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Photoinduced characteristics in $La_{0.67}Ca_{0.33}MnO_3$ film

K. X. Jin · C. L. Chen · S. G. Zhao

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Abstract A systematic investigation of photoinduced properties is carried out in $La_{0.67}Ca_{0.33}MnO_3$ film prepared on $LaAlO_3$ (100) substrate by magnetron sputtering method. At $T < 270$ K, the resistivity of film induced by laser increases because of the demagnetization effect of manganites. The photoinduced relaxation character of film indicates that the time constant increases with increasing temperature, which is attributed to the growing thermal fluctuation. After laser irradiation, the resistivity returns to the original value and the relaxation time seems to be independent of temperature. In insulating state, laser irradiation induces the reduction in resistivity of film due to the excitation of small polarons.

Introduction

The perovskite manganites REMnO$_3$ (RE is the trivalent rare earth cation, such as La, Pr, Nd, and Cd) are usually an anti-ferromagnetic semiconductor or insulator. If the trivalent rare earth cation is partially substituted with the divalent alkaline earth cation A (A = Ca, Sr, Ba, and Pb), the doped manganites $RE_{1-x}A_xMnO_3$ have exhibited a colossal magnetoresistance (CMR) effect [1–3], which can be qualitatively explained with Zener's double exchange model [4] and the cooperative Jahn-Teller effect [5]. In the past 10 years, research on CMR has attracted growing attention due to their unusual properties and potential applications in high density magnetic heads. The doped manganites are strongly correlated electron systems and application of various external fields, such as electric field, high pressures, X-ray irradiation, could affect their transport properties [6–10]. Laser irradiation, being the external stimuli, also offers a convenient method to vary the concentration of charge carriers and induce the changes in the physical properties of manganites [11–14]. Most research on photoinduced properties are focused on the charge ordering manganites [15, 16]. The photoinduced resistance change in charge ordering film has been observed at room temperature and the relaxation process has also been investigated, which is promising for photonic device application [17]. There are few reports about the photoinduced relaxation character of typical manganites with the metal to insulator transition [18] although it is very significant because the relaxation represents the photoinduced process and reflects the intrinsic physical mechanism of photoinduced effect. Based on these considerations above, we have prepared nano-scale $La_{0.67}Ca_{0.33}MnO_3$ (LCMO) film and investigated the photoinduced characteristics and relaxation process of film irradiated by laser.

K. X. Jin (✉) · C. L. Chen
Department of Applied Physics, Northwestern Polytechnical University, Xi'an 710072, China
e-mail: jinkx@nwpu.edu.cn

S. G. Zhao
Department of Basic Sciences, Xi'an University of Science and Technology, Xi'an 710054, China

Experimental details

The powder with LCMO nominal composition was prepared by solid state reaction technique with repeated grinding and sintering at 1,200 °C for 10 h. Then the polycrystalline sample was pressed from the powder and sintered at 1,250 °C for 10 h. The film was deposited on $LaAlO_3$ (LAO)-(100) single crystal substrate by magnetron sputtering method and subsequently annealed at 800 °C in air for 1 h in order to improve epitaxial character of the deposition. The structure of samples was investigated using D/MAX-rA X-ray diffractometer. The thickness of thin film was about 90 nm (measured by DEKTEK-3 surface profilometer). The sample was placed in a closed-circuit liquid nitrogen cryostat with the quartz-glass window, the temperature range of which varied from 77 to 400 K. The light source used in the experiment is Nd:YVO_4 continuous wave laser. The average power level is 20 mW and wavelength is 532 nm. The resistivity is measured using the UT50 digital universal meter, and the measuring current is less than μA order of magnitude. The sample and cryostat completely reach the heat balance, and the resistivity caused by current thermal effect has peaked.

Results and discussion

Figure 1 shows X-ray diffraction (XRD) patterns of bulk and film. The bulk of LCMO is single phase with pseudo-cubic structure. Besides (100) and (200) diffraction peaks of LAO substrate, only (100) and (200) diffraction peaks of film appears, indicating that the film has better epitaxial character with pseudo-cubic structure. The lattice mismatch between the thin film and substrate is less than 2% estimated from XRD data.

The magnetoresistance MR (H = 0.4 T) and the photoinduced relative change in resistivity PR are defined as $(R_0 - R_H)/R_0$ and $(R_p - R_0)/R_0$, respectively, where R_H is the resistivity with application of magnetic field, R_p is the resistivity of LCMO film irradiated by laser, and R_0 is the resistivity without any external field. Figure 2 shows the resistivity and MR of film as a function of temperature. The film without application of external fields exhibits typical metal–insulator transition at the peak resistivity temperature (T_p = 270 K). The small polaron model is given by:

$$R(T) = R_0 T \exp(E_{hop}/K_B T) \quad (1)$$

where E_{hop} is the effective hopping energy and K_B is Boltzmann's constant. The ln(R/T) as a function of 1,000/T at T > 270 K is shown in the inset of Fig. 2. The solid line is the fit curve using the formula and the small polaron mechanism works very well. The effective hopping energy is about 67 meV estimated from the fitting data. E_{hop} represents the hopping energy of localized carriers in transport properties and the film with T_p about 270 K has effective hopping energy about 67 meV, which is consist with experimental results suggested in the literature [19].

At H = 0.4 T, the resistivity decreases in whole measuring temperature range shown in Fig. 2. The maximum MR value is 21.4% at T = 250 K. The photoinduced effect on the resistivity of film is shown as Fig. 3. The resistivity

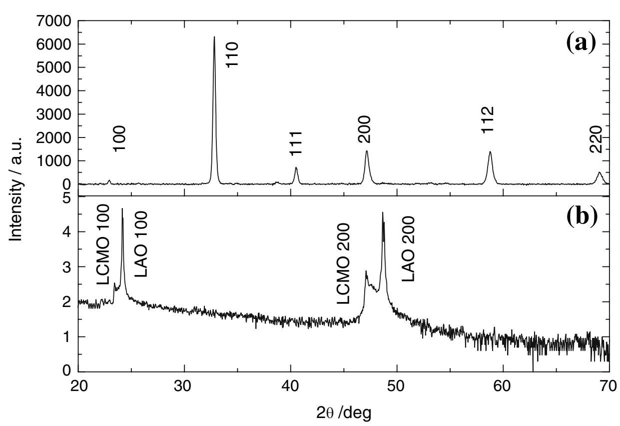

Fig. 1 X-ray diffraction patterns of $La_{0.67}Ca_{0.33}MnO_3$ bulk and film, (**a**) bulk and (**b**) film. The intensity of film is given in log scale

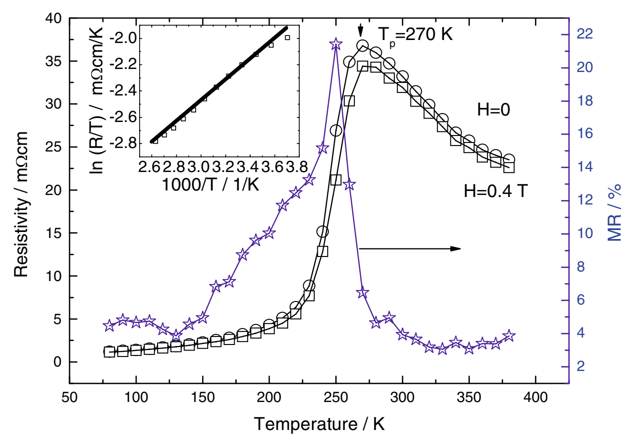

Fig. 2 Temperature dependence of resistivity and MR. The ln(R/T) versus 1,000/T curve is shown in the inset and the solid line is the fit curve using the small polaron model

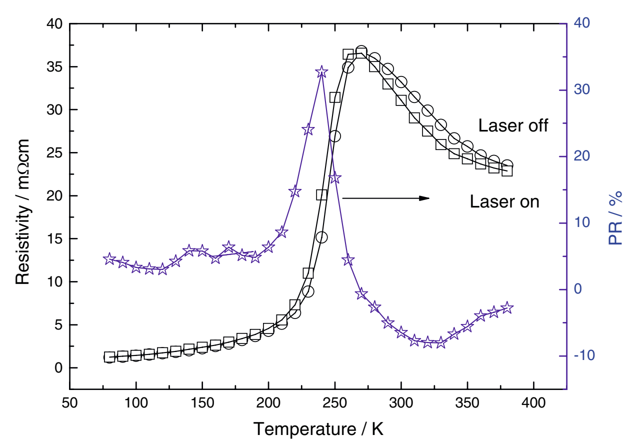

Fig. 3 Temperature dependence of resistivity and PR

is measured until resistivity of film irradiated by laser does not change. The resistivity of film irradiated by laser is higher than that without laser irradiation in the metallic state, while the resistivity is lower than that in the insulating state. There exists a maximum value of PR about 32.7% at $T = 240$ K. The transport of manganites is closely related to the spin system of e_g carriers and localized t_{2g} spin core in Mn ions. At $T < 270$ K, the double exchange effect is favorable. According to Pauli exclusion principle, only when the spin orientation of jumping e_g electrons is identical with that of t_{2g} spin core in the acceptor Mn^{4+} ions, the 2*p* electrons in O^{2-} ions can satisfy Hund's rule. The e_g electrons of Mn^{3+} ions jump more easily between Mn^{3+} and Mn^{4+} ions through O^{2-} ions and the film forms metallic conduction. With increasing temperature, the localized e_g electrons and the lattice distortion forms small polarons, so the transport of film is small polaron hopping conduction in insulating state. The magnetic field may align the spin cores of nearest Mn ions and reduce the scattering of e_g electrons, thereby enhance double exchange effect, which favors the transfer of e_g electrons and decreases resistivity. The light source used in the experiment is 2.34 eV, and laser could excite the down-spin e_g electrons, which destroys the ferromagnetic coupling between the upward-spin e_g and t_{2g} electrons in Mn^{3+} ions, as a result weakens double exchange effect, and increases resistivity. Namely, this is so-called photoinduced demagnetization of manganites [20, 21]. The external field effect on manganites is attributed to the change in spin system of e_g carriers and localized t_{2g} spins in Mn ions, which changes the transport properties of film by double exchange effect in metallic state. In insulating state, laser can excite hopping of small polarons, which results in the decrease of resistivity.

The basic experimental setup and schematic of the relaxation character are shown in Fig. 4, which is composed of the triggering timing system and the resistivity recording system. The photoinduced time character of film is shown in Fig. 5. The resistivity increases nonlinearly with increasing irradiation time at $T = 80$ K and it decreases with irradiation time at $T = 310$ K, which is consist with the photoinduced change of resistivity in Fig. 3. The photoinduced relaxation characters of film at $T = 130$ K, 180 K, 230 K have also been measured and have the same tendency as that at $T = 80$ K. The sample exhibits the transient photoconductivity effect. It means that the resistivity changes with laser irradiation and then restores to the original value when laser is switched off. The resistivity versus time curves after laser irradiation are also shown in Fig. 5.

The experimental data of photoinduced time relaxation is fitted into the formula:

$$R(t) = R_0 + A\exp[-(t/\tau)] \quad (2)$$

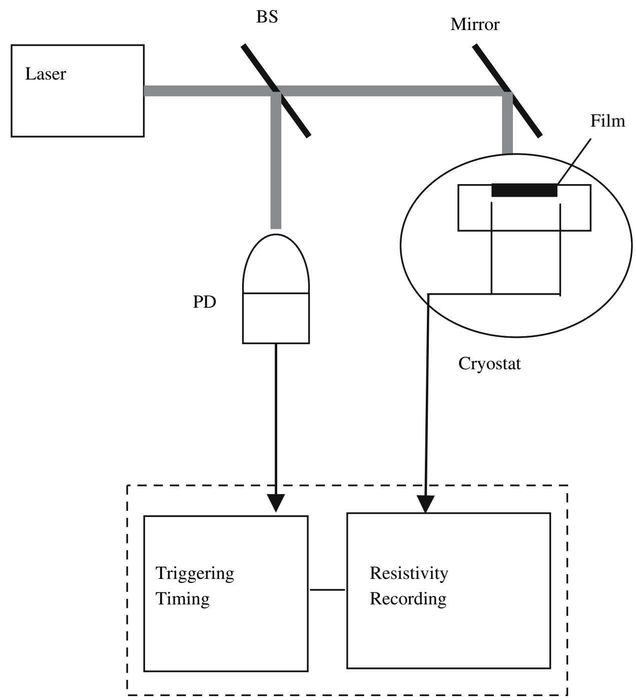

Fig. 4 A schematic view of the experimental facility. PD is the photodiode. BS is the beam splitting

where $R(t)$ is the resistivity at irradiation time t and τ is the time constant. The solid lines are the fitting curves shown in Fig. 5. The fitting parameters of photoinduced character at different temperatures are listed in Table 1. In metallic state, the time constant τ increases with increasing temperature when laser is on. The time constant is characteristics of photoinduced relaxation process, and there exists the similar phenomena in magnetization and spin glasses of manganites [22, 23]. Therefore the relaxation of photoinduced character relates with the demagnetization process of manganites. When temperature is lowered well below Curie temperature (near T_p), the double exchange interaction gradually becomes stronger and the ferromagnetic correlations are enhanced. Compared to thermal effect, the perturbation effect of laser irradiation on the system is strong and the relaxation process of photoinduced demagnetization is quick. With increasing temperature, the thermal fluctuation grows and the ferromagnetic correlations are weakened. The perturbations of laser irradiation are relatively weakened and the time of demagnetization process is increasing with increasing temperature. In insulating state, the time constant τ is about 15.45 s when laser is switched on. The relaxation process is hopping of small polarons. The small polarons are the quasi-particles with lattice distortion and have the bulk mass. Therefore the relaxation time is longer than that of film in metallic state.

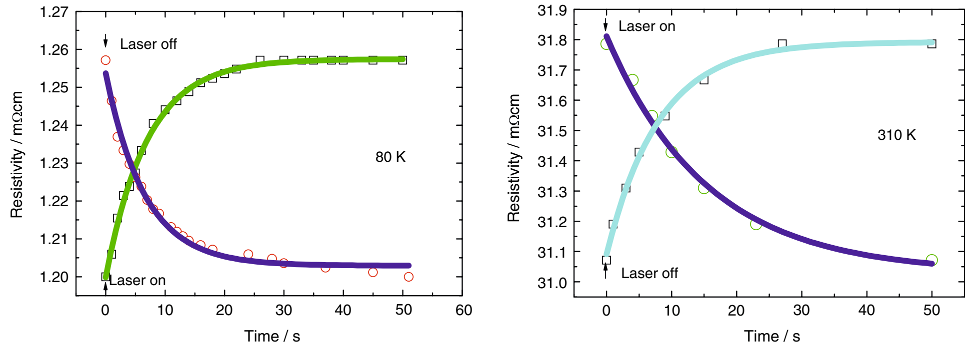

Fig. 5 Time characters of the photoinduced relaxation process at T = 80 K and 310 K. The solid lines are the fitting curves

Table 1 Fitting parameters of the relaxation process

Temperature		A	τ
T = 80 K	Laser on	–4.84	7.04
	Laser off	4.26	–6.78
T = 130 K	Laser on	–6.10	10.33
	Laser off	5.15	–6.58
T = 180 K	Laser on	–0.017	11.39
	Laser off	0.018	–6.65
T = 230 K	Laser on	–0.188	11.70
	Laser off	0.178	–6.84
T = 310 K	Laser on	65.67	–15.45
	Laser off	–58.94	8.09

The τ is the time constant

The time constant τ is independent of temperature and almost is a constant about 6.7 s in metallic state after laser irradiation. The time constant τ is about 8 s in insulating state, which is much lower than that of laser irradiation. The manganites are strongly correlated electron systems with the charge, spin, orbital, and lattice degrees of freedom, the equilibrium of which results in special properties. The perturbation of laser irradiation changes the equilibrium of these freedoms and induces the change in resistivity. When the laser is off, the system returns to the original equilibrium state and the relaxation is process of the recovery in balanced freedoms, which is the intrinsic character and seems to be independent of temperature.

Conclusions

The nano-scale $La_{0.67}Ca_{0.33}MnO_3$ film has been deposited by magnetron sputtering method from the nominal bulk target. The transport properties of film induced by the continuous wave laser and magnetic field have been investigated. The different external fields effect on manganites is attributed to the change in spin system of e_g carriers and localized t_{2g} spins in Mn ions. The photoinduced relaxation character of film has been investigated in details. The film has different relaxation characters at different phases, which is ascribed to the intrinsic mechanism of manganites. After laser irradiation, the system returns to the original state and this process seems to be independent of temperature.

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References

1. Von Helmholt R, Wecker J, Holzapfel B, Schultz L, Samwer K (1993) Phys Rev Lett 71:2331
2. Jin S, Tiefel TH, McCormack M, Fashtnacht RA, Ramesh R, Chen LH (1994) Science 264:413
3. Jin KX, Chen CL, Wang SL, Wang YL, Wang YC, Song ZM (2004) J Appl Phys 96:1537
4. Zener C (1951) Phys Rev 82:403
5. Millis AJ, Littlewood PB, Shraiman BI (1995) Phys Rev Lett 77:175
6. Jin KX, Chen CL, Zhao SG, Song ZM (2006) J Mater Sci 41:3881
7. Haghiri-Gosnet A-M, Renard J-P (2003) J Phys D: Appl Phys 36:R127
8. Asamltsu A, Tomioka Y, Kuwahara H, Tokura Y (1997) Nature 388:50
9. Liu XJ, Moritomo Y, Nakamura A, Tanaka H, Kawai T (2001) Phys Rev B 64:100401
10. Rana DS, Thaker CM, Mavani KR, Kuberkar DG, Malik SK (2005) Solid State Commun 133:505
11. Jin KX, Chen CL, Zhao SG, Song ZM (2006) Mater Sci Eng B 127:285
12. Dionne GF (1996) J Appl Phys 79:5172
13. Fiebig M, Miyano K, Tomioka Y, Tokura Y (1998) Science 280:1925
14. Smolyaninov II, Smolyaninova VN, Davis CC, Cheong S-W, Greene RL (2001) Phys Rev Lett 87:127204
15. Takuko N, Ogimoto Y, Nakamura M, Tamara H, Izumi M, Miyano K (2005) Phys Rev Lett 95:17404
16. Miyano K, Tanaka T, Tomioka Y, Tokura Y (1997) Phys Rev Lett 78:4257
17. Smolyaninova VN, Rajeswari M, Kennedy R, Overby M (2005) Appl Phys Lett 86:71922
18. Cauro R, Gilabert A, Contour JP, Lyonnet R, Medici M-G, Grenet J-C, Leighton C, Schuller IK (2001) Phys Rev B 63:174423
19. Song XF, Lian GJ, Xiong GC (2005) Phys Rev B 71:214427

20. Matsuda K, Machida A, Moritomo Y, Nakamura A (1998) Phys Rev B 58:R4203
21. Anderson PW, Hesegawa H (1955) Phys Rev 100:675
22. Coey JMD, Ryan DH, Buder R (1987) Phys Rev Lett 58:385
23. Chamberlin RV, Mozurkewich G, Orbach R (1991) J Appl Phys 56:1714