Thermal Stabilization of Localized Surface Plasmon Resonance Transducers

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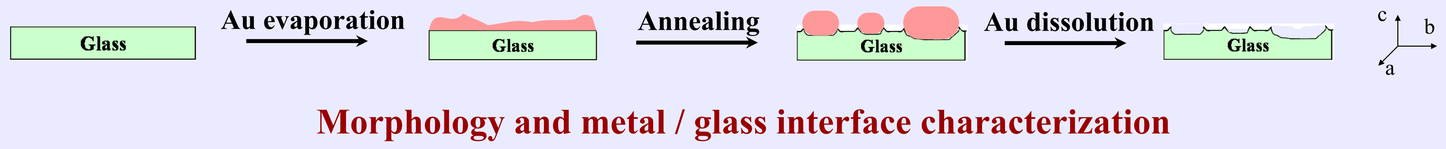
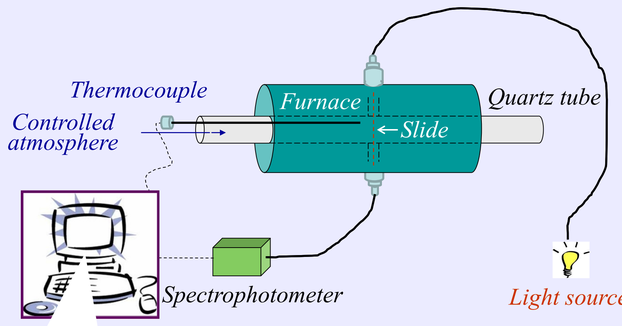
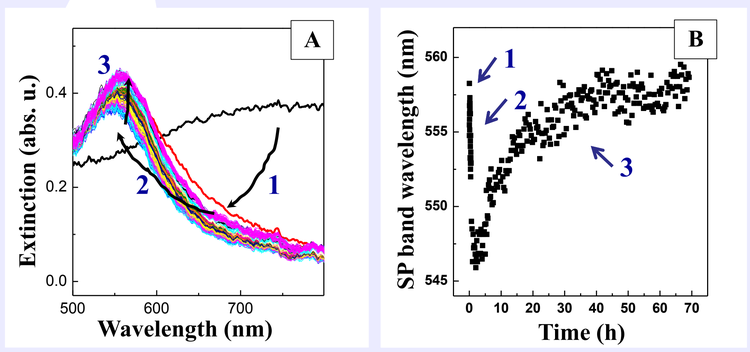
Gold island films prepared by resistive evaporation on glass were stabilized by high-temperature annealing at temperatures close to or higher than the glass transition of the substrate. The stabilization is attributed to partial embedding of the gold islands in the glass. The morphology and optical response of partially-embedded Au island 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 simplicity of the preparation and the high refractive index sensitivity achieved point to applications of stabilized Au island films as transducers for localized surface plasmon sensors.

High-temperature annealing kinetics

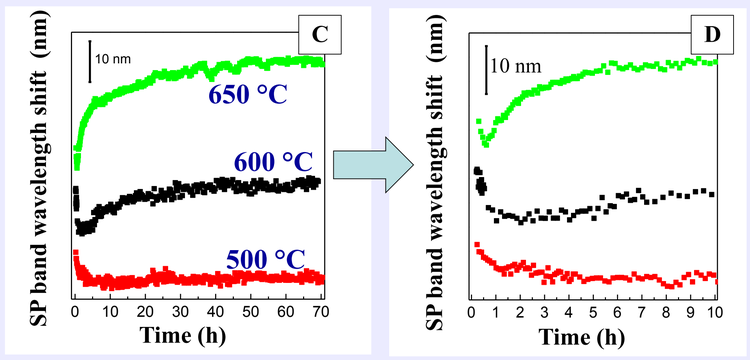


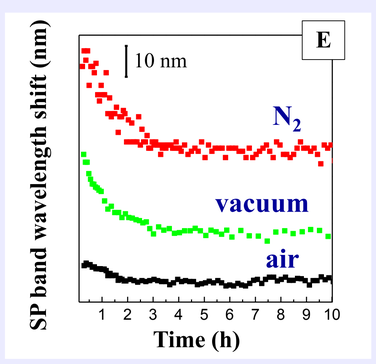


In situ UV-vis measurements



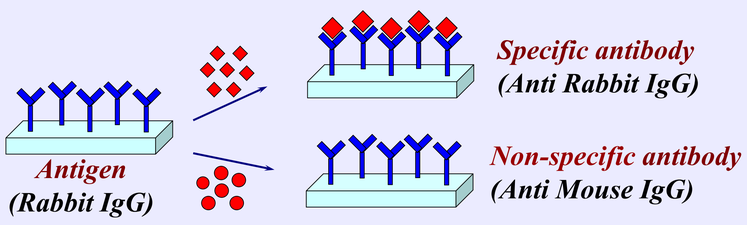
1) *SP band formation (~5min) – transformation to islands*
2) *SP blue shift (3-5 h) – should be studied further*
3) *SP red shift (up to ca. 40 h) – embedding*





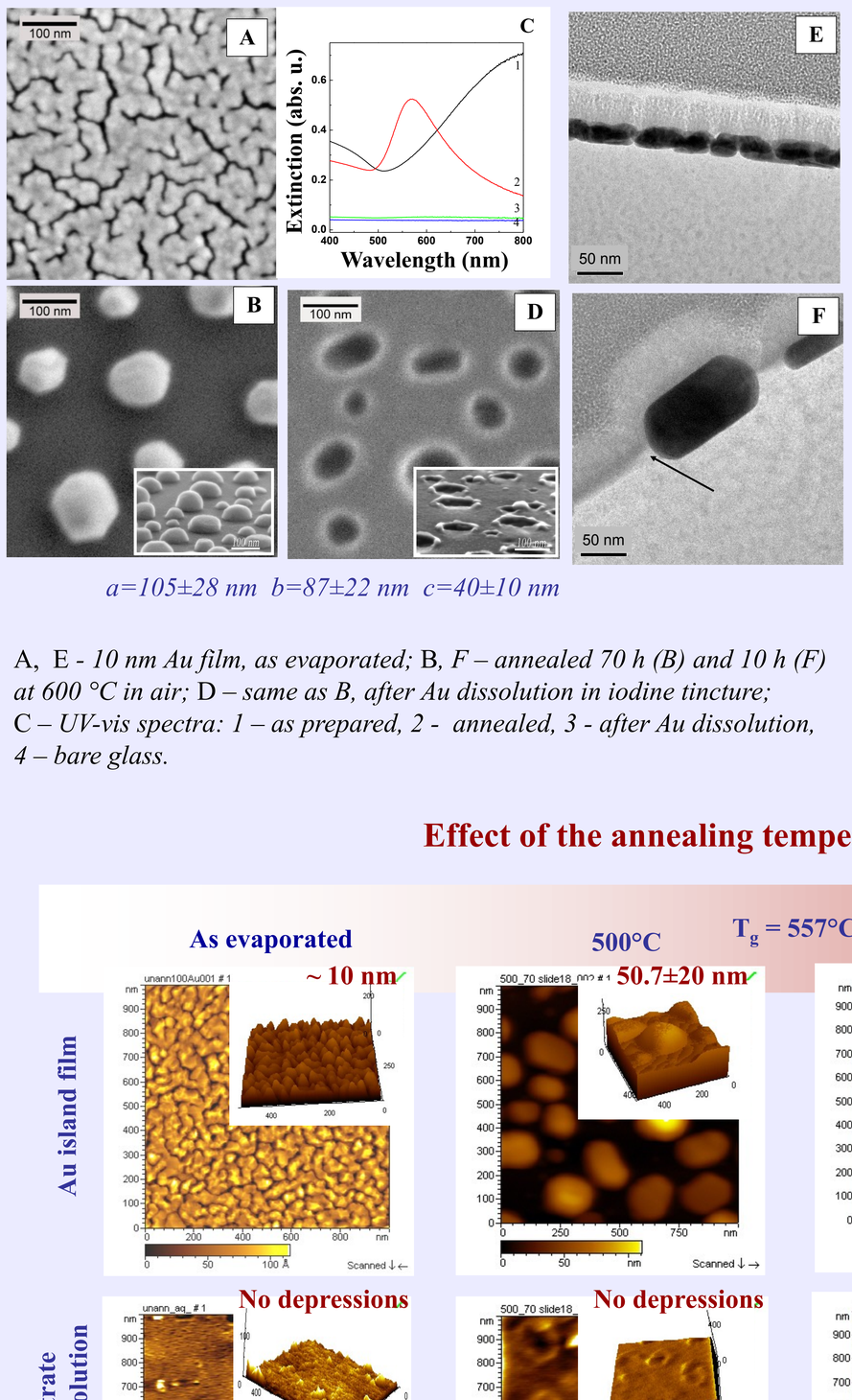
A - transmission UV-vis spectra in air;
B - E– evolution of the SP band wavelength during annealing:
B – in air, at 600 °C;
C – in air, at different temperatures;
D – zoom in on the first 10 h in C;
E – in different atmospheres, annealed at 600 °C.

Specific protein recognition



Morphology and metal / glass interface characterization

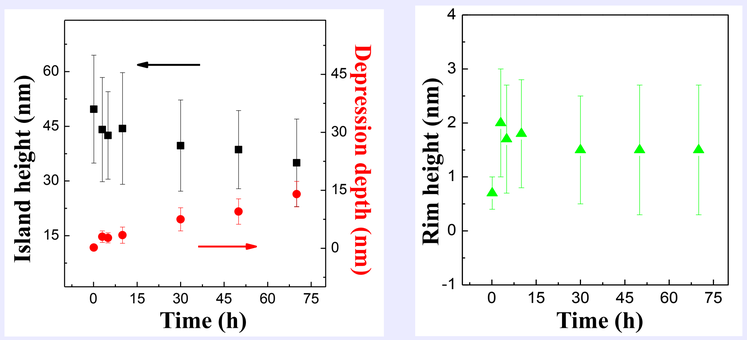
SEM and cross-sectional TEM



a=105±28 nm b=87±22 nm c=40±10 nm

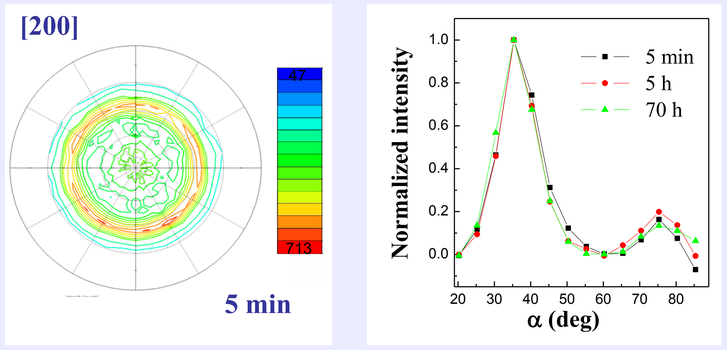
A, E - *10 nm Au film, as evaporated;* B, *F – annealed 70 h (B) and 10 h (F) at 600 °C in air;* D *– same as B, after Au dissolution in iodine tincture;*
C *– UV-vis spectra: 1 – as prepared, 2 - annealed, 3 - after Au dissolution, 4 – bare glass.*

AFM



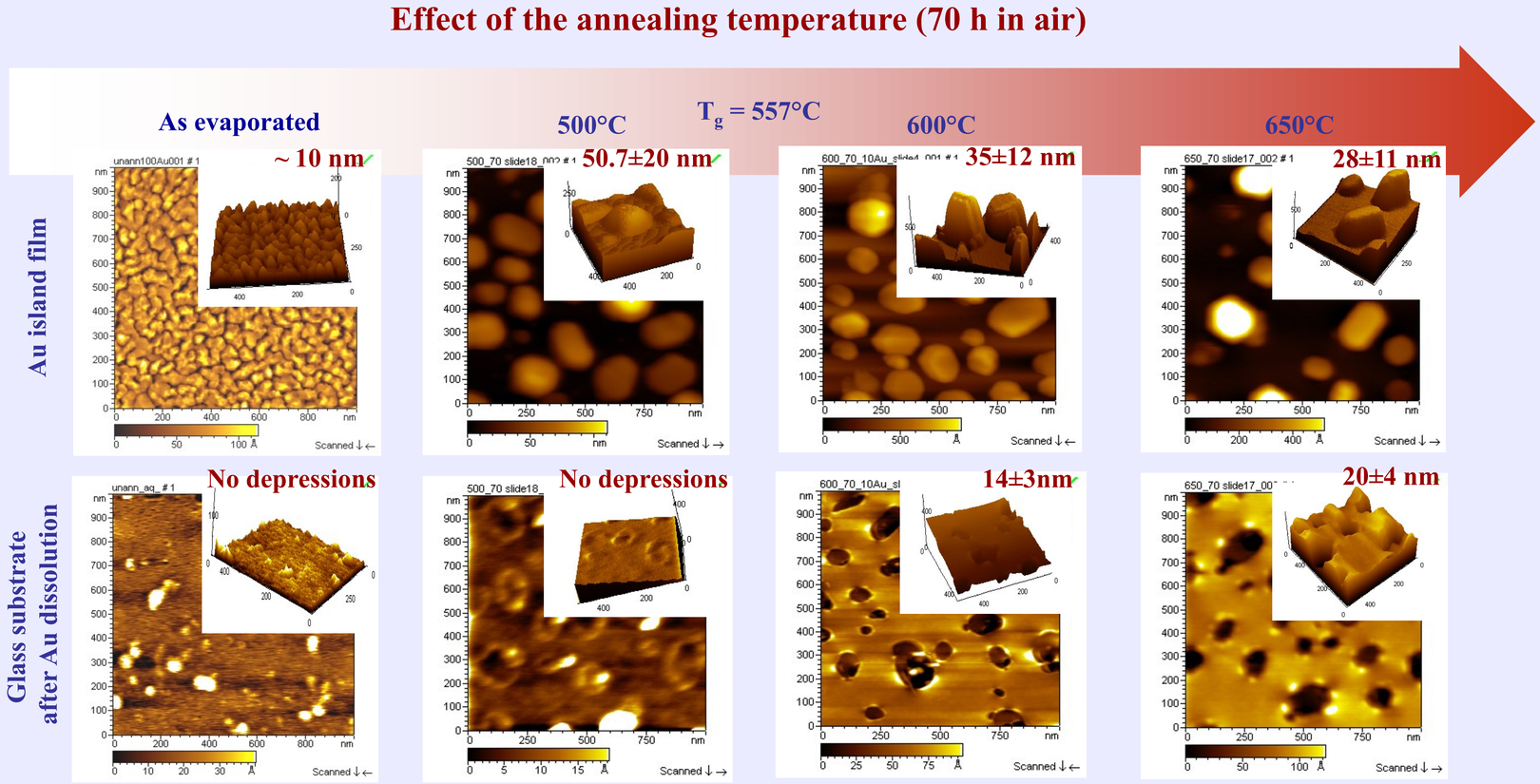
Island height + depression depth ≈ 50 nm, remains constant.
Rim forms in the first minutes of annealing

XRD: Pole figures



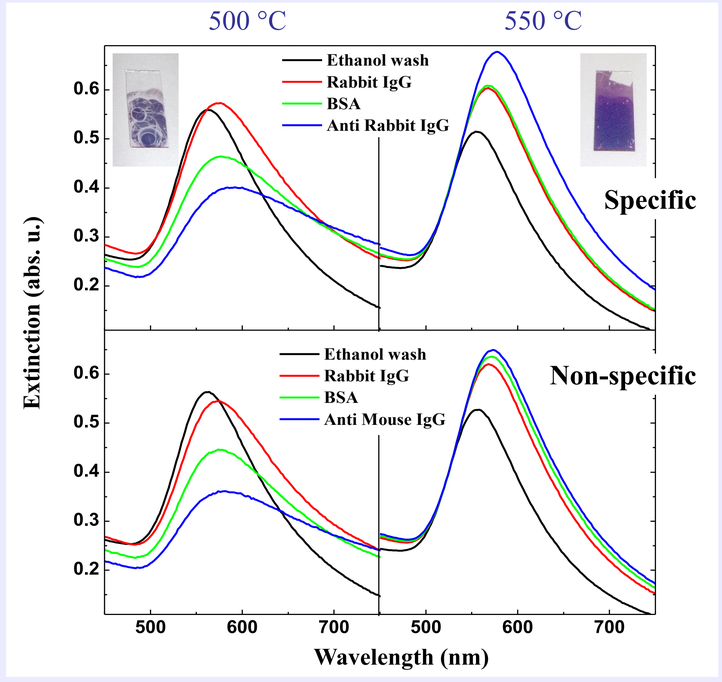
Conclusion: embedding with minimal island reshaping.

Effect of the annealing temperature (70 h in air)



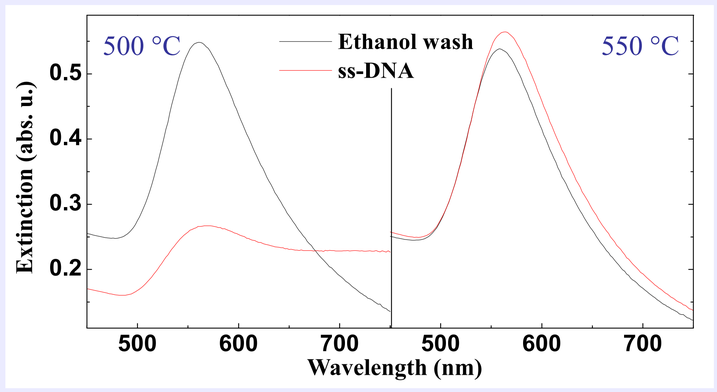
Conclusion: Embedding occurs at a temperature close to the T_g of the glass substrate.

Au island films annealed 10 h at 600 °C in different environments (air, N_2 and vacuum) show a similar morphology. The glass surface after gold dissolution contains depressions of ca. 8 nm in all cases.



The analytes were adsorbed from 1 μM solutions in PBS.

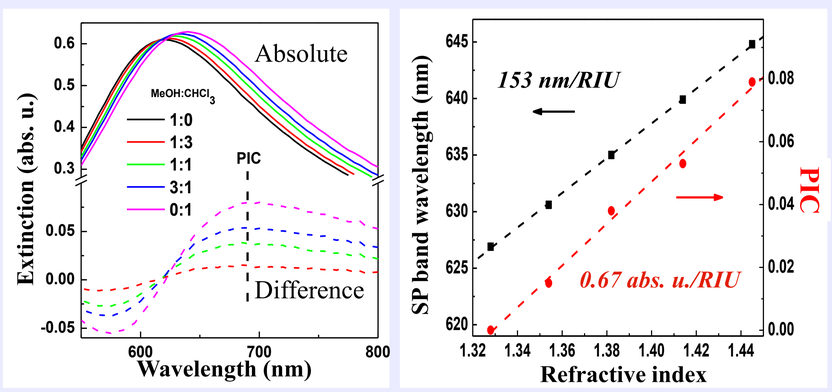
Self-assembly (SA) of ss-DNA



SA overnight of a disulfide-modified 43-base ss-DNA from a 1μM solution in PBS, on Au islands annealed at indicated temperatures.

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).