Radio Frequency Glow Discharge Optical Emission Spectroscopy

Depth Profiling Analysis of Thin Anodic Alumina Films as Potential Reference Materials


As in any form of chemical analysis, the quality of information obtained from a depth profiling experiment is only as good as the reference materials that are used to calibrate the instrument. In the case of depth profiling, calibration must take place in terms of chemical composition as well as distribution with respect to the specimen surface.

The nature of applications requiring such analyses is such that it is difficult to justify, much less prepare, large suites of reference materials. The ability to work from a single material motif, which would afford great flexibility but also provide high selectivity and control, would be very useful for a large number of surface and thin films analysis laboratories.

Anodic oxidation of electropolished, high-purity aluminum sheets in the so-called “barrier film forming electrolytes” such as neutral borate, phosphate, tartrate, and citrate solutions, leads to the growth of thin alumina films with thicknesses less than 1 μm (1). These films are amorphous and highly uniform in thickness, with flat and sharply defined metal/oxide interfaces.

Furthermore, films having fine distributions of impurities (termed "delta function marker layers") can be prepared routinely by anodic oxidation of electropolished aluminum specimens in appropriate electrolytes. In the present context, a "delta function layer" refers to a very thin band of material relative to the whole film, where the species of interest has no distribution beyond the well-defined, narrow dopant layer. (In mathematics, this is a function changing from zero to infinity and back to zero with no breadth. In terms of dopants, a single atomic layer is the closest approximation.) Of specific importance here is the fact that the distributions of impurities in the films can be revealed directly and independently by transmission electron microscopy (TEM) of ultramicrotomed sections.

As a preliminary evaluation of the use of such films as standards for assessment of the potential of various sputter-depth profiling techniques, selected films were analyzed by radio frequency glow discharge optical emission spectroscopy (rf-GD-OES) depth profiling (2). The rf-GD-OES method provides rapid (>1 μm/min), uniform sputtering of insulating layers such as the barrier-type films (BTF), with depth resolution capabilities approaching those of secondary ion mass spectrometry (SIMS) (3). The authors believe that the data presented here illustrate the potential of both the electrochemical means of producing high-quality film standards and the use of rf-GD-OES in the domain of surface science.

Experimental

In the present work, 99.99% pure aluminum sheets of 0.2-mm thickness, 300-mm width, and 500-mm length were used as the standard starting materials. The impurity levels for Cu (30 ppm), Fe (20 ppm), and Si (20 ppm) (likely determined by inductively cou-
pled plasma–OES) were provided by the manufacturer. The sheets were cut into 15-mm wide and 50-mm long strips and degreased in acetone. Subsequently, half of each individual specimen, 15 mm × 25 mm, was shielded by formation of a 400-nm-thick oxide film in a dilute ammonium pentaborate ([NH₄]₂B₁₀O₁₆) solution in a manner described elsewhere (4). Such preliminary shielding is essential to secure uniform polishing of a precise area without the anodic current concentrating at the water line during electropolishing.

After partial shielding, the specimens were electropolished individually at a constant current density of 150 mA/cm² in a solution consisting of 20 vol% of concentrated (60%) perchloric acid and 80 vol% of absolute ethanol at temperatures below 10 °C for 4 min. The polishing solution was stirred gently with a glass rod throughout electropolishing. The resultant specimens, of mirror-like appearance, were rinsed thoroughly with absolute ethanol and finally dried in a warm air stream. The electropolished aluminum specimens were then anodized under various conditions, as described later.

Ultramicrotomed sections (≈10 nm thick) of the aluminum substrate and barrier film were prepared by mounting in an epoxy resin and trimming the specimen with a diamond knife, as described in detail by Woods and co-workers (5) and examined by TEM on a TECNAI (FEI, Hillsboro, OR) F20 field-emission, high resolution instrument operated at 200 kV. The anodized substrates were depth profiled using a Jobin Yvon/HR victims (Edison, NJ) RF 5000 rf-GD-OES instrument at an argon pressure of 0.41 mbar by applying a 13.56 MHz rf potential at a power of 40 W, where the highest depth resolution is achieved. The area of analysis was 4 mm in diameter, so the lateral resolution of the technique is quite limited compared with methods such as SIMS or the electron spectroscopies. The RF 5000 instrument uses a Paschen-Runge polychromator arrangement, in which each of the photomultiplier tubes is sampled in parallel at a rate as high as 2 kHz. In the experiments described here, the sampling time was 0.01 s at the analytical transitions of Al(I) (396.15 nm), Cr(I) (425.43 nm), H(I) (121.57 nm), Cu(I) (324.75 nm), V(I) (437.92 nm), Si(I) (288.15 nm), P(I) (177.50 nm), and Fe(I) (385.99 nm).

Previous rf-GD-OES studies, using a more sensitive monochromator system, produced detection limits for many transition metals in aluminum matrices that were much less than 20 ppb (6). It is expected that the limits of detection for these elements in the base aluminum alloys used here should be in the area of ≈0.05 ppm. Detection limits for nonmetal elements have not been studied in detail; with the exception of a value of ≈1 ppm determined for nitrogen in steel matrices (7). Experience suggests that the sensitivity for hydrogen is more than an order of magnitude better than for nitrogen. Therefore, given the higher sputtering rates of aluminum alloys versus steel samples, it is reasonable to expect that the detection limits for H in these alloys should be much lower than 0.1 ppm.

Results and Discussion

General features of anodic alumina films. The ability to form and verify very precise, well-structured films is the first target for the generation of thin-film reference materials. Figure 1a is a transmission electron micrograph of an ultramicrotomed section of the aluminum substrate and its anodic film formed in 0.1 M (NH₄)₂B₁₀O₁₆ solution at 20 °C at a constant current density of 5 mA/cm² up to a potential of 200 V; (b) high-resolution transmission electron micrograph of the oxide/metal interface of (a).

Figure 1. (a) Transmission electron micrograph of an ultramicrotomed section of the aluminum substrate and its anodic film formed in 0.1M (NH₄)₂B₁₀O₁₆ solution at 20 °C at a constant current density of 5 mA/cm² up to a potential of 200 V; (b) high-resolution transmission electron micrograph of the oxide/metal interface of (a).
Thin barrier oxide films were formed in the presence of sodium chromate (Na₂CrO₄) and ammonium metavanadate (NH₄VO₃) to generate fine impurity regions containing chromium and vanadium. In these solutions, barrier oxide films form simultaneously both at the oxide/electrolyte and metal/oxide interfaces by the outward migration of Al³⁺ ions and inward migration of O²⁻ ions, respectively (9–11). At the oxide/electrolyte interface, low levels of chromium or vanadium species are incorporated into the growing oxide from the electrolyte. As a result, fine bands of a few nanometers thickness of chromium or vanadium enrichment are formed at precise depths from the surface in the barrier oxide films. Importantly, such narrow bands of chromium or vanadium enrichment are revealed clearly and directly by transmission electron microscopy of ultramicrotomed sections.

A transmission electron micrograph of an ultramicrotomed section of the aluminum substrate and a barrier oxide film formed in a 0.1 M Na₂CrO₄ solution at 20 °C at a constant current density of 5 mA/cm² up to a potential of 120 V; (b) rf-GD-OES depth profile of (a) at a pressure of 0.41 mbar Ar and an rf power of 40 W.

A dark band of material. The film is amorphous and appears featureless in the TEM micrograph. The film is highly uniform in thickness, about 236 nm, giving a film growth ratio of 1.18 nm/V, in agreement with that obtained from the kinetic equation given by Harkness and Young (8). This is a direct and very important consequence of the oxide growth kinetics, which are represented by

\[ i = A \exp(BV/d) \]  

where \( i \) is the ionic current density, \( V \) is the potential across the oxide film of thickness \( d \), and \( A \) and \( B \) are experimental constants (8).

Figure 1b shows a high-resolution transmission electron micrograph of the oxide/metal interface. It is evident that the interface is atomically flat. Crossed lattice fringes of spacing 0.236 nm, corresponding to <111> planes, are observed clearly in the aluminum substrate. The area shown in Figure 1 is limited over a distance of less than 1 μm. It is important to note, however, such uniformity in the film thickness and flatness of the metal/oxide interface prevails all over the surface.

**Cross-sectional TEM and GD-OES depth profiling of barrier oxide films.** Thin barrier oxide films were formed in the presence of sodium chromate (Na₂CrO₄) and ammonium metavanadate (NH₄VO₃) to generate fine impurity regions containing chromium and vanadium. In these solutions, barrier oxide films form simultaneously both at the oxide/electrolyte and metal/oxide interfaces by the outward migration of Al³⁺ ions and inward migration of O²⁻ ions, respectively (9–11). At the oxide/electrolyte interface, low levels of chromium or vanadium species are incorporated into the growing oxide from the electrolyte. As a result, fine bands of a few nanometers thickness of chromium or vanadium enrichment are formed at precise depths from the surface in the barrier oxide films. Importantly, such narrow bands of chromium or vanadium enrichment are revealed clearly and directly by transmission electron microscopy of ultramicrotomed sections.

A transmission electron micrograph of an ultramicrotomed section of the aluminum substrate and a barrier oxide film formed in a 0.1 M Na₂CrO₄ solution at 20 °C at a constant current density of 5 mA/cm² up to a potential of 120 V; (b) rf-GD-OES depth profile of (a) at a pressure of 0.41 mbar Ar and an rf power of 40 W.

An rf-GD-OES depth profile of the film is presented in Figure 2b. The signal intensity of aluminum is fairly stable and constant throughout the analysis of the film. The subtle periodic variation observed in the signal intensity of Al(I) is not due to variations in aluminum concentration in the film, but arises from an optical interference effect as photons emitted in the plasma pass through the oxide film and reflect off of the metal/oxide interface. This sort of interference effect is observed more clearly with thicker films (see Figure 1 in reference 11) and can be used to monitor oxide film thicknesses in real time (14, 15). As the sputtering proceeds, the signal intensity of aluminum exhibits a very sharp increase at the oxide/metal interface, which is followed by a gradual increase until a steady state value is reached. This slight rounding-off is due to the sputter-induced curvature at the crater edges/walls relative to the overall depth in the center. The width of the transition at the oxide/metal interface, which is a measure of depth resolution, is determined from the onset of the steep, linearly rising portion of the Al(I) profile to the point where the signal intensity starts to deviate from the straight line. The width of transition determined in this manner is ~3 nm at a depth of 140 nm from the surface.

Turning to the Cr(I) profile, the band of chromium enrichment is revealed clearly as a narrow peak, of full width at half maximum (fwhm) of about 5 nm, along with a distribution of chromium species in the uppermost layer. The peak associated with the band is located at a depth of 19 nm from the surface, in agreement with the TEM image presented in Figure 2a. Furthermore, the distributions of hydrogen and copper are revealed clearly. Hydrogen is present throughout the film, with concentrations greater at the near-surface regions due, perhaps, to hydration of the outermost portions of the film. A hydrogen content as low as 35 ppm has been reported recently by Morisaki et al. (16) for a barrier film formed in a borate solution using tritium-labeled water and
Liquid scintillation counting. Excellent sensitivity for the detection of hydrogen is evident here for the rf-GD-OES technique. The signal intensity of copper remains at a background level, indicating that the copper content in the oxide film is below the detection limit.

However, enrichment of copper is evident in the metal substrate immediately beneath the interface. A similar enrichment is also observed with hydrogen that has an assayed value (likely determined by gas extraction) in the metal of ~0.1 ppm. The enrichment is usually confined to a thin layer, only a few nanometers thick, and arises from the preferential oxidation of aluminum during electropolishing and anodizing (17). Interestingly, however, enrichments of Fe and Si are not observed, even though the sensitivities for detection of these elements are similar to that of Cu. This difference is associated with the ways that these impurities are dispersed in the aluminum matrix. While the Cu impurities are present mostly in solid solution, the Si and Fe impurities, with their very limited solubilities in the aluminum matrix, are present locally at grain or cellular boundaries. Through the use of magnetron sputter-deposited metastable 1.4 at%Fe-Al alloy, where iron is present in solid solution, it has been shown recently that an enrichment of iron similar to that of copper takes place during anodic oxide growth due to preferential oxidation of aluminum (18).

Figure 3a shows a transmission electron micrograph of an ultramicrotomed section of a barrier film formed in an ammonium metavanadate solution at 20 °C at a constant current density of 5 mA/cm² to 200 V. Over the flat aluminum substrate, an ~236 nm thick oxide film is observed. A narrow dark band at a depth of 16 nm from the surface (indicated by the white arrow) represents a region of vanadium enrichment that separates an inner pure alumina layer and an outer layer doped with vanadium species. These features are basically similar to those observed with the film formed in the Na₂CrO₄ solution, though differences are evident.
For example, the width of the band is only about 2 nm, which is narrower than that of the layer formed in the chromate solution. Interestingly, fine voids are observed above the band of vanadium enrichment, identified by the lighter contrast as shown by the black arrow. The mechanism of void formation and its association with the band of vanadium enrichment will be discussed in detail elsewhere (19).

The rf-GD-OES depth profile obtained from the film formed in the metavanadate solution is shown in Figure 3b. Apart from the near-surface regions where vanadium species are present, the signal intensity of aluminum is constant through the analysis of the film, with the periodic variation in the Al(I) response being due to the optical interference effect. The signal intensity for the aluminum exhibits a very sharp increase at the metal/oxide interface. The width of transition, as determined in the manner described above, is only 5 nm. A further expansion of the time axis is presented in Figure 3c. The narrow band of vanadium enrichment, observed in the TEM micrograph, is revealed clearly at a depth of 16 nm from the surface, displaying a narrow peak with an fwhm of ~4 nm (Figure 3b). The presence of the fine voids above the band of vanadium enrichment is also disclosed clearly in the Al(I) response as, at the depths where fine voids are observed in Figure 3a, the signal intensity of aluminum exhibits a minimum. Further, at the depth where the band of vanadium enrichment is present, the signal intensity of aluminum exhibits a narrow plateau region where the signal intensity of aluminum is about 70% of that in the "pure" alumina region beneath. From the comparison of the physical picture provided by the TEM and the composition profile in the optical signals, it is evident that the rf-GD-OES is able to generate a depth profile that agrees precisely with the compositional and structural features of the film.

Preparation of an anodic alumina film with delta function marker layers. Through anodic oxidation of aluminum, thin alumina layers with delta function marker layers can also be prepared readily, cheaply, and routinely. A typical example of a barrier oxide film with a delta function marker layer is shown in Figure 4. Over the flat aluminum substrate, an ~59-nm-thick barrier oxide film of high uniformity is observed. A dark, narrow band having a width of about 2 nm runs parallel to the flat metal/oxide interface and represents a region of chromium enrichment. In contrast to the film formed in sodium chromate solution depicted in Figure 2a, the oxide film above the band here contains no chromium species. The present film was formed by anodizing the electropolished specimen in a 0.1 M ammonium pentaborate solution at 20 °C at a constant current density of 5 mA/cm² up to a potential of 200 V. The specimen was then dipped in a solution consisting of 20 g/L CrO₃ and 35 mL/L H₃PO₄ at 90 °C for 10 min. The anodic alumina dissolves in the hot chromic acid–phosphoric acid solution, without any attack to the substrate metal, yielding very flat aluminum substrate, as shown in Figure 4. Importantly, the aluminum surface generated in this manner is covered with a thin, hydrated alumina film, about 3.5 nm thick, doped with Cr₂O₃ and PO₄³⁻ (18, 19). After the chromic acid–phosphoric acid treatment, the specimen was rinsed thoroughly with distilled water, dried in a warm air stream, and finally anodized to 50 V in a 0.1 M ammonium pentaborate solution at 20 °C and at a constant current density of 5 mA/cm².

Figure 5 shows the resulting rf-GD-OES depth profile of the film. The band of chromium enrichment has been revealed clearly at a depth of 6.6 nm from the surface as a narrow peak with an fwhm of about 4 nm. Also seen are the distributions of hydrogen, boron, phosphorus, and copper. Chromium and phosphorus, present in the film covering the initial surface, are now observed separately — the reason for which has already been described in detail elsewhere (3). Briefly, during anodic oxidation, Cr₂O₃ and PO₄³⁻ ions in the film covering the initial surface are incorporated into the anodic film that grows simultaneously at the oxide/electrolyte and metal/oxide interfaces through outward migration of Al³⁺ ions and inward migration of O²⁻ ions, respectively. Due to the relative charge mobility, the PO₄³⁻ ions migrate inward at a rate of 0.51 relative to that of the O²⁻ ions. Conversely, Cr³⁺ ions formed by the
Concerning the delta function marker layer shown in Figure 4, it is important to note that the depth of this marker layer can be varied readily by controlling the thickness of the primary barrier film which is related to the forming voltage during anodic oxidation. Very simply, the ratio of the depth of the band to the total thickness of the barrier oxide film is a constant of 0.11. In reference to this, an example is shown in Figure 6, which is similar to that of Figure 5, except that the film is formed with an increased thickness of 358 nm. Only chromium and phosphorus profiles are presented here for simplicity. The location of the metal/oxide interface, determined from the aluminum profile, is also indicated. In this film, therefore, the chromium marker layer is expected to be located at an increased depth of 39 nm from the surface. The marker layer has been revealed clearly as a narrow peak with an fwhm of only 5 nm, and located at a depth of ~40 nm. The small peak observed in the trailing edge of the chromium profile is due to the presence of “nano-sized” \( \text{Cr}_2\text{O}_3 \) particles that are plugging flaws (voids) in the initial hydrated oxide film (21), and is observed consistently in all films formed in this manner.

Cross-sectional transmission electron microscopy of sputtered craters. Beyond the ability to form thin, uniform films with sharply defined and controlled distributions of impurities for possible application as reference materials, the use of anodic alumina has another important advantage in sputter depth profiling analysis. A key feature is the fact that, through ultramicrotomy, thin (~10 nm) cross-sectional specimens can be prepared readily. This offers the unique opportunity to examine features such as microscopic roughening, atomic mixing, implantation of primary ions, and so forth, associated with the sputtering process at atomic resolution using modern analytical transmission electron microscopy.

Figure 7 is a TEM micrograph of an ultramicrotomed section of an aluminum substrate and its barrier film, sampled from the central region of the

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RF-GD-OES

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Figure 5 (above, top). RF-GD-OES depth profile of the delta function marker layer structure shown in Figure 4.

Figure 6 (above, bottom). RF-GD-OES depth profile of a delta function marker layer as in Figure 4, though with an oxide thickness of 358 nm. The oxide/metal interface is identified by the vertical line.

high-field assisted dissociation of \( \text{Cr}_2\text{O}_3 \), migrate outward at a rate of 0.74 relative to that of \( \text{Al}^{3+} \) ions, yielding spatially segregated distributions observed in the profile. Again, the aluminum profile exhibits a sharp increase at the metal/oxide interface, where the width of transition is only about 2 nm.
RF-GD-OES

sputtered crater produced in a partial depth profiling analysis by rf-GD-OES. The electropolished specimen was anodized to a potential 300 V at a constant current density of 5 mA/cm² in a 0.1 M ammonium pentaborate solution at 20 °C, resulting in the formation of a 358-nm-thick film. The specimen was then partially depth-profiled to a depth of about 320 nm from the surface at an Ar pressure of 0.41 mbar and an rf power of 40 W. Over the flat aluminum substrate, a residual barrier film of a uniform thickness of 39 nm is observed. (Residue of the TEM embedding epoxy resin is also observed at the film surface.)

It is evident that the exposed surface is very flat, even at the subnanometer level, indicating very smooth sputtering with no significant microroughening in the crater center during rf-GD-OES analysis. Note that there is some curvature at the crater edges as noted in the discussion of Figure 4, but this is relatively far removed from the crater center. Furthermore, the residual film appears largely intact, though a fine bubble-like texture is observed at a depth of ~3 nm from the surface. The micrograph here was taken under slightly under-focused conditions to reveal the texture clearly with minimal damage. Interestingly, the bubble-like texture was not evident initially, but developed relatively rapidly (~10 s), on examination of the film section at an appropriate high magnification in transmission electron microscope. In the near-surface region of the film, the presence of implanted Ar atoms is expected. Therefore, it is most likely that the development of fine, bubble-like texture is due to radiation-induced (via the electron beam heating of the thin specimen) agglomeration of implanted Ar atoms and subsequent formation of fine Ar bubbles, a few nanometers in size. In rf-GD-OES analysis, films are sputtered with Ar⁺ ions of very low (~50 eV) energy. Therefore, it is somewhat surprising that argon ions are implanted to a depth of about 3 nm in such a low-energy sputtering situation. Clearly, the alumina coating will have some porosity that affects the penetration depth of ions and neutrals, such as the argon discharge gas. This is a topic that will be looked at in greater detail in the future, again illustrating the opportunities afforded by the complementary use of the BTF materials, transmission electron microscopy, and rf-GD-OES.

Conclusions

Anodic oxidation of electropolished, high-purity aluminum specimens in appropriate electrolytes provides a readily implemented, cheap, and routine method for the production of thin (~1 mm) anodic films having very fine distributions of impurities or with delta function marker layers. The films are amorphous in structure and extremely uniform in thickness, with atomically flat oxide/metal interfaces as confirmed by cross-sectional transmission electron microscopy. The thickness of the produced oxide films is controlled easily and precisely by the forming voltage. The fine distributions of impurity species or delta function marker layers are revealed directly by cross-sectional TEM with structural details, such as the presence of voids, clearly identified. In view of these unique features, anodic alumina films may be used as standards for the assessment of analytical potential and performance of sputter depth profiling techniques. The use of the anodic alumina film system also offers unique opportunities to examine various phenomena associated with film sputtering, because cross-sectional specimens, 10 nm thick, can be prepared readily through ultramicrotomy. Use of modern analytical transmission electron microscopy in combination with energy-dispersive x-ray spectroscopy and electron energy loss spectroscopy will allow the compositional, structural, and geometrical details of the near-surface regions of the sputter craters to be examined at atomic-scale resolution.

The generation of these finely structured films has also allowed the further demonstration of the rf-GD-OES technique as a valuable part of the surface and thin film analysis arsenal. Although not stressed in the context of the use of the films as standards, the rf-GD-OES experiments are very rapid (typically less than 1 min for the examples here). In addition, the method has benefits...
such as lower capital costs and lower levels of operator skill than required for methods such as SIMS and Auger spectroscopy. As illustrated in the profiles of hydrogen content in the films, the elemental coverage and sensitivity are very important features, as well. In general, rf-GD-OES should experience a great deal of growth in the areas of electronic materials characterization and corrosion science, as these applications present the further challenges of insulating surfaces that are difficult by other charged particle methods.

Finally, the films given as examples in the present work are available on request to coauthor K. Shimizu by e-mail at shimizuk@econ.keio.ac.jp.

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