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Synthesis and characterization of barium titanate films on Ti-coated Si substrates by plasma electrolytic oxidation

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ABSTRACT

Barium titanate ($BaTiO_3$) films were synthesized on Ti/Si substrates by plasma electrolytic oxidation using 0.5 M $Ba(OH)_2$ as the electrolyte. A potentiostatic mode with the voltages ranging from 30 to 70 V was used to synthesize the films. X-ray diffraction results show that cubic $BaTiO_3$ films were successfully produced on Ti/Si substrates. From analyses of the induced currents, the occurrence of spark discharge, and the surface morphology, it is found that electrochemical oxidation occurred at voltages below 40 V, while plasma electrolytic oxidation predominated at voltages above 60 V. A mixed electrochemical oxidation and plasma electrolytic oxidation regime was present at voltages between them. The $BaTiO_3$ films made by PEO exhibited better corrosion properties than those of synthesized by electrochemical oxidation. The dielectric constant increased with the increasing reaction voltages, due to the formation of thick and dense $BaTiO_3$ films.

1. Introduction

Perovskite oxides belong to an interesting class of materials that exhibit a variety of dielectric [1], ferroelectric [2], and piezoelectric [3] characteristics, as well as giant magnetoresistivity [4]. Among those perovskite oxides, $BaTiO_3$ has been extensively studied [5–19]. Previous investigations have revealed that $BaTiO_3$ films can be prepared by many solution-based synthesizing methods including sol–gel [5,6], hydrothermal (HT) [7–15], electrochemical [16], hydrothermal–electrochemical (HT–EC) [17–20], hydrothermal–galvanic couple (HT–GC) [21–23], and plasma electrolytic oxidation (PEO) [24–26] techniques. Of them, PEO is a surface modification and coating technique, which exhibits superior adhesion with the substrate and significantly high growth rates [27,28].

Different from conventional electrochemical techniques, PEO is characterized as a distinct group of surface modification processes mainly due to the occurrence of spark discharge on the electrode surface [27]. Schreckenbach et al. [24] firstly prepared $BaTiO_3$ on bulk Ti substrates by using the PEO technique in $Ba(OH)_2$ electrolytes. Many efforts have then been devoted to synthesize $BaTiO_3$ films with high crystallinity, dielectric property, biocompatibility, and corrosion resistance by varying processing parameters of PEO [25,26,29–31]. In those studies, bulk Ti substrates were commonly used as the electrode to make the $BaTiO_3$ films, while Ti thin films have rarely been employed to synthesize the films by PEO. Since Ti thin films can be deposited onto various types of substrates including insulating materials, PEO can then be performed on many Ti-coated substrates, which leads to many more applications including corrosion resistant dielectrics and capacitors.

Here, we focused on investigating the synthesis of $BaTiO_3$ films on Ti-coated Si substrates by PEO. Applied voltages, one of the key processing parameters, were varied to study the effect of voltages on the growth and characteristics of the films. Corrosion resistance and dielectric property of the obtained $BaTiO_3$ films have also been explored.

2. Experiments

Ti thin films were firstly deposited on n-type (100) Si substrates by a DC magnetron sputtering technique. The deposition parameters are: Ti target (purity 99.99%), Ar flow rate 21.7 sccm, working pressure 0.159 Pa, and d.c. power 300 W. The deposition time was 1 h and the resulting thickness of Ti films was approximately 1.2 ± 0.1 μm. The as-deposited Ti/Si specimens (1.7×1.7 cm^2) were used as the working electrode and Pt foil was employed as the counter electrode. The exposure area of the specimen for the polarization test was 1.7 cm^2. The distance between the working electrode and the Pt foil was 5 cm. A potentiostatic mode was conducted during the synthesis with the voltages ranging from 30 to 70 V. The reaction time was kept at 3 min while the temperature was fixed at 70 °C. The electrolytes consisted of 0.5 M $Ba(OH)_2$ (Sigma-Aldrich, Germany) and the pH value of the electrolyte was 14. The induced currents were in-situ monitored to examine the electrochemical behaviors. After PEO, the obtained specimens were cleaned in the phosphoric acid (pH = 5) to remove the $BaCO_3$ contamination. Finally, the specimens were thoroughly washed with de-ionized water and then dried.

Crystal structures of the as-deposited Ti films and those after PEO were determined by X-ray diffraction (XRD; MXP3, MAC Science, Japan) with a Cu ($\lambda_{Cu\ k\alpha} = 0.154$ nm) excitation source operated at 40 kV and 30 mA. Surface and cross-sectional morphologies of the

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obtained films were investigated by field-emission scanning electron microscopy (FE-SEM; JEOL JSM-6700F, Japan) operated at 3 kV.

The polarization test was carried out with a three-electrode configuration (Electrochemical Workstation, CHI 6088D, USA). The specimens were used as the working electrode and platinum was employed as the counter electrode, while Ag/AgCl (sat. KCl) was the reference electrode. The reaction area of the specimens was 0.2 cm^2. Potentiodynamic polarization was performed with a scan rate of 10 mV/s in the 3.5 wt.% NaCl solution at room temperature. In dielectric measurements, gold dots (0.42 mm^2) deposited onto $BaTiO_3$ using a shadow mask were used as the top contact while Ti films were employed as the bottom contact. The dielectric constant and dielectric loss were determined using a probe station equipped with an impedance analyzer (Agilent, 4292A, USA).

3. Results and discussion

3.1. Reaction current

The reaction current vs. reaction time curves during the synthesis on the Ti films that were potentiostatically polarized at various voltages are plotted in Fig. 1. As shown, the initial maximum reaction current increased with voltages. When the voltages were in the range of 30–40 V, the reaction currents firstly decreased rapidly, then increased to a maximum, and finally decreased to a steady value. It is possible that at the beginning Ti films dissolved into the alkaline solution and then formed titanium oxide layer on the Ti surface, which may hinder the dissolution and suppress the reaction current. After that, the electrolytic currents started to increase, which is mainly due to the reactions of Ba^{2+} ions with the titanium oxides. This leads to the formation of $BaTiO_3$ and further induces dissolution of Ti. As the $BaTiO_3$ layer covered fully over the Ti surface, the reaction current reached the steady state. It indicates that the formation mechanism of $BaTiO_3$ in the range of 30–40 V may be mostly due to electrochemical oxidation of Ti in the electrolyte [32].

Different current behaviors were observed at voltages varying from 50 to 70 V. In the voltage range of 50–55 V, the current first increased rapidly and then followed by a gradual decrease accompanied by apparent current fluctuation, which did not occur at 30–40 V. Fluctuation of reaction current increased with applied voltages. The current fluctuation is one of the characteristics of PEO [28]. The fluctuating current attributed to the vaporization of the electrolyte on the surface of the electrode, which accompanied by the formation of luminous gas [28]. Nevertheless, another main characteristic of PEO, spark discharge, was not observed between 50 and 55 V. This implies that the growth mechanisms of $BaTiO_3$ may be mixed electrochemical oxidation and PEO at 50–55 V. When the voltages reached 60 V, spark discharge that is one of the major characteristics of PEO started to occur [27].

3.2. Crystallinity and microstructure

X-ray diffraction patterns of the as-deposited Ti films and those after electrochemical synthesis at different voltages ranging from 30 to 70 V are shown in Fig. 2a. Distinct diffraction peaks at $2\theta = 22.0$ (100), 31.4 (110), 45.0 (200), 50.6 (210), 55.9 (211) and 65.5° (220) belong to cubic $BaTiO_3$ (JCPDS 31-0174) [33]. To quantify the XRD results, the relative peak intensities of $BaTiO_3$ were evaluated by calculating the ratio of integrated intensities of the $BaTiO_3$ diffraction peaks to integrated intensities of overall diffraction peaks. The relative peak intensities of $BaTiO_3$ synthesized at voltages of 30–70 V are displayed in Fig. 2b. As depicted in the figure, the relative intensity of $BaTiO_3$ slowly increased with the voltage below 55 V and increased rapidly afterwards. Apparently, the applied voltage affects significantly the growth of the films. The occurrence of spark discharge at voltages higher than 60 V yields local fusion of films, which significantly enhance the growth of $BaTiO_3$.

Surface morphologies of the Ti-coated substrates and those after the electrochemical synthesis at various voltages are revealed in Fig. 3. The surface of the as-deposited Ti films exhibited a flaky nanogranular

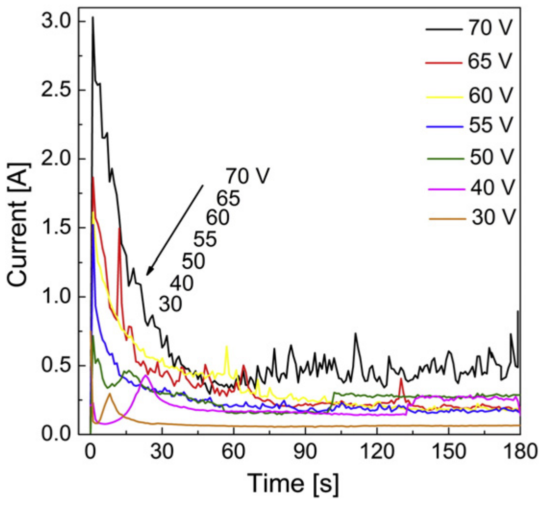

Fig. 1. Electrolytic current vs. reaction time of the obtained $BaTiO_3$ films synthesized over Ti/Si in 0.5 M $Ba(OH)_2$ electrolytes at various voltages ranging from 30 to 70 V.

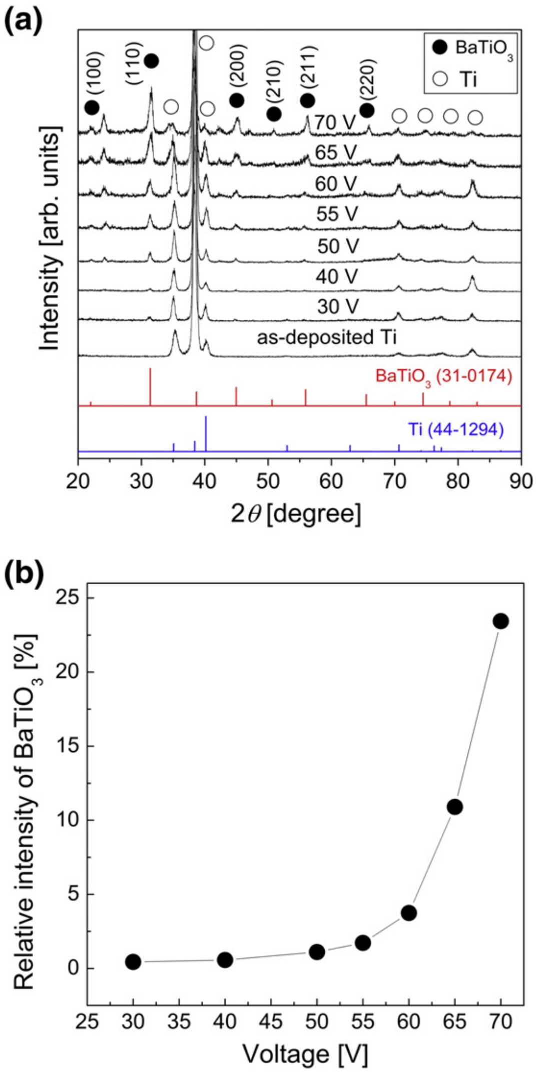

Fig. 2. (a) X-ray diffraction patterns of $BaTiO_3$ films synthesized over Ti/Si at various voltages for 3 min. (b) Relative peak integrated intensities of $BaTiO_3$ films formed over Ti films as a function of applied voltages.