

## Functionalization of silicon surfaces with Si-C linked $\beta$ -cyclodextrin monolayers

Corinne Lagrost,<sup>\*a</sup> Gilles Alcaraz,<sup>b</sup> Jean-François Bergamini,<sup>a</sup> Bruno Fabre<sup>a</sup> and Iuliana Serbanescu.<sup>a</sup>

<sup>a</sup> *Sciences Chimiques de Rennes, UMR 6226 CNRS-Université de Rennes 1, Equipe MaCSE, , Campus de Beaulieu, F-35042 Rennes, France. Fax: 33 22323 6732; Tel: 33 22323 5940; E-mail: corinne.lagrost@univ-rennes1.fr*

<sup>b</sup> *Laboratoire de Chimie de Coordination, CNRS, Equipe AOC, 205 route de Narbonne, F-31077 Toulouse, France.*

### Reagents

The chemicals used for cleaning and etching of silicon wafer pieces (30% H<sub>2</sub>O<sub>2</sub>, 96-97% H<sub>2</sub>SO<sub>4</sub>, 50% HF and 40% NH<sub>4</sub>F solutions) were of VLSI semiconductor grade (Riedel-de-Haën). Acetone (min. 99.8%, Carlo Erba), methanol (min. 99.9%, Carlo Erba), toluene (HPLC grade, VWR), *N,N*-dimethylformamide DMF (anhydrous, SDS), methylene chloride (anhydrous analytical grade, SDS) and absolute ethanol (puriss, Riedel-de-Haën) were used without further purification. Undec-10-enoic acid (Acros, 99%) and ethyl undecylenate (Aldrich, 97%) were passed through a neutral, activated alumina column to remove residual water and peroxides.

### Synthesis of heptakis{6-deoxy-6-[undec-10-enamido]}- $\beta$ -cyclodextrin

An anhydrous DMF solution (20 mL) containing undec-10-enoic acid (0.678g, 2.800 mmol) and 1-hydroxybenzotriazol monohydrate (0.603g, 3.937 mmol) was cooled to 0°C and 1-(3-dimethylaminopropyl)-3-ethylcarbodiimide hydrochloride salt (EDCCl) (0.710g, 3.704 mmol) was added. The solution was stirred for 1h at 0°C and then for 1h at room temperature. A slurry of heptakis(6-deoxy-6-amino)- $\beta$ -cyclodextrin (0.582g, 0.516 mmol) and *N*-ethylmorpholine (0.524g, 0.472 mL) in anhydrous DMF (20 mL) was subsequently transferred to the first solution. Stirring was continued for 4 days at room temperature giving a clear yellow solution. DMF was removed by trap-to-trap distillation. Water was added and the resulting suspension was filtered. The filtrate was discarded and the solid was copiously rinsed with ether and dried under vacuo to give an off-white powder (0.862g, 72.9%). In the following, this solid was used without any further purification. <sup>13</sup>C NMR (CDCl<sub>3</sub>, 75 MHz)  $\delta$  174.5 (C=O), 139.0 (CH=CH<sub>2</sub>), 114.1 (CH=CH<sub>2</sub>), 102.4, 84.0, 73.2, 72.9, 70.5, 39.8, 36.3, 33.8, 29.5, 29.2, 28.9, 26.0; ESI-MS *m/z*: 2314.4 ([M+Na]<sup>+</sup>).

### Covalent attachment of the $\beta$ -cyclodextrin-terminated monolayer on flat silicon(111) surfaces

A single side polished silicon(111) shard ( $1.5 \times 1.5 \text{ cm}^2$ , 1-5  $\Omega \text{ cm}$ , *p*-type, boron doped, thickness =  $525 \pm 25 \text{ }\mu\text{m}$ , Siltronix) was sonicated for 10 min successively in acetone, methanol and ultra-pure 18.2 M $\Omega \text{ cm}$  water. It was then cleaned in 3:1 v/v concentrated  $\text{H}_2\text{SO}_4/30\% \text{ H}_2\text{O}_2$  at 100°C for 30 min, followed by copious rinsing with ultra-pure water.

**Caution:** *The concentrated  $\text{H}_2\text{SO}_4:\text{H}_2\text{O}_2$  (aq) piranha solution is very dangerous, particularly in contact with organic materials, and should be handled extremely carefully.*

The surface was etched with ppb grade 40% aqueous argon-deaerated  $\text{NH}_4\text{F}$  for 15 min to obtain atomically flat Si(111)-H.<sup>1</sup> It was then dipped in argon-deaerated ultrapure water for several seconds, dried under an argon stream and transferred immediately into a Pyrex Schlenk tube containing ca.  $10^{-2} \text{ mol.dm}^{-3}$  heptakis{6-deoxy-6-[undec-10-enamido]}- $\beta$ -cyclodextrin (heptapodant  $\beta$ -cyclodextrin, in the following) in 10 mL of toluene, previously deoxygenated at 100°C for 15 min then at rt for 1.5 hr. The solution was thoroughly purged with argon for 30 min, the Schlenk tube was sealed with paraffin film (Parafilm M), and irradiated for 5 h in a Rayonet photochemical reactor (300 nm). The cyclodextrin-modified surface was then rinsed copiously with DMF, absolute ethanol and ultra-pure 18.2 M $\Omega \text{ cm}$  water, and dried under an argon stream.

### Covalent attachment of the $\beta$ -cyclodextrin-terminated monolayer on porous silicon(100)

A double side polished silicon(100) shard ( $1.5 \times 1.5 \text{ cm}^2$ , 1-5  $\Omega \text{ cm}$ , *p*-type, boron doped, thickness =  $275 \pm 25 \text{ }\mu\text{m}$ , Siltronix) was sonicated for 10 min successively in acetone, methanol and ultra-pure 18.2 M $\Omega \text{ cm}$  water. It was then cleaned in 3:1 v/v concentrated  $\text{H}_2\text{SO}_4/30\% \text{ H}_2\text{O}_2$  at 100°C for 20 min, followed by copious rinsing with ultra-pure water. The sample was then dipped in 50% HF for 1 min and dried under an argon stream. It was pressed against an opening in the cell bottom using a FETFE (from Aldrich) O-ring seal and the ohmic contact was made on the polished rear side of the sample with the steel bottom cap (any conducting material was not dropped to avoid surface contamination for subsequent FTIR investigation). A platinum counter electrode was used. The hydrogen-terminated porous Si(100) surface was produced by applying a current density of 50 mA  $\text{cm}^{-2}$  for 2.5 min in 50% HF/ethanol (MOS grade)/ ultra-pure 18.2 M $\Omega \text{ cm}$  water (2:2:1 vol). The surface was then rinsed with ethanol and dried under an argon stream. After monitoring of the FTIR spectrum of hydrogen-terminated porous Si(100), the sample was transferred into a Pyrex Schlenk tube containing ca.  $10^{-2} \text{ mol.dm}^{-3}$  heptapodant  $\beta$ -cyclodextrin in 10 mL of toluene, previously deoxygenated at 100°C for 15 min then at rt for 1.5 hr. The solution was thoroughly purged with argon for 30 min and irradiated for 5 h with white light using a halogen bulb. The cyclodextrin-modified porous surface was then rinsed as described for the flat Si(111) surface.

---

<sup>1</sup> C. P. Wade and C. E. D. Chidsey, *Appl. Phys. Lett.*, 1997, **71**, 1679.

## **Covalent attachment of the ester-terminated monolayer on flat silicon(111)**

The silicon(111) surface was decontaminated and etched using the same conditions as those described for the preparation of the  $\beta$ -cyclodextrin-terminated monolayer. The ester-modified surface was prepared from neat ethyl undecylenate heated at 170°C overnight under a constant flow of argon. It was then rinsed copiously with THF and methylene chloride, and dried under an argon stream.

## **Monolayer characterization**

### ***FTIR spectroscopy characterization of porous Si(100) surfaces***

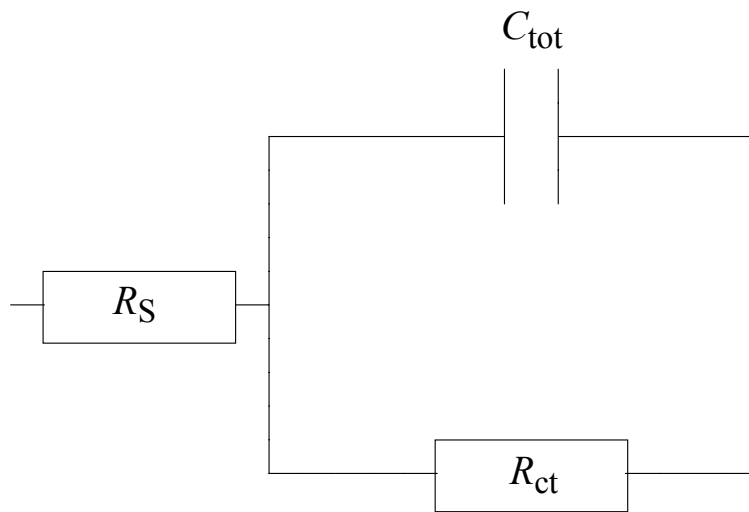
FTIR spectra were acquired using a Nicolet Model 205 FT-IR spectrometer in the transmission mode (100 scans, 4  $\text{cm}^{-1}$  resolution and automatic gain). The porous silicon was mounted on a home-made Teflon sample mount.

### ***Electrochemical characterizations***

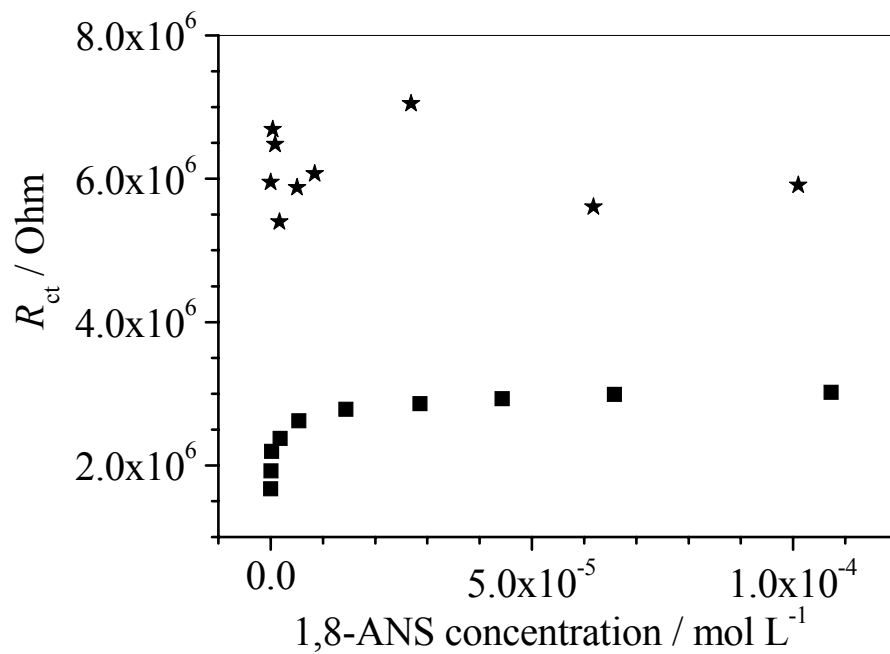
The cyclic voltammetry and impedance spectroscopy measurements were performed with an Autolab electrochemical analyzer (PGSTAT 30 potentiostat/galvanostat from Eco Chemie B.V., equipped with the GPES/FRA software) in a self-designed three-electrode Teflon cell. The working electrode, modified Si(111) (geometrical area: 0.28  $\text{cm}^2$ ), was pressed against an opening in the cell bottom using a FETFE (from 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 was a platinum foil and aqueous SCE was used as the reference electrode. All reported potentials are referred to SCE. All electrochemical measurements were carried out inside a home-made Faraday cage, at room temperature ( $20 \pm 2$  °C) and under a constant flow of argon.

After 36 h-incubation of the modified Si(111) sample in aqueous 1 M KCl, impedance spectroscopy measurements were performed in this electrolytic medium containing 2 mM  $\text{K}_3\text{Fe}(\text{CN})_6$  and 2 mM  $\text{K}_4\text{Fe}(\text{CN})_6$  at 0.2 V vs SCE (i.e. the formal potential of the used redox couple) using a 5 mV amplitude and a frequency range from 100 kHz to 0.01 Hz. The charge-transfer resistance  $R_{\text{ct}}$  of the monolayer was obtained by fitting the experimental data with a classical Randles circuit, neglecting the Warburg contribution (scheme 1). The titration curve with 1,8-ANS as a guest molecule was recorded using two stock solutions : 0.2 mM and 2 mM of 1,8-ANS in aq 1 M KCl containing 2 mM  $\text{K}_3\text{Fe}(\text{CN})_6/\text{K}_4\text{Fe}(\text{CN})_6$  to avoid dilution effect. After each addition of guest, impedance spectra were recorded after 3 min equilibrating time. For comparison purposes, fig.1 shows the variations of  $R_{\text{ct}}$  for both the ester and  $\beta$ -CD modified monolayers with increasing concentrations in 1,8-ANS. While the  $R_{\text{ct}}$  of the  $\beta$ -CD modified monolayer monotonously increases, the  $R_{\text{ct}}$  values corresponding to the ester modified monolayer show “stochastic” variations around 6 M $\Omega$  that cannot be fitted with a Langmuir isotherm.

Impedance measurements were also performed with a  $\beta$ -cyclodextrin modified surface, after storing for 3 days left in aq. 1 M KCl. This sample was used in a former experiment and, then, was saturated with 1,8-ANS. Impedance analysis gave the same results than 3 days before, suggesting that the cyclodextrin layer is stable.



**Scheme 1.** Equivalent electrical circuit used for fitting the experimental data where  $R_s$  is the solution resistance,  $R_{ct}$  the monolayer charge-transfer resistance and  $C_{tot}$  is the total capacitance.



**Figure 1.** Variations of  $R_{ct}$  values for  $\beta$ -CD (■) and ester (★) -modified monolayers with the 1,8-ANS concentration