Lattice Imperfection of Calcium Titanate Thin Films

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Thin films of calcium titanate were grown by a magnetron sputtering method. The change of defect structure and element distribution were studied in these thin films by SIMS, x-ray rocking curve measurements, and RBS, related with A-site / B-site cation ratios in perovskite structure. The thin film process had a tendency of creation of a large amount of defects and the wide range of solid solution at room temperature. The crystal distortion was increasing with deviation from the stoichiometric composition. These excess solved elements easily precipitated in annealing process, and macro defects were created. The interdiffusions between substrates and thin films were remarkable at higher annealing temperature.

1. INTRODUCTION

The titanate perovskites play a very important role in technology as well as in basic solid state chemistry because of their ferroelectric behavior and unique crystal structure. Recently, perovskite thin films have been extensively studied in the past few years for uses in nonvolatile memory applications and thin film capacitors. Several deposition techniques were being exploited for the growth of ferroelectric thin films[1]. It is noted that any thin film process accommodates more cation stoichiometric variation (A-site / B-site ratio) in perovskite structure than the conventional bulk ceramic processings. The variability in composition and defect structures are crucial to some properties[2].

In the bulk ceramics, the A-site / B-site ratio is virtually unit in barium titanate[3-4], but it can be quite large, up to 1%, in calcium titanate[5]. To clarify the effects of A-site / B-site ratio, calcium titanate, therefore, is the best materials among alkali earth titanate perovskites. The object of this study is determined the effect of A-site / B-site ratio on some properties of thin films. In the present report, we focus on a behavior of crystal imperfection in the calcium titanate perovskite, that have various A-site / B-site ratios. Characterizations of these materials were carried out by X-ray rocking curves measurement, SIMS and RBS.

2. EXPERIMENTAL PROCEDURE

The depositions of calcium titanate were carried out using a radio frequency magnetron sputtering system with a horizontal substrate holder 3cm away from a sputtering target. The sputtering target of calcium titanate was fabricated from $CaCO_3$ and TiO_2 powders, with some mole ratios of Ca/Ti, by a conventional ceramic powder processing : The powder mixtures were calcined, and pressed, and then sintered at 1350°C for 1h in air and finally shaping in 7.5cm-diameter.

Commercial available polished $SrTiO_3(100)$ (hereafter denoted as STS) wafers were used as substrates. To compare the result to the other substrates, MgO(100)(denoted MGO) and fused quartz glasses (denoted as GLS) were also used. To get high quality films, we adopted a reverse sputter etching process before deposition. When the chamber was evacuated below 10^{-4} Pa, the substrate was heated to the required temperature. Argon gas was then introduced to a pressure of 1 Pa. The overall sputtering conditions for the deposition of calcium titanate are summarized Table 1. Film thickness was measured by Dektak 3030 profiler.

After deposition of calcium titanate on the substrates, the elementary depth profiles in the samples were determined using depth-profile analysis with SIMS (CAMECA IMS-4f). For primary ions, $^{133}Cs^+$ or O^+ ions accelerated to 10kV were used. To maintain constant electric potential at insulator sample surface, gold films were coated with sputtering.

RBS and channeling measurements were carried out using 2- and 1-MeV He^+ ions. The angular dependencies of the back scattered yield near a <100> axis of $SrTiO_3$ substrates were obtained by rotating the crystal around the axis with an increasing tilt angle. The depth window for

integration of the back scattered yield was set to the Ti portion of the RBS spectra from 20 to 50nm. The resulting films and substrate were also characterized X-ray rocking curve measurement. The surface texture and average composition were evaluated by SEM with EDAX and optical microscopy.

Table 1.
Sputter Deposition Parameters

Substrates	MgO(100)
	Nb:SrTiO$_3$(100)
	Glass, Quartz, Pt
Target Stoichiometry	CaTiO$_3$
RF Power	150W
Growth Temperature	25°C to 600°C
Background Pressure	~4x10^{-4} Pa
Growth Pressure	1 Pa
Oxygen Flow Rate	0 sccm
Growth Rate	0.75 to 1.90 Å/sec

* Films were cooled in vacuum after growth. No oxygen was introduced.

3. RESULTS AND DISCUSSION

3.1. Effect of substrates on crystal orientation.

Crystalline structure and orientation of the thin films with various substrates are listed in Table 2. Although all thin films were in amorphous state at lower growth-temperature, crystallite phase with a perovskite structure was grown above 600°C. The high aligned crystals were obtained with the STS-substrates, and the polycrystals, with other substrates. The sample surface with STS was very smooth because of the epitaxial characteristics. It is noted that the polycrystal also has a pseudo cubic structure. The strontium titanate (100) plane corresponds to the calcium titanate (101) or (020) plane, whose lattice mismatch is moderate with values about 2%. In pseudo cubic system, (101) and (020) plans are the same as each other. On the contrary, it is over 9% with MgO (100) plane, 0.421nm, which is considered to be a reason of the random oriented growth with MGO.

3.2. Compositional dependence of crystallinity.

Figure 1 shows the EDAX results of thin films. The composition of thin films shifted to a side rich in Ti element. The secondary phase was not observed in as-grown thin films throughout all the compositional area in the present study, and the Vegard rule was valid.

The A-site / B-site ratios (hereafter, A/B ratio) within a single-phase region is generally narrow in the bulk ceramics of alkaline earth titanate perovskites. In barium titanate, it is virtually invariant[3-4], and it is more substantial in strontium titanate (100-1000ppm)[6-7]. In calcium titanate it can be slightly large, up to 1%[5]. In any case, it does not exceed a few % in bulk ceramics that is in a thermodynamic equilibrium state. For the case of thin films of calcium titanate, anomalous solubility

Table 2
Summary of X-Ray Results

Deposition Temperature (°C)	Glass	MgO	SrTiO$_3$
25	Amorphous	-----	-----
300	Amorphous	Amorphous	Amorphous
400	Amorphous	-----	-----
500	Amorphous	-----	-----
600	Polycrystalline	Polycrystalline	Highly Aligned

limit, which expanded almost to 10% in both sides of Ti and Ca, was observed. The secondary phase easily precipitated in the sample near stoichiometric composition, that was annealed about 900°C. This behaviour clearly indicates that the anomalous solid solution is in a metastable state.

In strontium titanate system, relatively large excess of SrO can be accommodated by insertion of individual layers of SrO between blocks of perovskite structure, i.e. "Ruddlesden and Popper type defects[8]," that have been directly observed using transmission electron microscopy[9]. To clarify mechanism and structure of anomalous solid

solution (e.g. which is dominant, point defect mode or extended defect mode with Ruddlessden Popper type?), some studies such as TEM and diffusion experiments must be done in future.

A large amount of defects is believed to decrease the crystallinity. A rocking curve of the Ratherford back scattered yield is one of nice indexes of cystallinity[10]. Figure 2 shows an example of angular dependencies near a <100> axis of STS. The observed behavior of the angular half-width and depth suggests the presence of some kind of lattice imperfection in the Ca rich sample.
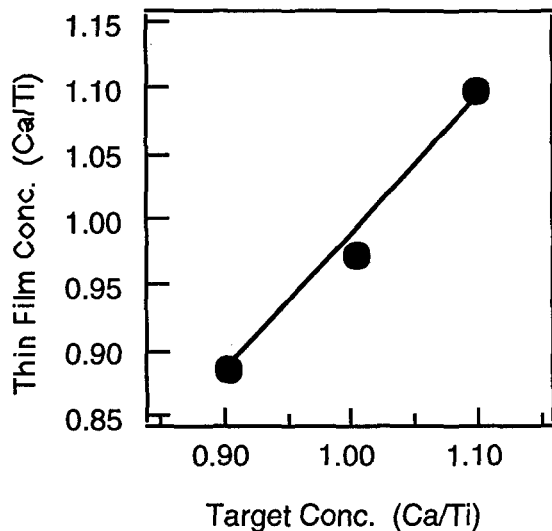

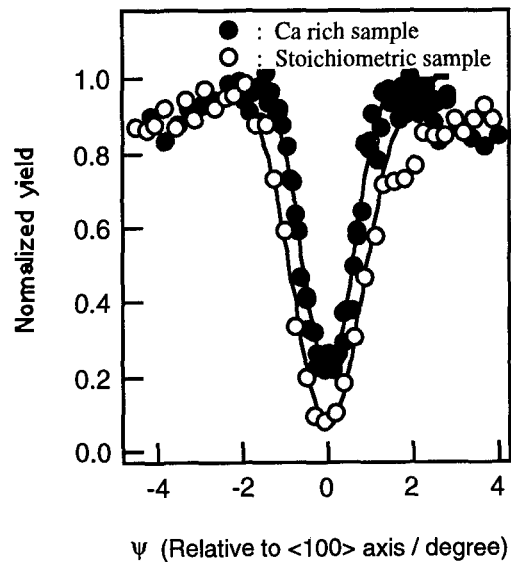Fig.1. Thin film A/B ratios measured by EDAX vs. Target ratios.

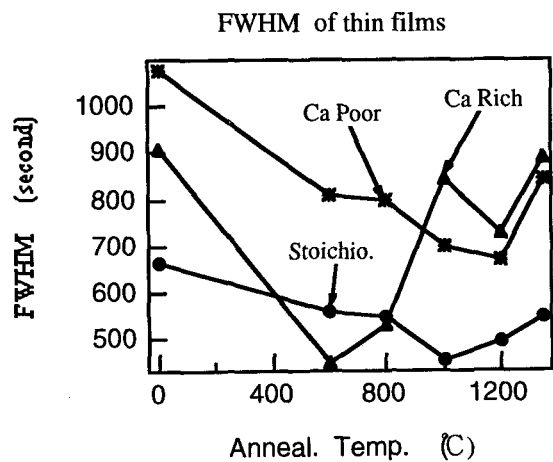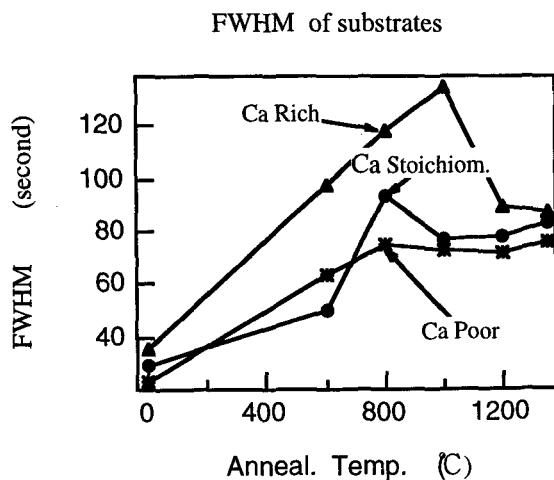Fig.2. RBS Channeling angular sacan vs.Target ratios.

Fig.3. FWHM of x-ray rocking curves vs. annealing temperature

3.3. Annealing Effect.

Above mentioned, the present thin films are metastable, so some reactions were expected to occur to the direction of equilibrium during anneling, that is, the relaxation of the lattice mismatch between thin films and substrates, the precipitation of excess element, and interdiffusion between thin films and substrates.

To evaluate the relaxation of crystal lattice distortion in the thin films, x-ray rocking curve measuement was carried out. Seen in Figure 3 the tendency of the change of FWHM for the x-ray rocking curve was not consistent and complex. However, many macro defects were observed on the surface after annealing, so it is considered that some reaction occured to the relaxation of the lattice distortion.

As described at section 3.2. excess TiO_2 component easily precipitated. Fourthermore, interdiffusion were characterized by SIMS technique. According to Figure 4, it is clear that the diffusion of calcium ions occured in the STS. Strontium ions diffused through planar defect grown at annealing and segregated on the surface of thin films. Contamination such as silicon also had a tendency to segregate at the planar defects. Although the diffusion coefficient of Ca ions in STS
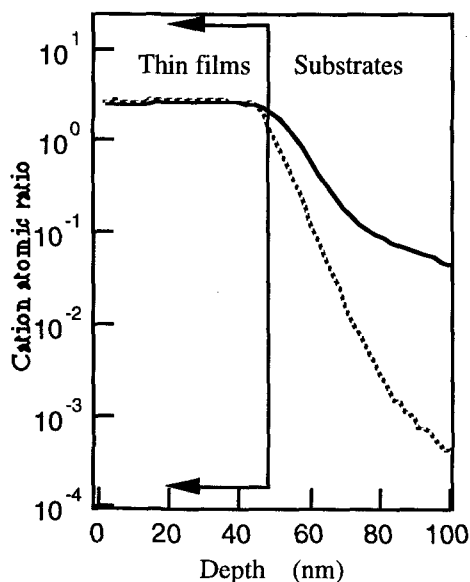
was few order magnitude smaller than reported values[11], the diffusion amount is enough for FWHM of the x-ray rocking curves to increase with annealing temperature(Fig.3.).

4. Summary.

The change of defect structure and element distribution were studied in calcium titanate thin films, related with A-site / B-site cation ratios in perovskite structure. In thin films, a large amount of defects were introduced at the thin film process and the wide range of solid solution stably exists at room temperature. The crystal imperfection was increasing with deviation from the stoichiometric composition. These metastable elements easily precipitated inannealing process, and macro defects were created. The inter diffusion between thin films and substrates were observed at higher annealing temperature.

Fig.4. Ca distribution in annealed and non-annealed samples.
Doted line : Rel. Ca int. in non-annealed sample
Solid line : Rel. Ca int. in the sample annealed at 1200°C

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