

Characterization of BaPbO₃ and Ba(Pb_{1-x}Bi_x)O₃ thin films

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Abstract

BaPbO₃ and Ba(Pb_{1-x}Bi_x)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 Ω sq⁻¹ (resistivity ≈ 1.07 × 10⁻⁴ Ω cm) 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(Pb_{1-x}Bi_x)O₃ films could stabilize the perovskite phase, though the sheet resistance is raised over 10 Ω sq⁻¹ at x = 0.3.

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1. Introduction

BaPbO₃ (BPO) has the perovskite structure and was first synthesized by Hoppe and Blinne [1]. It is orthorhombic with lattice constants $a = 6.024 \text{ \AA}$, $b = 6.065 \text{ \AA}$ and $c = 8.506 \text{ \AA}$ [2]. BaPbO₃ is a conductive phase with a resistivity about 3×10^{-4} to $8 \times 10^{-4} \text{ \Omega cm}$ for bulk ceramics at room temperature [2]. Ba(Pb_{1-x}Bi_x)O₃ compounds with $0.05 \leq x \leq 0.30$ have been shown to exhibit superconductivity below 13 K and metallic conductivity at the room temperature [3]. With increasing Bi substitution, the T_c 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 PbTiO₃ buffered MgO 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 re-

sistivity of 2.6×10^{-3} and $0.7 \times 10^{-3} \text{ \Omega cm}$, respectively. Wang et al. [12] prepared BaPbO₃ films on Al₂O₃ substrate by solution method, showing an average resistivity of about $1 \times 10^{-3} \text{ \Omega cm}$. However, there is little researches about BaPbO₃ and Ba(Pb_{1-x}Bi_x)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 $1.4 \times 10^{-3} \text{ \Omega cm}$. Gilbert et al. [5] have reported that Ba(Pb_{1-x}Bi_x)O₃ films deposited on glass substrate by rf sputtering shows optimum superconductivity at $x = 3.0$. 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 Pt/Ti/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(Pb_{1-x}Bi_x)O₃ films are conducted and discussed.

2. Experimental

Barium 2-ethylhexanoate (Ba(C₄H₉(C₂H₅)CHCOO)₂), lead 2-ethylhexanoate (Pb(C₄H₉(C₂H₅)CHCOO)₂) and bismuth acetate (Bi(CH₃COO)₃) were used as starting

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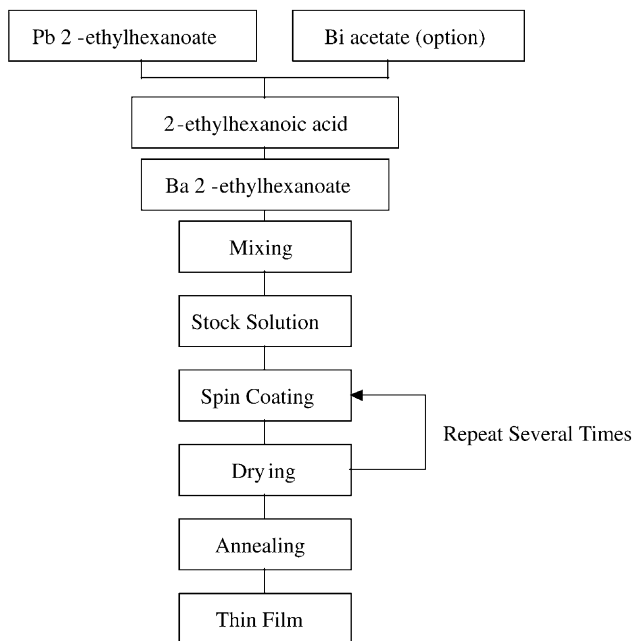


Fig. 1. Process flow chart of BaPbO₃ and Ba(Pb_{1-x}Bi_x)O₃ thin films.

materials. The substrate was made from a 3 in. p-type (100) Si wafer with a resistivity of 10 Ω cm and a bottom electrode in a configuration of 1500 Å Pt/200 Å Ti/2000 Å SiO₂/Si. The mixed solutions were diluted to an appropriate concentration and stirred for 12 h. These solutions were deposited on the Pt/Ti/SiO₂/Si substrate by spinning coating. Then, the wet films were annealed at different temperatures for 1 h. The process flow chart is shown in Fig. 1. The film thickness was determined by α stepper and cross-checked by scanning electron microscope (SEM). Thickness of 500 nm BPO films was obtained for electrical characterization. Meanwhile, X-ray diffraction (XRD, Siemens D5000) and field emission scanning electron microscope (FESEM, Hitach S-4000) were used to study the phase transition and microstructure, respectively. Additionally, four-point probe technique was used to investigate the resistivity for various compositions and annealing conditions. The 1 mA current was from a Keithley 237 high voltage source unit and the voltage was measured by a Keithley 182 sensitive voltage meter. We use the sheet resistance R_s (unit Ω sq⁻¹, resistivity $\rho = R_s \times t$, $t = 670$ nm) to present the results.

3. Results and discussion

3.1. Phase evolution of BaPbO₃

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 BaCO₃ and PbO were observed for all samples. With increasing Pb/Ba ratio, it was found that the intensity of

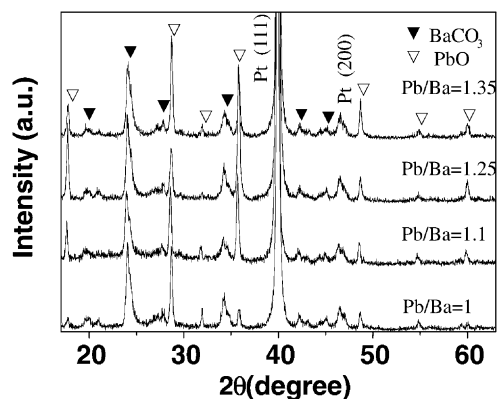
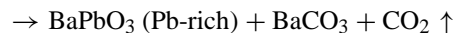


Fig. 2. XRD patterns of BaPbO₃ thin films annealed at 550 °C.

PbO peaks raises but those of BaCO₃ peak at $2\theta \sim 24^\circ$ remains the same.

Fig. 3 displays the XRD patterns for BaPbO₃ thin films with composition Pb/Ba = 1 and annealed at different temperatures for 1 h. At 550 °C, as shown in Fig. 3, no BaPbO₃ but only BaCO₃ and PbO were observed. At 600 °C, BaPbO₃ and BaCO₃ 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 BaCO₃, 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 BaPbO₃ 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 BaPbO₃ phase is completed by the reaction of BaCO₃ and BaPbO₃ (Pb-rich). According to the XRD analysis, this presents a two-stage reaction as follows:

Stage 1: BaCO₃ + PbO



Stage 2: BaPbO₃ (Pb-rich) + BaCO₃ → BaPbO₃ + CO₂ ↑

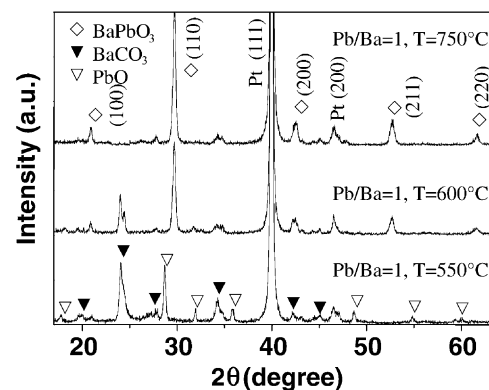


Fig. 3. XRD patterns of BaPbO₃ thin films annealed at different temperature.

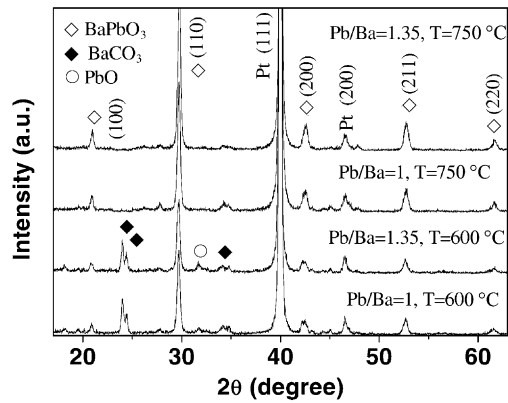


Fig. 4. XRD patterns of BaPbO₃ thin films with two Pb/Ba ratios annealed at 600 and 750 °C.

The BaPbO₃ (Pb-rich) is an intermediate during phase formation.

Fig. 4 illustrates XRD spectra for BaPbO₃ thin films with two Pb/Ba = 1 and 1.35 annealed at 600 and 750 °C. As shown in Fig. 4, BaPbO₃ starts to form when the annealing temperature reaches 600 °C but BaCO₃ 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 °C, the intensity of major peaks of BaPbO₃ rises and BaCO₃ phase disappears. This is consistent with the argument we mentioned in Fig. 3, which BaCO₃ dissolves in BaPbO₃ (Pb-rich) to form a stoichiometric BPO phase. Furthermore, at 750 °C, with the composition of Pb/Ba = 1.35, a single pure BaPbO₃ phase could be obtained without BaCO₃. This also implied that Pb-excess would be an facilitating process in the formation of perovskite BaPbO₃ phase. Since PbO evaporation during heat treatment only become significant over 850 °C, it is quite surprisingly to note that BPO phase can accommodate such excess lead in the solid solution.

Fig. 5 shows that the BPO thin film become unstable after heat treatment at 800 °C for different durations. The

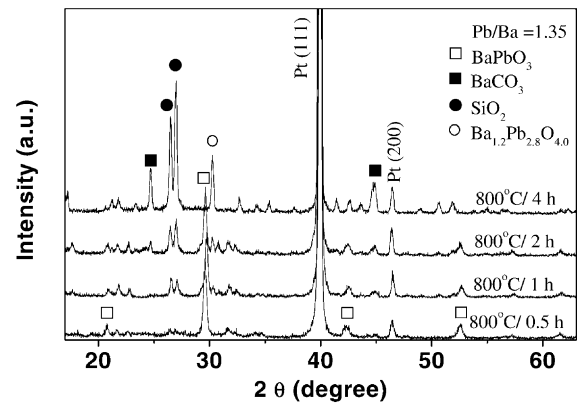


Fig. 5. BPO phase decomposes and silicon dioxide diffuses up from the substrate at 800 °C.

growing up peaks around $2\theta = 26.4\text{--}26.9$ are very much likely to be the SiO₂ 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. SiO₂, BaCO₃ and Ba_{1.2}Pb_{2.8}O_{4.0} (JCPDS 47-0877, $2\theta = 30.1$) were detected after BPO decomposed at 800 °C for 4 h. Azuma et al. [11] reported that the BPO reacted with SiO₂/Si substrate over 550 °C but did not decompose on MgO substrate even over 800 °C. From this observation, it is clear that the BPO phase could not survive over 800 °C in the case of Pt/Ti/SiO₂/Si substrate. The reacting problem between BPO phase and silicon substrate is currently unresolved.

The surface roughness and morphology of thin films are quite important for the applications of the electrode for memories or the bonding layer. The hillock formation on the metal thin film surface is a serious problem and could cause detrimental effects on ferroelectric properties such as short circuit in electronic device and the reduction of capacitor yield. Fig. 6 illustrates the morphology of BaPbO₃ thin films. Thin films with composition of Pb/Ba = 1 and 1.35

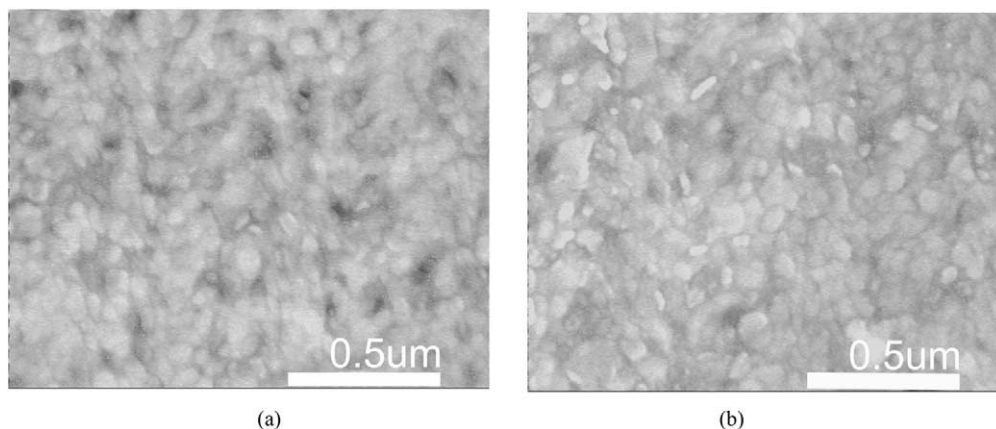


Fig. 6. FESEM micrographs of BaPbO₃ thin film (a) Pb/Ba = 1 and (b) Pb/Ba = 1.35.

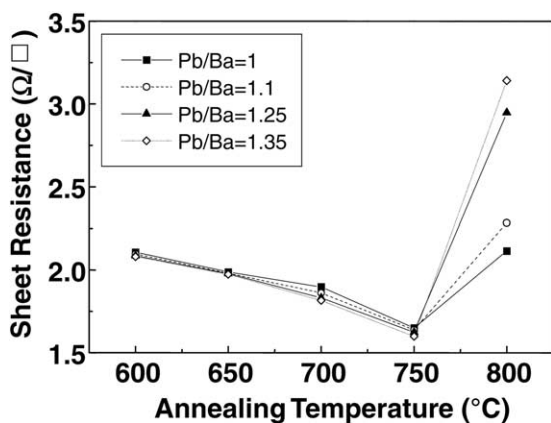


Fig. 7. Sheet resistances of BPO thin films with four different Pb/Ba molar ratios annealed at different temperatures.

both have the same small grains and are smooth enough for the practical applications.

3.2. Conductivity of $BaPbO_3$ and $Ba(Pb_{1-x}Bi_x)O_3$

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 $1.6 \Omega \text{sq}^{-1}$ (resistivity $\approx 1.07 \times 10^{-4} \Omega \text{cm}$) 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 = $10.58 \times 10^{-6} \Omega \text{cm}$). 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, $Ba(Pb_{1-x}Bi_x)O_3$ thin films were prepared and annealed at 750 °C. Fig. 8 shows the sheet resistance of $Ba(Pb_{1-x}Bi_x)O_3$ 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 $10 \Omega \text{sq}^{-1}$ as $x > 0.25$. This is thought

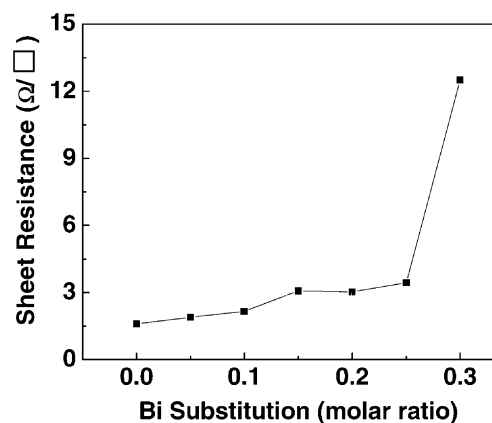


Fig. 8. Sheet resistances of $Ba(Pb_{1-x}Bi_x)O_3$ thin films annealed at 750 °C.

to be due to that $Ba(Pb_{1-x}Bi_x)O_3$ shows semiconductor properties in the range $0.35 \leq x \leq 1$ [1].

It is also suspected that $Ba(Pb_{1-x}Bi_x)O_3$ may not be so stable at higher Bi content. To reveal the phase stability, both $BaPbO_3$ and $Ba(Pb_{1-x}Bi_x)O_3$ 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 $BaPb_{1+y}O_3$ and $Ba(Pb_{1-x}Bi_x)O_3$ thin films have been prepared on the Pt/Ti/SiO₂/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 $1.6 \Omega \text{sq}^{-1}$ (resistivity $\approx 1.07 \times 10^{-4} \Omega \text{cm}$) 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 lose its good conductivity when the substitution of Bi is over 25 mol%.

Acknowledgements

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