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OXYGEN METASTABLE DEFECTS IN CALCIUM TITANATE THIN FILMS

H. Haneda[1*], *I. Sakaguchi*[2], *S. Hishita*[1], *T. Ishigaki*[1] *and T. Mitsuhashi*[1]

[1]National Institute for Research in Inorganic Materials,1-1 Namiki, Tsukuba, Ibaraki 305-0044
[2]Core Research for Evolution Science and Technology of Japan Science and Techonology Corporation, c/o National Institute for Research in Inorganic Materials, Namiki, Tsukuba, Ibaraki 305-0044 Japan

Abstract

Metastable defects of oxygen in calcium titanate thin films with perovskite structure were studied. Thin films of calcium titanate were deposited by a magnetron sputtering method. The oxygen defects were evaluated, using the results of oxygen diffusion experiments. The thin film process had tendencies of creation of a large amount of oxygen point defects and the wide range of non equilibrium solid solution at room temperature. The crystal distortion was increasing with deviation from the stoichiometric composition. Although the metastable defects were decreasing due to the annealing, annealed samples had more oxygen defects in a few magnitude orders than single crystals.

Keywords: calcium, diffusion, metastable defect, oxide ion, perovskite, sputtering, thin film, titanate

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. Their properties such as electrical conductivity are very sensitive with defect structure, so many reports about defect chemistry have been done [1]. However the effect of defects has still not been clarified, e.g., one can not understand the calcium effect on anti-reduction property in the barium titanate ceramics. The unsatisfactory understanding is believed to be caused mainly by an exist of metastable defects, that are common defects in perovskite structures [2]. 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, so they have generally a lot of metastable defects.

In the bulk ceramics, the A-site/B-site ratio is virtually unit in barium titanate [3, 4], and 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

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[*] Author for correspondence: fax: +81-298-52-7449; e-mail: haneda@nirim.go.jp

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earth titanate perovskites. 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.

Experimental procedures

The depositions of calcium titanate were carried out using a radio frequency magnetron sputtering system with a horizontal substrate holder 3 cm away from a sputtering target. The sputtering targets of calcium titanate were fabricated from $CaCO_3$ and TiO_2 powders, with some mole ratios of Ca/Ti, by a conventional ceramic powder processing. Commercial available polished $SrTiO_3$ wafers with (100) large planes were used as substrates. Sputtering procedure has been described in detail elsewhere [6]. The thin films were characterized with a secondary mass-spectrometer (SIMS, CAMECA IMS-4f), RBS, SEM and XRD. Some samples were annealed in oxygen atmosphere at various temperatures.

Diffusion coefficients of oxide ion in thin films were determined by a solid-gas exchange technique [7]. The thin films were diffusion-annealed in ^{18}O-enriched oxygen gas with 5 kPa pressure. The ^{18}O diffusion profiles (concentration *vs*. depth) were measured using SIMS with $^{133}Cs^+$ as the primary ion, an accelerating voltage of 10 kV, and a beam current of 5 to 20 nA. The detail experimental procedure of the exchange reaction and the isotope analysis with a secondary ion mass spectrometer have been described elsewhere [8]. The following relation was used to calculate the diffusion coefficients, D_1 in thin films and D_2 in substrate for double layers [9]:

$0<x<-l$

$$\frac{c(x,t)-c_1}{c_0-c_1}=\sum_{n=0}^{\infty}\alpha^n\left(erfc\left[\frac{(2n+1)l+x}{2\sqrt{D_1t}}\right]-\alpha\ erfc\left[\frac{(2n+1)l-x}{2\sqrt{D_1t}}\right]\right)$$

$-l<x<\infty$

$$\frac{c(x,t)-c_1}{c_0-c_1}=2k/(k-1)\sum_{n=0}^{\infty}\alpha^n\left(erfc\left[\frac{(2n+1)l+kx}{2\sqrt{D_1t}}\right]\right)$$

where,

$$k=\left(\frac{D_1}{D_2}\right)^{1/2},\quad \alpha=\frac{1-k}{1+k}$$

where $c(x,t)$ is concentration of ^{18}O isotope at the penetration depth, x, c_0, the concentration in gas phase, c_1, natural abundance of ^{18}O, t, the duration of diffusion annealing, l, thickness of the thin film, and $erfc=1-erf$ (erf the Gaussian error function).

Results and discussion

Characterization of thin films

Crystalline structure and orientation of the thin films were characterized by XRD, SEM and RBS. The thin films were in amorphous state at the lower growth-temperature, whereas the high aligned crystallite phase with a perovskite structure was obtained, when the substrate temperature was above 873 K. The crystalline sample surfaces were very smooth because of the epitaxial growth characteristics [10], shown in Fig. 1. It is noted that they had pseudocubic structures. The strontium titanate (100) plane corresponds to the calcium titanate (101) or (020) plane, whose lattice mismatch is moderate with values about 2%.

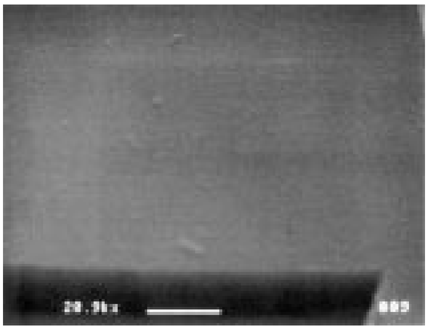

Fig. 1 The SEM photograph of highly aligned calcium titanate thin films deposited at 873 K (bar: 0.8 μm)

An energy dispersion spectroscopy (EDS) analysis with SEM indicated that the composition of thin films shifted to few % in Ti side compared with the target compositions. The secondary phase, however, was not observed in as-deposited thin films throughout all the compositional area in the present study, and a Vegard's rule was valid for the lattice constants. In any case of the alkali earth titanate perovskites, the solid solution range 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 limit, that expanded almost to 10% in both sides of Ti and Ca, was observed.

A large amount of defects is believed to decrease the crystallinity. A rocking curve of the Rutherford back scattered (RBS channeling) yield is one of nice indexes of cystallinity [11]. According to the results of the RBS channeling, the observed behavior of the angular half-width and depth suggests concentration of lattice imperfection in the Ca-rich sample more than near the stoichiometric composition.

Diffusion coefficients of oxide ions in thin films

Typical concentrations of ^{18}O *vs*. penetration depth in some kinds of samples are presented in Fig. 2. Figure 2(a) shows an effect of the cation ratio, Ca/Ti on the diffusion profiles of oxide ions in the as-deposited samples at 1176 K for 5 min with 200 hPa of ^{18}O-enriched oxygen gas. Oxygen diffusivity was increasing with increasing Ca/Ti ratio. As for annealed samples, the slope of oxygen isotope concentration near stoichiometric composition took a minimum value, seen in Fig. 2(b). One can obtain diffusion coefficients from the depth profiles using Eq. (1). The lines in Fig. 2. indicate fitted values with Eq. (1).

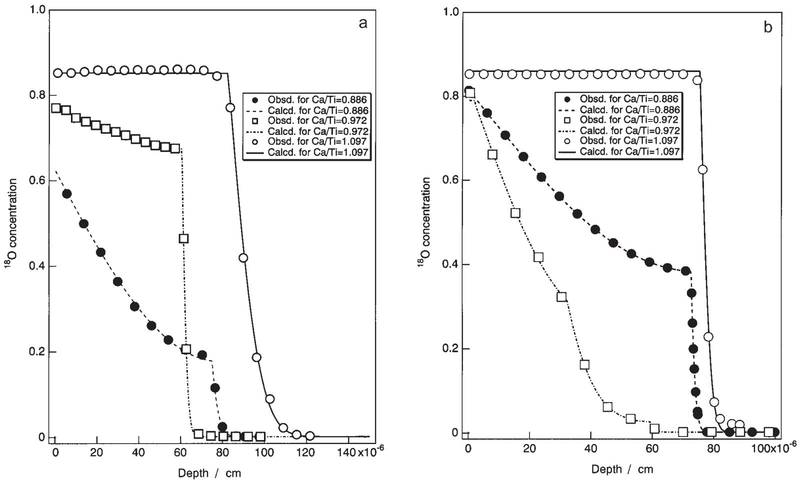

Fig. 2 Typical diffusion profiles of ^{18}O ions in calcium titanate thin films with various composition a – non-annealed, b –annealed at 873 K

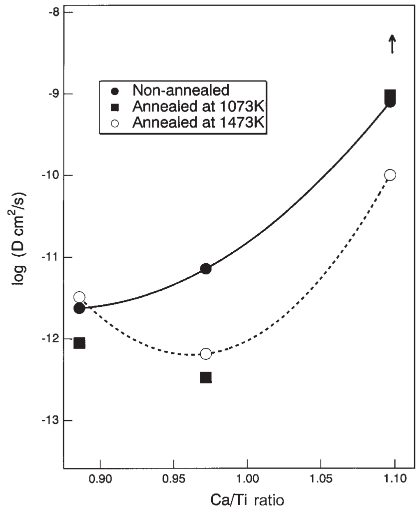

Fig. 3 Diffusion coefficients *vs*. compositional ratio, Ca/Ti, of oxide ions in calcium titanate thin films

To clarify the compositional effect on diffusion coefficient, the diffusion coefficients are plotted *vs*. the Ca/Ti ratios in Fig. 3. Although for as-deposited thin films the diffusion coefficient simply increased with the Ca/Ti ratio from these curves, the ten-

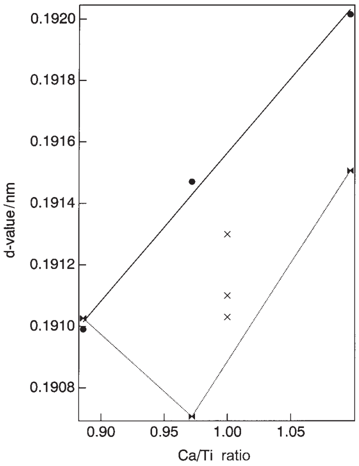

Fig. 4 The *d*-values of (200) of calcium titanate thin films in pseudo-cubic system. Closed circle non-annealed, hund drum symbols: annealed at 1073 K and crosses: data for $CaTiO_3$ in JCPDS card (42–423) [14]. All thin films, deposited at 873 K

dency of diffusion coefficients took a minimum value at the composition near cation stoichiometric in the samples annealed at 1073 K for 5 h in the air before diffusion annealing. The *d*-values of (200) for pseudocubic lattice are presented in Fig. 4. They have a Vegrad's rule in full compositional range. On the other hand, the *d*-value was minimum near stoichiometric composition. According to these results, as-deposited samples are considered to have a lot of oxygen defects that were increased with increasing Ca/Ti ratio and in metastable state. These defects caused the large *d*-values. For annealed-samples,

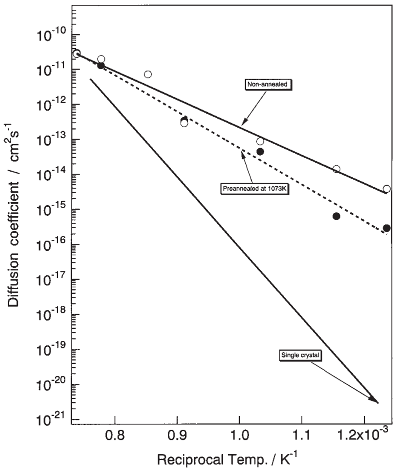

Fig. 5 Arrhenius plots for various calcium titanates near stoichiometric compositions. Open circles and solid lines for non-annealed samples deposited at 873 K, closed circles and dashed line for pre-annealed ones deposited at 873 K, and solid line for extrapolated values for single crystal, respectively

annihilation of metastable defects was faster near stoichiometric composition than Ca-excess and Ti-excess samples.

Sakaguchi *et al.* have reported the diffusion coefficients in calcium titanate single crystals at the temperature range between 1120 K and 1316 K [12]. According to their results, the activation energy had been 385 kJ mol^{-1}, corresponding to that for migration of oxygen vacancy. The temperature dependencies of the present results are plotted in Fig. 5 with the extrapolated values for the single crystal, accompany with the results for the single crystal. The diffusion coefficients in the thin films are always higher than those of single crystals, that indicates that the films have more oxygen vacancy concentration than single crystal. Since the concentration for single crystal is believed to corresponds to the equilibrium one, the excess oxygen vacancies of the thin films are in the metastable state. Seen in Fig. 5, the concentration of the metastable defects was decreasing during the pre-annealing before the oxygen diffusion experiments. The concentration of the metastable oxygen defects were maintained during the oxygen diffusion annealing, because the temperature dependences were expressed as the single Arrhenius relations, respectively, including the data above the temperature of pre-annealing in air before diffusion annealing in ^{18}O.

To clarify the annealing effects on the oxygen diffusion coefficients in the thin films, the diffusion coefficients were evaluated *vs.* the pre-annealing temperature. These results are illustrated in Fig. 6. The tendency of the pre-annealing effect is not so simple. The diffusion coefficients took a minimum value at the sample pre-annealed at 1073 K. The decreasing of the diffusion coefficient can be interpreted by a reason that the metastable oxygen vacancies annihilated during the pre-annealing. Their increasing is considered to be caused by the inter-diffusion between the thin film and the substrate.

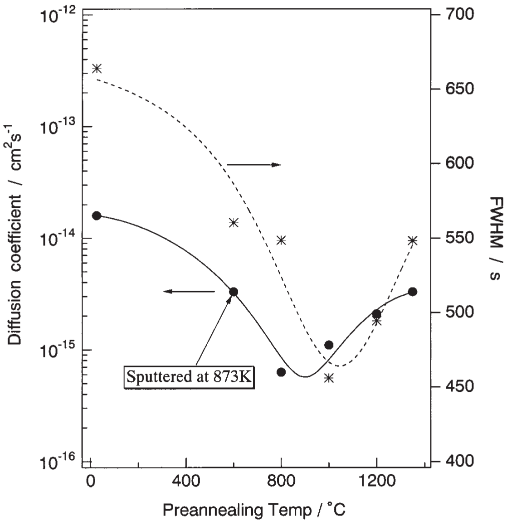

Fig. 6 Diffusion coefficients and FWHM of the X-ray rocking curve *vs.* pre-annealing temperature. Closed circles and solid line: diffusion coefficients, and stars and dashed line: FWHM, respectively

When the inter-diffusion occurred, the crystallinity was decreasing. The FWHM of the X-ray rocking curve indicates a crystallinity of sample. The results are also shown in Fig. 6. Seen in this figure, the tendency of FWHM is similar to that of the diffusion coefficient, that supports our interpretation of the increasing of the diffusion coefficient at higher pre-annealing temperatures. The annihilation mechanism of metastable oxygen defects will be discussed in other papers [13].

Conclusions

Oxygen self-diffusion coefficients in calcium titanate thin films with the perovskite structure were measured to evaluate the relative concentrations of the oxygen vacancy. The oxygen vacancy concentration is larger in few magnitude orders than that expected from the data for single crystals. Since these vacancies in the thin films were in metastable state, they were disappearing during the pre-annealing before the oxygen diffusion experiment. However, many metastable vacancies remained, after plenty annealing time.

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