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Supplementary Information

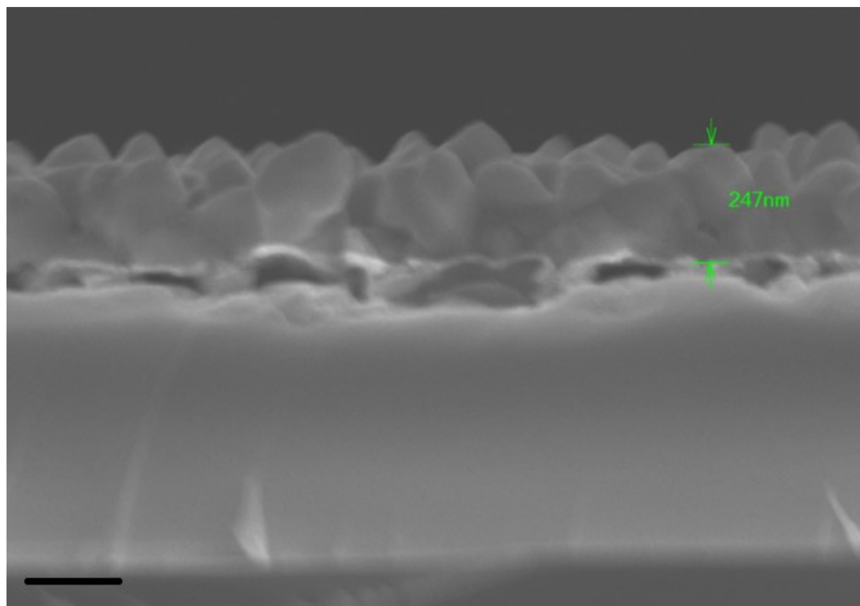


Figure S1. SEM image of a sample in cross section used for method calibration. The scale bar is 200 nm.

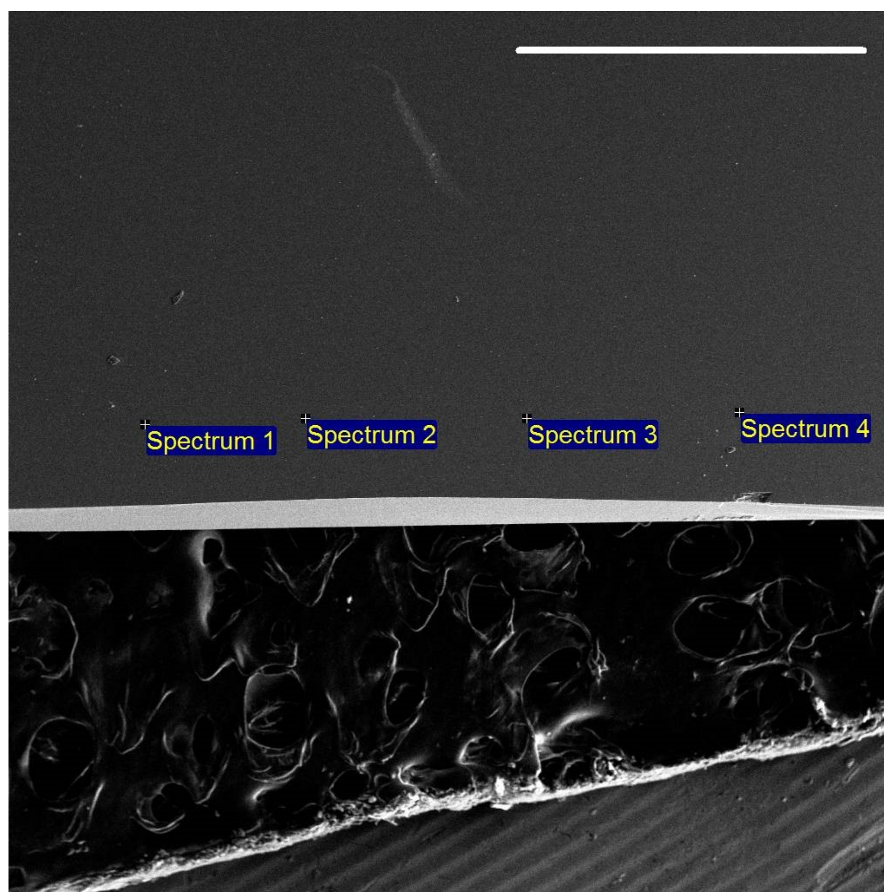


Figure S2. SEM image of sample near the edge. Points "Spectrum 1" – "Spectrum 4" represent places for EDS analysis. The points are placed close enough to the edge that the film thickness at the point of analysis is as close as possible to the thickness measured by the SEM. However, the distance to the edge should be more than 100 μm to avoid interaction of the generated X-rays with the end of the sample. The scale bar is 1 mm.

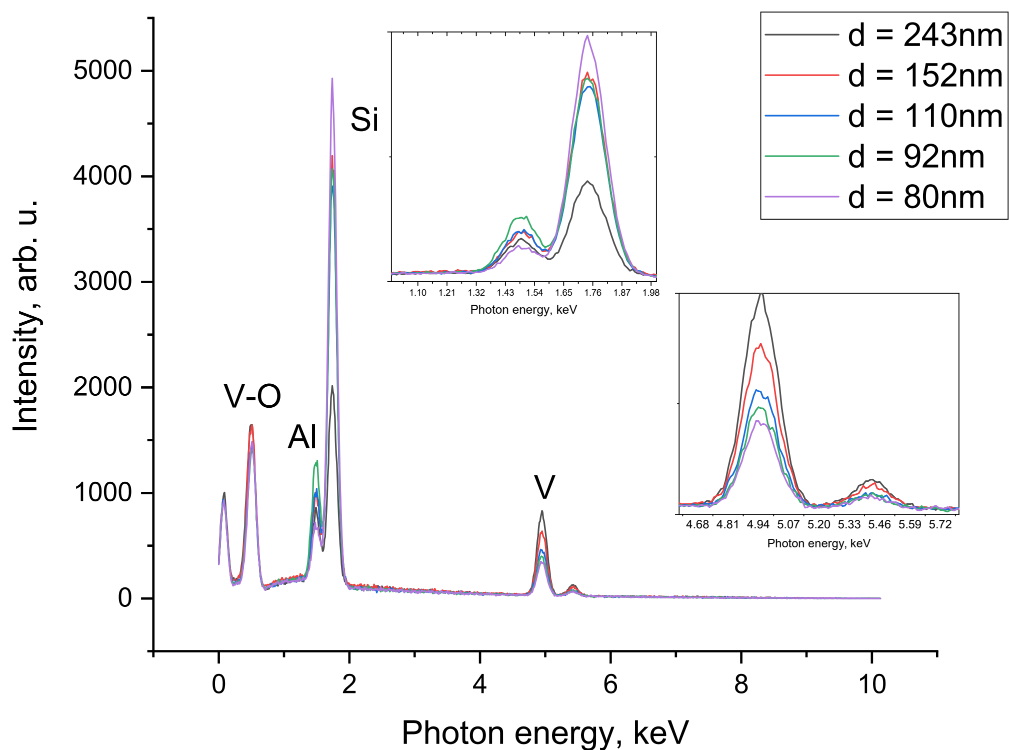


Figure S3. EDS spectra of a multilayer structure consisting of a variable thickness vanadium dioxide film, a 70 nm thick aluminium layer, and a 300 nm thick oxide layer on a silicon substrate.

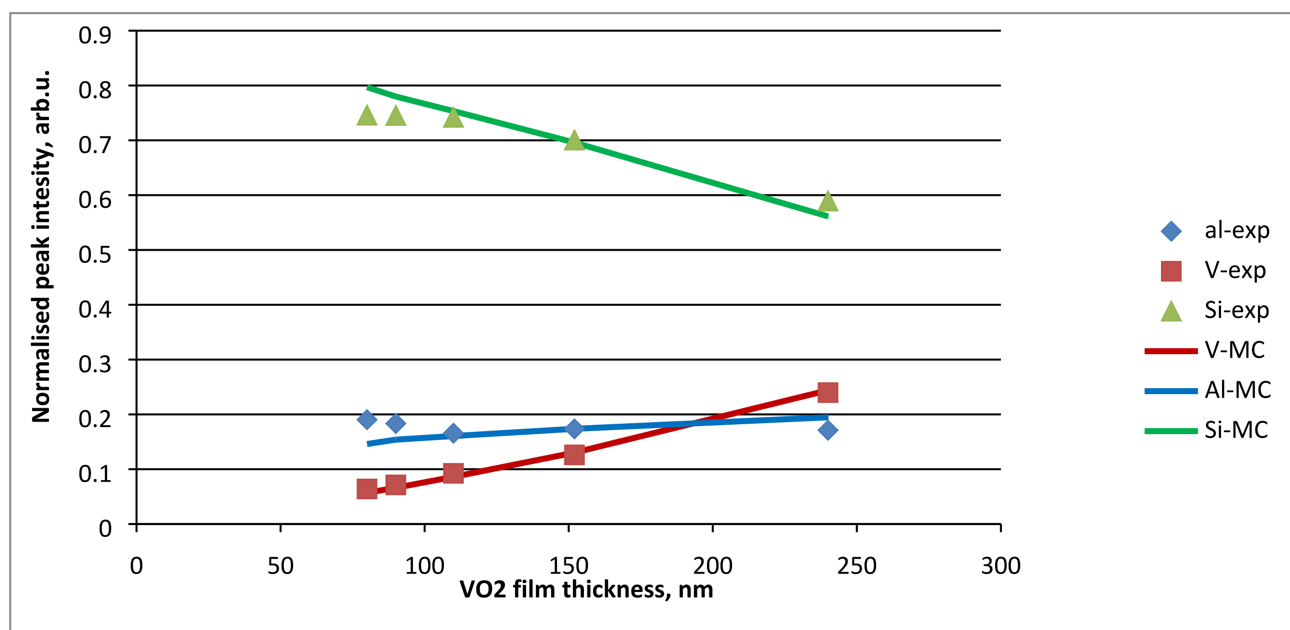


Figure S4. Normalised intensities of vanadium, aluminium and silicon peaks as a function of vanadium dioxide film thickness. Dots show experimental results, solid lines - Monte Carlo simulation results.

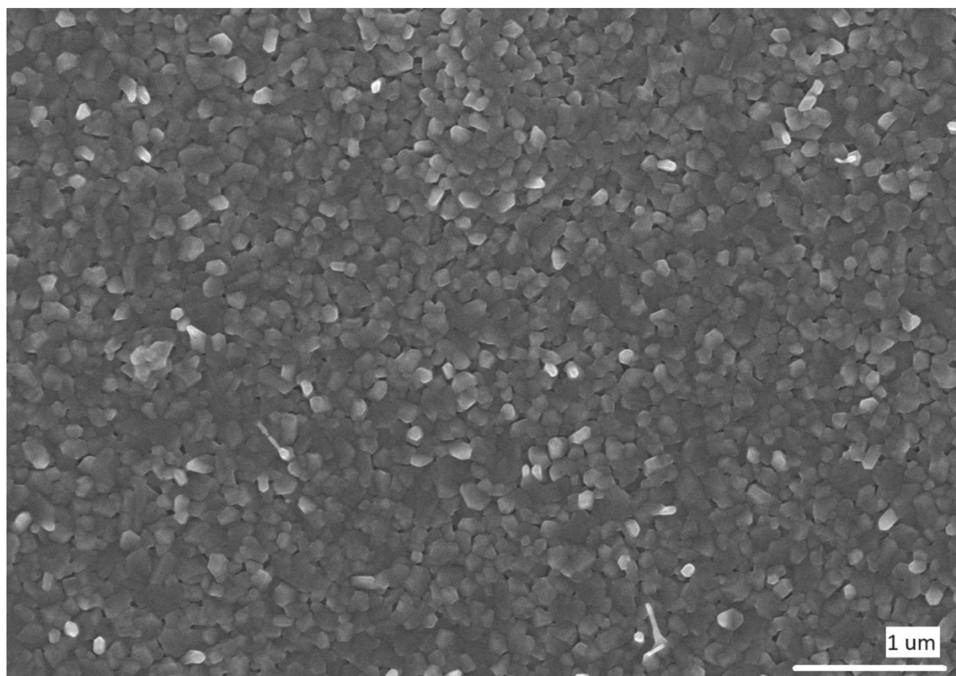


Figure S5. SEM image of the VO_2 film grown on aluminium surface (near point A in Fig.3) at 490 °C and carrier gas fraction n= 1.

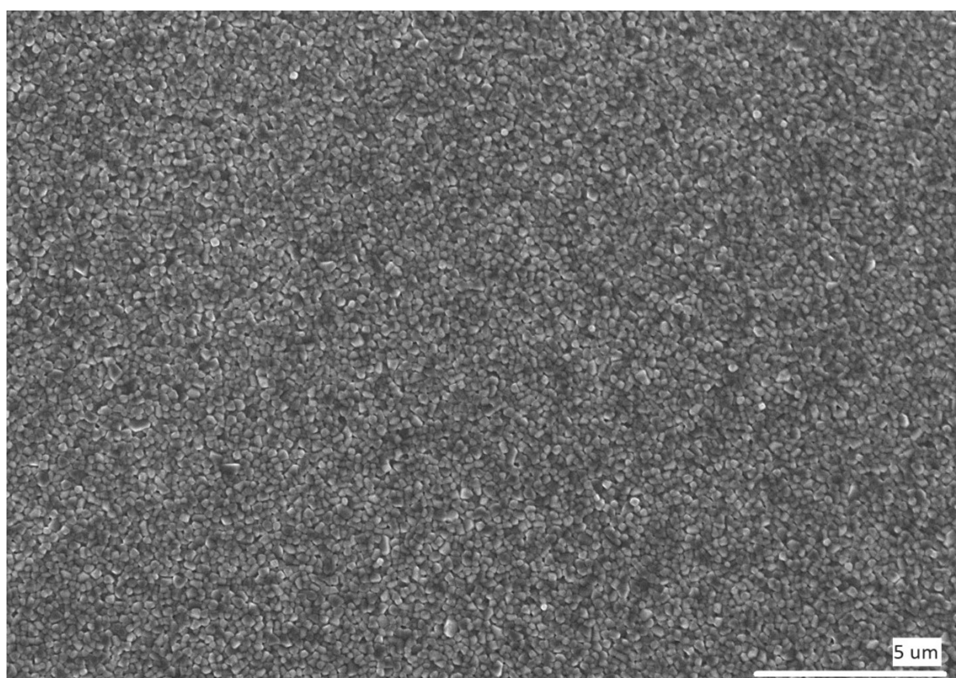


Figure S6. SEM image of the VO_2 film grown on silicon dioxide surface (near point D in Fig.3) at 490 °C and carrier gas fraction n= 1.

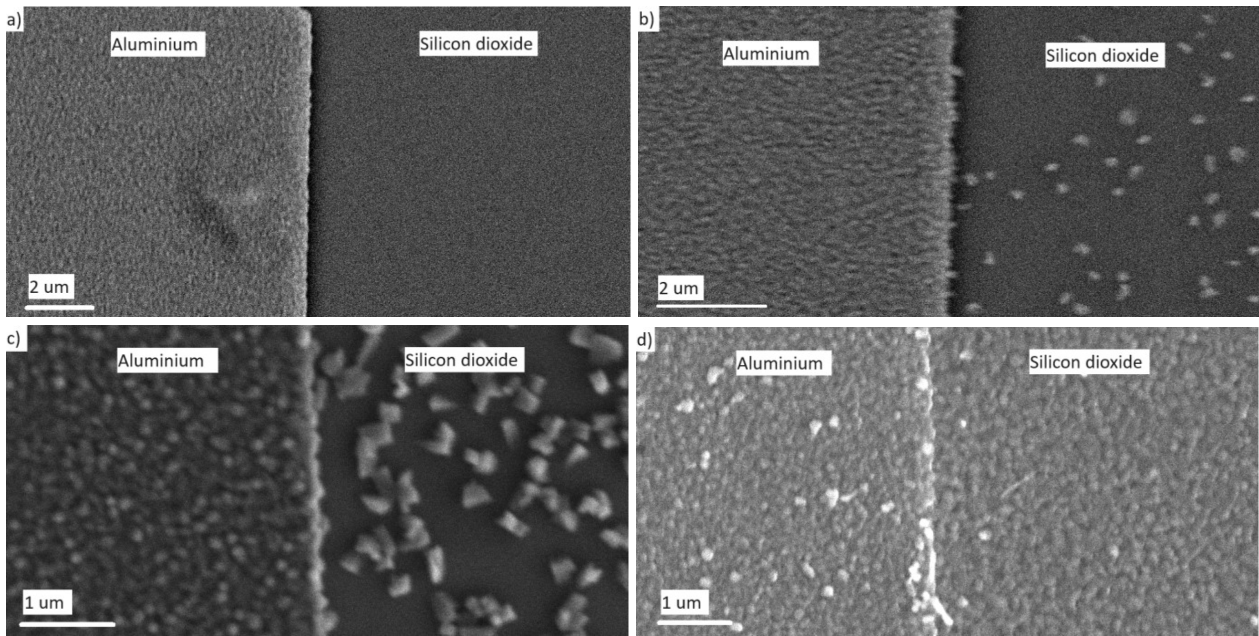


Figure S7. Surface of the SiO_2/Al interface boundary after VO_2 synthesis at different times – a) 5 minutes, b) 10 minutes, c) 30 minutes and d) 60 minutes.

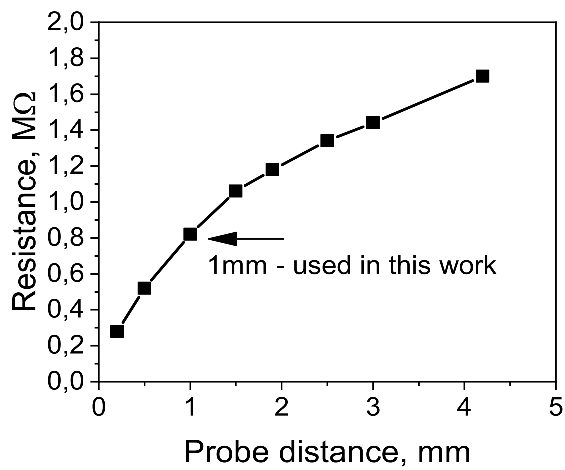


Figure S8. Dependence of the measured resistance on the distance between the probes. The sample is the 150 nm VO2 film grown on the silicon dioxide surface.

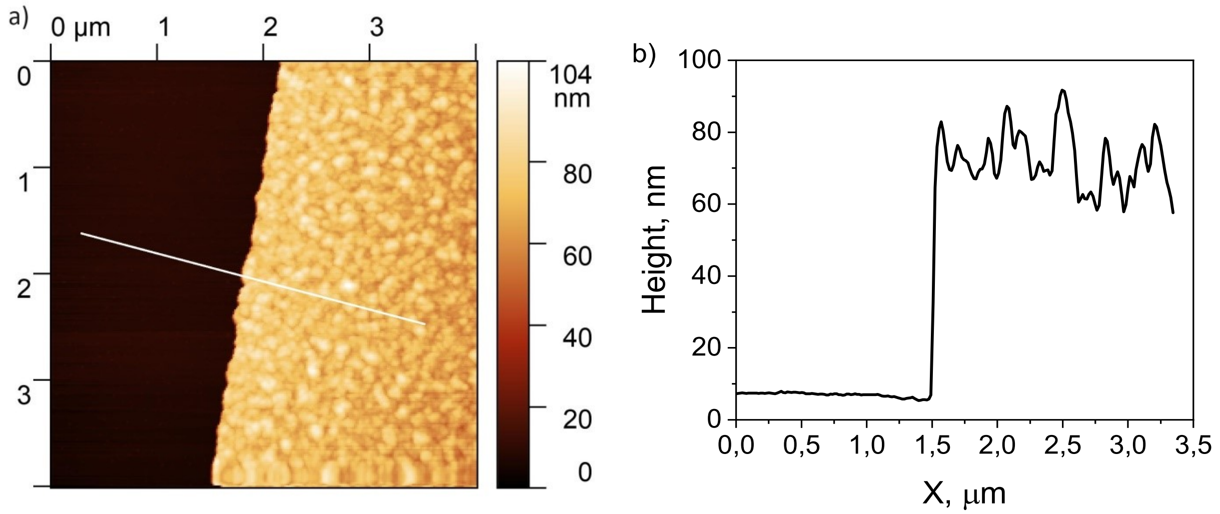


Figure S9. a) AFM image of the SiO_2/Al interface before growth process. Average roughness height is 23nm. b) Height profile of the aluminium step.

Growth selectivity

Consider the phenomenon of surface migration admolecules in the model of one-dimensional diffusion according to Fick's law. In a general form, the equation of the balance of the concentration balance of admolecules on the surface N(x,y,t) can be represented as follows:

$$\frac{\partial N}{\partial t} = J1 - J2 + D\Delta N \qquad \text{(S1)}$$

Where J1 is the flux of admolecules adsorbed from the gas mixture. J2 - flux of molecules desorbing from the surface, D - diffusion coefficient.

The pressure in the reactor is 266 Pa, at this pressure there will be a boundary layer of gas flow and the transfer of precursor to the substrate will be determined by the diffusion in the boundary layer. The flux of molecules to the surface in this case will be defined by the expression

$$J1 = \frac{k_D}{RT}(p - p_s) \qquad \text{(S2)}$$

Where p is the partial pressure of the precursor in the gas, ps is the partial pressure of the precursor near the surface, kd is the mass transfer coefficient, R is the universal gas constant.

Assuming that the process of desorption of admolecules from the surface of silica is thermally activated, with reaction constant A and activation energy Ea, the flux of adsorbing from the surface will be equal to:

$$J2 = N * c_d = N * A * exp(-\frac{Ea}{kT}) \qquad (S3)$$

Where c_d is the probability of a molecule to leave the surface, Ea is the activation energy of the desorption process.

Equating J1 and J2, we obtain the equilibrium concentration at which the adsorption and desorption processes balance each other. Let us denote it as N_0

$$N_0 = \frac{k_D \frac{p}{T}}{A \cdot exp(\frac{-Ea}{kT})} \qquad (S4)$$

Consider the case of aluminium and silicon oxide lateral interface. Assume that all precursor molecules hitting the aluminium surface immediately participate in the reaction and do not participate in further diffusion. Precursor molecules hitting the inert surface diffuse, desorb, and participate in the film formation reaction only when the limiting concentration is exceeded.

The stationary solution of equation (1) at the material boundary will be as follows

$$N(x) = A_1(\exp(\sqrt{D}x) + A_2(\exp(-\sqrt{D}x) + C \qquad (S5)$$

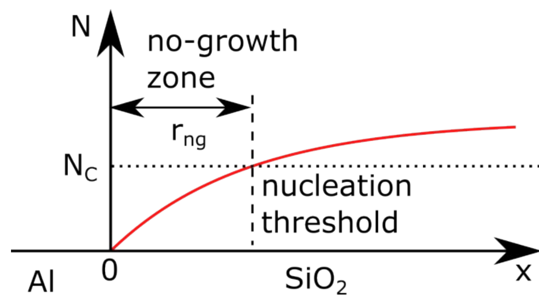
The boundary conditions will be as follows:

N(0) = 0, since all admolecules hitting the aluminium surface are immediately trapped.

N(∞) = N0, since far from the boundary an equilibrium concentration will be established

Given the boundary conditions, the concentration distribution of admolecules will be:

$$n(x) = n_0(1 - e^{-\sqrt{D}x}) \qquad (S6)$$



Solving the equation n(x) = Nc, we obtain the value $x=r_{ng}$ at which the concentration of admolecules exceeds the critical one.

$$r_{ng} = -\frac{1}{\sqrt{D}} ln(1 - \frac{N_c}{N_0}) \quad (S7)$$

Considering expression (S4)

$$r_{ng} = -\frac{1}{\sqrt{D}} ln(1 - \frac{N_c \cdot T \cdot A \cdot exp(-\frac{E_a}{kT})}{k_D \cdot p}) \quad (S8)$$

Thus, as T increases, the no-growth region increases, i.e. the selectivity increases. Increasing the precursor partial pressure p leads to the opposite result.

Expression (S1) does not take into account the consumption of precursor molecules for film formation, which will start at N>Nc. In such a case, the capture of the precursor by the formed film will have to be taken into account and expression (S6) will be time dependent. However, this model is quite suitable for the description of precursor depletion regions, which determine the growth selectivity.