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ELECTROTECHNICAL LABORATORY

1-1-4, Umezono, Tsukuba-shi, Ibaraki, 305 Japan

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Solid State Division, Oak Ridge National Laboratory
Oak Ridge, TN 37831-6056 U.S.A.

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We have studied the transport and structural properties of $(Ca, Sr)CuO_2$, $Sr_{1-y}Nd_yCuO_2$, and $Sr_{1-x}CuO_{2-\delta}$ thin films grown by pulsed-laser deposition. Stoichiometric "infinite layer" $(Ca, Sr)CuO_2$ thin films grown over a large range of growth conditions are insulators, while superconductivity is observed in $Sr_{1-y}Nd_yCuO_2$ films with T_c(onset)~28K for y=0.10. A Nd solubility limit of y=0.10 is observed with the appearance of a new phase with c~0.37nm for y>0.10. In addition, the transport and structural properties of $Sr_{1-x}CuO_{2-\delta}$ thin films grown by pulsed-laser deposition support the contention that the tetragonal phase is capable of accommodating a significant density of alkaline-earth deficiencies up to $x \geq 0.3$. Resistivity measurements indicate a significant change in the carrier density of the CuO_2 planes as Sr vacancies are introduced. In addition, an enigmatic anomaly in resistivity at 185K is observed for $Sr_{0.85}CuO_{2-\delta}$ thin films. Magnetic measurements on these samples indicate that, although a significant drop in resistivity at 185K is observed, it is not due to a superconducting transition. Hall measurements, as well as changes in resistivity with film growth conditions, suggest that the majority carriers in these $Sr_{1-x}CuO_{2-\delta}$ thin films are electrons even with the Sr-vacancies present.

The tetragonal phase of $(Ca,Sr)CuO_2$ is the simplest structure containing the CuO_2 planes necessary for high-temperature superconductivity.[1,2] The presence of four-fold coordinated Cu atoms in the CuO_2 sheets suggests the possibility of electron-doping, and electron-doped superconductivity has been realized through trivalent doping on the alkaline-earth site.[3-5] Despite the absence of apical oxygen coordinated to Cu in the structure, some have suggested that hole-doping, through the introduction of alkaline-earth vacancies, may also be possible.[6] The observation of superconductivity in bulk $(Ca, Sr)_{1-x}CuO_2$ has motivated additional investigations on this subject.[6-11] In addition to studying the properties of bulk material produced by high-pressure synthesis, parallel efforts with epitaxial thin films of this material are being pursued.[12-22] Tetragonal $(Ca, Sr)CuO_2$ single crystal thin films of the "infinite layer" defect perovskite structure have been grown by pulsed laser deposition over a wide range of growth conditions.[12-18] Superconductivity in trivalent-doped $SrCuO_2$ thin films has been reported.[23,24] In addition, some interesting evidence for superconductivity in $(Ca, Sr)CuO_2$ thin films at temperatures as high as 170K has been reported, although these results have been difficult to confirm.[14] To understand the superconducting properties of this material, it is useful to consider the transport and structural properties of chemically-doped, defect-doped and undoped material.

In addressing these issues, we have studied the transport and structural properties of $(Ca, Sr)CuO_2$, $Sr_{1-y}Nd_yCuO_2$ and $Sr_{1-x}CuO_{2-\delta}$ thin films grown by pulsed-laser deposition. Tetragonal, "infinite layer" thin films were grown by pulsed-laser deposition as has been described elsewhere.[18] Ceramic target pellets of $(Ca, Sr)CuO_2$, $Sr_{1-x}CuO_2$ and $Sr_{1-y}Nd_yCuO_2$ were prepared from high-purity Nd_2O_3, $CaCO_3$, $SrCO_3$ and CuO, intimately ground and mixed using an automatic agate mortar, pressed into pellet form, and fired in air. Several iterations of grinding, pelletizing, and firing were made to ensure homogeneity and decomposition of the carbonate in the finished targets as monitored by XRD. After growth, the films were cooled in either vacuum or an oxygen atmosphere. X-ray diffraction measurements were made using a 2- circle diffractometer (SCINTAG, Ge detector) with Cu Kα radiation. An omega scan (rocking curve) through the (200) reflection of the substrate was made initially to align each sample. Peak positions and integrated intensities of the reflections in θ-2θ scans were determined by least-squares fitting Pearson VII type functions. The film reflection positions were corrected for systematic errors by using three orders of the substrate reflections to construct an internal standard correction curve. Resistivity measurements were made using a standard four-point technique with a measuring current of ~0.01-3μA. In addition, Hall measurements were performed on selected samples.

Stoichiometric $Ca_{1-x}Sr_xCuO_2$ films were grown by single-target pulsed- laser deposition for the entire range of composition $0.15 \leq x \leq 1.0$. X-ray diffractometry indicates that these $Ca_{1-x}Sr_xCuO_2$ thin films are essentially single crystals with extremely narrow diffraction peaks, complete in-plane crystalline alignment with the (100) $SrTiO_3$ substrate, and virtually no impurity phases present. Fig. 1. shows the resistivity for stoichiometric $Ca_{1-x}Sr_xCuO_2$ thin films grown at 600°C in 200mTorr O_2 and subsequently cooled in 760 Torr O_2. For all compositions, the films are insulators with room temperature resistivity on the order of 0.2 to 2Ω-cm. However, the magnitude and temperature dependence of the resistivity is a strong function of both the temperature and oxygen pressure during film growth. Fig. 2. shows the resistivity for $SrCuO_2$ thin films grown under significantly different oxygen pressures and temperatures. A $SrCuO_2$ thin film grown at 600°C in 200mTorr and cooled in 760 Torr O_2 has a resistivity ρ(300K) ~1Ω-cm with ρ(25K) ~7000Ω-cm. In contrast, a $SrCuO_2$ film grown at 550°C in 2mTorr O_2 and cooled in vacuum has a resistivity ρ(300K) ~0.05 Ω-cm with ρ(25 K) ~ 0.2 Ω-cm. This apparent increase in carrier density as the films are grown in more reducing conditions suggests that the majority charge carriers are electrons. This is consistent with Hall measurements that show a negative Hall coefficient for these $SrCuO_2$ films, and is consistent with the presence of four-fold coordinated Cu atoms in the CuO_2 planes.

Electron-doping by trivalent substitution in $SrCuO_2$ has been shown to increase the carrier density leading to superconductivity.[3-5] We have grown $Sr_{1-y}Nd_yCuO_2$ thin films by pulsed-laser deposition, and have obtained similar results. Fig. 3. shows the resistivity for a $Sr_{0.9}Nd_{0.1}CuO_2$ thin film with T_c (onset) ~ 28K. The transition is quite broad, however, and shows a finite resistance down to 8K. It is unclear why the superconducting transitions for these films are so broad and are at a lower temperature than that observed for the bulk samples (40K). *X*-ray diffraction indicates that the *c*-axis lattice parameter for the films is slightly larger than that observed for bulk samples, and may indicate significant strain in the films.

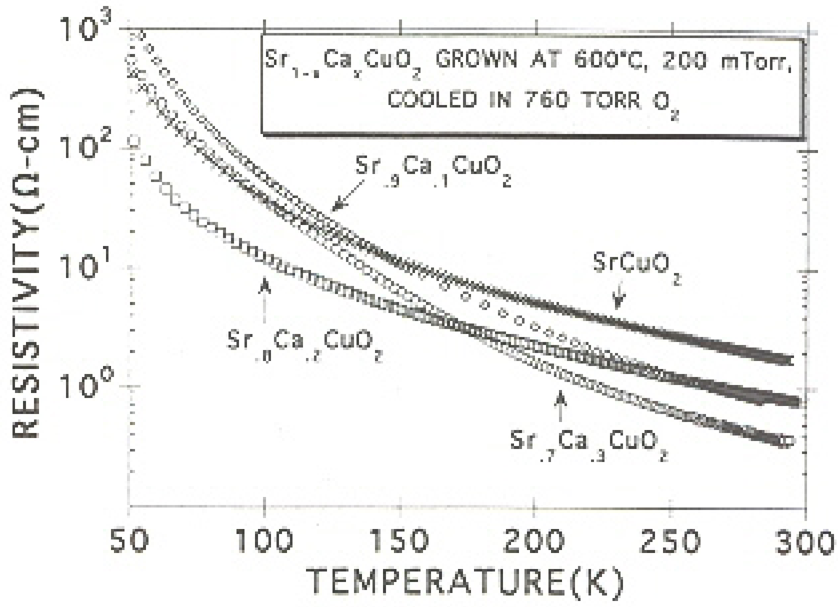

Fig. 1 Temperature dependence of the resistivity for $(Ca,Sr)CuO_2$ thin films grown at 600°C in 200 mTorr by pulsed-laser deposition.

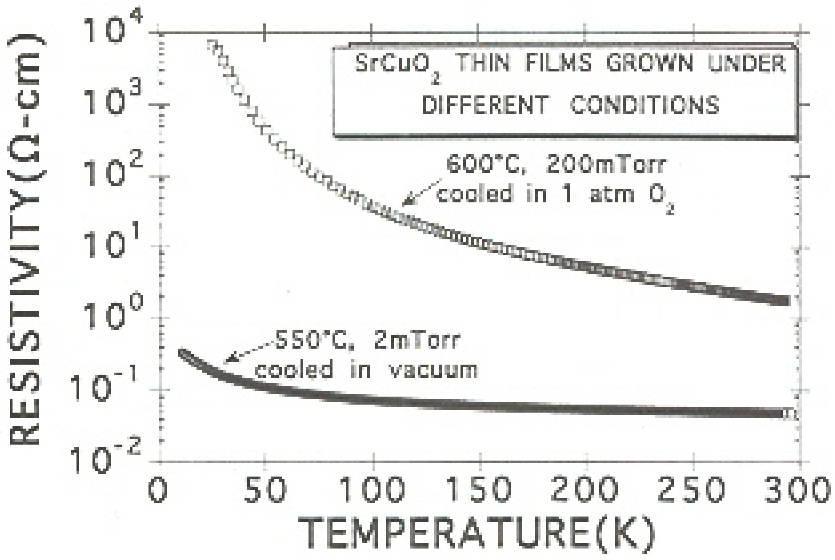

Fig. 2 Temperature dependence of the resistivity for $SrCuO_2$ grown under oxidizing (600°C, 200 mTorr O_2, cooled in 760 Torr O_2 after growth) and reducing (550°C, 2 mTorr O_2, cooled in vacuum) conditions.

For film growth conditions that lead to superconducting films, a solubility limit for Nd substitution is observed at $y \sim 0.1$. For Nd content higher than y=0.1, a new phase is seen in the *X*-ray diffraction data, as shown in Fig. 4, with a d-spacing of ~0.37nm. This new phase is metallic, but no superconducting transition has been observed. It is interesting to note that while $Sr_{1-y}Nd_yCuO_2$ films with y>0.1 grown at 700°C and 50mTorr contain this impurity phase, films with y>0.1 grown at lower temperatures can be obtained which consist only of the infinite layer phase as determined by *X*-ray diffraction.

In addition to stoichiometric (Ca, Sr)CuO_2 and (Sr, Nd) CuO_2 thin films, tetragonal $Sr_{1-x}CuO_{2-\delta}$ thin films of the "infinite layer" defect perovskite structure were grown over a rather extensive range of non-stoichiometry, with the films accommodating a significant density of Sr-vacancies. All of the $Sr_{1-x}CuO_{2-\delta}$ films discussed in this study were grown on (100)-oriented $SrTiO_3$ at 550°C in 1-2mTorr O_2 at a growth rate of

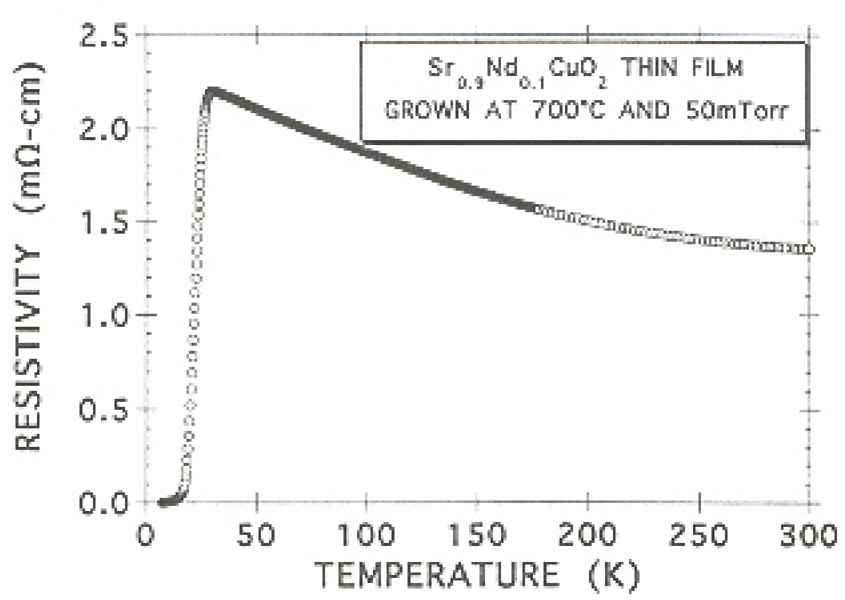

Fig. 3 Resistivity for a $Sr_{0.9}Nd_{0.1}CuO_2$ thin film grown at 700°C in 50 mTorr O_2.

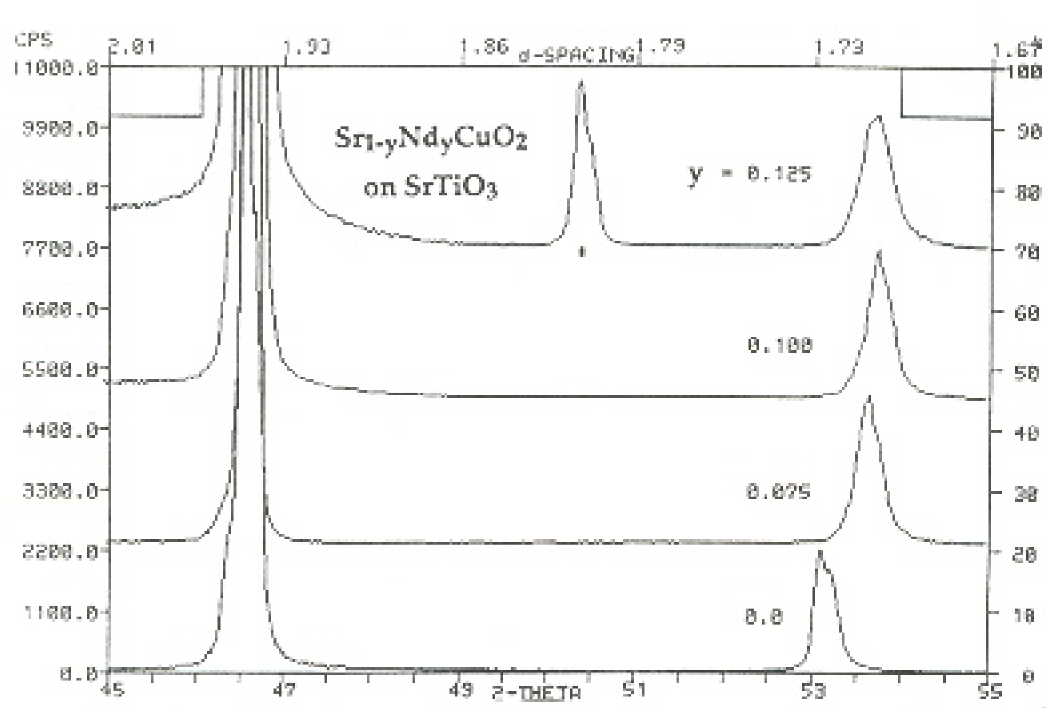

Fig. 4 *X*-ray diffraction for $Sr_{1-y}Nd_yCuO_2$ thin films grown at 700°C showing the appearance of an impurity phase for $y > 0.1$.

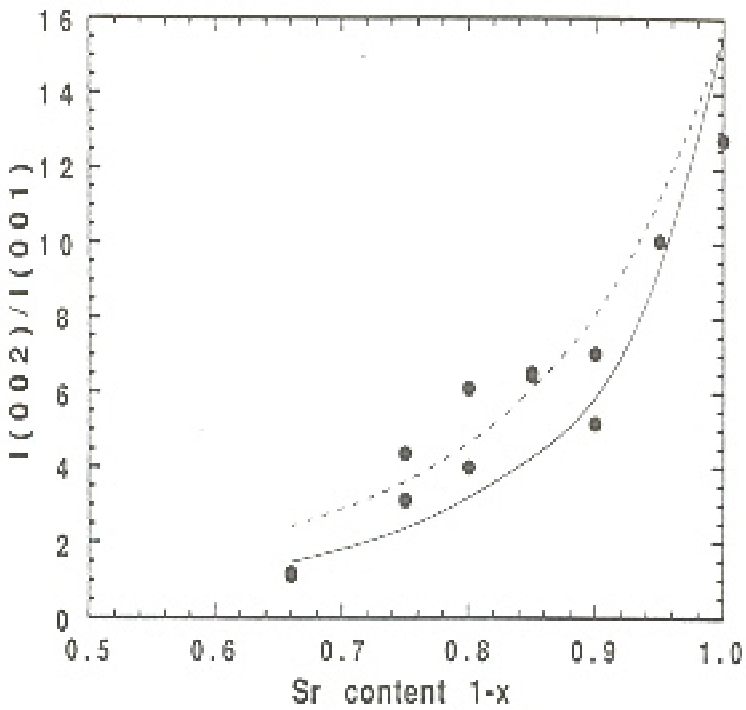

Fig. 5 *X*-ray diffraction intensity ratio, I(002)/I(001), for $Sr_{1-x}CuO_{2-\delta}$ thin films grown by pulsed laser deposition. The curves show the calculated intensity ratio assuming the incorporation of vacancies on the alkaline-earth site for a constant oxygen content of 2 atoms per formula unit (solid line) and a variable oxygen content of 2-x atoms per formula unit (dashed line). The model for the calculated intensity variations utilized the observed variation in the c lattice parameter and a = 3.904 Å, and also includes temperature factor, Lorentz, and polarization corrections.

0.02nm/sec. The films were then cooled in vacuum. In general, we find that lower oxygen pressures and growth temperatures lead to $SrCuO_2$ thin films with lower resistivities, which is consistent with an electron-doped system.[3-5] Film thickness was approximately 100nm. We find that the tetragonal phase is capable of accommodating a significant density of alkaline-earth deficiencies up to $x \leq 0.3$. Films with $x \leq 0.33$ consisted only of the "infinite layer" phase as determined by *X*-ray diffraction. For films grown from targets with Sr- deficiencies greater than 0.33, peaks were indexed to the expected $Sr_{1.75}Cu_3O_{5.13}$ phase, the end-member of the $Sr_{1.75-x}Ca_xCu_3O_{5.13}$ solid solution thermodynamically stable.[25] In order to determine if vacancies were being incorporated into the film structure, the intensity ratio, *I*(002)/*I*(001), was measured and compared to a calculated intensity ratio assuming the presence of Sr-vacancies in the structure. As seen in Fig. 5, there is close agreement between the calculated and measured intensity ratios indicating that vacancies are indeed being accommodated in the structure. The other likely structural model with Cu filling the vacant Sr-sites does not reproduce the observed intensity variation.

One can consider the effect of Sr-vacancies on the transport properties of the CuO_2 planes. Speculation suggests that such defects may lead to hole-doping of the CuO_2 planes in the infinite layer structure despite that only electron-doping has been realized in the superconducting copper oxides possessing four-fold coordinated copper atoms with no apical oxygen atoms present. If the film composition is the same as the pulsed-laser deposition target composition, then the non-stoichiometry in $Sr_{1-x}CuO_{2-\delta}$ must be either accommodated by an enhanced formal valence of Cu (increased hole content) and/or a reduced oxygen content (constant hole content). It is probable that both factors are operative. Unfortunately, we lack an independent measure of the oxygen content of the films, so we write the general formula as $Sr_{1-x}CuO_{2-\delta}$ where δ is probably significantly less than *x*. Fig. 6. shows the resistivity for $Sr_{1-x}CuO_{2-\delta}$ thin films grown from targets which were Sr-deficient with $0 \leq x \leq 0.25$.

Several rather interesting observations can be made regarding this data. Note first that, as the deficiency is initially increased, the resistivity decreases at all temperatures, suggesting that the alkaline-earth vacancies are contributing charge carriers to the CuO_2 planes. It is important to consider the initial decrease in resistivity with the introduction of Sr-vacancies more carefully. Based on simple arguments, one might expect these Sr-vacancies to contribute holes to the system. We have performed Hall measurements on $SrCuO_2$ and $Sr_{0.85}CuO_{2-\delta}$ thin films, and find that in both cases, a negative Hall coefficient is obtained. Bond valence sum analysis[26] of stoichiometric $SrCuO_2$ films also suggest that the CuO_2 layers of $SrCuO_2$ are intrinsically electron-doped for all growth conditions examined. These results, however, do not rule out the possibility that holes which are low in density and/or not very mobile exist in the films. The most consistent view is that the majority carriers in these "infinite layer" $Sr_{1-x}CuO_{2-\delta}$ thin films are electrons, and that the introduction of Sr-vacancies produces additional holes as the Cu valence changes to accommodate these vacancies. In addition, it is important to recognize that the introduction of Sr-vacancies tends also to create oxygen vacancies as well due to charge balance considerations.

In addition to this decrease in resistivity, an anomaly in the resistivity at ~185K is observed for $Sr_{1-x}CuO_{2-\delta}$ as *x* approaches 0.15. This resistivity anomaly is most clearly seen in the $Sr_{0.85}CuO_{2-\delta}$ samples, where a 15-20% drop in resistivity occurs with an onset at ~185K. We want to emphasize that this feature in the resistivity is reproducible.All of the $Sr_{0.85}CuO_{2-\delta}$ thin films grown under these conditions exhibit this behavior, although the growth parameter space (e.g., *T*, *P*(O_2), ablation

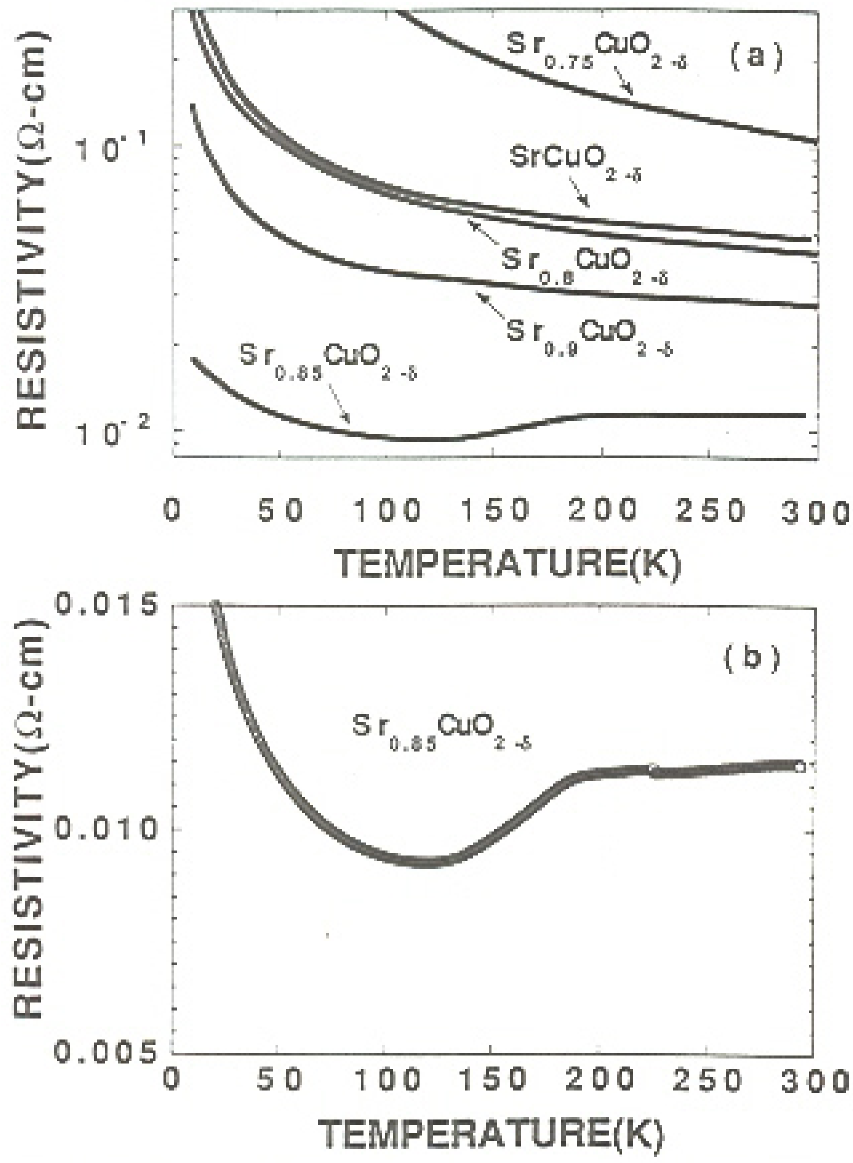

Fig. 6 A log plot of resistivity as a function of temperature for (a) $Sr_{1-x}CuO_{2-\delta}$ thin films grown at 550°C and 2 mTorr oxygen by pulsed laser deposition. A linear plot (b) for the $Sr_{0.85}CuO_2$ thin film is also shown highlighting the anomaly at ~185 K.

plume characteristics) necessary for obtaining films showing this behavior is somewhat narrow. In addition, the anomaly is stable with sample aging, showing reproducible resistivity data several days after film growth.

The origin of this anomalous behavior in the resistivity of $Sr_{0.85}CuO_{2-\delta}$ thin films at 185K remains unclear. Magnetization measurements made with a SQUID magnetometer on $Sr_{0.85}CuO_{2-\delta}$ samples give no indication of any magnetization response down to 4.2K. In addition, we have also measured the magnetoresistance of these samples in fields up to 8 Tesla. In all cases, the anomaly remains virtually unaffected by magnetic field. Based upon these measurements, it certainly does not appear that the drop in resistivity at 185K is a result of any superconducting transition. However, efforts are continuing to determine the origin of this anomaly in the resistivity.

For Sr-deficiencies $0 \leq x \leq 0.15$, increasing the vacancy density decreases the resistivity in the thin film. For Sr-deficiencies $x>0.15$, this trend is reversed. Fig. 7. shows the resistivity at 300K as a function of Sr-deficiency. Clearly, increasing the Sr-vacancy density for $x>0.15$ results in higher resistivities and a disappearance of the anomaly. This occurs even though the intensity ratios shown in Fig. 5 indicate that vacancies are continuing to be incorporated into the structure. In addition, there appears to be one-to-one correspondence between the *c*-axis lattice parameter and the resistivity of these films. Fig. 8. shows the *c*-axis lattice parameter as a function of Sr-deficiency. Initially, the introduction of Sr-vacancies results in a reduction in the *c*-axis lattice parameter. However, this trend is dramatically reversed for $x>0.15$, which is also the vacancy concentration where the resistivity begins to increase with increasing x and the resistive anomaly disappears. The sample-to-sample variation for a given composition apparent from the scatter of the data in Fig. 8 is exactly mimicked by the *R(T)* data. Apparently, the introduction of vacancies in excess of $x>0.15$ leads to a significant, yet subtle, change in the defect structure of these "infinite layer" thin films. Efforts are in progress to understand this behavior.

In conclusion, we have studied the transport and structural properties of (Ca, Sr)CuO_2, $Sr_{1-y}Nd_yCuO_2$, and $Sr_{1-x}CuO_{2-\delta}$ thin films grown by pulsed-laser deposition. Stoichiometric "infinite layer" (Ca, Sr)$CuoO_2$ thin films grown over a large range of growth conditions are insulators, while superconductivity is observed in $Sr_{1-y}Nd_yCuO_2$ films with T_c(onset)~28K for y=0.10. A Nd solubility limit of y=0.10 is observed with a new phase with c ~ 0.37nm resulting for $y>0.10$. We have also investigated the effects of Sr-vacancies on the transport and structural properties of $SrCuO_{2-\delta}$ thin films. Our results show that the introduction of vacancies leads initially to a decrease, with a subsequent increase in resistivity as the concentration of vacancies is increased. In all cases, the majority charge carriers are electrons as determined by Hall measurements. No superconducting transition was observed for temperatures down to 8K. These changes in resistivity, however, are found to correlate with the *c*-axis lattice parameter. In addition, an interesting anomaly in the resistivity is observed for $Sr_{0.85}CuO_2$ thin films in the form of resistivity drop at 185K. Additional magnetic measurements indicate that this drop in resistivity is not a manifestation of a superconducting transition, although its origin remains enigmatic.

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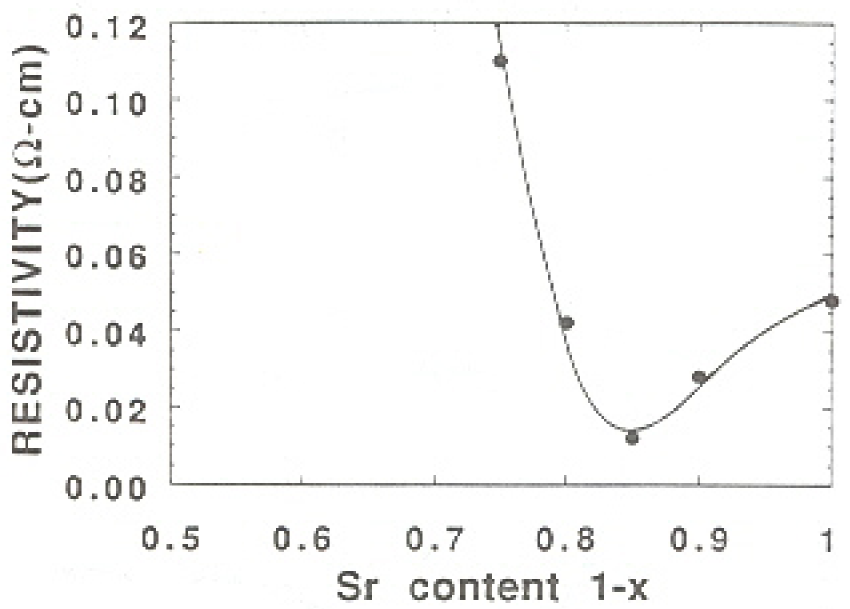

Fig. 7 Resistivity, measured at 300 K, as a function of Sr-deficiency for $Sr_{1-x}CuO_{2-\delta}$ thin films grown at 550°C and 2 mTorr oxygen.

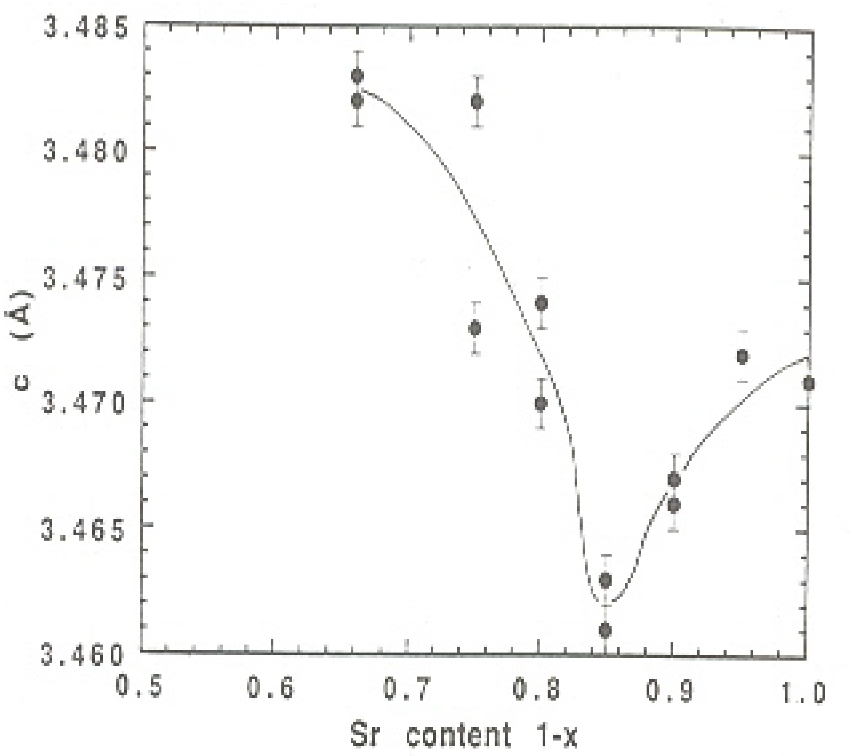

Fig. 8 *C*-axis lattice parameter as a function of Sr-deficiency for $Sr_{1-x}CuO_{2-\delta}$ films grown at 550°C and 2mTorr oxygen.

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