# Nanostructured Gold Films on Glass: Morphology, Optical Properties and Stabilization

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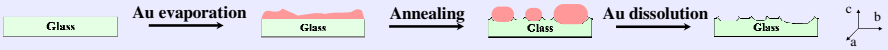
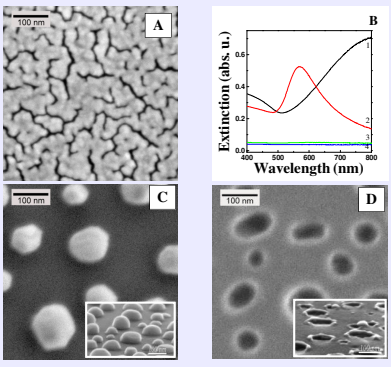
Gold island films prepared by resistive evaporation on glass, as well as citrate-stabilized Au nanoparticles (NPs) immobilized on aminosilane-modified glass, were stabilized by high-temperature annealing at a temperature close to the glass transition of the substrate. The stabilization is attributed to partial embedding of the gold nanostructures in the glass. The morphology and optical response of partially-embedded Au nanostructured films were exceedingly stable toward immersion in solvents, drying, and self-assembly of biological molecules.

The kinetics and the temperature dependence of the annealing of percolated Au films were studied using a special oven designed for *in situ* optical measurements under controlled atmosphere. Changes in the surface plasmon (SP) band during annealing were correlated with the development of Au film morphology, i.e., island formation and embedding in the glass substrate.

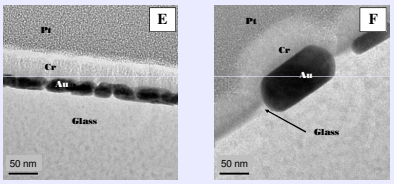
The refractive index sensitivity (RIS) of Au island films was studied systematically and was found to depend on the wavelength of the SP maximum extinction. The results may be useful in the preparation of Au island films with tunable morphology and optical response for application in LSPR sensing.




## Morphology: HRSEM and cross-sectional TEM



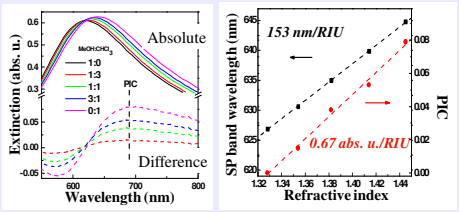

*a=105±28 nm b=87±22 nm c=40±10 nm*




A, E - *10 nm Au film, as prepared;*
C, *F – annealed 70 h (C) and 10 h (F) at 600 °C;*
D – *same as C, after Au dissolution in iodine tincture;*
B – *UV/vis spectra: 1 – as prepared, 2 - annealed, 3 - after Au dissolution, 4 – bare glass.*

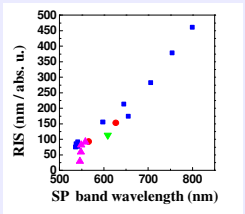
## Refractive index sensitivity (RIS)

*RIS measurements of 10 nm Au island film annealed at 550ºC*




*Transmission spectra were measured in mixtures of methanol (n=1.33) and chloroform (n=1.45).*

*Correlation between the RIS and SP band wavelength*

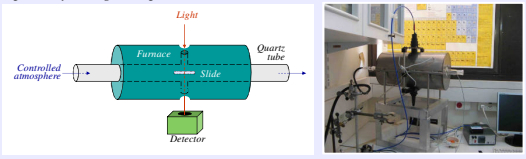



- *7.5, 10 nm Au island films, annealed 10h at 550ºC*
- *10 nm Au island film, annealed 10h at 600ºC*
- *2-15 nm Au island films, annealed 10h at 550ºC*
- *Au NP films*

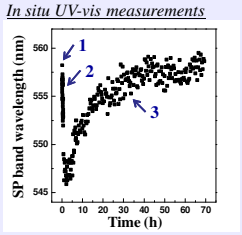
**Conclusion: the RIS can be estimated from the position of the SP band wavelength.**

## Kinetics: High-temperature annealing (600 °C)

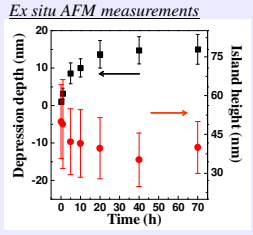
*Specially-designed optical oven*




*In situ UV-vis measurements*




*Ex situ AFM measurements*

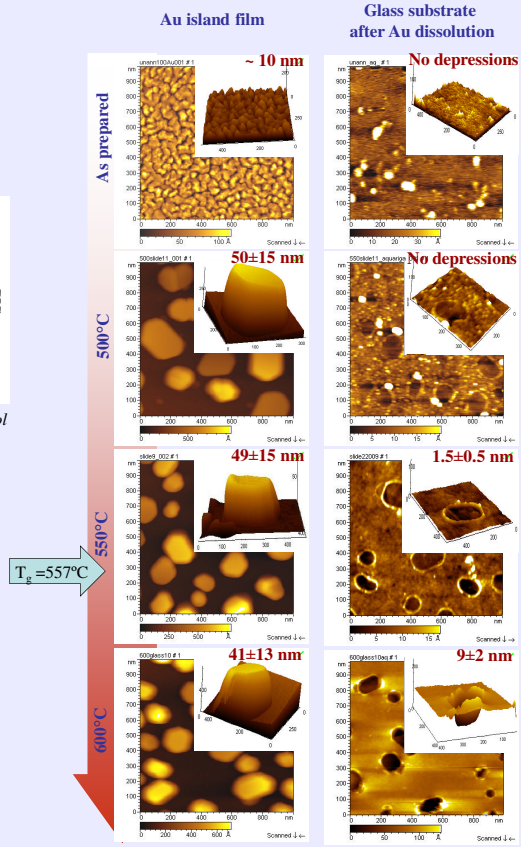



1) *SP band formation (~5min)*
2) *SP blue shift (3-5 h) – possibly change in island morphology*
3) *SP red shift (up to ca. 40 h) – embedding*

*Island height + depression depth ≈ 50 nm, remains constant*

**Conclusion: embedding with minimal island reshaping.**

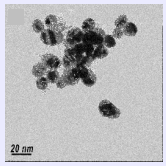
## The effect of annealing temperature: AFM



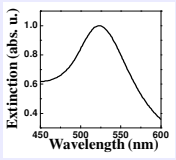

**Conclusion: embedding occurs at a temperature close to the $T_g$ of the glass substrate.**

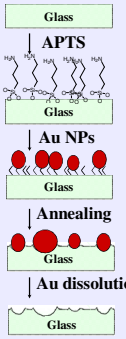
## Citrate-stabilized Au nanoparticles (NPs)

*TEM image*

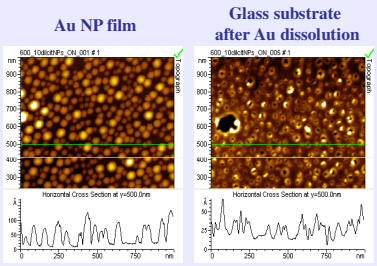



*UV/vis spectrum*

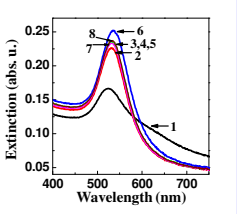



*AFM images: Morphology of Au NP films annealed 10h at 600 ºC*

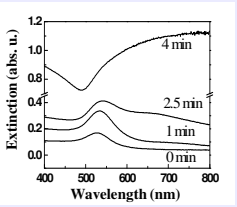



*Optical stability of Au NP films*




*1 – Au NP film as prepared; 2 – annealed; 3-5 – three sequential EtOH wash and dry cycles; 6 – $C_{18}SH$ monolayer + EtOH wash and dry; 7 – UV/ozone + EtOH wash and dry; 8 – immersion in PBS, followed by washing in water and drying*

*Electroless Au deposition on Au NP films*




*Electroless Au deposition was performed in 25 ml of 0.4 mM hydroxylamine hydrochloride + 0.25 ml of 0.1% chloroauric acid + 2.25 ml water.*