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Tunable superconductivity in parent cuprate $Pr_2CuO_{4\pm\delta}$ thin films*

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We studied the role of oxygen in $Pr_2CuO_{4\pm\delta}$ thin films fabricated by the polymer assisted deposition method. The magnetoresistance and Hall resistivity of $Pr_2CuO_{4\pm\delta}$ samples were systematically investigated. It was found that with decreasing oxygen content, the low-temperature Hall coefficient (R_H) and magnetoresistance changed from negative to positive, similar to those with the increase of Ce-doped concentration in $R_{2-x}Ce_xCuO_4$ (R = La, Nd, Pr, Sm, Eu). In addition, we observed that the dependence of the superconducting critical temperature T_c with R_H for the $Pr_{2-x}Ce_xCuO_4$ perfectly overlapped with that of $Pr_2CuO_{4\pm\delta}$. These findings point to the fact that the doped electrons induced by the oxygen removal are responsible for the superconductivity of the T'-phase parent compounds.

Keywords: $Pr_2CuO_{4\pm\delta}$ thin film, superconductivity, polymer assisted deposition

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1. Introduction

Studying the parent compounds of high-T_c superconductors is crucial for unveiling the underlying mechanism of high-temperature superconductivity, as well as providing significant clues to explore new superconductors. Parent compounds of the cuprates have been long considered as antiferromagnetic Mott insulators, which can be tuned to superconductors by hole or electron doping.[1] For example, Sr^{2+} cation substitute La^{3+} cations in hole-doped $La_{2-x}Sr_xCuO_4$ or Ce^{4+} cation substitute R^{3+} cations in electron-doped $R_{2-x}Ce_xCuO_4$ (R = La, Nd, Pr, Sm, Eu).[2] Besides the Ce-doped concentration, superconductivity of the electron-doped cuprates depend heavily on the oxygen content. In 1995, the superconducting critical temperature of the under-doped $Pr_{2-x}Ce_xCuO_4$ (PCCO) was enhanced with respect to that of the optimally doped compound when the sample was submitted to a protected annealing process.[3] In 2008, superconductivity was induced in parent thin films T'-R_2CuO_4 (R = Nd, Pr, Sm, Eu, Gd) by low-temperature annealing under the high-vacuum environment.[4] This discovery seemingly challenged the commonly accepted model that high-T_c superconductivity results from doping extra carriers into Mott insulators.

The intrinsic physics of superconductivity in the parent compounds is still under debate. Optical conductivity measurements on $Pr_2CuO_{4\pm\delta}$ (PCO) thin films have disclosed that the AFM-correlated pseudogap is absent in this system, which indicates that the T'-phase parent cuprates are metallic and superconductivity develops at low temperature.[5] In fact, it is unavoidable that the presence of unwanted oxygen defects during the sample preparation in turn introduces extra carriers into the CuO_2 planes and leads to superconductivity. Wei *et al.*[6] found that the superconducting T'-La_2CuO_4 thin film can be tuned into an insulator by substituting Sr^{2+} for La^{3+}. They suggested that the T'-phase parent cuprates are Mott insulators, while the intrinsic defects, most likely oxygen vacancies, are the sources of the effective carriers in these materials. Moreover, dynamical mean field theory (DMFT) studies demonstrate that the parent compounds may be described as weakly correlated Slater insulators rather than the strongly correlated charge transfer insulators.[7,8] Electrical transport measurement is a common but powerful method to explore the intrinsic electronic state in various superconductors. Plenty of studies in $R_{2-x}Ce_xCuO_4$ materials[9–13] support the idea that the negative magnetoresistance (MR) and nonlinear magnetic field dependence of Hall resistivity can be associated to the antiferromagnetic order, Fermi surface reconstruction, quantum phase transition, etc., which contributed to the understanding of the mechanism of high-T_c superconductivity. Regretfully, systematic electrical transport investigations have been seldom addressed in the parent system.

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In this paper, we carried out systematical MR and Hall resistivity measurements on superconducting PCO thin films which were synthesized on $SrTiO_3$ (STO) substrates by the polymer assisted deposition method. With the decrease of oxygen content, the low-temperature MR gradually changes from negative to positive. Meanwhile, the low-temperature Hall coefficient R_H undergoes a sign reversal, suggesting that the dominant carriers change from electrons to holes. These behaviors are quite similar to those observed in $R_{2-x}Ce_xCuO_4$ materials. Furthermore, a T_c versus R_H plot for both PCCO and PCO samples shows a perfect overlap of the data points of the two compounds. Our results imply that the carriers induced by the oxygen removal benefit the superconductivity in the T'-phase parent cuprates.

2. Preparation and measurements

Until now, the superconducting parent compounds have been successfully synthesized by metal–organic decomposition (MOD)[4] and molecular beam epitaxy (MBE) methods.[6,14,15] In general, it is hard to buy naphthenates of rare-earth elements used in MOD. On the other hand, MBE facilities are very expensive, and it is of low-efficiency during the thin film preparation. Therefore, developing a high-efficiency and inexpensive method for preparing superconducting parent thin films is of high technological relevance. Polymer assisted deposition (PAD) is a newly developed method, which has the advantages of easy operation, low cost, and stable precursor solutions.[16,17] In Fig. 1(a), a schematic diagram of PAD method is presented. In the first stage of the process, metal ions are electrostatically bound to the polymer in deionized water, forming a uniform and stable solution. Afterwards, the solution is applied onto a substrate through either spin-coating or dipping. Finally, the coated substrate is treated at a desired temperature in an oxygen-controlled environment to remove the polymer and enable the growth of the metal-oxide film.

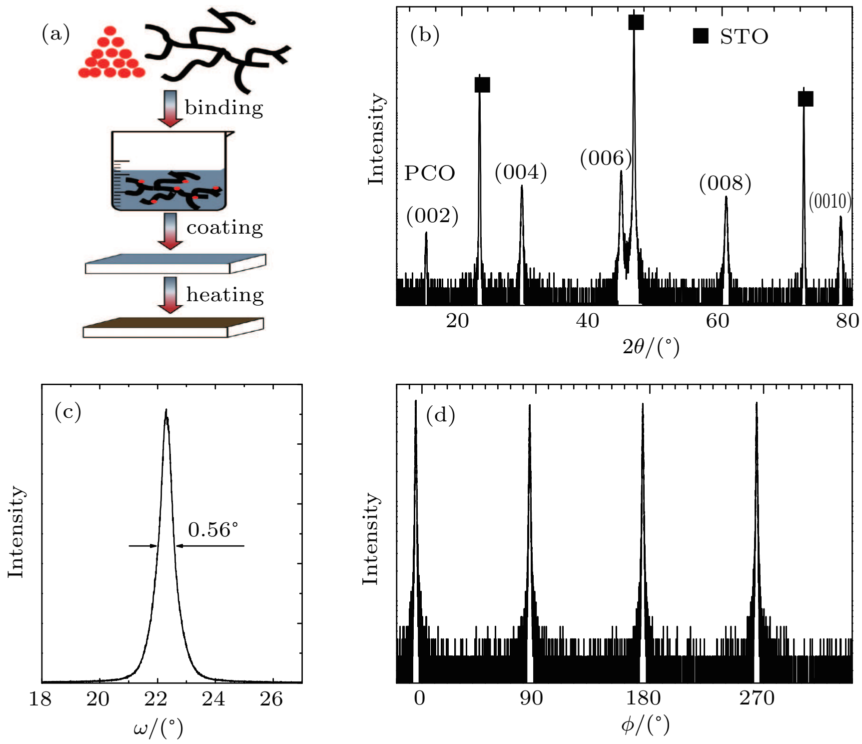

Fig. 1. (a) Schematic diagram of polymer assisted deposition method with metallic ions represented by red dots and polymeric chains by thick dark lines. Panels (b)–(d) show XRD 2θ-scans, ϕ-scan, and rocking curve of (006) diffraction peak of the $Pr_2CuO_{4\pm\delta}$ film on the $SrTiO_3$ (001) substrate, respectively.

To prepare high-quality superconducting PCO thin films, the metal ion sources are Pr and Cu nitrates, and the organic compounds are polyethylenimine (PEI) and ethylenediaminetetraacetic acid (EDTA). The concentration of Pr (Cu) metal ions in the solution was determined by inductively coupled plasma-atomic emission spectroscopy measurement. Then the precursor solution was obtained by mixing Pr solution and Cu solution at a certain stoichiometric ratio. In order to avoid a Cu deficiency, we enriched Cu by 50% in the precursor solution. The precursor solution was spin coated on STO substrates. The polymer was pyrolyzed by heating gradually from room temperature to 550 °C in the air. After that, the samples were sintered and crystallized at 850 °C for one hour in a tubular furnace under 200 Pa oxygen pressure. Finally, the films were annealed in low-oxygen pressure of about 1 Pa at various temperatures. The film thickness measured by scanning electron microscope is about 60 nm.

To characterize the structure and crystallinity of the PCO thin films, we measured the $\theta/2\theta$, ϕ-scan, and rocking curve of (006) diffraction peak of the samples using x-ray diffractometer. The XRD 2θ-scan of the PCO film on STO (001) is shown in Fig. 1(b). All peaks are sharp and can be indexed to (00l) of the T'-structure, indicating that the film shows a single phase and c-axis orientation. Figure 1(c) exhibits a small full width at half maximum of the rocking curve of the (006) diffraction peak, meaning that the sample has a good epitaxy as also evidenced by the ϕ-scan data with the approximately equal peak intensities in Fig. 1(d). Subsequently, electrical transport properties were measured in a 9 T physical property measurement system. In order to improve the measurement accuracy, all samples were patterned into standard Hall bridge structures. The magnetic field was applied perpendicular to the film surface during the MR and Hall resistivity measurements.

3. Results and discussion

In Fig. 2, we present the temperature dependence of the resistivity for various PCO thin films. With the decrease of the temperature, the resistivity of US3, US21, and US19 samples shows an upturn at the temperature $T_{\min}$. Considering that c_0 should have a positive correlation with the relative oxygen content of the samples,[18] we calculated the c-axis lattice constants c_0 of PCO films (see Table 1) by Bragg diffraction formula $2d\sin\theta = n\lambda$, where $d = c_0$, λ(Cu $K\alpha$) = 1.54056 Å, and $n = 8$ if we set 2θ to be the angle of (008) peak. It is worth mentioning that $T_{\min}$ gradually decreases as c_0 reduces and the upturn behavior disappears for S22, S19, S11, and S3.

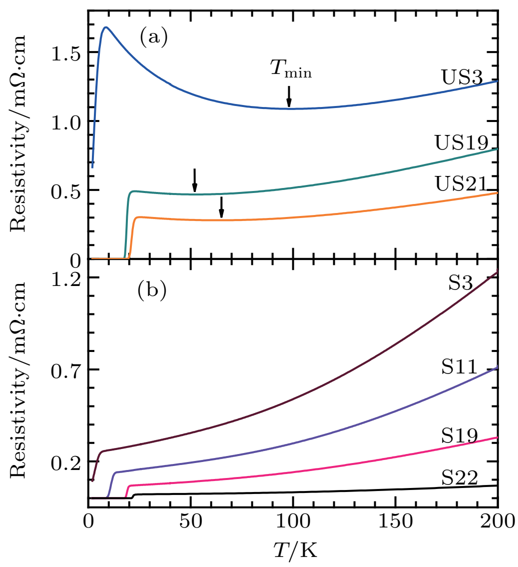

Fig. 2. Resistivity as a function of temperature for $Pr_2CuO_{4\pm\delta}$ films with various oxygen contents. (a) The resistivity of the samples US3, US19, and US21 shows an upturn at the temperature defined as $T_{\min}$. (b) The resistivity versus temperature of S22, S19, S11, and S3 samples shows a good metallic behavior. The number in the sample label presents the superconducting transition temperature.

In the underdoped region of Ce-doped cuprates, the low-temperature resistivity also shows an AFM-induced upturn, which gradually disappears with the increase of Ce concentration.[11,19] High magnetic field can suppress this upturn behavior, resulting in a negative MR.[13] Figure 3 displays the field dependence of MR, with the applied field parallel to the c-axis ($B \parallel c$). The MRs of US3, US21, and US19 samples are negative at the low temperature and turn into positive at the high temperature as shown in Figs. 3(a)–3(c). We define the transition temperature as T_0, which has a consistent tendency with $T_{\min}$ (as shown in Table 1). Besides, the low-temperature negative MR fades away with reducing oxygen content (Fig. 3(d)). We conclude that the mechanisms of the upturn and negative MR in US3, US21, and US19 samples are related to the antiferromagnetic order the same as those in the under-doped region of Ce-doped cuprates and the AFM can be erased just by the oxygen removal.

Table 1. Summary of the transport properties and lattice structure constant c_0 of PCO films. T_c is the superconducting transition temperature at which the resistance becomes a half of the normal state value. T_0 represents the transition temperature of MR from negative to positive of US3, US21, and US19 samples. RRR is the resistance ratio of R(300 K)/R(30 K) and c_0 is the c-axis lattice constant.

Sample	T_c/K	$T_{\min}$/K	T_0/K	c_0/Å	RRR
US3	2.5	98	105 ± 5	12.213	1.2
US21	21.2	65	75 ± 5	12.212	2.5
US19	18.7	52	55 ± 5	12.211	2.4
S22	21.9			12.205	4.8
S19	18.9			12.202	7.8
S11	11.0			12.201	8.0
S3	2.7			12.199	7.2

The Hall coefficient R_H can illuminate the nature of material carriers. For example, the low-temperature R_H in the $R_{2-x}Ce_xCuO_4$ system varies from negative to positive as the Ce-doped concentration increases, corresponding to the carriers varying from electrons to holes.[9,12,20] Figure 4(a) exhibits R_H as a function of temperature for various samples. The R_Hs of US3, US19, and US21 are negative in the whole temperature range, suggesting that the electron is predominant in the transport process. The sign reversal of R_H arises in S22 and S19 as the temperature increases, i.e., from positive to negative, which reveals a competition between electron and hole carriers. The R_Hs of S11 and S3 are positive below 150 K, indicating that the dominant carriers are holes.

Figures 4(b)–4(d) display the Hall resistivity ρ_{xy} at various temperatures for US3, S22, and S3, respectively. For US3 and S3, the ρ_{xy} as a function of magnetic field exhibits a good linear behavior, indicating that the samples have a single band characteristic. The low-temperature ρ_{xy} of the S22 sample is nonlinear to the magnetic field, which implies the coexistence of electron and hole bands. For Ce-doped cuprates, Fermi surface of the optimum doped samples is reconstructed by antiferromagnetic order.[12,21,22] Therefore, we can surmise that Fermi surface of the parent compounds can be gradually adjusted by changing the oxygen content.

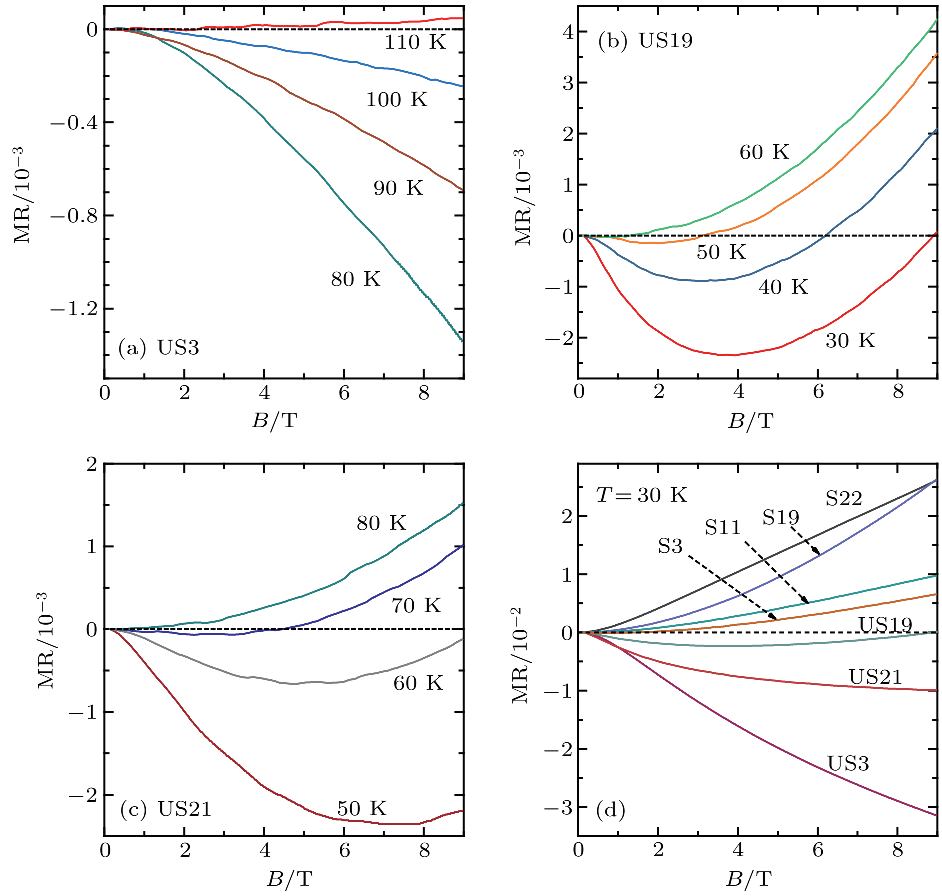

Fig. 3. (a)–(c) MR versus magnetic field B for US3, US19, and US21, respectively. (d) MR curves for various $Pr_2CuO_{4\pm\delta}$ films at $T = 30$ K.

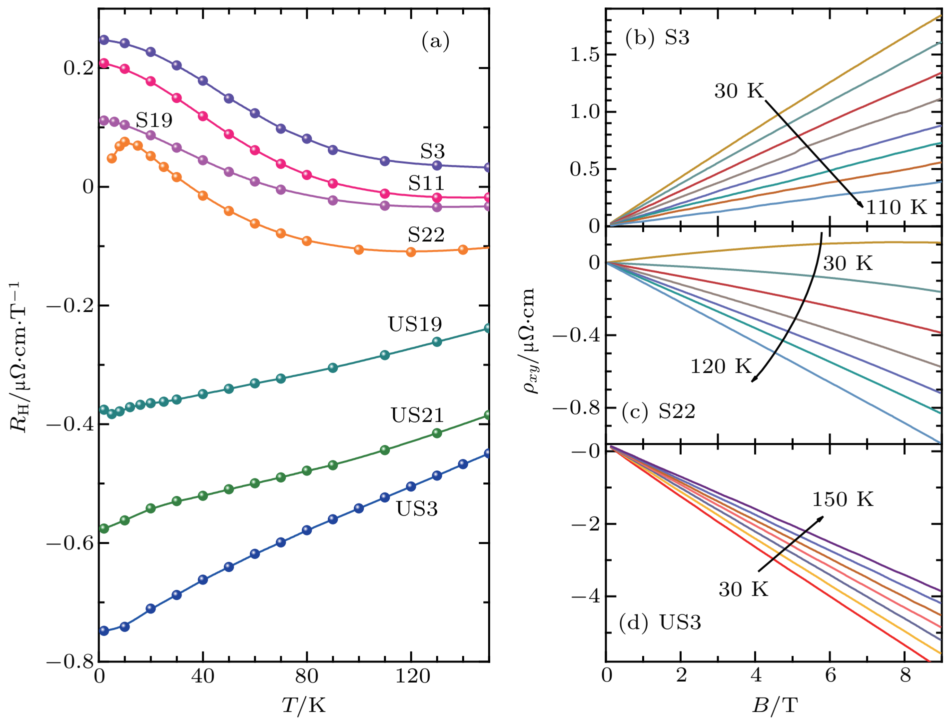

Fig. 4. (a) Normal state Hall coefficient R_H versus temperature for $Pr_2CuO_{4\pm\delta}$ films measured at $B = 9$ T ($B \parallel c$). (b)–(d) Hall resistivity ρ_{xy} versus B for S3, S22, US3.

As mentioned above, it can be concluded that, for MR and Hall resistivity, the effects of varying oxygen content in PCO thin films are similar to those of varying Ce concentration in PCCO. Such phenomenon indicates that the oxygen removal can induce carrier doping. This finding seemingly supports the scenario that superconductivity in parent compounds is obtained via doping a Mott insulator, symmetric to the hole-doped side. We note that this view has been clarified in the recent angle resolved photoemission spectroscopy (ARPES) results as well.[6,23]

Unfortunately, it is extremely difficult to measure the accurate oxygen content which also plays a non-ignorable role in $R_{2-x}Ce_xCuO_4$. Song *et al.*[24] studied $Pr_{1-x}LaCe_xCuO_4$ samples with different Ce concentrations and annealing processes using ARPES. They found that the effective electron number estimated from Fermi surface volume could unify the effect of Ce doping and deoxygenation. For electrical transports, R_H is the most qualified quantity reflecting the information of carriers. Therefore, we try to set R_H as the horizontal axis to study the evolution of T_c in both PCCO and PCO systems. As shown in Fig. 5, we find that all the data from distinct groups, various measuring conditions, and different samples obey the same rule, i.e., T_c increases at first and then decreases as R_H increases. Especially, T_c always reaches its maximum near $R_H = 0$, which indicates that the balance between the electron and hole bands is beneficial to the superconductivity of electron-doped cuprates, consistent with the electrostatic tuning results of $Pr_{1.85}Ce_{0.15}CuO_4$.[25]

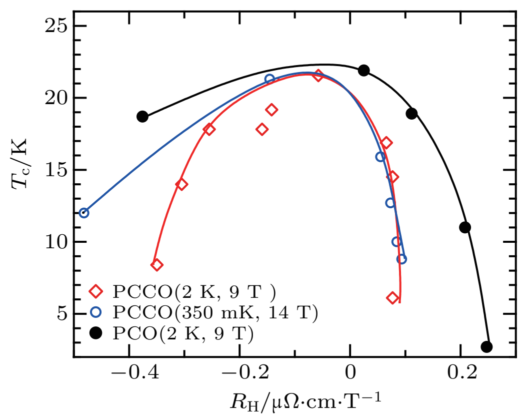

Fig. 5. T_c versus R_H of both PCO and PCCO. PCCO (2 K, 9 T) and PCCO (340 mK, 14 T) data derive from Refs. [12] and [20], respectively. The solid curve is a guide to the eye.

For the underdoped PCCO samples, the R_H rapidly decreases as the temperature decreases, independent of the magnetic field.[12,26] Therefore, the clear difference between two groups of data of PCCO is mainly attributed to the temperature distinction. However, we cannot exclude the influence of antiferromagnetic order and disorder. The PCCO data show a perfect overlap in the overdoped region because the R_H is hardly dependent on the temperature and linear with magnetic filed in this region. As shown in Fig. 5, we can see that the T_c of PCO is always greater than that of PCCO samples at a fixed R_H value. This can be well explained by the fact that the disorder introduced by Ce doping is more than that by deoxygenation.[3] Furthermore, for the two-dimensional disordered system, the disorder-induced changes in Hall coefficient should be proportional to the correction to resistivity, i.e., $\Delta R_H/R_H = 2\Delta R/R$.[27] However, one can see from Figs. 2 and 4(a) that the changes in Hall coefficient induced by oxygen removal are independent of those in resistivity. Besides, the *RRR* of S11 as listed in Table 1 is greater than that of S19, indicating that there are less disorders in S11 samples. Therefore, the T_c reduction should not result from the disorder effect. This finding can explain why T_c in the parent compounds are even higher than those of the optimal Ce-doped samples[18] and also support that the superconductivity in T'-phase parent cuprates stems from doping effect induced by the oxygen removal.

4. Conclusion

In summary, a series of high-quality superconducting PCO thin films have been prepared by polymer assisted deposition method. The magnetoresistance and Hall effect of superconducting PCO thin films with various oxygen contents are systematically studied. It is found that for the magnetoresistance and Hall resistivity, the effect of oxygen removal in PCO is similar to that of the Ce doping in $R_{2-x}Ce_xCuO_4$. In addition, we find that Hall coefficient R_H is an efficient parameter to depict the evolution of T_c in the electron-doped cuprates. We argue that doped electrons induced by the oxygen removal are the cause of the superconductivity in T'-parent compounds.

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