

Sub-20 Nanometer Electron Beam Induced Deposited Gold Plasmonic Nanostructures

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Introduction:

Photons provide a very fast medium with which to transfer information, but photonic devices' sizes are limited by the diffraction limit. The smallest photonic devices are in the order of 100 nanometers. In order to use photons in a smaller device, one can employ surface plasmons. Surface plasmons are resonant modes formed from oscillations of the conducting band in a metal when they interact with an electromagnetic wave. The modes propagate along the metal and semiconductor substrate with the same frequency as the incoming light but a shorter wavelength allowing for smaller devices [1].

We studied gold (Au) because, when deposited on silica, it has short wavelength surface plasmons when interacting with visible light according to Maxwell's equations (see Figure 1) [2, 3].

Our method for studying Au involved using electron microscopy. We used electron beam induced deposition (EBID) to create our structures. EBID provides a method that is reproducible and has high resolution. EBID is a direct write lithography method that uses a focused electron beam (e-beam) in an electron microscope. The beam breaks the bonds in a precursor molecules located in the vacuum chamber into volatile and nonvolatile components.

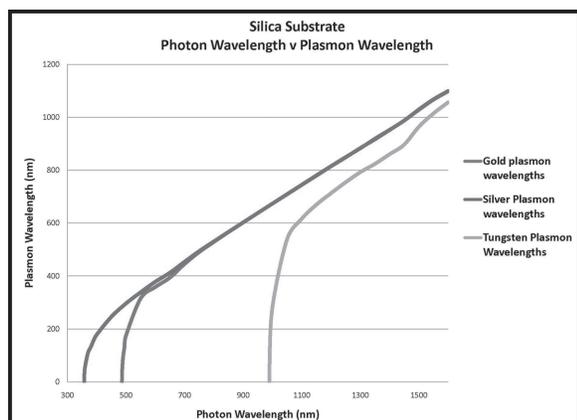


Figure 1: This graph is a simulation of using the solutions to Maxwell's equations. The plasmon wavelength becomes very small in the visible light range for Au, Ag, and tungsten.

The nonvolatile component, in our case gold, will stick to the substrate, while the volatile component, carbon, remains in the chamber or the electron microscope. EBID devices have a large amount of carbon contamination. In order to develop structures, it is important to remove any contamination in the structures. We annealed the devices in the presence of oxygen to help remove contamination [4].

The purpose of this project was to create Au nanodots and improve their carbon to Au ratio using annealing.

Experimental Procedure:

Au nanodots were deposited by e-beam-induced deposition using a scanning electron microscope (SEM, JEOL JSM-6700-F). A silicon membrane substrate was milled to about 100 nm, using a dimpling machine and ion milling. A gold precursor powder, dimethylgold(trifluoro)acetylacetonate [Me₂Au(tfac)], at 65°C, was used as the Au source. The vacuum chamber was 4×10^{-4} Pa, and the beam current was 30 pA at 30 keV. A pattern with a line of dots was pre-determined using the microscope's computer software. Nanodots were deposited for times between 4 seconds to 12 seconds in rows of 4 to 10 dots.

Deposited nanodots were analyzed by two microscopes. A transmission electron microscope (TEM, JEOL 2100) with energy dispersive x-ray spectroscopy (EDS) was used to determine if Au was present in the dots [5]. A scanning transmission electron microscope (STEM, JEOL JEM-2500SES) with electron energy loss spectroscopy (EELS) was used to image the sample and determine if carbon was present [5].

To remove carbon contamination from the Au dots we annealed the samples. The first set of dots was annealed at 400°C for 10 minutes. The second set of dots was annealed at 200°C for 10 minutes.

The dots were then reanalyzed using STEM.

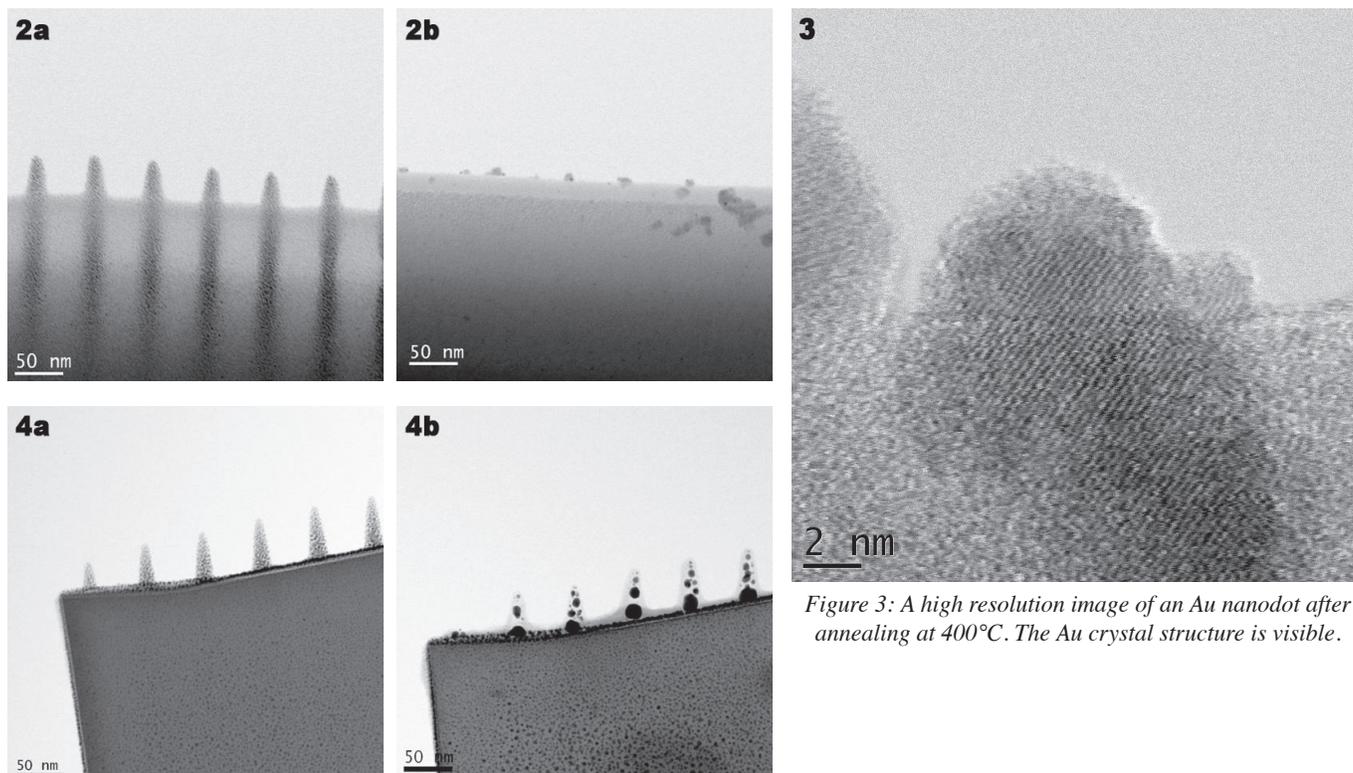


Figure 2, top: STEM bright field images of Au nanodots deposited for 8 seconds. [2a] was taken before annealing at 400°C and [2b] was taken after annealing. Gold is dark and carbon is light.

Figure 4, bottom: STEM bright field images of Au nanodots deposited for 8s. [4a] was taken before annealing at 200°C and [4b] was taken after annealing. One can see the how the gold agglomerated after annealing.

Results and Conclusions:

EDS and EELS confirmed that the dots were composed of gold with carbon contamination.

Annealing at 400°C for 10 minutes was too abrasive such that only $9.1\% \pm 5.4\%$ of the original dot remained (Figure 2). An interesting affect was that the gold crystallized during annealing (Figure 3).

Annealing at 200°C for 10 minutes caused the gold to crystallize as well as agglomerate (figure 4). The lower annealing temperature created dots that were closer to our goal of creating pure gold nanodots since the gold particles became larger.

Future Work:

We would like to adjust the temperature and time of annealing for optimal carbon removal. There are other methods for removing carbon including plasmon etching and incorporating gas assisted EBID.

Also, sample preheating has been shown to help the purity for tungsten and could be employed for gold [7].

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References:

- [1] Atwater, H. "The promise of plasmonics" *Scientific American*. April, 56-63, (2007).
- [2] Murray, A. W. and Barnes W. L. "Plasmonic Materials" *Advanced Materials*, 19, 3771-3782, (2007).
- [3] Refractive Index database. Refractiveindex.info (2010).
- [4] van Dorp, W and Hagan, C. "A critical review of focused electron beam induced deposition" *Sub-10 nm focused electron beam induced deposition*, 5-73 (2008).
- [5] Williams, D. and Carter, B. *Transmission Electron Microscopy*, 5- 11, 131-152, 573-585, 637-651. (1996).
- [6] Brydson, R. *Electron Energy Loss Spectroscopy*, 1-26 (2001).
- [7] Sychugov I., Nakayama Y., and Mitsuishi K. "Composition Control of E-beam Induced Nanodeposits by Surface Pretreatment and Beam Focusing" *J. Phys. Chem. C. Volume 113*. Page 21516-21519 (2009).