Hematite pillar structures formed by electrohydrodynamic instability

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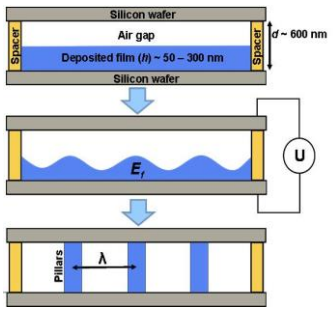
Abstract

Soft lithographic methods developed to structure organic resists are increasingly used to pattern inorganic materials. We combine sol-gel chemistry and a recent lithographic method, ie.electrohydrodynamic instability, to produce sub-micrometer patterns in polymer films to create hematite pillar structures. Hematite is an attractive candidate as a photoanode for solar energy driven splitting of H_2O in photoelectrochemical cells due to its abundance, low cost, chemical stability in aqueous environment and suitable band gap. However, hematite has a short hole diffusion length, therefore micro- and nanostructuring its morphology is a great interest.

Electrohydrodynamic (EHD) Instabilities



An electro-statically induced pressure across the interface:

$$p = -\frac{1}{2}\varepsilon_0\varepsilon_f(\varepsilon_f - 1)E_f^2$$

ε_0, ε_f: dielectric constants of vacuum and the film.

$$E_f = \frac{U^2}{\varepsilon_f d - (\varepsilon_f - 1)\cdot h}$$

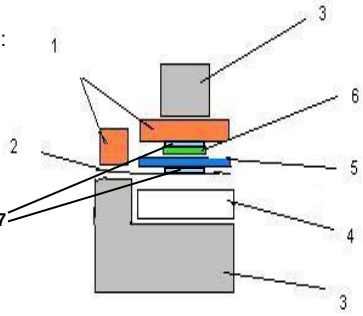
E_f: electric field in the film.

$$\lambda = 2\pi\sqrt{\frac{2\gamma}{-\partial p/\partial h}}$$

λ: distance between pillars.

The film is deposited by spin-coating.
Spontaneous pillar formation under electric field.

EHD setup



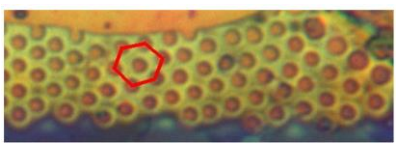
Parameters:
30V, 145°C, 2 - 3 hours

1 – copper electrodes;
2 – aluminium foil;
3 – holder;
4 – elastic material;
5 – Si wafer with the spacers;
6 – Si wafer with the film;
7 – conducting paste

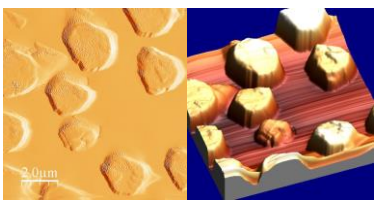
Results

a) Only polymer

Hexagonal array of PMMA pillars



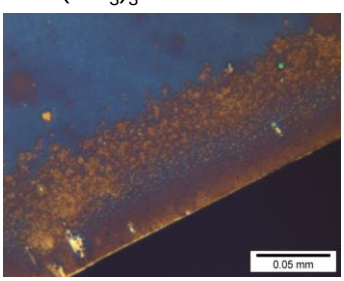
0.05 mm

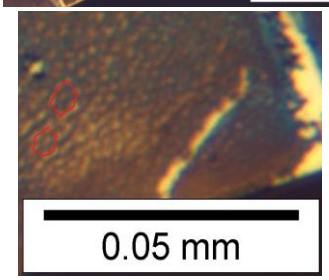


AFM images of PMMA pillars.

b) Polymer + iron-salt

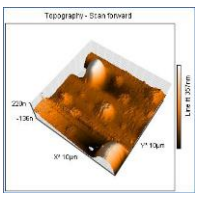
$Fe(NO_3)_3$ + PMMA film



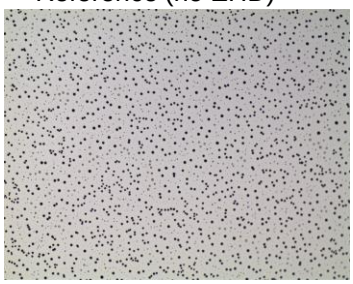


c) Organic Fe-precursor, no polymer!

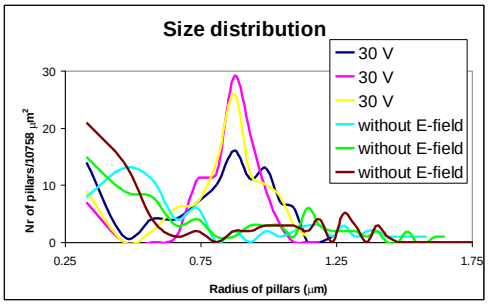
Fe(acac)+bzac+MeOH+octanol



Reference (no EHD)



After EHD (30V, 22°C, 20 min)



Conclusions

-Polymer+EHD forms pillars 2.3 μm diameter, 100 nm height.
-Blending iron salt with polymer promising, because portion of pillars shows Fe incorporation
-No electric field necessary, when organic Fe-oxide precursor solution used
-Electric field decreaees size and sharpens size distribution
- Thermal treatment of the films resulted in hematite pillars.

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