Journal of Electronic Materials, Vol. 21, No. 10, 1992

Fabrication of Bi(Pb)-Sr-Ca-Cu-O Superconducting Thin Films by Rapid Thermal Annealing

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Superconducting Bi(Pb)-Sr-Ca-Cu-O thin films were successfully fabricated on MgO substrates by dc sputtering and rapid thermal annealing. No furnace annealing was used in the process. The superconducting thin films, deposited by dc sputtering for 8 hr and rapid thermally annealed at 845° C for 60 sec, showed a superconducting transition onset temperature of 110 K and a zero resistance transition temperature of 86 K. Highly oriented films with the c-axis normal to the substrate surface were obtained. To our knowledge, this is the first time that Bi(Pb)-Sr-Ca-Cu-O superconducting thin films have been fabricated using rapid thermal annealing.

Key words: High T_c superconductor, Bi-Sr-Ca-Cu-O, thin films, rapid thermal annealing

I. INTRODUCTION

The early application of high transition temperature superconductors depends on the feasibility of fabricating high quality thin films. For the BiSrCaCuO superconductor material system, many superconducting thin film deposition techniques have been studied, including electron beam evaporation,[1,2] sputtering,[3,4,5] laser ablation[6,7,8] and molecular beam epitaxy.[9,10] In general, the as-deposited BiSrCaCuO films are not superconducting and require a high temperature post-annealing step to achieve superconductivity. The annealing is usually performed in a furnace with the temperature ranging from 800 to 900° C and the annealing time period ranging from a few min to several hr. There is significant interdiffusion between the superconductor and the substrate, causing many problems in thin film preparation. Recently, there have been some reports on in-situ deposition of Bi(Pb)SrCaCuO thin films with substrate heating.[5,11,12,13] Rapid thermal annealing (RTA) is another desirable way to anneal the superconducting thin films without excessive interdiffusion. In this work, superconducting Bi(Pb)SrCaCuO thin films were fabricated by dc sputtering and rapid thermal annealing. To the best of our knowledge, this is the first time that Bi(Pb)SrCaCuO thin films have been achieved with rapid thermal annealing.

II. EXPERIMENT

There exists three superconducting phases with T_c = 9 K, 80 K and 110 K in the BiSrCaCuO system which correspond to nominal compositions of 2:2:0:1, 2:2:1:2 and 2:2:2:3, respectively.[14] The preparation procedure of partially substituting Pb for Bi has been shown to be effective in lowering the sintering temperature for obtaining the 110 K superconducting phase.[15] In this paper, the Bi(Pb)SrCaCuO thin films was deposited using dc sputtering method. The dc sputtering process was similar to that described in a previous publication[14] and will be only briefly mentioned here. The sputtering target had a diameter of 54 mm and a thickness of 3 mm. The nominal composition was $Bi_{1.6}Pb_{0.4}Sr_2Ca_2Cu_3O_x$. It was made by hot pressing the thoroughly mixed Bi_2O_3, PbO, $SrCO_3$, $CaCO_3$ and CuO powder mixture at 700° C and 1000 psi for 1 hr and followed by sintering at 845 C for 24 hr. MgO single crystal wafer, (100) orientation, double side polished, was used as the substrate. Sputtering was carried out under pure argon gas with a pressure of 0.05 millibar. The applied discharge was typically run at 165 V and 75 mA. The substrate was placed on a stationary holder at a distance of 40 mm from the target. The substrate holder was kept at room temperature and the deposition rate was typically 2.5 nm/min.

The as-deposited films are amorphous and can be converted into polycrystalline form by rapid thermal annealing. The RTA was performed using an AG Associates Heatpulse model 410 in the temperature control mode. The temperature profile was designed so that the deposited thin film can be heated up rapidly by tungsten-hallogen lamps with a ramp rate of 125 C/sec, maintained at a constant temperature for 30 to 120 sec, and then ramped down to 250° C with a rate of 125° C/sec. All RTA cycles were performed in an atmospheric environment. After RTA, the resistance of the thin films were measured by a standard four-point measurement. Gold wire contacts to the samples were held in place with silver paste. The phase structure in the thin films

(Received March 3, 1992)

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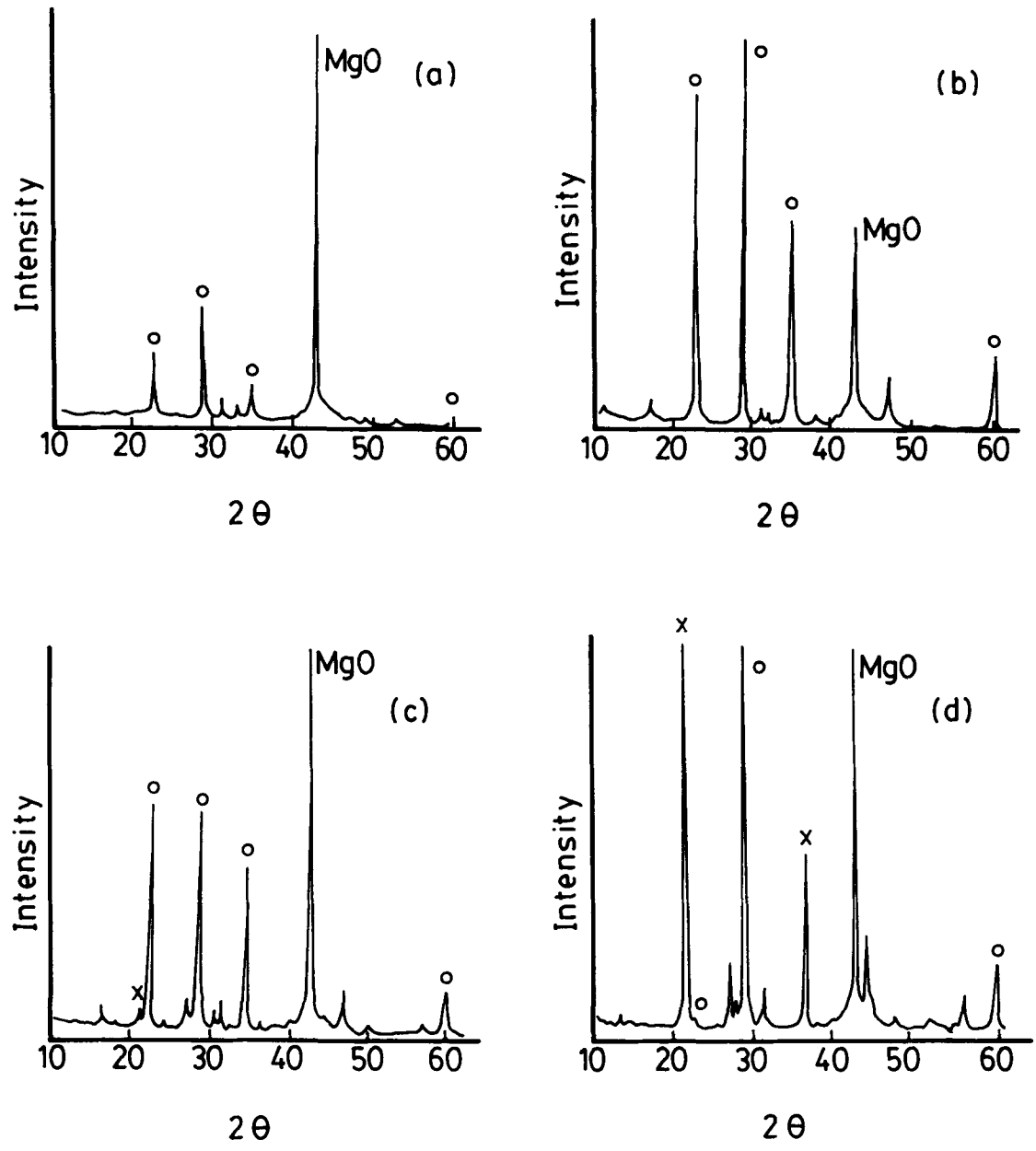

Fig. 1 — X-ray diffraction patterns of superconducting thin films deposited by dc sputtering for 2 hr and rapid thermally annealed for 60 sec at (a) 795° C (b) 820° C (c) 845° C and (d) 895° C. The vertical axis is x-ray intensity. The horizontal axis is two times the diffraction angle. 0 represents (2212) phase and x represents (2201) phase.

was analyzed by x-ray diffraction and the corresponding surface morphology by scanning electron microscopy (SEM), respectively.

III. RESULT AND DISCUSSION

Two series of experiments were carried out in this work to find out the important parameters in rapid thermal processing of Bi(Pb)SrCaCuO superconducting thin films.

The RTA temperature was first varied as a process parameter. In this experiment, thin films deposited by dc sputtering for 2 hr were used as samples of study. These films were then RTA treated for a fixed period of 60 sec with different RTA temperatures of 795, 820, 845 and 895° C.

The as-deposited amorphous films are converted into polycrystalline structure by RTA. The x-ray diffraction patterns of the annealed films, shown in Fig. 1, reveal that they are mainly composed of (2212) phase, with some (2201) phase observed. The films annealed at 820 and 845° C show zero resistance at temperatures of about 50 and 40 K, respectively. The onset transition temperature is 80 K. The films annealed at too low (795° C) or too high (895° C) a temperature are not superconducting. The range of temperature measurement is from 10 to 300 K. The SEM micrograph (Fig. 2) reveals that the films consist of platelike crystalline grains distributed among a pastelike matrix. The higher the annealing temperature, the longer the plates and the larger the proportion of the platelike structure.

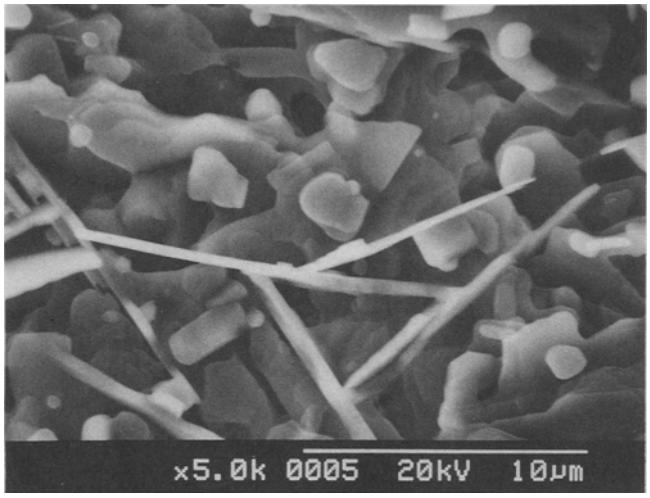

Fig. 2 — Scanning electron micrograph of superconducting thin film deposited for 8 hr and rapid thermally annealed at 845° C for 60 sec, which typifies the microstructure of RTA treated Bi(Pb)SrCaCuO thin films.

The x-ray patterns confirm the existence of (2212) superconducting phase and the SEM micrograph shows distinct and separate phases. This indicates that zero resistivity of the thin films is linked with the fact that the superconducting phases are interconnected. The films annealed at 820° C consists of larger proportion of (2212) phase which is indicated by the relatively high diffraction intensity of (2212) phase compared to that of the MgO substrate so that fair superconductivity is obtained. The cause of nonsuperconductivity for films annealed at 795° C can therefore be ascribed to the low proportion of (2212) phase, which again is indicated by the relatively low diffraction intensity of (2212) phase compared to that of MgO. For the films annealed at 895° C, large amounts of (2201) phase are observed. The connectivity of (2212) phase is reduced significantly such that no superconductivity is observable. The phenomenon also occurred in furnace annealing situations, where the (2223) phase are observed to decompose to (2201) phase and superconductivity is degraded seriously when annealing is performed at too high a temperature (895° C).[14]

The above results indicate that the RTA process is capable of converting the amorphous phase into crystalline superconducting phase in an appropriate temperature range and within a very short time interval. The difficulty of Pb-loss still remains, since the annealing atmosphere is not controlled in this experiment. This is implied by the fact that only the (2212) phase is attainable in all annealed samples. The proportion of (2212) phase could be increased by extending the annealing time. This is, however, not a good practice. Because the purpose of using RTA technique for post annealing treatment is to prevent the film-substrate interaction which is important when semiconducting materials such as silicon or GaAs are used as substrates.

The lattice mismatch between MgO and Bi(Pb)-SrCaCuO films is significant. It will induce a cer-

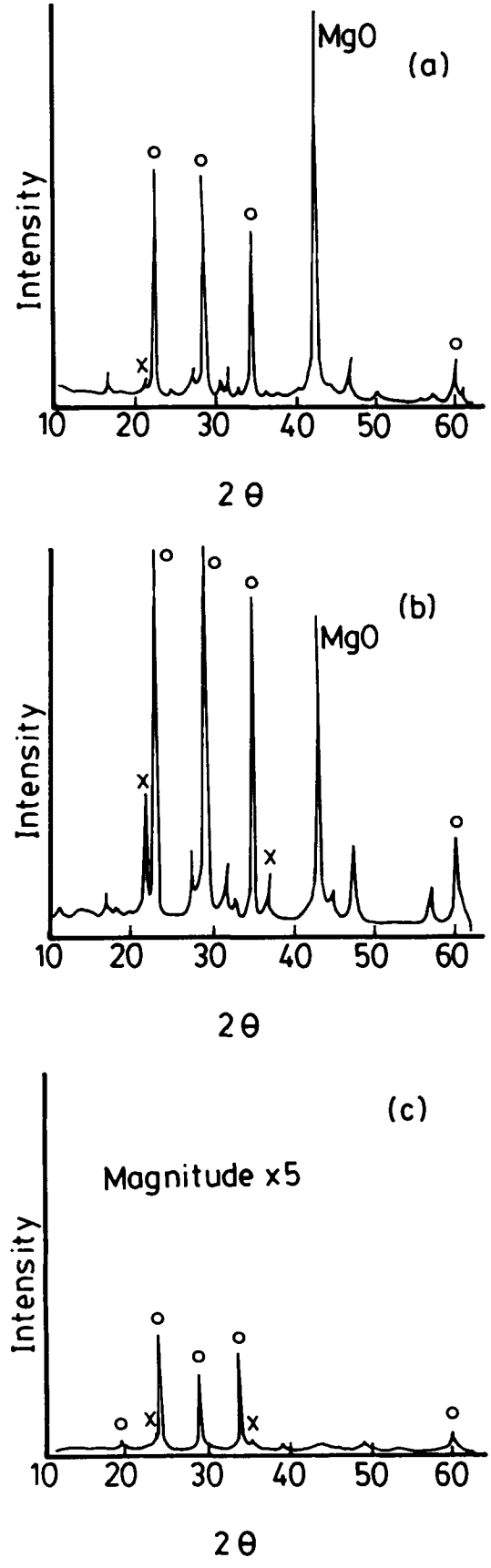

Fig. 3 — X-ray diffraction patterns of superconducting thin films deposited by dc sputtering for (a) 2 hr (b) 4 hr and (c) 8 hr and rapid thermal annealed at 845° C for 60 sec. The vertical axis is x-ray intensity. The horizontal axis is two times the diffraction angle. 0 represents (2212) phase and x represents (2201) phase.

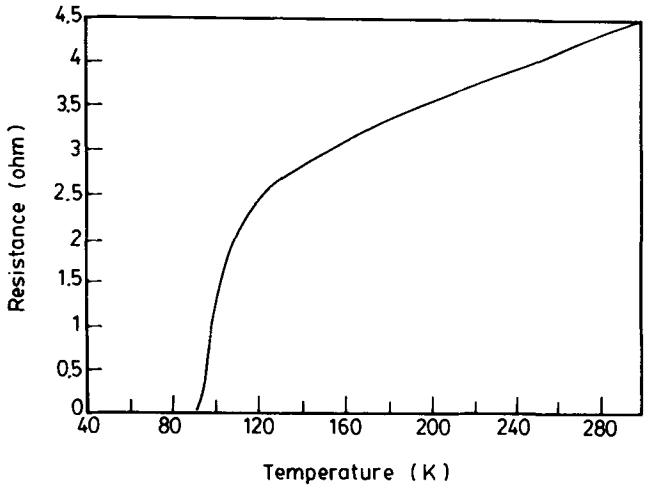

Fig. 4 — Resistivity vs temperature of superconducting thin film deposited for 8 hr and rapid thermally annealed at 845° C for 60 sec.

tain degree of lattice distortion in the film in contact with the substrate. The superconductivity will be degraded when the films are very thin. It is, therefore, of interest to increase the film thickness and investigate the corresponding change in RTA conditions on properties of Bi(Pb)SrCaCuO films. The deposited film thickness was then varied in a second series of experiments. The film thickness was proportional to the dc sputtering time. Since the deposition rate was about 2.5 nm/min, the films deposited for 2, 4 and 8 hr had average thicknesses of 300, 600 and 1200 nm, respectively. These films were all RTA treated at 845° C for 60 sec. The 845° C annealing temperature was chosen based on previous results using furnace annealing.[14] The x-ray diffraction patterns are shown in Fig. 3. The result reveals that the diffraction intensity of the (2212) superconducting phase increases with film thickness and is most prominent for the thickest films which were deposited for 8 hr. Highly c-axis oriented structure was obtained for this group of films. A representative resistance vs temperature characteristic is shown in Fig. 4. The highest zero resistance transition temperature was found to be 86 K and the transition onset temperature was 110 K.

The improvement in crystallography and superconductivity due to increase in film thickness infers that there is significant lattice distortion to the layer of Bi(Pb)SrCaCuO film adjacent to the MgO substrate, although the interdiffusion between MgO and Bi(Pb)SrCaCuO is reported to be insignificant. Another advantage of increasing the film thickness is that the Pb-loss of the layer beneath the surface of the films should be reduced. This is indicated by the occurrence of high transition onset temperature in Fig. 4 which must be caused by the possible existence of (2223) phase but the proportion is too small to be detected by x-ray diffraction technique. A relative Pb-loss measurement is made for thin films deposited for 2 and 8 hr by using secondary ion mass spectroscopy (SIMS). The superconducting thin film deposited for 8 hr contains 3.3 times more Pb than the film deposited for 2 hr.

IV. CONCLUSION

In summary, superconducting thin films of nominal $Bi_{1.6}Pb_{0.4}Sr_2CaCu_2O_x$ compositions have been fabricated by dc sputtering and rapid thermal annealing for the first time. No furnace annealing is required. Highly oriented films with the c-axis normal to the substrate surface are obtained. The film thickness and rapid thermal annealing temperature are two important parameters in determining the superconducting properties of $Bi_{1.6}Pb_{0.4}Sr_2CaCu_2O_x$ thin films. When the 8-hr deposited films, having a thickness of 1200 nm, are rapid thermally annealed at 845° C for 60 sec, the superconducting thin films are composed predominantly of the (2212) phase. The superconducting thin films have a zero resistance transition temperature of 86 K and a transition onset temperature of 110 K.

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