

# Nickel Titanium Nanowire Growth Using Electrochemical Step Edge

Scott Roberts  
Department of Materials Science & Engineering  
Carnegie Mellon University

Advisor: Reg Penner  
Department of Chemistry  
University of California Irvine

## Table of Contents

|                                  |     |
|----------------------------------|-----|
| List of Figures .....            | ii  |
| Key Terms.....                   | iii |
| Abstract.....                    | 1   |
| Introduction and Background..... | 2   |
| Procedure .....                  | 3   |
| Results and Discussion.....      | 5   |
| Conclusions.....                 | 11  |
| Acknowledgements .....           | 12  |
| References.....                  | 13  |

## List of Figures

|  |    |
|--|----|
| Figure 1. Metal nanowire Growth on HOPG.....   | 2  |
| Figure 2. Experimental Setup .....   | 3  |
| Figure 3. An illustration of nucleation and growth of a wire.....  | 4  |
| Figure 4. CV for the $\text{TiCl}_3$ , ammonium fluoride, and ammonium sulfate solution. ....                                    | 5  |
| Figure 5. <sup>4</sup> Pourbaix diagram for Ti.....  | 5  |
| Figure 6a-c. Titanium deposited on HOPG at -1.7V for 400 seconds. ....   | 6  |
| Figure 7. Photoluminescence measurements of the titanium wires. ....   | 7  |
| Figure 8a-c. Nanowires grown at -1.7V for 5s and -0.7V for 1000s. Figure 8d. EDAX measurements. ....                             | 8  |
| Figure 9. NiTi wires created by a CV with the cycle 0V $\rightarrow$ -2.5V $\rightarrow$ 2.5V $\rightarrow$ 0V at 50mV/sec. .... | 9  |
| Figure 10. a) Normal looking wires. b-d) Smaller very faint wires on the same sample.....  | 9  |
| Figure 11. EDAX analysis of Figure 10 wires Ti: Blue. Ni: Green. Si: Orange. Cl: Purple.....                                     | 11 |

## **Key Terms**

Activation Energy – The energy required to make a process occur.

Cyclic Voltammetry (CV) – An electrochemistry technique where a constantly varying voltage is applied across a cell and the resultant current is measured.

Electrodeposition – Depositing ions from a solution onto a cathode in an electrochemical cell.

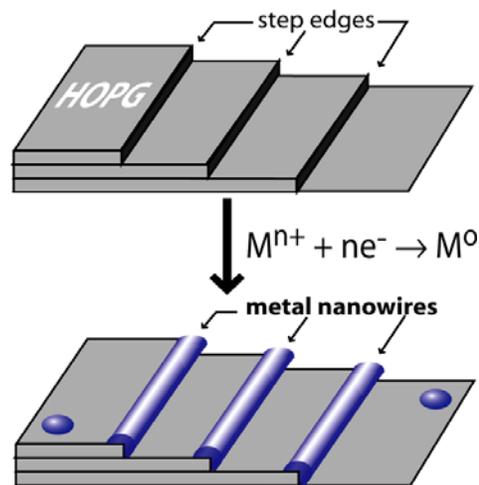
Nucleation – The formation of a new phase within another. In this paper, the formation of a metal grain on the cathode from the ionic solution.

## **Abstract**

With the increased popularity of using nanowires for complex sensing applications, it has become desirable to create a more rudimentary switching mechanism. A simple temperature-activated mechanical switch can be created with shape memory alloys. To date, no attempts have been made to grow nanostructures with a shape memory effect, leaving open the question of whether the effect will scale down to such small sizes. Ti or TiO<sub>x</sub> were first synthesized; it is unknown exactly which was formed as photoluminescence measurements were inconclusive. We have not yet successfully grown NiTi wires, although a series of closely nucleated particles along the step edges of HOPG has been achieved. They were determined to contain both Ni and Ti via EDAX analysis. The atomic ratio of the NiTi wires is roughly 30:70, outside of the range of a shape memory effect, although evening the ratio should be simple. The remaining work is to increase nucleation density and test for the shape memory effect.

## Introduction and Background

There are many different methods of creating nanowires. They include template synthesis, physical vapor deposition, or lithographically patterning the wires onto a substrate. However, most of these methods cannot create a metal nanowire of lengths greater than  $10\mu\text{m}$ <sup>1</sup>. In this paper a different method of synthesis, electrochemical step edge decoration (ESED), was used. In this method, highly ordered pyrolytic graphite (HOPG) was used in order to grow nanowires on the step edges (Figure 1). HOPG is desirable because it has many atomic step edges which decrease the required energy for nucleation of particles out of solution when compared to nucleation on a flat surface. The decrease in energy required to nucleate greatly increases the nucleation density of particles along the step edge, making wires out of all the nuclei along the step edge. Since there is little nucleation on the faces of the HOPG there should be very few crossed wires as the step edges should run close to parallel.



**Figure 1. Metal nanowire Growth on HOPG**

While a shape memory effect has been seen in various FCC nanowires (gold, copper, nickel, etc.) it is only exhibited those with cross sectional diameters less than  $2\text{nm}$ .<sup>2</sup> To this point, nobody has tried to create larger nanowires out of traditional shape memory alloys. In this case, a nickel titanium alloy was chosen over the other candidates of copper-aluminum-manganese, copper-aluminum-nickel and copper-zinc due to the challenges of ternary alloy depositions and the well-established biocompatibility of nickel titanium shape memory alloys. This experiment would also provide a good way of testing for the existence of the shape memory

effect at very small scales. To this point, measurements have been done successfully on indium-thallium thin films, but they were seen to have grains well over  $10\mu\text{m}$  wide, much larger than the width of even the thickest nanowires<sup>3</sup>. It will be interesting to see if the effect is strong enough to exist at smaller scales since it is a stress-induced phase transformation. However, at the nanoscale surface energies become much more influential than at the macroscale, so the shape restoration force may not be enough to overcome forces which have become more dominant at small scales.

From a device viewpoint, a nanowire possessing the shape memory effect could be used as a mechanical switch for nanodevices. Instead of having an electrical feedback system measuring temperature and responding to see if it is safe to run, the wire's change in shape could act as a circuit breaker to either make or break an electrical connection at its transformation temperature.

## Procedure

To actually make nanowires on the step edges, a solution must first be created. The solution contains metal ions which can be deposited electrochemically onto the graphite step edges. The experimental setup can be seen in Figure 2. A circuit is created by putting (1) a counter electrode, (2) a reference electrode, and (3) a working electrode all into (4) a solution. The reference electrode is a saturated KCl calomel electrode (which all measurements will be against) and the working electrode is a metal cylinder coated with Teflon and a small space at

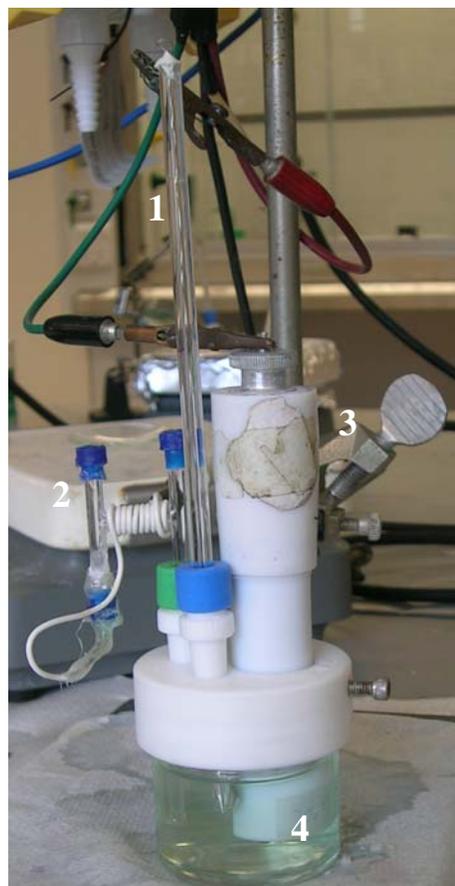
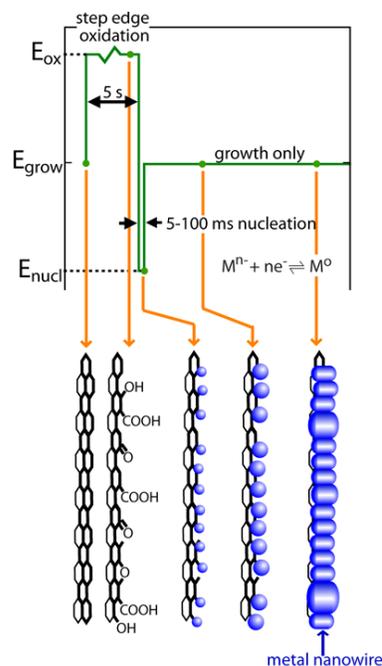


Figure 2. Experimental Setup

the tip allowing for the exposure of a small piece of HOPG (approximately 1x1mm<sup>2</sup>) to the solution. Prior to the insertion of the HOPG into the working electrode, its surface is cleaved with a piece of scotch tape in order to attain a smooth, uncontaminated surface.

Initially, only deposition of titanium from solution was attempted since it is difficult to electrodeposit from an aqueous solution. 99.99% pure titanium was dissolved into concentrated HCl by the reaction  $2\text{Ti} + 6\text{HCl} \rightarrow 2\text{TiCl}_3 + 3\text{H}_2$ . The first step is to run a cyclic voltammetric (CV) measurement to determine the potential ions begin to deposit. These points can be determined by ‘humps’ in the current of the negative voltage region of a CV (seen below in Figure 4).

After that, ions from the solution must be deposited. There are a number of ways this can be accomplished. First, a single deposition potential can be used. That involves setting the potentiostat to the desired voltage for a given amount of time and allowing the ions to nucleate and grow from the solution. A two step procedure can also be used where a very negative nucleation pulse is done for a short amount of time to promote a lot of nuclei along the step edges followed by making the potential less negative, allowing the nuclei to slowly grow. This works because the activation energy of nucleating new particles is larger than that of grain growth, so during the deposition step no new particles should form and only old ones should be able to grow. Finally, adding an initial oxidation step prior to the nucleation pulse can increase nucleation density along the step edges even more. The oxidation pulse is a positive potential around +0.8V for

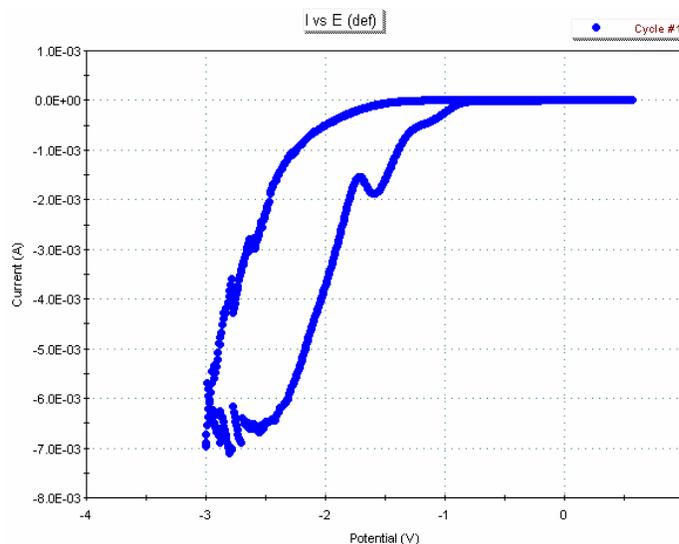


**Figure 3. An illustration of nucleation and growth of a wire.**

approximately 5 seconds.<sup>1</sup> Its purpose is to negatively charge the step-edges so they will attract the positively charged metal ions. Figure 3 illustrates this method of growing wires. All of these methods were done using PowerSuite software to regulate and record the voltages and resultant currents.

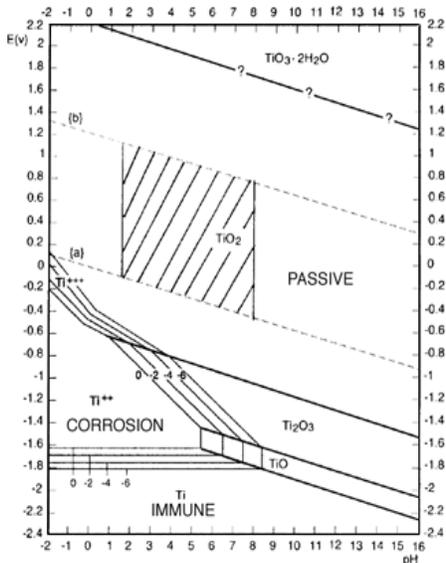
## Results and Discussion

Initially, only the  $\text{TiCl}_3$  solution was run through a CV, and no deposition was observed. Then, a 50 ml solution of 0.1M ammonium fluoride, 0.1M ammonium sulfate, and 15 drops of 0.1M  $\text{TiCl}_3$  was made and a CV was run. As can be seen in Figure 4, there is a well pronounced beginning at approximately -1.4V which is



**Figure 4. CV for the  $\text{TiCl}_3$ , ammonium fluoride, and ammonium sulfate solution.**

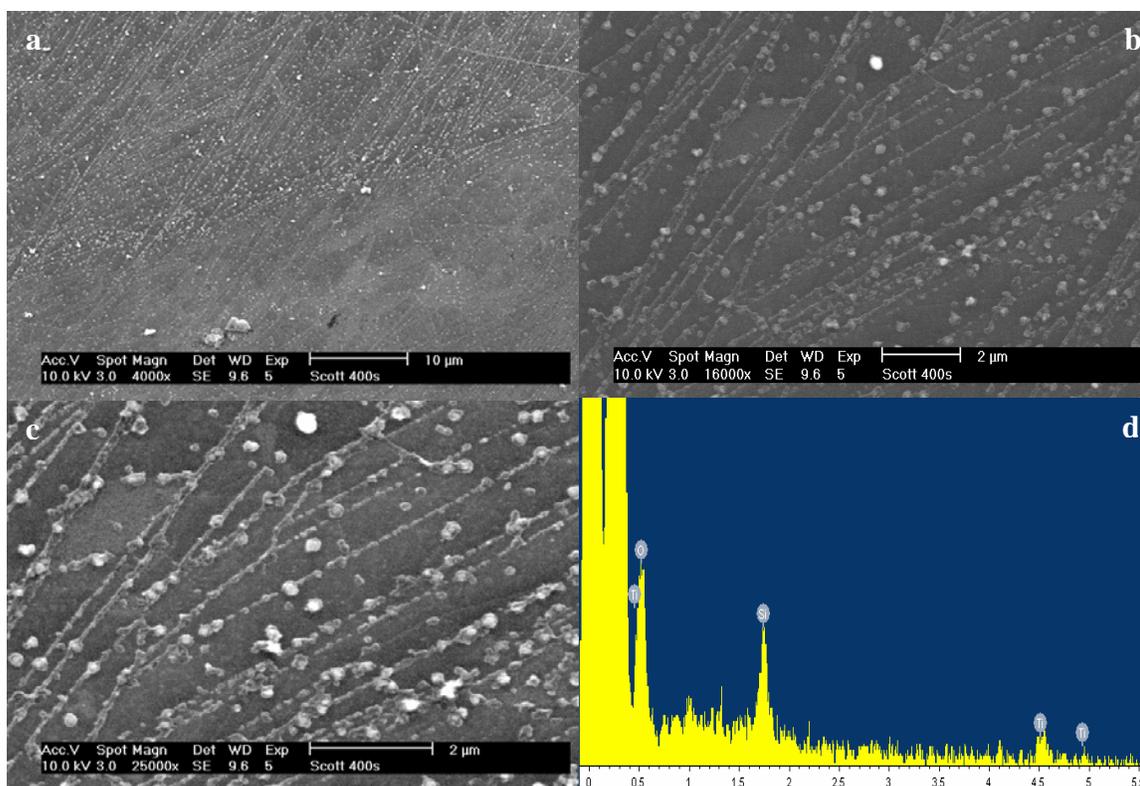
near the value found from a Pourbaix diagram of somewhere been -1.56 and -1.36 (Figure 5, add



**Figure 5.<sup>4</sup> Pourbaix diagram for Ti. Voltages are vs. hydrogen electrode.**

0.241V to the voltages to convert to SCE). The current becomes very large and erratic as the voltage becomes more negative because hydrogen bubbles begin to grow on the graphite and change the amount of surface area exposed to the solution.

Next deposition with a single potential was used. A large range of times and voltages were tested, with the best results being found at -1.7V for 400s. Images obtained via SEM can be seen in Figure 6a-c. There is a strong

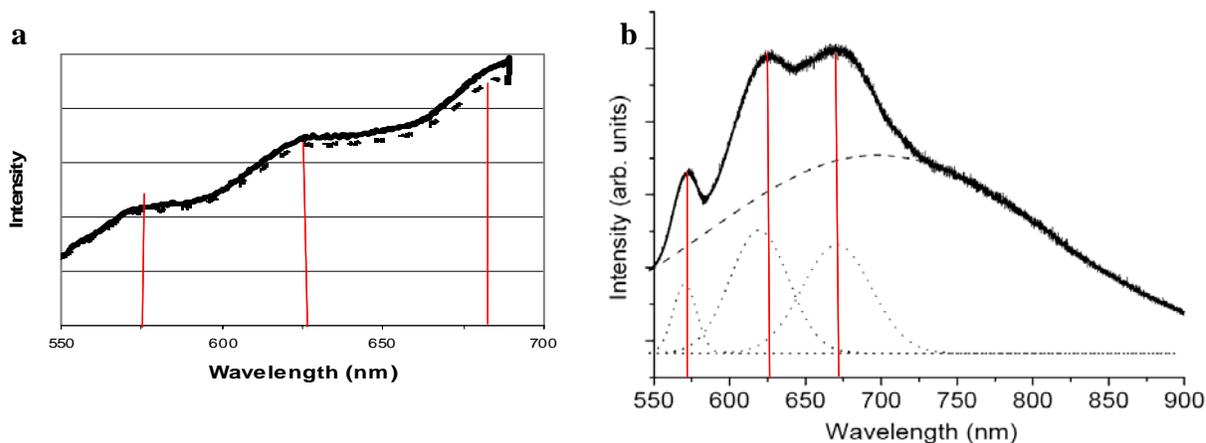


**Figure 6a-c. Titanium deposited on HOPG at -1.7V for 400 seconds.**

**Figure 6d. EDAX measurements of the Ti wires.**

preference for step edge nucleation and the density is high enough to form nearly continuous wires. Lower voltages produced less continuous wires and higher voltages created a film on the surface. Energy dispersive spectroscopy (EDAX) measurements of the wires were taken, and the presence of titanium on graphite was confirmed (Figure 6d).

However, there was still the possibility of the deposited material being a titanium oxide. In order to determine if titanium or titanium oxide had deposited, photoluminescence measurements were performed. The results can be seen in Figure 7a. Unfortunately, when the spectrum of the deposited wires on HOPG was compared to that of HOPG alone the peaks (Figure 7b) appeared to be in approximately the same positions. It is still undetermined if the bulk of the wires are titanium or titanium oxide, though it is expected that at least the surface is



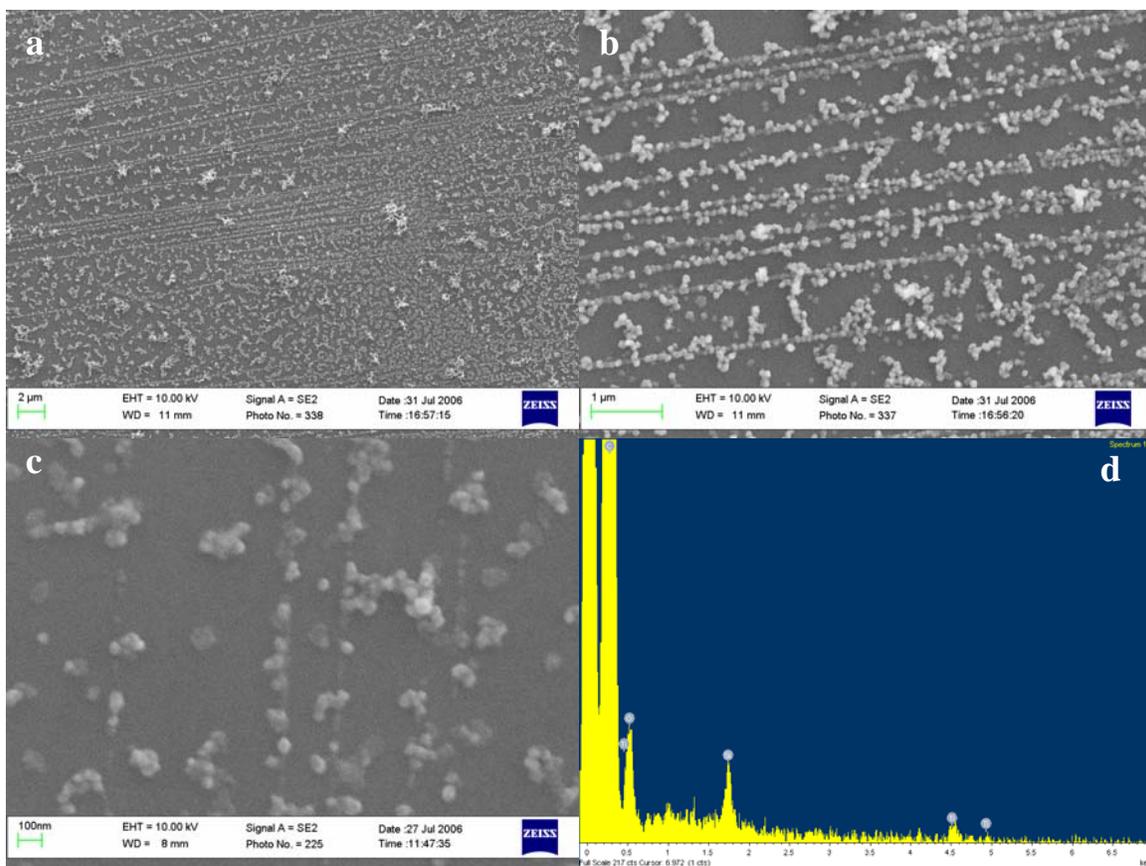
**Figure 7. Photoluminescence measurements of the titanium wires.**

**Figure 7b. Photoluminescence measurement of HOPG.<sup>5</sup>**

oxidized since titanium oxidizes readily in an oxygen atmosphere as well as in an aqueous solution.<sup>6</sup>

With the ability to deposit titanium confirmed, a new solution of 0.1M ammonium sulfate, 0.1M ammonium fluoride, 15 drops of 0.1M  $TiCl_3$ , and 15 drops of 30mM  $NiSO_4$  was created. First, a number of single deposition potentials and times were attempted. While some of these produced somewhat promising results (-1.7V for 60s was the best), none of the wires appeared fully continuous under an optical microscope, and there were always large particles on the surface that were considerably wider than the largest wires.

Next, a two step deposition method using nucleation and growth potentials was used. The nucleation step was done at values between -1.5V to -2.4V for time periods from one to one hundred seconds. Then a smaller growth potential from -0.5V to -1.3V was used with times between 100 and 1000 seconds. As can be seen in Figures 8a-8c, this method produces very small spherical particles that grew from the step edge. The main problem with this method is the particles tended to grow vertically into large chunks and the nucleation density along the step edges isn't high enough. These two factors prevent continuous wires from forming. Also,



**Figure 8a-c. Nanowires grown at -1.7V for 5s and -0.7V for 1000s. Figure 8d. EDAX measurements.**

surprisingly, no nickel was detected during EDAX analysis even though nickel should be easier to deposit than titanium (Figure 8d).

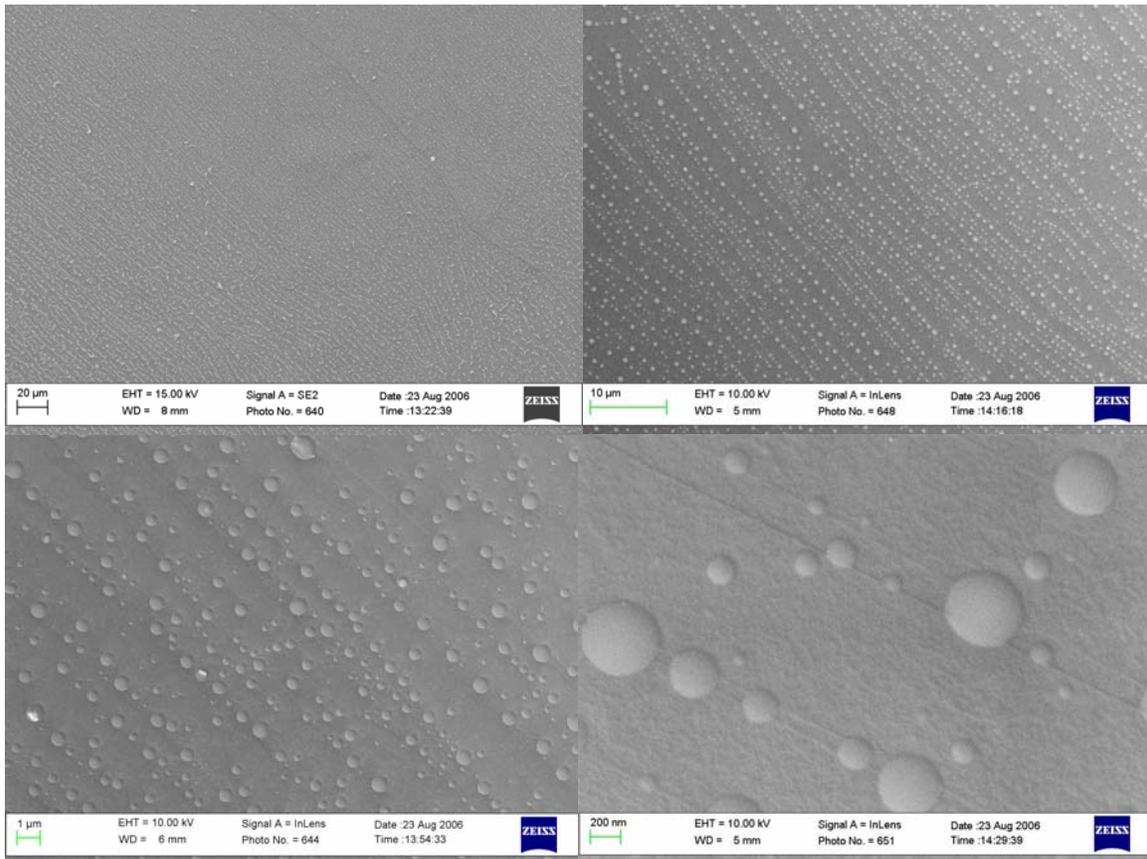
The next method of growth was the three-pulse method. First, an oxidation pulse of approximately 5 seconds at +0.8V was applied. Then, a very short nucleation pulse between -1.5V and -2.4V was applied for 50-300ms. Following that, a long growth potential from -0.3V to -1.0V for times between 30 to 1000 seconds was used. Typically, the wires grew faster for this method than the previous ones, but they still had the same general appearance under optical microscopy as both of the previous methods. They didn't appear continuous, there were lots of large particles on the surface, and the wires tended to be very thick and rough.

The final method used to produce wires was with a cyclic voltammetric test. It was found that by cycling through a range of negative potentials and back through the positives the wires would grow, be stripped, grow some more, and then be stripped again as the process was cycled numerous times. This created moderately sized



**Figure 9. NiTi wires created by a CV with the cycle 0V → -2.5V → 2.5V → 0V at 50mV/sec.**

nanowires with minimal growth on non-step edges since those particles tended to be stripped off in the positive potential range while the particles that nucleated on the step edges won't be completely stripped. Therefore the step edge particles wouldn't have to renucleate. An optical



**Figure 10. a) Normal looking wires. b-d) Smaller very faint wires on the same sample.**

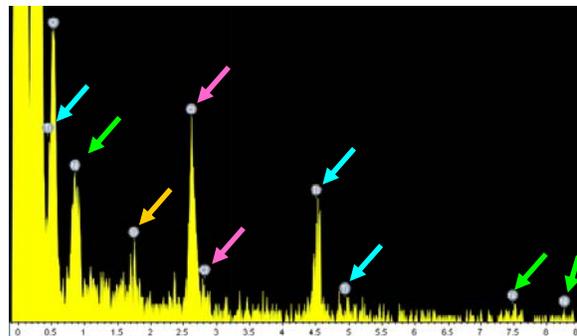
**0.3V → -2.2V → 2.5V → 0.3V @ 30mV/sec repeated 3 times.**

micrograph of these wires can be seen in Figure 9. As usual, there are a few of the larger clumps of material, but there are also long continuous somewhat thin wires (appearing a faint blue color under a dark filter in the optical microscope). Limits for deposition were then adjusted, ranging from -2.7V to +2.7V with scan rates from 20mV/sec to 100mV/sec. Multiple cycles were also utilized to determine if repeated stripping and deposition would create better wires. Three cycles was found to be optimal, as for more cycles nucleation would begin on terraces and fewer there wouldn't be enough growth of the particles. Faster deposition sweep rates (50mV/sec, 75mV/sec, and 100mV/sec) tended to not allow enough particles to nucleate and resulted in very space deposition. Slower sweep rates (10mV/sec, 20mV/sec) would create films on the surface and had excess hydrogen gas production, creating a bubble in the solution which broke the circuit. Stirring the solution during deposition would prevent the bubble from forming, but it would also tear off nucleated particles. The optimal deposition rate was found to be 30mV/sec. It was eventually discovered that starting the deposition scan at a slightly positive voltage instead of at zero mimicked the oxidation pulse used in the earlier three-step method. The best starting point for CV scans was found to be +0.3V where a positive current would be maintained until 0V. It managed to increase the preference for nucleating along step edges, practically eliminating the growth of particles on terraces. It created both the larger looking normal wires that appear discontinuous underneath an optical microscope as well as very faint, thinner wires which sometimes appeared to be continuous (brown looking under the dark filter). When inspected via SEM (Figures 10a-d) the smaller wires were non-continuous, though they showed superb preference for growth on the step edge. Three general sizes of particles can be seen since the deposition cycle was repeated three times, and during the most negative portion of the

deposition cycle most of the nuclei should form. Those which formed in later cycles should be expected to be smaller since they would have had less time to grow.

Figure 11 shows the EDAX analysis of these smaller wires. With this method nickel peaks appear, as well as a slightly mysterious chlorine peak. The chlorine was probably due to the sample being handled without gloves and then sitting unexamined for two weeks while the SEM was under repairs. The silicon peaks seen in

this and prior EDAX measurements could be from the ammonium fluoride combining with the acidic solution to form hydrofluoric acid which has the ability to etch away the glass container the solution was stored in (prepared solutions were



**Figure 11. EDAX analysis of Figure 10 wires Ti: Blue. Ni: Green. Si: Orange. Cl: Purple**

usually kept up to three days, though this sample was created with a completely fresh solution, so an appreciable amount of silicon may not have been etched). However, the presence of both nickel and titanium, and the uniformity of particles nucleated suggest that an alloy was formed so there aren't separate titanium and nickel particles.

## Conclusions

It is possible to synthesize Ti or TiO nanowires from an aqueous solution containing ammonium fluoride, ammonium sulfate, and titanium chloride. Nickel titanium nanowires can be deposited from a similar solution except with the addition of nickel sulfate. So far, the optimal deposition method for NiTi wires was a CV starting at +0.3V, to -2.2V, to +2.5V, back to +0.3V repeated three times at 30mV/sec. This exploits the preference for step edge nucleation and prevents practically any other nuclei from forming. Further work only needs to be done on increasing nucleation density along step edges which could be accomplished by either seeding

the step edges with a small amount of a material which has a very high nucleation density for the NiTi to grow on, or to try and slightly tweak the growth potentials to provide more time for nucleation.

### **Acknowledgements**

I would like to thank Reg Penner and his lab for all of their help and Megan Bourg for the suggestion of the initial solution to plate titanium from. Thanks to the IM-SURE program, UCI, the National Science Foundation and the Zeiss Center for their funding and support, as well.

## References

- <sup>1</sup> Walter, E C., B J. Murray, F Favier, G Kaltenpoth, M Grunze, and R M. Penner. "Noble and Coinage Metal Nanowires by Electrochemical Step Edge Decoration." The Journal of Physical Chemistry (2002). <[http://chem.ps.uci.edu/~rmpenner/PDFs/70\\_JPCB\\_106\(2002\)11407.pdf](http://chem.ps.uci.edu/~rmpenner/PDFs/70_JPCB_106(2002)11407.pdf)>.
- <sup>2</sup> Park, Harold S., Ken Gall, and Jonathan A. Zimmerman. "Shape Memory and Pseudoelasticity in Metal Nanowires." Physical Review Letters (2005). <<http://dx.doi.org/10.1103/PhysRevLett.95.255504>>.
- <sup>3</sup> Sonu, Chong Ho, and Thomas J. O'keefe. "Characterization of Phase Transformation Behavior." Materials Characterization 33 (1994): 311-319.
- <sup>4</sup> Gleixner, Stacy. "The Characterization of Particulate Ti Debris: Ch. 5." 27 Sept. 2000. San Jose State University. Summer 2006 <<http://www.engr.sjsu.edu/WofMatE/projects/srproject/srproj5.html#fig14>>.
- <sup>5</sup> Henley, S J., J D. Carey, and S R P. Silvia. "Room Temperature Photoluminescence From Nanostructured Amorphous Carbon." Applied Physics Letters (2004): 6236-6238. Summer 2006 <<http://epubs.surrey.ac.uk/nanoelectronics/9/>>.
- <sup>6</sup> Lu, Gang, Steven L. Bernasek, and Jeffrey Schwartz. "Oxidation of a Polycrystalline Titanium Surface by Oxygen and Water." Surface Science 458 (2000): 80-90.