

Effects of Current Density and Temperature on the Morphology and Electric Property of Anodic Films on Aluminum

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The growth of anodic alumina films in a neutral electrolyte proceeds at both film/electrolyte and film/substrate interfaces giving a duplex structure. The oxide layer formed at the former interface includes electrolyte anions, while a pure alumina layer is formed at the latter interface. The thickness ratios of each layer respectively represent transport numbers of Al^{3+} and O^{2-} if incorporated anions are immobile in the film (1). The film thickness and the incorporated anion content as well as transport numbers of both ions must affect the dielectric properties of the film as a capacitor material. However, the correlation between film structure and electrolytic conditions is not fully understood (2). For the further clarification of anodic film growth mechanism, more detailed characterization of anodic films in relation to electrolytic conditions is advantageous. Recently we (2-4) reported that the change in current density or temperature change associated with the change in electric field strength induces the notable change in film composition such as anion incorporation. In the present paper, the effect of current density and electrolyte temperature on the microstructure, composition and electric properties of anodic barrier films formed in a neutral borate solution was studied.

High purity (99.99%) aluminum sheets were electropolished in a 4:1 mixture of ethanol-perchloric acid solution before anodizing. Anodic films were formed in a mixture of 0.5 mol dm^{-3} boric acid and 0.05 mol dm^{-3} sodium tetra-borate solutions at 20°C at constant current densities of 1 Am^{-2} , 5 Am^{-2} , 10 Am^{-2} , 50 Am^{-2} and 100 Am^{-2} up to 80V. This upper voltage was selected to avoid electric breakdown events frequently observed at the higher voltage. Anodizing temperature was changed in the range of 10°C to 80°C . A quantitative electrochemical measurement called the "pore-filling (PF)" technique (5-7), i.e. re-anodizing, was used for the evaluation of film thickness and imperfections. For this evaluation, voltage - time ($V-t$) curves were measured during re-anodizing at 1 A m^{-2} in a mixture of 0.5 mol dm^{-3} boric acid and 0.05 mol dm^{-3} sodium borate solutions at 20°C , where initial voltage jump (V_j) is suggested to be proportional to the film thickness. Anodic film structure was observed by a transmission electron microscope (TEM, Hitachi H-9000) operated at 300kV. Cross sections of the films in the thickness of 30nm to 50 nm were prepared by an ultramicrotome with a diamond knife attached. Glow discharge optical emission spectroscopy (GD-OES, Jobin-Yvon JY5000RF) is used for measuring depth-profiles of constituent elements in the films accompanied by argon ion sputtering at the power of 40W. Electric properties such as capacitance and resistance were measured after Au sputtering on the anodized specimens to make MIM capacitors. Relative permittivity is determined by using the permittivity of vacuum $\epsilon_0 : 8.85 \times 10^{-12}$ and film

thickness.

Experimental results showed that the thickness of anodic films formed in boric acid - borate solution had a linear relation with the log of current density in the current range of 1 Am^{-2} to 50 Am^{-2} associated with 20% decrease of the thickness. Anodizing ratio changed from 1.6 nmV^{-1} to 1.3 nmV^{-1} at the above condition. Boron content in the film, as well as the ratio of incorporated depth to the film, increases also linearly with the log current although latter change is lower. Concerning the electrolyte temperature, film thickness increases linearly and boron content decreases also linearly as well as the ratio of incorporated depth with increasing temperature. These results suggest that the increase in current density leads to higher voltage sustainability of the film, presumably caused by higher anion content.

Next, the electric properties of the films in relation to the electrolytic conditions were examined. Resistance of the film decreases with the log current in the range from 1 Am^{-2} to 100 Am^{-2} . Capacitance increases roughly linearly with the log current. Concerning the electrolyte temperature, the resistance increases almost linearly with increasing temperature in the range from 10°C to 60°C . However, the resistance shows an extraordinary high value at 80°C . Capacitance decreases linearly with increasing temperature similarly to the resistance in the range from 10°C to 60°C except a very low value at 80°C .

To verify the exceptional values of the resistance and the capacitance for the film formed at 80°C , cross sections of the films were examined by TEM. The thickness of the film increases linearly with the increase of log current in the range from 1 Am^{-2} to 50 Am^{-2} . The thickness is rather higher at 100 Am^{-2} than that associated with 50 Am^{-2} . This may be affected by the local pore formation on the surface of the film as observed for the film formed at high current density (2,7). Concerning the electrolyte temperature, the thickness increases almost linearly with increasing temperature in the range from 10°C to 60°C . However, numerous fine pores are observed on the film surface formed at 80°C . This must be the cause of unusual high value of resistance and unusual low value of capacitance at 80°C .

Then, relative permittivity was estimated by use of the film thickness and capacitance. It decreases with the increase in the log current from 11.3 for 1 Am^{-2} and 10.9 for 50 Am^{-2} . The permittivity increases with the increase in temperature from 10.9 for 20°C and 12.1 for 60°C when anodic films were formed at 50 Am^{-2} . Therefore, we can conclude that the relative permittivity increases with the decrease of anion incorporation accompanied by current decrease and temperature increase, at which electric field strength decreases, whereas voltage sustainability decreases.

References

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