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Fabrication of conductive oxide polycrystalline $BaPbO_3$ films by chemical solution deposition and their electrical resistivity

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Abstract $BaPbO_3$ films were fabricated by a chemical solution deposition on the SiO_2/Si(100) and MgO(100) substrates followed by a post-deposition annealing at the temperatures between 673 and 1073 K under oxygen flow. Polycrystalline $BaPbO_3$ films were formed together with secondary phases such as PbO and Pb_3O_4 onto MgO(100) substrates at around 750 K, and the films were crystallized into single phase of $BaPbO_3$ above 823 K. Endothermic peak in differential thermal analysis due to crystallization of $BaPbO_3$ was observed at 750 K, which is consistent with crystallization temperature of $BaPbO_3$ estimated from X-ray diffraction. The electrical resistivity depended on the annealing temperature even in the single phase $BaPbO_3$ films, the lowest resistivity of 3×10^{-6} μΩ·m which was comparable to that of bulk $BaPbO_3$ was achieved at the annealing temperature of 873 K.

Keywords Perovskite-type $BaPbO_3$ · Electrical properties · Chemical solution deposition · MgO substrate

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1 Introduction

Ferroelectric and leakage current properties of ferroelectric capacitor films are strongly affected by interfacial quality as well as work functions of electrode materials. In general, Pt is used as electrodes for $Pb(Zr,Ti)O_3$ thin film capacitors due to its large differences of work function between Pt electrode and $Pb(Zr,Ti)O_3$. However, it is reported that Pb diffused into a Pt electrode layer during annealing process [1] which led to rough interface between Pt electrodes and $Pb(Zr,Ti)O_3$ films. [2, 3] Perovskite-type $BaPbO_3$ is a conductive oxide which shows superconductivity at extremely low temperatures [4] and metallic conductivity with an electrical resistivity of 3~8 μΩ·m at room temperature [5, 6]; therefore, conductive oxide $BaPbO_3$ films have a potential as a promising electrode material for $Pb(Zr,Ti)O_3$ thin film capacitor as well as $SrRuO_3$. In fact, compared to Pt electrodes, leakage current density and the fatigue properties were improved by using $BaPbO_3$ electrodes. [2, 3] However, most reports focused on the ferroelectric properties of ferroelectric thin film capacitors using the $BaPbO_3$ electrodes, few reports have investigated the effect of the preparation condition on structural and electric properties of $BaPbO_3$ films fabricated by a chemical solution deposition (CSD) method.

Furthermore, epitaxial growth of $BaPbO_3$ films is expected on single crystal substrates. In fact, a $BaPbO_3$ was heteroepitaxially grown on $SrTiO_3$(100) and (111), and perovskite $BiFeO_3$ was heteroepitaxially grown onto the epitaxial $BaPbO_3$ electrodes films. [7] By in-plane rotation of 45° in in-plane direction, the lattice mismatch between *a*- or *c*- axes of $BaPbO_3$ to *a*-axis of MgO is approximately 2%. Therefore, it is also expected that $BaPbO_3$ films hetero-epitaxially grow on single crystal MgO(100) substrates with some strain. However, no one report $BaPbO_3$ films on the MgO(100). In the present study, we fabricated the $BaPbO_3$ films onto MgO(100) substrates and investigated the influence of annealing temperature on structure, surface morphology and electric properties of the $BaPbO_3$ films.

2 Experiments

$BaPbO_3$ films were prepared by CSD method. The 2-ethylhexanoates based precursor solutions of 10 at.% of Pb-rich $BaPbO_3$ was provided by Kojundo Chemical Laboratory Co. LTD. Precursor solution was spin-coated with 4000 rpm for 50 s on SiO_2/(100)Si and MgO(100) substrates. The spin-coated films were dried at 423 K for 1 min and calcined at 623 K for 5 min. After spin coating and calcination had been repeated four or five times, the films were sintered at the temperature between 673 and 1073 K for 10 min under oxygen gas flow using a rapid thermal annealing system. The oxygen gas flow rate during the annealing was around 80~100 ml/min. The film thicknesses after annealing was approximately 200 nm for five spin coatings. The surface morphology was observed by scanning electron microscopy (SEM; Hitachi S-5000). Their crystal structure and orientation were determined by an X-ray diffraction (XRD) analysis (PANalytical X'Pert PRO MPD) with Cu-*Kα* radiation. Electrical properties were measured using an *I–V* meter at room temperature.

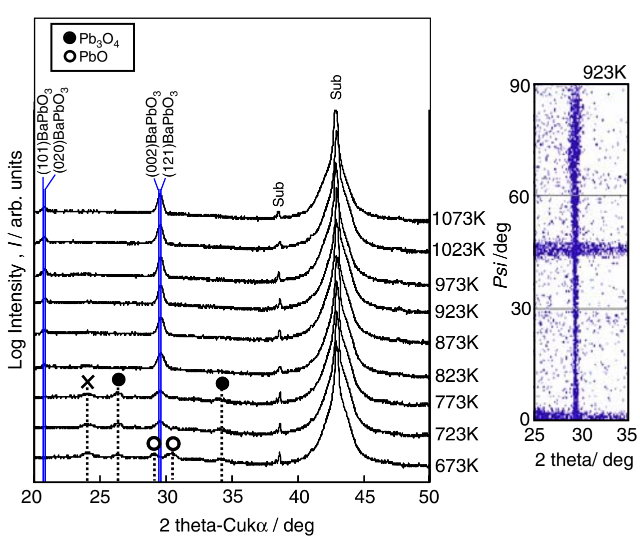

Fig. 1 An the XRD patterns for the films on MgO(100) substrates heat treated at various temperatures. An XRSM for the film annealed at 923 K. Above 823 K, single phase of polycrystalline $BaPbO_3$ films were obtained

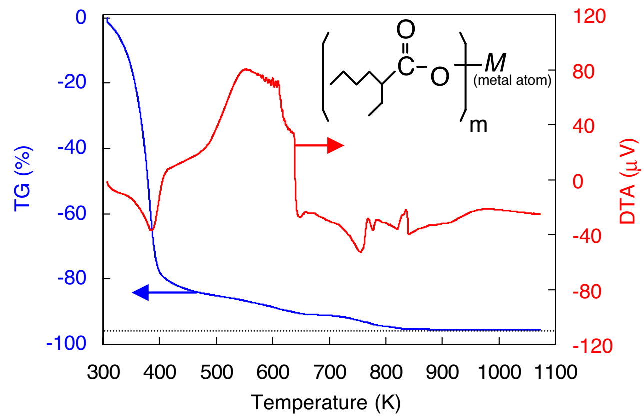

Fig. 2 Thermogravimetry (TG)–differential thermal analysis (DTA) curves of a 2-ethylhexanoates based precursor solution of 10 at.% of Pb-rich $BaPbO_3$

3 Results and discussion

Figure 1 shows the X-ray diffraction patterns of the films deposited on MgO(100) substrates followed by heat treatment at various temperatures. At annealing temperature of 673 K, lead oxide phases such as PbO (open circle) and Pb_3O_4 (filled circle) appeared together with unknown phase (×). As the annealing temperature increased to 723 K, $BaPbO_3$ phase was formed although the secondary phases of Pb_3O_4 and unknown phase still existed. Above 823 K, $BaPbO_3$ single phase was obtained and then the diffraction peak intensity of $BaPbO_3$ (002) and (121) became stronger with increasing annealing temperature. The film orientation was confirmed by an X-ray reciprocal space mapping (XRSM) for the film annealed at 923 K. Diffraction peak located around $2\theta = 29°$ showed the line-shape pattern along the inclination direction. This indicates that the $BaPbO_3$ films deposited on MgO(100) substrates were polycrystalline films.

Figure 2 shows thermogravimetry (TG)–differential thermal analysis (DTA) curves of a 2-ethylhexanoates based precursor solution used in this study. It is found that organic solvent evaporated below 400 K from the significant decrease in the TG curve. An endothermic peak in the DTA curve was observed at 750 K, which is attributed to crystallization of $BaPbO_3$. The TG curve was not constant until around 825 K, indicated that some organic components remained and organics might be blocking crystallization process of $BaPbO_3$. In fact, the secondary phases disappeared and single phase of $BaPbO_3$ was formed above constant region of TG curve.

Figure 3 shows the SEM and optical images of the $BaPbO_3$ films on MgO(100) substrates annealed at various temperatures. At any annealing temperatures, the grain sizes were 50–100 nm in diameter and we could not find drastic grain growth with elevating annealing temperature. However, many pores were observed among the grains. In Fig. 3(e)–(g), the optical permeability of the films seems to be changed due to annealing temperature.

Figure 4(a) shows the current (I) vs voltage (V) characteristics of the $BaPbO_3$ films annealed at various temperatures. The electric properties were measured by a four point proving method using the Mo probes at room temperature. The proportional relationships between current and voltage could be confirmed in all annealing temperatures except 723 K due to its high electrical resistivity which is consistent with the optical image as shown in Fig. 3(e). Figure 4(b) shows the electrical resistivity of the $BaPbO_3$ films annealed at various temperatures. The lowest electrical resistivity of approximately 3 μΩ·m was achieved at the annealing temperature of 873 and 923 K. Above 973 K, the electric resistivities monotonically increased and reached to 80 μΩ·m at 1073 K, although well crystallized single phase of $BaPbO_3$ films had formed at that temperature. According to our previous study, [8] polycrystalline $Pb(Zr,Ti)O_3$ films were crystallized at around 923 K, suggests that $BaPbO_3$ films is suitable for bottom electrode of the $Pb(Zr,Ti)O_3$ films. Therefore, we fabricated the $Pb(Zr,Ti)O_3$ films on the $BaPbO_3$ film electrodes using the same technique in this study and evaluated the ferroelectric properties. The $Pb(Zr,Ti)O_3$ layer annealed at the same temperature of the $BaPbO_3$ film electrode of 923 K. However, because of high leakage current and dielectrically breakdown, it could not confirm the ferroelectricity.

4 Summary

We fabricated the $BaPbO_3$ films on MgO(100) substrates by a CSD method at various annealing temperatures under

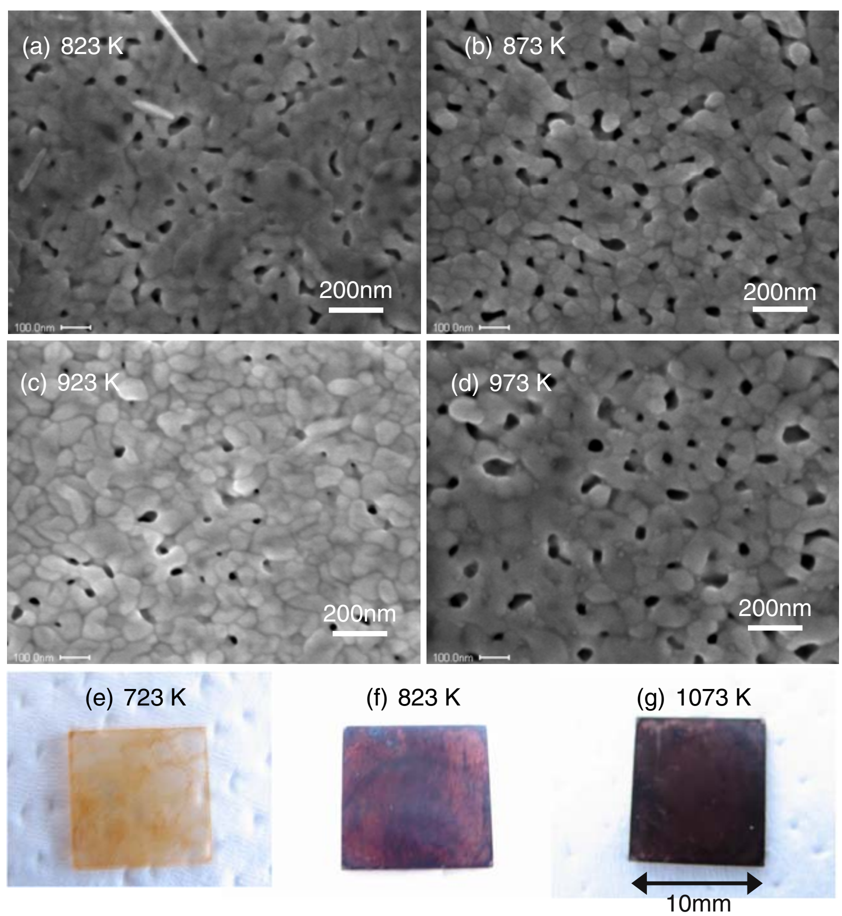

Fig. 3 (**a**)–(**g**) SEM and optical images for the $BaPbO_3$ films on MgO(100) substrate annealed at various temperatures

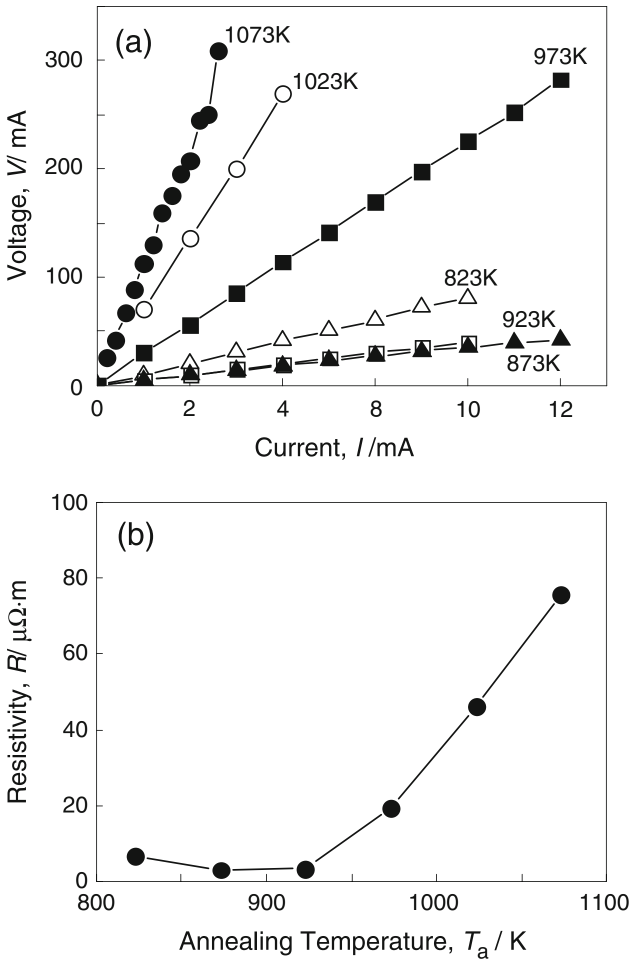

Fig. 4 Current (*I*) vs voltage (*V*) characteristic (**a**) and electrical resistivity (**b**) of the $BaPbO_3$ films annealed at various temperatures. The low electrical resistivity of approximately 3×10 μΩ·m was obtained at the annealing temperature of 873 and 923 K

oxygen gas flow, and investigated film structure and electric properties. As a result, following results were obtained. Above 823 K, the single phase of the polycrystalline $BaPbO_3$ films were formed on the MgO(100) substrates and crystallinity increased as the annealing temperature increased. The lowest resistivity of 3×10^{-6} μΩ·m was attained in the polycrystalline $BaPbO_3$ film at the annealing temperature of 873 K. However, above 923 K, the electrical resistivity rapidly increased with increasing annealing temperatures.

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