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Enhanced thermoelectric power factor of $Bi_2Sr_2Co_2O_y$ thin films by incorporating Au nanoparticles

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ABSTRACT

c-Axis oriented $Bi_2Sr_2Co_2O_y$ thin films imbedded with Au nanoparticles were prepared by pulsed laser ablation a ceramic $Bi_2Sr_2Co_2O_y$ target with a small piece of Au foil overlapped. It was found that the incorporation of Au nanoparticles, about 5–15 nm in diameter, did not disrupt the *c*-axis orientation of the films. Fortunately, the incorporation of Au nanoparticles decreased the resistivity of $Bi_2Sr_2Co_2O_y$ films while maintained the Seebeck coefficient almost unchanged, thus resulted in an enhanced power factor. Possible mechanisms were proposed to explain the results. This work demonstrated a promising approach to optimize the thermoelectric performance of layered cobaltite thin films.

1. Introduction

Thermoelectric (TE) materials can convert thermal energy directly into electricity and vice versa, making them attractive for applications in waste heat recovery and Peltier cooling. The efficiency of thermoelectric materials is generally evaluated by the dimensionless figure of merit $ZT = (S^2/\rho\kappa)T$, where S, ρ, κ and T are Seebeck coefficient, electrical resistivity, thermal conductivity, and absolute temperature, respectively [1]. Therefore, the performance of TE materials can be enhanced by either increasing the power factor S^2/ρ or decreasing the thermal conductivity κ, which is the sum of the lattice and the carrier contribution.

Among all the TE materials explored, layered cobaltites have received increasing attention to the TE community in the past decade, particularly to those who are interested in high-temperature applications in air, because of their good TE performance, low cost, high thermal and chemical stability, and environmental benignity [2–4]. Various approaches were used to enhance the TE performance of the layered cobaltite bulks, such as improving the *c*-axis texture degree, optimizing the carrier concentration by doping, and introducing metallic nanoparticles (NPs) into the thermoelectric matrix [5–11]. *ZT* value of about 0.61 at 1118 K was reported for $Ca_3Co_4O_9$ polycrystalline bulks, a typical layered cobaltite, through ion doping and incorporating metallic Ag NPs into the TE matrix [11]. For localized heating or cooling, thin films are required in many particular applications. However, there are very few reports on the improvement of TE performance of thin film samples. In this work, we reported the enhancement of TE performance of thin films of layered cobaltite by incorporating metallic gold nanoparticles (Au NPs). *c*-Axis oriented $Bi_2Sr_2Co_2O_y$ (BSCO) thin films imbedded with Au NPs were fabricated on $LaAlO_3$ (001) single crystalline substrates by pulsed laser deposition (PLD) technique. By incorporating Au NPs into BSCO thin films, we found the power factor of the films was enhanced comparing to that of pure BSCO over a wide range of temperature. In addition, the thermal conductivity of the BSCO:Au NPs composite thin films was expected to decrease due to the enhanced phonon scattering on the Au NPs as well as the interface between the Au NPs and the BSCO TE matrix. Therefore, the TE performance of BSCO thin films could be improved by introducing Au NPs into the films.

2. Experimental

c-Axis oriented BSCO thin films imbedded with the Au NPs were fabricated on $LaAlO_3$ (001) single crystalline substrates by pulsed laser ablating a BSCO ceramic target, on which a piece of fan-shaped Au foil (99.99%) was attached. The distance between the target and the substrate was about 50 mm. An excimer laser with 308 nm radiation was used for the film deposition with a laser energy density of 1.5 J/cm^2 and a repetition rate of 3 Hz. The deposition temperature was monitored to be about 680 °C and the oxygen pressure in the PLD chamber was about 60 Pa. The Au concentration in the deposited BSCO films can be easily controlled by changing the area of Au foils. Three fan-shaped Au foils with $\omega = 0°$, 25° and 45° were used in this work

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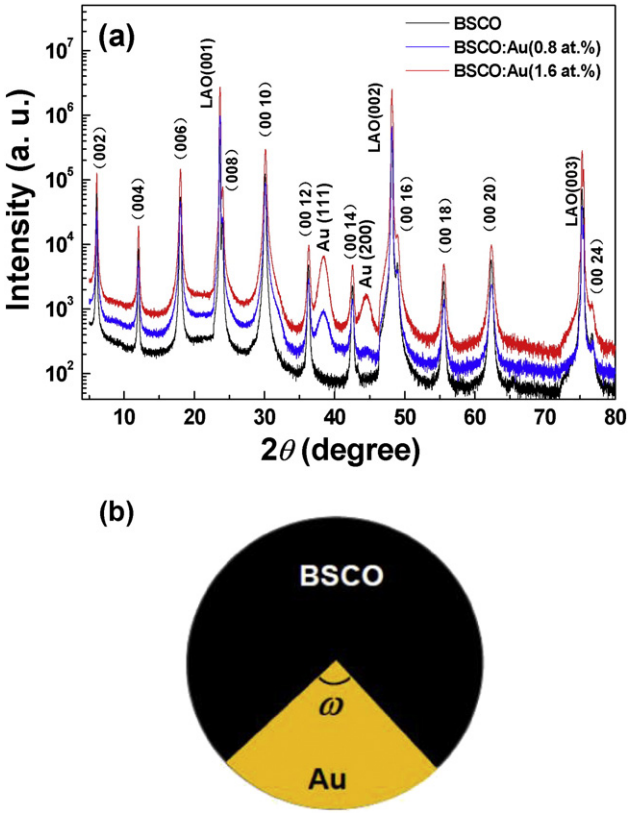

Fig. 1. (a) XRD θ-2θ scan of BSCO:Au composite thin films on $LaAlO_3$ (001) substrates. (b) The schematic image of BSCO:Au composite target.

(Fig. 1b), and the atomic ratio between Au and BSCO in the corresponding BSCO:Au composite films was about 0, 0.8 and 1.6%, respectively. It should be mentioned here that when we increased the Au atomic concentration to about 3.7% in the BSCO film (a fan-shaped Au foil with $\theta = 90°$ was used). The Seebeck coefficient of the resulting composite film decreased greatly, resulting in a reduction in TE performance.

The film thickness was measured by a Dektak 150 Surface Profiler and all film samples used in this work had thickness about 80 nm. The crystal structure of the films was identified by a Philips X'Pert 4-circle diffractometer with *CuKα* radiation. The Au concentration and chemical band in the composite films were determined by X-ray photoelectron spectroscopy (XPS) measurements. The microstructure were analyzed by a field-emission transmission electron microscopy (TEM, Tecnai G2 F20) equipped with an energy-dispersive X-ray spectroscopy (EDS) detector. The room temperature carrier concentration and mobility of the films was determined via Hall effect measurement by using a Physical Properties Measurement System (PPMS, Quantum Design Inc.). The temperature-dependent electrical resistivity and Seebeck coefficient were simultaneously measured using the dc four-probe method in Hall bar geometry by a LSR-3 measurement system (Linseis, Germany) with a heating rate of 5 K/min. To make the ohmic contact, silver paste was used for the terminal connections.

3. Results and discussion

Fig. 1a shows the typical XRD θ–2θ scans of the BSCO:Au composite thin films on $LaAlO_3$ (001) single crystalline substrates fabricated by pulsed laser ablation of the target. Schematic diagram of the target of BSCO with Au foil overlapped is shown in Fig. 1b. Except the diffraction peaks from the $LaAlO_3$ (LAO) and Au, all peaks in these three films can be indexed as 00ℓ diffractions from BSCO phase, suggesting that the resulting BSCO films are pure phase and *c*-axis oriented. As the concentration of Au in the films increases, the intensity of the Au diffraction peaks becomes stronger. In addition, the Au peaks also become broader, indicating that the size of Au particles in the films become smaller with the increase of the Au concentration. This might because that some small Au nanoparticles tend to agglomerate when the amount of Au in the films increases. We roughly estimate the average size of the Au particles in the films by the Au (111) peaks using the Scherer formula $D = (K\lambda)/(B\cos\theta)$, where D is the average size of the particles, K is the correction factor ($K = 0.89$), λ is the wavelength of X-ray ($\lambda = 0.15405$ nm), B is the full width at half maximum (FWHM) of Au (111) peaks shown in Fig. 1 and θ is the Bragg diffraction angle. The estimated D is about 5.4 and 8.0 nm for the films with the Au atomic concentration of 0.8 and 1.6%, respectively. We also estimated the number density of Au nanoparticles in these two films, which was about 4.94 and 8.02×10^{13}/cm^3, respectively.

Fig. 2a is the XPS survey spectra of a BSCO:Au composite thin film. It reveals that the cation ion ratio of Bi:Sr:Co in the film is about 1.00:1.03:1.06, which is very close to that of the nominal composition of this material. Moreover, the XPS measurement also reveals that the Au atomic concentration in this film is about 1.6%. Fig. 2b shows the Au 4f XPS core-level spectra of this film. The peaks of Au $4f_{5/2}$ and Au $4f_{7/2}$ are located at 87.6 and 84.0 eV, respectively, which correspond to the normal XPS spectra of metallic Au [12]. This result demonstrates that Au does not enter into the crystal lattice of BSCO but exists as a metallic phase in BSCO matrix.

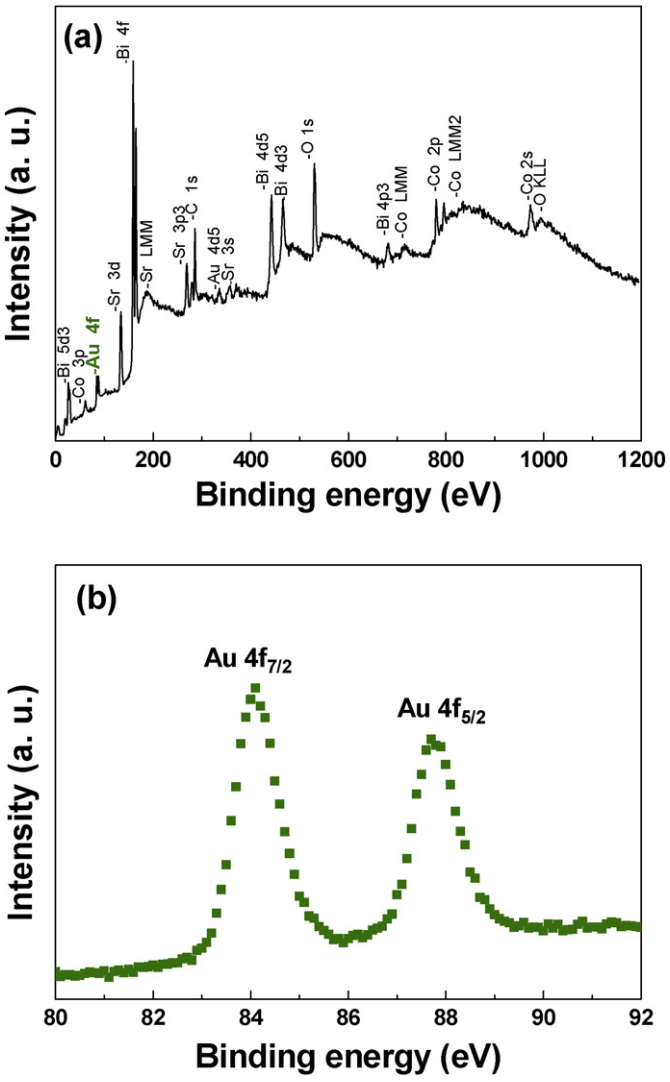

Fig. 2. (a) XPS spectra of BSCO:Au composite thin film with the Au atomic concentration of about 1.6%. (a) Survey scan and (b) high resolution core-level spectra of Au 4f.