

Effect of Lattice Strain on Ferroelectric Properties of Epitaxially Grown BaTiO₃ Thin Films by Reactive Evaporation

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Ferroelectric BaTiO₃ thin films have been epitaxially grown by reactive evaporation. The thickness variation of lattice spacings and dielectric constants are caused by the two-dimensional stress due to the lattice mismatch and the difference in the thermal expansion coefficients between an epitaxial layer and a substrate. The thickness dependence of the relative dielectric constant ϵ_r can be explained by Landau-Ginsburg-Devonshire thermodynamic theory.

Keywords: BaTiO₃/ Thin film/ Epitaxial growth/ Reactive evaporation/ Lattice strain/ Ferroelectricity

Recently, thin films of ferroelectric oxides are widely studied for the applications in nonvolatile memories, infrared sensors, and electro-optic devices. BaTiO₃ is known as a typical ferroelectric oxide having relatively large dielectric constants. We report structural and dielectric properties of epitaxially grown BaTiO₃ thin films.

BaTiO₃ films are grown by a reactive evaporation method [1]. Essentially, this method is a co-evaporation of metal elements under an oxygen atmosphere [2]. The local oxygen pressure near the substrate is 10^0 – 10^1 Pa. The deposition rate is about 0.2 nm/s. The substrate temperature is 700°C. The (100) SrTiO₃ and the (100) oriented Pt single crystal thin film (100 nm) grown on MgO (100) are used as substrates.

Atomic force microscope (AFM) observation has

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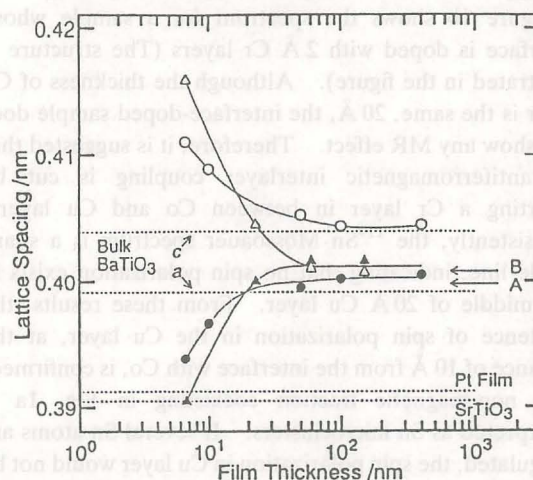


Figure 1. Lattice spacings as a function of film thickness. The lattice spacings of bulk BaTiO₃ and SrTiO₃ and *a* of Pt film on MgO are given by the dashed lines. ○, ●: lattice spacings *c* and *a* on Pt/MgO; △, ▲: *c* and *a* on SrTiO₃.

SOLID STATE CHEMISTRY —Artificial Lattice Compounds—

Scope of research

*Syntheses of oxide thin films by reactive evaporation and ceramics by solid state reaction and their characterizations are studied. The main subjects are: preparation and characterization of ultrathin films of high-*T_c* superconductors: investigation of growth mechanism of thin films by in situ reflection high-energy electron diffraction: phase diagram of Bi₂O₃-SrO-CaO-CuO system: preparation and observation of dielectric properties of ferroelectric thin films: preparation and characterization of metallic and ferromagnetic SrRuO₃ thin films: preparation and characterization of artificial superlattices comprising of oxides, metals, and semiconductors.*



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shown that a two-dimensional growth occurs from the initial stage on SrTiO₃ substrate and an island growth occurs on Pt substrate. The island structure changes into a continuous layer when the thickness is over 1.2 nm. *In situ* reflection high-energy electron diffraction (RHEED) observation has revealed that the initial nuclei on Pt have perovskite structure.

In Fig. 1, the lattice spacings a and c of BaTiO₃ films determined from X-ray diffraction are given as a function of film thickness [3]. The lattice spacing a decreases and c increases with decreasing film thickness. The ultrathin films with the thickness below 10 nm show a large contraction along the a -direction by accommodating elastically the lattice mismatch between BaTiO₃ and Pt or SrTiO₃. A large elongation along the c -direction originates from the large contraction of the a -axis.

For the films with the thickness over 50 nm, the lattice spacings get close to the bulk values due to the introduction of misfit dislocations. The lattice spacings, however, are not in agreement with the bulk values even at a thickness of 400 nm. Figure 2(a) shows thermal expansion curves for BaTiO₃, MgO, and SrTiO₃. While the BaTiO₃ film is cooled from the growth temperature of 700°C to room temperature, the lattice of the BaTiO₃ film may not be contracted according to its thermal expansion curve due to the strong effect from the substrate. If the lattice spacing of the BaTiO₃ film grown on the both substrates with the thickness larger than 50 nm is the same to the bulk value at the growth temperature of 700°C and is contracted according to the thermal expansion curve for the substrate, the lattice spacing a would be varied with temperature as shown in Fig. 2(b). The lattice spacing a 's of 0.4007 nm (B) for SrTiO₃ and 0.3999 nm (A) for Pt/MgO at the room temperature derived from the curves of Fig. 2(b) are in good agreement with those from X-ray measurement.

Figure 3 shows the thickness dependence of the observed relative dielectric constant ϵ_r for the BaTiO₃ films grown on Pt/MgO substrate. ϵ_r increases with increasing film thickness and is saturated to $\epsilon_r \sim 700$ which is larger than bulk value along the c -axis. We have calculated the thickness dependence of ϵ_r by the Landau-Ginsburg-Devonshire thermodynamic theory [4]. For BaTiO₃ in tetragonal state ($P4mm$), the spontaneous polarization, P_s , is determined to be $P_s^2 = \{-\alpha_{11} + [\alpha_{11}^2 - 3\alpha_{111}(\alpha_{11} - 2Q_{12}H)]^{1/2}\} / 3\alpha_{111}$ (i), where H is a two-dimensional stress; α_1 , α_{11} , and α_{111} are dielectric stiffness and higher-order stiffness coefficients at constant stress; and Q_{12} is a cubic electrostrictive constant. We can relate H to a lattice strain x_1 ($= (a_0 - a_c)/a_c$) as $x_1 = Q_{12}P_s^2 + (s_{11} + s_{12})H$ (ii), where a_0 is a lattice spacing determined from X-ray diffraction and a_c is a calculated lattice spacing of strained structure extrapolated to room temperature (point A in Fig. 2(b)); and s_{11} and s_{12} are elastic compliance coefficients. Thus, ϵ_r is given by $\epsilon_r = 1 + \eta_{33} = 1 + [2\epsilon_0(\alpha_1 - 2Q_{12}H + 6\alpha_{11}P_s^2 + 15\alpha_{111}P_s^4)]^{-1}$ (iii). The dotted line in Fig. 3 is a calculated curve for the thickness dependence of ϵ_r using Eqs. (i)–(iii), bulk values of dielectric parameters [5, 6] and X-ray data in

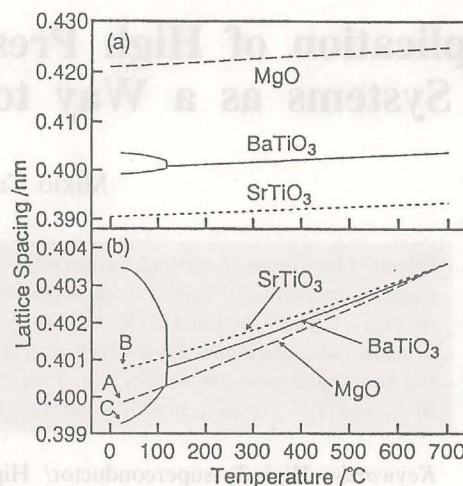


Figure 2. (a) Thermal expansion curves of BaTiO₃, MgO and SrTiO₃. (b) The calculated thermal expansion curves for the BaTiO₃ films grown on Pt/MgO and SrTiO₃, where the thermal expansion of the film is dominated by the substrate.

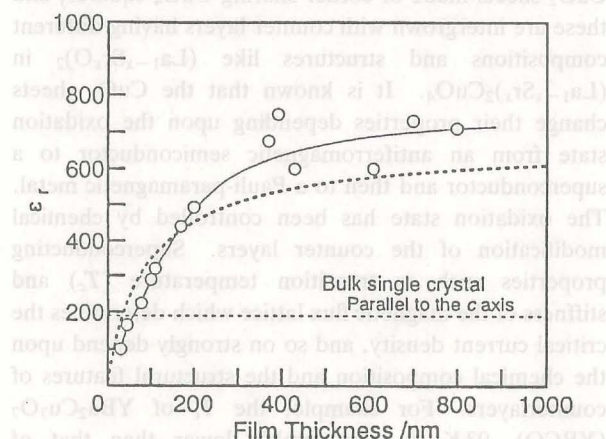


Figure 3. Relative dielectric constant ϵ_r as a function of film thickness at room temperature. Calculated curve of ϵ_r is given by dashed line.

Fig. 1. The agreement between the experimental results and the theoretical curve is fairly good, indicating that the thickness dependence of ϵ_r originates from the two-dimensional stress in BaTiO₃ films due to the lattice mismatch and/or the difference in the thermal expansion coefficient.

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