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Electronic Supplementary Information for

The Rapid Formation of Functional Monolayers on Silicon Under Mild Conditions

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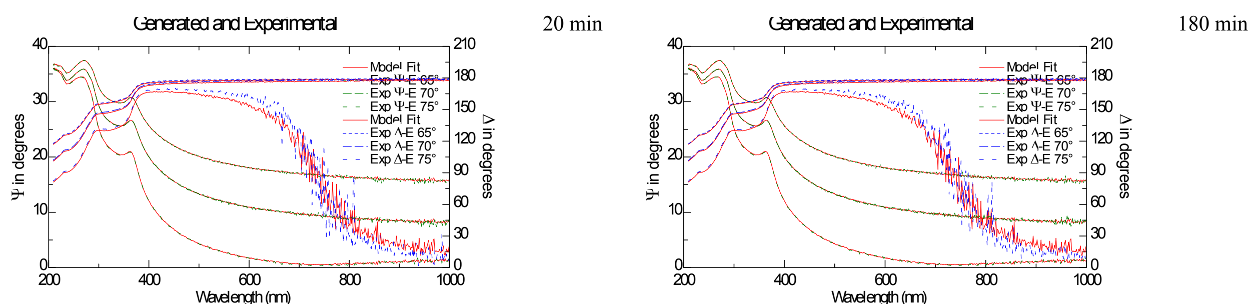

Figure S1. Representative experimental Ψ and Δ data and best-fit models (—) for spectroscopic ellipsometry measurements for the attempted grafting of DEB from dichloromethane (DCM) solutions (substrate: phosphorous-doped, 8-12 Ω cm, Si(100)−H). Reaction times are indicated in figure. The incidence angles were 65, 70 and 75° (graphs from top toward bottom). Ellipsometry determines the complex reflectance ratio $\rho = r_s / r_p = \tan \Psi \exp(i\Delta)$, where r_P and r_S are the Fresnel reflection coefficients for light polarized parallel and perpendicular to the plane of incidence, respectively. The angle Ψ is the ratio of the changes in amplitude for the s and p polarizations after reflection. The angle Δ relates to the difference in the phase shift after reflection for the two polarizations. Refinement using the Cauchy approximation (see §2.2.2 in main text) indicated no DEB monolayer formed from a 5 mM DEB solution in DCM in the dark and at room temperature.

XPS analysis of the fractional surface coverage of surface silicon atoms by DEB molecules in the monolayer

Fractional ML coverage can be extracted from XPS data according to the model of Cicero et al:

$$\frac{N_{ML}}{N_{Si}} = \frac{\lambda_{Si,Si}\, d_{ML}}{\lambda_{C,ML}\, N_C} \frac{I_C/SF_C}{I_{Si}/SF_{Si}} \frac{\rho_{Si}}{N_{Si}} \frac{\exp\left[-d_{ML}/(\lambda_{Si,ML}\sin\theta)\right]}{1 - \exp\left[d_{ML}/(\lambda_{C,ML}\sin\theta)\right]}$$

where d_{ML} is the monolayer thickness obtained from XRR, N_C is the number of carbon atoms in the molecule, $\lambda_{\alpha,\beta}$ is the inelastic mean free path of electrons emitted from α travelling through β ($\lambda_{Si,Si}$ = 16 Å, $\lambda_{C,ML}$ = 36 Å, $\lambda_{Si,ML}$ = 41.5 Å),[1] I_α and $SF\alpha$ are, respectively, thephotoelectron counts and the instrument-specific sensitivity factor for the element α, ρ_{Si} is the Si atoms per unit of volume (0.05 Å^{-3}), N_{Si} is the number density of atoms for the Si(100) surface (0.068 Å^{-2}), θ is the takeoff angle between the surface and the analyzer (90° in our case).

S2

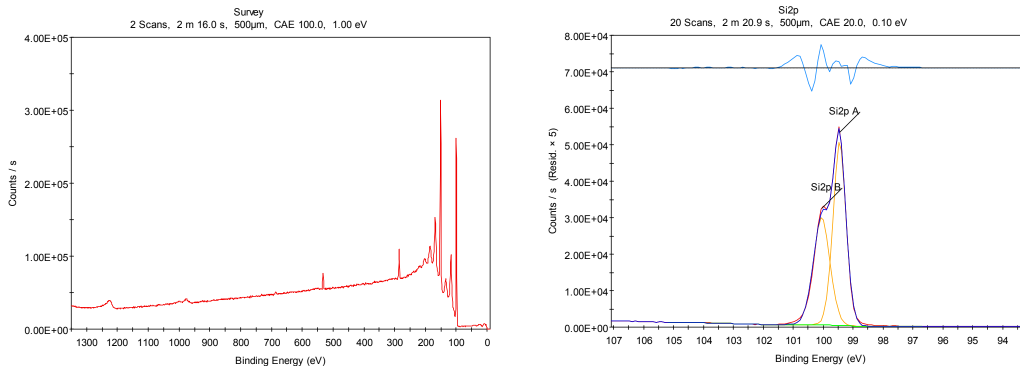

Figure S2. Representative survey and Si 2p high-resolution XPS spectrographs for freshly etched Si(100)−H samples (phosphorous-doped, 8-12 Ω cm). The average C/Si ratio was 0.12 ± 0.02

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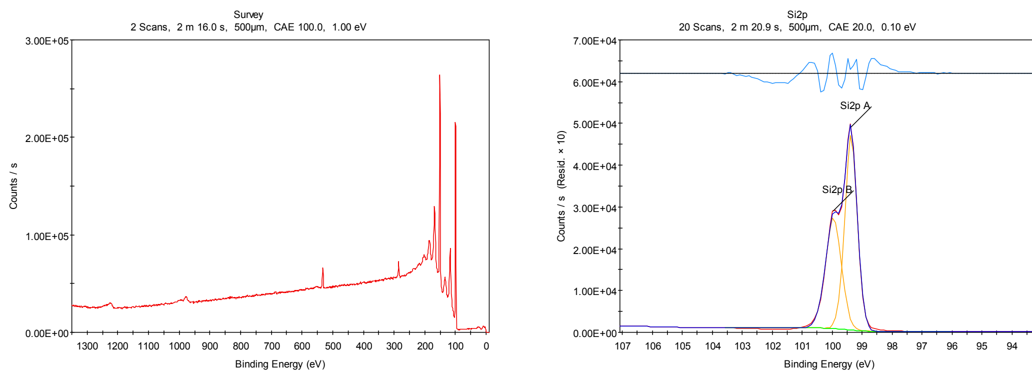
S3

a)



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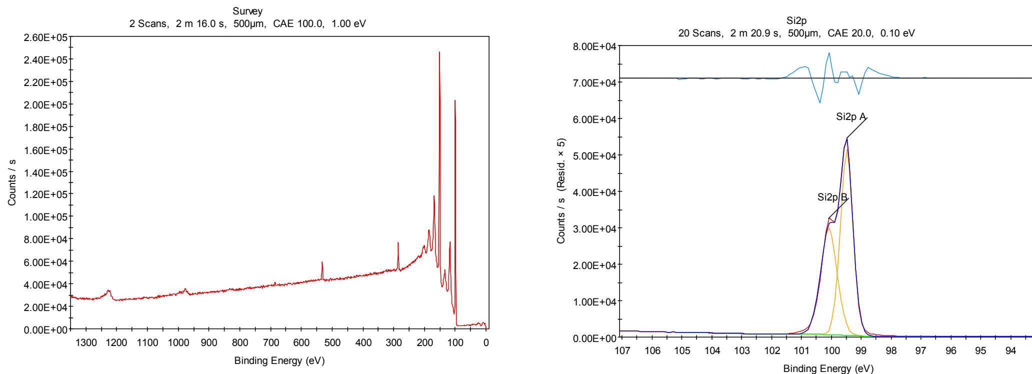


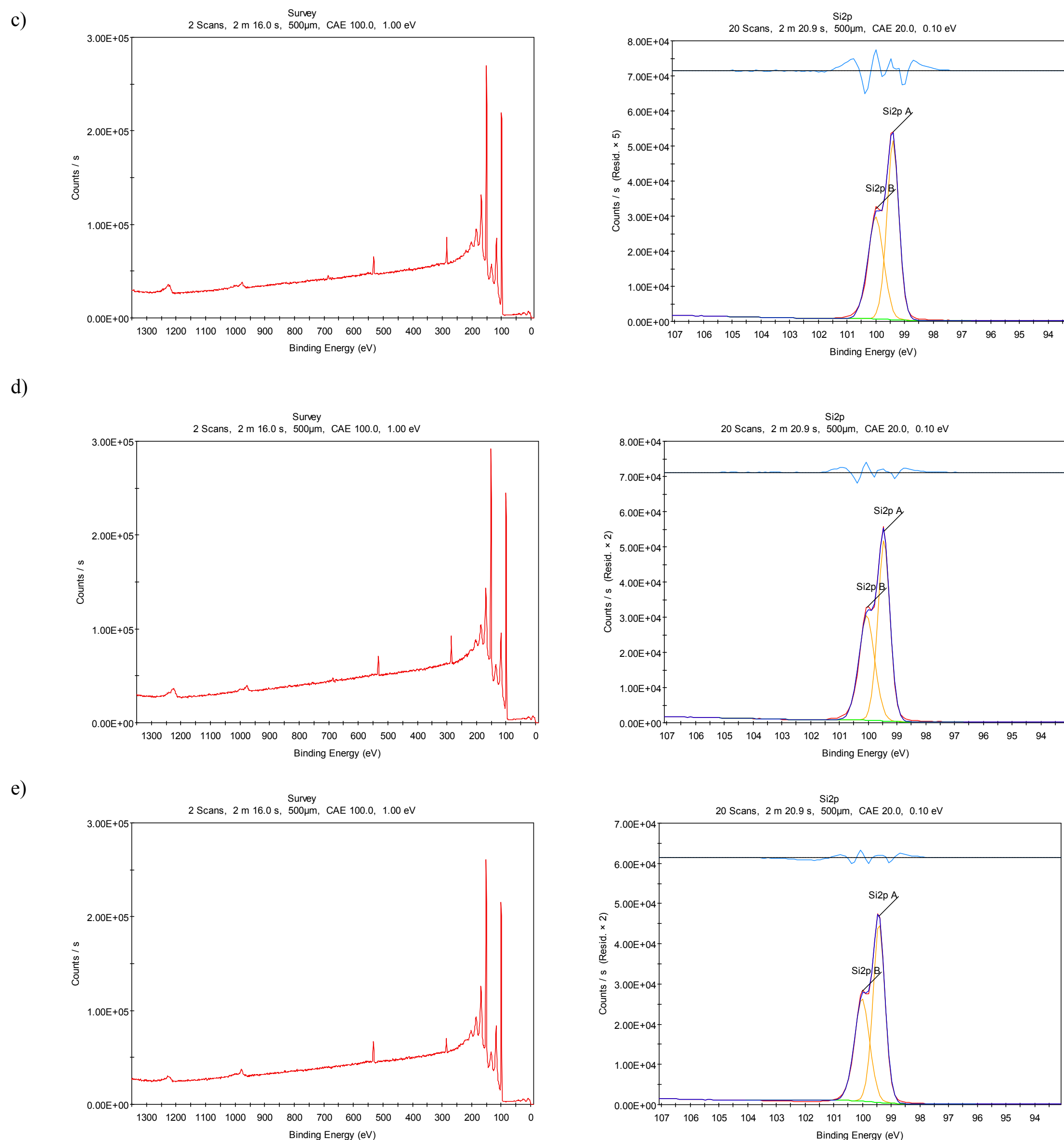
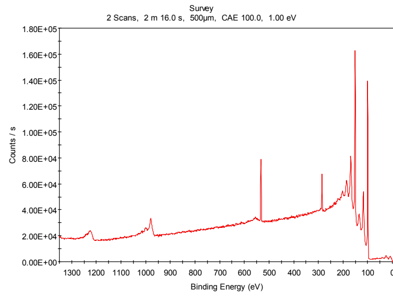
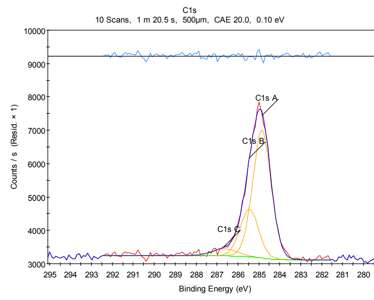


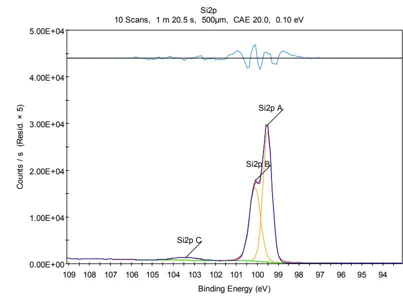
Figure S3. Representative survey and Si 2p high-resolution XPS spectrographs for the attempts to graft DEB from: dichloromethane solutions (substrate: phosphorous-doped, 8-12 Ω cm, Si(100)−H). Reaction times were: ((a), 20 min), ((b), 30 min), ((c), 60 min), ((d), 120 min), ((e), 180 min). Monolayer d values estimated from the attenuation of the substrate Si signal (see footnote 30 in the main text) were equal to 0 nm for all reaction times. No evidence of monolayer formation is found for the DEB/DCM system.

S4

a)







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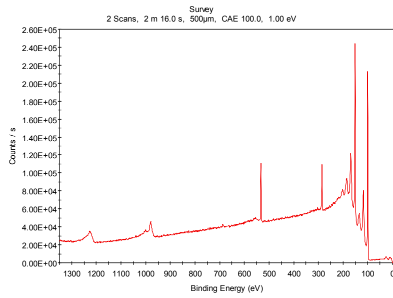

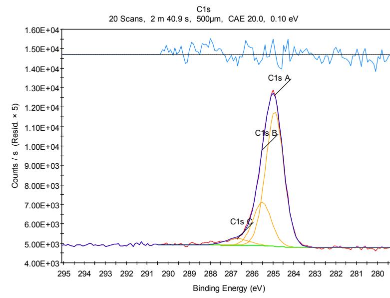

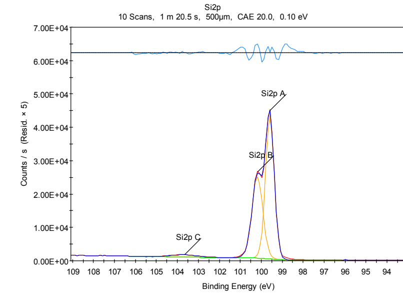

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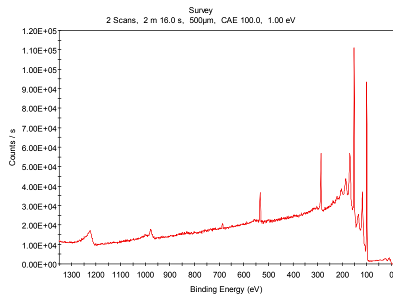

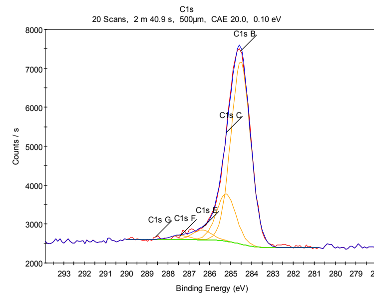

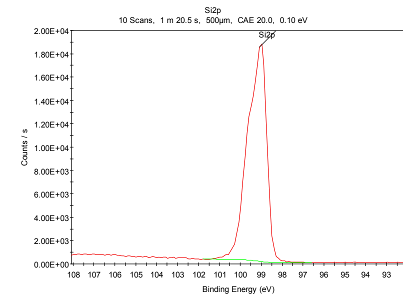

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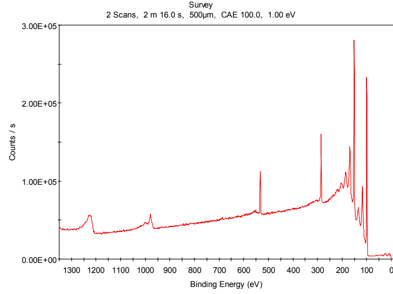
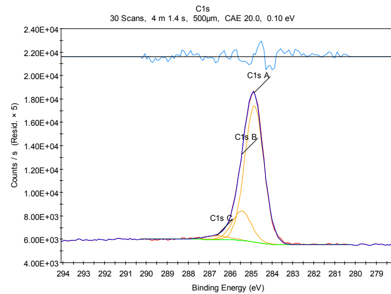
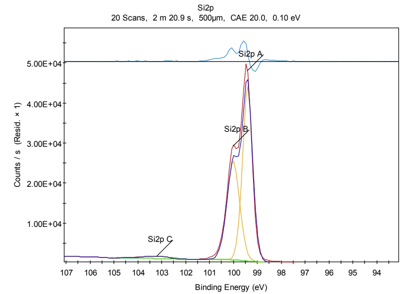






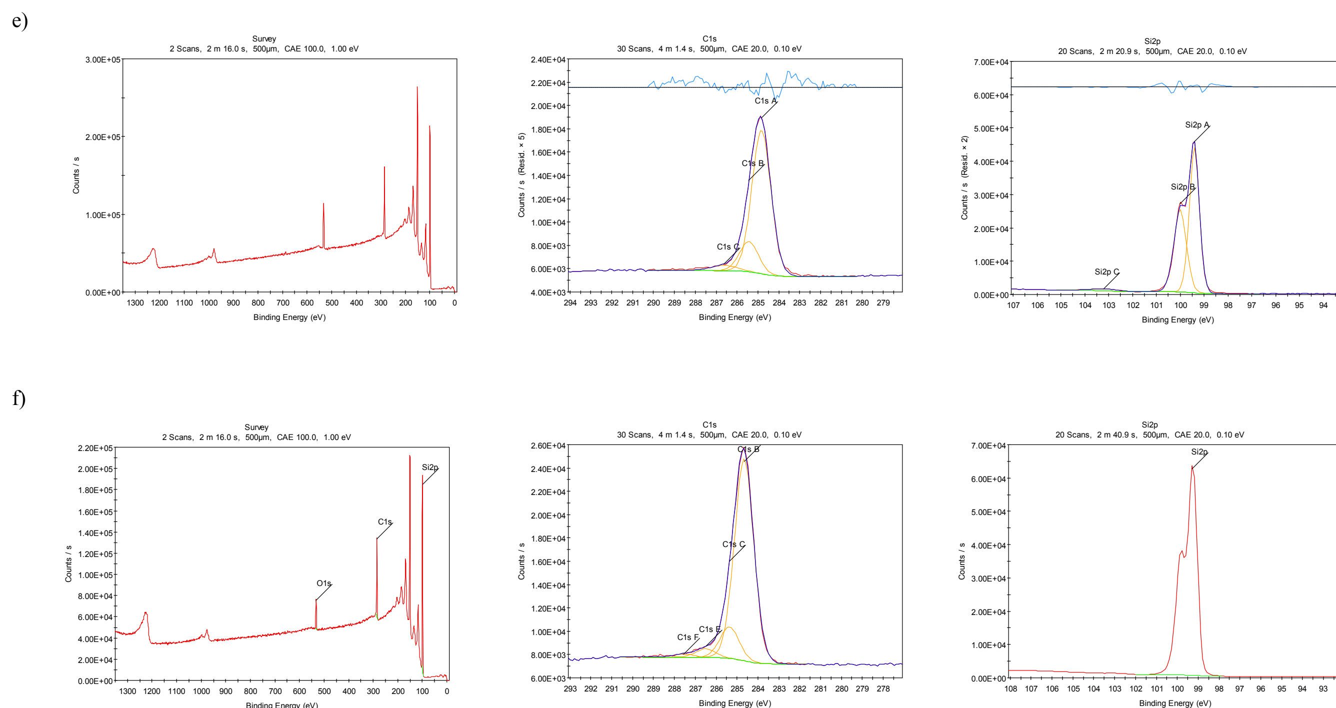
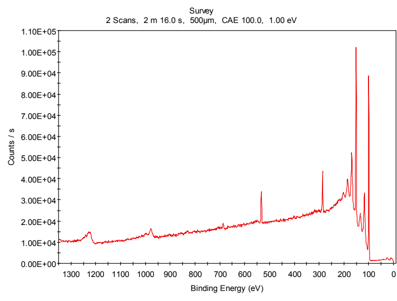
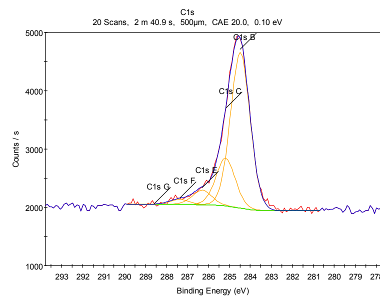


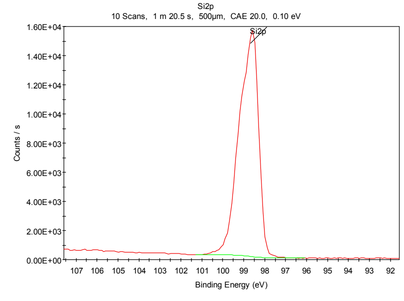
Figure S4. Representative survey, C 1s and Si 2p high-resolution XPS spectrographs for the grafting of DEB from acetonitrile solutions (substrate: phosphorous-doped, 8-12 Ω cm, Si(100)−H). Reaction times were: ((a), 10 min), ((b), 20 min), ((c), 30 min), ((d), 60 min), ((e), 120 min), ((f), 180 min). Average atomic C/Si ratios were: 0.19 (a, 10 min), 0.22 (b, 20 min), 0.30 (c, 30 min), 0.33 (d, 60 min), 0.36 (e, 120 min) and 0.40 (f, 180 min). Values of film thickness, as estimated from the attenuation of the substrate Si 2p signal (see footnote 30 in the main text) were: 0.6 nm (a), 0.7 nm (b), 0.8 nm (c), 1.0 nm (d), 1.1 nm (e), 1.1 nm (f). The high-resolution C 1s signal was generally fitted with three component peaks; the major component at 285.0 eV (76%, 1.0 eV fwhm) is assigned to the methylene carbons of the adsorbate.[2] The binding energy component at 285.6 eV (19%, 1.0 eV fwhm) and the higher binding energy component at 286.8 eV (5%, 1.4 eV fwhm) are tentatively assigned to an asymmetry in the main peak,[3] and to either oxygen-bound carbon atoms (C–O),[4] or sp-hybridized carbon-bound carbon, respectively.[5] On hydrogenated silicon surfaces, the assembly of monolayers of 1-alkynes is likely to result in sp^2 hybridization at the surface.[6] The growth of sp^2 structures is kinetically more facile than that of sp^3 structures (*i.e.*, 1-alkene adsorbates),[6-8] possibly by a factor of up to 6:1.[9] XPS data does support the existence of some oxidized carbon in the film, and this is in line with entropic considerations.[10] The C 1s peak decomposition may indicate that a non-negligible number of C–O bonds exist in monolayers of DEB. The structure of the adventitious C–O bond is still highly debated, although contamination has been reported in several studies.[2-4, 10] For instance, Kramer and co-workers suggests that a shift from 285 to 286.5 eV is likely to be associated to the core ionization of monohydroxyl carbon atoms (–Si–CHC(OH)–).[3] Zuilhof and co-workers have more recently suggested that the emission at 286.5 eV may also include emissions from –C≡C– groups.[5]

S5

a)







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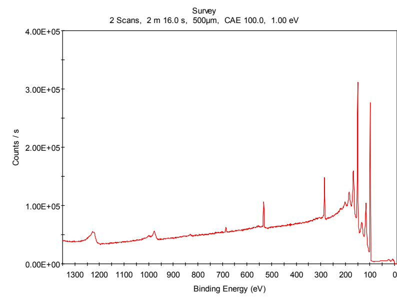

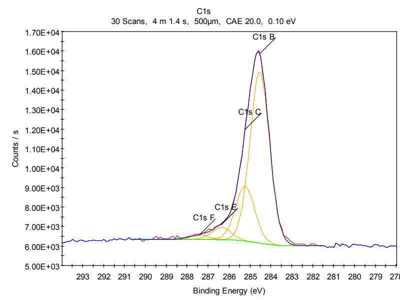

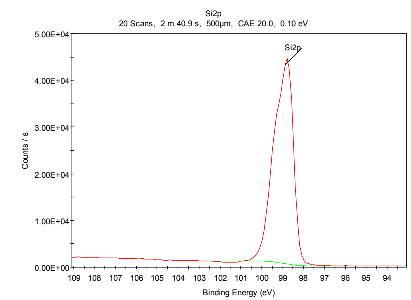

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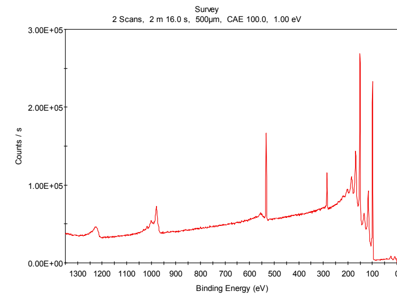

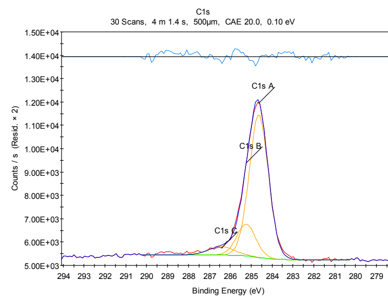

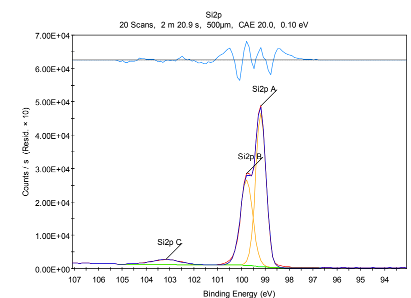

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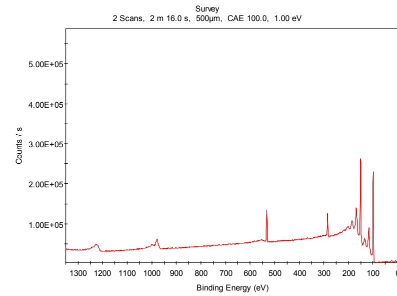

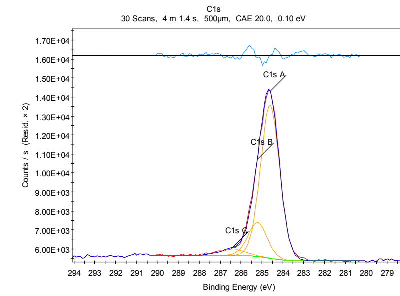

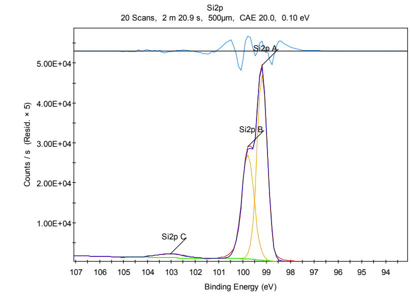

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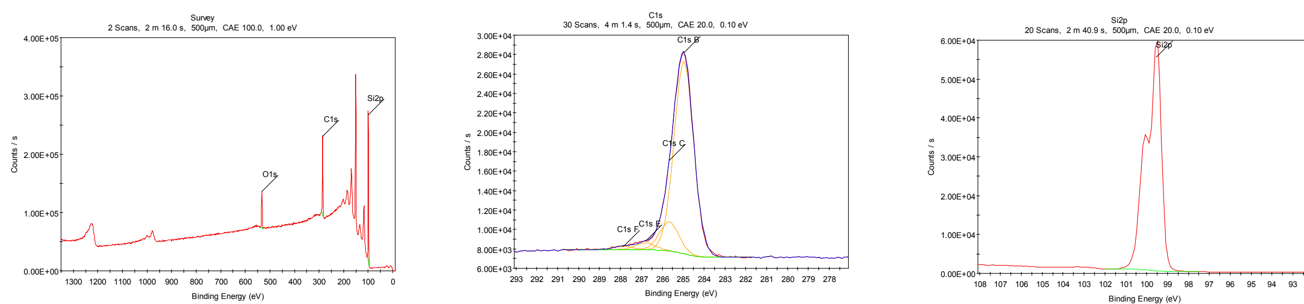

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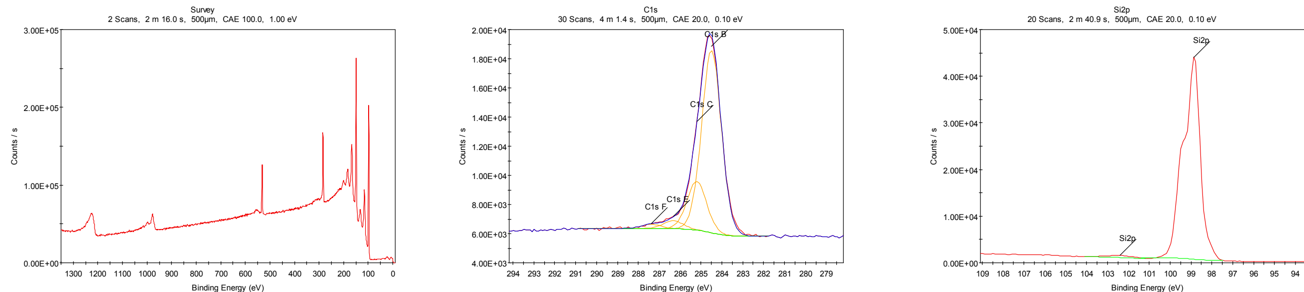


Figure S5. Representative survey, C 1s and Si 2p high-resolution XPS spectrographs for the grafting of DEB from acetonitrile solutions (substrate: boron-doped, 10-20 Ω cm, Si(100)−H). Reaction times were: ((a), 10 min), ((b), 20 min), ((c), 30 min), ((d), 60 min), ((e), 120 min), ((f), 180 min). Average atomic C/Si ratios were: 0.22 (a, 10 min), 0.25 (b, 20 min), 0.18 (c, 30 min), 0.23 (d, 60 min), 0.43(e, 120 min) and 0.36 (f, 180 min). Values of film thickness, as estimated from the attenuation of the substrate Si 2p signal (see footnote 30 in the main text) were: 0.5 nm (a), 0.6 nm (b), 0.7 nm (c), 0.8 nm (d), 0.9 nm (e), 1.0 nm (f).

S6

d	**9.70(7) Å**
SLD	**$13.6x10^{-6}$ Å^{-2}**
Roughness	**5.5(10) Å**

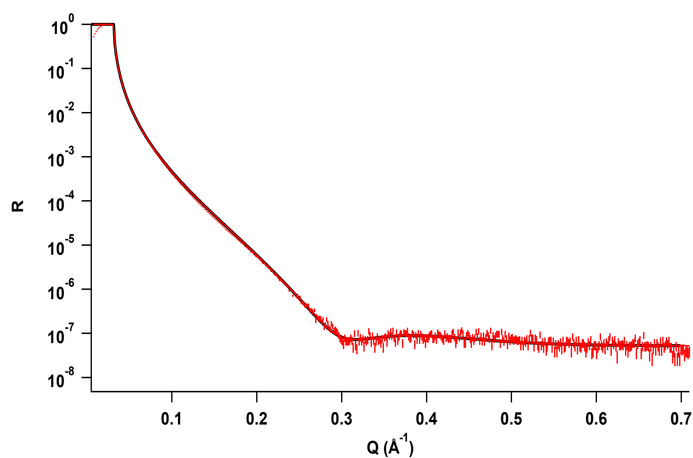
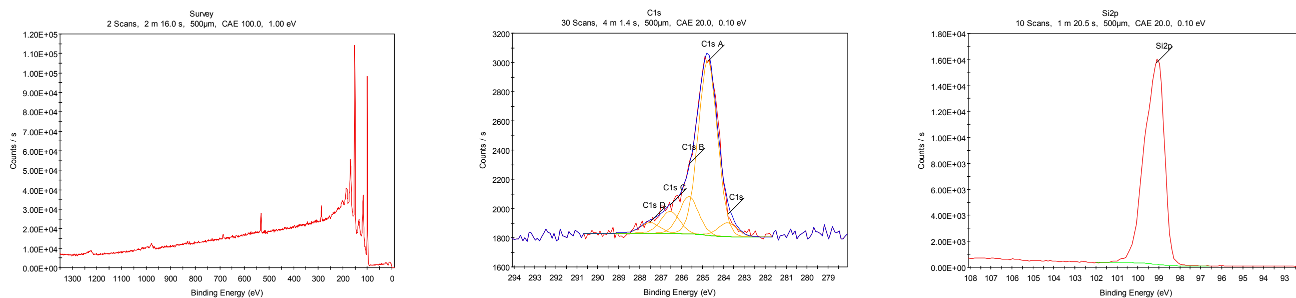


Figure S6. Measured and refined (—) XRR profiles for DEB films on n-type Si(100) surfaces. Reaction time was 120 min. The refined value of scattering length density, is 13.6×10^{-6} Å^{-2}. The XRR-determined film thickness is 9.7(7) Å.

S7

a)



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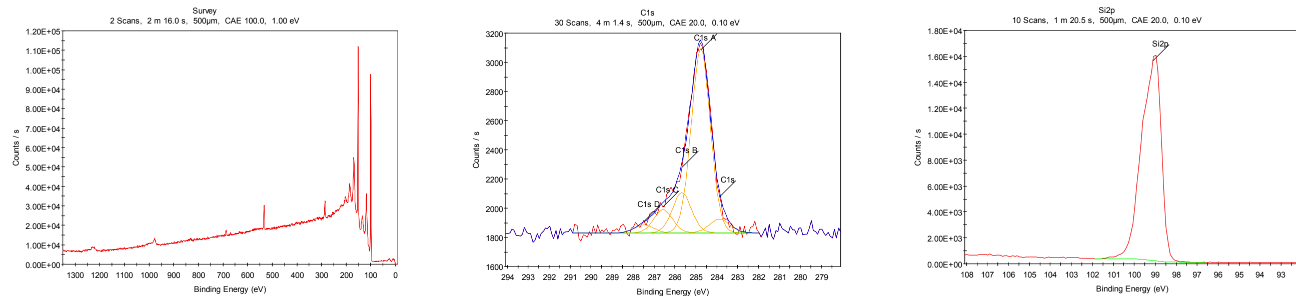

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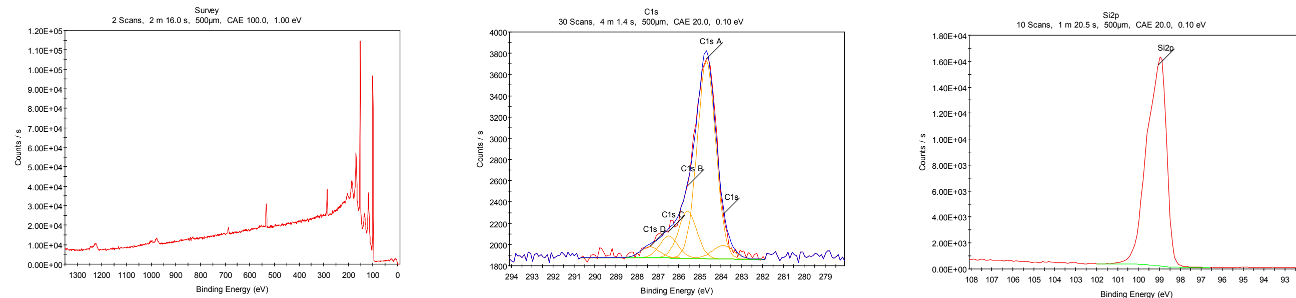

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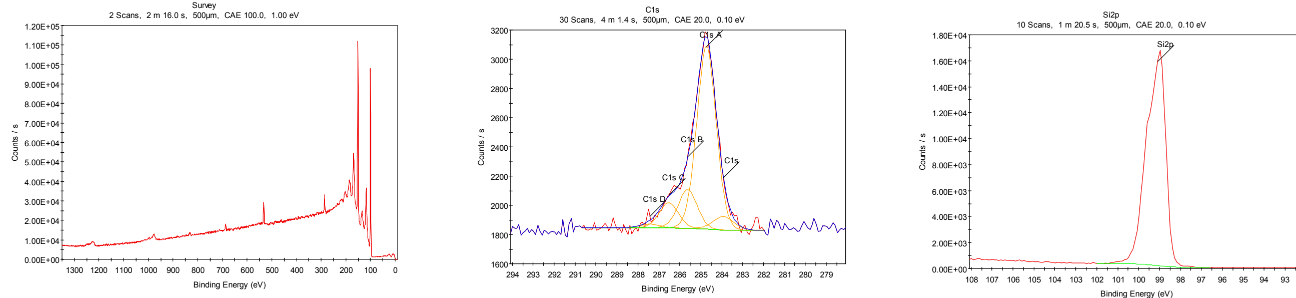

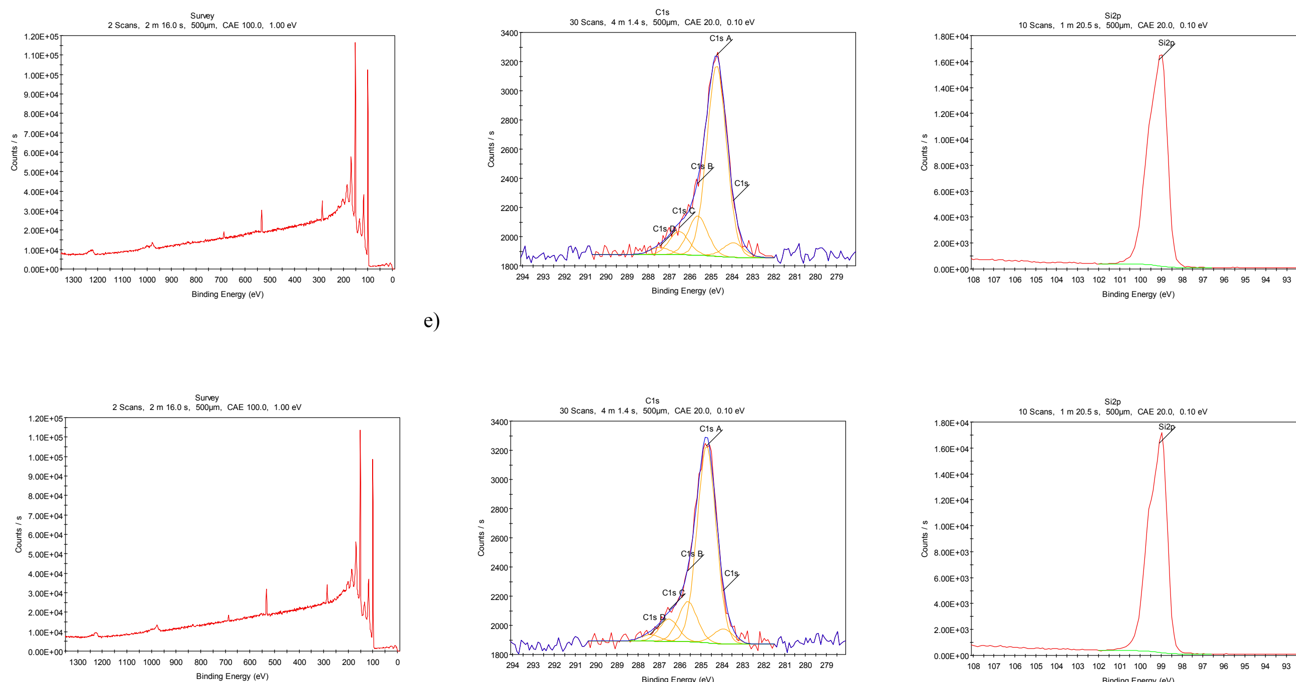

Figure S7. Representative survey, C 1s and Si 2p high-resolution XPS spectrographs for the attempts to graft 1,8-nonadiyne from: acetonitrile solutions (substrate: phosphorous-doped, 8-12 Ω cm, Si(100)−H). Reaction times were: ((a), 10 min), ((b), 20 min), ((c), 30 min), ((d), 60 min), ((e), 120 min), ((f), 180 min). Atomic C/Si ratios were: 0.09 (a, 10 min), 0.10 (b, 20 min), 0.14 (c, 30 min), 0.10 (d, 60 min), 0.10 (e, 120 min) and 0.10 (f, 180 min). Values of film thickness, as estimated from the attenuation of the substrate Si 2p signal (see footnote 30 in the main text) were 0 nm for all reaction times.

S8

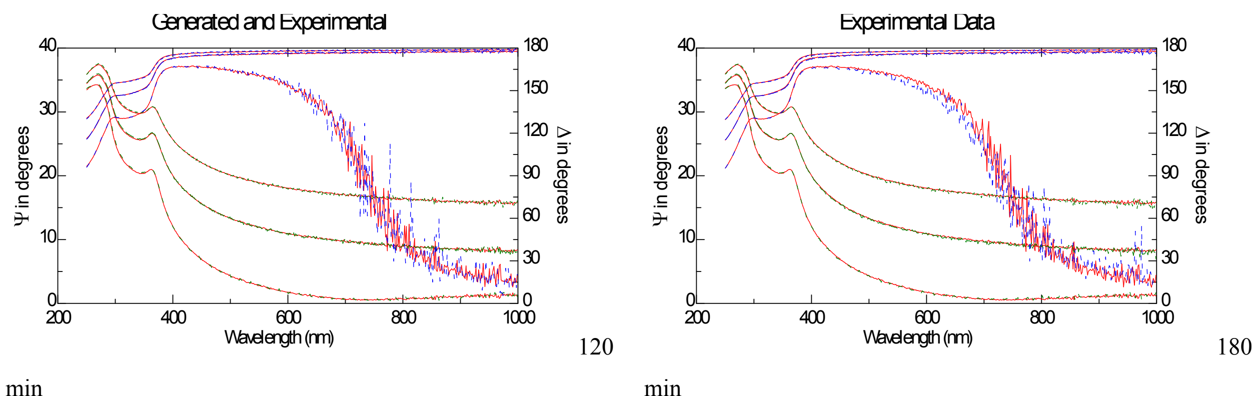

Figure S8. Representative experimental Ψ and Δ data and best-fit models (—) for spectroscopic ellipsometry measurements for the attempted grafting of DEB from THF solutions (substrate: phosphorous-doped, 8-12 Ω cm, Si(100)−H). Reaction times are indicated in figure. Cauchy approximation (see §2.2.2 in main text) indicated no monolayer was formed from a 5 mM 1,8-nonadiyne solution in THF in the dark and at room temperature.

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