

Homogeneously and gradually anchored self-assembled monolayer by tunable vapor phase-assisted silanization

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Electronic Supporting Information

Determination of the Surface Energies

The surface energies of ODMS monolayers were estimated as a function of exposure time. We used the Fowkes-van Oss-Chaudhury-Good model.¹ It describes the total surface energy as a combination of dispersive interactions (Lifshitz-van der Waals) and polar interactions (Lewis acid-base).

$$\gamma^{total} = \gamma^{LW} + \gamma^{AB}$$

where γ^{LW} is the dispersive (or Lifshitz - van der Waals) component. Chaudhury demonstrated that the dispersion (London), induction (Debye) and dipole (Keesom)

contributions to the apolar component are additive. γ^{AB} refer to the polar (or Lewis acid-base) components and is given by

$$\gamma^{AB} = 2\sqrt{\gamma^+\gamma^-}$$

where the electron donor parameter is designated as γ^- (basic component) and the electron acceptor one is designated as γ^+ (acidic component). Then, using the Dupré equation gives

$$\gamma_L(1 + \cos \theta) = 2(\sqrt{\gamma_S^{LW}\gamma_L^{LW}} + \sqrt{\gamma_S^+\gamma_L^-} + \sqrt{\gamma_S^-\gamma_L^+})$$

Three independent equations are obtained by measuring the contact angle of three liquids (2 polar and 1 dispersive) for which the parameters γ_L^+ , γ_L^- and γ_L^{LW} are known.

Liquids	$\gamma_L^{total} (mJ / m^2)$	$\gamma_L^{LW} (mJ / m^2)$	$\gamma_L^{AB} (mJ / m^2)$	$\gamma_L^+ (mJ / m^2)$	$\gamma_L^- (mJ / m^2)$
Water	72.8	21.8	51.0	25.5	25.5
Glycerol	64.0	34.0	30.0	3.92	57.4
α -bromonaphtalene	44.4	44.4	≈ 0	0	0

1. C.J. Van Oss, R.J. Good and M.K. Chaudhury, *Langmuir*, 1988, **4**, 884.

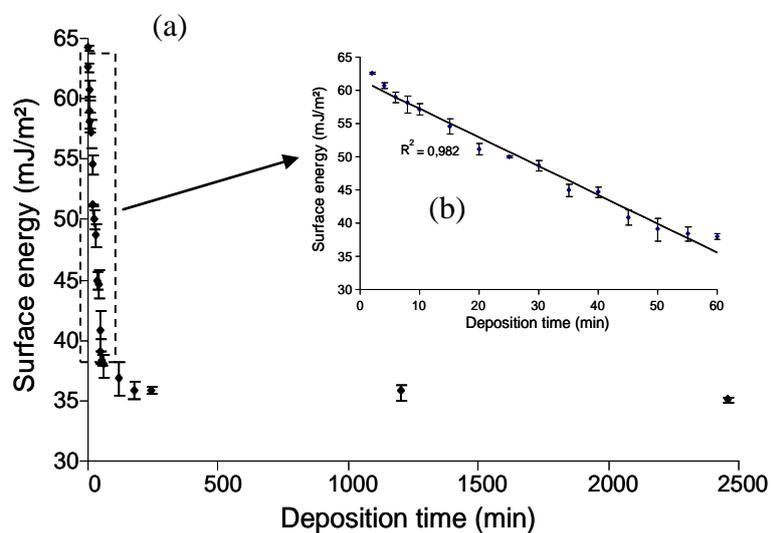


Figure 1. (a) Total surface energy as a function of the exposure time (grafting of ODMS at 60 °C) and (b) magnification for time comprised between 2 and 60 min. The reported errors refer to the standard deviation for each independent experiment.

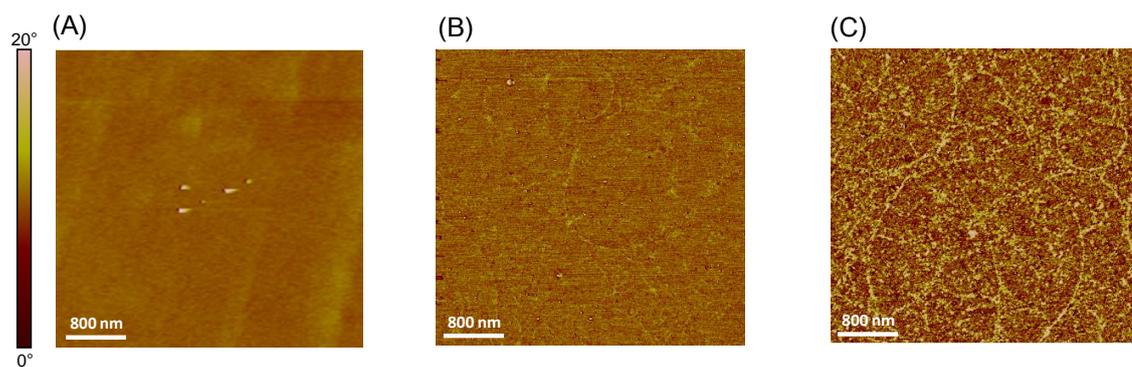


Figure 2. AFM phase images of ODMS-grafted silicon obtained after grafting time of 4 min, 40 min and 60 min (pictures (A), (B) and (C) respectively).

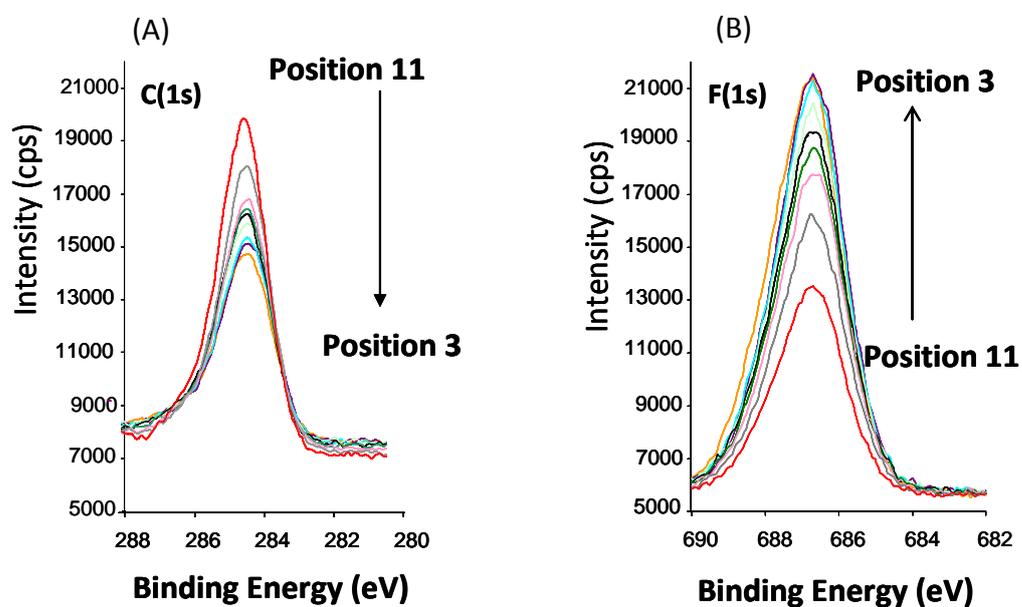


Figure 3. Intensity of C1s (A) and F1s (B) atomic concentration collected on 11 different locations of a silicon wafer firstly exposed to ODMS vapour for 10 min at 110 °C and then exposed to HFDMC vapor for 30 min at 25 °C.

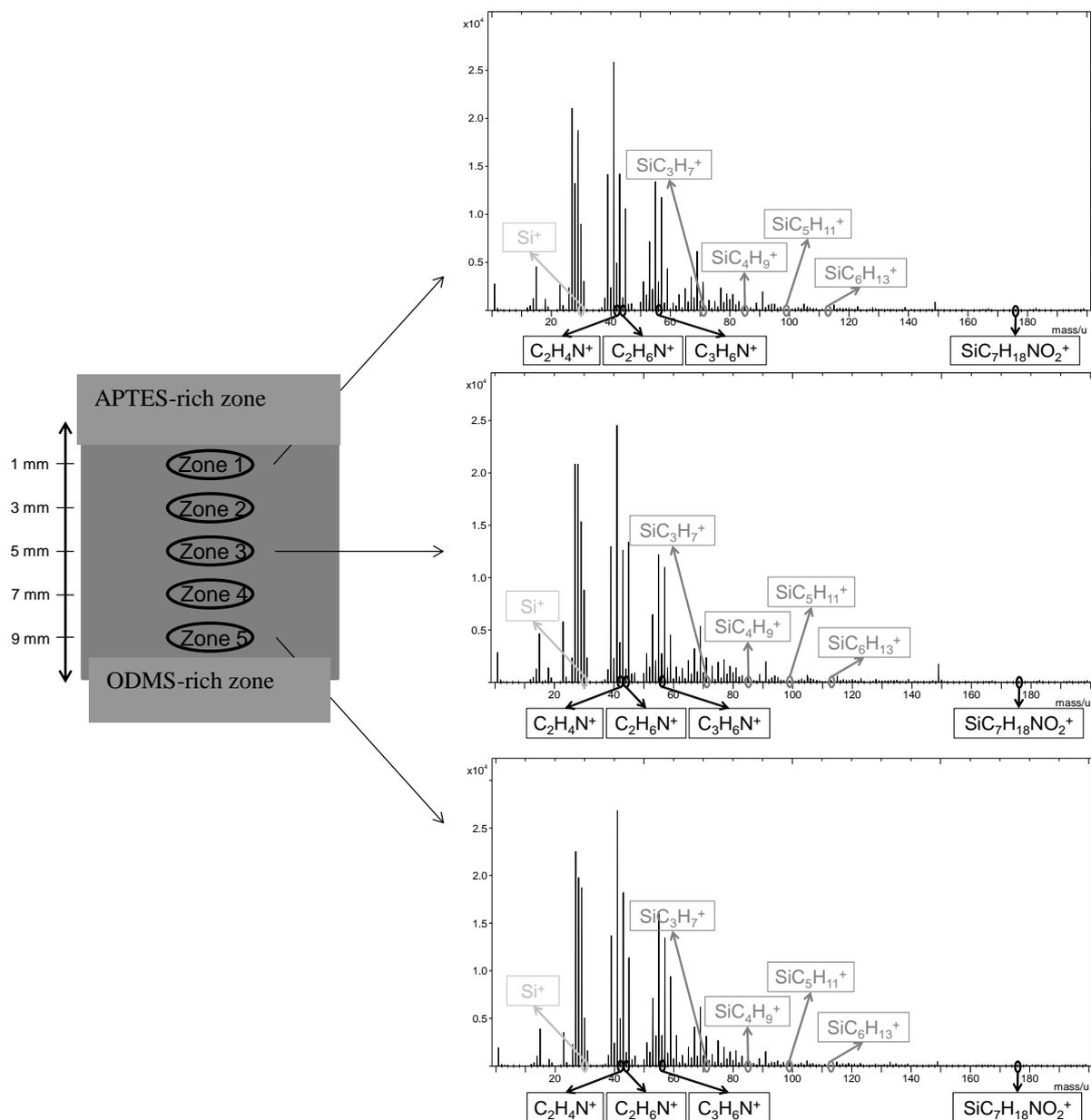


Figure 4. ToF-SIMS positive ion mass spectra of three different locations of a silica surface gradually grafted with ODMS (10 min, 110 °C) and subsequently backfilled with APTES (15 min, 25 °C, ethanol solution).