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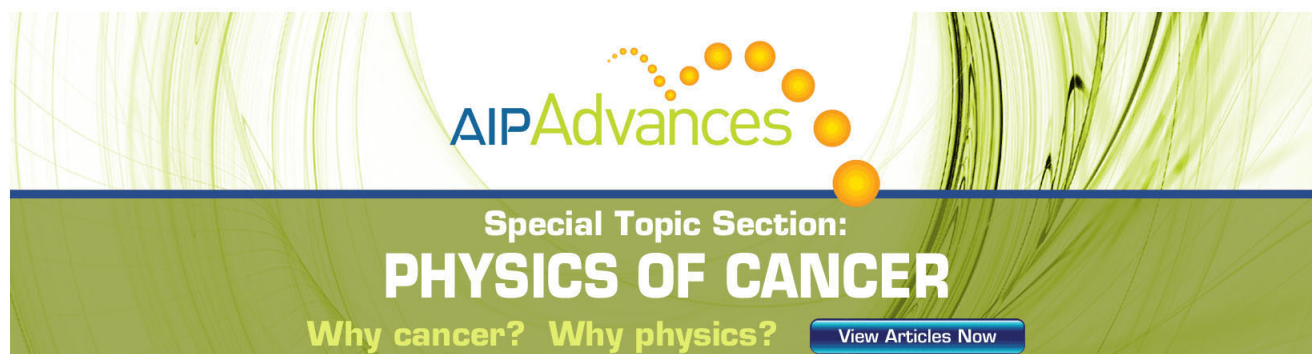
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Hexagonal pore arrays with a 50–420 nm interpore distance formed by self-organization in anodic alumina

A. P. Li,[a] F. Müller, A. Birner, K. Nielsch, and U. Gösele

Max-Planck-Institute of Microstructure Physics, Weinberg 2, 06120 Halle, Germany

Self-organized hexagonal pore arrays with a 50–420 nm interpore distance in anodic alumina have been obtained by anodizing aluminum in oxalic, sulfuric, and phosphoric acid solutions. Hexagonally ordered pore arrays with distances as large as 420 nm were obtained under a constant anodic potential in phosphoric acid. By comparison of the ordered pore formation in the three types of electrolyte, it was found that the ordered pore arrays show a polycrystalline structure of a few micrometers in size. The interpore distance increases linearly with anodic potential, and the relationship obtained from disordered porous anodic alumina also fits for periodic pore arrangements. The best ordered periodic arrangements are observed when the volume expansion of the aluminum during oxidation is about 1.4 which is independent of the electrolyte. The formation mechanism of ordered arrays is consistent with a previously proposed mechanical stress model, i.e., the repulsive forces between neighboring pores at the metal/oxide interface promote the formation of hexagonally ordered pores during the oxidation process. © *1998 American Institute of Physics.* [S0021-8979(98)00423-X]

I. INTRODUCTION

Ordered nanochannel-array materials have attracted increasing attention in recent years due to their utilization as templates for nanosize structures, such as magnetic, electronic, and optoelectronic devices.[1,2] Anodic porous alumina, which has been studied in detail in various electrolytes over the last five decades,[3] has recently been reported to be a typical self-ordered nanochannel material.[4,5] Self-organization during pore growth, leading to a densely packed hexagonal pore structure, has been reported for anodization in both oxalic and sulfuric acid solutions.[4–6]

When aluminum is oxidized to alumina, the volume expands by roughly a factor of 2 since the atomic density of aluminum in alumina is a factor of 2 lower than in metallic aluminum. The oxidation takes place at the entire metal/oxide interface, which leads to compressive stresses in the layer. However, the material can only expand in the vertical direction, therefore the existing pore walls are pushed upwards. On the other hand, Al^{3+} ions are mobile in the oxide under the electric field and some of the Al^{3+} ions reaching the oxide/electrolyte interface are injected into the electrolyte without contributing to the oxide formation. Moreover, the hydration reaction of the oxide layer takes place at the oxide/electrolyte interface leading to a dissolution and thinning of the oxide layer; this process is more evident in phosphoric or sulfuric acids. As a result, under the usual experimental conditions, the expansion of aluminum during oxidation leads to less than twice the original volume, but strongly depends on experimental conditions like the electrolyte concentration or anodizing voltage. Our group has recently proposed a model based on mechanical stress to explain this self-ordering formation.[6] It was suggested that the repulsive forces between neighboring pores caused by mechanical stress at the metal/oxide interface promote the formation of hexagonally ordered pore arrangements. The explanation should be supplemented by more experimental results.

In this work, ordered domains with a rather larger interpore distance (in other words, the center-to-center distance between neighboring pores) were observed by using much higher voltages and phosphoric acid solution as electrolyte. The structural characteristics of these self-ordered arrangements anodized in sulfuric, oxalic, and phosphoric acids have been studied. The results can help to elucidate the self-ordering mechanism.

II. EXPERIMENTAL TECHNIQUES

A detailed report on porous alumina formation can be found in Refs. 4–7. Here, we just give a brief description of the preparation of our samples. First, high purity (99.999%) aluminum foils were degreased in acetone and cleaned in a mixed solution of $HF:HNO_3:HCl:H_2O = 1:10:20:69$. Subsequently, the aluminum was annealed under nitrogen ambient at 400 °C for 3 h, and then electropolished in a 25:75 volume mixture of $HClO_4$ and C_2H_5OH. The mean roughness of the polished surface was measured by atomic force microscopy to be 3 nm over a 3 μm sq scan area. A metallographic examination showed the grain sizes of the annealed foils to be 100–200 μm.

Anodization was conducted under constant cell potential in three types of aqueous solutions, sulfuric, oxalic, and phosphoric acids, that were used as electrolytes. The aluminum foils were mounted on a copper plate serving as the anode and exposed to the acid in a thermally isolated electrochemical cell. During anodization, the electrolyte was rigorously stirred or recycled using a pump system. The values of the voltage, current, and temperature were recorded via

computer. 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 to facilitate observation of the pores. This etching process also leads to some pore widening, so the observed pore diameters do not reflect the intrinsic properties of the anodization process. In our analysis we therefore concentrate on the interpore distances rather than on the pore diameters. While the pores nucleate at the surface at almost random positions, periodic pore arrangements were observed at the bottom of the layers using a scanning electron microscope (SEM, JEOL JSM-6300F).

The volume expansion during oxidation was determined by measuring the layer thicknesses. The step height between the aluminum surface and the alumina surface at the edge of the anodized regions was measured with a mechanical profiler, and the overall thickness of the alumina was measured in an optical microscope after removal of the substrate. The ratio of both values corresponds to the relative thickness of the alumina layer grown and the aluminum layer consumed, i.e., the volume expansion factor.

III. RESULTS AND DISCUSSION

With a 10 wt % phosphoric acid solution the best periodic arrangements can be obtained under an anodization voltage of 160 V. The resulting interpore distance is about 420 nm. In Fig. 1, we present the pore arrangements anodized in sulfuric, oxalic, and phosphoric acid solutions under optimum parameters, where SEM micrographs of the porous films are shown with the same magnification. The periodic pore arrangements seen in Figs. 1(a)–1(c) with pore distances of 60, 95, and 420 nm were obtained in sulfuric, oxalic, and phosphoric acid solutions under voltages of 25, 40, and 160 V, respectively. Almost perfect hexagonal ordered domains can be seen over a wide range of pore distances.

For disordered pore arrangements in anodic alumina, the dependence of the interpore distance on the anodic voltage, the electrolyte, and its concentration has been studied, and it was reported that the anodic voltage has a major effect on both pore diameter and distance, i.e., the pore distance increases linearly with voltage.[8] For our ordered pore arrays, the dependence of pore distance on the anodic voltage is compared with reported data on disordered pore arrays in Fig. 2 for the three types of electrolyte. The samples anodized under voltage ranges of 19–160 V show pore distances ~ 50–420 nm. The solid line was drawn according to the formula obtained from random porous alumina arrays in Ref. 8. The linear relationship between the pore distance and the anodic voltage for disordered pore arrays describes the results for the ordered pore arrangements well. Moreover, it can also be found that, for phosphoric acid, the pore distances are a little bit larger than the fitting values, while for oxalic and sulfuric acids they are a little bit smaller. A similar electrolyte dependence was also found for disordered pore arrays.[9] All these mean that the morphology has a similar formation mechanism for both ordered and disordered pore arrangements. Numerous publications have been devoted to the investigation of the morphology of disordered
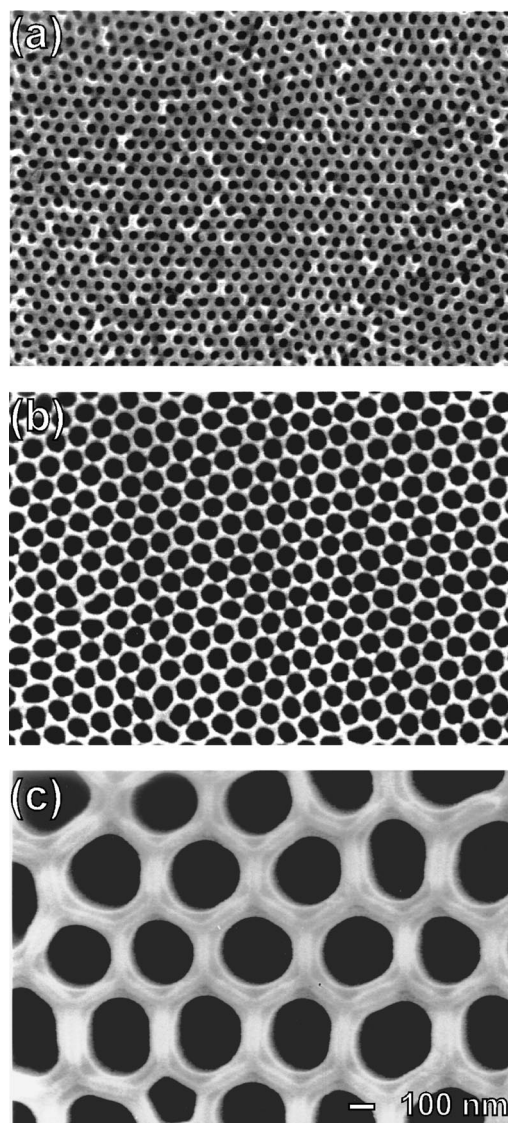

FIG. 1. SEM micrographs of the bottom view of anodic alumina layers. Anodization was conducted in 0.3 M (1.7 wt %) sulfuric acid at 10 °C at 25 V (a), 0.3 M (2.7 wt %) oxalic acid at 1 °C at 40 V (b), and 10 wt % phosphoric acid at 3 °C at 160 V (c). Pore opening was carried out in 5 wt % phosphoric acid at 30 °C for 30 min (a), 35 °C for 30 min (b), and 45 °C for 30 min (c). The thickness of the oxide films was approximately 120 μm.

arrangements of porous alumina.[10] Pores of virtually tubular shape with semispherical bottoms and a more or less hexagonal outside alumina cell are a logical consequence of expanding circles, evenly distributed over the surface in a (111) type of arrangement (starting from active sites), and merging after their perimeters hit each other. Since the pores nucleate at the surface at almost random positions, the pore arrangements fabricated are disordered.

In order to study stresses in the film, we have examined the relative ratio of the thickness of the alumina layer grown and the aluminum layer consumed. The volume expansion factor can be changed quite dramatically from about 0.8 up to 1.7 by varying the experimental anodization parameters. The volume expansion factors for optimal oxidation parameters, leading to hexagonal pore arrangements, are shown in Table I. Although the oxidation parameters, e.g., voltage, temperature, electrolyte, and concentration, are quite differ-
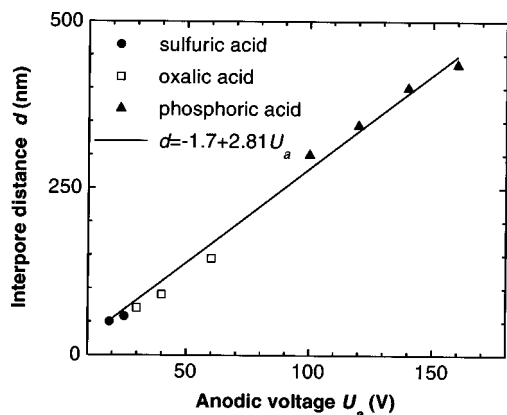
FIG. 2. Interpore distance d in self-organized porous alumina vs anodic voltage U_a for sulfuric, oxalic, and phosphoric acid solutions. The solid line represents the relation $d = -1.7 + 2.81 U_a$ (after Ref. 8).
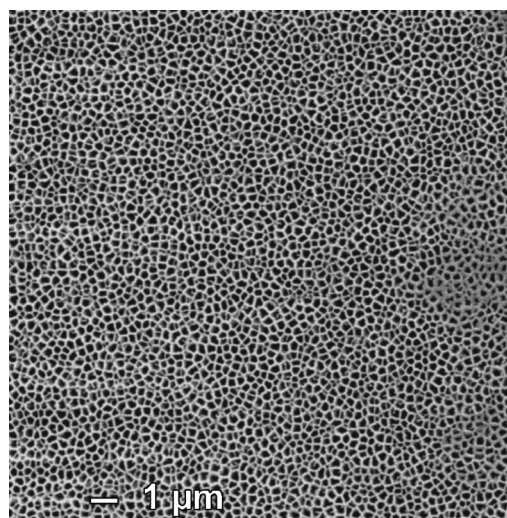

FIG. 3. Disordered pore arrangements of anodic alumina layers (bottom view) anodized in 10 wt % phosphoric acid at 120 V. Pores were opened in 5 wt % phosphoric acid at 45 °C for 30 min.

ent for the samples anodized in the three types of anodic acid, the relative alumina thickness ratios, i.e., the volume expansions, are very close to 1.4 in order to obtain ordered pore arrangements. That is to say, the best ordering is achieved for a moderate expansion factor of 1.4, independent of which electrolyte is used. In contrast, Fig. 3 shows the morphology of porous alumina with a volume expansion factor of 0.85 that was anodized in phosphoric acid under 120 V. Volume shrinkage, leading to tensile stress, was observed. We can hardly see any ordered domains in the structures. A series of studies show that ordered pore arrangement occurs in a stable anodic state, i.e., stable voltage and current. However, under a lower voltage, although the anodic process is very stable, the pore arrangements become more disordered since the volume expansion factors become smaller. Under a higher voltage, the volume expansion increases and sometimes cracks can be observed which explains the unstable current, and the arrangements are disordered too. All these results indicate that the volume expansion of the aluminum during oxidation plays an important role and a moderate expansion value is most suitable for self-organized formation in anodic alumina.

If aluminum is anodized to a γ-alumina barrier layer without pores, the volume expansion factor was reported to be about 1.28.[11] The specimens used in the present experiments were electrochemically polished and annealed. Stresses within the film arising from surface roughness and residual stresses were therefore minimized. Moreover, the

anodic alumina film is known to be extremely fine grained. Therefore, epitaxial stresses arising from lattice expansion are confined to a few atomic layers. A rough calculation of the magnitude of this stress may be made under the assumption that stresses arise from the volume change which occurs when aluminum is converted to porous aluminum oxide. The linear elastic strain at the metal/oxide interface is given by $(\sqrt[3]{V_R} - 1)$ where V_R is the volume expansion factor for porous alumina. For a classical cellular material with open cells,[12] the Young's modulus E_p is related to the porosity ρ and to the bulk property of the dense material according to

$$E_p = E_{alo}(1-p)^2, \qquad (1)$$

where E_{alo} corresponds to bulk aluminum oxide. This relationship has been widely used to estimate stress in porous silicon.[13,14] The volume expansion factor for porous alumina in the present experiment is about 1.4, and this corresponds to a linear strain of 0.12. If the porosity is 0.10,[6,9] stress in porous alumina is calculated to be 4.0×10^3 MPa (Young's modulus for the aluminum oxide film is 4.1×10^4 MPa).[15] For the anodic aluminum oxide without pores, the observation of compressive stress at low current densities appears qualitatively consistent with the estimated stress of 3.6×10^3 MPa although the observed stress ($\sim 2 \times 10^2$ MPa) is much less.[11] This enables us to assume that the actual stresses in these self-organized layers are of the order 4.0×10^3 MPa or less, which mainly depends on the volume expansion since the exact stresses are hard to measure experimentally in these self-ordered structures.

To study the structural characteristics of the ordered pore arrangements, Fig. 4 shows SEM micrographs of porous alumina which were anodized under the same conditions as those in Fig. 1 in lower magnifications. It can be found that the pore configurations contain many perfectly ordered domains. Within the domains, hexagonal pore arrangements with the same orientation of the pore lattice were observed. But the domains are only 1–3 μm, and they are separated from neighboring domains with different lattice orientations by grain boundaries. That is to say, the ordered pore arrange-

TABLE I. Ratio of the thickness of the alumina layer grown to the thickness of the aluminum layer consumed under different anodization conditions which lead to the self-ordered hexagonal pore arrangements.

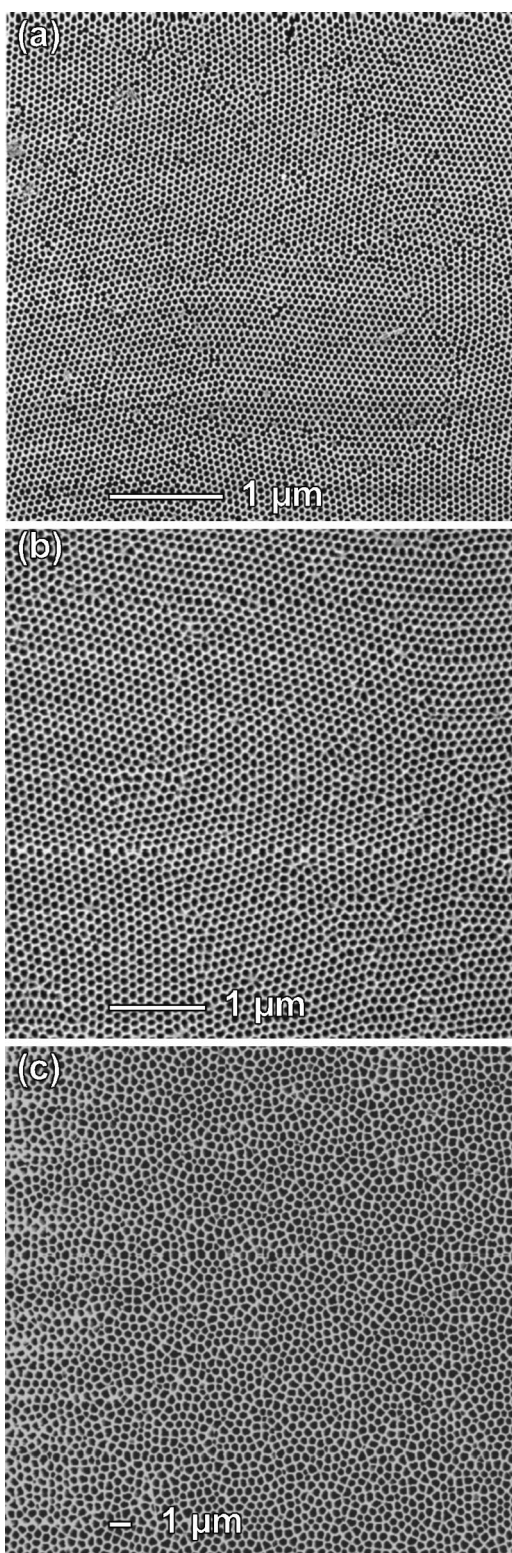| Electrolyte (acid)	Concentration (wt %)	Voltage (V)	Temperature (°C)	Thickness ratio of alumina to consumed Al
Oxalic	2.7	40	1	1.42
Sulfuric	20	19	1	1.41
	1.7	25	10	1.40
	1.7	25	1	1.36
Phosphoric	10	160	3	1.45

FIG. 4. Lower magnification SEM micrographs of porous alumina anodized in sulfuric (a), oxalic (b), or phosphoric acid (c). The anodization conditions are the same as those in Fig. 1.

ments show polycrystalline structures. Moreover, although the anodized structures were formed in the three types of electrolyte under quite different anodic voltages and, as a result, have different pore distances, the ordered domains are of almost the same size and no dependence on pore distance was observed. If it is assumed that the ordered domain size is

related to the stress and its relaxation in the alumina layer, then the constant size of ordered domains may be explained in terms of a similar stress value in the ordered structures. For the film anodized in phosphoric acid, the pore distance is about 420 nm (for a voltage of 160 V), 4–7 times larger than that anodized in sulfuric or oxalic acid. Therefore, for a given domain size it contains a much smaller number of pores and this can be used to explain why it is hard to find relatively larger regular domains in films anodized in phosphoric acid. Details of the characteristics of ordered domains and their boundaries need further investigation.

IV. CONCLUSIONS

We have observed self-organization of two-dimensional pore arrays with 50–420 nm interpore distances in porous anodic alumina. The self-organization process can occur during growth with oxalic, sulfuric, as well as phosphoric acid as an electrolyte. A proportionality of the interpore interval to the anodic voltage has been observed for the hexagonally ordered pore arrangements. The pore arrangements show polycrystalline structures with ordered domains having diameters of a few micrometers. The volume expansion of aluminum during oxide formation was examined. For all three types of electrolyte, optimal conditions for the growth of ordered arrangements are accomplished by moderate expansion of the aluminum, whereas no ordered domains can be observed in the cases of contraction or very strong volume expansion. The self-organized formation of hexagonal pore arrangements can be explained using a mechanical stress model.

ACKNOWLEDGMENTS

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