Evaporated Gold Island Films for Special Optical Applications

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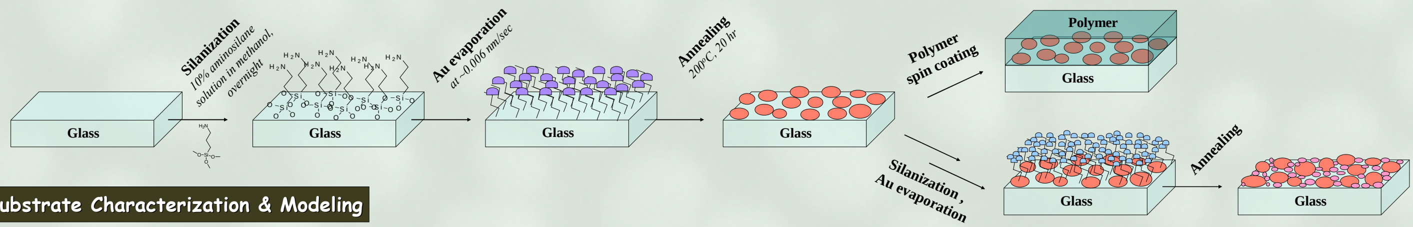
Abstract

Evaporated gold island films subjected to electromagnetic radiation show a localized surface plasmon (SP) resonance exhibited as enhanced light scattering, the appearance of a SP absorption band, and enhancement of local electromagnetic fields. These unique properties have been applied to chemical and biological sensing using transmission localized surface plasmon resonance (T-LSPR) spectroscopy and surface-enhanced Raman spectroscopy (SERS). Development of these and other applications requires optimization of the morphology and optical properties of the island films.

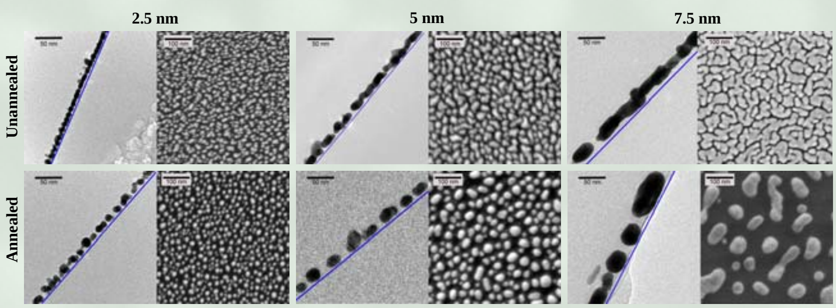
Tuning of the Au film morphology can be achieved by variation of the evaporation conditions (rate, substrate modification with adhesion layer) and post-deposition treatment (annealing at moderate temperatures). Consecutive evaporation steps provide gold films with a unique hierarchical structure. The 3D shape of the gold islands was studied by high-resolution scanning electron microscopy (HRSEM) and cross-sectional transmission electron microscopy (TEM). Extinction UV-vis spectra of evaporated Au films were measured and simulated using the Maxwell-Garnett mean field approximation and the experimentally determined geometrical parameters of the island ensemble.

Application of T-LSPR spectroscopy to gas sensing was demonstrated using the structural sensitivity of polymer films to different gases. T-LSPR transducers were fabricated by spin-coating of a polymer film onto Au island films (5 nm nominal thickness, evaporated on silanized glass and annealed). The optical response of the transducers to controlled amounts of analyte vapors was distinctly different between vapors of good compared to poor solvents, suggesting possible use in gas recognition.

Gold island films with various morphologies were studied as substrates for SERS, using Rhodamine 6G (R6G) as a model analyte. Substantial enhancement of the SERS signal was achieved when using the hierarchical film roughness obtained by a two-step evaporation procedure.

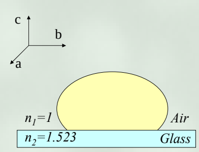


Substrate Characterization & Modeling

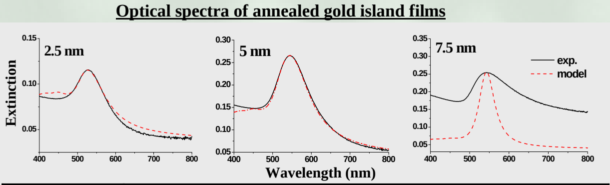


Cross-sectional TEM (left) and HRSEM (right) images

Nominal thickness (nm)	a (nm)	b (nm)	c (nm)	Q
2.5	15±3	13±3	13±2	0.29
5	30±7	24±5	22±6	0.27
7.5	71±42	43±15	39±8	0.19



Optical spectra of annealed gold island films



Nominal thickness (nm)	Q	Average particle radius (nm)		n_d
		Exp.	Model	
2.5	0.29	6.9	9	1.26
5	0.27	13	10	1.44
7.5	0.19	25.5	25.5	1.44

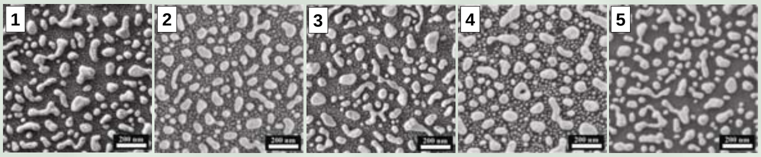
$$\frac{\varepsilon_c-1}{\varepsilon_c+2}=Q\left(\frac{\varepsilon-n_d^2}{\varepsilon+2n_d^2}\right)$$

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

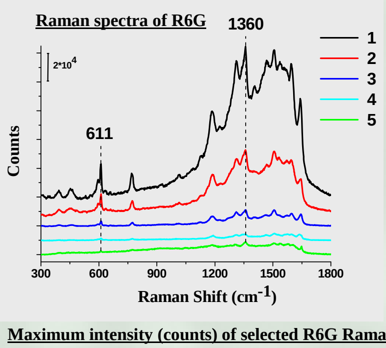
**Doremus, R. H. J. Appl. Phys. 1966, 37, 2775-2781;Thin Solid Films 1998, 326, 205-210.*

Simulated transmission spectra were generated using TFCalc 3.5 optics software, using the effective dielectric constant ε_c calculated from the Doremus equation. The refractive index of the surrounding medium was adjusted between $n_{air}=1$ and $n_{glass}=1.523$.

Surface-Enhanced Raman Spectroscopy



Raman spectra of R6G



- 1 ➢ *7.5 nm Au annealed + silane + 2.5 nm Au*
- 2 ➢ *7.5 nm Au annealed + silane + 2.5 nm Au annealed*
- 3 ➢ *7.5 nm Au annealed + 2.5 nm Au*
- 4 ➢ *7.5 nm Au annealed + 2.5 nm Au annealed*
- 5 ➢ *7.5 nm Au annealed*

Phodamine 6G (R6G) was adsorbed from $5\cdot10^{-5}$ M solution in ethanol. Raman spectra were measured at λ_{ext} = 633 nm, P = 25 mW, acquisition time = 30 sec.

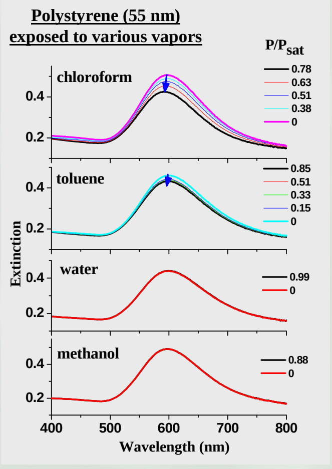
Maximum intensity (counts) of selected R6G Raman peaks

Raman frequency \ Sample	1	2	3	4	5
611	23691	12332	9964	1788	3089
1360	104684	42896	11652	4758	9050

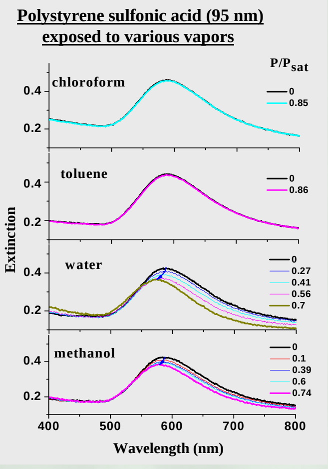
Gas Sensing

T-LSPR transducers were fabricated by spin-coating of polymer layers onto Au island films (5 nm nominal thickness, evaporated on silanized glass and annealed).

Polystyrene (55 nm) exposed to various vapors



Polystyrene sulfonic acid (95 nm) exposed to various vapors



Summary

- Evaporated Au island films were studied as possible candidates for T-LSPR sensing and SERS substrates. Upon annealing the islands undergo coalescence and attain an oblate spheroid shape, increasing the average island size and separation between islands and decreasing the relative contact area with the substrate.
- The optical response of polymer-coated T-LSPR transducers is sensitive to vapor analytes. Vapors of good solvents induce polymer 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. Polymer-coated Au island systems are therefore promising transducers for gas sensing in an array configuration (fingerprinting).
- The Raman spectrum of Rhodamine 6G adsorbed on a two-layer hierarchical Au island film was substantially enhanced relative to that obtained with a regular Au island film. Such substrates are therefore promising for surface-enhanced Raman spectroscopy (SERS) and can be optimized by controlling various morphological and interfacial parameters of the hierarchical system.