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STM AND X-RAY DIFFRACTION TEMPERATURE-DEPENDENT GROWTH STUDY  
OF SrRuO<sub>3</sub> PLD THIN FILMS

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ABSTRACT

SrRuO<sub>3</sub> (SRO) has recently found a number of applications in different fields, e. g. as a buffer layer for the growth of high temperature superconductor (HTS) YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7-x</sub> films and as a bottom electrode for ferroelectric or high dielectric constant thin film capacitors and nonvolatile data storage. The growth of high crystallinity SRO films with good structural and electrical properties is the prerequisite for each of these applications. In this paper we describe the affect of one growth parameter, temperature (T), on the crystalline quality, epitaxial substrate relationship and resulting electrical properties. SRO films were deposited on LaAlO<sub>3</sub> single crystal substrates by pulsed laser deposition at substrate temperatures (T<sub>s</sub>) ranging from room temperature (RT) up to 800° C with a nominal film thickness of 150 nm range. The resulting films were characterized by x-ray diffraction, 4-point transport, and STM.

The films' microstructures, as revealed by STM, evolved from polygranular at RT to a layered plate-like structure at higher deposition temperatures, T<sub>s</sub>. Increasing T<sub>s</sub> was marked first by increasing grain size, then a stronger orientational relationship between film and substrate, finally followed by the development of increased connectivity between grains to an extended island or condensed layered state. The transition from polygranular to layered structure occurred at T<sub>s</sub> > 650° C. Increased conductivity paralleled the changes in microstructure. The surfaces of all of the films were relatively smooth; the oriented films are suitable for use as conductive templates in multilayer structures.

INTRODUCTION

MASTER

Deposition of metallic SrRuO<sub>3</sub> (SRO) thin films has been a topic of much interest recently [1-4] due to its thermal and chemical stability and the compatibility of its growth parameters (e.g. temperature) and perovskite structure with several technologically important materials. For example, SRO has been used as a buffer layer for the growth of highly oriented superconducting YBa<sub>2</sub>Cu<sub>3</sub>O<sub>7-x</sub> (YBCO) on MgO substrates [5] and as a normal-metal layer in edge-geometry superconducting heterostructure configurations [6,7]. In addition, the high electrical conductivity and thermal stability of SRO make it a candidate for base electrode material in ferroelectric thin film capacitors [8-10] with non-volatile data storage applications.

The goal of this study was to determine the lowest deposition temperature at which heteroepitaxial growth of SRO films with optimum crystallinity, epitaxy, and conductivity could be achieved by pulsed laser deposition (PLD) methods on LaAlO<sub>3</sub> (100) single crystal substrates. Further, it was deemed useful to determine the effect of higher temperature growth on film properties, particularly temperatures at which further epi-layers, such as YBCO, might be deposited. Previously, we reported on the effect of temperature on changes in microstructure and

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conductivity [2] but without the complete microstructural changes throughout the entire room temperature to 825°C temperature range, including the fine structure present in the grain of the low temperature films ( $T_s < 650^\circ\text{C}$ ). The entire evolution of the micro- to nano-structure as a function of temperature is included in this work.

## EXPERIMENT

A pulsed-laser deposition (PLD) technique was used to deposit SRO thin films. The SRO target was prepared from a mixture of  $\text{SrCO}_3$  and Ru metal powders in the appropriate molar ratio which was ground together then heated in air at 1200°C for about 12 hours. The regrinding and heating procedure was repeated a second time before the resulting finally pressing into disks. The PLD was carried out using a XeCl excimer laser ( $\lambda = 308 \text{ nm}$ ) operated at repetition rates of 10 Hz and producing 20 ns pulses with an energy density of 2 J/cm<sup>2</sup>. The (100)  $\text{LaAlO}_3$  (LAO) wafers were cleaned using a sequence of acetone, methanol, and de-ionized water rinses before loading them into the vacuum chamber for SRO depositions.

The surface morphology of the SRO films was characterized with a Digital Instruments Nanoscope III scanning tunneling microscope (STM). Typical tunneling conditions were 70 to 80 pA current setpoint at 1.0 to 1.3 eV bias. Results using either mechanically cut or electrochemically etched Pt-Ir tunneling tips were identical. RMS surface roughness was determined from the STM images using the Digital Instruments software.

The microstructure of the films was characterized by x-ray diffraction (XRD) measurements using a Siemens D5000 four-circle diffractometer with  $\text{Cu K}_\alpha$  radiation. The full width at half maximum (FWHM) was determined from the  $\omega$ -rocking curve at 46.2°.

## RESULTS

All of the films were conductive enough to easily perform STM characterization. Figure 1 presents a composite of the STM images covering the complete set of nine films grown at  $T_s$ 's ranging from RT to 825°C at about 100°C increments. The images represent typical 100 nm x 100 nm areas of the surface of each film chosen to show the fine structure of the grains or that of the layered surface, in the case of the films grown above 600°C. In the latter case, the step heights are about ~ 6 to 8 Å, of the order of a unit cell.

Figure 2 shows the STM root-mean-square roughness (RMS) as a function of  $T_s$  for a 1  $\mu\text{m}$  x 1  $\mu\text{m}$  square area of the surface of each of these films. A comparison of this data with the corresponding x-ray  $\omega$ -rocking curve (c-axis tilt) FWHM and intensity for the films grown at  $T_s \geq 450^\circ\text{C}$ , figure 3, reveals an apparent correlation between the RMS roughness and the crystallinity/epitaxy of the films, assuming equal volume. The FWHM values range from 1.3° to 0.74°. STM characterization showed that for the 5 lowest  $T_s$ 's, films (with the exception of the RT film) grain size increased with increasing T but not smoothly. A large jump occurs between the 350°C and 450°C films.

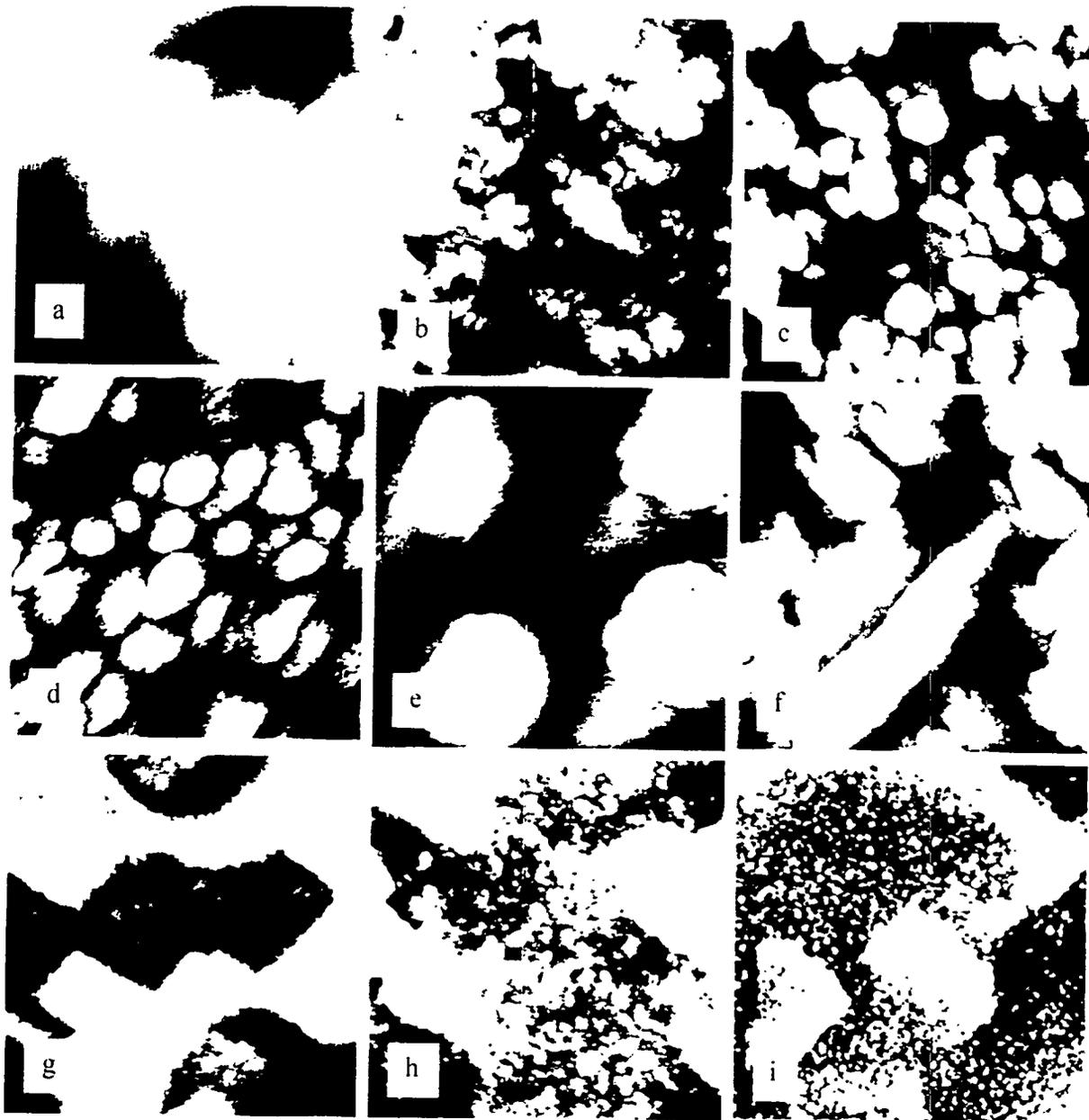


Figure 1. 100 nm x 100 nm STM images of the surfaces of SrRuO<sub>3</sub> thin films grown on LaAlO<sub>3</sub> (100) substrates by PLD: a) RT (RMS = 114 Å); b) 150° C (RMS = 20 Å); c) 250° C (RMS = 30 Å); d) 350° C (RMS = 23 Å); e) 450° C (RMS = 30 Å); f) 550° C (RMS = 19 Å); g) 650° C (RMS = 8 Å); h) 750° C (RMS = 10 Å); and i) 825° C (RMS = 22 Å).

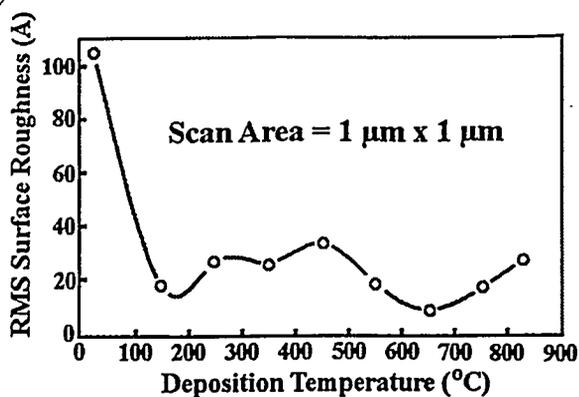


Figure 2. Root-mean-surface roughness ( $\text{\AA}$ ) of the  $\text{SrRuO}_3$  thin films plotted as a function of deposition temperature ( $^{\circ}\text{C}$ ) (modified from reference [5]).

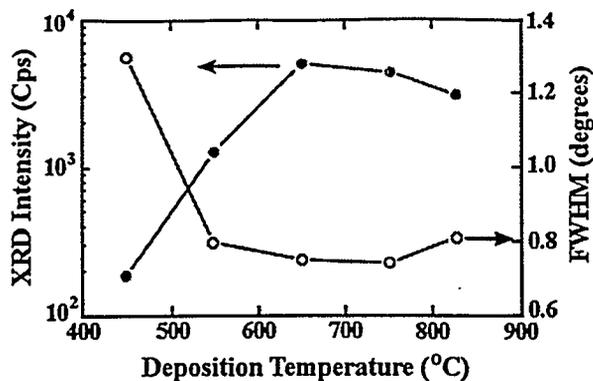


Figure 3. X-ray (004) reflection  $\omega$ -rocking curve intensity (left) and FWHM (right) as a function of  $\text{SrRuO}_3$  thin films deposition temperature ( $^{\circ}\text{C}$ ).

The RT temperature film not only stands out as the roughest film, its RMS roughness value is nearly 4 x that of the next roughest film and its grain size is comparable to the  $450^{\circ}\text{C}$  film.

The STM images also revealed that the  $250^{\circ}\text{C}$  and  $350^{\circ}\text{C}$  films consist of grains ( $\sim 10 - 15$  nm, respectively) made up of subunits which are approximately the same size as the grains ( $\sim 2 - 3$  nm across) that comprise the  $150^{\circ}\text{C}$  film. No obvious evidence for epitaxy or crystallinity is apparent in the STM images of the films grown below  $450^{\circ}\text{C}$ , i.e. the grains are not faceted, layered, or obviously aligned along the substrate crystallographic directions. This does not, however, rule out the possibility that they might be polycrystalline since no x-ray was done on films deposited below  $450^{\circ}\text{C}$ .

A large jump in roughness can be observed at  $450^{\circ}\text{C}$  which corresponds with the large, nearly 4-fold increase in grain size seen in the STM image for that film, figure 1e. These grains, in turn, consist of subunits about equal in size to the grains in the  $350^{\circ}\text{C}$  film. Some subunits appear to be faceted, consistent with the presence of a weak, broad x-ray  $\omega$ -rocking curve peak.

Although the  $550^{\circ}\text{C}$  film, figure 1f, consisted of discrete grains, the film was highly textured with grains oriented in two orthogonal directions; the x-ray  $\omega$ -rocking curve peak FWHM was nearly as narrow as for the three films grown at higher  $T_s$ . Grains growing in the two directions were, however, not the same length, one direction preferred over the other. Although the resistivity of the  $550^{\circ}\text{C}$  film was not measured, extrapolation between the data for the  $450^{\circ}\text{C}$  and  $650^{\circ}\text{C}$  films reported previously [2] suggests that the resistivity for the  $550^{\circ}\text{C}$  film is less than an order of magnitude lower than that for the high  $T_s$  films, probably due in part to grain boundary scattering.

For  $T_s \geq 650^{\circ}\text{C}$  the films consisted of coalesced layers interspersed with faceted depressions (not shown in the higher resolution images, figure 1g, h, and i). These depressions ranged in depth from  $\sim 2.5$  to  $3.5$  to  $15$  nm for the  $650^{\circ}\text{C}$ ,  $750^{\circ}\text{C}$ , and  $825^{\circ}\text{C}$  films, respectively. The trend is the higher the  $T_s$  the larger the coalesced layer and the larger and deeper the depressions. Resistivity

was regrettably not measured for the 750°C and 825°C films, but the 650°C film's resistivity, reported earlier [2] was comparable or only slightly higher than that for the 775°C film.

## CONCLUSIONS

The RMS roughness and relatively large grain size for the RT film is consistent with growth not controlled by diffusion, as is the case for the films grown at 150°C, 250°C, 350°C, and 450°C where one sees the classical increase in grain size with temperature. The large jump in grain size and apparent faceting of grain subunits for the 450°C film is probably due to an onset of crystallization and or epitaxy. By 550°C epitaxy is clearly evident from the orthogonal orientation of the film's elongated grains. By 650°C the films had coalesced into extended layers with fully faceted terrace edges consistent with full 3-D epitaxy.

The T-dependent surface roughness data appears to have some correlation with the corresponding x-ray  $\omega$ -rocking curve peak FWHM and inversely with the intensity: the better the film crystallinity/epitaxy the smoother the film and vice versa. Although the intensity is strongly influenced by alignment, particularly for the films with narrow FWHM, and, therefore, not to be taken too seriously, more careful alignment would have only meant even higher not lower intensity values. For the three highest  $T_S$  films, the increasing lateral dimensions and depth of the depressions left after incomplete coalescence of the layers with increasing  $T_S$  explains the increase in RMS with  $T_S$  but not the x-ray peak broadening and decreasing intensity, even after correcting for integrated peak area. The latter trends are likely traced to changes in crystallinity and/or film-substrate epitaxial relationships.

Although there are surface "nano-pits" in the extended layers of the three films grown at the highest  $T_S$ s, their depth is only a fraction of the film thickness, ranging from < 3 nm (650°C) to 15 nm (825°C) out of 100 to 150 nm, the total film thickness. With the presence of twin boundaries reported earlier [2] on a scale smaller than the size of the coalesced layers, it is not clear how much of a role the nano-pits play in determining the film resistivity. Although the density of these nano-pits is higher for the 650°C film, they are also smaller and shallower than for the other higher  $T_S$  films.

The above structural data compliments the previously reported RT transport [2] measurements which suggested that the optimum  $T_S$  for high quality base-electrode SrRuO<sub>3</sub> films grown on LaAlO<sub>3</sub> (100) under the present growth conditions is between 650°C and 750°C.

Future work will focus on a more systematic study of the growth process, epitaxy as a function of substrate, and role of structure on the transport properties. Work in progress involves the simultaneous growth of SRO on LAO and SrTiO<sub>3</sub> as a function of temperature to understand the role of compressive versus tensile stress on strain, epitaxy, and electronic properties. Both the low and high temperature regimes will have fuller characterization and growth in the critical temperature range, 500°C to 800°C, will be explored at a finer grid.

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#### REFERENCES

1. C.B. Eom, R.J. Cava, R.M. Fleming, J.M. Phillips, R.B. Vandover, J.H. Marshall, J.W.P. Hsu, J.J. Krajewski, and W.F. Peck, *Science* **258**, 1766 (1992).
2. Q.X. Jia, F. Chu, C.D. Adams, X.D. Wu, M. Hawley, J.H. Cho, A.T. Findikoglu, S.R. Foltyn, J.L. Smith, and T.E. Mitchell, *J. Mater. Res.* **11**, 2263 (1996).
3. K.P. Fahey, B.M. Clemens, and L.A. Wills, *Appl. Phys. Lett.* **67**, 2480 (1995).
4. P. Tiwari, X.D. Wu, S.R. Foltyn, M.Q. Lee, I.H. Campbell, R.C. Dye, R.E. Muenchausen, J.F. Smith, and T.E. Mitchell, *Phil. Mag. B* **69**, 1101 (1994).
5. P. Tiwari, X.D. Wu, S.R. Foltyn, M.Q. Lee, I.H. Campbell, R.C. Dye, and R.E. Muenchausen, *Appl. Phys. Lett.* **64**, 634 (1994).
6. L. Antagonize, K. Char, T.H. Geballe, L.L.H. King, and A.W. Sleight, *Appl. Phys. Lett.* **63**, 1005 (1993).
7. R. Domel, C.L. Jia, C. Copetti, G. Ockenfuss, and A.I. Braginski, *Supercond. Sci. & Tech.* **7**, 277 (1994).
8. C.B. Eom, R.B. Vandover, J.M. Phillips, D.J. Werder, J.H. Marshall, C.H. Chen, R.J. Cava, R.M. Fleming, and D.K. Fork, *Appl. Phys. Lett.* **63**, 2570 (1993).
9. S.Y. Hou, J. Kwo, R.K. Watts, J.Y. Cheng, and D.K. Fork, *Appl. Phys. Lett.* **67**, 1387 (1995).
10. Q.X. Jia, X.D. Wu, S.R. Foltyn, and P. Tiwari, *Appl. Phys. Lett.* **66**, 2197 (1995).