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Functionalization of Si(111) surfaces with alkyl chains terminated by electrochemically polymerizable thienyl units†

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A Si(111) surface has been derivatized with a thiophene-terminated alkyl monolayer which was subsequently photoanodically oxidized in the presence of thiophene to yield a strongly adherent and smooth conducting film.

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.[1–3] 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. For example, the reaction of Si(111)–H with alkenes,[4–10] aldehydes,[11,12] electrochemically reducible aryldiazonium salts,[13–15] Grignard[16–19] and organolithium[20,21] reagents or halogenated derivatives,[22–26] led to the robust and covalent attachment of organic films terminated with either a poorly reactive methyl group[6–8,11,12,16–19,22–25] or other much more reactive moieties, such as sulfonamides,[4,5] esters,[8,9] alcohols[8,9] and aromatic compounds.[13–15,20,21,26] 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. 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, prepared etching a clean silicon shard in deoxygenated ammonium fluoride 40% for 20 min,[9,16] was reacted photochemically at 300 nm for 3 h with ethyl undecylenate to provide an ester-terminated alkyl monolayer, Si(111)–$C_{10}H_{20}COOC_2H_5$. Then, the ester groups were converted into di(2-thienyl)carbinol moieties over 1 day by reaction with commercially available 1 M 2-thienyllithium in anhydrous THF. The thickness of the thiophene-terminated monolayer (Si(111)–$C_{10}H_{20}C(2\text{-thienyl})_2OH$) estimated by ellipsometry was 20.3 ± 0.8 Å, about 4 Å greater than the value determined for the ester-terminated monolayer (16.2 ± 0.6 Å).

The ATR-FTIR spectra of the ester- and thiophene-modified Si(111) surfaces are shown in Fig. 1.[27] The vibration bands attributed to the methylene stretching are observed at 2920 ($\nu_{as}(CH_2)$) and 2851 ($\nu_s(CH_2)$) cm^{-1}, irrespective of the nature of the terminal group. After the reaction with the 2-thienyllithium, the band corresponding to the ester group at 1739 cm^{-1} disappears and is replaced by another at 1663 cm^{-1} together with a broad absorption at 3420 cm^{-1} attributed to internally hydrogen bonded O–H. In the 3200–3000 cm^{-1} region, several weak bands are visible assigned to the =C–H stretching of attached thiophene.[28] The absorption at 1663 cm^{-1} agrees well with that observed in the IR spectrum of 1-(2-thienyl)-1-propanone at 1665 cm^{-1} indicating the formation of 2-thienylketone units in the monolayer. Their presence can be reasonably explained by the steric hindrance caused by the attached di(2-thienyl)carbinol moieties in the monolayer which would inhibit disubstitution as the reaction nears completion. By contrast, this type of reaction in solution has been reported to yield almost quantitatively the disubstituted product in the presence of a large excess of the organolithium derivative.[29] However, the overall conversion of the ester groups to di(2-thienyl) carbinol moieties is expected to be high ($>80\%$) as judged by the weak intensity of the band at 1663 cm^{-1} and the C(1s) : S(2p) ratio of 10.2 determined by XPS, very close to 9.5 corresponding to the attachment of two thienyl rings at the end of each alkyl chain.

Analysis of the thiophene-terminated monolayer by high-resolution electron energy loss spectroscopy (HREELS) provides further evidence of the presence of the attached aromatic rings. The most intense bands are observed at 704, 836, 1064, 1235, 1430 and 3095 cm^{-1}. The two first correspond to the =C–H out-of-plane deformation and the C–S–C ring stretching respectively.[28,30,31] It must be noted that the presence of a band at 840–790 cm^{-1} is characteristic of 2-monosubstituted thiophenes.[32] The C–H in-plane bending vibrations are observed at 1064 and 1235 cm^{-1}, whereas the band at 1430 cm^{-1} is assignable to the C=C stretching.

The electrochemical properties of the modified Si(111) surface have been investigated in thoroughly dried CH_3CN + 10^{-1} M Bu_4NClO_4 and under illumination using a 8 V/20 W optical fiber. A cyclic voltammogram of the thiophene-modified monolayer at 0.02 V s^{-1} showed an irreversible anodic shoulder at *ca.* 0.95 V *vs.* 10^{-2} M Ag/Ag$^+$, corresponding to the electropolymerization of the attached 2-thienyl units. In order to obtain higher coverage of a conducting material, the thiophene-terminated monolayer was photoelectrochemically oxidized at 0.9 V in the presence of 5×10^{-2} M of thiophene. Under these conditions, green-colored, 30–1000 nm thick polythiophene films were generated. The room-temperature electron conductivity measured by a four-probe method was *ca.* 10^2 S cm^{-1} for a 100 nm thick film. The important consequence

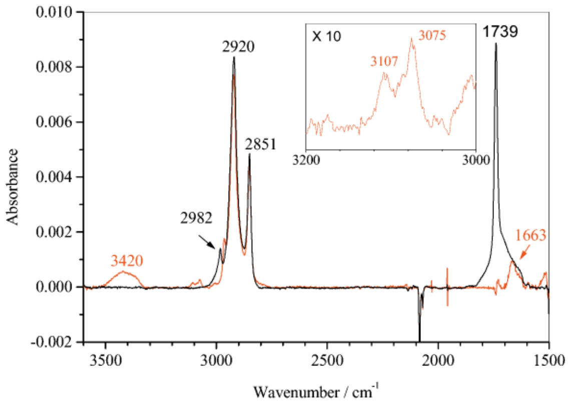

Fig. 1 ATR-FTIR spectra of Si(111)–$C_{10}H_{20}COOC_2H_5$ (black) before and (red) after reaction with 2-thienyllithium; (inset) =C–H stretching region of thiophene. The negative peak at 2084 cm^{-1} is the Si–H stretch from the Si(111)–H surface that was used as the reference for background subtraction.

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† Electronic supplementary information (ESI) available: cyclic voltammograms corresponding to the photoelectropolymerization of thiophene onto Si(111)–$C_{10}H_{20}C(2\text{-thieryl})_2OH$. See http://www.rsc.org/suppdata/cc/b2/b208446e/

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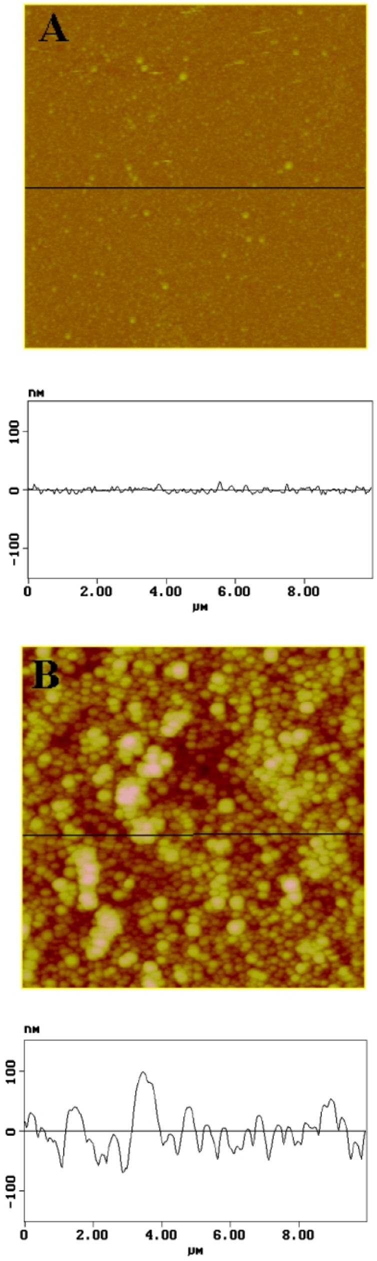

Fig. 2 AFM (10 × 10 µm^2) images and cross-section views for 40 nm thick polythiophene films deposited onto (A) Si(111)–$C_{10}H_{20}C(2\text{-thienyl})_2OH$ and (B) hydrogen-terminated Si(111).

of the presence of the attached thienyl units is that the conducting 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 evident by AFM (Fig. 2).

While contact-mode AFM images taken in ambient air showed a globular structure for all of these films, the smoothest film was that deposited on the thiophene modified surface. For example, for a 40 nm thick film, the mean roughness R_a was 3.6 nm (Fig. 2(A)) *vs.* 28 nm (Fig. 2(B)) in the case of polythiophene deposited on H-terminated silicon. This trend was even more marked for a much thicker film (400 nm) which showed a 12–15 times smoother surface, *i.e.*, R_a = 12 nm *vs.* 140 nm. Polythiophene deposited on ester modified silicon exhibited morphological characteristics almost indistinguishable from those obtained with H-terminated silicon which demonstrates that such differences could not be attributed to a monolayer effect. Similar results have also been reported for a pyrrole-terminated monolayer[20] and highlights that the covalent attachment of the electropolymerizable units is required for improving the junction between the conducting material and the semiconductor.

Patterning and the study of the electrical properties of this novel functionalized silicon surface are currently under investigation.

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