Fabrication of Metallic Nanoparticle Arrays

Christine Chin
Mechanical Engineering, Massachusetts Institute of Technology

NNIN REU Site: Michigan Nanofabrication Facility, University of Michigan
NNIN REU Principal Investigator: Professor L. Jay Guo, Applied Physics and Electrical Engineering & Computer Science, University of Michigan, Ann Arbor
NNIN REU Mentor: Brandon Lucas, Applied Physics, University of Michigan, Ann Arbor
Contact: c_chin@mit.edu, guo@eecs.umich.edu

Abstract:

Localized surface plasmon resonance (LSPR), a collective electron density oscillation found exclusively in metallic nanostructures, is a phenomenon that is of practical significance. The LSPR response of nanoparticles to changes in their surrounding dielectric environment may be exploited to use nanoparticle arrays as sensing platforms for biological or chemical sensors. This project focuses on the fabrication of such platforms using the method of nanoimprint lithography (NIL). NIL provides a way to produce significant areas of monodispersed nanoparticles of controlled size, shape and composition directly onto a wide range of substrates using a two-dimensional nanoblock array mold. Using this method of fabrication, we will study how the surface plasmon resonance of our fabricated Ag and Au nanoparticle arrays is affected as their composition as well as dielectric environment changes.

Introduction:

Localized surface plasmon resonance has been studied extensively over the past decade due to its utility as the backbone of many photonic technologies. Using spectroscopy, our LSPR biosensors will perform refractive index sensing by transducing changes in the surface refractive index into wavelength shifts of the LSPR extinction maximum.

The extinction maximum that we witness is the result of light absorption and scattering that occurs as light is shined onto our patterned sensing platforms. The electric field component of the incident light interacts with the particle electrons, causing them to collectively oscillate. LSPR is sensitive to the size, composition and shape of the nanoparticles as well as their orientation, spacing and dielectric environment. An abundance of nanofabrication techniques have been employed to produce the desired nanostructures utilized for LSPR biosensors with varied degrees of success as measured by the previously mentioned parameters that affect LSPR. Nanoimprint lithography is a very powerful method that allows for great particle fabrication control. Other alternative methods such as nanosphere lithography possess inherent fabrication limitations that allow for little particle orientation control, long range order, as well as particle geometric variation.

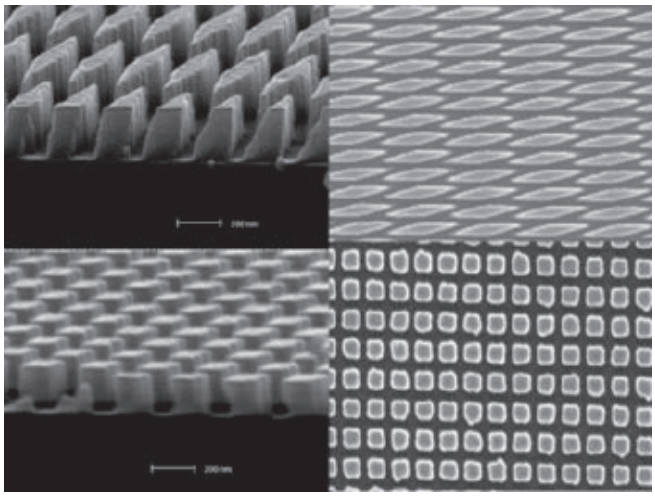


Figure 1: Fabricated metallic nanoparticle arrays.

Fabrication of Nanoparticle Arrays:

All glass substrates were cleaned in a 1:1 piranha solution of H_2O_2:H_2SO_4 for 15 minutes. Once soaked in solution, the substrate was rinsed with copious amounts of DI:H_20 and finally blown dry using N_2. A layer of mR-I 8020 photoresist was spin-coated onto the surface of the substrate to the appropriate thickness then baked on a hot plate at 140°C for 5 minutes to remove any solvents. A nanoimprinter was used to imprint a mold with periodic square nanoparticle features with in-plane widths of ~ 110 nm and particle spacing of ~ 100 nm directly onto the prepared substrate at 180°C and 670 psi. After imprinting, the residual layer of resist was removed using reactive ion etching (RIE). A select recipe of 20 sccm of O_2 at 50 watts of power and 20 mTorr was used to etch the polymer away. Following the polymer etch, a very thin layer of titanium followed by a layer of metal was deposited onto the surface of the substrate using an electron beam evaporator. Metals generally have poor adhesion properties, therefore the titanium adhesion layer was essential in fabricating metallic nanoparticles directly onto a substrate. Lift-off was performed by placing the substrate in a beaker of acetone and then placing the beaker of acetone in an ultrasonic bath. The finished sample was rinsed with methanol and IPA, and dried with N_2 to completion. SEM images of our fabricated nanoparticle arrays are illustrated in Figure 1.

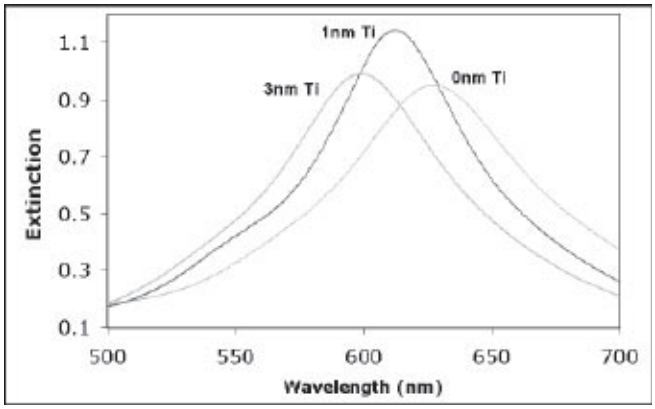
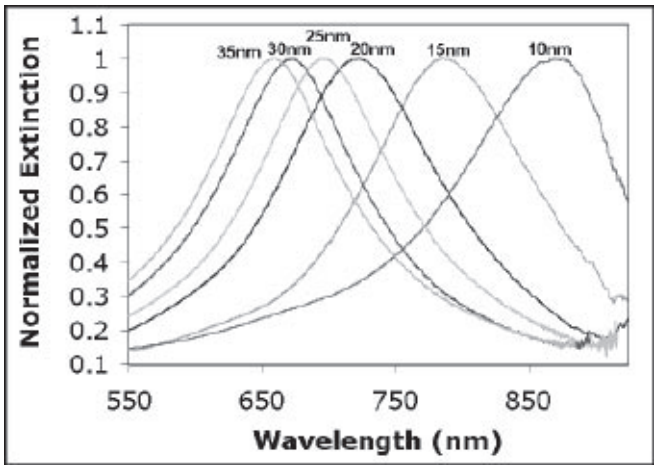


Figure 2: Adhesion layer testing on 20 nm silver nanoparticles.

Figure 3: Metal layer testing on gold nanoparticles.



Testing:

Optical extinction measurement tests were conducted using a Nikon TE300 Eclipse inverted microscope (20x objective) with transmitted broadband light coupled into an Ocean Optics SD2000 fiber-coupled spectrometer. Adhesion layer testing was first conducted to study the effects on the resonance of the metallic nanoparticles. 20 nm gold nanoparticles, as well as silver nanoparticles with adhesion layers of 0 nm, 1 nm and 3 nm were tested. As shown in Figure 2, a consistent resonance peak shift to shorter wavelengths was observed as the thickness of the titanium layer increased. In addition, the 1 nm adhesion layer uniquely exhibited a stronger resonance than other adhesion layer thicknesses. The effect of the metal thickness on the LSPR was also studied. Gold and silver nanoparticles of ranging thicknesses using a 1 nm titanium adhesion layer were fabricated and tested. Figure 3 illustrates the consistent shift of the wavelength peak to shorter wavelengths as the metal thickness increased. Silver nanoparticles exhibit a sharper resonance peak and therefore allow for better shift detection than gold nanoparticles. The consistent trend in shifts shows that NIL is able to produce metallic nanoparticle arrays that are very easily tunable.

We lastly performed refractive index testing to test the sensitivity of our nanoparticles. A flow cell setup was used to flow different concentrations of a glycerol/water solutions over our sensing platforms. The change in the refractive index of the surface resulted in a shift of the resonance peak. Silver nanoparticles exhibited higher sensitivity than gold nanoparticles, as can be seen in Figure 4. A greater shift in wavelength resulted in response to a change in refractive index for silver nanoparticles.

Results and Conclusions:

During the duration of this project, we not only successfully demonstrated the fabrication of nanoparticle arrays by nanoimprint lithography, but we additionally identified the optimal adhesion layer thickness for LSPR and examined the LSPR dependence on metal thickness of nanoparticles. And lastly, by performing refractive index sensing experiments, we were able to observe a stronger response from Ag nanoparticles of smaller height.

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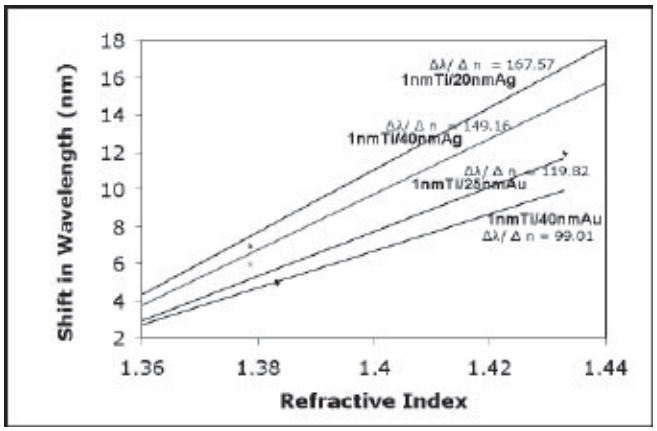

Figure 4: Refractive index testing.