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MICOSTRUCTURAL STUDY OF CMR FILMS AS A
FUNCTION OF GROWTH TEMPERATURE, AS-DEPOSITED
AND ANNEALED

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MICROSTRUCTURAL STUDY OF CMR FILMS AS A FUNCTION OF GROWTH TEMPERATURE, AS-DEPOSITED AND ANNEALED

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ABSTRACT

The properties encompassed by the family of complex metal oxides span the spectrum from superconductors to insulating ferroelectrics. Included in this family are the new colossal magneto-resistive perovskites with potential applications in advanced high density magnetic data storage devices based on single or multilayer thin films units of these materials fabricated by vapor phase deposition (PVD) methods. The realization of this potential requires solving basic thin film materials problems requiring understanding and controlling the growth of these materials. Toward this end, we have grown $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ and $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ on LaAlO_3 single crystal substrates by pulsed laser and RF sputter deposition at temperatures from 500 to 900 C and annealed at over 900C for about 10 hours. The evolution of the microstructure of these films was studied by scanning probe microscopies and transmission electron microscopy (TEM).

The results of SPM characterization showed that at the lower end of the growth temperature range, the as-grown films were polygranular with grain size increasing with temperature. The 500 C as-grown films appeared to be amorphous while the 750 C film grains were layered with terrace steps often one unit cell high. In contrast, films grown at 900 C consisted of coalesced islands with some 3-D surface crystals. After annealing, all films had coalesced into very large extended layered islands. The change in microstructure was reflected in a decreased resistivity of coalesced films over their unannealed granular precursors. Previous reported work on the growth of $\text{La}_{0.84}\text{Sr}_{0.16}\text{MnO}_3$ and $\text{La}_{0.8}\text{Sr}_{0.2}\text{CoO}_3$ grown demonstrated the sensitivity of the microstructure to substrate and deposition conditions. Films grown on an "accidental" vicinal surface grew by a step flow mechanism.

INTRODUCTION

The properties encompassed by the family of complex metal oxides span the spectrum from superconductors to insulating ferroelectrics and includes in this family the magneto-resistive oxide perovskites (currently referred to as colossal magneto-resistive (CMR) films to distinguish them from the multilayer giant magneto-resistive (GMR) films). The CMR films have potential applications in advanced high-density magnetic data storage devices based on single or multilayer thin films units of these materials fabricated by vapor-phase deposition (PVD) methods. Reproducibly fabricating perovskite thin films by PVD to optimize properties for magnetic data storage applications faces the same challenges that were encountered for the growth of the superconducting oxide films. The literature abounds with growth study articles for $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ (YBCO) deposition (see for example 1). All the same considerations apply to the PVD growth of the metal oxide magnetic films, $\text{La}_{1-x}\text{A}_x\text{MO}_{3-y}$, (A = Ca, Ba, Sr; M = Mn). The parametric deposition space is the same multidimensional and interdependent matrix as for YBCO: substrate lattice match, substrate temperature, deposition rate, target quality, gas composition and pressure. The sensitivity of the microstructure to the growth conditions, shown in Figure 1, was reported previously^{2,3} for the growth of $\text{La}_{0.84}\text{Sr}_{0.16}\text{MnO}_3$ and $\text{La}_{0.8}\text{Sr}_{0.2}\text{CoO}_3$ films. In addition to the usual deposition variables

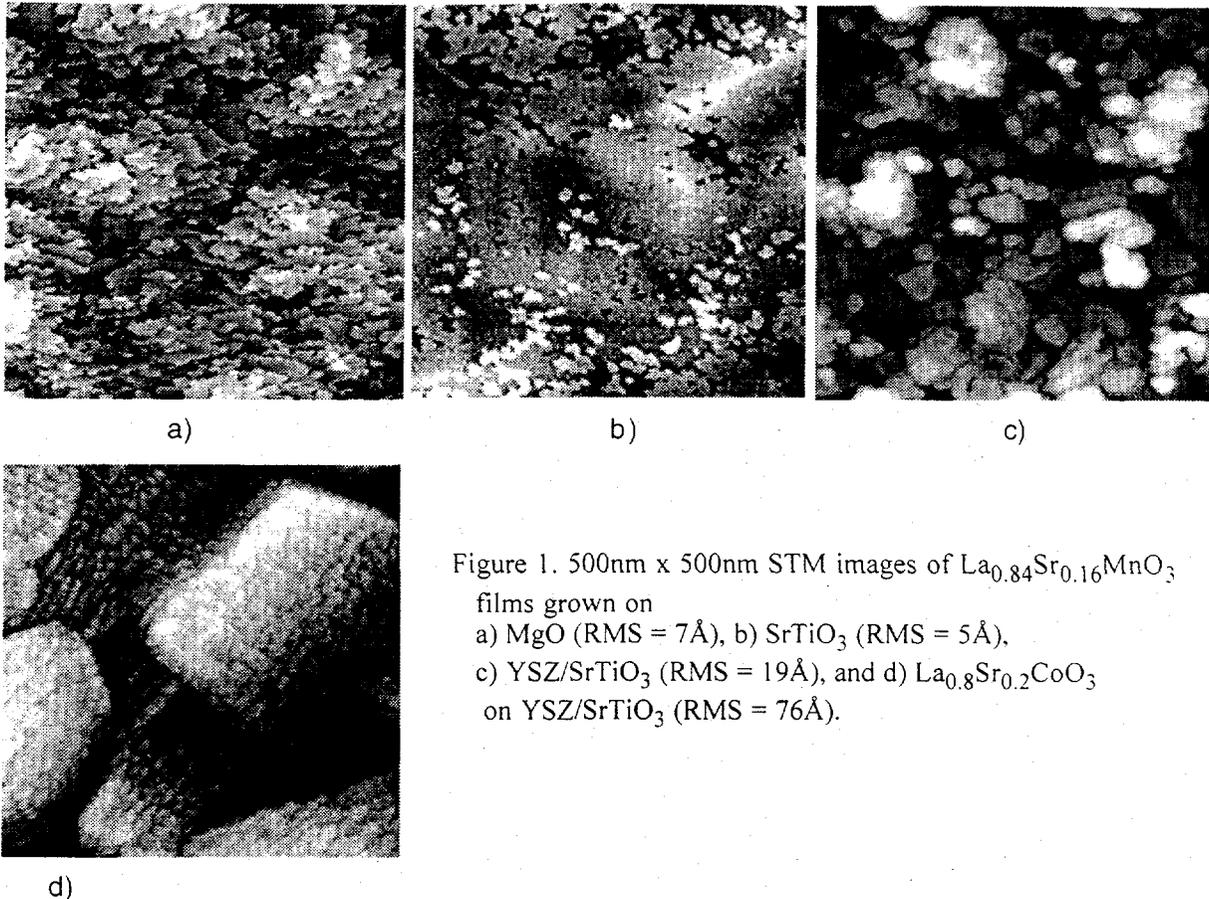


Figure 1. 500nm x 500nm STM images of $\text{La}_{0.84}\text{Sr}_{0.16}\text{MnO}_3$ films grown on
 a) MgO (RMS = 7Å), b) SrTiO_3 (RMS = 5Å),
 c) YSZ/ SrTiO_3 (RMS = 19Å), and d) $\text{La}_{0.8}\text{Sr}_{0.2}\text{CoO}_3$
 on YSZ/ SrTiO_3 (RMS = 76Å).

addition to the usual deposition variables like temperature, one needs to worry about the annealing procedure, i.e. time and temperature, that is used to complete processing of the films in order to optimize the MR properties as has been reported by other groups.⁴⁻⁶ The final La site dopant $M(1)$ concentration x and oxygen stoichiometry and distribution, which have a profound affect on the MR properties⁷, are often not exactly known and difficult to determine.

Recent work reported by Hundley, et. al.,⁸ showed the correspondence between the resistivity and large negative magnetoresistance peak near the ferromagnetic transition which for our annealed $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ films was about 250C. This was true only for the annealed samples. In the present paper we report on the results of some preliminary growth studies of $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ and $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ ferromagnetic oxide CMR films grown by pulsed-laser and RF off-axis sputter deposition methods at temperatures from 500C to 900C, focusing primary attention on film microstructure, crystallinity, and epitaxy as a function of substrate growth temperature. The as-deposited and post-deposition annealed films will be compared to illustrate the change in structure as a result of the annealing process.

EXPERIMENTAL

We have grown $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ and $\text{La}_{0.7}\text{Sr}_{0.3}\text{MnO}_3$ on LaAlO_3 (100) single crystal substrates by pulsed laser (PLD) and RF sputter deposition at temperatures from 500 to 900 C. The PLD films were deposited with a $\text{La}_{0.7}\text{A}_{0.3}\text{MnO}_3$ target composition at a 5 Hz rep. rate for 20 minutes in a 200

mTorr oxygen atmosphere. The thickness was about 100 nm for a deposition rate of 5 nm/min. After deposition, the samples were cooled in 300 Torr of oxygen to room temperature in 30 min. (the heater was off after the deposition, and cool by itself) and annealed at over 900C for about 10 hours. Multiple samples were made in the same run for different measurements. Half of the samples were annealed at 950 C in flowing oxygen for 10 hrs.

The sputter-deposited films were made by off-axis RF magnetron sputtering at a power level of 120 watts on $\text{LaAlO}_3(100)$ substrates at sputter gas pressures of Ar @ 6×10^{-3} torr and O_2 @ 1.5×10^{-3} torr. Deposition rates were 2 nm/min with total film thicknesses of 150 to 200 nm. Deposition temperatures ranged from 550 to 900 C. The targets purchased were 0.67La, 0.33(Ca or Sr), 1.0Mn Oxide. Post-deposition anneals were done in flowing oxygen for 10 hours at 950C.

Films stoichiometry was determined by Rutherford backscattering (RBS) measurements. The evolution of the microstructure of all of the films was characterized using atomic force (AFM) and scanning tunneling microscopy (STM), film surface conductivity permitting.

Several of the samples were examined by TEM either in plan or cross-sectional view to determine crystallinity and in- or out-of-plane epitaxial relationships with the substrate crystal orientations. Plan-view and cross-sectional TEM specimens were prepared by conventional grinding and polishing methods followed by Ar-ion milling with liquid nitrogen specimen cooling during milling. The specimens were examined at room temperature using a Phillips CM30 analytical electron microscope.

RESULTS AND DISCUSSION

RBS measurements showed the film cation stoichiometry to be within 2% of the target cation stoichiometry for both the PLD and sputter deposited films.

In the case of both deposition methods, the results of STM and AFM characterization for the as-deposited films showed that at the lower end of the growth temperature range, the as-grown films were polygranular with grain size increasing with temperature (Figures 2a, b, and c (PLD), and 3a, b, and c (sputter-deposited)). From the AFM image Figure 2a, the 500 C as-grown PLD films appeared to be amorphous in while the 750 C film grains were layered with terrace steps often one unit cell high suggesting that that film is epitaxial with respect to the substrate normal. The in-plane orientation is not known. In contrast, films grown at 900 C consisted of coalesced islands. The PLD film, Figure 2c, had some 3-D surface crystals on the surface, with two different in-plane orientations, either parallel to the (100) or (110) directions. The 500C PLD film was found to be semiconducting with no temperature dependent resistivity peak.⁹ The sputtered films showed the same trend in grain size; the 750C film grew by dislocation-mediated process.

The annealing process resulted in a dramatic change in microstructure. After annealing, all films had coalesced into very large extended layered islands (Figures 2d, e, and f (PLD) and 3d, e, and f (sputter-deposited)). Although all films were annealed at the same temperature for the same period of time, they differed significantly in final appearance. This result is probably due, in part, to the difference in diffusion mechanism. The as-grown film growth is controlled by molecular diffusion while during annealing bulk dominates island growth. The AFM image of the 500C, annealed PLD film (not shown) showed a scattered covering of surface >200 nm particles not present in the unannealed sample or in the corresponding STM image of the same film. They appeared as "holes" in the STM image and were probably insulating. The 500C sputter-deposited films were probably grown on an "accidental" vicinal surface, the growth proceeding by a step flow mechanism.

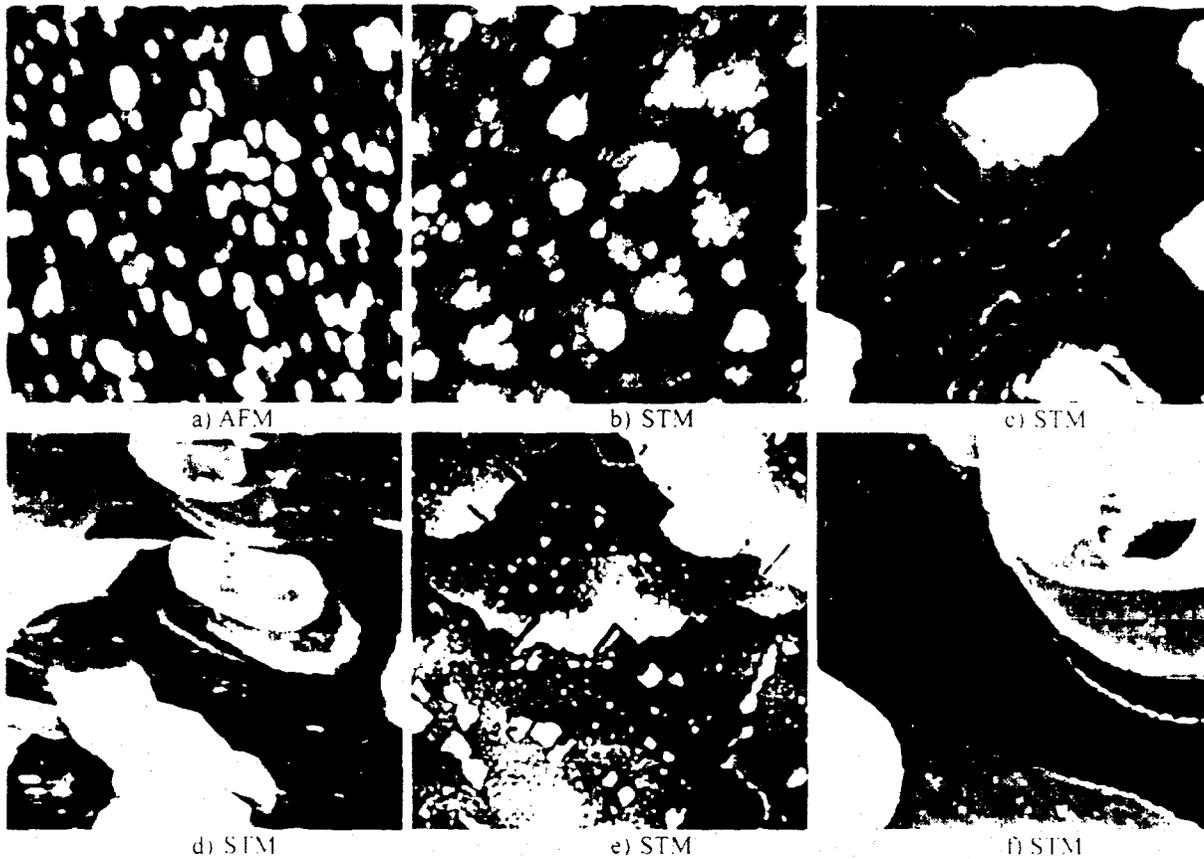


Fig. 2. 500 nm^2 images of pulsed-laser-deposited $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ films grown on $\text{LaAlO}_3(100)$ substrates. a) to c) are as-deposited films grown at 600C, 750C, and 900C, respectively. d) through f) are the corresponding films after annealing at 950C for 10 hours in 300 mTorr flowing O_2 .

The steps visible in the images of the annealed films are unit-cell high. In general, the change in microstructure was reflected in a higher transition temperature and decreased resistivity of the coalesced films over their unannealed granular precursors.

The TEM results, shown in Figure 4, compliment those from STM and AFM. As can be seen in Figure 4a, an amorphous ring is seen with no sharp Bragg reflection for the 500C as-deposited film. That result along with the microstructure shown in the plan-view is typical of an amorphous PLD films. The 500C, annealed film, on the other hand, is epitaxial, Figure 4b, but has a poorly developed misfit dislocation network. Also present in the micrograph, one can see possible threading dislocations (dark, curved, continuous lines in photo). In contrast to the 500C, annealed film, the 900C, annealed film, seen in Figure 4c, is epitaxial and has a well developed misfit dislocation network. There is evidence of twinning (orthogonal pattern of dark lines connecting nodes of misfit dislocation network). Both the 500C and 900C, annealed films have sharp Bragg reflections indicative of epitaxy, but closer examination of the spot for the 900C films reveals splitting of diffraction spots, Figure 4d, consistent with twinning evident in 4c. Some of the splitting may also be associated with diffraction from the misfit dislocation network itself. Some splitting was also observed in the 500°C film after annealing, but it was not nearly as pronounced consistent with the poorly developed misfit dislocation network.

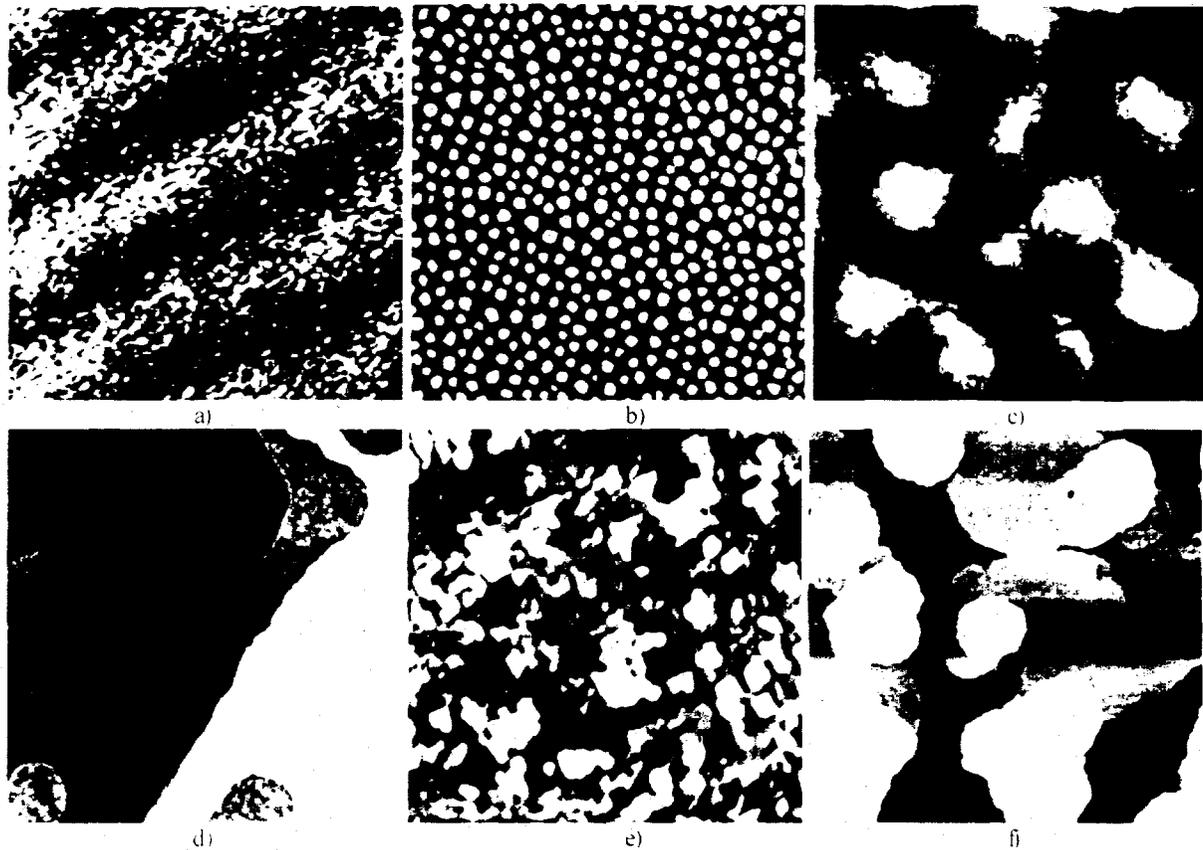
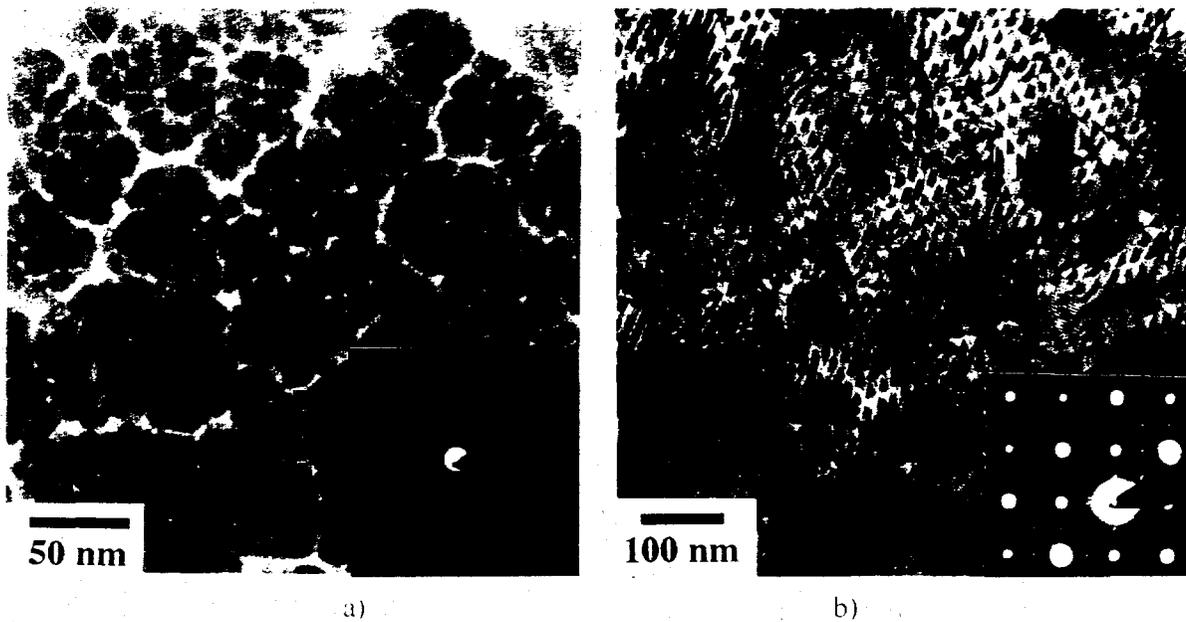


Fig. 3. 500 nm^2 STM images of RF off-axis sputter-deposited $\text{La}_{0.7}\text{Ca}_{0.3}\text{MnO}_3$ films grown on $\text{LaAlO}_3(100)$ substrates. a) through c) are as-deposited films grown at 500C, 600C, and 750C. d) through f) are the corresponding films after annealing at 950C for 10 hours. The 600C films appears to have grown by a step flow mechanism unintentionally on a vicinal surface.



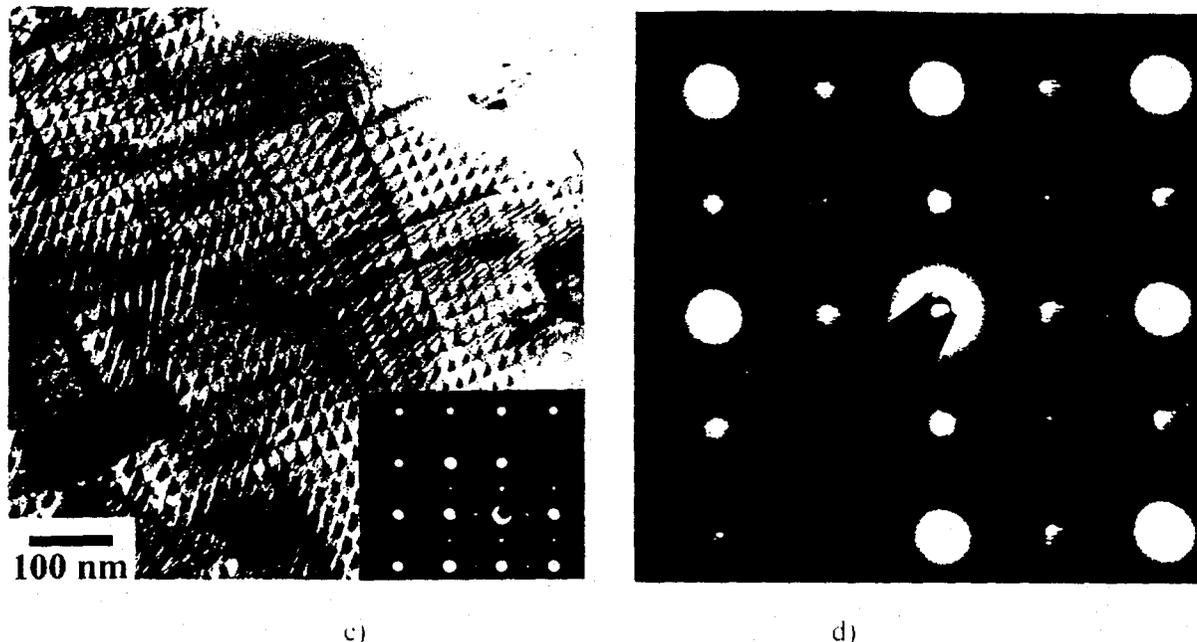


Figure 4. Bright-field, plan view TEM photomicrographs of a) an amorphous LCMO film deposited by PLD at 500°C. b) same film as in a) after annealing at 950°C for 10 hrs., c) an epitaxial LCMO film deposited at 900°C and annealed as in b). Figure 4d) is an enlargement of the diffraction pattern from 4c showing splitting of diffraction spots consistent with twinning evident in 4c.

Issues that still need to be resolved include the role of the microstructure and defects on the MR properties and the magnetic domains. The change in microstructure on annealing improved the magnetoresistive properties, but it is still not clear whether other changes other than the macroscopic ones observed in this study contribute to the change in properties. Future work will focus on correlating microstructure with magnetic and resistive properties using magnetic force and electric force microscopies.

REFERENCES

1. I. D. Raistrick, and M. E. Hawley, "Scanning Tunneling and Atomic Force Microscope Studies of Thin Sputtered Films of $\text{YBa}_2\text{Cu}_3\text{O}_7$ ", in *Interface in High Temperature Superconductors*, eds. Subhash Shinde and David A. Rudman, chapter 2, p. 28 (Springer-Verlag, NY, NY, 1993).
2. E.L. Brosha, B.W. Chung, F.H. Garzon, I.D. Raistrick, R.J. Houlton, and M.E. Hawley, *J. Electrochem. Soc.* **142** (5), 1702 (1995).
3. B.W. Chung, E.L. Brosha, F.H. Garzon, I.D. Raistrick, R.J. Houlton, and M.E. Hawley, *J. Mat. Res.* **10**(10), 2518 (1995).
4. R. von Helmolt, J. Wecker, B. Holzapfel, L. Schultz, and K. Samwer, *Phys. Rev. Lett.* **71**, 2331 (1993).
5. S. Jin, T.H. Tiefel, M. McCormack, R.A. Fastnacht, R. Ramesh, and L.H. Chen, *Science* **264**, 413 (1994).
6. H.L. Ju, C. Kwon, Q. Li, R.L. Greene, and T. Venkatesan, *Appl. Phys. Lett.* **65**, 108 (1994).
7. P. Schiffer, A.P. Ramirez, W. Bao, and S-W. Cheong, preprint.
8. M.F. Hundley, M. Hawley, R.H. Heffner, Q.X. Jia, J.J. Neumeier, J. Tesmer, J.D. Thompson, and X.D. Wu, *Appl. Phys. Lett.* **67**(6), 860 (1995).
9. M.F. Hundley, unpublished measurement.