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Effect of magnetic field on the capacitance of the $La_{0.5}Ca_{0.5}MnO_3$-based heterojunction

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Effects of interface decoration and ac frequency, under which the impedance is measured, on the magnetoelectric property have been experimentally studied for the heterojunctions of $La_{0.5}Ca_{0.5}MnO_3/SrTiO_3$:Nb and $La_{0.5}Ca_{0.5}MnO_3/LaMnO_3(3nm)/SrTiO_3$:Nb. It is found that the impedance of the junction can be well described by an effective circuit of two *R*–*C* sub-circuits in series well above 100 K. Magnetocapacitance emerges and develops as temperature decreases, and shows a strong frequency-dependent character. The maximal magneto-capacitance, under a field of 5 T, is ∼30 and ∼35% with and without the buffer layer, respectively. The incorporation of the $LaMnO_3$ layer shifts the upper temperature limit for significant magnetocapacitance from ∼120 to ∼200 K. Shrinkage of the depletion layer of the junction under magnetic field may be a main reason for the magnetoelectric effect observed here.

1 Introduction The magnetoelectric effect of the materials has received intensive attention in recent years because of its fundamental and technological importance. Although ferromagnetic and ferroelectric orders are difficult to coexist for perovskite oxides because of their conflicted requirements on structural asymmetry, recent work indicates the compatibility between helical spin structure and ferroelectricity, showing the abundant physics underlying this effect [1]. On the other hand, based on the magnetic field-induced permittivity change a promising technique for information storage could be developed: The stored data can be read via their influence on capacitance, instead of resistance [2, 3]. This technique is advantageous over the conventional one in the sense that it significantly depresses the thermal effect.

There are great theoretical and experimental efforts to explore effective magnetoelectric materials. Compounds that show considerable magnetocapacitance (MC), such as $LuFe_2O_4$ (Ref. [4]) and La_2NiMnO_6 (Ref. [5]), have been reported. Materials undergoing a ferroelectric–paraelectric transition are also found to show significa magnetoelectric effect [6, 7]. Unfortunately, the materials with considerable MC are scarce.

An alternative candidate of the magnetoelectric materials is the heterostructure. It has been found that the capacitance of the manganite-based junction undergoes considerable variations upon the application of a magnetic field [8, 9], and the maximal MC of the $La_{0.5}Ca_{0.5}MnO_3$(LCMO)/$SrTiO_3$:Nb (0.7 wt%) junction, for example, can be as high as ∼200% under a field of 5 T [9]. The mechanism for the magnetoelectric effect here could be ascribed to the complex change of the interface of the junction, instead of permittivity. However, it is still not very clear how the MC occurs and responses to the change of the interfacial state. In this paper, we performed a comprehensive study on the MC effect of the LCMO-based junctions. Special attention has been paid to the effect of interface decoration and ac frequency, under which the impedance of the junction has been measured, on the MC effect. It is found that the MC emerges and develops as temperature decreases, and shows a strong frequency-dependent character. The maximal MC, under a field of 5 T, is ∼30 and ∼35%, respectively, without and with buffer layer. The incorporation of the $LaMnO_3$ (LMO) layer shifts the upper limit for significant MC from ∼120 up to ∼200 K.

2 Experiments The manganite junctions were fabricated by growing, via the pulsed laser ablation technique, the 100 nm thick p-type LCMO films on a (001)-orientated n-type $SrTiO_3$:0.05 wt%Nb (STON) substrate ($3 \times 1\ mm^2$ in dimension) and a STON with a 3 nm LMO cover layer, respectively. Here LCMO was chosen because of its abundant magnetic properties. In the deposition process, the temperature of the substrate was kept at 720 °C, and the oxygen pressure at ~10 Pa for the LMO layer and ~80 Pa for the LCMO layer. The film thickness was determined by deposition time.

The LCMO-based junctions thus obtained are p–n junctions in character. These junctions are usually treated as Schottky junctions, since the depletion width in $La_{0.5}Ca_{0.5}MnO_3$ is very thin [10]. As electrodes, two copper pads were deposited on LCMO and STON, respectively. Appropriate electric pulses have been applied to the Cu-STON contact to get a soft electric breakdown, which can lead to an Ohmic contact. The resistance is ~15 Ω for the Cu-STON contact and ~160 Ω for the Cu-LCMO contact, at the ambient temperature. The capacitance was measured by a ZM2353 LCR meter, in the parallel circuit mode with a ac amplitude of 0.5 V. The capacitance collected under low ac voltage fluctuates severely below ~60 K, and reliable data can be obtained only above the ac voltage of 0.5 V. The data recorded under the voltage of 0.015 and 0.5 V are similar well above 60 K.

3 Results and discussions Figure 1 shows the capacitance (C) of the junctions as a function of frequency (f), measured under different temperatures. Let us focus our attention first on LCMO/STON. Around ambient temperature, the capacitance is essentially frequency-independent when f is low, and decreases rapidly above 20 kHz due to the Cu-LCMO contact as will be shown below. With the decrease of temperature, the C–f curve shows an upright shift, nearly rigidly, until the temperature of 60 K. Below 60 K, a re-shaping of the C–f curve takes place, leading to a strong f-dependence of the capacitance in the whole frequency range studied. Taking the capacitance at 20 K as an example, it decreases monotonically from ~21 nF for $f = 40$ Hz to ~7.2 nF for $f = 200$ kHz. As will be seen later, this could be an intrinsic property of the junction since the influence of the contact circuit may be unimportant below 200 kHz at 20 K, where the contact resistance could be extremely low. At a first glance, LCMO/LMO/STON is similar to LCMO/STON. However, a careful analysis of the C–f relation reveals the emergence of a second process at a temperature below 180 K, demonstrated by the occurrence of an inflection in the C–f curve with the decrease of frequency (marked by red arrows). Comparing this process with that at 60 K, and noting the evolution of the C–f dependence with temperature, we found that it is this process that dominates the low temperature capacitance. The inset plot in Fig. 2(b) shows the modification of magnetic field to this process.

Because of the presence of the LCMO-STON and the Cu-LCMO interfaces, the behavior of the junction may be described by an effective circuit of two R–C sub-circuits in series [inset in Fig. 1(a)]. As shown in Fig. 1(a), a satisfactory agreement between the calculated (solid lines) and observed (symbols) results has been obtained, adopting appropriate fitting parameters. The dielectric loss, defined as $\tan\vartheta = (\omega CR)^{-1}$, can also be well reproduced by the same set of parameters (not shown), where R is the real part of the impedance of the junction, and $\omega = 2\pi f$. The deduced parameters are, for example, for $T = 300$ K, $R_J = 2.2 \times 10^3\ \Omega$, $R_C = 155\ \Omega$, $C_J = 39$ nF, and $C_C = 1$ nF, where R_J/R_C and C_J/C_C are the resistance and capacitance of junction/contact, respectively. With the decrease of temperature, R_J undergoes an exponential growth, with an activation energy of ~34 meV, whereas R_C a parabolic decrease, $R_C \approx 19.1 + 0.00274(T\text{-}76)^2$, in the temperature range from 120 to 300 K. In contrast, C_C is nearly constant. According to this analysis, the capacitance drop under high frequencies bears a close relation with the Cu-LCMO contact, and the growth of the threshold frequency upon cooling is a consequence of decreased contact resistance. Similar conclusions are obtained for the LCMO/LMO/STON junction, which has been approximated by the same model considering the absence of a clear interface between LCMO

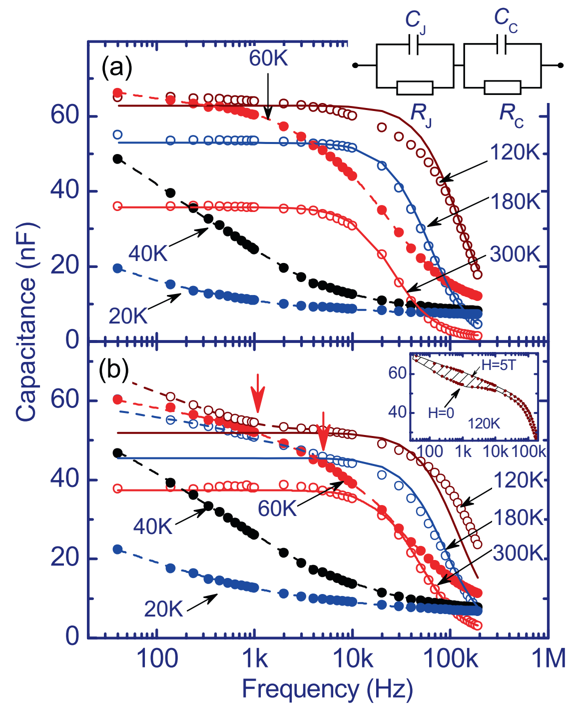

Figure 1 (online color at: www.pss-a.com) Frequency-dependent capacitance of the LCMO/STON (a) and LCMO/LMO/STON (b) junctions, measured in the temperature range from 20 to 300 K without magnetic field (only selective data are shown for clarity). The inset plot in (a) is a schematic diagram for the effective circuit describing the impedance of the junction. Shaded area in the inset plot in (b) shows the capacitance change in magnetic field for a typical temperature 120 K. Symbols and solid lines represent the experiment and theoretical results, respectively. Dashed lines are guides for the eye.

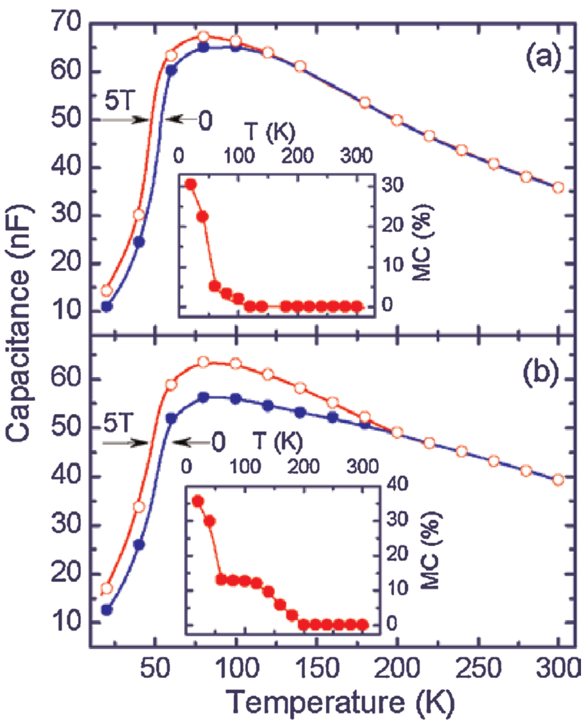

Figure 2 (online color at: www.pss-a.com) Capacitance as a function of temperature for the LCMO/STON (a) and LCMO/LMO/STON (b) junctions, measured under the fields of 0 and 5 T and the ac frequency of 1 kHz. Inset plots show the corresponding magnetocapacitance.

and LMO, though well fitting is obtainable only above 200 K. The C–f and $\tan\vartheta$–f relations cannot be reproduced using constant parameters when temperature is lower than 60, which indicates the frequency of C_J and R_J.

With the decrease of temperature, the capacitance first increases, then decreases. A summary of the capacitance at different temperatures is presented in Fig. 2. Without buffer layer, the capacitance is, for $f = 1$ kHz, $\sim$11 nF at 20 K, and grows rapidly with the increase of temperature, reaching the maximum of $\sim$65 nF at 80 K. The incorporation of the LMO layer does not affect the general C–T relation but depressing the maximal capacitance. The emergence of a maximal capacitance is a feature that has been observed in other manganite junctions before [8, 9], and can be ascribed to $SrTiO_3$. As reported, the dielectric properties of $SrTiO_3$ undergo an abnormal variation below $\sim$60 K [11, 12]. It is interesting to note the reduction of the maximal capacitance in LCMO/LMO/STON, which could be a signature of an enhanced built-in potential in depletion layer. In fact, an internal photoemission measurement has revealed a growth by $\sim$18% of the Schottky barrier in LCMO/LMO/STON compared to LCMO/STON (not shown). The most remarkable observation is the coincidence of the character temperature for the strong frequency dependence and the temperature for the dielectric anomaly of $SrTiO_3$. This may suggest the existence of a close relation between the dielectric relaxation in the junction and the dielectric anomaly of $SrTiO_3$.

Magnetic field causes a significant growth of capacitance. As shown in Fig. 2 and the inset plots, the MC takes the maximal value of, for example, for LCMO/STON, $\sim$30% at $\sim$20 K (the lowest temperature of the present experiment), drops sharply with the increase of temperature, and vanishes above $\sim$100 K [inset plot in Fig. 2(a)]. In contrast, the MC of LCMO/LMO/STON persists up to a much higher temperature ($\sim$200 K), with a maximal MC of $\sim$35%, also at 20 K [inset plot in Fig. 2(b)]. The MC obtained here is obviously smaller than that reported by Xie et al. [9] The reason may be that the Nb content in the present junctions is much low.

To get a clear picture on the effect of magnetic field and frequency, we present the C–f and R–f relations in Figs. 3(a)–3(d), measured under different dc biases and magnetic fields at a fixed temperature of 20 K. The dc field used by the measurements varies between -0.6 and 0.4 V. Analyses of the current–voltage characteristics give the interfacial barrier of $\sim$0.68 eV for the LCMO-based junctions studied here. Electric breakdown does not occur up to the reverse bias of 1 V. These results indicate that the dc field from -0.6 to 0.4 V will not affect the junction significantly. From a first glance, similar results are obtained for the two junctions. A significant growth of C and a corresponding decrease of R occur simultaneously upon the application of magnetic field. The capacitance is, for the LCMO/STON junction, $\sim$10.9 nF without magnetic field and $\sim$14.3 nF under a field of 5 T at a frequency of 1 kHz, while the corresponding resistance changes from $\sim 3.1 \times 10^4$ to $2.1 \times 10^4\,\Omega$. Positive bias enhances the capacitance and depresses the resistance whereas a negative bias yields an opposite effect. As shown in Figs. 3(e) and 3(f), either the MC or the magnetoresistance (MR) displays a strong dependence on frequency: The former increases from $\sim$18.4% for $f = 200$ kHz to $\sim$30.4% for $f = 1$ kHz, while the latter from ~ -17 to ~ -33% for similar frequency change.

Noting the success of the effective circuit above 120 K, the impedance of the junction at low temperatures may also be described by this circuit adopting frequency-dependent C_J and R_J. According to Catalan [13], a MC can be obtained if MR is finite even C_J and C_C are unchanged. As experimentally revealed, magnetic field indeed causes a reduction in R_J. However, as indicated by a simple calculation, a negative MC, instead of a positive one, is resulted if R_C, C_J, and C_C are constant. This is inconsistent with the experimental results. Further analysis shows that a capacitance growth can be produced by the decrease of R_C, and the relative change is $\sim$2% for the reduction of R_J from 20 to 0 Ω (The contact resistance is $\sim$20 Ω at $\sim$100 K for LCMO/STON as proved by the curve fitting. It could be much smaller at low temperatures noting its monotonic decrease on cooling), which is much lower than that observed here. These results actually imply the change of C_J under magnetic field. There are two different mechanisms for the variation of C_J. It has been proposed that the magnetic field makes the antiferromagnetic phase in the LCMO film, which is proved to be phase-separated at low temperatures, more conductive, leading to an increase of the effective area of the capacitor,

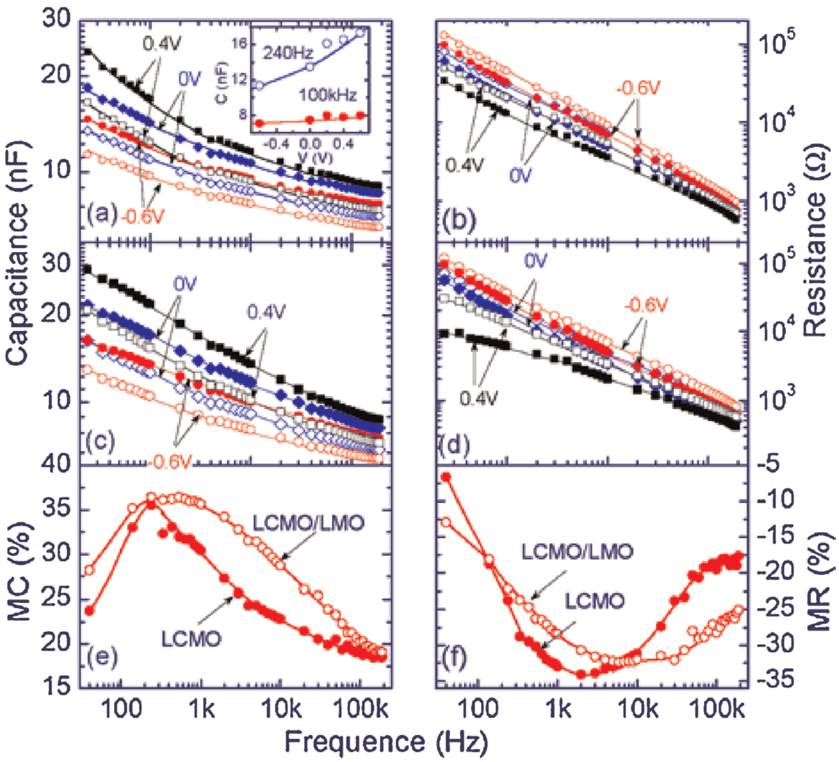

Figure 3 (online color at: www.pss-a.com) Capacitance and resistance for the LCMO/STON [(a), (b)] and LCMO/LMO/STON [(c) and (d)] junctions, measured under different electric and magnetic fields. Hollow and solid symbols correspond to $H = 0$ and 5 T, respectively. The inset plot displays the bias dependence of the capacitance. Magnetocapacitance and MR are respectively shown in (e) and (f), obtained without dc bias. Labels in the figure mark the dc voltage on the junction.

thus a growth of capacitance. An alternative explanation is the field-induced change of the depletion layer. As is well known, the capacitance of the LCMO/STON junction is mainly determined by depletion layer. It grows (decreases) as the depletion width decreases (increases). When the charge carriers at the LCMO-STON interface are activated by magnetic field, the carrier exchange between LCMO and STON will be enhanced, thus the depletion width diminished.

As mentioned above, the frequency dependence of *C* suggests the presence of dielectric relaxation in the junction. This behavior appears accompanying the dielectric anomaly of $SrTiO_3$, and could be a signature of dielectric correlation between electric dipole moments. It has been suggested that the antiferroelectricity or quantum paraelectricity occurs in $SrTiO_3$ below ~60 K [11, 12]. The evolution of the frequency dependency of the capacitance with dc biases deserves special attention. It is found that the low frequency capacitance grows much more rapidly with the increase of the bias voltage than the high frequency one does [inset plot in Fig. 3(a)]. This means an intensifying of the frequency-dependent nature of the capacitance under positive biases. With this in mind and considering the shrinkage of the depletion layer under electric biases, dielectric relaxation may mainly undergo at the interface of the junction. What of special interest are the similar effects of the dc bias and the magnetic field. As shown in Fig. 3(a), either an electric bias or a magnetic field causes an upward shift of the *C–f* curves. The similarity of the *C–f* curves measured under different conditions is obvious. For example, the *C–f* curve collected under a bias of 0.4 V coincides essentially with that obtained under a bias of −0.6 V and a magnetic field of 5 T. curves. This may indicate a reduction of the depletion width in magnetic field as occurred in electric field. In this scenario, the frequency dependence of the MC and MR can also be understood.

The incorporation of the LMO layer enhances the frequency-dependent feature of the capacitance, thus shifts the upper temperature limit for significant magnetocapacitance from ~120 to 200 K. In general, a greater MC is expected in LCMO/STON. However, the presence of the LMO layer may activate the response of interface layer to magnetic field. As reported [14], for the $La_{0.6}Sr_{0.4}MnO_3$/STO film, the insertion of an intermediate LMO layer plays a role enhancing the ferromagnetism of the interfacial layer, though its detailed mechanism is not very clear. It is possible that the LMO reduces the hole content, which is ~0.5 for the present LCMO film, of the adjacent LCMO layer, enhancing the interfacial ferromagnetic ordering.

It seems that the MC occurs accompanying the dielectric relaxation. This feature is especially obvious in LCMO/LMO/STON. As shown by the inset plot in Fig. 1(b), magnetic field affects the capacitance mainly by modifying frequency-dependent process. Why the dielectric relaxation process is especially sensitive to magnetic field is till not very clear. Further studies in this regard are desired for a thorough understanding of the MC effect of the junction.

4 Conclusions Effects of interface decoration and ac frequency, under which the impedance is measured, on the magnetoelectric property have been experimentally studied for the heterojunctions of $La_{0.5}Ca_{0.5}MnO_3$/$SrTiO_3$:Nb and

$La_{0.5}Ca_{0.5}MnO_3$/$LaMnO_3$(3nm)/$SrTiO_3$:Nb. It is found that the impedance of the junction can be well described by an effective circuit oftwo *R–C* sub-circuits in series well above 100 K. Magnetocapacitance emerges and develops as temperature decreases, and shows a strong frequency-dependent character. The maximal magnetocapacitance, under a field of 5 T, is $\sim$30 and $\sim$35% with and without the buffer layer, respectively. The incorporation of the $LaMnO_3$ layer shifts the upper temperature limit for significant magnetocapacitance from $\sim$120 to $\sim$200 K. Shrinkage of the depletion layer of the junction under magnetic field may be a main reason for the magnetoelectric effect observed here.

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