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Benchmarking surface sensitivity of LSPR sensors: comparison of experimental methods

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Summary:
Localized surface plasmon resonance (LSPR) principle-based biosensing methods enable the detection of various target molecules. When illuminated by a light source, oscillation of the free electrons occurs on the surface of the metal nanoparticles, thus enhancement of the scattering and absorption can be observed. The plasmon decay plays a major role in the signal enhancement from immobilized molecules. Therefore, estimating the field enhancement profile is the key to LSPR sensor benchmarking. Here, we compare two techniques utilizing Layer-by-Layer (LbL) and atomic layer deposition (ALD)

Keywords: localized surface plasmon resonance (LSPR), plasmonic nanostructure, refractive index sensing, plasmon decay length, layer-by-layer (LBL), atomic layer deposition (ALD)

Background, Motivation and Objective

LSPR sensors have been in the scientific focus, due to their great advantages, such as real-time monitoring of label-free molecular interactions, high sensitivity and selectivity. The detection of target molecules (e.g., proteins, DNA, etc.) can be estimated from the peak shift of the extinction spectra [1], which corresponds to changes of the refractive index surrounding plasmon nanoparticles. The scale of sensors' optical response depends greatly on the plasmonic structures and their field confinement and enhancement. Therefore, to maximize the performance and the signal, it is crucial to precisely define and control the size, shape, interparticle distance, and material properties with respect to the size of target molecules [2]. These properties affect the plasmon decay length of the metal nanoparticles, which helps us to define the effective sensing range of the sensors. For many nanoparticles with a diameter of 50–100 nm, their plasmon decay length can be observed in an exponential decay, around 5–10 nm, which can be compared to the size of protein molecules [3].

Mapping the field enhancement around the plasmonic nanoparticles is a crucial part in optimizing the performance of the sensors. Plasmon penetration depth can be studied in many ways: one research used a less invasive technique, applying biomolecules [4] on the gold nanoparticles.

However, one of the most frequently chosen methods for immobilization is the layer-by-layer (LBL) deposition method, which gives us an opportunity to precisely control the number of the layers and to characterize our sensors while offering a cost-effective, reliable solution. The layers are built from two different solutions (where one is positively charged, the other is negatively charged), which overlap one another at a molecular level, thus a homogenous optical material is created [5].

Another method to create precisely controlled conformal ultra-thin layers on the nanoparticles, is the atomic layer deposition (ALD) technique, which is a chemical synthesis process, where the gas-phase deposition is under high vacuum conditions [6]. Multiple self-terminating surface reactions are repeated precisely in order to grow the layers. ALD is particularly effective for modifying metallic surfaces; it can be used to funetune plasmonic characteristics, or to protect them from contamination and oxidation [7].

In this work, we study the effect of utilizing polyelectrolyte bilayers (created by LBL deposition) with different thicknesses on the target signal, to determine the signal's dependency on the distance from the particles. Furthermore, we compare the results to the measurements with ALD technique.

Description of the New Method or System

The samples containing the nanoparticles were created by annealing thin (8nm) Au film deposited by magnetron sputtering on a borosilicate glass wafer, which was followed by reactive ion

etching cut up to 12×7 mm sensors (Fig.1), which were oxygen plasma cleaned prior to use.

Fig. 1. The uniform thin film-based LSPR sensor on a glass wafer

LBL deposition was carried out by utilizing a microfluidic system, which enabled the control of the fluids during the experiment. Each additional layer on the gold nanoparticles caused a shift of the resonance peak positions that were detected by a spectrometer.

For the LBL deposition, 0.1mM polystyrene sulfonate (PSS) and 0.1 mM polyallylamine hydrochloride (PAH) were used in 0.1 M NaCl buffer. Both solutions were alternatively pumped over the chip, with water injection in between every step. The decay length (l_d) is calculated using the LSPR shift ($\Delta\lambda$) and the layer thickness (d). One bilayer of PAH/PSS is around ~4 nm, and the refractive index of n = 1.5. The measurements were carried out in a microfluidic chamber integrated into an LSPR experimental setup.

In the case of the ALD technique, trimethylaluminium (TMA) and oxygen were used as precursors. Growth per cycle (GPC) was 0.156 nm per cycle; the thickness of the film can be controlled by the number of cycles. The following Al_2O_3 layer thicknesses were applied on different chip samples: 1, 2, 4, 8, 16, 32, 64, 128 nm.

Results

The optical spectra of the sensors were taken in air (n=1) before and after ALD treatment. The layer thickness was measured with ellipsometry on a calibration piece of Si wafer. Figure 2. shows scanning electron microscope (SEM) images of selected nanoparticles.

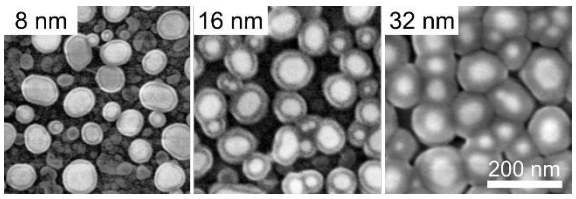

Fig. 2. SEM images of selected AuNPs covered by Al_2O_3 layers deposited by ALD.

The results of the ALD and LBL depositions and the peak shifts are presented in Figure 3. ALD offers a better solution for mapping the plasmon field around the nanoparticles, since the layer properties are more defined than in the case of LBL.

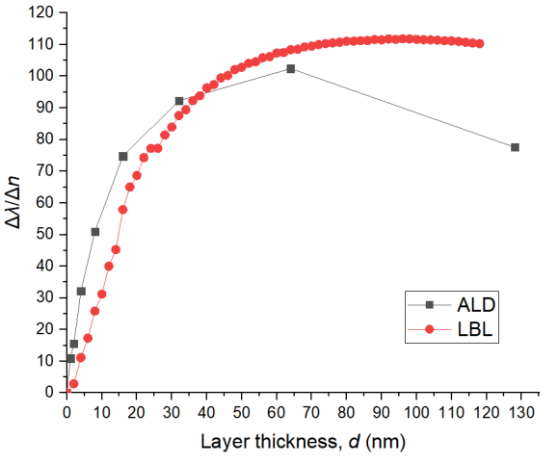

Fig. 3. Comparison of the ALD and LBL results.

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