Effects of ferroelectric polarization and converse piezoelectric effect induced lattice strain on the electrical properties of $La_{0.7}Sr_{0.3}MnO_3$ thin films

R. K. Zheng,[a)] J. Wang, X. Y. Zhou, Y. Wang, H. L. W. Chan, and C. L. Choy
Department of Applied Physics and Materials Research Center, The Hong Kong Polytechnic University, Hong Kong, China

H. S. Luo
The State Key Laboratory of High Performance Ceramics and Superfine Microstructure, Shanghai Institute of Ceramics, Chinese Academy of Sciences, Shanghai 201800, China

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Thin films of $La_{0.7}Sr_{0.3}MnO_3$ (LSMO) have been grown on the ferroelectric $0.68Pb(Mg_{1/3}Nb_{2/3})O_3-0.32PbTiO_3$ (PMN-PT) single-crystal substrates. The ferroelectric polarization of the PMN-PT induces a large decrease in the resistivity and an upward shift in the Curie temperature of the LSMO films, which was interpreted in terms of the ferroelectric polarization induced large reduction of the biaxial tensile strain in the LSMO films. The resistivity of the LSMO films can be dynamically tuned by applying dc electric fields across the polarized PMN-PT. The analyses of the results indicate that the electric field induced lattice strain via converse piezoelectric effect in the PMN-PT controls the strain states and hence the resistivity and Curie temperature of the LSMO films.
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I. INTRODUCTION

Since the discovery of the colossal magnetoresistance effect in perovskite-type $R_{1-x}A_xMnO_3$ (where R and A are trivalent rare-earth and divalent alkaline-earth ions, respectively) manganites, intensive efforts have been devoted to this system to disclose the mechanism underlying their behaviors.[1] Numerous previous studies have shown that the electrical, magnetic, and structural properties, e.g., magnetic structure, magnetic anisotropy, Curie temperature, resistivity, and magnetoresistance, for both bulk and thin film samples can be modified by imposing lattice strains on the samples.[2–4] The strains in bulk samples can be altered by chemical pressure via ion substitution or the application of external hydrostatic pressure. As for thin films, the strains are usually achieved by the lattice mismatch between thin films and substrates via growing thin films with various thicknesses on different types of substrates.[4–6] However, this method cannot isolate lattice strain effects from property changes due to other negative variables such as the oxygen nonstoichiometry, crystalline quality, small changes in the composition, lattice relaxation, and thickness dependence of the strain distribution, which also play important roles in influencing the properties of thin films.[7–9] To screen off these nonintrinsic strain effects on the properties of thin films, it is better to keep all these negative variables constant when one examines the properties of thin films. An ideal method is to study the properties of thin film on the *same* thin film sample whose strain state could be dynamically tuned while all above mentioned negative variables could be kept constant.

Perovskite-type $(1-x)Pb(Mg_{1/3}Nb_{2/3})O_3-xPbTiO_3$ (PMN-PT) single crystals with compositions near the morphotropic phase boundary (e.g., $x=0.32$) are excellent ferroelectrics. They also possess outstanding piezoelectric and converse piezoelectric effects.[10–12] Therefore, the lattice strain of the PMN-PT, and hence the strain states of thin films grown on them, can be tuned by the ferroelectric polarization and converse piezoelectric effect in the PMN-PT. In this paper, we report the growth of prototypical colossal magnetoresistance $La_{0.7}Sr_{0.3}MnO_3$ (LSMO) thin films on the ferroelectric and piezoelectric PMN-PT single-crystal substrates and studied the effects of ferroelectric polarization and converse piezoelectric effect induced lattice strain on the electrical properties of the LSMO films. We found that the ferroelectric polarization and converse piezoelectric effect induced lattice strain in the PMN-PT tuned the strain state and hence the resisitivity and Curie temperature of the LSMO films. The results indicate that the electric field induced lattice strain via the converse piezoelectric effect is an effective method which can be used to control the strain states and hence the properties of perovskite-type thin films.

II. EXPERIMENTAL PROCEDURES

High quality PMN-PT single crystals with a size of about $\Phi 48\times 80$ mm^2 were grown by a modified Bridgman technique at the Shanghai Institute of Ceramics. The experimental details for the growth of the PMN-PT single crystals were described elsewhere.[12] The single crystals were cut into small pieces of $10\times 5\times 0.42$ mm^3 rectangular size with the plane normal to the $\langle 001\rangle$ direction and polished until the average surface roughness Ra is less than 8 Å. Such polished single crystals were used as substrates to grow the LSMO films. The LSMO films were fabricated on the (001)-oriented PMN-PT substrates using the dc magnetron sputtering in an argon-oxygen flow ($Ar:O_2=1:1$) under a total pressure of 4.35 Pa and at a substrate temperature of 680 °C. After deposition, the LSMO films were slowly cooled to room

[a)]Electronic mail: zrk@ustc.edu

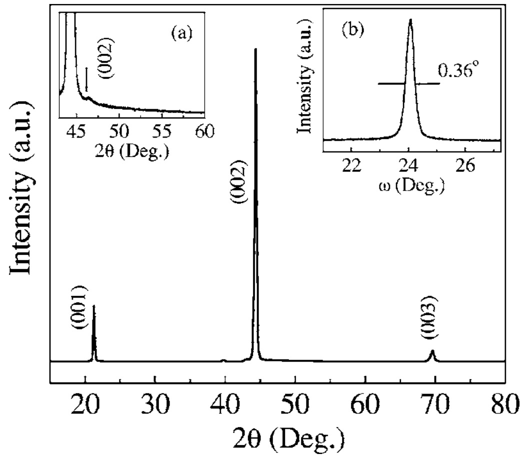

FIG. 1. XRD pattern of the LSMO film grown on the PMN-PT substrate. Inset (a) shows the expanded view of the PMN-PT and LSMO (002) reflections. Inset (b) shows the rocking curve of the LSMO (002) reflection.

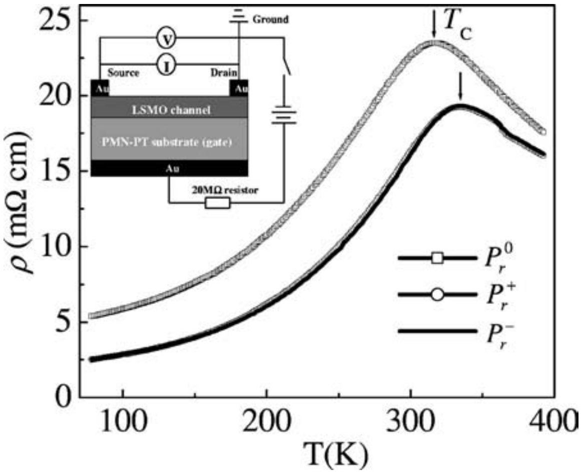

FIG. 2. Temperature dependence of the resistivity for the LSMO film at different polarization states of the PMN-PT. The P_r^0, P_r^+, and P_r^- represent unpolarized, positively polarized, and negatively polarized states, respectively. The inset shows a schematic diagram of the LSMO/PMN-PT ferroelectric FET and measurement circuit.

temperature *in situ* and postannealed in air at 700 °C for 30 min.

Because the PMN-PT is a ferroelectric material, the LSMO/PMN-PT is a ferroelectric field effect transistor (FET) in which the LSMO and the PMN-PT are the channel and gate insulator, respectively. The resistivity of the LSMO films between the source and the drain was measured using the measurement circuit schematically shown in the inset of Fig. 2. The external dc electric field was applied across the PMN-PT through the gate and the drain. A loaded resistor of 20 MΩ was inserted in series between the gate and the dc voltage meter in order to protect the current and voltage meters in case the applied electric fields cause dielectric breakdown of the PMN-PT.

The x-ray diffraction (XRD) measurements were performed using a Philips XPert x-ray diffractometer equipped with Cu $K\alpha$ radiation of wavelength $\lambda=1.5418$ Å. Field-emission scanning electron microscopy measurements indicate that the LSMO films have a thickness of ~50 nm. Low frequency ferroelectric hysteresis loop of the PMN-PT was measured using a standard Sawyer-Tower circuit. The measurements indicate that the PMN-PT single crystals show a square ferroelectric hysteresis loop with a remanent ferroelectric polarization of ~30 $\mu C/cm^2$ at room temperature (not shown here).

III. RESULTS AND DISCUSSION

Figure 1 shows the XRD θ-2θ linear scan from the LSMO/PMN-PT. It is seen that strong $(00l)$ ($l=1$, 2, and 3) reflections from the PMN-PT substrate were obtained, indicating that the PMN-PT single-crystal substrate is highly $(00l)$ oriented. Note that the reflections from the LSMO film have been covered by the strong reflections from the PMN-PT. Nevertheless, a weak LSMO (002) reflection appears at the right side of the PMN-PT (002) reflection, as shown in the inset (a) of Fig. 1. The rocking curve taken around the LSMO (002) reflection has a full width at half maximum of ~0.36° [inset (b) of Fig. 1], indicative of good crystallinity of the LSMO films.

Figure 2 shows the temperature dependence of the resistivity for the LSMO film when the PMN-PT is in different polarization states. For the PMN-PT at unpolarized state (hereafter be referred to as P_r^0), the resistivity of the LSMO film increases with decreasing temperature from 393 K and reaches the maximal value around 316 K. With further decrease of the temperature the LSMO enters into the ferromagnetic state, and hence the resistivity begins to decrease rapidly. To probe into the effects of the ferroelectric polarization induced lattice strain and the ferroelectric field effect on the electrical properties of the LSMO film, we applied a large positive dc voltage of 504 V, corresponding to an electric field of 1.2 kV/mm which is much larger than the coercive field of the PMN-PT, across the PMN-PT substrate at 310 K so that the PMN-PT be positively polarized (hereafter, be referred to as P_r^0). The resistivity of the LSMO film between the source and the drain was measured after the electric field had been turned off. As seen in Fig. 2, the resistivity of the LSMO film decreases in a wide temperature range from 77 to 393 K after the PMN-PT was positively polarized. Moreover, the insulator to metal transition temperature T_P shifts to a higher temperature by ~18 K. As is known, the LSMO is a p-type material, the majority of the charge carriers in the LSMO channel are positive holes. The application of a positive voltage to the gate will polarize the PMN-PT such that the electric dipole moments in the PMN-PT point upward into the LSMO channel, leading to a depletion of the positive holes in the LSMO channel. Thus, if only the ferroelectric field effect is considered, the resistivity of the LSMO channel should increase if the PMN-PT was positively polarized. Indeed, the channel resistivity in similar manganite-based ferroelectric FET, e.g., $La_{1-x}A_xMnO_3$ (A $=Ca,Sr,Ba$)/$Pb(Zr_xTi_{1-x})O_3$, always increases if the $Pb(Zr_xTi_{1-x})O_3$ gate was polarized positively.[13–16] Clearly, the ferroelectric field effect cannot account for the decrease in the resistivity and increase in T_P of the LSMO film in the LSMO/PMN-PT ferroelectric FET. On the other hand, we note that previous studies have shown that the ferroelectric field effect induced magnitude of the decrease (or increase) in the channel resistivity for manganite-based ferroelectric FET reaches the maximal value close to T_P but decreases with decreasing/increasing temperature from T_P.[13–16] However, the resistivity of the LSMO film in the LSMO/PMN-PT ferroelectric FET decreases by a similar amount in a wide temperature range from 77 to 393 K.

To get insight into the ferroelectric field effect in the LSMO/PMN-PT, we polarized the PMN-PT negatively (hereafter, be referred to as P_r^-) after the measurements of the resistivity for P_r^+. Again, the resisitivity of the LSMO film was measured after the external dc electric field was turned off. We found that the resisitivity of the LSMO channel also decreases in a wide temperature after the PMN-PT was negatively polarized. The resistivity of the LSMO for P_r^- is almost the same as that for P_r^+. The T_P for P_r^- also coincides with that for P_r^+. As mentioned above, a positive polarization of the PMN-PT will lead to a depletion of the holes in the channel and hence gives rise to an increase in the resistivity and a decrease in T_P, while a negative polarization of the PMN-PT will lead to opposite effects on the resistivity and T_p. If the ferroelectric field effect in the LSMO/PMN-PT plays a role in influencing the resisitivity and T_P, the resisitivity and T_P for P_r^- should deviate from those for P_r^+, that is, the resistivity for P_r^- should be smaller than that for P_r^+ while the T_P for P_r^- should be higher than that for P_r^+. Nevertheless, the real situation is that the resisitivity and T_P for P_r^- is almost the same as those for P_r^+, i.e., $\rho_{P_r^-}/\rho_{P_r^+}$ and $T_{P_r^-}/T_{P_r^+} \approx 1$ This implies that the ferroelectric field effect in the LSMO/PMN-PT is negligible. It is known that the ferroelectric field effect is closely related to the absolute number of charge carriers in the channel material.[17] For a fixed doping level, the charge carrier density is usually determined by the thickness of the thin film. If the film is thin enough so that the absolute number of the charge carriers in the channel is small, the ferroelectric polarization will then lead to a large relative change in the total number of the charge carriers in the channel and thus a strong ferroelectric field effect. In the LSMO/PMN-PT, the thickness of the LSMO is ~50 nm which is about 12 times larger than that in the $La_{0.8}Sr_{0.2}MnO_3/Pb(Zr_xTi_{1-x})O_3$ ferroelectric FET where the resistivity ratio of the two polarization states, i.e., $\rho_{P_r^-}/\rho_{P_r^+}$, is ~1.28 at room temperature.[15] Thus, it is estimated that the ferroelectric field effect induced relative change in the total number of the charge carriers in the present LSMO channel could be very small because the thickness of the LSMO film is relatively large. This may be why the ferroelectric field effect is not observed.

We noted that the ferroelectric polarization of the PMN-PT not only results in the accumulation or depletion of holes in the LSMO channel but also gives rise to an expansion of the lattice of the PMN-PT along the direction of the electric field because the electric field causes the rotation of the ferroelectric domains towards the direction of electric field. The ferroelectric polarization induced expansion of the lattice of the PMN-PT is to cause lattice strain in the LSMO film and hence influence the electrical properties of the LSMO film. To look into this point, we measured the resistivity of the LSMO film as a function of electric field and the

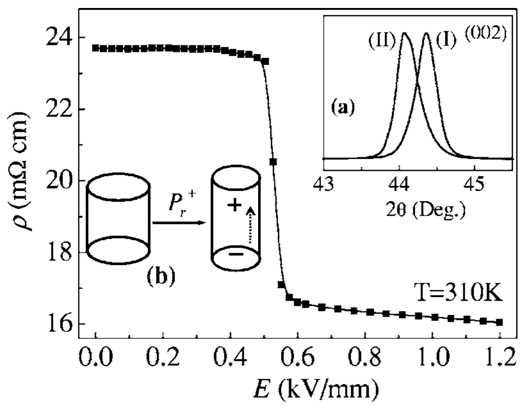

FIG. 3. Electric field dependence of the resistivity for the LSMO film. Note that the electric field was applied across the unpolarized PMN-PT. The inset (a) shows the XRD patterns of the PMN-PT (002) reflections for the PMN-PT at unpolarized (I) and positively polarized (II) states, respectively. The inset (b) shows a schematic diagram of the ferroelectric polarization induced expansion of the lattice of the PMN-PT along the direction of the electric field; the dotted arrow represents the direction of the electric dipole moments.

c-axis lattice constant of PMN-PT before and after the PMN-PT was positively polarized, respectively. As shown in Fig. 3, the resistivity of the LSMO is almost independent of the electric field for $E < 0.5$ kV/mm but shows a drastic decrease by ~30% between $E = 0.5$ kV/mm and $E = 0.575$ kV/mm. For $E > 0.575$ kV/mm, the resistivity decreases slightly with increasing electric field. We stress here that the PMN-PT (002) reflection clearly shifts to a lower 2θ angle after the PMN-PT was positively polarized [inset (a) of Fig. 3]. This implies that the *c*-axis lattice constant expands while the in-plane *a*- and *b*-axis lattice constants contract in order to maintain the Poisson ratio, as schematically shown in the inset (b) of Fig. 3. The ferroelectric polarization induced changes in the lattice constants are to cause lattice strains in the LSMO film. We thus conclude that the large decrease in the resistivity for P_r^+ and P_r^- is related to the ferroelectric polarization induced lattice strain effect. We note that the resistivity of the LSMO film cannot spontaneously restore to its initial value when the electric field is reduced to zero but can restore to its initial value when the PMN-PT is depolarized by heating it to a temperature higher than paraelectric to ferroelectric transition temperature. All these results demonstrate that the large decrease in the resistivity in a wide temperature range and the upward shift in T_P for P_r^+ and P_r^- are mainly caused by the ferroelectric polarization induced lattice strain which could modify the relative strength of the double-exchange (DE) interaction and suppression of the Jahn-Teller (JT) electron-lattice interaction in the LSMO film.

As is known, the electron-lattice interaction favors the localization of charge carriers, while the DE-induced ferromagnetism demands the active hopping of charge carriers. It is the competition between these two interactions that is mainly responsible for the electrical transport and magnetic properties of the LSMO film. Since the lattice constants of the PMN-PT ($a \sim b \sim c \sim 4.02$ Å) Ref. 10 is much larger than that for the bulk LSMO ($a = b = c \sim 3.88$ Å),[18] in-plane biaxial tensile strain is thus expected in the LSMO films grown

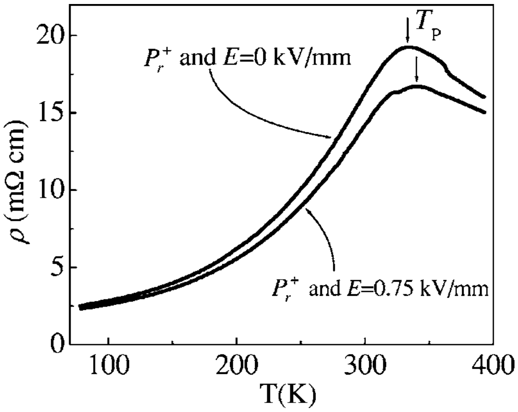

FIG. 4. Temperature dependence of the resistivity for the LSMO film when a field of 0 kV/mm or +0.75 kV/mm is applied to the positively polarized PMN-PT.

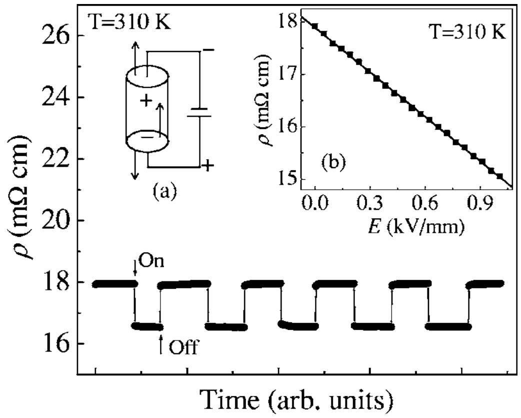

FIG. 5. The resistivity response of the LSMO film as a function of time while a 0.5 kV/mm electric field was switched on and off at 310 K. Inset (a) shows a schematic diagram of the electric field induced elongation of the lattice of the PMN-PT via the converse piezoelectric effect. Inset (b) shows the electric field dependence of the resistivity measured at 310 K.

on the PMN-PT. As discussed above, the ferroelectric polarization of the PMN-PT causes an increase in the c-axis lattice constant and a decrease in the in-plane a- and b-axis lattice constants of the PMN-PT. Such changes of the lattice constant could lead to a large reduction of the biaxial tensile strain in the LSMO film. The reduction of the biaxial tensile strain, on one hand, reduces the in-plane Mn–O bond length and thus enhances the strength of the DE interaction. In addition, recent theoretical and experimental investigations have shown that the electron-lattice interaction in thin films is very sensitive to the biaxial strain.[19–21] A compressive strain will increase the "bare" electron hopping amplitude and thereby reduce the relative strength of the JT electron-lattice interaction, while a biaxial tensile strain will increase the JT distortion, favoring localization of charge carriers.[19] Thus, the reduction of the biaxial tensile strain in the LSMO film, on the other hand, could reduce the relative strength of the electron-lattice interaction in the LSMO film. Therefore, the ferroelectric polarization induced decrease in the resistivity and enhancement in T_P can be qualitatively understood based on above pictures.

Figure 4 shows the temperature dependence of the resistivity for the LSMO film under zero and a 0.75 kV/mm electric field which was applied across the already positively polarized PMN-PT. As compared with that under zero electric field, the resisitivity of the LSMO was further reduced by the application of 0.75 kV/mm electric field, which is particularly pronounced near T_P where the resistance decreases by $\sim$14%. Simultaneously, the T_P shifts to a higher temperature by $\sim$7 K. These effects of the electric field on the resisitivity and T_P could be due to the electric field induced lattice strain via the converse piezoelectric effect in the PMN-PT. To clarify this problem, we measured the resistivity response of the LSMO film as a function of time while a 0.5 kV/mm electric field was switched on and off, as shown in Fig. 5. One can find that the resistivity can be modulated between the low- and high-resistivity states by switching on and off the electric field. The resistivity decreases sharply by $\sim$7.8% once the electric field was switched on and restores to its initial value upon the removal of the electric field. Such modulation of the resistivity by the electric field was also observed at other temperatures (not shown here). It is known that ferroelectric materials possess piezoelectric and converse piezoelectric effects after they have been polarized. Namely, polarized ferroelectrics will generate electric charges once they are subjected to mechanic deformation (i.e., piezoelectric effect). Conversely, when electric fields are applied across polarized ferroelectrics, stress and strain will occur in the ferroelectrics (i.e., converse piezoelectric effect). More specifically, applying a voltage with the opposite polarity as the poling voltage across the polarized ferroelectrics will cause the lattice of ferroelectrics to be compressed along the direction of the electric field, while applying a voltage with the same polarity as the poling voltage across the polarized ferroelectrics will cause the lattice of ferroelectrics to expand along the direction of the electric field, as schematically shown in the inset (a) of Fig. 5. In the LSMO/PMN-PT, if a positive electric field (e.g., 0.5 kV/mm) was applied across the positively polarized PMN-PT, the lattice of the PMN-PT will further expand along the c axis and contract perpendicular to that direction. This causes an enhancement of the DE interaction and a reduction of the electron-lattice interaction. As a result, the resisitivity of the LSMO decreases sharply. If the electric field was switched off, the lattice of the PMN-PT rapidly restores to its initial positively polarized state. Accordingly, the tensile strain in the LSMO film restores to its initial state, and hence the resistivity increases. Therefore, the repeated modulation of the resistivity by switching on and off the electric field can be understood based on the converse piezoelectric effect induced lattice strain effect.

To obtain more detailed insight into the effects of the converse piezoelectric effect in the LSMO/PMN-PT, we show the electric field dependence of the resistivity for the LSMO film at 310 K in the inset (b) of Fig. 5. Note that the PMN-PT was positively polarized before the measurements of the resistivity. The resistivity at 310 K decreases linearly with increasing electric field, which can be well fitted using Eq. (1):

$$\rho = 17.89 - 2.82E. \tag{1}$$

The converse piezoelectric effect induced in-plane compressive strain ε_T in the PMN-PT is proportional to the magnitude of the electric field and can be expressed as

$$\varepsilon_T = d_{31}E. \tag{2}$$

Here, the d_{31} is the transverse piezoelectric constant of the PMN-PT. From Eq. (2), one may conclude that the in-plane compressive strain ε_T in the PMN-PT increases linearly with increasing electric field. This implies that the in-plane tensile strain in the LSMO film was increasingly reduced with increasing electric field. Combining Eq. (1) with Eq. (2), the relation between the resistivity and the in-plane compressive strain in the PMN-PT can be expressed as

$$\rho = 17.89 - 2.82\varepsilon_T/d_{31}. \tag{3}$$

Equation (3) directly demonstrates that the resistivity at a fixed temperature decreases as the electric field induced in-plane compressive strain in the PMN-PT increases.

IV. CONCLUSIONS

We have studied the effects of ferroelectric polarization and converse piezoelectric effect induced lattice strain on the electrical properties of the LSMO films which have been grown on the ferroelectric PMN-PT single-crystal substrates. The ferroelectric polarization of the PMN-PT induces a large decrease in the resistivity and an upward shift in the Curie temperature of the LSMO films, which was discussed in terms of the PMN-PT ferroelectric polarization induced reduction of the tensile strain in the LSMO films. The ferroelectric field effect in the LSMO/PMN-PT ferroelectric FET is negligible. More importantly, we found that the resistivity of the LSMO films can be dynamically tuned by the electric field induced lattice strain via the converse piezoelectric effect in the PMN-PT. These approaches of using ferroelectric polarization and converse piezoelectric effect of ferroelectrics provide routes to tune the physical properties of perovskite-type thin films.

ACKNOWLEDGMENTS

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