Nanoporous structures from anodisation of non-planar aluminium surfaces

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Abstract. We report about a novel combination of two etching techniques for generating nanostructures, which individually are well established: (i) metal tip etching in NaOH, as e.g. used for STM or atom probe tip making, and (ii) anodic oxidation of aluminium for the generation of self-organised ordered pores. The non-planar geometry in both these etching processes allowed us to follow the electric field mediated orientation of pattern growth observable in the SEM. Surface-near porosity is found from both etching processes, however only anodisation leads to continued growth of deep channel-like pores. FIB cross-sections of the cone and tip regions are found suitable to study the oxide-metal interface distribution and their dependence with anodisation time and current, even grain boundaries between the two opposite regions of deep pores are observed.

1. Introduction

Anodisation of aluminium foils is one of the most successful methods to generate a self-organised ordered nanochannel membrane, resulting in mostly amorphous anodic aluminium oxide (AAO) [1-2]. Most studies concentrate on perfectly planar surfaces and the mechanism of self-ordering is believed to be due to strain-equilibration induced during volume change upon oxidation [3]. Advantages of AAO over other nanopore membranes include the tunable pore diameter (via acid choice and concentration and voltage), e.g. from 3-500 nm, the homogeneity of pores, their high degree of order and the inertness of $\text{Al}_2\text{O}_3$ towards most fill-in materials. Applications of AAO are found for electrodeposition of metallic nanowires [4-5], growth of ordered CNTs for field emission, or membranes and masks for PVD deposition or ion sputtering.

The motivation for studying anodisation of highly non-planar starting materials, such as ultra-sharp Al-nanotips, is therefore based on two prospects: (i) by following the pore formation in cross-section with continuously varying surface curvature, improved understanding of the general self-organisation mechanism could be obtained. (ii) There are prospective applications for nanoporous materials, including their composites after filling of the pores, for which a sharply pointed tip-shape of the support is a more useful functional nanostructure, rather than a slab-shaped membrane.

2. Aluminium nanotips

2.1. Fabrication via NaOH etching

NaOH solution is traditionally used to fabricate W nanotips via an electrochemical etching method [6], e.g. for STM, nanoindentation, or nanomanipulation applications. The electrochemical etching
technique also can be used to fabricate Ni nanotips via a NaCl solution [7]. We adapted this electrochemical etching method to fabricate Al nanotips. At the anode, an Al wire with 0.125 mm diameter was dipped into a 1 M NaOH solution. The etching voltage was 8 V dc. In this method the processes can be separated into two stages (“two-stage etching method”).

First stage: An Al wire was immersed into the NaOH solution with a depth of 2 mm followed by turning on the etching power. The initial current was relatively high, around 2.9 mA. The current rapidly dropped to 1.0 mA within several seconds then slowly decreased. When the current dropped to about 1.0 µA, the etching circuit was switched off. During this process Al in the immersed wire dissolved into the solution and the wire diameter decreased.

Second stage: The etched tip was then immersed 150 ~ 200 µm deeper and further into the etching electrolyte. When the etching circuit was switched on again, the typical etching current was about 70 – 80 µA in the beginning. When the current has dropped to 50 – 55 µA, the etching process was completed and a sharp tip fabricated successfully. The tip was then taken out from the electrolyte and washed thoroughly by distilled water.

Sharp Al nanotips with conical shape were gained via the method described above. However, some other shapes can also be achieved by electrochemical etching. When we used a cutter to cut the Al wire, the tip was roughly formed in a roof-like shape with a sharp edge. Although the cutting-sharpness remained within the tens of micrometer range, it can be refined to achieve submicrometer radius via electrochemical etching. This etching is similar to the first stage in the method mentioned above. The immersed wires shaped roughly like a roof were etched until the etching current reached 0.4 mA. Then the wire was taken out from the NaOH solution. Roof-like tips with fine edges were obtained. In this method just one stage of etching was used, we refer to it as “one-stage etching method”.

![Figure 1. SEM images (secondary electrons) for two Al nanotips, FEI Inspect F FEGSEM, 15 kV: (a), (b) conical nanotip at 2 magnifications; (c) roof-shaped nanotip](image)

2.2. SEM characterization
SEM was used to observe the fabricated tips. Figure 1 shows a typical conical nanotip with different magnified images (a), (b). The apex sharpness of this conical tip can achieve values below 50 nm. There is significant porosity in the surface layer due to amorphous oxide, which needs to be carefully distinguished from the anodization induced oxide in the next section. Figure 1(c) shows a roof-like tip obtained by the one-stage etching method.

3. Nanopore fabrication by anodization of non-planar structures: aluminium nanotips
A variety of nanotips with different geometry were anodized in 0.6 M oxalic acid with 33 V anodizing voltage for various anodizing time (15 min, 20 min, 25 min, 30 min, 50 min). Then these anodized Al nanotips were cut by focused ion beam (FIB) for in situ observation of their cross-sections by SEM (using a dual-beam JEOL/Orsay FIB). A central section can clearly show the growth behaviour of the pores into the depth of the structure under the boundary conditions of opposite surfaces of the nanotip.
During the FIB milling process very small milling current with short milling times were applied to decrease re-deposition effects which can remarkably degrade observation of the cross-sections. Figure 2 (left) shows an originally conical tip after anodization for 15 min and (right) its cross-section prepared by FIB milling imaged by SEM.

![Figure 2](image)

**Figure 2.** One of the original conical tips after anodization (left) and its cross-section (right) prepared via FIB milling. FEGSEM SE images.

During FIB milling, it is difficult to exactly cut the conical tips along their central axis. The pore channels therefore vary in contrast and visibility, and the pore direction is not always parallel to the cutting plane. Thus the roof-like tip shape was considered as preferred option. Figure 3(a) shows an SEM overview of the same tip as of figure 1(c) after anodization for 30 min, emphasizing the roughness of the roof-prism planes in contrast to the fine pore structure within the FIB cross-section. The geometry of the FIB milling setup, using two trenches, is shown as inset. Figure 3(a) also clearly separates FIB artefacts, seen as vertical tracks, from true pore structure, which is curved independent of the ion milling direction.

![Figure 3](image)

**Figure 3.** FIB cross-sections drilled into the roof-shaped Al-nanotip of figure 1(c). (a) overview with FIB cross-section placement as inset. (b) central Al core and curved Al₂O₃ pores. FEGSEM-SE images, 10 kV. Field of view of inset in (a) of 100 µm.

Figure 3(b) is a magnified image of the central area, where the two opposite oxide layers for the cross-section of this roof-like tip are seen to merge at a grain boundary (top left). Towards the bottom right, the oxide layers remain separated by the non-anodized central area of residual pure aluminium.
4. Discussion
The SEM images of the FIB cross-sections above prove that nanopores were generated in both conical and roof-like nanotips. Both shapes of tips show a 3D-disordered porous surface-near region of around 500 nm thickness, which is surprisingly sharply separated from the ordered nanochannel array below.

In the intermediate layer, where an ordered pore array phase can be found, the channels of pores are not as straight as they would be generated in a planar substrate situation. This could be a result from the generation-speed of these pores being different with different positions. The pores near the apex of the tip generate slower than further in the body of the tip. This different generation-speed can also be proven by the channel length of pores near the apex of the Al metal phase being shorter than in the area far away from the apex of the Al phase towards the wire body. One conclusion can be gained that the generation speed of anodic alumina nanopores can be affected by the surface shape (the geometry) of the substrate, hence to influence the channel geometry of pores.

Figure 3 also shows pore channels are mostly perpendicular to the interface between the phase of regular pores and the Al metal phase. And these channels are also perpendicular to the interface near the tip surface and between the disordered pore phase and the regular pore phase. This phenomenon can be explained by the anodizing electric field which is perpendicular to the surface of Al metal during the anodization process. Therefore it can be an evidence for proving that the pores grow along the direction of the anodizing electric field. In other words, via variation of the electric field direction, the pattern of pore formation can be significantly altered.

From Figure 3 it is also evident that at the centre of the regular pore phase on the thin side of the tip, no aluminium remained. Instead, a very fine bright layer is seen, formed by the combined bottom barriers below the pores. This remaining barrier layer was not dissolved into oxalic acid solution during the anodization even though the aluminium metal has already been totally consumed. This phenomenon can be explained due to the electric field vanishing suddenly as a consequence of the entire aluminium metal being converted into the insulating phase of anodic alumina. The anodic alumina cannot be dissolved by oxalic acid without assistance by an electric field.

5. Conclusions
Sharp Al nanotips with different shapes were obtained via electrochemical etching in NaOH solution. Nanoporous structures were generated in nanotips via anodization. Cross-sections of two tips with different shape were prepared via FIB milling and observed by SEM. The preparation of the cross-section of a roof-like anodic tip was more successful, as the inner cross-sections become a 2D geometry, rather than a 3D pore distribution. There is evidence to prove that the pore-generation as well as the pore-structure can be affected by the choice of substrate geometry and that the local electric field direction plays a significant role during the anodization.

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