Effect of microstructure on the thermoelectric properties of CSD-grown $Bi_2Sr_2Co_2O_y$ thin films*

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Three $Bi_2Sr_2Co_2O_y$ thin films with different microstructures have been prepared by chemical solution deposition on $LaAlO_3$(001) through varying the annealing temperature. With the decrease in the annealing temperature, both the size and *c*-axis alignment degree of grains in the film decrease as well, leading to an increase in the film resistivity. In addition, the decrease in the annealing temperature also results in a slight increase in the Seebeck coefficient due to the enhanced energy filtering effect of the small-grain film. The nanostructured $Bi_2Sr_2Co_2O_y$ film with an average grain size of about 100 nm shows a power factor comparable to that of films with larger grains. Since the thermal conductivity of the nanostructured films can be depressed due to the enhanced phonon scattering by grain boundary, a higher figure of merit is expected in $Bi_2Sr_2Co_2O_y$ thin film with grains in nanometer size.

Keywords: thermoelectric properties, $Bi_2Sr_2Co_2O_y$ thin films, microstructure, chemical solution deposition

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1. Introduction

Thermoelectric (TE) materials can convert thermal energy directly into electricity, making them attractive for waste heat conversion applications. The performance of a TE material is evaluated by the dimensionless figure-of-merit $ZT = (S^2/\rho\kappa)T$, where S is the Seebeck coefficient, ρ is the electric resistivity, κ is the thermal conductivity, and T is the absolute temperature. Therefore, good TE materials should possess a large Seebeck coefficient, low resistivity, as well as low thermal conductivity.

Layered cobalt oxides have attracted great attention from the thermoelectric community, particularly from those who are interested in high-temperature applications, because of their good thermoelectric performance and excellent chemical stability at high temperature in air.[1,2] $Bi_2Sr_2Co_2O_y$ (abbreviated as Bi-222) is a prime example of a layered cobaltite, and its bulk forms have been extensively studied.[3–6] For miniaturizing TE devices, thin film technology is advantageous because it is compatible with the microelectromechanical system. Moreover, thin film TE devices can achieve very high cooling power densities and very fast cooling. Researchers, including us, have recently reported the growth and TE properties of high-quality *c*-axis-oriented Bi-222 thin films by using pulsed laser deposition or chemical solution deposition (CSD) techniques.[7–11] TE measurements of these *c*-axis-oriented Bi-222 thin films showed that their power factor (S^2/ρ) is comparable to that of single crystals, suggesting their promising applications in thin film TE devices. It is known that the microstructure can greatly influence the carrier and phonon transport as well as carrier-phonon interactions in TE materials, and therefore can influence the parameters ρ, S, and k. One common route which has been exploited to improve the performance of a TE material is by tuning its microstructure. In this paper, we have prepared three Bi-222 films with different microstructures by using the CSD technique through varying the annealing temperatures, and investigated the effect of microstructure on TE properties of the films. We found that the high-temperature power factor S^2/ρ of nanostructured film with a grain size of about 100 nm is very close to that of films with larger grains. Since the thermal conductivity decreases with the grain size, higher ZT is expected in the Bi-222 thin film with grains in the nanometer size.

2. Experiments

Three Bi-222 thin films were prepared by using a CSD method on $LaAlO_3$ (001) substrates at different annealing temperatures of 600, 700, and 800 °C in flowing high purity oxygen with pressure slightly higher than 1 atm. The annealing time is about 2 h, and the thickness of all film samples is about 150 nm. The crystal structure of the films was measured using X-ray diffraction (XRD) with CuKα radiation. The microstructure was analyzed by field-emission scanning electron microscope (FE-SEM). Energy-dispersive X-ray spectroscopy analysis indicates that the actual cation ratio in these films was all very close to the nominal composition. The four-probe electrical resistivity and the Seebeck coefficient were mea-

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sured in air using a commercial equipment (Linseis, LSR-3) from room temperature to 600 °C.

3. Results and discussion

Figure 1(a) presents the XRD θ–2θ scan curves of three Bi-222 films on $LaAlO_3$ (001) substrates annealed at 600, 700, and 800 °C, respectively. Apart from the peak from $LaAlO_3$ (00l) substrates, all peaks in these three films can be indexed to Bi-222 (00l) diffractions, indicating that the films are pure phase and consist predominantly of c-axis-oriented grains. The ω scans of these three films shown in Fig. 1(b) clearly demonstrate that the diffraction peaks become narrower as the annealing temperature increases from 600 to 800 °C, which suggests that the average grain size in films increases. Additionally, the diffraction peaks are stronger for the films annealed at higher temperature, thus indicating a higher degree of crystallinity.

SEM images of these three Bi-222 films annealed at different temperatures are shown in Figs. 2(a)–2(c). All films are composed of densely packed grains with plate-like shape. It is shown that the grain grows rapidly with rising annealing temperature, and the average grain size is about 100, 300, and 700 nm, respectively, for the films annealed at 600, 700, and 800 °C. In addition, the crystalline quality and the grain alignment along the c axis of the films are also improved as the annealing temperature rises.

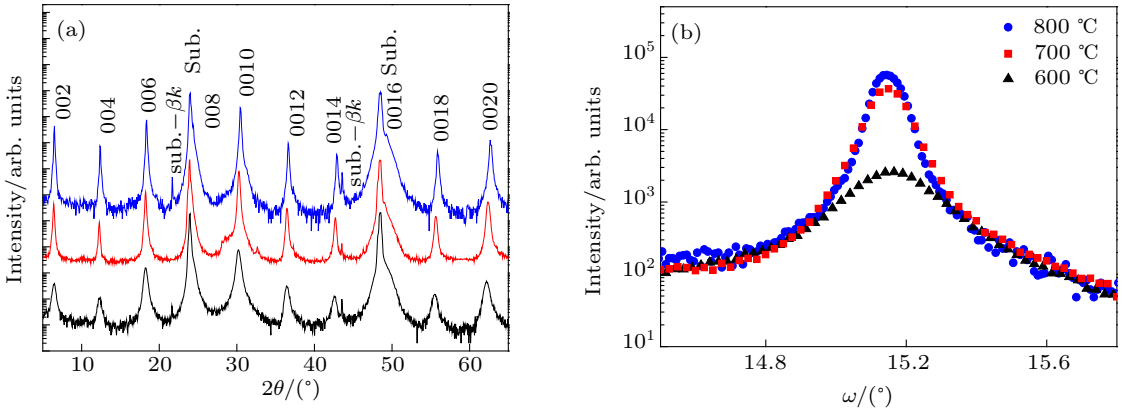


Fig. 1. (color online) (a) XRD-2 θ–2θ patterns and (b) rocking curves of three Bi-222 thin films on $LaAlO_3$ (001) substrates grown by the CSD method at annealing temperature of 600, 700, and 800 °C.

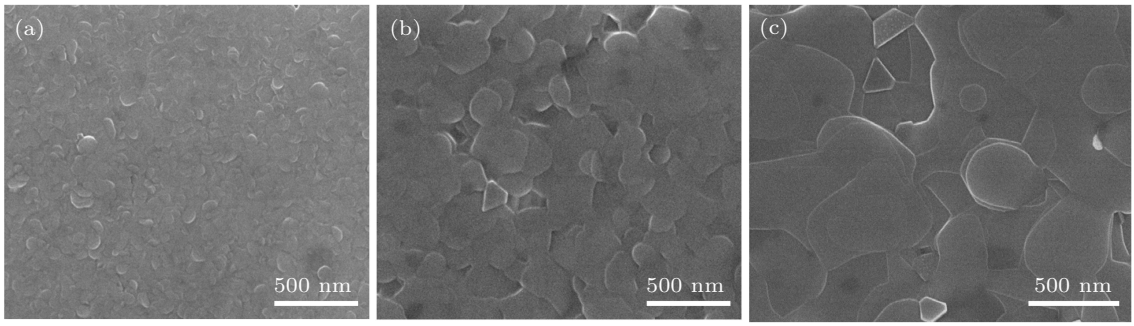


Fig. 2. SEM images of three Bi-222 thin films grown by the CSD method annealed at (a) 600 °C, (b) 700 °C, and (c) 800 °C.

TE properties of these three Bi-222 films are characterized by the temperature dependence of resistivity ρ, Seebeck coefficient S, and power factor S^2/ρ. Figure 3(a) shows $\rho(T)$ curves of these three films as a function of temperature, up to 600 °C. By decreasing the annealing temperature, the resistivity of the film increases in the whole measured temperature range. The increase in the resistivity for film with smaller grains annealed at lower temperatures is mainly due to the enhanced carrier scattering from grain boundary because the reduction in grain size results in an increase in the grain boundary density. Secondly, there are more other crystal defects in the films annealed at lower temperatures due to the deterioration of the crystalline quality. The scattering of carriers by other crystal defects can increase the film resistivity. Finally, a small part of grains do not grow along the c axis of the film as the annealing temperature is decreased. The reduction of c-axis alignment degree of grains in films can also lead to an increase in the resistivity due to the strong anisotropic nature in resistivity for Bi-222 phase ($\rho_c/\rho_{ab} \sim 10^4$).[12] In addition, Fig. 3(a) shows that the $\rho(T)$ behavior of the film annealed

at 600 °C is quite different from that of the other two films annealed at higher temperatures. The $\rho(T)$ curve for the former film exhibits a transition from metallic-like conduction to semiconting-like conduction, while the $\rho(T)$ curves for the two latter films exhibit a metallic-like behavior throughout the measured temperature range. Similar metallic-like conduction can be observed for pure-phase Bi-222 polycrystalline bulks with grain size in several micrometers.[5–7] The difference in conduction behavior between the nanocrystalline and microcrystalline samples has also been observed in $La_{0.5}Sr_{0.5}CoO_3$, and has been discussed in terms of a size-induced metal-to-insulator transition.[13]

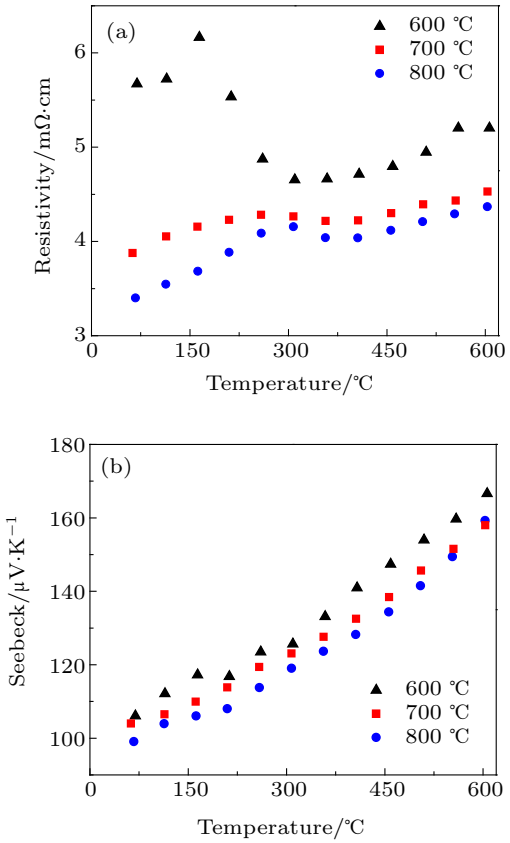


Fig. 3. (color online) Temperature-dependent (a) resistivity and (b) Seebeck coefficient of three CSD-grown Bi-222 thin films under different annealing temperatures.

Figure 3(b) shows the variation of the Seebeck coefficient (S) with temperature for these three Bi-222 films measured from room temperature to 600 °C. The S value for each film is positive in the whole measured temperature range, indicating a conduction mechanism mainly governed by holes. Moreover, S(T) behaviors of these three films do not show obvious difference from each other, and are all similar to that of the bulk samples. However, film with smaller grains annealed at lower temperatures has a slightly larger S. The slight enhancement of the thermopower in the small-grain films might be related to the filtering energy effect of the carriers. According to the theory of Moyzhes *et al.*, the contribution to S of carriers with low energy is negative.[14] The presence of boundary potential barrier can filter low-energy charge carriers traversing the boundary, which increases the average carrier energy, and consequently S.[15] On one hand, the reduction of grain size leads to an increase in the grain boundary density, thereby enhancing the effective filtering. On the other hand, film with smaller grain size has a higher barrier, which can block more carriers with low energy, and improve S.[16]

Figure 4 displays the dependence of the calculated power factor (PF) on temperature of these three Bi-222 films. At lower measured temperature, the film with smaller grain size has a smaller power factor due to its much larger resistivity value in this temperature range. However, at a higher temperature range (300–600 °C), the differences among the power factor values for these three films are very small. This result is expected since Bi-222 phase is a promising TE candidate in moderate and high temperature range. We have no thermal conductivity data of these films due to the difficulty in measuring κ for film sample as thick as a few hundred nanometers. However, we can speculate that the film with smaller grains will have a lower thermal conductivity when considering the fact that the thermal conductivity can be significantly reduced by the increased phonon scattering at grain boundary. Therefore, a higher ZT is expected in the films with grains of about 100 nm.

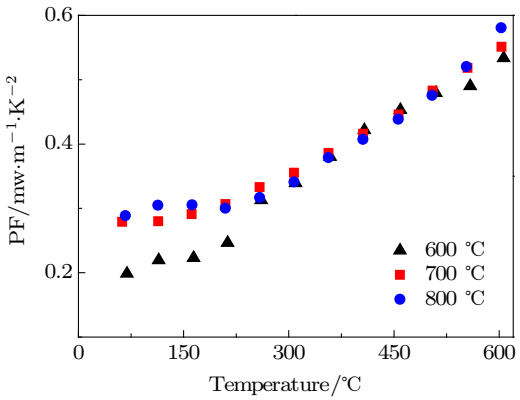


Fig. 4. (color online) Calculated power factor (PF) versus temperature of three CSD-grown Bi-222 thin films under different annealing temperatures.

4. Conclusion

The $c-$axis-oriented $Bi_2Sr_2Co_2O_y$ thin films have been grown on $LaAlO_3$ (001) by using the CSD technique in the annealing temperature range of 600–800 °C. With decreasing annealing temperature, both the size and c-axis alignment degree of grains in the films were reduced, which lead to an increase in the film resistivity due to the enhanced grain boundary scattering and the strong transport anisotropy nature of Bi-222. In addition, the decrease in annealing temperature also resulted in a slight increase in the Seebeck coefficient, which was considered to be caused by the enhanced carrier energy filtering effects of small-grain film. Bi-222 film with the average grain size of about 100 nm annealed at 600 °C showed a power factor comparable to that of the films with larger grains. Considering the fact that the thermal conductivity can be reduced

in nanoscale materials, a higher ZT can be expected for the nanostructured Bi-222 thin films annealed at lower temperatures.

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