Proceedings of the ICSC–F'96 Jaszowiec '96

MOCVD OF HIGH QUALITY $LuBa_2Cu_3O_{7-\delta}$ THIN FILMS

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Epitaxial $LuBa_2Cu_3O_{7-\delta}$ films were prepared by flash evaporation MOCVD on $LaAlO_3$, $SrTiO_3$, $LaSrGaO_4$ and $ZrO_2(Y_2O_3)$ single crystalline substrates. The highest T_c and j_c (77 K, 100 Oe) values were 89 K, 2.7×10^6 A/cm^2 ($LaAlO_3$) and 88 K, 1.5×10^6 A/cm^2 ($SrTiO_3$) respectively. The occurrence of secondary phases inclusions in $LuBa_2Cu_3O_{7-\delta}$ films correlates with the possibility of epitaxial relations with the film matrix or the substrate.

PACS numbers: 68.55.-a, 81.15.Hi

It is well known that single phase $LuBa_2Cu_3O_{7-\delta}$ ceramics cannot be obtained. However, single crystals of $LuBa_2Cu_3O_{7-\delta}$ were successfully grown by self-flux technique [1]. $LuBa_2Cu_3O_{7-\delta}$ phase can be also obtained as a thin film by pulsed laser deposition (PLD) and MOCVD [2, 3]. Peculiarities of $RBa_2Cu_3O_{7-\delta}$ phase with R^{3+} of the smallest ionic radius (Lu^{3+}) are important for better understanding of properties of the whole R-series. In the paper we report our recent results on structural and superconducting characteristics of $LuBa_2Cu_3O_{7-\delta}$ thin films prepared by MOCVD.

Epitaxial $LuBa_2Cu_3O_{7-\delta}$ films on $LaAlO_3$ (001), $SrTiO_3$ (001), $LaSrGaO_4$ (001) and $ZrO_2(Y_2O_3)$ (001) single crystal substrates were prepared by flash evaporation MOCVD as described elsewhere [3]. X-ray diffraction (XRD) study of the films (DRON-3M, SIEMENS D5000 diffractometers) was used to determine phase composition, orientation and lattice parameter c of $LuBa_2Cu_3O_{7-\delta}$. Cation stoichiometry was determined using EDX analysis and sputtered neutral mass spectrometry (SNMS) (Leybold INA-3). AC susceptibility measurements ($\chi(T)$) were performed in the range of 10–100 K using APD Cryogenics magnetometer. $j_c(T)$ dependences were found from the imaginary part of $\chi(T)$ as described in [4]. Scanning electron microscopy (SEM) with Jeol JEM-2000 FXII was used to study the films surface morphology. Transmission electron microscopy (TEM) studies of the films were performed with a Philips CM30ST electron microscope operating at 300 kV. Atomic force microscopy (AFM) experiments were carried out with NANOSCOPE.

It is widely known that j_c, T_c, lattice parameter c and some other characteristics of $YBa_2Cu_3O_{7-\delta}$ thin films are strongly dependent on deposition temperature and $p(O_2)$ [5–7]. The dependences of j_c(77 K) and c values of $LuBa_2Cu_3O_{7-\delta}$ thin films prepared at $T = 800°C$ on $LaAlO_3$ (001) and $SrTiO_3$ (001) substrates on $p(O_2)$ reveal the optimum value of 1.05 ± 0.10 Tr in the investigated range of 0.82–1.5 Tr. The similar dependences were found for FWHM of (00l) peaks and T_c values, however, the dependence is less profound for T_c, in agreement with the results of [5].

The increase in c parameter originates from a higher defect density in crystal structure of the film [6, 7]. The defect density increases with approaching growth conditions to the stability border of $LuBa_2Cu_3O_{7-\delta}$ ($p(O_2)$ lower than optimal) and with reducing of cation mobility during the growth ($p(O_2)$ higher than optimal). The optimum $p(O_2)$ is quite close to that of CuO/Cu_2O equilibrium, the similar behaviour is known for $YBa_2Cu_3O_{7-\delta}$ [5].

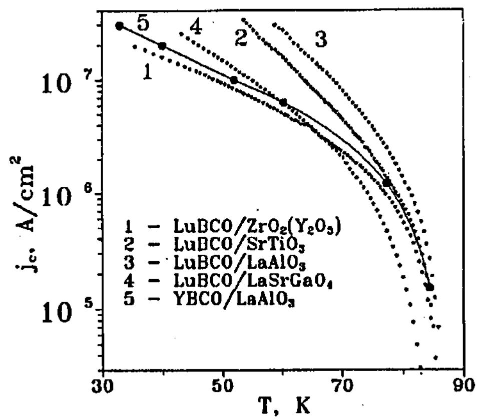

Fig. 1. Temperature dependences of j_c of $LuBa_2Cu_3O_{7-\delta}$ thin films on different substrates and $YBa_2Cu_3O_{7-\delta}$ film on $LaAlO_3$ as a reference.

The temperature dependences of j_c of $LuBa_2Cu_3O_{7-\delta}$ thin films on $LaAlO_3$ and $SrTiO_3$ grown under the optimum conditions are compared in Fig. 1. The higher j_c in the films on $LaAlO_3$ reflects the smaller lattice mismatch with $LuBa_2Cu_3O_{7-\delta}$. Using dependences of a and b parameters for $RBa_2Cu_3O_7$ on R^{3+} radii, derived from structural data in [8], $a = 3.80$ Å and $b = 3.87$ Å were found for R = Lu. Thus, the mismatch of $LuBa_2Cu_3O_{7-\delta}$ $(a + b)/2$ parameter with a pseudocubic lattice parameter of $LaAlO_3$, $SrTiO_3$ and $ZrO_2(Y_2O_3)$ is 1.1%, 1.8% and 6% respectively. The increase in j_c with a temperature decrease is much steeper for $LuBa_2Cu_3O_{7-\delta}$ films than for $YBa_2Cu_3O_{7-\delta}$ in agreement with the observations for PLD films [9]. The film on $LaSrGaO_4$ ($a = 3.84$ Å) was deposited under conditions optimized for $LaAlO_3$. Some contribution of a-oriented phase deteriorating superconducting characteristics was detected by XRD in the film.

A surface morphology of $LuBa_2Cu_3O_{7-\delta}$ films on $LaAlO_3$ and $SrTiO_3$ substrates reveals two specific features: (1) an absence of *a*-oriented $LuBa_2Cu_3O_{7-\delta}$ crystallites of the distinctive elongated shape on the film surface (in agreement with XRD study), irrespective of the film thickness and deposition $p(O_2)$ used; (2) a significant disturbance of $LuBa_2Cu_3O_{7-\delta}$ matrix flatness. According to AFM study, the outgrowths of $LuBa_2Cu_3O_{7-\delta}$ observed were about 1000 Å in height at a film thickness of 3000 Å.

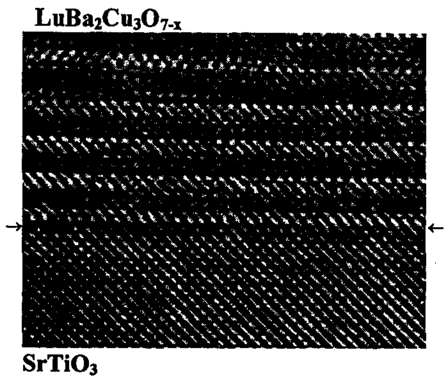

Fig. 2. TEM microphotograph of an interface area of $LuBa_2Cu_3O_{7-\delta}/SrTiO_3$.

TEM study of films on $LaAlO_3$ and $SrTiO_3$ revealed an epitaxial film-substrate interface (Fig. 2) with lattice mismatch resolved by the misfit dislocations. Any deviations of a cation composition of the film from the stoichiometry of $LuBa_2Cu_3O_{7-\delta}$ phase led to an appearance of inclusions of other phases. Usually observed secondary phases in the films were CuO, $BaCuO_2$, Lu_2O_3 and $Lu_2Cu_2O_5$. The presence of all these phases was proved by XRD also, except for the $Lu_2Cu_2O_5$ inclusions observed by TEM only. An occurrence of the secondary phase inclusions depends on the possibility of epitaxial relations with $LuBa_2Cu_3O_{7-\delta}$ matrix or substrate (Table). If no epitaxial relation takes place, the inclusion tends to appear on the film surface. Thus, protruding CuO precipitates of a size up to 1 μm were often observed on the film surface, this means that CuO impurity tends to be pushed out of the growing film. A density of the $LuBa_2Cu_3O_{7-\delta}$ outgrowths decreases drastically near CuO precipitates, probably an enhanced surface cation mobility takes place in the copper-enriched regions [10].

R_2O_3 and $R_2Cu_2O_5$ are generally considered to be non-equilibrium phases to $RBa_2Cu_3O_{7-\delta}$ [11, 12]. To explain their presence in the film, the following reasons can be proposed: (1) a contribution of surface energy could change an equilibrium phase diagram; (2) non-equilibrium phases could be nucleated in the gas phase [13] and afterwards be stabilized kinetically due to the epitaxial relations with $RBa_2Cu_3O_{7-\delta}$ (Fig. 3).

Concluding, the influence of the deposition $p(O_2)$ conditions on the properties of $LuBa_2Cu_3O_{7-\delta}$ films is rather similar to that in the case of $YBa_2Cu_3O_{7-\delta}$ films. The occurrence and orientation of secondary phases inclusions in

TABLE

Secondary phases, their occurrence and epitaxial relations to $LuBa_2Cu_3O_{7-\delta}$ or substrate ($LaAlO_3$).

Phase	Syngony, lattice parameters	Occurrence	Orientation
CuO	monoclinic, $a = 4.685$ Å, $b = 3.423$ Å, $c = 5.132$ Å, $\beta = 99.52°$	film surface	random
$BaCuO_2$	cubic, $a = 18.285$ Å	film surface or inside LuBCO matrix	no data
Lu_2O_3	cubic, $a = 10.39$ Å	film–substrate interface or inside LuBCO matrix	$(001)_{LuBCO} \parallel (001)_{Lu_2O_3}$, $(100)_{LuBCO} \parallel (110)_{Lu_2O_3}$
$Lu_2Cu_2O_5$	orthorhombic, $a = 10.698$ Å, $b = 3.4102$ Å, $c = 12.358$ Å	film–substrate interface	$(01{-}1)_{LaAlO_3} \parallel (001)_{Lu_2Cu_2O_5}$, $(011)_{LaAlO_3} \parallel (013)_{Lu_2Cu_2O_5}$

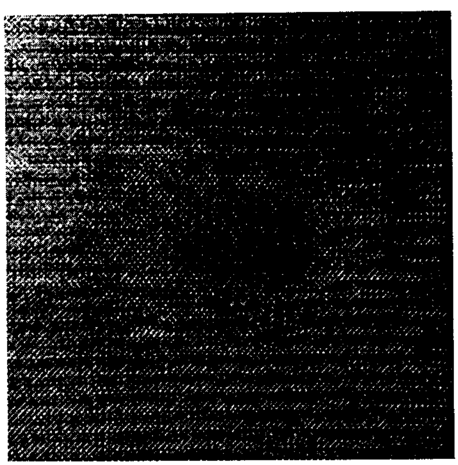

Fig. 3. Coherent Lu_2O_3 inclusion in the matrix of $LuBa_2Cu_3O_{7-\delta}$ film.

$LuBa_2Cu_3O_{7-\delta}$ films correlate with a possibility of epitaxial relations with $LuBa_2Cu_3O_{7-\delta}$ matrix or the substrate.

This work was supported by INTAS program (grant 93-936), RFBR (grant 96-03-33027) and Russian National Program on HTSC (grant 93-045). S.V.S. acknowledges the support of ISSEP. Prof. M. Berkowski is acknowledged for supplying us with $LaSrGaO_4$ substrates.

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