Photoinduced resistivity changes in Bi$_{0.4}$Ca$_{0.6}$MnO$_3$ thin films

V. N. Smolyaninova, M. Rajeswari, R. Kennedy, and M. Overby
Department of Physics, Astronomy and Geosciences, Towson University, Towson, Maryland 21252

S. E. Lofland
Department of Chemistry and Physics, Center for Material Research and Education, Rowan University, Glassboro, New Jersey 08028-1701

L. Z. Chen and R. L. Greene
Department of Physics and Center for Superconductivity Research, University of Maryland, College Park, Maryland 20742

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We report charge-ordered Bi$_{0.4}$Ca$_{0.6}$MnO$_3$ thin films with charge-ordering temperature near room temperature, and observation of large photoinduced resistivity changes in these films associated with melting of the charge ordering by visible light. Films grown under small compressive strain exhibit the largest photoinduced resistivity changes. The lifetime of the photoinduced low-resistance state is on the order of half a minute. These photoinduced resistivity changes in thin films of Bi$_{0.4}$Ca$_{0.6}$MnO$_3$ make them very promising for photonic device application. © 2005 American Institute of Physics. [DOI: 10.1063/1.1868869]

Doped rare-earth manganites $R_{1-x}A_x$MnO$_3$ ($R$ being a trivalent rare-earth and $A$ being a divalent alkaline-earth ion) exhibit a large diversity in electronic, magnetic, and orbital states due to the complex interplay of the corresponding degrees of freedom. One of the most intriguing properties of manganites is charge ordering (CO), wherein holes are localized at fixed positions of the Mn$^{4+}$ ions. Application of magnetic field, electric field, or electromagnetic wave irradiation drastically modifies the charge-ordered state, inducing an insulator-to-metal transition. A photoinduced insulator-to-metal transition in manganese oxides is especially interesting from the point of view of creating photonic band-gap materials, which allow control of dispersion and propagation of light. One can anticipate that a high refractive index contrast between the photoinduced conducting and insulating phases of CO manganites would be sufficient for development of a photonic crystal material. Once created, such a material would be quite unusual, since its properties could be easily tuned by application of a modest electric or magnetic field. In addition, since conductive properties, and therefore optical contrast, of the CO manganites are very sensitive to temperature, one could expect the development of rewritable photonic devices.

Recently, we observed permanent photoinduced reflectivity changes in a charge-ordered Bi$_{0.4}$Ca$_{0.6}$MnO$_3$ single crystal, and demonstrated that this phenomenon can be potentially used for creation of various photonic crystal materials. However, since visible light penetrates into the bulk of this material only to a depth of about 300 nm, thin films of Bi$_{1-x}$Ca$_x$MnO$_3$ with CO at room temperature are necessary for photonics applications. Preparation of such thin films presents quite a few challenges, since as a rule, thin-film properties differ from the properties of bulk material due to strain effects, changes in the magnetic and electron transport properties, etc.

The main results of this work is the first preparation of charge-ordered Bi$_{0.4}$Ca$_{0.6}$MnO$_3$ thin films with CO temperature near room temperature, and observation of large photoinduced resistivity changes in these films. This development became possible due to the key role of strain on the photo-sensitivity of thin Bi$_{0.4}$Ca$_{0.6}$MnO$_3$ films. It opens real possibilities for photonics device applications of these materials.

Thin films were grown by the pulsed-laser deposition technique from a polycrystalline target with nominal composition of Bi$_{0.4}$Ca$_{0.6}$MnO$_3$. The substrates used were [100] LaAlO$_3$ (LAO), which has a pseudocubic crystallographic structure with $a=3.79$ Å, and [100] SrTiO$_3$ (STO) with $a=3.905$ Å of a cubic structure. The laser energy density on the target was about 1.7 J/cm$^2$, and the deposition rate was 10 Hz. The LAO and STO 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. After deposition, the samples were slowly cooled to room temperature at a pressure of 400 Torr of oxygen. $\theta/2\theta$ scans show that films are epitaxial and single phase. The width of rocking curves, 0.04° for films grown on LAO and 0.3° for films grown on STO, shows good crystallinity of these films. Direct current resistivity was measured by a four-probe method. For sample illumination we used a continuous argon laser with 514, 488, 476, and 457 nm wavelengths, which has power of 150 mW in multiline mode.

Bulk Bi$_{0.4}$Ca$_{0.6}$MnO$_3$ has a CO temperature of 330 K. At the CO transition, the temperature dependence of the resistivity has a kink (a change in derivative) accompanied by a peak in the temperature dependence of magnetization. Our target material has similar properties: the CO temperature ($T_{CO}$) is 333 K, as indicated by the temperature dependence of the resistivity (Fig. 1) and by a peak in the temperature dependence of magnetization (not shown).

The rise in resistivity at the CO temperature in thin films is not as sharp as observed in the bulk material, as was noted previously for the charge-ordered thin films of a different composition. The CO temperature for thin films on LAO is lower than for the bulk: $T_{CO}=274$ K for 120-nm-thick film and 256 K for 40 nm. On the contrary, the films grown on STO have CO temperature $T_{CO}=347$ K, which is higher than...
the $T_{\text{CO}}$ of the bulk material. Our preliminary resonant and nonresonant x-ray scattering measurements on these films detected peaks associated with charge ordering below CO temperatures, consistent with the resistivity measurements. Such significant difference in CO temperatures for thin films grown on different substrates indicates the large effect of substrate-induced strain in thin films of Bi$_{1-x}$Ca$_x$MnO$_3$. The lattice parameters of LAO and STO are 3.79 and 3.905 Å respectively, while corresponding lattice parameter for Bi$_{0.4}$Ca$_{0.6}$MnO$_3$ is $V^{1/3} = 3.81$ Å. Therefore, films grown on LAO have small compressive strain, while films grown on STO are under tensile strain. Previously reported studies of charge-ordered Nd$_{0.5}$Sr$_{0.5}$MnO$_3$ and Pr$_{0.5}$Ca$_{0.5}$MnO$_3$ thin films of different thicknesses on STO and LAO do not show any significant difference in $T_{\text{CO}}$ for films of different thicknesses or grown on different substrates. A detailed study of strain effects on CO in Bi$_{1-x}$Ca$_x$MnO$_3$ films will be published elsewhere.

Light-induced resistivity changes in Bi$_{0.4}$Ca$_{0.6}$MnO$_3$ thin films are shown in Fig. 2. For this experiment we used a four-in-line electrical contact configuration, as shown in [Fig. 2(a) inset]. The distance between voltage contacts was approximately 0.3 mm. The space between voltage contacts was illuminated with full power (150 mW) multilength (514, 488, 476, and 457 nm) argon laser light. The laser beam was slightly focused with a 100 mm focal length lens, producing an illuminated region on the sample of approximately diameter of 0.05 mm and power density at the illuminated region of approximately $5 \times 10^4$ W/cm$^2$.

When the 40 nm film grown on STO was illuminated with argon laser light, its resistivity decreased approximately by a factor of 2 [Fig. 2(a)]. This change persisted up to 295 K with laser light on. The photoinduced resistivity change was not studied at higher temperature, since we do not have an optical access in the high temperature setup. When the illumination was switched off, the resistivity of the sample returned to its previous value [Fig. 2(a)]. A much more striking effect was observed for the 40 nm film grown on LAO. When this film was illuminated, its resistivity decreased by about one order of magnitude, almost returning to the value of resistivity for temperatures above the CO transition [Fig. 2(b)]. These data were taken while the sample temperature was ramped up at a rate of 2 K/min. This allows us to notice that the resistivity decreases rather slowly under illumination, and also returns slowly to its higher value, when the light is switched off [Fig. 2(b)]. This photoinduced change persists up to the CO temperature (256 K). This indicates that the observed photoinduced resistivity change is associated with melting of the CO.

FIG. 1. Temperature dependence of resistivity of Bi$_{0.4}$Ca$_{0.6}$MnO$_3$ polycrystalline target and thin films of different thicknesses grown on LAO and STO substrates. The CO temperatures are indicated with the arrows.

Thicker films (120 nm on LAO and STO) exhibit a much smaller photoinduced effect. The result for a 120 nm on LAO is shown in Fig. 2(c). Such a remarkable change in the photoinduced effect for films of different thicknesses suggests that the substrate induced strain plays a significant role in properties of the charge-ordered thin films of Bi$_{0.4}$Ca$_{0.6}$MnO$_3$. It appears that in thinner films, which are more strained, the charge ordering is weaker, or less stable, and therefore more susceptible to the argon laser light illumination, than that for thicker, more relaxed films, which exhibit very small photoinduced resistivity changes. The influence of strain on the CO of thin films was reported previously. It was noted that the CO in Pr$_{0.5}$Ca$_{0.5}$MnO$_3$ thin films grown on STO and LAO was destroyed by the application of a much weaker magnetic field than that required for a bulk material of the same composition. However, thinner films of Pr$_{0.5}$Ca$_{0.5}$MnO$_3$ were less susceptible to the influence of magnetic field than thicker films, while our results show that the CO in thinner films of Bi$_{0.4}$Ca$_{0.6}$MnO$_3$ can be more easily destabilized by light than that in thicker films. CO transition in bulk Bi$_{0.4}$Ca$_{0.6}$MnO$_3$ is accompanied by a structural transition, which leads to a sharp increase of lattice parameters $a$ and $c$ ($a=c$) and a sharp decrease of lattice parameter $b$. Such changes provide lattice distortion necessary for existence of the CO phase. They are typical for all the CO materials.

FIG. 2. Photoinduced resistivity changes for Bi$_{0.4}$Ca$_{0.6}$MnO$_3$ thin films: (a) 40 nm on STO, (b) 40 nm on LAO, and (c) 120 nm on LAO. Inset shows experimental current and voltage contact configuration with respect to the illuminated region. All temperature dependencies are taken on warming. Temperature dependencies of resistivity without illumination are shown with the dashed line. Solid line represents temperature dependencies of resistivity of illuminated samples. Arrows indicate the temperatures at which laser light was switched on or off.

Compressive strain should reduce in-plane lattice parameters ($a$ and $c$) in films grown on LAO resulting in smaller lattice distortion, which could make the CO weaker in these samples. On the other hand, tensile strain provided by STO substrate should increase in-plane lattice parameters, result-
This increase in the relaxation time with intensity is in agreement with our previous results, where for much higher power density (approximately $5 \times 10^7$ W/cm$^2$), permanent (more than 1 h) photoinduced optical reflectivity changes were observed.

In conclusion, we have developed charge-ordered Pr$_{0.7}$Ce$_{0.3}$MnO$_3$ thin films with CO temperature near room temperature. We have observed large photoinduced resistivity changes in these films associated with melting of the CO by visible light with wavelength around 500 nm. The substrate-induced strain makes the CO less stable and more susceptible to breakdown by illumination with visible light. Thus, thinner films grown on different substrates exhibit a larger drop in resistivity under illumination than do thicker films. The largest photoinduced resistivity changes were observed for thin, 40 nm, films grown under small compressive strain (on LAO). The lifetime of the photoinduced low-resistance state is of the order of half a minute and increases with intensity. Reported photoinduced resistivity changes in thin films of Bi$_{0.4}$Ca$_{0.6}$MnO$_3$ make this material very promising for photonic device application.

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\[ R(t) = R_0 \exp(-t/\tau) \]

**FIG. 3.** (a) Time dependence of resistance of a 40 nm Bi$_{0.4}$Ca$_{0.6}$MnO$_3$ film on LAO at $T=100$ K with 29% of full laser power switched on and off. Solid lines are fits to the exponential time dependence $\Delta R = \exp(-t/\tau)$. (b) Dependence of the time constant $\tau$ on intensity expressed as a percent of full laser power for the relaxation process after light was switched off at $T = 100$ K.

**References**


