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Structural and thermoelectric properties of Bi$_2$Sr$_2$Co$_2$O$_y$ thin films on LaAlO$_3$ (100) and fused silica substrates

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We have grown Bi$_2$Sr$_2$Co$_2$O$_y$ thin films on LaAlO$_3$ (100) and fused silica substrates by pulsed laser deposition. The films on LaAlO$_3$ are c-axis oriented and partially in-plane aligned with multiple domains, while the films on fused silica are preferred c-axis oriented without in-plane alignment. The Seebeck coefficient and resistivity of films on both substrates are comparable to those of single crystals. An oxide p-n heterojunction was formed by depositing Bi$_2$Sr$_2$Co$_2$O$_y$ film on Nb-doped SrTiO$_3$ single crystal, which showed a rectifying behavior. These thin films and heterostructures may be used for future thermoelectric applications. © 2009 American Institute of Physics. DOI: 10.1063/1.3072803

Layered cobalt oxides have attracted great attention as a promising candidate for thermoelectric applications since the discovery of large Seebeck coefficient and relatively low resistivity in Na$_2$Co$_2$O$_4$. Among various layered cobalt oxides, Bi$_2$Sr$_2$Co$_2$O$_y$ shows a high thermoelectric figure of merit ZT=S$^2$T/($\rho$k)$\sim$1.1 at over 700 °C, where S is the Seebeck coefficient, T is the temperature, $\rho$ is the electric resistivity, and k is the thermal conductivity. Similar to Na$_2$Co$_2$O$_4$, Bi$_2$Sr$_2$Co$_2$O$_y$ has a layered structure consisting of misfit layers of triangular Co–O planes and square lattice planes of the other metal oxide. The CdI$_2$-type CoO$_2$ subcell, in which electrons are strongly correlated, serves as electronic transport layers to achieve the large Seebeck coefficient and low electric resistivity, while the distorted rocksalt-type Bi$_2$Sr$_2$O$_4$ subcell enhances phonon scattering to achieve the low thermal conductivity. Bi$_2$Sr$_2$Co$_2$O$_y$ single crystal and polycrystalline bulk samples have been studied, and $S_{ab} \sim 130$ V/K and $\rho_{ab} \sim 6$ mΩ cm were reported for single crystals at room temperature. Many thermoelectric applications such as thermochrometry-on-a-chip, DNA microarrays, fiber-optic switches, and microelectrothermal systems have been cited for thermoelectric thin films. So far, no Bi$_2$Sr$_2$Co$_2$O$_y$ thin films have been reported. In this paper we report structural and thermoelectric properties of Bi$_2$Sr$_2$Co$_2$O$_y$ films grown by pulsed laser deposition (PLD). The excellent properties in these films open up tremendous opportunities for future thermoelectric applications.

Bi$_2$Sr$_2$Co$_2$O$_y$ thin films were grown by PLD from a ceramic Bi$_2$Sr$_2$Co$_2$O$_y$ target on (100) oriented single crystal LaAlO$_3$ and amorphous fused silica substrates. The fused silica substrate has low thermal conductivity, an additional advantage for thermoelectric applications. An excimer laser with 248 nm radiation was used for PLD with a laser energy density of 1.5 J/cm$^2$ and a repetition rate of 3 Hz. An oxygen pressure of 40 Pa (300 mTorr) was maintained during the film growth at substrate temperatures of 690–730 °C. The deposition rate was $\sim$0.18 nm/pulse. After the deposition, the films were cooled to room temperature within 5 min in 8×10$^4$ Pa (600 Torr) oxygen. Energy dispersive x-ray spectroscopy analysis of different spots on the surface of a film showed a Bi: Sr: Co ratio of 1.00:1.08:0.95 with an error of about 10%.

Figure 1(a) shows a typical x-ray diffraction (XRD) $\theta$-2$\theta$ scan of Bi$_2$Sr$_2$Co$_2$O$_y$ thin films on (1 0 0) LaAlO$_3$ taken on a Philips X’Pert Pro MRD four-circle diffractometer with Cu Kα radiation. Only peaks from diffractions of (00l) Bi$_2$Sr$_2$Co$_2$O$_y$ planes were observed besides the substrate peaks, indicating that the film is c-axis oriented. The $\omega$-scan of the Bi$_2$Sr$_2$Co$_2$O$_y$ (0 0 16) peak showed a full width at half maximum of 0.4°, further confirming the excellent c-axis orientation of the film. The $\theta$-2$\theta$ scan for the Bi$_2$Sr$_2$Co$_2$O$_y$ film on amorphous fused silica is shown in Fig. 1(b). In addition to strong Bi$_2$Sr$_2$Co$_2$O$_y$ (0 0l) reflections, there are several weak peaks representative of other orientations. We calculated the degree of c-axis orientation A by using the equation $A=(P-P_0)/(1-P_0)$, where $P=\Sigma I_{(00l)}/\Sigma I_{(hkl)}$ is for films and $P_0$ for the random oriented powders ($I$ is the peak intensity of a Bragg reflection) and an $A$ value of 1 corresponds to a perfect c-axis orientation. We find that $A$ for the film on fused silica is about 0.75.

The $ab$-plane texture information was investigated by XRD pole figures using a Bruker D8 diffractometer with the general area detector diffraction system (GADDS) system. Figure 2(a) shows the result for a Bi$_2$Sr$_2$Co$_2$O$_y$ thin film on LaAlO$_3$ (001) substrate. For the 2 0 8, 1 1 2, and 0 2 10 reflections, 12 spots overlap with the continuous Debye rings, indicating the existence of three different in-plane ori-
tent domains aligned 30° apart from each other in addition to randomly oriented regions. The small splitting of these spots was due to the small differences in the lattice parameters. The Debye rings for a thin film on fused silica substrate are continuous and smooth, indicating that the film is polycrystalline, fine grained, and has no in-plane texture. Figure 2(b) is a cross-sectional high-resolution transmission electron microscopy (HRTEM) image of a Bi$_2$Sr$_2$Co$_2$O$_y$ film on LaAlO$_3$ (001) substrate performed on a JEOL 3011 HRTEM system. Different layers within the film, as well as superlattice structures within the layers, are clearly visible in the image. The light band in the image shows the existence of regions of amorphization or delamination in the film. These structural defects provide additional scattering to electron and phonon transport, which will influence the thermoelectric properties of the film.

The resistivity versus temperature curves for two 300 nm thick Bi$_2$Sr$_2$Co$_2$O$_y$ thin films on LaAlO$_3$ (001) and fused silica substrates (5 × 5 mm$^2$ in size) are shown in Fig. 3(a), measured using a van der Pauw geometry on a dip probe inside a liquid helium tank. A metal-insulator transition is observed at about 140 K, which has been attributed to the decrease in the effective carrier number due to a pseudogap formation. The room temperature resistivity for film on LaAlO$_3$ is about 3 m$\Omega$ cm, similar to the $ab$-plane resistivity of Bi$_2$Sr$_2$Co$_2$O$_y$ single crystal and much smaller than that of the polycrystalline bulk. The room temperature resistivity for the film on fused silica is larger possibly due to the much larger $c$-axis resistivity than the $ab$-plane resistivity and the polycrystalline nature of the films. The Seebeck coefficient was measured using a Quantum Design physical properties measurement system (PPMS) system with a thermal transport option. The measurement was carried out in vacuum (10$^{-5}$ Pa) with a four-probe steady-state mode. The sample was 3 mm wide and 10 mm long. A resistive heater was connected to one end of the film, while the other end was mounted on a cold sink. The temperature gradient was measured by two thin film Cernox chip thermometers, and it was maintained at typically 0.5 K for the measurement. Figure 3(b) shows the temperature dependence of the Seebeck coefficient for two 300 nm thick Bi$_2$Sr$_2$Co$_2$O$_y$ thin films on LaAlO$_3$ and fused silica substrates. The temperature dependence is similar to those of other layered cobalt oxides such as Na$_x$CoO$_2$ and Ca$_x$CoO$_2$. The positive $S$ values indicate a hole transport. The room temperature $S$ of the film is about 125 $\mu$V/K on LaAlO$_3$ and 110 $\mu$V/K on fused silica. They are close to the single crystal value.
temperature of the Bi$_2$Sr$_2$Co$_2$O$_y$ layer. The deviation may be explained by the formation of the pseudogap in Bi$_2$Sr$_2$Co$_2$O$_y$ below the metal-insulator transition.\textsuperscript{21}

In conclusion, c-axis oriented Bi$_2$Sr$_2$Co$_2$O$_y$ thin films with multidomain in-plane texturing have been grown on single crystal LaAlO$_3$ (001) substrate by PLD, while the films on fused silica substrates are preferred c-axis oriented without in-plane texture. The Seebeck coefficient and resistivity of the films on both substrates are very similar to those in single crystal samples. The $p$-$n$ heterojunction using the Bi$_2$Sr$_2$Co$_2$O$_y$/Nb-doped SrTiO$_3$ structure shows a rectifying property. The availability of these thin films and heterostructures opens up opportunities for various thermoelectric applications.

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