

Supporting Information

Atomic-Scale Insights into the Oxidation of Aluminum

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Experimental Methods

- The aluminium sample was prepared by ultramicrotomy giving a thickness of ~20-10 nm on the edge.
- Samples were plasma cleaned for 15 minutes in an Ar 75%, O 25% mix to remove any surface carbon contaminants from the sample before imaging, such that all amorphous surface contrast comes from Al₂O₃ only. (This lack of contamination is confirmed by EELS – see Figure S2)
- Imaging was performed on an image-corrected FEI TITAN 80-300kV field-emission environmental transmission electron microscope at 300kV with a probe current of ~6 nA. A mass-flow controlled catalytic reaction system was capable of providing controlled pressures of gas mixtures and allowed careful control over atmospheric pressure.
- To control oxygen pressure, experiments were initially performed in high vacuum (3×10^{-7} Torr) to remove the oxide film, subsequently pure oxygen was added into the microscope chamber to pressures of: 3×10^{-5} Torr, 3×10^{-6} Torr and 3×10^{-7} Torr.
- The topmost oxide layer is considered a fiducial marker, for keeping track of where the oxide interface is relative to the surface of the metal and to account for any potential specimen drift that could occur from frame to frame. This is crucially important for identifying that that growth proceeds initially via layer-by-layer oxidation of surface Al atoms, etching into the aluminium lattice, before lateral oxide growth. Image noise is reduced by using a bilateral (edge-preserving filter) – see Fig S4 for unfiltered figure. All images are calibrated for pixel size, p , using the Al{111} spacing observable in the Fourier transform (FT) of the high resolution TEM images. Other lattice spacings were measured from the peak maxima present in radial FT profiles with measurement errors considered as $8p$.
- Electron dose rate is determined using the built-in calibration of the phosphorus screen.
- Image alignment procedure was performed during post-processing to remove image drift semi-automatically, first by using an iterative Sobel filter technique to find the edges of the specimen as a reference for alignment. Any minor remaining issues with drift were then corrected by manual alignment between frames.

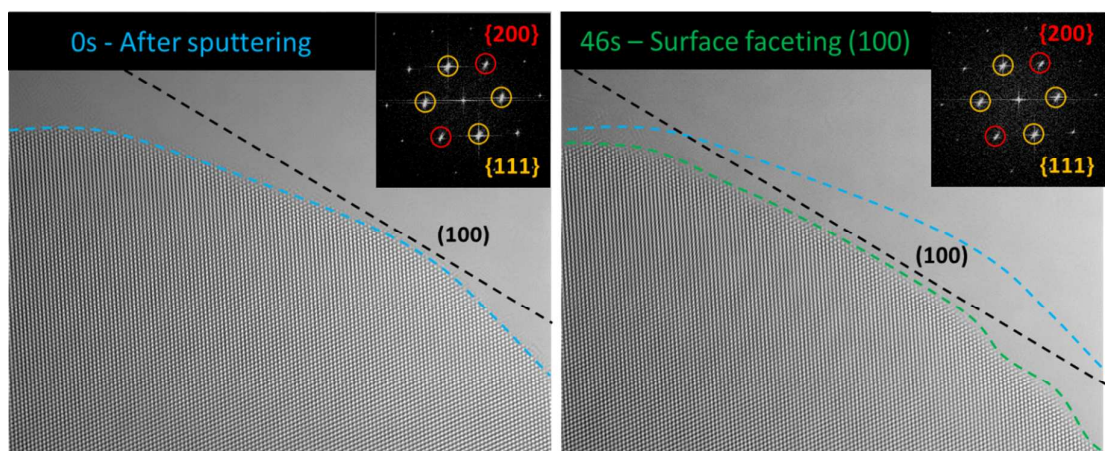


Figure S1: High flux electron beam irradiation causes oxide removal and surface faceting of an aluminium (100) surface, likely due to rearrangement of aluminium atoms to minimise surface energy. The dashed blue line shows the initial curved edge at 0s after sputtering is complete and the green line shows the straighter edge at 46s after sputtering. The black dashed line is drawn parallel to the {100} plane as a reference. Crystal viewed along [011] direction. Full series provided in SI video SV1.

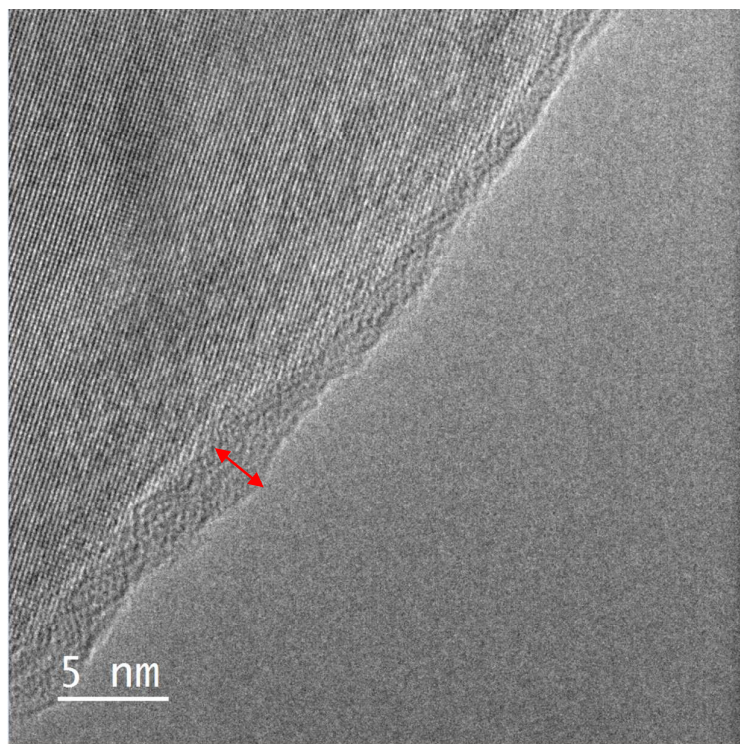


Figure S2: Representative image of initial oxide layer (100) before sputtering. Thickness of oxide at arrow: 2.6nm.

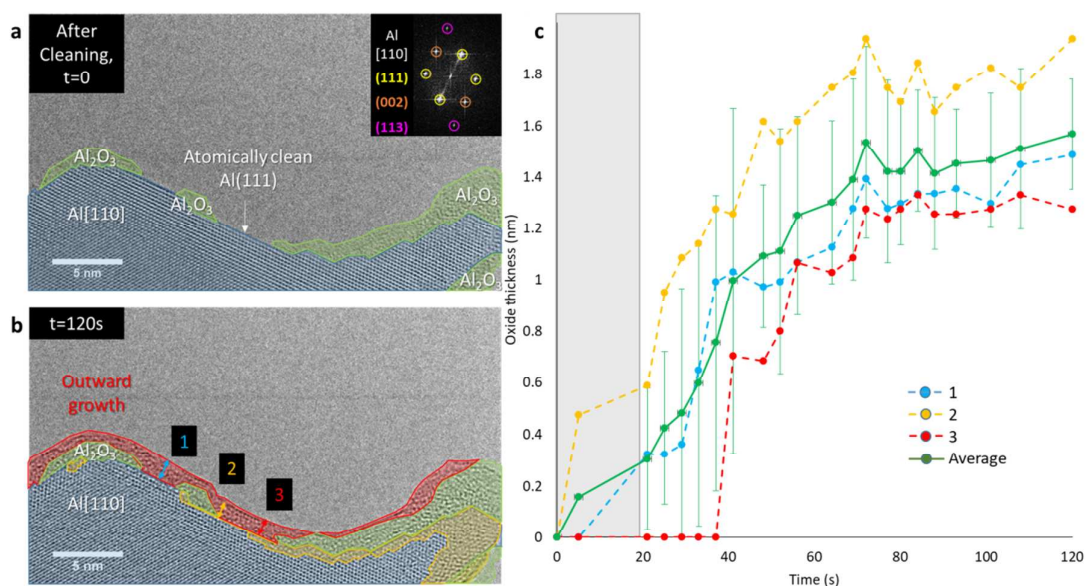


Figure S3: a,b) TEM images showing different stages of the oxidation of the (111) facet, annotated to show the inward and outward growth. The speed of growth presented in Figure 4 is determined by averaging different points on the surface as illustrated by the graph in (c), where 1,2 and 3 are different points that growth is measured laterally on the surface. The grey shaded region is where oxygen gas is let into the vacuum of the ETEM so the gas pressure increases to 3×10^{-5} Torr after ~ 20 s.

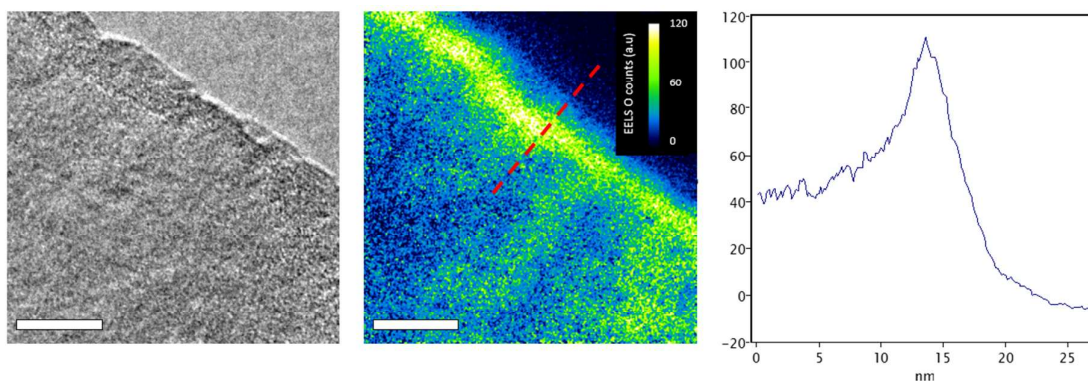


Figure S4: TEM image (left) and O-K edge map extracted from an EEL spectrum image (centre) of a fully-thickened oxide on Al(100). (Scale bar: 10nm). Intensity scan across the O-K edge (right) shows a lower level of oxide on the outer edge

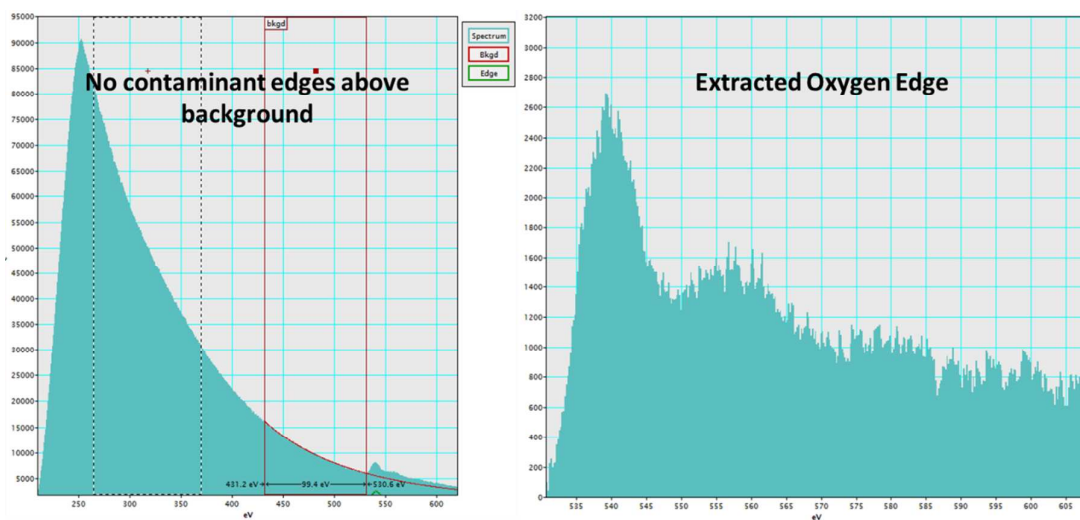


Figure S5: Left: EELS high-loss spectrum taken from full spectrum image region in Fig S2, showing smooth background with no visible signs of contaminant elements in oxide. Right: Characteristic oxygen K edge extracted from spectrum.

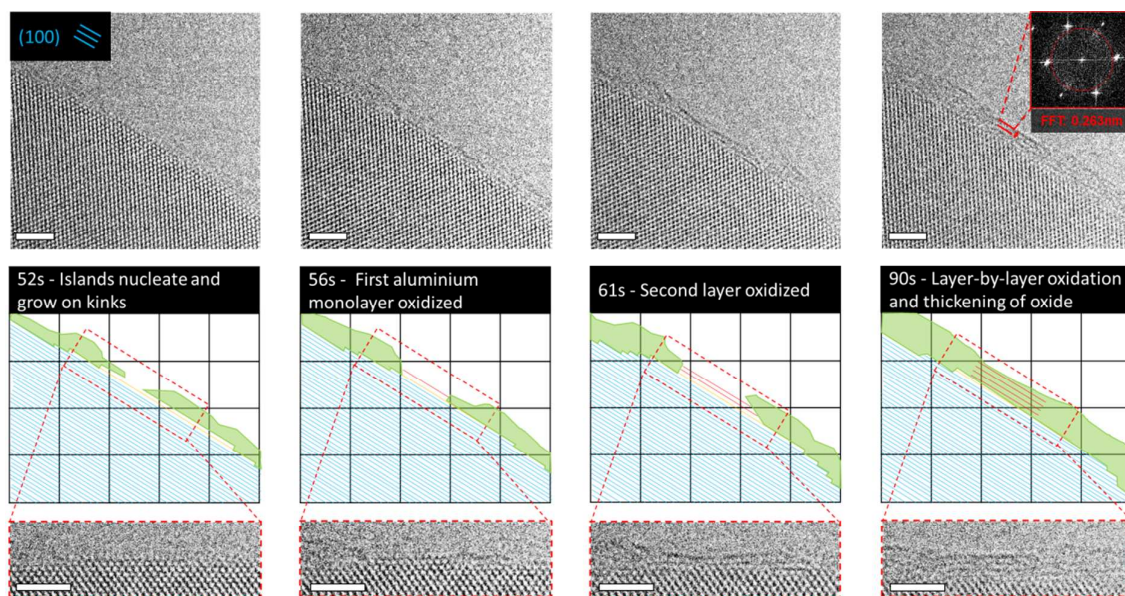


Figure S6: Figure 2 presented without bilateral filter (edge preserving noise reduction).

Supporting videos:

SI videos SV1 and SV2 showing oxidation of Al(100) (SV1) and Al(111) (SV2) at an oxygen pressure of 3×10^{-5} Torr (variable electron flux). Stills from these videos are presented in the main text (SV1, Figures 1,2; SV2: Figure 3). SI video SV3 shows imaging above critical electron flux ($12,000 \text{ e}\text{\AA}^{-2}\text{s}^{-1}$) with instant recrystallisation of oxide while SI video SV4 is below critical flux ($11,000 \text{ e}\text{\AA}^{-2}\text{s}^{-1}$) showing no crystallisation of oxide (SV4).