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Citation: *Applied Physics Letters* **90**, 212111 (2007); doi: 10.1063/1.2741407

View online: <http://dx.doi.org/10.1063/1.2741407>

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Epitaxial behavior and transport properties of $\text{PrBaCo}_2\text{O}_5$ thin films on (001) SrTiO_3

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(Received 5 March 2007; accepted 27 April 2007; published online 24 May 2007)

Highly conductive $\text{PrBaCo}_2\text{O}_{5.5+\delta}$ thin films were grown on (001) SrTiO_3 by pulsed laser deposition. Microstructural studies from synchrotron x-ray diffraction and transmission electron microscopy reveal that the as-grown $\text{PrBaCo}_2\text{O}_{5.5+\delta}$ films are a -axis oriented with excellent single crystallinity. Two domain structures with c axes in the plane directions parallel to the substrate surface were found with an atomic sharp interface. Transport property and isothermal magnetoresistance measurements for both as-grown and post-annealing were done to understand the physical properties of the films. An abnormal positive magnetoresistance effect was observed in the postannealed films, which suggests that the spins in the system are polarized easier.

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Perovskite oxides with high ionic conductivity have practical applications in solid oxide fuel cells, chemical membranes, and gas sensors.¹ Among many possible compositions with perovskite structure, perovskite cobalt oxide family is particularly attractive for the electrodes due to the low electrical resistivity and high ionic conductivity. This family of cobalt oxides also displays many interesting physical phenomena, such as anomalous magnetoresistance effects and spin-glass behavior. For instance, strontium-doped lanthanum-cobalt oxide shows excellent mixed electrical and ionic conductivity² and at low temperature exhibits very interesting strong correlation behavior and pinning interactions.³

The oxygen-deficient ordered double perovskites $\text{RBaM}_2\text{O}_{5+\delta}$ (where R is a rare earth element and $M=\text{Mn, Fe, Co}$) have been the subject of a number of investigations because of their wide ranges of stoichiometry and concomitant variable transition metal oxidation states. The low temperature structural properties of these compounds have been studied in detail^{4–8} and some data are available on their high temperature oxygen chemistry.^{9–12} Recently, Streule *et al.*⁸ have measured high rates of oxygen uptake in $\text{GdBaB}_2\text{O}_{5+x}$ ($B=\text{Mn, Co}$) together with clear indications that the ordered vacancies are important to this process. We have also observed facile oxygen uptake in $\text{PrBaCo}_2\text{O}_{5+x}$ (PBCO) powders and determined the oxygen diffusion and surface exchange rates.¹⁰ Similar rapid surface exchange kinetics were observed on thin films of PBCO prepared by pulsed laser deposition.¹¹ In this letter, we report the low

temperature transport phenomena and magnetic properties of the highly epitaxial PBCO thin films on single crystal (001) SrTiO_3 (STO) substrates. Two types of domains and spin-glass interaction behavior in magnetoresistance studies were found in the highly epitaxial PBCO thin films.

A KrF excimer pulsed laser deposition system with a wavelength of 248 nm was employed to fabricate the PBCO thin films on (001) STO substrates. An energy density of about 2.0 J/cm^2 and a laser repetition rate of 5 Hz were adopted during film deposition. A single phase PBCO target prepared for the film deposition, as described previously,¹¹ was used. Single-crystal (001) STO ($c_{\text{STO}}=3.905 \text{ \AA}$) was selected as the substrate for epitaxial growth of PBCO thin films due to the good lattice match, about -2.2% , estimated from the standard crystal lattice parameters of PBCO ($c_{\text{PBCO}}=7.6343 \text{ \AA}$) and STO. The optimal growth conditions were found to be at temperatures higher than 850°C and in an oxygen pressure ranging from 200 to 300 mTorr. Microstructure, crystallinity, and epitaxial behavior of the as-grown PBCO films were characterized by x-ray diffraction θ - 2θ scan, high resolution synchrotron x-ray diffraction, and transmission electron microscopy (TEM). The transport properties of both the as-grown and after-annealing samples were measured by resistance measurements in the temperature range from 50 to 450 K using the four probe method. The magnetic properties of the films were determined by the corresponding isothermal magnetoresistivity measurements using a Quantum Design superconducting quantum interference device (SQUID) magnetometer.

Figure 1 is an x-ray θ - 2θ diffraction contour plot of an as-grown PBCO thin film showing that the as-grown films are predominantly a -axis oriented. The rocking curve mea-

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FIG. 1. X-ray diffraction θ - 2θ scans of As-grown PBCO/STO thin film.

surement of the (200) reflection has a full width at half maximum of 0.1° , compared to a resolution-limited width of the STO (200) of 0.007° , indicating that the film on STO substrate has excellent single crystallinity and epitaxial behavior. More precise radial scan synchrotron studies performed along the STO [200] in plane direction showed the interface relationship to be $(100)_{\text{PBCO}} \parallel (001)_{\text{STO}}$ and $[001]_{\text{PBCO}} \parallel [100]_{\text{STO}}$. Both PBCO (200) and (004) peaks were observed, indicating that the as-grown PBCO films are a axis oriented with two different domain structures in the directions parallel to the substrate surface.¹¹

The crystallinity and epitaxial quality of the as-grown films were further investigated by TEM. A dark field cross sectional TEM image [Fig. 2 (top)] shows that two types of

FIG. 2. Cross sectional TEM studies show the crystallinity and epitaxial behavior of the as-grown PBCO thin film on STO (top). SAED pattern taken only in the area covering the film, indicating the film has excellent single crystallinity (inset in top). High resolution TEM image shows the interfacial structure and epitaxial quality of the film (bottom).

FIG. 3. (Color online) Temperature dependence of resistance in the field of 0 and 6 T for (a) as-grown film and (b) after-annealing film.

domain structures exist on the interface, which agrees with the synchrotron studies. The selected area electron diffraction (SAED) pattern taken only in the inset of area covering the film is shown in Fig. 2 (top). The sharp electron diffraction spots with no satellites indicate that the films have good single crystallinity. The electron diffraction pattern also confirms that the film is a axis oriented with the c axis along the interface. High resolution cross sectional TEM studies have demonstrated that as-grown films have excellent epitaxial behavior and a sharp atomic interface, as seen in Fig. 2 (bottom).

Transport property measurements from both the as-grown and postannealed PBCO films have been done to understand the physical properties of the highly epitaxial PBCO films. The postannealed film is the as-grown PBCO film that was *in situ* annealed in the deposition chamber with an oxygen pressure of 400 Torr at the same temperature for 30 min before it is slowly cooled down with a rate of $5^\circ\text{C}/\text{min}$. The temperature dependences of resistance for both the as-grown and postannealed films in the fields of 0 and 6 T are shown in Figs. 3(a) and 3(b), respectively. The resistances dramatically decrease with increasing temperature in the range of 50–700 K, indicating that the films have typical semiconductor behavior at low temperatures. In the same temperature region, the resistivity for the postannealed PBCO film is much smaller than that from the as-grown film, as seen in Figs. 3(a) and 3(b). This phenomenon implies that with the postannealing treatment, oxygen is introduced into the PBCO film, resulting in a reduction of the defect concentration relative to the as-grown films. This can be understood from the defect chemistry of the perovskite materials where the conductivity of PBCO film is related to the oxygen vacancy concentration $[V_o^{\bullet\bullet}]$ in the film. During the postannealing, the reduction reaction can be represented by

Thus, after annealing, thin film absorbed oxygen and reduced the oxygen vacancy concentration and produced more charge carriers, resulting in the increasing conductivity of the film.

The magnetic field effect on the transport properties for as-grown and post-annealing films was studied by isothermal magnetoresistivity measurements. The samples were cooled down with zero field from room temperature to the highest prescribed temperature, at which the change in the resistance of the sample with the applied magnetic field was measured

FIG. 4. MR of thin films as a function of the applied fields for (a) as-grown sample and for (b) after-annealing sample at registered temperatures.

from 0 to 6 T. The applied field was back then decreased to 0 T with a ramping up and down rate of about 0.05 T/min. The sample was cooled down again afterwards in zero field to the lower prescribed temperature. The route should be followed to make sure that the sample is prepared fresh without any field history before doing any measurement. The isothermal magnetoresistance (MR) for both of the samples is shown in Fig. 4. The as-grown sample shows positive MR at 150 K, but negative MR at 100 K. For the postannealed sample, however, MR at 150 K is negative in the magnetic field below 5.6 T and shows the maximum in magnitude at 4.6 T. The negative MR at 100 K is much larger than that for the as-grown sample (for example, -7.8% for the postannealing sample while 3.1% for the as-grown sample at 6 T). It indicates that the postannealing procedure results in the spins in system to be polarized easier. The increased charge carrier concentration after the postannealing may result in the stronger spin polarization,¹¹ which is strongly dependent on the oxygen nonstoichiometry. A small negative MR at 70 K relative to that at 100 K suggests that there exists a ferromagnetic transition around 100 K, which makes the largest negative MR around this temperature. But this temperature is much lower than that in bulk samples in which the ferromagnetic transition temperature is above 150 K for the samples with various oxygen contents.⁸ These phenomena may arise from the tensile strain, which leads to

a narrow bandwidth and weakens the ferromagnetic interactions. In fact, the strain effect on the ferromagnetic temperature was often observed in many other systems.¹³

In conclusion, the highly conductive PBCO thin films have been epitaxially grown on (001) STO by pulsed laser ablation. Microstructure studies reveal that the as-grown PBCO films are *a* oriented and have excellent single crystallinity. Two types of domain structures with *c* axes in the plane directions parallel to the substrate surface were found with excellent epitaxial behavior and atomic sharp interface. The present study on transport properties of both as-grown and after-annealing films demonstrates that the PBCO thin films have a typical semiconductor behavior with a spin-glass interaction behavior in the MR effect study at low temperature.

This research is partially supported by the Department of Energy under DE-FG26-07NT43063 and the State of Texas through the TcSUH.

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