SUPERCONDUCTING FILMS MADE BY SPIN-COATING WITH ACETATE SOLUTIONS

D. I. dos Santos
Universidade Estadual Paulista - Campus Bauru
Departamento de Física
Av. Engº Luis E. C. Coube
Bauru, São Paulo, Brasil - 17033

C. L. Carvalho, R. R. da Silva, and M. A. Aegerter
Universidade de São Paulo
Instituto de Física e Química de São Carlos
São Carlos, São Paulo, Brasil - 13560

U. Balachandran and R. B. Poeppel
Materials and Components Technology Division
Argonne National Laboratory
Argonne, IL 60439 U.S.A.

Metallic silver substrates were spin-coated with several layers of mixed acetate solutions containing bismuth, lead, strontium, calcium, and copper. The viscosities of the cation solutions were modified by the addition of polyvinyl alcohol. The films were heat treated at various temperatures in air, oxygen, and 1% oxygen (balance nitrogen) atmospheres. Bismuth cuprate films with transport critical current densities ≈500 A/cm^2 were obtained. New conditions of coating and sintering to produce superconducting films were studied.

INTRODUCTION

Bi-based copper oxide superconducting ceramics have been extensively investigated since the discovery of the Bi-Sr-Ca-Cu oxide system by Maeda et al. (1). Much work has been performed to obtain quality films of this material so that it can be used in practical applications such as electronic devices or magnetic shields. Major techniques of thin-film growth have been applied, including chemical vapor deposition (2), magnetron sputtering (3), laser ablation (4), laser evaporation (5) and molecular beam epitaxy (6). However, most of these techniques are very complicated and expensive and do not always yield good results. On the other hand, several relatively simple and inexpensive techniques, such as spin-coating, dip-coating, spraying, or screen-printing, proved to be useful in producing films with transition temperature above 100 K (7) and transport critical current density (J_c) of $\approx 10^3$ A/cm^2 at 77 K (8).

We chose to study spin- and dip-coating techniques that deposit stoichiometric acetate solutions of the Bi-Sr-Ca-Cu-O system on metallic-silver substrates. Precursor solutions with large range of viscosities were obtained by the addition of polyvinyl alcohol (PVA). Several heat-treatment schedules were followed for the films, and preliminary results showed a zero-field J_c in excess of 500 A/cm^2 at 77 K for lead-doped samples.

EXPERIMENTAL DETAILS

The solutions with stoichiometric compositions Bi:Sr:Ca:Cu = 2:2:1:2 and (Bi,Pb):Sr:Ca:Cu = (1.6,0.4):2:2:3 were prepared by dissolving bismuth, calcium, and copper acetates, strontium (and lead, in the case of the doped solution) nitrate in glacial acetic acid and water at room temperature. Changes in pH were achieved with ammoniumhydroxide. The final solution was quite stable when kept at ambient laboratory conditions. Various amounts of PVA were added to change the viscosity of the solutions. Attempts to change viscosity were also made with

polyacrylic and tartaric acids but these acids did not produce homogeneous solutions, and consequently good films were not obtained.

Figure 1 shows the change in viscosity and pH of a solution as a function of PVA concentration. No significant difference was observed in the viscosity of the lead-doped and undoped solutions. The dip-coating technique did not produce uniform coatings. Some experiments to deposit the solution on a substrate by spreading it with a spatula, in a magnetic field of ≈0.5 T, were also performed.

The solution used to prepare films by spin-coating had a viscosity of ≈100 cP at 30°C. Spinning velocity was ≈3500 r/min. The substrates used (small silver plates) were coated with 10

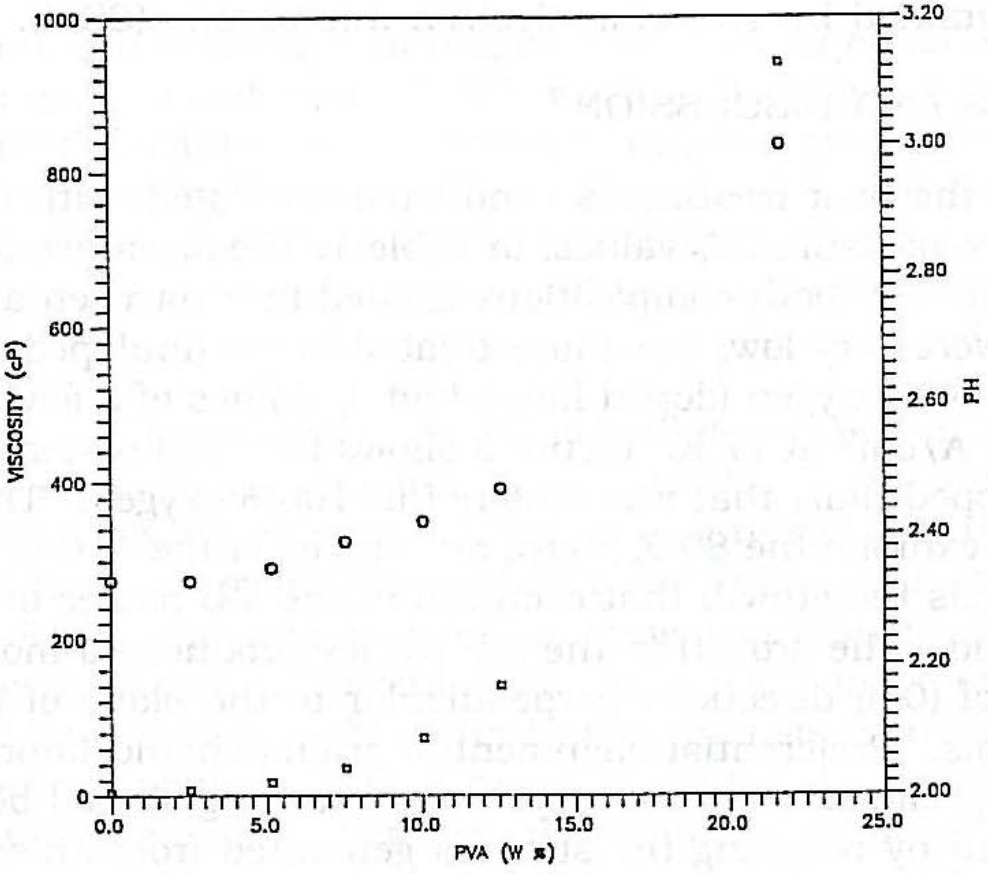

Figure 1 Change in viscosity (circle) and pH (square) of cation solution as a function of polyvinyl alcohol addition.

layers to achieve a thickness after heat treatment of 2 to 5 μm for both compositions. The films were heated to 600°C after deposition of each layer of coating. The spin-coating and heating processes were repeated approximately 10 times.

The final sintering was conducted at ≈850°C for periods of less than 1 h. The heat treatment atmospheres were air, oxygen, and 1% oxygen (balance nitrogen) gas mixtures. In all cases, the heating and cooling rate was 0.5°C/min and 2°C/min, respectively. Many of the films treated in air were completely volatilized during sintering at 850°C even for a short period of time. Transport critical current densities at 77 K were measured by the four-point probe technique, applying a criterion of 1 μV/cm. The principal uncertainty in calculating J_c was that of the cross-sectional area. We estimated the accuracy of the stated values as ±15%. The crystalline phases formed in the films were investigated by X-ray diffraction (XRD); the microstructural features were examined by scanning electron microscopy (SEM).

RESULTS AND DISCUSSION

Some of the heat treatments conducted are listed, with their respective measured J_c values, in Table 1. The J_c values obtained for the films of both compositions treated in a nitrogen atmosphere were very low, but those treated in air (undoped films) and in 100% oxygen (doped films) had J_c values of a few hundred A/cm^2 at 77 K. Figure 2 shows the XRD pattern of one of the doped films that was sintered in 100% oxygen. The pattern exhibits the 80 K phase and traces of the 110 K phase and reveals the growth that occurred in the a-b planes of the compound. The growth in the a-b planes produced a moderate texture of (00l) directions perpendicular to the plane of the thick films. Preferential alignment of grains should improve the J_c of a specimen in several ways: microcracking should be minimized by reducing the stresses generated from anisotropic thermal expansion coefficients, weak-link networks may be improved by reducing the number of grain boundaries from one end of the specimen to the other, and superconductivity within the grains is preferred in the a-b plane and will thus be at a

Table 1. Heat-treatment conditions and J_c (at 77 K) of spin-coated films

Composition	Temp./Time	Atmosphere	J_c (A/cm^2)
Bi:Sr:Ca:Cu 2:2:1:2	825°C/10 min	1% O_2–99% N_2*	≈5
		air	300–400
(Bi,Pb):Sr:Ca:Cu (1.6,0.4):2:2:3	825°C/10 min	1% O_2–99% N_2*	≈10
	825°C/10 min	100% O_2	340–550

*Below ≈760°C, cooling was performed in 100% O_2.

maximum if a-b planes lie in the direction of current transport. Because only a moderate amount of grain alignment resulted in the spin-coated films, the J_c obtained was only ≈500 A/cm^2.

To explore the possibility of aligning the microcrystals in the solution after the addition of PVA, we coated some substrates by spreading the solution with a spatula, under a magnetic field ≈0.5 T. Although we could observe differences between the XRD patterns of films prepared by the two different techniques, namely, spin-coating (zero-field condition) and spreading by spatula, no significant difference in X-ray spectra was observed.

Figure 3, an SEM micrograph of the lead-doped film made by spin-coating and sintering at 825°C in 100% oxygen, shows that long grains (≈300 μm) originate from a few nuclei and that between the long grains are equiaxed fine grains that are very dense. Such large grains were not present in films sintered in a 1% oxygen [balance nitrogen] atmosphere. The increased J_c [from ≈10 to ≈500 A/cm^2] found in the films sintered in air or 100% oxygen appears to be a result of improved contact between grains, and is, perhaps, associated with the large size of the grains. Similar results have been obtained with $YBa_2Cu_3O_x$ superconductors (9,10). In poorly sintered specimens, even

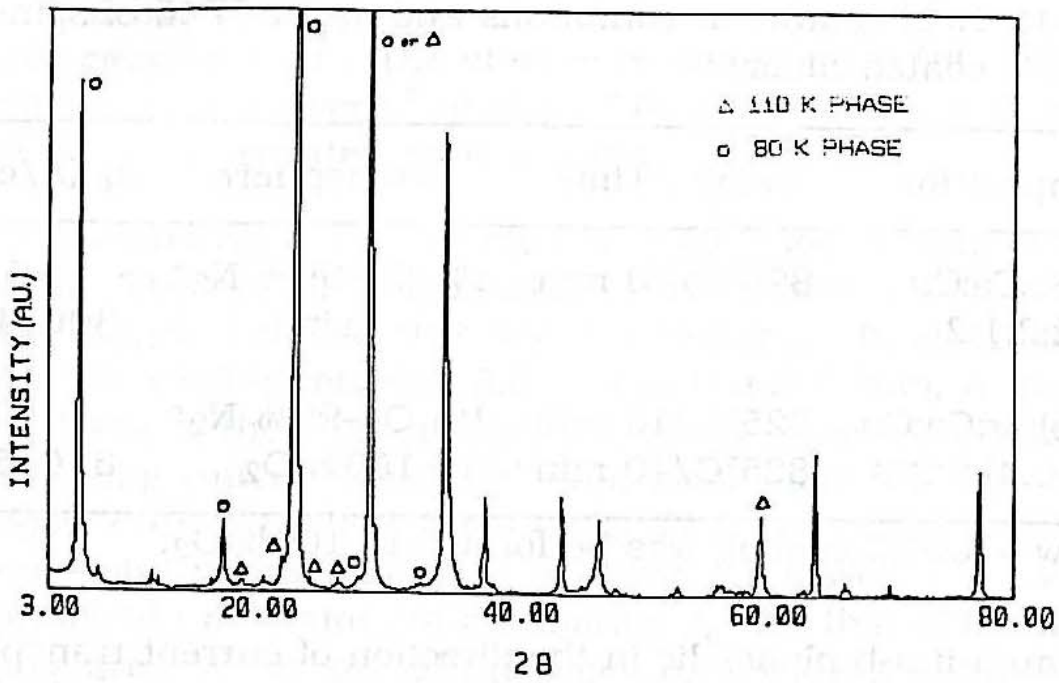

Figure 2 X-ray diffraction pattern of lead-doped bismuth cuprate film made by spin-coating.

Figure 3 SEM micrograph of lead-doped bismuth cuprate film, showing elongated grains.

those with long grains, J_c values are low, simply because the fraction of the cross-sectional area available for transport of electric current is small.

CONCLUSIONS

The results that we obtained for coatings prepared by spin-coating acetate solutions of the Bi-Sr-Ca-Cu-O system are very promising, compared with the best results obtained on bulk superconductors with films made by solution techniques, e.g., spray pyrolysis or metallo-organic decomposition, reported in literature. The work now in progress includes substrates such as MgO, $SrTiO_3$, and sapphire. The sintering temperature, time, and oxygen pressure will be varied to optimize the best processing conditions to obtain high transport critical current densities.

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