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Preparation of (0 2 0)-oriented $BaTi_2O_5$ thick films and their dielectric responses

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Abstract

Barium dititanate ($BaTi_2O_5$) thick films were prepared on a Pt-coated Si substrate by laser chemical vapor deposition, and ac electric responses of (0 2 0)-oriented $BaTi_2O_5$ films were investigated using several equivalent electric circuit models. $BaTi_2O_5$ films in a single phase were obtained at a Ti/Ba molar ratio ($m_{Ti/Ba}$) of 1.72–1.74 and deposition temperature (T_{dep}) of 908–1065 K as well as $m_{Ti/Ba} = 1.95$ and $T_{dep} = 914$–953 K. (0 2 0)-oriented $BaTi_2O_5$ films were obtained at $m_{Ti/Ba} = 1.72$–1.74 and $T_{dep} = 989$–1051 K. $BaTi_2O_5$ films had columnar grains, and the deposition rate reached 93 $\mu m\,h^{-1}$. The maximum relative permittivity of the (0 2 0)-oriented $BaTi_2O_5$ film prepared at $T_{dep} = 989$ K was 653 at 759 K. The model of an equivalent circuit involving a parallel combination of a resistor, a capacitor, and a constant phase element well fitted the frequency dependence of the interrelated ac electrical responses of the impedance, electric modulus, and admittance of (0 2 0)-oriented $BaTi_2O_5$ films.

Keywords: Films; $BaTiO_3$ and titanates; Impedance; Dielectric properties; $BaTi_2O_5$

1. Introduction

Ferroelectricity of barium dititanate ($BaTi_2O_5$, BT_2) has not been realized until recently despite considerable study on the BaO–TiO_2 quasi-binary system. We first prepared a ferroelectric $BaTi_2O_5$ single crystal and reported its high relative permittivity along the *b*-axis ($\varepsilon' = 20{,}000$) and its high Curie temperature ($T_C = 750$ K).[1,2] The first-principle calculation showed that the piezoelectric response of $BaTi_2O_5$ is comparable to that of $PbTiO_3$; thus, $BaTi_2O_5$ is a promising candidate for a new lead-free ferroelectric material.[3] Since piezoelectric force is directly related to film thickness, a *b*-axis-oriented $BaTi_2O_5$ thick film is required to achieve a large mechanical force in a practical actuator.

Although the preparation of $BaTiO_3$ films by chemical vapor deposition (CVD) has been extensively studied because of its wide use in ferroelectric devices such as capacitors and actuators,[4–8] the preparation of $BaTi_2O_5$ films by CVD has rarely been reported. Yu et al. reported the formation of the $BaTi_2O_5$ phase in their study of $BaTiO_3$ epitaxial growth by aerosol CVD[9]; however, the ferroelectricity of $BaTi_2O_5$ was not yet realized. To study $BaTi_2O_5$ films, we prepared ferroelectric $BaTi_2O_5$ epitaxial thin films by laser ablation[10]; however, its deposition rate around 0.1 $\mu m\,h^{-1}$ should be increased to prepare thick $BaTi_2O_5$ films for practical applications. Laser chemical vapor deposition (laser CVD) is advantageous to obtain oriented and thick $BaTi_2O_5$ films at a high deposition rate. Laser CVD preparation of Y_2O_3–ZrO_2, Al_2O_3 and CeO_2 thick films was demonstrated at high deposition rates of more than several hundreds of micrometer per hour with significant orientation growth.[11–13]

For the characterization of dielectric materials, ac impedance spectroscopy has been widely used. Although the ac electric response has been conventionally analyzed by a Debye-type relaxation process using the equivalent electric circuit model involving a parallel combination of resistor (R) and capacitor (C) elements, deviations from the Debye-type response are commonly observed. Thus, a non-Debye-type element,[14] the so-called constant phase element (CPE), has often been used to explain these deviations. Masó et al. recently proposed an equivalent circuit model involving a parallel combination of R, C and the CPE to characterize the frequency-dependent electrical responses of the $BaTi_2O_5$ single crystal,[15] in which the CPE would correlate with cooperative dipolar interactions.

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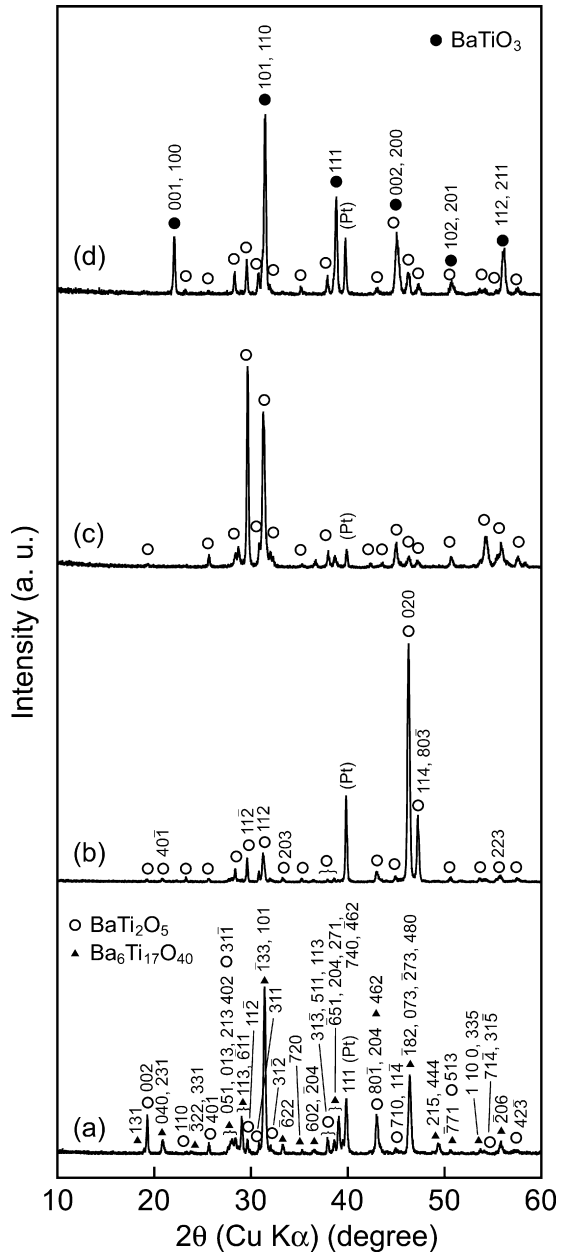

Fig. 1. XRD patterns of Ba–Ti–O films prepared at various $m_{Ti/Ba}$ and T_{dep}: 1.95 and 1020 K (a), 1.74 and 978 K (b), 1.74 and 957 K (c), and 1.06 and 1014 K (d), respectively.

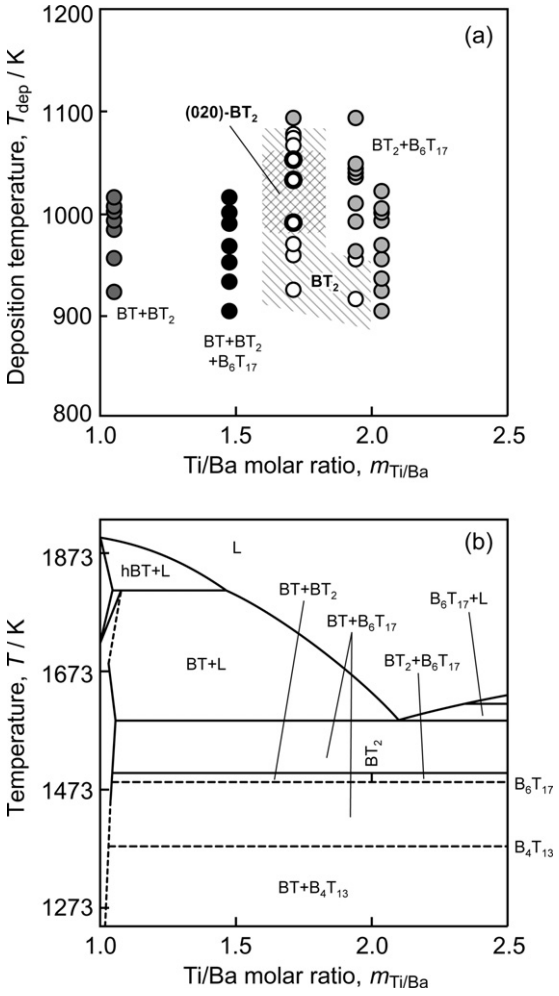

Fig. 2. Effects of Ti/Ba molar ratio and deposition temperature on the phase of Ba–Ti–O films (a), The hatched area indicates optimal deposition conditions for single-phase $BaTi_2O_5$ films. Phase diagram for the BaO–TiO_2 quasi-binary system (b).[16]

In the present study, we have prepared (0 2 0)-oriented $BaTi_2O_5$ thick films on a Pt-coated Si substrate by laser CVD, and the ac electric responses of the films were investigated using several equivalent electric circuit models.

2. Experimental procedure

$BaTi_2O_5$ thick films were prepared on a Pt-coated Si substrate by laser CVD with a continuous-wave mode Nd:YAG laser (wavelength: 1064 nm). Details of the laser CVD apparatus and the procedure have been reported elsewhere.[12] The substrate was placed on a hot stage, and a thermocouple was inserted near the substrate to measure the deposition temperature (T_{dep}). The substrate was heated on a hot stage at a pre-heating temperature (T_{pre}) of 773 K. A laser beam 15 mm in diameter was introduced through a quartz window to irradiate the entire substrate. As the laser power (P_L) increased from 52 to 93 W, T_{dep} increased from 918 to 1092 K. Barium dipivaloylmethanate ($Ba(dpm)_2$) and titanium diisopropoxy-dipivaloylmethanate ($Ti(OiPr)_2(dpm)_2$) precursors were evaporated at 563 K and 433–444 K, respectively. Their vapors were carried into a chamber with Ar gas, and O_2 gas was separately introduced into the chamber through a double-tube gas nozzle. The total pressure (P_{tot}) in the chamber was maintained at 400 Pa. Deposition was conducted for 600 s.

The crystal phase of the films was analyzed by X-ray diffraction (XRD, Rigaku RAD-2C) using Cu Kα X-ray radiation. The surface and cross-sectional microstructure of these films was observed by a scanning electron microscope (SEM, Hitachi S-3100H), and their dielectric properties were measured by an ac impedance spectroscope (Hewlett-Packard HP4194) in air from 298 to 1100 K in a frequency range between 2×10^2 and 10^6 Hz. Gold paste was used as an electrode. The ac electric responses