

ELECTRONIC SUPPLEMENTARY INFORMATION

Surface band structure of aryl-diazonium modified p-Si electrodes determined by X-ray Photoelectron Spectroscopy and electrochemical measurements

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1. XPS overlayer model

The evaluation of the thickness d of the grafted layer can be obtained using the closed overlayer model developed by Briggs *et al.*¹ The value can be determined by solving the following equation:

$$\frac{I_{C1s}}{I_{Si2p}}(d) = \frac{I_{C1s}^{\infty} \left[1 - \exp\left(-\frac{d}{\lambda_{C1s}^o}\right) \right]}{I_{Si2p}^{\infty} \exp\left(-\frac{d}{\lambda_{Si2p}^o}\right)} \quad (1)$$

with $\lambda_{Si2p(C1s)}^o$ the mean free path for photoelectron of Si 2p(C 1s) in the overlayer. The values calculated for a solid layer of polystyrene ($\lambda_{Si2p}^o = 36 \text{ \AA}$ and $\lambda_{C1s}^o = 32 \text{ \AA}$) are used in this study.²

I_{Si2p}^{∞} is the Si 2p photoelectron intensity of a clean, semi-infinite, silicon crystal. I_{C1s}^{∞} is the C 1s photoelectron intensity for a semi-infinite, solid layer of the considered grafted layer. These two values are estimated according to:³

$$I_X^{\infty} = a \cdot n_X \cdot \sigma_X \cdot \lambda_X \cdot T(KE_X) \quad (2)$$

with $T(KE)$ the transmission function of the analyser, σ_X the photoionization cross section and n_X the elemental density. Due to the dispersion of the photoionization cross-section in the literature, a high uncertainty is introduced in the estimation of $I_{C1s}^{\infty}/I_{Si2p}^{\infty}$ (from 1 to 2.2).

2. XPS C1s core level spectra

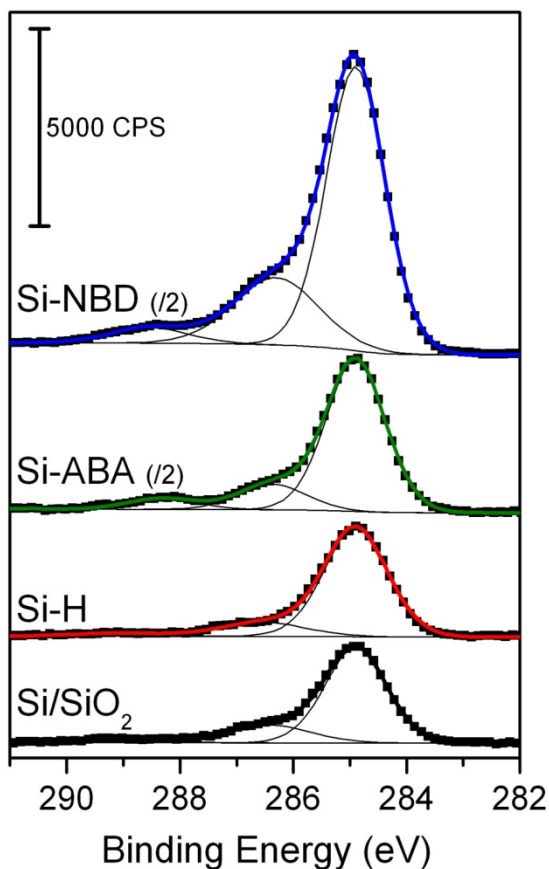


Figure S1 presents the C 1s core level spectra for different silicon surfaces (raw surface, after formation of Si-H, after grafting with ABA and NBD). In regards of the spectra resolution, only three peaks were used for curve-fitting. The first one attributed to adventitious carbon was used to calibrate the spectra in energy at 284.9 eV. It should be noted that this peak is not modified, in terms of width and shape, after grafting of an organic layer (Full width at half maximum (FWHM) stays between 1.21 and 1.30 eV). Thus, the energy calibration is not affected by the grafting of molecules.

Figure S1. C 1s core level spectra for Si/SiO₂, Si-H, Si-ABA and Si-NBD surfaces; black squares are

experimental data and colored lines represent the curve-fitting results.

3. Mott-Schottky analysis

Data from electrochemical impedance spectroscopy are used to obtain Mott-Schottky plots for each electrode. This allows the calculation of the charge carrier density, N_a (the density of acceptors for a p-type semiconductor), and the flat band potential E_{fb} , which are key parameters of a semiconductor electrode, from the following equation:

$$C_{sc}^{-2} = \frac{2}{qN_a\epsilon_s\epsilon_0} \left(E_{fb} - E - \frac{kT}{q} \right) \quad (3)$$

with ϵ_s , the relative dielectric permittivity (11.8 for silicon) and ϵ_0 , the permittivity of vacuum; $-kT/q$ has its general meaning and a value of -25 mV at 20°C. In the depletion region, a linear C_{sc}^{-2} vs E is predicted and the flat band potential is determined from the intercept.

In our case, an uncommon behavior is observed for the Mott-Schottky plot as shown in Figure S2. The E_{fb} values estimated from the linear part in figure S2.a depend on frequency and shift from 0.14 to -0.01V when the frequency decreases. Theoretically, E_{fb} is estimated at 0.42 V vs. NHE when taking into account the calculated valence band position in surface (0.58 V for a naked p-Si surface in 1.0 M HCl)⁴ and the energy difference between E_{vb} and E_f (the Fermi level) for a silicon sample with $N_a = 1 \times 10^{16}$ cm⁻³ (close to our silicon samples). The values obtained in conditions close to those of our experiments vary from 0.37 V (in 1M H₂SO₄)⁵ to 0.487 V vs NHE (in 0.1M HCl).⁶ The slope measured for the Mott-Schottky plots of Figure S2.a led to $N_a = 3.9 \times 10^{13}$ cm⁻³, which is two order of magnitude smaller than the expected value for a 1-10 Ω cm silicon wafer. This unusual behavior can be explained by the presence of deep surface states trapping the charge carriers. For the p-type silicon, they are expected to be in the middle of the gap.⁷

Figure S2.b presents a magnification of the same Mott-Schottky curves between 0.2 to 0.7 V where a

second linear region is observed. The values of E_{fb} and N_a obtained in this case are in agreement with the expected values for p-type silicon. E_{fb} presents a relatively constant value of 0.46 ± 0.04 V for a frequency range of 10^3 to 10^4 Hz. The acceptor density obtained in this case ($N_a = 9.8 \times 10^{15} \text{ cm}^{-3}$) is in the range calculated from the conductivity of the wafer (1.5×10^{15} - $1.5 \times 10^{16} \text{ cm}^{-3}$ for 1-10 $\Omega \cdot \text{cm}$ p-type Si). The appearance of this second domain can be explained by the depletion of the deep electronic surface states when increasing the potential and the fact that a sufficient energy difference exists between the Fermi level and the valence band ($|E_{vb}-E_{f|vol} \approx 0.2 \text{ eV}$) to allow the observation of a linear region. The flat-band potentials, E_{fb} , and charge carrier densities, N_a , for the different modified and unmodified silicon surfaces are estimated using this linear domain where the Mott-Schottky equation is valid.

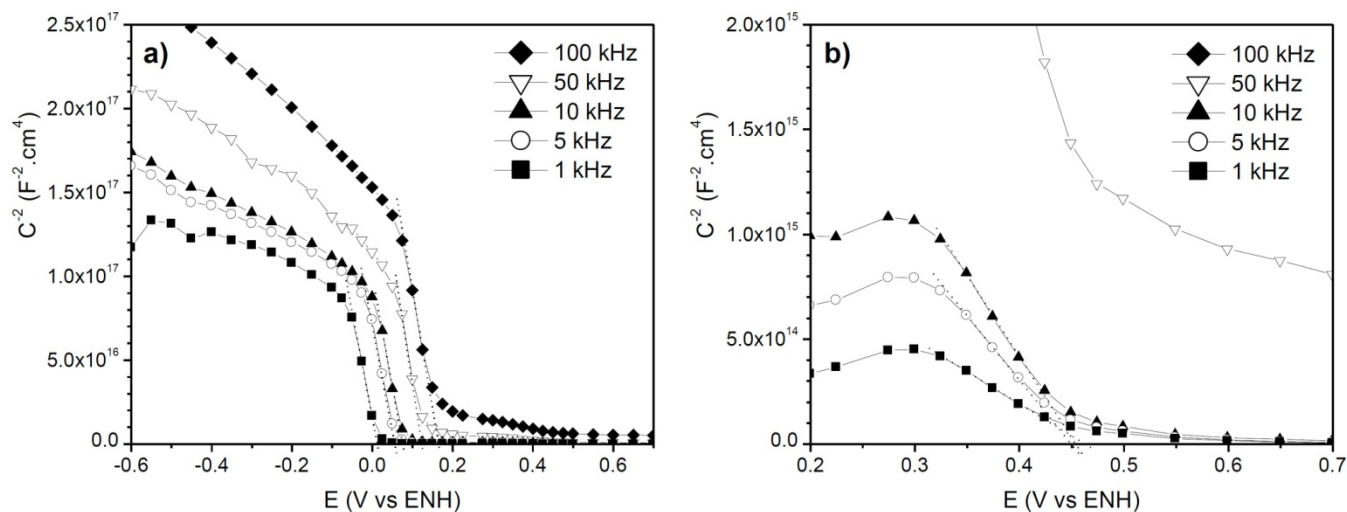


Figure S2. Mott-Schottky plots for a p-Si (111) electrode in 1 mol L⁻¹ HClO₄. a) Potential range from -0.6 to 0.7 V; b) Potential range from 0.2 to 0.7 V.

4. Semiconductor/electrolyte band diagram

With the N_a and E_{fb} values obtained from Mott-Schottky plots, the energy diagram of each electrode can be established according to the general principle described in Figure S3. In addition to the known

values for silicon ($E_g = 1.12$ eV, $\chi_{si} = 4.05$ eV),⁸ other parameters needed to know obtain this diagram include the work function (Φ), determined from the measured open circuit potential (E_{oc}) for each sample and considering the energy position of NHE (-4.5 eV). Also, the shift of the Fermi level position toward the valence band, $|E_{vb}-E_f|_{vol}$ is calculated from the charge carrier density according to:

$$|E_{vb} - E_f|_{vol} = \frac{kT}{q} \ln\left(\frac{N_v}{N_a}\right) \quad (4)$$

with N_v the density of states in the valence band:

$$N_v = 2 \left(2\pi m_h^* \frac{kT}{h^2} \right)^{\frac{3}{2}} \quad (5)$$

Using an effective mass for holes of $m_h^* = 1.15 m_0$ ⁹ and a temperature of 295 K, $N_v = 3.01 \times 10^{19} \text{ cm}^{-3}$, the band bending (E_{bb}) in the space charge layer is given by:

$$E_{bb} = |E_{oc} - E_{fb}|$$

(6)

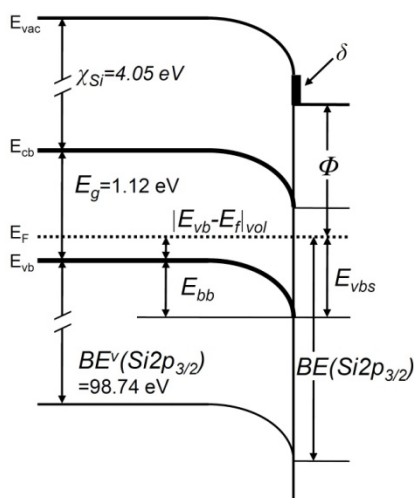


Figure S3. Diagram of surface energy band position for a semiconductor and the different values accessible by XPS and Mott-Schottky measurements.

E_{vbs} represents the position of the valence band at the surface relative to the Fermi level and can be obtain by:

$$E_{vbs} = E_{bb} + |E_{vb} - E_f|_{vol}$$

(7)

For comparison, E_{vbs} can be estimated from XPS measurements taking into account the Si 2p_{3/2} binding energy with respect to the valence band in bulk silicon ($BE^v(\text{Si } 2p_{3/2}) = 98.74(4) \text{ eV}$)¹⁰ and the measured values of Si 2p_{3/2} binding energy $BE^m(\text{Si } 2p_{3/2})$:

$$E_{vbs} = BE^m(\text{Si } 2p_{3/2}) - BE^v(\text{Si } 2p_{3/2}) \quad (8)$$

The E_{vbs} values obtained by the two methods, gathered in Table 2 in the paper, are in good agreement for the silicon samples before and after modification. The surface potential step (δ) is important for an evaluation of the silicon surface electron affinity determining the surface band positions. It represents the electron affinity shift between the surface and the bulk of the silicon sample. This parameter is expected to change with surface modification. It can be calculated according to:

$$\delta = \Phi - E_g - \chi_{si} + E_{vbs} \quad (9)$$

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