Electron-doped superconductivity in $Sr_{1-x}Ca_xCuO_{2-\delta}$ infinite layer thin films

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Abstract

Thin films of infinite-layer compound $Sr_{1-x}Ca_xCuO_{2-\delta}$ have been prepared by rf magnetron sputtering. For an optimum level of oxygen vacancy superconductivities were observed ($T_{c\ onset}$=42 K and 50 K, $T_{c\ (\rho=0)}$=11 K and 20 K). Structural and transport data suggest that the doping mechanism is electron-type. The superconducting transitions were also confirmed by *ac* susceptibility. Further increase of doping showed to destroy superconductivity.

Key words: Infinite-layer; Electron-dope superconductivity; Oxygen vacancy

1. Introduction

The "infinite-layer" [1] compound $ACuO_2$ (where A is an alkaline earth (AE) metal) can be chemically doped, by partial substitution of rare earth atoms such as La, Nd, or Gd for Sr, to become an electron-doped (n-type) superconductor in both bulk [2] and film [3] samples. Another situation is when vacancies may be incorporated on A lattice site according to the structure formula $(Sr_{1-x}AE_x)_{1-y}CuO_{2\pm\delta}$. In this case superconductivity with a maximum T_c > 100 K has been observed [4,5]. The much higher T_c values suggest that the superconductivity results from hole doping (p-type). However, the detailed nature of the pertinent doping mechanism has not yet been conclusively identified. Even when only the Sr-vacancies are present, the high quality $Sr_{1-x}CuO_{2-\delta}$ thin films clearly showed the tendency of electron doping [6]. The idea is that the competition between the oxygen deficiency (δ) and the AE deficiency may result in additional carriers as the Cu valence changes to accommodate these vacancies. It strongly suggests that n-type superconductivity is possible in the AE stoichiometric infinite-layer system by just reducing the oxygen content.

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2. Experimental

Desired compositional mixtures of $SrCO_3$, $CaCO_3$, and CuO were calcined at 950^{o}C for 20 hours, pressed into plates, and fired at 980^{o}C for 20 hours. $Sr_{1-x}Ca_xCuO_{2-\delta}$ thin films with infinite-layer structure were grown by single target off-axis *rf* magnetron sputtering on $SrTiO_3$ (100), at temperatures between 450^{o}C and 600^{o}C.

3. Results and discussion

Oxygen deficiencies in $Sr_{1-x}Ca_xCuO_{2-\delta}$ thin film could be induced either by reducing partial pressure of oxygen or by increasing substrate temperature (T_s). In order to introduce sufficient oxygen vacancies in the

$Sr_{1-x}Ca_xCuO_{2-\delta}$ ($x = 0.4$) infinite-layer phase, we reduced the partial pressure of oxygen (O_2/Ar = 1/3) with the fixed total pressure of 2.66 Pa. In addition, after the film deposition, an *in-situ* vacuum annealing was carried out for 60 min at temperatures between 450^{o}C and 550^{o}C.

Figure 1 shows the variation of the lattice parameter c as a function of T_s. It shows clearly that lattice constant c decreases systematically with increase of T_s. Enhancement of the number of oxygen vacancies in the CuO_2 sheets would enhance the electrostatic attraction between the intermediate AE layers, and thus the c lattice parameter should shrink [6]. At the same time, more vacancies in the CuO_2 sheets means addition of electrons to Cu-O bonds that will expand a lattice parameter [5]. Indeed, the a-axis lengths observed by the in-plane lattice checking are 0.39154 nm, 0.39246 nm and 0.39340 nm for samples prepared at T_s = 510^{o}C, 515^{o}C and 530^{o}C, respectively.

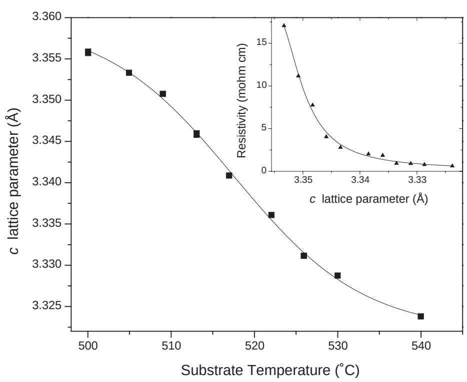

Fig. 1. Variation of the lattice parameter c as a function of T_s. Inset: the relation between the room temperature resistivity and the lattice parameter c.

The transport properties of the films were measured along the in-plane direction. For most samples prepared at lower T_s, the temperature dependence of resistivity shows semiconducting behavior. The room temperature resistivity of the films tends to decrease with decrease of c lattice parameter (inset of Fig. 1), suggesting electron doping through the increase of oxygen vacancies in CuO_2 plane.

For an optimum level of oxygen vacancy, two typical superconducting transitions with $T_{c\ onset}$ = 42 K and 50 K and $T_{c\ (\rho=0)}$ = 11 K and 20 K were obtained for sample A and B (for both, c = 0.33409 nm and a = 0.39293 nm), respectively (Fig. 2). The transitions are somewhat broad, indicating some inhomogeneity. In addition, we have measured the temperature dependence of *ac* susceptibility. In the inset of Fig. 2, the diamagnetic drops at 40 - 50 K can be observed, and there are two sharp decreases at 15 K and 22 K, respectively, for sample A and B.

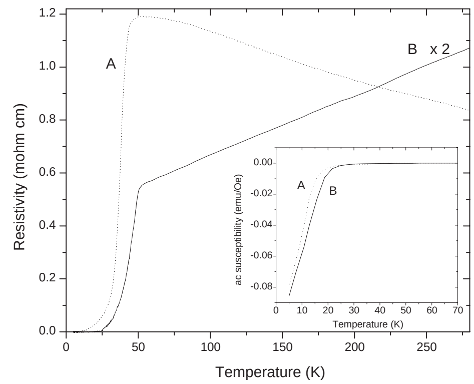

Fig. 2. Temperature dependence of resistivity for the superconducting sample A and B. The inset shows the temperature dependence of *ac* susceptibility, measured with *ac* field amplitude of 1 Oe and frequency of 997 Hz in the absence of *dc* field.

As the doping level is increased further, we observe metal-like conductivity over a wide temperature range, however, no sharp resistive drop is found. The disappearance of superconductivity strongly suggests that further increase of T_s will induce too many oxygen deficiencies in CuO_2 planes and thus destroy superconductivity. It is possible that the structural changes could also affect the resistivity.

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References

[1] T. Siegrist, S. M. Zahurak, D. W. Murphy and R. S. Poth, Nature **324** (1988) 231.

[2] N. Ikeda, Z. Hiroi, M. Azuma, M. Takano, Y. Bando, and Y. Takeda, Physica C **210** (1993) 367.

[3] S. Karimoto, K. Ueda, M. Naito, and T. Imai, Appl. Phys. Lett. **79** (2001) 2767.

[4] M. Azuma, Z. Hiroi, M. Takano, Y. Bando and Y. Takeda, Nature **356** (1992) 775.

[5] H. Shaked, Y. Shimakawa, B. A. Hunter, R. L. Hitterman, J. D. Jorgensen, P. D. Han and D. A. Payne, Phys. Rev. B **51** (1995) 11784.

[6] R. Feenstra, X. Li, M. Kanai, T. Kawai, S. Kawai, J. D. Budai, E. C. Jones, Y. R. Sun, J. R. Thompson, S. J. Pennycook and D. K. Christen, Physica C **224** (1994) 300.