Thin films of YBa2Cu3O7, YBa2Cu3O7:Ag, and Bi2CaSr2Cu2O8 have been grown by spray pyrolysis of aqueous nitrate solutions. Substrate temperatures in the range of 300°C to 875°C have been investigated. Following deposition, the films were annealed in flowing oxygen at 960°C for YBa2Cu3O7 and 850°C for Bi2CaSr2Cu2O8. The unit cell size of YBa2Cu3O7:Ag did not change from that of YBa2Cu3O7 but the X-ray diffraction patterns for the YBa2Cu3O7:Ag films show that the (001) reflections are greatly enhanced over all others. A Tc of 81K with a ΔTc of 3K has been measured for YBa2Cu3O7:Ag films and a Tc of 74K with a ΔTc of 3K has been measured for YBa2Cu3O7. These films were all grown on MgO substrates. The Bi2CaSr2Cu2O8 films are multilayer and have Tc of 65K with a very broad transition. The materials were characterized by X-ray diffractometry, scanning electron microscopy, and resistive superconducting transition measurements.

Introduction

Reproducible growth of high quality oxide superconducting films is a goal which is important for many potential applications of the high Tc superconductor materials. Spray pyrolysis of aqueous nitrate solutions1,2,3,4 enables good reproducibility of composition from layer to layer. One of the advantages of the spray pyrolysis procedure for thin film growth is that desired concentrations of dopants can be incorporated simply by adding the nitrate of the dopant as either a substitution for or in addition to the component elements of YBa2Cu3O7. Substitution for or in addition to the component elements increases the tendency for preferential orientation. Although preferential orientation has been observed for YBa2Cu3O7:Ag films, the relative changes in intensity of the (001) reflections compared to all other peaks has not been as great. The presence of silver in the film has increased the tendency for preferential orientation. Although preferential orientation has been occasionally observed in our YBa2Cu3O7 films, the relative changes in intensity of the (001) peaks compared to all other peaks has not been as extensive or as consistent prior to the addition of Ag. The unit cell sites for the YBa2Cu3O7 and YBa2Cu3O7:Ag films are listed in Table 1. Within experimental error the unit cell size has not changed with the addition of the silver indicating that silver has not been incorporated into the lattice of YBa2Cu3O7. Examination of the YBa2Cu3O7:Ag films using optical microscopy shows the presence of metallic appearing inclusions which may be elemental silver, although the peaks common to silver could not be seen in the X-ray diffraction pattern.

Sample Preparation

The solutions used for growth of the YBa2Cu3O7 films were prepared by dissolving Y2O3, BaCO3 and CuO in nitric acid to make the solution equivalent to 0.05 mole/l of YBa2Cu3O7. To make the YBa2Cu3O7:Ag composites, quantities of AgNO3 were added to the 0.05 mole/l YBa2Cu3O7 solution such that the solution was equivalent to 0.05 mole/l of Bi2CaSr2Cu2O8. The solutions were sprayed onto a MgO substrate using oxygen as the propellant gas. The substrate temperature was at 325°C-350°C to initiate film nucleation and coating of the substrate, after which the temperature was increased to 875°C for 10 minutes. From 875°C the samples were cooled over a period of one hour to 350°C and sprayed again. The heating/spraying cycle was repeated 2-4 times for the YBa2Cu3O7 or YBa2Cu3O7:Ag samples. The sprayed film on the MgO substrates at 960°C was then transferred to a tubing furnace and annealed in flowing oxygen at 960°C for a period of 10 minutes. The samples were cooled to room temperature at the rate of 50°C/hour.

The Bi2CaSr2Cu2O8 samples were sprayed onto MgO substrates at 500-600°C then transferred to a tubular furnace for annealing. Annealing was under flowing oxygen at 840°C-850°C for 10 minutes then cooled rapidly by withdrawing the samples from the furnace while still under flowing oxygen. Adhesion of YBa2Cu3O7 to the MgO substrate was much better than for the Bi2CaSr2Cu2O8 film.

Characterization and Discussion

An X-ray diffraction pattern for a typical YBa2Cu3O7 film shows the most intense reflections are the (013), (015) and (100) which occur in the range of 2θ = 32.5°-32.9°. The (003), (005), (006), and (007) reflections at 2θ = 22.8°, 38.4°, 46.9°, and 54.9° exhibit much lower intensity. An X-ray diffraction pattern for a YBa2Cu3O7:Ag composite film on MgO is shown in Figure 1. The (001) reflections are by far the most predominant reflections for the YBa2Cu3O7:Ag film with the other reflections for YBa2Cu3O7 having relatively low intensity. The presence of silver in the film has increased the tendency for preferential orientation. Although preferential orientation has been occasionally observed in our YBa2Cu3O7 films, the relative changes in intensity of the (001) peaks compared to all other peaks has not been as extensive or as consistent prior to the addition of Ag. The unit cell sites for the YBa2Cu3O7 and YBa2Cu3O7:Ag films are listed in Table 1. Within experimental error the unit cell size has not changed with the addition of the silver indicating that silver has not been incorporated into the lattice of YBa2Cu3O7. Examination of the YBa2Cu3O7:Ag films using optical microscopy shows the presence of metallic appearing inclusions which may be elemental silver, although the peaks common to silver could not be seen in the X-ray diffraction pattern.

Table 1. Unit Cell Dimensions of Oxide Superconductors

<table>
<thead>
<tr>
<th>n</th>
<th>a (Å)</th>
<th>b (Å)</th>
<th>c (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>YBa2Cu3O7</td>
<td>3.829(±0.004)</td>
<td>3.847(±0.005)</td>
<td>11.683(±0.07)</td>
</tr>
<tr>
<td>YBa2Cu3O7:Ag</td>
<td>3.829(±0.009)</td>
<td>3.897(±0.006)</td>
<td>11.720(±0.05)</td>
</tr>
<tr>
<td>Bi2CaSr2Cu2O8</td>
<td>5.43(±0.03)</td>
<td>5.43(±0.03)</td>
<td>30.29(±0.16)</td>
</tr>
</tbody>
</table>

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X-ray diffraction patterns for Bi$_2$CaSr$_2$Cu$_2$O$_8$ films on MgO show that the films are multiphase. Diffraction peaks corresponding to those identified as belonging to Bi$_2$CaSr$_2$Cu$_2$O$_8$ have been indexed to a tetragonal unit cell. The calculated unit cell dimensions are listed in Table 1 and are consistent with values reported in the literature for Bi$_2$CaSr$_2$Cu$_2$O$_8$.

Figures 2, 3 and 4 show scanning electron micrographs of YBa$_2$Cu$_3$O$_7$, YBa$_2$Cu$_3$O$_7$:Ag and Bi$_2$CaSr$_2$Cu$_2$O$_8$ films on MgO substrates. Figures 2A, 3A, and 4A show a view of the respective film surface whereas Figures 2B, 3B, and 4B show edge views of the respective films and substrates which had been cleaved. In comparing the morphology of the YBa$_2$Cu$_3$O$_7$ and YBa$_2$Cu$_3$O$_7$:Ag films with the YBa$_2$Cu$_3$O$_7$ film, it has a more irregular surface with individual granules protruding through the surface of the film. The surface of the YBa$_2$Cu$_3$O$_7$:Ag film is much more uniform in that the individual grains do not protrude through nor stand above the surface of the film. One possible reason for the increased uniformity or eroded appearance is that the silver which was originally dispersed throughout the film diffused and coalesced upon annealing. The diffusion of the silver into and through the YBa$_2$Cu$_3$O$_7$ grains may have aided in the fusion of the individual YBa$_2$Cu$_3$O$_7$ grains into a more uniform material containing fewer voids. The YBa$_2$Cu$_3$O$_7$:Ag material appearance and the preferred orientation shown in the X-ray diffraction patterns for the films are suggestive that a liquid may have been present during the annealing, possibly as a result of partial melting or dissolution of the YBa$_2$Cu$_3$O$_7$ in molten silver. Figures 2B and 3B show that both YBa$_2$Cu$_3$O$_7$ and YBa$_2$Cu$_3$O$_7$:Ag have conformed to the surface of the MgO substrates. The YBa$_2$Cu$_3$O$_7$:Ag film, however, has a few voids and the film adhered better to the substrate while being cleaved. The thicknesses of the two films were approximately 7 μm and 3 μm respectively.

Figure 4 shows SEM images of the Bi$_2$CaSr$_2$Cu$_2$O$_8$ film on MgO substrates. The morphology of the Bi$_2$CaSr$_2$Cu$_2$O$_8$ material is quite different from that of the YBa$_2$Cu$_3$O$_7$ layers. Bi$_2$CaSr$_2$Cu$_2$O$_8$ forms platelets which are on the substrate such that the layer has many voids. The random fashion in which the platelets attach to the substrate and to one another precludes substantial surface contact and may contribute to the poor adherence of the film. The thickness of the Bi$_2$CaSr$_2$Cu$_2$O$_8$ film shown in Figure 4B is approximately 1-2 μm. We have not added Ag to the growth solution nor have we optimized the growth and annealing conditions which may improve the morphology and adherence of the Bi$_2$CaSr$_2$Cu$_2$O$_8$ films.
Figure 3B. Scanning electron micrograph showing an edge view of cleaved YBa$_2$Cu$_3$O$_7$:Ag/MgO.

Figure 4A. Scanning electron micrograph showing growth habit of Bi$_2$CaSr$_2$Cu$_2$O$_8$.

Figure 4B. Scanning electron micrograph showing edge view of Bi$_2$CaSr$_2$Cu$_2$O$_8$/MgO.

Figure 5. Plot of resistance versus temperature for YBa$_2$Cu$_3$O$_7$:Ag.

Electrical resistance measurements of annealed films were made using a 10µA, 100 Hz constant current source and the in-line four point probe technique. Contacts to the oxide films were by indium coated, spring loaded pressure contacts. Figure 5 shows a plot of resistance versus temperature for a film of YBa$_2$Cu$_3$O$_7$:Ag on MgO. The transition temperature for this sample is 81K, the $\Delta T_c$ is 3K and the zero resistance occurred at 78K.

Table 2 contains the $T_c$ and $\Delta T_c$ for selected films of YBa$_2$Cu$_3$O$_7$, YBa$_2$Cu$_3$O$_7$:Ag, and Bi$_2$CaSr$_2$Cu$_2$O$_8$. The $T_c$ represents the temperature at which the resistance became 50% of its value at the onset of superconductivity. The $\Delta T_c$ is the temperature interval over which the resistance decreased from 90% to 10% of its value at onset. The values of $T_c$ are slightly higher for films of YBa$_2$Cu$_3$O$_7$:Ag than for films of YBa$_2$Cu$_3$O$_7$ while the $\Delta T_c$ value has not been greatly influenced. The very large $\Delta T_c$ for the Bi$_2$CaSr$_2$Cu$_2$O$_8$ film is consistent with the type of properties expected for a multiphase material.

Table 2. Measured $T_c$ and $\Delta T_c$ for YBa$_2$Cu$_3$O$_7$ and YBa$_2$Cu$_3$O$_7$:Ag Films on MgO

<table>
<thead>
<tr>
<th>Molar Ratio (Ag/YBa$_2$Cu$_3$O$_7$)</th>
<th>$T_c$(K)</th>
<th>$\Delta T_c$(K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>74</td>
<td>3</td>
</tr>
<tr>
<td>0.04</td>
<td>74</td>
<td>3</td>
</tr>
<tr>
<td>0.06</td>
<td>81</td>
<td>3</td>
</tr>
<tr>
<td>0.2</td>
<td>81</td>
<td>3</td>
</tr>
</tbody>
</table>

**Conclusions**

Spray pyrolysis of nitrate solutions followed by annealing in oxygen provides a viable technique for the preparation of polycrystalline oxide superconductor materials. Film thicknesses measuring 3-8 µm can easily be grown on MgO substrates. Films with $T_c$ of 74K and a transition width of 3K have been achieved for YBa$_2$Cu$_3$O$_7$ whereas for the silver composite films we have achieved $T_c$ of 81K and a transition width of 3K. The YBa$_2$Cu$_3$O$_7$:Ag films exhibit preferred orientation and appear to have fewer voids. A $T_c$ of 65K has been achieved for Bi$_2$CaSr$_2$Cu$_2$O$_8$ on MgO although the transition width is wide and the material is not single phase.
Acknowledgements

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References


