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Defect Formation and Carrier Doping in Epitaxial Films of the "Parent" Compound $SrCuO_2$: Synthesis of Two Superconducting Descendants

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DEFECT FORMATION AND CARRIER DOPING IN EPITAXIAL FILMS OF THE "PARENT" COMPOUND $SrCuO_2$: SYNTHESIS OF TWO SUPERCONDUCTING DESCENDANTS

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The infinite layer or parent compounds $ACuO_2$ (A: Ca-Sr-Ba) constitute the simplest copper oxygen perovskites that contain the CuO_2 sheets essential for superconductivity. The stabilization of these basic "building blocks" as epitaxial films, therefore, provides alluring opportunities towards the search for new superconducting compounds and elucidation of the underlying mechanisms. In this work, general trends of the defect formation and carrier doping for epitaxial films of the intermediate endmember $SrCuO_2$ are reviewed. First results are presented from successful attempts to induce hole-doped superconductivity via the processing-controlled incorporation of charge reservoir layers.

DEFECT FORMATION AND CARRIER DOPING IN $SrCuO_2$ FILMS.

$Sr_xCuO_{2\pm\delta}$ films were epitaxially grown on (100) $SrTiO_3$ substrates either by codeposition via single target pulsed-laser ablation [1] or atomic layer stacking of Sr(O) and CuO monolayers using RHEED-controlled laser-MBE [2]. Substrate temperatures were about 500–550°C. To investigate the nature of the majority charge carriers, reversible changes in the oxygen content were induced via low temperature (350°C) anneals at variable oxygen pressures. Since oxygen adds holes to the electronic system, hole-like and electron-like contributions lead to different dependencies of the resistivity on the oxygen pressure. Effects from key synthesis parameters are summarized in Fig. 1.

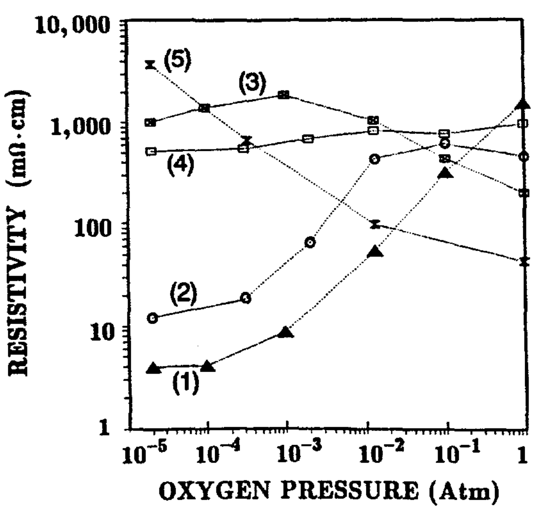

Fig. 1 Variation of the resistivity at 300 K with oxygen pressure during low temperature annealing (350°C) for codeposited $Sr_xCuO_{2\pm\delta}$ infinite layer films: (1) x = 0.85, (2) x = 1.0, (3) x = 1.2; (1)–(3): 550°C/2 mTorr; (4) x = 1.0 (550°C/200 mTorr); (5) x = 1.0 (500°C/200 mTorr).

(i) The resistivity for films grown at low oxygen pressures decreases upon Sr-vacancy incorporation. Opposite to high-pressure synthesized bulk ceramics [3], the A-ion vacancies lead to *electron-doping* rather than hole-doping; (ii) Hole-doping is enhanced (electron-doping reduced) at higher oxygen pressures and lower substrate temperatures.

Similar conclusions hold for films grown with the laser-MBE technique. With this technique, the Sr/Cu composition is instantly variable and the layer-by-layer deposition may be adjusted to optimize continuity of a streaky RHEED pattern and the magnitude of induced intensity oscillations. As reported in [2], this optimization tends to produce Sr-deficient films, indicating perhaps the existence of a *natural tendency* towards A-ion deficiency in the thin film $SrCuO_2$ infinite layer matrix. Hall and thermoelectric power measurements confirm the observed electron-doping characteristics. Taking into account the correlation with the oxygen pressure during epitaxial growth, we assume that the electron-doping in the Sr-deficient films results from oxygen vacancies in the $CuO_{2-\delta}$ sheets. Although relatively low resistivities were in fact obtained, superconductivity was not observed for any of the Sr-deficient films.

INCORPORATION OF CHARGE RESERVOIR LAYERS.

The absence of hole-doping in the Sr-deficient films indicates that charge reservoir layers containing apical oxygen atoms may be needed to induce (hole-doped) superconductivity. This conclusion is supported by the onset of hole-doping for the Sr-rich "infinite layer" films and the observation of high densities of planar defects in superconducting bulk specimens [3]. Two methods for the controlled introduction of such charge reservoir layers were explored in the present study, schematically depicted in Fig. 2.

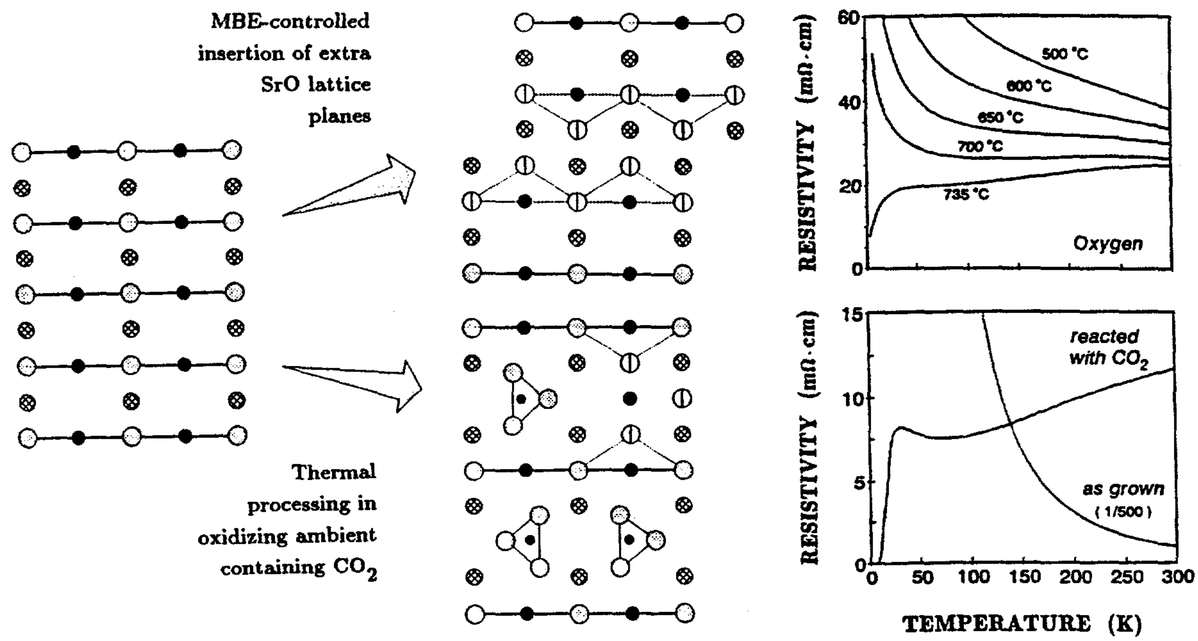

Fig. 2 Schematic representation of the introduction of charge reservoir layers in the $SrCuO_2$ infinite layer lattice. Partially occupied oxygen sites are indicated by open circles with vertical line. The onset of superconductivity is illustrated on the right.

The first method involves the MBE-controlled "insertion" of extra SrO lattice planes between n unit-cell thick $SrCuO_2$ codeposited blocks ($n = 3$–9). The Ruddlesheim-Popper phases aimed for have the structure formula $Sr_{n+1}Cu_nO_{2n+1}$ [4]. Although hampered by an island-like growth mechanism, the extra SrO monolayer deposits were effective in inducing hole-doping (as grown) and superconductivity after high temperature oxygenation (~ 750°C) and rapid cooling [5]. The second method involves the substitution of Cu atoms by CO_3 radicals via post-growth thermal processing. Accordingly, $SrCuO_2$ films were annealed in oxidizing ambient (air) containing ~400 ppm of added CO_2 [6]. A new phase appeared for annealing temperatures around 700°C, identified as isomorphic with the oxycarbonate $SrCuO_2(CO_3)$ [7]. The presence of carbon atoms on substitutional lattice sites was confirmed by ion beam analysis using the $^{12}C(p,p)C^{12}$ enhanced elastic backscattering cross section for protons incident at 1.73 MeV. The hole doping giving rise to superconductivity in this oxycarbonate phase presumably results from excess oxygen in mixed occupancy (Cu,C) lattice planes [7].

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