

Nano-Composite Barrier Anodic Aluminum Oxide for ICD Capacitors

A.C. Geiculescu^{*}, J.L. Stevens^{**}, T.F. Strange^{***}

*St. Jude Medical, CRMD, Capacitor Operation, 6220 Moorefield Memorial Highway,
Liberty, SC, 29657, USA (* cgeiculescu@sjm.com; ** jstevens@sjm.com; *** tstrange@sjm.com)*

ABSTRACT

Anodizing of aluminum in acid solutions has been widely used to produce nano-porous coatings on aluminum for architectural or decorative purposes. This amorphous oxide can be grown electrolytically to thicknesses of many microns with a relatively well organized array of nano-pores extending nearly down to the metal surface. Aluminum oxide for normal electrolytic capacitor applications is produced by different formation processes without the use of prior anodization. However, this nano-crystalline oxide forms in the tensile stress state which can lead to localized ruptures within the dielectric film. Present work shows that by adding a hydrothermal treatment between the anodization and the barrier layer formation step, one can produce a nano-composite barrier layer while maintaining an amorphous oxide layer adjacent to the metal. It is expected that this structure will offer the low stress, high stability of amorphous oxide while maintaining high capacitance typical of nano-crystalline oxide.

Keywords: anodic film; aluminum; capacitors; field emission microscopy; transmission electron microscopy;

1 INTRODUCTION

Barrier aluminum oxide in either amorphous or crystalline state (γ -Al₂O₃) can be prepared by anodic oxidation depending on the growth conditions. Anodizing prior to barrier layer formation is commonly used to produce amorphous high voltage aluminum oxide since anodized oxides have compressive stress rather than the tensile stress found in crystalline oxide. The lower ionic conductivity of crystalline oxide though make it more attractive for the electronic components industry, because it permits the use of a thinner dielectric, with a higher dielectric constant, providing substantially higher capacitance than amorphous oxide [1-3].

One way to make a high capacitance crystalline oxide but taking advantage of the low stress and the high stability properties of the amorphous oxide is to prepare a nano-crystalline composite layer by depositing a hydrous oxide layer on the anodized aluminum substrate before the barrier layer formation. The hydrous oxide is pseudoboehmite (PSB), an oxohydroxide containing excess water with approximate composition AlO(OH)·H₂O [4]. PSB is not a significant barrier to ion or water transport and has a low density, 2.47 g/cm³. Subsequent barrier layer growth however, uses the PSB crystallites as seeds for transformation of the amorphous anodic oxide to γ '-oxide.

The transformations to a more dense oxide unfortunately, result in shrinkage that causes high tensile stress and leaves microscopic voids and/or oxygen trapped within the oxide, which are responsible for the electrical instability of the composite oxide

film. Subsequent stress relaxation occurs by cracking, with cracks extending from the surface to the internal voids and frequently to the base of the metal [5]. Such relaxation is undesirable in electronic devices, as it could result in extremely damaging current surges or other electrical instabilities. A reformation is needed to restore the barrier oxide to its original state. Unfortunately, only a fraction of the internal voids are removed this way. Therefore, oxide dielectrics with enhanced long-term stability are needed.

In the present study, crystalline aluminum hydrous oxide [AlO(OH)] films have been grown on anodized aluminum (Al) substrates by reaction with hot deionized water. Further formation in citric acid to produce a nano-composite oxide is expected to combine the properties of both types of oxides. However, a more detailed knowledge of oxide structure and its growth sequence is required. The surface of all oxide films was characterized by field emission scanning electron microscopy (FE-SEM) and X-ray diffraction (XRD). Furthermore, thin sections were prepared with the help of a focused ion beam (FIB) instrument and they were examined by transmission electron microscopy (TEM). The collected diffraction patterns of the oxide layers were expected to reveal a new insight into the oxide structure and growth process. In addition, ramp-build-time tests of rise time (tV_n) after two-hour boil in DI-water have been conducted for stability studies to assess the tendency for self-relaxation/deformation.

2 EXPERIMENTAL PROCEDURE

2.1. Preparation of Alumina Films

A high purity (99.98 %) aluminum (Al) foil (PF, Pechiney world trade, 114 μ m thick) with high surface area (20:1, obtained by electrochemical etching and chemical widening) and high cubicity texture was used in the present study as substrate for films growth. For this foil ~ 85% of the area was oriented with the (100) plane parallel to the surface and ~15 % in (111) direction.

Hydrous oxide films were grown by hydration in DI-water, at 95 °C for 12 min on 1-1.2 cm² Al strips anodized for 10 min in 10 % H₂SO₄, at 15 °C, using a current density of 0.1 A/cm². The barrier layer film was obtained upon a formation step in a 500-800 μ S/cm citric acid solution at 85 °C. Oven relaxation was at ~ 500 °C for 4 min followed by a 90 sec depolarization in forming solution and reformation. All samples had three heat relaxation/reformation steps after the first formation plus a heat/acid/rinse/reform step for passivation followed by a final anneal at 300 °C. The acid used was a 2 % H₃PO₄ solution at 70 °C.

2.2. Films Characterization

2.2.1 X-Ray Diffraction

The crystallographic structure of the films formed upon hydration at 95 °C for 12 min was determined by XRD. Analyses were carried out on an X'Pert PRO MPD Philips goniometer equipped with a multilayer parabolic mirror (1/2° fixed divergence slit; 0.04rad soller slits; Ni filter) and a receiving 0.009 parallel plate collimator with 0.04 rad soller slits. The incident radiation was obtained from a ceramic tube with copper anode operating at 45 kV and 50 mA. A miniproportional detector was used to collect the diffracted beam. Scans with 3° constant omega were performed on a 2-theta (2θ) range of 5 to 75°.

2.2.2 Scanning Electron Microscopy

The surface of the grown films on Al substrate was observed with a Hitachi FE-4800. An electron beam with 1.5 keV acceleration voltage and 7-10 μA current was used for imaging. Working distance was kept at ~ 1.5 mm while both SE detectors were mixed for better detail. Prior to the FE-SEM analysis, all films were coated with a 2 nm Pt/Pd layer from a 208 HR/MTM20 Crossington Sputter unit.

2.2.3 Transmission Electron Microscopy

Specimens to be examined by TEM were thinned using a Hitachi FB2000A focused ion beam (FIB). A beam of Ga ions radiating parallel to the plane of the sample face was used to cut sections of ~ 50 nm thickness. These thin sections of the oxide films on Al substrate were examined with a Hitachi HD-2300 TEM. A beam with 200 kV acceleration voltage and 20-30 μA current was used for imaging. Electron diffraction patterns were generated using a beam diameter of 200-300 nm at 200 kV and 80-85 nA current.

2.2.4 Stability Testing

Standard crystalline oxides produced by the conventional citric acid forming process along with the composite anodized-hydrated-formed oxides were subjected to a ramp-build-time test in 85 °C citric acid solution using 0.5 mA/cm² current density, after they were boiled for two hour in deionized (DI)-water. The rise times were measured and used to assess the stability of the grown oxides, and in turn the level of defects/voids present that need repairing.

3 RESULTS AND DISCUSSIONS

Two sets of samples were prepared for this study: one set had samples anodized only and the second one had samples anodized and hydrated followed by the formation step. The anodization and hydration processes were expected to help the nucleation of γ'-Al₂O₃ to produce mostly a crystalline film. An additional set followed the standard formation process, with no anodization step, and it was used for comparison in stabilities studies.

Figures 1a and 1b present the surface and cross-sectional FE-SEM views of a porous, anodized film formed on the highly

etched surface of the PF Al foil, after 10 min anodization and with no subsequent hydration or formation. The 0.4 μm layer consists of nano-pores, with 10-20 nm diameter, self-organized into a cellular structure with local areas approximating a hexagonal-close-packed [hcp] array. Cross sectional view shows that the tunnels that were not originally round after widening tend to keep their square corners indicating that anodization proceeds almost entirely into the original metal substrate without affecting the original tunnel opening. This fact reinforces the notion that anodization is a dissolution and partial re-precipitation process and can contribute to tunnel merging just as widening does. Because the pores extend nearly to the metal surface, this film is not usable for dielectric purposes.

Figure 2 shows the effect of anodizing time on the porous oxide thickness and tunnel opening diameter for the PF foil. One can see that the tunnel opening diameter is not significantly affected during anodizing. The porous oxide builds up at an approximately exponential rate into the original tunnel wall. Figure 3 shows a tunnel of the anodized PF foil that has been hydrated at 95 °C, for 12 min, in DI-water and formed in citric acid. A residual hydrous oxide layer that was not completely removed by the H₃PO₄ treatment is still visible inside the tunnels. A corn-flakes structure with fine, lacy edges, having 100 – 150 nm size petals and 20 – 30 nm particle size, as presented in Figure 4, was found to be the signature look for this crystalline hydrate layer that gets converted to crystalline barrier-type γ'-alumina in the formation process by field-assisted dehydration. The hydrate was identified by XRD (Figure 5) as being pseudoboehmite (PSB). Figure 6 shows a cross-section of a broken tunnel in a typical crystalline oxide foil. Note the highly textured appearance of the crystalline barrier layer and the platelet-structured residual hydrate on the tunnel interior.

Figure 7 shows a TEM micrograph of a fully converted nano-composite oxide detailing a multi-layer structure with amorphous material next to the metal for stress-relief while the upper converted layers have been formed into nano-crystalline barrier oxide. This is the image of a tunnel cross-section. This oxide was produced by anodizing to fabricate a porous layer thicker than needed for incorporation into the barrier oxide. After anodizing, it was hydrated and formed in a citric acid solution without any heat or phosphoric acid treatments that might disturb the structure of the freshly formed nano-composite oxide layers.

Formed foil was FIB micro-sampled and thinned to produce extremely thin sections needed in the HD-2300 TEM. These cross-sections have been labeled with numbers 1 through 6 to identify the different layers of materials seen. The diffraction patterns of these layers are presented in Figure 8. Layer 1 shows the delicate residual hydrate left on the inner surface of the tunnel adjacent to the electrolyte. Although it cannot be seen, the hydrate is believed to be present inside the pores of the amorphous anodized oxide seen in Layer 2. Layers 3 and 4 show the typical granularity of the crystalline barrier layer oxide. The diffraction spots of crystalline Al oxide are very clear. Layer 3 appeared to be slightly more disordered but still quite crystalline. Layer 5 has the smooth, featureless appearance of amorphous barrier layer oxide (diffuse rings), while Layer 6 shows a very clean, crystalline pattern that belongs to the high cubicity Al substrate.

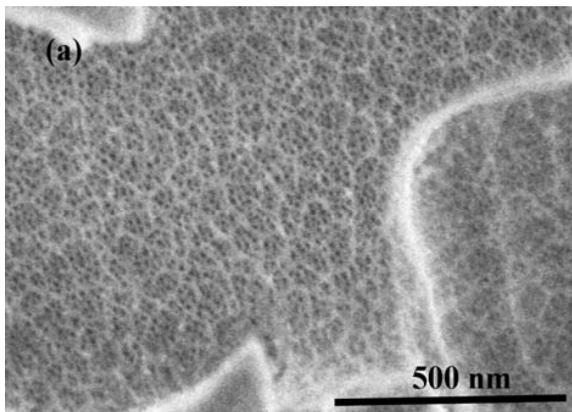


Figure 1. FE-SEM micrograph of anodized PF foil (a) surface view; (b) cross-section view.

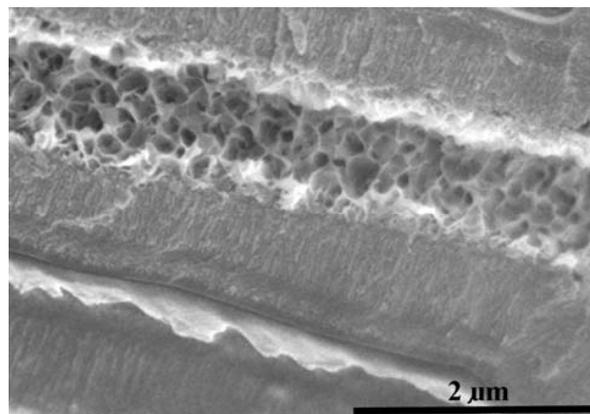


Figure 3. Cross-sectional FE-SEM micrograph of a tunnel showing a layered nano-composite oxide structure including the residual PSB film.

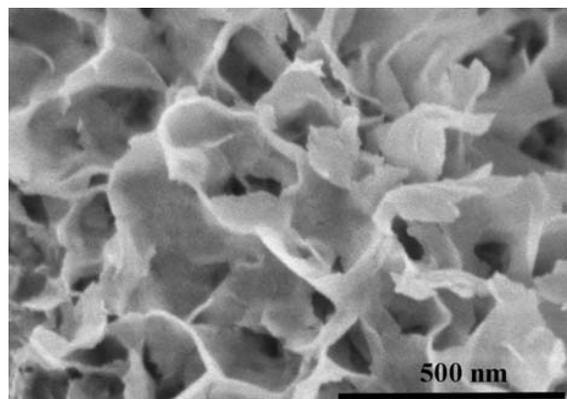
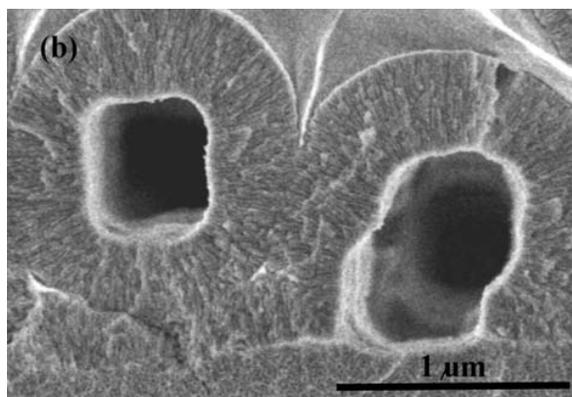


Figure 4. FE-SEM micrograph of the hydrous oxide film, obtained by hydration at 95 °C for 12 min.

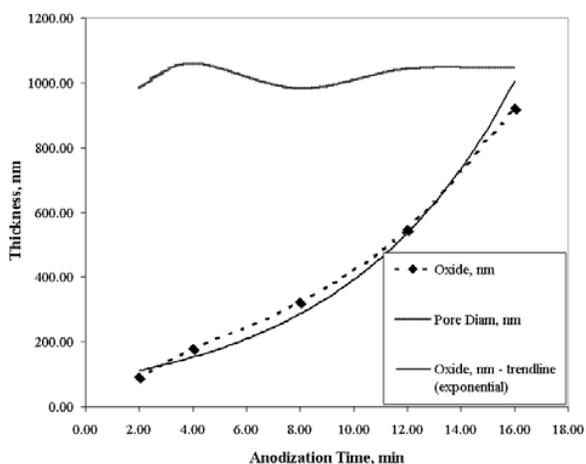


Figure 2. Effect of anodization time on oxide thickness and tunnel pore diameter.

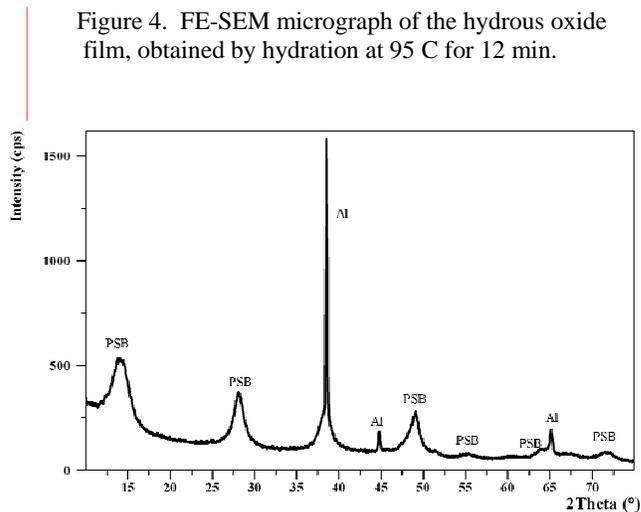


Figure 5. XRD pattern of the hydrous oxide film prepared by hydration at 95 °C for 12 min.

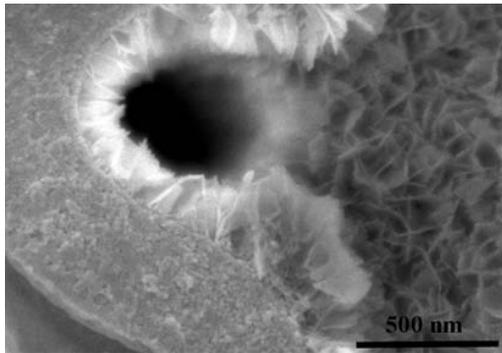


Figure 6. FE-SEM micrograph of a broken tunnel.

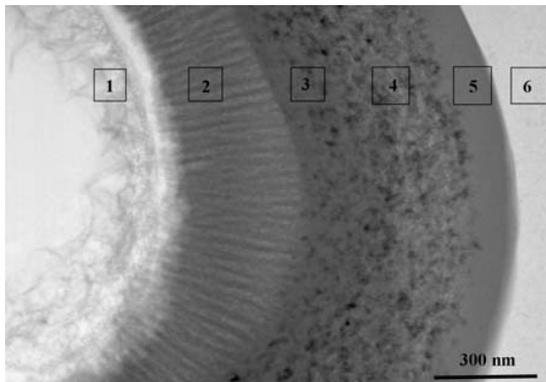


Figure 7. TEM cross-section of an anodized, hydrated and barrier oxide formed tunnel [Sample imaged by Hitachi High Technologies America (HTA), Inc.].

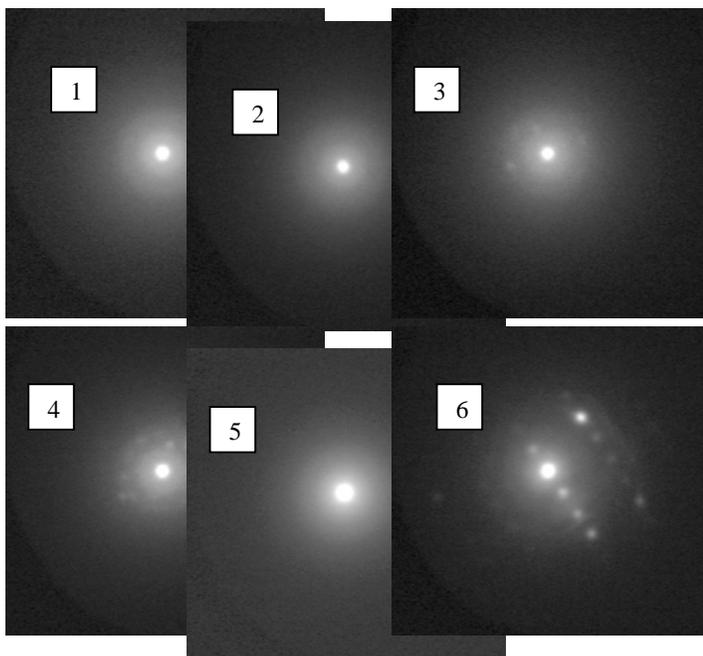


Figure 8. TEM diffraction patterns of the nano-composite multilayer found in an anodized, hydrated and barrier oxide formed Al tunnel [Sample imaged by Hitachi-HTA].

A comparison between standard oxide and the nano-composite oxide is shown in Table 1. It can be noted that the standard crystalline (X) oxide dielectric ratio value is at the low end of the generally accepted 0.9 to 1.1 nm/V. The presence of the amorphous (Am) under layer did not have a positive effect either, as it lowered the field strength by about 7 % (higher dielectric ratio). However, despite the lower capacitance of the nano-composite oxide, the lower residual stress as shown by the excellent rise times after two-hour boil in the boiling water test is indicative of much higher oxide stability.

Table 1. A comparison between an Al oxide prepared by a standard formation process and a nano-composite process.

	<u>Standard Form</u>		<u>An/Hy/Form</u>	
	Hydrate	X	Am	X
Thickness Avg, nm	177	454	135	346
St. Dev.	11	21	19	30

Dielectric ratio, nm/V	0.89		0.96	
tV _n (Rise Time), sec	15 – 3		1 - 3	

An = anodization; Hy = hydration; Form = formation

4 CONCLUSIONS

The novel combination of an anodizing step with a hydrothermal step prior to formation, provided an improved process for the production of high-stability crystalline anodic aluminum oxide for electrolytic capacitors. The hydration step was used to convert the nano-porous amorphous oxide obtained by anodization to a crystalline precursor material for later formation of the barrier oxide layer. A highly crystalline oxide layer was formed in this study, with stability similar to amorphous oxide and capacitance within 85 to 95 % of that of standard crystalline oxide, versus the 60 % level seen for conventional amorphous oxide. The degree of crystallinity and the very high resistance to the boiling water ramp-build-test were distinguishing features of the formation process used. Despite the fact that the conditions for the lowest two hour boil rise time (tV_n) coincided with the lower capacitance values, a considerable window for highly stable oxide exists for PF foil. The need for parameters optimization dictates possible further work in this area.

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