

## Electrochemical processes of barium titanate thin film and structural analysis by X-ray diffraction

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A new process to prepare barium titanate thin film with electrochemical method has been developed. During the electrochemical process, the cyclic voltammogram is susceptible to the surface condition of barium titanate thin film, so that the difference of each cyclic electrochemical properties can be examined. The deposited barium and titanium metal layers on copper substrate were oxidated under the fixed potential. Electrochemical behaviors of those thin films have also been investigated.

### 1. INTRODUCTION

Barium titanate-based ceramics are the most widely used dielectric materials in the fabrication of ceramic capacitors. The barium titanate thin film are desired in electroceramics applications such as ferroelectrics, condensers and optoelectrics. Barium titanate powders have been produced by the solid-state reaction, sol-gel[1] and oxalate coprecipitation methods[2]. Since the first formation of barium titanate thin film with a vacuum deposition technique by Feldman[3], the preparation of barium titanate thin film has received much attention because of the material's suitability for large-volume microcircuit capacitors based on its exceptionally high dielectric constant. These are classified into two methods to obtain barium titanate thin film: physical vapor deposition such as vacuum deposition[4], DC diode sputtering[5] and RF-magnetron sputtering[6] or chemical process such as spray coating, dip coating of metal organic compounds and chemical vapor deposition[7]. Iijima[8] prepared ferroelectric barium titanate thin film on Pt epitaxial film and SrTiO<sub>3</sub> substrate by activated reactive evaporation. These methods generally need higher temperature to crystallize barium titanate after forming an amorphous film on the substrate. In this study, the preparation of barium titanate thin film on copper substrate by an

electrochemical method is described. The reaction temperatures of electrochemical method are much lower than those needed in the conventional methods.

### 2. EXPERIMENTAL PROCEDURE

In the electrochemical process, the copper substrate is used as the working electrode(cathode), Pt plate as the counter electrode(anode) and Ag/AgCl as the reference electrode. Prior to experiment, the copper substrate was degreased in acetone, chemically etched in nitric acid, and then cleaned ultrasonically in redistilled water. Ethyl alcohol was used as nonaqueous solution with the addition of titanium tetrachloride and barium acetate to electrochemically deposit titanium and barium metal layer on copper substrate with various potentials and currents. The electrolyte solutions bubbled with nitrogen gas to deaerate the dissolved oxygen for 30 minutes. After the thin films of the titanium and barium metal layers were deposited, the anodic oxidation was carried on in the dilute boric acid solution with an applied voltage between 3 and 5 V. The thin films were analyzed by scanning electron microscopy(SEM), X-ray diffraction and potentiodynamic experiment.

In the potentiodynamic experiment, the cyclic

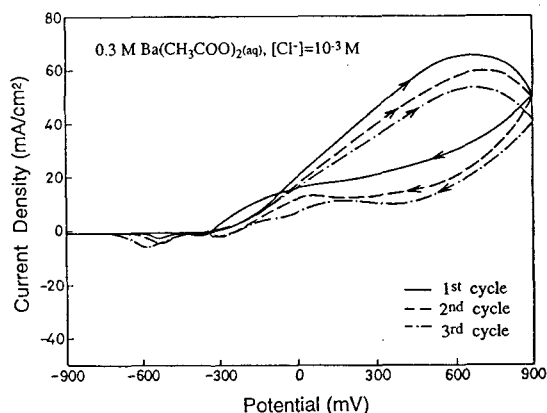


Fig. 1 Cyclic voltammograms of deposited barium metal in 0.3 M barium acetate solution with  $10^{-3}$  M  $\text{Cl}^-$

voltammogram scanned from -1000 mV to 1000 mV at the scanning rate of 30 mV/min is susceptible to the surface condition of barium titanate thin film, so that the difference of each cyclic electrochemical properties can be examined. In order to minimize the IR drop in the solution, the reference electrode was positioned as closely as possible to the working electrode about 0.2 mm.

### 3. RESULTS AND DISCUSSION

Fig. 1 showed the cyclic voltammograms of the first, second and third scans resulting from potential cycling in 0.3 M barium acetate electrolyte with  $10^{-3}$  M  $\text{Cl}^-$ . The relation between Tafel slope and barium ion concentration was shown in Fig. 2. The Tafel slope decreased with barium ion concentration increasing within the first to the third cycle. Thus, the activity of the thin film decreased as barium ion concentration increasing. It could reduce the anodic oxidation velocity.

In the nonaqueous solution of titanium tetrachloride and barium acetate, the titanium and barium metal were simultaneously electrodeposited on the copper substrate. Then, the deposited barium-titanium metal film underwent anodic oxidation in 0.05 M boric acid solution. The cyclic voltammogram of deposited barium-titanium oxide and titanium oxide was illustrated in Fig. 3. Because the formation of barium metal affected weekly surface properties of thin film, the curves of barium-

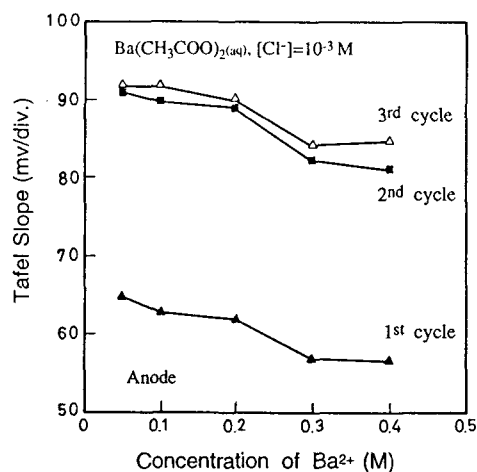


Fig. 2 The relation between Tafel slope and  $\text{Ba}^{2+}$  concentration with  $10^{-3}$  M  $\text{Cl}^-$

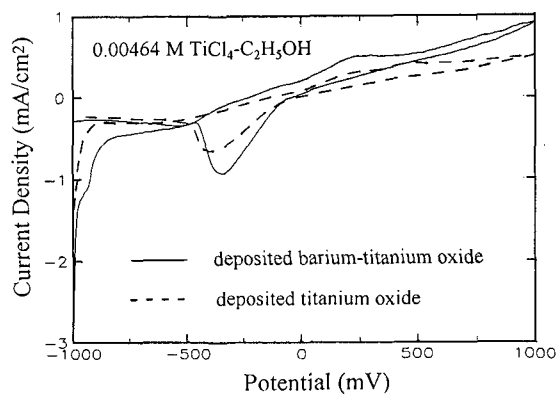


Fig. 3 Cyclic voltammogram of deposited barium-titanium oxide and titanium oxide

titanium oxide and titanium oxide were similar. Anodic oxidation velocity decreased with the potential of electrodeposition increasing in 90 coul/cm<sup>2</sup>.

The X-ray diffraction patterns of the thin films formed in 0.128 M  $\text{TiCl}_4$  by the electrodeposition and anodic oxidation on the deoxygen copper substrate was shown in Fig. 4. The Titanium oxide diffraction pattern was observed. The SEM photographs of the surface of the thin films formed on the deoxygen copper and the copper substrate were shown in Fig. 5. The surface morphology of the thin films appeared that smaller grains were existed on the deoxygen copper substrate than on the copper substrate. Since the crystal structure of

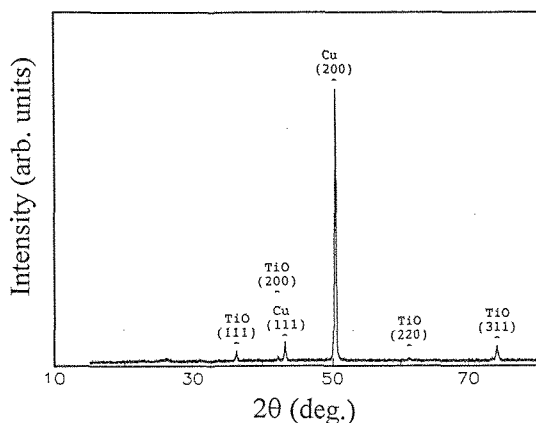


Fig.4 X-ray diffraction pattern of deposited titanium oxide on deoxygen copper substrate

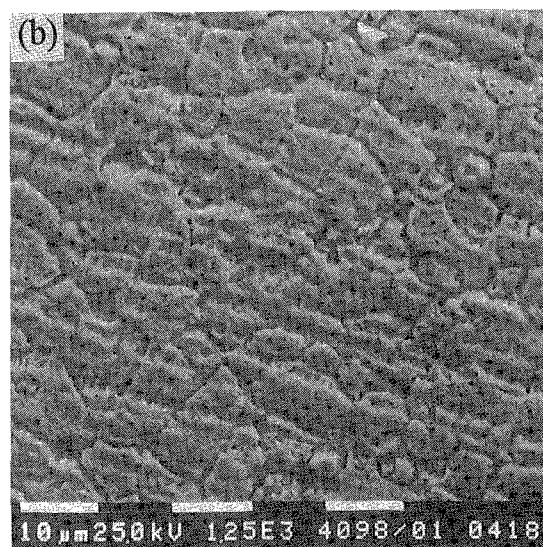
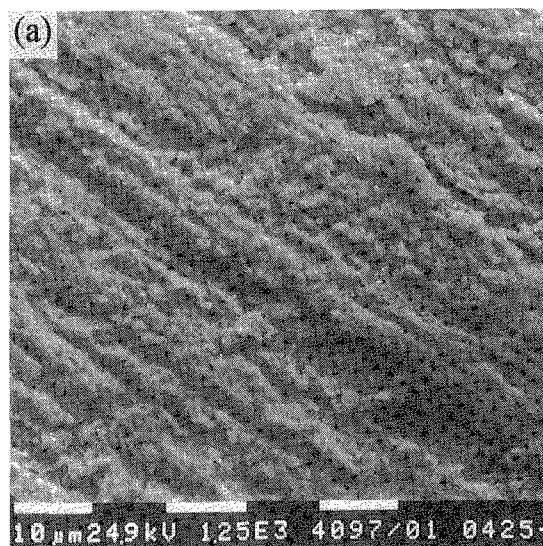


Fig.5 Comparison of deposited titanium oxide on different copper substrate (a) on deoxygen copper substrate (b) on copper substrate

surface on the deoxygen copper and copper substrate were different, the crystal orientations were effected during electrodeposition of titanium metal.

In the low titanium tetrachloride concentration electrolyte, the surface almost deposited nothing on copper substrate and the Ag/AgCl reference electrode was dissolved. In the reference electrode, the lower chlorine ion concentration caused the AgCl coating to dissolve completely. However, the higher chlorine ion concentration had the same effect by forming soluble complex ions. Hence, the concentration of chlorine ion in the potentiodynamic experiment was 0.01856 M. The deposited thin film in the higher concentration of electrolyte was amorphous. At different potentiodynamic environment, the deposited titanium oxide apparently appeared the light sensitivity.

#### 4. CONCLUSION

The preparation of deposited barium-titanium oxide thin film with electrochemical method has been investigated. It showed that the oxides films on the copper substrate were composed of titanium oxide and barium-titanium oxide. The results suggested a strong possibility that the thin film of barium titanate can be formed on copper substrate by electrochemical method.

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