New high-temperature superconducting phase spread alloy thin films

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We have prepared $Gd_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ phase spread alloy thin films with well-defined variations in the concentration of Pr across a single substrate. Their Pr concentrations were independently determined from electrical resistivity and Auger electron spectroscopy measurements. The results from both methods are in good agreement with each other. Using this technique several high-temperature superconducting thin-film alloys may be grown under virtually identical conditions. As an example of an important application of this technique, we measured the changes in the films' resistivities and critical temperatures (T_c) induced by decreasing their oxygen concentration. The observed shifts in T_c of the oxygen-deficient samples appear to be slightly dependent on their Pr concentrations.

It is well-known that the $PrBa_2Cu_3O_{7-\delta}$ (PrBCO) compound is not superconducting.[1] When a superconductor of the type $REBa_2Cu_3O_{7-\delta}$, where RE is a rare earth or yttrium, is doped with Pr, the Pr substitutionally enters into the RE site and the superconducting critical temperature (T_c) is depressed.[1,2] In the case of $Gd_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$, superconductivity ceases when $x\approx0.5$.[3] Although much work has been performed on $RE_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ alloy single crystals, including resistivity[1-3] and magnetization[4] measurements, as well as Mössbauer spectroscopy,[5] few experiments have been performed on thin films.[6] Since the structural and physical properties of ceramic films, such as resistivity and T_c, can vary between samples grown under *nominally* identical conditions, the *simultaneous* preparation of several different samples on the same substrate is a definite advantage. In the present work, we describe a simple technique for growing several ceramic phase spread alloy thin films on a single substrate, under identical growth conditions. A $Gd_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ phase spread alloy sample is then used to study changes in T_c when its oxygen concentration is decreased.

The preparation method is a combination of the traditional phase spread alloy and the nonaligned, chopped power, oscillatory (NACHOS) growth techniques.[7] Briefly, the samples were prepared via magnetron sputtering, at a substrate temperature of approximately 750 °C, from two targets, $PrBa_2Cu_3O_{7-\delta}$ (PrBCO) and $GdBa_2Cu_3O_{7-\delta}$ (GdBCO). The deposition rates were calibrated from the positions of low-angle finite-size x-ray peaks of thin films.[7] The [100] oriented MgO substrates were rectangular, typically 5×10 mm^2, and the films were approximately 5×7 mm^2. The substrates were mounted on a heater block whose position in the chamber was controlled via a computer-driven stepping motor. During growth, they were placed to one side of each target, outside the glow discharge, with their long dimension pointing away from the discharge. The material, be it GdBCO or PrBCO, was deposited for a short period of time, corresponding to a fraction of a unit cell. The substrate was subsequently moved near the other target, and the procedure repeated multiple times [see Fig. 1(b) inset]. The Pr

concentration gradient was adjusted by varying the position of the substrate and/or deposition times.

The thicknesses of the resulting films, measured using contact profilometry, were typically 2000 to 3000 Å, with less than a 10% variation across the films. X-ray diffraction data revealed crystalline growth along the c axis with no impurity phases. The preparation method and structural studies assure that the films were indeed alloys because: (1) much less than a unit cell was deposited per cycle (according to the deposition rate calibration), and (2) $\theta-2\theta$ x-ray scans revealed sharp [001] peaks, with no evidence of superlattice peaks. Two samples were simultaneously prepared; one was analyzed via Auger spectroscopy, and the other used to determine the temperature-dependent resistivity $\rho(T)$.

Samples used in $\rho(T)$ measurements were photolithographically patterned into five strips approximately
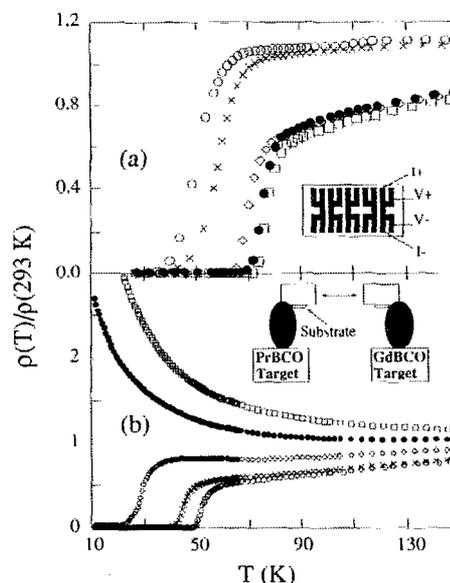

FIG. 1. Resistivity data from two patterned phase spread alloy films as a function of temperature. In sample (a), $\rho(293\ K)=0.81$, 1.03, 1.43, 2.93, and 4.14 mΩ cm with increasing Pr concentration. In sample (b), $\rho(293\ K)=0.99$, 1.16, 2.06, 2.08, and 2.44 mΩ cm. The photolithography pattern and NACHOS growth technique are shown in the insets.

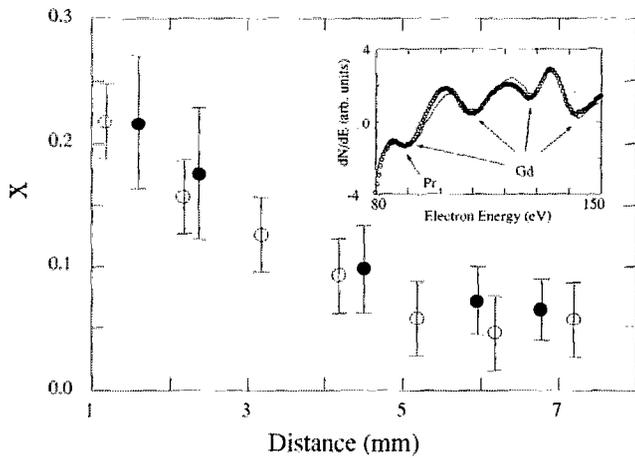FIG. 2. Pr concentration in the $Gd_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ phase spread alloy thin film of Fig. 1(a), determined from Auger ($\bigcirc$) and resistivity measurements ($\bullet$). The x axis is the distance from the edge of the film. The Auger data were adjusted horizontally to match the center data point with the center of the film, with a resulting uncertainty of ± 0.5 mm. The error bars in the resistivity data result from the 90% and 10% resistivity points. Inset shows a typical Auger scan; the solid curve represents a fit to the weighted average of data obtained from pure PrBCO and GdBCO single thin films plus an arbitrary linear background. In this case, the fit yielded $x = 0.16$. The positions of Gd and Pr peaks are indicated.

FIG. 3. Critical temperatures (determined from the 50% resistivity points) of as-grown samples ($\bigcirc$) and deoxygenated ($\delta \approx 0.3$) samples ($\bullet$) with identical Pr concentration profiles. The error bars represent the 90% and 10% resistivity range. Inset shows the shifts in temperature of the 50% resistivity points ($T_c - T_c^{\mathrm{deox}}$) due to deoxygenation as a function of the Pr concentration x; the error bars represent the maximum and minimum possible values of ($T_c - T_c^{\mathrm{deox}}$) consistent with the 90% and 10% resistivity points.

0.5-mm wide [Fig. 1(a) inset]. The resistivity of each strip was measured using a four-probe method. Since the direction of the Pr gradient was perpendicular to the strips, the range of concentration δx in any one of them was very small (this is quantified below). The measurements shown in Fig. 1 demonstrate the versatility of the phase spread alloy growth method: both semiconducting and superconducting samples can be grown.

An ultrahigh vacuum (UHV) low-energy electron diffraction (LEED) Auger system (at 30 mA and 1500 or 1600 V) was used to directly determine the Pr concentration. Prior to the measurements, the film's surface was sputtered with argon ions to remove surface contaminants. Calibration data was obtained from pure PrBCO and GdBCO thin films under nominally identical conditions. The Pr concentration of the phase spread alloys as a function of substrate position was determined by fitting the 80–150-eV Auger data to a weighted average of the two sets of data obtained from the pure films. An adjustable linear background was also included in the fit to take into account the different surface and acquisition conditions of each measurement. An example of such a fit is shown in the inset of Fig. 2.

The Pr concentration along the gradient direction of the sample corresponding to Fig. 1(a), determined both from the Auger measurements and by comparing the T_c's of the different strips with published bulk values,[8] are shown in Fig. 2. The Auger and resistivity data are in good quantitative agreement with each other, within experimental error. From this information, we estimate the range of Pr concentration within each strip to be small ($\delta x \lesssim 0.02$). This corresponds to transition widths $\delta T_c \lesssim 3.6$ K. The observed transition widths of the Pr-rich strips were ap-
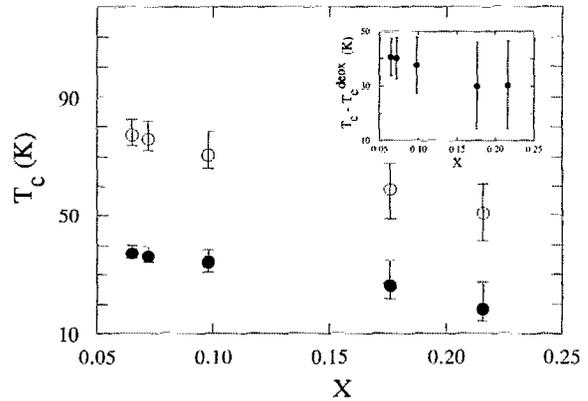
proximately 9 K, which indicates that factors other than the Pr concentration gradient, such as sample imperfections, also contribute to the broadening.

As an important application of these films, we studied the effect of oxygen depletion on their T_c. The oxygen content of the sample used to obtain the Auger data shown in Fig. 2 was decreased (prior to patterning) by annealing at 250 °C in flowing Ar gas for approximately 30 min. In the absence of a better method for determining the oxygen concentration of these thin films, their oxygen deficiency was estimated to be $\delta \approx 0.3$ from a similar treatment of a fully oxygenated GdBCO thin film. We note that such a determination of the oxygen concentration may not be correct, since there is no evidence that the oxygen dynamics in PrBCO is the same as in GdBCO. In Fig. 3 we compare the T_c's (defined by their 50% resistivity points) of the oxygenated and deoxygenated strips. The shifts in T_c (Fig. 3 inset) appear to be larger for strips with lower Pr concentrations, although an accurate determination of this difference is difficult to assess due to the sizable transition widths. We note that similar trends have been observed in $Er_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ and $Sm_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ oxygen-deficient single crystals.[9]

In conclusion, we have developed a convenient method for preparing several high-temperature superconducting phase spread alloy films on a single substrate. The Pr concentration in $Gd_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ films determined from Auger electron spectroscopy is in good quantitative agreement with $T_c(x)$ measurements. The shifts in T_c of oxygen-deficient $Gd_{1-x}Pr_xBa_2Cu_3O_{7-\delta}$ phase spread alloys with respect to fully oxygenated ones appear to be greater in those with lower Pr concentrations.

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