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Electro-assisted formation of organothiols self-assembled monolayers on polycrystalline copper surfaces

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General context: organothiols films grafted on copper
- Organothiol Self-Assembled Monolayers (SAMs) can be successfully adsorbed on noble (Au) and oxidizable metals (Cu, Zn, Ni). They can be used as protective coatings against corrosion, lubricants, lithographic patterns, molecular (bio)sensors, … [1]
- Oxidation state of the substrate surface is a key factor for the SAMs formation => an electrochemical reduction pretreatment of the Cu oxides layer can be exploited to form reproducible high quality films [2].
- Molecular adsorption process has an important impact on the SAMs characteristics: passive self-assembly (open circuit potential) vs. active electro-assisted assembly (cathodic polarization of Cu) [3].

Two experimental approaches and methodologies
- General context: organothiols films grafted on copper
- Passive adsorption
- Active adsorption

Results and discussion

Chemical composition: XPS (active method)
- Charge density: S2s & S2p, C1s increases
- Thiolate-S-Cu bond at 162.3 eV => no unbound thiol (164 eV) or oxidized species (> 164 eV)
- Reduction of the oxides layer (Auger Cu_KLL)
- Hydrocarbon contaminations: CH/S = 25.6 => th. = 13

Electrochemical stability (CV, cath. desorption)
- Protection against corrosion (pol. curves)

Structure and organization: PM-IRRAS
- ν(CH3) = 2920 cm⁻¹ and ν(CH2) = 2850 cm⁻¹ => in both cases, densely packed monolayers with alkyl chains in a trans zig zag conformation
- Intensity of CH2 bands more important with the active adsorption process => modification of the alkyl chain inclination and orientation relative to the substrate surface due to the cathodic polarization of Cu

Local characterization: SECM
- Active adsorption reinforces the insulating features of the grafted films (decreasing of I/I0) => Homogeneous surfaces
- = Active adsorption

Conclusions and perspectives
- Efficiency of active electro-assisted adsorption of organothiols on copper => formation of SAMs with excellent properties of organization, protective against corrosion, with high electrochemical stability, and formed with a significant saving of time comparatively to the passive methodology (10min vs. 2h).
- Perspectives: variation and optimization of experimental conditions with other substrates and surfactants [3], use of ionic liquids to reduce hydrocarbon contaminations, ...

References

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