

# **OPTIMIZATION OF LOCALIZED SURFACE PLASMON RESONANCE (LSPR) TRANSDUCERS**

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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, 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:  $R=m(n_2-n_1)(1-\exp[-d/l])$ , where m is the bulk RI sensitivity (RIS),  $(n_2-n_1)$  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

#### **Importance of the decay length**

For a prominent response, binding event (e.g., an the 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).

dt 10

Au Antibody Just right

#### Gold nano-islands and polyelectrolyte coating



Polyelectrolyte multilayer





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.

Left and center – plan view; right – 30° tilt, In-Lens (left) and chamber mounted Everhart-Thornley (right) SE detectors, 10-20 kV; coated with 2-3 nm Cr.

#### **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*.

## **Polyelectrolyte multilayers**



#### Each PAH/PSS bilayer is 2.09 ± 0.03 nm thick

**Left**: Changes in the extinction spectrum with layer growth; **right**: Change in the peak wavelength and intensity, for 3 nm (nominal thickness) islands.

(measured by spectroscopic ellipsometry; n = 1.56 in the visible range)

Adsorption solution: 1 mM (monomer) polyelectrolyte in 0.1 M aqueous NaCl; 15 min per deposition step.

### Maximizing the response

Incremental wavelength shift —— 3nm for the adsorption of a 2.1-🗕 5nm polyelectrolyte nm-thick 🗕 – – 6nm 🗕 7.5nm an existing bilayer on →— 9nm polyelectrolyte multilayer of thickness; varying Au thicknesses nominal are indicated. Calculated using 35 40 eq 1 and the extracted *m* and *I*.

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).

20 25 30

Adsorption distance (nm)

#### **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**

⊤ ⊣140



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

The result: *I* and *m* are strongly correlated, and increase with the nominal thickness.

Left: Decay length / and refractive index sensitivity (RIS) m (both for wavelength shift) vs Au nominal thickness. **Right:** RIS vs decay length, for the various Au transducers studied (nominal thicknesses indicated).

Error bars represent standard deviation or average standard error (larger of the two) of four samples per Au size.

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

# 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 the specific to application.

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