



# Distance Sensitivity in Localized Surface Plasmon Resonance Systems

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## Background

Nanostructured metal (e.g., gold) surfaces support localized surface plasmon resonance (LSPR) excitation, exhibited as an optical extinction band in the visible range. The LSPR band (intensity and wavelength) is sensitive to changes in the refractive index near the metal nanostructures, resulting in changes in the extinction spectrum upon molecular binding.

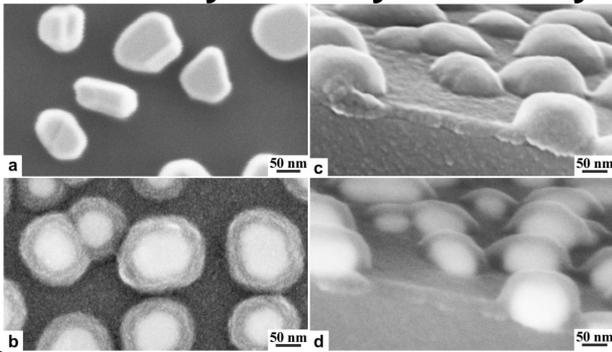
### The issue

In biosensing, the common need for a recognition interface comprising bulky receptors raises the issue of the decay length of the plasmon evanescent field. A model assuming exponential decay of the evanescent wave gives the relationship  $R = m\Delta\eta[1 - \exp(-2d/l_d)]$  where  $R$  is the response (as intensity change or wavelength shift),  $m$  is the bulk refractive index sensitivity,  $\Delta\eta$  is the change in the effective refractive index associated with the adsorbate,  $d$  is the effective thickness of the adsorbate layer, and  $l_d$  is the plasmon field decay length.

### The solution

Determine the decay length of metal nanoisland systems using a layer-by-layer (LbL) scheme of alternate adsorption of oppositely-charged polyelectrolyte layers. The method provides regular film growth and control over the thickness on the nanometer scale.

## Polyelectrolyte multilayers on gold nano-island films

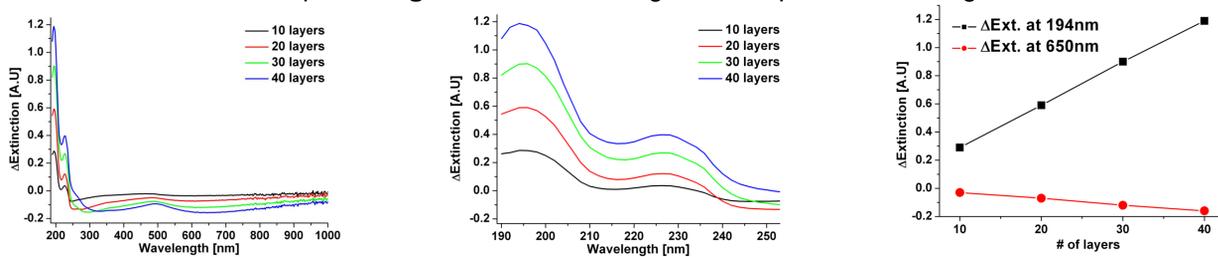


High-resolution SEM images of a gold nano-island film on glass substrate (10 nm nominal thickness, annealed at 550 °C for 10 hrs).

(a) Pristine Au nano-island film. (b-d) Nano-islands coated with a polyelectrolyte multilayer (8 pairs of PAH/PSS), prepared in 1.0 M NaCl. (b) Top view and (c, d) isometric projection (20° tilt). Samples b-d coated with 3 nm Cr and scanned using the (b, c) In-lens and (d) SE detectors at 10 kV.

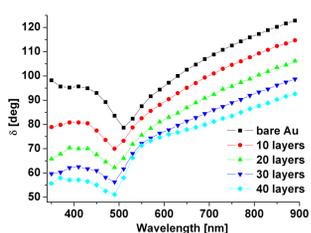
## Regularity of layer growth

**Left:** Transmission UV-vis spectra of polyelectrolyte multilayers on a continuous gold layer on quartz; **middle:** Growth of the PSS aromatic peaks; **right:** Extinction change at two specific wavelength.



PAH/PSS prepared in 0.1 M NaCl. Au substrate: 20 nm evaporated on silanized quartz, annealed at 200 °C for 20 hrs.

## Spectroscopic ellipsometry



Ellipsometric spectrum

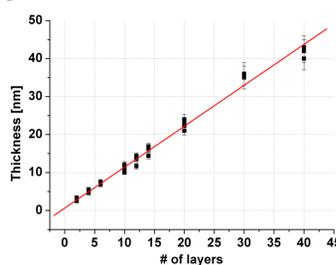
PAH/PSS prepared in 0.1 M NaCl. Au substrate: 20 nm evaporated on silanized glass, annealed at 200 °C for 20 hrs.

1. Fit a Cauchy model to find layer thickness:

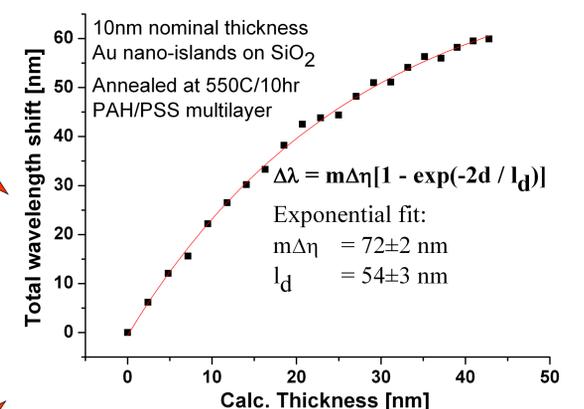
$$n(\lambda) = A + B / \lambda^2 + C / \lambda^4$$

$$k(\lambda) = k_1 \cdot \exp[k_2 \cdot (E - E_b)]$$

2. Fit a linear model to find layer number / thickness relationship



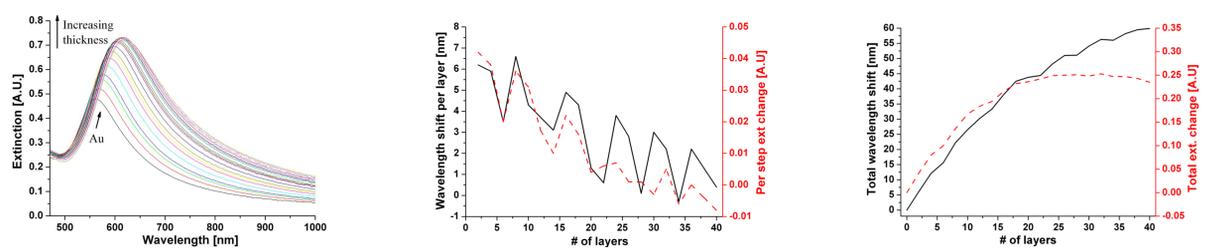
## Finding the decay length



Fitting an exponential model to the wavelength shift of the plasmon peak with increasing polyelectrolyte thickness, yields the decay length.

## Localized surface plasmon response

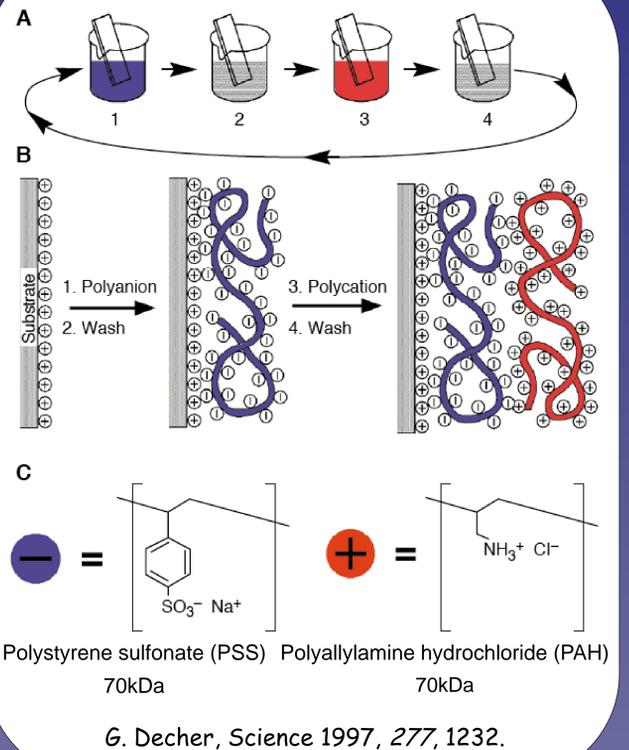
**Left:** Changes in the extinction spectrum with layer growth; **middle:** Change in the plasmon peak of each layer; **right:** Total change in the plasmon peak.



PAH/PSS prepared in 0.1 M NaCl. Au island film substrate: 10 nm nom. thickness evaporated on glass, annealed at 550 °C for 10 hrs

## Conclusions

LbL assembly of polyelectrolyte multilayers may be applied to the evaluation of the localized plasmon decay length in gold nano-island systems, using a simple procedure and analysis. This approach will be used for determining the decay length of various Au island systems, in order to gain understanding of factors affecting the decay length and to optimize the response of localized plasmon transducers.



## Film thickness using AFM

A 'window' was created in the polyelectrolyte film using the cantilever in the contact mode.

The thickness (measured in the ac mode) of 18 layers is approx. 30 nm.

9 double layers (PAH/PSS) prepared in 1.0 M NaCl. Au substrate: 20 nm evaporated on silanized glass, annealed at 200 °C for 20 hrs.

