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Epitaxial growth of high $T_c$ superconducting Y-Ba-Cu-O thin films on (001)MgO by a chemical spray pyrolysis method

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A chemical spray pyrolysis method has been applied to grow epitaxial films of a high $T_c$ Y-Ba-Cu-O compound (YBCO) on (001)MgO. Films as thin as 0.6 μm in thickness were found to exhibit excellent superconducting transition behavior. For films up to 2 μm in thickness, typical values of $T_c$, onset, $T_c$ zero and transition width (90%-10%) were measured to be 82, 76, and 1.5 K, respectively. Both plan-view and cross-sectional transmission electron microscopy revealed that the orientation relationships between the epitaxial films and the substrate are [001]YBCO/[(001)MgO and (110)YBCO/(200)MgO. Twins, which may be perceived as domains that are rotated 90° along the c axis of the thin films with respect to the substrate, were found to be copiously present. The influences of the configuration of the oriented growth of overlayer thin films on the superconducting properties are addressed. The advantages of the chemical spray pyrolysis in producing superconducting thin films are outlined.

I. INTRODUCTION

The discovery of superconductivity above 30 K in La-Ba-Cu-O system and above 90 K in Y-Ba-Cu-O system has generated phenomenal interest in the research and development of high $T_c$ superconductors.\textsuperscript{1,2} One of the major fronts in the global efforts to deploy the high $T_c$ superconductors for practical applications and to determine their fundamental properties is the preparation and characterization of superconducting thin films. Electron beam evaporation, dc and rf sputtering, laser evaporation, molecular-beam epitaxy, metalorganic deposition, screen printing, dipping pyrolysis, and chemical spray pyrolysis methods were all successfully applied to grow high $T_c$ superconducting thin films.\textsuperscript{3-10} Chemical spray pyrolysis has been shown to be a simple and inexpensive method for the preparation of superconducting thin films.\textsuperscript{10-12} In this paper, we report the growth of high $T_c$ superconducting Y-Ba-Cu-O thin films on (001)MgO by a chemical spray pyrolysis technique with particular emphasis on the epitaxial growth of Y-Ba-Cu-O thin films on (001)MgO. Growth of superconducting thin films with preferred orientations on single-crystal substrates were reported extensively in the literature.\textsuperscript{6,13-22} However, the preferred growth was mostly inferred from Rutherford backscattering channeling along normal directions of the substrates, x-ray diffraction in $\theta$-2$\theta$ scan mode with a conventional diffractometer or reflected high-energy electron diffraction. These techniques, although convenient and powerful in many aspects, are relatively inept in providing microstructural information and quantitative data on the oriented growth of thin films on single-crystal substrates. Transmission electron microscopy has gained prominence in the study of thin films for its high spatial resolution and high sensitivity in phase detection and the capability to characterize microstructural defects in details in recent years. Cross-sectional transmission electron microscopy (XTEM) has been found to be especially useful in the determination of the interface structure and depth distribution of microstructures of heteroepitaxially grown thin films on various substrates.\textsuperscript{23}

II. EXPERIMENTAL PROCEDURES

An aqueous solution with atomic ratio of Y, Ba, and Cu of 1:2:3 was prepared by dissolving appropriate amounts of Y(NO$_3$)$_3$, 5H$_2$O, Ba(NO$_3$)$_2$, Cu(NO$_3$)$_2$, 3H$_2$O into 18 M Ω cm in resistivity de-ionized water. The typical concentration of Y in the aqueous solution was about 1000 ppm. The aqueous solution was sprayed onto a heated substrate maintained at a temperature in the range of 200–400°C. Typical thicknesses of the as-deposited samples were about 2–5 μm. The samples were then preheated at 400°C for 30 min in air with a heating rate of about 40°C/h from room temperature to 400°C. Final heat treatments were performed in O$_2$ ambient at 800–980°C for 5–60 min. The cooling rates were either 1.5 or 2°C/min following annealings at high temperatures. Plan-view and cross-sectional transmission electron microscopy, scanning electron microscopy, x-ray diffraction, and electrical resistivity measurements were applied to characterize the thin films. A standard four-point probe in a closed cycle refrigerator was used for electrical resistance measurement. The x-ray data were obtained with CuKa radiation in $\theta$-2$\theta$ mode with a scan rate of 0.5°–2°/min by means of a conventional x-ray diffractometer. Plan-view samples were prepared by mechanically grinding the samples to about 50 μm in thickness followed by ion milling to electron transparency. For thicker films, the samples were also ion milled from film side for short periods of time at the...
end of sample preparations to facilitate simultaneous examinations of the overlayer thin films and the substrate. Cross-sectional samples were prepared following the procedures outlined by Sheng and Chang.\textsuperscript{24}

### III. RESULTS AND DISCUSSION

Thin films exhibiting sharp superconducting transition and with a high $T_c$ onset were reproducibly obtained by annealing the preheated samples at 950°C for 20 min followed by slow cooling to 200°C with a cooling rate of 1.5°C/min. Typical thicknesses of the films were 1–2 µm. However, excellent superconducting transition behavior was found for films as thin as 0.6 µm in thickness. The electrical resistivity of the annealed films at room temperature is about 100 µΩ cm. The temperature dependence of resistivity showed $T_c$ onset at 82 K and $T_c$ zero at 76 K with a superconducting transition width of about 1.5 K. An example is shown in Fig. 1. X-ray diffraction pattern revealed that the films are highly preferentially oriented with respect to the MgO substrates with the c axis parallel to the normal of the substrate surface. As seen in Fig. 2(a), only diffraction lines corresponding to (001) planes ($l = 1, 2, ... 9$) of the modified perovskite structure thin films, which were reported to have a nominal composition of $\text{Y}_2\text{Ba}_2\text{Cu}_3\text{O}_y$ were present in the x-ray diffraction pattern. However, peaks from the other phases of the Y-Ba-Cu-O system were not detected. For comparison, x-ray diffraction pattern of a randomly oriented superconducting Y-Ba-Cu-O thin film is shown in Fig. 2(b). The modified perovskite structure thin films are herein referred to as YBCO thin films. High-resolution lattice imagings of the cross-sectional samples also indicated that the (001) planes of the films are parallel to the (001)MgO planes. An example is shown in Fig. 3. The somewhat irregular appearance of fringes near the YBCO/MgO interface in contrast to the straight fringes shown in Figs. 3(a) and 3(b), respectively, is probably an artifact resulting from ion milling. However, the effects due to interactions between overlayer films and the substrate cannot be ruled out at this time. TEM plan-view micrographs showed that the orientation relationships between the epitaxial YBCO thin films and the MgO substrate are $[001]\text{YBCO}/[001]\text{MgO}$ and $[110]\text{YBCO}/(200)\text{MgO}$. An overlapping $[001]\text{YBCO}/[001]\text{MgO}$ diffraction pattern is shown in Fig. 4. Misorientations of YBCO thin films with respect to the substrate by a rotation around [001]MgO axis up to 10° were found. The observations indicated that the grains of the thin films had a tendency to rotate towards the orientations so that the overlayer films exhibited definite orientation relationships with respect to the MgO substrate which are presumably of a low-energy state. A high density of twins was observed in many regions of the films as shown in Fig. 5. The areal fraction of twins was measured to be about the same as the "direct" epitaxy. The twinned regions in the modified perovskite structure thin films may be perceived as domains that are rotated 90° along the c axis with respect to the substrate.\textsuperscript{13}

![Figure 1](image1.jpg)

**FIG. 1.** The temperature dependence of electrical resistivity of a superconducting YBCO thin film.

![Figure 2](image2.jpg)

**FIG. 2.** X-ray diffraction patterns of (a) preferentially and (b) randomly oriented thin films on (001)MgO.

![Figure 3](image3.jpg)

**FIG. 3.** High-resolution images of a cross-sectional sample showing lattice fringes of (001) planes from regions (a) near and (b) at a distance away from the YBCO/MgO interface.
Epitaxial thin films were previously grown on different substrates with a variety of techniques. Most of the results indicated a textured growth with the c axis perpendicular to the plane of the substrate surface (c-axis orientation).\textsuperscript{13,15,18,20–22} However, there were reports that preferred orientation of the overlayer thin films is such that the a axis is normal to the substrate surface (a-axis orientation) or both c axis and a axis are perpendicular to the substrate plane (c/a orientation).\textsuperscript{6–14,16–19} Previous reports indicated that the film orientation is very process dependent.\textsuperscript{19} The mechanisms for the nucleation and growth of textured films remain poorly understood at this time. In the present study, preferred growth of thin films with the c axis perpendicular to the interface plane was found. This configuration was considered to favor a large critical current in one of the recent reports.\textsuperscript{13} There was also speculation that c-axis oriented grains have metallic conduction in all directions of the film, while the a-axis oriented grains have metallic conduction in only one direction.\textsuperscript{25}

The spray pyrolysis method offers a number of advantages in preparing superconducting thin films. In addition to simplicity and low cost, precise control of the composition, high deposition rate, amenable to large area and nonplanar geometry applications will also be of significant value to the fabrication of cryoelectronic devices. The versatility of the process to prepare thin films with many metal components speedily is expected to play an important role in the search for new high \( T_c \) superconductors with different compositions and structures.

### IV. SUMMARY AND CONCLUSIONS

Modified perovskite structure superconducting Y-Ba-Cu-O thin films, 0.6–2 \( \mu \)m in thickness, were epitaxially grown on (001) MgO by a chemical spray pyrolysis method. Plan-view and cross-sectional transmission electron microscopy, scanning electron microscopy, x-ray diffraction, and electrical resistivity measurements were applied to characterize the thin films.

For films annealed at 950 °C for 20 min followed by slow cooling to 200 °C with a cooling rate of 1.5 °C/min in \( O_2 \) ambient, typical values of \( T_c \) onset, \( T_c \) zero, and superconducting transition width were measured to be 82, 76, and 1.5 K, respectively. The orientation relationships of the epitaxial thin films and the substrate were determined to be [001]YBCO// [001]MgO and (110) YBCO// (200) MgO. Twins were found to be copiously present in the epitaxial regions. The areal fraction of twinned regions was found to be about the same as that of "direct" epitaxy.

The influences of the configuration of the oriented growth of overlayer thin films on the superconducting properties are addressed. The advantages of the chemical spray pyrolysis in producing superconducting thin films are outlined.

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\textsuperscript{1} G. Bednorz and K. A. Müller, Z. Phys. B 64, 189 (1986).


