Effects of dielectric film surface on oxygen diffusion

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The oxygen diffusivity in BaTiO3 thin films heteroepitaxially grown on SrTiO3 substrates was investigated using a gas/solid exchange technique with 18O-isotope-enriched gas. Deformation of the BaTiO3 lattice and inhibition of the oxygen diffusivity occurred simultaneously when the YSZ layer, which is assumed to be catalytic for the 18O/16O exchange reaction, was deposited on BaTiO3. The mechanism for the reduction in oxygen diffusivity due to the YSZ cover layer is discussed in terms of residual stress in the strained BaTiO3 layer.

Key-words : Oxygen diffusion, Secondary ion mass spectrometry, Oxygen vacancy, Dislocation, Deformation, Barium titanate, Lattice constant

1. Introduction

In recent times, thin films of perovskite-type titanate, such as (Ba, Sr)TiO3 and Pb(Zr, Ti)O3, have been extensively studied because their high dielectric permittivity, which results from their ferroelectric nature, is regarded as useful for novel applications such as nonvolatile memory, integrated passive devices, and voltage-tunable capacitors.1,2,3 Simultaneous high capacitance and low dielectric loss are absolutely necessary for thin-film capacitors (TFCs). In addition, the fatigue behavior, which currently limits both the device reliability and lifetime, also has to be improved for the utilization of perovskite-type titanate in TFCs.

As suggested by earlier studies,3,4 degradation of the dielectric properties in oxide ceramics has been attributed to electromigration of the ionized oxygen vacancies toward the cathode. These schemes appear to be reasonable, since oxygen vacancies are regarded as positively charged defects and the degradation rate is enhanced by heating or application of a direct current electrical field. In the case of TFCs, degradation induced by an electric field is more serious than it is for bulk ceramics, since the field strength in the very thin dielectric layer often exceeds 1 MV/cm (=10 V applied to 100 nm-thick films), which could induce electromigration of defects. Therefore, an understanding of defect migration in TFCs is of great importance for further development of TFCs.

In this context, we attempted to characterize the defects in TFCs by performing diffusivity measurements, as the self-diffusion coefficient at a certain temperature, Ds(T), is determined by the concentration of the defects responsible for the observed diffusion behavior. The gas-solid exchange (GSE) method using an oxygen isotope enriched gas, e.g., 18O2, is a conventional technique for evaluating oxygen diffusivity in oxides.5,6,7 In the GSE method with oxygen isotope tracers, Ds(T) is evaluated by fitting the observed oxygen isotope concentration profile, C(x, t, T), according to Eq. (1) using the so-called error function

\[
\frac{C(x, t, T) - C_{bg}}{C_s - C_{bg}} = \text{erf}(\frac{x}{\sqrt{4D_s(T) \cdot t}})
\]  

(1)

Here, C(x, t, T) is the 18O concentration at a certain depth (x) from the surface after a certain GSE reaction period (t), Cbg is the background concentration of 18O (in general, the natural abundance of 18O ≈ 0.002), and Cs is the surface concentration of 18O.8 It should also be noted that the 18O concentration (C) is defined as the abundance of 18O under an assumption that the abundance of 16O is negligibly low.

For evaluation of Ds(T) with Eq. (1), C, has to be constant (the same as the 18O concentration in the gas phase) during whole GSE treatment period. In other words, the reaction rate for oxygen molecule (O2) splitting at the sample surface must be high enough and the oxygen diffusivity has to be the rate-limiting process determining the C(x, t, T) profile. In general, the GSE treatment has to be performed at high temperature to enhance the surface reaction rate. On the other hand, performing GSE treatment at high temperature is not always appropriate for studying defect structures, since GSE treatments at overly high temperatures can lead to annihilation of the defects to be studied.9,10 This problem is particularly serious for non-equilibrium systems, since changes in the structure and concentration of defects during GSE treatment prevent us from accessing the defect structures with Eq. (1), and non-equilibrium structures relax and disappear under thermal treatment even at relatively low temperatures. Therefore, the GSE treatment must be performed at a sufficiently low temperature to keep the defect structures frozen. In our previous study, we demonstrated that covering the sample surface with a “catalytic layer” is an effective way to perform GSE treatment at a lower temperature. In fact, a very thin yttrium-stabilized zirconia (YSZ) layer formed on the sample surface worked as a catalytic layer and enabled us to measure the Ds(T) of SrTiO3 at relatively lower temperatures.11

Hence, in this study, we fabricated BaTiO3 thin films with very thin “catalytic” YSZ cover layers to study the defect structures in BaTiO3 thin films heteroepitaxially deposited on a SrTiO3 substrate. As a result, we found that the YSZ cover layer in these
structures was not a simple catalytic layer but obviously reduced the oxygen diffusivity in BaTiO3 beneath it. In this paper, we discuss the oxygen migration behavior in YSZ/BaTiO3/SrTiO3 heterostructures in terms of lattice deformation and residual stress in the BaTiO3 layer.

2. Experimental

First, 300-nm-thick BaTiO3 films were fabricated on the (100) faces of Nb-doped SrTiO3 single-crystal (SrTiO3:Nb) substrates by pulsed laser deposition (PLD). We used nominally undoped BaTiO3 ceramic targets, and an ArF excimer laser, operated at a pulse energy of approximately 1 J/cm² and at a pulse repetition frequency of 6 Hz, was used for laser ablation of the target. The pressure in the deposition chamber was kept at 2.66 Pa by introducing pure O2 gas into the deposition chamber, and the substrate temperature was kept at 873 K during deposition. Subsequently, a thin YSZ layer was deposited on the resultant BaTiO3 film by PLD as a catalytic layer to enhance \(^{18}\)O/\(^{16}\)O exchange at surface. The conditions for deposition of the YSZ layer were same as those for BaTiO3 deposition, except a YSZ target was used. The thickness of the YSZ layer was approximately 15 nm, which is suitable for GSE treatments.11) Some samples were annealed at 600°C (873 K) for 6 h in pure O2 gas (0.1 MPa) after deposition of the YSZ cover layer. Thus, we obtained three different types of samples, as listed in Table 1.

The GSE treatment was performed by heating the specimens at 573–873 K for 0.5–12 h in an \(^{18}\)O atmosphere. Here, the term "\(^{18}\)O atmosphere" denotes that enrichment with the \(^{18}\)O isotope was more than 90%. The oxygen pressure for GSE treatment was set to 0.02 MPa. The GSE experiments were performed soon after the samples were prepared. Finally, the \(^{18}\)O tracer distribution in the films was analyzed by depth profiling using a secondary ion mass spectrometer (SIMS) (IMS-4F, Cameca, France) with \(^{133}\)Cs as the primary ion beam. The SIMS beam spot covered a raster area of 100 \(\mu\)m \(\times\) 100 \(\mu\)m on the sample surface, and the analytical area was defined as 50% of this raster area using a dynamic transfer system.

The surface morphology of each deposited sample was characterized with an atomic force microscope (AFM) (MODEL MMAFM-2, digital instruments, California, U.S.A.). The chemical composition was confirmed by X-ray fluorescence (XRF) (MaggiX PRO, Philips, Eindhoven, the Netherlands), and the crystal-line structures were evaluated by X-ray diffraction (XRD) (MRD, Philips, Eindhoven, the Netherlands), and the film thickness and microstructures were evaluated with a high-resolution transmission electron microscope (HR-TEM) (JEM-2100F, JEOL, Tokyo, Japan). Thin-slice specimens for HR-TEM were prepared by mechanical polishing with abrasive papers, after which thin sections were made by low-incidence-angle Ar-ion milling (Precision Ion Polishing System (PIPS), Gatan, Inc., Pleasanton, CA).

3. Results and discussion

The obtained films were flat on the atomic scale. The typical root-mean-square roughness values were 0.87 nm for Sample-A, 0.98 nm for Sample-Z, and 0.95 nm for Sample-Za, as evaluated by AFM measurement. These results indicate that the YSZ top layer did not lead to surface roughness.

Figure 1 shows a typical depth profile of \(^{18}\)O-abundance after GSE treatment for 6 h at 873 K. Note that the \(^{18}\)O-abundance \((A)\) is defined using concentration of \(C\) and \(^{16}\)O concentration \((C')\) as Eq. (2), when we neglect concentration of very rare isotope, \(^{17}\)O. The absolute value of \(C\) and \(C'\) cannot be obtained by SIMS analyses, and the observable value using SIMS is \(A\). When we assume that total oxygen concentration \((C + C')\) in our sample is homogeneous, we can use \(A\) instead of \(C\) for diffusivity analyses.

\[
A(x, t, T) = \frac{C(x, t, T)}{C(x, t, T) + C'(x, t, T)}
\] (2)

In this figure, the origin of the depth scale \((x = 0)\) was set as the BaTiO3 surface for Sample-A and as the YSZ/BaTiO3 interface for the other samples. First, we focus on \(^{18}\)O abundance at \(x = 0\) \((A_0)\) to see whether YSZ layer worked as expected as a catalytic layer. The \(^{18}\)O-abundance profiles of Samples-Z and Za show that the YSZ layer actually worked as catalytic layer, since \(A_0\) for these samples with YSZ cover layer was close to 1.0. For the sample without the YSZ layer (Sample-A), the value of \(A_0\) was also close to 1.0. These results show that both the naked BaTiO3 surface and the surface covered by YSZ had sufficiently high reactivity for the \(^{18}\)O/\(^{16}\)O exchange reaction. Therefore, the GSE conditions employed in this study are useful for investigating the oxygen diffusivity in the heteroepitaxial BaTiO3 films. Although the catalytic YSZ layer was needed for diffusivity study on SrTiO3 in the previous GSE study, catalytic layer was not essentially necessary for GSE study for BaTiO3 prepared in this study. However, the diffusivity in the film with and without YSZ cover layer was significantly different as described below.

Now, we focus on the depth profiles of the \(^{18}\)O-abundance. In Sample-A, the \(^{18}\)O-abundance was nearly constant at around 1.0 over the whole depth range. This means that \(D_0(873 \text{ K})\) was very high in the as-deposited BaTiO3 films in this study. This behavior confirms that the reactivity of the naked BaTiO3 surface for \(^{18}\)O/\(^{16}\)O exchange was sufficiently high, because almost all \(^{16}\)O was replaced by \(^{18}\)O within the limited time. In contrast, the \(^{18}\)O-abundance in BaTiO3 layer of Sample-Z steeply decreased with depth, and the \(^{18}\)O-abundance in the deeper part was close to the natural abundance of \(^{18}\)O \((\approx 0.002)\). These results mean that the oxygen diffusivity in Sample-Z was very slow compared with

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Table 1. Sample preparation conditions and identifications

| Sample ID | YSZ cover layer | Annealing at 600°C in pure O2 gas |
|-----------|-----------------|----------------------------------|
| Sample-A  | No              | No                               |
| Sample-Z  | Yes             | No                               |
| Sample-Za | Yes             | Yes                              |

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![Figure 1](image-url)
that in Sample-A and indicates that the formation of the YSZ layer affected the oxygen diffusion behavior in the BaTiO3 layer beneath it.

Comparison of Sample-Za with Sample-Z indicates that the very slow oxygen diffusivity in Sample-Z was not simply due to the presence of the YSZ cover layer. In fact, the 18O-abundance was very high even in the deeper part of Sample-Za, indicating that the diffusivity in Sample-Za was much faster than that in Sample-Z. Therefore, it can be presumed that formation of the YSZ layer induced a specific film structure in which the oxygen diffusivity was reduced. This comparison also indicates that the low-diffusivity structure was relaxed by annealing in O2 gas.

Figures 2(a) and 2(b) show cross-sectional HR-TEM images of the BaTiO3/SrTiO3Nb interface regions of Sample-A and Sample-Z. First, these HR-TEM observations confirm that BaTiO3 films were epitaxially grown on the SrTiO3Nb substrates. In addition, these images indicate that the in-plane lattice misfit between BaTiO3 and SrTiO3 (about 3%) resulted in the formation of many dislocations. Assuming that thickness of the sample slices for HR-TEM observation was approximately 50 nm, the average dislocation densities of Sample-A and Sample-Z were estimated to be $7.2 \times 10^{14}$ and $7.6 \times 10^{14}$ m$^{-2}$, respectively. These results indicate that there were no noticeable differences between Sample-A and Sample-Z in terms of the dislocation density. In general, dislocation pipes act as fast mass transport paths because of their irregular structure and low density. However, because Samples-A and Z were similar from the viewpoint of dislocation density, the difference in diffusion behavior between Samples-A and Z cannot be explained in terms of the dislocation density. As the 18O-abundance in the deeper part of Sample-Z was close to the natural abundance of 18O, as mentioned above, the dislocations found in HR-TEM images cannot actually be fast diffusion paths for oxygen in these samples.

It is also noteworthy that the deposition of the YSZ cover layer did not lead to incorporation of extrinsic elements into the BaTiO3 films. In fact, as shown in Fig. 3, the YSZ/BaTiO3 interface was well defined in the composition profile, and no clear evidence for any reaction occurring between the YSZ and BaTiO3 lattice was found. The results in this figure indicate that the thickness of the interfacial layer was less than 5 nm from the viewpoint of the concentration distributions of Y and Z at the interface. Thus, it is clear that the difference in the oxygen diffusion behavior between Sample-A and Sample-Z did not originate from diffusion of extrinsic elements.

Figures 4(a)–4(c) show reciprocal space maps for the asymmetric (303) reflection. In these maps, the horizontal axes correspond to the reciprocal lattice parameter for the out-of-plane axis ($c^*$), and the vertical ones correspond to that of the in-plane axis ($a^*$). The measure of reciprocal space is defined by Eq. (3.a) using wavelength of X-ray ($\lambda$) used for diffraction measurement and real space d-spacing ($d$). As the Cu-Ka radiation ($\lambda = 0.15405$ nm) was used for this measurement and the diffraction spots shown in Fig. 4 are indexed as (303) spots, lattice parameter of a-axis and c-axis of the sample can be determined from these results using Eqs. (3.b) and (3.c).

$$a = \frac{\lambda}{2d}$$

$$a$-parameter = 3 \times d_{300} = 3 \times \frac{\lambda}{2 \times a_{300}^*} = \frac{\lambda}{(0.15405 \text{ nm})}$$

$$c$-parameter = 3 \times d_{003} = 3 \times \frac{\lambda}{2 \times c_{303}^*} = \frac{\lambda}{(0.15405 \text{ nm})}$$

Since the (303) spots of both BaTiO3 and SrTiO3 were found on the same reciprocal plane, it is evident that the BaTiO3 films were epitaxially grown on the (100) SrTiO3 substrate. Here, the positions of the spots for SrTiO3 were different from those for SrTiO3 in both the $a^*$ (in-plane) and $c^*$ (out-of-plane) directions. The disagreement between the in-plane lattice parameters ($a_0$) of SrTiO3 and BaTiO3 means that the $a_0$ of BaTiO3 was different from that of SrTiO3, suggesting that the BaTiO3 lattice was not completely restricted by that of SrTiO3. This result is consistent...
it is clear that the lattice parameters of BaTiO3 in Samples-A and introduced by the YSZ cover layer was relaxed by annealing.

presence of the YSZ cover layer, since the lattice deformation lattice parameter could not have been simply determined by the induced by the formation of the YSZ cover layer. However, the broad diffraction spot is not a well-defined measure of the crystallinity of BaTiO3 films in this study. The diffraction spots for the SrTiO3:Nb substrate show splitting and diffusion due to mosaic structures formed in SrTiO3:Nb substrate. This mosaic structure of the substrates should be reproduced by the films deposited on them. Therefore, we cannot analyze the shapes of the diffraction spots of BaTiO3 here, and our discussion is confined only to the lattice parameters.

In the literature, there are many reports of increases in the lattice parameters of oxides due to the introduction of non-stoichiometry. Thus, it is reasonable to assume that the expanded lattice parameter of BaTiO3 in Sample-Z was due to oxygen deficiency. Thus, we have to explain why deposition of the YSZ layer on the BaTiO3 layer induced oxygen deficiency in BaTiO3. Recently, some studies focusing on the oxidation reaction during the PLD process have suggested that the growing films were sometimes oxidized by extraction of oxygen from the oxide substrate. In the PLD process, the composition of fragment arriving at the substrate surface is not always the same as the composition of the oxide target, and an additional oxygen source is needed to crystallize a film with the same composition as the target.

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Under this assumption, we next discuss why the oxygen diffusivity in the BaTiO3 layer of Sample-Z was significantly slower than that in the other two samples. At the present stage, we are not able to quantitatively discuss the oxygen diffusion mechanism, because the diffusivity in Sample A was too fast to measure precisely. Thus, we discuss the possible mechanism qualitatively.

Diffusivity is a product of the density of the defects responsible for the diffusion behavior and their hopping rate. Since oxygen vacancies are the dominant defects in oxygen-deficient BaTiO3 and are the major players in the oxygen diffusion behavior, it is reasonable to suggest that the oxygen diffusivity of BaTiO3 should be simply determined by the density of oxygen vacancies. Indeed, post-deposition annealing at 600°C in pure O2 gas suppressed 18O tracer diffusivity of sample-A (not shown), indicating that annihilation of oxygen defect by annealing resulted in relatively low oxygen diffusivity. However, the results obtained in this study suggest that the concentration of oxygen vacancies in Sample-Z, the sample with the lowest oxygen diffusivity, was very high compared to those of the other samples. Consequently, the oxygen vacancy hopping rate must have been lowered in Sample-Z.

The most probable reason for the lowered hopping rate is lattice deformation, as illustrated in Fig. 5. The change in the

Fig. 4. Reciprocal space map for the asymmetric (303) reflection for (a) Sample-A, with the BaTiO3/SrTiO3 structure, (b) Sample-Z, with the YSZ/BaTiO3/SrTiO3 structure, as-prepared, and (c) Sample-Za, with the YSZ/BaTiO3/SrTiO3 structure, after annealing in O2 gas. The c* and c axes correspond to the reciprocal lattice parameters for the in-plane and out-of-plane axes, respectively, and the dashed lines shown here are guides for eyes.

with the HR-TEM images, where the formation of misfit dislocations resulting from lattice relaxation was observed. The out-of-plane parameter (c0) of BaTiO3 was larger than a0 in all samples, indicating that BaTiO3 had tetragonal symmetry.

A noticeable difference between Sample-A and Sample-Z was found in the c0 of BaTiO3. In fact, the reciprocal space mapping indicated that the c0-parameter of BaTiO3 in Sample-Z was much larger than that of Sample-A. This lattice expansion was likely induced by the formation of the YSZ cover layer. However, the lattice parameter could not have been simply determined by the presence of the YSZ cover layer, since the lattice deformation introduced by the YSZ cover layer was relaxed by annealing. From the comparison between Fig. 4(c) and Figs. 4(a) and 4(b), it is clear that the lattice parameters of BaTiO3 in Samples-A and Za were nearly identical, while the lattice parameters of BaTiO3 in Sample-Z were different. Since both Samples-Z and Za had YSZ cover layers on top, it is clear that the expansion of the c0-parameter of BaTiO3 in Sample-Z was not simply due to the presence of YSZ layer, and must instead be due to specific structures existing only in the as-deposited film with the YSZ cover layer.

The broadening of the diffraction spots shown in these figures should also be discussed. In general, the full-width-at-half-maximum (FWHM) of the diffraction spot is a measure of the crystallinity, and streak patterns are a good indication of lattice strain. However, the broad diffraction spot is not a well-defined measure of the crystallinity of BaTiO3 films in this study. The diffraction spots for the SrTiO3:Nb substrate show splitting and diffusion due to mosaic structures formed in SrTiO3:Nb substrate. This mosaic structure of the substrates should be reproduced by the films deposited on them. Therefore, we cannot analyze the shapes of the diffraction spots of BaTiO3 here, and our discussion is confined only to the lattice parameters.
lattice parameter observed in Sample-Z is likely due to the introduction of oxygen deficiency. In particular, formation of oxygen vacancies by deposition of YSZ is the most reasonable explanation for the lattice expansion observed in Sample-Z. Because the lattice is restricted by the structure of the substrate, the lattice expansion of Sample-Z appeared as uniaxial strain, not as isotropic strain, in contrast to sample-A with isotropic strain. As a result, the in-plane lattice parameters of BaTiO3 in Samples-A, Z, and Za were nearly the same, although the out-of-plane lattice parameter was changed by the presence of the YSZ cover layer. In fact, the BaTiO3 in Sample-Z was likely under compression stress to maintain in-plane lattice parameter of Sample-A. Absolutely, the model described in Fig. 5 is a schematic illustration for visualizing our points. Further study, such as evaluation of migration barrier in strained BaTiO3 using molecular dynamics simulation, is necessary to obtain further clear and quantitative discussion on oxygen migration behavior.

Comparison of this study and our previous study11 supports our conclusion. In our previous study, we investigated the oxygen diffusivity in SrTiO3 homoepitaxially deposited on a SrTiO3 substrate. In that study, the oxygen diffusivity was found to be a function of cation non-stoichiometry, i.e., the Sr/Ti ratio, in the films, although the YSZ cover layer acted as a catalytic layer enhancing the 18O/16O exchange reaction. On the other hand, this study revealed that the lattice strain and residual stress are the primary parameters governing the oxygen diffusivity in heteroepitaxial BaTiO3 films. The apparent difference between our present study on BaTiO3 and our previous study on SrTiO3 is likely due to the difference between the film structures, i.e., the heteroepitaxy with lattice mismatch and homoepitaxy without lattice mismatch at the interface. The lattice mismatch at the interface is an important origin of the variation in oxygen migration behavior in the BaTiO3 films prepared in this study.

As described above, stress and strain likely have huge impacts on the oxygen migration behavior in BaTiO3, and it is important to manage the mass transport in BaTiO3 when the material properties can be degraded by migration of defects and impurities. The possibility of the inhibiting the oxygen vacancy migration by introducing stress and strain found in this study will likely be very important for further development of TFCs.

4. Conclusions

The oxygen diffusivity in BaTiO3 heteroepitaxial films deposited on a SrTiO3:Nb substrate was studied using the GSE method with a YSZ cover layer as a catalyst to enhance the 18O/16O isotope exchange rate at relatively low temperature. The oxygen diffusivity of the BaTiO3 with the YSZ cover layer was very slow compared to that of the BaTiO3 without the YSZ cover layer. Characterization of the BaTiO3 structure revealed that the BaTiO3 lattice with the YSZ cover layer had expanded in the out-of-plane direction, and the dependence of the lattice parameter of the resultant BaTiO3 on the annealing conditions indicated that deposition of the YSZ cover layer induced oxygen vacancies in the BaTiO3 lattice. From these results, we concluded that the BaTiO3 with the YSZ cover layer showed very slow oxygen diffusivity because of the increased oxygen migration barrier resulting from the lattice strain and residual stress. That means that oxygen diffusion in strained BaTiO3 was inhibited in spite of the high oxygen vacancy concentration. These results indicate that management of the lattice strain and residual stress in BaTiO3 will be very important for designing of TFC devices with extended lifetimes, because these parameters are correlated with the mass transport properties.

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