Journal of Alloys and Compounds, 195 (1993) 643–646
JALCOM 7548

Electrical resistivity of $PrBa_2Cu_{3-x}Ga_xO_{7-y}$ (001) and (105) oriented thin films

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Abstract

In the past almost all studies on the anisotropy of the transport properties in 1-2-3 materials were performed on single crystals. This study is focused particularly on the anisotropy of the specific resistivity ρ as measured on almost single domain thin films of $PrBa_2Cu_{3-x}Ga_xO_{7-y}$. Gallium doped $PrBa_2Cu_3O_{7-y}$ was deposited on (305) $SrTiO_3$ to obtain (105) oriented, almost single domain thin films [1]. The films are deposited by rf magnetron sputtering in a one-step process, at low deposition rate. A relatively simple route for the preparation of single-phase gallium doped $PrBa_2Cu_3O_{7-y}$ target material by a citrate synthesis and pyrolysis [2] is presented.

1. Introduction

A much higher barrier resistivity than that of $PrBa_2Cu_3O_7$ (PrBaCuO) is desirable for applications in ramp type YBaCuO/PrBaCuO/YBaCuO junctions. Modification of PrBaCuO by doping with gallium on the Cu(1) sites gives the opportunity to control the conductivity. The specific resistivity of $PrBa_2Cu_3O_{7-y}$ can easily be modified by the gallium doping level [3]. This research concerns doping levels in the range $0 \leq y \leq 0.1$, both in polycrystalline sintered material and in epitaxial thin films. As observed by Hiroi [4] in the $YBa_2(Cu_{3-x}Fe_x)O_{7-y}$, a microdomain structure will form for those systems with high doping levels. In the case of iron doping in YBaCuO (micro) clustering of Fe atoms will occur for doping levels $x > 0.12$. In the analog situation of gallium in PrBaCuO ($PrBa_2Cu_{3-x}Ga_xO_{7-y}$) we tried to prevent the formation of gallium-rich domains at higher doping levels by using a highest doping level of $x = 0.1$.

A relatively simple route for the preparation of single-phase gallium doped $PrBa_2Cu_3O_{7-y}$ target material by a citrate synthesis [2] is presented. The gallium doped $PrBa_2Cu_3O_{7-y}$ thin films are studied for their transport properties because of the possible application as a non-superconductive inter or barrier layer in superconductive electronics. The temperature dependencies of the specific resistivity for $PrBa_2Cu_{3-x}Ga_xO_{7-y}$ will be discussed in terms of the variable range hopping model. Furthermore this doped material allows us to study the transport mechanism in this variable range hopping (VRH) system [5].

2. $PrBa_2Cu_{3-x}Ga_xO_{7-y}$ powder preparation and analyses.

A procedure for obtaining homogeneous single-phase gallium doped $PrBa_2Cu_{3-x}Ga_xO_{7-y}$ by citrate synthesis and pyrolysis is developed. In contrast to the solid-state (diffusion) reactions, this procedure results in single-phase, sub-micron powdered, PrBaCuGaO material after only one calcination and a relatively short high temperature treatment. The atomic mixing of constituents after the citrate synthesis followed by pyrolysis makes this possible, because long range diffusion is unnecessary. The procedure for obtaining gallium doped $PrBa_2Cu_3O_{7-y}$ is a modified recipe for obtaining $YBa_2Cu_3O_{7-y}$ as described by Blank et al. [2]. The recipe consists of 3 steps, which are (1) dissolving the metals or oxides in (citric) acidic solutions followed by neutralisation, (2) pyrolysis of this solution and finally (3) a calcination and reaction treatment at high temperature. The modification, as refered to Blank [2], is the replacement of Y_2O_3 by Pr_6O_{11} and a partial substitution of CuO by Ga. Because the gallium oxides are very stable in acidic environments these materials were not usable. Instead we used pure gallium, that could be dissolved in nitric acid as easy as all other oxides used. The powder thus obtained can directly be processed to a sputter target, which is obtained after pressing and a sinter treatment at typically 930 °C for 10 hrs.. Powder XRD shows good 123 crystallinity, without signs of other phases. Good crystallinity and stoichiometry was also confirmed by HRTEM. Figure 1 shows a HRTEM picture of the calcinated and

0925-8388/93/$06.00

reacted powder $PrBa_2Cu_{2.95}Ga_{0.05}O_{7-y}$. From these TEM measurements we could also conclude that the powder was of very good micro crystallinity. Micro clustering of gallium could not be observed up to the doping levels used. Using X-ray fluorescence (XRF) the atomic concentrations were determined at Pr:1.00(±5%), Ba:2.00(±3%), Cu:2.95(±1%) and Ga:0.05(±1%). As shown by Blank [2], the carbon content is less than 0.2 % in the calcinated powder.

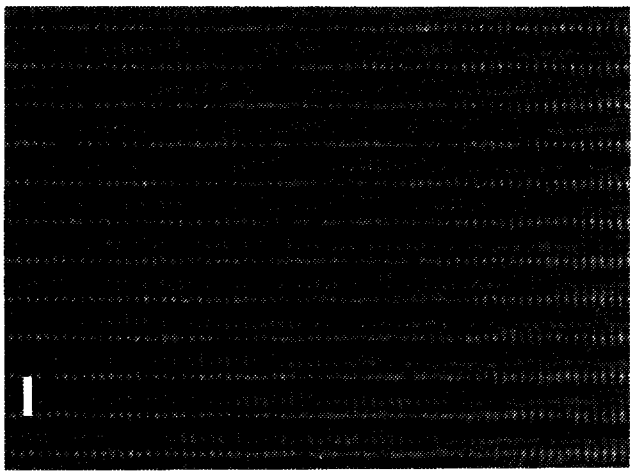

Figure 1. HRTEM picture of $PrBa_2Cu_{2.95}Ga_{0.05}O_{7-y}$ powder in the [110] direction. The bar indicates the length and direction of the c-axis.

2.1 Recipe

The recipe holds for 0.1 mol $PrBa_2Cu_{3-x}Ga_xO_{7-y}$ (x=0.05). $BaCO_3$ (39.47 gr., 0.2 mol Ba) is dissolved in 60 ml nitric acid HNO_3 (65%), Pr_6O_{11} (17.02 gr., 0.1 mol Pr) is dissolved in 60 ml HNO_3 (65%). Add 10 ml HNO_3 (65%) to 50 ml (0.05 mol Ga) of a standard solution 0.1 M Ga in HNO_3 (65%). Dissolve CuO (23,46 gr., 0.295 mol Cu) in this acidic solution. Put all three acidic solutions together and add 240 gr. (granular) citric acid. Adjust the pH of this solution to 3.5-4 using NH_4OH. The solution should stay clear without precipitates. This solution is heated to pyrolysis on a hot-plate. The contents will become viscous and will swell before combustion. This pyrolysis is better done with small quantities of solution (250 ml) in an oversized Pyrex breaker in order to keep your kitchen clean. To remove nitric and carbon compounds from the obtained powder after pyrolysis, a calcination for typically 5 hr. at 800 °C in flowing O_2 is performed. A single phase, fine powered material is obtained when the calcinated powder is milled for a short time (typically 15 min.) and reacted at a temperature of 930 °C for 15 hrs.. The reaction and cooling (1 °C/min) to room temperature is done in flowing O_2 at ambient pressure. The thus obtained powder can directly be processed to a sputter target.

3. Thin films

3.1 Sputter deposition optimization of PrBaCuGaO

The optimization of sputter parameters for thin PrBaCuGaO films regarded the resistivity and smoothness of the film. The dependence of the film resistance at room temperature on the substrate temperature during deposition shows a clear minimum, as can be seen in figure 2. This minimum of the resistivity can be expected for a non-granular, fully oxydized PrBaCuO film [6]. The substrate temperature for which a minimal resistivity was found was taken as the best deposition temperature for the thin PrBaCuGaO films. The other sputter parameters, such as argon and oxygen partial pressures and flows were the same as for optimal YBaCuO deposition.

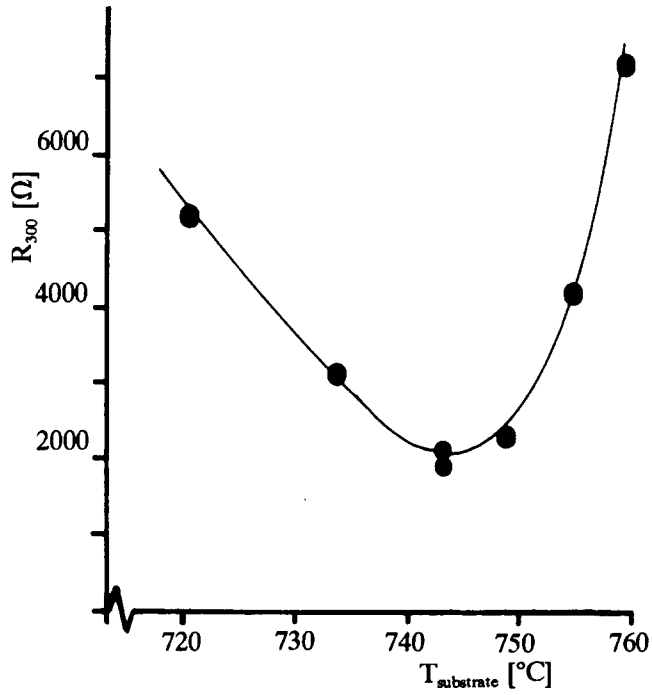

Figure 2. Film resistance (at room temperature) as a function of the substrate temperature during deposition for $PrBa_2Cu_{2.95}Ga_{0.05}O_7$ on (001) $SrTiO_3$.

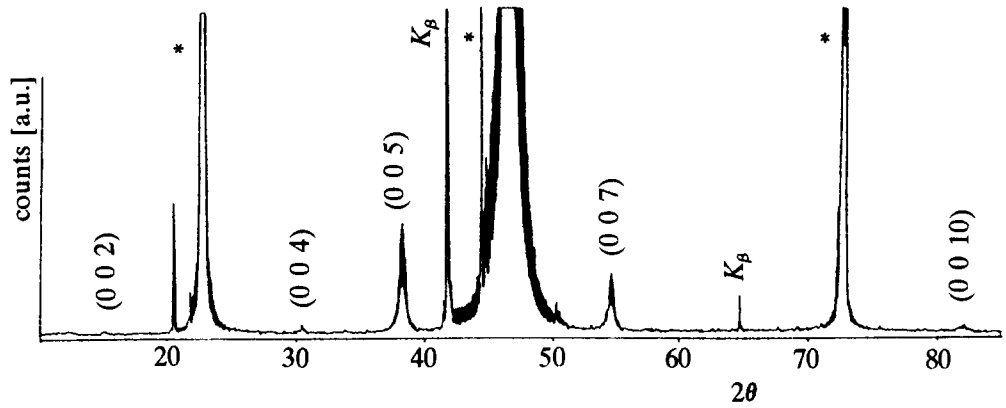

Figure 3. $2\theta/\theta$ XRD scan on a $PrBa2Cu_{2.95}Ga_{0.05}O_7$ film on (001) $SrTiO_3$. The $SrTiO_3$ substrate peaks are labelled with "*". Reflections from the PrBaCuGaO are labelled with their corresponding indices.

3.2 Thin film analysis of $PrBa_2Cu_{2.95}Ga_{0.05}O_7$

The chemical composition of the thin films has been compared to the target material by Auger Electron Spectroscopy. The results in atomic percents:

at.%	Pr	Ba	Cu	Ga
Target	22±2	40±2	8.5±0.7	0.6±0.1
Film	22±2	37±1	11.2±0.9	0.7±0.1

These values show that the chemical compositions of the target and the films are essentially the same, except for a slightly higher copper content of the thin film.

The x-ray diffraction (XRD) experiments were performed on a Philips Materials Research Diffractometer (MRD) equipped with parallel beam x-ray optics. As can be seen in figure 3, PrBaCuGaO grows with the c-axis perpendicular to a (001) oriented $SrTiO_3$ substrate, because only the (00*l*) reflections can be observed. A similar result is obtained when growing PrBaCuGaO films on (305) $SrTiO_3$ substrates. A $2\theta/\omega$ scan (figure 4) on a PrBaCuGaO film deposited on a (305) $SrTiO_3$ substrate, directed along the $SrTiO_3$ [001] direction, revealed the (00*l*) peaks from the PrBaCuO material. The (009) and (0012) reflections from the PrBaCuO coincided with the (003) and (004) reflections of the $SrTiO_3$, respectively. By scanning reciprocal space no other reflections, related to different oriented material, could be observed. These results confirm that the c-axis of the PrBaCuO is tilted over 31° when referred to the surface normal and parallel to the [001] $SrTiO_3$ direction. These results agree with the measurement of the (104) PrBaCuGaO reflection, that was found at the right θ, ω, ϕ and ψ values. The rocking curve of this reflection reveals a full width at half maximum (FWHM) of 0.5°, indicating a very well textured film.

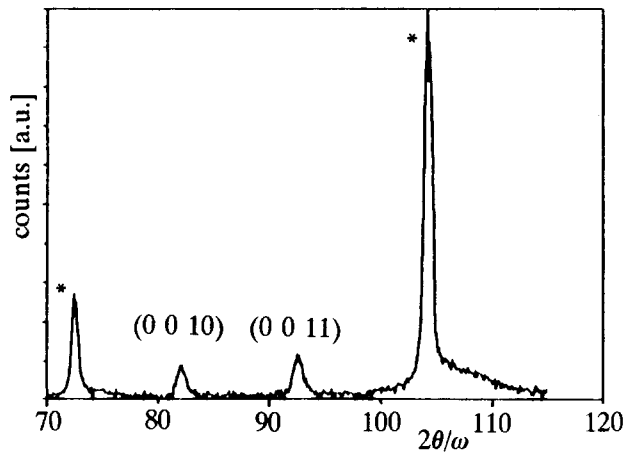

Figure 4. $2\theta/\omega$ XRD scan along the $SrTiO_3$ [001] directions on a PrBaCuGaO film on (305) $SrTiO_3$. $SrTiO_3$ substrate peaks are labelled with "*". Reflections from the PrBaCuO are labelled with their corresponding indices.

3.3 Anisotropy and temperature dependence of resistivity

The anisotropy measurements of the resistance of thin films of PrBaCuO and PrBaCuGaO on (305) $SrTiO_3$ substrates show an anisotropy ratio of about 2 between the a-b and c-direction, as measured on films deposited on (305) $SrTiO_3$. This is a relatively low value compared to a factor of 50 for YBaCuO [1] grown on (305) substrates, which approaches the values measured in single crystals [7]. The low value of the anisotropy can be due to an inherent property or an imperfect morphology of the thin film.

A single activation energy model for the resistivity

predicts an exponential temperature dependent resistivity $\rho \sim \exp(\Delta_0/T)$. According to Fisher [8] et al, this model is valid for oxygen deficient $PrBa_2Cu_3O_6$ and $YBa_2Cu_3O_6$, but more complicated models, such as variable range hopping, have to be used in case of the fully oxygen loaded $PrBa_2Cu_3O_7$ and $YBa_2Cu_3O_7$. We find for the gallium doped PrBaCuGaO that a single activation energy model is not valid. For all films it was found impossible to describe the resistivity with a single activation energy Δ_0, because a log ρ to (1/T) plot resulted in very curved lines.

Instead, the fully oxydized gallium doped $PrBa_2Cu_{3-x}Ga_xO_7$ films, like bulk $PrBa_2Cu_3O_7$ material, can indeed be described better as a variable range hopping system with a resistivity $\rho = \rho_0 \cdot \exp[(T_0/T)^{1/4}]$. This temperature dependency is valid in the case of a constant density of states and hopping in 3 dimensions [5,9]. As can be seen in figure 5, the VRH model also gives a limited approximation of the temperature dependent resistivity. This figure presents the a-b plane resistivity as measured on $PrBa_2Cu_{2.95}Ga_{0.05}O_7$ films on both (001) and (305) $SrTiO_3$ at optimal deposition temperature (746 °C). The estimated value of T_0 is approximately $\sim 10^7$K.

The absolute values of the resistivity $\rho(T)$ of the gallium doped PrBaCuO films are one order of magnitude higher than those of the undoped PrBaCuO films, as can be seen in figure 6. The $\rho(1/T^{1/4})$ dependencies have a similar slope with $T_0 \sim 10^7$K. We can suggest an increase of the film resistivity in case of gallium doping due to the lower density of states without significant changes of the localization nature in PrBaCuO and Ga-doped PrBaCuGaO films.

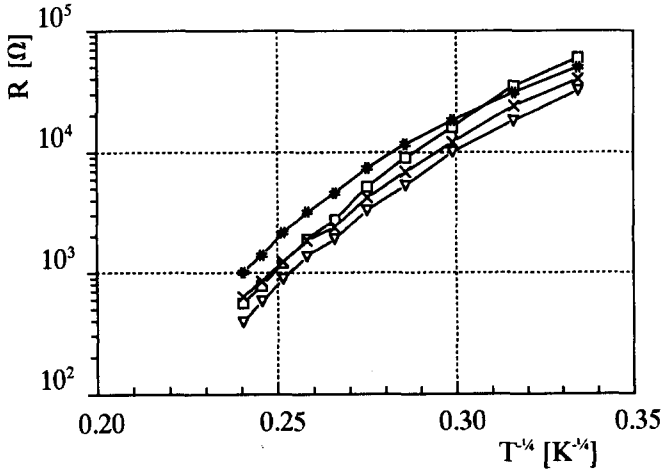

Figure 5. Temperature dependence of the resistance of a $PrBa_2Cu_{2.95}Ga_{0.05}O_7$ film , plotted as a function of $\rho = f(1/T^{1/4})$. #:(001) $SrTiO_3$, ×:(305) $SrTiO_3$ both run 209, □:(001) $SrTiO_3$, ▽:(305) $SrTiO_3$ both run 207. The deposition temperature was 746 °C for all films.

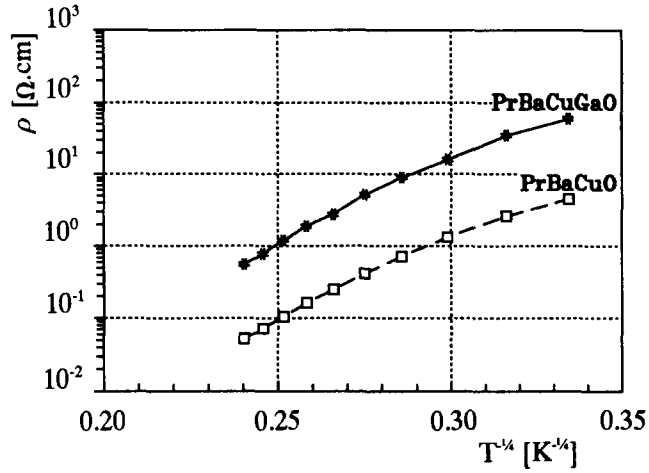

Figure 6. Comparison of the resistivity of the gallium doped and undoped PrBaCuO epitaxial films, plotted as a function of $\rho(1/T^{1/4})$.

4. Conclusions

It is shown that PrBaCuGaO can be grown epitaxially on $SrTiO_3$ (001) and (305) substrates by rf magnetron sputtering from a stoichiometric target. The target and films have essentially the same chemical composition. On (305) $SrTiO_3$ substrates PrBaCuGaO can be grown coherently tilted, which allows in principal anisotropy measurements on one thin film [1]. PrBaCuGaO showed a smaller anisotropy for the resistivity than YBaCuO, which can be due to an inherent property or an imperfect morphology.

The Variable Range Hopping model gives a better fit of the resistivity of PrBaCuGaO than the single activation energy model. The T_0 is estimated at $\sim 10^7$K for both cases.

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