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ALUMINUM OXIDE FILMS

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The present invention relates to a new and improved type of thick, relatively non-porous aluminum oxide film. For years, aluminum oxide films have been used for a variety of purposes in the electronics arts. Perhaps the most important of these uses has been as an insulator between the electrodes of an electrolytic capacitor. Here such films have been extremely advantageous because of their dense character and their high dielectric constant. However, even in this use, it has been desired to obtain films possessing the basic characteristics of aluminum oxide, but which are thicker than the presently used oxide films which do not exceed 1 mil in thickness. With such thicker films, higher voltage applications are made possible.

The object of the present invention is to produce a new and improved variety of aluminum oxide film which is characterized by being thicker than, but similar to, the prior art aluminum oxide dielectric films. Further objects of the invention, as well as the advantages of it, will be apparent from the balance of this specification, as well as the appended claims.

Briefly, the above aims are achieved by first oxidizing the surface of aluminum electrode in an ionogen, such as oxalic acid, sulfuric acid, phosphoric acid, or the like so as to produce a comparatively porous columnar inert film, then depositing aluminum metal within the pores of the so-produced film, and finally oxidizing the so-deposited metal in an ionogen, such as boric acid, which is capable of forming an extremely dense adherent oxide layer which effectively fills the pores of the first produced oxide.

The extreme simplicity of the present invention makes it extremely difficult to describe in the usual detailed manner. The first oxidation treatment is carried out by utilizing usual anodic oxidation procedures and electrolytes, such as oxalic, sulfuric, phosphoric, or the like, which are known to produce comparatively porous oxide films of columnar structure. In general, voltages up to about 400 volts and current densities of from 5 to about 40 amps. per square centimeter can satisfactorily be employed during this step. The temperature of the electrolyte is a comparatively immaterial factor, although it is in general preferred to use temperatures of from about 20° C. up to about the boiling point of the electrolyte.

The deposition of aluminum within the pores of the oxide film produced as set forth in the preceding paragraph is slightly more difficult than the formation of the initial oxide layer. To accomplish the deposition, the oxide layer is preferably immersed within a plating bath, at approximately room temperature, such as are commonly employed in the deposition of aluminum, and is connected as a cathode in such a bath. A suitable electrolytic composition comprises the dispersion of toluene in a toluene solution of a fusion product of ethyl pyridiniumbromide and aluminum chloride with or without additional agents such as methyl-t-butyl ether. More specifically, this plating bath has a composition of 32% by weight of the fusion product of one mol of ethyl pyridiniumbromide and two mols of aluminum chloride, 67% of toluene and 1% of methyl-t-butyl ether. Other plating baths are well-known to the art and are preferably baths wherein the electrolyte is dissolved in an organic solvent such as pyridine in which electrical deposition can take place at room temperatures. The precise voltages and currents used throughout such deposition are well-known to the art. In general, the deposition of the aluminum should be carried out just until the point at which this metal is visible on the surface of the oxide film being treated, when viewed through a comparatively low power microscope, for example, a common microscope of 200 power. Further deposition of the aluminum is apt to destroy the advantageous results obtained by, in effect, creating a second layer of aluminum on top of the initial base oxide layer; the second layer of aluminum then being converted to an oxide film of normal thickness. For certain applications, a floating electrode structure of this type may be desirable, but such ramifications are outside the broad scope of the present invention.

Following the aluminum deposition procedure specified in the preceding paragraph, a final oxide film is produced by immersing the coated aluminum body in an electrolyte, such as an aqueous solution of boric acid, in which an extremely dense non-porous oxide film can be obtained in a manner known to the art for the same periods used presently in the formation of oxide films. In general, in the formation of this second oxide film, voltages up to about 600 volts are satisfactory, utilizing an initial current density of 40 amps. per square centimeter, when the electrolyte consists of a saturated solution of boric acid held at its boiling point.

It is contemplated that the broad teachings of the present inventive concept will be extended to other valve metals, such as, for example, tantalum, zirconium, and the like, and to extremely thick adherent dielectric films to be produced on them by the expedient of first depositing a comparatively porous oxide film, then filling the pores of this initial film with a metal, such as the base metal, and then oxidizing the final deposited metal so as to produce an extremely dense adherent film. It is to be understood that within the confines of this invention, it is substantially immaterial whether the second metal used to fill the pores of the first oxide layer is the same or another valve metal as the initial base material.

It is further contemplated that the broad teachings of the invention as developed by further experimentation will show that extremely advantageous aluminum oxide and other valve metal oxide films can be obtained by first oxidizing these metals to produce a porous oxide layer, then orienting the initial oxide films, as by the use of electric field of reasonably high intensity, and then finally forming an extremely dense oxide layer as described above within the pores of the so-oriented initial porous oxide layer without the use of a second metal to fill the pores of the first layer.

As many apparently widely different embodiments of my invention may be made without departing from the spirit and scope hereof, it is to be understood that my invention is not limited to the specific embodiments hereof except as defined in the appended claims.

What is claimed is:

1. The process of forming an insulating layer of oxide upon aluminum comprising the steps of anodically forming a porous layer of oxide upon the aluminum, electrodepositing a coating of aluminum within the pores of the oxide layer, and converting said deposit into the oxide.

2. The process of forming a heavy insulating layer of oxides upon an aluminum comprising the steps of anodically oxidizing the aluminum at a voltage of up to about 400 volts and a current density of from about 5 to about 40 amperes per square centimeter, plating a coating of

aluminum within the pores of the oxide layer, and converting said aluminum to the oxide.

3. An aluminum body having a non-conductive and non-porous aluminum oxide layer of a thickness greater than 1 mil in which said body is provided with a comparatively porous aluminum oxide layer, the pores of which are filled with denser aluminum oxide.

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