Nanoimprinted Plasmonic Nanoparticles for Biosensor Applications

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Abstract

Localized surface plasmon resonance (LSPR), free-electron density oscillations found in gold (Au) and silver (Ag) nanoparticle (NP) systems, has been studied extensively over the last decade in part because of the NP's ability to behave as nanoscopic transduction elements. In this study, metallic nanoparticle arrays (NPAs) were fabricated using the mold-based nanoimprint lithography (NIL) technique. The NIL approach, compared to other methods, allowed the complete control of the fabrication of nanopatterns possessing different sizes, shapes and interparticle spacing on a variety of substrates. The ability of these NPAs to transduce changes in their dielectric environment was exhibited through a controlled study using electron-beam deposited silicon dioxide (SiO_2). Additionally, the ability of these plasmonic NPAs to detect biological interactions was demonstrated using a high-affinity biotinstreptavidin model system.

Introduction

Surface plasmon resonance (SPR) biosensors have been utilized extensively to study biological interactions by monitoring changes in the resonance condition (i.e. critical angle and reflectance) of a suitably modified metal film. Similarly, its nanoparticle (NP) system analog known as localized surface plasmon resonance (LSPR) can be monitored using UV-Vis spectroscopy to transduce changes near the NP surface. These changes result in shifts of the resonance wavelength that is characterized by enhanced absorption and scattering of the NP system. Therefore, a suitably modified NP system offers the ability to also detect bimolecular interactions with commercially available spectroscopic systems.

Nanoparticle Array Fabrication

Glass substrates were first cleaned in a piranha solution, thoroughly rinsed with deionized water and dried using nitrogen (N_2). Nanoimprint resist was spin cast onto the substrates to achieve the appropriate film thickness and baked on a hot plate to remove residual solvent. Imprinting was performed by heating the mold and substrate assembly above the resist glass transition temperature while in the imprint chamber, followed by an increase in the chamber pressure for approximately 5 minutes. The mold-substrate assembly was then cooled and separated to yield an imprinted pattern as shown in Figure 1. The final NP (Figure 1) was achieved by residual layer removal using oxygen (O_2) plasma reactive-ion etching (RIE), and Au electron-beam evaporation to the desired thickness and lift-off.

Experimental Methods

Extinction measurements of our fabricated NP system were accomplished through UV-Vis spectroscopy using a system comprised of an inverted microscope (Nikon TE300) and miniature spectrometer (Ocean Optics HR4000). In order to ascertain the distance-dependent dielectric response of Au NPAs possessing different height characteristics (40 nm; 60 nm; 80 nm),

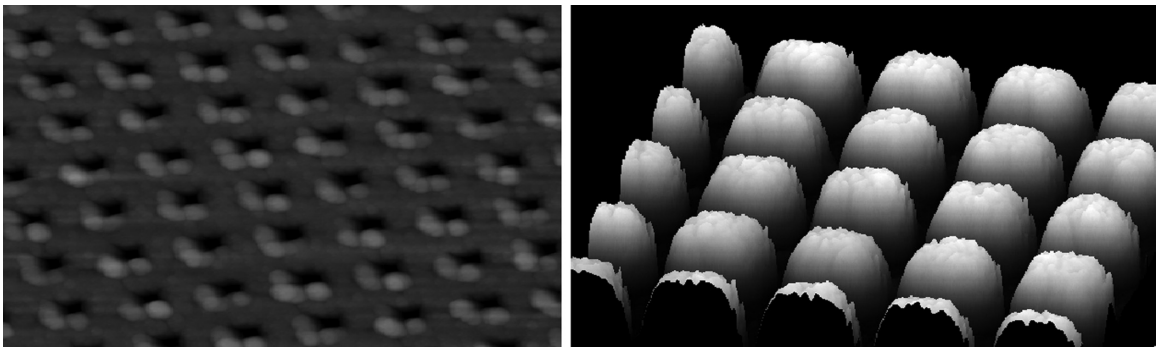

Figure 1: AFM images of imprinted sample and Au NPA.

evaporation of SiO_2 was performed to modify the dielectric environment of the NPA in a controlled manner. After ascertaining the initial resonance wavelength of the NPAs in ambient, extinction measurements were performed for multiple SiO_2 layer depositions on each NPA, iteratively.

Next, a Au NPA possessing a height of 40 nm was used to detect the specific binding interaction of a biotin-streptavidin system. This was accomplished by biotinylating the NPA through overnight incubation in a commercially available biotin-thiol self-assembled monolayer. The sample was incorporated into the experimental setup with a custom made flow cell that allowed increasing concentrations of streptavidin to flow across the biotinylated NPA surface using a peristaltic pump. Changes in LPR were acquired in real-time using data acquisition software. A standard commercially available SPR system was used as a control for the biological experiment.

Experimental Results

Figure 2 shows the resulting resonance shift due to changes in the SiO_2 layer thickness. It was found that the resonance peak amplitude, width and wavelength all increase with increasing SiO_2 layer thickness. Additionally, the 40 nm NPA was found to be the most sensitive to the SiO_2 layer thickness. All NPA systems also show a reduction in sensitivity as the oxide layer increases, and approach a saturated response. This demonstrates the ability of these NPAs to detect changes that occur only in the surrounding nano-environment. Figure 3 shows the ability of the NPAs to detect and monitor in real-time the specific binding of the biotinstreptavidin system. Each exposure of the biotinylated NPA to increasing streptavidin concentrations, followed by a wash in phosphate buffered solution to remove unbound streptavidin, were clearly observed for both the LSPR and SPR systems. The saturation of biotin binding sites with streptavidin was clearly observed through the saturated LSPR response which occurred much faster and at lower concentrations than found in the SPR system.

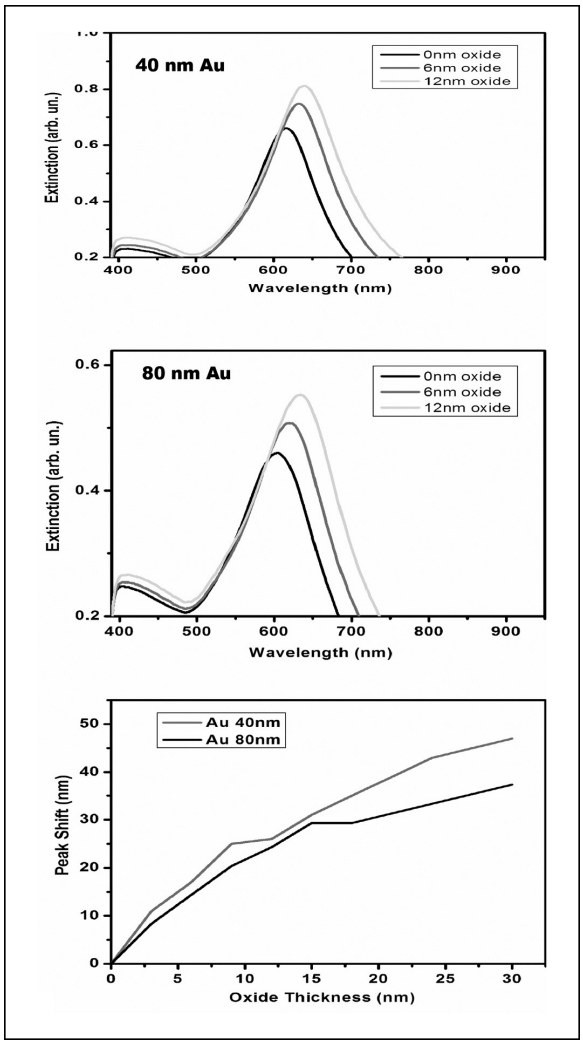

Figure 2: SiO_2 dielectric layer testing.

Conclusions

The ability of Au NPAs to detect changes in the local dielectric was exhibited using electron-beam evaporation of SiO_2. An increase in oxide film thickness caused an increase in the amplitude, width and wavelength of the LSPR. Shorter Au NPA constructs were found to be more sensitive to increases in oxide layer thickness. Additionally, all NPAs exhibited a reduction in their dielectric sensitivity with increasing oxide layer thickness and approached saturation. The relevance of these NPAs to biosensor applications was demonstrated through the detection of specific binding in a biotin-streptavidin system.

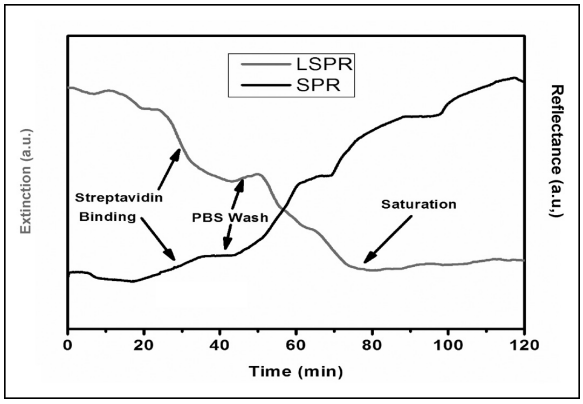

Figure 3: Streptavidin detection.

Acknowledgements

I would like to thank the National Science Foundation (NSF), Intel Foundation, Professor L. Jay Guo, Brandon Lucas, Dr. Vladimir Chegel, Dr. Sandrine Martin, Prof. Guo's research group, Michigan Nanofabrication Facility staff members, the National Nanotechnology Infrastructure Network Research Experiences for Undergraduates, and fellow NNIN REU 2007 interns at the MNF site for their help and support. Also, I would like to thank Professor Lawrence Josbeno for introducing me to the program.