CHEMISTRY LETTERS, pp. 379-382, 1991.

Preparation of $YBa_2Cu_3O_{7-x}$ and $Bi_2Sr_2CaCu_2O_y$ Films by Electrodeposition Technique

Hideki MINOURA,* Keiji NARUTO, Hiroyuki TAKANO, Eiji HASEO,
Takashi SUGIURA, Yasusada UENO, and Tamio ENDO†
Department of Applied Chemistry, Faculty of Engineering, Gifu University,
Yanagido 1-1, Gifu 501-11
†Department of Electrical Engineering, Faculty of Engineering,
Mie University, Kamihama-cho 1515, Tsu 514

The high-temperature superconducting $YBa_2Cu_3O_{7-x}$ and $Bi_2Sr_2CaCu_2O_y$ phases have been prepared by the electrodeposition of the corresponding precursors from the baths containing salts of the constituent metals in dimethylsulfoxide-H_2O mixture solvent followed by a suitable heat treatment. The use of this solvent was found to contribute to a significant improvement in the deposition process.

Since the discovery of high-temperature superconducting materials in 1986,1) many works have been devoted to the fabrication of thin superconducting films. In the various film preparation techniques which have been extensively studied, the electrodeposition technique for getting the corresponding precursors is a unique one which is a room temperature process that does not require vacuum technology, suitable for mass-production and large-area fabrication, and capable of depositing onto surfaces with any shapes and of controlling deposition rate and film properties by electrical parameters. To our knowledge, however, only one research paper on the preparation of superconducting materials *via* the electrodeposition has been published so far, which is on the Pb(Bi)-Sr-Ca-Cu-oxide films by Maxfield *et al.*2) This technique involves two processes; the electrochemical deposition process and the subsequent heat-treatment process, which is the case for most of other film preparation techniques.

The high-temperature superconductors contain alkaline earth metals and rare earth metals, which have much more negative deposition potentials than the hydrogen evolution. This necessitates the use of aprotic solvents, careful dehydration of electroplating baths, and application of high voltage. Actually Maxfield *et al.* used dimethylsulfoxide (DMSO) as an aprotic solvent and carefully dehydrated the baths and applied potentials as negative as -4 V to -5 V *vs.* Ag/Ag^+.[2)] These are consistent with that the redox potentials of Sr/Sr^{2+} and Ca/Ca^{2+} are -3.42 V and -3.40 V *vs.* Ag/Ag^+, respectively.

Our finding described in the present paper is, in contrast, the preparation of precursor films with lower applied voltages by using a DMSO-H_2O mixture solvent. The ideas behind this are as follows.

i)Alkaline earth metals and rare earth metals having extremely negative deposition potentials have a strong tendency to be oxidized in water. If the deposition of those metals as oxidized states occurs, the free energy change for the deposition of those constituents must be significantly reduced, which in turn results in a significant shift in apparent deposition potentials toward positive direction.

ii)Precursors composed of oxidized form of the alkaline earth metals and rare earth metals may not be undesirable but rather preferable for getting superconducting oxide phases through a subsequent annealing.

The purpose of the present study is to confirm them experimentally and then to explore the possibility of getting the precursors for both Y-Ba-Cu-oxide (YBCO) and Bi-Sr-Ca-Cu-oxide (BSCCO) superconducting phases with more ease.

The electrodeposition experiments were carried out under the potentiostatic configuration using an Ag plate working electrode (substrate), a Pt counter electrode and an Ag/Ag^+ reference electrode immersed in the plating bath at room temperature. The plating bath contains nitrate salts of the constituent metals and tetra-n-butylammonium perchlorate (TBAP) as a supporting electrolyte in DMSO-H_2O mixture solvents. The resulting precursors for YBCO system were heated initially at 500 °C for 1 h, subsequently at 900 °C for 30 min, followed by a slow cooling down to 300 °C for 5 h in air. Those for BSCCO system were heated initially at 600 °C for 1 h, subsequently at 800 °C for 5 min, followed by a slow cooling down to 400 °C for 4 h in air. Potential values in the present paper are with respect to Ag/Ag^+ reference electrode. Samples were characterized by using XRD, SEM, EPMA, and ESCA.

The voltammogram in DMSO-H_2O mixture (10:1 in volume) containing 20 mM $Y(NO_3)_3 6H_2O$, 40 mM $Ba(NO_3)_2$, 60 mM $Cu(NO_3)_2 3H_2O$ and 200 mM TBAP exhibits four cathodic steps which might correspond to the reduction of three constituent metals and proton. Based on the voltammogram, we carried out the electrolysis experiments under constant potentials between

Table 1. EPMA data (atomic %)

Electrolytic potential	Element Y	Ba	Cu
-1.4	3	3	94
-1.6	16	36	48
-1.8	15	31	53
-2.0	25	28	47

-1.4 and -2.0 V. Chemical composition of as-deposited films thus obtained are summarized in Table 1. These values scattered up to 10%, therefore, the most typical values were employed in this table. It is interesting to note that both yttrium and barium are deposited at potentials more negative than -1.6 V without competition with hydrogen evolution which was observed to start at around -2.0 V.

Such a remarkable and very favorable shift in the deposition potentials is attributable to the deposition in the form of hydroxide/oxide. Overall reactions are expressed as follows,

$$Ba^{2+} + 2H_2O + 2e \rightarrow Ba(OH)_2 + H_2$$
$$2Y^{3+} + 6H_2O + 6e \rightarrow 2Y(OH)_3 + 3H_2.$$

The calculation of free energy change based on the above reactions gives anodically shifted redox potentials, which are -1.46 V for Ba/Ba^{2+} and -1.27 V for Y/Y^{3+}. The deposition potentials for calcium and strontium are likewise calculated to be -1.21 V and -1.27 V, respectively. The shift in the deposition potential of those alkaline earth metals as high as 2 V has to be noticed.

We observed that the electrolytic current rapidly decreased with time in the electrolyte containing either barium source or yttrium source, which is attributable to the formation of non-conducting hydroxide/oxide layer. This fact confirms that the deposition occurs in the form of hydroxide/oxide. ESCA analyses of as-deposited films also confirmed the existence of oxygen through the film. Interestingly, on the other hand, from the bath containing salts of every constituent metal, the electrolysis continues with a slight decay in current at the initial stage. It is probably due to the simultaneously deposited metallic copper which offers sufficient conductivity. Therefore, it is possible to prepare films with any thickness by changing the quantity of electricity passed.

Annealing the precursors in air gives superconducting YBCO and BSCCO phases. Typical X-ray diffractograms are shown in Fig.1. When deposition potential is more positive than -2.0 V in the electrolyte described above for YBCO system, *e.g.*, -1.6, -1.8 V, the sample thus obtained tends to be contaminated with Y_2BaCuO_5 and CuO phases.

SEM photographs of as-deposited and annealed samples for YBCO system are displayed in Fig.2.

In conclusion, we have demonstrated that employing DMSO-H_2O mixture

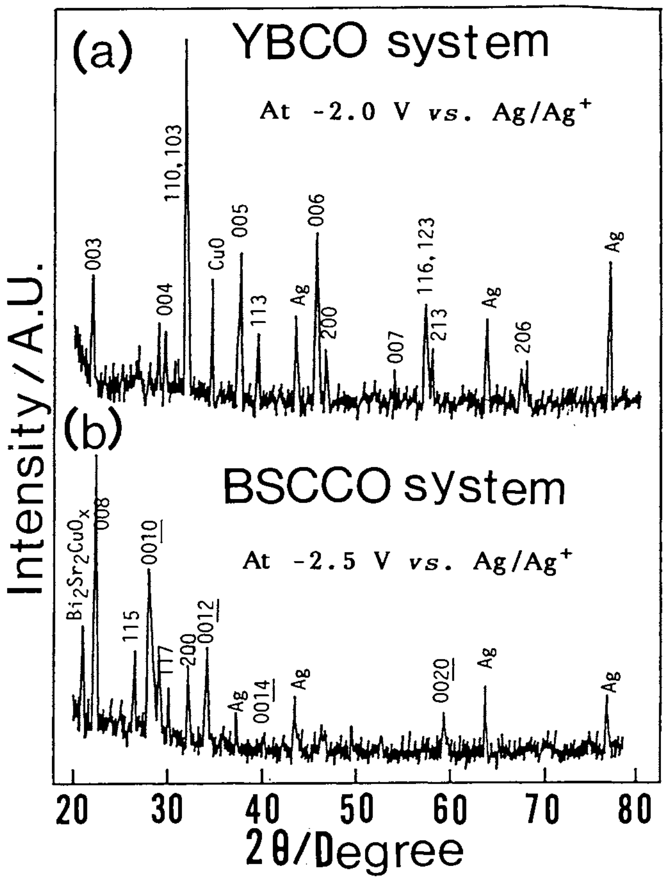
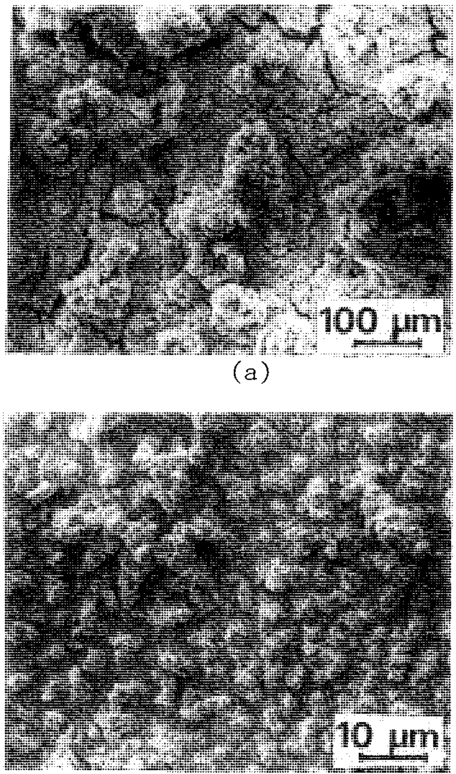


Fig.1.X-Ray diffractogram of annealed samples.
(a)YBCO system (b)BSCCO system



(a)

(b)

Fig.2.SEM photographs of YBCO phases.
(a)As-deposited
(b)Annealed
Electrolytic potential;-2.0 V

as a solvent gives rise to a significant improvement in the fabrication process of high-temperature superconducting phases *via* the electrodeposition technique in the following way, i)The electrodeposition of precursors takes place with much lower applied voltages, so that the competitive hydrogen evolution is virtually avoided. ii)Deliberate drying during the electrolyte preparation and the electrolysis is unnecessary. iii)The solubility of salts of constituent metals in a non-aqueous solvent is increased by mixing with water, which leads to wider selection of the chemical composition of the plating bath.

More detailed analyses of the deposition process are now in progress along with the detailed characterization of the films including the electrical properties.

References

1)J.G.Bednorz and K.A.Müller, *Z.Phys. B*, 64,189(1986).
2)M.Maxfield, H.Eckhardt, Z.Iqbal, F.Reidinger, and R.H.Baughman, *Appl. Phys.Lett.*, 54,1932(1989).

(Received November 21, 1990)