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# Molecular-beam epitaxy and deposition of high- $T_c$ superconductors

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We have grown thin, highly oriented, polycrystalline  $\text{DyBa}_2\text{Cu}_3\text{O}_{7-x}$  films using molecular-beam epitaxy (MBE) techniques that show the onset of superconductivity at temperatures above 90 K and complete transitions at temperatures as high as 87 K. These films have critical current densities as high as  $5 \times 10^5$  A/cm<sup>2</sup> at 4.2 K. Films were grown in a modified Varian 360 MBE machine using effusion sources containing the metal constituents, along with a gaseous oxygen source. The early stages of deposition were monitored with reflection high-energy electron diffraction (RHEED). The best films were obtained on  $\text{SrTiO}_3$  substrates at substrate temperatures of 600–750 °C. At these temperatures, the initial stage of growth is dominated by epitaxy of copper islands. At lower temperatures, the growth is amorphous, while at higher temperatures, copper may not be incorporated into the film. Copper incorporation is also affected by oxygen flux. In all cases, the films are semiconducting or insulating as grown, and become superconducting only after high-temperature oxygen anneals. We comment on the prospects for obtaining true epitaxy superconducting phase *in situ*.

## I. INTRODUCTION

Practical uses of the new high-temperature superconductors will require materials with critical current densities, in excess of  $1 \times 10^5$  A/cm<sup>2</sup>. In addition, thin films are necessary for many applications of superconductors, such as electronics. To date, high critical currents in high-temperature superconductors have been demonstrated only in single crystals of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ <sup>1</sup> or in thin, highly oriented films of  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  on  $\text{SrTiO}_3$ .<sup>2,3</sup> High critical current thin films have been produced by electron-beam evaporation<sup>2-4</sup> and by sputtering.<sup>5,6</sup> Critical currents as high as  $1.2 \times 10^7$  at 4.2 K<sup>7</sup> and  $1.6 \times 10^6$  at 77 K<sup>6</sup> have been recently achieved in sputtered thin films. All of these films are not superconducting as deposited, but can be made so by furnace annealing in oxygen. While the composition of the films is determined by the deposition, the final crystal structure is determined primarily by the annealing procedure.

$\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  and similar compounds have a layered, oxygen deficient perovskite structure which can be thought of as a stable three-layer superlattice of the hypothetical perovskites  $\text{YCuO}_3$ <sup>-y</sup> and  $\text{BaCuO}_3$ <sup>-z</sup>. The structure is orthorhombic, with lattice constants  $a = 3.89$  Å,  $b = 3.82$  Å,  $c = 11.69$  Å.<sup>8</sup> The intrinsically layered structure of these compounds suggests that if they could be formed epitaxially during the deposition, then other, possibly metastable super-

conductors might be engineered. In addition, novel device structures might be formed by building heterostructures with the superconductors along with insulators, semiconductors, and metals with related crystal structures.

In this paper, we discuss the initial results of our investigation into the possibility of using molecular-beam epitaxy (MBE) techniques<sup>9</sup> to form the superconducting structure during deposition. There are several obstacles to the attainment of this goal. In contrast to the simplicity of most of the material systems in which MBE has been successfully achieved, at least three pseudoternary and six pseudobinary compounds of various crystal structures, in addition to the three oxides, exist in the equilibrium phase diagram.<sup>10</sup> In experiments on bulk synthesis, the  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  structure (to be referred to here as the 123 structure) forms above 800 °C, and undergoes a tetragonal to orthorhombic transition upon cooling to 700 °C.<sup>11</sup> In addition, oxygen can evolve from the material at temperatures as low as 200 °C,<sup>12</sup> transforming the material from a superconducting metal to a non-superconducting semiconductor or insulator. Thus, it may be unrealistic to expect to obtain superconductors directly from a high-temperature vacuum process with low oxygen pressures. However, the tetragonal  $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$  structure is stable with as few as six oxygens per unit cell ( $x = 1$ ),<sup>13</sup> so most of the advantages of epitaxy are preserved if this layered perovskite structure can be obtained during

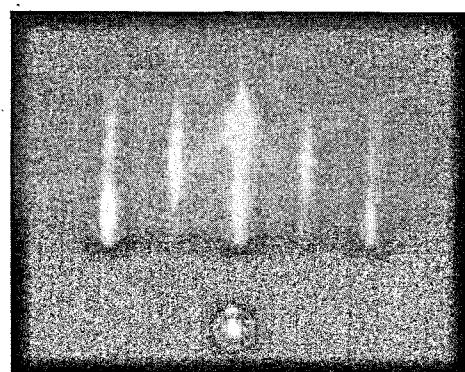
growth, requiring only a low-temperature oxygen anneal to obtain the superconductor.

Despite these obstacles to epitaxy of the superconductor, we have been successful in obtaining high critical current thin films of the high-temperature superconductor  $\text{DyBa}_2\text{Cu}_3\text{O}_{7-x}$  (DBCO) using MBE techniques. During the deposition, we have observed epitaxy of several phases, including copper, which depend on the choice of substrate material, substrate temperature, and flux composition.

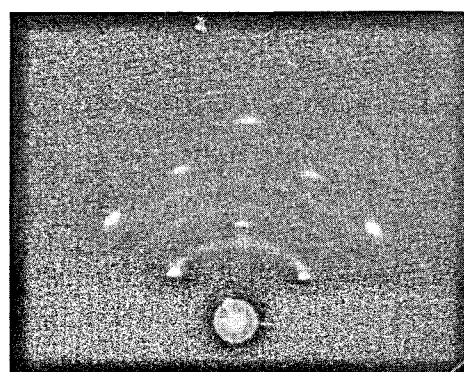
## II. MBE SYSTEM CONFIGURATION

The MBE system used for this work is a Varian 360 which has been previously used for growth of III-V compounds. To improve the oxygen pumping capability of this system, a turbomolecular pump and a titanium sublimation pump have been added to the usual configuration of the system. A precision leak valve introduces oxygen into a tube which

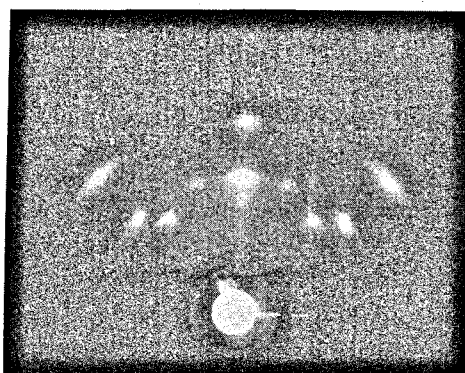
terminates near the substrate. Copper, barium, and dysprosium beams are obtained from effusion cells with pyrolytic boron nitride (PBN) crucibles. Solid chunks of barium are used; these must be protected from extended exposure to the atmosphere. Solid dysprosium was selected from among the elements which form high- $T_c$  superconductors<sup>14,15</sup> for its high vapor pressure (more than three orders of magnitude higher than yttrium), its relatively low cost, and the closeness of its ionic radius to that of yttrium, which has been the most studied element. Dysprosium is also magnetic, which may be an advantage for high critical current applications. At temperatures near its melting point, elemental copper in PBN crucibles emitted bursts of nitrogen, presumably due to a reaction with the PBN. To obtain stable fluxes of copper, we used a eutectic alloy of copper and lanthanum as the source of copper. In addition to lowering the melting point, the lanthanum may have helped passivate the crucible by forming a nitride.



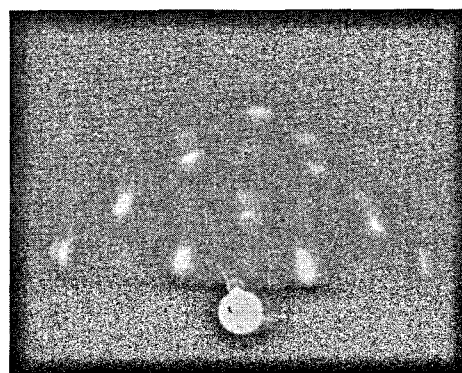
(a)



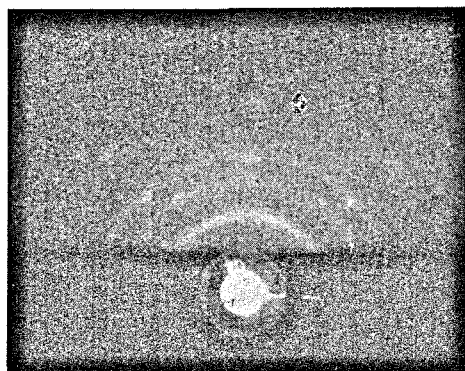
(d)



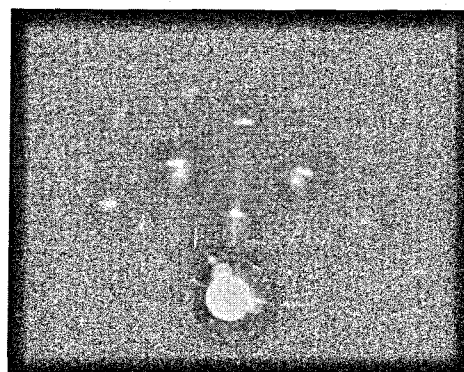
(b)



(e)



(c)



(f)

FIG. 1. RHEED pattern observed on [100] azimuth (a) from clean  $\text{SrTiO}_3(001)$  prior to growth, (b) after 1.5 min growth of DBCO (VSC67), (c) after 5 min of growth, (d) after 10 min of growth, (e) after 4 h and 12 min of growth, and (f) VSC65 after 11 min of growth.

Substrates were chem-mechanically polished and cleaned in solvents and then soldered onto molybdenum blocks. For growths at high temperature, the back sides of the substrates and the blocks were coated with titanium, platinum, and gold to improve wetting of tin solder. Prior to growth, the fluxes of each source were measured by an ion gauge in the growth position. Post-growth composition measurements by electron microprobe allowed calibration of the relative fluxes. Barium flux was observed to drastically increase the emissivity of the ion gauge filament. Both barium and dysprosium appear to be good getterers. For many of the growths, the barium and dysprosium fluxes were periodically shuttered; this was found to be ineffective for forcing the film into the desired  $c$ -axis oriented growth. The fluxes were set to obtain a growth rate of about  $0.65 \text{ \AA/s}$  for the 123 structure. Typical oxygen fluxes range from  $5\text{--}10 \times 10^{-6}$  Torr gauge pressures at the substrate. Substrates were heated to  $800^\circ\text{C}$  before growth to obtain reconstructed surface diffraction patterns. As the grown films are unstable in humid air, they are immediately annealed in oxygen at  $550^\circ\text{C}$  following growth. They are then further annealed at  $750$  and at  $850^\circ\text{C}$  for 1 h each to obtain good superconducting properties.<sup>4</sup>

### III. DEPOSITION ON $\text{SrTiO}_3\{100\}$

Although we have obtained superconducting films with zero resistance at 67 K on  $\{1\bar{1}02\}$  sapphire, and at 85 K on  $\{100\}$  yttria stabilized cubic  $\text{ZrO}_2$ , the best films have been obtained on  $\{100\}$   $\text{SrTiO}_3$  substrates. These substrates also show the strongest tendency towards oriented epitaxy during deposition, based on observations of spots in reflection high energy electron diffraction (RHEED) patterns. Figure 1(a) shows a photograph of a typical RHEED pattern observed along a  $[100]$  azimuth from a clean  $\text{SrTiO}_3$  substrate prior to growth. Streaked,  $2 \times 2$  patterns are typically seen, indicating a smooth, reconstructed surface. Depositions of DBCO on  $\text{SrTiO}_3$  have been made under a variety of growth conditions, summarized in Table I. At substrate temperatures below about  $500^\circ\text{C}$  (VSC76, 77) deposition of DBCO

results in a rapid disappearance of the diffraction pattern, indicating that the deposited film is amorphous. After the high-temperature oxygen anneal, these films become superconductors of reasonably good quality if the compositions are close to being stoichiometric. For substrate temperatures between  $500$  and  $720^\circ\text{C}$  (VSC62, 63, 64, 66, 67), a distinctive pattern of diffraction spots, shown in Fig. 1(b), is seen for the first few minutes of growth. These spots then give way to a ring pattern characteristic of polycrystalline growth, shown in Fig. 1(c), which diminishes in intensity through the deposition. For temperatures below  $580^\circ\text{C}$ , no diffraction pattern appears after the rings fade away. At higher temperatures, the ring pattern is replaced by a new pattern of spots, shown in Fig. 1(d), which persists until the end of the deposition, as seen in Fig. 1(e). The initial pattern has been identified<sup>9</sup> as that of metallic copper, which forms in islands on the  $\text{SrTiO}_3$ . The islands are epitaxially aligned with the substrate, the interface plane being predominantly  $\{110\}\text{Cu}$  and some  $\{100\}\text{Cu}$ . These islands become randomly oriented as the growth proceeds, resulting in the ring pattern of Fig. 1(c). The spots in the diffraction pattern shown in Fig. 1(d) correspond well to those expected for  $\text{Dy}_2\text{O}_3$ . The diffraction pattern at the end of growth, Fig. 1(d), contains both the  $\text{Dy}_2\text{O}_3$  spots and a second set of spots which may indicate the growth of one of the barium-dysprosium oxides.<sup>16</sup> It should be noted that our best films have been obtained in the substrate temperature range  $580\text{--}720^\circ\text{C}$ , where this growth pattern is observed. The presence of unoxidized copper, at least in the initial phase of growth, suggests the existence of kinetic barriers to oxidation of the copper, similar to the case of aluminum deposited under an oxygen flux.<sup>17</sup> This suggests that the use of oxidants other than molecular oxygen, such as ozone, atomic oxygen, ionized oxygen, nitrous oxide, or solid oxidants such as  $\text{Cu}_2\text{O}$  or  $\text{Sb}_2\text{O}_3$ <sup>17</sup> may be beneficial. Preliminary experiments (VSC70) show epitaxy of copper even in very high fluxes of  $\text{N}_2\text{O}$ .

At substrate temperatures above about  $750^\circ\text{C}$ , the incorporation of copper is sensitive to the precise conditions of growth. For nominal fluxes of copper (VSC65, 91) the copper incorporation is significantly less than unity. Figure 1(f)

TABLE I. Summary of DBCO growth conditions.

Sample No.	$T_{\text{substrate}}$	Oxygen flux ( $10^{-6}$ Torr)	Composition <sup>a</sup>	$T_c$ : 10%–90%	Comments
62	$650\text{--}600^\circ\text{C}$	7–6	$\text{Dy}_{17}\text{Ba}_{37}\text{Cu}_{46}$	88–84 K	Shuttered; $J_c = 3.1 \times 10^5$ at 4.2 K
63	$710\text{--}720^\circ\text{C}$	6–7	$\text{Dy}_{16}\text{Ba}_{34}\text{Cu}_{50}$	91–88 K	Shuttered; $J_c = 7.7 \times 10^4$ at 4.2 K
64	$600\text{--}640^\circ\text{C}$	7	$\text{Dy}_{18}\text{Ba}_{34}\text{Cu}_{48}$	92–89 K	Shuttered; $J_c = 4.8 \times 10^5$ at 4.2 K
65	$807\text{--}810^\circ\text{C}$	7–9	$\text{Dy}_{23}\text{Ba}_{77}$	Insulating	Shuttered
66	$470\text{--}500^\circ\text{C}$	7	$\text{Dy}_{18}\text{Ba}_{34}\text{Cu}_{48}$	90–88 K	Shuttered
67	$570\text{--}600^\circ\text{C}$	7	$\text{Dy}_{17}\text{Ba}_{38}\text{Cu}_{46}$	86–82 K	
68	$580\text{--}610^\circ\text{C}$	100–500	$\text{Dy}_{29}\text{Ba}_{71}$	Insulating	Shuttered; clear, pink, and green tint
70	$540\text{--}600^\circ\text{C}$	400–800	$\text{Dy}_{34}\text{Ba}_{46}\text{Cu}_{20}$	Insulating	Oxidant: $\text{N}_2\text{O}$ ; shuttered, clear, pink, and green
77	$300^\circ\text{C}$	7	$\text{Dy}_{18}\text{Ba}_{32}\text{Cu}_{50}$	89–78 K	Shuttered
85	$720^\circ\text{C}$	8	$\text{Dy}_{12-9}\text{Ba}_{17-16}\text{Cu}_{61-75}$	86–57 K	100% excess copper flux
88	$780^\circ\text{C}$	8	$\text{Dy}_9\text{Ba}_{19}\text{Cu}_{72}$	82–58 K	100% excess copper flux
91	$780^\circ\text{C}$	8	$\text{Dy}_{21-12}\text{Ba}_{37-41}\text{Cu}_{42-36}$	Insulating	
93	$780^\circ\text{C}$	8	$\text{Dy}_{14}\text{Ba}_{28}\text{Cu}_{58}$	64–16 K	50% excess copper flux

<sup>a</sup>Electron microprobe.

shows the RHEED pattern for VSC65 showing spots and streaks indicating epitaxial growth of one or more unidentified phases. The sharp, elongated set of spots is consistent with that expected for BaO, which has a 0.3% lattice match to SrTiO<sub>3</sub>. Increased copper fluxes at these temperatures (VSC85, 88, 93) appear to increase the copper incorporation to unity and result in copper-rich samples. Although copper loss is reasonable in view of the volatility of Cu<sub>2</sub>O,<sup>18</sup> the sensitivity to growth conditions is not understood at present.

Observations of the RHEED patterns of pure copper deposited on SrTiO<sub>3</sub> indicate that copper desorbs at temperatures above 680 °C. Oxygen flux was not observed to affect the copper desorption on SrTiO<sub>3</sub>. Growth of DBCO films in oxygen fluxes larger than  $5 \times 10^{-5}$  Torr resulted in copper loss at temperatures as low as 580 °C. Growth of films was attempted in oxygen pressures up to about 1 mTorr, but these growths resulted in films completely devoid of copper and were detrimental to the reliable operation of the system. The volatility of Cu<sub>2</sub>O is also reflected in the fact that *in situ* Auger analyses of the surfaces of the DBCO films immediately after deposition almost always found severe deficiencies of copper.

#### IV. STRUCTURE AND PROPERTIES OF FILMS

The DBCO films as grown are not superconducting and are unstable in air. They are typically dark brown and shiny. After the stabilization anneal in oxygen at 550 °C, the films have none of the orthorhombic superconducting phase, as determined by x-ray diffraction studies. At this stage, the copper-rich films have copper and cupric oxide, while the copper deficient films show signs of BaCuO<sub>2</sub> and Dy<sub>2</sub>BaCuO<sub>5</sub>. Due to the closeness of the SrTiO<sub>3</sub> lattice spacing to that of DBCO (especially its tetragonal forms), it was difficult to rule out the presence of aligned phases. After the full high-temperature anneal, the orthorhombic distortion made very clear the presence of DBCO aligned to the substrate.

Resistive transitions were measured using the four-point technique with silver paint contacts and low current densities. Several examples of resistive transitions are shown in Fig. 2. The sharp superconducting transitions and linear increase of normal state resistivity with temperature in some of the samples is thought to indicate that the contribution of impurity phases at grain boundaries is small. It is not clear at this point whether the quality of the transitions depends on the growth conditions at all, or whether the composition of the films is the most important factor.

A more demanding test of film quality is the critical current density. Magnetization hysteresis loops have been measured for three of our best films in a vibrating sample magnetometer in fields up to 15 kOe. We use the Bean formula<sup>19</sup> to obtain the average critical current density:  $J_c = 30M(H)/R$ , where  $R$  is the average radius of the sample (in cm) and  $M(H) = \Delta M(H)/2$  is one-half of the change in magnetization across the hysteresis loop (in emu/cm) for fields perpendicular to the plane of the sample. Our best film, sample VSC64, has a  $J_c$  at 3 kOe of  $4.8 \times 10^5$  A/cm<sup>2</sup> at 4.2 K and  $3.9 \times 10^4$  A/cm<sup>2</sup> at 77 K. Sample VSC62 has a slightly lower

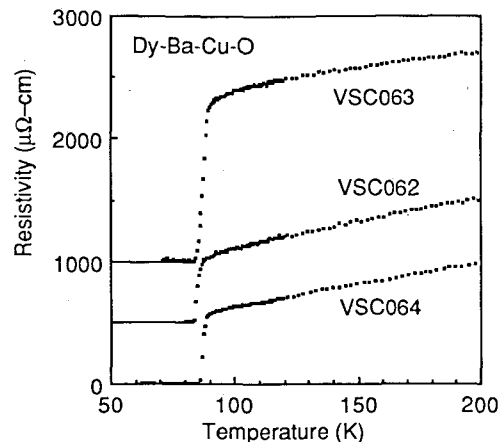


FIG. 2. Resistivity vs temperature for VSC62, 63, 64. The data for VSC62 and 63 are displaced upward for clarity.

$J_c$ , while that of VSC63 is lower by an order of magnitude.

The films show varying degrees of orientation to the substrate. In highly oriented films, observation of x-ray diffraction from the (102) and (012) planes of the 123 structure reveals the orientation of the  $c$  axis relative to the substrate. The best film, sample VSC64, shows strong alignment of the  $a$  or  $b$  axes of the crystalline grains along the SrTiO<sub>3</sub> [100] axis perpendicular to the substrate (the long axis,  $c$  in the plane of the substrate), with some  $c$  axis oriented gains, as well as a small amount of random orientation. Samples VSC62, 63, 76, and 77 show more  $a$  or  $b$  orientation than  $c$  orientation, but not nearly as much as sample VSC64. Random orientations exist in large amounts in VSC76 and 77, in small amounts in VSC63, and VSC62 shows almost none. Furthermore, in the plane of the film VSC62, 63 and 64 have the oriented grains aligned both along the  $\langle 100 \rangle$  axes of SrTiO<sub>3</sub>, as well as along the  $\langle 110 \rangle$  axes, while in VSC76 and 77, only  $\langle 100 \rangle$  alignments are observed. All the films have varying amounts BaCuO<sub>2</sub> as an impurity phase, although in VSC62 and VSC64 it appears only in trace amounts.

#### V. CONCLUSIONS

We have shown that deposition of DyBa<sub>2</sub>Cu<sub>3</sub>O<sub>7-x</sub> by molecular-beam epitaxy techniques, followed by high-temperature oxygen annealing, can result in highly oriented superconducting thin films. However, epitaxy of copper, possibly Dy<sub>2</sub>O<sub>3</sub>, and other, nonsuperconducting phases occurs during the deposition. The present work is only the first stage in the exploration of the possibilities for molecular-beam epitaxy. A wide range of growth conditions have yet to be tested. In view of the high quality of the films obtained at this early stage, and the variety of epitaxial growths so far observed, the outlook for obtaining epitaxy of the layered perovskite structure of the high- $T_c$  superconductors is encouraging. In this respect, the recent results of Lathrop *et al.*,<sup>20</sup> who obtain superconducting films *in situ* using O<sub>2</sub> pressures of  $6.5 \times 10^{-4}$  Torr, suggest that epitaxy is indeed possible.

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