Electronic Supplementary Information

Confined Crystallization of Anatase TiO_2 Nanotubes and Its Implications on Transport Properties

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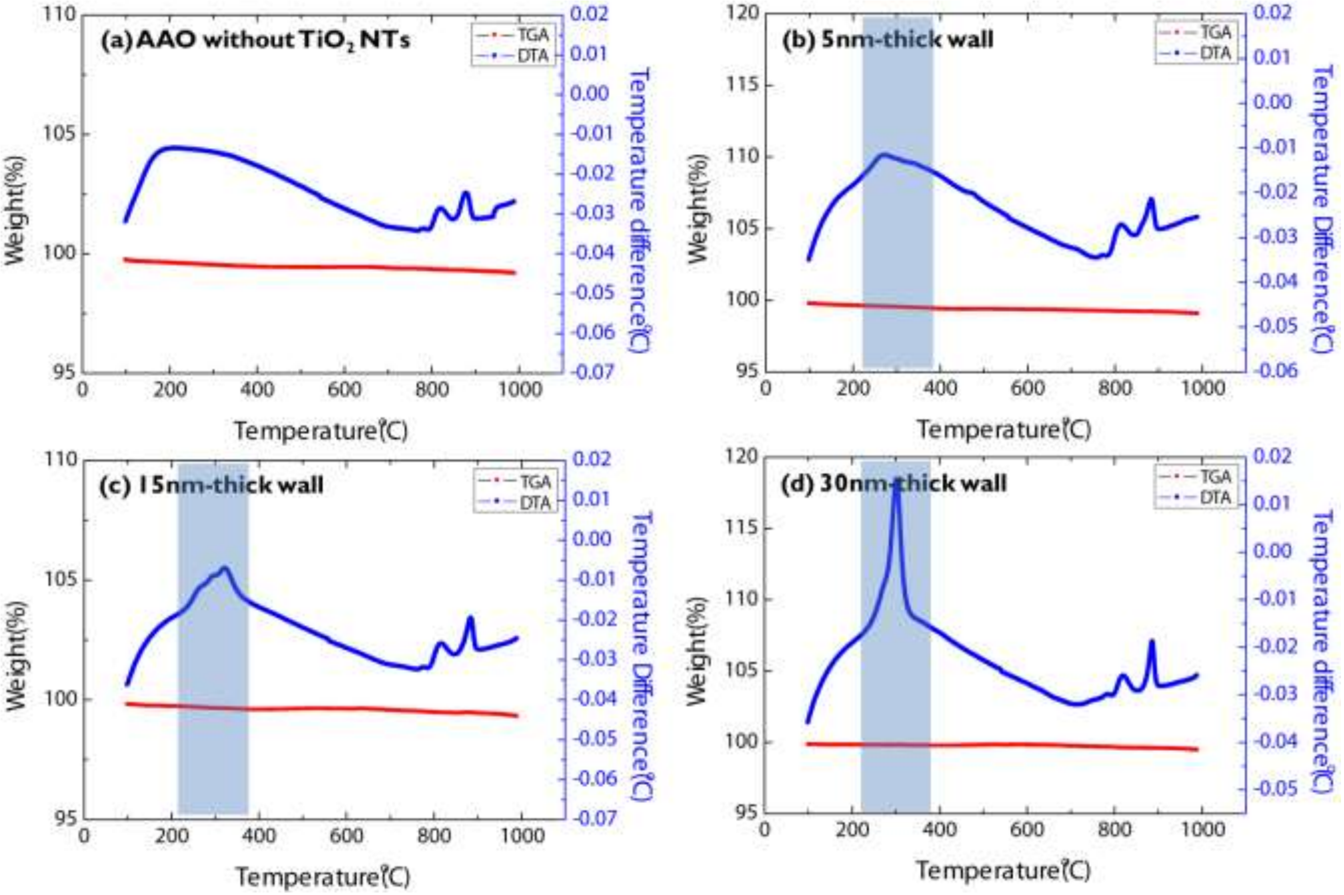

Figure S1. Measured thermal gravimetric analysis (TGA) and differential thermal analysis (DTA) results of porous alumina templates with different TiO_2 wall thicknesses. Pale blue zones indicate the amorphous-anatase phase transformation.

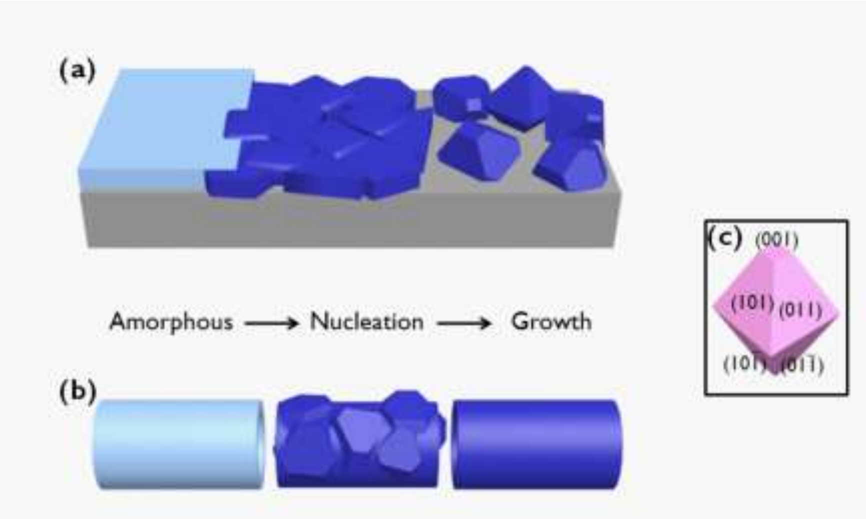

Figure S2. Schematic depictions for the explanation of the difference in crystallization behaviors between TiO_2 thin films (a) and nanotubes (b), drawn in an exaggerated scale. Light and dark blue denote amorphous and anatase TiO_2, respectively. (c) An equilibrium crystal shape of anatase TiO_2 in accordance with the Wulff construction.

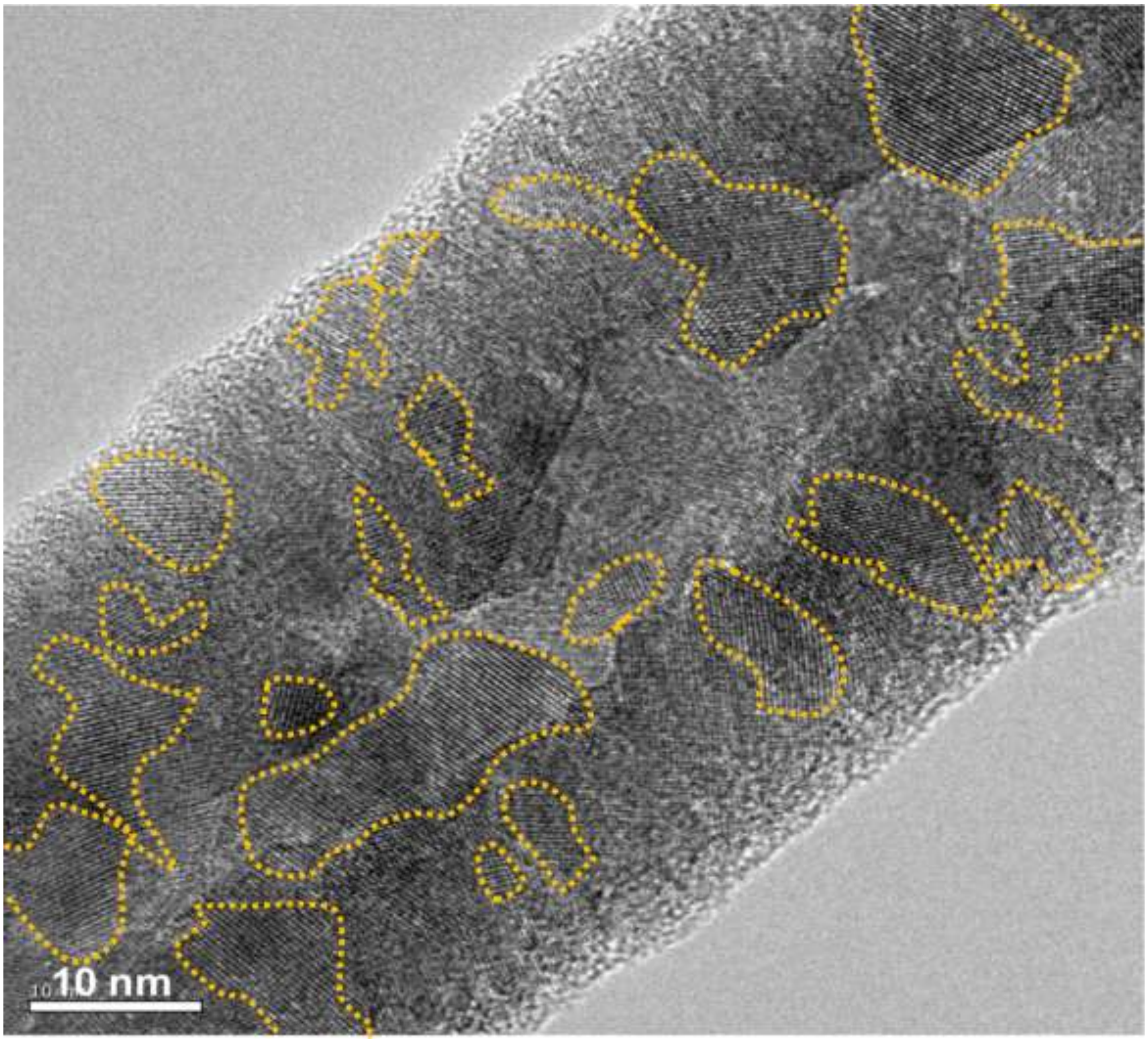

Figure S3. TEM of a TiO_2 nanotube as-deposited by ALD at 300°C. It shows highly crystalline grains, and the dimensions are comparable to the wall thicknesses.

Evaluation of grain boundary and surface defects as a function of nanotube wall thickness

For the evaluation of the total grain boundary area (A_{GB}) and the total surface area (A_S), a geometrical model of the nanotubes was used, as detailed in **Figure S4**. The model is based on the observations obtained from the TEM morphological analysis of different anatase TiO_2 nanotubes with variable wall thicknesses. The following assumptions were made:

- The polycrystalline nanotube is divided into several elements, i.e. single crystals with arc segmented geometry, which are described by four parameters, in cylindrical coordinates: the radial length (l_r), the outer and inner arc length ($l_{\theta,e}$ and $l_{\theta,i}$) correlated through the arc segment angle θ, and the axial length (l_z). **Figure S5** shows the basic representation of a crystal element and the corresponding parameters which define it.
- It is assumed that the radial length of the elements, independently of wall thickness, is equivalent to the wall thickness (e). That is to say that the crystals grow from the outer wall to the inner wall in a columnar-type way, which is reasonable from our TEM observations and from the literature available on ALD [Ref. S1].
- Both the axial length and the arc length depend on the wall thickness, as shown in **Figure S5**.
- The axial length was measured by TEM and is plotted *versus* the wall thickness in Figure 4 in the main text. These data were fitted to an equation of the type:

$$l_z = 4{,}0 + \frac{291{,}0}{1 + 10^{\frac{12{,}5 - e}{3{,}0}}} \qquad (1)$$

which is also included in Figure 4. l_z tends to a maximum of around 300 nm for the thickest layers and a minimum of around 4 nm for the thinnest layers, which is consistent with the experimental data. The crystal axial length remains constant for layers thicker than 15 nm as long as the same annealing conditions are used.

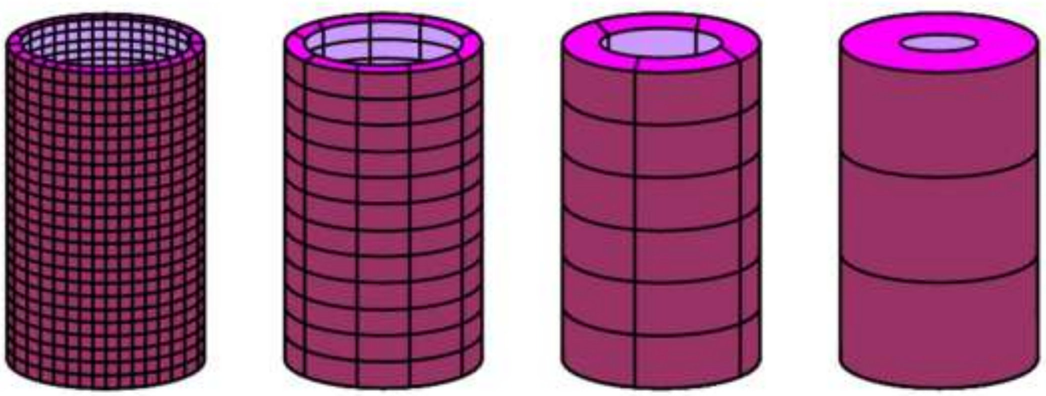

Figure S4. Geometrical model of TiO_2 nanotube crystal size distribution as a function of wall thickness

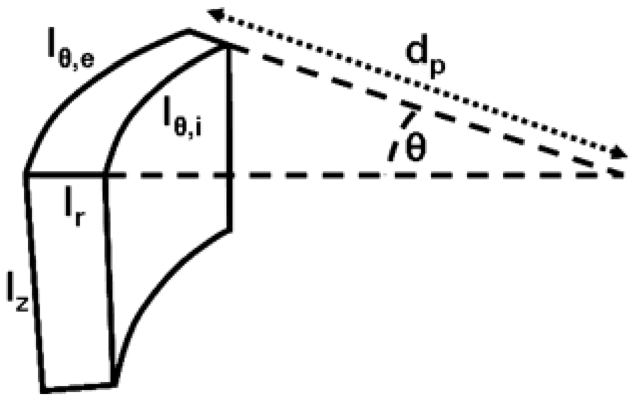

Figure S5. Basic representation of a single crystal element of the TiO_2 nanotube with the geometrical parameters that define it.

- The dependence of the arc length on the wall thickness is estimated considering three facts:
  - The dependence of the arc length angle (θ) follows the similar trend to the axial length, given in this case by equation (2).

$$\theta = 0{,}194 + \frac{6{,}089}{1+10^{\frac{10-e}{2}}} \qquad (2)$$

- $l_{\theta,i}$ and $l_{\theta,e}$ are calculated using the general formula $l_\theta=\theta\cdot r$, where r is the inner (r_p-e) or the outer (r_p) nanotube radii.
- The outer and inner arc lengths and the radial length tend to the same value for the thinnest nanotube walls, that is, the wall thickness.
- The maximum inner and outer arc lengths possible are that of a unique single crystal along the whole nanotube segment (when θ=2π), as evidenced from TEM observations for wall thicknesses greater than 15 nm.

Using these facts, we can calculate the change in the dimensions of a single crystal element as a function of the thickness, which will allow estimating the variation of A_{GB} and A_S with the wall thickness of a nanotube.

Calculation of A_{GB}:

For the calculation of the total area of the grain boundaries (contact surface among the different crystals), we have to consider both the contact area between the grains located at the same level ($A_{GB,para}$), i.e. the interfaces parallel to the nanotube axis, and the contact area between the grains located at consecutive levels ($A_{GB\text{-}perp}$), i.e. the interfaces perpendicular to the nanotube axis.

$A_{GB,para}$ is calculated counting the number of parallel interfaces for each θ(e) and multiplying by the radial length (e) of the single crystal element and the total length of the nanotube (L). This is given by eq. (3).

$$\mathrm{A}_{\mathrm{GB,para}} = \left[Integer\left(\frac{2\pi}{\theta}\right) - 1 \right] \cdot e \cdot L \qquad (3)$$

$A_{\mathrm{GB,perp}}$ is calculated by counting the number of levels (L/l_z) and multiplying by the area of the complete arc segment of the nanotube (θ=2π). This is given by eq. (4).

$$\mathrm{A}_{\mathrm{GB,perp}} = \pi \cdot (d_p - e) \cdot e \cdot \frac{L}{l_z} \qquad (4)$$

Then, the total grain boundary area is taken as the sum of equation (3) and (4). The dependence is complex, as it is related to e, l_z(e) and θ(e), given by eqs. (1) and (2).

Calculation of $\mathbf{A_{surf}}$:

In this case, the calculation is rather simple, as it corresponds to the sum of the outer and the inner areas of the nanotube wall, given by the sum of eqs. (5) and (6), accordingly.

$$\mathrm{A}_{\mathrm{surf,o}} = \pi \cdot d_p \cdot L \qquad (5)$$

$$\mathrm{A}_{\mathrm{surf,i}} = 2 \cdot \pi \cdot \left(\frac{d_p}{2} - e\right) \cdot L \qquad (6)$$

This shows a linear dependence with thickness.

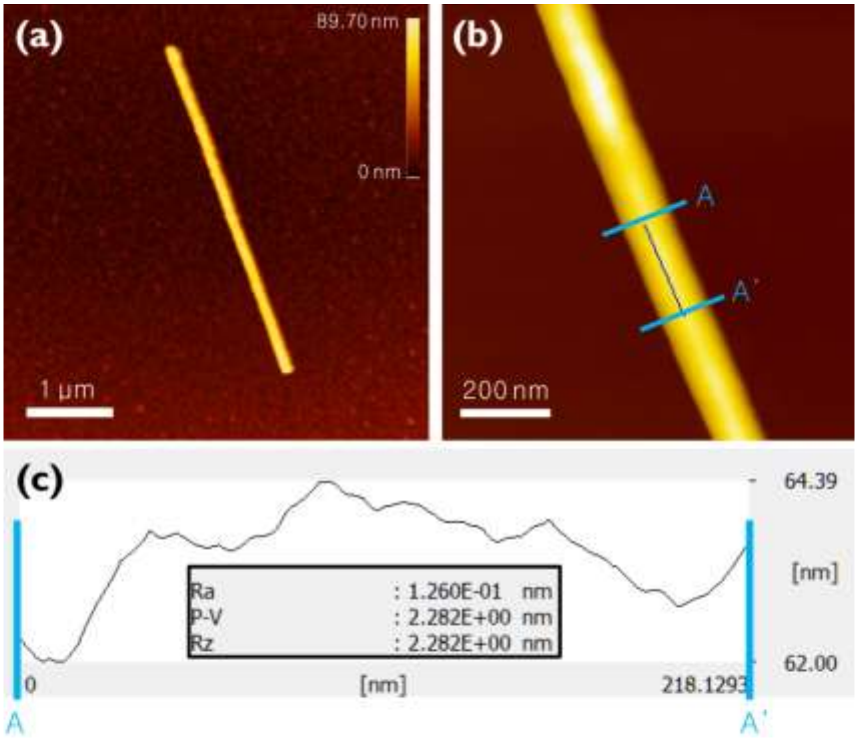

Figure S6. Atomic force micrographs and surface roughness analysis of a TiO_2 nanotube.

Roughness-related parameters given in Fig. S6-c (*R_a*, *P-V*, and *R_z*)

(1) Average surface smoothness: R_a

This is the average value of the absolute value of the partial differences between a standard reference surface and an appointed surface.

$$R_a = \frac{1}{S_0}\int_{Y_B}^{X_T}\int_{X_L}^{X_R} |F(X,Y) - Z_0|\, dXdY$$

(2) Maximum difference in height: *P-V*

The difference between the maximum and the minimum among the Z data of an appointed surface.

$$P - V = Z_{max} - Z_{min}$$

(3) Average surface smoothness over n points: R_z

This can be defined as the difference between the mean peak value from the maximum peak to n/2 peak and the mean vale value from the minimum vale to n/2 vale on an appointed surface.

[n: an even number between 2 and 30]

References

[S1] V. Miikkulainen, M. Leskelä, M. Ritala, R.L. Puurunen, "Crystallinity of Inorganic Films Grown by Atomic Layer Deposition: Overview and General Trends." *J. Appl. Phys.* **113**, 021301 (2013)