Fabrication of BSCCO Films using CVD Process

Sang-Heon Lee[a]
Department of Electronics Information and Communication Engineering, Sun Moon University, Asan, Chung nam 336-840, Korea

[a]E-mail : shlee@sunmoon.ac.kr

(Received June 22 2004, Accepted July 29 2004)

BiSrCaCuO thick films were fabricated by plasma enhanced chemical vapor deposition, and the crystallinity and the superconducting properties were investigated. The superconductivity was achieved at 20 K with an onset temperature of around 90 K in the film prepared at 720 °C. From X ray diffraction analysis, the main superconducting phase in the films was the low Tc phase at 700 ~ 750 °C and the high Tc phase at 750 ~ 800 °C.

Keywords : BSCCO, Chemical vapor deposition, Thick films, Low Tc phase, High Tc phase

1. INTRODUCTION

Chemical vapor deposition (CVD) is thought to be one of the most desirable methods for preparing superconducting BiSrCaCuO films. CVD can control the film thickness to within a mono atomic layer accuracy for the growth of compound semiconductors, which is one of the key technologies for the fabrication of oxide superconducting films. Low temperature processing is very important for the application of films to superconducting devices because a chemical reaction of the superconductor with the substrate is apt to proceed t high temperature. Recently, fabrications of superconducting films at lower temperatures have been attempted using plasma assisted CVD because the decompositions of the metal organic sources are accelerated and the oxygen gas is activated in the plasma. However, as deposited BiSrCaCuO superconducting films with critical temperatures higher than 10 K have not been obtained by using either thermal CVD or plasma assisted CVD at less than 800 °C . If low temperature deposition can be achived by thermal CVD, as well as physical vapor deposition methods, from the viewpoints of the simplicity and the reliability of the apparatus and its amenability to large scale processing. A low deposition rate improves the film thickness control and the properties of the films and lowers the deposition temperature because the lower deposition rate allow enough time for the migration of deposits on the surface. However high growth temperatures of over 750 °C[1] have been required to grow superconducting thick films. Thus, a concerted effort has been made to decrease the growth temperature to enable CVD to be applied to electronic processes, because a reaction between the superconductor and the substrate proceeds at such a high temperature[2]. In this paper, we discuss the fabrication of BiSrCaCuO thick films by using CVD, their crystallinity, and their superconducting properties.

2. EXPERIMENTAL PROCEDURE

A magneto microwave plasma type apparatus was used for growing the superconducting thick films. The frequency of the microwave, which was generated by a magnetron, was 2.45 GHz. The tetramethylheptadione complexes of Sr, Ca and Cu were employed as metal sources. For the bismuth source, $Bi(ph)_3$, was utilized because of its superior volatility and chemical stability. Evaporation temperatures of 100 ~ 200 °C and an Ar gas carrier flow rate of 50sccm were used to transport the metal organic source to the reactor. Ar gas carrying each metal organic source and oxygen gas as an oxidant were mixed prior to entering the reactor. The depositions were carried out on single crystal (100) MgO substrates located on Inconel alloy susceptors. The deposition rates employed were 0.5 nm/min. Oxygen gas was an oxidant. MgO (100) single crystals polished with phosphonic The crystallinity was investigated by X-ray diffraction (XRD). The chemical composition of the films was determined by inductively coupled plasma (ICP) spectroscopy. The electrical properties were determined by the conventional four probe method.

3. RESULTS AND DISCUSSION

The effect of the plasma enhancement on the composition of the prepared thick films is shown in Fig. 1. Fig. 1 shows the XRD patterns of BiSrCaCuO thick films prepared at higher than 750 °C with the deposition rate of 0.5nm/min. The chemical compositions for film were $Bi_{2.0}Sr_{2.0}Ca_{2.0}Cu_{3.0}O_x$ and $Bi_{2.3}$ $Sr_{2.0}Ca_{2.3}Cu_{3.0}O_x$, respectively.

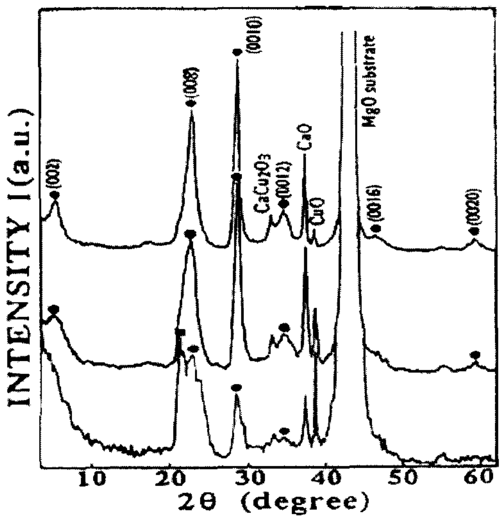

Fig. 1. XRD patterns of the films prepared at 750 °C and (b) 700 °C.

The main diffraction peaks for film (a) and (b)are assigned to the high Tc phase ($Bi_{2.0}Sr_{2.0}Ca_{2.0}Cu_{3.0}O_x$) with the c-axis perpendicular to the (100) MgO substrate. The lattice constant, c, for the high Tc phase of the films (a) and (b) was estimated to be 37.1 Å from the (0010), (0012) and (0014) diffractions. The XRD patterns of the BiSrCaCuO thick films prepared at lower than 750 °C with a deposition rate of 0.14 nm/m are in Fig. 2.

The chemical compositions for the thick films in Fig.2 (a)-(c) were $Bi_{2.0}Sr_{2.0}Ca_{2.0}Cu_{3.2}O_x$, $Bi_{2.3}$ $Sr_{2.0}Ca_{2.3}Cu_{4.1}O_x$ and $Bi_{2.1}Sr_{2.0}Ca_{2.2}Cu_{3.7}O_x$, respectively. In the films (a) and (b) prepared 750 °C and 720 °C, respectively, however, mainly the diffraction peaks for the low Tc phase were not observed, while the chemical compositions of the films were close to that of the high Tc phase. In the films (c) prepared at 700 °C the low Tc phase and the semiconductive phase coexisted. CaO, CuO and $CaCu_2O$ diffraction peaks other than from the superconducting phase were also observed in the films prepared at less than 750 °C. This results suggests that the Ca layer and Cu-O layer of the superconducting phases are hardly constructed at the low temperature ; therefore, not the high Tc phase, but the low Tc phase and the semiconductive phase for which the numbers of Ca and Cu-O layers are less than those in the high Tc phase, are formed.

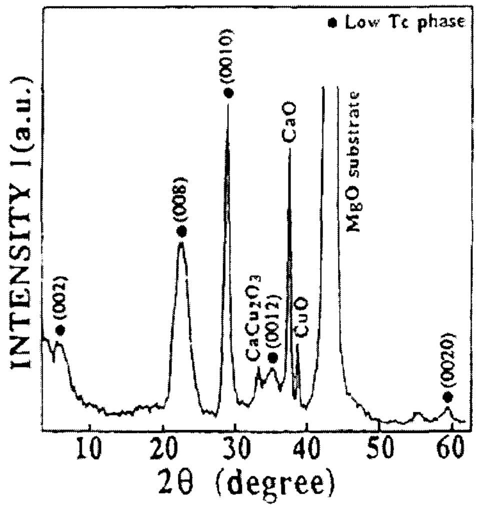

Fig. 2. XRD patterns of the BiSrCaCuO thick films prepared (a) 750 °C, (b) 720 °C and (c) 700 °C at a deposition rate of 0.14 nm/mim for 4hours. ● : low Tc phase.

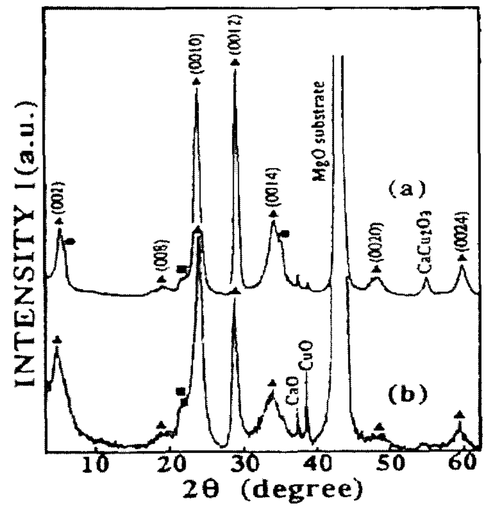

Fig. 3. XRD pattern of the film deposited at 700 °C at a deposition rate of 0.06 nm/mim for 8 hours.

The film in Fig. 3 was prepared at 700 °C at a lower deposition rate than the film in Fig. 2 (c). The decomposition rate for the film in Fig. 3 was 0.06 nm/mim which was half that for the film in Fig. 2 (c). As shown in Fig. 3, the diffraction peaks for the low Tc phase were observed while those of the semiconducting phase were not observed, unlike the film with the deposition rate of 0.14 nm/mim. This result indicates that the insertion of the Ca and Cu-O layers to the perovskite related structure is prompted by lowering the deposition rate.

Figure 4 shows the temperature dependences of resistance for the films as a function of the deposition temperature. The onset temperatures were achieved at around 100 K in the films prepared at higher than 800 °C. The onset temperatures of the films prepared at c, d, e arein Fig. 2 for 250, 220 and 700 °C, 750 °C and lower were around 90 K. Full superconductivity was achieved at 75 K in the film prepared at 850 °C, and Tc, 0 of films, decreased with decreasing deposition temperature. The Tc, 0 of the film prepared at 800 °C. It is speculated that the high Tc phase, mainly include in the film (b) is more weakly linked than the low Tc phase in the film (c), likely because the high Tc phase of the film (c) contains many intergrowth defects, judging from the brod diffraction peaks for the film (b) as shown in Fig. 1 (b). Film (d) prepared at 72 °C exhibited full superconductivity at 20 K while films (e) and (f) prepared at 700 °C did not reach the zero resistance at higher than 15 K.

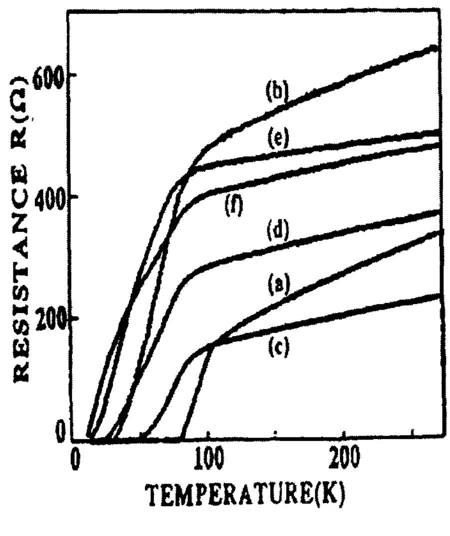

Fig. 4. Temperature dependences of the resistance for the films prepared at (a) 850 °C, (b) 800 °C, (c) 750 °C, (d) 720 °C, (e) 700 °C , and (f) 700° C.

4. CONCLUSION

The effects of plasma enhancement on BiSrCaCuO thick films grown by CVD were investigated. BiSrCaCuO thick films were fabricated by plasma enhanced chemical vapor deposition, and the crystallinity and the superconducting properties were investigated. The superconductivity was achieved at 20 K with an onset temperature of around 90 K in the film prepared at 720 °C. From X ray diffraction analysis, the main superconducting phase in the films was the low Tc phase at 700 ~ 750 °C and the high Tc phase at 700 ~ 750 °C.

REFERENCES

[1] J. Yang, D. Shi, X. Wang, A. Liu, and G. Yuan, “Fabrication of YBCO coated conductors using magnetron sputtering”, Physica C, Vol. 341, p. 2499, 2000.

[2] G. Celentano, C. Annio, V. Boffa, L. Cioneta, F. Fabbri, Gambradella, V. Galluzzi, and A. Mancini, “Superconducting and structural properties of YBCO thick films grown on biaxiaaly oriented architecture”, Physica C, Vol. 341, p. 2501, 2000.

[3] Y. Dimitriev and E. Kashchieva, “Charge-density-wave transport properties”, J. Mater. Sci., Vol. 10, No. 2, p. 1419 , 1995.