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Preparation of 110K Bi(Pb)SrCaCuO superconducting thin films by r.f. magnetron sputtering and their response to microwave radiation

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Abstract

Bi(Pb)SrCaCuO thin films containing a high ratio of Pb (Pb/Bi>1), about 0.5μm thick, were deposited on single crystal $LaAlO_3$, $SrTiO_3$ and MgO substrates by using a heavily Pb doped single composite oxide target. The film deposited on (001) MgO at a substrate temperature of 170°C and sintered at 852-862°C for 1hour in air showed zero resistivity at 110K. The highest critical current density of $4.6x10^4$ Amp/cm^2 at 77K has been measured on the film grown on (100) $LaAlO_3$. The dependence of the high-Tc (2223) and low-Tc (2212) phase concentrations on annealing temperature was also studied by X-ray diffraction. The highest fraction of the 2223 phase was obtained on the film annealed at 862°C for 1 hour. Microwave response measurements were carried out on a film patterned into a 150 μm wide and 1 cm long meander-type structure using standard photolithography and wet chemical etching. The result showed that the microwave response contains a non-bolometric component.

1. Introduction

It is well established that the high-Tc(110-K) phase in the $Bi_2Sr_2Ca_{n-1}Cu_nO_x$(n=1,2,3) system with ideal composition $Bi_2Sr_2Ca_2Cu_3O_{10}$ can be promoted and stabilized by the partial substitution of Bi by Pb[1]. The effect of Pb doping is that it considerably decreases the formation temperature, which is quite close to the melting point, for the 110-K phase[2]. The Pb rich environment also makes it more stable which allows control of the formation of the phase in a wide temperature range.

More recently, metalorganic deposition has been used successfully to fabricate epitaxial thin films of the Pb doped low-Tc phase onto (100) $LaAlO_3$ substrates. Jc values up to 10^5 and 10^6 Acm^{-2} were measured at 77 K and at 45 K, respectively, in zero field[3]. The epitaxial nature of 80 nm thin films of the low-Tc phase deposited on (100) $LaAlO_3$ substrates by metalorganic deposition, has been confirmed by neutron diffraction study[4].

Many kinds of processes for the partial substitution of Bi by Pb have been used in preparing superconducting thin films of the 110-K phase, including sintering at high temperatures in Pb-rich atmosphere[5] and use of a sputtering target containing Pb[6]. The influence of Pb doping on formation of the 110-K phase was extensively examined by Kula et-al[7] using Pb doped targets at different Pb/Bi ratios up to 1.25 by a DC magnetron sputtering technique. They reported that their data suggest that even higher Pb doping should be desirable for fabrication of the 110-K phase films with very narrow superconducting transition. They have also reported that the annealing temperature range was quite narrow for the preferential growth of the 110-K phase.

In this work we present the effect of the sintering temperature on the formation of the 110-K phase in heavily Pb doped, < 0.5μm thick sputtered thin films and their response to microwave radiation. We have also shown that the 110-K single step transition can be obtained for a range of sintering temperatures, at least 10K.

2. Experimental

The films were deposited on polished $LaAlO_3$, $SrTiO_3$ and MgO substrates by rf magnetron sputtering from single composite oxide BiPbSrCaCuO targets with cationic ratio of 2:2.5:2:2.15:3.3 following Kula et al[7]. In order to prepare targets the appropriate amounts of Bi_2O_3 (99.9%), PbO (99.9%), CuO (99%), $Sr(NO_3)_2$ (99%) $CaCO_3$(99%) powders were intimately mixed and ground by ball milling for 24 h using ZrO_2 media in an appropriate amount of 2-propanol. The powder slurry was then dried on a hot plate, being constantly stirred

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with a magnetic stirrer to prevent segregation. Next the dried powder was annealed at 650°C for 10 h and ground with a pestle and mortar and pressed into a 50 mm-diameter disk. The disk was again annealed at 675°C for 4 h. The sputtering conditions during film deposition are listed in Table I. The deposition time was about 4 h resulting in average film thicknesses of approximately 0.4μm.

The chemical composition of as-deposited films was analyzed by Electron Probe X-ray Microanalysis (EPMA) for each batch. After deposition, the films were sintered in a wide temperature range from 820°C to 875°C for 1h in air. The films were slowly heated to the desired temperature and cooled with ramping rate 1°C/minute above 500°C. The annealed films were characterized by X-ray diffraction (XRD) using a Cu target (40 KV, 20 mA) and by Scanning Electron Microscopy (SEM). The superconducting transition temperatures (Tc) were measured using the conventional four point contact technique with a measuring current of 100μA, and a lock-in amplifier as the voltage detector. The critical current density, Jc, was measured on unpatterned films. In both cases current and voltage leads were directly attached to the film surface with silver paste. The films were patterned into a 150μm wide 1 cm long meander type structure using standard photolithography and wet chemical etching for microwave response measurements.

3. Results and Discussion

The EPMA measurements on as-deposited films revealed that the initial cationic ratio of BiPbSrCaCu oxide was around 1.63:1.85:1.80:1.70:3 (normalized to Cu) for the films showing zero resistivity above 110K, when they are annealed at between 852°C and 862°C. In this composition the Pb/Bi ratio fluctuates between 0.92 and 1.4, while the Sr/Ca ratio remains above 1. It was found that the film quality was very sensitive to the Bi concentration: films containing a high ratio of Bi with respect to other components showed island like grain structure after high temperature annealing, even when the initial Pb/Bi ratio was larger than 1. When the Bi concentration was very low, the superconducting properties of the film were very poor with Tc around 80 K. Films which had a stoichiometry close to the optimized one were sintered at different temperatures from 820°C to 875°C for 1h in air. XRD patterns of those films revealed that the 80-K phase and Ca_2PbO_4 formed together in the early stage of high temperature annealing (Fig 1. a). Ca_2PbO_4 is a highly reactive intermediate phase aiding the formation of the 110-K phase. The 110-K phase has started to grow at 835°C when the peaks attributed to Ca_2PbO_4 were smaller

Table 1. rf magnetron sputtering conditions for a standard deposition.

RF power	50 watt
Sputtering atmosphere	$2x10^{-2}$mbar Ar
Substrate temperature	170°C
Substrate-to-target distance	60mm
Sputtering rate	0.025nm/s

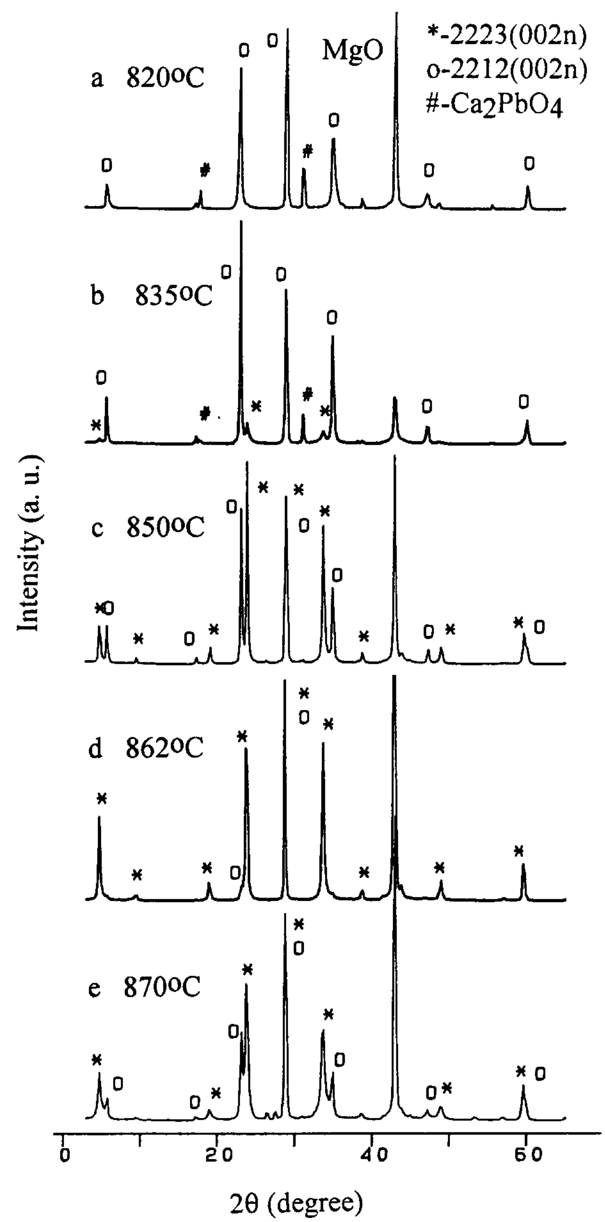

Figure 1. XRD pattern of the the films annealed at different temperatures for 1 h in air, on MgO substrate

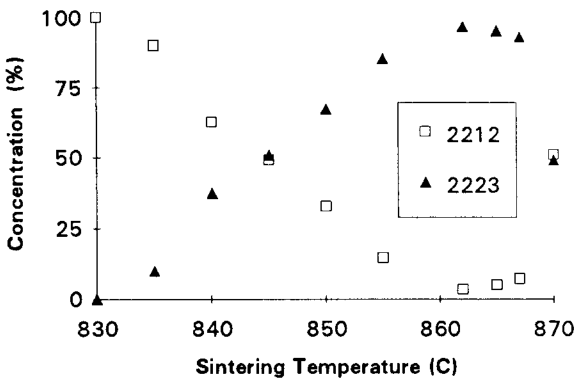

Figure 2. The variation of 110-K and 80-K phase concentration with sintering temperature for the films sintered at different temperatures for 1h in air.

(Fig 1. b). The 110-K phase became dominant against the 80-K phase while Ca_2PbO_4 was not detected at 850°C. The volume fraction of the 110-K phase in the film increased and of the 80-K phase decreased further for annealing temperatures up to 862°C. At 862°C the highest ratio of the 110-K phase was observed (97%). Above this temperature the 80-K phase has started to appear again, together with some impurity phase, (Sr,Ca)CuO (not detectable by XRD). This variation of the 110-K and 80-K phase concentration with annealing temperature, estimated from the intensity ratio of the low-angle peaks of both phases, is illustrated in fig. 2.

The resistivity measurements (Fig 3.) were in a very good agreement with XRD spectra. It is quite clear that Tc-onset increases with increasing ratio of the 110-K phase and remains almost constant for a wide temperature range. Tc-zero is slightly decreased at the beginning of the 110-K phase formation because of the segregation of phases. It reached 108K at 850°C, in spite of the existence of a large amount of 80-K phase. If this result is joined to the result of the single step transition being observed for all samples, it can be seen that 110-K phase is formed without intergrowth of the 80-K phase, an effect of Pb doping[2]. Tc-zero decreases for sintering above 862°C with the start of decomposition of the 110-K phase into the 80-K phase and (Sr,Ca)CuO impurity phase in the shape of huge needles (Fig. 4). This result implies that the formation of the 110-K phase can be controlled in a wide temperature range in heavily Pb doped films to get good microstructure and high current density.

The films grown under the same conditions as used for MgO substrate on $LaAlO_3$ and $SrTiO_3$ single crystal substrates were also characterized. While XRD patterns of films grown on $LaAlO_3$ substrates were similar to the films deposited on MgO, the 80-K phase was dominant on $SrTiO_3$ (Fig 5.). Resistivity measurements of films on $SrTiO_3$ exhibited a wide transition and reached zero resistivity at 102K, while it was 108K and 110K for $LaAlO_3$ and MgO, respectively, with a narrow transition width of 6K (Fig 6.). The presumed epitaxial growth[4] of films deposited on $LaAlO_3$ substrates would account for its smooth surface relative to the rough texture of films on MgO (Fig. 4). The highest critical current density, Jc, of 4.6×10^4 A cm^{-2} at 77K using 1μV/mm voltage criterion, has been measured on an unpatterned film grown on $LaAlO_3$. It was 8×10^3A cm^{-2} at 77K on the MgO substrate. The approximate resistivity values at Tc-onset temperature are 1.08×10^{-3} and 1.53×10^{-3}Ωcm, respectively, for samples mentioned above.

Figure 7. shows the microwave response[8,9], Vmr, of a 110K BiPSCCO film using a 33.5 GHz sweep oscillator

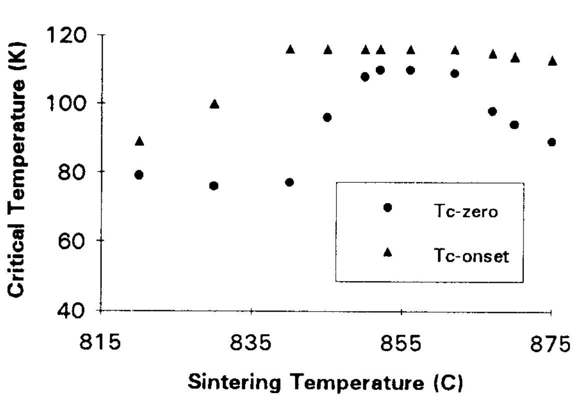

Figure 3. The variation of the Tc-zero and Tc-onset temperature with sintering temperature for samples sintered at different temperatures for 1h in air.

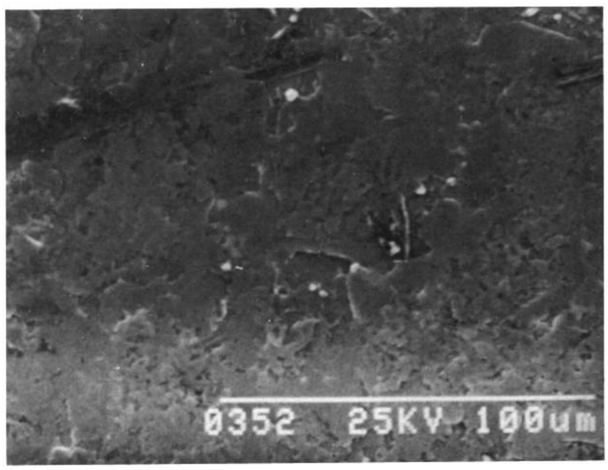

Figure 4. SEM surface image of film grown on $LaAlO_3$ substrate.

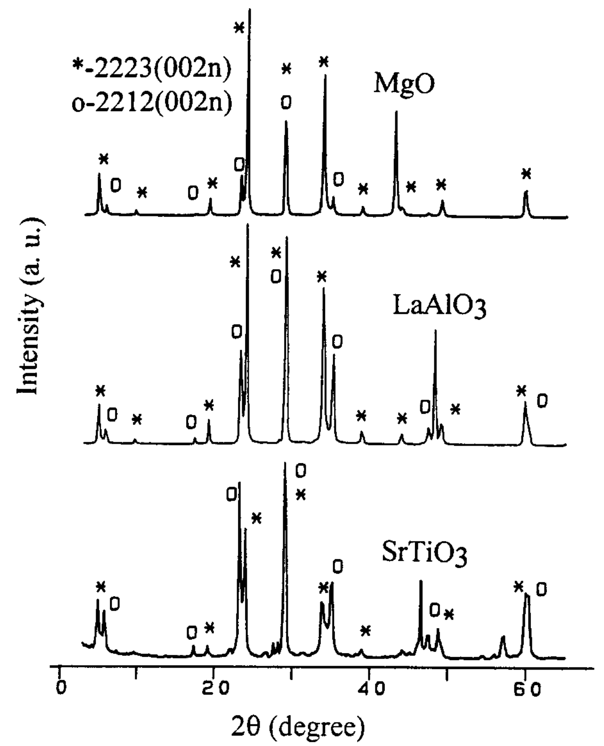

Figure 5. XRD patterns of the films grown on different substrates and annealed at 855°C for 1h in air.

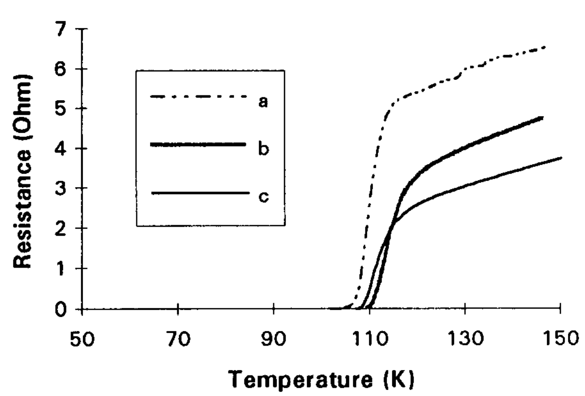

Figure 6. The temperature dependence of resistivity for the samples grown on $SrTiO_3$(a), MgO(b) and $LaAlO_3$(c) single crystal substrates, and sintered at 855°C for 1h in air.

at a bias current of 0.1mA and a chopping frequency of 161 Hz with a Teflon (PTFE) window. Three normalized curves are presented in the same figure: R vs. T, dR/dT vs. T and Vmr vs. T. The comparison of the curves shows that the microwave response is not proportional to dR/dT and therefore is non-bolometric. Two peaks were observed in the transition ranges of the 80-K and 110-K phases, while the R vs. T curve shows a single step transition.

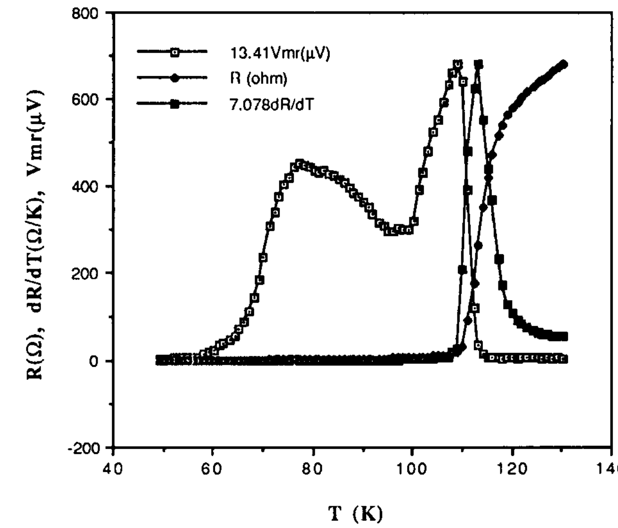

Figure 7. The comparison of R, dR/dT and microwave response curve of a Bi(Pb)SrCaCuO thin film.

4. Conclusion

The effect of sintering temperature on heavily Pb doped, < 0.5 μm thick, sputtered thin films has been studied, and shown that a 110-K single step transition can be obtained in a temperature range as wide as 10K. To prevent intergrowth of the 80-K phase during the formation of 110-K phase, the initial Pb/Bi ratio in as-deposited films can be extended to between 0.9<Pb/Bi<1.4. A (Sr, Ca)CuO impurity phase formed in the needle structure can be minimized by decreasing the Cu content in the as-deposited composition.

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