Diffusion behavior of Ag electrodes into (Bi$_{1/2}$Na$_{1/2}$)TiO$_3$ ceramics

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The diffusion of silver, Ag, as the electrode material in (Bi$_{1/2}$Na$_{1/2}$)TiO$_3$ (BNT) ceramic was studied by means of a secondary ion mass spectrometry (SIMS). The Ag diffusion along the grain boundary was confirmed. The diffusion coefficient of Ag in BNT is almost equal to that of Pb-based ceramics. The intergranular fracture is considered to be associated with the grain boundary diffusion of Ag. The apparent diffusion coefficients of Ag were obtained using SEM images of cross sections after Ag diffusion. The temperature dependence of Ag apparent diffusion in BNT ceramics was described by 2.3 x 10$^{-3}$ cm$^2$/s of pre-exponential factor and 132.2 kJ/mol of the activation energy in the temperature range of 700–900°C as diffusion treatment.

Key-words : Lead-free piezoelectric ceramics, Ag, Electrode, Diffusion, SIMS, Perovskite

1. Introduction

Perovskite piezoelectric ceramics Pb(Zr,Ti)O$_3$ (PZT) have dominated the commercial market for electromechanical devices because of their superior properties.1,2,3 However, lead-free materials have recently been demanded from the viewpoint of environmental protection and enforcement of the legislation such as the Restriction of Hazardous Substances (RoHS).4 In particular, actuators and high power piezoelectric applications have a large market in piezoelectric devices; thus, the development of lead-free piezoelectric materials is strongly demanded in these fields. As the lead-free piezoelectric candidates various perovskite-structured ferroelectrics, such as BaTiO$_3$ (BT), (Bi$_{1/2}$K$_{1/2}$)$_2$TiO$_3$ (BKT), (Bi$_{1/2}$Na$_{1/2}$)$_2$TiO$_3$ (BNT), (K,Na)NbO$_3$ (KNN), and (Bi$_{1/2}$Na$_{1/2}$)$_2$TiO$_3$ (BNT)-based solid solutions, have recently been actively studied.5–18 BNT ceramics are expected to be one of the superior candidates for lead-free piezoelectric materials owing to their friendly for current manufacturing process, low materials cost, and relatively high piezoelectric properties.11–18 In particular, BNT-based ceramics are an excellent high-power piezoelectric properties with low mechanical losses for ultrasonic applications.19 However, piezoelectric strain constant $d_{33}$ values are still not as large as those of PZT. To cover the low $d_{33}$ values of BNT, it is generally considered that a multilayer structure is very effective for actuator and high power applications because the total displacement can be increased proportionally to the layer number of the multilayer structure.

Kawada et al. demonstrated the fabrications of multilayer ceramic actuators (MLCAs) using lead-free piezoelectric ceramics, (K,Na)NbO$_3$-based ceramics and Nichel inner electrode, which showed excellent piezoelectric properties.20 However, in the case of Bi-based compounds, basically, MLCAs could not be fabricated using the base-metal electrodes such as Ni. This is because, according to the Ellingham diagram,21 the pO$_2$ level of Bi/NiO is located in the range of 10$^{-10}$–10$^{-12}$ atm, that is higher than that of Ni/NiO in all temperature range. In other words, Bi-based oxides are easier to be reduced than nickel electrode, then, Bi-based oxides cannot be sintered in a reducing atmosphere which does not oxidize nickel. Therefore, we need to use precious metals such as Au, Pt, Ag, and Ag–Pd for Bi-based MLCAs. We demonstrated MLCAs using (Bi$_{1/2}$Na$_{1/2}$)$_2$TiO$_3$ (BNT)-based ceramics as the active layers and Pt electrodes as the inner electrodes.22 Then, the prototype of BNT-based actuator indicated a large displacement, and we could not observe any apparent delamination around the interface between Pt electrodes and active layers. Normally, the Ag–Pd electrodes have been widely used for the PZT-based MLCAs, considering cost efficiency. Nguyen et al. tried to fabricate MLCAs using (Bi$_{1/2}$Na$_{1/2}$)$_2$TiO$_3$ (BNT)-based ceramics as the active layers and Ag–Pd electrodes as the inner electrodes.23 When the co-firing temperature was approximately 1100–1130°C, the Ag–Pd electrodes were not perfectly active and electrical properties of the MCLA were deteriorated as compared with those of bulk ceramics. As the other example, we demonstrated MLCAs using BKT as active piezoelectric layers and Ag–Pd (7:3) as inner electrode.24 When they were co-fired at a high temperature over 1050°C for long time, the internal electrodes in BKT-based MCLA were almost disappeared. From these reports, interfacial behaviors such as diffusion and reaction between piezoelectric active layers and electrodes are quite important and essential to obtain their performance fully. Previously, diffusion behavior of Ag as the electrode material in BKT ceramics were studied.25 Activation energy of Ag in BKT was almost equal to that in Pb-based ceramics, so that, the diffusion mechanism seemed to be the same each other. However, the diffusion path of Ag in BKT has not been clear because of the small grain size (<1 μm) in that study.25 Therefore, in this study, we selected BNT ceramics as a large grain size (<15 μm). The purpose of this study is to evaluate the diffusion behavior of Ag such as the volume and grain boundary diffusion in BNT. And then, we compare these data with those of Pb-based ceramics.

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2. Experimental procedure

Ceramic samples of (Bi_{1/2}Na_{1/2})TiO_3 (BNT) were prepared by a conventional solid-state reaction. Reagent-grade oxide of Bi_2O_3, Na_2CO_3, TiO_2 with 99.6% purity were used as the starting materials. These materials were mixed by ball milling and calcined at 850°C for 2h. After calcining, the ground and ball-milled powders were pressed into 20 mm in diameter and about 10 mm in thickness. The final sintering was carried out by an ordinary firing method at 1140°C for 2h in an alumina crucible in air. The crystal structures and lattice constants of the sintered ceramics were determined using an X-ray diffractometer (Rigaku; RINT2000). These ceramics were cut and polished for various physical and electrical measurements. For the obtained ceramics, densities were measured by the Archimedes method and microstructures were observed by scanning electron microscopy (SEM: Hitachi S-2400).

Sintered bodies were cut into test pieces of 4 × 4 × 2 mm³. Sample surface was polished and finished by several grade diamond pastes, to get a mirror plane. And then, silver electrode (H-4580, SHOEI CHEMICAL INC.) was coated on single surfaces. Samples with Ag electrodes were heated at the specified temperature for various time as diffusion annealing (800°C for 3h, 850°C for 2h and 900°C for 1h).

Ag diffusion profiles and ion images in BNT ceramic were acquired by secondary ion mass spectrometry (SIMS; CAMECA IMS-4f). The samples after the diffusion annealing were modified to observe the cross section. Gold 40 nm thick was deposited to maintain the uniform electric field of sample surfaces prior to analysis. A normal induced electron gun was used to prevent charge-up by primary ion irradiation. In measurement, ¹³³Cs⁺ accelerated with a voltage of 10 kV was used as a primary ion and was irradiated to the sample surface. The intensity of ¹⁰⁷Ag⁺, TiO⁻ was measured as secondary ions sputtered by primary ions.

Ag diffusion profiles were obtained by the step scan method using spot primary beam. The step scan method was applied to obtain the diffusion profiles in deeper side up to 300 micron. Details of the experimental set-up for the Ag diffusion measurements are described elsewhere. Intensity profiles of ¹⁰⁷Ag⁺ and TiO⁻ were obtained. To evaluate the diffusion coefficient D, the observed profiles were fitted to the diffusion equation. The equation was a solution to the diffusion equation obtained by assuming a constant concentration of ¹⁰⁷Ag⁺ at the sample surface and diffusion in a semi-infinite medium.

3. Results and discussion

The BNT ceramics showed a single phase perovskite structure with rhombohedral symmetry from the XRD measurement. The relative density ratio of observed density over theoretical one was 99.6% in BNT ceramic. Figure 1 shows SEM microstructures of prepared BNT ceramic. This picture showed homogeneous and pore less microstructure. Average grain size for BNT ceramic was approximately 13 μm. The grain size of BNT is much larger than that of BKT. It is expected that the diffusion path could be distinguished to volume diffusion and grain boundary diffusion. The resistivities of samples were the order of 10¹¹Ω cm. From these measurements, fabricated samples in this study indicated almost similar properties as compared with the previous reports.

The Ag profile obtained by step scan method was shown in Fig. 2. In this figure, the fitted curve from the diffusion equation was also shown. The obtained diffusion coefficient of Ag at 900°C for 1h was 9.1 × 10⁻⁹ cm²/s. Other samples analyzed by using the same methods indicated similar diffusion coefficients of Ag. As compared with the grain boundary diffusion coefficient for Pb-based ceramics, these values are nearly the same order of magnitude. However, it was difficult for us to obtain the Arrhenius plot and equation from these diffusion coefficients. It is because we can not distinguish between volume and grain boundary diffusion due to the limitation of space resolution in our experimental set-up of SIMS. To solve this problem, we need to wait further analysis by using nano-SIMS for example. Figure 3 shows the ¹⁰⁷Ag⁺ image in BNT ceramic annealed at 900°C for 1h.
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1 h as silver diffusion annealing. In image in Fig. 3, the interface between Ag electrode and BNT ceramics was clearly observed. Figure 3 shows that the Ag diffuses into the sample from the surface and moves rapidly through the grain boundary. In this figure, volume diffusion was hardly observed, and it was clarified that the grain boundary plays a role as high diffusion path. As compared with BKT, the diffusion path of Ag into BNT was revealed.25) That is considered because the grain size of BNT is larger than that of BKT.

Figure 4 shows a SEM micrograph of the fracture surface of BNT after Ag diffusion. In this figure, the region of silver paste at the top, that of intergranular fracture under the electrode interface, and that of transgranular fracture beneath it, clearly showing separation into the region of intergranular and transgranular fracture. To find out whether this fracture was caused by Ag diffusion, fracture processes were observed by changing the temperature of Ag diffusion. The diffusion coefficient ($D_{Ag}$) was obtained from the depth ($x$) of the region of intergranular fracture from the sample surface by using $x = 2\sqrt{D_{Ag}t}$. This diffusion coefficient is an apparent diffusion coefficient ($D_{Ag}$) in terms of using $x = 2\sqrt{D_{Ag}t}$, where $x$ is the diffusion length, $D$ is the apparent diffusion coefficient, and $t$ is the annealing time. The diffusion coefficients were summarized as a function of reciprocal temperature, and result is shown in Fig. 5. The temperature dependence of $D_{Ag}$ was written by the Arrhenius equation, $D = D_0 \exp(-E_a/RT)$, where $D_0$, $E_a$, $B$, and $T$ are the pre-exponential factor, activation energy, gas constant, and annealing temperature, respectively. The temperature dependence of Ag apparent diffusion in BNT ceramic was described by $D_0 = 2.3 \times 10^{-3}$ cm$^2$/s of pre-exponential factor and $E_a = 132.2$ kJ/mol of the activation energy.

The activation energy of the apparent diffusion in BNT is almost equal to that in PZT, so that, the diffusion mechanism seems to be the same.29) These result agree well considering the precision of the experiment, probably due to the intergranular fracture of BNT in Fig. 4 being caused by the grain boundary diffusion of Ag.

4. Conclusions

Diffusion behavior of silver, Ag, as the electrode material in dense (Bi0.5Na0.5)TiO3 (BNT) ceramic was studied by means of a secondary ion mass spectrometry (SIMS). The Ag diffusion along the grain boundary was confirmed. The grain boundary diffusion of Ag exerted a great influence on the physical and chemical strength of the grain boundaries of BNT ceramics, proving that grain boundaries had an important function in the interfacial behaviors of electrodes. The diffusion coefficient for BNT ceramics and the grain boundary diffusion coefficient for Pb-based ceramics are nearly the same order of magnitude.29) Apparent diffusion coefficient of Ag in BNT ceramics were obtained. The temperature dependence of Ag in BNT was written by $2.3 \times 10^{-3}$ of pre-exponential factor and 132.2 kJ/mol of activation energy. The activation energy of the apparent diffusion in BNT is almost equal to that in PZT, so that, the diffusion mechanism seems to be the same.29)

References