Effects of Photoinduced Hole Doping on Normal-State and Superconducting Transport in Oxygen-Deficient $YBa_2Cu_3O_y$

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The effects of photoinduced hole doping, caused by persistent photoconductivity, on the normal and superconducting properties of $YBa_2Cu_3O_y$ ($6.35 \leq y \leq 6.70$) thin films are studied using a high-power-density He-Ne laser light. Substantial photoinduced enhancements of both the normal conductivity and T_c are found for all the films. Hall measurements reveal that the number of photoinduced holes depends only on the photon dose and is independent of the oxygen content. The enhanced T_c has a nearly quadratic correlation with the hole density similar to that observed in $YBa_2Cu_3O_y$ when the hole density is varied by adding oxygen to the CuO_x chain.

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Since high-T_c cuprates exhibit a sharp insulator-to-metal transition under carrier doping, considerable attention has been focused on the idea of modulating the carrier density and thus the superconducting properties of these materials by electric field effects [1] or photoexcitation [2–8]. Many photoconductivity experiments have been carried out, for example, on insulating $YBa_2Cu_3O_y$ (YBCO) single crystals [2] and La_2CuO_4 single crystals [3]. In $YBa_2Cu_3O_{6.3}$ single crystals irradiated by laser pulses, a transient photoinduced increase in conductivity of more than 10 orders of magnitude with a lifetime of 10–50 ns was observed [2]. Later, a more striking phenomenon, persistent photoconductivity (PPC) in semiconducting YBCO thin films with $y \sim 6.4$, was discovered by Kudinov *et al.* [4,5]. They showed that high-power Ar laser illumination induces a remarkable decrease in the resistivity which persists completely at 100 K even after the laser is switched off [4]. A photoinduced semiconductor-to-metal transition and even metastable superconductivity at 5 K after prolonged illumination were also indicated. Subsequently, the photoinduced enhancement of superconductivity was confirmed in YBCO thin films with an initial T_c of less than 25 K [6] and then in films with a T_c of as high as 82 K [7]. Although Nieva *et al.* [8] reported a photoinduced change in the Hall coefficient at room temperature in conjunction with the T_c enhancement, the relation between the density of photoinduced holes and both the normal-state and superconducting properties has not been clarified yet. The microscopic mechanism underlying these phenomena is also still controversial [5,6].

In this Letter, we report on the photon dose dependences of normal conductivity, transition temperature T_c, and the hole density determined by Hall measurements at low temperatures for YBCO thin films with different oxygen deficiencies. It is clearly shown that photoinduced hole doping effects exist even for relatively high oxygen content ($y \sim 6.7$) and that the number of photoinduced holes is independent of the oxygen content. These measurements not only allow us to elucidate the mechanism underlying these phenomena but also to compare the effects of carrier doping induced by photoexcitation with those induced by the addition of oxygen and the electric field effect.

The samples were prepared from $YBa_2Cu_3O_y$ ($y = 6.9$–7) (001) epitaxial thin films grown on $SrTiO_3$ (100) substrates by coevaporation method. Details of the thin-film preparation have been described elsewhere [9]. As-deposited thin films showed a T_c (1 $\mu\Omega$ cm) of 89–90 K and a typical critical current density J_c of 2×10^6 A/cm^2 at 77 K. Two successively deposited films, both 100 nm thick, were selected and cut into four pieces. After depositing Au contact pads using a metal mask, they were annealed in flowing $Ar+O_2$ gas to obtain samples with different oxygen deficiencies. We adopted an O_2 volume fraction of 0.5%–2% and the annealing temperature of 400–460 °C. After annealing for 0.5 h, the samples were cooled to 200 °C in 1 min and then slowly cooled in a furnace.

The four reduced samples had T_c values of 73, 45, 26, and lower than 1.5 K, and resistivity ρ (at 300 K) values of 0.60, 1.09, 1.86, and 3.45 mΩ cm, respectively, indicating a systematic correlation between T_c and ρ. Furthermore, the ρ-T curve showed an apparent downward deviation from the T-linear dependence as reported in high-quality oxygen-deficient single crystals [10]. These facts confirm that the samples contain very little inhomogeneous oxygen distribution and grain-boundary weak links. The oxygen contents of the four samples estimated by comparing the T_c values to those published by Veal and Paulikas [11] were 6.70, 6.45, 6.40, and 6.35. These samples were patterned using standard photolithography and ion milling techniques to produce 10 μm wide and 100 μm long constrictions with the necessary voltage and current contacts.

The photoconductivity measurements were carried out using a 632.8 nm He-Ne laser which was coupled to a multimode optical fiber with a power density of up to 66 W/cm^2. The setup for these measurements has been already detailed elsewhere [7]. The fiber end (core diameter=50 μm) was fixed to the substrate with an alumina guide and introduced into a temperature-stabilized cryo-

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stat. Thus an area of the constriction slightly larger than the length of the voltage probe region (30 μm) was uniformly illuminated. Since the samples were surrounded by He gas in the cryostat, oxygen absorption during illumination could be avoided. Moreover, the illumination-induced temperature rise was less than 0.5 K, hence no substantial influence of sample heating was expected. In the present experiments, the samples were illuminated with various photon doses at a temperature of 80 K or 90 K (for $y=6.70$ sample). The Hall coefficient R_H was measured in a 1 T magnetic field parallel to the c axis using a standard field inversion technique.

Figure 1(a) shows the evolution of the resistive transition curve with various photon doses d_{ph} for a sample with $y=6.35$. Before illumination, this sample shows an apparent resistivity upturn below 60 K, indicating it is in an incipient localization regime near the semiconductor-to-metal transition. With initial photon dose d_{ph}, ρ decreases dramatically. This decrease in ρ is accompanied by a clear T_c enhancement. For $d_{ph} > 5\times10^{22}$ photons/cm^2, the variation of the curve is characterized by a parallel (similar in shape) shift with less pronounced enhancements in T_c and normal conductivity σ, although no definite saturation is observed. The conductivity enhancement $\Delta\sigma/\sigma$ for the largest dose of 5.8×10^{25} photons/cm^2 is approximately 100%, which is the same as the value reported by Kudinov *et al.* [5] for $y\sim6.38$. The maximum T_c enhancement $\Delta T_{c\,\max}$ is approximately 15 K, which is the largest value ever reported for homogeneous samples.

Figure 1(b) shows the evolution of the resistive transition curves with various photon doses for $y=6.40$, 6.45, and 6.70. All of these samples exhibit a parallel shift in the curve accompanied by increases in T_c and σ. Their $\Delta T_{c\,\max}$ values are approximately 8, 4, and 4 K, respectively. They are smaller than the value for the $y=6.35$ sample but substantially larger than those observed for metallic films by Nieva *et al.* [6].

Figure 2 shows the temperature dependence of $1/R_He$ before and after illumination with a dose of approximately 1.5×10^{24} photons/cm^2. The samples with $y<6.5$ show very weak temperature dependence except near the transition region, while a substantial dependence is observed for $y=6.70$. The latter shows a nearly T-linear dependence at temperatures higher than 150 K. This tendency agrees qualitatively with the recent results for YBCO thin films with various oxygen deficiencies reported by Jones *et al.* [12]. The illumination induces a parallel shift in the curves for all the samples, which clearly indicates the photoinduced doping of additional holes. It is generally difficult to estimate the carrier density precisely for samples which show a strong temperature dependence of R_H. However, Jones *et al.* [12] have pointed out that $d(1/R_He)/dT$ or $1/R_He$ at a fixed temperature gives a good measure of the hole density p in $YBa_2Cu_3O_y$ where the impurity scattering may be neglected. Thus we hereafter consider $1/R_He$ at 80 or 90 K as the hole density p. We also calculated the temperature dependence of the co-

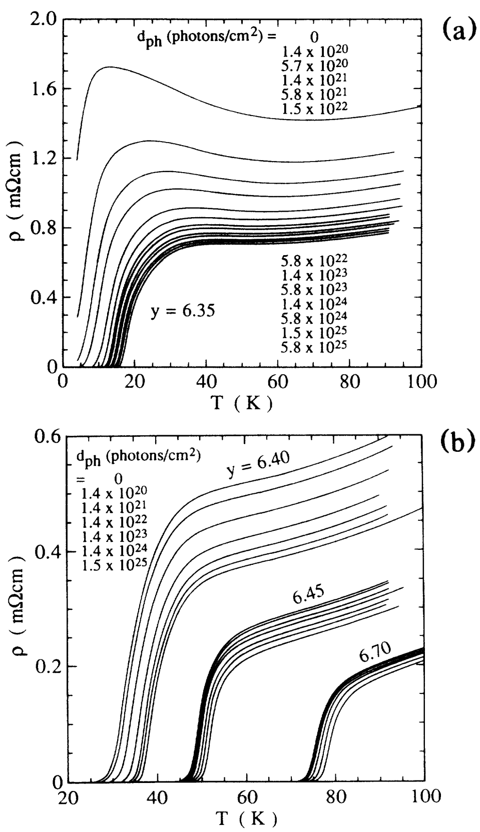

FIG. 1. (a) Photoinduced evolution of resistive transition curve for a $YBa_2Cu_3O_y$ thin film with $y=6.35$. The photon dose d_{ph} was varied from 0 to 5.8×10^{25} photons/cm^2 from the highest to the lowest curve. The photon dose for a 100 min illumination with a power density of 66 W/cm^2 is comparable to 1.2×10^{24} photons/cm^2. (b) Photoinduced evolution of resistive transition curve for $YBa_2Cu_3O_y$ thin films with $y=6.40$, 6.45, and 6.70. The dose was varied from 0 to 1.5×10^{25} photons/cm^2.

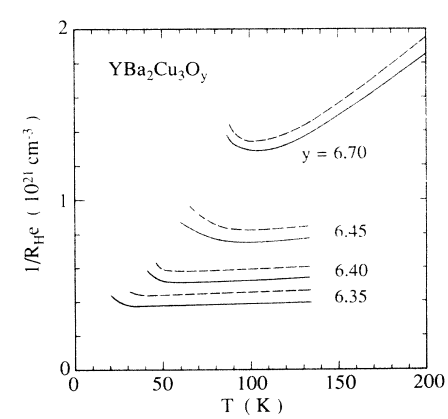

FIG. 2. Temperature dependence of $1/R_He$ before (solid lines) and after illumination (broken lines) with a photon dose of 1.4×10^{24} photons/cm^2 for $YBa_2Cu_3O_y$ thin films with $y=6.35$, 6.40, 6.45, and 6.70.

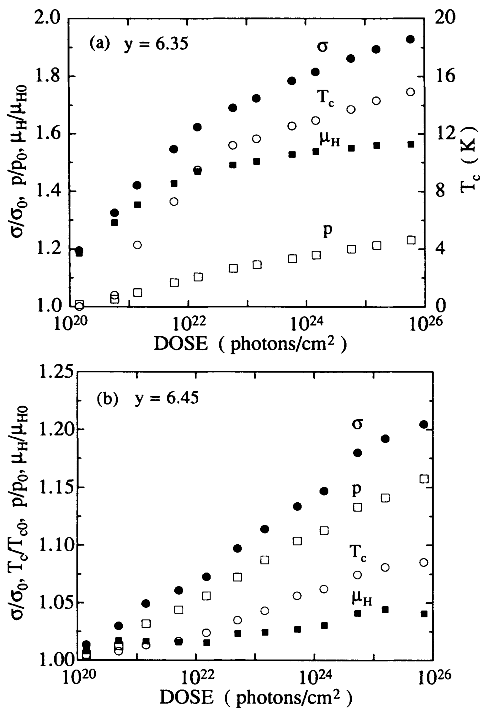

FIG. 3. Photon dose dependences of normalized normal-state conductivity and hole density defined at 80 K as well as T_c and Hall mobility ($\mu_H = R_H\sigma$) for $YBa_2Cu_3O_y$ thin films with (a) $y = 6.35$ and (b) $y = 6.45$. The bare T_c value is indicated for the former film.

tangent of the Hall angle $\cot(\theta_H)$ and found a photoinduced downward shift in the curves for $y = 6.35$ and 6.40, suggesting an increase in the scattering time or the mobility of holes. The samples with $y = 6.45$ and 6.70 had almost the same $\cot(\theta_H)$ vs T curve and only a very slight decrease in $\cot(\theta_H)$ was observed after illumination.

Figure 3(a) shows the photon dose (d_{ph}) dependence of the normal-state conductivity σ and p as well as T_c and the Hall mobility μ_H ($=\sigma R_H$) for the $y = 6.35$ sample. In spite of the rapid initial increases in both σ and T_c, p exhibits a monotonic and nearly logarithmic dependence on the photon dose over the entire dosage range. It is apparent that their rapid increases are mainly caused by the increase in the mobility. A similar logarithmic dependence of p on the photon dose is observed for $y = 6.40$, 6.45, and 6.70. The photon dose dependence of σ, T_c, p, and μ_H for $y = 6.45$ is shown in Fig. 3(b). All these parameters exhibit monotonic logarithmic increases with the photon dose in this sample.

In Fig. 4, T_c enhanced by the photon irradiation is plotted versus $1/R_He$ (which represents p) for all the samples. The most important fact to notice is that all the points for samples with different y values seem to coalesce into one correlation line between T_c and p. The correlation deduced from the recent results by Jones *et al.* [12] is indicated as a dashed line in the same figure. Their correlation line, obtained for several YBCO thin films

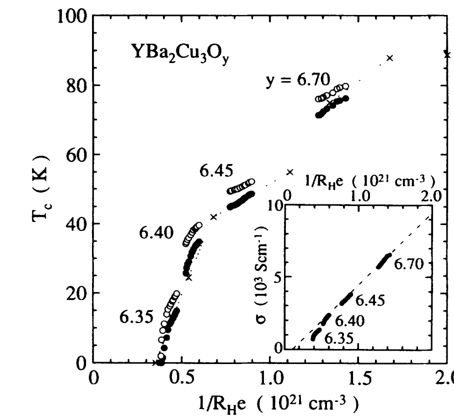

FIG. 4. Correlation of T_c enhanced by photon irradiation with $1/R_He$ (which represents the hole density) for $YBa_2Cu_3O_y$ thin films with different y values. The open and closed circles represent T_c midpoint and T_c defined at $\rho = 1$ $\mu\Omega$ cm. The hole density was defined at 80 K (for $y = 6.35$, 6.40, and 6.45) or extrapolated to this temperature (for $y = 6.70$). The dashed line represents the correlation deduced from the results reported by Jones *et al.* for thin films with different y values (Ref. [12]). Correlation of conductivity at 80 K with the hole density for the same films is also indicated in the inset. The broken line is a guide to the eye.

with various y values, agrees very well with our result if their hole density is multiplied by a factor of 0.4. This means that the photon irradiation has the same effects on the hole density and T_c as those of adding oxygen to the CuO_x chains and also strongly suggests that T_c is determined only by the hole density in the CuO_2 plane.

Another important fact is that the amount of photoinduced increase in p for the maximum photon dose for all the samples is nearly the same, approximately $(1-1.5) \times 10^{20}$ cm^{-3}. This fact as well as the results of Fig. 3 indicate that the number of photoinduced holes depends only on the photon dose and is independent of the oxygen content. It is also clear that $\Delta T_{c\max}$ for each sample is determined by this correlation line in $YBa_2Cu_3O_y$. The correlation between σ and p is also shown in the inset. It is evident that the critical hole density for both the metallic conduction and superconductivity is almost the same, approximately 4×10^{20} cm^{-3}. A linear correlation observed for $y > 6.40$ reinforces the idea that $1/R_He$ actually represents the hole density except for a constant factor.

There have been a large number of studies on the correlation between T_c and the carrier density in high-T_c cuprates. Earlier, Uemura *et al.* [13] pointed out a universal linear relation between T_c and n_s/m^* (superconducting carrier density over effective mass) for YBCO, $La_{2-x}Sr_xCuO_{4+\delta}$, and Bi-based cuprates. On the other hand, Whangbo and Torardi [14] reported a quadratic relation, $T_c = T_{c\max}[1 - \eta(p - p_{opt})^2]$, between T_c and p estimated from the bond valence sum for several high-T_c cuprates. Here, p_{opt} is the optimum hole concentration and η is a system-dependent parameter. Although a similar quadratic T_c correlation with the hole density deduced from the bond valence sum [15] or Hall measurements [12] was observed in $YBa_2Cu_3O_y$, there is some ambiguity due to the scattering of the data for the T_c range below 50 K. The result of Fig. 4 obtained by continuously varying p apparently indicates a nonlinear, nearly quadratic, correlation in this material. In contrast, Xi *et al.* [1] have recently reported a linear relation between T_c and p modulated by the electric field effect. This difference possibly arises from the fact that the zero resistance T_c for their 2-unit-cell-thick YBCO thin film represents the Kosterlitz-Thouless temperature T_{KT} which is proportional to n_s [16].

To explain the persistent photoconductivity in oxygen-deficient YBCO thin films, two different mechanisms have mainly been proposed. These are photoinduced charge transfer [4] and photoassisted oxygen ordering [6]. The first assumes the photoexcitation of the electron-hole pairs in the CuO_2 plane bands and also assumes the transfer of the excited electrons to the adjacent CuO_x chain planes where they are trapped in the localized O^- levels. In the second mechanism, photoexcitation in the CuO_x chain plane induces oxygen defect ordering so as to form longer chain segments. This results in the charge transfer of additional holes to the CuO_2 plane. This mechanism has close relevance to the experimental fact that a thermally activated oxygen reordering was observed near room temperature in oxygen-deficient YBCO quenched from high reduction temperatures [17]. The similarity in the characteristic time for thermally activated oxygen reordering, of several hours, to the relaxation time of PPC has been pointed out [8].

On the other hand, Kudinov *et al.* [5] have recently observed that the PPC efficiency and the relaxation parameters are strongly dependent on the oxygen content. For example, the PPC efficiency, as estimated from $\Delta\sigma/\sigma$ at room temperature, rapidly diminishes for $y \geq 6.45$. The amount of T_c enhancement observed by Osquiguil *et al.* [18] also shows a similar tendency. Kudinov *et al.* [5] attributed this PPC disappearance to the difficulty in the isolation between photogenerated electrons and holes for metallic films with a significant hybridization of the CuO_x and CuO_2 layers. However, our present study indicates that the efficiency of photoinduced hole doping is almost the same for films with different oxygen contents including the $y=6.70$ film. We have recently observed PPC and a T_c enhancement of approximately 1 K for a film with a T_c as high as 87 K and an estimated y of 6.80. These totally contradict the discussion presented by Kudinov *et al.* on the oxygen content dependence and rule out the first mechanism. In contrast, the substantial photoinduced doping even for large y values can be explained by the oxygen ordering mechanism, since oxygen ordering has a substantial influence on the superconducting properties of high-T_c YBCO thin films, as revealed by recent surface resistance measurements [19]. The significant enhancement in the doping efficiency for an elevated illumination temperature previously observed in some *in situ* films [7] and the photoinduced slight reduction in the c-axis parameter recently reported by Kawamoto and Hirabayashi [20] are also consistent with this mechanism.

In conclusion, we have shown that substantial persistent photoconductivity and T_c enhancement effects exist even in high-T_c YBCO thin films as well as in lower-T_c films with a lower oxygen content. Hall measurements clearly reveal that the enhancements of both T_c and conductivity for films with different oxygen contents result from the photoinduced doping of a similar amount of additional holes in the CuO_2 plane. These observations rule out the photoinduced charge transfer mechanism which assumes electron trapping and indicate that the photoassisted oxygen ordering in the CuO_x chain plane is the most probable mechanism of these unusual photoinduced phenomena in oxygen-deficient YBCO. The enhanced T_c exhibits a nonlinear, nearly quadratic, relation with the hole density similar to that observed when the hole is supplied by adding oxygen to the CuO_x chain.

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