

# Effects of oxygen depletion on photoinduced and transport properties of thin films of charge-ordered manganites

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In this paper, we report a study of conductive and photoinduced properties of charge-ordered  $\text{Bi}_{0.4}\text{Ca}_{0.6}\text{MnO}_3$  thin films with different oxygen contents. The oxygen content of the films was varied following different annealing or deposition protocols. Change in film's resistivity during annealing reflects oxygen dynamics at high temperatures. It was found that oxygen-deficient films exhibit a significant increase in the photoinduced resistivity changes and the lifetime of photoinduced conductive phase. Possible origin of this effect is discussed. © 2009 American Institute of Physics. [DOI: 10.1063/1.3195059]

## I. INTRODUCTION

Doped rare-earth manganese oxides have rich and complex physics.<sup>1-3</sup> This group of materials exhibits drastic change in properties under application of external fields (magnetic and electric field, x-ray, and visible light illumination) or variation in chemical composition.<sup>1-6</sup> A photoinduced phase transition in charge-ordered (CO) manganites is a subject of considerable recent interest<sup>7-14</sup> not only due to interesting fundamental physics but also because of potential applications. Insulator-to-metal transition in manganese oxides makes these materials attractive from the point of view of creating photonic and optoelectronic devices.<sup>5,7,14,15</sup> However, the origin of the photoinduced effects in manganites is not well understood at present. From this perspective, it is important to better understand the origin of the photoinduced effects and to be able to control the magnitude of photoinduced changes and their lifetime.

Electronic, magnetic, orbital, and structural degrees of freedom are interconnected in manganites. Slight compositional variation may produce drastic change in properties. Bulk manganites have been found to be quite robust with respect to oxygen content.<sup>16</sup> On the other hand, the oxygen content can be varied more significantly in manganite thin films, strongly affecting their transport properties.<sup>17,18</sup> Oxygen deficiency induces significant changes in properties of the manganites, which are in ferromagnetic metallic ground state in the case of full oxygen stoichiometry. In thin films of  $\text{La}_{0.7}\text{Sr}_3\text{MnO}_3$ , the fully oxygenated state is metallic below the ferromagnetic transition temperature, while oxygen depletion can produce insulating state in the whole temperature range.<sup>18</sup> These thin films develop photoconductivity, while fully oxygenated thin films of the same composition are not photosensitive.<sup>18</sup> Oxygen deficiency in the manganite thin films from the ferromagnetic metallic part of the phase diagram also leads to switching behavior<sup>10</sup> or erasure of photoconductivity by magnetic field,<sup>8</sup> which makes the oxygen-deficient manganites interesting for device applications.

However, the effects of oxygen deficiency on properties

of CO manganites were not studied previously. Since bulk oxygen content in bulk manganites is very robust, thin films offer a unique opportunity to study the effects produced by variation in oxygen content in these materials. From the applied point of view, it is also important to find conditions at which the oxygen depletion occurs. The process of annealing in different gases, which is reported in this study, was monitored by resistivity measurements.

Large photoinduced decrease in resistivity and even photoinduced insulator to metal transition in CO manganites (bulk and thin films) was found in stoichiometrical (fully oxygenated) materials.<sup>5,14,15</sup> These photoinduced changes in the CO manganites are attributed to the destruction of the CO by light, which leads to the delocalization of the charge carriers and increase in conductivity. In this paper, we report strong influence of oxygen content on photoinduced and transport properties of CO  $\text{Bi}_{0.4}\text{Ca}_{0.6}\text{MnO}_3$  thin films.

## II. EXPERIMENTAL

Pulsed laser deposition (PLD) technique was used to grow thin films of  $\text{Bi}_{0.4}\text{Ca}_{0.6}\text{MnO}_3$  (the film thicknesses were around 40 nm) from a polycrystalline target with the same nominal composition. The substrates used were (100) oriented  $\text{LaAlO}_3$  (LAO), (100) oriented  $\text{SrTiO}_3$  (STO), and (001) oriented  $\text{NdCaAlO}_4$  (NCAO). The substrates were kept at a constant temperature of 800 °C during the deposition. The deposition was carried out at a pressure of 400 mTorr of flowing oxygen (if not indicated otherwise). The laser energy density on the target was about 1.7 J/cm<sup>2</sup>, and the pulse repetition rate was 10 Hz. After deposition the samples were slowly cooled, 20–40 °C/min, to room temperature at a pressure of 400 Torr of oxygen. X-ray  $\theta$ -2 $\theta$  scans showed that films were single phase, and  $\varphi$  scans confirmed epitaxiality. The width of rocking curves, 0.1°–0.2°, showed good crystallinity of these films.

Light-induced resistivity changes in  $\text{Bi}_{0.4}\text{Ca}_{0.6}\text{MnO}_3$  thin films were measured in four-in-line electrical contact configuration, as shown in Fig. 3 (inset): constant current was passed through the sample via the outer contacts, while voltage was measured using the inner contacts. The distance between voltage contacts was approximately 300  $\mu\text{m}$ . The

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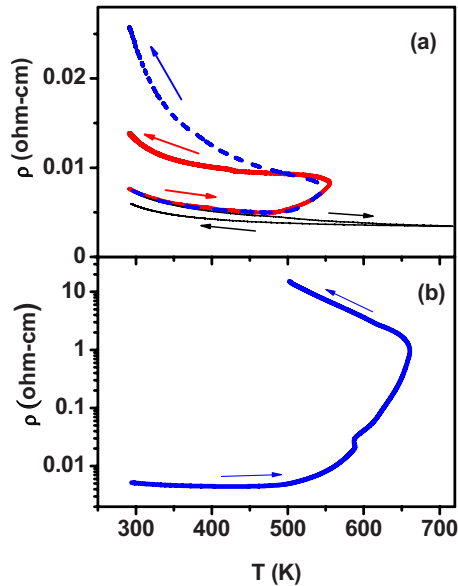


FIG. 1. (Color online) Temperature dependence of resistivity of  $\text{Bi}_{0.4}\text{Ca}_{0.6}\text{MnO}_3$  thin films grown on LAO on heating and cooling in (a) air (thick solid line), argon (dashed line), and oxygen (thin solid line); (b) in argon. The arrows indicate cooling or warming for each curve. The heating and cooling rates are 2 K/min.

area between the voltage contacts was illuminated with 140 mW multiwavelength (514, 488, 476, and 457 nm) unfocused argon-ion laser light, so that this area was fully covered by laser beam. High temperature resistivity was measured by a four-probe method in a tube furnace in flow of air, argon, or oxygen.

### III. RESULTS AND DISCUSSION

#### A. High temperature resistivity changes

Figure 1 shows the temperature dependence of resistivity,  $\rho(T)$ , for  $\text{Bi}_{0.4}\text{Ca}_{0.6}\text{MnO}_3$  thin films grown on LAO during heating and cooling in the flow of different gases with warming/cooling rate of 2 K/min. When the sample is heated in air above 480 K [Fig. 1(a)], the resistivity of the sample starts to increase. This annealing-induced increase is irreversible, and on cooling to room temperature the resistivity is higher compared to the room temperature  $\rho$  of the sample before annealing. After the similar process in argon flow, the resistivity returns to a much higher room temperature value. On the contrary, when the sample is annealed in oxygen, the resistivity of the sample is slightly reduced during cooling to room temperature [Fig. 1(a)]. When the film is heated in argon to a higher temperature (650 K), the resistivity changes by several orders of magnitude [Fig. 1(b)]. After the process of annealing shown in Fig. 1(b), the film becomes more transparent, while processes shown in Fig. 1(a) does not change the transparency of the film. On the other hand, heating the film to 720 K in the flow of oxygen does not alter the resistivity of the film significantly. We suggest that these changes reflect the oxygen dynamics in the film during annealing: the increase in the resistivity (annealing in air or argon) corresponds to the oxygen depletion, while the decrease in the resistivity corresponds to oxygenation of the film.

X-ray diffraction showed that the out of plane lattice parameter of the film after annealing in argon is slightly (by 0.01 Å) larger than the lattice parameter of as-prepared film. After annealing in oxygen, the lattice parameter remains the same within experimental uncertainty. Annealing in argon to a higher temperature [Fig. 1(b)] causes a significant increase in the lattice parameter (by 0.087 Å). There are two processes, which could change the lattice parameters of the thin films after annealing: change in oxygen stoichiometry and relaxation of strain. Since the lattice parameter of LAO, 3.79 Å, is slightly smaller than the lattice parameter of bulk  $\text{Bi}_{0.4}\text{Ca}_{0.6}\text{MnO}_3$ ,  $V^{1/3}=3.81$  Å, thin films grown on LAO are under small compressive strain.<sup>15</sup> Compressive strain leads to the increase in the out-of-plane lattice parameters, since in-plane lattice parameters are stretched. The relaxation of strain, which could occur under annealing, should lead in this case to the decrease in the lattice parameters, which is not observed experimentally. Perhaps the annealing temperature and/or annealing time are not sufficient to induce the relaxation of strain in our films. This means that the other factor, change in oxygen stoichiometry, is responsible for the increase in the lattice parameters in films annealed in air and argon. Indeed, the increase in the lattice parameter due to a decrease in the oxygen content was observed in bulk manganites of different compositions after annealing with a Ti getter.<sup>16</sup> The values of the changes in the resistivity and the lattice constants may vary slightly from film to film, but the general tendency remains the same under similar annealing conditions. The thin films grown on other substrates showed similar results indicating the loss of oxygen during annealing.

#### B. Photoinduced resistivity changes

Figure 2 shows the temperature dependence of resistivity,  $\rho(T)$ , for  $\text{Bi}_{0.4}\text{Ca}_{0.6}\text{MnO}_3$  thin films grown on LAO. As temperature decreases, the  $\text{Bi}_{0.4}\text{Ca}_{0.6}\text{MnO}_3$  thin films undergo a transition to a CO state.<sup>15,19</sup> The onset of the charge ordering is marked by a kink (a change in derivative) in the temperature dependence of resistivity (indicated by arrows in Fig. 2). This transition in the thin films is not as sharp as in the bulk materials.<sup>15,20</sup> Our x-ray scattering studies on these films showed the presence of superlattice peaks associated with charge ordering below charge-ordering temperatures consistent with the  $T_{\text{CO}}$  determined from the resistivity measurements.<sup>19</sup>

The charge ordering in this material can be partly destroyed by visible light:<sup>15</sup> the resistivity of as-made sample under illumination is considerably smaller than  $\rho$  of the sample measured without illumination [Fig. 2(a)]. The difference between  $\rho(T)$  taken with and without illumination decreases as temperature approaches the charge-ordering temperature  $T_{\text{CO}}$ , and there are no appreciable photoinduced effects above  $T_{\text{CO}}$ .

After annealing in argon following the process shown in Fig. 1(a), the resistivity of the film increases, and the photoinduced resistivity changes become significantly larger than in as-made film [Fig. 2(a)]. The annealed film undergoes the charge-ordering transition at approximately the same tem-

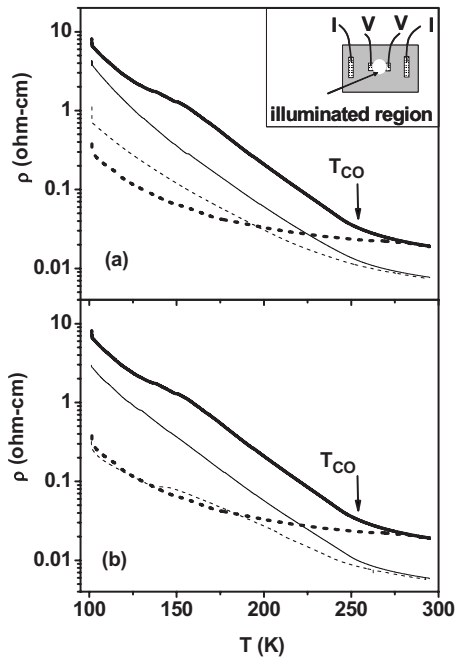


FIG. 2. Temperature dependence of the resistivity of the  $\text{Bi}_{0.4}\text{Ca}_{0.6}\text{MnO}_3$  thin film grown on LAO: solid lines—taken on cooling without illumination; dashed lines—taken on warming with illumination for the (a) as-grown film (thin lines) and film annealed in argon (thick lines); for the (b) film annealed in argon (thick lines) and film annealed in oxygen after annealing in argon (thin lines). The arrows indicate the charge-ordering temperature. The inset shows the experimental current and voltage contact configuration with respect to illuminated region.

perature, as as-made film: the kink in the  $\rho(T)$ , which occur at the charge-ordering temperature is at the same temperature for the annealed and as-made films ( $T_{\text{CO}}$  is indicated by arrows in Fig. 2). Figure 2(b) shows comparison of the photoinduced changes for the film annealed in argon and the same film subsequently annealed in oxygen. The photoinduced effect is reduced in the film annealed in oxygen if compared with the film treated in argon. The resistivity of the film annealed in oxygen is also smaller than  $\rho(T)$  of the film annealed in argon. This indicates that the oxygen content of the  $\text{Bi}_{0.4}\text{Ca}_{0.6}\text{MnO}_3$  thin films strongly influences the magnitude of the photoinduced resistivity changes in this material: the photoinduced effect can be enhanced by reducing the oxygen concentration, and this process can be reversed by subsequent restoration of the oxygen content. Oxygen-deficient films grown on STO and NCAO exhibit qualitatively similar enhancement of the photoinduced resistivity changes. The increase in the resistivity in the oxygen-deficient films can be attributed to localization effects due to disorder introduced by oxygen vacancies in oxygen-deficient films.

Oxygen deficiency in the  $\text{Bi}_{0.4}\text{Ca}_{0.6}\text{MnO}_3$  thin films can be also produced by growing thin films in reduced partial oxygen pressures lower than the optimal pressure for full oxygen stoichiometry.<sup>17</sup> Figure 3 shows the temperature dependence of the resistivity (with and without illumination) of  $\text{Bi}_{0.4}\text{Ca}_{0.6}\text{MnO}_3$  thin film grown on LAO in reduced (100 mTorr) partial pressure of oxygen and resistivity of the same film subsequently annealed in oxygen. Similar to the results shown in Fig. 2(b), annealing in oxygen reduces the magni-

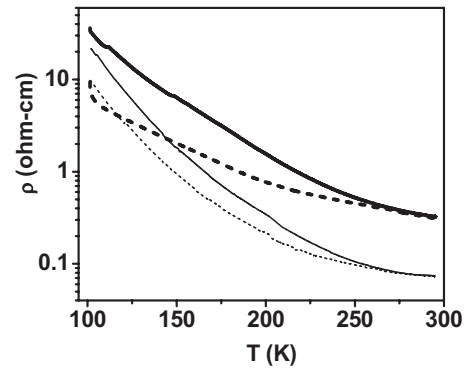


FIG. 3. Temperature dependence of the resistivity of the  $\text{Bi}_{0.4}\text{Ca}_{0.6}\text{MnO}_3$  thin film grown on LAO in reduced (100 mTorr) partial pressure of oxygen: solid lines—taken on cooling without illumination; dashed lines—taken on warming with illumination for the as-grown film (thick lines) and film annealed in oxygen (thin lines).

tude of the photoinduced effect and also reduces the resistivity of the film, showing that the oxygen content influences the magnitude of the photoinduced resistivity changes.

Photoinduced conductivity was observed in oxygen-deficient thin films of  $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$  (ferromagnetic conductor in fully oxygenated state).<sup>18</sup> It was suggested that the origin of this effect is similar to the proposed explanation of photoinduced enhancement of superconductivity in cuprates.<sup>21,22</sup> In this model, the electron (from electron-hole pair created by incoming photon) is trapped at the oxygen vacancy, while the hole contributes to conduction. This mechanism could be also responsible for enhancement of the photoinduced effect in CO manganites. However, another explanation of this effect is also possible: the disorder introduced by the oxygen vacancies weakens the charge ordering, so it can be more easily destroyed by light. Perhaps both mechanisms play a role in enhancement of photoinduced effects in CO oxygen-deficient  $\text{Bi}_{0.4}\text{Ca}_{0.6}\text{MnO}_3$  thin films.

### C. Lifetime of photoinduced conductive phase

When a  $\text{Bi}_{0.4}\text{Ca}_{0.6}\text{MnO}_3$  thin film is illuminated with visible light at fixed temperature, the material undergoes a transition to a more conductive phase reflecting the process of destruction (or partial destruction) of the charge ordering by light.<sup>15</sup> When illumination is switched off, the material gradually returns to its original CO state (Fig. 4). These time dependencies can be fitted to the exponential law:  $\Delta R \propto \exp(-t/\tau)$ . The lifetime  $\tau$  of the photoinduced conductive phase is significantly larger for oxygen-deficient sample: at  $T=160$  K, the time constants  $\tau$  are 92 and 359 s for the as-prepared and annealed in argon samples, respectively. The time constants  $\tau$  of as-prepared and oxygen-deficient samples differ significantly in a wide temperature range below the charge-ordering temperature (Fig. 5). When an oxygen-deficient film was treated in oxygen following the process shown in Fig. 1(a), the time constants  $\tau$  were reduced significantly at all temperatures (Fig. 5) when compared to the oxygen-deficient film. However, the time constants of this film did not return back to the values of the as-made film. Similarly, the magnitude of the photoinduced resistivity changes in the film treated in oxygen after annealing in argon

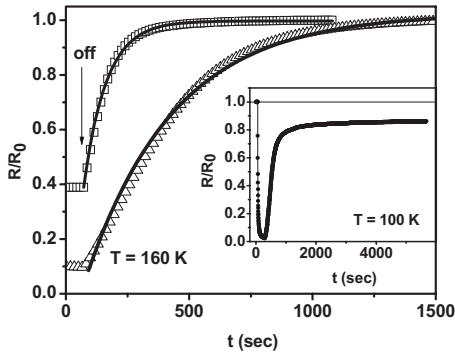


FIG. 4. Time dependence of normalized resistance  $R/R_0$  of as-made (squares) and annealed in argon (triangles)  $\text{Bi}_{0.4}\text{Ca}_{0.6}\text{MnO}_3$  films on LAO at  $T=160$  K with illumination and after illumination was switched off ( $R_0$  is resistance before illumination). The solid lines are fits to the exponential time dependence  $\Delta R \propto \exp(-t/\tau)$ . The inset shows time dependence of the normalized resistivity as illumination was switched on and off for the first time after cooling to  $T=100$  K. Time at which the light was switched off is indicated with arrows.

was reduced when compared with the film annealed in argon, but still larger than in the as-prepared film. (Perhaps longer annealing in oxygen would result in complete reversibility of effects produced by annealing in argon.) This shows sensitivity of the magnitude and lifetime of photoinduced resistivity changes on oxygen content of  $\text{Bi}_{0.4}\text{Ca}_{0.6}\text{MnO}_3$  thin films.

The inset of Fig. 4 shows the “persistent” photoinduced resistivity changes in oxygen-deficient sample at  $T=100$  K. The sample was cooled to  $T=100$  K and illuminated with laser light. After illumination was switched off, the resistance of the sample does not return to its initial value but reaches a smaller value (smaller than the initial resistance  $R_0$  by 15% for this film). Repeated switching of illumination on and off results in return of the resistance to the same reduced value ( $0.85R_0$  in this case). This effect is observed only after first illumination after cooling. For the subsequent measurements at higher temperatures, the value of the resistance before illumination  $R_0$  is equal to the final value.

If enhancement of the photoinduced effect in oxygen-deficient  $\text{Bi}_{0.4}\text{Ca}_{0.6}\text{MnO}_3$  thin films is due to electron trapping by oxygen vacancies, the electrons would need to overcome a potential barrier to recombine with holes. This could make the lifetime of the photoinduced CO conducting phase

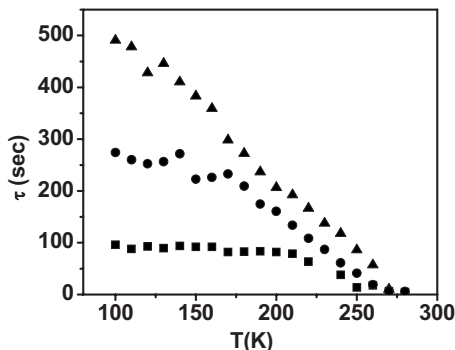


FIG. 5. Temperature dependence of the time constants  $\tau$  for the process of transition from photoinduced conductive state to the original state after illumination was switched off for  $\text{Bi}_{0.4}\text{Ca}_{0.6}\text{MnO}_3$  on LAO as-made film (squares), annealed in argon (triangles), and subsequently annealed in oxygen (circles). The data were taken on warming.

in oxygen-deficient  $\text{Bi}_{0.4}\text{Ca}_{0.6}\text{MnO}_3$  thin films longer and could also explain the persistent photoinduced effect (Fig. 4, inset).

#### IV. CONCLUSIONS

We have found that resistivity of the  $\text{Bi}_{0.4}\text{Ca}_{0.6}\text{MnO}_3$  thin films increases with oxygen depletion during annealing in argon or air. The process of oxygen depletion during annealing starts at rather low temperature, around 500 K. This information is important not only for manganite thin films but might also be found insightful for the thin films of other oxides. Higher annealing temperatures lead to larger oxygen depletion and higher resistivity values. Oxygen-deficient  $\text{Bi}_{0.4}\text{Ca}_{0.6}\text{MnO}_3$  films exhibit a significant increase in the photoinduced resistivity changes and the lifetime of photoinduced conductive phase. Two mechanisms can possibly contribute to the enhancement of photoinduced effects in CO  $\text{Bi}_{0.4}\text{Ca}_{0.6}\text{MnO}_3$  thin films: (1) trapping of electrons by the oxygen vacancy, while the holes (from electron-hole pair created by incoming photon) contribute to conduction; and (2) weakening of the charge ordering by the disorder introduced by the oxygen vacancies, so it can be more easily destroyed by light.

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