

Effect of Potential Changes on Pore Ordering During the Anodization of Aluminum - Period Doubling and Splitting Experiments

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Anodic porous alumina is an excellent example of a self-ordered nano-structured material that is well-suited as a template for growing metallic nanowires for applications in magnetic, electronic and opto-electronic devices [Ref. 1, 2]. The pores form a hexagonally ordered structure with short-range order and vertical orientation. Pore size can be varied from 4nm-300nm by controlling the conditions during electrochemical oxidation of aluminum [Ref. 3, 4, 5]. Masuda et al showed that short range ordering can be achieved by a double anodization process [Ref. 3] Although, there has been a lot of work done to obtain ordered porous alumina with well-defined pore diameter and spacing, the short-range order is generally observed in very narrow ranges of applied potential (195V for phosphoric acid, 40V for oxalic acid and 25V for sulfuric acid) [Ref. 8]. Here, we show that the pore diameter and spacing can be changed (either increased or decreased) while maintaining short-range order by changing the applied potential during the second anodization.

High purity (99.999%) aluminum foils were first degreased using acetone and iso-propanol solutions in sequence. They were subsequently cleaned using HF:HNO₃:HCl:H₂O (1:10:20:69) mixture and then annealed at 500C for 4-5hrs. The aluminum surface was electropolished using perchloric acid-ethanol mixture and dried before the anodization process. Anodization was carried out using 0.3M sulfuric acid at 25V at 3C overnight and the porous alumina formed during the first anodization was removed by wet chemical etching. A second anodization was performed at twice the initial potential (50V) in 0.3M oxalic acid for 2-3 hours and subsequently removed by wet etching. The samples were characterized by SEM at all stages of the experiment.

From Fig. 1 and 2, it can be seen that by doubling the potential during the second anodization, the pore spacing is also doubled while still maintaining short range order. We have also performed similar experiments starting with 40V, 0.3M oxalic acid and changing to 20V, 0.3M sulfuric acid which leads to period splitting to half of that obtained at 40V (Fig. 3 and 4). It is clear from the images that the size and shape of the corrugations on the aluminum surface after removing the oxide from 1st anodization influences the pore arrangement during 2nd anodization. Similar experiments are currently being performed over a wide range of pore-spacing and diameter by changing the electrolyte and the applied potential during the second anodization and will be discussed. This simple yet powerful technique can be used as a tool to increase the potential ranges over which good local ordering can be achieved.

References

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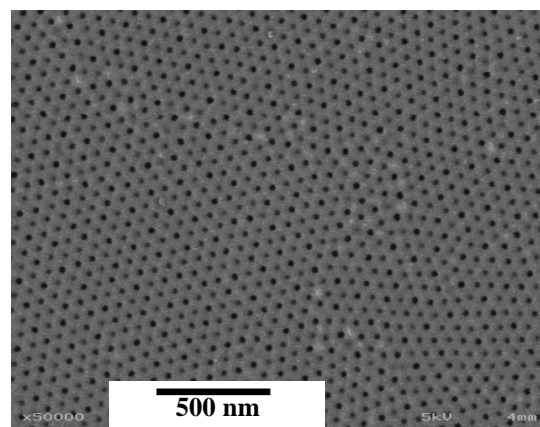


Fig. 1 Porous alumina surface after 2nd anodization (1st anodization – 25V, 2nd anodization 50V) Pores initially nucleate with the same pore density as that from the 1st anodization but only half the number of pores are stable and grow over time

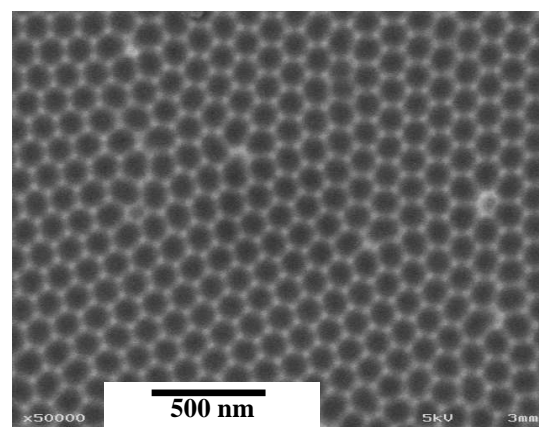


Fig. 2 Aluminum surface after removing the porous alumina formed by 2nd anodization – Good local ordering with double the period is clearly seen comparing to Fig. 1

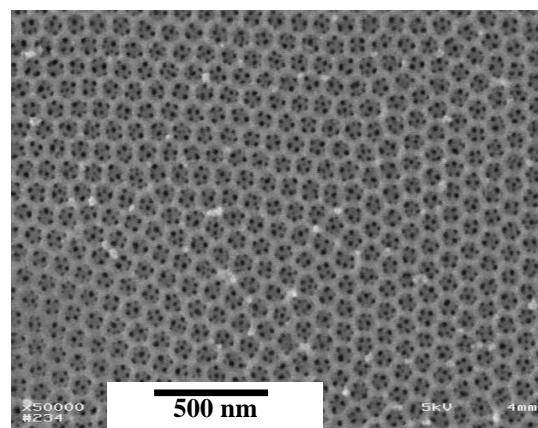


Fig. 3 Porous alumina surface after 2nd anodization (1st anodization – 40V, 2nd anodization 20V) The initial pore density is much higher than the equilibrium pore density and some pores merge during subsequent growth

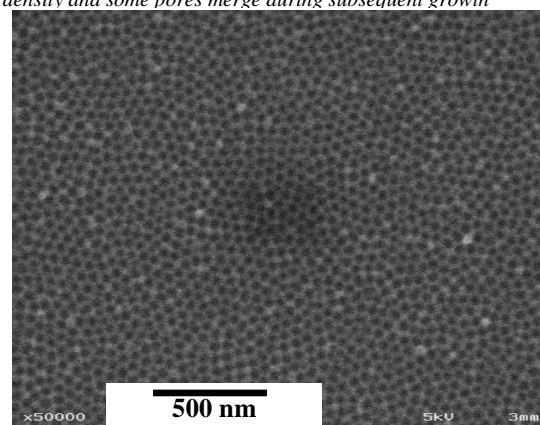


Fig. 4 Aluminum surface after removing the porous alumina formed by 2nd anodization – Local ordering (though not very good) with half the period is seen comparing to Fig. 3