

## Interfacially Controlled Transient Photoinduced Superconductivity

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(Received 1 August 2006; published 27 October 2006)

We report on a large *transient* photoinduced enhancement of the superconducting critical temperature ( $\Delta T_c = 23$  K) in epitaxial  $\text{YBa}_2\text{Cu}_3\text{O}_{6.7}/\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$  bilayers upon visible light illumination. The effect relaxes with a characteristic time of 100 s at low temperatures, which is 4 orders of magnitude faster than the *persistent* photoconductivity or *persistent* photoinduced superconductivity previously found in single high- $T_c$  superconducting films. This result is discussed in terms of light induced charge transfer through the interface similar to what happens in semiconductor junctions.

DOI: [10.1103/PhysRevLett.97.177005](https://doi.org/10.1103/PhysRevLett.97.177005)

PACS numbers: 74.78.Fk, 73.50.Pz, 74.25.Fy, 74.62.Yb

Interfaces often give rise to novel physical phenomena induced by competing interactions. Recent work has claimed interesting charge transfer phenomena at interfaces between complex oxides [1,2]. These may originate from band bending (as found earlier at semiconductor interfaces) [3,4] or from other effects peculiar to the oxide structure and/or bonding like modified orbital structure and polarity mismatch. Oxide-oxide interfaces thus gather a variety of degrees of freedom which can be exploited to modify the electronic structure and to tailor novel properties and behaviors [5,6]. In this connection, modulating charge transfer at oxide interfaces with light illumination, besides leading to new photogenerated effects, may provide a path to explore the complex phase space of transition metal oxides. In this Letter, we report on novel photoinduced effects in  $\text{YBa}_2\text{Cu}_3\text{O}_{6.7}/\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$  (YBCO/LCMO) bilayers and show that the charge transfer across interfaces between strongly correlated oxides can be manipulated using light excitation.

Many complex transition metal oxides, including cuprates and manganites, are strongly correlated electron systems close to a metal-insulator transition. Consequently, small changes in the carrier density may produce large changes in the resistivity. The salient feature, however, is the strong coupling between charge, spin, and orbital degrees of freedom, which is at the foundation of a rich set of coexisting phases with similar ground state energies. Small external perturbations may shift this delicate balance between different phases and may induce dramatic changes in the physical properties. Light illumination of complex oxides provides a convenient way to induce new properties through modifications of the carrier density and changes in this interplay between different phases. For example, it is known that underdoped high temperature superconductors ( $\text{R}\text{Ba}_2\text{Cu}_3\text{O}_\delta$ , ( $R = \text{Y}, \text{Gd}$ ) with  $6 < \delta < 7$ ), exhibit *persistent* photoconductivity (PPC) and *persistent* photoinduced superconductivity (PPS) which is accompanied by a decrease in the Hall coefficient and a structural contraction of the  $c$  axis [7–10]. These photoinduced changes increase with oxygen deficiency and have been related to

an increase of the carrier density and mobility [11], which is more pronounced in the UV part of the spectrum [12]. The mechanism invoked to explain photoinduced effects relies on the oxygen deficient Cu-O chain layers that contribute with holes to the  $\text{CuO}_2$  planes through electron capture or oxygen ordering [10,13].

While low temperature ( $T < 30$  K) *persistent* photoconductivity has also been reported in hole doped manganites with a small oxygen deficiency, less than 0.1 per formula unit, *transient* photoconductivity is found for oxygen deficient samples with larger oxygen deficiency [14,15]. The *persistent* effects have been explained as due to the extra photogenerated electron hole pairs and trapping of electrons in oxygen vacancies, much in the same fashion as in high- $T_c$  cuprates [15,16]. In addition, a *persistent* transition into a ferromagnetic-metallic state upon x-ray illumination has been observed in otherwise antiferromagnetic-insulating samples [17,18], indicating that the effect of light may affect the balance between antiferromagnetic-insulating and ferromagnetic-metallic phases. Although a clear picture of the mechanism explaining the photoinduced effects in the manganites has not emerged yet, it seems that photocarrier generation by itself cannot explain the observed effects and new ingredients related to the mesoscopic phase separation need to be considered [18,19].

Here we report on photogenerated effects in bilayers of oxygen depleted YBCO and LCMO. Contrary to single YBCO films that exhibit *persistent* photoconductivity, we find *transient* photoconductivity with a relaxation time on the order of 100 seconds and substantially larger enhancements ( $\Delta T_c = 23$  K) of superconductivity. This novel mechanism of photoinduced superconductivity is discussed in terms of enhanced recombination of photogenerated holes in the YBCO at the interface with the manganite.

YBCO/LCMO bilayers were sputtered on (100)  $\text{SrTiO}_3$  (STO) substrates at high pressure (3.4 mbar) in pure oxygen at high temperatures (900 °C). This technique provides a highly thermalized and ordered growth at a slow rate

(1 nm/min) allowing an accurate control of the layer thickness. Oxygen content was adjusted *in situ* following a stability line of the pressure-temperature phase diagram during cool down [20]. This method has been shown to provide a reproducible control of oxygen content in YBCO thin films. Here we have studied  $N$  u.c.-YBCO<sub>6.7</sub>/40 u.c.-LCMO [ $N = 15, 12, 10, 8, 7, 6, 5, 4$  unit cells (u.c.)]. Low angle x-ray diffraction was used to measure the thickness of both LCMO and YBCO layers. The YBCO oxygen content was determined from the elongation of the out of plane lattice parameter [21]. Quantitative information about interface roughness was obtained from structural x-ray refinement analysis using SUPREX 9.0 software [22,23]. Four probe resistance measurements used sputtered Ag contacts and a 1000 W Hg-Xe arc lamp provided the optical excitation. An Au thin film sputtered on STO close to the sample was used as an additional reference thermometer to accurately measure the sample temperature under illumination.

Quantitative x-ray analysis of YBCO/LCMO bilayers using the SUPREX software revealed flat interfaces with negligible interdiffusion and rms roughness of the top layer of 0.7 nm. High angle x-ray diffraction was used to determine the position of the (005) Bragg peak to calculate the out of plane YBCO  $c$ -axis lattice parameter. Oxygen content was adjusted using the dependence of oxygen stoichiometry on the  $c$ -axis lattice parameter for oxygen deficient YBCO <sub>$\delta$</sub>  [21]. Calibration YBCO single films showed  $c = 11.67 \pm 0.01$  Å which corresponds to an oxygen content  $\delta = 6.7$ .

Four-point resistivity measurements of deoxygenated bilayers show an increased resistance and a reduced critical temperature compared to fully oxygenated samples of the same thicknesses. Both are due to the reduced oxygen content of single YBCO films [8,9]. Figure 1(a) shows the resistance curves of a bilayer with a YBCO layer thickness of 12 u.c. (14 nm). In the dark (open symbols)  $T_c = 43$  K is much lower than 87 K, which corresponds to a fully oxygenated bilayer of the same thickness. Under light exposure [line in Fig. 1(a)]  $T_c$  increases to 66 K, a large increase of 23 K, but the  $T_c$  of the fully oxygenated sample is not recovered. This  $T_c$  increase is much larger than that of single YBCO films with the same deoxygenation sequence (corresponding to an oxygen content  $\delta = 6.7$ ). For comparison, Fig. 1(b) shows the resistance curves of a single YBCO<sub>6.7</sub> film (85 u.c.) in the dark and under illumination. The  $T_c$  increase ( $\Delta T_c = 3.6$  K) is much smaller than the one corresponding to the bilayer and consistent with earlier measurements of similar films [11]. The increase of the  $c$ -lattice parameter upon deoxygenation is larger in bilayers ( $\Delta c = 0.07$  Å) than in single films ( $\Delta c = 0.02$  Å), suggesting different dynamics of the oxygen (out) diffusion in bilayers as compared to single films. The change in the critical temperature upon deoxygenation,  $\Delta T_c^{\text{ox}}$ , is known to scale linearly with the change

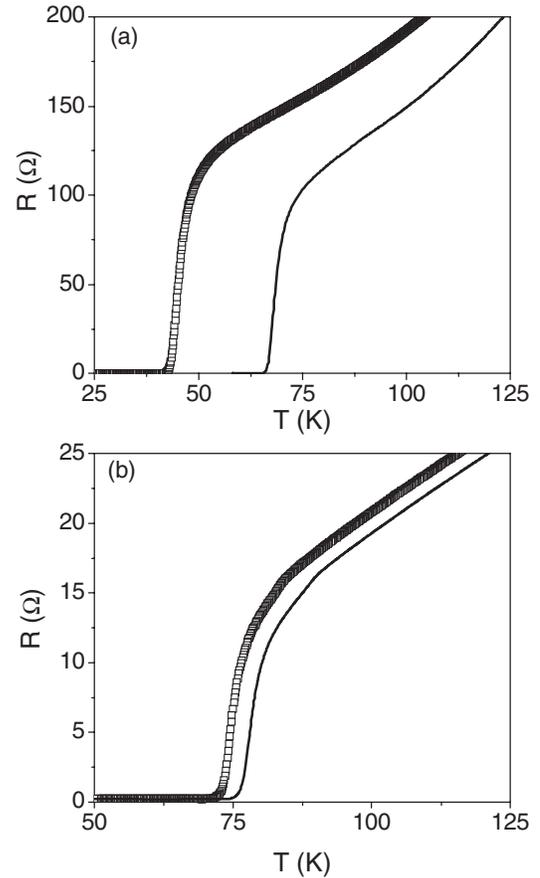


FIG. 1. (a) Resistance curves vs temperature for a bilayer with 12 u.c. YBCO<sub>6.7</sub>/40 u.c. LCMO, in the dark (open symbols) with  $T_c = 43$  K, and under illumination (solid line). The change in the critical temperature is  $\Delta T_c = 23$  K. (b) Resistance curves for a single YBCO<sub>6.7</sub> thin film in the dark (open symbols) and during illumination (line). The enhancement of  $T_c$  under illumination is 3.6 K.

in the  $c$ -lattice parameter,  $\Delta c$ , in oxygen depleted films [20]. The similar  $\frac{\Delta T_c^{\text{ox}}}{\Delta c}$  values obtained for bilayers ( $\frac{\Delta T_c^{\text{ox}}}{\Delta c} = 714$  K/Å) and single films ( $\frac{\Delta T_c^{\text{ox}}}{\Delta c} = 750$  K/Å) suggest that bilayers may have smaller oxygen content than single films despite the similar deoxygenation sequence. The magnitude of the photo effect on  $T_c$  is thus likely related to the larger oxygen depletion in bilayers as compared to single films, which is known to result in larger  $T_c$  changes upon illumination [8,11].

Figure 2 shows the superconducting  $T_c$  before (open circles) and during (full circles) light exposure as a function of the superconducting layer thickness. For comparison we also include the YBCO thickness dependence of  $T_c$  for fully oxygenated bilayers. The decrease of  $T_c$  with decreasing YBCO thickness arises from the interplay between the YBCO superconductivity with the LCMO which is restricted to 10 unit cells from the interface for fully oxygenated samples as described previously [24].  $T_c$  of oxygen depleted samples in the dark (open circles) show a

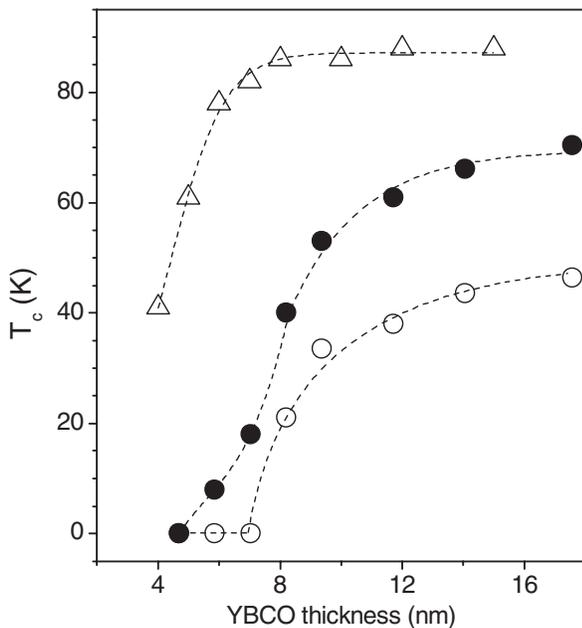


FIG. 2. Superconducting transition temperature ( $T_c$ ) as a function of YBCO thickness for samples that are fully oxygenated in the dark (open triangles), deoxygenated in the dark (open circles), and deoxygenated during illumination (solid circles). Lines are guides to the eye.  $T_c$  is depressed for oxygen deficient bilayers. Notice the  $T_c$  enhancement for bilayers with YBCO thickness larger than 4 u.c.

similar dependence on YBCO thickness. A pronounced  $T_c$  increase is observed under illumination (solid circles). Note that below 4 unit cells YBCO is not superconducting with or without light. Samples with YBCO thicknesses of 5 and 6 u.c. (5.9 and 7 nm, respectively) are superconducting when measured under light exposure, but remain metallic in the dark. It is worth remarking that for a YBCO thickness larger than 8 unit cells (where samples in the dark are superconducting), the change of  $T_c$  upon illumination is basically thickness independent, pointing to the importance of the interface in this photogenerated superconductivity.

The resistance is reduced upon illumination, consistent with an increase in the carrier density as previously observed in YBCO single films [9–11]. However, the illumination effects described above are *transient* [i.e., even at low temperatures the initial values (before irradiation) are recovered with a characteristic time constant when the light is turned off]. Figure 3(a) shows the time dependence of the resistance of a bilayer at 100 K. The characteristic *transient* time  $\tau$  for the decrease (increase) of the resistance is 350 s (150 s). The asymmetry may be related to the difference in time constants between the diffusion process of holes into the YBCO during the illumination part, and the faster recombination process happening concurrently within the LCMO. For comparison with the bilayer, we

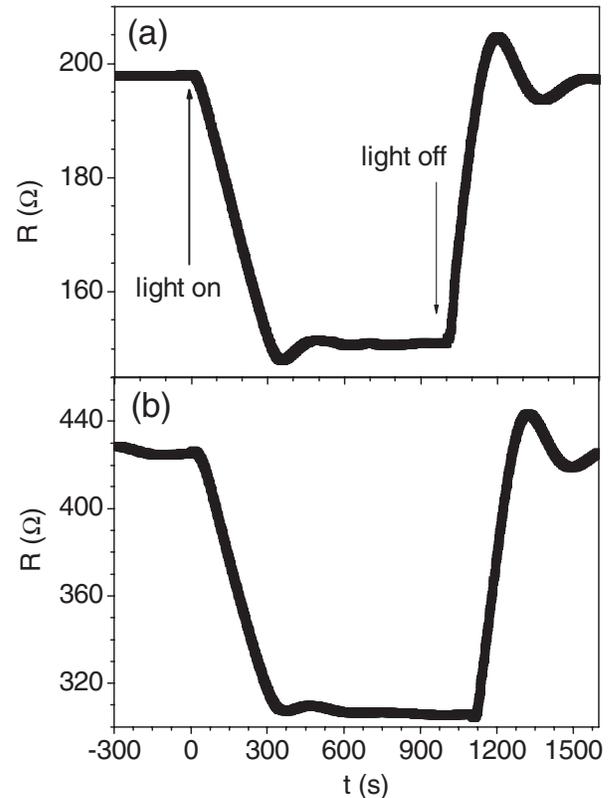


FIG. 3. Time dependence of the resistance when the light is switched on ( $t = 0$  s) and off for (a) a 12 u.c. YBCO<sub>6.7</sub>/40 u.c. LCMO bilayer, and (b) a 60 u.c. LCMO film, both at  $T = 100$  K. The relaxation times for the bilayer and the single LCMO film are similar and show that the effect is *transient* even at low (100 K) temperatures.

show the transient behavior of the resistance with illumination of a *single manganite film* prepared with the same deoxygenation sequence [Fig. 3(b)]. Note that the effect is transient as previously reported for deoxygenated manganites [14, 15], and that the characteristic times are similar to the bilayers. This implies that the manganite layer dominates the relaxation times of the photogenerated superconductivity. Of course, the superconductivity is expected to originate from the YBCO. In fact, single YBCO films with the same oxygen content ( $\delta = 6.7$ ) show persistent effects at these low temperatures, indicating that the transient effect observed in bilayers has a different origin. Moreover, at temperatures in between the critical temperatures in the dark and under illumination the samples can be driven superconducting by light (see Fig. 4) with a transient response, controlled by the manganite, which points to the key role played by the interface in the mechanism of photoinduced superconductivity operating here.

The correlation between the behavior of the single LCMO films and the bilayers studied imply that the effects are due to interfacial and/or electron transfer effects. The enhancements of the superconducting transition temperatures must occur in the YBCO layer, probably produced by

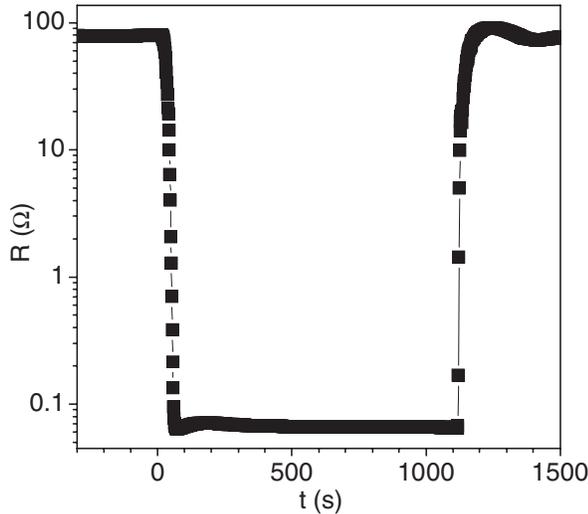


FIG. 4. Time dependence of the resistance for a 12 u.c. YBCO<sub>6.7</sub>/40 u.c. LCMO bilayer at  $T = 50$  K signaling the transition from the metallic to the superconducting state under illumination. The effect is *transient*, since even at low temperatures the initial value of the resistance is recovered on a short time scale when the light is turned off.

an increase in the number of holes. However, since the effect is transient unlike in single YBCO films, the enhanced relaxation must be caused by the LCMO. A simple way that this can occur is through hole transfer across the interface from the YBCO into the LCMO, where a faster recombination process can occur. Massive hole transport from YBCO to LCMO had been suggested as a possible explanation for a sizeable suppression of  $T_c$  in superlattice structures elsewhere [25]. Another possibility to consider is the modulation of the critical temperature  $T_c$  via changes in the LCMO magnetic properties with light. This alternative scenario, related to the interplay between ferromagnetism and superconductivity, is not supported by the present data. Since the superconducting  $T_c$  was shown to decrease almost linearly with the magnetic moment of the manganite layer [24,26], a reduced magnetization would produce an increased  $T_c$ . However, the changes in the magnetic properties of LCMO imply an enhanced magnetism with light irradiation [15]. In support of this, we have observed a 15 K shift of the metal-insulator transition to higher temperatures. The metal-insulator transition change suggests an enhanced magnetic moment, since the transition occurs at the Curie temperature.

In summary, we find a novel photoinduced superconductivity phenomenon occurring in S/F cuprate-manganite

bilayers. Contrary to previous observations in cuprate single films where the effect of illumination is *persistent*, in these bilayers it is *transient*. Furthermore, the enhancement upon white light illumination of the critical temperature in bilayers can be of considerable magnitude. These results are an illustration of light induced charge transfer across interfaces between strongly correlated oxides. The large transient changes of the resistivity and the superconducting critical temperature hold the potential for the development of novel devices in this type of nanostructured materials.

Work supported by US Department of Energy, the National Science Foundation, and CICYT MAT No. 2005 06024.

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