Physica C 217 (1993) 146–150
North-Holland

PHYSICA C

Anomalous transport and structural properties of $Sr_{1-x}CuO_{2-\delta}$ thin films

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Received 6 August 1993

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 $x \leq 0.3$. 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 the resistivity at 185 K 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 185 K is observed, it is not due to a superconducting transition. Hall measurements, as well as changes in the 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 $SrCuO_2$ 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 oxygens 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 170 K have been reported, although these results have been difficult to confirm [14]. To understand the superconducting properties of this material, specifically regarding whether hole-doping is possible, it is useful to consider the transport and structural properties of chemically-doped, defect-doped and undoped material.

To address these issues, we have studied the transport and structural properties of $Sr_{1-x}CuO_{2-\delta}$ thin films grown by pulsed-laser deposition. We find that the tetragonal phase is capable of accommodating a significant density of alkaline-earth deficiencies up to $x \leq 0.3$. Changes in the X-ray diffraction intensity ratio, $I(002)/I(001)$, are consistent with the presence of Sr-vacancies in the structure. In addition, we find some rather interesting behavior, particularly in the transport properties of $Sr_{1-x}CuO_{2-\delta}$ thin films, as the Sr-deficiency is increased. In particular, resistivity measurements indicate a significant change in the carrier density of the CuO_2 planes as Sr vacancies are introduced. In addition, an interesting anomaly in resistivity at 185 K 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 185 K is observed, it is not due to a superconducting transition. Hall measurements, as well as changes in the resistivity with film-growth conditions, indicate that the majority carriers in these $Sr_{1-x}CuO_{2-\delta}$ thin films are electrons despite the presence of Sr-vacancies in the structure.

0921-4534/93/$06.00

$Sr_{1-x}CuO_{2-\delta}$ films were grown by pulsed laser deposition as has been described elsewhere [18]. Ceramic target pellets of $Sr_{1-x}CuO_{2-\delta}$ were prepared from high-purity $SrCO_3$ and CuO, intimately ground and mixed using an automatic agate mortar, pressed into pellet form, and fired in air at 900°C. 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. All of the films discussed in this study were grown on (100)-oriented $SrTiO_3$ at 550°C in 1-2 mTorr O_2 at a growth rate of 0.02 nm/s. 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]. After growth, the films were cooled in vacuum. The film thickness was approximately 100 nm. X-ray diffraction measurements were made using a two-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 ~3 μA. In addition, Hall measurements were performed on selected samples.

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. 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. 1, 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.

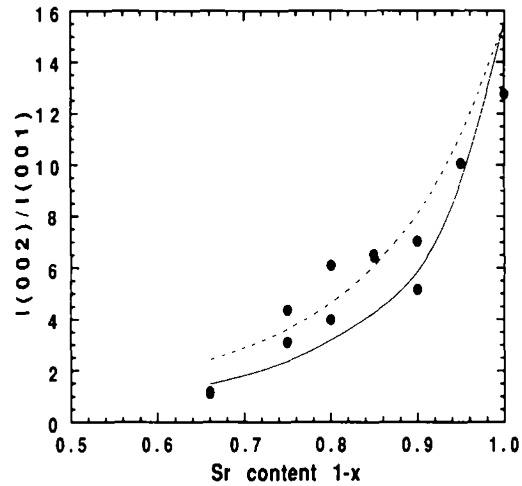

Fig. 1. X-ray diffraction intensity ratio, $I(002)/I(001)$, for $Sr_{1-x}CuO_{2-\delta}$ thin films grown by pulsed laser deposition. The curves show the calculated intensity ratio assuming the incorporation of vacancies on the alkaline-earth site for a constant oxygen content of 2 atoms per formula 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.

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 finite-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 $Sr_{1-x}CuO_2O_{2-\delta}$ 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. Figure 2 shows the resistiv-

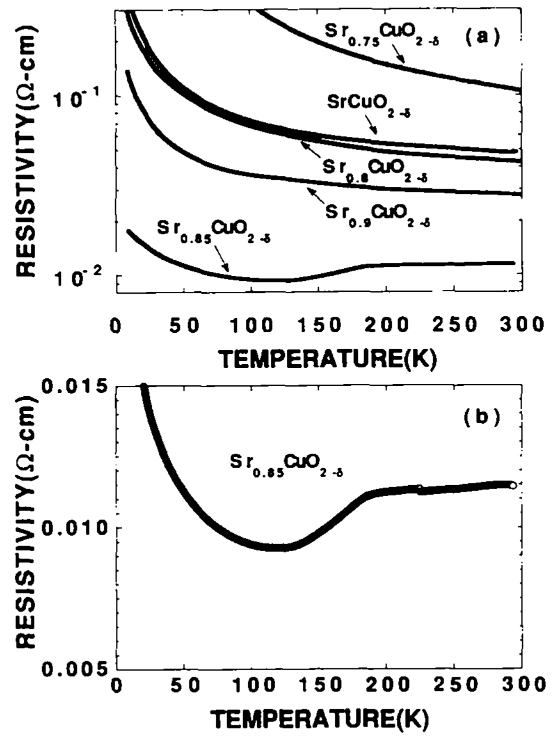

Fig. 2. A log plot of the resistivity as a function of temperature for (a) $Sr_{1-x}CuO_{2-\delta}$ thin films grown at 550°C and 2 mTorr oxygen by pulsed laser deposition. A linear plot (b) for the $Sr_{0.85}CuO_2$ thin film is also shown, highlighting the anomaly at ~185 K.

ity for $Sr_{1-x}CuO_{2-\delta}$ thin films grown from targets which were Sr-deficient with $0 \le x \le 0.25$. 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 ~185 K 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 the 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 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 185 K 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 4.2 K. In addition, we have also measured the magnetoresistance of these samples in fields up to 8 T. In all cases, the anomaly remains virtually unaffected by the magnetic field. Based upon these measurements, it certainly does not appear that the drop in resistivity at 185 K is a result of any superconducting transition. However, efforts are continuing to determine the origin of this anomaly in the resistivity.

For Sr-deficiencies $0 \le x \le 0.15$, increasing the vacancy density decreases the resistivity in the thin film. For Sr-deficiencies $x > 0.15$, this trend is reversed. Figure 3 shows the resistivity at 300 K as a function of the Sr-deficiency. Clearly, increasing the Sr-vacancy density for $x > 0.15$ results in higher resistivities and in a disappearance of the anomaly. This occurs despite the fact that the intensity ratios shown in fig. 1 indicate that vacancies are continuing to be

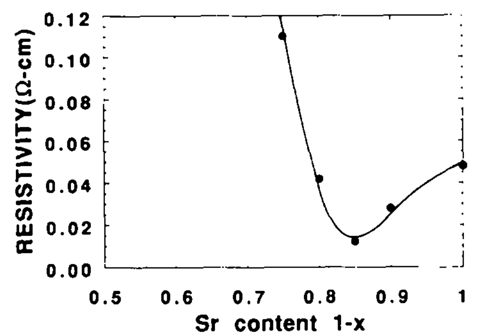

Fig. 3. Resistivity, measured at 300 K, as a function of the Sr-deficiency for $Sr_{1-x}CuO_{2-\delta}$ thin films grown at 550°C and 2 mTorr oxygen.

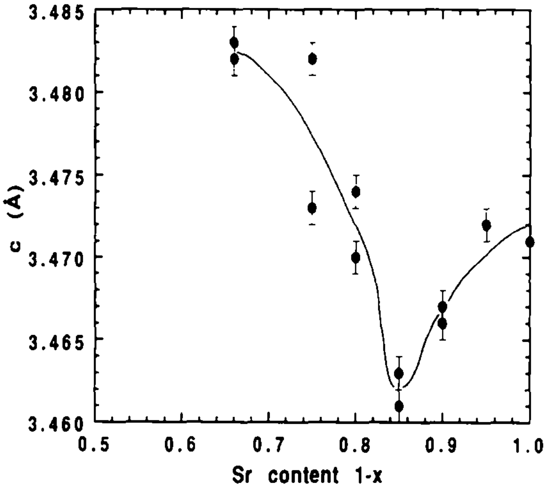

Fig. 4. C-axis lattice parameter as a function of the Sr-deficiency for $Sr_{1-x}CuO_{2-\delta}$ films grown at 550°C and 2 mTorr oxygen.

incorporated into the structure. In addition, there appears to be a one-to-one correspondence between the c-axis lattice parameter and the resistivity of these films. Figure 4 shows the c-axis lattice parameter as a function of the 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. 4 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 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 the 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 8 K. These changes in the 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 a resistivity drop at 185 K. Additional magnetic measurements indicate that this drop in the resistivity is not a manifestation of a superconducting transition, although its origin remains enigmatic.

Acknowledgements

We would like to thank P.H. Fleming for assistance with substrate preparation. This research was sponsored by the Division of Materials Sciences, US Department of Energy under contract DE-AC05-84OR21400 with Martin Marietta Energy Systems, Inc.

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