EFFECT OF PROCESS PARAMETERS ON THE NANOPOROUS STRUCTURE OF ANODIZED ALUMINA[1]

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Abstract

Nanoporous alumina fabricated by the anodizing of Al provides unique, advantageous characteristics such as uniformity, high pore density, controllable pore dimensions, highly ordered structure and simple synthesis procedures. Nanoporous alumina membranes have applications in diverse fields such as tissue engineering, drug delivery, biosensors and templates to synthesize nanowires or nanotubes. The performance of nanoporous surfaces and nanoporous membranes is highly dependent on the pore morphology, size and chemistry as well as their density and homogeneity. One of the fascinating aspects of anodized alumina nanoporous structure is its tunability in pore size, pore density, inter-pore distance and pore depth by simply changing the anodizing parameters, such as current, voltage, time, electrolyte chemistry, electrolyte concentration and temperature. To control the anodizing of Al and obtain desirable properties, an understanding of anodizing conditions on the film characteristics is important. In this study a statistical analysis of the effect of process variables on the nanoporous structure of anodized alumina is examined. Such studies can be extended to anodizing other materials such as niobium and tantalum for various applications including energy storage.

Keywords: Anodization; Nanporous; Alumina; Membrane.

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1 INTRODUCTION

There are several applications for nanoporous structures synthesized during the anodization of alumina. Nanoporous structures obtained from anodized alumina have been used in tissue engineering as substrates for cell cultivation, to immobilize drugs in pores in drug delivery systems, in biosensors and as templates to fabricate nanowires or nanotubes.[1-4] The performance of the nanoporous structure of anodized alumina is highly dependent on the pore morphology, size and chemistry as well as their density and homogeneity. Therefore, it is important to be able to control these attributes.

Anodized alumina membranes provide advantageous characteristics such as uniformity, high pore density, controllable pore dimensions, highly ordered structure and simple synthesis procedures.[1,5-8] In addition, alumina is electrically insulating, with high chemical stability. Anodized alumina is biocompatible[9] and has good adhesion with the metallic aluminum as its base and support.[10] Completely anodized alumina is optically transparent.[11]

One of the fascinating aspects of anodized alumina nanoporous structures is its tunability in pore size, pore density, inter-pore distance and pore depth by simply changing the anodizing parameters, such as current, voltage, time, electrolyte chemistry, electrolyte concentration and temperature.[1,12-15] Pore sizes of the anodized aluminum can vary in a wide range of 5 to 500 nm.[1,12] In anodized alumina, the pore aspect ratio (pore diameter vs. pore depth) can reach values more than 1:1000 and these pores could have a narrow size distribution.[1] To control a anodizing of aluminum and obtain desirable properties, the knowledge of the effect of different anodizing conditions on the film characteristics is important. Identifying the effect of different fabrication parameters governing the synthesis of alumina films with controlled nanoscale pore structure will help in not only manufacturing tailored, pre-designed porous structure but also avoiding the current practice of trial-and-error procedures.

In previous studies conducted on the effect of different parameters on porous structure of the anodized alumina (either obtained from Al foils or thin films), mainly pores are considered regular and uniform and there has been no statistical study on the pore size distribution. In this study, the effect of Al foil surface preparation on anodized alumina structure was studied and was compared with the anodized alumina fabricated by anodizing of the thin film of Al deposited on silicon wafer. The effect of different anodizing parameters on the nanoporous structure was also investigated using an analysis of the pore attributes derived from studying pore size distributions.

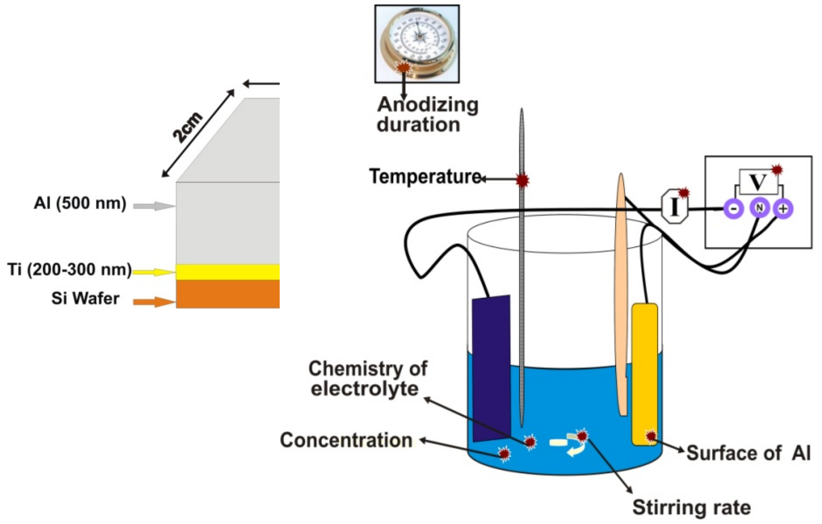


Figure 1: Al thin film sputter deposited on silicon wafer (left) and the cell and experimental parameters used for anodizing (right).

2 MATERIALS AND METHODOLOGY

A 500 nm thin film of Al (0.5% Cu) was sputter deposited on a silicon wafer. To provide the adhesion between the Si wafer and the deposited aluminaum a thin layer of Ti (200-300 nm) was used as the intermediate (Figure 1(a)). These samples were used as the working electrode (positive electrode, anode). A 314 stainless steel foil was used as the cathode. A saturated calomel electrode (SCE) was used as the reference electrode and the electrolyte was oxalic acid. The variables applied in anodizing were concentration of electrolyte (0.3, 1.5 and 3 wt% oxalic acid), applied potential (40 V, 50, 60 V and 80 V), temperature (0, 20, 40 °C) and the effect of time (5, 10, 20, 50, 60, 75, 100 and 240 minutes). Also the effect of stir rate and surface properties were studied. The anodizing set up and the parameters which can be used as anodizing variables are shown in Figure 1 (b). The nanoporous structure of the surface of the anodized alumina was characterized after each anodizing step. To study the structure of the pore bases, the surface layer of the anodized alumina was removed. This alumina layer was removed by soaking in aqueous H_3PO_4 (6wt%) and H_2CrO_4 (1.8 wt%) mixture in 50°C for 4-5 minutes and the porous structure under the first anodizing layer was studied.

To study the effect of the surface, Al foils (99.999% Al, Al Shim Stock Roll, 6” thickness) with different surface conditions were used. Different surfaces were prepared by a combination of annealing, mechanical polishing, and electropolishing, or a combination of them. Etched and unetched surfaces in each condition were also investigated. Annealing was done in Argon atmosphere at 400°C for 2 hours. Scratching was done using 80 grit sand paper. Electropolishing was conducted in a mixture of ethanol:perchloric acid (4:1 v) at room temperature in 60V for 20 seconds in the presence of a stainless steel cathode.

During anodizing, the current changes vs. time were measured and recorded. The temperature changes during the experiments were also controlled. For evaluating the nanoscale structure of anodized samples and investigating the effect of different parameters on these structures, scanning electron microscopy (SEM) was used. SEM characterization of the membranes was performed using a Hitachi S-4700 Cold Cathode Field Emission Scanning Electron Microscope. The SEM was conducted using a 5 kV accelerating voltage and 10-11 mm working distance. Various sections of the membrane were scanned at different magnifications in each case. To look at the cross-section of the samples a dual beam FIB microscope (Hitachi S-4700 Cold Cathode Field Emission SEM) was used.

For each process condition, two samples were prepared. In each sample at least two different locations were imaged by SEM. For measuring the pore diameters, their size distribution, and their uniformity, all pores were measured by using plot digitizer. In this software, one can define a scale for a .JPG image and base on that scale the x and y position of each point could be read by the software. Edges of all pores were defined and the pore diameters were calculated based on these measurements. In each image minimum and maximum of the pore sizes, standard deviation of them, average of pore sizes, the histogram of their frequency, the cumulative distribution of the pore sizes and the width of the distribution were calculated. To have a good accuracy of the data, this analysis method was repeated in images with different magnifications. For each process condition, the experiment was repeated twice. Both of the samples were SEM imaged in 2 different spots. In each spot for each sample around 150 pores were measured. The density of the pores was measured in 5 different areas of 500 nm^2 in each SEM image. All results for each specific condition were compared to each other and the accuracy of the measurement of pore size, pore density and pore distribution were proved.

3 RESULTS AND DISCUSSION

Figure 2 shows the effect of different Al surfaces on the anodized film structure. The effect of different surface preparation methods on Al foils were compared to the surface of Al sputter deposited on a Si wafer. In Figure 2(a), the anodized structure of the as-received Al foil is shown. Figure 2(b) shows the anodized structure of the Al foil after electropolishing. Figures 2(c), 2(d) and 2(e) show the anodized structure of the electropolished Al foil after annealing; scratching, and scratching followed by annealing, respectively. Figure 2(f) relates to anodizing of the Al film that was sputter deposited on a Si wafer. All these samples are anodized in 3 wt% oxalic acid, in 40V, for 100 minutes, at 20ºC. Figures 3 and 4 represent the histograms and cumulative frequency distributions of pore sizes after anodizing the different Al surfaces. Table 1 summarizes the effect of surface preparation of anodized alumina on the various pore size attributes.

Figure 2(a) shows that the pores mainly form along the pre-existing surface defects. The anodized surface of electropolished Al is shown in Figure 2(b). It can be seen that the trend of the pore size distribution of the anodized electropolished surface (Figure 3(b)) is similar to the anodized as-received Al foil (Figure 3(a)). The maximum pore size shifted slightly to larger size (27 nm in comparison to 22 nm maximum pore size on anodized as-received Al foil) and the pore distribution is slightly shifted to larger pore sizes. As seen in Table 1, a small increase in pore sizes and their deviations in d_{50}, d_{90} and mean pore size were also observed. In addition, the anodized surface of the electropolished Al foil shows a larger standard deviation of 3.6 compared to the anodized surface of the as-received Al foil (3.1). It could be observed that even though electropolishing has not significantly affected the pore size and distribution, it has decreased the pore density from 250 to 169 pores/μm^2 (32.4% decrease).

Electropolishing is known as an effective factor in surface preparation. Electropolishing removes the natural oxide layer of the Al. It also decreases the roughness of the surface. It has been reported that electropolishing improves the regularity of the anodized porous structure. Also electropolishing conditions affect the cell sizes of anodized alumina besides their configuration. Yu et al reported that different electropolishing conditions can create surfaces with a wide range of roughness. They have reported that electropolished surfaces with higher roughness cause smaller average pore sizes after anodizing and therefore electropolishing conditions could be used as a method to control the tunability of pore sizes formed during anodization. However, choosing inappropriate electropolishing conditons can also increase surface roughness. Further, electropolishing delays the pore formation on the surface, while in as-received surfaces pore formation occurs immediately after initiating the anodizing process. For the same reason, electropolishing may prevent pore formation in anodizing with electrolytes that have low dissolution ability.

Since electropolishing generally smoothens the surface and removed the surface defects such as oxides or scratches, less pore nucleation locations are available. Here, the decrease in pore density is in agreement. The reason that the pore sizes are shifted slightly to larger amounts could be related to this lower pore density. When the number of pores are decreased the applied voltage and the resulting current density is consumed for oxidation and dissolution of less pores. Therefore it could be expected that in this case field-assisted dissolution be stronger and pores become deeper and wider.

Figures 2(c) and 3(c) show that annealing before electropolishing form larger pores in comparison with the electropolished sample. Table 1 shows that d_{50}, d_{90}, mean pore size and maximum pore size have shifted to larger pores. Annealing before electropolishing increased the range of the pore sizes and the width of distribution. Wider pore sizes increased the pore size standard deviation and the resulting surface had lower uniformity in pore size. Annealing increased the pore density from 169 to 266 pores/μm^2 (57.3% increase). It has been suggested that annealing reduces the internal stresses in the samples, promotes the crystalline quality of Al and prevents further oxidation of Al surface. It is reported that annealing improves the pore structure regularity of the anodized alumina. Annealing causes larger grains in aluminum. Annealing increases grain size and therefore causes long-range order in oxide which leads to higher pore structure regularity. There has been no prior report on the effect of annealing on pore size and density.

Figure 2(d) shows the effect of scratching on the anodized surface. It could be observed that anodizing the scratched sample after electropolishing (Figure 2(d)) created larger pores than the sample which was anodized after electropolishing of the as-received sample (Figure 2(b)). Table 1 shows that d_{50}, d_{90}, mean pore size and maximum pore size have shifted to larger sizes. Also, a comparison between Figure 3(b) and 3(d) shows that scratching caused a wider range of pore size and according to Table 1 pore size standard deviation increased from 3.6 to 5.9. Finally, scratching increased the pore density from 169 to 358 pores/μm_2 (111.8% increase). These observations can be explained by the theory of pore nucleation from pre-existing surface defects. An increase of pore size can also be explained by the mechanism of non-uniform electric field which helps the alumina dissolution.

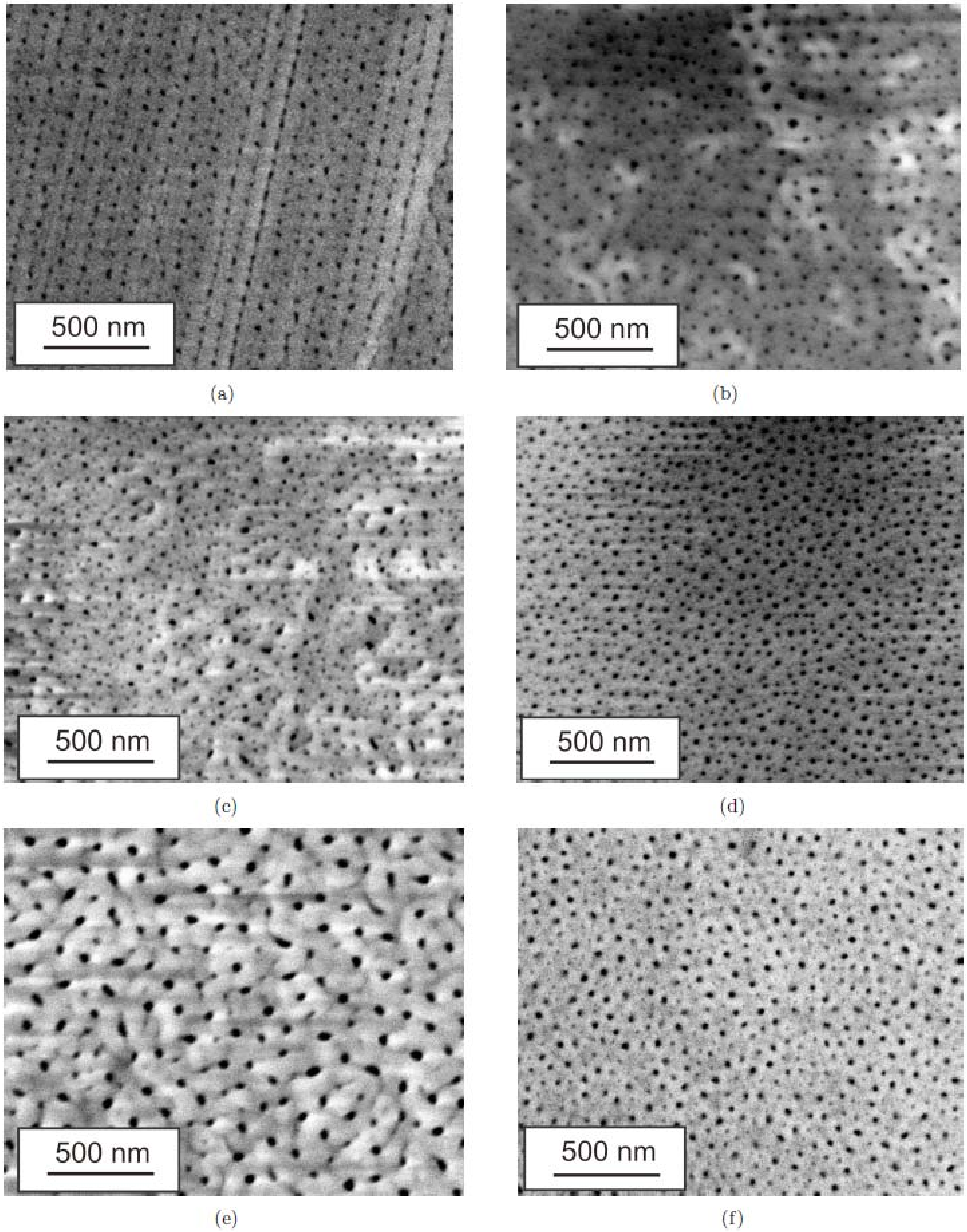
Figure 2(e) shows the anodized surface structure of the Al foil that was annealed after scratching and was also electropolished before being anodized. Comparing this image to Figure 2(d) indicates that annealing reduced the pore density from 358 to 80 pores/μm^2 (77.6%). It confirms that pre-existing stresses in the sample can produce sites for pore nucleation. Another reason for lowered pore density in the annealed sample can be larger grain sizes due to annealing which provides fewer grain boundaries. Since grain boundaries ae preferred sites for pore nucleation, reduction of grain boundaries can lead to lower pore density.

Figure 3(e) shows that annealing increased the width of the pore size distribution. The density of small pore (<10 nm) was reduced and the pore size distribution shifted to larger pore sizes. The d_{10}, d_{50}, d_{90}, mean pore size and maximum pore size are larger than the sample which was scratched without annealing (Table 1). This pore size enlargement can be related to lower pore density which affects the current density distribution and increase of the current density and therefore field-assisted solution in pore sites. This focus of current density on pores can be the explanation for their growth in comparison with the sample with higher pore density. Comparing this image with Figure 2(c) showed that the sample which was scratched before annealing produced larger pores. Figures 3(d) and 3(e) show that scratching results in a wider pore size distribution. These images show two peaks for the maximum pore size distribution, suggesting that scratching decreased the homogeneity of pore sizes. This observation is also supported by an increase of standard deviation of the related samples, as listed in Table 1.

Figure 2(f) relates to the anodizing of the Al that was sputter deposited on Si wafer. It could be observed that pores are not grown larger than 35 nm and shows a pore density of 257±29 pores/μm^2. These results show the importance of the surface preparation on pore size, pore distribution and anodized pore structure. It is extremely important to know all steps taken to prepare an anodized sample. Electropolishing is a very common method for sample preparation. When the anodizing is applied for thin films or aluminum films which are in contact with other materials there are some limitations for electropolishing. Also some additional reactions during anodizing due to the existence of a second material has been reported which affects the efficiency and potential of the anodizing conditions. These differences and limitations suggest that further studies are needed on anodizing of sputter-deposited Al films.

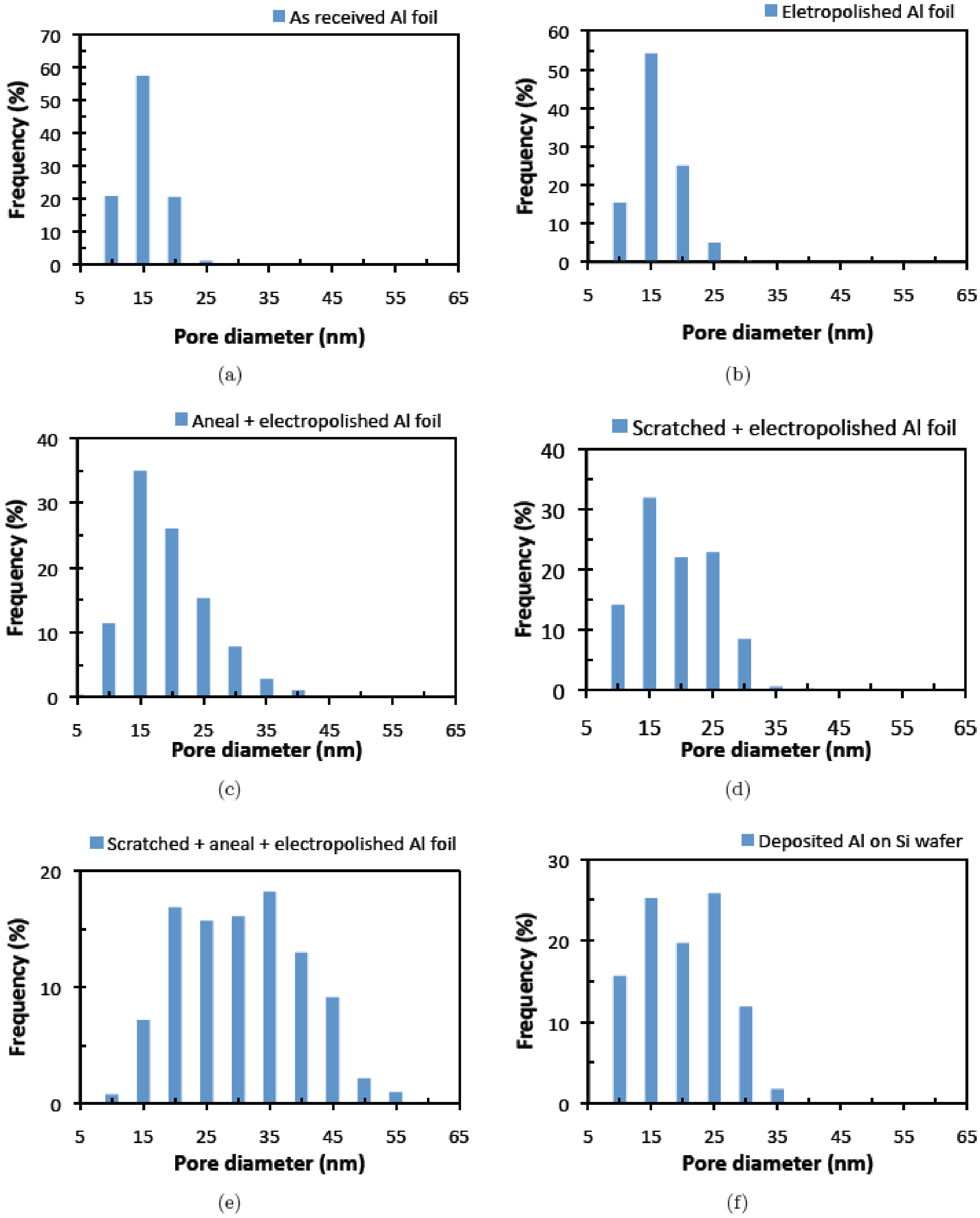
Table 1: Effect of surface preparation on pore size attributes of anodized alumina

Surface preparation	d10 (nm)	d90 (nm)	d50 (nm)	Maximum pore size	Mean Pore size (nm)	Standard deviation (nm)	Mode (nm)	Pore density $(\#/\mu m^2)$
As received Al foil	9±0.7	17±0.7	13±0.7	22	13±0.7	3.1	12.5±2.5	250±16
Electropolished Al foil	9±0.7	18±2.1	14±1.4	27	14±1.4	3.6	12.5±2.5	196±18
Aneal + electropolished Al foil	9±0.7	25±1.4	17±0.7	38	17±0.7	6.3	12.5±2.5	266±34
Scratch + electropolished Al foil	9±1.4	24±0.7	17±0.7	35	17±0.7	5.9	12.5±2.5 22.5±2.5	358±38
Scratch+aneal+ electropolished Al foil	16±0.7	40±1.4	28±1.4	53	28±0.7	9.4	17.5±2.5 32.5±2.5	80±6
Al deposited on Si wafer	9±1.4	26±0.7	17±1.4	34	17±0.7	6.5	12.5±2.5 22.5±2.5	257±29



(a) (b) (c) (d) (e) (f)

Figure 2: Effect of surface preparation on anodized alumina surface structure after anodizing in 3 wt% oxalic acid at 20ºC in V=40V for 100 minutes (a) as-received aluminum foil (b) electropolished aluminum foil (c) annealed + electropolished aluminum foil (d) scratched + electropolished aluminum foil (e) scratched + annealed + electropolished aluminum foil, (f) aluminum sputter-deposited on silicon wafer.

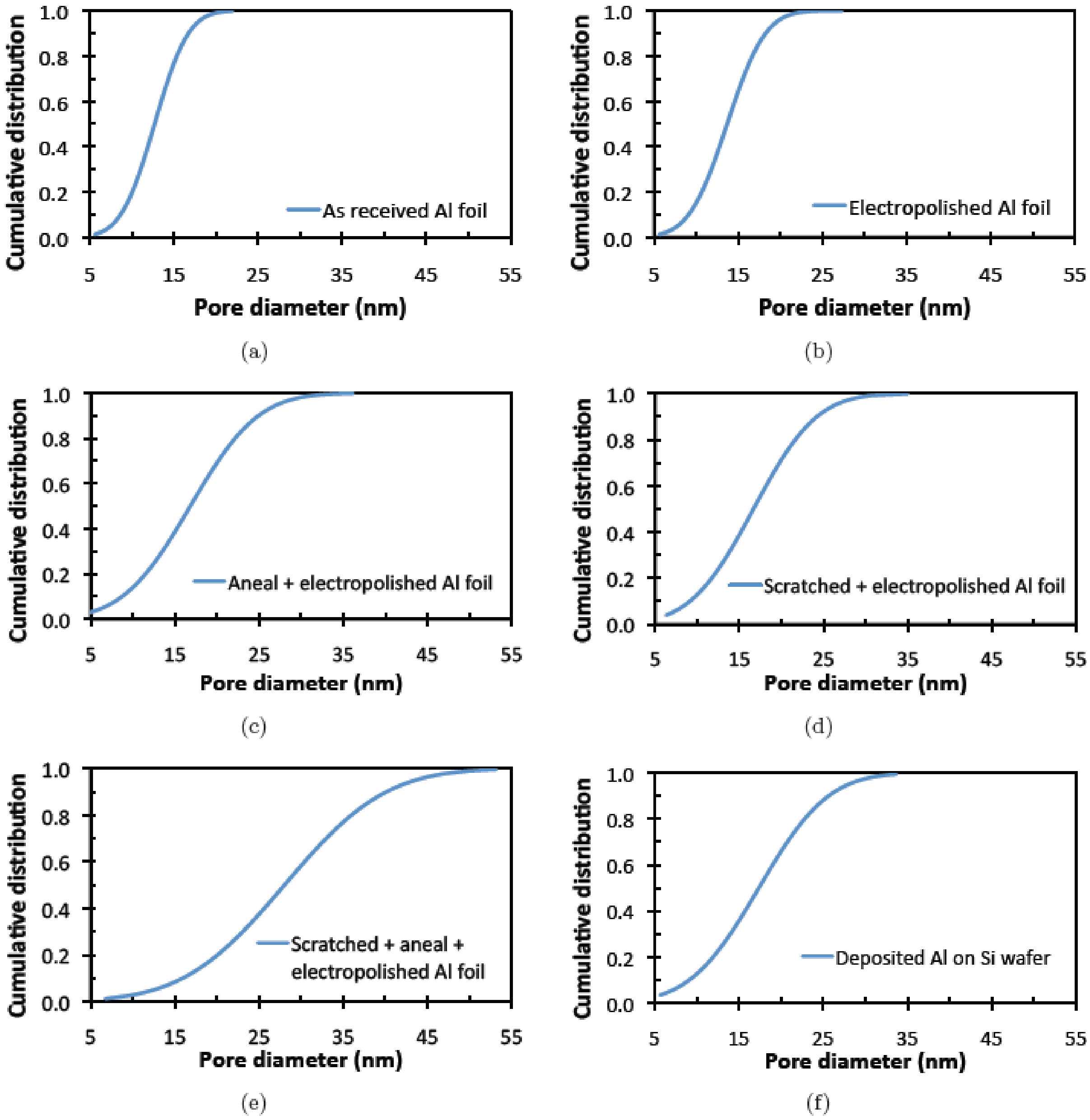


(a) (b)

(c) (d)

(e) (f)

Figure 3: Effect of surface preparation on pore size distribution after anodizing in 3 wt% oxalic acid at 20ºC in V=40V for 100 minutes (a) as-received aluminum foil (b) electropolished aluminum foil (c) annealed + electropolished aluminum foil (d) scratched + electropolished aluminum foil (e) scratched + annealed + electropolished aluminum foil, (f) aluminum sputter-deposited on silicon wafer.



(a) (b) (c) (d) (e) (f)

Figure 4: Effect of surface preparation on cumulative pore size distribution after anodizing in 3 wt% oxalic acid at 20ºC in V=40V for 100 minutes (a) as-received aluminum foil (b) electropolished aluminum foil (c) annealed + electropolished aluminum foil (d) scratched + electropolished aluminum foil (e) scratched + annealed + electropolished aluminum foil, (f) aluminum sputter-deposited on silicon wafer.

5 CONCLUSIONS

To investigate the effect of process parameters on the nanoporous structure of the anodized alumina, it is important to be aware about the surface condition that the anodizing is performed on. Each individual parameter could show different effects when the range of the other variables change. Surface preparation has a major effect on pore size and distribution of the anodized alumina. Stresses existing in Al are considered to be the sources of pore nucleation. These results indicate that detailed studies on the anodizing of sputter deposited Al films are required to understand the effect of process parameters such on the nanoporous structure of anodized films.

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