Reshaping of Evaporated Gold Island Films

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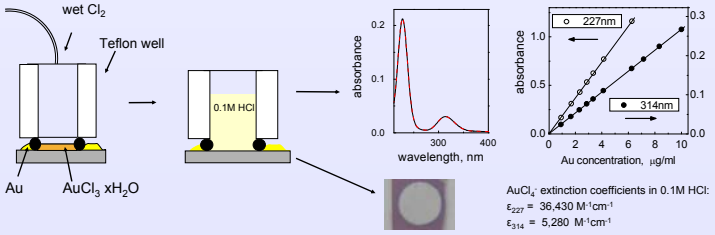
Controlled change of the morphology of Au island films upon chemical (interaction with a solvent) and electrochemical treatments was studied by transmission UV-vis spectroscopy and high-resolution SEM (HRSEM) imaging. Well-separated Au islands were formed using "RCA" treatment and electrochemical oxidation/reduction cycling, while sequential Pb underpotential deposition (UPD) / dissolution caused fast relocation of islands, resulting in a wormlike, near-percolated structure. The mean mass thickness and morphology of Au films were analyzed simultaneously using a specially developed procedure. The latter involves gas-phase chlorination of the Au followed by spectrophotometric analysis of the generated AuCl4-, presenting a simple method of measuring the mass thickness of Au films, potentially useful in various applications. Determination of the sticking coefficient of Au on solid substrates and the integrity of Au films upon surface treatment, are demonstrated.

Analysis of the mass thickness of Au films

Au chlorination | Chloride dissolution in selected area | Au film mass/thickness determination | Calibration curves



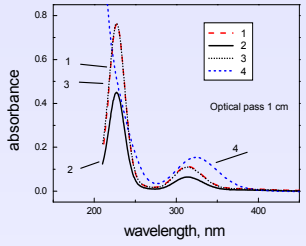
$AuCl_4^-$ extinction coefficients in 0.1M HCl:
ε_{227} = 36,430 $M^{-1}cm^{-1}$
ε_{314} = 5,280 $M^{-1}cm^{-1}$

Au chlorination reactions:

$Cl_2 + H_2O = HClO + HCl$

$HClO = HCl + 1/2O_2$

$Au + 3HClO + xH_2O = AuCl_3\ (x+3/2)H_2O + 3/4O_2$



Analysis validation:

Mass of 160 nm thick Au film on glass slide:

gravimetry – 1.62 ± 0.04 mg

chlorination – 1.61 ± 0.04 mg

1 – standard chloroaurate solution (4.2 μg/ml Au, 0.1M HCl)

2 – chlorination product of 5.0 nm Au film on polystyrene;

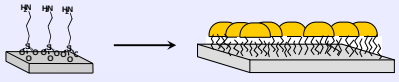
3 – scaled spectrum 2;

4 – 2mM NaClO + 0.1M HCl.

Sticking coefficient of Au adatoms on solid substrates

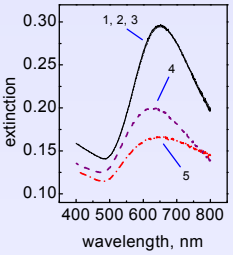
Au island film thermally evaporated on solid substrates: bare and aminosilane-modified glass, and Teflon.

Au evaporation rate rate: 0.005 nm/s.



Au film mass thickness, nm				Relative sticking coefficient of Au adatoms, Teflon/bare glass
QCM	Chemical analysis			
	Bare glass	Aminosilane-modified glass	Teflon	
0.2	0.24±0.02	0.26±0.01	0.06±0.01	0.25
0.6	0.65±0.06	0.63±0.01	0.15±0.06	0.23
1.2	1.19±0.03	1.19±0.03	0.30±0.05	0.25
1.8	1.74±0.07	1.74±0.04	0.72±0.08	0.41

Stability of Au island films in a solvent



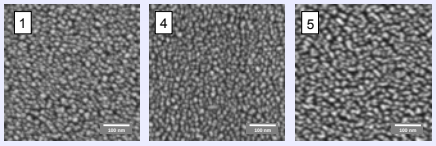
Slide treatment	Au film thickness, nm	
	Silanized glass	Bare glass
Untreated	3.11±0.08	3.06±0.04
Dipping for 30 min in DMSO	3.00±0.08	3.05±0.09
Sonication for 30 min in DMSO	3.02±0.03	1.57-2.70

1,2,3 – APTMS-modified glass slides after evaporation;

4 – slide 2 after dipping for 30 min in DMSO;

5 – slide 3 after 30 min sonication in DMSO.

HRSEM images of Au island films after solvent treatment

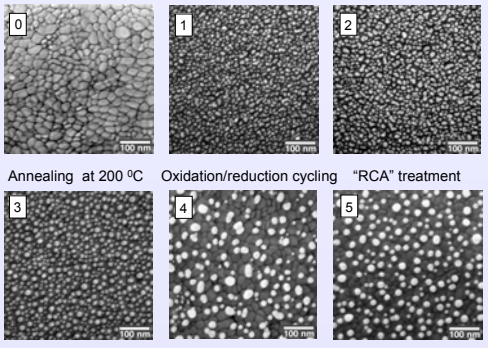


Chemical and electrochemical treatment of Au island films

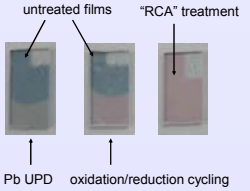
Au films preparation

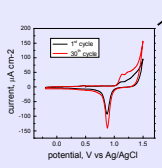
- ITO substrates (Delta Technologies) sonicated in acetone followed by "RCA" treatment (H_2O_2:NH_4OH:H_2O 1:1:5, 70 ^{0}C).
- 2.5 nm Au film evaporated on ITO at 0.01 nm/s and sample holder rotation speed of 42 RPM.
- After evaporation films were washed in 0.1M $HClO_4$ and dried under N_2 stream.
- Oxidation-reduction cycling in 0.1M $HClO_4$. Scan rate: 50 mV/s.
- Pb deposition solution: 5mM $PbClO_4$ + 0.1M $HClO_4$. Scan rate: 50 mV/s.

HRSEM images of Au island films after solvent and electrochemical annealing

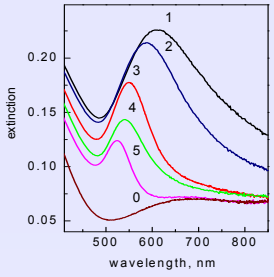


Appearance of 2.5 nm Au island films





Transmission UV-vis spectra

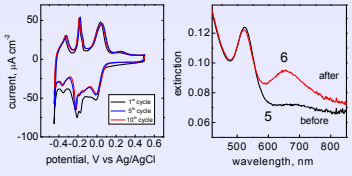


Au island film parameters

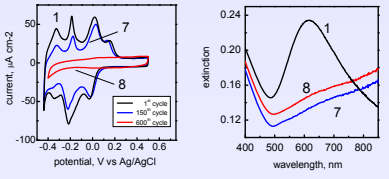
Slide treatment	Thickness, nm	Island area, %
Evaporated film	2.4 (QCM - 2.5)	40
Annealing at 200^0 C for 24 h	2.6	29
"RCA" treatment	2.3	24
Oxidation-reduction cycling	2.0	23
Pb UPD after "RCA" treatment	-	21

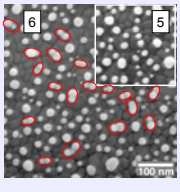
Transformation of Au island films induced by Pb deposition-dissolution in the UPD potential region

Pb deposition-dissolution on "RCA" treated film

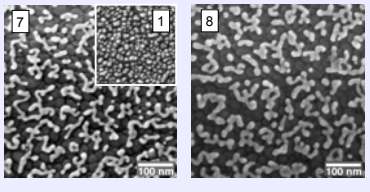


Au-Pb alloying during prolonged cycling





- Au islands showing partial coalescence



Conclusions

- Treatment of Au films with wet chlorine vapor followed by spectrophotometry presents a simple and effective scheme for mass thickness determination of ultrathin Au films on solid substrates. Determination of the mass thickness of ultrathin Au films allows control of the thin films integrity during post-deposition chemical or electrochemical modification.
- Combination of solvent and electrochemical treatment allows controlled change of the morphology and optical properties of Au island films on solid substrates: The island size, shape and separation can be varied from individual nanoparticles and nanoparticle pairs to wormlike, near-percolated structures.