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KAPL-3164

UC-25, Metals, Ceramics
and Materials
(TID-4500, 47th Edition)

FABRICATION OF ALUMINUM OXIDE FILMS

A. B. Hance, L. R. Hanrahan

July 27, 1966

Issue Date September 23, 1966

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ABSTRACT

This report describes a simple, low-cost procedure for the forming of Al_2O_3 films from common household aluminum foil. A method for accurately controlling the film thickness is described for self-supporting films of Al_2O_3 ranging from several hundred to 1000 Å thick. The method can be used for anodizing a smooth aluminum surface to form an Al_2O_3 surface layer of uniform thickness ranging from ~100 Å to 1000 Å.

FABRICATION OF ALUMINUM OXIDE FILMS

A. B. Hance, L. R. Hanrahan

INTRODUCTION

This report describes a process for the preparation and application of aluminum oxide films of thicknesses in the 100 to 1000 Å range. In the research and development program at the Knolls Atomic Power Laboratory we found a need for thin aluminum oxide films for use in two different experiments—first, a suitable backing layer for a low-density potassium chloride transmission dynode (Goetze);^{1,2} and second, a thin film for the target surface of an electron multiplier used for detecting energetic positive ions.

The following film requirements had to be satisfied in order to support the low-density potassium chloride layer of the transmission dynode. The thicker films of 500 Å or more had to be strong, easily formed, non-organic, of known uniform thickness, and capable of being stretched and mounted on a thin, flat stainless steel frame. In deciding on a suitable material, aluminum oxide, nickel, and VVNS (polyvinyl acetate copolymer) were considered. Aluminum oxide fulfilled all the requirements.

SAMPLE PREPARATION

In the preparation of dense, polycrystalline aluminum oxide films, as shown by Harris,³ ordinary light-duty household aluminum foil (0.7 mils thick) is used. The aluminum is first anodized on both sides, using an ammonium citrate solution (3 wt %). The apparatus used is shown in Figure 1. The initial current through the electrolyte decreases exponentially with time to ~6 mA. At this time the maximum attainable film thickness has been achieved, and the process is terminated. The anodized film is then rinsed with reagent-grade acetone and distilled water. To facilitate handling, the anodized aluminum is placed between two 3-in. square glass plates, each containing a 2-in.-diam hole. The plates are held together with a pair of clamps. The next step is removal of the aluminum oxide from one side of the anodized surface. Sodium hydroxide (8M) is painted on the dull side and allowed to stand for 8 to 10 min (for 750 Å films, an exposure time of 8 min is used). The film is then rinsed in water to remove any sodium hydroxide residue. The aluminum metal is removed from the anodized face by applying HCl (4M) with a soft brush at the perimeter of the film area. The HCl flows across the face of the film, which is held in a near-vertical position. Next, the film is rinsed with distilled water, using the same application technique that was used for the acid.

Examinations under a microscope show small particles of aluminum that adhere to the film and are difficult to remove. This also has been observed by others.³ The particles are very sparsely deposited and prove to be of little importance in the application discussed here.

The glass plates clamping the aluminum which surrounds the oxide foil are placed in a manipulator (Figure 2). The manipulator contains a vacuum tweezer (Ultrasonic Laboratories, Inc. - Model VG-100) and suction cup assembly which securely affixes it to a stainless steel holding frame for contact with the foil. The construction of the manipulator gives three degrees of freedom and permits one to position the holder frame flat on the oxide surface. The inexpensive throwaway frame consists of two identical flat pieces of 0.010-in.-thick stainless steel between which the film is mounted. The highly polished stainless steel is "wetted" with reagent-grade methyl alcohol before contact is made with the film. The alcohol provides lubrication between the film and frame. After the film is dry, the edge may be trimmed. It was found that a highly polished surface on the holder provided a better surface adhesive bond between film and frame than did a rough surface.

A 300-Å layer of pure aluminum is vacuum-deposited on the side of the film which is not in contact with the stainless steel frame. The aluminum is deposited, assuming inverse square law evaporation from a point source. After the foil is aluminized, the second half of the stainless steel holder is spot-welded to the surface that contains the $\text{Al}_2\text{O}_3 + \text{Al}$ films. Thus, the sandwiched films are protected on either side.

Within practical limits, films of any desired thickness can be made by using different anodizing potentials. A value of 13.7 A/volt is used

TWO BEAKERS ARE USED TO PREVENT ELECTRODES FROM SHORTING DURING ANODIZATION

FIGURE 1. Anodizing System.
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FIGURE 2. Film-Frame Manipulator.
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to determine the voltage for the proper thickness.³ A calibrated area of a sample of the several films is weighed on an ultramicrobalance ("Rodder, Model E"). Films used for the transmission dynode were 750 Å thick. Using 3.42 gm/cc for the density of aluminum oxide, a 750 Å film should weigh 26 $\mu\text{g}/\text{cm}^2$. Weights calculated from known cell voltages for several samples agreed closely with actual weighings of the films on the ultramicrobalance. Weighings were also made on several foils coated with aluminum to confirm the thickness of the metal layer.

The procedure for coating the self-supporting backing layer of aluminum oxide plus aluminum is as follows: The stainless steel frame containing the two foils is placed in a special vacuum chamber (Figure 3). By use of Goetze's technique,^{1,2} an ~1-mil-thick layer of KCl (between 2 and 5% of normal density) may be coated onto the aluminized foil. A complete transmission dynode cross section is shown in Figure 4. The low-density KCl layer is vapor-deposited in a dry argon atmosphere at a system pressure of 2 torr. Since excess moisture in a crystalline sample may explode when heated under reduced pressure, the KCl is melted into small balls before loading into the rhenium canoe filament. This technique of

FIGURE 3. Vapor Depositing Chamber.

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FIGURE 4. Transmission Dynode Cross Section.

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FIGURE 5. Thin Film Target Dynode.
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forming small fused balls also facilitates weighing and loading the sample. The canoe filament is loaded with 8 mg of fused KCl and is then heated until the KCl is completely vaporized. A distance of 1 in. separates the loaded filament from the frame containing the transmission dynode. The transmission dynode is secured by a jig that exposes only the aluminized oxide film which is to be coated. It was found to be impractical to attempt removal of the porous KCl layer from the transmission dynode. Any washing agent completely destroys the film.

It is imperative that the low-density KCl layer be kept very dry during transfer from the coating system to the electron multiplier test setup. Therefore, a simple plastic dry-bag arrangement with rubber gloves attached to the sides was used to transport the completed dynode to the electron multiplier. Dry nitrogen at atmospheric pressure was in the dry bag during transfer.

In the second application, a target surface was needed for energetic positive ions. The target consists of a stainless steel block ($\sim 1\frac{1}{2} \times 1\frac{1}{32} \times \frac{1}{8}$ in.) polished to near optical flatness. Figure 5 shows a cross section of the block and aluminum oxide film. The procedure used to fabricate the film in the first application was used in the second, except that a larger area of aluminum oxide was needed to cover the block. It is advisable to dry the finished target assembly with heat lamps prior to its insertion in a vacuum system. This prevents any gas trapped between film and block from blistering the smooth film area upon exposure to a lower pressure. A used or radioactively contaminated dynode can be reactivated by stripping off the oxide film and applying a new film layer. We have also vapor-deposited a pure aluminum film on a flat, polished stainless steel surface and then anodized the aluminum layer to the desired film thickness of aluminum oxide.

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CONCLUSION

It was found that the method described here proved to be a simple and inexpensive way of fabricating thin films of aluminum oxide of known thickness. The films of this thickness are extremely strong and can be handled easily.

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