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

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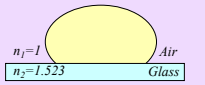
Ultrathin (typically <10 nm thick) gold island films evaporated on transparent substrates show a localized surface plasmon (SP) extinction in the visible-to-NIR range (550-800 nm). Changes in the dielectric properties of the contacting medium influence the excitation of surface plasmons and hence the 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, 3850]. 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 modeled 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) compared to poor (methanol and water) solvents. The response is fast (~15 sec) and reversible. Gold island systems coated with polymeric films of different properties can thus be 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*



$$\frac{\varepsilon_c - 1}{\varepsilon_c + 2} = Q\left(\frac{\varepsilon - n_d^2}{\varepsilon + 2n_d^2}\right)$$

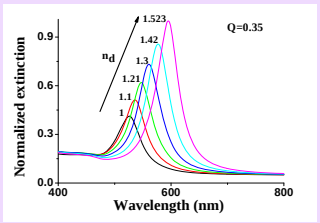
*Doremus, R. H. J. Appl. Phys. 1966, 37, 2775-2781; Doremus, R. Thin Solid Films 1998, 326, 205-210

- ε_c effective dielectric constant of a granular metal layer embedded in a dielectric medium,
- ε dielectric constant of the bulk metal,
- Q volume fraction of the metal,
- n_d refractive index of the surrounding medium

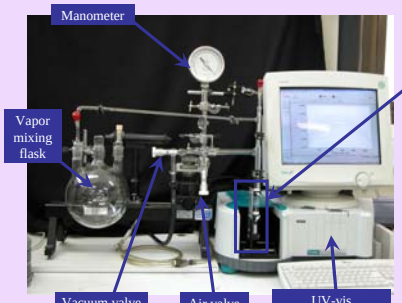
Simulated transmission spectra were generated using TFCalc 3.5 optics software, using the effective dielectric constant ε_c calculated from the Doremus equation. Changes in island morphology were accounted for by variation of the parameter x:

$$n_d = x \cdot n_1 + (1-x) \cdot n_2$$

- x fraction of Au island surface in contact with air

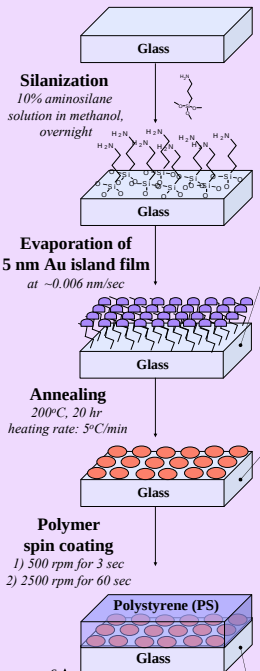


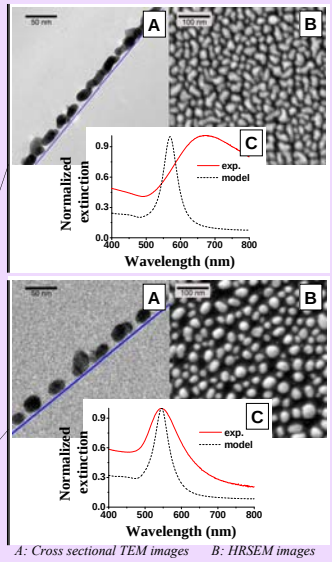
Experimental setup



- ✓ *The system is pumped down to low vacuum (~300 Pa)*
- ✓ *Organic solvent (analyte) is evaporated in the mixing flask, and the flask is separated*
- ✓ *The system is pumped down, filled with air/N_2 and a substrate is inserted into the cell*
- ✓ *The measuring cell is pumped down*
- ✓ *Gas mixture is transferred to the measuring cell*
- ✓ *UV-vis spectrum is measured at various relative pressures of the analyte (P/P_{sat})*

Substrate preparation and characterization

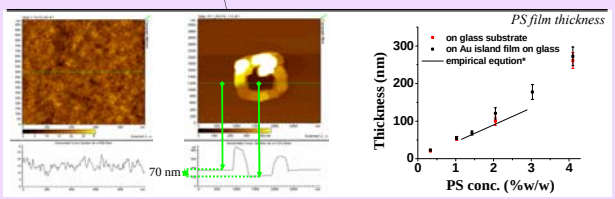




A: Cross sectional TEM images B: HRSEM images
C: Normalized transmission spectra

The model spectra were calculated for Q=0.337, n_d=1.21

	Unannealed			Annealed		
	a	b	c	a	b	c
Average particle dimension (nm)	30.2±8.6	18.9±4.3	13.3±1.6	30.3±7.4	23.7±5	21.9±5.9
Particle density (μm^{-2})	1000			700		
Average particle volume (nm^3)	5038.9			10537.9		
Volume fraction (%)	42.8			33.7		

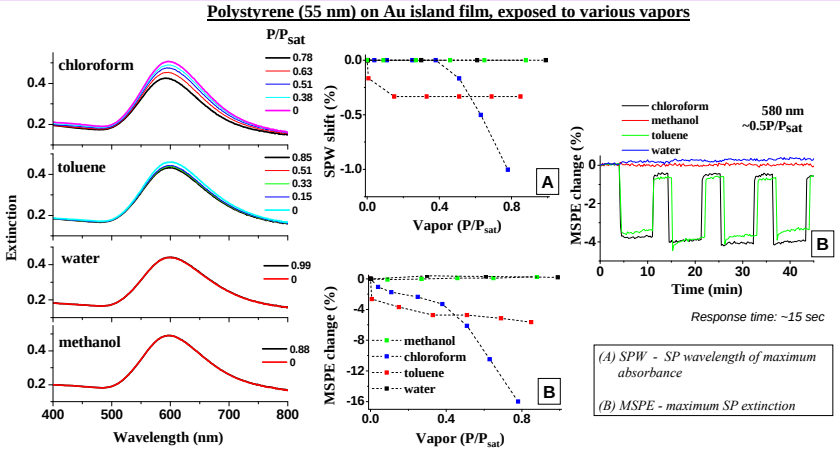


AFM images of a PS film spin-coated on Au island film from 1.5% PS solution in toluene.

**Schubert, D. W.; Dunkel, T. Mat. Res. Inn. 2003, 7, 314-321.*

T-SPR Spectroscopy

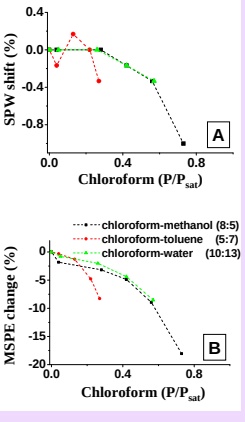
Polystyrene (55 nm) on Au island film, exposed to various vapors



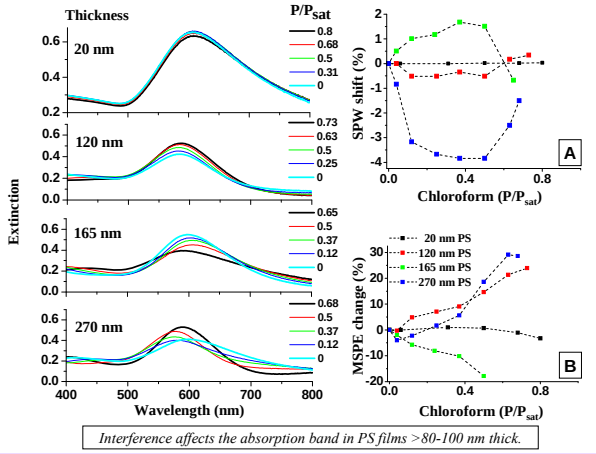
(A) SPW - SP wavelength of maximum absorbance

(B) MSPE - maximum SP extinction

Polystyrene film (55 nm) in vapor mixtures

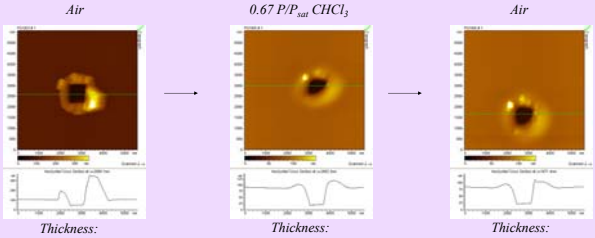


Polystyrene films in chloroform vapor



Interference affects the absorption band in PS films >80-100 nm thick.

In-situ AFM: PS structural change in chloroform vapor



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 oblate spheroid shape, 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). Interference effects in T-SPR transducers with thick polymer coatings can be used for fingerprinting. Gold island systems coated with polymeric films are therefore promising transducers for gas sensing.