

ADHESION OF ELECTROGRAFTED NITROBENZENE FILMS ON SILICON SURFACES AS A FUNCTION OF THE APPLIED POTENTIAL: AN AFM STUDY

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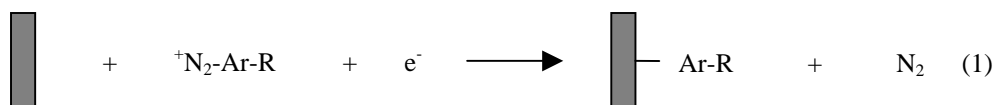
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Abstract:

We report the formation of multilayer nitrobenzene films attached to silicon surfaces. Thin films are grafted to the surface via the electrochemical reduction of aryl diazonium salts. As a function of the final applied potential, the coating is more or less strongly attached to the surface as evidenced by AFM. For a final potential more cathodic than -0.8V/Ag wire in our electrolytic medium, coating can be removed from the surface by the mechanical friction of the AFM tip. A nanoscale pattern can be then obtained and the free restored surface becomes again available for a later grafting.

Diazonium compounds are known to easily form radicals in chemical reactions, and the electrochemical reduction of aryl diazonium salts on various conductive surfaces is a very effective means for generating thin films containing a wide range of chemical functionalities. Attack of the electro-generated radical at the surface leads to covalent attachment (eq 1).

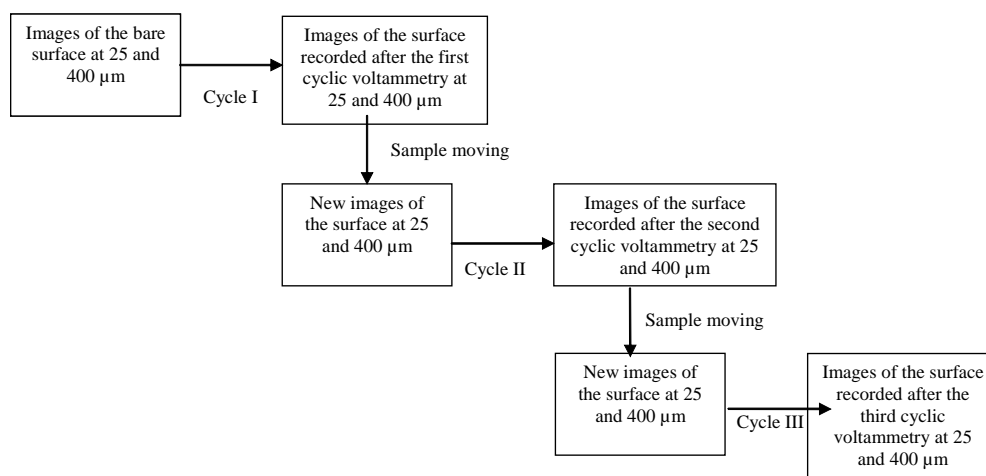


The thin film that is initially grafted does not completely impede the further reduction of diazonium ions; hence the generation of radical species and film growth may continue. The current work investigates the multilayer formation of nitrobenzene films by coupling *in situ* electrochemistry and AFM analysis. The deposition and imaging processes involve the following steps (scheme 1): (1) substrate, placed in the electrochemical cell in presence of the electrolytic solution, is first imaged in the contact AFM mode; (2) the tip is then withdrawn from the surface (5 μm), and electrochemical procedure is applied (cyclic voltammetry between the open circuit voltage and the chosen final potential); (3) after electrochemical process, the resulting coating was imaged by switching to AFM contact mode; (4) after withdrawing the tip, the sample is moved (from a few mm with a micro-control plate) and a new area is imaged. At that last position, a new voltammetry cycle is applied and the resulting surface modifications are again imaged by AFM. This protocol was set up because it makes it possible to check at the same time the homogeneity and the adhesion of the coating on a large range of the sample.

When the first cyclic voltammetry occurs, the resulting organic grafting is strongly attached to the surface whatever the final applied potential. No mechanical erosion of the coating was observed when we moved the sample after the first cycle and analysed a new area. The first organic layer is thus strongly attached to the surface leading to a covalent bond between the aryl radical and the substrate.

But when the number of cycles increases, and when the final potential becomes more cathodic than $-0.8\text{V}/\text{Ag}$ wire, a mechanical erosion of the coating by the tip is clearly observed. The images recorded at $40\ \mu\text{m}$ by $40\ \mu\text{m}$ clearly highlight a square of $5\ \mu\text{m}$ by $5\ \mu\text{m}$ formed by the precedent scanning of the tip at that same position. This phenomenon starts to be observed starting from the second cycle and is accentuated even more for the following cycles (fig. 1).

It is likely that strongly cathodic potentials promote very efficient formation of radicals from the diazonium solution. Those radicals can eventually react between them thus forming compounds which are not anchored to the surface of the sample. A polynitrophenylene multilayer film is formed which is not grafted to the surface and can be removed (or displaced), by simple mechanical effect, with the successive scans of the tip. Beyond a threshold potential ($-0.8\text{V}/\text{Ag}$ wire in our case), one notes the drive of the matter in contact with the tip even on surfaces said “new”, visible on the images by the formation of a square on the surface, corresponding in dimensions, with the preceding scanning. One can use this characteristic to structure the substrate at a sub-micronic scale.



Scheme 1: Steps of the experimental applied protocol combining in situ electrochemistry and AFM analysis

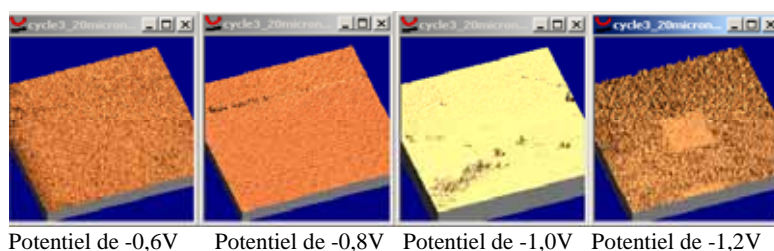


Figure 1: Images in contact AFM, $40\ \mu\text{m}$ by $40\ \mu\text{m}$, of the coating obtained after three cyclic voltammetry as function of the final applied potential.