Effect of Lattice Strain on Ferroelectric Properties of Epitaxially Grown BaTiO$_3$ Thin Films by Reactive Evaporation (SOLID STATE CHEMISTRY - Artificial Lattice Compounds)

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Effect of Lattice Strain on Ferroelectric Properties of Epitaxially Grown $\text{BaTiO}_3$ Thin Films by Reactive Evaporation

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Ferroelectric $\text{BaTiO}_3$ 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 $\varepsilon$, can be explained by Landau-Ginsburg-Devonshire thermodynamic theory.

Keywords: $\text{BaTiO}_3$/ 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. $\text{BaTiO}_3$ is known as a typical ferroelectric oxide having relatively large dielectric constants. We report structural and dielectric properties of epitaxially grown $\text{BaTiO}_3$ thin films.

$\text{BaTiO}_3$ 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 $10^6$--$10^7$ Pa. The deposition rate is about 0.2 nm/s. The substrate temperature is 700°C. The (100) $\text{SrTiO}_3$ 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

![Figure 1. Lattice spacings as a function of film thickness. The lattice spacings of bulk $\text{BaTiO}_3$ and $\text{SrTiO}_3$ and $\sigma$ of Pt film on MgO are given by the dashed lines. $\bigcirc$, $\blacklozenge$: lattice spacings $c$ and $a$ on Pt/MgO; $\Delta$: $c$ and $a$ on SrTiO$_3$.](image-url)

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shown that a two-dimensional growth occurs from the initial stage on SrTiO$_3$ 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 BaTiO$_3$ 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 BaTiO$_3$ and Pt or SrTiO$_3$. 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 BaTiO$_3$, MgO, and SrTiO$_3$. While the BaTiO$_3$ film is cooled from the growth temperature of 700°C to room temperature, the lattice of the BaTiO$_3$ 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 BaTiO$_3$ 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 $a$ of 0.4007 nm (B) for SrTiO$_3$ 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 $\varepsilon_r$ for the BaTiO$_3$ films grown on Pt/MgO substrate. $\varepsilon_r$ increases with increasing film thickness and is saturated to $\varepsilon_r \approx 700$ which is larger than bulk value along the $c$-axis. We have calculated the thickness dependence of $\varepsilon_r$ by the Landau-Ginsburg-Devonshire thermodynamic theory [4]. For BaTiO$_3$ in tetragonal state ($P4mm$), the spontaneous polarization, $P_s$, is determined to be $P_s = [-a_1 + \sqrt{a_1^2 - 3a_{11}(a_1 - 2Q_{12})}]^{1/2}/3a_{11}$ (i), where $H$ is a two-dimensional stress; $a_{11}$, $a_{12}$, and $a_{11}$ 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 $x_1 = (a_0 - a_1)/a_1$ as $x_1 = Q_1P_2 + (s_{11} + s_{12})H$ (ii), where $a_0$ is a lattice spacing determined from X-ray diffraction and $a_1$ 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, $\varepsilon_r$ is given by $\varepsilon_r = 1 + x_3 = 1 + [2a_0(a_0 - 2Q_{12}H + 5a_{11}P_2 + 15a_{11}P_4)]^{-1}$ (iii). The dotted line in Fig. 3 is a calculated curve for the thickness dependence of $\varepsilon_r$ using Eqs. (i)-(iii), bulk values of dielectric parameters [5,6] and X-ray data in Figure 3. Relative dielectric constant $\varepsilon_r$ as a function of film thickness at room temperature. Calculated curve of $\varepsilon_r$ 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 $\varepsilon_r$ originates from the two-dimensional stress in BaTiO$_3$ films due to the lattice mismatch and/or the difference in the thermal expansion coefficient.

References