For presentation at: ISTEC-MRS Intern. Workshop on Superconductivity BNL-68066
Honolulu, June 24-27, 2001.

NUCLEATION OF $YBa_2Cu_3O_{7-d}$ IN THE BaF_2 PROCESS

L. Wu*, V. F. Solovyov, H. J. Wiesmann, Y. Zhu, and M. Suenaga
Materials and Chemical Science Division, Energy Sciences and Technology Department,
Brookhaven National Laboratory, Upton, New York, 11973, USA

ABSTRACT

The nucleation of the c-axis aligned and non-c-axis $YBa_2Cu_3O_{\sim 6.1}$ (YBCO) from precursor films on [001]-cut $SrTiO_3$ was investigated for the so-called BaF_2 process. Specimens with different thickness were quenched from 735°C, then studied by transmission electron microscopy and x-ray diffraction techniques. Preceding the formation of YBCO nuclei, three intermediate phases of (Y,Ba) oxy-fluoride and a transition phase without F were found in the precursor films. These were structurally and chemically related to the nuclei of YBCO which was found to be deficient in Cu relative to its stoichiometric composition.

INTRODUCTION

The growth of the bi-axially aligned thick $YBa_2Cu_3O_7$ (YBCO) films on a flexible metallic substrate is essential to its use for electrical power devices. The BaF_2 post-deposition reaction process is one of the most promising methods for the fabrication of such tapes. In this process, the basic growth-rate-limiting process is determined by the removal rate of the reaction product HF from the surface of the film into the reaction atmosphere.[1] Also, the mechanism for the c-axis growth of YBCO layers is shown to be the epitaxial precipitation of YBCO onto the existing YBCO layer from a thin liquid layer. The Y-Ba oxy-fluoride decomposes at its interface with the liquid.[2] Here, we will present our observation related to the mechanism of the YBCO nucleation.

EXPERIMENTS

As described previously in detail, the stoichiometric precursor films were co-deposited by the evaporation of Y, Cu, and BaF_2.[3] Substrates were 3 mm x 10 mm x 0.5 mm polished [001] $SrTiO_3$ (STO). YBCO synthesis was performed in a 50 mm diameter quartz tube in a tube furnace. The flowing process-gas-mixture consisted of 100 mTorr of O_2 and 25 Torr of H_2O in N_2. The gas-flow rate and the temperature were kept at 0.2 *l*/min and 735° C, respectively. In order to study the nucleation process for YBCO, several specimens with different film thickness (1, 3, and 5 μm) were heated and quickly pulled out of the tube after prescribed the heat treatment times, (10, 20, 30, and 40 min.). All specimens were studied with x-ray diffraction (XRD) for the overall phase development while transmission electron microscopy (TEM) techniques were used for selected specimens for a detailed examination of the structural and the chemical evolution of the films.

RESULTS AND DISCUSSIONS

The morphology and phase composition of the precursor changed quickly with annealing times. After 10 minutes at 735° C, the precursor consisted of Cu_2O and a Y-Ba

oxy-fluoride (cubic, a=0.618 nm).[2] Moreover, the oxy-fluoride had a tendency to align its (111) plane parallel to the (001) plane of STO adjacent to the substrate, but no indication of YBCO nucleation. Further heat treatments of the films revealed that the heat treatment duration required for the nucleation of YBCO was dependent on the thickness of the films. After 20 minutes, c-axis oriented YBCO was observed by XRD in 1-μm thick film, but it was absent from 3- and 5-μm thick films. For 5-μm thick films, nuclei of YBCO were found by TEM in the specimen which was heated for 30 min., but there was no indication in XRD of the YBCO formation. After a 40 min. period there was clear indication of YBCO in XRD. However, the strongest lines from the film were (h00) lines indicating the growth of a substantial non-c axis oriented YBCO. Also, non-YBCO XRD lines in all of the heat-treated films were identified with those of Cu_2O, disordered (Y,Ba) oxy-fluoride and the newly found intermediate ordered oxy-fluoride phases.

In the 1–μm thick film specimen heated for 20 minutes, the thin (~60 nm) c-axis aligned YBCO layer was observed along the surface of the substrate, nearly covering the entire surface (Fig.1). The remaining areas were occupied by the (111) aligned oxy-fluoride. The dimensions of YBCO nuclei in the basal plane were far greater than along the c-direction. This suggests that once YBCO nucleates, its growth in the basal plane was rapid. Energy dispersive spectroscopy analysis shows that the YBCO layers at this stage were still deficient in Cu, i.e., $YBa_2Cu_{1.5\sim2}O_x$.

We had previously reported the possibility that the Y-Ba oxy-fluoride orders along its [111] direction at the precursor/STO interface region.[2] The periodicity of the ordered structure was three times its disordered (111) spacing and was nearly identical to that for the (001) spacing of YBCO. Here, we observed clear indications of such ordering taking place. In fact, two distinguishable ordered structures were observed in both 3- and 5-μm thick films which were heated for 20 and 30 minutes (Fig.1c). One of them is tetragonal lattice with a = 0.757 and c = 1.07 nm; the other is orthorhombic with a = 1.063, b = 1.078 and c = 1.07 nm. The structure relationships between the disordered oxy-fluoride and the ordered oxy-fluorides are as follows: $c_{O1} \sim c_{O2} \sim 3d_{O\text{-}F}^{111}$, $a_{O1} \sim 1/\sqrt{2}\, a_{O2} \sim 3d_{O\text{-}F}^{211}$ and $(001)_{O1,O2} \parallel (111)_{O\text{-}F}$, where subscripts O_1, O_2 and O-F represent ordered tetragonal and orthorhombic, and disordered oxy-fluorides, respectively. Both of these phases had epitaxial relationships with STO.

When the 5–μm thick specimen was heated for 30 minutes, in addition to small Y_2O_3 precipitates, and the disordered and ordered oxy-fluorides, YBCO nuclei and a new transitional phase (for convenience, we denote it as the T phase) were found at STO surface (Fig.2a and 2b). The composition of YBCO nuclei were the same as those found in the 1–μm thick film which was heated for 20 min. The T phase had a composition similar to that of YBCO nuclei, the average composition being $YBa_2Cu_{1.5\sim2.0}O_x$, and was aligned with its (001) plane parallel to the (001) plane of STO. The d-spacing of its (001) plane was 0.38 nm, which was larger than that of (111) plane of the disordered oxy-fluoride (0.357 nm), but was nearly one third of d-spacing of YBCO's (001) plane (1.168 nm). This T phase was formed by the replacement of F in the oxy-fluoride by Cu and O. This process causes an increase of its (111) d-spacing from that for the oxy-fluoride. Thus, we believe that this T phase is a transitional state in the formation of the YBCO nuclei from the oxy-fluoride. Furthermore, it appears that YBCO starts to nucleate right at the interface between this phase and STO as shown in Fig.3b. In some areas of the same specimen, non-(001) aligned oxy-fluoride grains were also found at the STO surface (Fig.3c). These might be the sites of the formation of very

large non-c-axis YBCO, (e.g., ~ 3 μm and ~ 100 nm along the a-b plane and the c-axis direction, respectively.) (Fig.3d) which were occasionally found in this specimen.

* E-mail: ljwu@bnl.gov, Fax: 631-344-4071, Tel: 631-344-3267.
This work was performed under the auspices of Division of Mat. Sci., Office of Basic Energy Sci., Office of Science, US Department of Energy under contract No. DE-AC02-98CH10886.

REFERENCES

1. V.F. Solovyov, H. J. Wiesmann and M. Suenaga, Physica C **353**, 14 (2001).
2. Lijun Wu, Y. Zhu, V. F. Solovyov, H. J. Wiesmann, A. R. Moodenbaugh, R. L. Sabatini, and M. Suenaga, To be published in J. Mater. Res.
3. V.F. Solovyov, H. J. Wiesmann, M. Suenaga and R. Feenstra, Physica C **309**, 269 (1998).

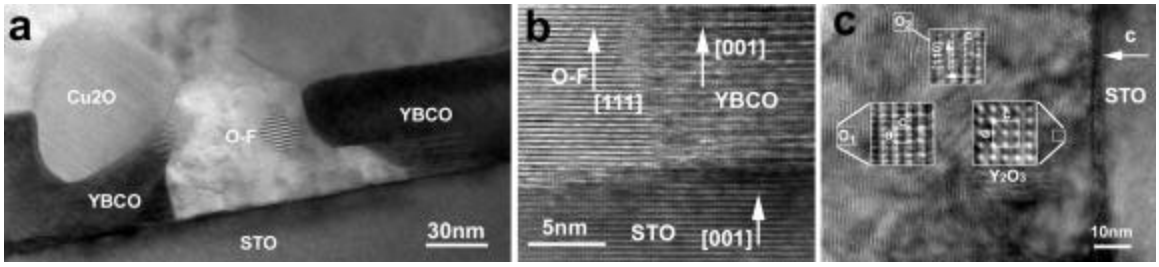


Fig.1 Morphology from a 1 μm thick film heated at 735°C for 20 min., (a) YBCO and the aligned oxy-fluoride at the STO surface and (b) high resolution image of the YBCO and the oxy-fluoride aligned with STO: $(001)_{YBCO} \parallel (001)_{STO}$, $(110)_{YBCO} \parallel (110)_{STO}$. (c) High resolution TEM images of two ordered oxy-fluorides (O_1 and O_2) and a small Y_2O_3 in a 3μm thick film heated for 30 minutes.

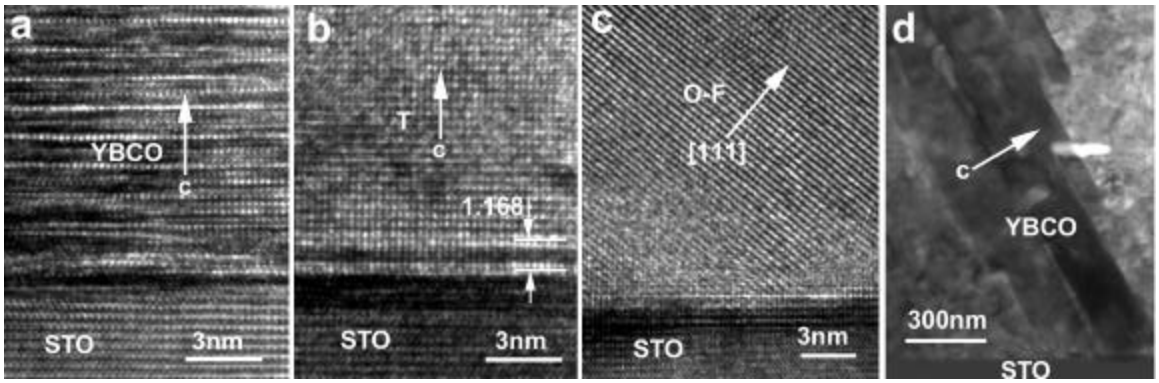


Fig.2 Morphology of YBCO and oxy-fluorides from a 5μm thick film heated for 30 min, (a) YBCO nucleus. (b) The transitional phase (T phase) showing one unit cell of YBCO formed at the STO surface. (c) a non-aligned oxy-fluoride at the STO surface, and (d) a non-c-axis YBCO grain.