Metallic state in La-doped $YBa_2Cu_3O_y$ thin films with n-type charge carriers

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We report hole and electron doping in La-doped $YBa_2Cu_3O_y$ (YBCO) thin films synthesized by pulsed laser deposition technique and subsequent *in-situ* postannealing in oxygen ambient and vaccum. The n-type samples show a metallic behavior below the Mott limit and a high carrier density of $\sim 2.8 \times 10^{21}$ cm^{-3} at room temperature (T) at the optimally reduced condition. The in-plane resistivity (ρ_{ab}) of the n-type samples exhibits a quadratic T dependence in the moderate-T range and shows an anomaly at a relatively higher T probably related to pseudogap formation analogous to underdoped $Nd_{2-x}Ce_xCuO_4$ (NCCO). Furthermore, ρ_{ab}(T), T_c and T with minimum resistivity (T_{min}) were investigated in both p- and n-side. The present results reveal the n-p asymmetry (symmetry) within the metallic-state region in an underdoped cuprate and suggest the potential toward ambipolar superconductivity in a single YBCO system.

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I. INTRODUCTION

High-T_c superconductivity in cuprates results from doping charge carriers into Mott insulators. The magnetic and superconducting properties of Mott insulators doped by holes (p-type) are different from those doped by electrons (n-type), showing asymmetry in the phase diagrams [1]. Moreover, their transport properties depend on the type of carriers, for example, in-plane normal-state resistivity exhibits quadratic temperature (T) dependence for n-type cuprates [2] while linear T dependence is seen for p-type cuprates with optimal doping [3,4]. Such comparisons of electron- and hole-doping asymmetry (symmetry) in cuprates should help to further our understanding of the cuprate superconductors [5,6]. The typical electron-hole asymmetry (symmetry) investigation is usually based on the cuprates with different crystallographic structure such as NCCO (T' structure) and $La_{2-x}Sr_xCuO_4$ (T structure). These materials have different parent Mott insulators, and thus, exhibit different properties even without doping [7]. Therefore, it is desirable to dope electrons and holes into a Mott insulator without changing the crystallographic structure and address the physics in both sides of such 'ambipolar' cuprate.

An ambipolar single-crystal cuprate was first achieved in $Y_{1-z}La_z(Ba_{1-x}La_x)_2Cu_3O_y$ (x=0.13, z=0.62) with charge carriers ranging from 7% of holes per Cu to 2% of electrons per Cu [8]. It was also found that $Y_{0.38}La_{0.62}(Ba_{0.87}La_{0.13})_2Cu_3O_y$ exhibits asymmetric behavior in magnetic ground states and transport properties between electron- and hole-doped sides [9]. However, this asymmetric comparison was limited to insulating state near the zero-doping region due to low carrier density in n-type samples. In order to fully investigate the n-p asymmetry (symmetry), more heavily electron-doped materials in YBCO system, which exhibit metallic and even superconducting behaviors, are desirable.

Effective reduction of the as-grown materials is necessary to dope n-type carriers in cuprates [10]. In general, the bulk single crystals are annealed at high T (850 °C-1080 °C) in low oxygen partial pressure (P_{O2}) for tens of hours to several days. For the thin-film growth, oxygen can be removed uniformly and efficiently with postannealing for several tens of minutes, since oxygen diffusion along the c-axis is much easier and the diffusion lengths are comparable to the film thickness [1]. Recently, an electrochemical technique was used to remove oxygen in pure YBCO thin films and achieve n-type metallic state [11]. However, carrier density of the n-type sample was still low ($\sim 2.5 \times 10^{20}$ cm^{-3}) and the metallic state was only observed above 120 K. Chemical doping is necessary for achieving higher electron density. Since La^{3+} possesses a higher valence state than Ba^{2+}, La substitution for Ba in YBCO is expected to provide additional electrons [8]. Therefore, one can expect that more electrons can be doped by varying the La content in $Y_{1-z}La_z(Ba_{1-x}La_x)_2Cu_3O_y$ and efficiently removing oxygen using thin-film growth method. In this work, we grow the $Y_{0.38}La_{0.62}(Ba_{0.82}La_{0.18})_2Cu_3O_y$ thin films using a pulsed laser deposition (PLD) process and shift the materials from p-type superconducting to n-type metallic states by postannealing in low P_{O2}. The resistivity of n-type samples exhibits a Fermi-liquid behavior and an anomaly at a certain T below which the resistivity begins to decrease rapidly. This behavior is similar to that of the underdoped non-superconducting NCCO, suggesting the potential of n-type superconductivity in YBCO system if electrons are further doped.

II. EXPERIMENTAL

The starting materials for the preparation of the ceramic target were pure cation oxides powders of Y_2O_3 (99.999 %), La_2O_3 (99.999 %), $BaCO_3$ (99.997 %) and CuO (99.9999 %). These were weighed and mixed according to the chemical formula of $Y_{0.38}La_{0.62}(Ba_{0.82}La_{0.18})_2Cu_3O_y$. The mixture was then fired at 850, 900, 900 °C for 10 h respectively, and at 980 °C for 20 h in air with regrinding between firings. On the final firing, the powder was pressed into disk-shaped pellet for the PLD process. Thin films with thickness of ∼260 nm were grown on (001) $LaAlO_3$ (LAO) substrates by a PLD system using the as-prepared target. The deposition T and P_{O2} for all samples were 760 °C and 200 mTorr, respectively. Since we cannot measure accurately the oxygen content, we label the films annealed at different conditions by carriers per Cu atom which is determined by the carrier densities (from Hall measurements) and volume of primitive cell of YBCO. Three p-type samples with carrier densities (at 300 K) of p=0.019, 0.034, 0.055 holes/Cu were obtained by *in situ* postannealing in the PLD chamber at 560 °C for 20 min in P_{O2}=0.02, 0.2 and 3 Torr, respectively. P-type sample with higher carrier doping of p=0.068 holes/Cu was obtained by re-annealing in a tube furnace at 600 °C for 30 min in air. N-type samples with carrier densities of n=0.02, 0.029, 0.034, 0.038 electrons/Cu were obtained by *in situ* postannealing at 640 °C in vaccum ($P_{O2}<10^{-5}$ Torr) for 10, 30, 50 and 80 min, respectively, and then cooling down to room temperature at 30 °C/min. In order to obtain higher electron doping of n=0.087 and 0.166, the samples annealed for 80 min were re-annealed in vaccum at 380 °C with a ramp rate of 30 °C/min for 0 min (with immediate cool down at T=380 °C) and 10 min, respectively. Note that this re-annealing process is critical for reduction of oxgen as confirmed by expansion of the c-axis (fig. 1 and fig. 5). The composition of the grown films was analyzed by the Rutherford Backscattering Spectrometry (RBS) and was found to approximately be the same as that of the target. The crystallographic structure of the thin films was measured by X-ray diffraction (XRD). The transport property measurements were made using a Quantum Design PPMS at temperatures ranging from 2 to 400 K. The resistivity was measured by four-probe method and Hall effects by Van der Pauw geometry with the magnetic field swept from -5 to 5 T.

III. RESULTS AND DISCUSSION

Figure 1 shows the θ-2θ XRD patterns of four $Y_{0.38}La_{0.62}(Ba_{0.82}La_{0.18})_2Cu_3O_y$ samples annealed in air and vacuum. Only (00l) peaks of thin films and LAO substrates (indicated with S(00l)) were clearly observed, where l is an integer, confirming the c-axis oriented epitaxial growth. The c-axis lattice constant, d, of the sample annealed in air was determined to be 11.728 $\AA$ which is less than that of the as-grown (in air) crystal $Y_{0.38}La_{0.62}(Ba_{0.87}La_{0.13})_2Cu_3O_y$ (11.763 $\AA$) [8]. This indicates that our samples have larger La composition substituted for Ba and thus, possess smaller d, which is in fair agreement with the established empirical relation [12]. (00l) peaks of the samples annealed in vacuum

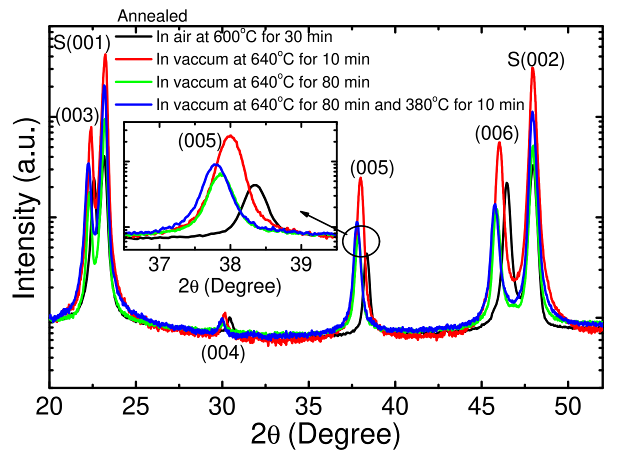

FIG. 1: X-ray diffraction patterns of $Y_{0.38}La_{0.62}(Ba_{0.82}La_{0.18})_2Cu_3O_y$ thin films. Inset: (005) peaks.

shift to smaller angles, compared with that of sample annealed in air, suggesting an expansion of the c-axis. It is known that d of $YBa_2Cu_3O_y$ increases as y decreases [13, 14]. This supports the fact that oxygen was removed as $Y_{0.38}La_{0.62}(Ba_{0.82}La_{0.18})_2Cu_3O_y$ films were annealed in low P_{O2} and vaccum.

Figure 2(a)-2(d) show the evolution of the T dependence of ρ_{ab} upon changing carrier doping levels at 300 K. The p- and n-type charge carriers were confirmed by Hall effects measurements in fig. 4. Samples with high hole-doping level show superconductivity, for example, sample with p=0.068 exhibits zero-resistance T_c of ∼8 K. As p decreases, and thus the oxygen content in the sample is reduced, T_c decreases and ρ_{ab} increases, the samples show evolution from superconductors to insulators (fig 2(b)). To further reduce oxygen content and obtain electron doping, thin films were annealed in vacuum. For low electron doping level, the sample exhibits insulating behavior (fig. 2(b)). As doping increases, ρ_{ab} goes down and the samples show metallic behavior at high T (fig. 2(c), (d)), although ρ_{ab} shows an upturn at low T. For n-type samples with n<0.087, the magnitude of ρ_{ab} within metallic region is above the Mott limit [15]. Moreover, the metallic behavior is already established at doping n=0.029 (5.0×10^{20} cm^{-3}) near Mott insulating state [9] and electron-electron scatterings are dominant in transport behavior which will be discussed in the following text. This suggests a bad metal behavior at low doping [17-19]. However, the sample with n=0.166 is obviously metallic since ρ_{ab} is below the Mott limit from ∼300 K down to the lowest T measured. The ρ_{ab} of the sample with highest doping (∼0.88 mΩ·cm at 300 K), to the best of our knowledge, is the lowest resistivity in n-type YBCO system [8-9,11].

In the moderate-temperature range, ρ_{ab} of the n-type samples is approximately proportional to T^2, as is demonstrated in fig. 3, indicating a conventional Fermi-liquid (FL) behavior due to electron-electron

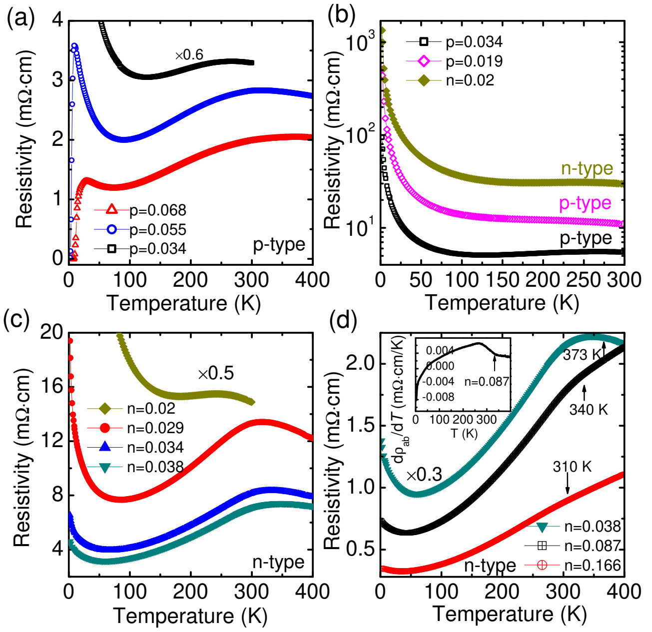

FIG. 2: The in-plane resistivity ρ_{ab} as a function of temperature for p-type and n-type thin films. The samples were labeled by the hole (p) and electron (n) doping at 300 K (per Cu atom) which is obtained by Hall measurement. Inset of (d) is the temperature derivative of ρ_{ab} for sample with n=0.087.

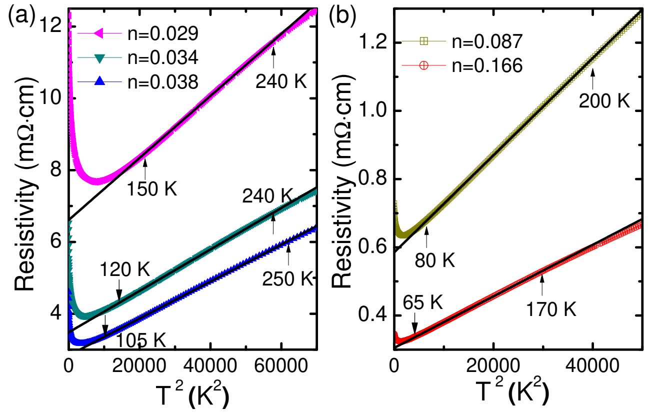

FIG. 3: ρ_{ab} of n-type samples as a function of T^2 for the same data shown in fig. 2. Solid line is the fitting to the data. Arrows indicate the T where ρ_{ab} deviates from Fermi-liquid behavior.

scattering [2]. By fitting the data to the equation $\rho_{ab}(\mathrm{T})=\rho_0+A_2T^2$, we can obtain the quadratic scattering rate A_2. A_2 decreases rapidly from $\sim 8.6\times10^{-5}$ to $\sim 7.5\times10^{-6}$ mΩ·cm·K^{-2} with increasing electron doping, as is shown in fig. 5. This behavior of A_2 is similar to those in NCCO as electron doping increases [20]. Interestingly, the magnitude of A_2 in our films are of the order of $10^{-6}-10^{-5}$ mΩ·cm·K^{-2} which is comparable to those of NCCO [2, 20]. The similarity in magnitude and evolution of A_2 between $Y_{0.38}La_{0.62}(Ba_{0.82}La_{0.18})_2Cu_3O_y$ and NCCO hint at the possibility that the electron-electron scattering in n-type cuprates is governed by essentially the same physics, regardless of the different crystallographic structures. As is marked by arrows, the FL regimes shift to lower T as the electron doping increases. It has been demonstrated that the ground state of heavily overdoped n-type cuprates is dominated by FL behavior [21]. The shift of FL regimes probably suggests the same ground state in n-type YBCO system if electrons are overdoped. In contrast, the quadratic dependence with T of ρ_{ab} is not observed in p-type samples.

At T above $\sim$ 250 K, weakening of the quadratic dependence of ρ_{ab} is observed for electron-doped samples [2]. ρ_{ab} even saturate and become non-metallic at higher T for n<0.087. For n=0.087 and 0.166, ρ_{ab} tends to saturate at higher T although it is metallic up to 400 K. The saturation of ρ_{ab} can also be observed in p-type samples. On close examination, for samples with $n\geq$0.038, ρ_{ab} begins to decrease rapidly at around the T marked by arrow (T_ρ) with decreasing T. T_ρ can be obtained by the T derivative of ρ_{ab} and is around the T where $\mathrm{d}\rho_{ab}/\mathrm{d}T$ starts to increase [22], as is shown in inset of fig. 2 (d). The steep decrease of ρ_{ab} is also observed in underdoped $Nd_{2-x}Ce_xCuO_4$ with x=0.025-0.075 and is related to the formation of pseudogap confirmed by optical spectra [22,23]. In $Nd_{2-x}Ce_xCuO_4$, T_ρ decreases as x increases and disappears at optimal doping of x=0.15. In our samples, T_ρ also decreases with increasing electron doping. Importantly, this anomaly in ρ_{ab} become less noticeable at higher electron doping which is similar to NCCO. Whether the pseudogap begins to evolve below T_ρ requires further investigation by optical spectroscopy. Nevertheless, the anomalies in ρ_{ab} of n-type films suggest the possibility of its being a precursor of superconductivity.

Figure 4 shows the Hall coefficients (R_H). The samples annealed in vaccum exhibit negative R_H all the way below 300 K, indicating electron doping. The electron density of optimally reduced sample is $\sim 2.87\times10^{21}$ cm^{-3} ($R_H\sim$ -0.00217 cm^3/C) at 300 K which is one order of magnitude higher than those in $Y_{0.38}La_{0.62}(Ba_{0.87}La_{0.13})_2Cu_3O_y$ single crystal ($\sim 2.2\times10^{20}$ cm^{-3}, $R_H\sim$ -0.028 cm^3/C) [8] and pure YBCO film ($\sim 2.5\times10^{20}$ cm^{-3}) [11]. The magnitude of R_H in insulating film with n=0.02 ($R_H\sim$ -0.018 cm^3/C at 300 K) increase more sharply at low T, which is similar to that of the single crystal with near electron doping ($R_H\sim$ -0.028 cm^3/C at 300 K) [8]. Futhermore, ρ_{ab} at 300 K of the insulating thin film exhibits similar value ($\sim$29 mΩ·cm) to that in single crystal ($\sim$30 mΩ·cm) [8]. These suggest that the crystal quality of our thin films is comparable to that of single crystal. As is shown in fig. 5, d continuously increases by hole depletion and electron doping across the zero-doping state, although it is moderate at higher electron-doping region, which indicates that electrons were continuously doped as oxygens were removed. Therefore, high carrier density and low ρ_{ab} in n-type thin films are caused by electron doping.

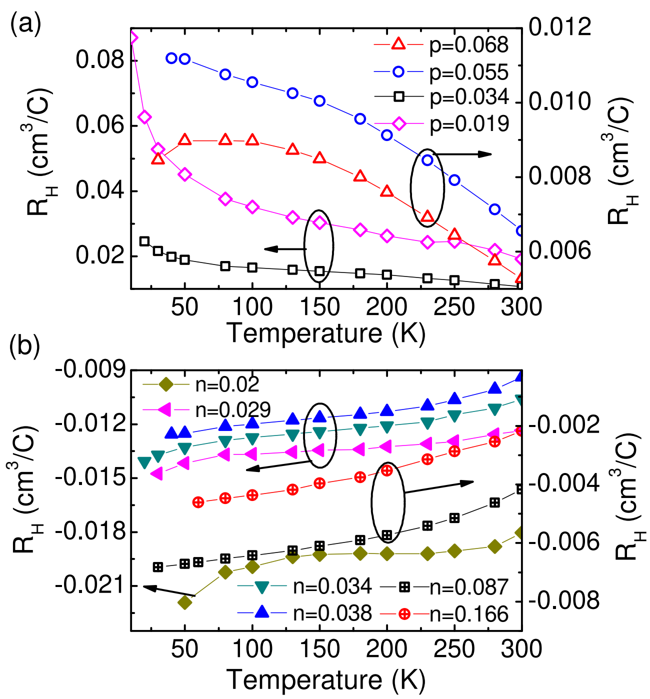

FIG. 4: The Hall coefficients R_H of p-type (a) and n-type (b) thin films as function of temperature.

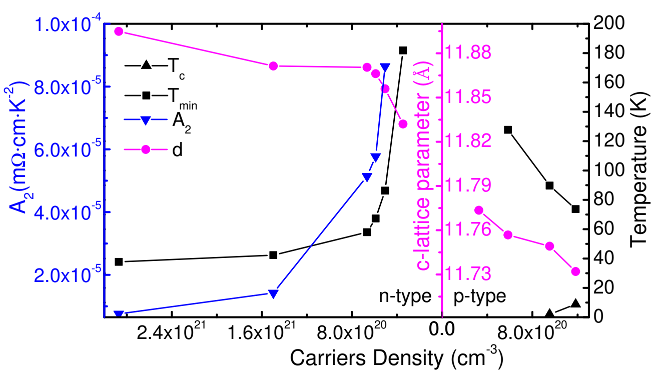

FIG. 5: Superconductivity transition temperature T_c, temperature with minimum resistivity T_{min}, c-lattice parameter d and quadratic scattering rate A_2 as a function of carriers density at 300 K. T_{min} is obtained by calculating the derivatives $d\rho_{ab}/dT$ and is the temperature when $d\rho_{ab}/dT$=0. A_2 is obtained from fitting ρ_{ab}(T)=ρ_0+A_2T^2 to data within $\rho_{ab}\propto T^2$ region shown in fig.3.

It is found that in all the samples with metallic state, even in superconducting p-type samples, ρ_{ab} exhibits insulating-like behavior below T with minimum ρ_{ab} (T_{min}). This behavior have been investigated in underdoped cuprates but its origin is still unclear [24-26]. We also show T_c and T_{min} as a function of carrier density at 300 K (n_{300K}) in fig. 5. T_{min} was found to share the same evolution as a function of doping in both n- and p-type thin films, mainly decreasing with increasing n_{300K}. However, T_{min} decreases much more rapidly in n-type samples, from 181.8 K at $n_{300K}\approx 3.46\times10^{20}$ cm^{-3} to 57.9 K at $n_{300K}\approx 6.65\times10^{20}$ cm^{-3}, than that in p-type samples, from 127.7 K at $n_{300K}\approx 5.8\times10^{20}$ cm^{-3} to 73.7 K at $n_{300K}\approx 1.18\times10^{21}$ cm^{-3}. At higher electron doping, T_{min} exhibits a slight drop and tends to saturate. Superconductivity emerges at $n_{300K}\approx 9.5\times10^{20}$ cm^{-3} (T_c=2 K) when T_{min}=89.7 K in p-type samples and T_c increases with decreasing T_{min}. However, superconductivity was not observed in n-type samples even if T_{min} was much lower than 89.7 K and the doping level of electrons was higher than that of holes. Interestingly, it was found that the amplitude of A_2 exhibits the same evolution as T_{min} with electron doping, suggesting an intimate relationship between electron-electron scattering and the metal-insulator transition in n-type YBCO system.

IV. CONCLUSION

In conclusion, metallic n-type La-doped YBCO thin films were successfully obtained by PLD technique and postannealing in vaccum. Above around T where metallic-insulating transition, the n-type samples exhibited T^2-dependent resistivity. At relatively higher T, ρ_{ab} showed an anomaly probably due to the formation of pseudogap which has been observed in underdoped NCCO. P-type samples were also investigated and showed different evolutions with doping in ρ_{ab}(T), T_c and T_{min}. The present work could be a significant step toward ambipolar superconductivity in YBCO system.

Acknowledgments

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