Supporting Information

The Kinetics and Mechanism of Long-Range Pore Ordering in Anodic Films on Aluminum

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Conceptual scheme of in-situ diffraction experiment

Figure S1 shows conceptual scheme of electrochemical cell used for the *in-situ* investigation of pore ordering in anodic films on aluminum. The cell consists of two concentric cylinders, which allow us to minimize the distance between the back capton window and the aluminum plate and as a consequence to minimize attenuation of the X-ray beam in an electrolyte solution.

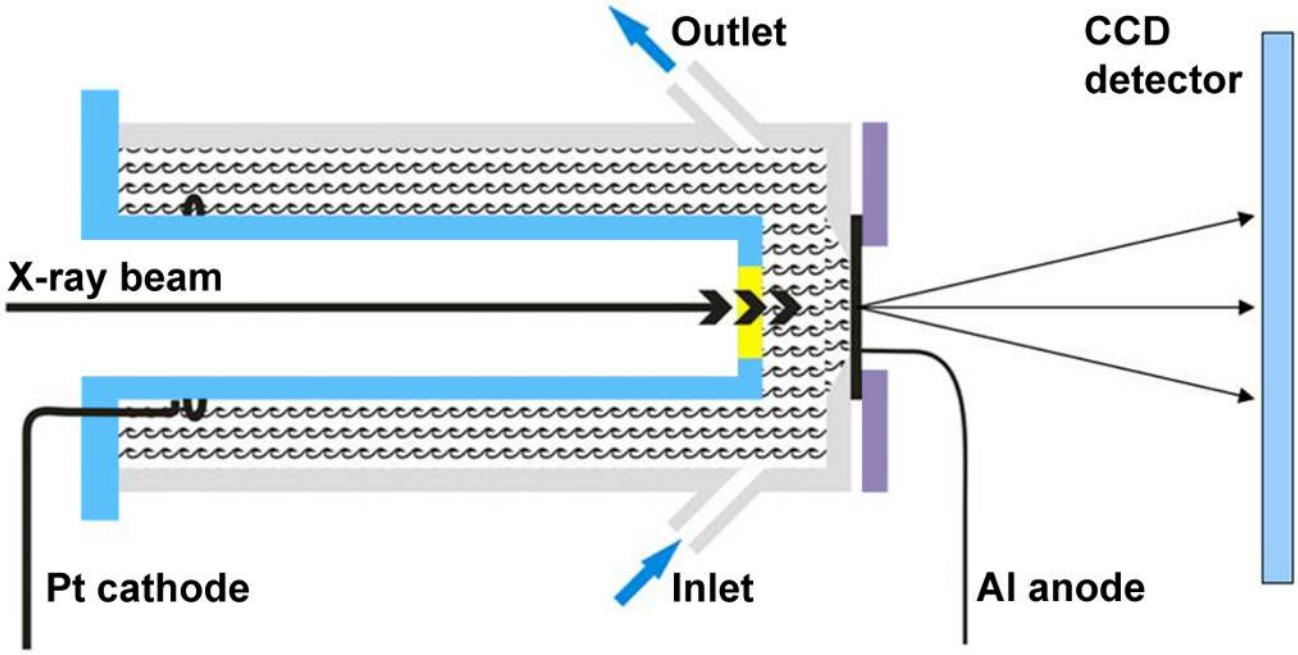

Figure S1. Schematic representation of the diffraction experiment.

SEM observation of porous structure at different oxidation time

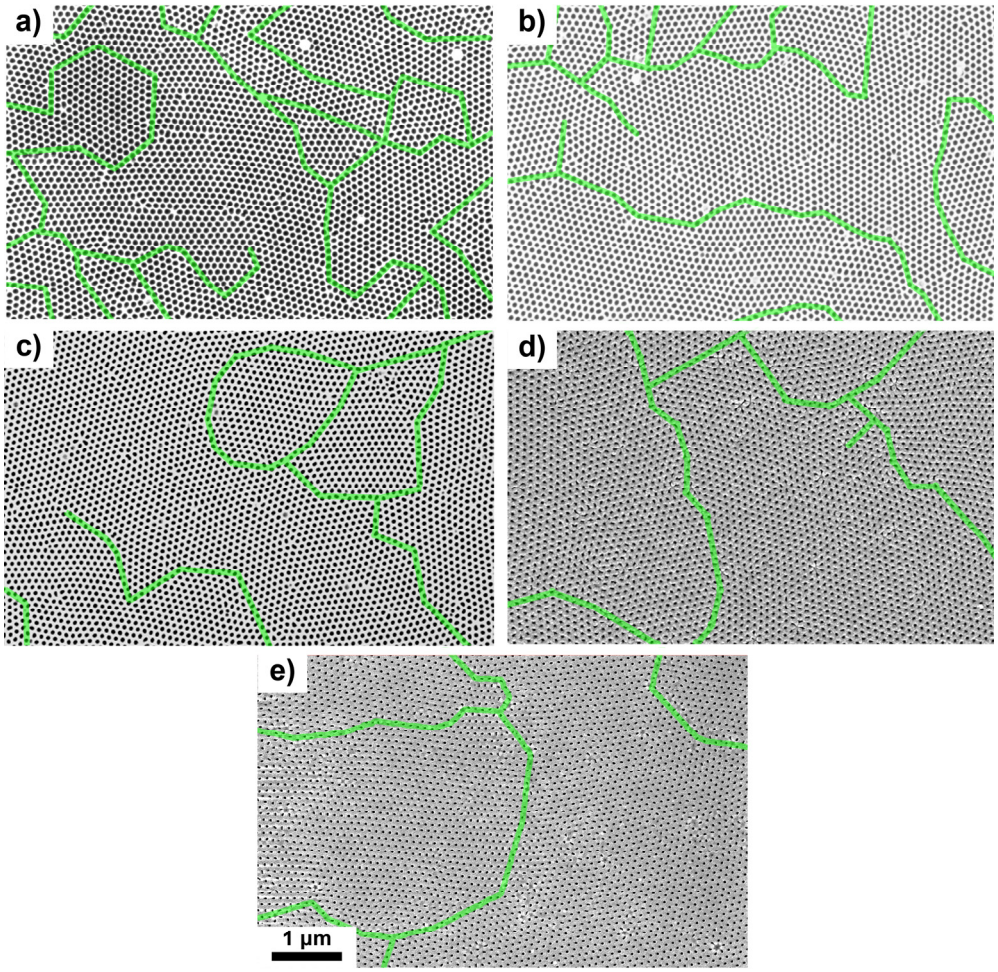

Figure S2. SEM images of bottom of anodic alumina films [40 V, 0.3 M $(COOH)_2$] after removal of the barrier layer by chemical etching. Green lines indicate boundaries between ordered regions.

Numerical simulations of pore ordering process

Numerical simulations of pore ordering process were carried out using a system of 1000×1000 domains with statistically distributed original in-plane orientation of pore lattice in $0 - \pi/3$ interval (taking into account 6-fold symmetry of AAO). Each domain contained 100 pores at the beginning of the simulation. Such structure is characteristic for AAO porous films at the early stages of anodization. An algorithm of the simulation included three major events: (i) domain boundary movement, (ii) domain death and (iii) merging of neighboring domains with similar in-plane orientations.

AAO growth rate in every domain was defined as a function of pore system orientation with Gaussian distribution of growth rates around optimal orientation:

$$U(\varphi) = U_0 + ke^{\frac{(\varphi-\varphi_{\max})^2}{2\sigma^2}}, \quad \text{(s1)}$$

where U_0 is a constant, depending on anodization conditions (i.e. voltage, temperature, electrolyte composition, etc.), φ is in-plane orientation of pore system in the domain ($0 < \varphi < \pi/3$), φ_{max} corresponds to an "optimal" in-plane orientation of lattice of pores and σ is a standard deviation from "optimal" orientation, having a meaning of orientational misalignment effect on AAO growth rate.

From an experimental point of view the value of σ could be estimated as a minimal achievable mosaicity of AAO porous structure. Analysis of Fourier transformed images of bottom side of AAO film obtained in long-term anodization experiment allowed to estimate this value as about 25º.

The speed of domain wall movement was defined to be proportional to the difference of pore growth rates in neighboring domains. It's worth noting that in frame of the model U_0 does not influence the ordering process. However in real situation this term depends on local temperature and potential distribution, which are far from been equal in different points of the sample, especially in case of anodization at high current densities. In the other words better in-plane orientational ordering would be achieved at minimal pore growth rates.

The domain death condition was applied in case the area of domain decreased below single pore area. An event of merging of neighboring domains was set in case of misalignment in in-plane orientation of neighboring domains did not exceed 7º (the value was obtained by analysis of Fourier transformed images of perfect single-domain areas of AAO).

Using these boundary conditions the structure was freed to evolve until the total quantity of domains decreased 10 times. Perimeter and average size of domains were computed on every time step of evolution process. The simulation was carried out using different parameters of σ.

The resulting time dependences of domain boundary perimeter were fitted well with a power law $P(t) = c \cdot t^d$, with d ranging from -0.5 for σ = 40º to -1.2 for σ = 5º (see Figure S3). It is worth noting

that the value of d = -0.54 ± 0.04 (close to experimental d = -0.57) was obtained for $\sigma \approx 30^{\circ}$. This orientational deviation is rather close to FWHM of AAO diffraction maximum in azimuthal direction.

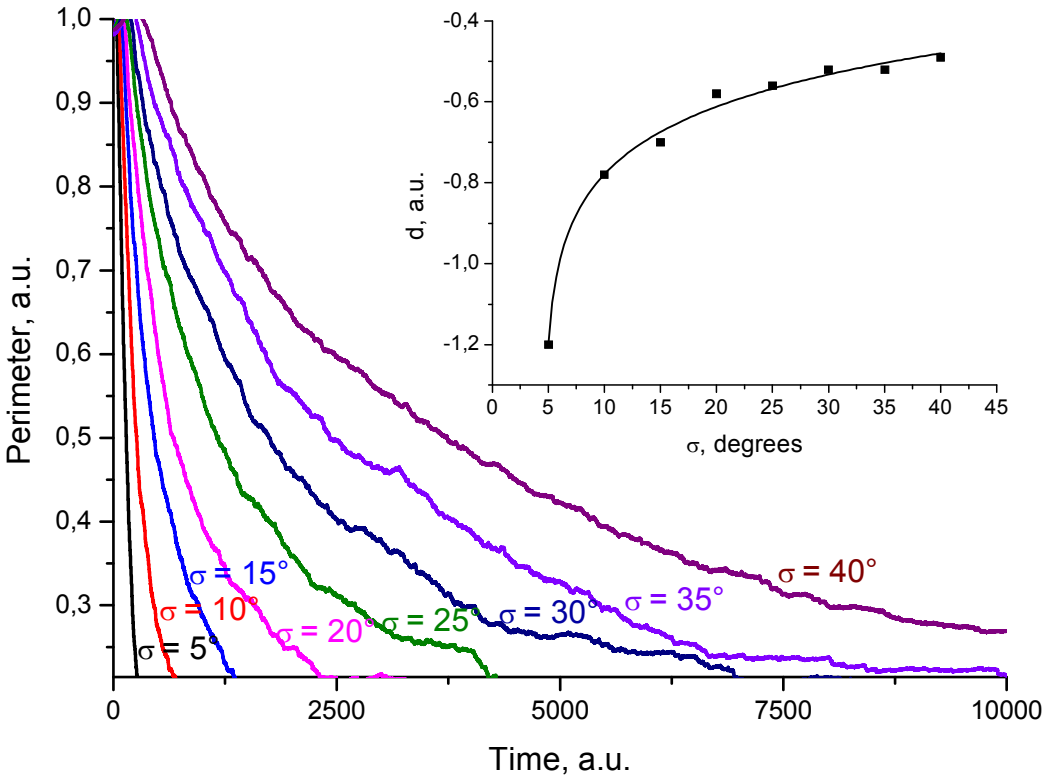

Figure S3. Modeled domain boundary perimeter time dependences for different values of standard deviation from "optimal" in-plane orientation σ. Inset illustrates power, d, as a function of σ.

Time dependence of the mosaicity of the porous oxide layer obtained in the modeled experiment also exhibited power law dependence, $\phi(t) = k \cdot t^{b}$, with b ranging from -0.2 for $\sigma = 40^{\circ}$ to -0.4 for σ = 5°. The value of b = -0.28 ± 0.02 was obtained for $\sigma \approx 30^{\circ}$ is rather close to experimental b = -0.20 (see Figure S4).

Thus the proposed model could be successfully applied to describe pore ordering process and structure evolution in anodic alumina films.

The experimental results and proposed model allows us to predict that the potential distribution at the Al-oxide interface and growth rate of AAO films play an important role in the appearance of long-range pore ordering. Both these values disturb growth front leading to disordering of AAO structure.

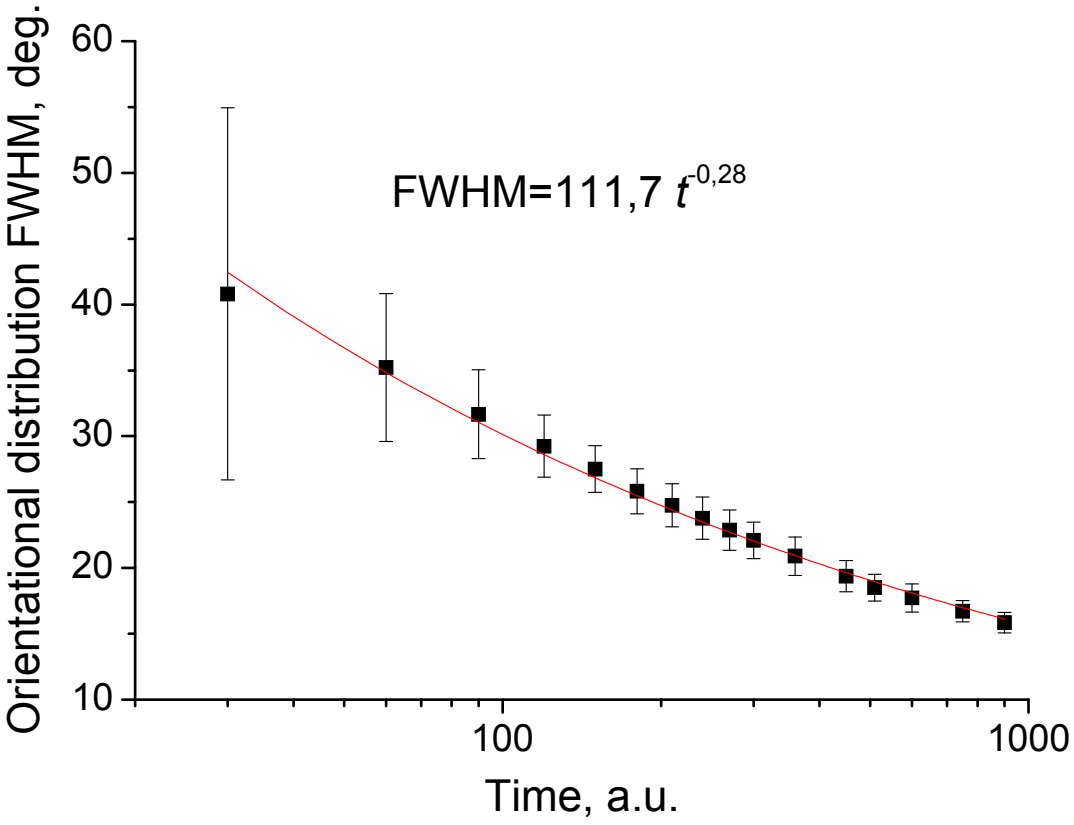

Figure S4. FWHM of in-plane orientational distribution of pores at AAO/aluminum interface as a function of anodization time.