Remodeling of Evaporated Gold Island Films

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Controlled change of Au island films morphology upon chemical (interaction with 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) and dissolution causes 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 $AuCl_4^-$, presenting a simple method of measuring the mass/thickness of Au films, potentially useful in various applications. Determination of the distribution of Au vapor flux in the evaporation chamber, the sticking coefficient of Au on solid substrates, and the integrity of Au films upon surface treatment, are demonstrated.

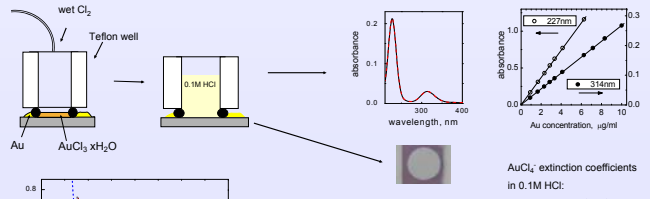
Analysis of the mass/thickness of Au films

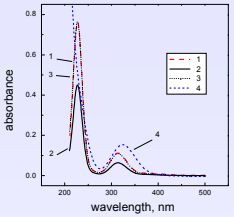
Au chlorination

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 $M^{-1}cm^{-1}$

literature data (0.2 – 2)M HCl:

ε_{314} = 5,480 - 5760 $M^{-1}cm^{-1}$

Au chlorination reactions:

$Cl_2 + H_2O = HClO + HCl$

$HClO = 2HCl + 1/2O_2$

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

Analysis validation

Mass of 160 nm thick Au film on glass slide:

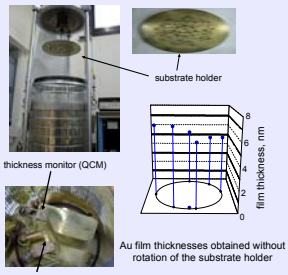
gravimetry – 1.62 ± 0.04 mg

chlorination – 1.61 ± 0.04 mg

1 – 4.2 μg/ml Au standard chloroaurate solution;
2 – after dissolution of the chlorination product of 5.0 nm Au film on polystyrene;
3 – scaled spectrum 2;
4 – 2mM NaClO + 0.1M HCl. Optical pass 1 cm.

Mass/thickness of Au films on solid substrates

Evaporation chamber for Au film preparation



Au film thicknesses obtained without rotation of the substrate holder

QCM	Au film thickness, nm* Chemical analysis: glass	APTMS silanized glass**	Teflon	Relative sticking coefficient of Au adatoms, Teflon/glass
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

*Au evaporation rate: 0.005 nm/s, substrate holder rotation speed 42 RPM.

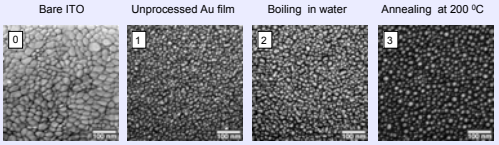
** Glass modified in 10% methanolic solution of aminopropyl trimethoxysilane (APTMS) overnight.

Chemical and electrochemical treatment of Au island films on ITO

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 °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.

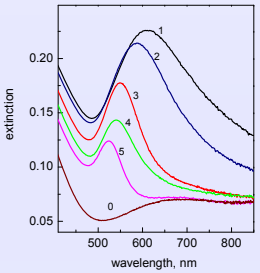
HRSEM images of Au island films after solvent and electrochemical annealing



Thickness of Au films, nm

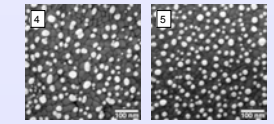
Untreated slides	QCM monitor	2.5
	Chemical analysis	2.4
Annealing at 200° C for 24 h		2.6
UPD of Pb		2.5
RCA treatment		2.3

Transmission UV-vis spectra

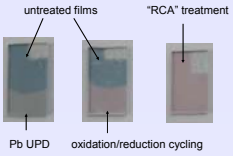


Oxidation/reduction cycling

"RCA" treatment

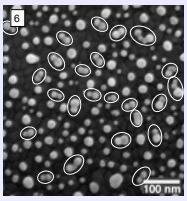


Appearance of remodeled Au films

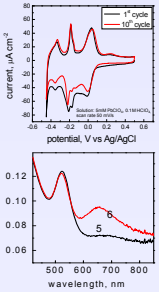


Transformation of Au island films induced by Pb deposition-dissolution

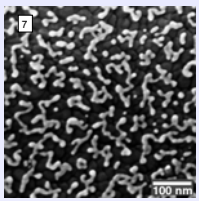
"RCA" treatment + Pb deposition-dissolution

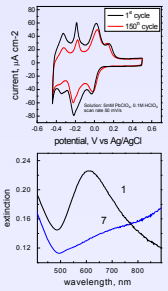


- Au islands showing partial coalescence



Prolonged cycling in Pb deposition solution

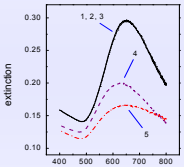




Stability of Au island films in a solvent

3.0 nm Au film evaporated at 0.01 nm/s on bare glass and on glass modified with APTMS.

1,2,3 – spectra of APTMS-modified glass slides after evaporation;
4 – spectrum of slide 2 after dipping for 30 min in DMSO;
5 – spectrum of slide 3 after 30 min sonication in DMSO.



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

Conclusions

- Treatment of Au films with wet chlorine followed by spectrophotometry presents a simple and effective scheme for mass/thickness determination of ultrathin Au films on solid substrates.
- The sticking coefficients of Au evaporated on bare and APTMS-modified glass are close to 1 and do not depend on the surface coverage. The sticking coefficient of Au adatoms on Teflon is ≈ 0.25 for thicknesses up to several monolayers of Au.
- Interaction of Au island films with solvents changes the films morphology with no Au detachment, for films evaporated on APTMS-modified glass and on ITO. Hence, the morphology and optical properties of Au island films can be remodeled using solvent treatment with no material loss.
- 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 to wormlike, near-percolated structures.