Dielectric properties of the compositionally graded BaZrxTi2-xO5 thin films prepared by sol-gel method

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Abstract. The downgraded and upgraded BaZrxTi2-xO5 (x=0, 0.01, 0.02, 0.03 and 0.04) films normal to Pt/Ti/SiO2/Si substrates were prepared by sol-gel method. The microstructure and dielectric properties of the compositionally graded BaZrxTi2-xO5 films were investigated. The single-phase downgraded and upgraded films were obtained as the films were annealed at 900 °C for 30 min. The downgraded BaZrxTi2-xO5 film had dense surface, while there were pores in the surface of the upgraded BaZrxTi2-xO5 film. The thicknesses of both upgraded and downgraded BaZrxTi2-xO5 films were about 500 nm. The values of permittivity ($\varepsilon_r$) for the downgraded and upgraded BaZrxTi2-xO5 films were 84 and 100, respectively, at 1 MHz.

1. Introduction

Since Akashi et al [1,2] reported that the BaTi2O5 single crystal showed ferroelectric properties and high relative permittivity ($\varepsilon_r$) only along the b-axis with high Curie temperature ($T_C$ = 750 K), the BaTi2O5 ferroelectrics, as a new lead-free ferroelectrics, has been widely investigated [3-6]. However, the remnant polarization ($P_r$) of BaTi2O5 ceramics and single crystal was very small. Yue et al [7] improved the $\varepsilon_r$ value of BaTi2O5 ceramics using Zr substitution. Due to the demand of device miniaturization, the Zr-substituted BaTi2O5 should be applied as the film form. To the best of our knowledge, there was no literature reported on the preparation of Zr-substituted BaTi2O5 thin film.

Recently, much attention has been paid to compositionally graded ferroelectric films due to many intriguing properties, such as the enhancement of dielectric and ferroelectric properties [8-11]. In this study, the compositionally graded BaZrxTi2-xO5 (x=0, 0.01, 0.02, 0.03 and 0.04) thin films normal to Pt/Ti/SiO2/Si substrates were prepared by sol-gel method, and then their microstructure and dielectric properties were investigated.

2. Experiment

The compositionally graded BaZrxTi2-xO5 (x=0, 0.01, 0.02, 0.03 and 0.04) films were prepared on Pt/Ti/SiO2/Si substrates by sol–gel method. The details of preparation of BaZrxTi2-xO5 precursors were introduced elsewhere [12]. The BaZrxTi2-xO5 films were spin-coated on Pt/Ti/SiO2/Si substrates in sequence at 3000 r/min for 25 s to achieve the compositionally graded BaZrxTi2-xO5 films. And then the as-coated films were heated at 350 °C for 15 min. Figure 1 shows the cross-sectional schematics of compositionally graded BaZrxTi2-xO5 thin films. From the substrate to the film surface, the “upgraded” (Fig. 1a) and “downgraded” (Fig. 1b) preparations were described with increasing and decreasing Zr content, respectively. Finally, the films were annealed at 900 °C for 30 min in the air ambient.

The crystalline structure of samples was analyzed by an X-ray diffractometer (XRD, Rigaku
Ultima III) with Cu Kα radiation. The morphologies were observed by a field emission scanning electron microscope (FESEM, JSM-6700F). To measure the dielectric properties, the top electrode with the area of \( 2.0 \times 10^{-3} \, \text{cm}^2 \) was fabricated by sputtering Au target. Dielectric properties were measured using a precision impedance analyzer (Agilent 4294A) at room temperature.

![Figure 1](image1.png)

**Figure 1** The cross-sectional schematics of the compositionally graded BaZrxTi_{2-x}O_{5} films: (a) Upgraded and (b) Downgraded

3. Result and discussion

Figure 2 shows the XRD results of the graded BaZrxTi_{2-x}O_{5} films. The single-phase upgraded and downgraded BaZrxTi_{2-x}O_{5} films were obtained. The microstructures of the graded BaZrxTi_{2-x}O_{5} films are shown in Fig. 3. The downgraded BaZrxTi_{2-x}O_{5} film had dense surface, while there were pores in the surface of the upgraded BaZrxTi_{2-x}O_{5} film. The thicknesses of both upgraded and downgraded BaZrxTi_{2-x}O_{5} films were about 500 nm, according to the cross-sectional morphologies.

![Figure 2](image2.png)

**Figure 2** XRD patterns of the compositionally graded BaZrxTi_{2-x}O_{5} films: (a) Downgraded, (b) Upgraded

Figure 4 depicts the frequency dependence of \( \varepsilon_r \) for the downgraded and upgraded BaZrxTi_{2-x}O_{5} films. With increasing the frequency, the \( \varepsilon_r \) decreased at low-frequency region and kept at the
almost constant values at high-frequency region. The $\varepsilon_r$ values of the downgraded and upgraded BaZrxTi2-xO5 films were 84 and 100, respectively, at 1 MHz.

![Figure 3](image)

**Figure 3** Surface and cross-sectional images of the compositionally graded BaZrxTi2-xO5 films:
Upgraded (a, c) and downgraded (b, d)

![Figure 4](image)

**Figure 4** Permittivity ($\varepsilon_r$) as a function of frequency for the graded BaZrxTi2-xO5 films

4. **Conclusion**

The downgraded and upgraded BaZrxTi2-xO5 films were prepared on Pt/Ti/SiO2/Si substrate by sol-gel method. The single-phase downgraded and upgraded films were obtained as the films were annealed at 900 °C for 30 min. The downgraded BaZrxTi2-xO5 film had dense surface, while there were pores in the surface of the upgraded BaZrxTi2-xO5 film. The thicknesses of both upgraded and
downgraded BaZr_{x}Ti_{2-x}O_{5} films were about 500 nm. The \( \varepsilon_r \) values of the downgraded and upgraded BaZr_{x}Ti_{2-x}O_{5} films were 84 and 100, respectively, at 1 MHz.

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