Growth mechanism of $YBa_2Cu_3O_{7-y}$ thin films on the metallic tapes by MOCVD

Y. Yoshida, I. Hirabayashi, H. Kurosaki, H. Akata, K. Higashiyama and Y. Takai

***abst*-We fabricated the $YBa_2Cu_3O_{7-y}$ (YBCO) thin film on the MgO single crystalline substrate and the cube textured (CUTE-Ag)-tape using metal organic chemical vapor deposition (MOCVD) method. It was confirmed that the *c*-axis oriented YBCO film grew on these substrates. The terraced surface and spiral growth pattern are clearly visible. Many Ag particles were observed on the terrace surface of the spiral steps. after heat treatment these particles concentrated at the edge of the spiral steps. The dependence of the terrace width on the substrate temperature is drastically changed at the certain temperature range between 750 and 800°C. At high temperatures, the terrace width of the films on MgO increases and reaches to about 90nm at 800°C, whereas those on CUTE-Ag tape is about 160nm at same temperature 800°C. The value of the supersaturation ratios are estimated as 50 and 15 from the terrace widths on MgO and CUTE-Ag. The results from the surface morphology and the microstructure suggest that there is a difference in the growth mechanism between the YBCO films on MgO and those on CUTE-Ag in the higher temperature region. We speculate that the quasi-liquid layer is more stable on the CUTE-Ag at higher temperatures than 750°C, and the growth mechanism of the YBCO films on the CUTE-Ag is mixed with the Vapor-Liquid-Solid (VLS) growth mode and the surface-active species (Surfactants) growth mode.**

***Index Terms*-thin film, metallic substrate, YBCO, MOCVD**

I. INTRODUCTION

The growth of high quality thin films of $YBa_2Cu_3O_{7-y}$ (YBCO) on metallic substrates is desirable for electric power and energy storage applications. It is well known that grain boundary misorientation in oxide superconductors has a large influence over the critical current density (*Jc*) value. It requires that the *in-plane* and *out-of- plane* alignment observed be high for high *Jc* values. Much progress has been made in satisfying these requirements using ion beam assited deposition (IBAD) [1], inclined substrate deposition (ISD) [2], rolled and annealed biaxially textured (RABITS) [3], surface oxidation epitaxy (SOE) [4] and cute-textured Ag tape (CUTE-Ag) [5] for the oriented YBCO thin film on metallic substrate.

Metalorganic chemical vapor deposition (MOCVD) has been shown to be a promising technique for the fabrication of device quality compound semiconductors and high T_c superconducting thin films. We studied the growth mechanism and the superconducting properties of YBCO thin films on MgO single crystalline substrate [6]and the metallic tape [5] using MOCVD method for the superconducting wire. Then we found the existence of the liquid layer on the growing surface of the YBCO films above the higher temperature than 750°C and proposed the possibility of the Vapor-Liquid-Solid (VLS) growth for this observation.[7-8]

In this paper, we fabricated the YBCO thin film on the CUTE-Ag tape and discussed the growth mechanism of the thin films, compared with the films on MgO substrates.

II. EXPERIMENTAL

We prepared YBCO thin films by cold-wall and hot-wall type MOCVD using liquid state sources. The sources of hot-wall type MOCVD are yttrium-tris-(2,2,6,6-tetramethylheptane-3,5-dine) 4-t-butylpyridine-N-oxide adduct ($Y(DPM)_3 \cdot 4tBuPyNO$), bis-dipivaroylmethanatobarium-tetraethylenepentamine adduct ($Ba(DPM)_2 \cdot 2tetaraene$) and copper-bis-(2,2,6-trimethylheptane-3,5-dione) ($Cu(TMHPD)_2$). The sources of cold-wall type MOCVD are barium-bis-(1,1,1,2,2,3,3,7,7,8,8,9,9,9-tetradecafluoronane-4,6-dione) tetra glyme adduct ($Ba(TDFND)_2 \cdot tetraglyme$), copper-bis-(1,1,1,2,2,3,3,7,7,8,8,9,9,9-tetradecafluorononane-4,6-dione) hydrate ($Cu(TDFND)_2 \cdot H_2O$) and the yttrium source is the same in the case of the hot-wall MOCVD. The MO source vapors were transported by Ar gas and mixed with oxygen gas. In the case of both cold-wall and hot-wall type MOCVD experiments, the flow rates of Ar and oxygen gases were maintained at 10, 30 and 228, 700 sccm, respectively. The pressure in the reactor was adjusted from 2.5 to 6.0 Torr. The temperatures of Y,

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Ba and Cu sources were kept respectively at 120, 150, and 115°C in the case of cold-wall MOCVD and 137, 151 and 123°C in the case of hot-wall MOCVD, which were higher than the melting points of the sources. MgO (100) single crystalline substrate and the CUTE-Ag tape were used as substrates. The substrate temperature was set at 600-800°C in the cold-wall system and 800-870°C in the hot-wall system. Using the conventional vapor phase growth, the films were deposited at rate of 1-2nm/min followed by cooling down to 200°C at 15°C/min under oxygen at 1 atm. The crystal structure of the deposited films was examined by θ-2θ X-ray diffraction (XRD) method. In particular, the *in-plane* orientation of the film is determined by X-ray pole-figure measurment by the Schulz reflection method. The critical temperature (T_c) of the grown films was measured by four-probe resistance measurement. The surface morphology of the films was investigated by atomic force microscopy (AFM). Cross sectional transmission electron microscopy (TEM) equipped with an energy dispersive x-ray spectroscopy (EDS) revealed the crystal structure.

III. Results and Discussion

A. Surface morphologies of the YBCO films on the CUTE-Ag tape

High-quality *c-axis* oriented films were obtained with a thickness of 150nm on the MgO and the CUTE-Ag substrate. The zero-resistance critical temperature (Tc_0) for the films on the MgO and the CUTE-Ag substrate are 82K and 83K, respectively. The crystalline axis of the *a*/*b*-axis oriented YBCO grains are aligned with the relationship of the mixture of YBCO[110] // MgO[100] and YBCO[100] // MgO[100]. This results was understood from the NCSL (the near-coincidence site lattice) model.

Screw dislocations are observed on the plate-like crystallites for the top-view image in Fig.1. They are nearly 1.2nm in height, and it agrees well to one-unit cell height along *c-axis* direction of the YBCO. Many precipitates appeared on the top of the terraces. These were polycrystalline Ag precipitates measured by the Auger spectra.

Fig.2 show the surface morphologies of the as-grown surface at room temperature and that at 550°C. The Ag precipitates were dispersed on the surface of the terrace at room temperature (Fig.2(a)) and condensed at the step edge at high temperature (Fig.2(b)). It is proven that Ag particles, which diffuse in YBCO layer, pass through to the surface in the growth of YBCO thin films. We presume that this phonomenon is similar to the role of surface-active species (surfactants) in the field of semiconcoductor technology.[9-12]

Furthermore fig.3 shows the dependence of the terrace width on the substrate temperature for several films on the MgO and the CUTE-Ag substrate. The terrace widths on CUTE-Ag substrate were increased as substrate temperature increase. These values reached 240nm at 850°C, which is wider than the terrace widths on MgO at same temperature.

It is known that the terrace widths vary with growth conditions. Supersaturation plays an important role in determining the terrace width of the spirals which originate from the screw dislocations. From the BCF theory[13], the terrace width y_0 is given by

$$y_0 = 19\, r_s^* \quad (1),$$

where r_s^* is the critical radius for 2-dimensional nuclei and is expressed in the form,

$$r_s^* = \gamma\, \Omega / RT \ln \alpha_s \quad (2).$$

In the above expression, γ, Ω and α_s are respectively the surface free energy for the side surface of 2-dimensional nuclei, molar volume and supersaturation ratio.

Using eqs. (1) and (2) and by measuring the terrace width of the spiral hill, the value of the supersaturation ratio can be determined if γ is given. Nishinaga and Scheel used the value of γ = 1.6 J/m[14] and we use this value in the calculation. Fig.4 shows the dependence of the supersaturation on the substrate temperature for several films on the MgO and the CUTE-Ag substrate, calculated from the terrace widths at each temperature. It is indicated the supersaturatio ratio rapidly changes at 750-850°C, which is a low value of about 50 on MgO and about 15 on CUTE-Ag at 850°C. In the Liquid phase epitaxy (LPE) method, it was reported that the supersaturation ratio is about 1.07 at above 1000°C[14]. These results suggest that the CVD growth mechanism on the CUTE-Ag substrate at the higher temperature is essentially the same as LPE method, proposed

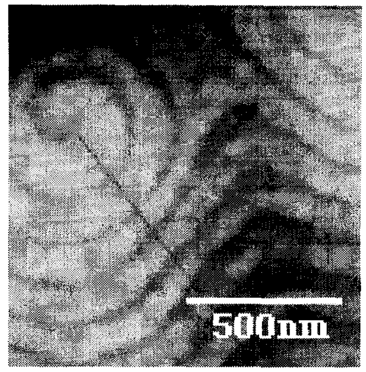

Fig.1. The surface morphology observed by AFM for the YBCO films on the CUTE-Ag.

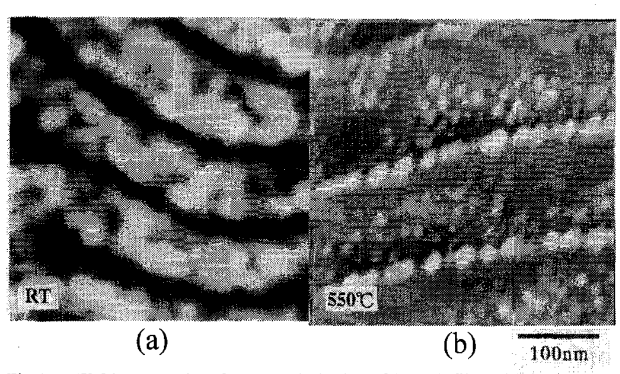

Fig.2. AFM images of surface morphologies of YBCO film with heat treatment. (a) Room temperature and (b) 550°C.

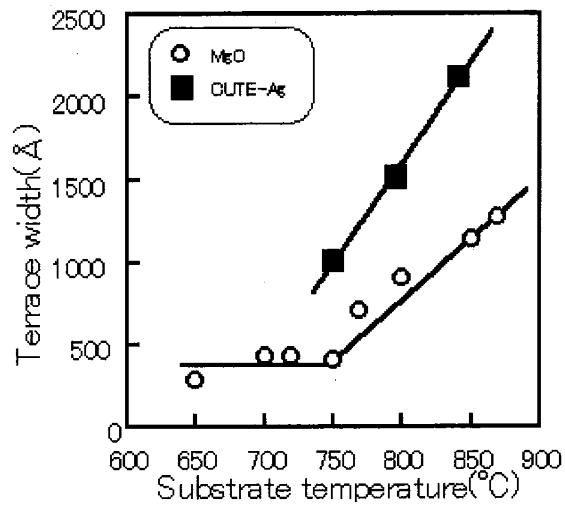

Fig.3. Dependence of the terrace width on the subtarte temperature. Circles (○) denote the terrace width on MgO and squares (■) are those on CUTE-Ag.

the possibility of the Vapor-Liquid-Solid (VLS) growth [7]. We assume the existence of the liquid layer at the surface is stable on the YBCO films on the CUTE-Ag substrate, compared with on MgO.

B. The microstructure between YBCO film and CUTE-Ag

Additional information on the growth of YBCO films on the CUTE-Ag substrate was obtainted from the cross-sectional TEM analysis. Fig.5 displays the cross-sectional TEM images between the YBCO and the CUTE-Ag substrate (a) and the microstructure of the YBCO film (b). These figures are taken with the incident beam parallel to <100> of the film. The interface between the YBCO layer and the substrate is sharp and clean. The YBCO films grow directly on the CUTE-Ag substrate, and there are no reaction products in the interface. TEM imaging reveals that the presence of steps in the CUTE-Ag substrate usually results in the formation of antiphase boundaries (see fig.5(a)). Furthermore, the TEM image of the YBCO layer indicates that the *c*-planes are not smooth; the films on the CUTE-Ag substrate contains many stacking faults which are marked by the arrows in fig.5 (b). On the other hand, the YBCO film on the MgO substrate deposited by the block by block method is free from stacking faults[15]. The microstructure of the YBCO film on the CUTE-Ag substrate is essentially equivalent to the films on MgO deposited by LPE method[16] and VLS growth mode[17].

Ag addition lowers the melting temperature of the Ba-Cu-O phase [18] and it enables us the "low-temperaturization" of LPE method.[19] We assume that the Ag diffused from the substrate on the surface of the YBCO films, and it enhanced the production of liquid phase in the VLS growth at the surface of YBCO/CUTE-Ag.

IV. SUMMARY

We discussed the growth mechanism of the YBCO epitaxial films deposited on the CUTE-Ag substrate by MOCVD, and compared with that on the MgO substrate. AFM images show an abrupt change in the terrace width of spiral growth features at approximately 750°C for films deposited on MgO and CUTE-Ag. Furthermore the terrace width on CUTE-Ag is broader than that on MgO at the same temperature. Many Ag precipitates appeared on the terrace measured by Auger spectra. It was confirmed that the absence of the Ag precipitates in the grains and the grain boundaries of the YBCO films from the cross sectional TEM images. These results suggest the Ag precipitates diffused from the substrate might promote the stable of the liquid layer in the growth of YBCO films on the CUTE-Ag substrate at higher temperatures.

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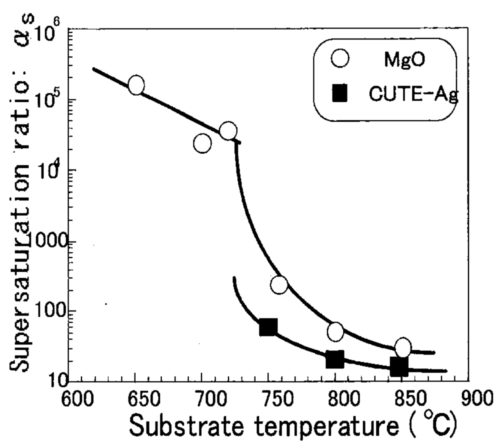

Fig.4. Dependence of the supersaturation ratio on the substrate temperature. Circles (○) denote supersaturation ratio on MgO and squares (■) are those on CUTE-Ag.

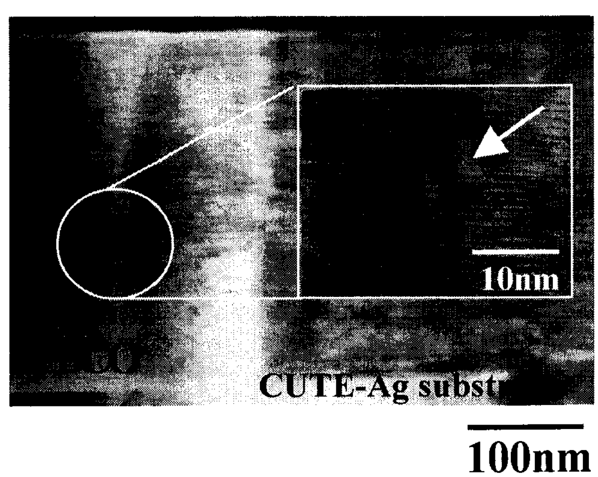

Fig.5. Cross-sectional TEM images between the YBCO film and the CUTE-Ag substrate.

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