JOURNAL OF SOLID STATE CHEMISTRY 100, 379–382 (1992)

LETTERS TO THE EDITOR

$Er_5Ba_7Cu_{12}O_y$ and $Er_4Ba_5Cu_9O_y$: New High-Temperature Superconductor Thin Films with Critical Transition Temperature in the 93–95 K Range

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Communicated by J. M. Honig, July 10, 1992

Epitaxial $Er_1Ba_2Cu_3O_{7-\delta}(001)$, $Er_5Ba_7Cu_{12}O_y(001)$, and $Er_4Ba_5Cu_9O_y(001)$ thin films on $LaAlO_3(100)$ substrates were prepared by molecular beam deposition and postannealing. Scanning electron microscopy and X-ray diffraction studies indicate that these films are single phase materials. For the $Er_1Ba_2Cu_3O_{7-\delta}(001)$, $Er_5Ba_7Cu_{12}O_y(001)$ [or $Er_{1.25}Ba_{1.75}Cu_3O_y(001)$], and $Er_4Ba_5Cu_9O_y(001)$ [or $Er_{1.35}Ba_{1.65}Cu_3O_y(001)$] thin films, four-point resistivity measurements show zero resistivity critical transition temperature ($T_{c,0}$) of 93, 95, and 93 K, respectively (uncertainty = ±0.5 K).

High-temperature superconductivity in the *R*–Ba–Cu–O system (*R* = Y, Eu, Sm, Gd, Nd, Dy, or Er) is of great scientific and technological interest (*1, 2*). The bulk $R_1Ba_2Cu_3O_{7-\delta}$ high-temperature superconductors are known to show critical transition temperature for zero resistivity ($T_{c,0}$) in the 93–95 K range. To our knowledge, thin films of $R_1Ba_2Cu_3O_{7-\delta}$ oxides have not shown $T_{c,0} > 92$ K. Superconductivity in the $RE_{1+x}Ba_{2-x}Cu_3O_y$ (*RE* = Eu, Nd, Dy, or Er) materials is very interesting. For bulk $Eu_{1+x}Ba_{2-x}Cu_3O_y$ and $Nd_{1+x}Ba_{2-x}Cu_3O_y$, T_c and the lattice constant c_0 decrease as the value of x increases from 0 to 0.5. Nd and Eu have larger ionic radii than Dy and Er but they are smaller than the Ba ions (within 15%) (*2–4*). In $Eu_{1+x}Ba_{2-x}Cu_3O_y$ and $Nd_{1+x}Ba_{2-x}Cu_3O_y$, it is thought that the excess Eu or Nd atoms substitute for Ba in the crystal structure of $R_1Ba_2Cu_3O_y$ (*2, 3*). For $Dy_{1+x}Ba_{2-x}Cu_3O_y$, it has been reported that the T_c is always 90 K, and it was suggested that for any composition with $x > 0$ the materials might be decomposing into multiple phases (*2, 3*). Recently, we reported on single phase epitaxial $Dy_{1.1}Ba_{1.9}Cu_3O_y(001)$ and $Dy_{1.3}Ba_{1.7}Cu_3O_y(001)$ thin films (*5*). In these oxides, the material was not found to decompose and the lattice constant c_0 as well as T_c decreased as observed for bulk $Eu_{1+x}Ba_{2-x}Cu_3O_y$ by T. Iwata *et al.* (*3*).

In this letter, we report on superconductivity in (single phase) epitaxial $Er_{1+x}Ba_{2-x}Cu_3O_y(001)$ thin films. We have discovered new compositions in the Er–Ba–Cu–O thin film system, $Er_{1.25}Ba_{1.75}Cu_3O)_y$ (or $Er_5Ba_7Cu_{12}O_y$) and $Er_{1.35}Ba_{1.65}Cu_3O_y$ (or Er_4Ba_5

0022-4596/92 $5.00

Cu_9O_y) for which the transition temperature for zero resistivity ($T_{c,0}$) is 95 and 93 K, respectively. We also report on epitaxial $Er_1Ba_2Cu_3O_{7-\delta}$ (001) thin films for which $T_{c,0}$ = 93 K.

The epitaxial $Er_1Ba_2Cu_3O_{7-\delta}(001)$ and $Er_{1+x}Ba_{2-x}Cu_3O_y(001)$ thin films on $LaAlO_3(100)$ substrates were prepared by molecular beam deposition of Er, BaF_2, and Cu in the presence of molecular oxygen (P_{O_2} = 5 × 10^{-6} Torr) followed by postannealing in wet and dry O_2 at 890°C, as described elsewhere (*6*). $Er_1Ba_2Cu_3O_{7-\delta}$, $Er_{1.15}Ba_{1.85}Cu_3O_y$, $Er_5Ba_7Cu_{12}O_y$ (or $Er_{1.25}Ba_{1.75}Cu_3O_y$), $Er_4Ba_5Cu_9O_y$ (or $Er_{1.35}Ba_{1.65}Cu_3O_y$), and $Er_{1.42}Ba_{1.58}Cu_3O_y$ thin films were prepared. The film thickness is about 1800 Å for all of the samples. Just after the samples were removed from the annealing furnace, silver pads were vapor-deposited on the films for four-point resistivity measurements. The resistivity was measured either by the Van der Pauw technique or by a collinear four-point probe in a liquid nitrogen cryostat. The crystal structure of all films was determined by X-ray diffraction. The surface morphology of the films was examined by scanning electron microscopy.

Figures 1a–c show the X-ray diffraction (XRD) data for the $Er_1Ba_2Cu_3O_{7-\delta}(001)$, $Er_5Ba_7Cu_{12}O_y(001)$, and $Er_4Ba_5Cu_9O_y(001)$ thin films. The figure show that all of the films are highly epitaxial with the *c*-axis oriented perpendicular to the surface. After correction for sample displacement errors (*5*), the lattice constant c_0 was determined as 11.65 ± 0.01 Å for all of these three films. A decrease in the lattice constant c_0 that was expected as the value of x in $Er_{1+x}Ba_{2-x}Cu_3O_y$ increased was not observed. The $Er_{1.15}Ba_{1.85}Cu_3O_y(001)$ film also showed epitaxy of the same quality (figure not shown).

The resistive transition for the $Er_1Ba_2Cu_3O_{7-\delta}(001)$ thin film is shown in Fig. 2, which shows $T_{c,0}$ of 93 ± 0.5 K. The resistance was measured by the Van der Pauw technique. The film size was 5 × 7 mm and

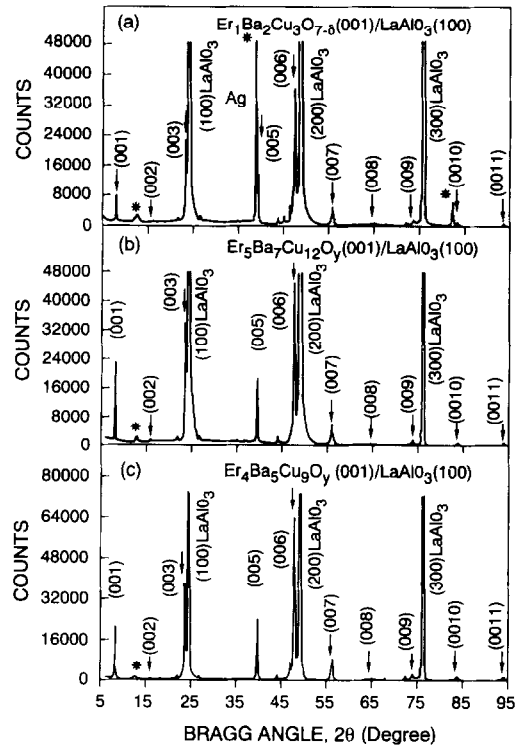

FIG. 1. X-ray diffraction patterns for epitaxial $Er_1Ba_2Cu_3O_{7-\delta}(001)$ and $Er_{1+x}Ba_{2-x}Cu_3O_y(001)$ thin films (Cu$K\alpha$ X-ray source): (a) diffracted beam intensity vs. Bragg angle 2θ (deg.) for $Er_1Ba_2Cu_3O_{7-\delta}(001)$; (b) diffracted beam intensity vs. Bragg angle 2θ (deg.) for $Er_5Ba_7Cu_{12}O_y(001)$ (or $Er_{1.25}Ba_{1.75}Cu_3O_y(001)$); (c) diffracted beam intensity vs. Bragg angle 2θ (deg.) for $Er_4Ba_5Cu_9O_y(001)$ (or $Er_{1.35}Ba_{1.65}Cu_3O_y(001)$).

the contact pads were located at the corners (1.5 × 1 mm). The film thickness is about 1800 Å as described earlier.

For $Er_5Ba_7Cu_{12}O_y(001)$ and $Er_4Ba_5Cu_9O_y(001)$ thin films, the $T_{c,0}$ values are 95 and 93 K (uncertainty = ± 0.5 K), respectively, as shown in Figs. 3a and b. The data were acquired by collinear four-point resistivity measurements. These are new compositions in the Er–Ba–Cu–O system which show >90 K $T_{c,0}$. The results were confirmed by susceptibility measurements.

The $Er_{1.15}Ba_{1.85}Cu_3O_y(001)$ thin film showed the onset of superconductivity just

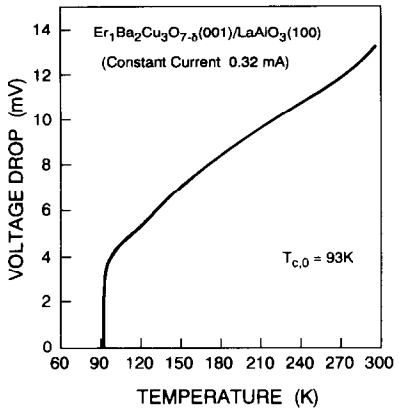

FIG. 2. Resistive transition for epitaxial $Er_1Ba_2Cu_3O_{7-\delta}$(001) thin films as measured by Van der Pauw technique. The voltage drop is proportional to resistivity of the thin film.

above 90 K but the resistance did not completely go to zero until 82 K. The $Er_{1.42}Ba_{1.58}Cu_3O_y$(001) sample has not been examined since its room temperature (two-point) resistance is higher by a factor of 2 in comparison to the resistance of other films, and a T_c of 90 K was not expected.

The surface morphologies of all of the films were examined by scanning electron microscopy. The surfaces of $Er_1Ba_2Cu_3O_{7-\delta}$(001), $Er_5Ba_7Cu_{12}O_y$(001), and $Er_4Ba_5Cu_9O_y$(001) thin films were found to be fairly smooth; there was no evidence of large particulates of any second phase. Small particulates were found on the surfaces of all of these films and their distributions were almost the same. However, there was evidence of cracking in all of the films. This is understandable since all films have a unique appearance in visual inspection. They are black but opaque under bright light. This implies that the films must have cracks, otherwise their optical behavior would defy the theories of light transmission through metallic substances.

The question arises of whether the epitaxial $Er_5Ba_7Cu_{12}O_y$(001) and $Er_4Ba_5Cu_9O_y$(001) thin films are single phase materials or whether they are decomposed into multiple phases. We suggest that the films are single phase materials for the following reasons: (1) If the material is decomposed into multiple phases, one of which is $Er_1Ba_2Cu_3O_{7-\delta}$, then epitaxy cannot be attained unless the other phases are also epitaxial. In other words, we cannot expect an epitaxial $Er_1Ba_2Cu_3O_{7-\delta}$(001) film mixed with large amount of a polycrystalline second phase. If the material were decomposed into two or more phases which grew epitaxially then the other phases should be observable in the XRD data (Fig. 1), which is not the case; (2) Our SEM studies on these films do not show large particulates of other phases on the surface, which are usually observed when other phases are present in large amount; (3) In

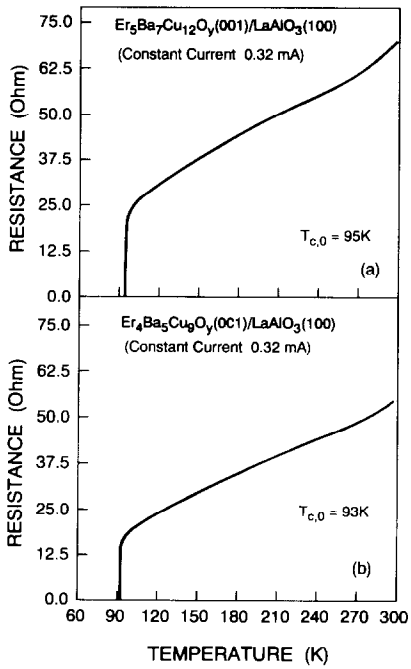

FIG. 3. Resistive transition for new high-temperature superconductor thin films as measured by collinear four-point resistivity measurements. The film thickness is not accurately known (about 1800 Å); hence the resistance values were not converted to resistivity: (a) resistive transition for $Er_5Ba_7Cu_{12}O_y$(001); (b) resistive transition for $Er_4Ba_5Cu_9O_y$(001).

Figs. 2 and 3, the resistive transition curves show that if the resistance were extrapolated below the critical transition temperature it would reach zero close to 0 K. This will not happen if the new $Er_5Ba_7Cu_{12}O_y(001)$ and $Er_4Ba_5Cu_9O_y(001)$ high-T_c superconductor thin films contain a large amount of second phase materials.

Hence, the results indicate that the $Er_5Ba_7Cu_{12}O_y(001)$ and $Er_4Ba_5Cu_9O_y(001)$ thin films are single phase materials which have $T_{c,0}$ in the 93–95 K range. In a phenomenological approach, we suggest that when the Er and Ba atoms in an Er–Ba–Cu–O compound are in whole numbers (≤ 7), a $T_{c,0}$ in the 93–95 K range is obtained. If this is true, then there might be a superstructure along the *a*- or *b*-axis; i.e., the substitution of Ba by Er atoms is ordered when a $T_{c,0}$ in the 93–95 K range is observed. Further investigation is in progress to understand the structure and superconductivity in these materials.

In conclusion, we have made epitaxial $Er_5Ba_7Cu_{12}O_y(001)$ and $Er_4Ba_5Cu_9O_y(001)$ thin films which show 95 and 93 K $T_{c,0}$ values.

Acknowledgments

This research was supported by Midwest Superconductivity Consortium (MISCON), Purdue University, under Department of Energy Grant DE-FG02-90ER45427. We thank MISCON staff for their encouragement and support of superconductivity research.

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