Anodic TiO_2 Films Doped with Alkali-Earth Oxides

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An electrolytic titanium capacitor consists of titanium substrate as the anode, dielectric film and an oxidizing liquid or solid electrolyte as the cathode, see Fig. 1. Carbon and a metal layer are added for electrical contact. The electrolyte provides a conducting path and a self-healing mechanism to the dielectric layer. The attractiveness of such electrolytic capacitors is in their high dielectric strength (over 7MV/cm). For a given capacitor geometry the stored energy is proportional to the product of capacitance and the square of the operating voltage. The goal of the present research is to increase capacitance by enhancing the dielectric constant of TiO_2 dielectric. Whereas titanium dioxide dielectric has a dielectric constant of 60 to 150, it may be possible to increased this value by incorporating alkali-earth + titanium oxides, such as barium titanate or strontium titanate, which are known for their high dielectric constant values. In this paper we present experimental work to test this hypothesis.

High purity titanium was doped with alkali earth elements, Ca, Mg, Ba, Sr, then anodized in an oxidizing electrolyte to incorporate titanate molecules in the growing TiO_2 film. Doping was carried out by diffusion treatments in vapors of the respective dopant elements at temperatures ranging from 870 to over 1400 ^{o}C. Concentrations range from non-detectable to a few atom percent. The composition of the diffusion layer was analyzed by X-ray photoelectron spectroscopy (XPS) and energy-dispersive x-ray spectroscopy (EDS). Surface topography was characterized by scanning electron microscopy and atomic force microscopy.

Composition and surface topography of anodic oxide films were analyzed by XPS, SEM and AFM. Properties of dielectric strength, leakage current, and stored charge density were measured to determine the effect of doping. Figure 2 shows a comparison between different capacitor anodes that were anodized to identical amounts of energy, and Table 1 shows preliminary results on the properties of un-doped and doped oxide films.

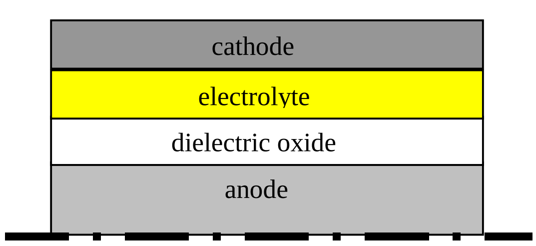

Fig 1. Schematic of an electrolytic capacitor.

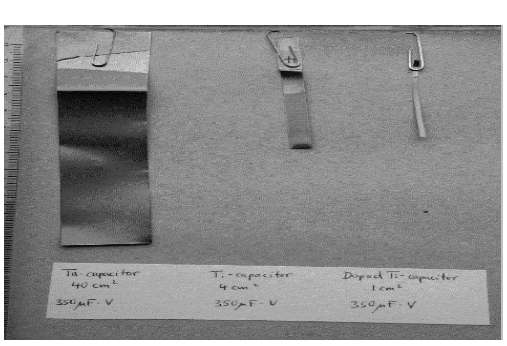

Fig 2. Comparison of Ta-, Ti- and Ca-doped Ti-electrolytic capacitors, each charged to 2μF at 175V.
A) Ta capacitor with surface area of 40 cm^2
B) Ti capacitor with surface area of 4 cm^2
C) Ca-doped Ti capacitor, surface area of 1 cm^2

Table 1. Electrical properties of various dielectrics

Dielectric	Dielectric constant	Dielectric strength, MV/cm	Charge density, μC/cm^2
Anodically formed Ta_2O_5 Film	25	7	15
Anodically formed TiO_2 Film	150	7.5	100
Anodically formed Ca-doped TiO_2 Film	250	7.5	150