Spatially resolved localized plasmon response of gold island films

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Abstract: Gold nanostructures are known to support excitation of localized surface plasmons (SPs) in the visible-to-near IR spectral range. The conditions of SP excitation are sensitive to changes in the dielectric properties of the immediate environment, opening possibilities for optical sensing. The refractive index sensitivity of Au island based transmission localized surface plasmon resonance (T-LSPR) transducers, defined as the change in extinction (plasmon intensity change, PIC) or the shift of the wavelength of maximum extinction per refractive index unit (RIU) change, was determined using different solvents as immersion media.

Mapping of the spatial distribution of the local RI sensitivity of T-LSPR transducers may enable sensor optimization for various applications. Binding of analyte to different types of sites, i.e., to the Au islands or to the substrate between the islands, is expected to show a different sensitivity. In this work the spatial variation in the T-LSPR response was studied using Au island films on glass substrates as model transducers, and Au nanoparticles (NPs) as an analyte probe. Site-specific NP binding was achieved using self-assembly schemes, verified by scanning electron microscopy (SEM) and atomic force microscopy (AFM) imaging.

Changes in the UV-vis spectra induced by spatially-resolved NP binding were measured.

Preparation

- Au evaporation
  - Thickness: 10 nm
  - Rate: ~0.006 nm/sec
- Annealing
  - 550°C, 10 hrs

Spatial selective immobilization

- On islands: SA of C18SH
- Between islands: SA of di-C10/MPTMS NPs

TOAB NPs

HRSEM AFM

Spatial selectivity: The chemical difference between the gold islands and the substrate was exploited for achieving preferential analyte binding to the islands or to the substrate. Thiol (-SH) chemistry was used for binding to the Au islands, whereas silane (-Si(OCH3)3) provided binding to the glass substrate.

The self assembly (SA) procedure:
1) Au island blocking with 1-octadecane thiol (C18SH);
2) SA of 1,10-decanedithiol (HS-C10-SH) - "On islands" or SA of 3-mercaptopropyl trimethoxysilane (MPTMS) - "Between islands";
3) Verification of the spatially resolved binding by SA of tetraoctylammonium bromide (TOAB) capped Au NPs.

Refractive index sensitivity:

The refractive index sensitivity of annealed gold island films was determined by transmission measurements in mixtures of methanol and chloroform (n1 = 1.33 to 1.45).

Summary:
- The bulk refractive index sensitivity of 10 nm Au island films, annealed, is 153 nm/RIU and 0.67 abs. u./RIU.
- Lateral control of molecular binding to Au island films was achieved using site-directed self-assembly schemes.
- The LSPR response to analyte binding to the gold islands as well as between the islands was measured.