FUNCTIONALIZATION OF Si(111) SURFACES WITH THIOPHENE-TERMINATED MONOLAYERS FOR THE ELECTRODEPOSITION OF COVALENTLY BOUND POLYTHIOPHENE

Bruno Fabre and Danial D. M. Wayner

Steacie Institute for Molecular Sciences, National
Research Council of Canada, Ottawa, Ontario K1A 0R6,
Canada

The organic functionalization of semiconductor surfaces constitutes an attractive approach for designing novel well-defined interfaces for numerous applications, such as molecular electronics, photovoltaic devices and chemical/biological sensing.[1,2] Among the various approaches, reactions of hydrogen-terminated silicon surfaces, Si(111)-H, have been demonstrated to be one of the most versatile to yield monolayers tailored with unique chemical and interfacial properties.

As an approach to achieving electronically conducting material/semiconductor junctions with attractive electrical properties, we propose here a simple and convenient route to functionalize Si(111)-H surfaces with a monolayer terminated by electrochemically polymerizable 2-thienyl units (Scheme 1).[3] These functional groups are used subsequently as anchoring sites for the thiophene electropolymerization.

The preparation of these derivatized surfaces proceeded in two steps. Firstly, *n*-doped Si(111)-H was reacted photochemically with ethyl undecylenate to provide a 16 Å thick ester-terminated alkyl monolayer ($-C_{10}H_{20}COOC_2H_5$). Then, the ester groups were converted into di(2-thienyl)carbinol moieties (20 Å thick $-C_{10}H_{20}C(2\text{-thienyl})_2OH$)) by reaction with 2-thienyllithium in THF. These surfaces were fully characterized by ATR-FTIR (Figure 1), XPS and HREELS.

The electrochemical oxidation of the thiophene-modified Si(111) surface in CH_3CN under illumination and in the presence of thiophene yielded a conducting polythiophene film. The important consequence of the presence of the attached thienyl units is that the film was much more adherent and smoother than that electrodeposited directly on Si(111)-H or on the ester-terminated monolayer. Polymer deposited on Si(111)-H could be completely removed upon rinsing with an organic solvent, such as CH_2Cl_2 or THF. In contrast, polythiophene grown on the thiophene modified surface could not be removed by sonication or the peel test. Moreover, the morphological differences between the polymer films were clearly evidenced by AFM (Figure 2). All of these observations are in agreement with those already reported for a pyrrole-terminated monolayer[4] and highlights that the covalent attachment of the electropolymerizable units is required for improving the junction between the conducting material and the semiconductor.

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(3) Fabre, B.; Lopinski, G. P.; Wayner, D. D. M. *Chem. Commun*., in press.
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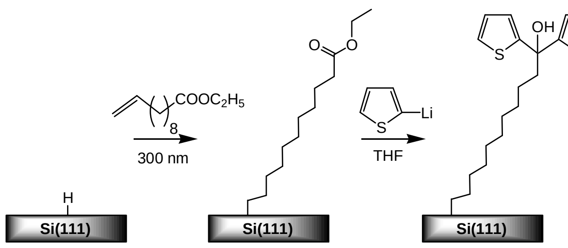

Scheme 1. Functionalization of Si(111)-H with a covalently bound thiophene-terminated alkyl monolayer .

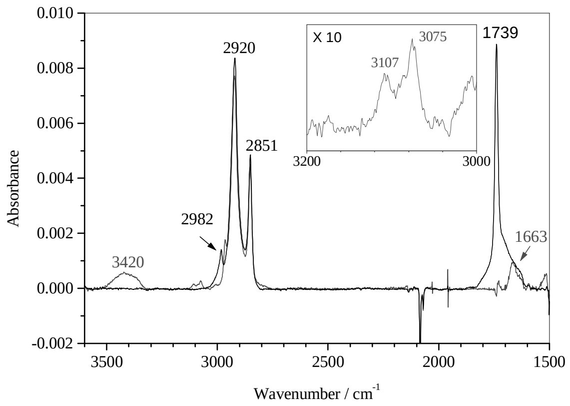

Figure 1. ATR-FTIR spectra of Si(111)-$C_{10}H_{20}COOC_2H_5$ (black) before and (red) after reaction with 2-thienyllithium; (inset) =C-H stretching region of thiophene.

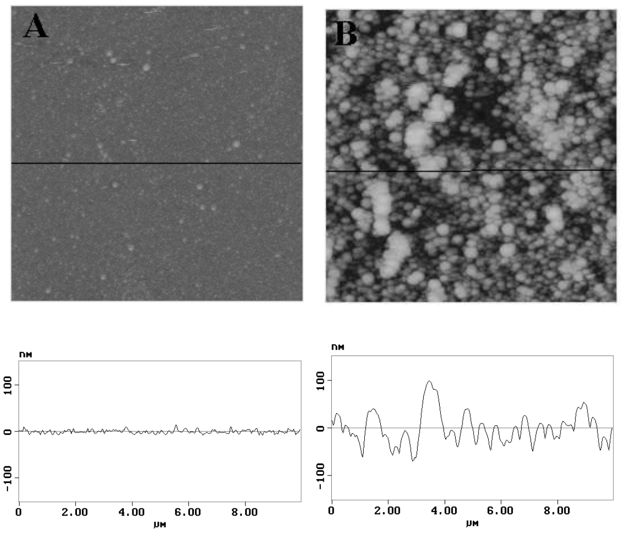

Figure 2. AFM (10 x 10 μm^2) images and cross-section views for 40 nm thick polythiophene films deposited onto (A) Si(111)-$C_{10}H_{20}C(2\text{-thienyl})_2OH$ and (B) hydrogen-terminated Si(111).