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Structure and dielectric properties of barium titanate thin films for capacitor applications

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Abstract

$BaTiO_3$ is a typical ferroelectric material with high relative permittivity and has been used for various applications, such as multilayer ceramic capacitors (MLCCs). With the tendency of miniaturization of MLCCs, the thin films of $BaTiO_3$ have been required. In this work, $BaTiO_3$ thin films have been deposited on Pt-coated Si substrates by RF magnetron sputtering under different deposition conditions. The films deposited at the substrate temperature from 550 °C–750 °C show a pure tetragonal perovskite structure. The films deposited at 550 °C–625 °C exhibit (111) preferential orientation, and change to (110) preferential orientation when deposited above 650 °C. The film morphologies vary with working pressure and substrate temperature. The film deposited at 625 °C and 4.5 Pa has the relative permittivity of 630 and the loss tangent of 2% at 10 kHz.

Keywords: A. Films; C. Dielectric properties; D. $BaTiO_3$; E. Capacitors

1. Introduction

A large number of lead-free electronic ceramics have been studied in recent years for various applications. Thin films of barium titanate ($BaTiO_3$) and other ferroelectric materials are widely studied for applications in miniaturized devices [1]. For example, $BaTiO_3$ with high relative permittivity is a promising material for applications in gigabit density dynamic random access memories (DRAMs) and multilayered ceramic capacitors (MLCCs). To meet the demand of the miniaturization of MLCCs and at the same time to keep the same capacitance, the thickness of the dielectric layers in the MLCCs has been reduced and reached below 1 μm [2]. Thin films of $BaTiO_3$ have been prepared by several techniques, including sol–gel process [3], pulsed laser deposition [4] and RF sputtering [5].

In this work, $BaTiO_3$ thin films have been prepared by RF magnetron sputtering. The effect of substrate temperature and working pressure on the structure, surface morphology and electrical properties of $BaTiO_3$ thin films have been investigated.

2. Experimental procedures

$BaTiO_3$ thin films were deposited by RF magnetron sputtering from the home-made ceramic targets. The substrates used in this work are $Pt/Ti/SiO_2/Si$ (100). A turbo-molecular pump backed by a rotary pump, was used to achieve a base pressure of 2.0×10^{-4} Pa. An RF power (Cesar1310, Dressler) was supplied to the $BaTiO_3$ target. The sputtering time was 3 h. The film thickness was measured by a stylus profiler (Dektak 6M, Veeco) and is approximately 300 nm. For electrical properties measurement, Pt top electrodes of 0.5 mm in diameter were deposited on $BaTiO_3$ films by RF sputtering.

The structures of the $BaTiO_3$ films were examined by an X-ray diffractometer (D/Max-2400, Rigaku) with Cu Kα radiation. The surface morphology and roughness are measured by an atomic force microscope (AFM, Dimension 3000, Veeco) and a field-emission scanning electron

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microscope (FESEM, JSM-7000 F, JEOL). The dielectric properties were investigated by using a precision impedance analyzer (4294A, Agilent).

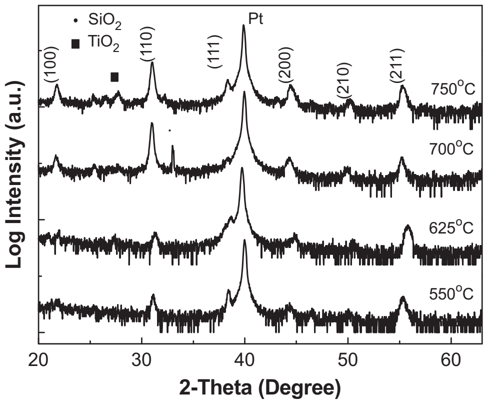

Fig. 1. XRD patterns of $BaTiO_3$ thin films deposited at temperatures from 550 °C to 750 °C.

Table 1
Relative intensities and FWHM of XRD peaks of $BaTiO_3$ thin films deposited from 550 °C to 750 °C.

Temperature (°C)	Relative Intensity/FWHM		(202)(220)
	(101)(110)	(111)	
550	0.2%/0.36	1.0%/0.39	–
625	0.1%/0.39	0.5%/0.47	–
700	4.1%/0.20	0.1%/0.36	0.2%/0.37
750	2.2%/0.25	0.3%/0.37	0.1%/0.41

3. Results and discussion

3.1. Structure of $BaTiO_3$ thin films

XRD patterns of $BaTiO_3$ thin films deposited at different substrate temperatures are shown in Fig. 1. It can be seen that all films show a pure tetragonal pervoskite structure. However, the film deposited at 550 °C exhibits quite weak crystallization. With increasing deposition temperature, (111) peak becomes weaker and the peaks of (100) and (110) gradually become stronger. Table 1 shows the analysis of the relative peak intensity (compared with Pt (111) peak) and the full width half maximum (FWHM). The strongest peak of the films is (111) for the films deposited from 550 °C to 625 °C, but changes to (110) above 625 °C which indicates a change of the preferential orientation from (111) to (110) around 625 °C [6].

It is shown that the $BaTiO_3$ ceramics has a tetragonal structure and the split in (002)/(200) peaks near 45°(2θ) indicates a tetragonal distortion. In contrast, the XRD patterns of the films, especially in (002)/(200) peaks splitting, indicate a pseudocubic phase. This result suggests that the tetragonal phase is more stable than the cubic phase in the thin films [7]. The pseudocubic phase occurs when the grain size decrease sufficiently so that the unit cell becomes less and less tetragonal as a result of the internal strain [5]. The broaden XRD peaks were observed, which manifests the decreased grain size. A core–shell model is used to explain the deformation in $BaTiO_3$ thin films [8]. In this model, a grain has a composite structure consisting of

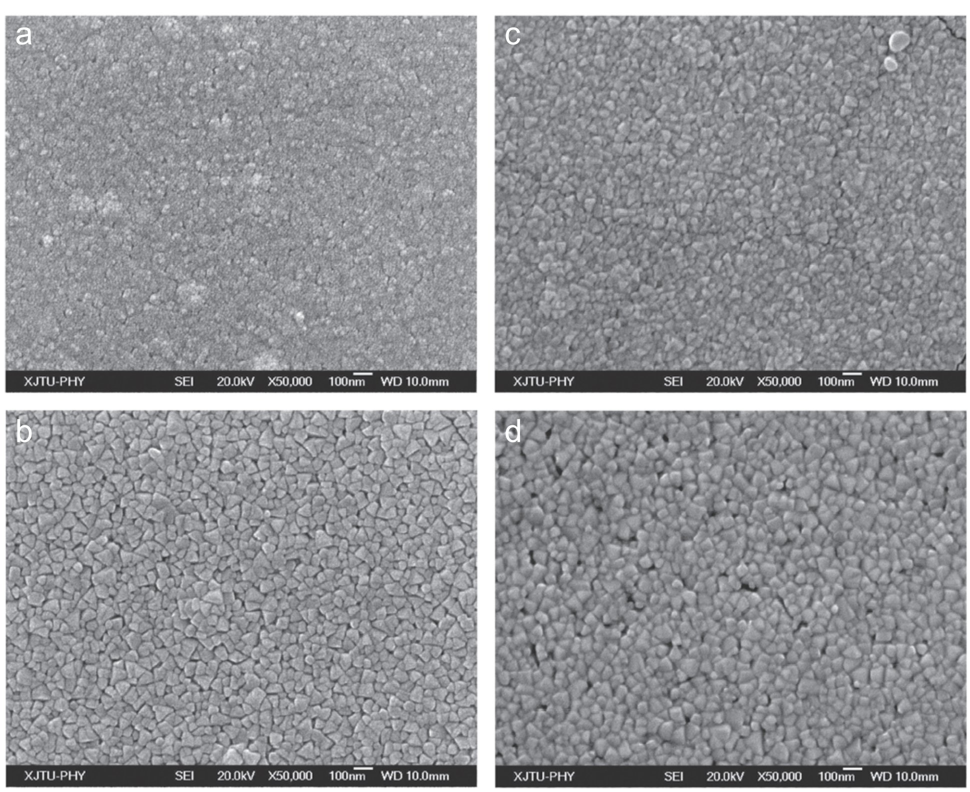

Fig. 2. SEM images of $BaTiO_3$ thin films deposited at (a) 2.9 Pa, (b) 3.5 Pa, (c) 4.0 Pa and (d) 4.5 Pa.

an inner tetragonal core, a gradient lattice strain layer (GLSL), and a surface cubic layer [9]. The lattice parameters (a and c) change continuously in the middle layer GLSL. As a result, we can observe that the peaks around 45° were broad, indicating a slight splitting of (002)/(200) and a small tetragonal distortion.

3.2. Surface morphologies

The SEM surface micrographs of $BaTiO_3$ thin films deposited under different pressures are shown in Fig. 2. It can be seen that the grain size becomes larger with increasing working pressure.

At 2.9 Pa, the grain boundaries are not clear. The film deposited at 3.5 Pa shows clear grain boundaries. But the grain size is not uniform. The film deposited at 4.0 Pa exhibits a smooth and densely packed structure with homogeneous grains. The average grain size is about 80 nm. However, when deposited at higher pressure, like 4.5 Pa, the film exhibits more pores compared with the film prepared at 4.0 Pa.

The surface morphologies of $BaTiO_3$ thin films was examined by an atomic force microscope. Fig. 3 shows the results for the films deposited from 550 °C to 750 °C. The roughness in RMS with the different depoisiton temperatures is 3.0 nm, 5.1 nm, 2.4 nm, 8.5 nm and 11.4 nm, respectively. The roughness of the films significantly increases when deposited above 650 °C. This result can be attributed to the following: the energetic particle bombardment on the growing film that leads to the ejection of previously deposited atoms, and the formation of islands which grow large enough to touch and coalescence during nucleation and growth on the substrate [10]. For the substrate temperature from 650 °C to 750 °C, it is likely that the particles arrive in the substrate with high energy and cross the energy barrier of nucleation. These high energy particles are more likely to develop into films with high porosity and high roughness [11].

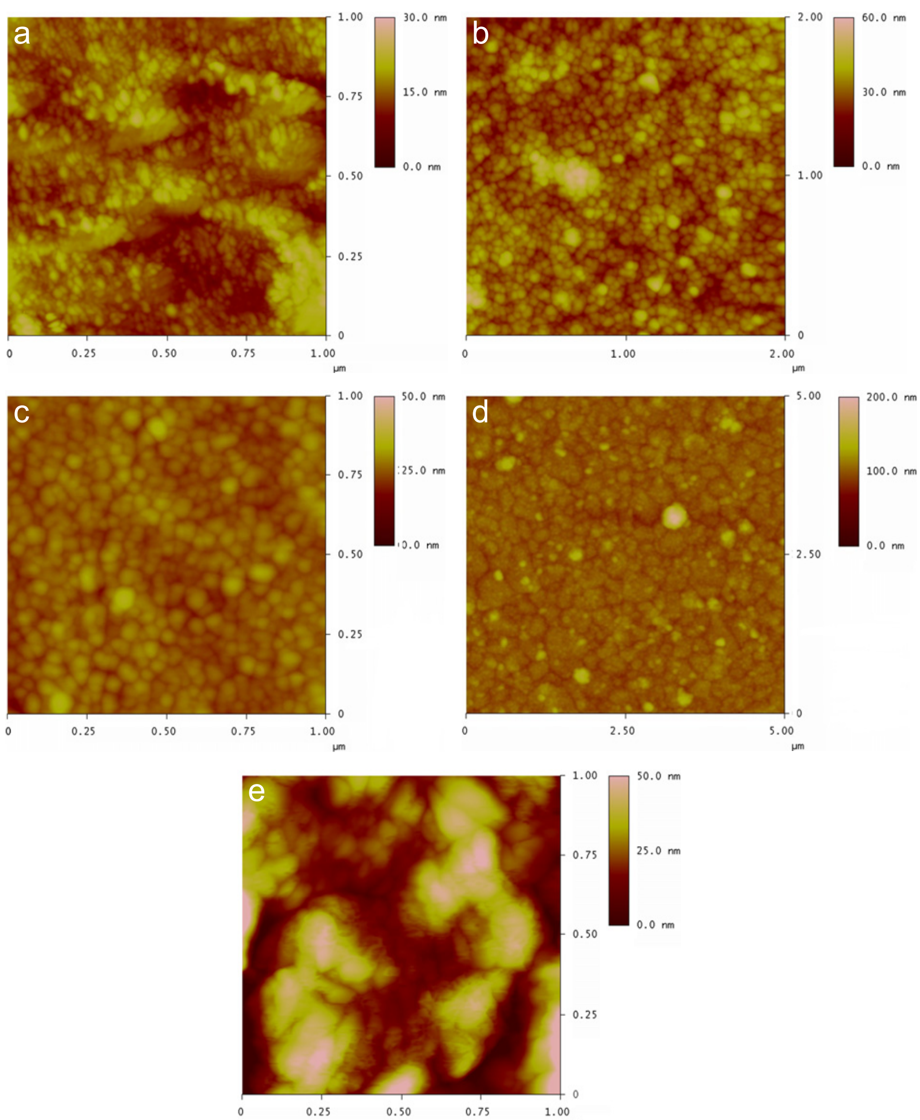

Fig. 3. AFM images of $BaTiO_3$ thin films deposited at (a) 550 °C, (b) 625 °C, (c) 650 °C, (d) 700 °C and (e) 750 °C.

3.3. Dielectric properties

Fig. 4 gives the relative permittivity (ε_r) and loss (tanδ) of $BaTiO_3$ thin films measured at room temperature as a function of frequency. These films were deposited under the following parameters: 160 W, 5% O_2, and the substrates temperature was set at 625 °C. The working pressure was set at 2.9 Pa, 3.5 Pa, 4.0 Pa and 4.5 Pa, respectively.

Fig. 5 gives the relative permittivity and loss tangent of $BaTiO_3$ thin films at 10 kHz. The film deposited under 4.5 Pa shows the improved properties with the relative permittivity of 630 and the loss of 2%.

The relative permittivity of $BaTiO_3$ thin films increases with working pressure. In $BaTiO_3$ ceramics, the relative permittivity decreases with increasing grain size. However, the tendency is reversed when the grain size is below a critical point, usually 1.1 μm [12]. In this work, the average grain size of $BaTiO_3$ thin films was below 100 nm and the relative permittivity increases with grain size. As manifested in Fig. 4, the relative permittivity decreases in the high frequency range and the loss increases obviously in this range. The possible reasons are the hypothesis of the influence of the contact resistance between the probe and the electrode and the electrode resonance due to high relative permittivity [13]. Similar frequency dispersion phenomenon was also reported in other ferroelectric thin films [14]. The dissipation factor in $BaTiO_3$ thin films is mainly caused by the contribution of the domain wall pinning, space charge polarization, interfacial diffusion, as well as secondary phases [15]. The dielectric loss remains low and steady as frequency is below 100 kHz.

The result suggests that the $BaTiO_3$ thin films are promising candidates for applications in thin film MLCCs [16].

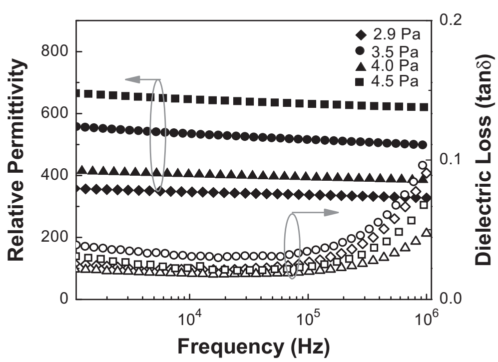

Fig. 4. Dielectric constant and loss tangent of the $BaTiO_3$ thin films deposited at 2.9 Pa, 3.5 Pa, 4.0 Pa and 4.5 Pa, respectively.

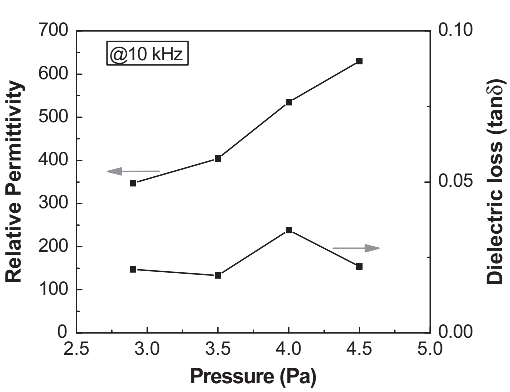

Fig. 5. Dielectric constant and loss tangent of $BaTiO_3$ thin films at 10 kHz.

4. Conclusion

$BaTiO_3$ thin films have been deposited under different deposition conditions. Crystallized $BaTiO_3$ thin films were deposited in the substrate temperature range from 550 °C to 750 °C. The films deposited from 550 °C to 625 °C show the (111) preferential orientation, while the films deposited above 650 °C show (110) preferential orientation. Weak tetragonal distortion was observed from the slight split in the (002)/(200) peaks indicating a pseudocubic phase occurred when the grain size decreased. The AFM and SEM images of the films show that the high substrate temperature led to large roughness. The grain size increases with working pressure. The film deposited at 625 °C and 4.5 Pa exhibits improved performance with the relative permittivity of 630 and the loss tangent of 2% at 10 kHz.

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