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An approach to control the interpore distances and nanopore diameters of 150-nm-thick thin aluminum films is reported here. The Al thin films were grown by sputtering on *p*-type silicon substrate and anodized with a conventional anodization process in a phosphoric acid solution. It was found that interpore distance and pore diameter are related to the aluminum grain size and can be controlled by annealing. The grain contours limit the sizes of alumina cells. This mechanism is valid for grain sizes supporting only one alumina cell and consequently only one pore. © *2010 American Institute of Physics*. [doi:10.1063/1.3291115]

Two-dimensional nanostructures based on a self-organization process have attracted a great deal of interest from the scientific community as a key method for nanofabrication in broad areas of nanotechnology due to their relative simplicity and low cost of synthesis. In particular, porous anodic aluminum oxide (PAA) films have attracted much interest due to the high degree of ordering, high pore density and uniformity. One of the properties of PAA membranes is the potential to fabricate an ordered template with desirable dimensions. For example, in order to grow nanowires[1] and nanotubes[2] inside nanopores with a high ratio of length to diameter and a thickness of several microns, PAA templates are needed. On the other hand, for the fabrication of arrays of nanodots,[3] it is important to reduce the alumina template thickness to a minimum in order to facilitate dot growth inside pores with better control of dot size and shape.

An excessive decrease in the aluminum (Al) layer (to a few nm) imposes additional conditions upon the formation and control of the PAA structure. In bulk Al and/or Al thick films under appropriate anodization conditions, very regular, self-ordered, honeycomblike, hexagonal arrays with a circular pore at the center can be obtained.[4–10] Al thin films on an Si substrate have two important intrinsic factors that become evident with decreasing thickness of the film layer: (i) decreases in Al grain size lead to a disordered, porous structures[11,12] and (ii) a SiO_2 interfacial layer is formed below the anodized Al film where the volume expansion of SiO_2 relative to Si induces a mechanical stress on the PAA.[13,14] These effects need to be better understood and controlled for technological application of nanoporous templates

with thicknesses of a few nanometers. As a consequence, growth of ordered pore arrays using Al thin films on Si has remained a challenge from scientific and technological points of view.

Here it is reported an approach to control the interpore distances and nanopore diameters of 150-nm-thick aluminum thin films deposited on *p*-type silicon substrates using a conventional anodization process in a phosphoric acid solution. The effects of the Al thin film grain size on nanopore formation, size and self-organization were investigated to gain deeper insight into the control of the PAA structures.

A 150-nm aluminum 99.99% thin film was deposited on *p*-type Si (111) substrate (1–10 Ω cm) using dc-magnetron sputtering at a pressure of 3×10^{-1} Pa with a deposition rate of 1.5 nm s^{-1}. The native silicon oxide of *p*-type Si was removed using 48% HF acid solution for 30 s prior to deposition of the Al film. The samples were annealed at 500 °C for 3, 6, 15, 18, and 24 h in a conventional furnace at a pressure of 3×10^{-4} Pa to relax the internal stress and to promote grain growth of the polycrystalline Al thin films.

The anodization was performed in a conventional cell using a platinum sheet as a cathode. The electrical contact was made on the backside of the Si wafer. An aluminum Ohmic contact was formed after deposition. The samples were anodized in an acidic aqueous solution of 1.3 mM H_3PO_4 at a constant voltage of 140 V for 10 min.[12] The bottom of the anodization cell was cooled with a Peltier System to ensure a constant temperature of 20 °C. During anodization, the electrolyte was vigorously stirred. Then, the samples were dipped into a solution of 2.8 M H_3PO_4 at 20 °C for 1 min to widen and enlarge the pores.[12] After the anodization process, the samples were rinsed in de-ionized water and dried in N_2 gas.

X-ray diffraction and atomic force microscopy (AFM) were used to investigate the crystalline structure and to determine the mean grain size and surface morphology of the

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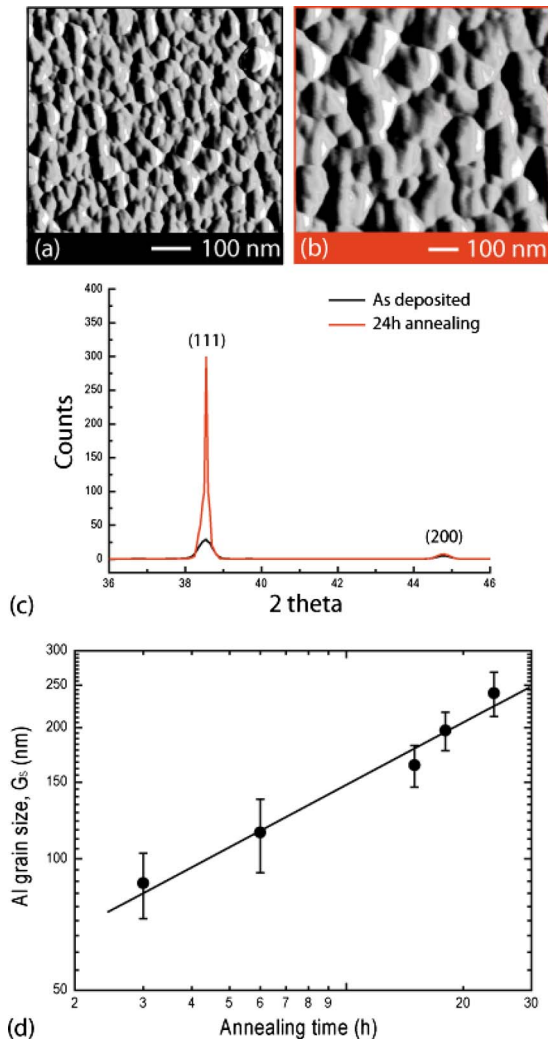
FIG. 1. (Color online) AFM images of Al thin films with different annealing times. (a) As-deposited, (b) 24 h, (c) x-ray diffractograms of the same samples, and (d) the relationship between annealing time and mean grain size, G_S.
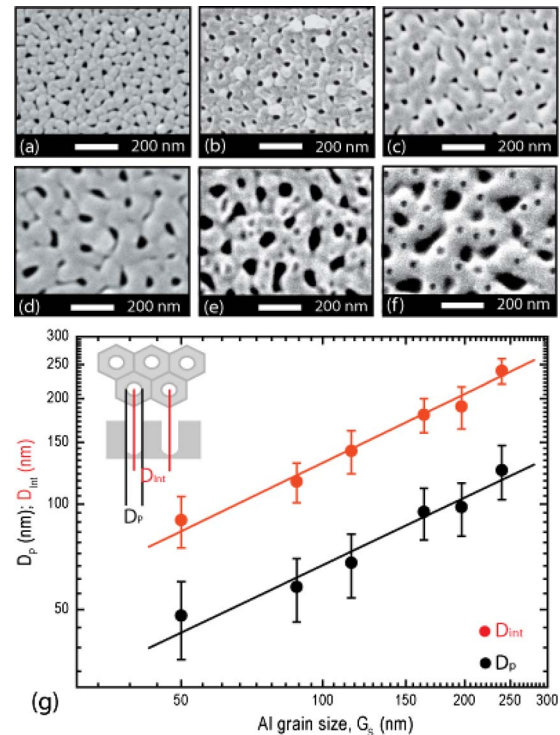

FIG. 2. (Color online) SEM images of anodized Al thin films with different annealing times. (a) As-deposited, (b) 3 h, (c) 6 h, (d) 15 h, (e) 18 h (f) 24 h, and (g) dependence of the D_p and D_{int} on G_S.

metallic Al thin films. Surface images of the PAA structures were obtained by scanning electron microscopy (SEM); cross sections of the samples were prepared in a focused ion beam and imaged with field emission SEM.

Figures 1(a) and 1(b) show the AFM images of the as-deposited Al thin film after annealing for 24 h. The AFM images of the as-deposited films consist of small grains of around 50 nm in diameter and larger grains with diameters of around 240 nm after annealing for 24 h. An increase in the mean grain size (G_S) and preferential orientation in the (111) reflection plane are observed in the diffractograms in Fig. 1(c). Figure 1(d) shows dependence of the G_S on the annealing time, measured by AFM for all samples. The as-deposited samples present small G_S due to the physical vapor-deposition process. This is generally carried out under supersaturation, leading to small critical nuclei spaced much closer to one another.[15] After annealing, the defects were released and G_S increased. For metals and alloys, including thin films, the dependence of G_S on annealing temperature is expected to be described by the expression

$$R = Bt^n,$$

where **B** is dependent on the annealing temperature and **n** is related to the specific material (for Al, it can vary from 0.4 to 0.5).[16] For the 150 nm sputtered Al films, the G_S growth presents a dependence similar to that of bulk Al, with an **n** value of 0.47. The limit of G_S has been found to be three times the film thickness for Al films.[16] It is noteworthy that there is a direct relationship between the film thickness and G_S.[17]

Figures 2(a)–2(f) show the SEM images of Al films anodized for 10 min after annealing for 0 to 24 h. Figure 1(g) depicts the relationship between the G_S of Al and the pore diameter (D_p) and interpore distance (D_{int}). The D_p and D_{int} of the material increase linearly with the G_s of Al from 48 to 125 nm and from 90 to 240 nm, respectively.

The values of D_{int} and D_p for PAA thin films obtained herein differ from those that would be obtained from anodization of bulk Al. For anodized bulk Al, D_{int} and D_p tend to increase linearly with applied voltage. The proportionality constants (PCs) of the applied voltage are 2.5 and 1.29 nm V^{-1} for D_{int} and D_p, respectively.[8] Similar PCs were found for films with thicknesses ≥ 1 μm. If the Al thin film anodization follows the same trend as bulk anodized Al structures, D_p and D_{int} should be 180 and 350 nm, respectively, in phosphoric acid solution at 140 V. Moreover, Sun *et al.*[12] reported that for Al thin films with thicknesses of 350–400 nm, mean pore sizes of 70–120 nm were obtained by employing the same anodization conditions used here.

Based on previous discussions, it is possible to infer that alumina hexagonal cells seem to be limited by the aluminum G_S. When G_S is large enough to nucleate more than one cell,
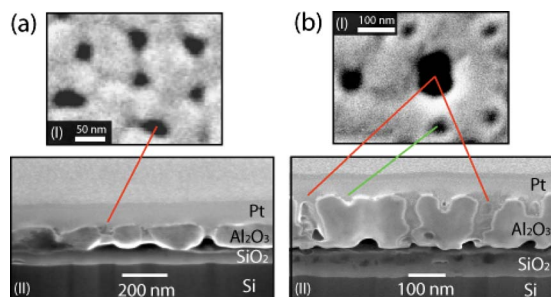
FIG. 3. (Color online) Amplified SEM images of the surfaces a(I) and b(I) and the cross-sections a(II) and b(II) of the same samples depicted in Figs. 2(a) and 2(f), respectively.

the mechanism that governs the expansion of the alumina cells will be the same as that of bulk aluminum.[4–10] However, it is likely that there is a limit to this behavior. When G_S is smaller than a critical size, the expansion of the alumina cells is physically limited by the Al G_S, as can be seen in Fig. 2(g). The small pores that appear in Figs. 2(e) and 2(f) show the limit of the alumina cells that correspond to the aluminum G_S.

Kokonou *et al.*[18] reported that for Al films with thicknesses of 500 nm anodized with electrolytes, oxalic, or sulfuric acid solutions, D_p values around 30–40 nm were obtained. This is in good agreement with the expected values calculated from the proportionality constant, 1.29 nm V^{-1}. However, when the Al film thickness was decreased to 30 nm, D_P decreased to values of around 10–15 nm. This could be related to the fact that in thin films the grain size is expected to be proportional to the thickness of the films when deposited at the same rate.

The cross sections I and II of Figs. 3(a) and 3(b) show an amplification of the surface and cross-sectional SEM images of the same samples depicted in Figs. 2(a) and 2(f), respectively. It is possible to observe the same structure along the film thickness (see arrows). Cross sections I and II of Figs. 3(b) clearly show the limits of the alumina cell formed by a big central pore surrounded by smaller ones. Due to the irregularity of the grain contours and their small sizes, the alumina cells are not exactly hexagonal, as found in bulk anodized aluminum. The small pores appear after chemical etching in defective regions due to a junction of two or more alumina cells. In fact, these regions are localized at the grain boundaries that limit the alumina cells. Chu *et al.*[19] demonstrated that for bulk Al oxide, the triple cell junction may not be as dense as the other parts of the cell wall. This is due to circularly distributed expansion forces from the centers of the alumina cells, leading to preferential dissolution of the triple point junctions. The SiO_2 layer at the interface of the alumina and Si substrate is due to the beginning of anodization of Si.

In summary, the influence of grain size on pore structures of Al thin films anodization of grown on Si has been discussed. It was demonstrated that D_p and D_{int} are directly related to the mean aluminum grain size, G_S. Therefore, the alumina cells growth is limited by the aluminum G_S and, for the conditions presented here, only one cell per grain will be formed. As a consequence, only one pore is nucleated per grain. The growth of the alumina cell is closely related to the behavior to the growth of aluminum G_S but it presents a limit. When G_S is large enough to nucleate more than one cell, the expansion of the alumina cells will be the same as that of bulk aluminum. It was demonstrated an approach to control the interpore distance and pore size of nanoporous alumina. The results help to clarify the key factors that control the growth of nanoporous Al_2O_3 thin films by anodizing Al films in the nanometric scale. As consequence, its possible to control and improve methods for production of such materials. Thus, these results open the possibility to rationaly design nanoporous Al_2O_3 arrays to several nanotechno logical applications, especially in template synthesis of nanodevices and nanostructures.

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