Characterization of BaPbO₃ and Ba(Pb₁₋ₓBiₓ)O₃ thin films

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Abstract
BaPbO₃ and Ba(Pb₁₋ₓBiₓ)O₃ films made from barium 2-ethylhexanoate, lead 2-ethylhexanoate and bismuth acetate were prepared by metal-organic deposition (MOD) method on Pt/Ti/SiO₂/Si substrate. The phase transition and the physical properties of these films were studied. The polycrystalline BaPbO₃ phase starts to form above 600°C and the Pb-excess addition would enhance the formation of single perovskite BaPbO₃ phase. With increasing annealing temperature, the optimum sheet resistance 1.6 Ωsq⁻¹ (resistivity = 1.07 × 10⁻⁴ Ωcm) could be obtained at 750°C. However, an annealing temperature over 800°C causes reactions between substrate and BaPbO₃ phase and results in sharp increase of resistance. On the other hand, the substitution of Pb by Bi in the Ba(Pb₁₋ₓBiₓ)O₃ films could stabilize the perovskite phase, though the sheet resistance is raised over 10 Ωsq⁻¹ at x = 0.3.

Keywords: Barium metaplumbate; Metal-organic deposition; Thin films; Resistivity

1. Introduction
BaPbO₃ (BPO) has the perovskite structure and was first synthesized by Hoppe and Blinne [1]. It is orthorhombic with lattice constants a = 6.024 Å, b = 6.065 Å and c = 8.506 Å [2]. BaPbO₃ is a conductor phase with a resistivity about 3 × 10⁻⁴ to 8 × 10⁻⁴ Ωcm for bulk ceramics at room temperature [2]. Ba(Pb₁₋ₓBiₓ)O₃ compounds with 0.05 ≤ x ≤ 0.30 have been shown to exhibit superconductivity below 13 K and metallic conductivity at the room temperature [3]. With increasing Bi substitution, the Tc would increase from about 9 K at x = 0.05 to a maximum of about 13 K at x = 0.3. The specimen with x larger than 0.35 could not show superconducting transition down to 4.2 K [4,5]. Due to its good conductivity, this material is a good candidate for a conductor paste in thick film capacitors [6], resistor [7], corrosion resistant coating for battery electrode [8], and electrode material for BaTiO₃ thin film applications [9,10]. Azuma et al. [9] have deposited BaPbO₃ films on Pt/TiO₂ buffered SiO₂ substrate by chemical solution method for BaTiO₃ thin film applications. He [11] also used a metal-alkoxide method to prepare BPO thin films on MgO and SiO₂/Si substrate, resulting in a room-temperature resistivity of 2.6 × 10⁻³ and 0.7 × 10⁻³ Ωcm, respectively. Wang et al. [12] prepared BaPbO₃ films on Al₂O₃ substrate by solution method, showing an average resistivity of about 1 × 10⁻⁵ Ω cm. However, there is little researches about BaPbO₃ and Ba(Pb₁₋ₓBiₓ)O₃ films prepared on the Si wafer. Luo and Wu [13] have reported that the lowest resistivity of BPO films they obtained on SiO₂/Si substrate by rf-magnetron sputtering is 1.4 × 10⁻⁵ Ω cm. Gilbert et al. [5] have reported that Ba(Pb₁₋ₓBiₓ)O₃ films deposited on glass substrate by rf sputtering shows optimum superconductivity at x = 0.3. However, the effects of Pb excess and Bi substitution on electrical properties of BPO films on Pt/Ti/SiO₂/Si are not studied. Accordingly, the Pr/Te/SiO₂/Si substrate was used in this research in order to study the phase evolution and the resistivity [14]. First of all, we investigated the phase evolution of the BaPbO₃ films with Pb/Ba ratio ≥1 annealed at different temperatures. Then, the sheet resistance of BaPbO₃ and Ba(Pb₁₋ₓBiₓ)O₃ films are conducted and discussed.

2. Experimental
Barium 2-ethylhexanoate (Ba(C₄H₇(CH₃COO))₂), lead 2-ethylhexanoate (Pb(C₄H₇(CH₃COO))₂) and bismuth acetate (Bi(CH₃COO)₃) were used as starting
Fig. 1. Process flow chart of BaPbO$_3$ and Ba(Pb$_{1-x}$Bi$_x$)O$_3$ thin films.

Fig. 2. XRD patterns of BaPbO$_3$ thin films annealed at 550 °C.

Fig. 3. XRD patterns of BaPbO$_3$ thin films annealed at different temperatures.

3. Results and discussion

3.1. Phase evolution of BaPbO$_3$

Fig. 2 shows the XRD patterns for the thin films annealed at 550 °C. For the Pb-excess investigation, four Pb/Ba ratios were chosen (Pb/Ba = 1, 1.2, 1.25, 1.35) and the phase of BaCO$_3$ and PbO were observed for all samples. With increasing Pb/Ba ratio, it was found that the intensity of PbO peaks raises but those of BaCO$_3$ peak at 2θ ~ 24° remains the same.

Fig. 3 displays the XRD patterns for BaPbO$_3$ thin films with composition Pb/Ba = 1 and annealed at different temperatures for 1 h. At 550 °C, as shown in Fig. 3, no BaPbO$_3$ but only BaCO$_3$ and PbO were observed. At 600 °C, BaPbO$_3$ and BaCO$_3$ were detected at the same time and PbO phase disappeared. Therefore, it is believed that the BPO should be a PbO-rich phase (due to the emergence of BaCO$_3$, i.e. the remaining composition of Pb/Ba ratio > 1), which more correctly, BPO phase forms from the composition with Pb/Ba ratio of 1 + y. This indicates that dissolution of BaO into PbO to form a BaPbO$_3$ phase, as reported by Chang et al. [15]. This phase transformation proceeds sharply at temperature of 750 °C as shown in Fig. 3. Therefore, the chemical stoichiometry of BaPbO$_3$ phase is completed by the reaction of BaCO$_3$ and BaPbO$_3$ (Pb-rich). According to the XRD analysis, this presents a two-stage reaction as follows:

Stage 1: BaCO$_3$ + PbO → BaPbO$_3$ (Pb-rich) + BaCO$_3$ + CO$_2$ ↑

Stage 2: BaPbO$_3$ (Pb-rich) + BaCO$_3$ → BaPbO$_3$ + CO$_2$ ↑

Fig. 3. XRD patterns of BaPbO$_3$ thin films annealed at different temperatures.
The BaPbO$_3$ (Pb-rich) is an intermediate during phase formation. Fig. 4 illustrates XRD spectra for BaPbO$_3$ thin films with two Pb/Ba ratios annealed at 600 and 750 $^\circ$C. As shown in Fig. 4, BaPbO$_3$ starts to form when the annealing temperature reaches 600 $^\circ$C but BaCO$_3$ still exists. Again, the Pb/Ba = 1.35 specimen shows that the BPO phase is a Pb-excess phase. With the annealing temperature up to 750 $^\circ$C, the intensity of major peaks of BaPbO$_3$ rises and BaCO$_3$ phase disappears. This is consistent with the argument we mentioned in Fig. 3, which BaCO$_3$ dissolves in BaPbO$_3$ (Pb-rich) to form a stoichiometric BPO phase. Furthermore, at 750 $^\circ$C, with the composition of Pb/Ba = 1.35, a single pure BaPbO$_3$ phase could be obtained without BaCO$_3$. This also implied that Pb-excess would be an facilitating process in the formation of perovskite BaPbO$_3$ phase. Since PbO evaporation during heat treatment only become significant over 850 $^\circ$C, it is quite surprisingly to note that BPO phase can accommodate such excess lead in the solid solution.

Fig. 4 XRD patterns of BaPbO$_3$ thin films with two Pb/Ba ratios annealed at 600 and 750 $^\circ$C.

The growing up peaks around 2$\theta$ = 26.4–26.9 are very much likely to be the SiO$_2$ phase (JCPDS 38-0360), which were regarded as an unidentified phase in Azuma et al. [11] report. The silicon dioxide from substrate diffuses up and the BPO phase decomposes as the heat treatment goes longer than 1 h. SiO$_2$, BaCO$_3$ and Ba$_{1.2}$Pb$_{2.8}$O$_{4.0}$ (JCPDS 47-0877, 2$\theta$ = 30.1) were detected after BPO decomposed at 800 $^\circ$C for 4 h. Azuma et al. [11] reported that the BPO reacted with SiO$_2$/Si substrate over 550 $^\circ$C but did not decompose on MgO substrate even over 800 $^\circ$C. From this observation, it is clear that the BPO phase could not survive over 800 $^\circ$C in the case of Pt/Ti/SiO$_2$/Si substrate. The reacting problem between BPO phase and silicon substrate is currently unresolved.

Fig. 5 illustrates the morphology of BaPbO$_3$ thin films. Thin films with composition of Pb/Ba = 1 and 1.35
both have the same small grains and are smooth enough for the practical applications.

3.2. Conductivity of BaPbO$_3$ and Ba$_{(1-x)Bi_x}$O$_3$

Fig. 7 demonstrates the room temperature sheet resistance of thin films with different Pb/Ba ratios. It shows that the sheet resistance decreases with increasing annealing temperature and reaches a minimum value at 750°C. In corresponding to the XRD patterns shown in Figs. 3 and 4, the minimum sheet resistance could be attributed to the formation of conducting BaPbO$_3$ phase and the reduction of BaCO$_3$ phase. As shown in Figs. 3 and 4, the BaCO$_3$ phase apparently declines with temperature up to 750°C so that the sheet resistance decreases. The minimum sheet resistance of 1.6 Ω sq$^{-1}$ (resistivity $\approx 1.07 \times 10^{-4}$ Ω cm) at room temperature was obtained at 750°C. The lower resistivity than the reported values [2,12,13] is attributed to the contribution from the conducting Pt layer (resistivity $= 10^{-5}$ Ω cm). However, the excess Pb seems not to reduce the sheet resistance significantly before 750°C and also results in the increase of sheet resistance at higher temperature of 800°C. As demonstrated in Fig. 5, it is understandable that the increased sheet resistance is caused by the decomposition of conducting BPO phase and presence of SiO$_2$ phase as a result of diffusion up materials from the substrate. It is noted that at 800°C, the higher the excess Pb is, the higher the resistance will be. This is thought to be due to the deteriorate effect of the excess Pb after decomposition, though the excess Pb is normally required to enhance the formation of BaPbO$_3$ phase before 750°C.

In order to further study the effect of Bi substitution, Ba$_{(1-x)Bi_x}$O$_3$ thin films were prepared and annealed at 750°C. Fig. 8 shows the sheet resistance of Ba$_{(1-x)Bi_x}$O$_3$ thin films obtained after annealing at 750°C. It is observed that within 0 $\leq x \leq 0.25$ the sheet resistance will slightly ascend with the increase of Bi substitution. However, the sheet resistance would increase dramatically over 10 Ω sq$^{-1}$ as $x > 0.25$. This is thought to be due to that Ba$_{(1-x)Bi_x}$O$_3$ shows semiconductor properties in the range 0.35 $\leq x \leq 1$ [1].

It is also suspected that Ba$_{(1-x)Bi_x}$O$_3$ may not be so stable at higher Bi content. To reveal the phase stability, both BaPbO$_3$ and Ba$_{(1-x)Bi_x}$O$_3$ samples were placed in a humidity-controlled box with humidity over 98% and it was found that Bi-substituted BPO phase was still stable over all range of substitution, while BPO decomposed. In the present study, we found that Bi can stabilize the perovskite phase, though its sheet resistance is slightly higher than BPO phase. The conducting nature of Bi-substituted BPO phase deserves more investigations.

4. Conclusions

Polycrystalline BaPb$_{1-x}$O$_3$ and Ba$_{(1-x)Bi_x}$O$_3$ thin films have been prepared on the Pt/Ti/SiO$_2$/Si substrate by using the metal-organic deposition (MOD) method. The annealing temperature at 750°C results in the lowest sheet resistance of the films, which is attributed to the dissolution of second phase and complete formation of BaPbO$_3$ phase. The minimum sheet resistance of 1.6 Ω sq$^{-1}$ (resistivity $\approx 1.07 \times 10^{-4}$ Ω cm) at room temperature was obtained by annealing the film at 750°C. Excess lead addition was used to enhance the formation of conducting BPO phase formation. However, conductivity seems not significantly improved before 750°C and also cause deteriorate effect at 800°C by the addition of excess lead. The Bi substitution could stabilize the perovskite phase in humidity but loose its good conductivity when the substitution of Bi is over 25 mol%.

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