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

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The diffusion of silver, Ag, as the electrode material in $(\text{Bi}_{1/2}\text{K}_{1/2})\text{TiO}_3$ (BKT) ceramic were studied by means of a secondary ion mass spectrometry (SIMS). Some analytical methods of SIMS were applied to obtain Ag diffusion coefficient in BKT ceramics. Depth profile of Ag showed a simple concentration gradient from the surface towards the deeper side in BKT ceramics. From these profiles, the diffusion coefficients of Ag were calculated and obtained by the analysis. The temperature dependence of Ag diffusion in BKT ceramics was described by $2.2 \times 10^6 \text{ cm}^2/\text{s}$ of pre-exponential factor and 296 kJ/mol of the activation energy in the temperature range of 700–900°C as diffusion treatments.

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

[Received January 31, 2015; Accepted May 22, 2015]

1. Introduction

Piezoelectric materials play an important role in electrical devices, such as actuators, piezoelectric motors, transducers, filters, and resonators. Most piezoelectric devices are composed of $\text{Pb}(\text{Zr},\text{Ti})\text{O}_3$ (PZT)-based piezoelectric ceramics because of their excellent properties.^{1),2)} However, PZT ceramics contain a large amount of PbO; therefore, lead-free piezoelectric materials are required from the viewpoint of environmental protection. Bismuth potassium titanate, $(\text{Bi}_{1/2}\text{K}_{1/2})\text{TiO}_3$ (BKT), is a typical ferroelectric material with a perovskite structure of tetragonal symmetry at room temperature (RT) and a relatively high Curie temperature T_c of 380°C.^{3)–6)} Additionally, BKT has a relatively high piezoelectric strain constant $d_{33} = 100 \text{ pC/N}$ from resonance method and normalized $d_{33}^* = 122 \text{ pm/V}$ from the measurement of field-induced strain.^{7)–12)} Therefore, BKT has attracted attention as a candidate of the lead-free piezoelectric actuators with wide working temperature range. However, it is not enough to use for practical actuators due to low d_{33} values.

To compensate for the low d_{33} values of BKT-based ceramics, it is generally considered that a multilayer structure is very effective for actuator 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, $(\text{K},\text{Na})\text{NbO}_3$ -based ceramics and Ni inner electrode, which showed excellent piezoelectric properties.¹³⁾ However, in the case of Bi-based compounds, basically, MLCAs could not be fabricated using the base-metal electrodes such as Ni in accordance with the Ellingham diagram. Therefore, we need to use precious metals such as Au, Pt, Ag, and Ag–Pd for Bi-based MLCA. Normally, the Ag–Pd electrodes have been widely used for the PZT-based MLCAs, considering cost efficiency. So we

demonstrated MLCAs using BKT as active piezoelectric layers and Ag–Pd (7:3) as inner electrode.¹⁴⁾ Then, the prototype of BKT-based actuator was co-fired with Ag–Pd (7:3) electrodes at 1045°C, and indicated good field induced strain behavior. Thus, the prototype was confirmed that it could effectively work as the actuator. On the other hand, the internal electrodes in BKT-based MLCA were almost disappeared when they were co-fired at a high temperature over 1050°C for long time.¹⁴⁾ As the other example, Nguyen et al. tried to fabricate MLCA using $(\text{Bi}_{1/2}\text{Na}_{1/2})\text{TiO}_3$ (BNT)-based ceramics as the active layers and Ag–Pd electrodes as the inner electrodes.¹⁵⁾ When the co-firing temperature was approximately 1100–1130°C, the Ag–Pd electrodes were not perfectly active and electrical properties of the MLCA were deteriorated as compared with those of bulk ceramics.¹⁵⁾ 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. Therefore, in this study, we tried to evaluate the diffusion behavior of silver into BKT ceramics as the preliminary work.

2. Experimental procedure

Ceramic samples of $(\text{Bi}_{1/2}\text{K}_{1/2})\text{TiO}_3$ (BKT) were prepared by a conventional solid-state reaction. Details for the fabricating procedure are described in elsewhere.¹⁰⁾ The final sintering was carried out by an ordinary firing method at 1050°C for 20 h 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 $4 \times 4 \times 2 \text{ mm}^3$. 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 (700°C for 6 h, 800°C for 3 h, 850°C for 2 h and 900°C for 1 h).

Depth profiles of silver in BKT ceramic were analyzed by

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[‡] This article was selected from the presentations at "STAC-8" (The 8th International Conference on the Science and Technology for Advanced Ceramics) held in Yokohama, Japan (2014), through the regular reviewing procedure.

Fig. 1. Sample modification for the analysis.

Fig. 2. SEM image of BKT ceramic.

secondary ion mass spectrometry (SIMS; CAMECA IMS-4f). The samples after the diffusion annealing were modified to observe the cross section as shown in Fig. 1. Gold 20 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.¹⁶⁾ In measurement, $^{133}\text{Cs}^+$ accelerated to 10 kV was used for primary ions. The intensity of $^{107}\text{Ag}^-$, TiO^- was measured as secondary ions sputtered by primary ions.

Silver diffusion profiles were obtained by two analytical methods such as the line analysis in high-resolution image and the step scan using spot primary beam. First, we try to get Ag profiles by the line analysis in ion images near the sample surface. The illustration was shown in Fig. 1(c). From this method, depth profiles in the area less than 100 micron can be obtained. Second, step scan method was applied to obtain the diffusion profiles in deeper side up to 500 micron. Before the step scan analysis, the several craters were formed by the primary beam, to remove Ag contamination during the polishing. The step scan analysis was carried out the bottom of craters as shown in Fig. 1(c). Intensity profiles of $^{107}\text{Ag}^-$ and TiO^- were obtained. To evaluate the diffusion coefficient D , the observed profile was fitted to the diffusion equation. The equation was a solution to the diffusion equation obtained by assuming a constant concentration of $^{107}\text{Ag}^-$ at the sample surface and diffusion in a semi-infinite medium.¹⁷⁾

3. Results and discussion

The BKT ceramics showed a single phase perovskite structure with tetragonal symmetry from the XRD measurement. From the calculation of lattice parameters, a lattice anisotropy c/a was 1.017, which is almost consistent with the previous papers.^{3)–6)} The relative density ratio of observed density over theoretical one was 97.9% in BKT ceramic. Figure 2 shows SEM microstructures of prepared BKT ceramic. This picture showed homogeneous and pore less microstructure. Average grain size for BKT ceramic was approximately 0.5 μm. The resistivities of samples were the order of $10^{11} \Omega\cdot\text{cm}$. From these measurements, fabricated samples in this study indicated almost similar properties as compared with the previous reports.^{7)–9)}

Figure 3 shows the $^{107}\text{Ag}^-$ and TiO^- images and line profile obtained from images in BKT ceramic annealed at 850°C for 2 h as silver diffusion annealing. In images in Figs. 3(a) and 3(b),

Fig. 3. High resolution images of (a) $^{107}\text{Ag}^-$ and (b) TiO^- , and (c) line profile from L1 of $^{107}\text{Ag}^-$ and TiO^- in BKT ceramics after diffusion-annealing at 850°C for 2 h.

Fig. 4. SIMS depth profiles on step scanning mode after diffusion-annealing at 850°C for 2 h.

the interface of Ag electrode and BKT ceramics were clearly observed. The line analysis was carried out along L1 in the images. The intensity profiles of $^{107}\text{Ag}^-$ and TiO^- were shown in Fig. 3(c). Ag in BKT ceramics showed the weak intensity and the constant values. From the result, it is unclear Ag diffusion in BKT ceramics. One possible reason is that Ag is fast diffusion species in BKT ceramics. So, we applied the step scan method to judge Ag diffusion in BKT ceramics. The Ag profile obtained by step scan method was shown in Fig. 4. In this figure, Ag has a long diffusion length in BKT ceramics, and is the fast diffusion species. In this figure, the fitted curve from the diffusion equation was also shown. The obtained diffusion coefficient of Ag at 850°C for 2 h was $3 \times 10^{-8} \text{ cm}^2/\text{s}$. Other samples were analyzed by above methods, to obtain the diffusion coefficient of Ag. The diffusion coefficients were summarized as a function of reciprocal temperature, and result is shown in Fig. 5. The temperature dependence of Ag diffusion in BKT ceramics was described as:

Fig. 5. Arrhenius plots of diffusion coefficient of $^{107}\text{Ag}^+$ in BKT.

$$D = 2.2 \times 10^6 \exp [-(296) (\text{kJ} \cdot \text{mol}^{-1})/RT] (\text{cm}^2 \cdot \text{s}^{-1})$$

The diffusion path of Ag in BKT ceramics is unclear in this study, because Ag diffusion profile is a simple character. In order to explain above feature, two possible diffusion paths are considered from the diffusion category.¹⁸⁾ One is that Ag diffuses in lattice in BKT. Another is that Ag diffusion occurs along the grain boundaries in BKT ceramics. This problem remains at this time, and then D values above would be called apparent diffusion coefficients.

Some studies on silver electrode diffusion had been under way in some Pb-based perovskite compounds.^{19)–21)} According Ling, silver as an electrode component diffuses and penetrates about 5 μm deep from the interfaces of $\text{Pb}(\text{Mg}_{1/3}\text{Nb}_{2/3})\text{O}_3$ ceramics annealed 800°C for 10 h.¹⁹⁾ The concentration is quite low, and the distribution of silver concentration in depth was not measured in this study. Slinkina et al. reported that silver diffuses and penetrates at least 100 μm deep from the electrode into $\text{Pb}_{0.95}\text{Sr}_{0.05}(\text{Zr}_{0.53}\text{Ti}_{0.47})\text{O}_3 + 1 \text{ mol } \% \text{ Nb}_2\text{O}_5$ (PZTN) ceramics and also reported diffusion coefficients D of silver.²⁰⁾ For example, observed D value at the temperature 750°C was $5 \times 10^{-7} \text{ cm}^2/\text{s}$, which is approximately 2 orders of magnitude higher than that in BKT at the same annealing temperature. Considering to their measurement technique,²⁰⁾ their D values are also apparent diffusion coefficients and then comparable to our results.

4. Conclusions

Diffusion behavior of silver, Ag, as the electrode material in

dense $(\text{Bi}_{1/2}\text{K}_{1/2})\text{TiO}_3$ (BKT) ceramic were studied by means of a secondary ion mass spectrometry (SIMS). Ag diffusion profiles showed a simple concentration gradient in BKT ceramics. So, apparent diffusion coefficients of Ag were obtained. The temperature dependence of Ag in BKT was written by 2.2×10^6 of pre-exponential factor and 296 kJ/mol of activation energy. At this time, Ag diffusion path in BKT ceramics is unclear. Next study, we would like to focus on the Ag distribution in BKT ceramics.

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