Reaction and Diffusion between PLZT Ceramics and Ag Electrode

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Diffusion properties of silver in PLZT were studied by means of a secondary ion mass spectrometry (SIMS). Diffusion profiles of silver ion were composed of two parts. The silver ion rapidly decreased near the surface, that showed a volume diffusion contribution. At inner part, the silver ion decreased very slowly due to a grain boundary diffusion. The sample with silver electrode has a tendency of a intergranular fracture, that is considered to be associated with the grain boundary diffusion of silver.

1. INTRODUCTION

Ferroelectric ceramics of lead-perovskite system are widely used as the ceramic capacitors, actuators and so on. Recently, application of those materials to a ferroelectric RAM and a replacement of SiO_2 in DRAM capacitor are extensively tried. These still remains some problems such as leakage current, fatigue, electrical breakdown, decrease of mechanical strength and so on for practical applications. To solve them, interaction between ferroelectric materials and electrodes must be studied. Especially, these problems are in close relation with reactions at interface and diffusion behavior. On manufactural processes of the ceramics and thin film, thermal treatments can cause the diffusion from the electrode to the ceramics and thin film. In this paper, we focused on the diffusion and reaction between PLZT ceramics and silver electrode. The diffusivities of silver ion along the grain boundary are also discussed. Because they plays an important role in the electrode reaction.

2. EXPERIMENT

A transparent PLZT (10/65/35, Taki Chemical Co.,Ltd.) was used in this experiment. One side of the sample surface was polished to optical flatness, and was painted with silver paste (Demetron Co., Ltd.). After samples were dried at 120°C, isothermal diffusion annealings were performed at 700°C to 900°C for desired duration in an air atmosphere. After the diffusion annealing at 700°C for 1h, fractured textures were observed with a scanning electron microscope (SEM, JEOL JSM-6400).

After the silver electrode was removed by nitric acid, the diffusion profiles of silver in PLZT were evaluated with a secondary ion mass spectrometry (SIMS, CAMECA IMS-4f).

3. RESULTS AND DISCUSSION

Figure 1 shows the SEM micrograph of a fractured surface in PLZT. The fracture mode was a intergranular fracture near the silver electrode, while that was a transgranular fracture for the area away from the silver electrode. The intergranular fracture shows that a mechanical strength of the grain boundary in PLZT was reduced. A boundary between the intergranular fractured area and the transgranular one was clearly observed. The boundary moves to the direction of the inside with increasing temperature. It is assumes that the diffusion from the silver electrode to PLZT ceramics is associated with the fracture mode.
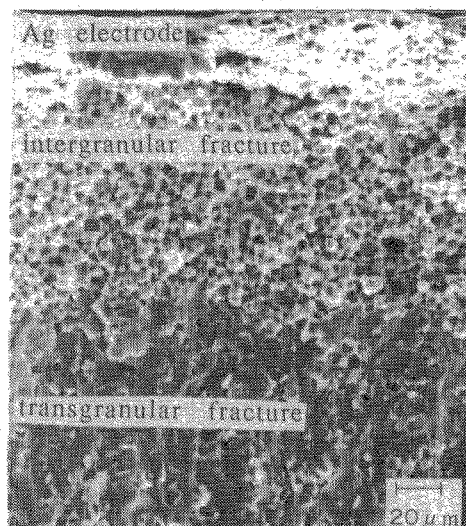

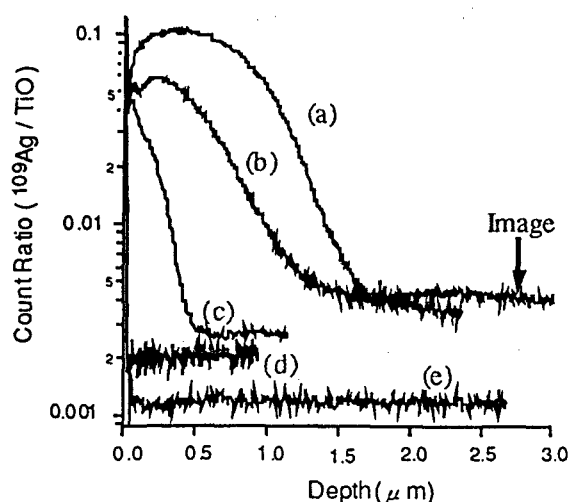Fig.1. SEM micrograph of the fracture surface in PLZT.

Fig.2. SIMS depth profiles of ^{109}Ag in PLZT
(a) at 900°C for 1h, (b) at 850°C for 2h,
(c) at 800°C for 3h, (d) at 700°C for 6h and
(e) no electrode

Figure 2 shows depth profiles of ^{109}Ag⁻ on various conditions in PLZT ceramics. Vertical-axis shows count ratio of ^{109}Ag⁻ which was normalized with TiO⁻. The intensity of TiO⁻ and ZrO⁻ in PLZT after diffusion annealings correspond well to those intensity in pure PLZT, which was constant for the depth. The profiles of Fig. 2 have characteristics as follows. On the profiles of (a)-(c), the profiles of ^{109}Ag⁻ ions are each composed of a part of high intensity near the surface and a tail part of low intensity far from the surface. On the profile of (d), only the tail part of low intensity is recognized, but a relative intensity is higher than that in pure PLZT sample without electrode. The reaction layer was observed at higher temperature.

The characteristic of the profile (e) is caused by obstructive ions as ^{91}Zr^{18}O⁻ whose mass is nearly 109 aum. On the other hand, profile of (a)-(d) have contribution of silver diffusion from electrode to PLZT ceramics. Still, the part of high intensity on depth profile of (a), (b) and (c) is caused by a volume diffusion of silver. The volume diffusion coefficient (D_v) is described by a following equation :

$$D_v = 0.12 \exp\{-(258\pm25)(kJ \: / \: mol) \: / \: RT\} \: (cm^2/s).$$

To clarify the mechanism of the tail part on depth profiles of Fig. 2, secondary ion image of ^{109}Ag⁻ ions were taken by using imaging mode of

SIMS (RAE) about 3μm depth from surface in PLZT polycrystal on the diffusional condition at 900°C for 1h. Silver ions were clearly observed at grain boundaries in polycrystalline PLZT. It directly shows that the tail part is caused by the grain boundary diffusion of silver. Products of the grain boundary width (d) and grain boundary coefficients (D_{gb}) were obtained by measuring the depth profile of ^{109}Ag⁻ ions at deeper part of Fig.2. If d is chosen 3Å, D_{gb} of silver is described by Arrhenius' low as follow:

$$D_{gb} = 43.50 \exp\{-(236\pm46)(kJ \: / \: mol) \: / \: RT\} \: (cm^2/s).$$

The D_{gb} values are about three orders magnitude higher than the D_v values. In other words, the grain boundary diffusion of silver in PLZT has the high diffusivity. Especially on Ag-diffusion samples less than at 700°C, it is assumed that silver ions diffuse from electrode to PLZT along the grain boundary.

It is considered that the fractured behavior near the electrode on Fig.1 is associated with the grain boundary diffusion of silver. In other words, it is considered that the mechanical strength of the grain boundary in PLZT was reduced by the grain boundary diffusion of silver. In this way, the grain boundary diffusion of silver is considered to make a contribution to the fracture behavior and electrical properties.

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