

Figure 1: (Left) Water contact angle data shows DMATMS reaction at  $135^{\circ}$ C,  $180^{\circ}$ C and  $250^{\circ}$ C saturate to a value of  $97\pm1^{\circ}$  and  $98\pm1^{\circ}$  and  $101\pm1^{\circ}$  respectively, suggesting only a very minor impact of the temperature on surface functionalization. The HMDS reaction, at  $135^{\circ}$ C and  $180^{\circ}$ C, saturates to a value of  $\pm 81^{\circ}$ . (Right) – the trimethylsilyl (TMS, Si-(CH<sub>3</sub>)<sub>3</sub>) surface concentration, measured by XPS. DMATMS reaction at  $250^{\circ}$ C results in  $\pm 2.1$  TMS/nm<sup>2</sup> after 300 s, close to the theoretical limit of 2.41 TMS/nm<sup>2</sup>, while the HMDS reaction at  $135^{\circ}$ C results in only  $\pm 1.5$  TMS/nm<sup>2</sup>.



Figure 2: The selectivity, defined as the normalized thickness difference between the growth and non-growth surface S=(N(g)-N(ng)) / (N(g)+N(ng)), as a function of the TiO<sub>2</sub> (ALD at 150°C) thickness on the growth surface (RBS). The DMATMS passivation at 250°C, 180°C and 135°C result in a selectivity of 0.95, 0.92 and 0.90 respectively, corresponding to 3.41 nm on hydroxylated SiO<sub>2</sub>. HMDS has only a selectivity of 0.13 for the same amount of growth on hydroxylated SiO<sub>2</sub>.



Figure 3: Scanning electron microscopy (SEM) images for 100 cycles of  $TiO_2$  ALD on (left) hydroxylated  $SiO_2$ , (middle) HMDS (135°C, 300s) passivated  $SiO_2$  and (right) DMATMS (250°C, 300s) passivated  $SiO_2$ . The hydroxylated  $SiO_2$  is fully covered with a smooth film of  $TiO_2$ , for HMDS the surface is almost fully covered in  $TiO_2$  but shows a rougher surface, while for DMATMS there are small islands of  $TiO_2$  visible after 100 cycles, indicating growth inhibition and island growth.