Supporting Information

**Surface Diffusion Control Enables Tailored Aspect Ratio Nanostructures in Area-Selective Atomic Layer Deposition**

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Saturation characteristics of the TiO$_2$ ALD process

We optimized the ALD parameters for the growth of TiO$_2$ on poly (methyl methacrylate) (PMMA) to ensure the saturation characteristics of the process. Therefore, we determined the TiO$_2$ film thickness from X-ray reflectivity measurements. The titanium tetrachloride (TiCl$_4$) pulse time was varied, while the water (H$_2$O) pulse time and the TiCl$_4$ and H$_2$O purge times were set arbitrarily large to 10 s. This ensures complete saturation of the surface with H$_2$O and an efficient removal of excess precursors and reaction products from the reactor. The number of cycles was 100, and the growth per cycle (GPC) as a function of the TiCl$_4$ pulse time shows saturation at a pulse duration of 0.1 s (Figure S1A). Then, the TiCl$_4$ pulse time was set to 0.1 s and the H$_2$O pulse time was varied, while the TiCl$_4$ and H$_2$O purge times were set arbitrarily large at 10 s. The GPC as a function of the H$_2$O pulse time shows saturation at a pulse duration of 3 s (Figure S1B).

**Figure S1.** Saturation characteristics of the TiO$_2$ ALD process. TiO$_2$ was grown from TiCl$_4$ and H$_2$O on PMMA. (A) GPC of TiO$_2$ as a function of the TiCl$_4$ pulse time. Saturation occurs at 0.1 s. (B) GPC of TiO$_2$ as a function of the H$_2$O pulse time. Saturation occurs at 3 s
**X-ray reflectivity of TiO$_2$ thin films on PMMA**

**Figure S2.** X-ray reflectivity of TiO$_2$ thin films on PMMA. TiO$_2$ reflectivity on PMMA (solid lines) as a function of the number of cycles. The dashed grey line is an exemplary simulation of the 300 cycles sample.
X-ray photoelectron spectroscopy

XPS spectra were recorded on PHI VersaProbe with an Al-anode (AlKα = 1486.6 eV) at a source angle of 45°. Charge neutralization of the sample surface was used, and spectra were referenced to the carbon 1s signal (C1s) at 284.8 eV. The TiO₂ thin films were deposited on SiO₂ and PMMA from 107 cycles of TiCl₄-H₂O resulting in a thickness of approximately 6 nm.

Figure S3. X-ray photoelectron spectroscopy of TiO₂ thin films. TiO₂ signals appear on PMMA (A) and SiO₂ (B) indicating growth on both surfaces. The characteristic TiO₂ Ti 2p₃/₂ peaks appear at 458.5 eV on SiO₂ and PMMA. An additional organic/inorganic TiCl₂ compound 2p₃/₂ peak appears on PMMA at a lower energy of 457.3 eV
Infrared spectroscopy

Figure S4. Infrared absorbance spectra of TiO₂ thin films grown on PMMA. Infrared absorbance of TiO₂ thin films as a function of the number of cycles and PMMA and Si references

Atomic force microscopy

Figure S5. Topography of a TiO₂ thin film grown on SiO₂. The roughness is 280 pm, and the scale bar 200 nm. The number of cycles was 100
Electron beam lithography patterns

We varied the area ratio of the no-growth area to the growth area according to Figure S6. The width of the growth area was fixed at 1 µm, and the width of the no-growth area was varied from 2 to 100 µm resulting in an area ratio from 2 to 100.

**Figure S6.** Electron beam lithography patterns and area ratio. Schematic representation of the PMMA patterns on SiO$_2$ that serve as substrates in the area-selective ALD process. The ratio of the no-growth area (PMMA) to the growth area (SiO$_2$) was varied and denoted by area ratio.

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\text{Area ratio} = \frac{A_{\text{NGA}}}{A_{\text{GA}}}
\]

GA = Growth area
NGA = No-growth area
Growth per cycle and area ratio in AS-ALD

The GPC on patterned substrates increases significantly when the number of cycles is beyond the selectivity window (Figure S7). Furthermore, it is independent of the area ratio in the investigated range indicating that the widths of the growth and no-growth areas are significantly larger than the diffusion length of species. Grillo et al. estimated the diffusion lengths of Ru adspecies on –OH terminated (growth area) and –CH₃ terminated (no growth area) SiO₂ to 50 and 140 nm.¹

Figure S7. Growth per cycle and area ratio in AS-ALD. GPC of TiO₂ in AS-ALD on patterned substrates as a function of the area ratio.
Iteration steps in kinetic Monte-Carlo

**Figure S8.** Iteration steps in kinetic Monte-Carlo. Number of particles in the growth area as a function of the number of iterations. Particles accumulate in the growth area as the number of iteration steps increases.
References

(1) Grillo, F.; Soethoudt, J.; Marques, E. A.; de Martín, L.; Van Dongen, K.; van Ommen, J. R.; Delabie, A. Area-Selective Deposition of Ruthenium by Area-Dependent Surface Diffusion. Chem. Mater. 2020, 32 (22), 9560–9572.
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