TEM Sample Preparation for Order-Disorder Temperature Analysis of Au-Cu Nanoparticles

Jordan Batschi

A senior thesis submitted to the faculty of
Brigham Young University
in partial fulfillment of the requirements for the degree of

Bachelor of Science

Richard Vanfleet, Advisor

Department of Physics and Astronomy

Brigham Young University

August 2014

ABSTRACT

TEM Sample Preparation for Order-Disorder Temperature Analysis of Au-Cu Nanoparticles

Jordan Batschi
Department of Physics and Astronomy
Bachelor of Science

Understanding of the nanoparticle order-disorder temperature is important and vital to ongoing research, yet experimental analysis is lacking and the scientific base of knowledge relies on computational models. Tripod polishing techniques were used to prepare Au-Cu TEM samples for experimentally determining the order-disorder temperature of Au-Cu nanoparticles. The tripod polishing process with diamond lapping films proved to affect the samples, with TEM EDS showing significant copper deficiency. Alternative methods of sample preparation are shown and compositionally analyzed. Through coating the nanoparticles with alumina, the sample was shown to be compositionally stable with the desired 50-50 ratio. Further research is required using the alumina capped Au-Cu samples to find the order-disorder temperature.

Funding through National Science Foundation grant DMR-0906385 is gratefully acknowledged.

Keywords: tripod polish, Au-Cu

Table of Contents

List of Tables and Figures

Chapter 1

Introduction

The properties of materials change dramatically accordingly to their atomic structure. While these effects are well known in bulk materials, the nanoparticle realm is lacking sufficient experimental data to have a well-defined set of characteristics. As the capabilities of technology continue to grow, nanotechnology increasingly becomes a viable method and its uses are varied. Immediate applications of nanoparticle use and their properties include dramatic increases of storage capabilities on hard disk drives. This research focuses on advancing the base of experimental scientific knowledge of the order-disorder temperature of nanoparticles.

Background

The basis of material science is that different materials have different atomic structures. Many materials are of a crystalline nature, built of a structured lattice of atoms, layered in atomic planes. These structures are classified by the unit cell which is repeated to form the lattice. The atoms forming the unit cell vary their position depending on the type of crystal, such as face centered cubic (FCC), face centered tetrahedral (FCT) or hexagonal close-packed (HCP). When some polyatomic crystals are formed, the placement of the atoms is random within the structure of the lattice. This structure of the crystalline material is called the disordered state. The ordered state exists when symmetry occurs and the planes of the lattice are not random, but rather one plane in the lattice is comprised completely of one type of atom and the subsequent plane is comprised completely of another (see figure 1). The order-disorder temperature is the point at which through kinetic energy the atoms within the structure move from the disordered state to the ordered one, or the other way around. Through making this transition, the state of the atoms is more favorable according to the potential energy of the entire system. The most common example of this is the transition of water to ice or vice versa.

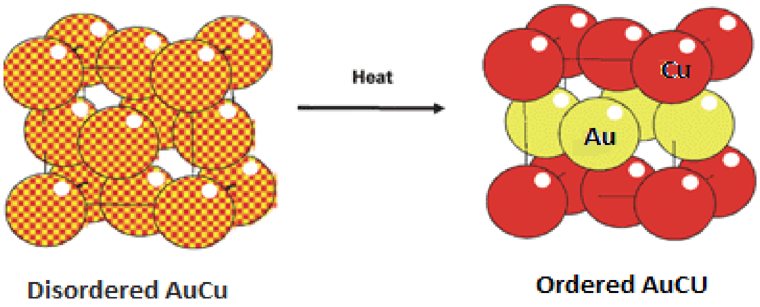

Figure 1: Phase transformation of Au-Cu from disordered to ordered state [1]

In some crystals, in order to achieve the ordered state, thermal energy is needed to allow the atoms to shift into another energy equilibrium. This amount of added energy is called the kinetics barrier, and acts as the energy obstacle from freely transitioning into a different state (see figure 2). This process of adding energy to the system or heating the crystal is called annealing. When annealing a disordered crystal, the higher temperature lowers the kinetics barrier. Through natural thermal fluctuations the energy state rises above the kinetics barrier and, when cooling,

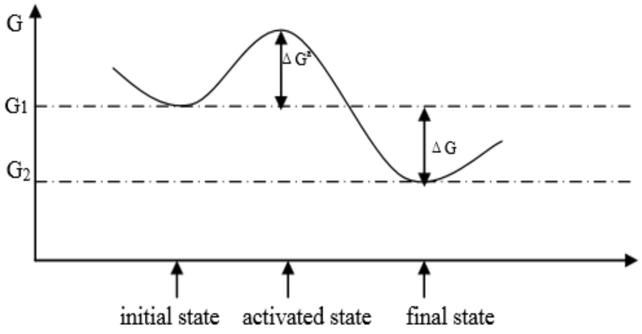

Figure 2: Kinetics barrier [2]

repositions into a symmetrical ordered state. These inter-crystalline transitions are important to the properties of the material and can affect the electric and magnetic aspects dramatically.

The kinetics and the energy needed for the transition of ordered to disordered states depend on the composition of the composite material. This relation is governed by the phase diagram of the material, which shows the different atomic structures, compositions and temperatures needed for a transition. The phase diagrams for bulk materials have been well defined experimentally. However, when dealing with nanoparticles or particles consisting of a few thousand or even hundreds atoms, the assumptions that can be made are limited. For example the boundary conditions of nanoparticles have increased importance when compared to a bulk model. As such, the phase diagram for bulk materials is a starting point for the experimental analysis of nanoparticle transitions, yet it cannot be assumed to be completely true for the nano-regime.

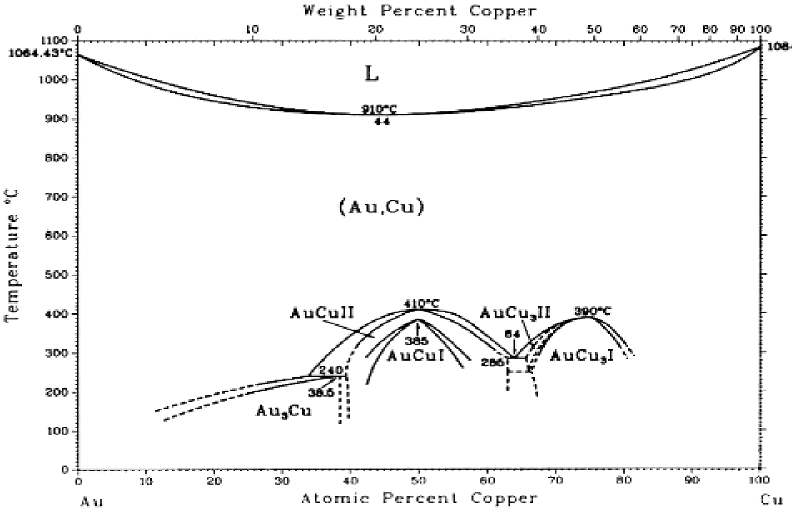

Figure 3: Phase diagram for Au-Cu in bulk material and the three different structures, the focus of this paper is on the central region [3]

Focus

The broad purpose of this research originated on different samples composed of different elements. These elements such as Ni-Pt, Co-Ni-Pt, and Fe-Pt were required to have certain magnetic and conductive properties with the goal to establish the order-disorder temperatures for these nanoparticle compositions. Through the manipulation of these properties, the particles could be used as bits on hard disk drive storages. Through applying a magnetic field, the magnetic moment of the particle could be switched and the orientation read as a 1 or a 0. As current hard disk drives are limited by the size and magnetic instability of the particles used, nanoparticles hold great potential for increasing areal storage density. Early on in the research, an Au-Cu sample was found to be ordered after annealing for an hour on a hot plate at an easily attainable temperature of 350 C. For this reason, finding the Au-Cu order-disorder temperature looked promising and is the focus of this research.

A set of Au-Cu samples had been prepared previously, with gold to copper atomic percentages ranging from 57-43 to 49-51. The bulk phase diagram for Au-Cu indicates the order-disorder temperature to occur when the atomic composition is 50-50, and this was used as the starting assumption for the nanoparticle realm. When analyzed, some of the samples had a significant compositional copper deficiency. When other samples with the same composition were prepared again, the same copper deficiency was found. These results lead to the focus on Au-Cu nanoparticles: to determine the cause of — and fix — the deficient atomic percentage of copper, as well as to determine the order-disorder temperatures for compositions of Au-Cu.

Chapter 2

Methods

As the nano-regime is so small and difficult, special techniques and methods must be employed for the analysis of nanoparticle samples. The resolution limitations from light microscopes are surpassed through using electrons with their small deBroglie wavelengths. A Tecnai F20 Transmission Electron Microscope (TEM) was largely used to obtain data for the set of Au-Cu samples. The TEM uses a beam of electrons that are emitted from a high voltage tungsten tip. This beam of electrons is then shaped through electromagnetic lenses, as opposed to the glass lenses for traditional microscopes. While the electrons allow for a higher resolution, they come with inherent problems. As electrons are charged they interact a great deal with whatever they come in contact. Because of this, special preparation techniques are required to be able to view the sample. While viewed in the TEM, the sample may be subjected to energy-dispersive X-ray spectroscopy (EDS) which measures the atomic compositions through the excitations and emission of electrons from the different electron levels. Diffraction imaging can also be used in the TEM, as the electrons pass through both the substrate supporting crystal structure, and through the “thin slit” of the atomic crystal structure of the nanoparticles.

The samples are made by collaborators from the University of Central Florida. Silicon wafers are used and exposed to oxygen to form an additional layer of silicon oxide. Through a co-sputtering technique, a high intensity beam of ions is aimed at targets, one of copper and one of gold. As the ions hit the targets, the copper and gold atoms are sputtered and dispersed evenly over the nearby silicon oxide surface. The wattages that are used for the sputtering affect the deposition rate of the copper or the gold; thus the samples are classified by the wattages used to make them, instead of their atomic composition which has additional inherent error involved. These copper and gold atoms form nanoparticles as they deposit, ranging from 2-10 nm in size. The samples can then be annealed at different temperatures; our samples are annealed at 350 C for 30 min. This annealing process heats up the atoms, and that thermal energy allows the transition over the kinetics barrier. Once over the kinetics hump they are then free to form into an ordered state.

Sample Preparation

After the sample has been made, it essentially must be thinned down to where electrons can pass though sufficiently to provide necessary contrast for EDS analysis, TEM diffraction mode, as well as visual images through a phosphorus screen. There are a variety of methods to do this, yet most are largely time consuming and expensive. The fastest, cheapest and the one used the most in this research is the tripod polishing method. A more precise, lengthy and expensive method is through using a Focused Ion beam.

Tripod Method

The tripod, or wedging method of polishing, is very mechanical in nature and depends highly on the preparer's skill level and previous experience. The previously made sample is cleaved into a 1mm x 2mm rectangle and washed with acetone to clean the nanoparticle surface, and then with methanol to remove any acetone residue. The sample is mounted to the glass post of the tripod (see figure 4) with a thin layer of MWH 135 wax (Quick Stick) with the particle side facing the glass embedded in the wax.

As the legs of the tripod are adjustable, they are set higher than the sample to form a wedge (see figure 6). Under a lubricant of deionized water, the sample is polished on consecutively finer diamond lapping films of grit sizes of 30µm, 15µm, 3µm, 1µm, 0.5µm and 0.1µm. The sample is then polished with colloidal silica with silica particles of 70-100 nm. Ideally, the substrate of colloidal silica is removed completely, leaving the nanoparticles supported on the layer of silicon oxide. After the sample is deemed thin enough by the preparer, it is placed in an acetone bath to dissolve the wax holding the sample in place. Once free of the tripod, the polished sample is rinsed again with acetone and methanol. After being cleaned the polished sample is mounted to a TEM grid of either titanium or molybdenum with Vishay M-Bond 610 epoxy so that the thin polished side is suspended over the hole (see figure 7). After the sample is securely mounted, it is cured on a hotplate at ~140 °C for five minutes.

Figure 5: Tripod Polisher

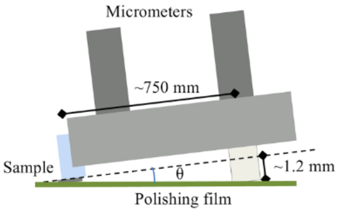

Figure 6: Schematic of tripod polisher (not to scale) [4]

Figure 4: Diamond lapping films green (30 µm) down to white (0.1µm)

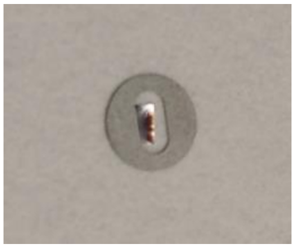

Figure 7: Finished polished sample on grid. Width of grid = 3mm

Focused Ion Beam

The Focused Ion Beam (FIB) uses a high intensity beam of ions from a liquid metal ion source, most commonly gallium, to essentially etch out the sample. The bombardment of ions sputters the material of the sample. This process removes the material with great precision of sub-micron scales. Due to the tilting ability of the sample stage, the desired thickness and size may be achieved. While in the vacuum chamber of the TEM, the etched out sample is mounted upon a TEM grid. The downside to this process is that it is long, taking hours to complete, and is also relatively expensive.

Challenges

There are many challenges involved in the production and analysis of the samples. These challenges include the physical structure of the actual sample, the instruments involved in taking data, and the inherent physics used to analyze the sample. Primarily, the sample must be as pristine as possible with little to no artifacts in the sample. Artifacts include colloidal silica buildup which obstructs the view of the nanoparticles underneath and potentially changes the composition of the underlying particles. Artifacts also consist of irregular structure in the sample, especially on the edge, particularly if the edge is not tapered off, but rather broken and jagged. Another artifact hindering the analysis of the sample sometimes occurs if the nanoparticles are stripped off through the polishing process, whether along the edge or in wide swaths down the middle.

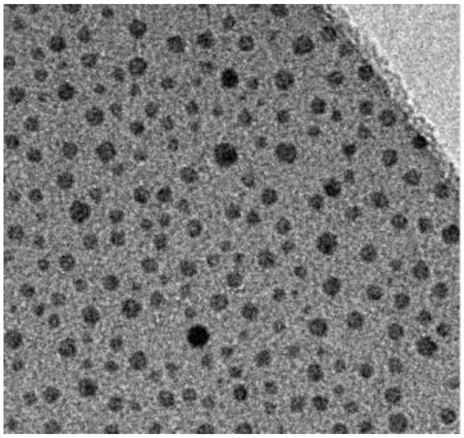

Figure 8: TEM image of Au-Cu 6-8 annealed at 350 C for 30 min

The sample preparation also determines the quality of the diffraction pattern found. If the silicon substrate is left too thick then the atomic lattice will overwhelm the weaker diffraction rings from the nanoparticle planes. Any of these artifacts limits the usefulness and reliability of the data gained from the sample.

The actual making of the sample and deposition of the nanoparticles also presents a challenge. The sputtering process which is used must first be put through a set of calibrations to get the 50:50 rates for copper and gold. These calibration samples are done using Rutherford Back Scattering (RBS), and must be recalibrated for each ion gun as well as according to the type and age of the target used. The sputtering process does assume linearity in the deposition rates. Thus, while the calibrations were done for a thicker layer of material, there may be differences from the intended compositional ratio in the actual composition of the sample.

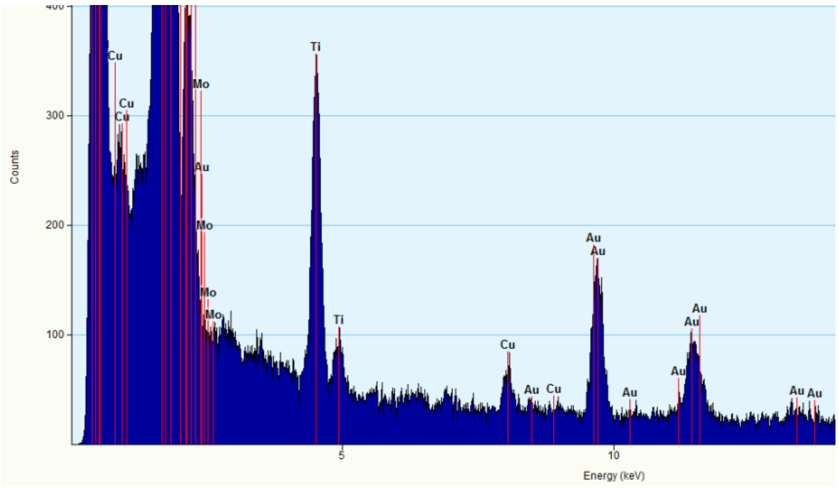

Figure 9: EDS of as-deposited Au-Cu 6-8

The physics used to analyze the compositional data in the TEM is also part of the challenge. As the incident electrons excite the atoms, the energy excites the electrons in the ground state, leaving holes in for which higher orbital electrons fall down to fill. As these electrons are bound in different energy levels, they produce distinct quantized amounts of energy when they drop down to lower energy levels. This energy is also distinct for the types of atoms from which it was emitted. Through theoretical atomic models and numerical factors based on the detector, the energy emitted can be used to determine which element it originated from. These numerical indicators, called *k*-factors are well known for some elements but are less known for others [4]. For some elements the *k*-factor is completely outside of the range of the detector.

There is also a specific manner in which the EDS process must be run to ensure accuracy. The EDAX detector in the TEM counts the packets of energy that are emitted and uses these numbers to determine composition. If the count rate of energy is too high, the sensor is damaged, if it is to low the data is limited by noise. All of these factors make it difficult to precisely measure the nanoparticles.

Chapter 3

Results

In order to determine and explore the patterns of composition, size and ordering, we took multiple EDS, TEM images, and diffraction patterns of all the samples. We initially had three different measurements with two different methods. The samples were made in Florida and compositionally measured using RBS and sent to faculty at BYU with the composition labeled as such. On average, we took data from the TEM EDS four times, from separate locations along the samples edge. We prepared the Au-Cu samples in August of 2013 through the tripod polishing technique previously described. Also as part of the recent preparation done during March through May of 2014, we used the FIB process in order to have a standard to compare methods. The Au-Cu as-deposited and annealed samples were again prepared using the tripod method March through May of 2014 to compare against the previous year's preparation.

The original compositions (marked as wattages used for the respective targets) of the samples sent from the UCF were: 5-7, 5-8, 6-7, 6-8, 6-9 which correlate to the atomic percentages (as determined by RBS) of gold to copper of: 52/48, 49/51, 57/43, 54,46, 51/49. When comparing to this standard, the sample results from 2013 varied and showed some significant copper deficiency. The results were: 28/71, N/A, 88/11, 87/12, 38/61.

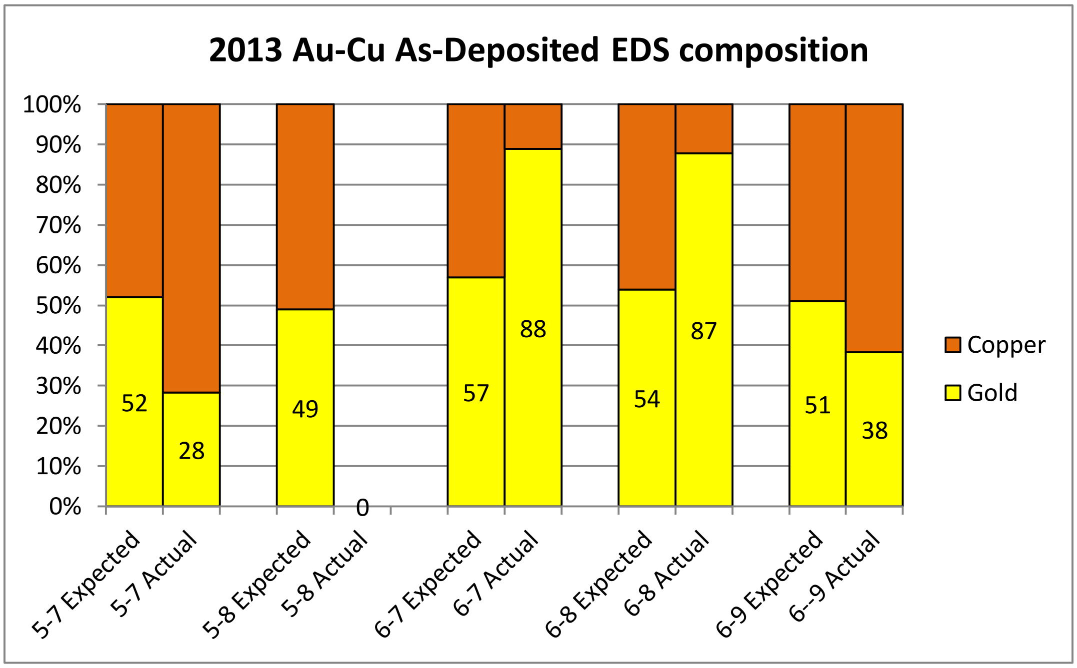

Figure 10: Old 2013 Au-Cu composition

The FIB technique however, done on a 5-7 sample, showed an agreement with the composition provided by the UCF. The samples were again prepared with the tripod polishing and when analyzed through EDS they again showed a large amount of copper deficiency. The results for the as-deposited samples were: 82/18, 83/17, 42/58, 70/30, 83/17 with standard deviations of 3.18, 0.8, 11.1, 9.6 and 1.4. The results for the 350 C annealed samples were: 77/23, N/A, 68/32, 71/29, 69/31 with standard deviations of 2.9, N/A, 11.6, 2.9 and 1.6.

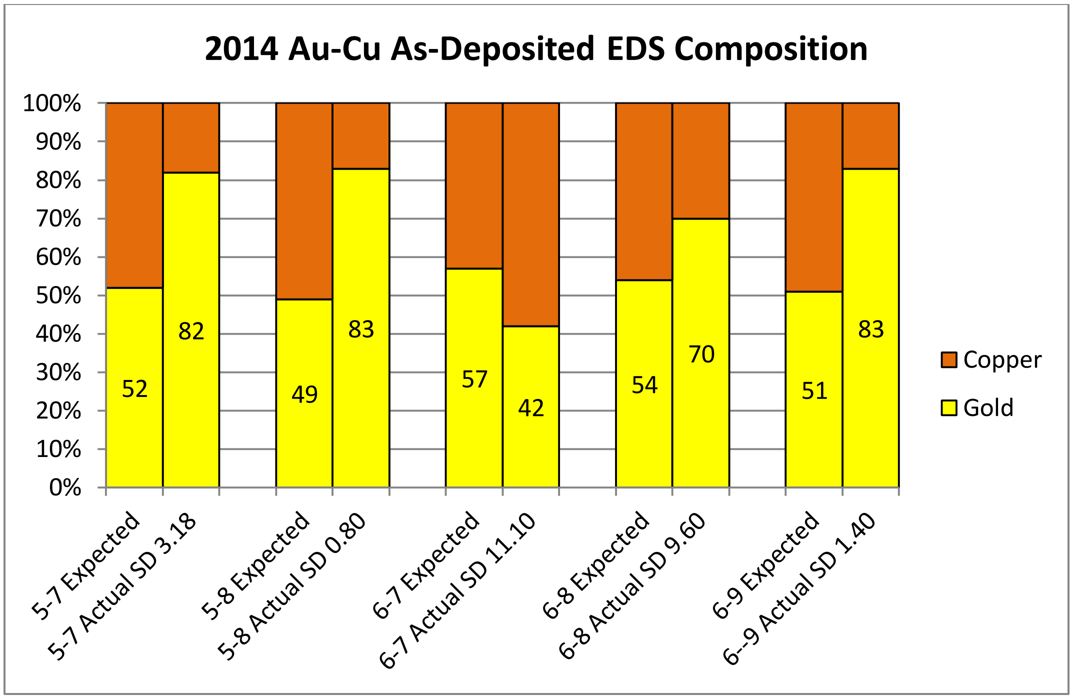

Figure 11: Au-Cu as-deposited composition

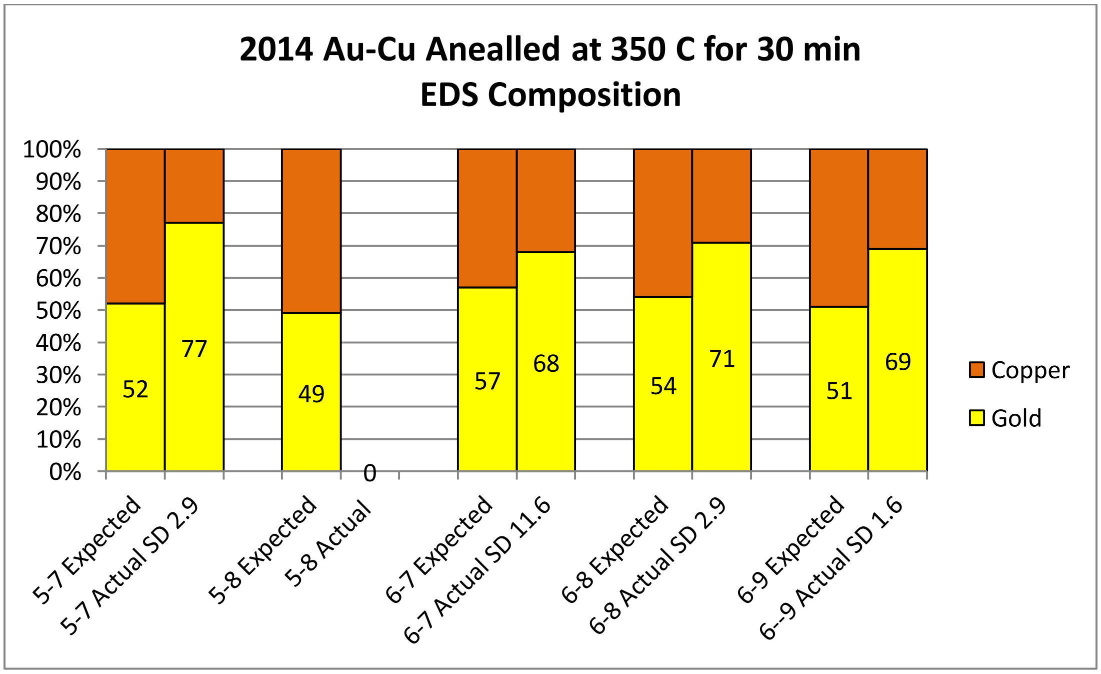

Figure 12: Au-Cu annealed composition

The samples were prepared three times in the same manner so as to test if there were any errors done in the preparation process previously. Since the new results from the tripod polishing method were similar for the old Au-Cu samples we concluded that something involved in the tripod polishing method must be causing the nanoparticles to lose copper. The following steps and materials used seemed to be most likely cause of copper diffusion: the acetone and methanol rinse of the sample, the crystal bond wax used to mount the sample, the deionized water used for lubricant during the polishing, as well as the colloidal silica used for the final polish.

Samples were subsequently prepared as well as possible while eliminating one of the possible culprit variables. The tests were prepared using the 6-9 as-deposited sample and the following tests done: without methanol, without acetone (using methylene chloride to dissolve the wax instead) and without colloidal silica. The results were: 80/20, 70/30, 63/37 with the standard deviations 4.95, 0.19 and N/A.

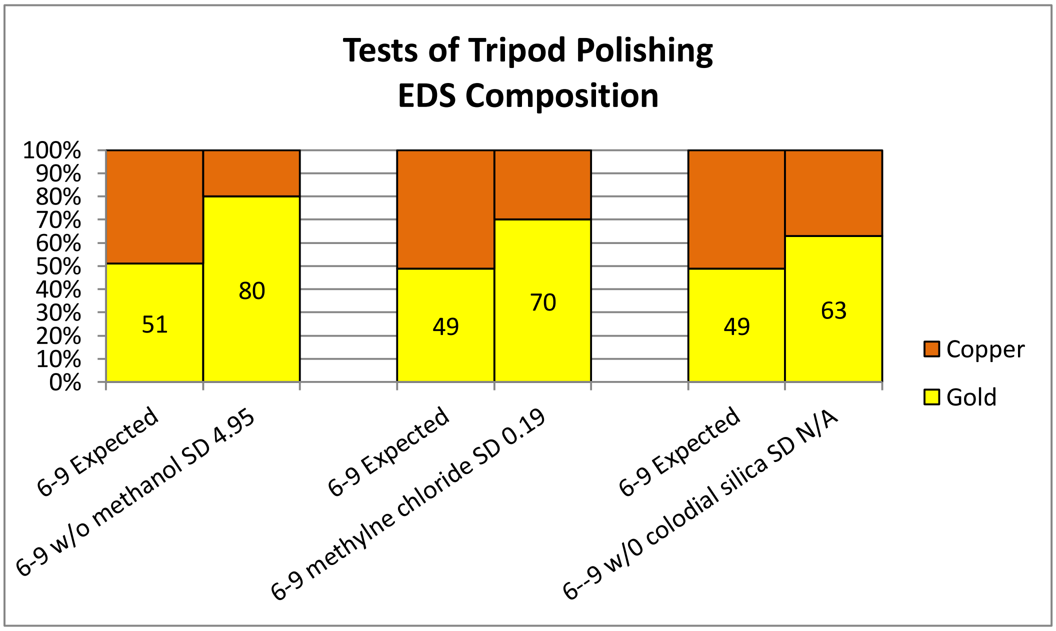

Figure 13: Au-Cu trials composition

In addition to testing the steps of the polishing process, the Au-Cu samples were coated with a layer of carbon and alumina to see if that would inhibit the loss of copper. The results for the carbon coated were skewed with no copper showing up at all in the EDS However, the alumina coated showed 48/52 and 48/52 for the as-deposited and annealed samples with standard deviations of 1.3 and 0.26.

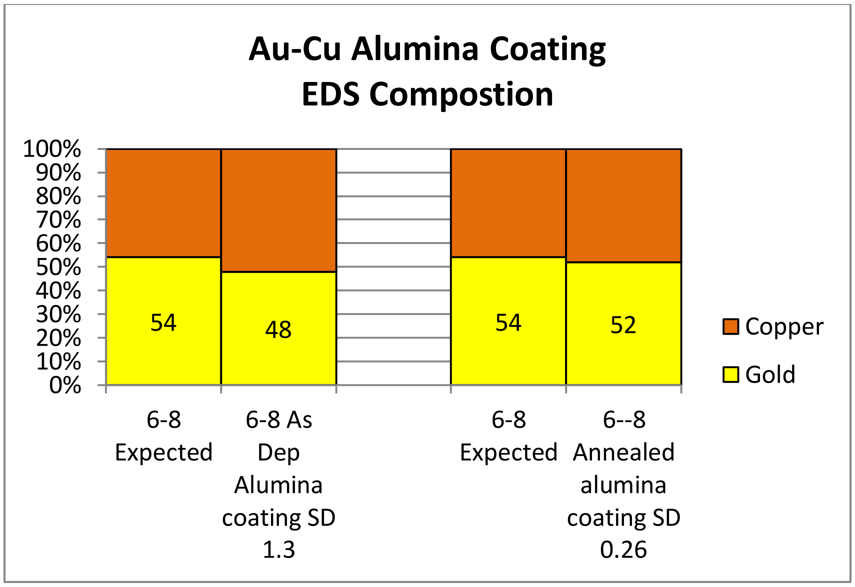

Figure 14: Au-Cu alumina coating compositions

Diffraction patterns were also taken of the samples through the TEM to see if the patterns/rings due to the ordering of the plane were visible. None of the diffraction patterns of the samples prepared contained the visible rings indicative of ordered nanoparticles.

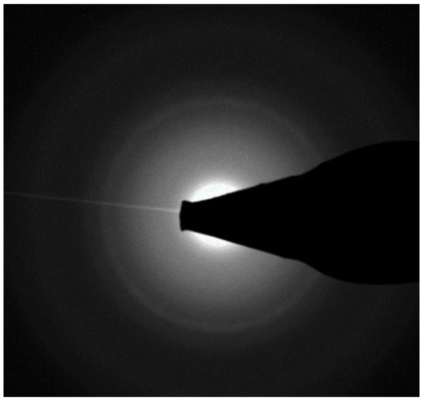

Figure 15: Diffraction pattern of Au-Cu 6-8 350 C alumina coated

Chapter 4

Analysis

The five data sets that were taken show an overall trend of copper deficiency. Since the RBS measurements show that the wattages used should produce a compositional atomic ratio of 50% to 50%, this is problematic. According to the bulk phase diagram (see figure 3) the Au-Cu requires an atomic composition centered on 50/50 to facilitate the order-disorder transition. The tripod polishing method is also the quickest way to produce TEM grade samples for analysis, so even though the FIB prepared sample agreed with the RBS and expected composition, it was deemed worthwhile to determine the cause of and resolve the copper deficiency in the Au-Cu samples.

Other composite nanoparticle samples have been prepared before using the tripod polishing technique without any noted change to composition. Due to this fact, the materials used in the tripod polishing process must lead to a diffusion of copper. However, there are a number of steps that are essential to the preparation process. The deposition of the nanoparticles on a substrate is obligatory, and some copper diffusion through amorphous silicon is known to exist [5]. The mounting of the sample to the tripod with some type of adhesive is necessary, as well as the solvent to remove it.

The data suggests that the copper atoms in the nanoparticles diffuse at least partially when subjected to the deionized water that is both present as a lubricant on the polishing wheel as well as the suspension for the colloidal silica. As the polishing proceeds, the wax that is holding the sample in place is polished away first. When this happens the sides and front edge are exposed prematurely to the deionized water, thus increasing the time that the nanoparticles are subjected to it. The compositional data for the trial where colloidal silica was not used also showed a slightly higher atomic percentage of copper, although more data would be necessary to have that confirmed within error bars. At the point in the process where colloidal silica is used, the substrate on the leading edge is all but polished away. As the colloidal silica is in an aqueous suspension, and as the silica particles polishes the remaining substrate, the nanoparticles that have been exposed from the wax are then exposed to the aqueous solution.

The compositional data for the Au-Cu alumina coated samples also support this theory. As the nanoparticles are capped with a layer of alumina, the copper is no longer free to diffuse when subjected to either acetone, methanol, or deionized water. The 6-8 wattages of the sample used correspond to atomic percentages of 54% Au to 46 % Cu, and the average of the three EDS compositions taken from 3 different spots is 52% Au to 48% Cu. With a standard deviation of 0.26, the result is within the desirable range of 50% Au to 50% Cu to see the order-disorder temperature.

In order to be able to determine the order-disorder temperature, the nanoparticles must be in the ordered state. Then through heating the sample on the hot stage in the TEM, the diffraction rings from the ordered planes of atoms will disappear at the order-disorder temperature for that composition. In addition, the alumina layer may affect the ordering and imaging of the underlying nanoparticles. However, as the focus of this research was to resolve the compositional problem of the Au-Cu nanoparticles, the lack of ordering in the annealed samples must be resolved in further studies to be able to determine the order-disorder temperature for the Au-Cu nanoparticles

Chapter 5

Conclusion

Through significant experimental data sets the nano-regime can be well mapped out and understood for applications and for a fundamental understanding of physics. Effects that are well known and studied at larger sizes may be dramatically different at the size of the diameter of a strand of human DNA. Theoretical models do not include all of the factors involved in the actual experimental methods and apparatuses, and extensive actual experimental data and studies must be done to ensure confidence in the results. Through understanding of nanoparticles and their attributes, nanotechnology and its uses will be revolutionized.

Bibliography

[1] Nguyen, H., Howard, L., Giblin, S., Tanner, B., Terry, I., Hughes, A., ... Evans, J. (2005). Synthesis of monodispersed fcc and fct FePt/FePd nanoparticles by microwave irradiation. *Journal of Materials Chemistry,* (15), 5136-5136.

[2] Zhang, L. (2013, January). *Kinetics vs. Thermodynamics: different but related*. Document posted in University of Utah *MSE 5034* online classroom, archived at http://www.eng.utah.edu/~lzang/images/lecture-1.pdf

[3] Okamoto, H., Chakrabarti, D., Laughlin, D., & Massalski, T. (1987). The Au−Cu (Gold-Copper) system. *Bulletin of Alloy Phase Diagrams, 8*(5), 454-474. (1987, January 1). Retrieved July 20, 2014.

[4] Jackson, A. (2012). *Experimental determination of the PT K edge K-factor for nanoparticle order-disorder transition analysis* (Undergraduate Thesis). Brigham Young University, Provo, UT.

[5] Fisher, D. J. (1998). *Diffusion in Silicon*. Scitech Publication.

Retrieved from: http://pearton.mse.ufl.edu/semic_properties/data/5029.pdf