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ELECTRON MICROSCOPY ANALYSIS OF THE INTERMEDIATE PHASES FORMED DURING THE NUCLEATION OF $YBa_2Cu_3O_{7-d}$ FILM

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Recently, considerable efforts have been made in growing bi-axially aligned thick $YBa_2Cu_3O_7$ (YBCO) films on a flexible, textured metallic substrate for electrical power applications. The BaF_2 post-deposition annealing process is one of the most promising methods. To understand the nucleation and growth mechanism of YBCO in this process, extended transmission electron microscopy analysis has been made[1]. Here, we report on the evolution of Ba-Y oxy-fluoride which is pertinent to the epitaxial YBCO nucleation process on $SrTiO_3$ (STO) substrate.

The stoichiometric ratio of Y, Cu and BaF_2 was evaporated on (001)-cut STO substrate. Subsequently, these films were annealed at 735°C in an O_2-H_2O-N_2 gas atmosphere and quenched after 10, 20, or 40 minutes. The morphology and phase composition of the precursor changed drastically with the annealing times, e.g. after 10 minutes heat treatment, the precursor consisted of fine grained Cu_2O and Ba-Y(Cu) oxy-fluoride (cubic, a=0.618nm) as shown in fig.1a. The oxy-fluoride tends to align its (111) plane parallel to the (001) plane of STO at the precursor/substrate interface region (fig.1b). Moreover, ordering along [111] direction occurred, as indicated in the fig.1b. After annealing for 20 minutes, an ~100nm thick layer composed of ordered oxy-fluorides and Y_2O_3 were formed in the vicinity of the STO substrate (fig.2a). The ordered oxy-fluorides and the Y_2O_3 were well aligned with the STO substrate. Further annealing results in the formation of an ~100nm thick YBCO layer, suggesting that the ordered structure is in an intermediate state for the disordered oxy-fluoride to nucleate YBCO.

High resolution images (fig.2a) and electron diffraction patterns (fig.2b and 2c) indicate that there are two kinds of ordered oxy-fluorides. One has a tetragonal lattice with a = 0.757 and c = 1.07 nm and the other is orthorhombic with a = 1.063, b = 1.078 and c = 1.07 nm. Quantitative microprobe EDS and EELS show that the average composition of the disordered oxy-fluoride is $(Y_{0.3}Ba_{0.7})(O_{0.15},F_{0.85})_2$ with a detectable amount of Cu. The ordered oxy-fluoride with tetragonal symmetry is deficient in Y but rich in F, compared with the disordered oxy-fluoride, while that with orthorhombic symmetry is rich in Y but deficient in F. The structure relationships between disordered oxy-fluoride and ordered oxy-fluorides follow: $c_T \sim c_O \sim 3d_{O\text{-}F}^{111}$, $a_T \sim 1/\sqrt{2}\ a_O \sim 3d_{O\text{-}F}^{211}$ and $(001)_{T,O} \parallel (111)_{O\text{-}F}$. The crystallographic relationships between STO substrate and the ordered oxy-fluorides are: $(001)_{STO} \parallel (001)_T \parallel (001)_O$ and $(110)_{STO} \parallel (110)_T \parallel (100)_O$, where subscripts T, O and O-F represent ordered tetragonal and orthorhombic, and disordered oxy-fluorides, respectively. We note that the ordered oxy-fluorides have a very close structural relationship with YBCO: $c_{YBCO} \sim c_{T,O}$, $a_{YBCO} \sim \frac{1}{2}\ a_T \sim 1/\sqrt{8}\ a_O$ and also have an epitaxial relationship with STO. These two intermediate ordered phases are expected to play an important role in the nucleation of c-axis oriented YBCO films on STO.

References

1. Lijun Wu, Y. Zhu, V. F. Solovyov, H. J. Wiesmann, A. R. Moodenbaugh, R. L. Sabatini, and M. Suenaga, Submitted to J. Mater. Res.
2. Work supported by US Department of Energy under contract No. DE-AC02-98CH10886.

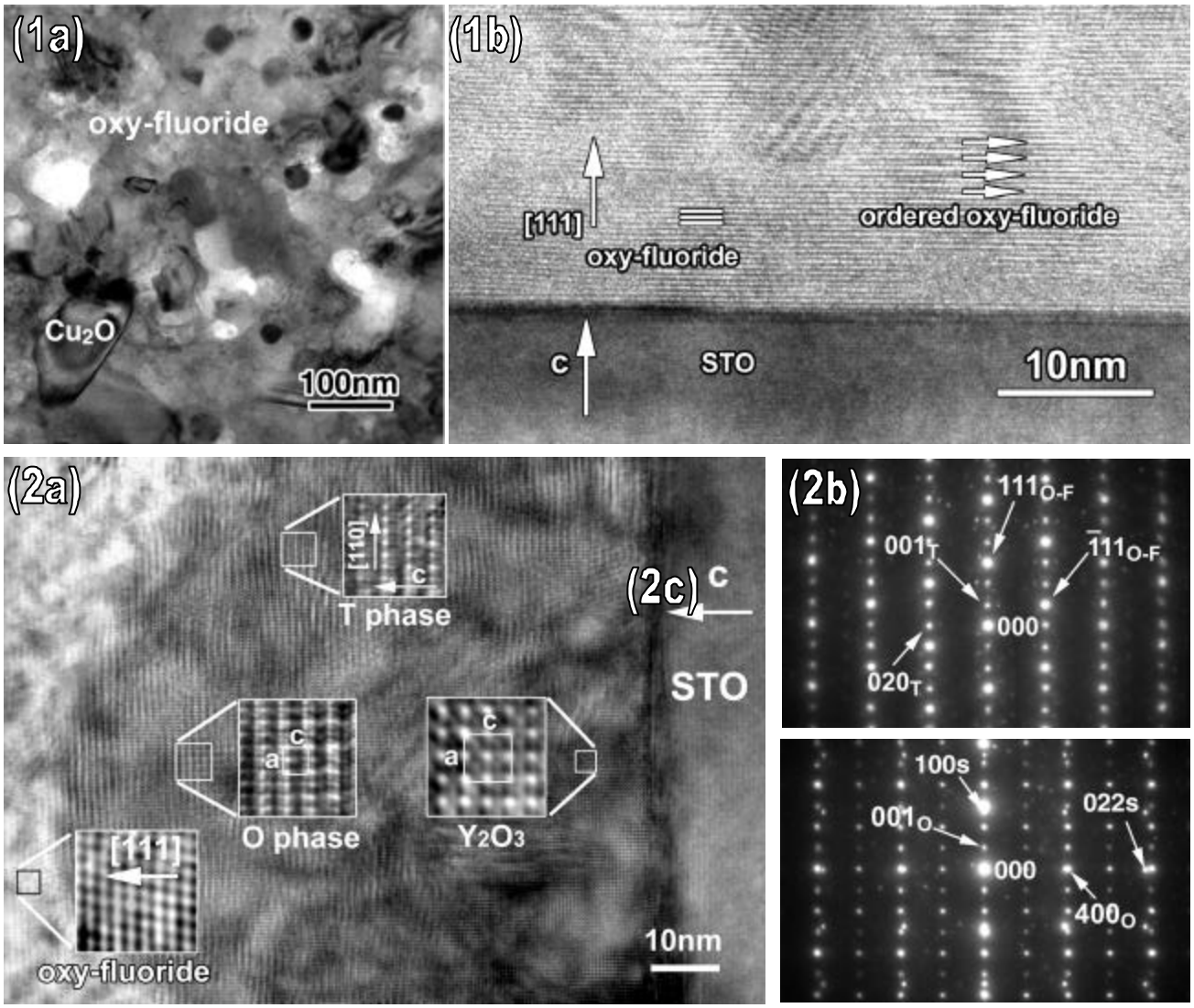

Fig.1 Morphology of the specimen after heat-treatment for 10 minutes. (a) Cu_2O and oxy-fluoride particles are randomly orientated in the area ~100nm away from the $SrTiO_3$ (STO) substrate. The black particles are Cu_2O, while the gray ones are oxy-fluoride. (b) In the vicinity of STO substrate (~100nm), oxy-fluoride tends to align its (111) plane parallel to the (001) plane of STO substrate. Moreover, structural ordering occurs along the [111] direction in some oxy-fluoride, resulting in the formation of ordered oxy-fluorides.

Fig.2 (a) High resolution images of the specimen annealed for 20 minutes, showing a layer (~100 nm thick) before the nucleation of YBCO. The layer consists of two ordered oxy-fluorides (T phase: tetragonal, a=0.757 and c=1.07nm, O phase: orthorhombic, a=1.063, b=1.078 and c=1.07nm) and Y_2O_3 phase. Both ordered oxy-fluorides and Y_2O_3 are aligned with their (001) plane parallel to the (001) plane of STO substrate. (b) Electron diffraction pattern taken from the area containing disordered oxy-fluoride and the T phase. (c) Diffraction pattern from the O phase and STO. Subscripts O-F, T, O and S represent oxy-fluoride, T phase, O phase and STO substrate, respectively.