Optical Transducers for Gas Sensing in Transmission Surface Plasmon Resonance (T-SPR) Spectroscopy

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Ultrathin (typically < 10 nm thick) gold island films evaporated on transparent substrates show a localized surface plasmon (SP) excitation in the visible-to-NIR range (550-800 nm). Changes in the dielectric properties of the contacting medium influence the excitations of surface plasmons and hence the SP absorption band, providing a scheme for optical sensing in the transmission surface plasmon resonance (T-SPR) mode [Kalyuzhny, Vaskevich, Schneeweiss, Rubinstein, Chem. Eur. J. 2002, 8, 3650]. In the present work the 3D shape of the gold islands was studied using high-resolution scanning electron microscopy (HRSEM), cross-sectional transmission electron microscopy (TEM), and atomic force microscopy (AFM). The shift of the wavelength of the SP band maximum upon change in the effective dielectric constant of the medium was measured using the experimental data on the island morphology.

The applicability of T-SPR spectroscopy to gas sensing was explored using polymeric coatings on the Au island films. T-SPR transducers were fabricated by spin-coating of polystyrene (PS) onto optimized Au island films (>5 nm-thick, Au, evaporated on silanized glass and annealed) [Doron-Mor, Barkay, Filip-Granit, Vaskevich, Rubinstein, Chem. Mater. 2004, 16, 3476]. The influence of chloroform vapor on PS film thickness, morphology and stiffness was examined by in-situ AFM under controlled atmosphere. The PS film undergoes significant thickness change upon exposure to chloroform vapor (up to ~35% increase in 20 nm films), thus presenting an effective and convenient platform for T-SPR gas sensing.

The optical response (change in the T-SPR spectra) of PS overlayers on Au island films to controlled amounts of vapor analytes was studied. Transducers with PS coatings show a different optical response to vapors of good (chloroform and toluene) and poor (methanol and water) solvents. The response is fast (~15 sec) and reversible. Gold island systems coated with polymeric films of different properties can be thus applied to gas sensing as a single sensor for concentration determination of a certain vapor, or to vapor recognition in an array (fingerprinting) configuration.

**Theoretical treatment: Maxwell-Garnett effective medium model**

\[ n_{\text{eff}} = \frac{\sum_{i} \phi_{i} n_{i}^{2}}{\sum_{i} \phi_{i} n_{i}^{2}} \]

where

- \( n_{\text{eff}} \) is the effective dielectric constant of a granular metal layer
- \( n_{i} \) is the dielectric constant of the bulk metal
- \( \phi_{i} \) is the volume fraction of the component i

The model spectra were calculated for Q=0.337, nd = 1.917, and A = 2.105. The experimental data was fitted for \( n_{Q} = 0.67 \). The optical response (change in the T-SPR spectra) of PS overlayers on Au island films to controlled amounts of vapor analytes was studied. Transducers with PS coatings show a different optical response to vapors of good (chloroform and toluene) and poor (methanol and water) solvents.

**Summary**

- The shape of gold islands evaporated on transparent substrates was studied by HRSEM and cross-sectional TEM. Upon annealing, the islands undergo coalescence and attain oblong, nearly spherical shapes, increasing the size and separation between islands and decreasing the relative contact area with the substrate. The reshaping leads to a sharper SP absorption band and a blue shift of the band maximum.
- The modified Maxwell-Garnett approximation provides a good prediction of the wavelength of maximum SP absorption for annealed (but not for unannealed) gold island films, using the experimental data on the island morphology.
- The optical response of T-SPR transducers with PS coatings depends on the solubility of PS in the analyte solvent. Vapors of good solvents (chloroform, toluene) induce PS swelling and thickness increase, manifested as a fast and fully reversible optical response to the presence of the analyte. No response is seen to poor solvent vapors (water, methanol).

**Bioactivities**

- Chloroform affects the absorption band in PS films (~80-100 nm thick).