PHYSICAL REVIEW B **80**, 075106 (2009)

Large photoconductivity and light-induced recovery of the insulator-metal transition in ultrathin $La_{0.7}Ce_{0.3}MnO_{3-\delta}$ films

E. Beyreuther,* A. Thiessen, S. Grafström, and L. M. Eng
Institute of Applied Photophysics, Dresden University of Technology, D-01062 Dresden, Germany

M. C. Dekker and K. Dörr
Institute for Metallic Materials, IFW Dresden, D-01171 Dresden, Germany

(Received 21 January 2009; revised manuscript received 30 June 2009; published 6 August 2009)

Tetravalent-ion-doped lanthanum manganite films typically suffer from overoxygenation in the as-prepared state, which in turn leads to an effective hole doping instead of the nominal electron doping. This problem can be overcome by post-deposition annealing in a reducing atmosphere, which, however, suppresses the phase transition from an insulating to a metallic phase at the magnetic ordering temperature so that the films are insulating in the whole temperature range. In the present work, reduced $La_{0.7}Ce_{0.3}MnO_{3-\delta}$ thin films were investigated with respect to their transport characteristics under photoexcitation. While the films are insulating in the dark, even the exposure to diffuse daylight recovers the insulator-metal transition (IMT). Excitation with continuous visible laser light further decreases the resistance by up to seven orders of magnitude and shifts the IMT to higher temperatures. The spectral, temporal, intensity, and temperature dependences of the photoconductivity have been investigated. The results suggest that (i) the manganite film shows a light-induced IMT and large photoconductivity, (ii) the substrate has an influence on the photoconductivity (through carrier injection into the film and/or substrate photoconduction) that grows with decreasing wavelength of the light, and (iii) an electron-doped metal state might be present under photoexcitation.

DOI: 10.1103/PhysRevB.80.075106 PACS number(s): 71.30.+h, 72.40.+w, 73.50.Pz, 75.47.Lx

I. INTRODUCTION

Mixed-valence perovskite manganites of the chemical composition $R_{1-x}A_xMnO_3$ with $x \in [0,1]$, R being a trivalent rare-earth cation, such as La or Pr, and A being a divalent cation, such as Ca, Ba, or Sr, have attracted enormous scientific interest over decades, as documented in numerous reviews, see, e.g., Refs. 1–4. The historical reason for this is the colossal magnetoresistance (CMR) effect, which appears in a certain composition range of those compounds, as well as their complex magnetic and electronic phase diagrams, which result from the sensitive coupling of electronic and lattice degrees of freedom exhibited by the manganites.

The present study combines two of the newer aspects in the research on mixed-valence manganites: (i) the control of the carrier concentration by photoexcitation and (ii) the physics of electron-doped manganites.

Photoconductivity phenomena have attracted great interest after an unusual response of a $Pr_{0.7}Ca_{0.3}MnO_3$ bulk crystal to photon exposure in the x-ray range was reported more than a decade ago.[5] The authors described a low-temperature photon-induced insulator-metal transition (IMT) associated with persistent photoconductivity. The latter was found to be reversible by heating and was accompanied by changes in the lattice structure. The effect was shown to be induced in the same compound also by infrared-to-visible photons.[6] Those findings triggered a variety of investigations on different manganites under various illumination conditions. Until now, there is no general understanding of the physical mechanisms which determine the photoresponse of manganites. Several types of phenomena and microscopic mechanisms are under debate. *Persistent photoconductivity* (PPC) is the light-induced decrease in the resistivity that remains after switching off the light. The original state can be recovered only by heating. PPC phenomena have been observed in metallic (mostly oxygen deficient)[7–11] and in insulating charge-ordered[12,13] (CO) manganites. Since the effect is often observed in *oxygen-deficient* samples, it was suggested that the underlying mechanism might be similar as in oxygen-deficient $YBa_2Cu_3O_{7-\delta}$ thin films (Ref. 8 and references therein). There, the photoconductivity is explained by the generation of electron-hole pairs with subsequent trapping of electrons at oxygen vacancies. Only heating can release the trapped carriers.

A *photoinduced insulator-metal transition* can occur in insulating manganites, as—for example—observed in $Pr_{2/3}Sr_{1/3}MnO_3$ films.[8] This effect is nonpersistent and results in a decrease in the resistivity by several orders of magnitude, comparable to the CMR effect. One approach to explain the effect, developed especially for charge-ordered manganites, is related to the electronic phase-separation scenario[14–16] in chemically homogeneous samples and suggests a melting of the CO state associated with the growth of ferromagnetic metallic islands, see also recent theoretical work.[17] For $Pr_{0.7}Ca_{0.3}MnO_3$ single crystals, phase separation in the sense of formation of conducting filaments under the simultaneous presence of both a static electrical field and illumination has been demonstrated by locally resolved reflection spectroscopy.[18,19]

Carrier injection from the substrate for films thinner than the absorption length of light has been addressed as a decisive additional process[20] but further work on this issue is very rare. Thus, the possible change in doping resulting from carrier injection from the substrate is an open point for most experiments on illuminated manganite films with a thickness of several 10 nm.

Considering the perspective for all-oxide photonic devices, it appears promising to realize an electron-doped manganite phase. The synthesis of *electron-doped* $LaMnO_3$ by doping with a tetravalent instead of a divalent *A* ion, which nominally leads to a mixed 2+/3+ valence of the Mn ions, has been discussed controversially for years (see, e.g., Ref. 21 and references therein for an overview). As-prepared films typically show hole doping due to overoxygenation[22,23] while ultrathin reduced films can indeed be electron doped according to x-ray spectroscopy results.[21] Disappointingly, recent investigations on $La_{0.7}Ce_{0.3}MnO_3$ (LCeMO) films[22–25] showed that the deoxygenation used to prepare the electron-doped state concomitantly leads to an insulating character of the samples.

In this paper, we discuss the photoresponse of as-prepared hole-doped and reduced electron-doped LCeMO ultrathin films on $SrTiO_3$ substrates. We show that the electron-doped LCeMO film is highly photoconductive and that the insulator-metal transition, which had been lost by deoxygenation, is recovered under illumination. The dependence of the photoconductivity on time, intensity, and wavelength has been investigated, along with similar measurements on a bare $SrTiO_3$ substrate. The results reveal both intrinsic photoconduction of the film itself and an influence of the substrate that strongly increases with the photon energy, in particular upon crossing the $SrTiO_3$ band gap. The results further indicate an electron-doped nature of the film in the metallic state.

II. EXPERIMENTAL

A 10-nm-thick epitaxial film of LCeMO was grown on a $SrTiO_3(100)$ (STO) single-crystal substrate by pulsed-laser deposition in off-axis geometry.[26,27] A stoichiometric target was ablated with a KrF excimer laser at a wavelength of 248 nm.

X-ray diffraction measurements were employed to ensure single-phase epitaxial growth. The films were additionally characterized by atomic-force microscopy (AFM) in the contact mode. The AFM measurements revealed an rms roughness of 1 nm as extracted from a scan area of 4 μm^2.

The sample was cut into two halves of $10 \times 5 \times 0.5\ mm^3$ each. One of them was deoxygenated by heating for 2 h in an ultrahigh vacuum at 670 °C. Both halves, the deoxygenated and the as-prepared one, were analyzed with regard to their manganese valence and thus to their doping type by x-ray photoelectron spectroscopy, as described in detail elsewhere.[21] The as-prepared film showed a Mn valence between +3 and +4 and is thus believed to be hole doped. The deoxygenated film turned out to be electron doped with a Mn valence between +2 and +3.

For transport measurements the samples were fixed on a sapphire slide sitting on the sample holder of an exchange-gas liquid-nitrogen optical cryostat (Optistat DN by Oxford Instruments). Normal wiring was used for the as-prepared film and coaxial wiring for the deoxygenated one. Metallic contacts were painted on the film surface by conductive silver paste. The resistance of the as-prepared film was measured by a Keithley 2700 digital multimeter in four-point geometry and that of the oxygen-deficient film by a Keithley 617 electrometer in two-point geometry with contact distances of 1 mm.

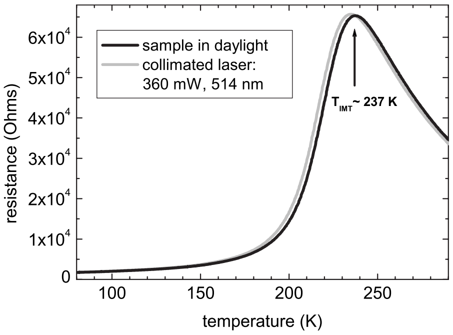

FIG. 1. Temperature dependence of the resistance of a 10-nm-thick LCeMO film in the as-prepared state with and without laser illumination.

To check a possible contribution of the $SrTiO_3$ substrate to the photoconductivity, transport measurements were additionally performed on a reference substrate which had undergone the same vacuum annealing treatment as the deoxygenated manganite film.

For exploring the photoresponse of the specimens, the sample surfaces were illuminated by an Ar^+ laser (Coherent Innova 90) operated in the cw mode at a wavelength of 514 nm. To investigate the spectral behavior of the photoresponse, additional photoconductivity measurements employing a monochromatized white-light source [1000-W xenon arc lamp coupled into a grating monochromator (Cornerstone 260 by Oriel Instruments)] were performed.

III. RESULTS AND DISCUSSION

First, we consider the transport and photoresponse behavior of the *as-prepared LCeMO film*, which was shown to be hole doped due to overoxygenation (see previous section). Figure 1 depicts the resistance-versus-temperature characteristics in the range between 300 and 80 K. The black curve, which was acquired with the sample exposed to daylight reaching the sample through the window of the optical cryostat, shows the insulator-metal transition which is typical for numerous mixed-valence manganite compounds. The insulating high-temperature phase changes to a metallic low-temperature phase at around 237 K. This value is reasonably consistent with the transition temperature of 260 K from the publication of Raychaudhuri *et al.*,[28] in which the phase diagram of the $La_{1-x}Ce_xMnO_3$ system was established for 50-nm-thick films. We attribute the lower transition temperature to the tensile strain and the thinness of our film. Exemplarily, at 300 and 77 K the cryostat windows were shadowed to achieve complete darkness of the sample chamber. The resistivity did not change in these cases, thus we assume that daylight does not induce any nonpersistent photoconductivity.

The gray curve in the same plot represents the transport characteristics under continuous illumination of the sample area between the two middle contacts of the four-point probe

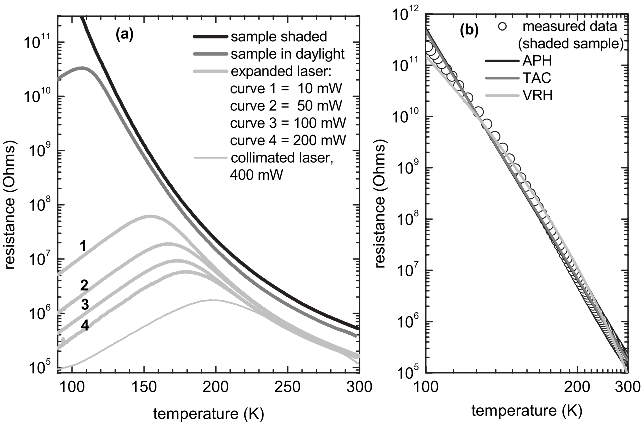

FIG. 2. (a) Temperature dependence of the resistance of the reduced LCeMO film in darkness (sample shaded), in diffuse daylight, and under laser illumination ($\lambda = 514$ nm) at different intensities. (b) Fit of the resistance-temperature characteristics of the shaded sample by three different transport models: APH, simple TAC, and VRH.

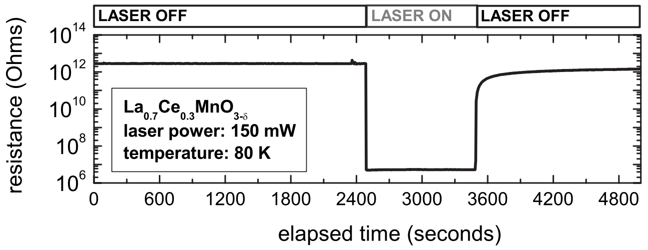

FIG. 3. Resistance of the reduced LCeMO film as a function of time while the sample illumination ($\lambda = 514$ nm) is switched on and off.

by the Ar^+ laser operated at a wavelength of 514 nm at an output power of 360 mW with a spot diameter of 1 mm. No significant change in the resistance can be stated, except a small shift of the curve along the temperature axis, which we attribute to sample heating.[29] An alternative explanation of the small resistance changes might be given in analogy to the argumentation of Jin *et al.*[30] In this paper an effect of the same order of magnitude is observed for 90-nm-thick $La_{0.67}Ca_{0.33}MnO_3$ films under very similar excitation conditions. The authors explain the resistance drop in the insulating range by photoexcitation of small polarons and the increase in the resistance in the metallic range by photoinduced demagnetization. It cannot be excluded with certainty that this scenario is valid here, too.

The transport behavior of the *reduced* LCeMO film appears completely different. In darkness, the film is highly resistive and no phase transition to a metallic phase is observed down to 80 K (Ref. 31) [Fig. 2(a), black line]. The resistance-versus-temperature characteristics can be fit by three different models that are commonly discussed for the insulating phase of manganite compounds,[2] namely, adiabatic polaron hopping (APH), simple thermal activation (TAC), and variable-range polaron hopping (VRH) [see Fig. 2(b)]. The first two fit the experimental data slightly better than the latter and reveal activation energies of 0.21 and 0.19 eV, respectively, which are typical values for insulating manganites (see, e.g., Ref. 14).

In contrast to the as-prepared LCeMO film, the reduced film is extremely sensitive to photoexcitation, as can be seen directly from the gray curves in Fig. 2(a). Already exposure to daylight (dark gray line) causes a resistance drop by as much as two orders of magnitude at 100 K, and recovers the insulator-metal transition at 110 K, which however occurs at a much lower temperature than in the as-prepared film.

The photoconductivity is larger if laser light is used: illumination of the sample area between the two electrical contacts by a laser beam of 1 mm diameter at a wavelength of 514 nm and 400 mW power results in a decrease in the resistance by seven orders of magnitude at 100 K and leads to an insulator-metal transition at around 200 K (thin light-gray line). The other (thick light-gray) curves of Fig. 2(a) were acquired with the whole sample surface illuminated by the laser beam after expansion by a telescope. It turns out that the IMT temperature as well as the magnitude of the resistance drop at a given temperature below the IMT increase systematically with the light intensity.

We note that the photoconductivity is not limited to the low-temperature metallic phase. Also in the high-temperature insulating phase a clear resistance drop upon laser illumination was observed. There, however, the resistance keeps its order of magnitude and its temperature dependence is characterized by a similar activation energy as under dark condition.

In a further measurement the resistance was recorded as a function of time while the laser was switched on and off. Thus, we explored the temporal recovery of the sample conductivity: as shown in Fig. 3, the main part of the observed photoconductivity exists only as long as the photoexcitation is present. After switching off the illumination, the resistance reaches the same order of magnitude as in the previous dark period, but remains somewhat below the initial value. Hence, also a small PPC is observed.

In order to investigate the observed photoconductivity effect as a function of the excitation wavelength, resistance-versus-temperature characteristics were acquired during illumination with selected wavelengths from a monochromatized white-light source. We measured complete R-T characteristics at excitation wavelengths of 700, 600, 500, 450, 400, and 380 nm while keeping the photon-flux constant.[32] Figure 4(a) represents the results for wavelengths of 700, 450, and 380 nm, with the latter corresponding to a photon energy slightly above the fundamental band gap of the $SrTiO_3$ substrate ($E_g = 3.2$ eV, i.e., 387 nm). For comparison, the R-T curve without illumination has been replotted. As can be clearly seen, even the long-wavelength excitation (700 nm) recovers the IMT. With increasing photon energy this process becomes more pronounced in the sense that the transition temperature goes up and the photoinduced conductivity increases.

Figure 5(a) shows the spectral dependence of the photoconductivity at 110 K in the wavelength range between 800 and 360 nm. We acquired the data starting in the infrared to avoid long-term relaxation processes from a preceding UV excitation. Even though the general tendency is a drop of the resistance with decreasing wavelength of the light, it be-

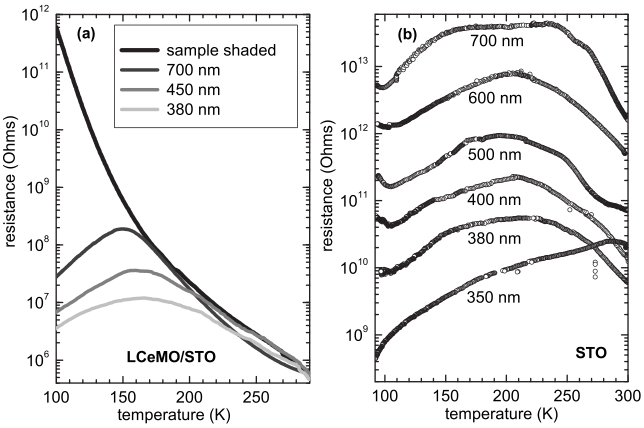

FIG. 4. Resistance-temperature characteristics at different illumination wavelengths, taken at constant photon flux, for (a) the $La_{0.7}Ce_{0.3}MnO_{3-\delta}$ film and for (b) the bare $SrTiO_3$ substrate.

comes clear that the photoconductivity-vs-wavelength characteristics shows several pronounced slope changes (kinks). The largest one is an increase in the conductivity by one order of magnitude occurring when the substrate band gap (387 nm) is reached.

In order to analyze the observed photoconductivity of the reduced $La_{0.7}Ce_{0.3}MnO_{3-\delta}/SrTiO_3$ sample, several questions need careful consideration: (i) Does only the film contribute to the observed photoconductivity, or is there substantial photoconduction in the substrate? (ii) Where do the charge carriers in the film originate from? Is there a significant carrier injection from the substrate? (iii) What is the nature of the charge carriers in the film? Is there indeed an underlying Mn^{2+}/Mn^{3+} mixed valence?

The spectral dependence of the photoconductivity near the band gap of the substrate [Fig. 5(a)] clearly reveals that the substrate contributes to the observed behavior. In order to come closer to an answer to question (i), a bare $SrTiO_3$ substrate was annealed and investigated in full analogy to the reduced LCeMO/STO sample. The temperature-dependent resistance under illumination in the wavelength range between 350 and 700 nm is displayed in Fig. 4(b). One notes several facts that clearly differ from the film results: the resistance is higher by at least three orders of magnitude for all wavelengths and the temperature dependence is different in that it shows a broad wavelength-independent resistance maximum around 200 K and an anomaly near 105 K, which we attribute to the structural cubic-to-tetragonal transition in $SrTiO_3$. Further, the normalized photoconductivity, defined as the relative change in the conductance under illumination, of the bare substrate is lower by a factor of around 40 (not shown in a figure). Finally, again regarding the spectral dependence of the resistance [Figs. 5(a) and 5(b)], the bare

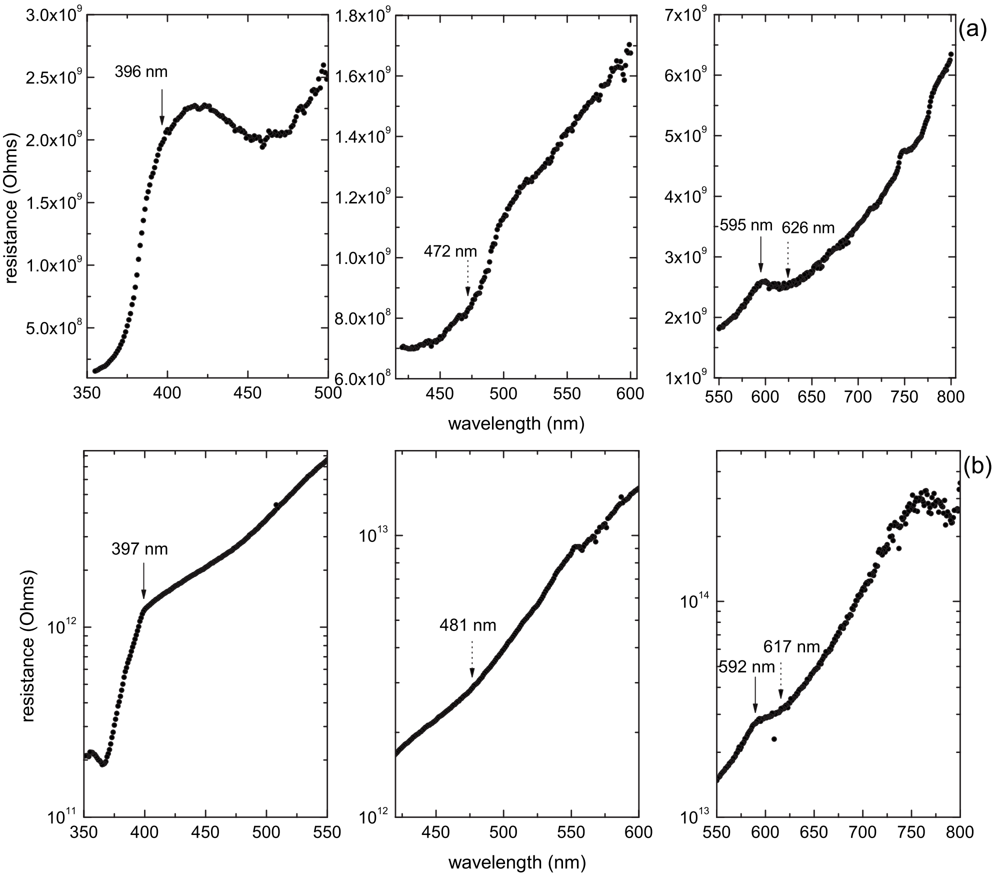

FIG. 5. Spectral dependence of the photoconductivity (a) of the $La_{0.7}Ce_{0.3}MnO_{3-\delta}$ film and (b) of the bare $SrTiO_3$ reference substrate, taken at 110 K under constant photon flux. Anomalies (points of slope change) appearing unambiguously in both samples are indicated by arrows. Note the logarithmic resistance scale in part (b).

substrate exhibits a decisively higher resistance dynamics across the measured wavelength range (resistance changes by three orders of magnitude) than the LCeMO sample (resistance changes by only one order of magnitude). These results seem to exclude a strong contribution of the substrate to the observed photoconductivity in the sense of parallel substrate conduction. It is, however, possible that an exchange of oxygen or charge carriers with the film may change the properties of the substrate, at least close to the interface with the film. This means that the comparison with the bare-substrate data gives a strong indication but no final evidence to rule out photoconduction in the substrate.

For the range of larger wavelengths ($\lambda > 500$ nm),[33] the temperature dependence of the resistance [Figs. 2(a) and 4(a)] is clearly typical for a manganite. It exhibits a rather narrow resistance peak, which systematically shifts to higher temperature with increasing irradiation power without changing its shape, but shows none of the features in the temperature dependence of the resistance observed for $SrTiO_3$ [Fig. 4(b)], and the activation energy in the insulating range is approximately the same as under dark condition. This gives sufficient evidence that the conduction essentially takes place in the film. It is worth noting that the broadened R-T characteristics under 450 and 380 nm irradiation [Fig. 4(a)] are different and do not support the above argument for the lower wavelength range. Here, a sizable substrate contribution to the measured photoconduction may be present.

Concerning the discussion of question (ii), the influence of the substrate becomes clear when Figs. 5(a) and 5(b) are compared where the spectral dependence of the resistance under illumination is shown for the LCeMO film and the $SrTiO_3$ reference. One notes several kinks occurring at the same wavelengths in both samples (near 390 nm, associated with the STO band gap, as well as near 480 and 590 nm). They may indicate a release of carriers from localized defect states in the $SrTiO_3$ bulk or at its interface. The carriers may be injected from the substrate into the film, as suggested in the work of Katsu *et al.*[20] As a second possible mechanism, photoconduction in an electronically or even chemically modified layer in the $SrTiO_3$ close to the interface may take place.

A strong injection of carriers into the film is expected to be irreversible on the time scale of some seconds[34] so the persistent part of the photoconductivity would grow with increasing carrier injection. The fact that most of the observed photoconductivity is transient (Fig. 3) for excitation energies below the $SrTiO_3$ band gap suggests the major part of the photoconductivity still to be caused by the light-induced release of carriers within the film. For photon energies above the substrate band gap the relaxation of the photoconductivity indeed becomes decisively slower (data not shown).

The nature of the doping, i.e., the Mn valence present in the conducting illuminated film—question (iii) from above—is of strong interest since it is possible that our experiment reveals the searched-for conducting electron-doped state of a manganite. Before illumination, the film is indeed in a mixed Mn^{2+}/Mn^{3+} state according to the x-ray photoemission spectroscopy analysis.[21] During illumination, carrier injection from the substrate may change the doping. Katsu *et al.*[20] present data indicating that the $SrTiO_3$ substrate behaves like an *n*-type semiconductor which under photoexcitation injects electrons into hole-doped manganites. In that experiment, the electron injection from the substrate was detected via changes in the resistance and magnetization revealing a clear reduction in the hole doping in the investigated $La_{1-x}Sr_xMnO_3$ films. In our experiment, the conductivity strongly increases at the STO band gap, implying an increasing absolute doping value. If the LCeMO film was in a hole-doped state, this would mean hole injection, in conflict with the observation of Katsu *et al.* This argument provides support for the assumption that an electron-doped conducting state is present in the irradiated film.

After having established that photoconduction essentially occurs in the LCeMO film for the larger wavelengths, let us consider the mechanism of photoconduction. It might be similar as in hole-doped manganites with a mixed Mn^{3+}/Mn^{4+} valence: charge carriers could be released from bound polaron states.[30] The Mn^{2+}/Mn^{3+} mixed valence allows for such states in a similar way as the Mn^{3+}/Mn^{4+} mixed valence. Further, an electronic phase separation in the sense of the presence of conducting paths in an insulating matrix is not in conflict with the present data.

IV. SUMMARY

In summary, we have studied the electrical transport behavior of an as-prepared and a reduced 10-nm-thick epitaxial $La_{0.7}Ce_{0.3}MnO_3$ film on $SrTiO_3$ under photoexcitation. The first film is in a hole-doped state, whereas our previous experiment characterized the second one to be electron doped. For the latter, we could demonstrate large photoconductivity of up to seven orders of magnitude at 100 K and the recovery of the insulator-metal transition under illumination. The strength of the effect is comparable to the CMR effect.

The investigation of the temporal behavior of the photoconductivity reveals that only a small part of the effect is persistent. The spectral dependence of the photoconductivity shows several kinks attributed to the $SrTiO_3$ substrate. Thus, the substrate needs to be taken into account for the understanding of the observed photoconduction. We could rule out a strong contribution from substrate photoconduction for the wavelength range above 500 nm, whereas excitation across the $SrTiO_3$ band gap leads to a strong drop of the resistance attributed to carrier injection into the film and/or substrate photoconduction.

Finally, we argue that the reduced $La_{0.7}Ce_{0.3}MnO_3$ film is likely to be electron doped. Thus, the present results suggest that photoexcitation may indeed induce a metallic electron-doped state in manganites. Further work on carrier injection and valence changes under illumination is needed to clarify this point.

ACKNOWLEDGMENT

This work was financially supported by the German Research Foundation (DFG) (FOR 520).

[*] elke.beyreuther@iapp.de

[1] A. Ramirez, J. Phys.: Condens. Matter **9**, 8171 (1997).

[2] J. M. D. Coey, M. Viret, and S. von Molnár, Adv. Phys. **48**, 167 (1999).

[3] M. B. Salamon and M. Jaime, Rev. Mod. Phys. **73**, 583 (2001).

[4] K. Dörr, J. Phys. D **39**, R125 (2006).

[5] V. Kiryukhin, D. Casa, J. P. Hill, B. Keimer, A. Vigiliante, Y. Tomioka, and Y. Tokura, Nature (London) **386**, 813 (1997).

[6] K. Miyano, T. Tanaka, Y. Tomioka, and Y. Tokura, Phys. Rev. Lett. **78**, 4257 (1997).

[7] J. Hao, G. He, D. Lu, and H.-K. Wong, Mater. Lett. **46**, 225 (2000).

[8] A. Gilabert, R. Cauro, M. G. Medici, J. C. Grenet, H. S. Wang, Y. F. Hu, and Q. Li, J. Supercond. **13**, 285 (2000).

[9] R. Cauro, A. Gilabert, J. P. Contour, R. Lyonnet, M. G. Medici, J. C. Grenet, C. Leighton, and I. K. Schuller, Phys. Rev. B **63**, 174423 (2001).

[10] Z. G. Sheng, Y. P. Sun, J. M. Dai, X. B. Zhu, and W. H. Song, Appl. Phys. Lett. **89**, 082503 (2006).

[11] H. Oshima, M. Nakamura, and K. Miyano, Phys. Rev. B **63**, 075111 (2001).

[12] I. I. Smolyaninov, V. N. Smolyaninova, C. C. Davis, B.-G. Kim, S.-W. Cheong, and R. L. Greene, Phys. Rev. Lett. **87**, 127204 (2001).

[13] S. Chaudhuri and R. C. Budhani, Europhys. Lett. **81**, 17002 (2008).

[14] W. Westhäuser, S. Schramm, J. Hoffmann, and C. Jooss, Eur. Phys. J. B **53**, 323 (2006).

[15] N. Kida, K. Takahashi, and M. Tonouchi, Phys. Rev. B **76**, 184437 (2007).

[16] M. Matsubara, Y. Okimoto, T. Ogasawara, S. Iwai, Y. Tomioka, H. Okamoto, and Y. Tokura, Phys. Rev. B **77**, 094410 (2008).

[17] K. Satoh and S. Ishihara, J. Magn. Magn. Mater. **310**, 798 (2007).

[18] M. Fiebig, K. Miyano, Y. Tomioka, and Y. Tokura, Science **280**, 1925 (1998).

[19] M. Fiebig, K. Miyano, Y. Tomioka, and Y. Tokura, Appl. Phys. Lett. **74**, 2310 (1999).

[20] H. Katsu, H. Tanaka, and T. Kawai, J. Appl. Phys. **90**, 4578 (2001).

[21] E. Beyreuther, S. Grafström, L. M. Eng, C. Thiele, and K. Dörr, Phys. Rev. B **73**, 155425 (2006).

[22] T. Yanagida, T. Kanki, B. Vilquin, H. Tanaka, and T. Kawai, Appl. Surf. Sci. **244**, 355 (2005).

[23] R. Werner, C. Raisch, V. Leca, V. Ion, S. Bals, G. Van Tendeloo, T. Chassé, R. Kleiner, and D. Koelle, Phys. Rev. B **79**, 054416 (2009).

[24] D. J. Wang, C. M. Xiong, G. J. Liu, Y. W. Xie, B. G. Shen, and J. R. Sun, Physica B **371**, 187 (2006).

[25] D. J. Wang, J. R. Sun, S. Y. Zhang, G. J. Liu, B. G. Shen, H. F. Tian, and J. Q. Li, Phys. Rev. B **73**, 144403 (2006).

[26] B. Holzapfel, B. Roas, L. Schultz, P. Bauer, and G. Saemann-Ischenko, Appl. Phys. Lett. **61**, 3178 (1992).

[27] C. Mitra, P. Raychaudhuri, G. Köbernik, K. Dörr, K.-H. Müller, L. Schultz, and R. Pinto, Appl. Phys. Lett. **79**, 2408 (2001).

[28] P. Raychaudhuri, C. Mitra, P. D. A. Mann, and S. Wirth, J. Appl. Phys. **93**, 8328 (2003).

[29] In order to estimate the magnitude of sample heating we assume one-dimensional heat conduction from the sample surface towards its rear side. The temperature difference ΔT between surface and rear side can be calculated as $\Delta T=\frac{Pl}{\lambda A}$ with P being the incident light power, l the sample thickness (here: 0.5 mm), A the illuminated area (here: 5×10^{-3} mm^2 for the unexpanded laser beam), and λ the heat conductivity of $SrTiO_3$ [10 W K^{-1} m^{-1} in the range between 100 and 300 K (Ref. 35)]. At a laser power of 100 mW our estimation gives a temperature difference of 1 K.

[30] K. X. Jin, C. L. Chen, and S. G. Zhao, J. Mater. Sci. **42**, 9617 (2007).

[31] To ensure that there is no metallic phase below 80 K the sample was later transferred into a liquid-helium cryostat for a resistivity measurement at lower temperatures: no phase transition was observed down to 5 K.

[32] The photon flux $\Phi=\frac{P}{h\nu}$, with P being the incident power at the sample surface, is proportional to $P\lambda$. In our measurement we used a value of $P\lambda=1260$ mW nm, which corresponds, for example, to an incident light power of 2.1 mW at a wavelength of 600 nm.

[33] Note that the value of 500 nm is somewhat arbitrary because the influence of the substrate grows continuously towards shorter wavelengths. However, for the discussion it is convenient to distinguish two different regimes of the photoresponse behavior.

[34] Y. T. Sihvonen, J. Appl. Phys. **38**, 4431 (1967).

[35] T. Mitsui and S. Nomura, in *Ferroelectrics and Related Substances: Oxides*, edited by K.-H. Hellwege and A. M. Hellwege, Landolt-Börnstein, New Series, Group III, Vol. 16a (Springer, New York, 1981).