



Coop Term Report
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1.0 Introduction

This is a report on the synthesis of indium antimonide (InSb) nanowires (NWs) by template assisted electrochemical deposition. This synthesis method has the advantage of being inexpensive in addition to yielding highly uniformly sized NWs. The NWs are characterized by powder X-ray diffraction (XRD) and scanning electron microscopy (SEM) with Auger and electron dispersive X-ray (EDX) spectroscopy. The report will be used as a reference for future experiments on electrochemical deposition of InSb or other III-IV group semiconducting compounds. In the first part of the report, the growth of InSb NWs is optimized by growing bulk thin films on various substrates under different voltage and current conditions using the same electrolyte solution used in related paper by M. Ibrahim Khan et al. [1] Once the techniques have matured, the future plans are to deposit InP, InAs, GaAs, and other III-V group NWs following this electrochemical method.

1.1 Brief Introduction Properties of InSb NWs

InSb is a Group III-IV compound semiconductor. The crystal structure of InSb is zincblende with a 0.648 nm lattice constant. InSb is known for its narrow band gap (0.18eV at room temp) and high electron mobility ($8 \times 10^4 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ at room temp), and it is sensitive to wavelength from 1~5 μm . Common applications of InSb are thermal imaging cameras, FLIR systems, infrared homing missile guidance systems, and in infrared astronomy. [2]

InSb is also a magnetoresistive material, and also an excellent candidate for low voltage and high speed transistors. [3] InSb NW is possibly useful for spintronics due to its strong spin-orbit coupling. A collaborator in the Netherlands plans to put contacts on these InSb NWs to create a single spin quantum dot device.

Typical ways of producing InSb are liquid phase epitaxy, hot wall epitaxy, or molecular beam epitaxy.[3,4] It can also be grown from organometallic compounds by metalorganic vapor phase epitaxy.[5] The above processes require high to ultra high level vacuum (10^{-5} to 10^{-9} torr), and the epitaxy processes involves highly reactive and toxic chemicals. Both of the above requirements are expensive to acquire and dispose.

NWs are 5 to 20 μm rods with diameter in the nanometer scale (10^{-9}) consist of metallic

(Zn, Pt, Au), semiconducting (Si, InP, GaAs, InSb, ZnO), or insulating materials (SiO₂). Quantum mechanical effects apply to these wires at such small diameter; specifically, quantum confinement will occur when the size of the NWs becomes smaller than the effective Bohr radius of the charge carriers. NW can be used in nano-circuits, creating logic gates by crisscrossing, or serve as waveguides and quantum dot devices.

1.2 Rationale and Experimental Objective

The rationale for experiment is to create an inexpensive method to mass-produce III-IV NWs or NWs of other compounds. The template electrodeposition method allows the synthesis of many very long (50um) wires with very good uniformity in wire diameter. [1,6] Anodic alumina membrane (AAM) is optically transparent, electrically insulating, thermally and mechanically robust and chemically inert, which is an ideal template for electrochemical deposition. The porous AAM can be purchased in 5nm to 200 nm diameter pores and in density of 10⁹ to 10¹² / cm². The AAM does not react with the highly acidic electrolyte solution, nor does it conduct electrons to affect the electrochemistry. Each electrochemical deposition on AAM would yield roughly 10⁹ individual NWs, so one 40 minute growth cycle can produce enough NWs to supply as many as ten other experiments. Several papers have already reported InSb NW growth with AAM, and the resulting InSb NWs show promising optical and quantum mechanical properties. [1,7] Due to these above reason, the project is initiated in hope that with the template electrodeposition technique, InSb NWs and NWs of different materials can be made.

The objective is to obtain a stable recipe for growing InSb NWs by template electrochemistry method and to develop techniques to extract these NWs from the template for characterization and, eventually, use in NW devices. The three key factors this experiment focuses to understand are the rate of deposition of InSb, dependencies of the composition, and appropriate characterization and imaging approaches.

1.3 Electrochemistry Basics

As shown in figure 1, the three electrode chemical cell consists of a few components: DC power supply, an electrolyte solution, two digital multimeters (DMM), a working electrode, which is the cathode where the reduction occurs, a counter electrode, which is the anode where the oxidation occurs, and a reference electrode, an electrode that is at equal potential with the solution.

The working electrode is connected to the DC power supply to the counter electrode. The interest of the experiment lies on the working electrode, where desired material is reduced onto. The reduction can be metallic ions, such as Fe^{3+} , Cu^{2+} , Zn^{2+} , or Group III&IV ions, Ga^{3+} , As^{3+} . In this report, the desired material is InSb from In^{3+} and Sb^{3+} ions. The desired working electrode should have a relatively small surface area compared to the counter electrode.

The surface of the counter electrode should be at least 100 to 1000 times larger than the working electrode so that the charge density can be dispersed. In aqueous reactions, the electrolysis of H_2O is unavoidable, with a larger surface area on the counter electrode; most of the reaction on the surface will be oxidation of H_2O to O_2 gas. An electrochemical cell with a smaller counter electrode can still be operational, but the counter electrode corrodes from the higher charge density. The oxidized metal ions can pollute the electrolyte solution.

The current of the three electrode system can be measured through the counter electrode, but not the voltage. The voltage of interest is the interfacial potential of the working electrode and the electrolyte solution, which will provide us with information of energy consumption of the electrochemical reaction on the desired product. The interfacial potential of the counter electrode varies with the change in applied voltage, so it cannot provide a reference. The solution is to connect the working electrode through a high impedance voltmeter to a third electrode, which will not have potential variant when the electrochemistry is active.

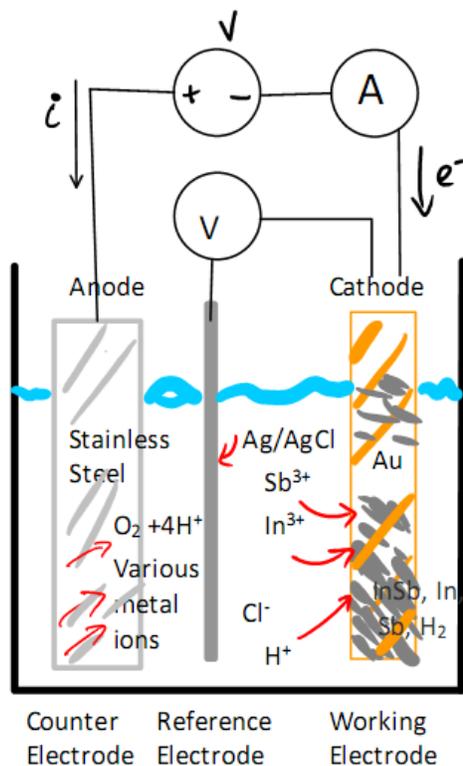


Figure 1. Three Electrode Cell

In most cases, the working electrode can be any smooth surfaces coated with gold, platinum, or just a broken n-type silicon chip. A preferred counter electrode is a thick sheet of a robust metal. Platinum, silver, and gold can be used, but the most cost effective choice is a stainless steel plate. The reference is preferably another oxidation electrode that does not interfere with the dominant reaction. In this report, an Ag/AgCl anodic electrode is used. Further explanation of the chemistry is discussed in section 2.1.2.

2.0 Experiments, Results, and Analysis

2.1 Introduction to the Electrochemistry Experiment

2.1.1 Fabrication Methods for Each Parts of the Electrochemical Cell

Teflon Cap - Two one inch slots for the working and the counter electrode, and the two holes are for the reference electrode. Openings and grooves on the Teflon cap is curved using milling machine. Four clamps are soldered on to screws and attached on the four corners of the block. For picture, refer to [Appendix I, Figure 1].

Gold/Platinum-Glass Electrodes- The Au and Pt electrodes is made by e-beam evaporation of 20nm of Cr and 200nm of Au or Pt on microscope slides. The slides are broken into 2 or 4 pieces. Microscope slides must be solvent cleaned to remove the oil that is always present on the "pre-cleaned" slides. Patterns on the slides are created with an aluminum metal mask. 4mm and 13mm diameter metal masks have been made. These Au and Pt electrodes are not suitable for counter electrodes, since Cr and Au will be oxidized. [Appendix I, Figure 2]

Anodic Alumina Membrane (AMM) - The AAMs are ordered from Synkera Technologies, Inc. They are around 48 um thick, and 13mm in diameter. One set of AAMs had 150nm pores, 2×10^9 pores/cm², and 32% porosity. Another set of AAMs had 35 nm pores, 10^{10} pores/cm², and 12% porosity. [Appendix I, Figure 3]

Silver Paint - The silver paint is a conductive adhesive that attaches the AMM to the 13mm Au-glass electrodes. The silver paint is purchased from Ted Pella Inc. [Appendix I, Figure 4]

Stainless steel - A piece of stainless steel cut to fit the holes on the Teflon cap. [Appendix I, Figure 5]

Ag/AgCl electrode - A conductive cathode and an Ag anode are inserted into a 100ml of 0.3M to 0.6M diluted HCl solution. 4ml of 10M HCl is added to 200ml of DI water for the diluted HCl solution. Two 6cm silver rods are oxidized for roughly 1 minute at 0.7 V applied voltage, and roughly 27mA of current. The two electrodes are stored in saturated KCl solution to prevent dissolving of AgCl layer on the electrode, as seen in Appendix I, figure 6. Only one of the Ag/AgCl electrodes is used in the actual experiment. The unused Ag/AgCl electrode is used as a reference to keep the potential of the used AgCl electrode constant. For the reported experiment,

the Ag/AgCl reference electrode is reoxidized after roughly ten experiments, as some of the AgCl had reduced into the containing KCl solution. [Appendix I, Figure 6]

Beakers used - Two 150 ml beakers, two 100 ml beakers, and three halved beakers are required. Three 80ml beakers are cut in half to be used as containers for the InSb electrochemical cell. The half-size beakers helped the working electrodes be more fully immersed with less solution. [Appendix I, Figure 7]

Electrolyte solution - The citric acid is ordered from Anachemia Science Inc., and the potassium citrate, indium(III) chloride, and antimony(III) chloride are ordered from Mallinckrodt Baker, Inc. All chemicals are of analytical grade without further purification. The electrolyte solution contained 0.17M of potassium citrate, 0.36M of citric Acid, 0.15M of indium(III) chloride(InCl₃), 0.1M of antimony(III) chloride(SbCl₃). The order to dissolve the chemical is potassium citrate, citric acid, indium chloride, and then lastly, antimony chloride. Deionized water (DI) is used. The beaker with the mixed chemicals is sonicated for 30 minutes to dissolve and thoroughly mix the precipitated chemicals. [Appendix I, Figure 8]

Potassium citrate and citric acid are relatively safe to work with. The citrate ions act as complexing agents for In and Sb ions, so they must be added before InCl₃ and SbCl₃. Both InCl₃ and SbCl₃ will form a solid form of hydrochloride with water without complexing agents. InCl₃ hydrolyzes when in contact with moisture air, so transferring from weighting scale to solution should be quick. SbCl₃ hydrolyzes extremely fast when in contact with any moisture, and the solid SbCl₃ will hydrolyze completely within three or four minutes when in contact with air. SbCl₃ hydrolyzation is very exothermic, so SbCl₃ should be added last to provide energy to dissolve InCl₃, which would otherwise require heating.

Citric Acid for Etching InSb - Concentrated citric acid can be used to etch InSb deposits. 50% citric acid is dissolved in water by weight, and then 70% citric acid is mixed with 30% H₂O₂ by volume just before etching begins. [Appendix I, Figure 9]

NaOH for Dissolving AAM - 3M NaOH stock solution is made to dissolve anodic alumina membrane for last stages of the experiment. NaOH pellets are purchased from Fisher Scientific Inc.

DC Power Supply and DMMS- Two DMMS, one DC power supply, four banana head to clamp wires, and two banana to banana wires. [Appendix I, Figure 10]

2.1.2 Electrochemical Cell Schematics and Reactions

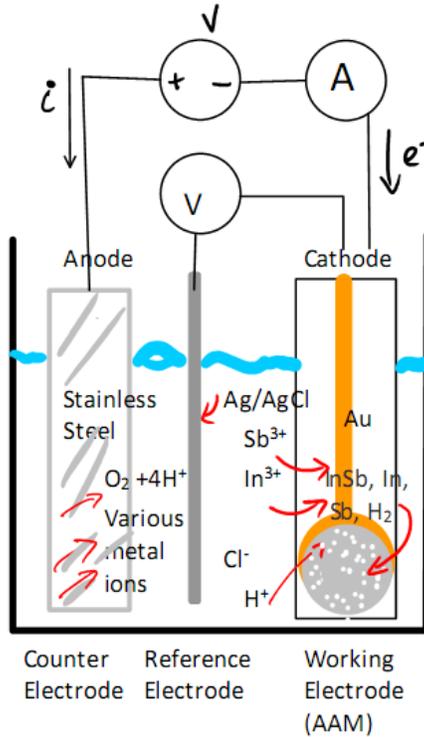


Figure 2. Three Electrode Cell with AAM (For physical image, refer to Appendix I, Image 11)

in the stainless steel, which can include Fe, Cr, C, Mo, and Ti. Fortunately, the deposition potential and the concentrations of these various metals are low enough to avoid being deposited on the working electrode. Having a larger surface area on the counter electrode can lower the charge density on the surface, which makes electrolysis of H₂O preferential, rather than oxidation of the electrode itself.

The reference Ag/AgCl electrode is connected through the working electrode through a voltmeter. The intended reference electrode is a manufactured Ag/AgCl electrode with glass tubing isolation in KCl solution, but the difference in accuracy between bare Ag/AgCl and isolated Ag/AgCl is in the millivolt range, which is not needed for the experiments. The small current in the voltmeter loop is small enough to not cause significant oxidation or reduction of the Ag/AgCl electrode. The potential difference between the two Ag/AgCl electrodes is around 13~14 mV initially and difference ranges from 35 to 40 mV after 30 trials, as measured by the voltmeter. The potential difference is caused by the different concentration of oxidation from Ag to AgCl on the Ag rod.

The electrolyte solution contains In³⁺, Sb³⁺, Cl⁻, and citrate ions. The working electrode is the reduction site, and the counter electrode is the oxidation site. The electrons flow to the working electrode, which cause In³⁺ and Sb³⁺ ions to deposit on the working electrode, in either solid In, Sb, or InSb. Electrolysis of water is also spontaneous when operating the three electrode system, so H₂ gas is also being reduced at the same time on the working electrode. The H₂ bubble will cause certain regions to be "blocked" from the electrolytes; however, in trials longer than 10 minutes, the effect is negligible. To prevent H₂ bubbles from accumulating on the working electrode, the solution is to place the reaction cell into an ultra sonic bath. On the stainless steel counter electrode, several oxidation reactions occur. The most obvious is the electrolysis of H₂O, which produces O₂ gas. The less visible oxidations would be oxidation of various metals

The current, I, is measured by the DMM. Applied voltage, V_{app} , is measured by the display on the power supply. The reference voltage, V_{ref} , is measured by taking the voltage difference between the Ag/AgCl electrode and the working electrode. **All the mention of voltage following this section will be referring to the reference voltage, V_{ref} , unless otherwise specified.**

Table 1: List of Possible Electrochemical Reactions

Working Electrode		Counter Electrode	
Reactions	Reduction Potential	Reactions	Oxidation Potential
$2 \text{In}^{3+} + 2\text{Sb}^{3+} + 6\text{e}^- \rightarrow 2\text{InSb}$ $2\text{H}^+_{(aq)} + 2\text{e}^- \rightarrow \text{H}_2_{(g)}$ $\text{In}^{3+}_{(aq)} + 3\text{e}^- \rightarrow \text{In}_{(s)}$ $\text{Sb}^{3+}_{(aq)} + 3\text{e}^- \rightarrow \text{Sb}_{(s)}$	$E_{red} = \sim -0.95\text{V}$ $E_{red} = 0\text{V}$ $E_{red} = \sim -1.0\text{V}$ $E_{red} = \sim -0.5\text{V}$	$2\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{H}^+$ Possible oxidation of Fe, Cr, C, Ti, Mo from Stainless Steel electrodes	$E_{ox} = 1.23\text{V}$
		Reference Electrode	

2.1.3 General Procedure for Electrodeposition

Procedure is intended for a clean room environment.

1. Set up the DC power supply and DMMs on to a stationary stool, and beaker stand onto the clean room wet bench.
2. Take out two halved beakers, two 150ml beakers, 1 plastic tweezers, Teflon beaker cap, Ag/AgCl electrode vial, and stainless steel electrode out of the electrode box.
3. Rinse the beakers with DI water and clean the halved beaker thoroughly for the electrochemistry.
4. Fill one halved beaker and two 150ml beakers with DI water, place plastic tweezers in one of the 150ml beakers.
5. Insert the reference Ag/AgCl electrode, stainless steel electrode, and the Au-Glass or AAM electrode, accordingly in to the slots on the Teflon beaker cap.
6. Take out the electrolyte solution from organic acid cabinet, and carefully pour the solution into the halved beaker until it is 90% filled. Clean outside of the electrolyte bottle carefully.
7. Place Teflon cap on top of the beaker, thus inserting the electrodes in the solution. [Appendix I, Figure 11]
8. Restrict the current output on the DC power supply to roughly 25 to 35mA. This step is very hard to calibrate, but it is crucial to limiting the reaction rate.
9. Connect the wirings accordingly to the contacts on the Teflon cap, and secure the wires on the edge of the wet bench with tape. [Appendix I, Figure 10,11]
10. Start the experiment with the appropriate voltage, while keeping track of the time, applied voltage, Ag/AgCl ref. voltage, current, and physical changes on the working electrode.
11. Adjust the current, voltage, or the V_{ref} with the voltage knob on the DC power supply according to the purpose of the experiment
12. After the deposition has finished, remove the working electrode by pulling it out from the top side of the Teflon cap. Rinse the working electrode in DI water gently.
13. Remove the counter electrode and reference electrode, rinse them in the other 150ml beaker, and then store them in their original containers.
14. Pour the electrolyte solution back into its original bottle to be reused next time.

2.1.4 General Properties of InSb Bulk Film Growth

The motivation for growing bulk InSb films is to understand the electrochemistry of InSb, such as growth rate, dependency of composition, and peculiar behaviors of the electrochemical deposition.

Shown by the electrode on the right in figure 3, the first general observation shows the deposition will start from the edge of the electrode and continue at a faster deposition rate comparing to regions in the center. However, with a smaller area electrode like the one on the left, the difference in growth rate and thickness is less obvious.

During the deposition, the current increase steadily due to increasing nucleation sites created by newly deposited InSb crystals. More nucleation sites allow more reaction to occur, thus lowering the resistance of the cell. At the same time as the InSb deposition, H^+ ions are forming H_2 gas from electrolysis of water. In ideal condition, without consideration of change in surface potential, the V_{ref} will be constant with respect to the applied voltage, since the number of each active cathodic reaction will be the same. When H_2 bubbles are produced, they will collect themselves on the surface of the InSb and block the InSb reaction site from the electrolyte solution. Consequently, the V_{ref} and current will fluctuate due to the change in surface area and the number of ongoing reaction. The fluctuation is more apparent when depositing with anodic alumina membranes.



Figure 3. Thin Au-glass electrode (Left), Thick Au-glass electrode (Right), both with InSb deposition

Note: Section 2.2, 2.3, 2.4, and 2.5 are moved to Appendix II due to exceeding page limit.

2.6 Experiment 6: Anodic Alumina Membrane Experiments

2.6.1 Anodic Alumina Membrane as Template

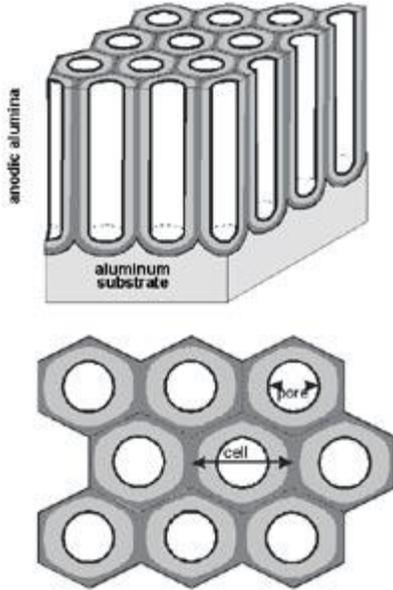


Figure 4. Illustration of AAM Growth Process (Top), and AAM Structure, from Synkera Technologies Inc.[9]

Anodic alumina membrane (AAM) is a self-organized nanostructure material containing a high density of uniform cylindrical pores that are aligned perpendicular to the surface of the materials and penetrate its entire thickness. [9] The diameter of the pores can range from 5 to over 200nm, so the feature size of the nanostructure can be easily controlled. AAM can also be dissolved easily with NaOH, so the NWs that are grown inside the membrane can be extracted easily without structurally compromising methods like sonication or plasma etching. AAM is also inert to non-halogenated solvents and acidic environments. The organized nanostructure and the ease of manipulation make AAM a good template material for deposition of NWs.

2.6.2 AAM Experiment Setup

In addition of section 2.2.1, the AAM experiment also requires an AAM electrode. 200nm of Au is first evaporated on the backside of the AAM as electrical contacts, and then the AAM is attached to the 13mm template Au-glass electrode by a small drop of silver paint. To prevent InSb from depositing on the edge and the contacts leading to the AAM, a thin layer of SU-8 photoresist is applied on the edges for insulation, as shown in Appendix I, figure 14. Only a very small volume of SU-8 photoresist is needed because SU-8 photoresist will creep outwards during the baking process. The SU-8 photoresist should be soft baked at 65C for 15 minutes and then hard baked at 95C for at least 45 minutes.

2.6.3 InSb Reaction Properties

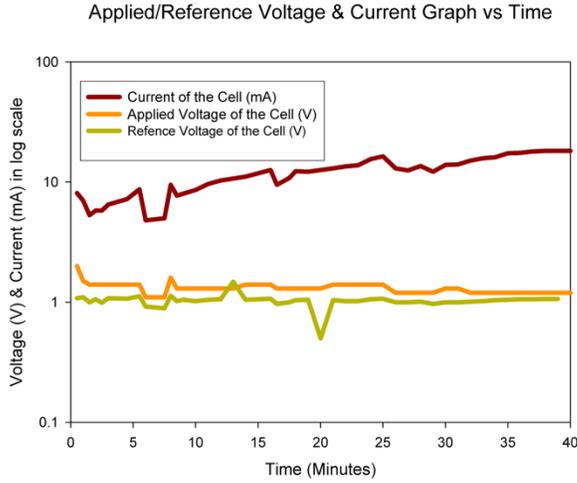


Figure 5. Graph of V_{app} , V_{ref} , & Current vs. Deposition Time

The steps for InSb deposition in AAM is exactly the same as described in section 2.1.3. During the deposition, the current increase steadily due to increasing nucleation sites created by newly deposited InSb crystals, as shown in figure 5. More nucleation sites allow more reaction to occur, thus lowering the resistance of the cell. As more InSb deposits, more surfaces are available for H^+ ions to form H_2 gas as well. At the same time, the V_{ref} will fluctuate due to the change in the dominating reactions. In

ideal condition, without consideration of change in surface potential, the V_{ref} will be constant with respect to the applied voltage, since the number of each active cathodic reaction will be the same. When H_2 bubbles are produced, they will collect themselves on the surface of the InSb and block the InSb reaction site from the electrolyte solution. With H_2 bubbles reducing the surface area and increasing nucleation sites from the newly formed InSb, different cathodic reactions, as listed in table 1, are competing with each other with respect to the changing surface potential and available reaction area.

To achieve stoichiometric ratio in between In and Sb, the current or V_{ref} should be kept constant. For example, InSb NWs on sample 32 are deposited in constant V_{ref} around 1.02 to 1.08V, so the applied voltage is adjusted with respect to the change in V_{ref} . The exact dependence of composition will have to be determined by the experiments detailed in section 2.3.3.

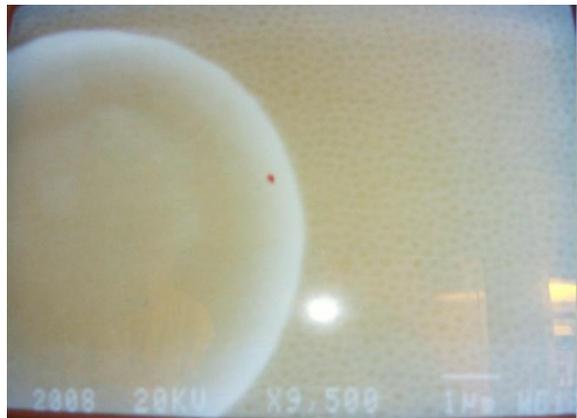


Figure 6. InSb spherical outgrowth on top of the porous AAM (Taken by an old SEM)

As shown in figure 6, the InSb does not grow uniformly past the thickness of the membrane. The InSb will form a spherical structure and expand outward, and eventually forming a crust on top of the AAM. The increase

in current from the 25 minute mark is due to the outward expansion of the reaction surface.

2.6.4 InSb NWs Extraction Method

Once the AAM electrode is removed from the cell and rinsed with DI water, the NWs is extracted from the vial shown in appendix I, figure 13 by following these steps:

1. Place the Glass electrode in a small beaker and rinse the electrode with acetone until the photoresist and the adhering silver paint dissolve. The AAM should fall off the electrode eventually.
2. Always handle the AAM with a plastic tweezers. Clean the AAM in boiling acetone for 10 minutes to remove the remaining photoresist, and then rinse the AAM gently with water for 5 minutes.
3. Place the AAM in a clean 80ml beaker with the gold side facing upward, and with a disposable pipette, drop three drops of 3M NaOH solution to dissolve the AAM.
4. Shake the beaker gently for 10 minutes, add three more drops of 3M NaOH solution, and then shake the beaker gently for another 10 minutes.
5. Once the AAM has dissolved, add 15 ml of DI water, and then sonicate the content for 15 minutes. The sonication should dissolve the AAM completely, while breaking the InSb NWs off the InSb crust.
6. Dilute the solution until the 80ml mark with DI water, and then transfer the solution to a vial, as shown in the appendix I, figure 13.
7. Add 20ml of DI water to wash out the precipitates in the bottom of the beaker into another vial, repeat the process until there is no visible precipitate in the beaker. This step is extremely important, since most of the NWs are obtained from these precipitates in the second wash vial.
8. To further dilute the NaOH and Al_2O_3 in the solution, centrifuge both vials, carefully remove 80% of the solution carefully, dilute the solution again, and then repeat these steps twice starting with centrifugation. **Note:** this step has not been done for sample 32, which is discussed in the following sections.

2.6.5 Sample Preparation for SEM, EDX, SAM, TEM, and XRD

In order to do Secondary Electron Microscopy (SEM), Energy Dispersive X-ray Spectroscopy (EDX), Scanning Auger Microscopy (SAM), or Transmission Electron Microscopy (TEM) analysis, the substrate must be conductive. For important samples, it is best to use nickel coated holey carbon film TEM grids; however, a cheaper alternative is to use small chips n-type or p-type silicon, as shown in Appendix I, figure 13. The silicon chip has to be BOE cleaned beforehand. To transfer the InSb NW on to the chip, shake the second wash vial gently, and then squeeze a small drop of the solution from the second wash vial on the silicon chip. Once the water on the chip is allowed to dry naturally, the InSb NW on the silicon chip is ready for SEM, SAM, or TEM analysis. For X-ray Diffraction (XRD), the silicon chip sample has to undergo long scanning time in order to obtain enough signals from the trace amount of InSb NWs on the surface. Another method for XRD is to do XRD of the InSb in the AAM before it has been dissolved.

2.6.6 Data Analysis

Three experiments with AAM have been completed, but only sample 32 is characterized. With only one sample, the reproducibility of the result is hard to determine, so only physical appearance and the composition will be discussed.

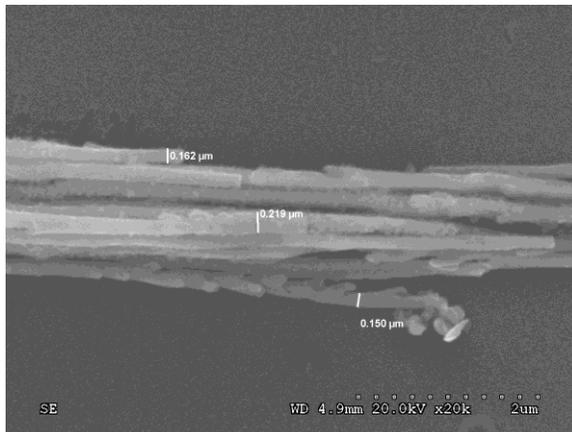


Figure 7. 20k X SEM of a group of InSb NWs

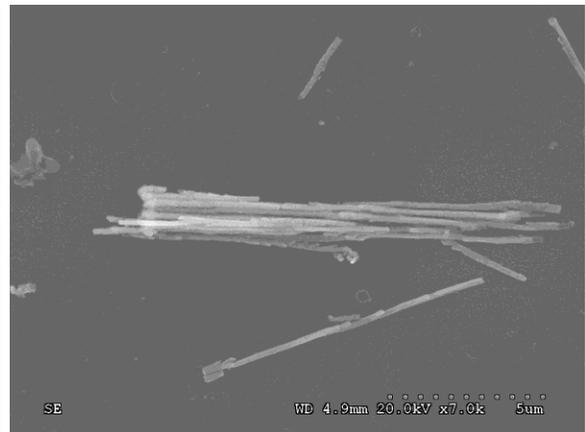


Figure 8. 7.0k X SEM, Group of NW and one 10nm NW

From the SEM Figures taken from EDX, the InSb NWs are roughly 10 to 15nm in length, and roughly 150nm in the diameter. The expected length of the NW is around the same

length as the thickness of the AAM, which is 40nm. Due to the sonication process that is required to break the NWs off the InSb crust, the NWs are broken off into shorter segments. The diameter is the same size as the pore diameter on the AAM as expected. There are branching on the NWs, such as the bottom NW in figure 7. The exact reason of this phenomenon is unknown.

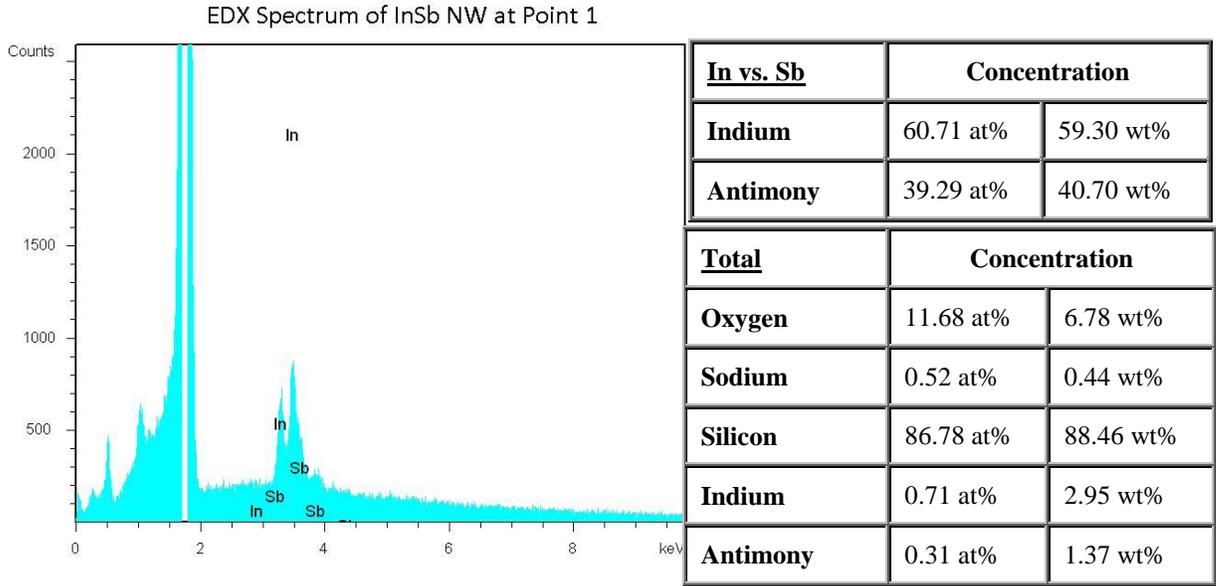


Figure 7. EDX spectrum and data for sample 32

Composition wise, the EDX revealed that the NWs are consisted of roughly 60% In and 40% Sb by number of atoms. The composition is close to stoichiometric ratio, which is a great result. Since In has a higher deposition potential, and Sb has a lower deposition potential, a stoichiometric ratio can be achieved by lowering the V_{ref} by 0.15 to 0.25V. Trace of sodium is also present in the EDX analysis. The signal of sodium is further confirmed with SAM results.

The mechanics of SAM is complex, and without going into detail, SAM is a surface

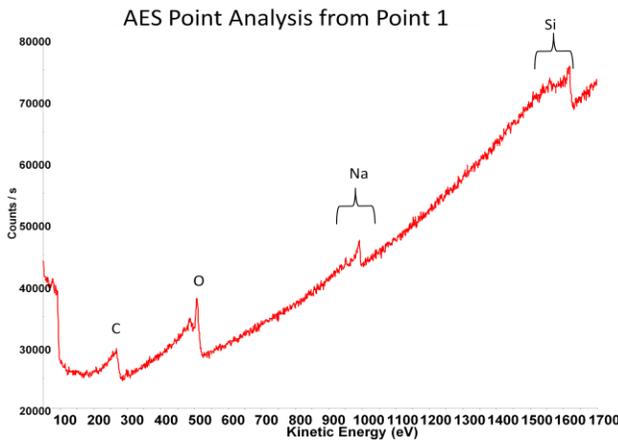


Figure 10. Auger Electron Spectrum of InSb NW

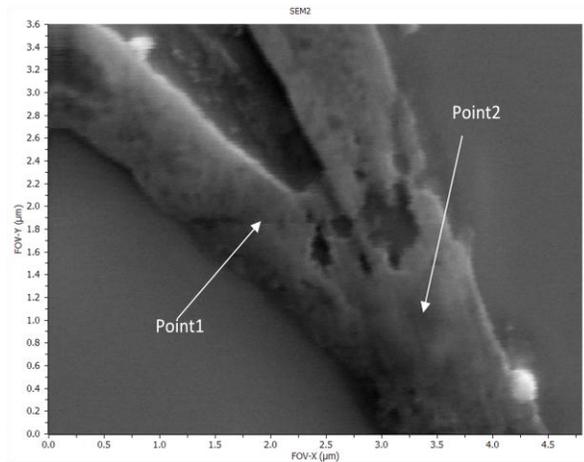


Figure 8. 25k X SEM Image of InSb NW

elemental analysis penetration depth around 8nm. Shown in figure 10 and figure 11, the surface of the NW is covered with at least 8nm of sodium hydroxide. The layer of NaOH is thick enough that the InSb signal cannot be obtained. There is no sodium signal from the silicon substrate surface from both EDX and SAM analysis, which is perplexing at first, because NaOH should recrystallize on the InSb as well as the surface of the silicon. Since NaOH is highly soluble in water, the NaOH should not crystallize on the InSb NWs while they are in solution. Thus, the only chance for it to recrystallize is during drying step of the sample preparation. It is suspected that the reason that the NaOH only crystallize on the InSb due to a lack of nucleation sites on BOE cleaned single crystal silicon. With further dilution described in section 2.6.4 step 8 and 9, the NaOH coating can be avoided.

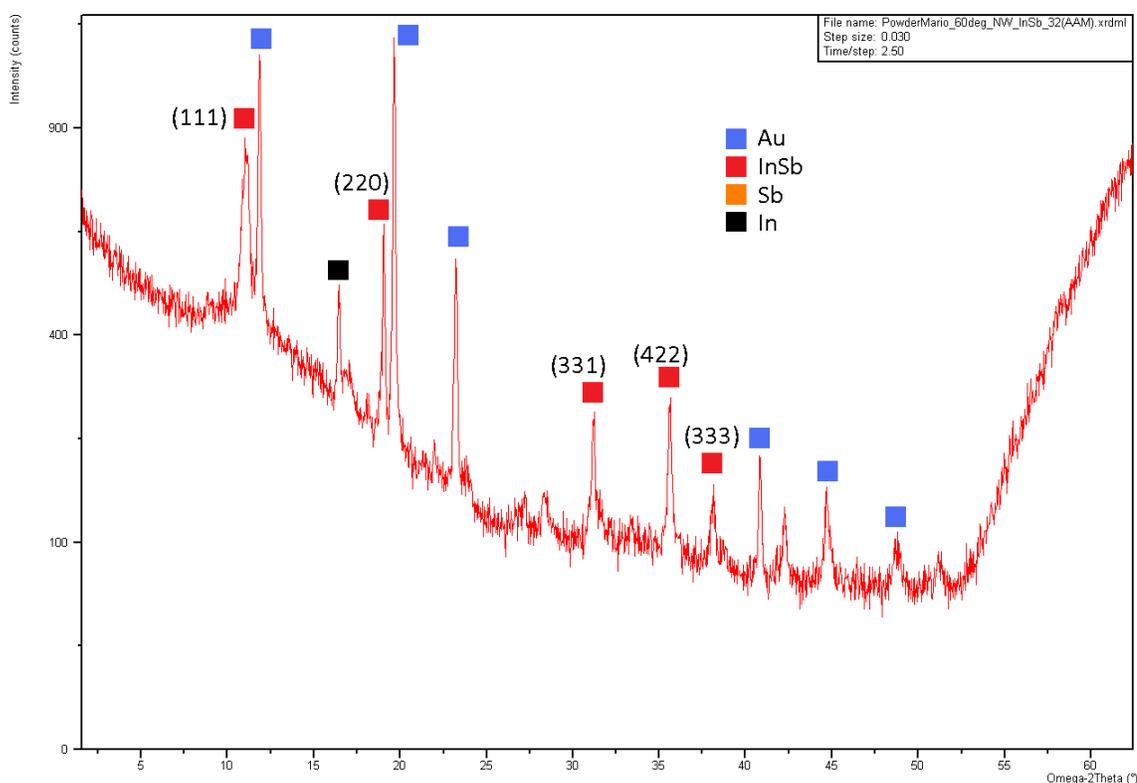


Figure 9. Powder X-Ray Diffraction Pattern of Sample 32 InSb on AAM Sample

Figure 12 shows the $\text{CuK}\alpha$ XRD spectrum of the InSb with the AAM still attached. The XRD peaks are identified by the X'pert data viewing program. Several orientations of InSb are present in the AAM sample with (111) and (220) being the two most prominent orientations to the surface. From the XRD spectrum, the crystal grain size can also be determined by the Scherrer equation $B = 0.9 \lambda / (t \cdot \cos \theta)$, where B is the full width at half maximum of the peak, λ is

the wavelength of the x-ray, t is the grain size, and θ being the angle of diffraction. The grain sizes are 2.7nm for (111) plane, 1nm for (220), and 0.5nm for (331), (422), and (333) plane. This XRD spectrum cannot be representative of the composition of the InSb NWs, since a large majority of the scan includes the InSb crust and the Al₂O₃ of the AAM. Unfortunately, the XRD result of the NWs on silicon substrate has not been obtained by the end of the work term.

2.6.7 Recommendation for Future AAM Experiments

The goal for the next AAM experiment would be to obtain stoichiometric InSb NWs. There are two possible options.

If the results from the experiments suggested in appendix II, section 2.3.3 indicates that the composition is largely voltage dependent, then a series of three experiment with constant V_{ref} of 0.85V, 0.9V, and 0.95V should be tested on 150nm pore AAM and 35nm pore AAM.

If the results from section 2.3.3 indicate that the composition is largely current density dependent, then the current should be kept constant at 8mA, 9mA, and 10mA for the 150nm AAM and 3mA, 4mA, and 5mA for the 35nm AAM. The voltage for constant current experiments can be kept higher than 0.8V by restricting the current knob on the DC power supply.

3.0 Conclusion

In summary, the experimental objective has yet to be reached, that is discovering a stable recipe for growing InSb NWs by template electrochemistry method. Fortunately, preliminary results have been obtained. The composition and growth rate of InSb depends not only depend largely on concentration, but also V_{ref} and current density of the surface. Sufficient data has been acquired to estimate the ranges of the parameters needed for future experiments.

From the analysis of various form of characterization, it has been shown in the report that InSb NWs has been successful deposited into the template AAM, and then extracted from the AAM for future applications. The spectroscopy and imaging data indicate the composition of the InSb NWs is near stoichiometric at 60% In to 40% Sb. The SEM image has shown that the NWs are of 150nm in diameter and roughly 10um in length. For future experiments, the objective is to fabricate InSb with 1:1 ratio between In and Sb, and improve the grain size by thermal annealing. With better purification technique, such as centrifugation, these InSb NWs will be available in various experimental photonics and semiconductor devices. In the further prospect, following the techniques that are applied in this experiment, development of recipe to create quality NWs with other Group III-IV semiconductors will commence in the near future.

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Appendixes

Appendix I. Pictures of Equipments

**Majority of the picture were taken in a photolithography room in AMPEL clean room, thus the yellow lighting.*

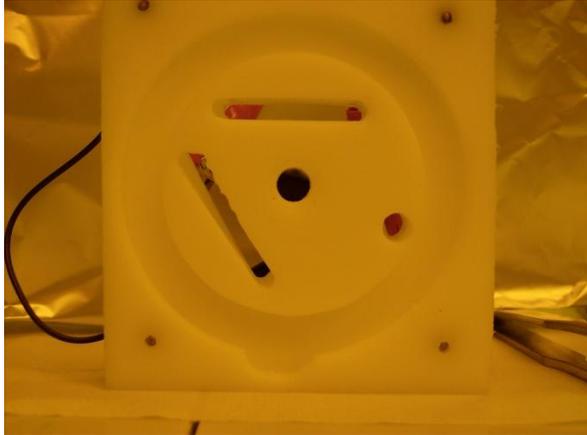
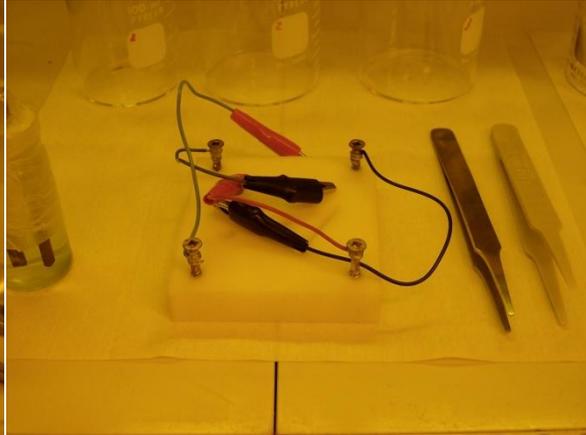


Figure 10. Teflon Cap, bottom view



top view

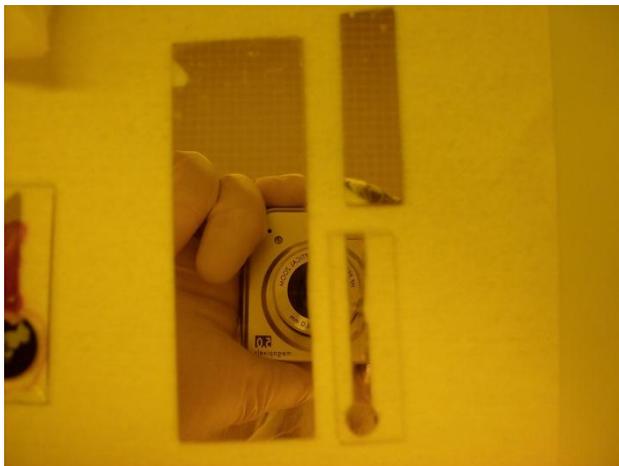


Figure 2. Gold/Platinum-Glass Electrodes

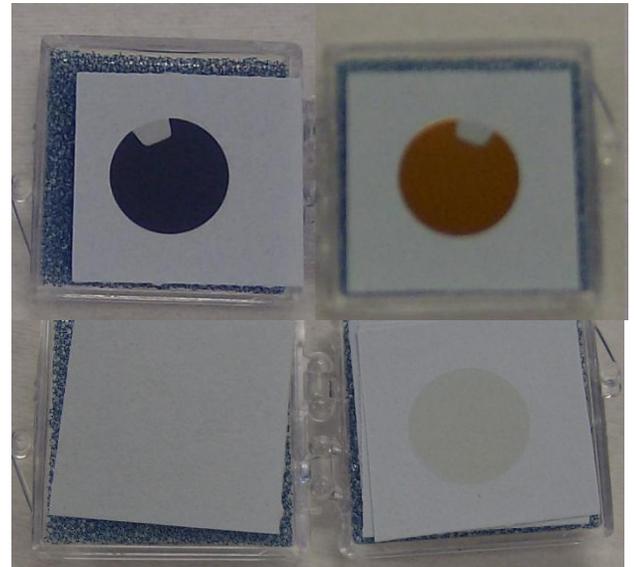


Figure 3. Anodic Alumina Membrane (AMM)

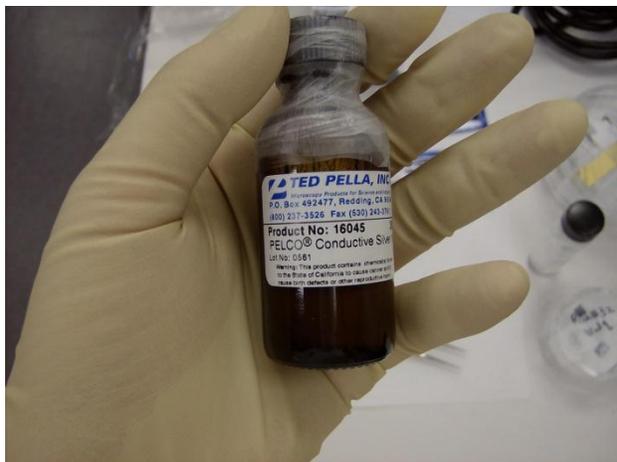


Figure 4. Silver Paint



Figure 5. Stainless steel

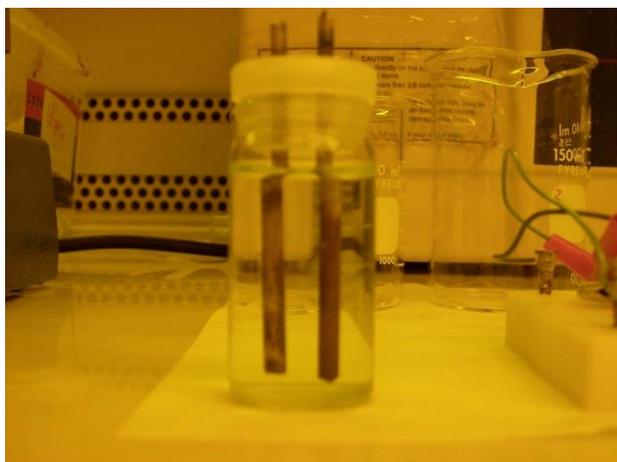
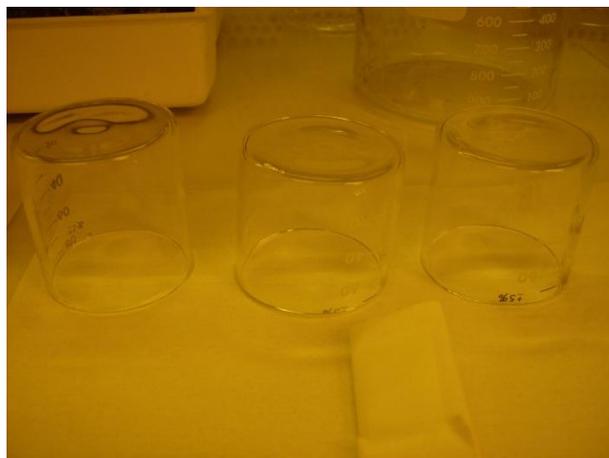


Figure 6. Ag/AgCl electrode



Figure 7. Various beakers used



halved 80ml Beakers



Figure 8. Electrolyte solutions

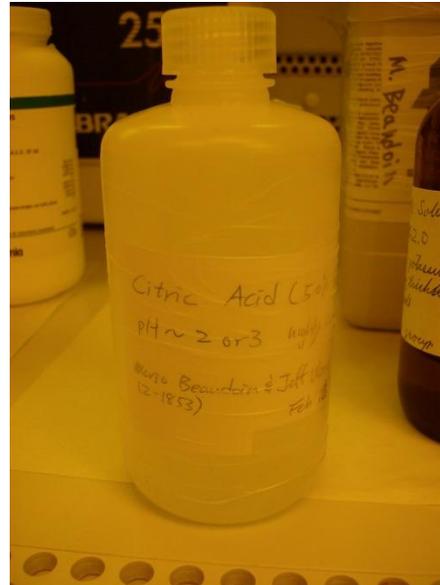


Figure 9. Citric Acid for Etching InSb

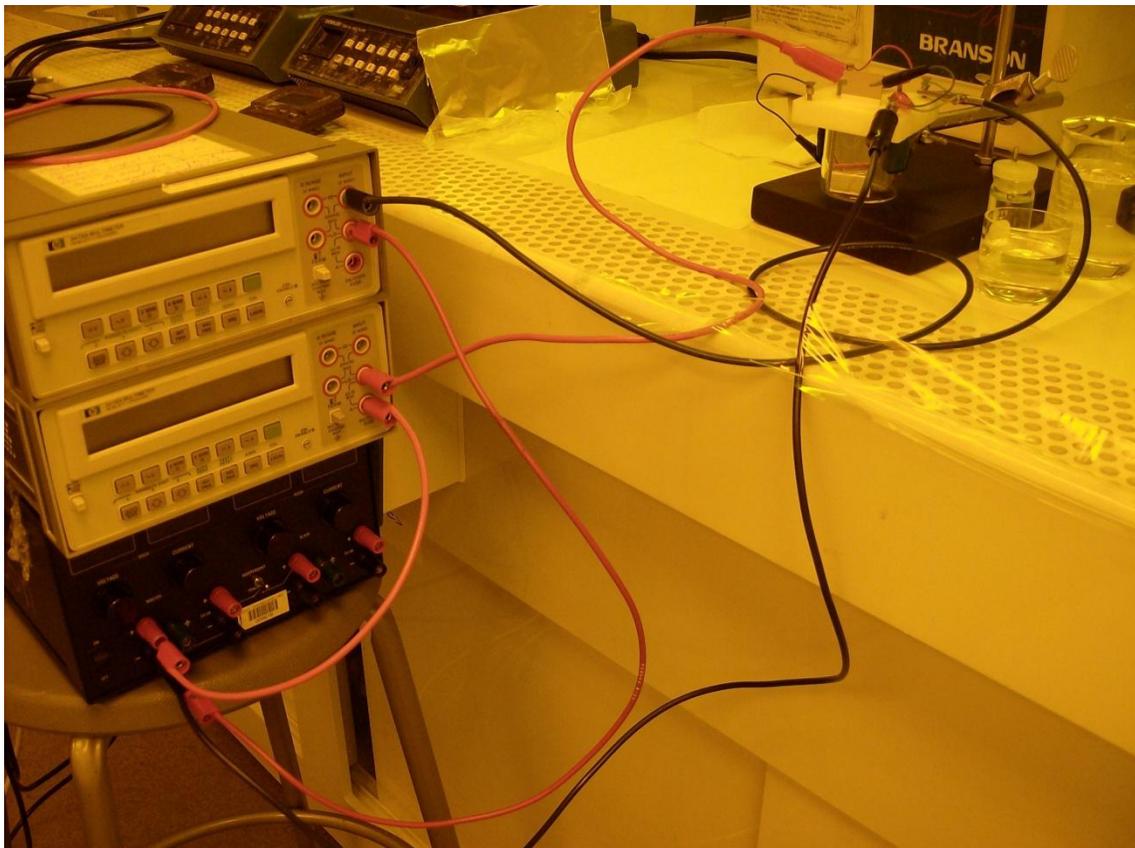


Figure 10. DC Power Supply and DMM Measurement tools

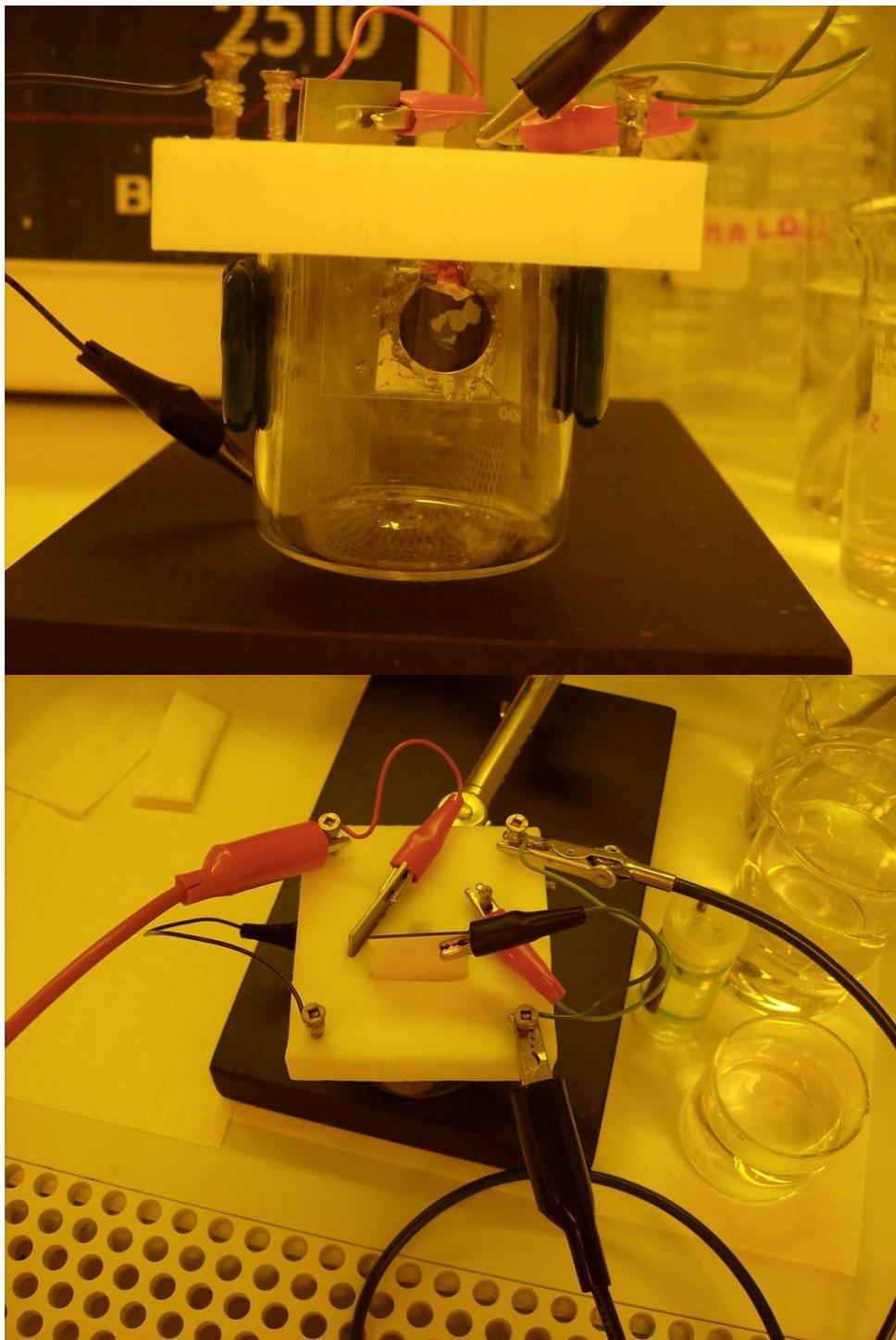


Figure 11. The Electrochemical Cell

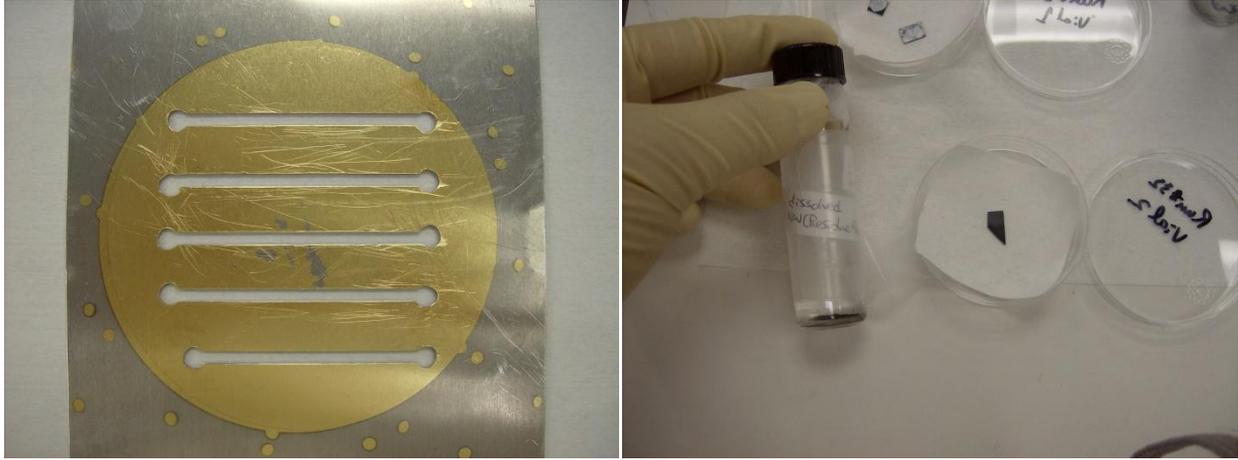


Figure 13. Vial for dissolved AAM and Silicon substrate for SEM



Figure 14. AAM electrode before deposition

Appendix II. Section 2.4 and 2.5

2.2 Experiment 1: Dependencies for Composition

The objective for this experiment is to determine which experimental parameters lead to a stoichiometric, 1:1 ratio, between In and Sb. The ratio of In and Sb in the deposition depends on the concentration of the In and Sb ions, the voltage applied for the deposition, and the time of the deposition. To achieve 1:1 ratio between In and Sb, careful control of these parameters is required. Sb is prone to deposit at lower applied voltage, around $\sim -0.5V$ to $\sim -1.0V$, while deposition of In occurs at a higher voltage around $-1.0V+$. With reference to previously published paper, the concentrations in the electrolyte solution is set to a 3:2 ratio between In^{3+} ions and Sb^{3+} ions for the best stoichiometric deposition. [1] Maintaining a 3:2 ratio between the concentration of In^{3+} and Sb^{3+} greatly reduces the dependence of voltage and time, but Sb is still reducing more rapidly than In in most cases. The difficulty in achieving 1:1 ratio InSb free of excess Sb or metallic Sb deposition is discussed in the end of this section.

The series of experiments for determining composition are carried out on Gold-Ti-glass or Pt-Cr- glass working electrodes, stainless steel counter electrode, and Ag/AgCl reference electrode. Compositions of the samples were obtained by powder X-ray diffraction (XRD).

Table 2: Experimental Parameters and Data for Composition

Sample ID	Composition	Substrate	Vapp	Vref	Current Density	Duration
5	only Antimony (Sb)	Au-Ti-Glass	1.2V	-0.8V	1 mA/cm ²	25 min
7	only Antimony (Sb)	Au-Ti-Glass	0.75V	-0.5V	1 mA/cm ²	20 min
15	InSb 100),(111), (220),(311), some Sb	Pt-Cr-Glass	1.2V	-0.87V	8.5 mA/cm ²	5 min
27	InSb (111), (220), (311)	Au-Ti-Glass	2V	-1V	40 mA/cm ²	4 min
32	InSb (111), (220), (331), (422), (333)	AAM + Au	1.3V	-1.05V	30.5 mA/cm ²	40 in

2.2.1 Dependence on Voltage and Current Density on the Surface

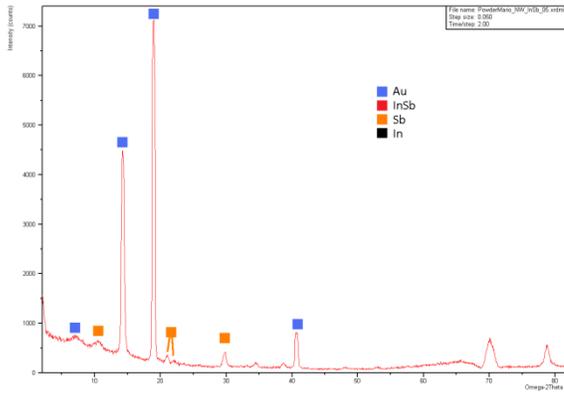


Figure 1. Powder X-Ray Diffraction Pattern of Sample 5

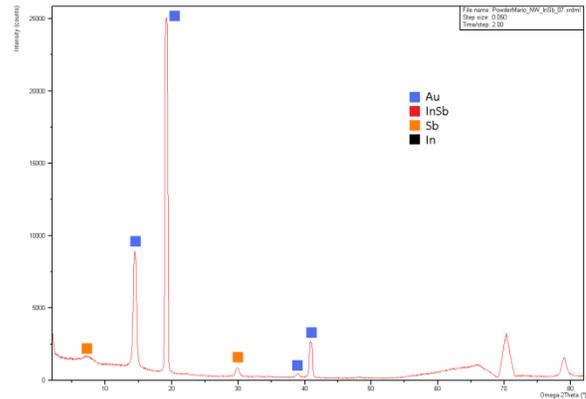


Figure 2. Powder X-Ray Diffraction Pattern of Sample 7

Sample 5 and 7 belongs to the group of initial tests. The initial tests do not use a stainless steel electrode, so the resistance of the electrochemical cell increases as Au and Cr oxidized, ranging from 400 to 600 ohms. The current is restricted to 3 mA. The surface of the working electrode has a current density of roughly $1\text{mA}/\text{cm}^2$ and a voltage of 0.5 to 0.8 V. In figure 1 and 2, XRD of sample 5 and 7 have only one characteristic peak from Sb is present. The other peaks are Au peaks from the electrode. This result indicates that Sb deposits at low current density and voltage as low as 0.5V, and no In and InSb can deposit at low current density.

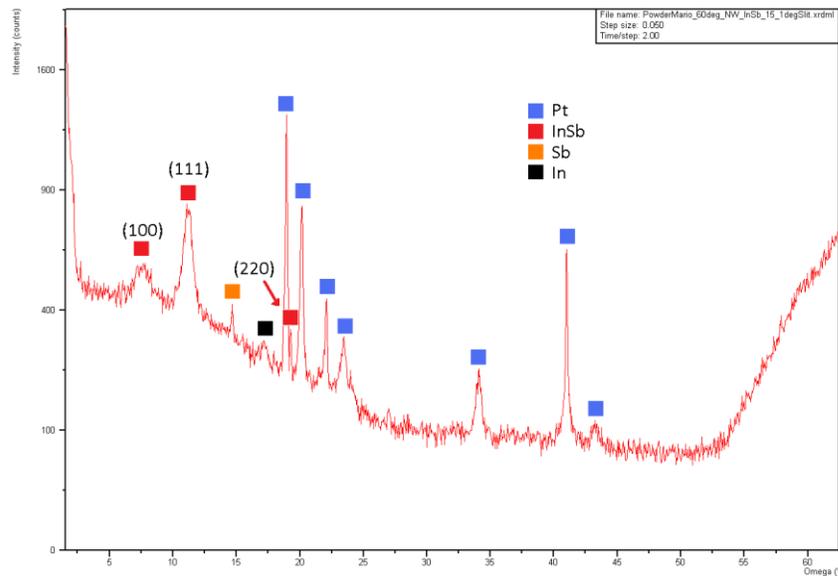


Figure 3. Powder X-Ray Diffraction Pattern of Sample 15, grown on Pt-glass electrode

Sample 15 is grown on Pt working electrode with a stainless steel counter electrode. The resistance of the cell is roughly 120 to 140 ohms, reference voltage is roughly 0.87 V, and the current density is roughly 9 mA/cm². In figure 3, XRD of sample 15 shows traces of InSb, but the intensities of the peaks are weak. The weak intensity means the crystallinity of the electrochemically deposited InSb is between amorphous to near polycrystalline. The grain size of the crystallines can be calculated by the full wave half maximum (FWHM) of the peak. $B = 0.9 \lambda / (t \cdot \cos \theta)$. The average grain size calculated from the (100), (111) plane is 0.9 nm.

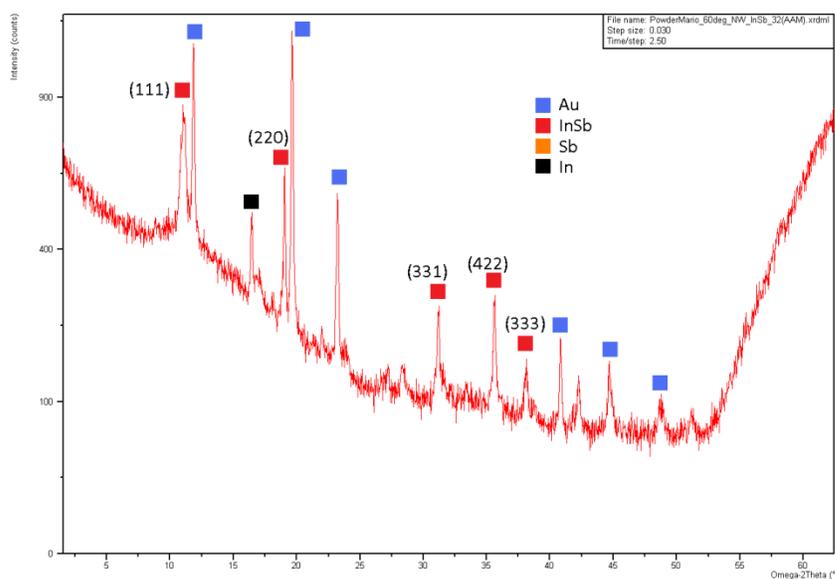


Figure 4. Powder X-Ray Diffraction Pattern of Sample 32 InSb on AAM Sample

Sample 32 is an AAM sample. For now, only the charge density of the AAM is investigated. The XRD pattern in figure 7 is taken after 20 minute of growth on AAM. The surface area for deposition is roughly 0.36 cm² and the current density is roughly 30 mA/cm², which is 3.5 times more than sample 15 and 30 times more than sample 5 and 7. Because AAM sample is deposited for a longer period of time than the other samples, intensity of peaks are stronger from different orientation of InSb. The grain sizes are 2.7nm for (111) plane, 1nm for (220), and 0.5nm for (331), (422), and (333) plane.

The Even though the quality of the crystalline is hard to determine from the XRD, the true significance of sample 32 is the absence of Sb. Indium deposition is more dominant than Sb deposition at higher Vref, 1.0V to 1.09V and proportionally higher current density, 30 mA/cm²; whereas Sb deposition is more dominant than In under lower current density and Vref, as shown in sample 5 and 7.

2.2.2 Difficulties with Controlling Composition

The composition of the electrochemistry is hard to control due to the constant change in reaction equilibrium between In and Sb depositions with changing surface area. The change in surface area leads to change in current density, impedance of the cell, and the voltage. With smaller surface area and a higher current density or higher voltage, In deposits preferentially, whereas Sb deposits in lower current density or lower voltage. The suggested approach to eliminate this problem is to use a potential stat power supply; however, such equipment is hard to acquire at the time of the experiment.

2.3 Experiment 2: Thickness vs. Growth Per Charge

Finding out the growth per charge of bulk InSb film helps us to understand how long and how much current is needed to deposit on the AAM, since AAM is a relatively expensive material. It is also useful to know the growth per coulomb to understand the behavior of InSb electrochemistry. Although the thickness of the material can only approximate the rate of growth; however, when the exact electrochemistry of InSb is unknown, no exact approximation can be made from calculating the electron transfer of the InSb redox. The experiment parameters and data table are included in the section 2.3.2 for ease of reading.

2.3.1 Characterization Methods



Figure 5. The DEKTAK Profilometer, from Veeco Instruments Inc.

Profilometry characterizes the surface by probing with a sub-micron thin stylus. It gives fast results, and it is the recommended method to characterize thickness for bulk films. The downside to profilometry is the requirement for a difference in height along the scanning line. The range of scan of the old Alpha Step 200 profilometer is often too short for the bulk film sample. The new DEKTAK profilometer in the AMPEL clean room has a much longer scanning range and better accuracy than the alpha step profilometer, but to prevent polluting the scanning tip,

the DEKTAK profilometer requires the sample to be clean and dust free.

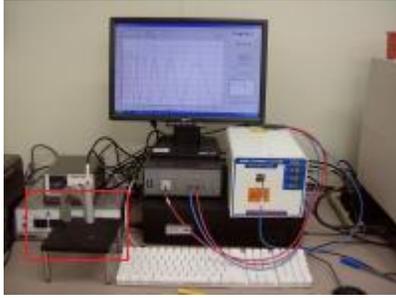


Figure 6. Filmetrix F200 Station

The Filmetrix F20 can operate in reflection spectroscopy mode or transmission mode. Since all the electrodes used are over 4mm, only reflection mode is applied. Filmetrix F20 is able to acquire reflective signals from multiple layers of thin films, which is a useful tool when fabricating highly ordered structures. Unfortunately, the instrument is hard to calibrate when the film is

too rough, which is often the case for electrochemically deposited InSb. Also, InSb absorbs near infrared spectrums (roughly 1.2 um+), which compromises the result. In figure 6, the red box indicate the light source and sample measuring stage.

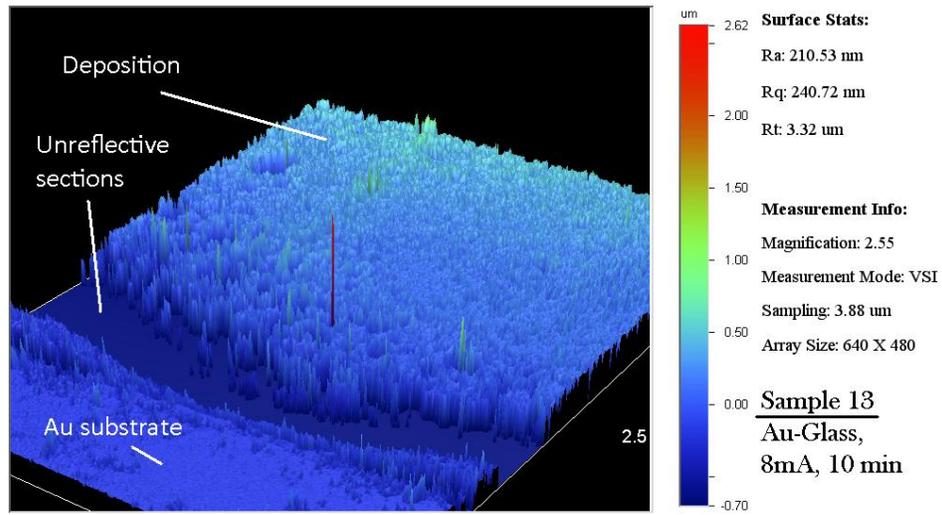


Figure 7. 3D rendering surface profile of sample 13 taken from the interferometer

Interferometer uses interference of two beams of light for characterizing surface topographies. It is able to determine surface roughness, measure the height of defects, and generate 3D models of the surface. It has two modes of operation, the phase shifting interferometry (PSI) and the vertical scanning interferometry (VSI). The PSI mode is used to see surface topography in sub-nanometer range, while VSI is used in scanning surface with higher discontinuities, such as InSb bulk film samples. [8] The interferometry is a great method for measuring reflective surfaces; however, InSb film is only reflective until roughly 700nm, roughly five to eight minutes of

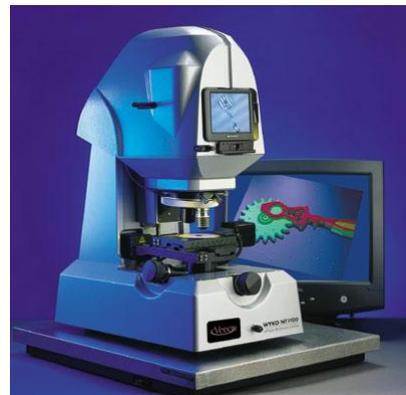


Figure 8. The Interferometer, Veeco Instrument Inc.[8]

deposition.

2.3.2 Thickness and Growth Rate Data Analysis

Table 3: Experimental Parameters and Data for Thickness and Growth Rate

Sample	Thickness (nm)	Growth per Charge (nm/C*cm ²)	V _{app}	V _{ref}	Current Density approximation	Duration
7	1000 to 1400	680	0.75V	-0.5V	1 mA/cm ²	20 min
13-Au	340 to 700	180	2.3V	-0.87V	8 mA/cm ²	8 min
15-Pt	~580	227	1.2V	-0.87V	8 to 9 mA/cm ²	5 min
18	~300 to 500	340	2.5V	-1.02	20 mA/cm ²	1min
34	23000	1200	1.8V	-0.9V	32 mA/cm ²	10 min

The growth The Experiment 7, 13, 15, 18 will be discussed first. By multiplying the time with the current density, the charge per area on the electrode can be calculated. Assuming all the electrons are transferred through redox reaction, the amount of charge per area can be related to the thickness of InSb deposited on the electrode. The deposition on sample 7 was mostly Sb, as described in the previous section. The Sb reduction requires significantly less electrons per reaction, so the thickness of sample 7 is almost double the rest of the samples with half as much charge per area.

Comparing sample 13 and 15, which both have InSb deposited with traces of Sb, the result shows that growing InSb on Platinum film electrode will have more growth per charge than growing InSb on Au film electrode.

When comparing sample 18 and 34, the result shows that when reference voltage is near -1 V, not only does the current increase greatly due to the high rate of InSb deposition, which has reduction potential around -0.95V; but the growth per charge also increases exponentially.

2.3.3 Recommendation for Future Composition and Grow

Since the composition and growth rate dependency experiment discussed above are not well planned, new experiments need to be done to confirm the reliability of the data. The following experiments should also be followed for future template nanowire growth with other materials.

The first set of suggested experiments is designed to observe the growth rate increase under static applied voltage. Static applied voltage is used to observe the change in V_{ref} over time, the increase of growth rate vs time, and decrease in resistance of the system vs. time. The data will show when the V_{app} need to be increased to maintain constant V_{ref} or constant current. The second set of suggested experiments is designed to determine the relationship between V_{ref} and the composition. This experiment is very important. It will also show which voltage is needed for 50:50 InSb NWs. The growth rate increases with longer deposition time, current usually increase while the V_{ref} stays constant. Experiment 3, the static current experiment, will determine if current density if the key to control the composition of the InSb. If the current stays the same, that means the V_{ref} will change with the adjustment of V_{app} . If the composition can be controlled with constant current, then that makes calculating the growth rate/thickness/amount of reactants really easy.

Table 4: Parameters for Suggested Composition and Growth Experiments

Exp #1 Parameters	6 trials, static $V_{app} = 1.2, 1.3, 1.4, 1.5, 1.6, 1.7$ V, 15 min each
Notes	Thickness of each sample should be measured every 2 min, 4 min, 8 min, 16 min, 20 min. Use thin Au-Glass working electrode.
Exp #2 Parameters	11 trials, static $V_{ref} = -0.5, -0.6, -0.7, -0.8, -0.9, -1.0, -1.1, -1.2, -1.3, -1.4, -1.5$ V, 15 min. per trial initially. Do additional 8min. and 20 min. trials for samples with InSb.
Notes	$V_{ref} = -0.5$ to -0.8 V should be all Sb, -0.9 to -1.1 V should be InSb, -1.2 to -1.5 V should be mostly In and InSb. Use thin Au-Glass electrode.
Exp #3 Parameters	6 trials, Static Current = 3, 5, 10, 15, 20, 35 mA/cm ² , 15min each
Notes	Use thin Au-Glass working electrode.

4.1 Experiment 3: Current Control attempts

Rationale: In the early stages of the experiment, the objective is to grow better quality InSb by increasing the V_{ref} to -1.5 V while keeping the current under 1mA to reduce growth rate. Since the current can only be restricted down to 3mA on the power supply, a method needs to be used to low the current of deposition under 0.5mA maintaining V_{ref} of -1.5 V . Connecting a parallel resistor seems to be the right idea, since most current will go through the least resistive path. If the current were unrestricted,

the cell would still feel the same amount of current regardless of the series resistor. Normally, the current is restricted to 5mA, so the current should divide in half when an equally resistive object is connected in parallel to the cell. The resistance of the cell is 120 to 300 ohms.

4.1.1 Reason for Failure and Suggestions for the future

Results: The result is that none of the attempts succeeded. Either the current diverted completely to the resistor, or the cell current did not change. The current still cannot be under 3mA when V_{ref} is -0.8 to -1V. The electrochemical cell acts like a current dependent resistor, whose resistance drastically increase with lower currents. This particular property makes direct current control extreme difficult, not to mention the attempt to couple the system as a current splitter. Fortunately, InSb deposition requires a minimum of 5mA, which is confirmed by results in later stage of the experiment. Lowering the deposition current below 1mA is unnecessary for future experiments.

4.2 Experiment 5: Achieving Uniformity

After the thickness and composition trials, attempts are made to obtain uniformity of the bulk film surface and uniformity in composition. From the interferometry data [insert ref] , the bulk film that is deposited on Au-glass sub has surface roughness root mean square (Rrms) of at least 150nm. Due to such high roughness, the light source is overly refracted for reflection spectroscopy, and the spiky surface profile obtained from interferometry and profilometry becomes hard to interpret. It is suspected that the roughness oriented from the glass microscope slides of the Au-Glass electrodes, so experiments are planned to test deposition of InSb on gold evaporated on silicon wafer to minimize surface defects.

4.2.1 Attempts and Nucleation Properties

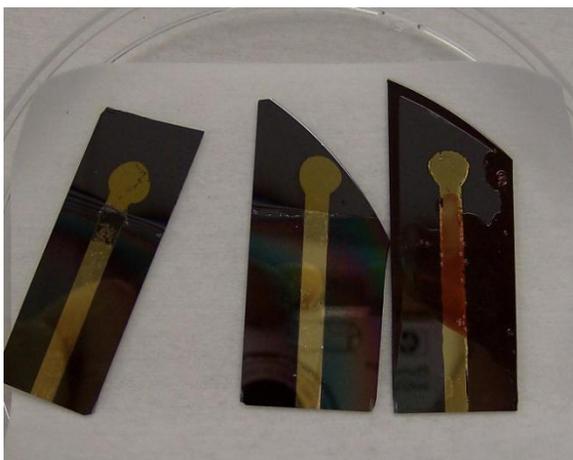


Figure 9. Au-silicon electrodes. Au-Si coated with P.R. (Right)

Figure 12 shows the Au on silicon wafer working electrodes. The electrodes are made by e-beam evaporation of 20nm of Ti and 200nm of Au on buffer oxide etch solution (BOE) treated silicon wafer. The patterns of the electrode are formed with an metal mask shown in appendix I, figure 12. A layer of insulating Si_3N_4 is deposited on back of the wafer and inactive

regions of the contact. The silicon is then broken in ten individual electrodes.

The result is shown in figure 13. The microscope Figure on the top left is sample 21 Au-Si electrode after one trial. Unlike all previous trials (sample 2 to 19), all of which have at least 500nm layer of InSb deposition, sample 21 has only trace amount of InSb deposited.

The reason for this phenomenon is suspected to be related to the need for nucleation of chemical reactions. The silicon wafer is defect free

on a molecular level, thus even with a crude e-beam gold evaporation, the surface of the gold is still very planar. To test this theory, scratch marks are put on the sample 21 surface, and the sample is reinserted for another round of electrochemical deposition. As seen in the bottom Figure, only the scratched portion has InSb deposition. From this result, it can be concluded that the deposition of InSb by electrochemistry requires heterogeneous nucleation with the deposition surface; however, the exact mechanism of the nucleation is still require further experimentation.

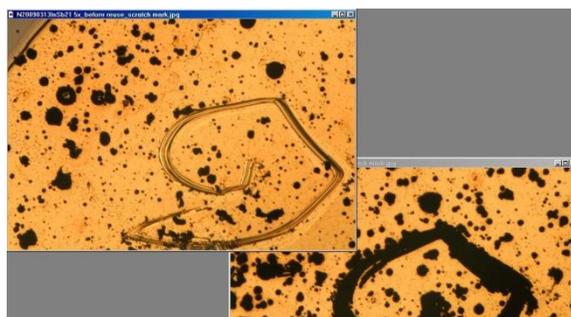


Figure 11. Sample 21 Au-Si electrode, After 1st trial(Left), After 2nd trial (Right)

4.2.2 Suggested Methods to Prepare the Surface

The silicon wafer fails as a good substrate to deposit uniform bulk film, so alternate substrates is needed. The current working electrodes used are still gold on glass electrodes; however, there is another option. Using the same type of Au-Si electrode, by oxidizing it in the electrochemical cell for ten seconds, small amount of gold will be oxidized into the solution, leaving small cavities on the surface as nucleation sites. This method is discovered by accidentally reversing the current on sample 20, which is also an Au-Si working electrode.