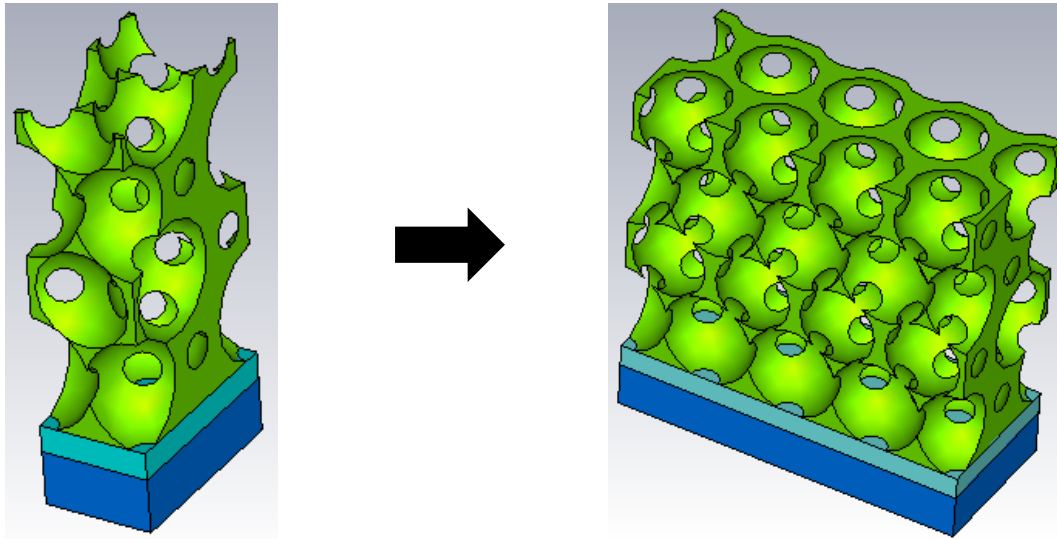


Figure 6.7. Schematic of a finite element method (FEM) model (left) of the Ni IO structure. Multiple copies (right) of a unit cell have been stacked side by side to illustrate the formation of the Ni IO structure.

The Ni content, areal fill fraction (AFF), on the topmost layer of the Ni IO structure may be varied by adjusting the height of the IO stack, as seen in Figure 6.8. The height of the IO stack

is set to be $z = 0$, when the IO model terminates exactly at four and a half layers of spherical cavities, *i.e.* the central plane of the top-most layer. When the height of the IO stack is varied slightly (by δz), the areal fill fraction of Ni in the top-most surface changes, and therefore changes the simulated reflectance spectra. The reflectance spectra was found to be very sensitive to the Ni content of the top-most layer.

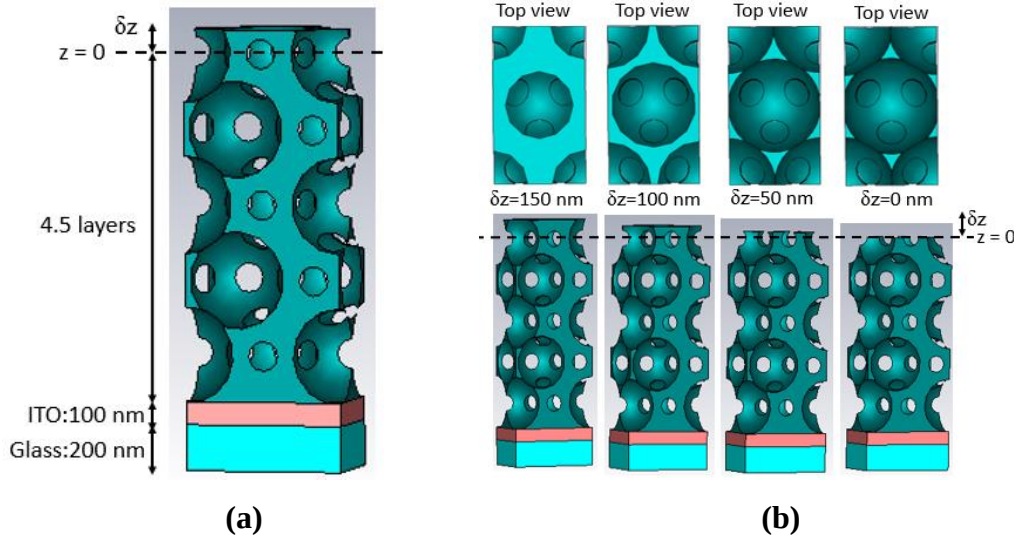


Figure 6.8. (a) Schematic of the finite element method (FEM) model used for the calculation of the reflectance spectra of the Ni inverse opal (IO) structure using $4\frac{1}{2}$ layers of hcp arrays of spherical cavities. (b) Schematic showing the differences in the areal fill fraction (AFF) of the top surface of the Ni IO model by a slight variation (δz) of the height of the IO stack.

The simulated polarized reflectance of a numerical model for a representative Ni IO structure is plotted in Figure 6.9. To emulate the measurement conditions of the ellipsometer the incident angle has been set at 20° with respect to the surface normal. The reflectance of the numerical model was simulated for different heights (δz) of the terminating layer. It was found that the longer wavelength reflectance varied by as much as 15% when the terminating layer δz was varied from 0 to 100 nm. Based on the SEM images of the Ni IO surface, it was determined that most of the IO surfaces terminated at an off-center plane of the terminating layer. The simulated in-plane p-polarized reflectance (pR) and the out-of-plane s-polarized reflectance (sR) were found to closely match with the measured pR and sR, when $\delta z \sim 75$ nm, as seen in Figures 6.9 (a & b). The simulated spectra generally agree with the measured results, including the resonance peak.

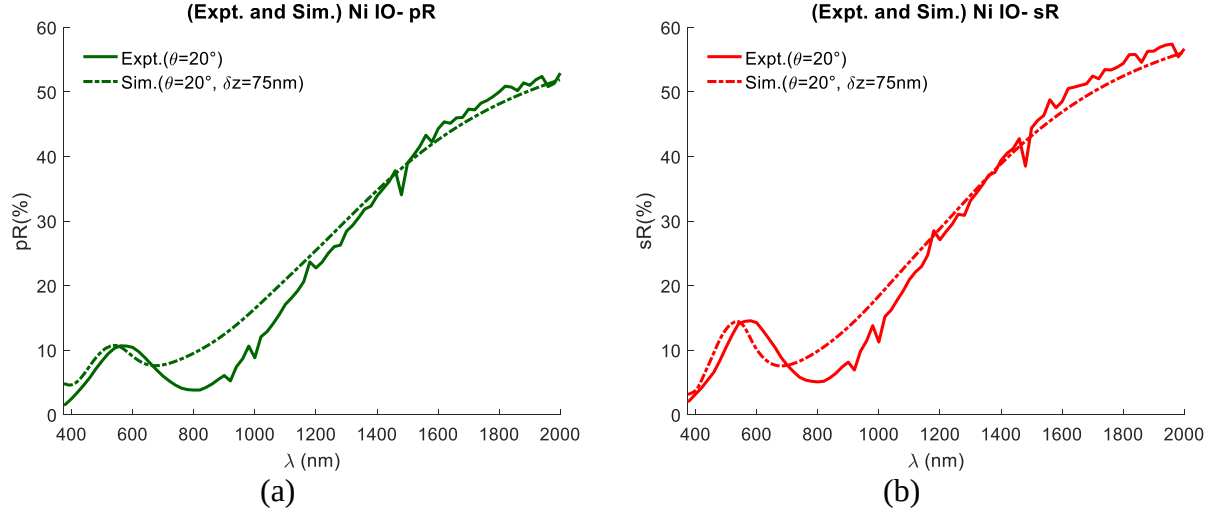


Figure 6.9. Comparison between the measured polarized reflectance and the simulated reflectance of a numerical model of a representative Ni IO structure at 20° incidence angle with the topmost layer terminating at an off-center height of $\delta z = 75$ nm. (a) Comparison of the in-plane p-polarized reflectance (pR). (b) Comparison of the out-of-plane s-polarized reflectance (sR).

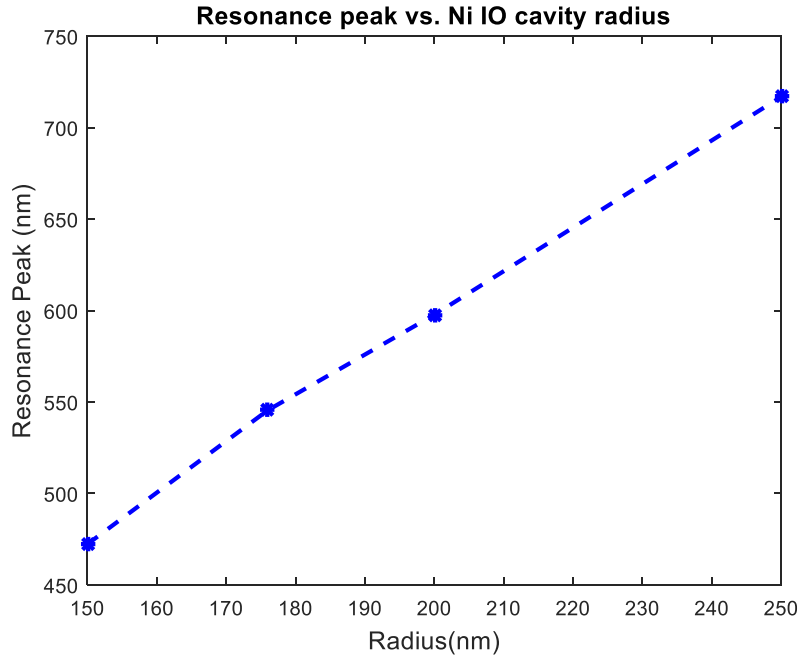


Figure 6.10. Shift of the resonance peak in the reflectance spectra in a Ni IO structure, as predicted by a FEM model, as a function of the air cavity radius. A blue (red) shift of the resonance reflectance peak with decreasing (increasing) diameter of the air cavities for a Ni IO structure is expected.

The same FEM model was also used to simulate the reflectance characteristics of a Ni IO structure for various cavity diameters to predict the shift in the reflectance spectra as the structural parameter was changed. For this simulation, the radii of the spherical cavities were varied from 150 nm to 250 nm (diameter varied from 300 nm to 500 nm). The model assumes the same structure as that of an IO template, with the spherical cavities in close contact with each other, as represented in Figure 6.7, and their periodicity changing as function of the radius of the spherical voids. The simulations show a blue (red) shift of the resonance peak with decreasing (increasing) diameter of the air cavities, as shown in Figure 6.10. Therefore, numerical modeling indicates that the reflectance spectra can be tuned by changing the structural parameter, *i.e.* diameter of the air cavities in an IO structure.

In summary, this work reports the fabrication procedure, and the corresponding reflectance spectra of a Ni IO structure (cavity diameter ~ 400 nm). The Ni IO structure is created using a self-assembled, regular hcp array of polystyrene microbeads as a template, which has a reflectance profile different than that of bulk Ni of similar volume fill fraction. The highly symmetric surface of the Ni IO structure was found to be relatively (for small angles) independent of the angle of incidence, θ , and independent of the angle of rotation, ϕ , of the surface. Full-wave numerical simulations were used to model the reflectance spectra of the IO structure, and indicated that the optical properties of the Ni IO structure can be tuned by engineering the structural characteristics, such as the radius and periodicity of the air cavities.

6.4 Controlled Laser Photomodification of a Ni IO Structure

The previous section discussed about the fabrication of inverse opal (IO) structures using an opal template, made with self-assembled, hexagonally close-packed (hcp) arrangements of monodispersed spherical polystyrene microbeads. This section will discuss about the synthesis and characterization of a Ni based photomodified inverse opal (PIO) nanostructures. It focuses on the synthesis and optical characterization of nickel-based photomodified IO (PIO) nanostructures formed by femtosecond laser annealing, which transforms the highly symmetric hexagonal close-packed structure of the IO to a controlled asymmetric (unidirectional zipper shaped) structure without the use of any lithographic techniques. While the IO exhibits a hcp array, of air cavities, typical of self-assembled structures, the laser annealing breaks the surface symmetry unidirectionally and yields a ‘zigzag’ or a ‘zipper’ shaped surface nanostructure in the PIO. The

laser annealing approach provides the unique capabilities to control the orientation of the zipper structure via the polarization of the laser and to selectively modify selected areas. Unlike the IO structures, the PIO nanostructures exhibit measured reflectance spectra which depend on the angle of rotation between the surface and the polarization of the incident light. A full wave numerical simulation of representative structures was used to model the reflectance spectra of the PIO structure.

6.4.1 Photomodified Inverse Opal (PIO) Structure of Ni

The Ni photomodified inverse opal (PIO) structure was formed by selectively annealing an area of approximately 0.25 cm^2 on a Ni IO surface (fabrication technique discussed in detail in Section 6.3) using a linearly polarized beam of a femtosecond laser (Spectra Physics, Solstice Ace). The parameters of the laser were as follows: 80 fs pulse duration, fluence of 100 mJ cm^{-2} , wavelength of 800 nm, and a beam diameter of $300 \text{ }\mu\text{m}$. An extended area of the sample was raster scanned with line spacing of $50 \text{ }\mu\text{m}$ and a scan speed of 3 mm s^{-1} . As illustrated in Figure 6.11, the beam is at normal incidence to the sample surface and is scanned along the x-direction. The Ni PIO surface normal points towards the positive z-direction.

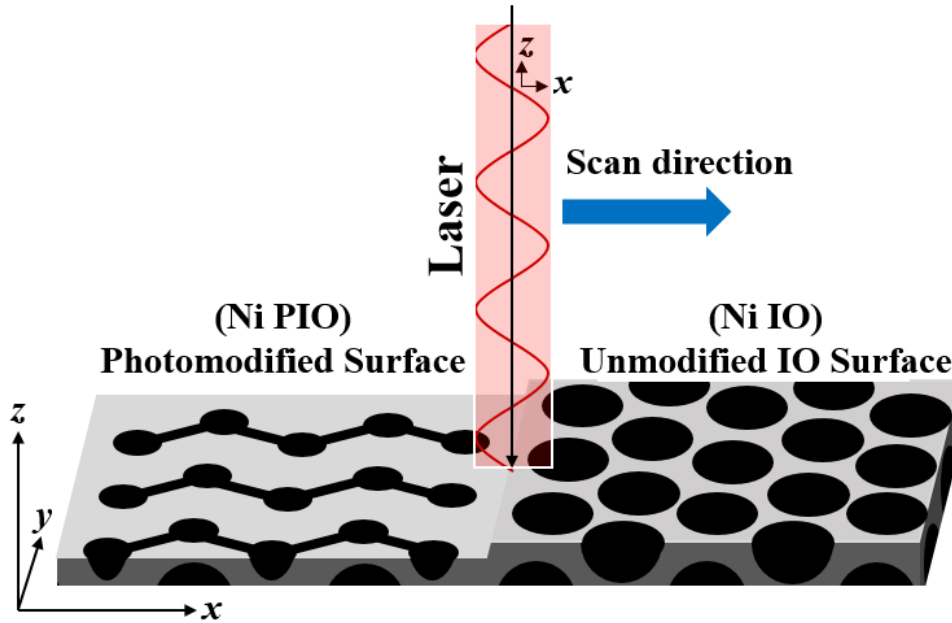


Figure 6.11. Schematic of the laser photomodification process, with the laser beam normal to the surface of the sample, polarized along the x-axis, and being scanned along the same direction.

The surface images of the Ni PIO structure were taken with a Hitachi S-4800 Field Emission Scanning Electron Microscope (FESEM). From the FESEM images of the PIO sample, Figure 6.12, a unidirectional break in symmetry is observed on the surface, with the channels of the zipper-shaped structure forming along the direction of the laser scan. The structural modification is evident from the observed reduction of the diameter of the surface cavities (~ 250 nm); the structure maintains the same periodicity (*i.e.* center-to-center distance of ~ 400 nm), and therefore, a thickening of the inter cavity walls is also observed.

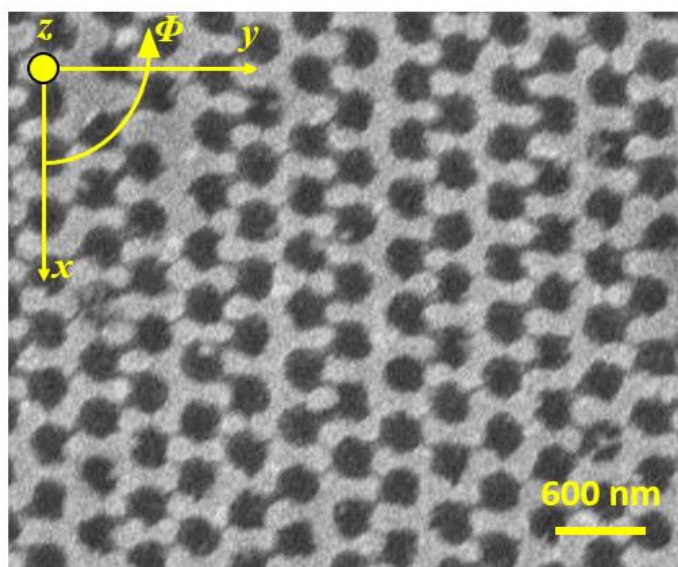


Figure 6.12. FESEM images of a photomodified (Ni PIO) surface. The laser beam was scanned along the x-axis.

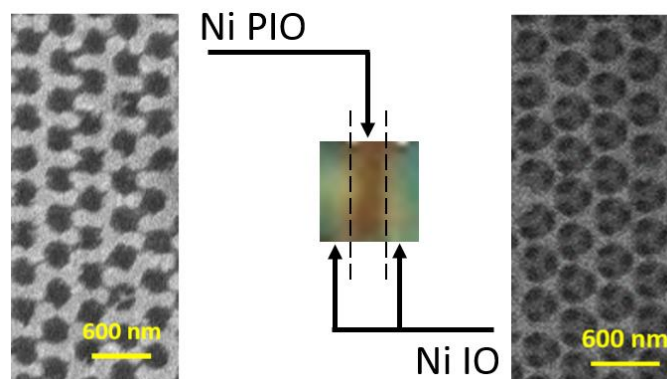


Figure 6.13. Optical (macroscopic) image showing the visible color difference between the unmodified green regions of the Ni IO surface from the reddish brown regions of the photomodified PIO surface, with representative SEM images of the IO and PIO structure shown on either side.

Optical inspection indicates that the color of the laser treated region changes from green to brownish red. Figure 6.13, shows a region on the Ni IO surface that has been photomodified by laser annealing, the representative FESEM structure for the two regions, IO and PIO, are shown on either side of the optical image.

The formation of the parallel zipper shaped structure is likely caused by localized heating, due to the E -field concentration that depends on the laser beam's intensity, scan direction, and polarization. The exposure time, and the intensity of the laser beam are found to be critical in forming these zipper shaped nanostructures, as overexposure yielded irregular islands of Ni, likely due to more complete melting of the surface nanostructures, as seen in Figure 6.14. Based on a full wave numerical simulation, discussed later, the interaction of light with the Ni IO surface appears to be confined within the first two layers of the IO structure. Therefore, the structural modification is thought to be confined to the top two layers.

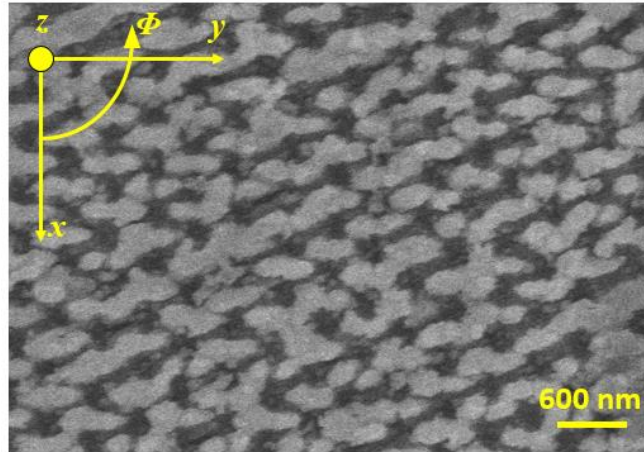


Figure 6.14. FESEM image of an overexposed region of the photomodified Ni PIO structure, complete melting of the surface nanostructures yield irregular islands of Ni.

The zigzag patterns give rise to continuous surface metallic pathways along the direction of the patterns (x -axis in Figure 6.12). In comparison, the surface continuity is interrupted at regular intervals along the orthogonal direction (y -axis in Figure 6.12). As a result, this nanostructure is expected to give rise to a reflectance that depends on the angle of rotation, ϕ , of the PIO sample for linearly polarized incident light. Figure 6.15 (a and b) shows the relationships between the various coordinate systems: rectangular coordinates (xyz) are most convenient for

describing the structure, while polar coordinates with angles of incidence (θ) and rotation (ϕ), where $\phi = 0^\circ$ along the yz-plane and $\phi = 90^\circ$ along the xz-plane, are used to describe the incident light for reflectance studies. Schematic of a unit cell, Figure 6.15b, shows the top view of the Ni PIO structure, along with the direction vectors. The structure has been discussed further in a later section that describes the numerical model.

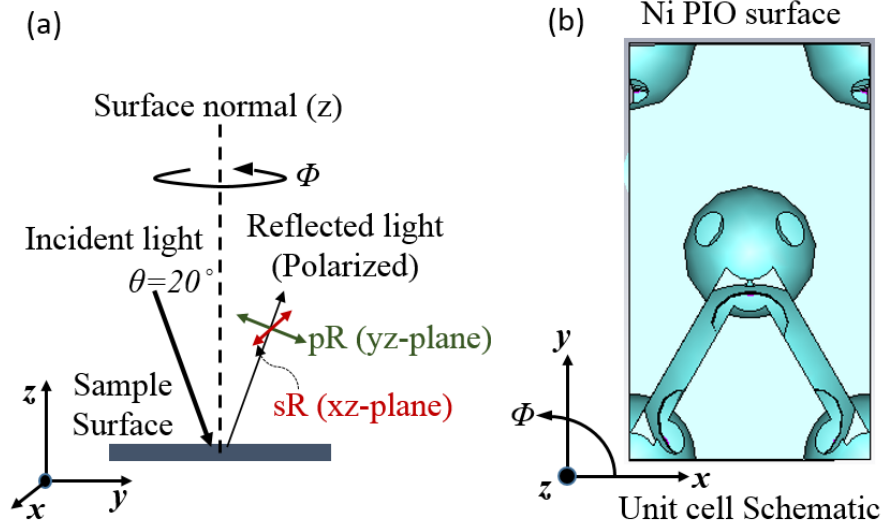


Figure 6.15. (a) Directional vectors with the p-polarized reflectance (pR), along yz-plane ($\phi = 0^\circ$) and the s-polarized reflectance (sR), along xz-plane ($\phi = 90^\circ$). (b) Schematic of a unit cell of a laser annealed Ni PIO surface.

6.4.2 Reflectance Measurement of the Ni PIO structure

Due to structural difference, the total reflectance spectra of the Ni PIO is different from that of the unmodified IO structure, as observed from the measurement in the integrating sphere of a spectrophotometer (incident angle, $\theta = 8^\circ$), Figure 6.16. Owing to the regular interruption in surface continuity, in one direction (y-axis in Figure 6.12) of the Ni PIO structure as opposed to the other (x-axis in Figure 6.12), the photomodified nanostructure, unlike the unmodified, symmetric IO structure, is expected to give rise to a reflectance that also depends on the angle of rotation, ϕ , with respect to linearly polarized incident light. In other words, the reflectance for the Ni PIO structure is expected to be different for x- and y-polarized light at $\theta = 0^\circ$, with measurements at a relatively small angle of $\theta = 20^\circ$ providing a reasonable approximations of these polarizations.

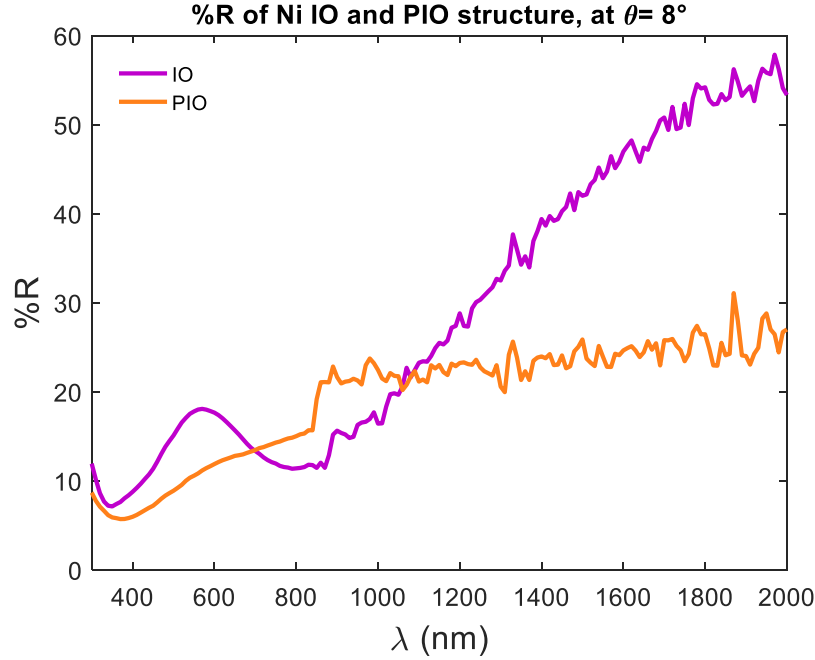


Figure 6.16. Reflectance from the Ni PIO surface when compared with the reflectance from the Ni IO surface.

To observe this angle of rotation based reflectance, the polarized reflectance of the PIO surface were measured using a J.A. Woollam V-VASE UV-VIS-NIR spectroscopic ellipsometer, at room temperature. The linearly polarized (along the yz -plane, Figure 6.12) incident beam was set at a small angle of $\theta = 20^\circ$, which is as close to normal incidence as permitted by the ellipsometer. At normal incidence ($\theta = 0^\circ$, and $\phi = 0^\circ$, *i.e.*, parallel to the yz -plane), the out of plane s - (parallel to the xz -plane, $\phi = 90^\circ$) and in-plane p - (parallel to the yz -plane, $\phi = 0^\circ$) polarizations represent polarization along x - and y - axes, respectively. The reflectance for the Ni PIO structure is expected to be different for x - and y -polarized light at $\theta = 0^\circ$ (and at the relatively small angle of $\theta = 20^\circ$), due to the break in symmetry of the structure in the xy -plane along the two orthogonal directions. Therefore, it is expected and was observed that the sR and pR spectra are different from each other, and from those of the Ni IO structure, Figure 6.17.

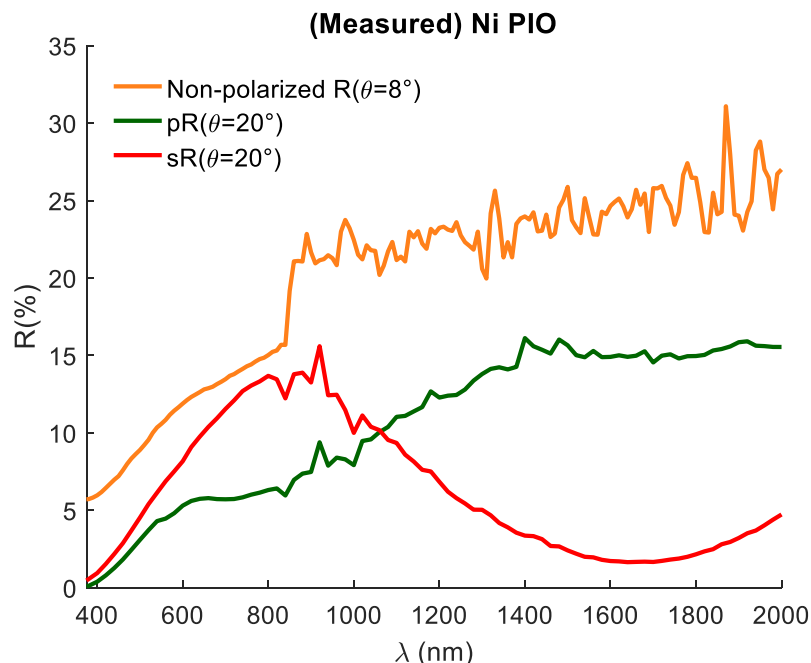


Figure 6.17. Ellipsometric measurement with respect to the surface normal of a photomodified Ni PIO structure. The measured s-polarized (along xz-plane), sR, and p-polarized (along yz-plane), pR, reflectance are plotted, for a linearly polarized incident ($\theta = 20^\circ$) beam. The measured non-polarized reflectance (near-normal incidence $\theta = 8^\circ$) of the Ni PIO structure is also compared with its polarized reflectance.

Figure 6.17 illustrates that the measured s- and p- polarized reflectance (sR and pR) of the Ni PIO structure, and as expected the spectra are indeed different. For instance, the sR reaches a peak at a wavelength of around 850 nm before declining in the near-infrared (nIR) range, and finally rising again beyond a wavelength of 1.7 μm . On the other hand, the pR spectra rises monotonically, and slowly, as the wavelength increases. Therefore, the in-plane (along yz-plane) p-polarized reflectance (pR) was measured and found to be weakly dependent on the wavelength, whereas the out-of-plane (along xz-plane) s-polarized reflectance (sR) was measured and found to be strongly dependent on the wavelength of light. Thus the unidirectional break in symmetry in the PIO surface gives rise to an angle of rotation (ϕ) dependent reflectance, as observed from the pR and sR spectra.

The non-polarized reflectance (specular and diffuse) of the Ni PIO measured ($\theta = 8^\circ$, with respect to the surface normal) in an integrating sphere of a spectrophotometer is also compared with the polarized reflectance. The relatively higher reflectance measured in the spectrophotometer may attributed to the total reflectance it measures as opposed to only the specular reflectance

measured by the detector of the ellipsometer. The photomodification process selectively alters the surface morphology of the IO structure, which leaves behind a very rough surface along with the unidirectional zipper shaped nanostructures. The surface roughness of the PIO structure causes a lot of the reflected light to be scattered that reduces the amount of specular reflectance recorded in the ellipsometer. Furthermore, the non-polarized reflectance increases with wavelength over the visible range, then saturates to around 20-25% at wavelengths greater than 800 nm, and does not show a resonance peak for an incidence angle of $\theta = 8^\circ$.

6.4.3 Numerical Modeling of the Ni PIO structure

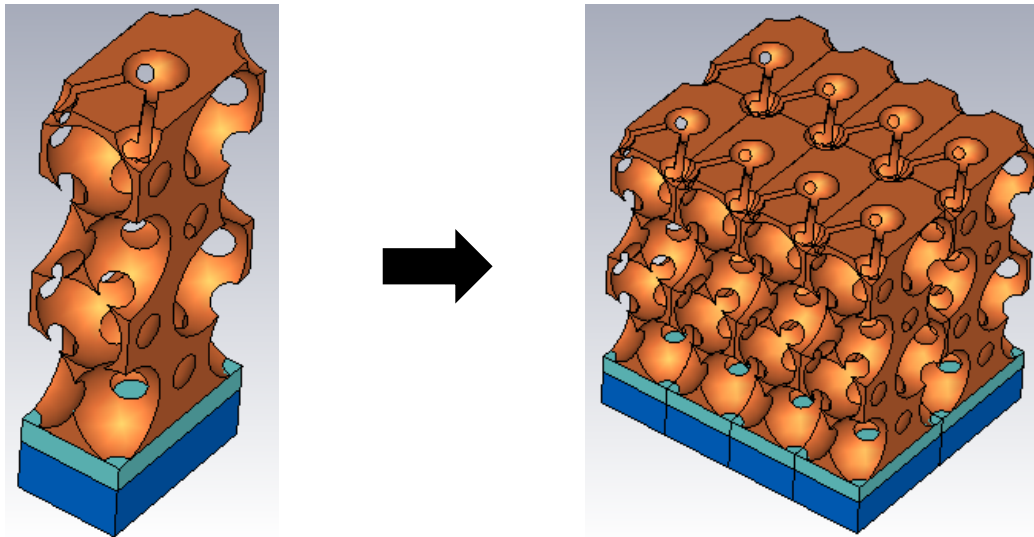


Figure 6.18. Schematic of a FEM model (left) used for the calculation of the reflectance spectra of the Ni PIO structure. Multiple copies (right) of the model have been stacked side by side used to illustrate the formation of the zipper shaped nanostructure on the surface of the Ni PIO.

A representative structure of photomodified Ni inverse opal (IO), Figure 6.18, was modeled using a full wave numerical simulation employing the finite element method (FEM) with CST Studio Suite, a commercially available electromagnetic field simulation software, using four and a half stacks of regular arrays of hcp spherical voids in a matrix of Ni frame, that resembles the cavities left behind by the polystyrene microbeads in the IO structure. The difference between the IO model and the PIO model is that the FEM model for the PIO structure has a modified top layer to emulate the features observed in the FESEM image of the Ni PIO surface Figure 6.12. Based on the structural morphology of the PIO structure, as seen in the FESEM images of the PIO surface,

the top surface of the PIO exhibited the formation of smaller cavities as a result of the photomodification process, while maintaining the same center-to-center distance (pitch) of 400 nm. Therefore, the model used for the reflectance simulation uses the same structure as the Ni IO for the bottom four layers, while the topmost layer has reduced size cavities of radius ($r < 200$ nm) with a pitch of 400 nm.

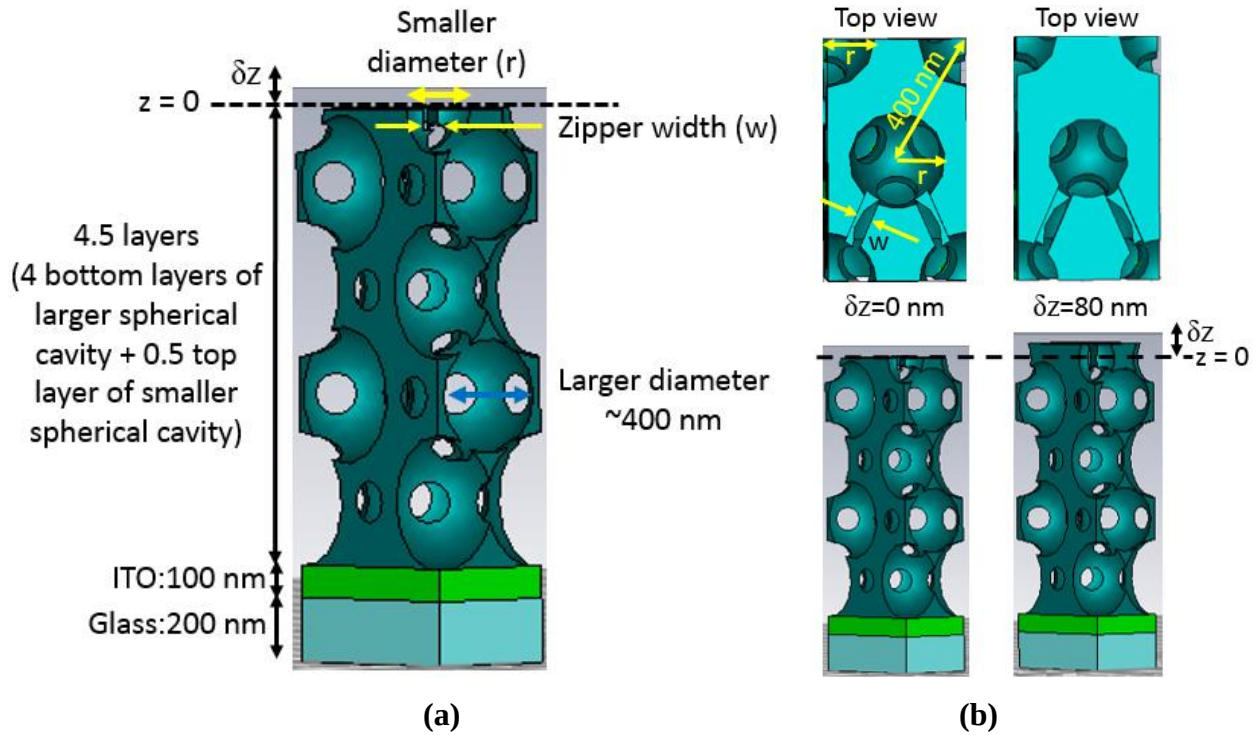


Figure 6.19. (a) Schematic of the FEM model used for the calculation of the reflectance spectra of the Ni PIO structure using $4\frac{1}{2}$ layers of hcp arrays of spherical cavities. The bottom four layers of the spherical cavity has the same dimensions as the IO structure, whereas the topmost layer is made of spherical cavities of a reduced diameter, as observed from the FESEM images of the PIO surface. Three of the cavities of the topmost layer are also selectively connected to each other by rectangular channels of width, w , to emulate the zipper structures. (b) Schematic showing the differences in the top surface fill fraction by a slight variation (δz) of the height of the PIO stack. The schematic also shows the dimension of the various structural features of the topmost surface when $\delta z = 0$ (surface at the central plane).

To emulate the zipper shaped structure on the surface, three of the five spherical cavities of the topmost layer are connected with a rectangular channel of width, w , and with a channel depth of r (the model assumes the zipper channel is only as deep as the topmost layer of the reduced diameter cavities). The radius of all the spherical cavities were adjusted accordingly so that the

cavities touch each other to form the circular channels seen in the FESEM images of the Ni IO structure. Although the Ni PIO structure in this model was thick enough to ignore the transmittance, and the reflectance at the Ni-ITO-glass interfaces, a 100 nm thick ITO layer was sandwiched between the Ni PIO structure, and a 200 nm thick glass layer for consistency with the actual PIO structure.

Like the model of the Ni IO structure, the Ni content (AFF) on the topmost layer of the Ni PIO structure may be varied by adjusting the height of the PIO stack, as seen in Figure 6.19b. The height of the PIO stack is set to be $z = 0$, when the PIO model terminates exactly at the central plane of the topmost layer. When the height of the IO stack is varied slightly (by δz), the areal fill fraction of Ni in the top-most surface changes, which was found to change the simulated reflectance spectra. The reflectance spectra was found to be very sensitive to the Ni content of the top most layer.

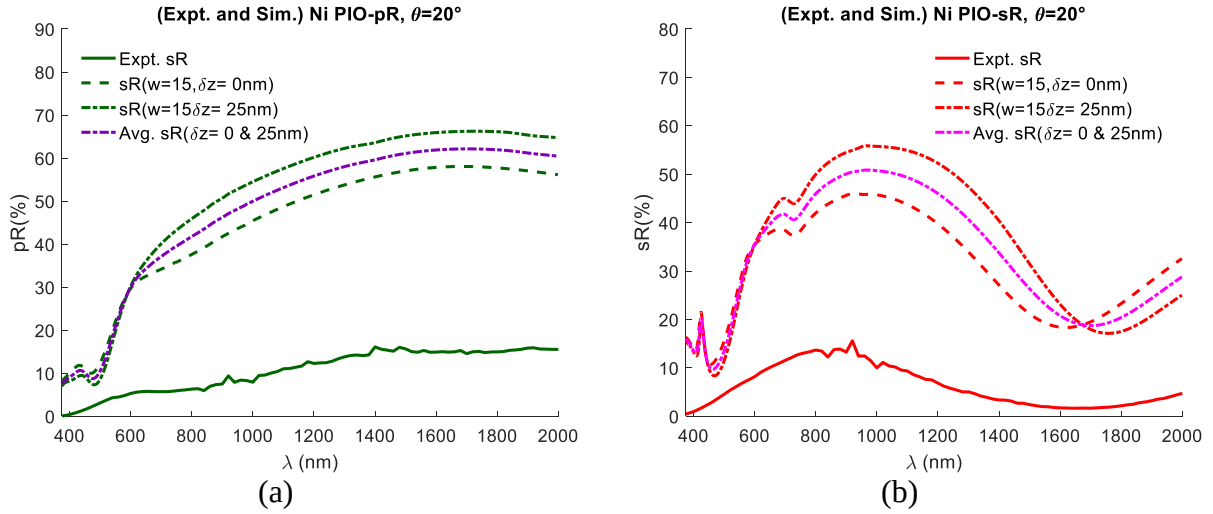


Figure 6.20. Comparison between the measured polarized reflectance and the simulated reflectance of a numerical model of a representative Ni PIO structure at 20° incidence angle with the topmost layer terminating at different off-center heights of $\delta z = 0$ and 25 nm, for a top layer cavity radius of, $r = 125$ nm and channel width of, $w = 15$ nm. (a) Comparison of the in-plane p-polarized reflectance (pR). (b) Comparison of the out-of-plane s-polarized reflectance (sR).

The simulated polarized reflectance of the numerical model for a representative Ni PIO structure is plotted in Figure 6.20. To emulate the measurement conditions of the ellipsometer the incident angle has been set at 20° with respect to the surface normal. The reflectance of the numerical model was simulated for different heights (δz) of the terminating layer. The model used

to plot the pR and sR in Figure 6.20 used a top layer cavity radius of 125 nm and a zipper channel width of 15 nm, which equates to a volume fill fraction of Ni ~33% and air ~67% in the top most layer.

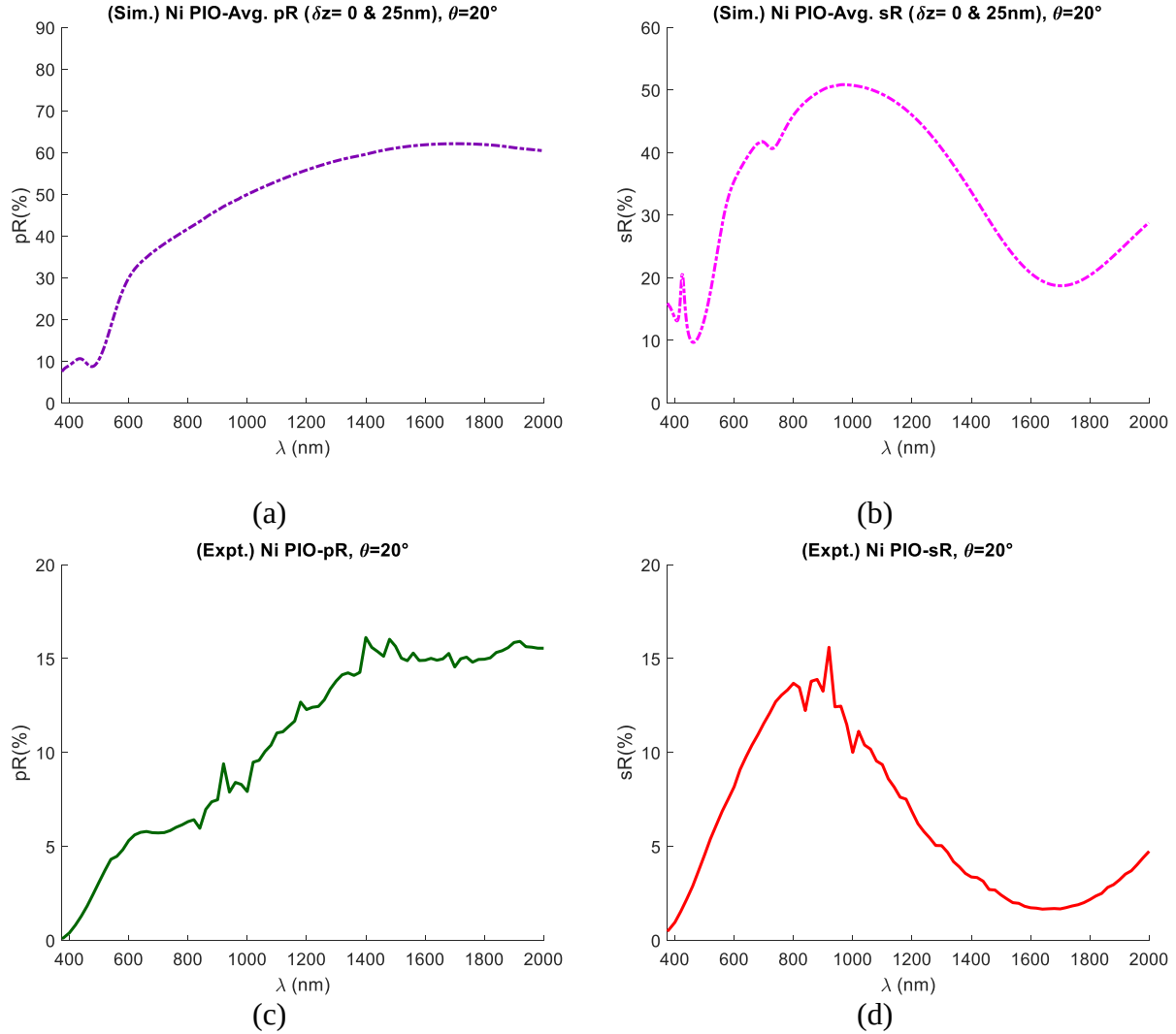


Figure 6.21. Comparing the measured (c & d) polarized reflectance with the simulated reflectance (a & b) of a numerical model of a representative Ni PIO structure separately at 20° incidence angle. The model assumes the topmost layer having a cavity radius of 125 nm and channel width of 15 nm. (a) Simulated average pR spectra (differential height (δz) of 0 and 25 nm). (b) Simulated average sR spectra (differential height (δz) of 0 and 25 nm). (c) Measured pR spectra of the PIO structure. (d) Measured sR spectra of the PIO structure.

It was observed that by sweeping the δz value from 0 to 100 nm, which effectively increases the Ni content of the top most layer by reducing the diameter of the opening of the spherical cavity

(see Figure 6.19b), the peak of the simulated sR spectra shifts from 926 nm (45.9%) to 1278 nm (65.8%). On the other hand, the trough of the sR spectra shifts from 1619 nm (18.3%) to beyond 2000 nm when δz value is swept from 0 to 100 nm. From varying the various dimensions of the PIO model, the structural parameter that yields the best fit for the strong wavelength dependence observed in the measured sR was the PIO model with the topmost layer cavity diameter of 125 nm, with a channel width of 15 nm. Figure 6.20 (a & b) plots the simulated pR and sR spectra for models assuming a differential height (δz) of 0 and 25 nm, the figures also plot the average spectra for both of these differential heights. When the plots are observed separately, Figure 6.21, the models appear to capture the strong wavelength dependence of the measured sR spectra, and the relatively weak wavelength dependence of the measured pR spectra. The model shows a strong angular (ϕ) dependence for the reflectance of the PIO structure. As the polarized reflectance is observed at different rotated angles, *i.e.* from the yz-plane (pR, $\phi = 0^\circ$) to the xz-plane (sR, $\phi = 90^\circ$), the simulated reflectance spectra of the Ni PIO structure changes from a monotonically rising curve, with respect to wavelength, to one that relatively acts as an optical band stop filter, which is similar in trend to the Ni PIO's measured polarized reflectance ($\theta = 20^\circ$), pR and sR, respectively.

In conclusion, while the model reasonably captures the trend of the sR and pR spectra of the PIO structure, it overestimates the reflectance. The low reflectance measured in the PIO structure is thought to be caused by the surface roughness, and the structural deviation present in the actual nanostructure that causes a scattering of the reflected light, which was not accounted for in the numerical model. Moreover, the ellipsometer is only able to measure the specular reflectance from the PIO surface, whereas the integrating sphere in the spectrophotometer can measure both the unpolarized specular and diffuse reflectance, which exhibits a reflectance that is nearly double the polarized reflectance in the long wavelength range, Figure 6.17. The relatively higher reflectance measured in the spectrophotometer is due to the diffuse reflectance of the scattered light from the rough surface of the PIO structure.

To summarize, this work reports the fabrication of a novel zipper shaped nanostructure by photomodification of a metallic IO structure using a laser annealing technique. The initial unmodified Ni IO structure is created using a self-assembled, regular hcp array of polystyrene microbeads as a template. Combining self-assembly techniques, which yield highly ordered regular arrays, with a femtosecond laser photomodification technique yields a novel nanostructure with controlled asymmetry, namely the zipper shaped PIO structure. The laser photomodification

process allows for a highly localized structural modification as dictated by the beam size, while also providing the potential of scalability for mass production. The reflectance of the Ni PIO structure responds differently along various angles of rotation of the surface, due to the differences in symmetry along the two orthogonal directions of the surface. Full-wave numerical simulations were used to model the reflectance spectra of the PIO structures. The results from this work confirm the ability to tune the reflectance spectra of nanostructures of the same material with similar volume fill fractions by photomodification, where the different optical responses can be attributed to the structural differences of the actual structure as opposed to the material properties of the solid.

6.5 Indium Antimonide (InSb) Inverse Opal (IO) Structure

6.5.1 Template Assisted Electrodeposition of InSb IO structure

As a III-V, direct band gap, semiconducting material, indium antimonide (InSb), has a lot applications especially in the field of infra-red detection due to its low bandgap of 0.17eV, which translates to a cut-off wavelength of $\sim 7\text{ }\mu\text{m}$, as discussed in Chapter 3 (Section 3.2). This allows InSb to effectively absorb light of wavelength of up to the mid-IR range of the spectrum. The actual absorption in a material can be increased significantly, if the initial reflectance can be suppressed. This sub-section will discuss about the anti-reflective properties of an InSb IO structure fabricated using a template assisted electrodeposition technique.

The template used in this case is the same opal template discussed earlier (Section 6.2), created by self-assembly of polystyrene microbeads (diameter $\sim 400\text{ nm}$) on an electrically conducting ITO coated ($\sim 180 - 200\text{ nm}$ thick) glass substrate. The InSb IO structure is synthesized by filling the void within the array of polystyrene microbeads by electrodeposition. The InSb was electrodeposited in a three-electrode electrochemical cell, using ITO coated glass substrate as the active electrode, a platinum (Pt) gauze as the counter electrode, and a silver/silver chloride (Ag/AgCl) (saturated 3M NaCl) reference electrode. All the potentials reported here, are in reference to this electrode (Ag/AgCl). The electrolyte for the electrodeposition of InSb consisted of an aqueous solution of 0.15 M indium chloride (InCl_3), 0.1 M antimony chloride (SbCl_3) along with complexing agents 0.36 M citric acid, and 0.17 M potassium citrate, at pH of 1.8 [27-29].

Using cyclic voltammetry, the electrodeposition voltage for depositing InSb on the ITO coated glass substrate was determined to be -0.7 V.

The thickness of the deposited InSb layer can be controlled by regulating the time of electrodeposition. The IO structure is formed, once the opal template or the arrays of polystyrene microbeads are etched away completely, see schematic in Figure 6.2a. This is achieved by submerging the electrodeposited opal template in tetrahydrofuran $[(CH_2)_4O, (THF)]$ at $40^\circ C$ for an hour, followed by a fresh treatment in THF for an additional hour to remove any remaining traces of polystyrene in the template, which leaves behind a semiconductor based, several microns thick, skeletal IO structure. The InSb IO structure visually appears black at this stage, but has a brilliant greenish iridescence when observed from certain angles due to structural coloration that arises from the symmetry, and the dimension of the IO structure. The surface images of the InSb IO structure was taken with a Hitachi S-4800 Field Emission Scanning Electron Microscope (FESEM), Figure 6.22.

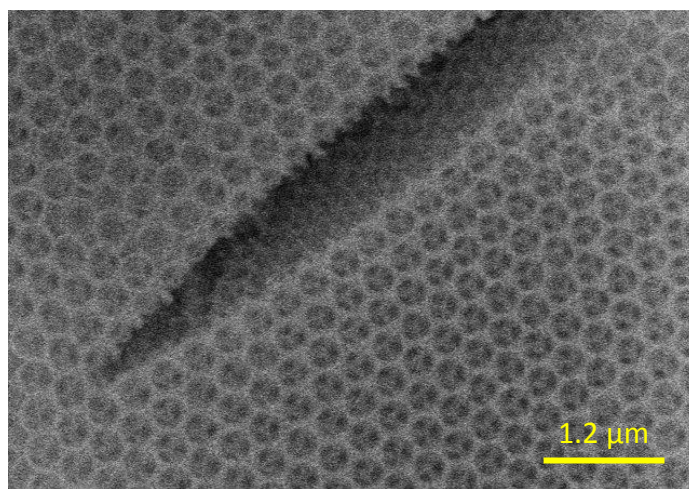


Figure 6.22. FESEM image of the InSb IO surface showing long range ordering in the IO structure. The center-to-center distance, inter-cavity pitch, between two adjacent cavities is ~ 400 nm, and the circular channels in the underlying inter-cavity walls are also clearly visible. The cracked region gives a glimpse of the thickness of the IO structure, and confirms it to be several microns thick.

A three-dimensional hcp arrangement with long range order was observed. The diameter of the air voids, and the center-to-center distance between adjacent cavities (inter-cavity pitch) in the InSb IO structure is consistent with that of the polystyrene beads (~ 400 nm). As expected, the thermal annealing of the opal structure increases the contact area between adjacent beads, which

in turn, creates the circular channels in the inter-cavity walls of the IO structures, as observed in the FESEM image. The cross-sectional FESEM image, Figure 6.22, of the InSb IO sample shows the structure to be several microns ($\sim\mu\text{m}$) thick. The IO thickness can be varied up to the thickness of the initial opal structure by regulating the electrodeposition time. The final thickness of the electrodeposited InSb was less than that of the initial stack of polystyrene beads

6.5.2 Reflectance Measurement of the InSb IO structure

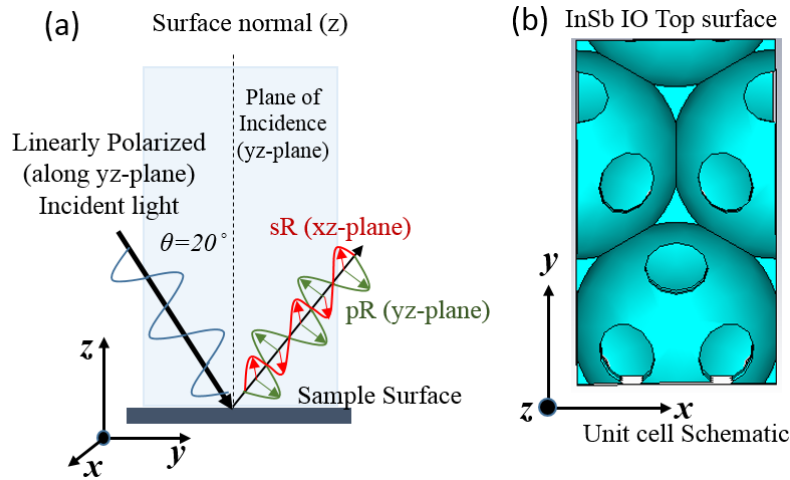


Figure 6.23. (a) Directional vectors for the (ellipsometry) polarized reflectance measurement for a linearly polarized incident light, with the p-polarized reflectance (pR), along yz -plane and the s-polarized reflectance (sR), along xz -plane. (b) Schematic of the unit cell of an InSb IO's top surface.

The symmetric nature of the nanostructure ensures the reflectance from the InSb IO surface to be independent of the angle of rotation. This was confirmed by taking a linearly-polarized reflectance measurement with an ellipsometer. Note that Figure 6.23a, shows the relationships of the rectangular coordinate systems for describing the structure, with the plane of incidence along the yz -plane. The p-polarized reflectance, pR, is along the yz -plane, and the s-polarized reflectance, sR, is along the xz -plane. Schematic of the unit cell, Figure 6.23b, shows the top view of the IO structure with the InSb filling up to middle of the terminating polystyrene bead layer (*i.e.* the cavity cross-section at the central plane of each spherical cavity), along with the circular channels, visible in each of the topmost hemispherical voids.

The s- and p-polarized reflectance were measured, at room temperature, using a J.A. Woollam V-VASE UV-VIS-NIR spectroscopic ellipsometer. The incident beam was set at a small angle of $\theta = 20^\circ$, as shown in Figure 6.23a, which is as close to normal incidence as permitted by the ellipsometer. At normal incidence ($\theta = 0^\circ$, and the plane of incidence along the yz-plane), the out of plane s (parallel to the xz-plane) and in-plane p (parallel to the yz-plane) polarizations represent polarization along x- and y- axes, respectively; measurements at $\theta = 20^\circ$ provide reasonable approximations of these polarizations for the InSb IO structures. The reflectance for the InSb IO structure is expected to be the same for x- and y-polarized light at $\theta = 0^\circ$, and similar at $\theta = 20^\circ$ due to the periodic nature and the symmetry of the structure in the xy-plane. Figure 6.24 illustrates that the measured s- and p- polarized reflectance (sR and pR) are indeed similar for the InSb IO structure.

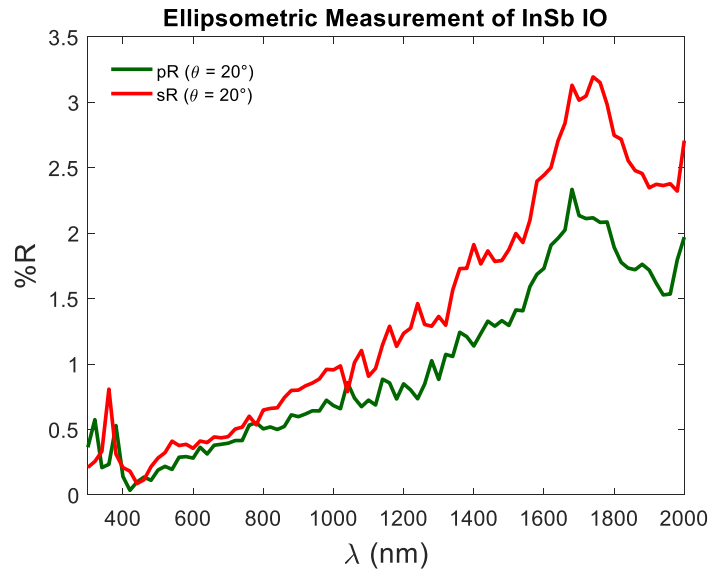


Figure 6.24. Ellipsometric measurement at $\theta = 20^\circ$ with respect to the surface normal for an InSb IO structure. The measured s-polarized (along xz-plane, sR, and p-polarized (along yz-plane), pR, reflectance, for a linearly polarized incident ($\theta = 20^\circ$) beam are plotted in the graph. The sR and pR are less than $\sim 0.5\%$ in the red end and $\sim 0.15\%$ in the violet end of the visible spectrum.

It is remarkable to note, that sR and pR, of the structure has a reflectance of around 0.5% in the red end and further reduces to $\sim 0.15\%$ near the violet end of the visible range of the wavelength spectrum. The small difference in the sR and pR profiles can be attributed to slight structural deviation in the actual nanostructure. The total reflectance (measured at $\theta = 8^\circ$, smallest angle allowed by the spectrophotometer), from a pure InSb wafer (bulk), is also compared with

the polarized reflectance spectra of the InSb IO structure, Figure 6.25. Bulk InSb has a measured average reflectance of $\sim 40\%$ in the wavelength range of 300 nm to 2 μm , whereas the average sR ($\theta = 20^\circ$) is $\sim 1.37\%$, and the average pR ($\theta = 20^\circ$) is $\sim 0.98\%$ in the same wavelength range.

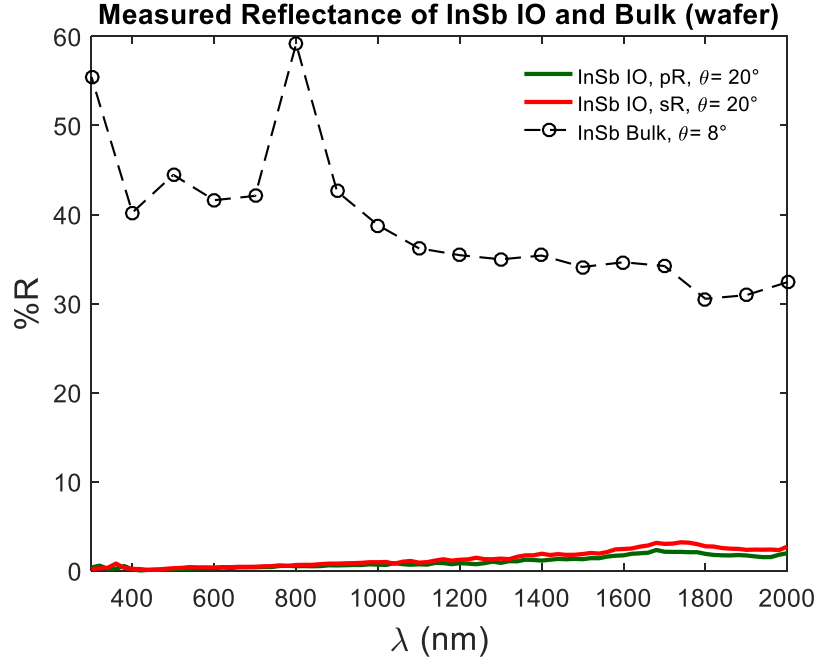


Figure 6.25. Comparison of the measured polarized reflectance (sR and pR) spectra of the InSb IO structure (cavity diameter ~ 400 nm) at $\theta = 20^\circ$ with the measured reflectance of a pure (bulk) InSb wafer at $\theta = 8^\circ$. The InSb IO structure has a very low reflectance surface when compared with its bulk counterpart.

In summary, this work reports the fabrication procedure, and the corresponding polarized reflectance spectra of an InSb IO structure (cavity diameter ~ 400 nm). The template assisted, electrodeposited InSb IO structure is created using a self-assembled, regular hcp array of polystyrene microbeads as a template. The InSb IO structure was found to have a remarkably low reflectance in the visible portion of the spectrum of light. Therefore, InSb IO structure can easily be used as a very efficient anti-reflective coating, and used in various sensing, and photovoltaic applications.

6.6 Reference

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7. CONCLUDING REMARKS

This thesis reports, explores, and discusses the optical and structural characteristics of some of the complex, novel structures of nanomaterials synthesized using various template assisted electrodeposition techniques. Ambient condition electrodeposition processes provide a relatively easy and a cost effective way to create intricate nanostructures, unlike the more sophisticated methods such as high temperature CVD, or time consuming atomic layer deposition (ALD) techniques. The fabrication and utilization of various intricately designed templates, discussed here, are found to be very versatile, and their various geometrical parameters can be tuned and adjusted during their self-assembly process, which makes the use of such template assisted technology so fascinating. Several, structures, such as the novel hierarchically branched nanostructures, reported here would be extremely difficult, time consuming and expensive, if not outright impossible, to realize using any of the other technologies available today.

The thesis reports and characterizes, in detail, about the fabrication techniques of geometrically tailored, highly crystalline, nanostructures of InSb, and other metals, using various material characterization techniques. NWs of InSb are extremely interesting from an optoelectronic point of view as they have exhibited light manipulation, in terms of having low reflectance, and band selective absorbance, depending on the structural parameters of the NWs, and have the potential for application in the next generation photovoltaic and optoelectronic devices. This thesis explores and reports on the fabrication techniques of such structurally complex architectures such as the vertically aligned straight NW arrays, and also discusses about hierarchically branched NW arrays. The optical characterization of such arrays of structures, accompanied by appropriate numerical modeling, show a wavelength dependent absorption spectra, whose properties can be tailored by tuning the geometrical dimensions of the structure. This idea of using vertically aligned arrays of NWs and nanostructures, realized by template assisted electrodeposition, may be extended to any other metallic or semiconducting material of interest. While template assisted electrodeposition has many advantages, it can sometimes be challenging to convert them effectively into working electrodes for electrodeposition. A couple of solution to this problem, including the selection and regulation of the conductor layer thickness and use of optically transparent graphene as electrode for electrodeposition, has been demonstrated and discussed.

Using the template assisted electrodeposition technique, it is also possible to electrodeposit vertically aligned arrays of semiconductor-metal NW based heterostructures (InSb-Ag was shown in this work) using graphene as an *in-situ* transparent conductor. As reported in this work, this preliminary structure with its low reflectance, has a lot of potential optoelectronic application, and can be used as a starting point for future research to design and integrate such structures for photovoltaic or photo-sensing applications.

Self-assembled opal templates created using single diameter, monodisperse, polystyrene beads, which structurally mimic their naturally occurring counterpart, are found to be quite versatile in their application in fields ranging from chemistry to biology to aesthetics to optoelectronics. The thesis discusses and reports the use of such a template to electrodeposit and fabricate intricately designed inverse opal (IO) nanostructures of both metals (Ni) and semiconductors (InSb). Due to the structural parameters of these IO nanostructures, they are found to have wavelength dependent optical characteristics that are very different from their bulk counterpart. The novel InSb IO structure, has the potential application of both as an *in-situ* antireflective (AR) coating, and as an active absorbing material for IR detectors and sensors made of the same compound.

The metallic, in this case Ni, IO structures have also been fabricated by a template assisted electrodeposition technique, and exhibit high level of structural symmetry. The Ni IO reported in this work have hcp arrangements of ~ 400 nm diameter air cavities, whose reflectance was found to be relatively independent of the angle of incidence (for small angles), θ , and independent of the angle of rotation, ϕ , along the surface normal. Unlike the highly absorbing InSb IO array, it has been calculated that the color, or the reflectance profile, of Ni IO structures can be controlled by adjusting the structural parameters of the spherical voids that make up the IO structure, which has many potential application in the field of structural coloring. The thesis also demonstrates a novel way to create a zipper shaped nanostructure using the Ni IO structures with a femtosecond laser photomodification technique that structurally transforms the highly symmetric hcp of the IO to a controlled asymmetric (unidirectional zipper shaped) structure without the use of any lithographic techniques. These photomodified inverse opal (PIO) structures, unlike their unmodified IO counterparts, exhibit a measured reflectance spectra that depend on the angle of rotation between the surface and the polarization of the incident light. The laser photomodification process allows

for a highly localized structural modification as dictated by the beam size, while also providing the potential of scalability for mass production.

The inherent complexity and uniqueness of these IO and PIO structures make them an excellent candidate for applications in anti-counterfeiting and product security. As reported in a recent article, cloned fake components, especially in the semiconductor industry, are becoming more and more difficult to distinguish from the authentic products [1]. It has been reported that despite all the sophisticated and expensive anti-counterfeiting techniques available at the present moment, ranging from tamper-evident tags and markings to holograms to radio frequency identification labels, aggressive counterfeiters have the ability to replicate these technologies within 18 months. This can be countered by incorporating and integrating complex nanostructures with structural coloration into devices, by fabricating hidden features or designs that can potentially make them nearly impossible for counterfeiters to replicate.

7.1 Reference

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COMPUTER SKILLS: MATLAB, PSPICE, CST Microwave Studio 3D EM Simulation Software, Microsoft Office.

ENGINEERING, FABRICATION & CHARACTERIZATION SKILLS:

- Anodization, Deep Reactive Ion Etching, Electrodeposition, Electrical Characterization, Energy Dispersive X-Ray Spectroscopy (EDX), Electron Beam Evaporator, Field Emission Scanning Electron Microscopy (FESEM), Optical Spectrophotometry, Photolithography, Wet chemical etching, and XRD (X-ray Diffraction).
- Extensive working experience in cleanrooms, under chemical hoods and in glove boxes.

PUBLICATIONS

- (Under Review) “Controlled Laser Photomodification of a Ni Inverse Opal Structure”, **Asaduzzaman Mohammad**, Albraa Alsaati, Piotr Nyga, David Warsinger, Alexander Kildishev, Amy Marconnet, David B. Janes. (2020).
- “Electrodeposition of InSb branched nanowires: Controlled growth with structurally tailored properties”, Suprem R. Das, Çem Akatay, **Asaduzzaman Mohammad**, Mohammad Ryyan

Khan, Kosuke Maeda, Russell S. Deacon, Koji Ishibashi, Yong P. Chen, Timothy D. Sands, Muhammad A. Alam, David B. Janes, J. App. Phys., 2014, 116, 083506.

- “Optical Characteristics of Vertically Aligned Arrays of Branched Silver Nanowires”, **Asaduzzaman Mohammad**, Doosan Back, Jieran Fang, Alex Kildishev, David B. Janes, Proceedings of 14th IEEE International Conference on Nanotechnology (Toronto, ON, Canada), (IEEE) 978-1-4799-4082-0, pp.563-566 (2014).
- “Wavelength-Dependent Absorption in Structurally Tailored Randomly Branched Vertical Arrays of InSb Nanowires”, **Asaduzzaman Mohammad**, Suprem R. Das, Mohammad Ryyan Khan, Muhammad A. Alam, David B. Janes, Nano Lett., 2012, 12(12), pp 6112-6118.
- "Electrodeposition of Indium Antimonide Nanowires in Porous Anodic Alumina Membranes", **Asaduzzaman Mohammad**, Suprem R. Das, Yong P. Chen, Timothy D. Sands, David B. Janes, Proceedings of 18th University Government Industry Micro/Nano Symposium (West Lafayette, IN), (IEEE) US 978-1-4244-4732-9, pp. 186-189 (2010).

CONFERENCE PRESENTATIONS

- “Wavelength Dependent Absorption in Vertically Aligned Indium Antimonide (InSb) Nanowire Arrays”, **Asaduzzaman Mohammad**, Mohammad Ryyan Khan, Muhammad A. Alam, David B. Janes, TMS 2015 Electronic Materials Conference (2015), Columbus, OH, USA.
- “Optical Characteristics of Vertically Aligned Arrays of Branched Silver Nanowires”, **Asaduzzaman Mohammad**, Doosan Back, Jieran Fang, Alex Kildishev, David B. Janes, 14th IEEE International Conference on Nanotechnology (2014), Toronto, ON, Canada.
- “Reflection and Transmission Properties of Thin Branched InSb NW Arrays Formed by Electrodeposition”, **Asaduzzaman Mohammad**, Suprem R. Das, Mohammad R. Khan, Muhammad A. Alam, David B. Janes, TMS 2012 Electronic Materials Conference (2012), State College, PA, USA.
- “Electrochemically Deposited Branched Indium Antimonide (InSb) Nanowire Arrays as “in-situ” Anti-reflective Structures”, **Asaduzzaman Mohammad**, Suprem R. Das, Mohammad Ryyan Khan, Muhammad A. Alam, David B. Janes, TMS 2011 Electronic Materials Conference (2011), Santa Barbara, CA, USA.

- “Vertical InSb Nanowire Arrays Electrodeposited into Porous Anodic Alumina Templates on Silicon Substrates”, Suprem Das, **Asaduzzaman Mohammad**, Yong Chen, Timothy Sands, David Janes, TMS 2010 Electronic Materials Conference (2010), Notre Dame, IN, USA.

ACADEMIC HONORS AND AWARDS

- **Committee for the Education of Teaching Assistants (CETA) Teaching Award**, Purdue University, **2012**.
- **Excellence in Teaching Award**, Department of Mathematics, Purdue University **2011**.
- **Title of Outstanding Graduate Instructor** Conferred by the Department of Mathematics, Purdue University, **2011**.
- **Magna cum Laude, B.Sc.**, Louisiana State University (LSU) **2007**.
- **Chancellor’s and Dean’s Honor List**, Louisiana State University, **2003 – 07**.
- **LSU Union Knight and Day Outstanding Student Employee Award**, Louisiana State University, **2007**.
- **LSU Non Resident Scholarship**, Louisiana State University, **2003 – 07**.

LINGUISTIC SKILLS

- **Advanced** (Fluent) conversational, reading and writing: Bengali (Bangla), English, and Hindi.
- **Intermediate**, conversational: Urdu.
- **Moderate**, conversational, reading, and writing: Arabic, and French.

PUBLICATIONS

- [1] A. Mohammad, S. R. Das, M. R. Khan, M. A. Alam, D. B. Janes, “Wavelength-Dependent Absorption in Structurally Tailored Randomly Branched Vertical Arrays of InSb Nanowires”, *Nano Lett.* 2012, 12, 6112-6118.
- [2] S. R. Das, C. Akatay, A. Mohammad, M. R. Khan, K. Maeda, R. S. Deacon, K. Ishibashi, Y. P. Chen, T. D. Sands, M. A. Alam, D. B. Janes, *J. App. Phys.* 116, 083506 (2014).
- [3] A. Mohammad, D. Back, J. Fang, A. Kildishev, D. B. Janes, “Optical characteristics of vertically aligned arrays of branched silver nanowires”, 2014 IEEE 14th International Conference on Nanotechnology (IEEE-NANO), 563-566.