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The preparation of YBCO epitaxial superconducting films by a chemical solution deposition process

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The utility of a chemical precursor solution for the production of $YBa_2Cu_3O_{7-x}$ superconducting films has been investigated. The homogeneous precursor solution made of metal acetates, 1,3-bis(dimethylamino)-2-propanol, and acetic acid was applied to [1 0 0] MgO substrates via spin-coating. Subsequent heating and sintering removed the organic components. The best epitaxial film obtained by this chemical solution deposition method has a T_c of 78 K. © *1999 Kluwer Academic Publishers*

1. Introduction

Since the discovery of high-temperature ceramic superconductors, there has been a great deal of interest in manipulating these materials into useful forms for use in a variety of practical applications [1]. In particular, there has been a strong demand for the development of superconducting films suitable for use in high-technology electronic devices such as those found in the microwave communication industry [2]. Several elaborate techniques have been developed for the production of superconducting films such as molecular vapor deposition [3] and laser ablation [4]. These techniques are well established and can produce high quality films. However, these techniques are usually slow and costly and may never be suitable for large scale industrial production. The chemical solution deposition (CSD) process, utilizing existing spin or dip-coating techniques may offer several advantages over other techniques for preparing superconducting films.

The difficulty in developing a chemical solution approach to producing superconducting films is the design of a suitable precursor solution with the characteristics necessary for film production. One of the major concerns in developing a solution precursor is attaining homogeneity of the constituent metals in solution. The constituent metals of a superconductor are chemically distinct, which results in their complexes having different physical properties such as solubility. For this reason it is difficult to achieve a homogenous solution containing all of the required metals. The problem is amplified by the need to produce a relatively viscous solution for use in the solution deposition process. Our approach to these problems has been to utilize organic bifunctional ligands capable of binding the constituent metal ions of a superconductor together. Using this method, the problem of the different solubilities of the individual metal components can be minimized. In addition, when the inevitable precipitation of the precursor does occur during thermal processing, the metal components will precipitate together rather than individually. In the past we have developed and studied several heterometallic systems utilizing multi-dentate ligands. Of those, 1,3-bis(dimethylamino)-2-propanol (bdmapH) has been found to be particularly useful in binding to several different metal ions. For example, we have synthesized several mixed metal complexes, Ba/Cu and Ln/Cu, where the bdmapH ligand functions as a cross-linking reagent to the Ba(II) and Cu(II) ions or Ln(III) (Y(III)) and Cu(II) ions. The major advantage provided by the bdmapH ligand is that, by binding to the metal centers, it significantly improves the solubility of metal compounds in organic solvents [5]. In this paper, the production of $YBa_2Cu_3O_{7-x}$ (YBCO) superconducting films by using a chemical precursor solution containing bdmapH and spin coating is described.

2. Experimental procedure

2.1. General procedures

All of the chemicals used were reagent grade and were used without further purification. Copper acetate and barium acetate were purchased from BDH, Inc. Yttrium acetate was purchased from the Strem Chemical Company. Since the yttrium and copper acetate starting materials were hydrated, the amount of water present was determined by thermogravimetric weight loss under oxygen using a Perking Elmer TGA-7. The compound 1,3-bis(dimethylamino)-2-propanol (bdmapH) was purchased from the Janssen Chemical Company. The spin-coating apparatus was a Laurell Technologies WS-200-4NPP-RV spin-coater. The spin-coating device was equipped with a small substrate vacuum chuck. Single crystal substrates of [1 0 0] MgO ($10 \times 10 \times 0.5$ mm^3) were purchased from Coating and Crystal

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Technology. Prior to being used crystal substrates were washed with ethanol to remove any contamination. The box furnace used was a Linburg Blue model 51700. The furnace was equipped with a Eurotherm model 808 programmable controller. All of the reactions were performed in air in a 10 mL beaker. The morphology of the film surfaces and the thickness of the films were investigated using a Jeol JSM-8500-LV or JSM-840 scanning electron microscope (SEM). Prior to making the thickness measurements the coated substrates were fractured to expose the central area of the film. Energy-dispersive X-ray spectroscopy (EDXS) was performed with a Tracor-Northern TN5500 instrument on the Jeol JSM-840 SEM. The critical onset temperatures were determined by magnetic susceptibility measurements performed on a Quantum Design MPMS SQUID magnetometer. X-ray powder diffraction experiments were performed on a Scintag XI powder diffractometer using CuKα radiation operating at 45 kV and 40 mA.

2.2. Synthesis and deposition of the precursor solution

The precursor solution for film 1 was prepared by dissolving $Y(O_2C_2H_3)_3 \cdot 2H_2O$ (50 mg, 0.17 mmol), $Ba(O_2C_2H_3)_2$ (85 mg, 0.33 mmol), $Cu(O_2C_2H_3)_2 \cdot H_2O$ (100 mg, 0.50 mmol) and bdmapH (146 mg, 0.66 mmol) in a 1 : 2 : 3 : 4 ratio in approximately 5 mL of acetic acid. The solution was stirred and heated until all of the metal salts were dissolved. The solution was then concentrated to approximately 0.3 M (based on Cu). The precursor solutions for films 2 and 3 were prepared in the same manner except that half of the acetic acid solvent was replaced with ethanol. In all cases, the dark blue solution was found to be stable for several weeks provided that stirring was continued and the flask was covered. The precursor solution was coated to the substrate via spin coating. The solution was applied to the surfaces of the [1 0 0] MgO substrates dropwise with a pipette. The substrates were then accelerated to 1500 r.p.m. in approximately 30 s. The spinning was continued for an additional 30 s. The initial precursor films were light blue in color and transparent. Once removed from the spin-coater the films were placed on a flat and level quartz plate.

2.3. Thermal processing of film 1

The plate containing the precursor-coated substrate was placed in the 400 °C preheated furnace. The film was then heated in air at 25 °C min^{-1} to 870 °C. The film was held at this temperature for approximately 1 h before being cooled to 400 °C at a rate of 10 °C min^{-1}. Shortly after being placed in the furnace the film became light brown in color. At this stage much of the volatile precursor had decomposed. The color of the film after high-temperature processing is dark blue or black and appears somewhat metallic. This coating and thermal processing was repeated an additional nine times to achieve the desired thickness. A final annealing was carried out in oxygen. This was achieved by placing the film under a quartz hood and flowing oxygen over the film. The rate of oxygen flow was measured to be approximately 20 cm^3 min^{-1}. During the final annealing the film was heated at a rate of 15 °C min^{-1} to 930 °C for 30 min. Following this the film was cooled at a rate of 10 °C min^{-1} to room temperature under oxygen.

2.4. Thermal processing of film 2

The precursor-coated substrate was placed in a 400 °C preheated furnace. The temperature was increased at a rate of 25 °C min^{-1} to 870 °C. The film was soaked at this temperature for approximately 1 h. Cooling was done at 10 °C min^{-1} to 400 °C. The coating and thermal processing was repeated an additional nine times. Annealing was performed by heating the film at 15 °C min^{-1} in flowing oxygen to 930 °C. The film was held at 930 °C for approximately 6 h before being cooled very slowly at the rate of 2 °C min^{-1} to room temperature under oxygen.

2.5. Thermal processing of film 3

The coated substrate was placed in the furnace at 25 °C and heated in air at 25 °C min^{-1} to 930 °C. The film was held at this temperature for approximately 30 min. The furnace was then cooled to 25 °C at a rate of 20 °C min^{-1} under oxygen. This process was repeated an additional 20 times to achieve the desired thickness. Annealing was performed by heating the film in flowing oxygen at 15 °C min^{-1} to 930 °C. The film was held at 930 °C for approximately 6 h before being cooled to room temperature at a slow rate of 2 °C min^{-1}. During this cooling the film was soaked at 400 °C and 300 °C for 6 h in oxygen.

3. Results and discussion

It has been reported previously that metallorganic precursor compounds can be used in the production of high-temperature superconducting films via a solution-deposition process [6]. The ligands used in these systems typically bond to a single metal center. While these ligands to improve the solubility of some of the metal compounds in solution, they do not address the problem of the solubility difference of different metal compounds. Therefore, non-homogenous precipitation of the different metal compounds often occur in these systems. While in the production of bulk powder samples this problem may be corrected by good mechanical mixing, in the production of film samples it will result in a loss of stoichiometry. The use of cross-linking reagents may address this problem since precipitation of the metal complexes containing more than one metal ion will retain stoichiometry during precipitation. The morphology of the films produced should also improve, since less rearrangement will be necessary in the solid state. Several examples of mixed metal compounds linked by bridging ligands, which may be useful as components in precursors for high-temperature superconductors are known [7]; however, few of them have been applied to produce superconducting materials [8]. We have investigated several ligands for their ability to form heteronuclear complexes with the constituent metals of the high temperature superconductor oxides. To date we believe the ligand 1,3-bis-dimethylamino-2-propanol (bdmapH) is the best. In independent syntheses we have isolated several mixed metal compounds using bdmap and acetate as cross-linking reagents. Although we have not been able to isolate any crystalline mixed-metal compounds directly from the dark blue solution, we believe that it is likely that some of the complexes formed in solution may be similar to those we obtained by independent syntheses, reported elsewhere [5].

Another advantage of cross-linking reagents is the enhanced solubility they bring to the precursor solution. In our studies we have found that 1 : 2 : 3 mixtures of $Y(O_2CCH_3)_3$, $Ba(O_2CCH_3)_2$ and $Cu(O_2CCH_3)_2$ are soluble in acetic acid provided the solution is kept very dilute or at high temperature. If the solution is concentrated or cooled to ambient temperature the result is the precipitation of one or more of the metal compounds. We have found that the addition of a small amount of bdmapH to a mixture of these acetates greatly enhances the solubility of the individual metal components. This ability to control the concentration of the precursor solution is important in the application of the precursor using either the spin-coating or dip-coating techniques. With these techniques the thickness of the film is largely controlled by the viscosity of the solution used. The viscosity of the precursor solution made with the bdmapH ligand can be easily adjusted by controlling the amount of solvent present. This allows the precursor solution to be coated easily using common solution-deposition techniques.

The substrates used in our work are [1 0 0] MgO and [1 0 0] $LaAlO_3$. The tetragonal lattice constants for MgO and $LaAlO_3$ are $a = 0.4203$ nm and 0.3790 nm, respectively [9]. Since the lattice constants for the orthorhombic YBCO superconductor are $a = 0.32$ nm and $b = 0.389$ nm, a closer lattice match is expected for $LaAlO_3$ [10]. The thermal lattice expansion characteristics of $LaAlO_3$ and MgO are similar, having expansion coefficients of $10 \times 10^{-6}\,^{\circ}C^{-1}$ and $8 \times 10^{-6}\,^{\circ}C^{-1}$ respectively. Both are therefore suitable as substrates for YBCO which has an expansion coefficient of $11–12 \times 10^{-6}\,^{\circ}C^{-1}$ [11(b)]. One of the principal uses for high T_c superconducting films is in high-frequency applications such as those found in the microwave communication industry [2]. For these applications the dielectric constant of the substrate should be as low as possible. The dielectric constants for MgO and $LaAlO_3$ are 10 and 25 respectively. Although MgO may be slightly better, both substrates are acceptable as substrates for use in microwave applications which require dielectric constants less than 100 [11]. We have observed that films produced on $LaAlO_3$ have very poor surface and superconducting properties. For this reason the work presented here involves only MgO substrates.

The nature of the solvent in a precursor solution is the other principal controlling factor in the substrate precursor interactions [12]. A precursor solution intended for use in film production must bind to the substrate material as well as the superconductor oxide. If the precursor does not coat evenly, forming droplets or islands, the production of high-quality oxide films will not be possible. Since the substrates commonly used to produce epiaxial microcrystalline films of YBCO are oxide materials, the initial solvent chosen for our precursor system was acetic acid. Acetic acid is an ideal polar solvent because it binds well with the polar oxide substrates and also allows for the formation of a viscous precursor solution. Unfortunately, acetic acid is corrosive and can slowly dissolve YBCO. This creates the problem of the previously coated layers of oxide being partially dissolved during the application of additional layers. The resulting film will be porous and thin. This problem has been observed in our first attempt to produce the YBCO film 1. The solvent used in the experiment for film 1 was glacial acetic acid. A SEM micrograph of a randomly selected area of this film is shown in Fig. 1. The black regions, comprising approximately 15% of the film, are the MgO substrate as confirmed by EDX and are evidence of incomplete coverage due to the corrosive nature of the solvent. The film consists of uniform round platelets measuring laterally 2–3 μm which lie parallel to the substrate surface. The microstructures observed in other similar metallorganic or sol-gel processes using spin coating have shown less uniform microstructures and often smaller grain sizes [6(a), 6(c), 6(g), 13]. The thickness of this film was measured to be approximately 0.5 μm by cross-sectional SEM. Film 1 does show an excellent X-ray powder diffraction pattern with only the $YBa_2Cu_3O_{7-x}$ peaks and substrate peaks appearing. Since only [0 0 ℓ] lines were observed in the diffraction scan, it can be concluded that the film shows a preferred epitaxial alignment along the c axis of the substrate. There is no evidence of other misaligned phases or impurities present, since, except for the MgO [2 0 0] reflection, no other reflections were observed Fig. 3. Despite the thin and porous nature of this film, the sample was found to be superconducting. The superconducting characteristics of the films were investigated by variable-temperature magnetic susceptibility measurements using a SQUID magnetometer. This was accomplished by cooling the films to 2 K in the absence of a magnetic field before warming the film to 300 K in a field of 100 G, which showed that film 1 has an onset critical temperature of approximately 60 K (curve A, Fig. 2).

The porous appearance of the film can be minimized by diluting the acetic acid solution. In the precursor solution used for film 2, approximately half of the acetic acid solvent was replaced by ethanol. Further dilution of the acetic acid solvent with ethanol resulted in the precipitation of a white powder. The results of diluting the acetic acid solvent dramatically improved the morphology of the film. This can be seen clearly from the randomly selected area of the film shown in the SEM micrograph of film 2 (Fig. 4). The film is denser, in comparison to film 1, and covers nearly the entire surface area of the substrate, although a few very small holes (less than 1 μm) are still present, which appear black on the micrograph. The entire film area is similar to the region shown except for some small cracks very close to the substrate edges. The film again consists of uniform round platelets; however, the platelets in this film are larger than those in film 1 with diameters ranging from 3 to 5 μm. A uniform and complete coverage of the materal with large grains is highly

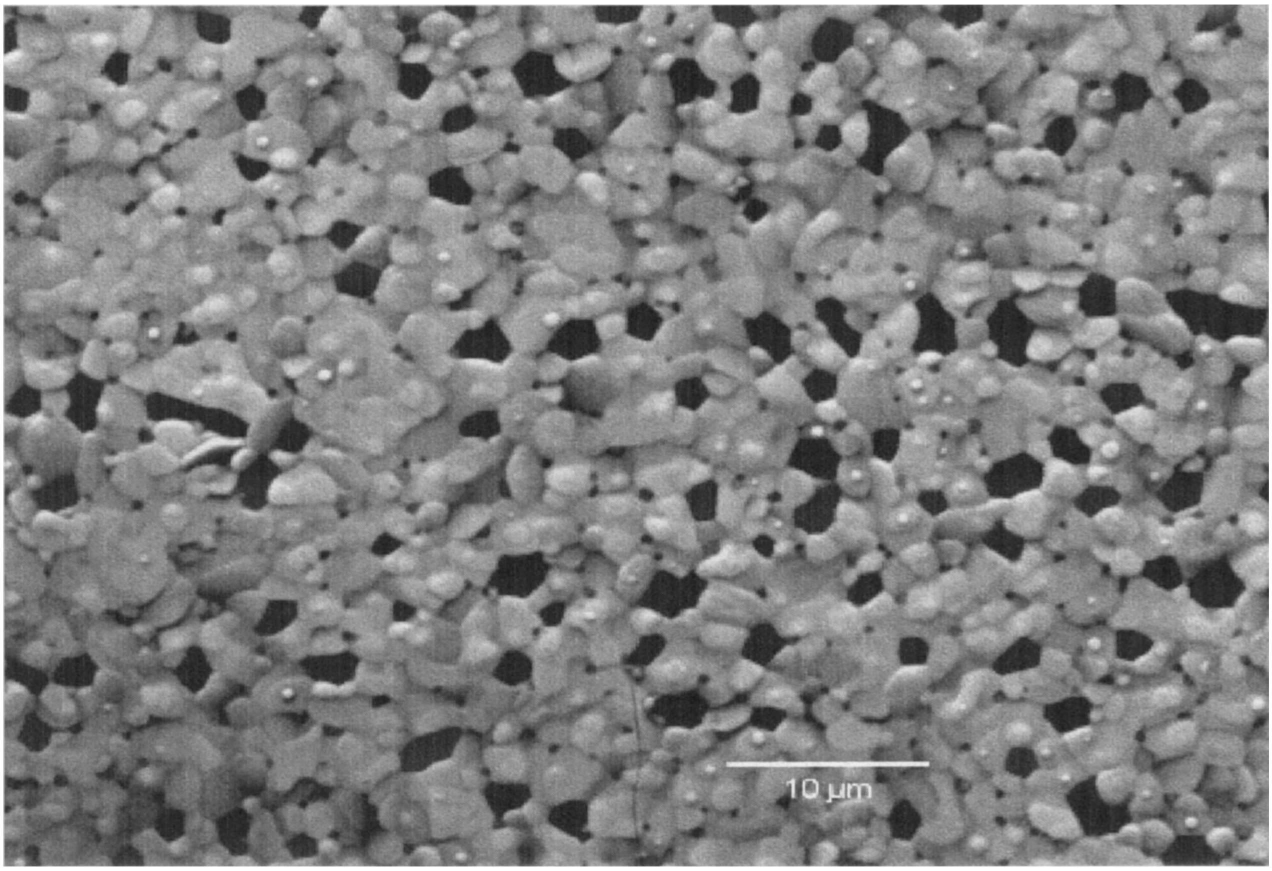

Figure 1 a SEM micrograph of film 1.

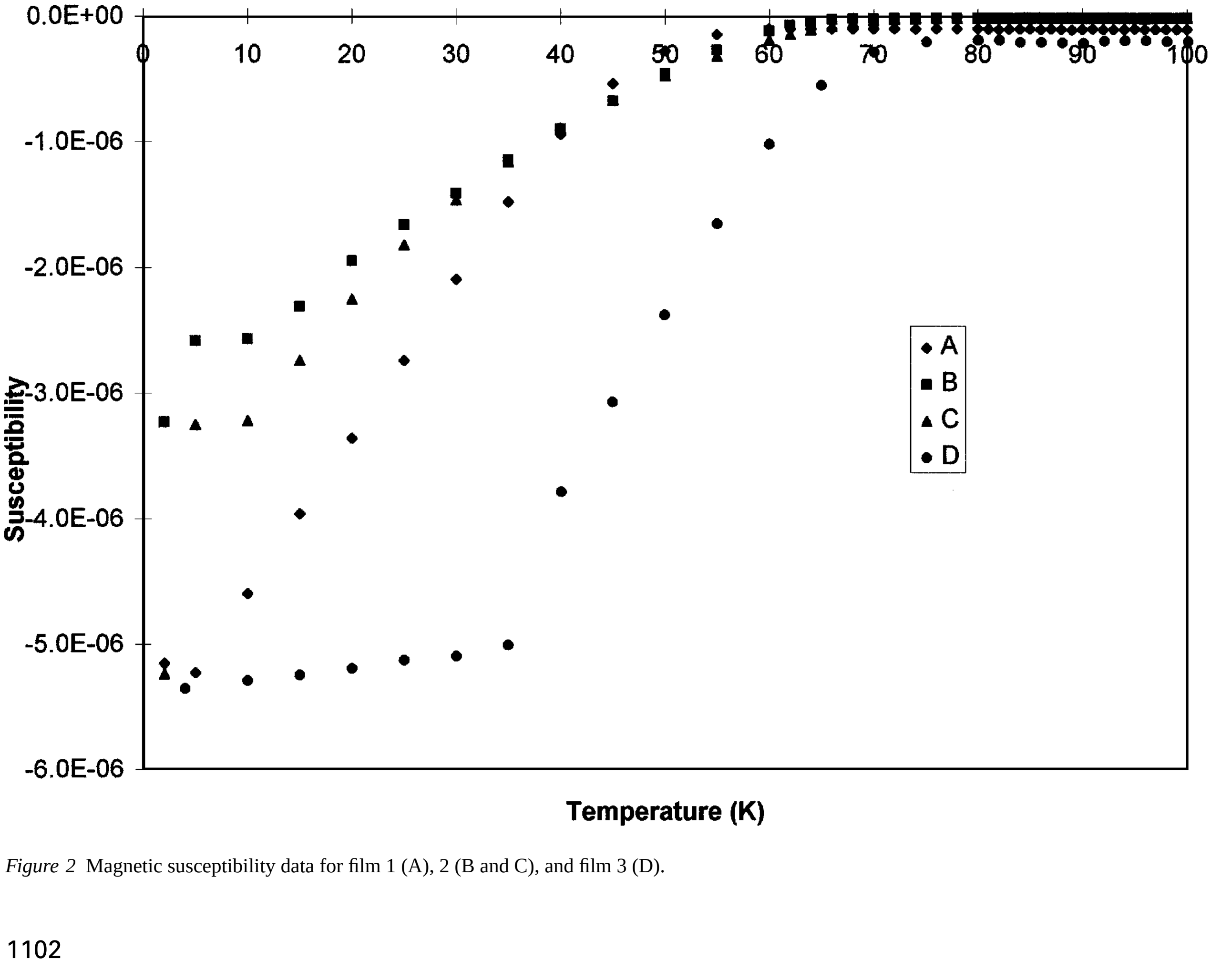

Figure 2 Magnetic susceptibility data for film 1 (A), 2 (B and C), and film 3 (D).

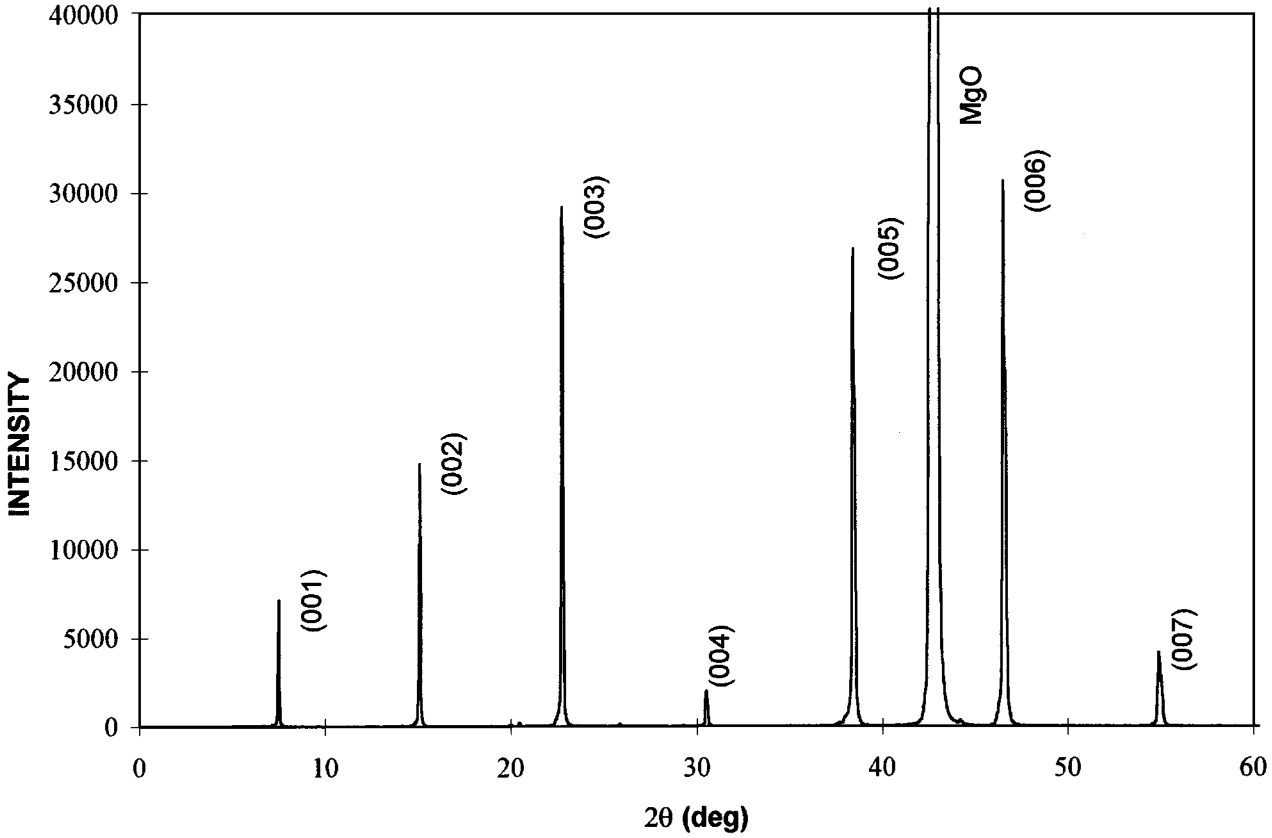

Figure 3 X-ray powder diffraction diagram for film 1. (The X-ray diffraction diagrams for films 2 and 3 are identical to that of film 1, except that the relative intensities of the MgO peaks decrease substantially.)

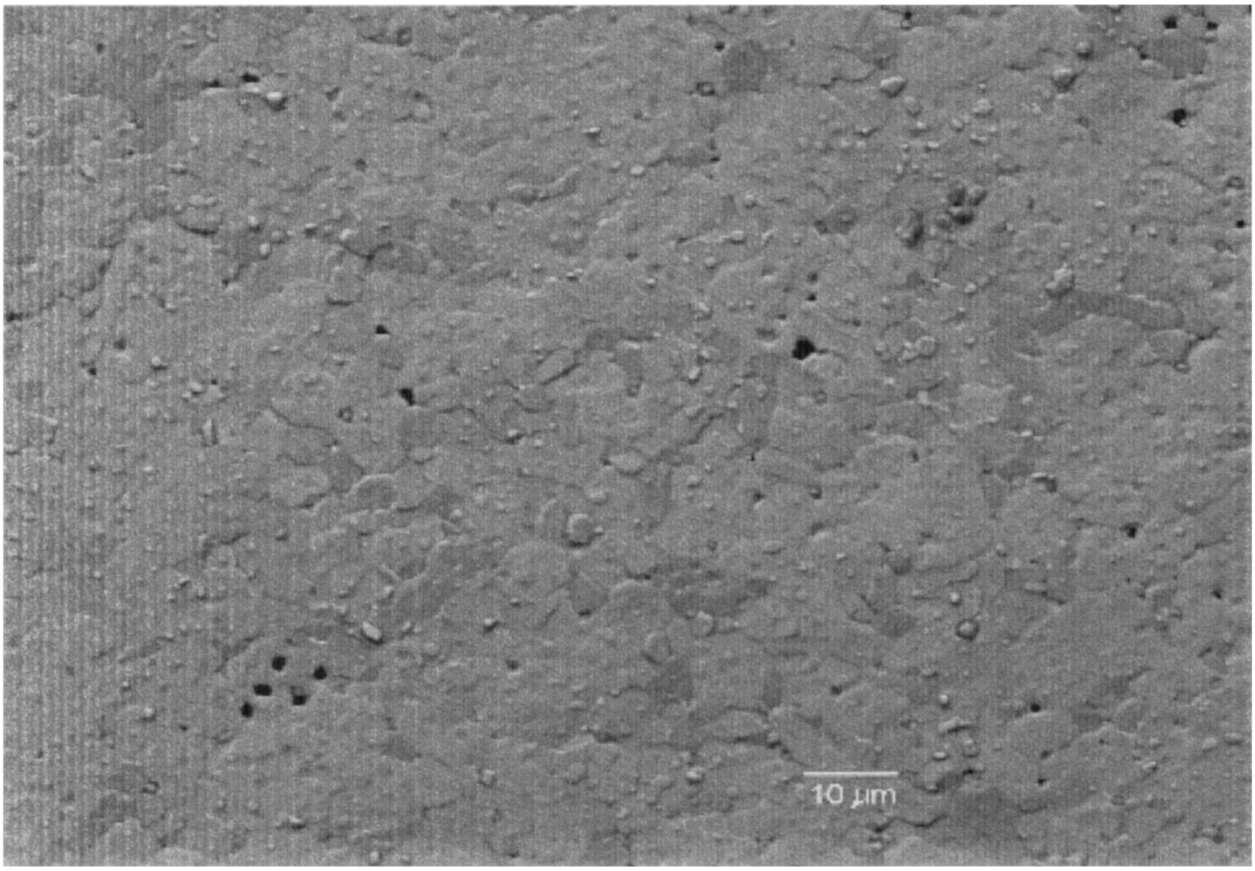

Figure 4 a SEM micrograph of film 2.

desirable in superconducting films, since grain boundaries are minimized [14, 1(a)]. We believe the high-quality microstructure observed in this film is directly related to the presence of the bdmapH cross-linking reagent in the precursor solution, since systems involving only metal acetates do not show this type of high-quality microstructure [6(e)]. The X-ray powder diffraction pattern of this film is again consistent with YBCO superconductor with an epitaxial alignment along the c axis on the substrate. Unfortunately, the critical temperature for this film is still only 68 K (curve B, Fig. 2). The optimal critical temperature for YBCO superconductor oxide is approximately 96 K. Several factors can contribute to a low critical temperature in ceramic superconductor films. Two of the most common contributing factors are oxygen deficiency and non-homogenous surfaces [15]. In an effort to improve the critical temperature of the films, a second annealing was performed on film 2. In this process the film was held at a 930 °C for approximately 6 h. The purpose of this extended high-temperature heating was to allow further crystallization to occur, thus improving the homogeneity of the surface. The film was then cooled very slowly (2 °C min^{-1}) to room temperature with 6 h delays at 300 °C and 400 °C in the hope that the oxygen content of the superconductor could be maximized. At high temperatures oxygen is lost in YBCO superconductor, and therefore annealing at a lower temperature in an oxygen-enriched atmosphere is necessary. This can be accomplished by either slowly cooling the film or soaking the film at a relatively low temperature [16]. The results of this second annealing did improve the morphology slightly, since the film showed less vacant areas. The superconducting property of the film did not however improve much, with the critical onset temperature still being only 74 K (curve C, Fig. 2). It has also been shown that very high-temperature treatments can partially fuse the grains of YBCO, which reduces boundaries and produces more homogenous films [6(a), 6(e), 17]. It should be noted, however, that prolonged exposure to very high temperatures may be damaging to the film, since melting of individual components of the superconductor may occur [18]. In an article by S. I. Shaw, eutectic melting was shown to occur at temperatures as low as 850 °C [19]. It has been commonly found, however, that much higher temperatures are often needed to attain high-quality materials [6(a), 6(d), 6(e), 6(f), 6(g), 13(a), 13(c), 17, 20]. In our work we have found that temperatures less than 930 °C produce non-superconducting films. Further high-temperature treatments were attempted at 970 °C, 980 °C and 990 °C for short periods of time (2 min) and prolonged low-temperature heating was attempted but no improvement in the films T_c was observed.

The thickness of film 2 was measured by cross-sectional SEM measurements which showed the film had a thickness of approximately 0.8 μm. It has been shown that very thin films can lead to low T_c values [6(e), 20]. Efforts were therefore made to produce a thicker film by applying additional coats. Further improvements in the film morphology were also desired. The thermal processing rate below the decomposition temperature should have a large effect on the morphology of the final film produced. Thermogravimetric

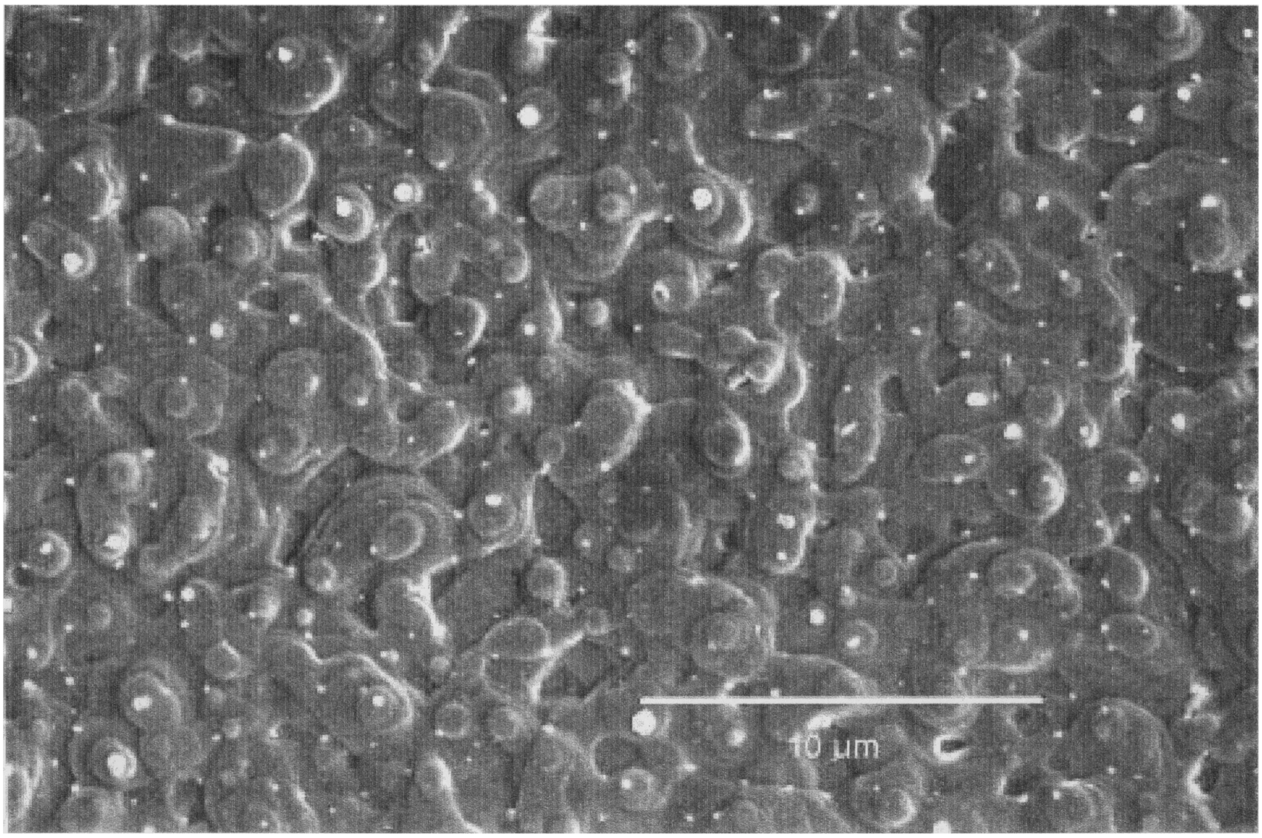

Figure 5 a SEM micrograph of film 3.

analysis of the dried precursor material has shown that approximately 95% of the precursor decomposition occur at temperatures below 412 °C. It was therefore thought that gradual heating from room temperature would result in an improvement in the morphology of the films. The techniques used in previously described metallorganic systems to decompose precursor films vary. In many cases the films were heated very rapidly [6(a), 6(c), 6(f)]. One possible explanation for this choice of processing method is that in these systems non-stoichiometric precipitation occurs if a slow heating process is used. We anticipated that a loss of stoichiometry by premature precipitation of individual metal ions during this gradual heating would not be a problem in our system due to the presence of the bdmapH cross-linking reagent. The resulting film 3 obtained after 20 coats indeed showed improved superconducting characteristics with a critical temperature of 78 K (curve D, Fig. 2). From the SEM image for this film it can be seen that film 3 is much more densely coated than films 1 and 2 with no observable uncovered areas. A few small (0.1–0.5 μm) particles of unknown composition also appear on the film surface. The nature of these unknown particles is being investigated. The film appears to be comprised of several stacked layers of platelets lying parallel to the substrate surface (Fig. 5). The platelets in the top layers appear smaller (1–2 μm) than those of the lower layers (3–4 μm). With the exception of a few small defects at the substrate edge, no cracking was observed in the film. The thickness of this film was found to be 1.2 μm. We have not been able to produce the YBCO film with a T_c above 80 K. Oxygen deficiency may be still a factor. However, it is also possible that the low T_c of our films were caused by carbon contamination, which is being examined in our laboratory.

4. Conclusions

The bdmapH precursor solution system has been shown to produce highly uniform superconducting films of YBCO using the spin-coating method via a relatively easy and inexpensive process. The principle factors responsible for the quality of the films produced are the presence of the bdmapH cross-linking reagent, the solvents, the thermal processing conditions, and the number of coats applied to the film. Future efforts will focus on improving the quality and T_c of the YBCO films as well as the application of the bdmapH precursor system to other copper-oxide-based superconducting films.

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References

1. (a) G. B. LUBKIN, *Phys. Today* **3** (1995) 20; (b) H. J. SCHEEL, *MRS Bull.* **9** (1994) 26; (c) T. H. TIEFEL, S. JIN, G. W. KAMMLOTT, J. E. GRAEBNER and R. B. VAN DOVER, *Appl. Phys. Lett.* **58** (1991) 1917; (d) T. H. GEBALLE, *Science* **259** (1993) 306; (e) H. OHTA, T. NAKAYAMA and M. AONO, *Riken Review II* **2** (1993) 3.
2. (a) P. D. GRANT and R. F. CLARK, in the Proceedings of the Symposium on Antenna Technology and Applied Electromagnetics Ottawa, August 1994, p. 581; (b) G. E. DIONNE, D. E. OATES and D. H. TEMME, *IEEE Trans. Appl. Supercond.* **5** (1995) 2083; (c) C. H. MULLER, F. A. MIRANDA, S. S. TONCHICH and K. B. BHASIN, *ibid.* **5** (1995) 2559; (d) G. C. LIANG, D. ZHANG, C. F. SHIH, M. E. JOHANASSON and R. S. WITHERS, *ibid.* **5** (1995) 2652.
3. (a) K. ZHANG, B. S. KWAK, E. P. BOYD, A. C. WRIGHT and A. ERBIL, *Appl. Phys. Lett.* **54** (1989) 380; (b) A. J. PANSON, R. G. CHARLES, D. N SCHMIDT, R. J. SZEDON, J. R. MACHIKO and A. I. BRAGINSKI, *Appl. Phys. Lett.* **53** (1988) 1756; (c) R. HISKES, S. A. DICAROLIS, J. L. YOUNG, S. S. LADERMAN, R. JACOWITZ and R. C. TABER, *Appl. Phys. Lett.* **59** (1991) 606; (d) H. SAKAI, Y. SHIOHARA and S. TANAKA, *Physica C* **228** (1994) 259.
4. (a) X. D. WU, T. VENKATESAN, A. INAM, C. CHANG, R. RAMESH, D. M. HWANG, L. NAZAR, B. WILKENS, S. A. SCHWARZ, R. T. RAVI, J. A. MARTINEZ, J. B. BARNER, P. ENGLAND, C. T. ROGERS, J. M. TARASON, R. E. MUENCHAUSEN, S. FOLTYN, R. C. DYE, A. R. GARCIA and N. S. NOGAR, *Proc. of MRS* **191** (1990) 129; (b) J. FROHLINGSDROF, W. ZANDER and B. STRITZER, *Solid State Commun.* **67** (1988) 965. (c) A. I. GOLOVASHIKIN, E. V. EKLINOV, S. I. KRASNOSVOBODTSEV and E. V. PECHEN, *Physica C* **153** (1988) 1455.
5. (a) S. WANG, Z. PANG, K. D. L. SMITH, YOU-SHENG HUA, C. DESLIPPE and M. J. WAGNER, *Inorg. Chem.* **34** (1995) 909; (b) S. WANG, Z. PANG and K. D. L. SMITH, *ibid.* **32** (1993), 4993; (c) S. WANG, S. J. TREPANIER and M. J. WAGNER, *ibid.* **32** (1993) 833; (d) S. BREEZE and S. WANG, *ibid.* **33** (1994) 5113; (e) S. WANG, Z. PANG, K. D. L. SMITH and M. J. WAGNER, *J. Chem. Soc. Dalton Trans.* (1994) 955.
6. (a) M. E. GROSS, M. HONG, S. H. LIOU, P. K. GALLAGHER and J. KWO, *Appl. Phys. Lett.* **52** (1988) 160; (b) S. J. GOLDEN, T. E. BLOOMER, F. F. LANGE, A. M. SEGADAES, K. J. VAIDYA and W. L. OLSEN, *Mater. Res. Soc. Symp. Proc.* **169** (1990) 755; (c) A. H. HAMDI, J. V. MANTESE, A. L. MICHELI, R. C. O. LAUGAL, D. F. DUNGAN, Z. H. ZHANG and K. R. PADMANABHAN, *Appl. Phys. Lett.* **51** (1987) 2152; (d) A. GUPTA, R. JAGANNATHAN, E. I. COOPER, E. A. GIESS, J. I. LANDMAN and B. W. HUSSEY, *Appl. Phys. Lett.* **52** (1988) 2077; (e) C. E. RICE, R. B. VAN DOVER and G. J. FISANICK, *Appl. Phys. Lett.* **51** (1987) 1842; (f) S.-T. LEE, S. CHEN, L. S. HUNG and G. BRAUNSTEIN, *Appl. Phys. Lett.* **55** (1989) 286; (g) P.-Y. CHU, I. CAMPION and R. C. BUCHANAN, *J. Mater. Res.* **8** (1993) 261.
7. (a) A. PURDY and C. F. GEORGE, *Inorg. Chem.* **30** (1991) 1971; (b) A. PURDY, C. F. GEORGE and J. H. CALLAHAN, *ibid.* **30** (1991) 2813; (c) W. BIDEL, J. DORING, H. W. BOSCH, H.-U. HUND, E. PLAPPERT and H. BERKE, *ibid.* **32** (1993) 502; (d) A. J. BLAKE, R. O. GOULD, P. E. Y. MILNE and R. E. P. WINPENNY, *J. Chem. Soc. Dalton Trans.* (1991) 1453; (e) U. CASELLO, P. GUERRIERO, S. TAMBURINI, S. SITRAN and P. A. VIGATO, *ibid.* (1991) 2145; (f) A. BENCINI, C. BENELLI, A. CANESCHI, R. L. CARLIN, A. DEI and D. GATTESCHI, *J. Am. Chem. Soc.* **107** (1985) 8128; (g) M. SAKAMOTO, M. TAKAGI, T. ISHIMORI and H. OKAWA, *Chem. Soc. Jpn.* **61** (1988) 1613; (h) A. J. BLAKE, P. E. Y. MILNE, P. THORNTON and R. E. P. WINPENNY, *Angew. Chem. Int. Ed. Engl.* **30** (1991) 1141; (i) C. BENELLI, A. CANESCHI, D. GATTESHI, O. GUILLOU and L. PARDI, *Inorg. Chem.* **29** (1990) 1750; (j) A. BENCINI, C. BENELLI, A. CANESCHI, A. DEI, D. GATTESCHI, *ibid.* **25** (1986) 572.
8. (a) N. N. SAUER, E. GARCIA, K. V. SALAZAR, R. R. RYAN and J. A. MARTIN, *J. Am. Chem. Soc.* **112** (1990) 1525; (b) S. KATAYAMA and M. SEKINE, *Mater. Res. Soc. Symp. Proc.* **180** (1990) 873; (c) H. S. KOO, C.K. CHIANG, Y. T. HUANG and G. C. TU, *ibid.* **180** (1990) 917.

9. (a) "Technical Data Sheet," RD # 4, (Coating and Crystal Technology, Inc., Kittanning, PA 16201) p. 3. (b) J.M. PHILLIPS, *MRS Bull*. **4** (1995) 35.
10. C. P. POOLE JR., T. DATTA and H. A. FARACH, in "Copper oxide superconductors" (Wiley-Interscience, New York, 1988) p. 92.
11. (a) J. H. HINKEN, in "Superconductor electronics, fundamentals and microwave applications" (Springer-Verlag, New York, 1989) p. 6; (b) R. BROWN; V. PENDRICK and D. KALOKITIS, *Appl. Phys. Lett*. **57** (1990) 1352.
12. J. B. WACHTMAN and R. A. HABER, in "Ceramic Films and Coatings" (Noyes Publications, New Jersey, 1993) p. 315.
13. (a) Y. MASUDA, R. OGAWA and Y. KAWATE, *J. Mater. Res*. **7** (1992) 819; (b) S. A. KRAMER, G. KORDAS, J. MCMILLAN, G. C. HILTON and D. J. VAN HARLINGER, *Appl. Phys. Lett*. **53** (1988) 156; (c) A. A. HUSSAIN and M. SAYER, *J. Supercond*. **5** (1992) 11.
14. Y. ZHU, J. TAFTO and M. SUENAGA, *MRS Bull*. **11** (1991) 54.
15. P. KUMAR, V. PILLAI, S. R. BATES and D.O. SHAH, *Mater. Lett*. **16** (1993) 68.
16. C. N. R. RAO, in "Chemistry of Advanced Materials" (Blackwell Science, London, 1993) p. 155.
17. D. S. GINLEY, E. L. VENTURINI, J. F. KWAK, R. J. BAUGHMAN and B. MOROSIN, *J. Mater. Res*. **4** (1989) 496.
18. R. S. ROTH, K. L. DAVIS and J. R. DENIS, *Adv. Ceram. Mater*. **2** (1987) 36.
19. S. I. SHAW, *Appl. Phys. Lett*. **53** (1988) 612.
20. P. MAY, D. JEDAMZIK, W. BOYLE and P. MILLER, *Supercond. Sci. Technol*. **1** (1988) 1.

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