

## Conducting ferrocene monolayer on non-conducting surfaces.

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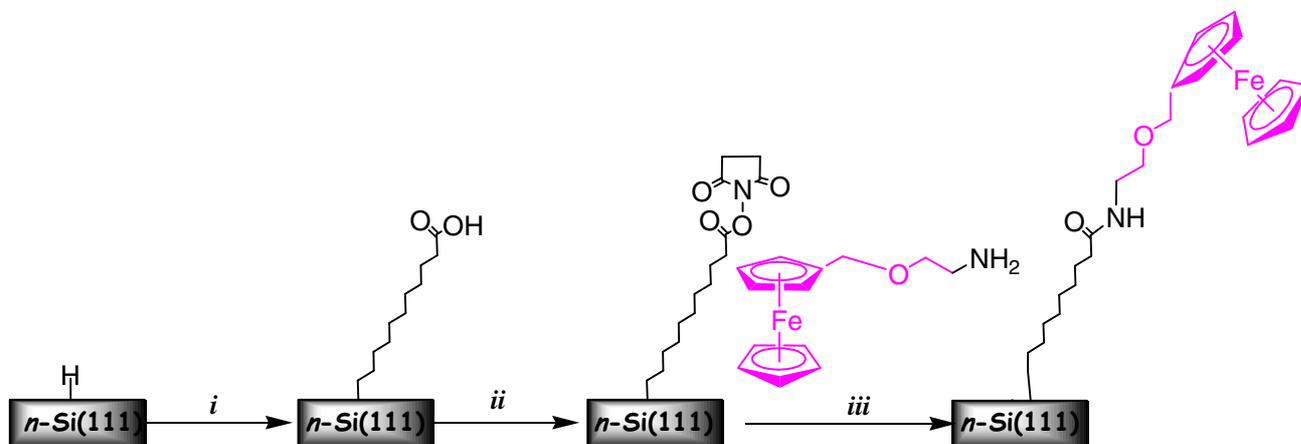
### Covalent attachment of the ferrocene-terminated monolayer on *n*-type silicon surface.

The covalent derivatization of Si(111) surfaces by a ferrocene-functionalized monolayer is depicted in Scheme S1 and was adapted from a previously reported procedure for *p*-type silicon surfaces.<sup>1</sup>

In order to limit the number of chemical steps, the direct grafting of an acid-terminated alkyl monolayer was performed using the reaction at 170°C under argon overnight of undecylenic acid<sup>2</sup> (Acros, 99%, previously passed through a neutral, activated alumina column to remove residual water and peroxides) with an hydrogen-terminated single side polished silicon(111) shard<sup>3</sup> (1.5 x 1.5 cm<sup>2</sup>, 1-5 Ω cm, *n*-type, phosphorus doped, thickness = 525 ± 25 μm, from Siltronix). The carboxylic acid-modified silicon surface was rinsed copiously with tetrahydrofuran and dichloromethane, then dipped in hot acetic acid for 2 x 20 min and dried under a nitrogen stream. It has been recently demonstrated that the rinsing in hot acetic acid leaves the functionalized surface smooth and perfectly free of physisorbed contaminants.<sup>4</sup>

2-Aminoethylferrocenylmethylether was synthesised in one step from commercially available (ferrocenylmethyl)trimethylammonium iodide (Strem Chemicals, 99%) following a previously reported procedure.<sup>5</sup>

The thickness measured by ellipsometry of the ferrocene-terminated monolayer was 26 Å, consistent with the calculations of energy minimization using the semi-empirical PM3 method giving 28 Å.



**Scheme S1.** Preparation of the ferrocene-terminated alkyl monolayer bound to *n*-Si(111) surfaces. *Reagents and Conditions:* (i) Undecylenic acid, 170°C, 20 hr; (ii) 0.1 M aq. NHS + 0.2 M aq. EDC, rt, 2 hr; (iii) CH<sub>2</sub>Cl<sub>2</sub>/0.05 M 2-aminoethylferrocenylmethylether, rt, 3 hr.

### Covalent attachment of the ester-terminated monolayer on *n*-type silicon surface.

The ester-terminated monolayer was prepared using the thermal reaction at 170°C overnight under argon of hydrogen-terminated silicon with neat ethyl undecylenate (Aldrich, 97%).<sup>6</sup> After cooling down to 40-50°C, the ester-modified silicon surface was rinsed copiously with toluene and dichloromethane, and dried under an argon stream.

### Cyclic voltammetry.

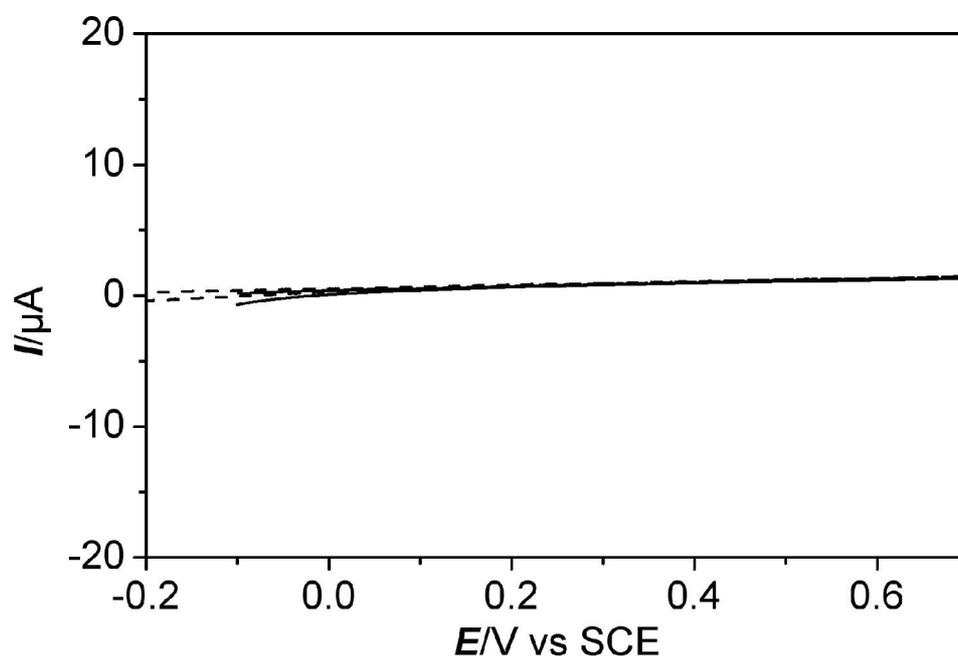
The cyclic voltammetry measurements were performed with an Autolab electrochemical analyzer (PGSTAT 30 potentiostat/galvanostat from Eco Chemie B.V.) equipped with the GPES software in a self-designed three-electrode Teflon cell. The working electrode, modified Si(111), was pressed against an opening in the cell bottom using a FETFE (Aldrich) O-ring seal. An ohmic contact was made on the previously polished rear side of the sample by applying a drop of an In-Ga eutectic (Alfa-Aesar, 99.99%). The counter electrode

### Supporting Information Section

was a platinum foil and the system  $10^{-2}$  M  $\text{Ag}^+ | \text{Ag}$  in acetonitrile was used as the reference electrode (+0.29 V vs aqueous SCE). The reported potentials are referred to SCE (uncertainty  $\pm 0.01$  V). Tetra-*n*-butylammonium perchlorate  $\text{Bu}_4\text{NClO}_4$  was purchased from Fluka (puriss, electrochemical grade). The ( $\text{CH}_3\text{CN} + 0.1$  M  $\text{Bu}_4\text{NClO}_4$ ) electrolytic medium was dried over activated, neutral alumina (Aldrich) for 30 min, under stirring and under argon. About 20 mL of this solution was transferred with a syringe into the electrochemical cell prior to experiments.

All electrochemical measurements were carried out inside a home-made Faraday cage in dark, at room temperature ( $20 \pm 2$  °C) and under a constant flow of argon. Solution resistance was compensated by electronic positive feedback

#### Characterization by cyclic voltammetry of the ferrocene modified layer in dark.



**Figure S1.** Cyclic voltammograms at  $0.1 \text{ V s}^{-1}$  of the ferrocene-terminated monolayer on *n*-type Si(111) in  $\text{CH}_3\text{CN} + 0.1$  M  $\text{Bu}_4\text{NClO}_4$  in dark: (---) in absence of ferrocene in solution; (—) after addition of  $10^{-3} \text{ mol.L}^{-1}$  of ferrocene in solution. This CV shows the "Non-Conducting" behaviour of such modified electrode in dark

**SECM measurements.** SECM measurements were performed using the CHI900B instrument from CH-Instruments equipped with an adjustable stage for tilt correction. The electrochemical cell was the one furnished with the SECM and was used in a typical three-electrode configuration for unbiased experiments. The tip electrode was a 5  $\mu\text{m}$  radius Pt disk ultramicroelectrode (UME, CH-Instruments) with a typical RG = 5–10 (RG is the ratio of the total electrode radius including the glass insulator over UME radius).<sup>7</sup> The reference electrode was an Ag/AgCl, aqueous KCl 3 M electrode. UME was characterized by cyclic voltammetry and by typical approach curves recorded on a Pt conductive substrate.

Two redox mediators were used: the ferrocene/ferrocenium (Fluka, >98%) and decamethylferrocene/decamethylferrocenium (Aldrich, 97%) at 1mM concentration in CH<sub>3</sub>CN (+0.1 M NBu<sub>4</sub>ClO<sub>4</sub>).

Approach curves were recorded under constant current mode at a tip-substrate distance expressed as  $L = d/a$  around 1 ( $d$  is the distance between the tip and the substrate and  $a$  is the radius of the UME). Fittings were performed using the approximate functions following the Bard–Mirkin formalism for  $\text{RG} < 10$ .<sup>7</sup>

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