

Transmission Surface Plasmon Resonance (T-SPR)
Spectroscopy: Gold Island Film Morphology
and Optical Response

A. Vaskevich,^{*} I. Doron-Mor,^{*} M. Lahav,^{*} Y. Feldman[#]
and I. Rubinstein^{*}

^{*}Department of Materials and Interfaces

[#]Chemical Services Department
Weizmann Institute of Science
Rehovot 76100, Israel

Evaporation of ultrathin (≤ 10 nm nominal thickness) gold films onto inert substrates leads to the formation of a layer of gold islands. Such films show a surface plasmon (SP) extinction peak in the visible or NIR region (550-800 nm), which depends on the island film morphology. In a series of recent publications¹⁻⁴ we have shown that the SP absorption band (intensity and wavelength of maximum absorbance) changes upon binding of various molecules to the surface. This new method of optical measurements was termed Transmission Surface Plasmon Resonance (T-SPR) spectroscopy.³ T-SPR spectroscopy was shown to be applicable to both chemically and physically adsorbed molecules, in liquid or gas phase, with measurements carried out either *ex-situ* or *in-situ* (real-time measurements).^{2,3} The stability of Au island films was substantially improved by using glass modified with 3-mercaptopropyl trimethoxysilane (MPTS) as well as polystyrene as substrates for Au island evaporation.⁴ The sensitivity of T-SPR spectroscopy and the possibility to control the island film morphology, optical properties and stability are key issues in possible application of this new technique.

Binding of Cu^{2+} ions to a self-assembled monolayer (SAM) of 3-mercaptopropanoic acid (MPA) on Au was used to demonstrate T-SPR sensing in aqueous solutions. UV/vis spectra of an MPA-modified Au island film before and after binding of Cu^{2+} ions are shown in Fig. 1, demonstrating the possibility to detect binding of a small cation to a receptor layer on Au by T-SPR spectroscopy.

Controlled etching of Au island film in cyanide solution was used to achieve additional control over film morphology. Continuous dissolution of Au island films on polystyrene in cyanide solution was monitored *in-situ* by transmission UV/vis spectroscopy (Fig. 2). Note that in the initial stages of the etching a change of shape of the extinction spectra is observed, i.e., the two upper curves in Fig. 2 nearly intersect. Further etching results in a gradual decrease of the extinction intensity and a blue shift of the SP band maximum. This spectral behavior is consistent with gradual Au dissolution and disappearance of small islands. An increase of the mean distance between islands is a reasonable explanation for the blue shift of the SP band. At later stages of the dissolution the SP band position becomes stable with a maximum at $\lambda \approx 545$ nm (inset in Fig. 2). The rate of dissolution is conveniently controlled by the cyanide concentration, providing improved control over the entire process. Additional control is achieved by chemical (electroless) re-deposition of Au on the dissolved islands (not shown).

¹ G. Kalyuzhny, A. Vaskevich, G. Ashkenasy, A. Shanzer, I. Rubinstein, *J. Phys. Chem. B* **104** (2000) 8238-8244.

² G. Kalyuzhny, M. A. Schneeweiss, A. Shanzer, A. Vaskevich, I. Rubinstein, *J. Am. Chem. Soc.* **123** (2001) 3177-3178.

³ G. Kalyuzhny, A. Vaskevich, M. A. Schneeweiss, I. Rubinstein, *Chem. Eur. J.* **8** (2002) 3849-3857.

⁴ A. Vaskevich, G. Kalyuzhny, N. Filip Granit, M. A. Schneeweiss, I. Lichman, E. Klein, I. Rubinstein, 201st ECS Meeting, Philadelphia, 2002, Abstract No. 58

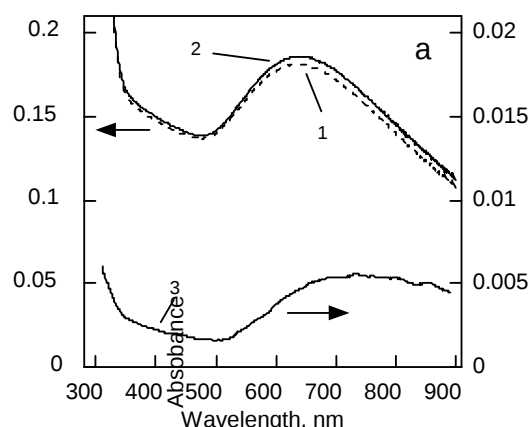


Figure 1. T-SPR sensing of the binding to a receptor layer on Au island film. Absolute spectra of a SAM of MPA on a Au island film before (1) and after (2) binding of Cu^{2+} ions from a 10 mM aq. CuSO_4 solution, and the difference spectrum (3) obtained by subtracting 1 from 2. Substrate: 1.5 nm (nominal thickness) Au film evaporated on MPTS-modified glass. All spectra were taken in air.

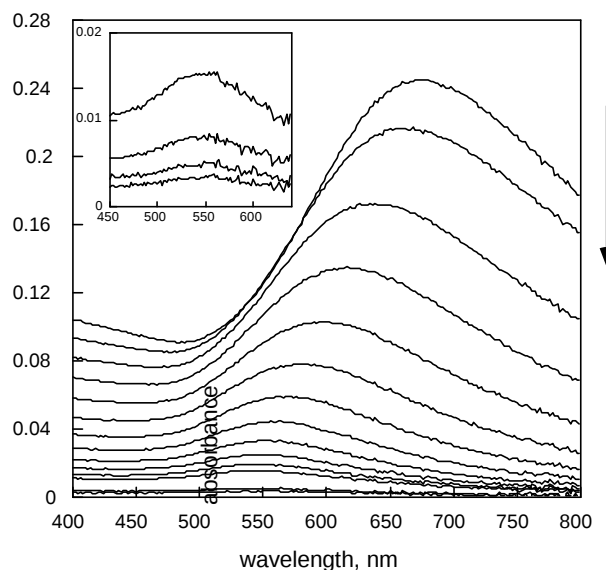


Figure 2. Evolution of the transmission UV/vis spectra of a 2.5 nm (nominal thickness) Au film evaporated on polystyrene, recorded during etching in a 2 mM aq. NaCN solution. Spectra recorded at time intervals of 30 s. Inset: Spectra taken at later stages of the dissolution, i.e., at 14, 16, 18, 20 min from the start.