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GROWTH OF $SrCuO_2$ EPITAXIAL THIN FILMS

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We report on the growth of $SrCuO_2$ thin films prepared by RF reactive magnetron sputtering onto (100) $SrTiO_3$ substrates. Epitaxial (001) $SrCuO_2$ films are obtained at 550°C in a sputtering pressure of 1-10mTorr of Ar. Off axis x-ray analysis reveals perfect in plane ordering. We find, depending on the preparation conditions, changes in the c-axis value, which may be due to a change in the Sr-Cu-O concentrations. These modifications are correlated to changes in the resistivity of the films.

1. Introduction

The discovery of high T_c superconductivity in the $(Sr_{1-x}Nd_x)CuO_2$[1] and $(Sr_{1-x}Ba_x)CuO_2$[2] compound brought a lot of attention to this material. The reason being that the structure of this so called "infinite layer compound", represents the "key ingredient" to all high T_c superconductors. It consists of a stack of planar CuO_2 planes separated by Sr (or Ca) planes and the $CaCuO_2$ structure corresponds to the n=∞ compound of the $Bi_2Sr_2Ca_nCu_{n+1}O_{6+2n}$ and $Tl_mBa_2Ca_nCu_{n+1}O_{4+m+2n}$ series. This material is presumably much less anisotropic that other cuprates since all the planes are separated by about 3.2-3.5Å. This may be a major advantage for potential applications over other high T_c materials.

Efforts to synthesize the $CaCuO_2$ structure started right from the beginning of the high T_c rush when it became clear that all cuprate superconductors contain CuO_2 planes and, especially after the discovery that T_c increases (at least until n=3) in the BiSrCaCuO and TlBaCaCuO systems when the number of CuO_2 planes stacked per unit cell increases. The structure turned out not to be stable at ambient pressure. Roth[3] demonstrated that 14% of Sr substitution on the Ca site allows to stabilize the compound. Single crystals $Ca_{0.86}Sr_{0.14}CuO_2$ were studied by Siegrist et al.[4] to precisely determine the structure. Tentative experiments to dope this insulating antiferromagnetic material failed until the use of high pressure techniques to synthesize the material. Superconductivity at 40K in the $SrNdCuO_2$[1] and now at 110K in $SrCaCuO_2$[5] has been reported in high pressure synthesized bulk materials. Superconducting thin films of $SrNdCuO_2$ have also been reported recently[6]. Such thin films are fascinating since they provide the opportunity to study the transport properties of this material in details, and especially to investigate its anisotropy. In this paper we describe the growth of highly oriented $SrCuO_2$ films and we discuss their transport properties.

2. Experimental

The $SrCuO_2$ films were RF sputtered from a stoichiometric target onto (100) $SrTiO_3$ substrates heated at 550°C. The substrates are glued with silver paste onto a stainless steel plate which can be heated to 900°C. The temperature is measured by a thermocouple inserted in the plate, just below the substrate. The sputtering atmosphere consists of pure Ar or of a mixture of Ar and O_2 (P_{Ar}/P_{O2} =7-8). The total sputtering pressure was between 1 and 10mTorr. The substrates are facing the targets with a target-substrate distance of 7cm. RF power was 100-125W for a target diameter of 5cm. In ~15% O_2 and at 125W power we estimate the rate to be 1.4Å/s. The power applied to the target turned out to be a crucial and sensitive parameter to get highly oriented single phase films, as discussed below. After deposition the films are cooled in the same atmosphere to room temperature.

3. Structural and transport properties.

Figure 1 shows a θ-2θ x-ray diffractogram of a 5000Å thick $SrCuO_2$ film grown at 550°C in a sputtering pressure of 5mTorr, with 15% O_2. As can be seen only (00L) reflections are visible. The very intense and narrow reflections (as compared to the substrate) indicate a high degree of crystallinity. The FWHM (full width half maximum) of the (002) reflection is 0.09°. The FWHM of the rocking curve around the (002) line is only 0.12°, confirming the growth quality. The inset of figure 1 is an off-axis x-ray showing a phi scan using the (101) $SrCuO_2$ plane reflections. The four peaks come from the symmetry of the structure and indicate perfect in plane alignment. Phi scan using the (101) planes of

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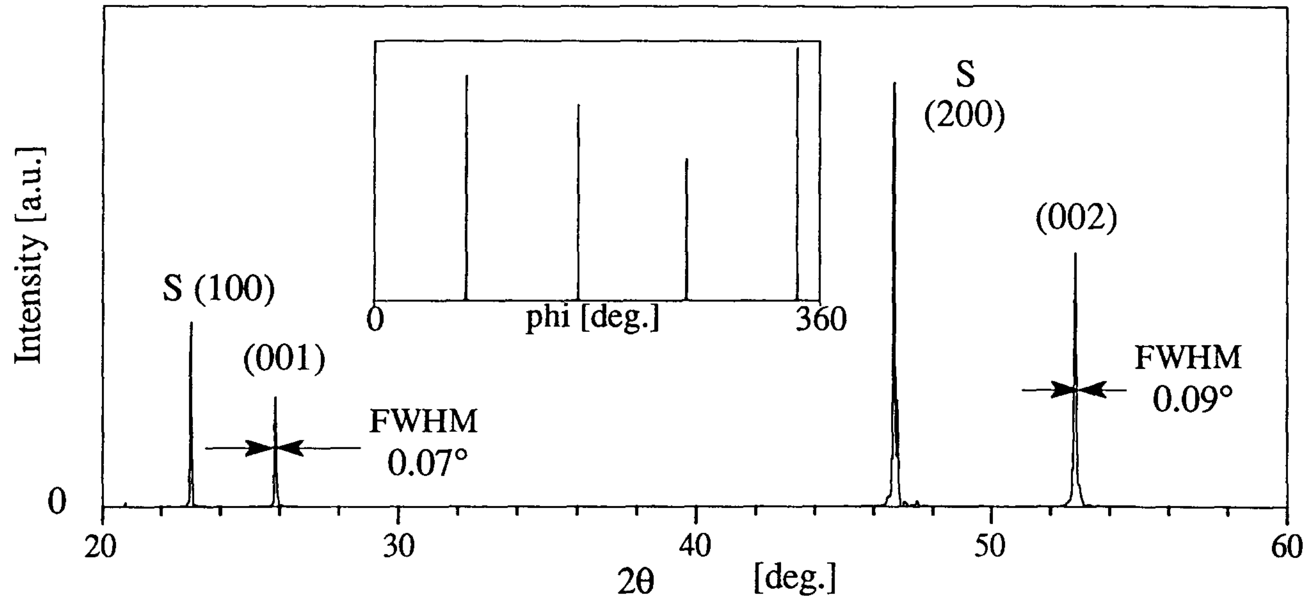

Figure 1 is a θ-2θ x-ray diffractogram of a $SrCuO_2$ sample grown with 15% oxygen. The inset is a phi scan using the (101) $SrCuO_2$ plane reflections.

the substrate shows that the a axis of the $SrCuO_2$ structure are aligned, as expected, with the (100)-(010) directions of the $SrTiO_3$ substrate, demonstrating the epitaxial growth.

To obtain such films we found that several parameters are determinant for the growth: the substrate temperature, the sputtering pressure, the presence or absence of oxygen during deposition, and the RF power applied to the target. We find, as others[6,7], that the substrate temperature has to be around 550°C. Higher substrate temperature leads to lower intensity peaks with the apparition of mixed orientations, presumably (110) and (111). The low sputtering pressure (1-10mTorr) seems to favors an excellent growth as demonstrated on figure 1. However, as it is well known for the deposition of $YBa_2Cu_3O_7$ thin films from single target[8], this technique is not ideal to insure a good stoichiometry transfer from the target to the substrate. Preliminary micro-probe analysis seems to indicate that the films are slightly Cu deficient.

Incorporation of oxygen during the growth seems to give a higher quality of crystallization, although good quality films can be obtained in pure Ar as shown on figure 2. We observed that thin films produced with oxygen have *a shorter c axis parameter*. Without O_2 the typical values for the c axis are between 3.507 and 3.521Å. This is much larger than the 3.43Å reported for bulk materials[9]. This is also larger than the values reported for thin films[6,10]. With oxygen the c axis shortens considerably to 3.44Å, a value much closer to the bulk. The effect of oxygen on the c axis length suggests that films deposited without oxygen (apart from the O_2 coming from the target) have O vacancies reducing the average Cu-O bond and thus, increasing the c parameter. This change in c axis length correlates with changes in transport properties which will be discussed below.

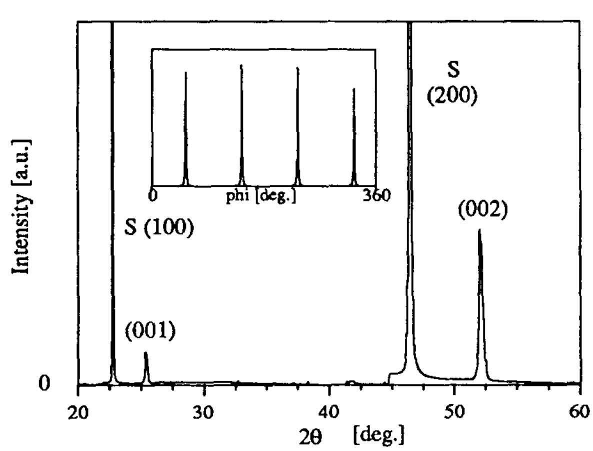

Figure 2 is a θ-2θ x-ray diffractogram of a $SrCuO_2$ sample grown without oxygen. The inset is a phi scan using the (101) $SrCuO_2$ plane reflections.

More striking is the effect of the RF power on the growth. With 100W RF power, two different phases are detected. Along with (001) $SrCuO_2$ we find the presence of $SrCu_2O_3$ as shown in Fig. 3. The peak at 54.65°, close to the (002) $SrCuO_2$ reflection for sample A (dashed line) is identified as a $SrCu_2O_3$ reflection. Notice the weak (002) $SrCuO_2$ line. The presence of this second phase is not related to the presence or absence of oxygen during the deposition. By increasing the power to 110W (125W with oxygen) the diffractogram is dramatically different as illustrated by sample B: the solid line on Figure 3. The $SrCu_2O_3$ disappears and the $SrCuO_2$ reflection is 100 times more intense. We already observed such a behavior in a preliminary study of $Ca_{0.86}Sr_{0.14}CuO_2$ films.

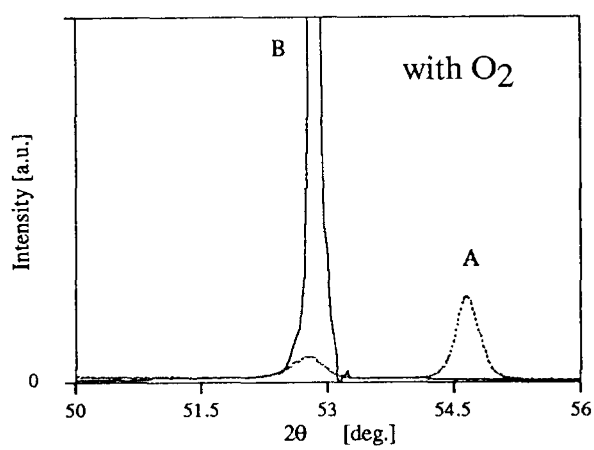

Figure 3 illustrates the effect of the RF power on the growth. The solid line is a sample grown with a 125W RF power. The dashed line is a sample grown with the same conditions but with a 110W RF power.

Figure 4 illustrates the effect of a reduction of the total pressure on the growth. The dashed line is the x-ray diffractogram of a sample grown at a total pressure of 4.3mTorr. The solid line is the diffractogram of a sample grown with the same parameters except that the total pressure was reduced to 0.7 mTorr. As can be seen the peak broadens with the appearance of a second peak. This can be interpreted as two different c axes in the sample. The peak positions are 51.9 and 52.6°, corresponding to 3.52 and 3.48Å respectively. It is not yet clear how the microstructure accounts for these two different c axis parameters but we note that superstructures have been observed in high pressure synthesized bulk samples[5]. Further investigations are necessary to understand if these two c parameters have the same origin as the superstructure observed by Azuma et al.[5].

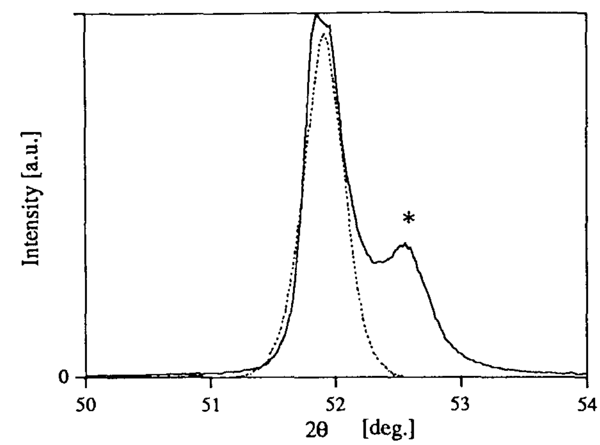

Figure 4 illustrates the effect of the total pressure on the growth. The dashed line is a sample grown at a total pressure of 4.3mTorr. The solid line is a sample grown with the same conditions but at a total pressure reduced to 0.7mTorr.

The surface quality of these films has been studied by SEM and STM. The SEM pictures look very smooth on the micron scale with only few particules on the surface. STM on a 5000Å thick sample shows also smooth surfaces with no particular features. The roughness on a 1/4μm x 1/4μm is on the order of 50Å.

Finally we want to discuss the transport properties of these films. We observe that oxygen prepared samples have a relatively low resistivity, on the order of 2500 μΩcm at room temperature. All these samples display a semiconducting behavior with no visible anomalies. Samples prepared without oxygen have much higher resistivity, typically larger than 100mΩcm. Some of these samples show anomalies in the R(T) curve. Three samples display a decrease of the resistance at temperatures between 140 and 180K. This decrease is 40% of $R(T>T_{anomaly})$ at most. The sample which shows the most pronounced anomaly, although prepared without oxygen, had a c axis parameter and a resistivity close to the oxygen prepared samples but, a markedly different behavior of the R(T) curve. This sample suggest that there is a general trend between the c axis value and the resistivity at room temperature. Magnetic measurements on samples showing anomalies in the R(T) curve were performed. One sample showed a decrease of the paramagnetic susceptibility at 90K, but none displayed any singularities at the temperature of the R(T) anomalies. Unfortunately, the sample showing the lowest resistivity along with the most pronounced decrease of resistivity degraded after the resistive measurements. Clearly, the origin of these anomalies are subtle effects, possibly related to the microstructure of the films.

4. Summary

We have grown $SrCuO_2$ thin films by RF reactive magnetron sputtering onto (100) $SrTiO_3$ substrates. Excellent quality epitaxial (001) $SrCuO_2$ films are obtained at 550°C in a sputtering pressure of 5mTorr with 15% O_2. We find that the c axis value changes dramatically with the incorporation of O_2 during the growth. We observe a correlation between the c axis value and the resistivity at room temperature. The shorter the c axis the lower the resistivity. Anomalies in the R versus T curve between 140 and 180K are observed for a few samples. These anomalies show at most a 40% decrease of the resistance with, up to now, no corresponding singularities in the susceptibility of the samples.

5. Acknowledgements

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