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X-ray photoemission study in $Re_{0.7}Ca_{0.3}MnO_3$ epitaxial films

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We have performed the x-ray photoemission experiments in the colossal magnetoresistive manganites $Re_{0.7}Ca_{0.3}MnO_3$ with Re=La, Pr, and Nd in order to study the Re dependence of electronic structures in this system. The samples are epitaxial films grown on $LaAlO_3$ substrates with pulsed laser deposition system. It is found that the binding energies of Mn $2p_{3/2}$ are 641.7 and 643.1 eV for $La_{0.7}Ca_{0.3}MnO_3$ and $Nd_{0.7}Ca_{0.3}MnO_3$, respectively. The shift of this energy level is related to the change in bond angle and/or bond length between Mn and oxygen. Moreover, two lines of O 1*s* core level are assigned as Mn–O (530 eV) and Re–O (533 eV). The intensity ratio of these two lines in $Nd_{0.7}Ca_{0.3}MnO_3$ is different from those in $La_{0.7}Ca_{0.3}MnO_3$ and $Pr_{0.7}Ca_{0.3}MnO_3$, suggesting that the ion redistribution between Re–O and Mn–O sites occurs with the Re substitution in these films. © *2009 American Institute of Physics*. [DOI: 10.1063/1.3062821]

I. INTRODUCTION

Perovskite manganites with chemical compositions $Re_{1-x}A_xMnO_3$, where Re is a rare earth (Re=La, Pr, Nd) and A is an alkaline-earth metal (A=Sr, Ba, Ca), have been widely studied because of their extraordinary physical properties such as the colossal magnetoresistance (CMR) and the strong correlation of spin, charge, and orbital orderings.[1,2] Their particular magnetotransport properties have been attributed to the double-exchange (DE) mechanism.[3–5] However, recent studies clearly indicate that DE cannot explain all the interesting features of the manganites. Some of the $Re_{1-x}A_xMnO_3$ compositions exhibit charge ordering (CO), which is crucially dependent on the effective radius of (Re, A) ion $\langle r_A \rangle$ or the e_g bandwidth and can be melted by applying magnetic field, electrical field, photon, or pressure.[6–8] In addition, the phase separation may be the origin of the CMR effect.[9–11] According to the DE model, the chemical potential may shift due to the change in the e_g bandwidth corresponding to either the lattice distortion or the change in $\langle r_A \rangle$. Therefore, it is interesting to investigate the distortion effects on the electronic structure of CMR materials. Among various techniques to detect the electronic structures, photoemission spectroscopy provides a direct information on the binding energy of each element,[12–15] and x-ray photoemission spectroscopy (XPS) is particularly surface sensitive. In this study, we report the XPS studies on the $Re_{0.7}Ca_{0.3}MnO_3$ (RCMO) thin film with Re=La, Pr, and Nd in order to study the Re dependence of electronic structures in this system. It is known that both $Pr_{0.7}Ca_{0.3}MnO_3$ (PCMO) and $Nd_{0.7}Ca_{0.3}MnO_3$ (NCMO) are insulators, undergoing a CO transition at $T_{CO} \sim 220$ K and a canted antiferromagnetic transition at $T_{ca} \sim 110$ K,[7,8] while $La_{0.7}Ca_{0.3}MnO_3$ (LCMO) is a ferromagnetic metal below the Curie temperature T_C (~ 250 K).[9] By comparing these three samples, the effects of lattice distortion on the electronic structure may be prevailed.

II. EXPERIMENT

The PCMO, NCMO, and LCMO thin films were deposited on $LaAlO_3$ (LAO) single-crystal substrate by using the pulsed laser deposition with a KrF (248 nm) laser in flowing O_2 atmosphere of 50 mTorr at the temperature of 800 °C. The phase purity of all the films was analyzed with x-ray diffraction (XRD) using Bruker D8 system. Temperature dependent resistivity measurements were carried out with a standard four-probe configuration in a closed-cycle refrigerator system. XPS measurements were performed at the National Synchrotron Radiation Research Center of Taiwan. With the present setup, the beam spot at the focal point is smaller than 100 nm. During the data analysis, the position of Fermi energy E_F was calibrated by measuring the gold spectra. Energy calibration was done by using the C 1*s* line at 285 eV.

III. RESULTS AND DISCUSSION

The XRD patterns exhibit only (00*l*) lines for LCMO, PCMO, NCMO, and LAO substrate as shown in Fig. 1, indicating the good crystalline structures of these films with a preferential growth along the *c* axis. The temperature dependent resistivity curves are shown in Fig. 2 to demonstrate that LCMO has a metal-insulator transition at $T_C \sim 250$ K while PCMO and NCMO are insulators. Among these three samples, the resistivity at 275 K of NCMO is one order higher than that of PCMO and three orders larger than that of LCMO.

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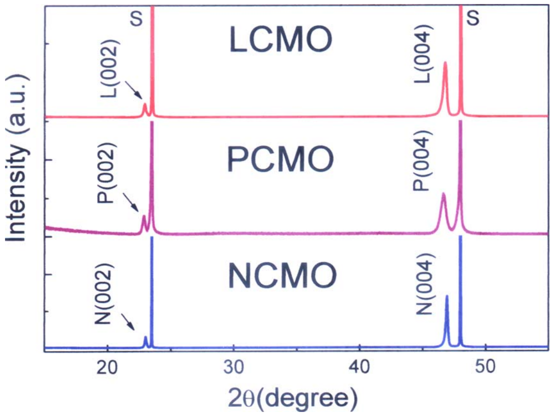

FIG. 1. (Color online) The XRD patterns of ReCMO (Re=La, Pr, Nd) thin films on LAO substrate. All lines are identified as (00*l*).

Figure 3 shows a typical XPS spectrum for ReCMO in a wide energy range with the incident photon energy *hv* =807 eV. Figure 4 is the detailed XPS pattern for (a) Re 4*d*, (b) Ca 2*p*, (c) Mn 2*p*, and (d) O 1*s* core levels. In Fig. 4(a), the lines of La $4d_{5/2}$ and $4d_{3/2}$ core level spectra are observed at 102 and 105 eV, respectively, which are close to the reference values of 103 and 106 eV. For Pr and Nd 4*d* core levels, only one line is observed and it is at 116 and 122 eV, respectively. The Ca 2*p* core level spectra shown in Fig. 4(b) are very similar for all three samples and the difference in binding energies (ΔE) between the levels of Ca $2p_{3/2}$ and $2p_{1/2}$ retains as a constant of 3.6 eV. In Fig. 4(c), the line positions of Mn $2p_{3/2}$ and $2p_{1/2}$ change with varying the Re ion. The binding energies of Mn $2p_{3/2}$ are 641.7, 643.1, and 642.2 eV for LCMO, PCMO, and NCMO, respectively. However, the values of ΔE between Mn $2p_{3/2}$ and $2p_{1/2}$ are slightly different. They are 11.83, 11.92, and 11.97 eV for Re=La, Pr, and Nd, respectively. These differences in the line positions and ΔE should be related to the changes in bond angles and/or bond lengths between Mn and oxygen with various Re ions. Figure 4(d) plots the O 1*s* spectra for three RCMO samples. In contrast to a single O 1*s* line in MnO,[13] there are two lines in the O 1*s* core level of ReCMO, one at around 530 eV and the other at about 532 eV. This feature reflects a chemical shift due to two different kinds of chemical bonding: 530 eV is associated with Mn–O bonding and 532 eV with the Re/Ca–O bonding. For LCMO and PCMO samples, the intensity of 530 eV line is comparable to that of 532 eV line, indicating that both bonds are equally favorable. On the other hand, in NCMO sample, the 532 eV line has a much higher intensity than the 530 eV line, indicating that the surface prefers Nd/Ca–O bonding. In conjunction with the data of *ρ*-*T*, the ion redistribution on the surface of NCMO may be related to the change in the electronic structure in this system.

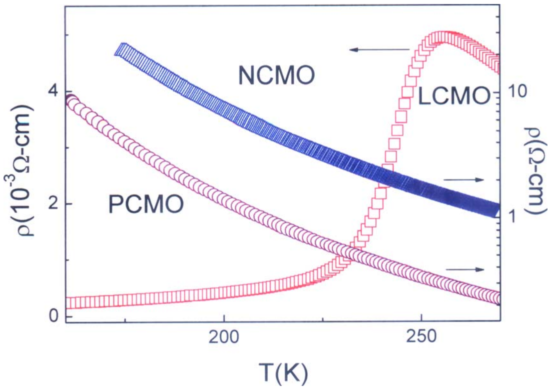

FIG. 2. (Color online) Resistivity vs temperature (*ρ*-*T*) with the left scale for LCMO and the right scale for NCMO and PCMO as indicated by arrows.

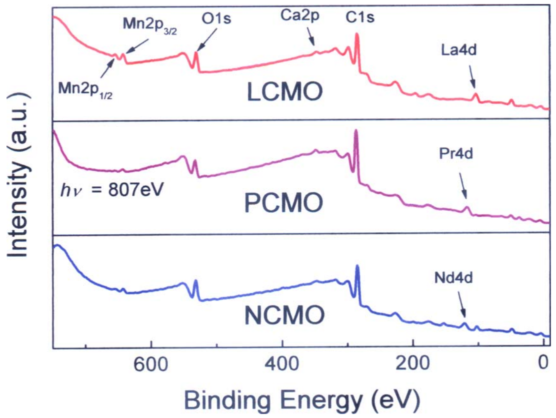

FIG. 3. (Color online) Photoemission spectra with a wide energy range for ReCMO samples, with the incident photon energy of 807 eV.

Figure 5 shows the Re dependence of photoemission spectra for (a) the shallow core level and (b) the valence band. In Fig. 5(a), the core lines of Ca 3*p*, O 2*s*, La 5*p*, Pr 5*p*, and Nd 5*p* can be clearly indexed by the arrows. Interestingly, there is no significant difference in O 2*s* core lines but a noticeable difference in Ca 3*p*, which is different from the result of Ca 2*p* and O 1*s*. In Fig. 5(b), the valence band comprises four distinct features labeled as *A*, *B*, *C*, and *D*. Feature *A* is just below the Fermi level. Feature *B* is located at around 2 eV, followed by feature C at 3 eV with a

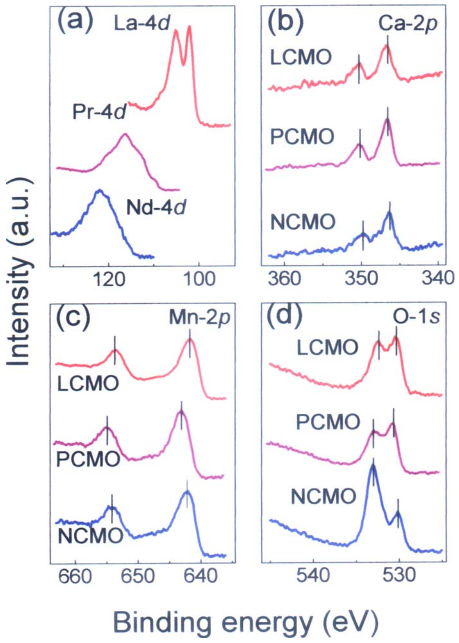

FIG. 4. (Color online) Photoemission spectra of (a) Re 4*d*, (b) Ca 2*p*, (c) Mn 2*p*, and (d) O 1*s* for various ReCMO samples.

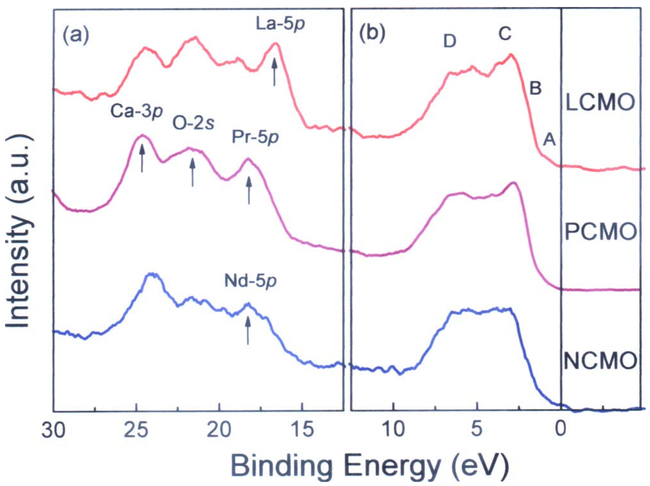

FIG. 5. (Color online) Redependence of (a) the shallow core level and (b) the valence-band photoemission spectra.

maximum intensity, and feature D between 6 and 7 eV. These four features are assigned to the Mn $3d$–O $2p$ bonding and O $2p$, Mn $3d$–t_{2g}/Pr $4f$, and Mn $3d$–e_g states with respect to *A-D*. However, these features smear out in NCMO sample, implying that the lattice distortion enhances the hybridization of various bonds.

IV. CONCLUSION

The photoemission study in various manganites is carried out and the results are correlated with the degree of lattice distortion. The significant energy shift in Mn $2p$ core level is attributed to the change in bond angles and/or bond lengths between Mn and oxygen. Moreover, two peaks on the O $1s$ core level are observed which is related to two different kinds of oxygen bonding. In particular, the intensity ratio of these two peaks in NCMO is different from those in LCMO and PCMO, suggesting that the substitution of Nd ion may trigger the ion redistribution between Re–O and Mn–O sites, which may affect the properties of electronic structure in this system.

ACKNOWLEDGMENTS

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