Self-organized formation of hexagonal pore arrays in anodic alumina

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The conditions for the self-organized formation of ordered hexagonal structures in anodic alumina were investigated for both oxalic and sulfuric acid as an electrolyte. Highly ordered pore arrays were obtained for oxidation in both acids. The size of the ordered domains depends strongly on the anodizing voltage. This effect is correlated with a voltage dependence of the volume expansion of the aluminum during oxidation and the current efficiency for oxide formation. The resulting mechanical stress at the metal/oxide interface is proposed to cause repulsive forces between the neighboring pores which promote the formation of ordered hexagonal pore arrays. © *1998 American Institute of Physics.* [S0003-6951(98)03510-4]

Porous oxide growth on aluminum under anodic bias in various electrolytes has been studied for more than 40 years.[1] Because of their relatively regular structure with narrow size distributions of pore diameters and interpore spacings, porous alumina membranes are used for the fabrication of nanometer scale composites.[2–4] In 1970, O'Sullivan and Wood[5] presented a model to describe the self-regulating pore growth. This model based on the electric field distribution at the pore tips is able to explain why pores grow at all and why their size distribution is quite narrow. This and further refined models[6–8] can give microscopic explanations for the dependence of, e.g., pore diameters and pore distances on applied voltage or electrolyte composition.

Just recently Masuda *et al.*[9,10] reported self-organized pore growth, leading to a densely packed hexagonal pore structure for certain sets of parameters. But highly regular polycrystalline pore structures occur only for a quite small processing window, whereas an amorphous pore structure can be obtained for a very wide range of parameters without substantial change in morphology. The former models based only on field distribution cannot easily explain this behavior. The self-organized arrangement of neighboring pores in hexagonal arrays can be explained by any repulsive interaction between the pores. In this work, the dependence of the structural properties on the anodization conditions have been investigated to gain more insight into the formation conditions of ordered pore arrays and to find a microscopic explanation of the repulsive forces.

In order to explain the effect of self-organization, the situation during steady state pore growth has to be considered (Fig. 1). Pores grow perpendicular to the surface with an equilibrium of field-enhanced oxide dissolution at the oxide/electrolyte interface and oxide growth at the metal/oxide interface.[5,8] While the latter is due to the migration of oxygen containing ions (O^{2-}/OH^-) from the electrolyte through the oxide layer at the pore bottom, Al^{3+} ions which simultaneously drift through the oxide layer are ejected into the solution at the oxide/electrolyte interface.[11] The fact that Al^{3+} ions are lost to the electrolyte has been shown to be a prerequisite for porous oxide growth, whereas Al^{3+} ions

which reach the oxide/electrolyte interface contribute to oxide formation in the case of barrier oxide growth.[12,13] The atomic density of aluminum in alumina is by a factor of two lower than in metallic aluminum. A possible origin of forces between neighboring pores is therefore the mechanical stress which is associated with the expansion during oxide formation at the metal/oxide interface. Since the oxidation takes place at the entire pore bottom simultaneously, the material can only expand in the vertical direction, so that the existing pore walls are pushed upwards. Under usual experimental conditions the expansion of aluminum during oxidation leads to less than twice the original volume, since Al^{3+} ions are mobile in the oxide under the electric field, so partly the oxidized aluminum does not contribute to oxide formation. Whereas relative cation transport numbers between 0.4 and 0.5 have been reported in literature independently of experimental conditions,[12,13] in our experiments the relative thickness of the porous alumina layer compared to the consumed aluminum was found to vary with voltage and electrolyte composition.

Since no oxide formation takes place at the oxide/electrolyte interface during porous oxide growth but all cat-
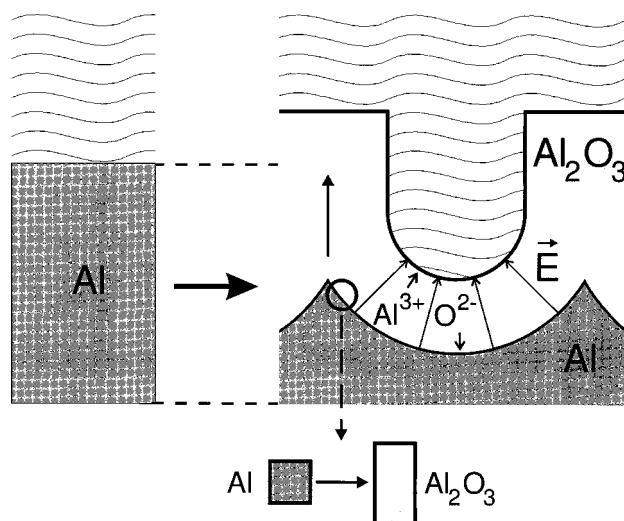

FIG. 1. Expansion of aluminum during anodic oxidation. On the left the level of the unoxidized metal surface is depicted.

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ions reaching the interface are ejected into the electrolyte, this observation can be explained by a variation of the relative transport numbers of Al^{3+} and (O^{2-}/OH^-) ions with voltage and electrolyte composition. Therefore we investigated the influence of the mechanical stress on the structural features by varying the forming voltage using two of the major anodizing acids.

The volume expansion during oxide growth was obtained by two different measurement techniques. On the one hand, the step height between the aluminum surface and the alumina surface at the edge of the anodized regions was measured with a mechanical profiler. The overall thickness of the alumina was determined by investigating the cross section in an optical microscope. The ratio of both values leads to relative alumina thickness. Since the alumina thickness varied between the edge and center of the sample by 20%, the accuracy of the measurement was estimated to be within 10%. The second method was based on measuring the current efficiency for oxide formation from the mass of the produced alumina and the charge flow during oxidation. Since the charge transfer over the anode is carried entirely by electrons that are generated by oxidation of Al to Al^{3+}, the current efficiency for oxide formation yields the ratio of aluminum which is transformed to Al_2O_3 to the total amount of oxidized aluminum. A current efficiency of 100% therefore corresponds to an expansion of the initial aluminum during oxide formation to double the volume. The weight of the alumina has to be corrected for the film porosity, which is approximately 10% as determined by SEM investigations on cleaved edges and in agreement with other results obtained for oxalic acid.[6] Incorporation of acid anions and OH^- also has to be considered as a potential source of error.[14,15] Overall the error is estimated to be about 10%.

High purity (99.999%) aluminum foils from Goodfellow were used as the starting material. Prior to anodizing, the aluminum was annealed under forming gas or nitrogen atmosphere at 500 °C in order to enhance the grain size in the metal and to obtain homogeneous conditions for pore growth over large areas. Subsequently, the foils were electropolished in a 4:4:2 by weight mixture of H_3PO_4, H_2SO_4, and H_2O. While the surface roughness of the aluminum foils was in the range of 5 μm before electropolishing, the roughness of the electropolished surface was typically between 20 and 30 nm on a lateral length scale of 10 μm. Porous alumina membranes prepared from nonannealed or from nonelectropolished aluminum foils did not exhibit any ordered pore domains. A more detailed analysis of the influence of the preparation conditions on the growth kinetics and structural properties of the porous alumina membranes will be reported elsewhere.[16]

The aluminum foils were mounted on a copper plate serving as the anode and exposed to the acid in a thermally isolated electrochemical cell. The diameter of the exposed area was 10 mm. While the anode temperature was kept constant at 1 °C, the temperature of the electrolyte deviated from that value by less than 0.1 °C. The electrolyte was rigorously stirred during anodization. In a first set of experiments, 0.3 M oxalic acid, as used by Masuda and Fukuda,[9] was used as the electrolyte. The anodization voltage was varied between 30 and 60 V. With oxidation times between 2
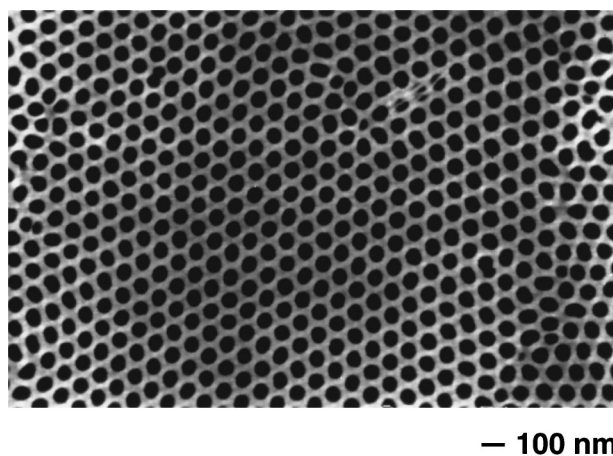

— 100 nm

FIG. 2. SEM bottom view of a porous anodic Al_2O_3 layer with ordered hexagonal pore structure after opening the pore bottoms by chemical etching [40 V, 0.3 M $(COOH)_2$, 1 °C].

and 4 days, layer thicknesses between 100 and 200 μm and aspect ratios (ratios of diameter and depth) of the pores of more than 1000 were obtained. After anodization, the remaining aluminum was removed in a saturated $HgCl_2$ solution. Subsequently, the pore bottoms were opened by chemical etching in 5 wt.% aqueous phosphoric acid.

While the pores nucleate at the surface at almost random positions, ordered pore domains of μm size were observed at the bottom of the layers (Fig. 2). The lattice constant within the ordered domains was approximately proportional to the voltage, in accordance with the literature, where proportionality of both pore and cell wall diameters to the voltage has been established.[5,6] The quality of the ordering of this structure depends on the anodization voltage. The best results were obtained for 40 V, which corresponds to the oxidation parameters given by Masuda and Fukuda.[9] Perfect hexagonal ordering is obtained within domains of μm size, which are separated from neighboring domains with different orientation of the pore lattice by grain boundaries. Thus, a polycrystalline pore structure is observed. When the voltage is increased to 60 V, ordered domains of comparable size, but also nonordered regions are observed in the sample. Lowering the voltage to 30 V leads to a much smaller size of the ordered domains, so that moderate voltages seem to be preferable in order to obtain highly ordered structures.

The volume expansion during oxidation was determined by measuring the layer thicknesses as well as the current efficiencies for oxide formation with consistent results. The dependence of the current efficiency on the forming voltage is given in Table I. The current efficiency is increasing with rising voltage. Optimal conditions for the formation of ordered structures occur at a current efficiency which corre-

TABLE I. Current efficiency for oxide formation in 0.3 M oxalic acid at 1 °C.

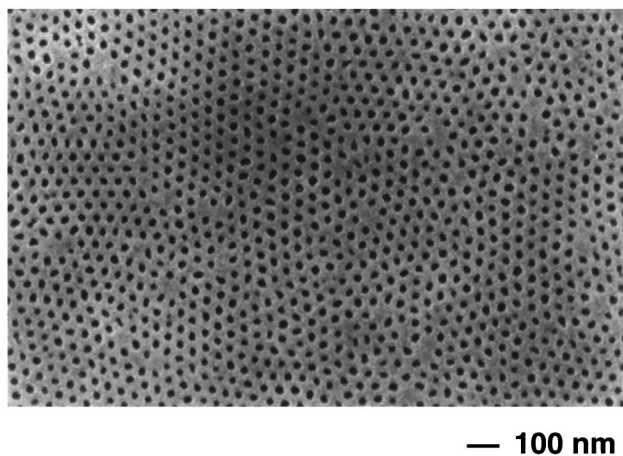| Voltage (V)	Current efficiency (%)
30	45
40	55
60	65

— 100 nm

FIG. 3. SEM bottom view of a porous alumina layer prepared in sulfuric acid (20 wt.% H_2SO_4, 18.7 V, 1 °C).

sponds to a moderate expansion of the aluminum during oxidation.

In order to check whether this condition for optimal ordering also holds for a different electrolyte, the voltage dependence of the alumina thickness and the ordering of the structures was investigated using 20 wt.% sulfuric acid at 1 °C. Although the applied voltages ranged only between 18 and 25 V, the anodizing current was on average 4 times higher than in the case of oxalic acid. With oxidation times between 1 and 2 days, alumina thicknesses of about 200 μm were achieved. The most regularly ordered structure, obtained with 18.7 V anodizing voltage, is shown in Fig. 3. Corresponding to the lower voltage, the feature size is roughly a factor of two smaller than with oxalic acid. Ordered domains with a hexagonal structure can be observed, although nonordered domains are also visible. The lower degree of perfection of the structure compared to that observed with oxalic acid is probably due to the higher growth rate and reduced interaction time for the self-organization process as well as to not entirely optimized anodization conditions. The relation between the anodizing voltage and the alumina layer thickness in relation to the consumed aluminum obtained by directly measuring the sample thickness, is shown in Table II. Due to the higher rate for chemical etching and the corresponding weight loss of the alumina, the directly

measured current efficiency values are significantly lower than those deduced from thickness measurements, especially for the lowest anodizing voltages. A strong increase of the volume expansion with the voltage can be observed. In addition to the sample prepared at 18.7 V, the samples anodized with 19 and 20 V to a minor extent also exhibit ordered domains. Again, conditions which lead to a moderate expansion of the aluminum during oxide formation, are most suitable for obtaining hexagonal ordered pore arrays. With volume contraction or very strong expansion during oxide formation, no ordered structures can be achieved. While in the case of contraction no repulsive forces between the pores are expected, large volume expansion may result in structural defects in the alumina and irregular pore growth. A large volume expansion is also associated with high anodizing voltages and growth rates and therefore with reduced interaction between the neighboring pores.

We conclude that in porous anodic alumina, ordered hexagonal pore arrays formed by a self-organization process during growth with oxalic as well as sulfuric acid as an electrolyte. A systematic dependence of the volume expansion of the aluminum during oxide formation on the anodizing voltage was observed. With both acids, optimal conditions for the growth of ordered structures are accompanied by a moderate expansion of the aluminum, whereas no ordered domains can be observed in the cases of contraction or very strong volume expansion. We suggest that the mechanical stress, which is associated with the expansion of the aluminum during oxide formation is the cause of repulsive forces between neighboring pores during the oxidation process, which lead to self-organized formation of hexagonal pore arrays.

TABLE II. Alumina layer thickness compared to the consumed aluminum layer using 20 wt. % H_2SO_4 at 1 °C.

Voltage (V)	Layer thickness (% Al layer)
25	162
20	134
19	141
18.7	122
18	86

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