Enhancement of photoinduced effects in Bi$_{1-x}$Ca$_x$MnO$_3$ thin films

V. N. Smolyaninova,[a] E. Talanova, Rajeswari M. Kolagani, G. Yong, R. Kennedy, M. Steger, D. Schaefer, and K. Wall
Department of Physics, Astronomy and Geosciences, Towson University, Towson, Maryland 21252

A considerable increase of the photoinduced resistivity changes and the lifetime of these changes were found in the Bi$_{0.4}$Ca$_{0.6}$MnO$_3$ thin films after depositing gold nanoparticles on the surface. A possible interpretation of this effect may be the enhancement of local electromagnetic field at the interface between the film and the metal nanoparticles due to the plasmon resonance, which may promote formation of larger volume of conducting phase producing larger magnitude and the lifetime of photoinduced resistivity changes. © *2007 American Institute of Physics.*
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Wide variety of electronic, magnetic, and structural states, their coexistence, and competition makes 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) a very attractive system for basic and applied studies. These materials are sensitive to application of magnetic, electric fields, x ray, or visible light irradiation.[1–5] Visible light can induce insulator to metal transition in charge-ordered manganites, revealing their potential for photonic device application.[3,6,7] A high refractive index contrast between the photoinduced conducting and insulating phases of charge-ordered manganites promises to be sufficient for the development of a photonic crystal material, which allows the control of dispersion and propagation of light. Since visible light penetrates into the bulk of this material only to a depth of about 300 nm, we have been studying photoinduced effects in thin films of Bi$_{1-x}$Ca$_x$MnO$_3$.[7] These thin films have the charge ordering transition around room temperature, a useful feature for device applications. Another important point for the development of manganite-based photonic devices is the possibility of coexistence of two phases with high refractive index contrast on a submicron scale, in this case charge-ordered insulating and charge-disordered metallic phases.[1,8–11] From this point of view it is important to be able to control the magnitude of photoinduced changes or the size of the conducting phase on a submicron level. We report considerable increase of the photoinduced resistivity changes in Bi$_{0.4}$Ca$_{0.6}$MnO$_3$ thin films after depositing gold nanoparticles on the surface, which may be attributed to the resonant enhancement of local electromagnetic field in the vicinity of the gold nanoparticles.

Thin films were grown by the pulsed laser deposition technique from a commercial polycrystalline target with nominal composition of Bi$_{0.4}$Ca$_{0.6}$MnO$_3$. The film thicknesses were around 50 nm. The substrates used were [100] oriented LaAlO$_3$ (LAO), [100] oriented SrTiO$_3$ (STO), and [001] oriented NdCaAlO$_4$ (NCAO). The laser energy density on the target was about 1.7 J/cm^2 and the pulse repetition rate was 10 Hz. The LAO and NCAO 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. θ-2θ scans showed that films were epitaxial and single phase. The width of rocking curves, less than 0.2°, 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, weak 476, and 457 nm wavelength lines, which has power of 150 mW in the multiline mode. Light-induced resistivity changes in Bi$_{0.4}$Ca$_{0.6}$MnO$_3$ thin films were measured using four-in-line electrical contact configuration, as shown in Fig. 1 (inset). The distance between voltage contacts was approximately 0.3 mm. The space between voltage contacts was illuminated with full power (140 mW) multiwavelength argon-ion laser light. Measurements were also done with 633 nm wavelength light of He–Ne laser of fixed 20 mW power. The laser beam had a width of 0.6 mm, which covered completely the area between the voltage contacts.

Figure 1 shows the temperature dependence of resistivity with and without illumination for the Bi$_{0.4}$Ca$_{0.6}$MnO$_3$ thin films grown on NCAO substrate. Below the charge ordering transition the resistivity starts to increase more rapidly and the temperature dependence of the resistivity has a change in derivative at the charge ordering temperature, T_{CO}=240 K. The rise of resistivity at the charge ordering temperature in

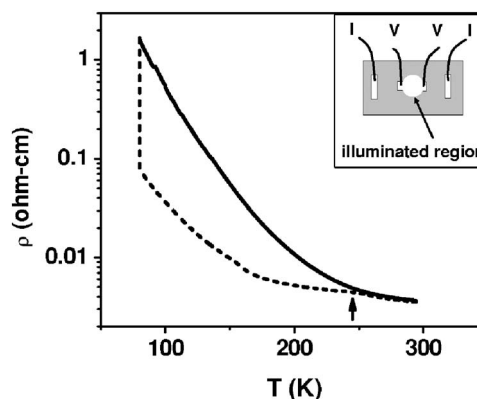FIG. 1. Temperature dependence of the resistivity of the Bi$_{0.4}$Ca$_{0.6}$MnO$_3$ thin film without illumination (solid line) and with illumination (dashed line) taken on warming. The charge ordering temperature is indicated with the arrow. The inset shows experimental current and voltage configuration with respect to the illuminated region.
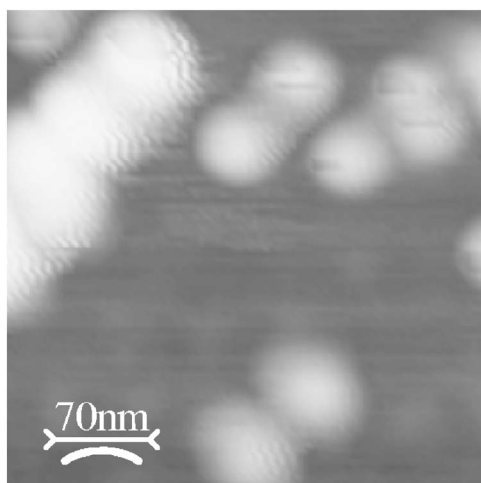
[a] Electronic mail: vsmolyaninova@towson.edu

FIG. 2. AFM image of gold nanoparticles on the surface of $Bi_{0.4}Ca_{0.6}MnO_3$ thin film.

FIG. 3. Time dependence of the resistivity of the $Bi_{0.4}Ca_{0.6}MnO_3$ thin film at $T=170$ K after laser illumination was switched on and off for sample with gold nanoparticles on the surface (squares) and without the nanoparticles (circles). Times at which the illumination was switched on and off are indicated by arrows. Solid lines are fits to the exponential time dependence $\Delta R \propto \exp(-t/\tau)$.

thin films is not as sharp as observed in the bulk material, as was noted previously.[7,12,13] Our x-ray scattering studies on these films show the presence of superlattice peaks associated with charge ordering below charge ordering temperatures, consistent with the resistivity measurements.[14]

When the sample was cooled down to the temperature of around 80 K and then illuminated with full power (150 mW) multiwavelength argon-ion laser light, its resistivity decreased by more than one order of magnitude (Fig. 1). This decrease of resistivity under illumination is associated with destruction of the charge ordering by visible light, as we reported previously.[7] The magnitude of the photoinduced changes is substrate dependent, proportional to the power of illumination, and do not depend on the wavelength of light for our experimental range.[7,11]

Above the charge ordering temperature illumination has no effect on the resistivity of the sample, and the temperature dependence of the resistivity taken with illumination has a kink at the charge ordering temperature, above which it coincides with the resistivity of the sample without illumination. This confirms that the photoinduced resistivity changes are associated with destruction of the charge ordering by light. However, illumination does not destroy the charge ordering completely in this material. At $T=80$ K the resistivity is still high, more than one order of magnitude higher than the resistivity above the charge ordering transition (Fig. 1). This indicates the presence of the charge-ordered insulating phase together with charge-disordered phase under illumination.

In order to study the effect of local electromagnetic field enhancement on the photoinduced resistivity changes, we deposited gold nanoparticles (40 nm diameter colloidal gold, aqueous solution) on the surface of $Bi_{0.4}Ca_{0.6}MnO_3$ thin films. These nanoparticles exhibit relatively wide plasmon resonance in the 500–600 nm frequency range.[15] The atomic-force microscope (AFM) image of the surface of a sample with gold nanoparticles is shown in Fig. 2. The size of the individual particles is around 40 nm in agreement with the information provided by the manufacturer. The AFM images indicate presence of both individual nanoparticles and clusters of nanoparticles on the surface of the film. The size of clusters and their geometrical configuration varied considerably, which implies further widening of the plasmon reso-

nance frequency range.[16] Thus, the wavelengths of laser light used in our experiments (488, 514, and 633 nm) match the plasmon resonance frequencies of the system.
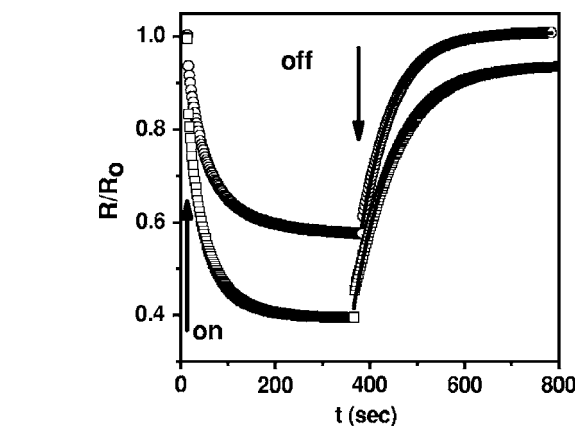
At fixed temperature, when the illumination of the sample is switched on, the resistivity drops considerably due to the destruction of the charge ordering by light, and when the illumination is switched off, the resistivity relaxes back (Fig. 3).[7,11] If the process is repeated, the resistivity exhibits the same changes (with or without gold particles on the surface), and does not have a progressively lower value with next illumination, as it was the case with x-ray induced resistivity changes in $La_{0.88}Sr_{0.12}MnO_3$ thin films.[5] These time dependencies can be fitted to the exponential law, $\Delta R \propto \exp(-t/\tau)$, where τ is a time constant. Under illumination, which partly destroys the charge ordering, the sample has more conductive charge-disordered phase. This phase is quasistable, i.e., has a substantial lifetime (characterized by a time constant τ) after the illumination is switched off, $\tau = 67$ s for the process shown in Fig. 3 (circles). Thus, for considerable time these two phases coexist without external stimuli. The temperature dependence of the lifetime of the photoinduced resistivity reduction is shown in Fig. 4. We have found a significant increase (up to 50%) of the photoinduced resistivity changes (Fig. 3) in the $Bi_{0.4}Ca_{0.6}MnO_3$
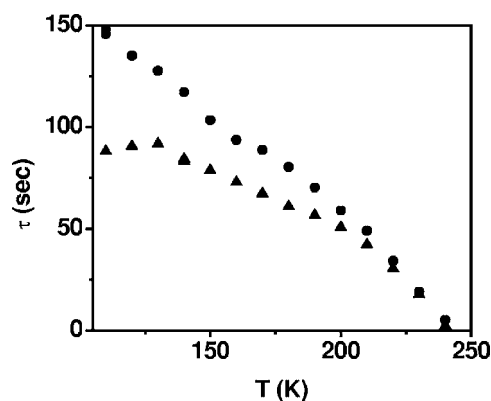

FIG. 4. Temperature dependence of the time constants τ for the process of transition from more conductive state to the charge-ordered state after illumination was switched off for sample with (circles) and without (triangles) gold nanoparticles on the surface.

thin film after covering the surface of the film with gold nanoparticles. This increase can be explained by the enhancement of local electromagnetic field in the vicinity of the gold nanoparticle due to the plasmon resonance.[15] Moreover, the lifetime of the photoinduced changes τ increases significantly after deposition of the gold nanoparticles on the surface of the film (Fig. 4). The difference between the lifetimes measured for the clean sample and the sample with gold nanoparticles decreases with the increase of the temperature and gradually disappears in the vicinity of the wide charge ordering transition. From our previous studies we have found that the magnitude and the lifetime of photoinduced resistivity changes increase, when intensity of illumination increases, which is probably due to the increase of the volume of conducting phase created by light. Therefore, enhanced electromagnetic field in the vicinity of gold particles, which may occur either due to the plasmon resonance or due to the related lightning rod effect,[17] promotes formation of larger volume of conducting phase producing larger magnitude and the lifetime of photoinduced resistivity changes. Experiments at different frequencies with different metal nanoparticles deposited in controlled manner (without clustering) would be useful to confirm the origin of the enhancement of the photoinduced resistivity changes.

Similar enhancement of photoinduced resistivity changes was observed for the films of $Bi_{0.4}Ca_{0.6}MnO_3$ grown on LAO and STO. To check whether this enhancement of photoinduced resistivity changes could be due to interaction of the surface with water, we studied the photoinduced resistivity changes in two parts of the same sample: one with colloidal gold and another with an equal amount of water dried on the surface. The sample treated with water did not exhibit enhancement of photoinduced resistivity changes.

To summarize, we have found that gold nanoparticles on the surface of the $Bi_{0.4}Ca_{0.6}MnO_3$ thin films produce a considerable increase of the photoinduced resistivity changes and the lifetime of these changes. This increase may be attributed to the enhancement of local electromagnetic field at the interface between the film and the metal nanoparticle due to the plasmon resonance. Enhanced electromagnetic field in the vicinity of gold particles due to the plasmon resonance could result in the formation of larger volume of conducting phase around the particles producing larger magnitude and

the lifetime of photoinduced resistivity changes. This phenomenon is interesting from the point of view of potential optoelectronic switching and memory device applications. For example, controlled deposition of gold nanoparticles on the $Bi_{0.4}Ca_{0.6}MnO_3$ film surface could lead to the controlled patterns of the photoinduced conducting phase in the charge-ordered insulating matrix leading to efficient optoelectronic switching.

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