In-situ photoemission study of Pr$_{1-x}$Ca$_x$MnO$_3$ epitaxial thin films with suppressed charge fluctuations

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We have performed an in-situ photoemission study of Pr$_{1-x}$Ca$_x$MnO$_3$ (PCMO) thin films grown on LaAlO$_3$ (001) substrates and observed the effect of epitaxial strain on the electronic structure. We found that the chemical potential shifted monotonically with doping, unlike bulk PCMO, implying the disappearance of incommensurate charge fluctuations of bulk PCMO. In the valence-band spectra, we found a doping-induced energy shift toward the Fermi level ($E_F$) but there was no spectral weight transfer, which was observed in bulk PCMO. The gap at $E_F$ was clearly seen in the experimental band dispersions determined by angle-resolved photoemission spectroscopy and could not be explained by the metallic band structure of the C-type antiferromagnetic state, probably due to localization of electrons along the ferromagnetic chain direction or due to another type of spin-orbital ordering.

Strongly correlated systems have attracted great interest because of their various interesting physical properties, such as metal-insulator transition, colossal magnetoresistance (CMR), and the ordering of spin, charge, and orbitals [1]. One of the peculiar features of these systems is their high sensitivity to external stimuli. Pressure as well as carrier concentration are among the most important parameters. The effects of carrier doping and chemical pressure on their electronic structures have been extensively studied by transport measurements and various spectroscopic methods, including photoemission spectroscopy, although it has been impossible to directly observe the electronic structures under high pressure. However, if one grows thin films epitaxially on single crystalline substrates, one can effectively perform photoemission measurements under (anisotropic) high pressure. As for the high-$T_c$ cuprates, Abrecht et al. [2, 3] performed an in-situ angle-resolved photoemission spectroscopy (ARPES) study of La$_{2-x}$Sr$_x$CuO$_4$ (LSCO) thin films grown on SrLaAlO$_3$ (001) substrates (under in-plane compressive strain), and found that the topology of the Fermi surface changed from that of unstrained bulk LSCO concomitantly with an increase of $T_c$ from 38 K to 40 K.

Effects of pressure should be particularly striking for charge-orbital-related phenomena since the charge and orbital degrees of freedom are strongly coupled to lattice distortion. In this sense, direct observation of pressure effects on the electronic structure of hole-doped perovskite manganites is highly attractive. The hole-doped perovskite manganites $R_{1-x}A_x$MnO$_3$, where $R$ is a rare-earth ($R =$ La, Nd, Pr) and $A$ is an alkaline-earth atom ($A =$ Sr, Ba, Ca), exhibit CMR and spin, charge, and orbital ordering [4, 5, 6, 7, 8]. Most of the half-doped manganites ($x \approx 0.5$) with a small bandwidth $W$ exhibit the so-called “CE-type” antiferromagnetic (AF) charge ordering (CO) with alternating Mn$^{3+}$ and Mn$^{4+}$ states within the (001) plane in the form of stripes [9]. The inter-stripe distance increases with further hole doping and such charge modulations persist at high temperatures as fluctuations well above the CO temperature $T_{CO}$ [10, 11]. Pr$_{1-x}$Ca$_x$MnO$_3$ (PCMO), where $W$ is the smallest, has a particularly stable CO state at low temperatures in a wide hole concentration range $0.3 \leq x \leq 0.7$ [12]. It is known that the magnetic and electronic phases of Mn oxides can be controlled in thin films grown on substrates with various lattice parameters. For example, La$_{0.5}$Sr$_{0.5}$MnO$_3$ thin films remain ferromagnetic (FM) on (LaAlO$_3$)$_{0.3}$-(SrAl$_{0.5}$Ta$_{0.5}$O$_3$)$_{0.7}$ (LSAT) substrates, but becomes A-type AF on SrTiO$_3$ (STO) substrates, and C-type AF on LAO substrates [13]. The CO states of (Nd$_{1-x}$Pr$_x$)$_{0.5}$Sr$_{0.5}$MnO$_3$ thin films were also found to be controlled by the strain effects from the substrates [14]. Recently, it was reported that PCMO thin films grown on STO (001) substrates have higher CO temperatures than bulk samples, indicating that in-plane tensile strain leads to the stabilization of the CO state [15].

In this work, we have studied the electronic structure of PCMO thin films grown on LaAlO$_3$ (LAO) substrates by photoemission spectroscopy. This work is the first experimental observation of the electronic structure of the strained manganites. The fabricated PCMO thin films were under compressive strain from the LAO substrates, which is considered to suppress CO or charge modulation [15]. From core-level photoemission studies, we found that the chemical potential shift as a function of hole doping was not suppressed in the doping region where
incommensurate charge fluctuations are observed in the bulk samples. From the valence-band spectra, we found that no new states appeared near the Fermi level \((E_F)\) with hole doping. These results are in striking contrast to the recent results of PCMO bulk samples reported by Ebata et al. [16], who concluded that the chemical potential pinning and the spectral weight transfer do occur, and are considered to be spectroscopic evidence for the suppression of incommensurate charge modulation in PCMO thin films grown on LAO.

The experiments were performed at beamlines 1C and 2C of the Photon Factory, High Energy Accelerators Research Organization (KEK), using a combined laser MBE photoemission spectrometer system [17]. Epitaxial thin films of PCMO with a thickness of about 400 Å were fabricated by the pulsed laser deposition method from ceramic targets of desired chemical compositions. Single crystals of LAO (001) were used as the substrates. Atomically flat step-and-terrace structures were observed by atomic force microscopy. The crystal structure was characterized by four circle x-ray diffraction measurements. The in-plane lattice constants of the PCMO thin films were the same as that of LAO \((a = 3.792 \text{ Å})\), confirming the epitaxial and coherent growth of the thin films on the substrates. For all the compositions, the out-of-plane lattice constants were longer than the in-plane lattice constants, indicating that the present PCMO thin films were under compressive strain [see Fig. 1 (c)]. In the LEED patterns, sharp \(1 \times 1\) spots were observed without surface-reconstruction-derived spots. The electrical resistivities were high and showed no jump as a function of temperature, indicative of a suppression of CO and the associated lattice distortion due to the compressive strain imposed by the LAO substrates. Details of the sample growth and characterization can be found in Ref. [18]. The photoemission spectra were taken using a Gamamdata Scienta SES-100 spectrometer. All the spectra were measured at room temperature, except for ARPES measurements (20 K). The total energy resolution was about 150–400 meV depending on photon energies. The Fermi level \((E_F)\) position was determined by measuring gold spectra.

From the core-level photoemission spectra, we found that all the spectra were shifted toward lower binding energies with \(x\), as plotted in Fig. 1 (a). Here, the “relative energies” are referenced to the core levels of the \(x = 0.4\) sample. The chemical potential shift \(\Delta \mu\) can be obtained from the average of the energy shifts of the O 1s, Ca 2p, and Pr 4d core levels as in the case of bulk PCMO [16]. Figure 1 (b) shows \(\Delta \mu\) thus determined plotted as a function of \(x\). The shift of the chemical potential is monotonic without any sign of suppression at least up to \(x = 0.5\), which is similar to bulk and thin film LSMO [19, 20] but is quite different from bulk PCMO [16]. The suppression of the chemical potential shift has been observed in the region of incommensurate charge fluctuations [10, 11] in bulk PCMO \((x > 0.3)\) at room temperature [16], La\(_{2-x}\)Sr\(_x\)NiO\(_4\) [21], and underdoped La\(_{2-x}\)Sr\(_x\)CuO\(_4\) [22]. Their origin has been attributed to dynamical stripe-type charge fluctuations, a kind of “microscopic phase separation” between hole-rich and hole-poor regions. That is, the suppression of the chemical potential shift occurs when the distance between stripes changes as a function of hole concentration. Such a “microscopic phase separation” may be absent in the PCMO thin films considering the suppression of charge modulation caused by the compressive strain effects from the LAO substrates. Figure 1 (b) shows \(\Delta \mu(\text{film}) - \Delta \mu(\text{bulk})\), plotted as a function of \(x\). Note that \(c/a\) extrapolates to 1 at \(x \sim 0.7\) in PCMO thin films on LAO substrates [18] [see Fig. 1 (c)]. Chemical potential shifts to higher energy by applying compressive strain. Figure 1 (d) shows interpolated \(\Delta \mu\) as a function of \(c/a\) and \(x\). This panel clearly shows the pinning of \(\Delta \mu\) in the paramagnetic insulating state region near \(c/a \sim 1\) for \(x \geq 0.3\), whereas the pinning disappears for smaller \(x\) and larger \(c/a\).

Figure 2 (a) shows the doping dependence of the valence-band photoemission spectra. Following Ref. [16], structures A, B, C, and D are assigned to Mn 3d - O 2p bonding, non-bonding O 2p, Mn 3d \(t_{2g}\) plus Pr 4f, and Mn 3d \(e_g\) states, respectively. A gap (absence of fi-
nite density of states at $E_F$) was seen for all values of $x$, which is considered to be a natural consequence of the insulating nature of the PCMO thin films. Structures A-D moved toward $E_F$ upon hole doping. This is contrasted with the results of bulk PCMO, where spectral weight transfer occurs near $E_F$ from high to low energies with hole doping as shown in the inset to Fig. 2(b). Sekiyama et al. [23] also reported finite intensity at $E_F$ in the insulating state of Nd$_{1-x}$Sr$_x$MnO$_3$. The main panel of Fig. 2(b) shows the valence-band spectra of the PCMO thin films near $E_F$. The overall shift of the spectra is attributed to the effect of the chemical potential shift, and no new states appeared near $E_F$ with hole doping. From the present spectra near $E_F$, we conclude that our PCMO thin films were good insulators without any dynamical “phase separation”.

The absence of chemical potential “pinning” and spectral weight transfer toward $E_F$ in the thin films, which were observed in bulk PCMO [10], are attributed to the suppression of incommensurate charge fluctuations due to the compressive strain effects from the LAO substrates, and are considered as the spectroscopic evidence for the change of the electronic structures due to the epitaxial strain effects from the substrates.

Figure 3(a) shows the ARPES spectra of a PCMO ($x = 0.4$) thin film taken with a photon energy of 88 eV. Here, the second derivatives of the energy distribution curves are plotted as a false-color image, where bright parts correspond to peaks or shoulders in energy distribution curves. Hereafter, $k_\parallel$ denotes the in-plane momentum expressed in units of $\pi/a$. The structures at $-(1.5-3)$ eV show weak dispersions and are assigned to the Mn 3$d_{g\uparrow}$ and $t_{2g\uparrow}$ bands. The structures at $-(3-7)$ eV show strong dispersions and are assigned to the O 2$p$ bands. There is no intensity at $E_F$, consistent with the insulating behavior of this film. The same plot for an LSMO thin film ($x = 0.4$) grown on an STO substrate is shown for comparison in Fig. 3(b) [24]. The dispersions of the O 2$p$ bands were similar between these two spectra, while those of the Mn 3$d$ bands were very different. The Mn 3$d_{g\uparrow}$ bands show a clear dispersion and cross $E_F$ in LSMO, but are weak and show only very weak dispersions in PCMO.

The magnetic ground state of the PCMO ($x = 0.4$) thin film may be inferred from the lattice constants and the phase diagram of LSMO proposed by Konishi et al. [13]. The $c/a$ of the PCMO ($x = 0.4$) films was 1.03 as shown in Fig. 1(c). From the phase diagram in Ref. [13], $c/a = 1.03$ and $x = 0.4$ is just at the boundary of the FM and C-type AF states. We confirmed that this film was not FM by magnetization measurements, and considered it to be in the C-type AF state. In the C-type AF state, FM metallic chains are formed along the c-axis. Therefore, we have performed normal emission ARPES measurements to study the out-of-plane band dispersions as shown in Fig. 3(a). For comparison, Fig. 3(b) shows the normal-emission ARPES spectra of an LSMO ($x = 0.4$) thin film taken from Ref. [24]. Here again, the dispersions of the O 2$p$ bands are similar between these two spectra. On the other hand, the dispersions of the Mn 3$d_{g\uparrow}$ bands are clear in LSMO (b), but very weak in PCMO (a). In order to interpret the experimental band dispersions, we have performed a tight-binding (TB) band-structure calculation with empirical parameters. Here, we have performed the calculation by assuming the C-type AF state for PCMO and the FM state for LSMO as shown in Figs. 4(c) and (d). In the case of LSMO, agreement between experiment and calculation is good.
except for the narrowing of the conduction band due to strong electron correlation. In the case of PCMO, the strong dispersion of the Mn 3d electrons appears to be localized along the ferromagnetic chain direction, probably due to disorder and/or electron correlation. This result is also consistent with the fact that in C-type AF materials the expected one-dimensional metallicity has not been observed so far.

In summary, we have performed an in-situ photoemission study of Pr$_{1-x}$Ca$_x$MnO$_3$ (PCMO) thin films grown on LaAlO$_3$ (LAO) substrates. From the core-level photoemission study, we found that unlike bulk PCMO, in strained films the chemical potential shifted monotonically with doping, implying the disappearance of incommensurate charge fluctuations. In the valence-band spectra, we found no spectral weight at the Fermi level ($E_F$) nor doping-induced spectral weight transfer toward $E_F$, also unlike bulk PCMO. The gap at $E_F$ was clearly seen in the experimental band dispersions determined by angle-resolved photoemission spectroscopy (ARPES) and could not be explained by the metallic band structure of the C-type AF state as previously proposed, probably due to the localization of electrons along the ferro-chain direction caused by disorder and electron correlation.

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