

Electrochemical processing of high- T_c Bi(Pb)–Sr–Ca–CuO thin films

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Abstract. Superconducting thin films of Bi(Pb)–Sr–Ca–CuO system were prepared by depositing the film onto silver substrate by d.c. electrodeposition technique with dimethyl sulphoxide bath in order to examine the effect of Pb addition to the BSCCO system. The films were deposited at the potential of -0.8 V vs saturated calomel electrode (SCE) onto the silver substrate. The different preparative parameters such as deposition potential, deposition time were studied and optimized. These films were then oxidized electrochemically at room temperature in an alkaline (1 N KOH) solution, and also at 600°C temperature in an oxygen atmosphere. The films showed the superconducting behaviour, with T_c values ranging between 85 K and 96 K, respectively.

Keywords. Superconductor; electrochemical deposition; thin films.

1. Introduction

The Bi(Pb)–Sr–Ca–CuO high- T_c cuprates with a nominal stoichiometry of $(\text{BiPb})_2\text{Sr}_2\text{Ca}_2\text{Cu}_3\text{O}$ were considered to be the most promising superconducting materials for practical applications. However, it is very difficult to synthesize a single high- T_c phase (2223 phase); as this Bi-system occurs in mixed state of phases belonging to the homologue series of $\text{Bi}_2\text{Sr}_2\text{Ca}_{n-1}\text{Cu}_n\text{O}_{2n+d}$ with specific transition temperature ranging from 20 K (2201 phase); 85 K (2212 phase) to 110 K (2223 phase) for $n = 1, 2$ and 3, respectively (Tarascon *et al* 1988).

Many studies have been attempted to obtain the 2223 phase; and this has been made possible by partial substitution of Bi by Pb in the Bi–Sr–Ca–CuO system (Sunshine *et al* 1988; Tokano *et al* 1988; Mizuno *et al* 1988). To establish the contribution of Pb in enhancing the T_c of superconductors, some reports (Nobumara *et al* 1989; Ramesh *et al* 1989; Zhang *et al* 1990) suggest that Pb atom replaces Bi substitutionally in the Bi–O layers, and takes part in lattice formation. Thus, Pb is not merely segregated in the grain boundaries. Also, since Pb is bivalent (or tetravalent) showing similarity in size with Bi, which is trivalent (or pentavalent), an alteration in the defect structure is expected. This suggests that Pb can be considered as an ideal candidate for doping: there is every possibility of vacant Bi-sites getting occupied by Pb atoms, thus offering stability to the lattice and resulting in an ordered crystal structure.

To prepare (2223) high- T_c phase superconductors, methods like coprecipitation, conventional solid state reaction

method etc were suggested (Cava 1988; Politis 1988; Tokano *et al* 1988). Superconducting thin films of Bi–Sr–Ca–CuO system have been successfully prepared by number of techniques like laser ablation, electron beam evaporation, magnetron sputtering, spray pyrolysis, electrochemical synthesis etc. Among these, the electrochemical synthesis is economical and environmentally friendly for depositing stoichiometric-alloyed films, with subsequent oxidation to achieve superconducting property (Maxfield *et al* 1989; Bhattacharya *et al* 1990; Pawar and Mujawar 1990, 1991a, b; Pawar and Pendse 1991; Pawar *et al* 1993, 1994).

In the present report, we discuss an attempt for deposition of Bi(Pb)–Sr–Ca–CuO films, from dimethyl sulphoxide (DMSO) bath, onto a silver substrate with subsequent oxidation, for fabricating thin-film superconductor, by d.c. electrodeposition technique. The two types of oxidation techniques namely: (i) electrochemical oxidation at room temperature; and (ii) furnace oxidation at high temperature in presence of oxygen atmosphere have been tried. The superconducting properties for both the oxidations have been compared and reported.

2. Experimental

The electrolytic baths were prepared by using reagent-grade nitrates of bismuth (18 mM), lead (4 mM), strontium (45 mM), calcium (30 mM), and copper (8 mM). The values of concentrations of Bi, Sr, Ca and Cu were decided from the mobility of these ions (Maxfield *et al* 1989). Concentration of Pb was decided by optimizing rate of deposition of its individual constituents. The total

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bath composition was adjusted to get Bi-Pb-Sr-Ca-Cu deposit in the required stoichiometry.

A conventional three-electrode system consisting of saturated calomel electrode (SCE) as the reference electrode, graphite as the counter electrode, and mirror-polished silver substrate as the working electrode was used. EG- and G scanning potentiostat model 362 with X-Y recorder was used for electrochemical deposition. The electrodeposition was carried out under potentiostatic condition, and at ambient temperature (300 K).

The cathodic polarization curves for electrodeposition of Bi, Pb, Sr, Ca, Cu and Bi-Pb-Sr-Ca-Cu alloy were studied. The deposited films were then oxidized using two different techniques. Electrochemical oxidation was carried out in an alkaline 1 N KOH solution for 20 min at a potential of +700 mV vs SCE at room temperature. In furnace oxidation technique, the films were oxidized at 600°C temperature for 15 min using auto-controlled furnace and then quenched down to room temperature. Microstructural properties of these films were studied with METZER optical microscope (magnification 500 \times) with CCTV attachment. X-ray diffraction pattern was recorded by using Phillips PW-1710 X-ray diffractometer using CuK_α radiations. The superconducting transition temperature was determined by resistivity (R - T) measurement, using conventional four-probe technique with silver paint contacts. An APD close-cycle refrigerator (model HC-2D) was used to cool the samples.

3. Results and discussion

It is well known that different metals from an electrolytic bath deposit at different potentials. The cathodic polarization curves for bismuth, lead, strontium, calcium, copper and Bi-Pb-Sr-Ca-Cu complex onto the silver substrate are shown in figure 1. From these curves it is evident that the deposition potential for Pb is smallest, while for Sr it is largest. The values of set potentials are obtained from cathodic polarization curve. The potentials for Bi, Pb, Sr, Ca, Cu and Bi-Pb-Sr-Ca-Cu complex onto the silver substrate are listed in table 1.

To obtain Bi-Pb-Sr-Ca-Cu-alloyed films with required stoichiometry of 2:2:2:3, the total bath composition was adjusted by considering the rate of deposition of each of its constituents. Figure 2 shows the variation of cathodic current density with deposition time. It was observed that the deposition current density showed a rapid decrease within first few sec which has been attributed to the formation of a double layer at the electrode-electrolyte interface, which causes an increase in the resistance. Subsequently, deposition current density showed a gradual increase with time. After few min, the current showed a gradual increase with deposition time and eventually, attained a steady state.

Figure 3 shows the variation of Bi(Pb)-Sr-Ca-Cu-alloyed film thickness with deposition time. For 40 min deposition period, thickness of the film is of the order of 2 to 3 microns. The films were oxidized electrochemically from an alkaline 1 N KOH solution for 20 min at a potential of +700 mV vs SCE at room temperature. Similarly the films were oxidized at 600°C for 15 min in preheated furnace and quenched down to room temperature.

Surface morphology of the as-deposited and oxidized Bi(Pb)-Sr-Ca-Cu-alloyed films were studied by using an

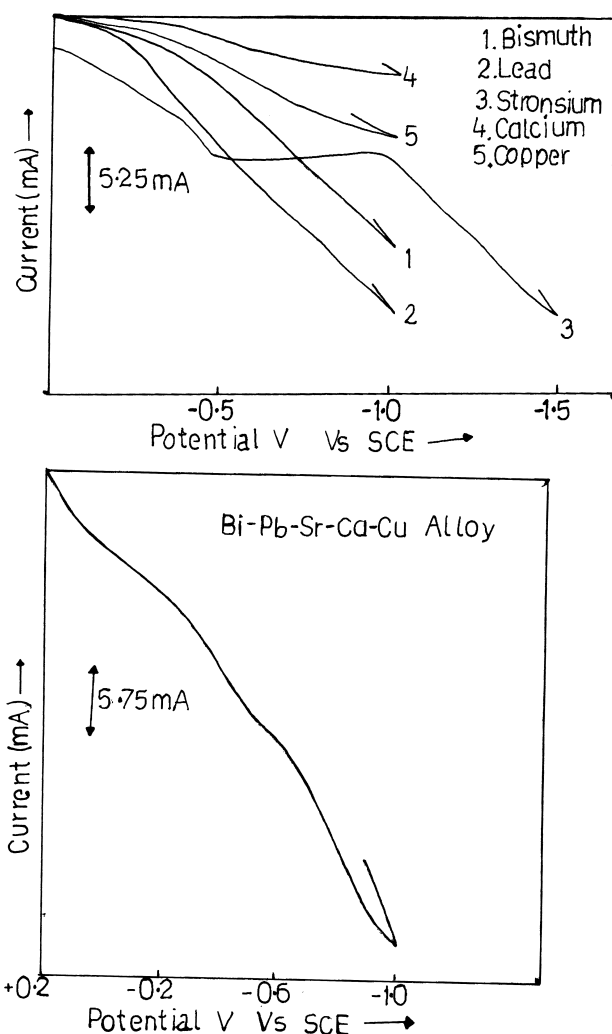


Figure 1. Cathodic polarization curves for Bi, Pb, Sr, Ca, Cu metals and Bi(Pb)-Sr-Ca-Cu alloy onto silver substrate.

Table 1.

Substrate	Electrodeposition potential, V vs SCE (saturated calomel electrode)					
	Bi	Pb	Sr	Ca	Cu	Bi-Pb-Sr-Ca-Cu
Silver	-0.6	-0.4	-1.1	-0.55	-0.6	-0.8

optical microscope with a CCTV attachment. The microstructure photographs show the films as being smooth, dense and uniform. While the as-deposited and electrochemically oxidized film is black, with furnace oxidation the colour changed to yellow. The as-deposited film was very dense with very small grains. The oxidation of the film showed an improvement in the grain size.

After oxidation the resulting films were examined by X-ray diffraction (XRD) technique under reflection mode. The XRD patterns of electrochemically and furnace-oxidized films are shown in figures 4 and 5, respectively. The XRD pattern and the microstructure show that the electrodeposited Bi(Pb)–Sr–Ca–Cu films are polycrystalline in nature. While the indexed XRD reflection corresponds to the Bi-2223 phase, the weaker underlined reflection corresponds to the Bi-2212 phase. Diffraction peaks from the silver substrate are also observed in the

pattern. The electrochemically oxidized film is mainly comprised of the high- T_c phase (2223), showing characteristic peaks at 0010, 0014, 0012, 0016 arb. units, together with a small amount of the low- T_c phase. The furnace-oxidized film mostly showed the low- T_c phase with a small amount of high- T_c phase. This might be due to transformation of the high- T_c phase to the low- T_c phase during annealing at higher temperatures. The C-parameter calculated from the XRD data of electrochemically oxidized film is 37.006 Å, which agrees with the standard C-parameter.

The variations in resistance with temperature are shown in figure 6. While for the electrochemically oxidized film the T_c is below 85 K, for the furnace-oxidized films the T_c is below 96 K.

Although the furnace-oxidized film show higher T_c (96 K) than electrochemically oxidized film (below 85 K), the authors strongly recommend using the room

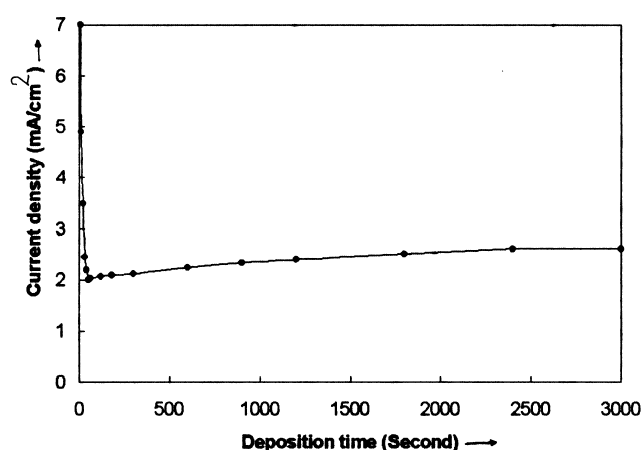


Figure 2. Variation of cathodic current density with deposition time during Bi(Pb)–Sr–Ca–Cu alloy deposition.

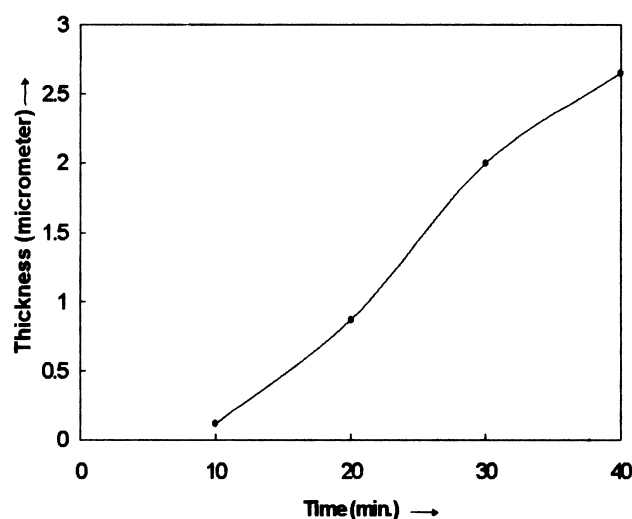


Figure 3. Variation of Bi(Pb)–Sr–Ca–Cu alloyed film thickness with deposition time.

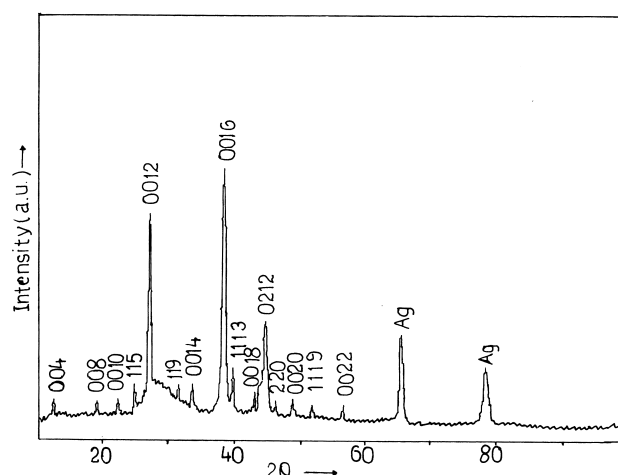


Figure 4. X-ray diffraction pattern for electrochemically oxidized Bi(Pb)–Sr–Ca–CuO films.

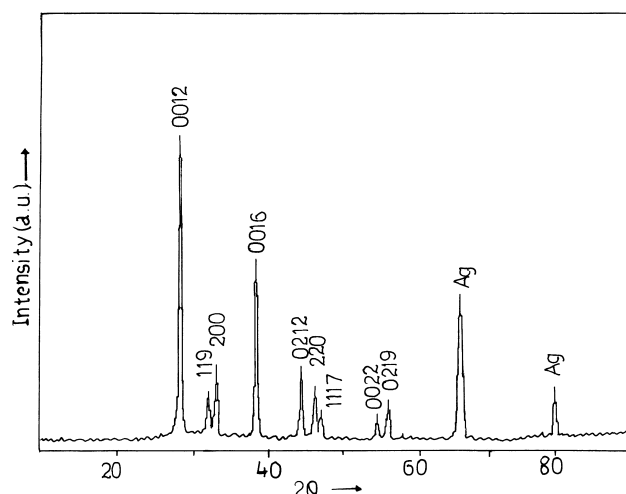


Figure 5. X-ray diffraction pattern for Bi(Pb)–Sr–Ca–CuO films oxidized at high temperature.

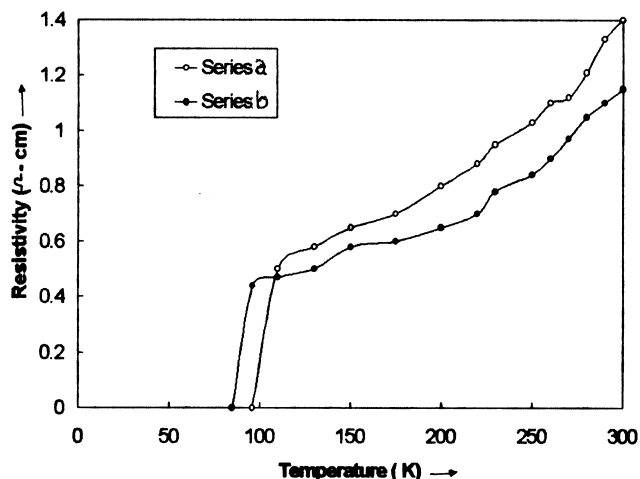


Figure 6. Temperature dependence of resistivity for a. electrochemically oxidized films and b. furnace oxidized films.

temperature electrochemical oxidation technique to obtain stable Bi 2223-thin films.

4. Conclusion

Attempts will be made to obtain both high- T_c phases in order to enhance the T_c value, and the stability by adjusting the perfect doping concentration of Pb in BSCCO film by electrochemical synthesis technique.

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