The influence of oxygen deficiency and the unbalance Bi/Sr in Bi$_2$Sr$_2$CuO$_{6+\delta}$ on metal-insulator transition

A.V.Pop$^1$, I. Matei$^1$ and V.Pop$^2$

$^1$ Babes-Bolyai University, Faculty of Physics, 400084 Cluj-Napoca, Romania

$^2$ Technical University Cluj-Napoca, Faculty of Materials Science and Engineering, Department of Physics, Technical University, Cluj-Napoca, Romania 400641, Cluj-Napoca, Romania.

E-mail: avpop@phys.ubbcluj.ro

Abstract. Epitaxial Bi:2201 superconducting thin films ($T_c \approx 7$K) with the composition Bi:Sr:Cu=2:1.95:1.01 and Bi:Sr:Cu=2.1:2:1.01 were deposited onto SrTiO$_3$ substrate by using different partial oxygen pressures ($f_{O_2}$) in the DC magnetron sputtering system. The compositions and structural characterization of the deposited films were carried out by (EDX), and X-ray diffraction measurements. The effect of Bi excess, Sr deficiency and the partial oxygen pressure in the sputtering gas on the metal-insulator transition are presented from the electrical resistivity data.

1. Introduction

The compound Bi-2201 is a convenient system for studying the normal state properties. The ‘2201’ phase in the Bi$_2$O$_3$–SrO–CuO bulk system is known to adapt itself to various Bi:Sr:Cu ratios [1–2]. In Bi$_{2+c}$Sr$_{2-x}$CuO$_{6+\delta}$ for $0<x<0.1$, the change in oxygen content induces the exchange of small amounts of Bi and Sr ions between the ‘BiO’ and ‘SrO’ sheets. Bi:2201 (T$_c<10$K) is one of the most interesting candidate to test the unusual properties of HTS, as the linear-T behavior of electrical resistivity in a large temperature range. Some reports revealed that Bi:2201 is superconducting with $T_c=6$-10K at a narrow range of Bi:Sr ratio [3]. The mismatch between BiO layers is reduced by the incorporation of extra oxygen in the BiO layer. The additional oxygen creates holes in the conducting band and lead to corrugation of CuO$_2$ plane, which influenced the normal and superconducting properties. Bi:2201 epitaxially thin films grown by RF sputtering on a SrTiO$_3$ substrate at $T_s=9$K presents a clear nonmetallic upturn near the superconducting transition [4]. Because of vacancies in the CuO$_2$ planes caused by expelling interstitial oxygen atoms (after the vacuum annealing or after some thermal treatments) the Bi:2201 superconductor is found to have a large residual resistivity [5]. By controlling the oxygen concentration $\delta$ (by successive annealing treatments of Bi$_2$Sr$_{1.6}$La$_{0.4}$CuO$_{6+\delta}$) the same film is changed from over doped to strongly under doped state [6]. Similarly results were obtained by the control of oxygen concentration in the sputtering gas [7-8].

Here we present results obtained from XRD and electrical resistivity of c-axis oriented epitaxial Bi:2201 thin films (with the composition Bi:Sr:Cu=2:1.95:1.01 and Bi:Sr:Cu=2.06:2:1.01) deposited onto SrTiO$_3$ substrate using a magnetron sputtering method. The effect of oxygen concentration in the
sputtering gas on the temperature dependence of electrical resistivity and lattice parameters is presented.

2. Experimental

Bi:2212 films with thickness of approximately 200 nm were deposited onto heated single crystal SrTiO$_3$ (100) substrate by using a cylindrical DC magnetron for the sputtering. The composition of the deposited films carried out by (EDX) is Bi: Sr: Cu = 2: 1.95: 1.01 (named sample F-Sr because is Sr deficient) and Bi: Sr: Cu = 2.06: 2: 1.01 (named sample F+Bi, because is Bi rich sample). The sputtering gas was a mixture of oxygen and argon with the partial pressure ratio f$_{O2}$/f$_{Ar}$ in the range 0.6/0.4 - 0.30/0.70. The deposition pressure was 1 mbar and the substrate temperature was 700°C. After deposition the films were annealed at 500°C in an oxygen atmosphere (1 mbar).

The epitaxial properties of the deposited films were characterized by X-ray diffraction (XRD).

The films were chemically patterned and equipped with silver sputtered contacts pads. The temperature dependence of the in-plane resistivity was measured by using a standard four contacts dc method.

3. Results and discussion

Figure 1 shows XRD patterns for the Bi excess film (named F+Bi) for f$_{O2}$ = 0.55. The XRD 2θ/θ−scanning patterns showed the presence of peaks associated exclusively to (00l) planes, and confirmed that the film had c axis orientation of Bi:2201 and c = 24.60 Å. By increasing the oxygen fraction f$_{O2}$ in sputtering gas, the length of c axis decrease to c = 24.46 Å for f$_{O2}$ = 0.60. Similar behavior was obtained for Sr excess film (F+Sr) (the increase of oxygen fraction in sputtering gas from f$_{O2}$ = 0.3 to f$_{O2}$ = 0.60, lead to the decreases of c axis length from c = 24.58 Å to c = 24.40 Å).

Figure 2 shows that temperature dependence of electrical resistivity ρ(T) for Bi:2201 films is sensitive to the oxygen concentration in sputtering gas and to the unbalance Bi/Sr. The room temperature resistivity increases monotonically with decreasing f$_{O2}$. For F+Bi film with oxygen fraction f$_{O2}$ = 0.55 electrical resistivity shows above 60K a linear temperature dependence and the maximum value of critical transition temperature T$_c$ = 7.6 K. Similar results were obtained for f$_{O2}$ = 0.45 in F-Sr film with T$_c$ around 8K. This behavior corresponds to a state near the optimum doping by holes in CuO$_2$ planes. The normalized conductivity (σ/σ$_{opt}$)$_{300K}$ (were σ$_{opt}$ is the conductivity for optimal doping) was used to characterize the oxygen doping (and the hole concentration p), because the Hall

![Figure 1. The X-ray diffraction patterns for F+Bi film deposited on SrTiO3 substrate by using in the sputtering gas an oxygen fraction fO2 = 0.55.](image-url)
number \( n_H \) varies nearly linearly with the number \( p \) of holes per Cu and with \((\sigma/\sigma_{op})_{300K}\), respectively [6].

\[ \rho \propto f \frac{\sigma}{\sigma_{op}} \]

**Figure 2.** Electrical resistivity versus temperature for Bi:2201 with Sr deficiency (F-Sr) and Bi excess (F+Bi). The insert show electrical resistivity versus \( \ln T \) in lower temperature region for Bi excess films. The vertical lines show the temperature range for linear dependence, for thin films obtained by \( f_{O_2} = 0.45 \) and 0.35.

Figure 3 shows that the critical temperature is a parabolic function of \((\sigma/\sigma_{op})\), in agreement by the empirical parabolic function: \( T_c/T_{c_{max}} = 1 - 82.6(p-0.16)^2 \) [9]. The increase of oxygen concentration \( f_{O_2} \) in the synthesis processes of F+Bi rich films lead to the change of holes concentration from under doped to optimal doped samples. For F-Sr films the change is from optimal doping to over doped. This behavior is in agreement by the observation that the addition of Bi cation caused an under doping effect (samples F+Bi) and the depletion of Sr ions lead to over doping effect [10].

**Figure 3.** The dependence of superconducting transition temperature \( T_c \) function of parameter \((\sigma/\sigma_{op})_{300K}\), for F+Bi films (square) and for F-Sr films (circle).
For $f_{O2}=0.45$ in F+Bi film ($T_c=6.9K$) the occurrence of insulating behavior start at the temperature $T_M=48K$, where $\rho(T)$ is minimum. By decreasing $f_{O2}$ below 0.35 the films loss the superconductivity and $T_M$ increases.

The insert of figure 2 shows the $\rho_{ab}$ data vs. $\ln T$ for under doped F+Bi films with $f_{O2}=0.35$ and 0.45. The plot gave almost a straight line in the temperature range 12K-38K. The logarithmic temperature dependence of electrical resistivity was obtained taking into consideration a model of strong correlated electronic system with a single particle self-energy of the marginal Fermi liquid, and in the presence of randomly distributed nonmagnetic impurities, [11].

4. Conclusions

Bi:2201 thin films with the composition Bi: Sr:Cu=2:1.95:1.01 and Bi: Sr:Cu=2.1:2:1.01 were deposited in situ onto SrTiO$_3$ substrate by DC magnetron sputtering by using different partial oxygen pressures ($f_{O2}$) in the sputtering gas.

By increasing $f_{O2}$, $\rho(T)$ changed from under doped regime to optimally doped for excess Bi films (F+Bi), and from optimally doped to over doped for Sr depleted films (F-Sr), respectively.

A log (1/T) behavior of $\rho(T)$ is present for $T\leq38K$ in the region of the metal – insulator (MI) transition of under doped (F+Bi) films.

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