OPTIMIZATION OF LOCALIZED SURFACE PLASMON RESONANCE (LSPR) TRANSUDCERS

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Background

Nanostructured metal (e.g., gold) surfaces support localized surface plasmon resonance (LSPR), i.e., charge density oscillations exhibited as an optical extinction band. The LSPR band is sensitive to changes in the refractive index (RI) near the nanostructures; hence, change of the RI as a result of, e.g., molecular binding to the metal nanostructures, leads to variations in peak wavelength and intensity. Such systems can thus be employed as optical transducers for chemical and biological sensing, using appropriate recognition layers for specificity. Here we study gold nano-island films prepared by evaporation on transparent substrates and annealing, offering simplicity and low cost.

In biosensing, for the need for a recognition interface comprising biomolecules raises the issue of the decay length of the plasmon evanescent field. The LSPR transducer response $R$ (as intensity change or wavelength shift) is commonly described by: \( R = m R(n_l - n) \left| 1 - \exp(-d/l) \right| \), where $m$ is the bulk RI sensitivity (RIS), $R(n_l - n)$ is the change in the effective RI associated with the adsorbate, $d$ is the thickness of the adsorbate layer, and $l$ is the plasmon decay length. Obtaining a maximal response requires optimization of the RIS $m$ and decay length $l$ of the LSPR transducer (see box on the right).

Gold nano-islands and polyelectrolyte coating

High-resolution SEM images of Au island films evaporated on glass slides, annealed 10 h at 580 °C. Left – samples of different nominal thicknesses (indicated); center and right – 10 nm (nominal thickness) islands, coated with 40 polyelectrolyte layers.

Building a multilayer: Transmission spectroscopy

Polyelectrolyte multilayers were grown on samples of various Au nominal thicknesses, until the peak wavelength approached a limiting value. Exponential regression to eq 1 provides $m$ and $l$.

Response to polyelectrolyte adsorption

Plasmon peak wavelength shifts (left) and intensity change (right) for the deposition of polyelectrolyte layers on Au island films of indicated nominal thicknesses.

Decay length and refractive index sensitivity

The RIS ($m$) and decay length ($l$) were extracted from the response plots using exponential regression to eq 1.

The result: $l$ and $m$ are strongly correlated, and increase with the nominal thickness.

Hence, choosing transducers with higher RIS may result in weaker response, due to mismatch between the large decay length and the biomolecule size.

Importance of the decay length

For a prominent response, the binding event (e.g., an antigen binding to an antibody) has to take place in a region of a strong field and occupy a large part of the region. Thus, the decay length, which defines the sensing volume, has to be optimized to the application (i.e., to the dimensions of the recognition layer and the analyte).

Polyelectrolyte multilayers

Each PAH/PSS bilayer is 2.09 ± 0.03 nm thick (measured by spectroscopic ellipsometry; $n = 1.56$ in the visible range)

Maximizing the response

Incremental wavelength shift for the adsorption of a 2.1-nm-thick polyelectrolyte bilayer on an existing polyelectrolyte multilayer of varying thickness; Au nominal thicknesses are indicated. Calculated using eq 1 and the extracted $m$ and $l$.

The strongest response for thin adlayers (e.g., biomolecules) is expected from small islands, despite their lower RIS, owing to better matching between the adlayer thickness and the small decay length (i.e., the available sensing volume).

Conclusions

We have shown that the decay length is directly correlated to the refractive index sensitivity (RIS), meaning that higher RIS does not always produce the strongest response. Transducer optimization for high performance requires matching of both parameters to the specific application.