

## Electronic Supplementary Information (ESI)

### Road for macroporous silicon stabilization by ultrathin ALD TiO<sub>2</sub> coating

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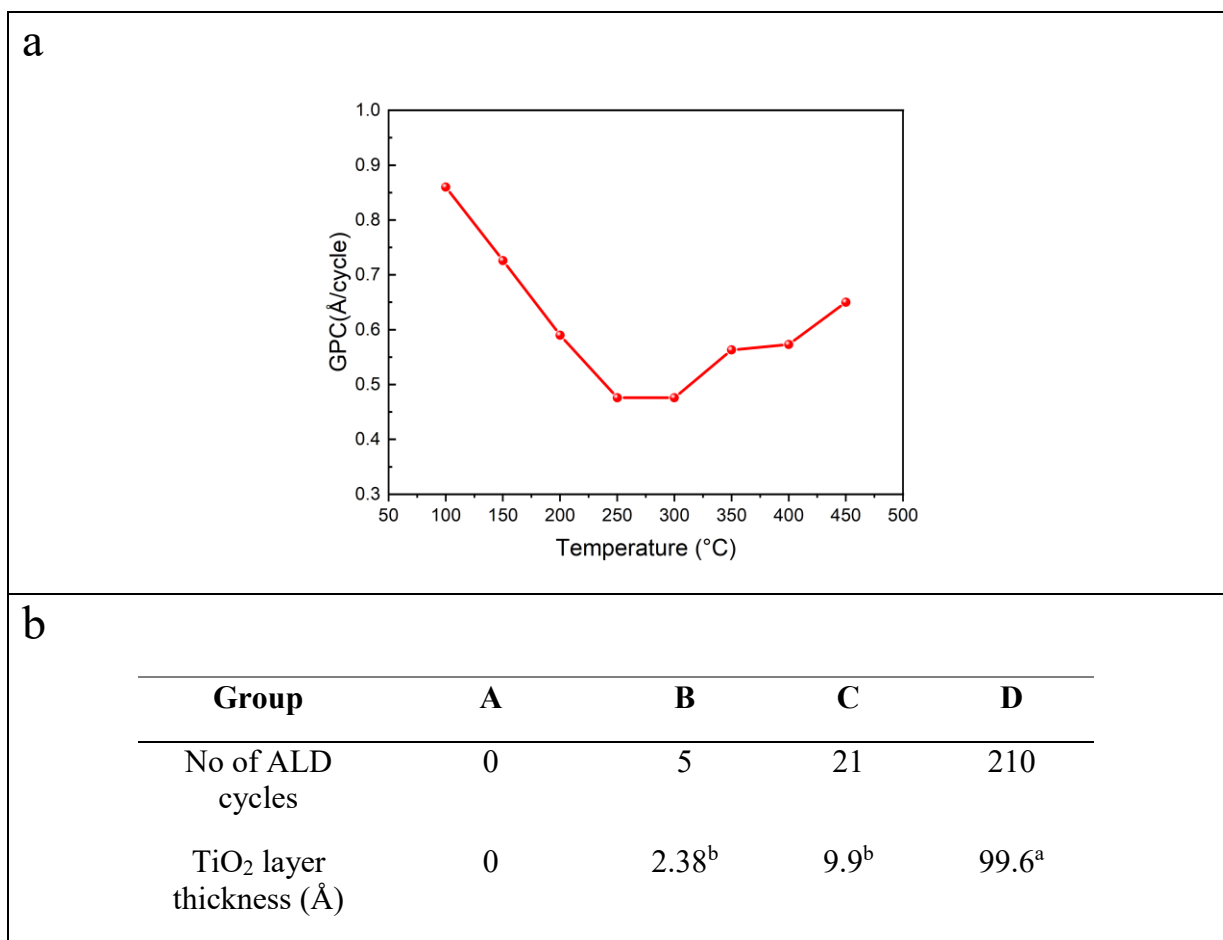
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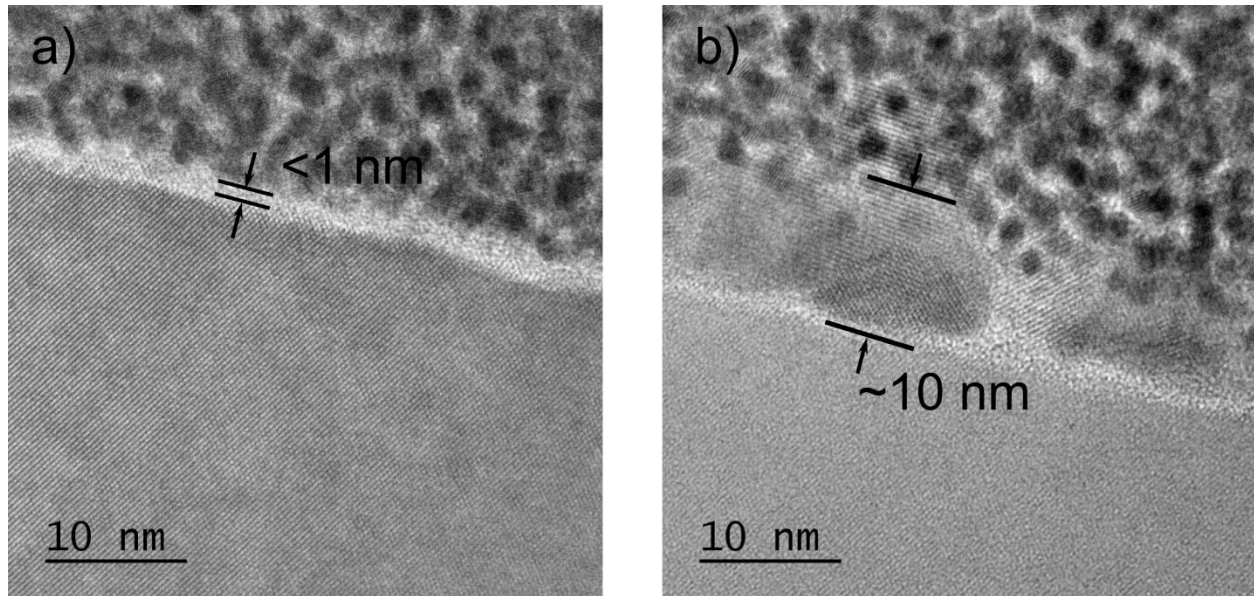
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## 1. ALD window



**Fig. S1:** (a) ALD window of TiO<sub>2</sub> deposition using the recipe described in the Experimental section. (b) Table summarizing the corresponding films thicknesses for each sample group as a function of the number of ALD cycles at 300°C. <sup>a</sup>Value measured thanks to SEM observation. <sup>b</sup>Values extrapolated as a function of the number of ALD cycles and the group B measurement.

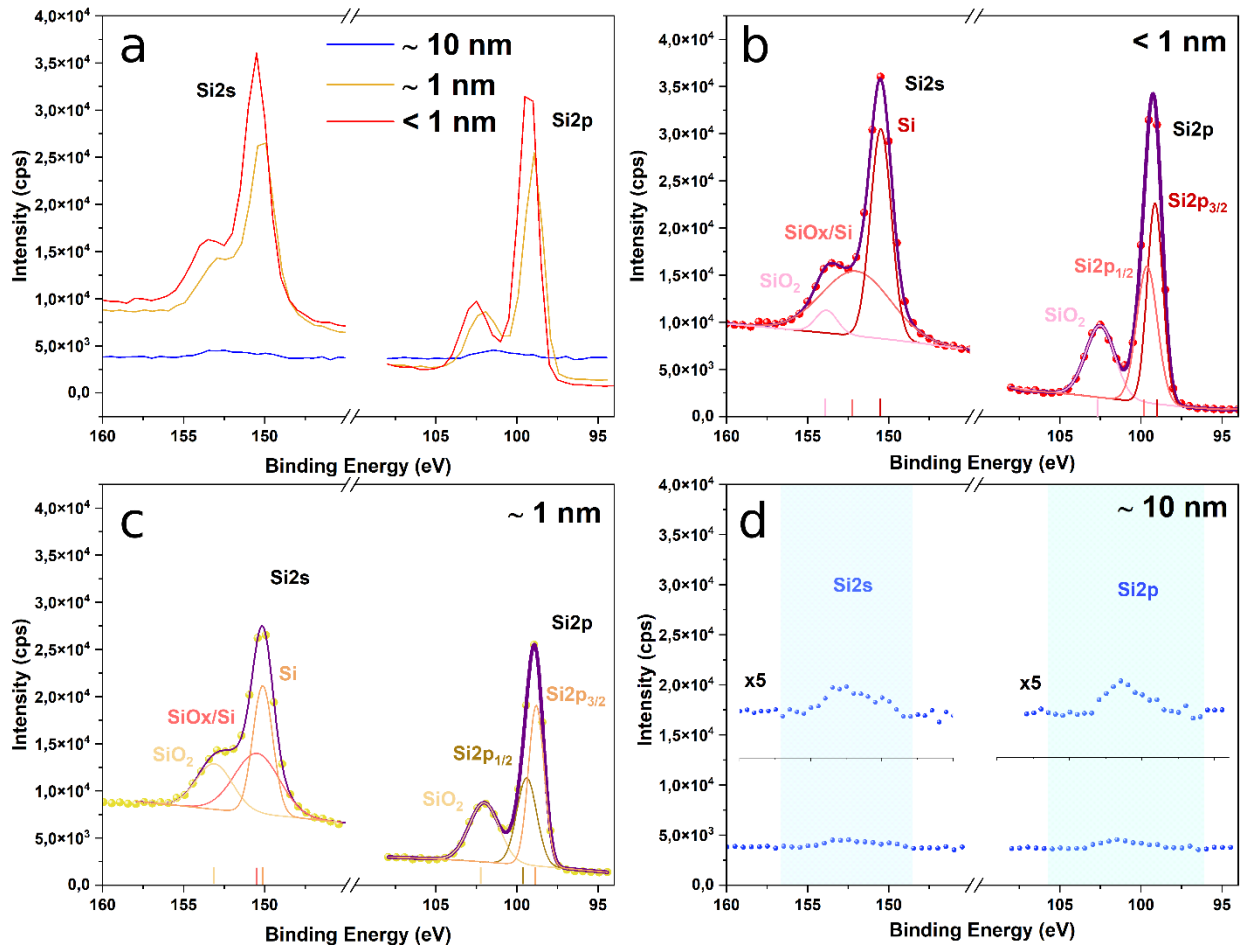
## 2. TEM images of TiO<sub>2</sub> layers for samples from Groups B and D



**Fig. S2:** (a) TEM observation of the sub 1nm-thick TiO<sub>2</sub> layer deposited on flat porous silicon. One can observe the roughness is low, typical from thin ALD films. (b) TEM observation of the ~10 nm-thick TiO<sub>2</sub> layer deposited on flat porous silicon. The layer presents inhomogeneous growth of TiO<sub>2</sub> grains. The presence of these grains is explained by the fact that ALD process is done after desoxidation step. This leads to the formation of such grains as Si-H bond are present during the first ALD cycles<sup>1</sup>.

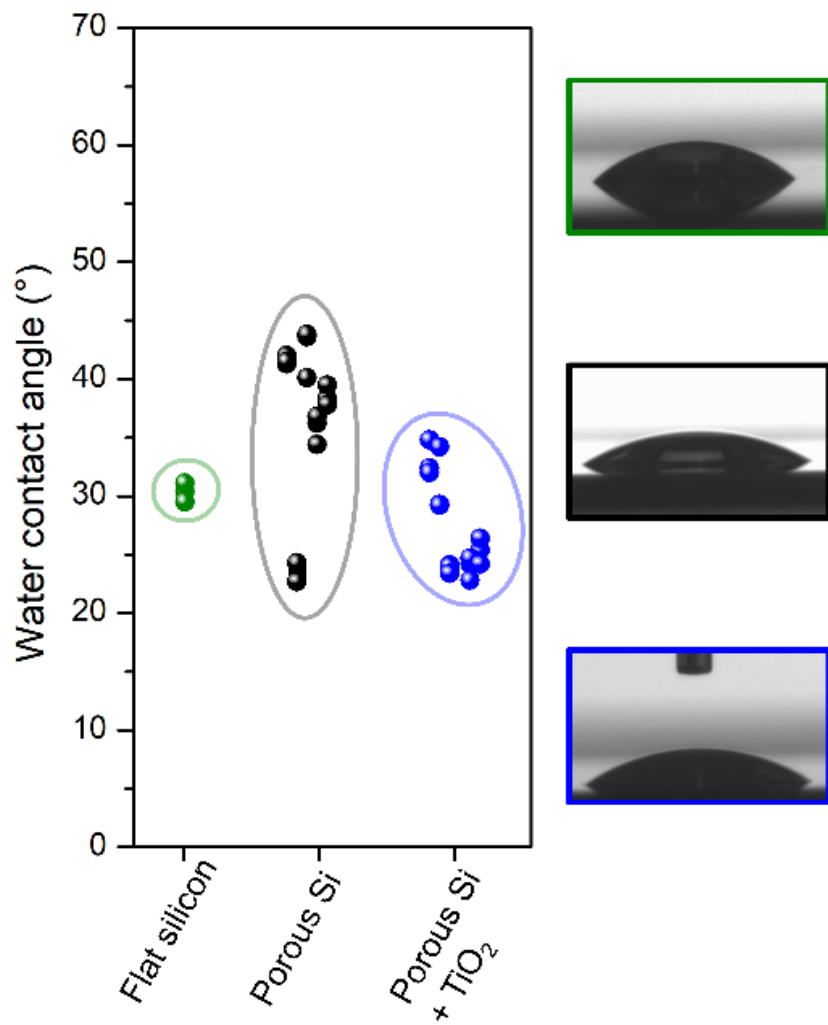
### 3. Detailed high-resolution XPS spectra of the Si 2s and 2p peaks

Figure S3 shows the high-resolution XPS spectra of the Si 2s and 2p peaks. Figure S3a present a comparison between the three samples, whereas Figures S3b, S3c and S3d present, respectively, the detail for group B (<1 nm of TiO<sub>2</sub> on PSi), C (~1nm of TiO<sub>2</sub> on PSi) and D (~10 nm of TiO<sub>2</sub> on PSi) samples. The Si 2p and Si 2s peaks are much less intense when thicker TiO<sub>2</sub> layers are covering the porous silicon.



**Fig. S3:** Detailed high-resolution XPS spectrum of the Si 2s and Si 2p peaks for the various samples: (a) comparison of all three samples; (b) group B sample; (c) group C sample; (d) group D sample. In (b), (c) and (d), solid dots correspond to the experimental data, whereas the solid purple line corresponds to the fit.

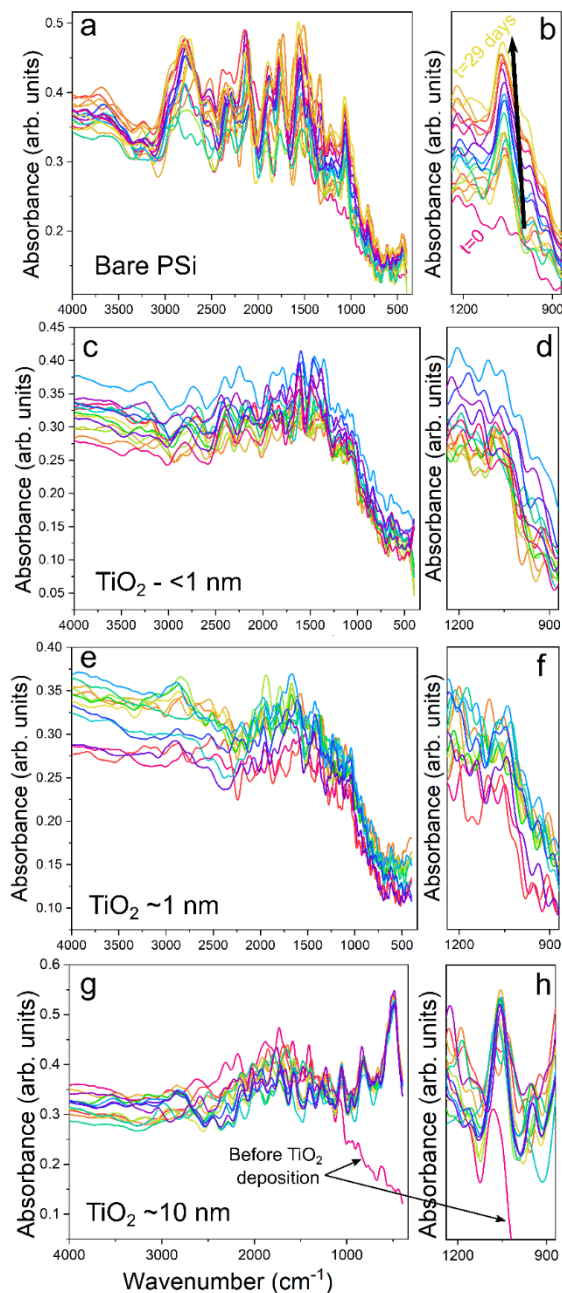
#### 4. Water contact angle measurements



**Fig. S4:** Measured water contact angle of flat (green), porous (black) and ~10nm TiO<sub>2</sub> coated porous silicon (blue) silicon and associated pictures (insets).

## 5. Complete FTIR spectra (400 to 4000 $\text{cm}^{-1}$ )

Figure S5 shows the FTIR spectra (ranging from 400 to 4000  $\text{cm}^{-1}$ ) of one sample from each sample group, representative of the observed oxidative/stabilization processes. Figure S5 b, d, f and h focus on the energetic band of interest (from 900 to 1200  $\text{cm}^{-1}$ ). These views allow to better show the oxidation occurring for bare PSi (Fig. S5a and b) over the 700 hours of the experiment. Note that we observed that the frequency of the Si-O-Si vibration shifts up to 1075  $\text{cm}^{-1}$ , which can be related to a growing angle of the Si-O-Si bridge.<sup>2,3</sup>



**Fig. S5:** FTIR spectrum used for the monitoring of the oxidation of the group A (bare PSi), B (<1 nm of  $\text{TiO}_2$  on PSi), C (~1 nm of  $\text{TiO}_2$  on PSi) and D (~10 nm of  $\text{TiO}_2$  on PSi) samples over 700 hours. Spectra a, c, e, g show the 400-4000  $\text{cm}^{-1}$  band and spectra b, d, f, h focus on the 900-1200  $\text{cm}^{-1}$  band.

## 6. Evolution of the absorption band at 620 nm of MB in aqueous solution

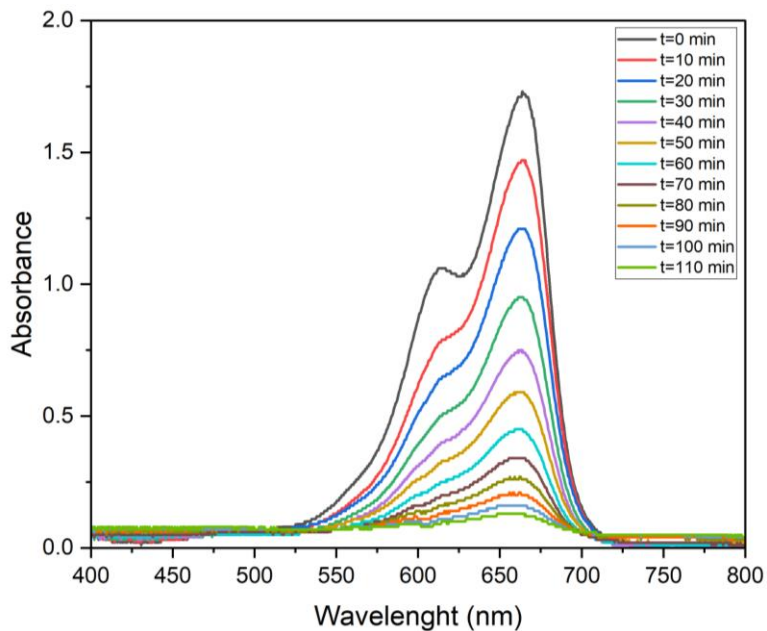


Figure S6: Evolution of the absorption band at 620 nm of MB (MB in solution  $C_0 = 5.6 \times 10^{-3}$  mol/L) under light exposure in the presence of a group D sample ( $\sim 10$  nm  $\text{TiO}_2$  deposited on porous silicon).

## 7. Luminescence spectra

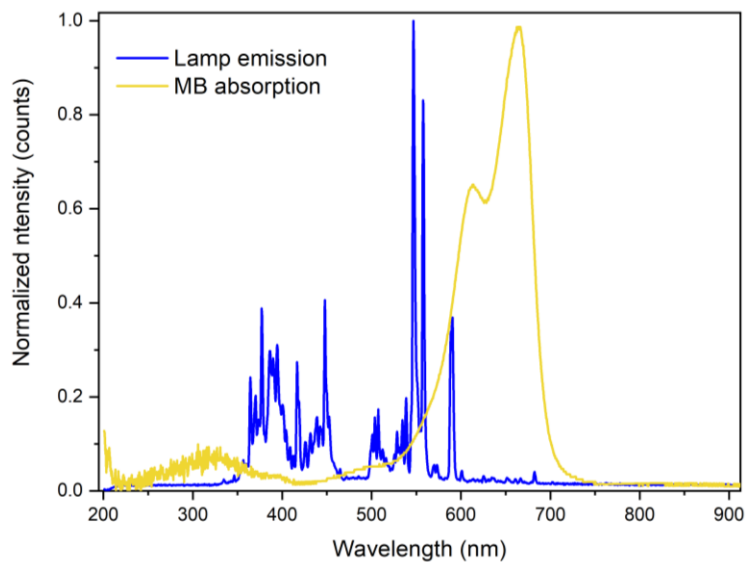


Fig. S7: Measured spectra of the lamp emission (blue line) and MB solution absorption (yellow line).

## 8. Apparent rate constants of MB degradation

**Table S1** – Apparent (pseudo-first) rate constants ( $k$ ) of MB degradation upon illumination (350-680 nm) using ALD TiO<sub>2</sub> coated (various cycles) n-type PSi. The kinetic constants were obtained from the fit of the linear part of the curves in Figure 4b.

Sample	Apparent rate constant $k$ (min <sup>-1</sup> )
Group B (< 1 nm)	0.02002
Group C (~1 nm)	0.01515
Group D (~10 nm)	0.02112
Control solution	0.01142

## 9. References

1. D. R. G. Mitchell, D. J. Attard and G. Triani, *Thin Solid Films*, 2003, **441**, 85-95.
2. D. Gräf, M. Grundner, R. Schulz and L. Mühlhoff, *Journal of Applied Physics*, 1990, **68**, 5155-5161.
3. D. B. Mawhinney, J. A. Glass and J. T. Yates, *The Journal of Physical Chemistry B*, 1997, **101**, 1202-1206.