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Nanoparticle Spectroscopy: An Alternative for Classical Surface Plasmon Spectroscopy

By Prof. Dr. Silvia Mittler
Department of Physics & Astronomy
University of Western Ontario

The thickness of thin solid films on a substrate surface can be measured with various optical methods such as ellipsometry, surface plasmon spectroscopy, interference methods, and waveguide spectroscopy, depending on the nature of the substrate. In most of these cases the refractive index of the material under consideration needs to be known for data analysis. Only an experimental set-up which allows at least two independent measurements, e.g. a waveguide experiment with at least two modes, allows one to determine refractive index and film thickness independently from each other.

For gold substrates, surface plasmon spectroscopy has had an enormous impact for thin film characterization, because the surface plasmon resonance can be easily measured and simulated with the help of a Fresnel equation based matrix formalism. This yields an exact value for the optical film thickness, a combination of film thickness and refractive index which are not completely independent from each other. If more information on the film material is known, e.g. a dn/dc curve, the molar concentration in [mol/cm^2] can be given. Because of its extreme sensitivity this method is commercialized by Biacore and used extensively by biological and medical researchers for testing recognition reactions on surfaces.

Figure 1. Discrete Dipole Approximation Simulation of gold nanoparticle half spheres in water

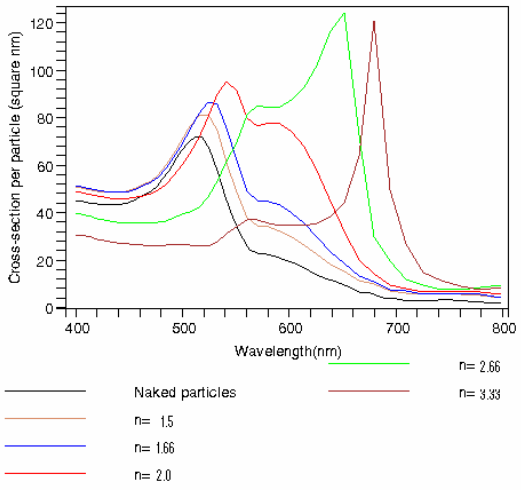
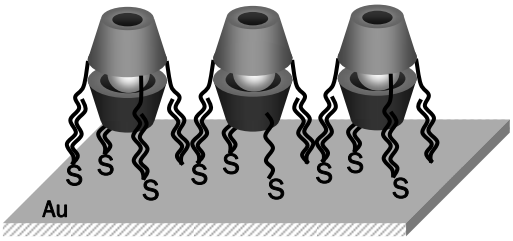


Figure 2. Supermolecular structure of Calix[4]arene heterodimer on gold.



Here we show that gold nanoparticles which have a surface plasmon absorption band can be in principle used for the same application. It has been known for quite some time that the surface plasmon resonance band of nanoparticles shifts towards the red when the nanoparticle size is increased.

With the help of Discrete Dipole Approximation (DDA) simulations we have found that by applying a thin film coating on a gold nanoparticle of a fixed size a similar effect can be observed, when the dielectric constant of the coating is systematically increased. Figure 1 shows such a simulation of gold nanoparticle half spheres with a diameter of 7 nm and a coating thickness of 7 nm simulated in water. In order to prove this simulated behavior we have implemented a supramolecular system as an ultra thin coating on gold nanoparticles. Figure 2 shows a supramolecular structure self-assembled out of two different calix[4]arens and a guest molecule. The calix[4]arene heterodimer is designed in such a fashion that when the sulphur moiety binds to a gold substrate, the capsule should not be allowed to re-open and release the guest. Calculations and measurements of these self-assembled films have yielded a film thickness of 50 ± 2 Å. However, the refractive index of the film depends on the dielectric constant or the refractive index of the guest molecule. Filling with $CHCl_2$ leads to a refractive index of 1.463, with two dichloromethane molecules (CH_2Cl_2) to 1.480 and with a ferrocenium ion to 1.466.

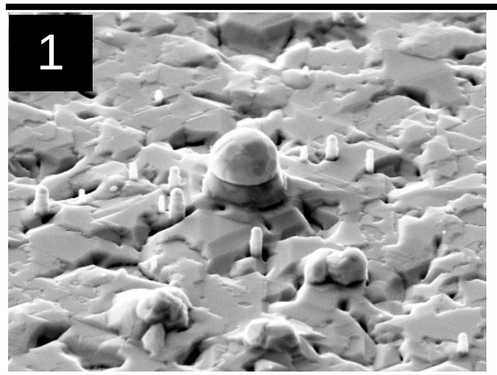
Gold nanoparticles were deposited on a transparent glass substrate as an incomplete gold film by e-beam evaporation. Absorption spectroscopy has shown clearly the existence of gold nanoparticles by

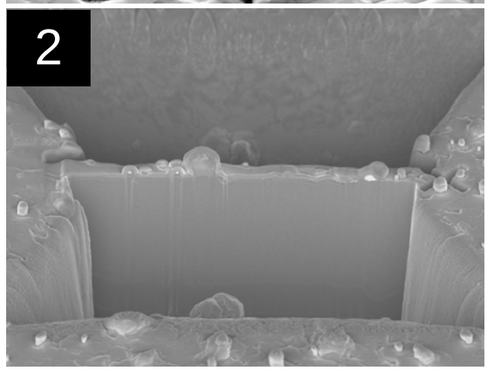
(Continued on page 4)

TEM Specimen Preparation

Western's Nanofab has recently installed an Ascend Instruments nanomanipulator in the FIB/SEM CrossBeam Instrument. The primary application of this new tool is the preparation of thin sections for Transmission Electron Microscopy (TEM). Focused Ion Beam (FIB) milling is a very powerful tool for preparing thin sections for electron microscopy analysis. In combination with the instrument's high resolution SEM imaging capabilities, we are now able to prepare site-specific sections of sub-micron sized features.

The procedure, outlined below, requires approximately two hours to complete.





1. A feature of interest is located with the Scanning Electron Microscope (SEM) in the FIB/SEM CrossBeam. (Sample courtesy of Prof. Ray LaPierre, McMaster University).

2. The region of interest is coated with platinum, in-situ, using the CrossBeam's gas injection system. This layer protects the surface of the feature during subsequent FIB milling. The surrounding substrate is removed by FIB milling, leaving a 1 micron thick lamella containing the feature of interest.

3. At the tip nanomanipulator rod is mounted an 'end effector' – a sharp Mo or Cu tip. The tip is positioned just above the region of interest on the sample.

4. Using the FIB, a pair of tines are machined at the tip of the end effector. The spacing is slightly less than the thickness of the lamella prepared in step 2.

5. With the left and bottom sides of the lamella cut free, the end effector is positioned onto the right side of the lamella. This procedure is accomplished by viewing both the SEM and FIB secondary electron images while lowering the end effector onto the sample. The alignment of the tines with the sample in plane of the sample surface is observed and adjusted in the FIB image and the height is visualized in the SEM image.

6. With the lamella securely held between the tines, the right side is cut free and the sample is lifted clear, again while monitoring the position with both the FIB and SEM electron images.

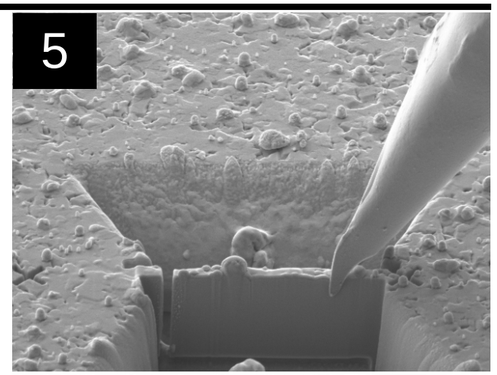
7. After the lamella is lifted clear of the substrate, the final thinning and polishing is performed by FIB milling. Progress is monitored in situ by SEM – the rod can be rotated to allow both front and back to be imaged and the thickness to be measured. A final thickness of 100nm is typical.

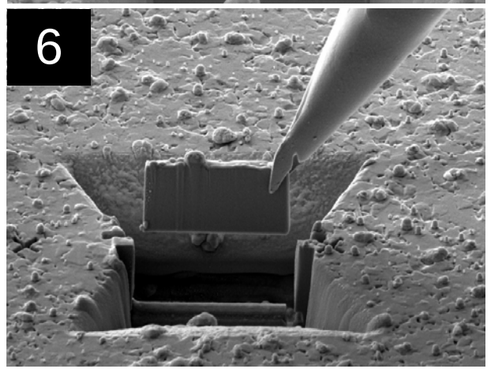
8. The nanomanipulator rod is withdrawn from the microscope through a loadlock without venting the microscope chamber. After the tip of the end effector is folded over and removed from the nanomanipulator rod, it can be directly mounted in a standard 3mm diameter TEM sample holder.

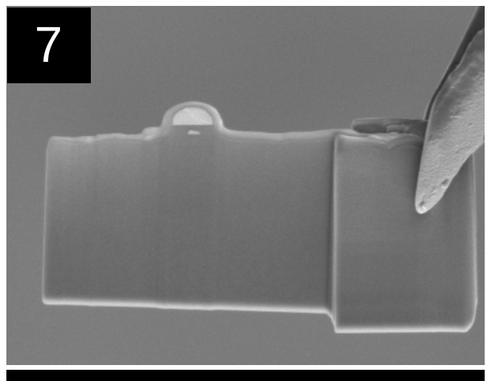
FREE TEM SAMPLES

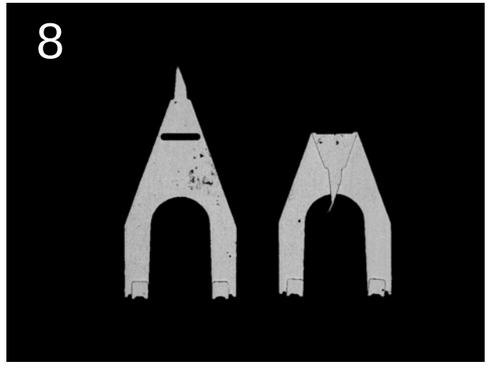
For a limited time, we are soliciting requests for TEM lift-out sample preparation. Samples will be prepared free-of-charge in exchange for feedback from subsequent TEM analysis.

Please contact Todd Simpson
tsimpson@uwo.ca
519-661-2111 x86977









The Nanofabrication Laboratory

University of Western Ontario
Physics & Astronomy Building Rm 14
London, Ontario N6A 3K7

Phone: 519-661-2111
Fax : 519-661-2033

Rick Glew, Lab Manager
Ext. 81458 Email: rglew@uwo.ca

Nancy Bell, Lab Technician
Ext. 81457 Email: nbell2@uwo.ca

Todd Simpson, Research Scientist
Ext. 86977 Email: tsimpson@uwo.ca

Silvia Mittler, Laboratory Director
Ext. 88592 Email: smittler@uwo.ca

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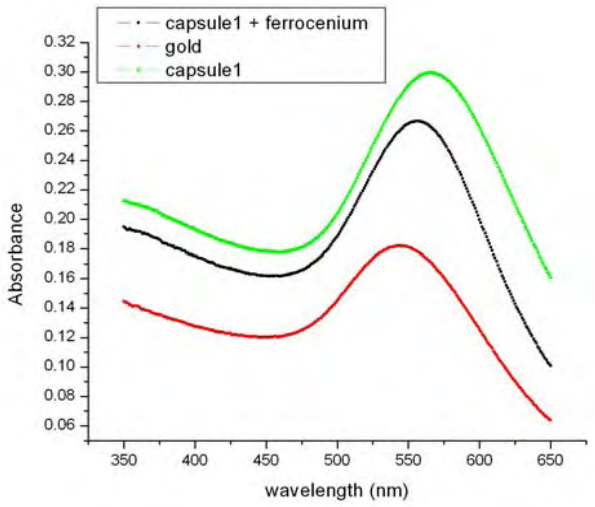
a plasmon absorption band with a maximum around 545 nm (figure 3). Coating these nanoparticles with dichloromethane filled and ferrocenium filled heterodimer capsules leads to a red shift as predicted. The n=1.466 film (ferrocenium filled) shows a peak at 560 nm whereas the n=1.488 (dichloromethane filled) species peaks at 575 nm. The higher the refractive index of the film, the greater the red shift from the uncoated particle spectrum.

In principle, this system of nanoparticles shows extremely sensitive information about a coating placed on them. For example, pancake shape objects, which will show a different plasmon resonance band in a polarization direction parallel and perpendicular to the substrate. If one uses evanescent waveguide absorption spectroscopy on asymmetric particles and these nanoparticles are placed in the evanescent field of a wave-guide, they should yield two independent measurements in s- and p-polarizations, yielding both parameters; refractive index and film thickness as independent parameters.

Simulations with DDA can verify our results but in the moment there is no rigorous theory which allows to calculate the thickness and the refractive index of a coating, by feeding the nanoparticle shape and the position of the plasmon bands as parameters into a calculation.

This new technology is promising and is extremely sensitive; nevertheless a rigorous theory for simple data analysis is still missing.

Figure 3. Absorption Spectroscopy of gold nanoparticles on a transparent glass substrate..



This work was only possible in a close collaboration between the synthetically active group from the Department of Chemistry, Johannes Gutenberg University, Mainz, Germany: Ganna Podoprygorina, Volker Böhmer, with the experience in theoretical physics of Patrick Ronney and Chitra Rangan from Department of Physics, University of Windsor, Canada and Songbo Xu, a PhD student of the Department of Physics and Astronomy, University of Western Ontario, Canada. The authors like to thank Nancy Bell and Rick Glew from the Nanofabrication Facility at The University of Western Ontario for the fabrication of the gold substrates. This work was supported financially by NSERC, the Ontario Photonics Consortium (through Ontario Research and Development Challenge Fund (ORDCF)), CFI and OIF, the Canadian CRC program as well as the Deutsche Forschungsgemeinschaft (SFB 625).

Ordered Arrays of Gold Colloidal Particles

Dr. Todd Simpson of The University of Western Ontario presented a talk at the Materials Research Society Fall meeting in Boston on the fabrication of ordered arrays of gold colloidal particles. The talk and accompanying paper detail recent results of experiments performed in the Nanofab with Professor Ian Mitchell.

Colloidal chemistry can be used to synthesize and functionalize nanoparticles for a variety of applications. Integration of colloidal particles into microfabricated structures for sensor function remains a challenge. In this study we investigate the use of nanohole arrays to produce ordered, non close-packed arrays of gold colloids. Using Focused Ion Beam (FIB) techniques, we are able to produce nanosieve structures in silicon nitride membranes with hole diameters down to 35nm with spacings as small as 50nm. When a colloidal suspension is 'filtered' through the nanosieve, it is possible to size the holes so that individual colloids cannot pass through, but are trapped and block subsequent flow, resulting in a single colloid, trapped at each hole (shown schematically in figure 1). In this way, arrays of non-touching colloids can be fabricated. Figure 2 shows lines of 100nm Au colloids on 150nm pitch prepared by this technique.

Figure 1.

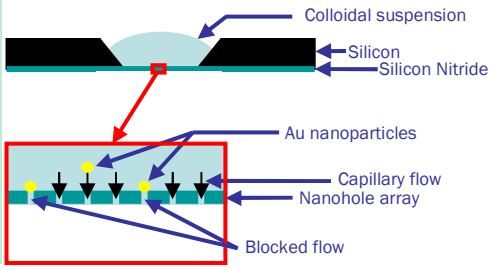


Figure 2.