Silver and Gold:

An Investigation into the Surface of a Daguerreotype

Travis Kohler, Ralph Wiegandt, Brian McIntyre, Nicholas Bigelow, Alex Shestopalov, and Nicholas Brandreth
Department of Physics and Astronomy, University of Rochester, Rochester, NY 14627

Abstract

In 1839 Louis Jacques-Mandé Daguerre discovered a way to save an image as seen from the human eye, changing the world forever. This process involved putting polished silver in contact with a halogen, sensitizing the surface, and then exposing the silver to an image. Following this exposure, the image would be developed by introducing mercury vapor. In 1840 Hippolyte Fizeau discovered a way to increase the quality of the image, gilding. This process involves coating the plate in a solution of gold chloride and sodium thiosulfate, heating the plate, and then rinsing the remaining solution off

Figure 1: Study Collection Daguerreotype SC_58

Advances in nanotechnology have lead to the discovery that the surface of a daguerreotype is actually a mosaic of silver and gold nanoparticles. In order to understand more about the techniques used and discover what happens when gold nanoparticles come in contact with the silver substrate we are using X-ray Photoelectron Spectroscopy (XPS) and Scanning Electron Microscopy (SEM). In addition to this technique we are currently refining a process to extract a lamella with a Focused Ion Beam (FIB) for use in the Transmission Electron Microscope (TEM). This project was supported in part by NSF award PHY-1156339.

X-ray Photoelectron Spectroscopy

The XPS scans for elements present by irradiating the sample with x-rays then reading the kinetic energy of the escaping electrons. For our tests we:

- Cut Historic Daguerreotype into 1cm by 1cm square (Figure 2)
- Placed the sample in the XPS
  - Scanned the surface
  - Etched the sample with argon ions for 60 seconds
  - Loop for 21 etchings
- Analyzed Data

Figure 3 plots 1000 counts vs binding energy of the electron. The z direction is depth

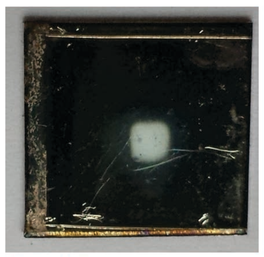

Figure 2: Daguerreotype post XPS etching

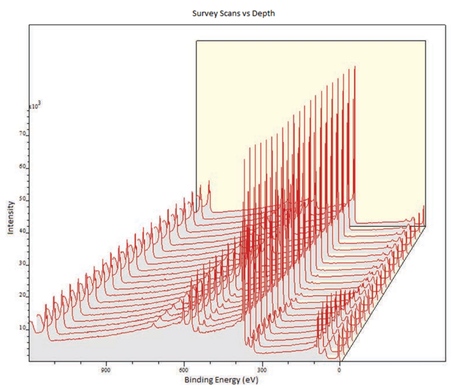

Figure 3: 3D compilation of Survey Scans

XPS (continued)

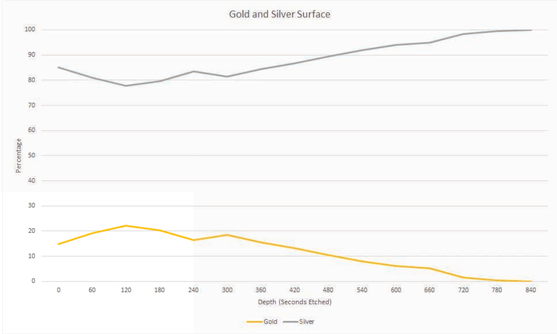

Figure 4: Percentage of Gold and Silver Present

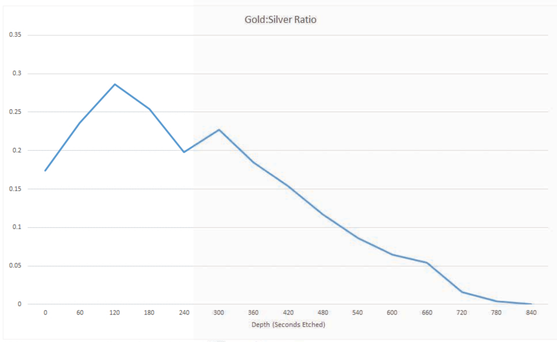

Figure 5: Ratio of Gold to Silver Present

Etching depth varies with inconsistencies in the material. Because of that, depth will be defined in units of seconds etched.

The topmost layers of the daguerreotypes are of the most interest. Figures 4 and 5 show the relation of gold to silver in this nanostructure.

There is an increase in the gold to silver ratio at 120 seconds. This suggests that the gold is absorbed into the silver and not just pooling on the surface

Focused Ion Beam Trenches

Milling the trenches

- Deposit platinum
- Mill deep on one side (Figure 6)
  - 30 kV 4nA 3 passes 300 seconds
  - 30 kV 1nA 3 passes 300 seconds
- Mill less deep other side (Figure 7)
  - 30 kV 2nA 3 passes 300 seconds
  - 30 kV 1nA 3 passes 300 seconds
- Clean up both sides Lowering the amperage to prevent redeposition
  - 30 kV 120 pA 3 passes 200 seconds
  - 30 kV 50 pA 1 pass 60 seconds

This leaves behind a 100 nm wide lamella ready for extraction (Figure 8).

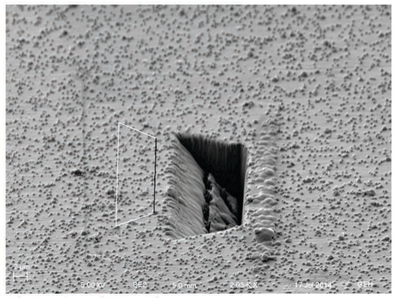

Figure 6: Left Trench

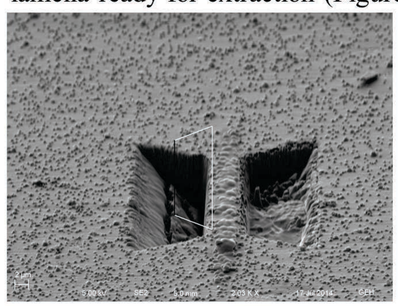

Figure 7: Left and Right Trench

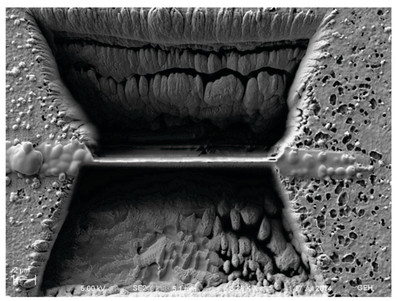

Figure 8: Lamella

The Next Step

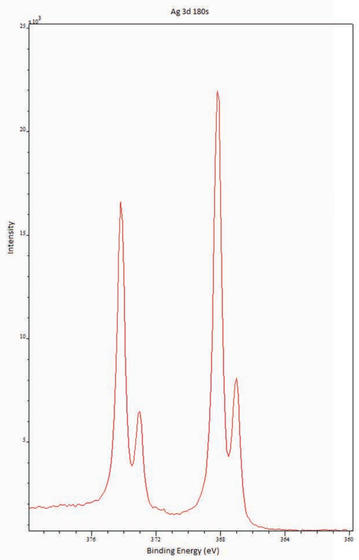

Figure 9: Ag 180s Etched

More analysis on the Gold Silver nanostructure needs to be done. Our next steps are:

- Create 4 plates using standardized sensitization.
- Gild 1 for the length of time for a satisfactory image (roughly 1 minute)
- Over gild the rest at n+1 minutes
- XPS and FIB the plates to determine the effects gilding has on the surface.

Our XPS scan found a silver halide present at depth of 180 seconds. This could explain daguerreotypes reaction to light. The next steps are:

- Etch slower to see how much halide is present
- XPS on daguerreotypes known to react to light
- Create new daguerreotypes with different sensitization

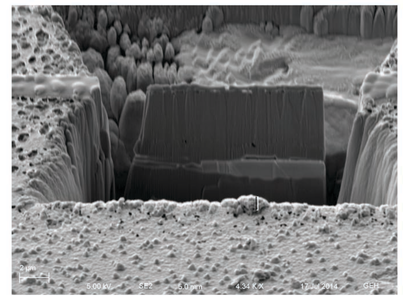

Figure 10: Freed Lamella

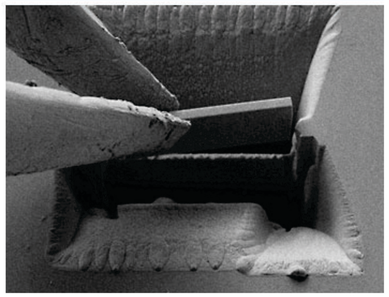

Figure 11: kleindiek Microgripper. Retrieved July 29, 2014, from: http://www.nanotechnik.com/mgs2-em.html

Now that we can make lamellas reliably, we need to determine a way to extract them and put them on a TEM grid. The TEM will provide a better understanding of the grain structure of the surface. Our next step is to use the Microgripper shown in Figure 11.

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