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SHORT COMMUNICATION

Preparation of $Y_{1-x}Yb_xBa_2Cu_3O_{7-y}$ Superconducting Films by Chemical Vapor Deposition

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Abstract−High Tc $Y_{1-x}Yb_xBa_2Cu_3O_{7-y}$ films were prepared on $SrTiO_3$(100) substrates by chemical vapor deposition method. $Yb_1Ba_2Cu_3O_{7-y}$ films were obtained at higher oxygen partial pressure compared with $Y_1Ba_2Cu_3O_{7-y}$ films at the same deposition temperature. Tc,o (R=0) decreased about 1.5 K when Y was fully substituted with Yb. The c-axis lattice parameter of $Y_{1-x}Yb_xBa_2Cu_3O_{7-y}$ films also decreased as the amount of Yb(x) increased.

Key words: CVD, Superconductor, Thin Films, YBaCuO, YbBaCuO

INTRODUCTION

Since the discovery of the high Tc oxide superconductor by Bednorz and Müller [Bednorz and Müller, 1986], many intensive studies have been conducted to find a new superconducting material with higher Tc. As a result, new high Tc superconductors such as YBaCuO [Chu et al., 1987], BiSrCaCuO [Maeda et al., 1988], TlBaCaCuO [Sheng et al., 1988] and HgBaCaCuO [Putulin et al., 1993] have been found. The preparation techniques for the thin films of those superconductors have also caused a great deal of interest due to wide applicability to microelectronics.

Recently, the methods such as laser ablation, evaporation, sputtering, molecular beam epitaxy (MBE) and chemical vapor deposition (CVD) have been successfully used to fabricate the thin films of these oxides. Among these techniques, the CVD method, which is one of the very promising methods due to its high productivity and simplicity, has been used to fabricate the BiSrCaCuO superconducting films [Endo et al., 1996] as well as YBaCuO films [Watanabe et al., 1989] with high Tc's and high Jc's. We also succeeded in fabrication of YBaCuO films with Tc,o of 87 K and Jc higher than 10^4 A/cm^2 at 77 K) by CVD method at low temperature (650 °C) by controlling the oxygen partial pressure [Lee et al., 1992].

It has been well known that a variety of LnBaCuO (Ln=lanthanide element) shows superconductivity (except Ln=Ce, Pr, Pm and Tb) above 77 K and has the same crystal structure with $Y_1Ba_2Cu_3O_{7-y}$. However, most research on thin film fabrication was carried out for a Y-based 123 system, and very limited investigations were made for other lanthanide-based 123 systems. In particular, there are few reports on the preparation of other LnBaCuO films by CVD method even though the formation temperature of 123 phase is affected depending on the kinds of lanthanide elements [Morita et al., 1990].

In this work, we substituted Y in the $Y_1Ba_2Cu_3O_{7-y}$ by Yb, which has a larger localized magnetic moment than Y. The purpose for that is to increase a non-superconducting phase that has been known to play a role as flux pinning center. $Y_{1-x}Yb_xBa_2Cu_3O_{7-y}$ superconducting films were prepared on $SrTiO_3$(100) substrates by chemical vapor deposition method by using molecular oxygen as an oxidant. The phase formation and the superconductivity of $Y_{1-x}Yb_xBa_2Cu_3O_{7-y}$ films were investigated by X-ray diffraction (XRD) patterns and electrical resistance of the films by standard ac four-probe method, respectively.

EXPERIMENTAL

Source materials used were beta-diketone chelates of $Y(thd)_3$, $Yb(thd)_3$, $Ba(thd)_2$, and $Cu(thd)_2$ (thd=2,2,6,6-tetramethyl-3,5-heptanedionate) (Strem Co., Ltd). These chelates were evaporated at 126-132 °C. The source vapors of Y/Yb, Ba, and Cu were transported into the hot zone by Ar gas, respectively, and oxygen gas was introduced separately. The oxygen partial pressure was controlled by changing the Ar/O_2 ratio using mass flow controller (MFC). The CVD reactor was a hot-wall type, described in detail elsewhere [Lee et al., 1991].

Deposition of films was performed on $SrTiO_3$(100) single-crystal substrates placed normal to a gas stream at 750 °C at a reduced pressure of 4 torr. The oxygen partial pressure was 0.0248 torr and the deposition time was 30 min. After deposition, the films were cooled to 400 °C at a cooling rate of 15 °C/min and held for 30 min in an oxygen pressure of 760 torr. The deposition rate of the films was about 1 μm/h. X-ray diffraction (XRD) were obtained to examine the phase formation and the crystallographic orientation of the films deposited. Electrical resistance and current density were measured by using a four-probe method and dc four-probe method.

RESULTS AND DISCUSSION

Table 1 shows the electric properties [Tc,o and ΔT(=Tc, onset-Tc,o)] of the $Y_{1-x}Yb_xBa_2Cu_3O_{7-y}$ films (x=0-1.0) prepared at 750

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Table 1. Electrical properties for the $Y_{1-x}Yb_xBa_2Cu_3O_{7-y}$ (x=0-1.0) thin films on $SrTiO_3$(100) at substrate temperature 750 °C and Po_2= 0.0248 torr

$Y_{1-x}Yb_xBa_2Cu_3O_{7-y}$	Substrates ($SrTiO_3$(100))		
	Tc, 0 (K)	Δ T (K)	Tc, onset (K)
x=1.0	86.5	1.5	88
x=0.81	87.5	1.0	88.5
x=0.64	87.0	1.5	88.5
x=0.38	87.5	1.0	88.5
x=0.18	88.0	1.0	89.0
x=0	88.5	1.0	89.5

°C with an oxygen pressure of 0.0248 torr. The reactor pressure was 4 torr. It can be seen that the films showed good superconductivity with a narrow ΔT over 77 K when x was changed from 0 ($Y_1Ba_2Cu_3O_{7-y}$) to 1.0 ($Yb_1Ba_2Cu_3O_{7-y}$). Tc,o of the films deposited on $SrTiO_3$ substrates was measured as 86.5-88.5 K when x, substitution of Yb for Y, was increased from 0 to 1.0.

Fig. 1 shows the XRD patterns of the $Y_{1-x}Yb_xBa_2Cu_3O_{7-y}$ films deposited on $SrTiO_3$(100) substrates at 750 °C with an oxygen pressure of 0.0248 torr. It can be seen that c-axis oriented texture was developed regardless of the substitution amount of Yb. XRD peaks from Yb_2O_3, $YbCu_2O_5$ and 211 phase appeared for Yb-substituted specimen but were weakened for the $Yb_1Ba_2Cu_3O_{7-y}$ specimen where the whole Y was substituted with Yb. Y and Yb are competitively reacted to the different paths, based upon the difference of the reactivity between Y and Yb, resulting in that Yb is less reactive than Y. Therefore, if Y and Yb coexist at the same temperature, the superconducting phase is not completely formed, 123 phase, stable 211 phase, Y_2O_3 and $Yb_2Cu_2O_5$ are existing in an incomplete reaction state, respectively.

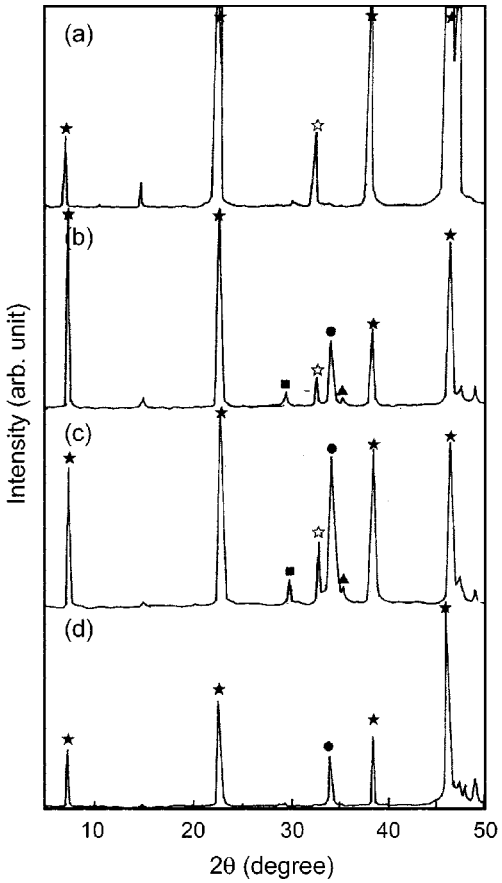

Fig. 1. XRD patterns of $Y_{1-x}Yb_xBa_2Cu_3O_{7-y}$ (x=0-1.0) thin film on $SrTiO_3$(100) substrates (a) x=0.0, (b) x=0.38. (c) x=0.64 and (d) x=1.0.
[■: Yb_2O_3, ▲: Yb_2BaCuO_5, ●: $Yb_2Cu_2O_5$, ★: $Y_{1-x}Yb_xBa_2Cu_3O_{7-y}$ (*00l*), ☆: $Y_{1-x}Yb_xBa_2Cu_3O_{7-y}$ (103)].

It has been reported that the fine particles of non-superconducting phases act as a pinning center in R.E.-123 films [Li et al., 1992]. Therefore, it is expected that these second phases may be beneficial for Jc improvement acting as flux pinning in $Y_{1-x}Yb_xBa_2Cu_3O_{7-y}$ films. Lee et al. [Lee et al., 1993] reported that $Yb_1Ba_2Cu_3O_{7-y}$ films were formed at a lower oxygen partial pressure at the same deposition temperature than $Yb_1Ba_2Cu_3O_{7-y}$ films. This means that the 1/T-Po_2 phase stability line is different for Y-Ba-Cu-O and Yb-Ba-Cu-O system. The Yb-123 phase may be stable at lower temperature than Y-123 phase because the Yb-123 phase was stable at higher oxygen partial pressure compared with Y-123 phase. Therefore, it is thought that the phases such as yttria, $Yb_2Cu_2O_5$ and 211 phase, which may be in equilibrium with 123 phase, could appear at the deposition temperature.

Hon et al. [Hon et al., 1993] also reported the presence of second phases in Y-123 films prepared by sputtering method. It is thought that the formation mechanism of $Y_{1-x}Yb_xBa_2Cu_3O_{7-y}$ films consists of two reaction paths. One is the reaction path correspond-

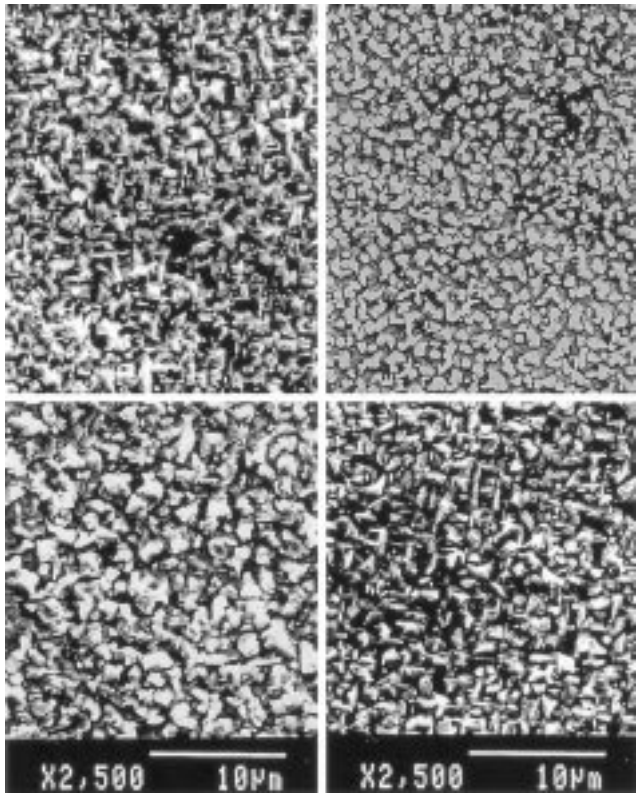

Fig. 2. Surface SEM micrographs of the $Y_{1-x}Yb_xBa_2Cu_3O_{7-y}$ (x= 0-1.0) thin films on $SrTiO_3$(100) at substrate temperature 750 °C and Po_2=0.0248 torr (a) x=0.0, (b) x=0.38, (c) x= 0.64, (d) x=1.0.

ing to Y-Ba-Cu-O system and the other is that of the Yb-Ba-Cu-O system. Impurity phases should be in equilibrium with the 123 phase at the deposition condition; therefore, the presence of an impurity phase suggests the reaction path of 123 phases. Based on the phases formed in deposited films, the reaction paths are suggested as following for Y-123 and Yb-123, respectively.

$$\text{Y(Yb)-123: } Y(Yb)_2O_3 + 2CuO \rightarrow 4BaCuO_2 + Y(Yb)_2Cu_2O_5$$
$$\rightarrow 2Yb_1Ba_2Cu_3O_{7-y}$$

Fig. 2 shows the SEM micrographs of the $Y_{1-x}Yb_xBa_2Cu_3O_{7-y}$ films with x=0, 0.38, 0.64 and 1, respectively. Microstructure reveals that the two dimensional alignment of 123 grains are not good compared with those prepared at higher temperature [Li et al., 1992]. In the $YbBa_2Cu_3O_{7-y}$ and $YBa_2Cu_3O_{7-y}$ thin films appears a two dimensional alignment of 123 grains but $Y_{1-x}Yb_xBa_2Cu_3O_{7-y}$ thin films with both the Y and Yb present show plate-like particles thought to be second phase. These particles are considered to act as an effective flux pinning center in the system.

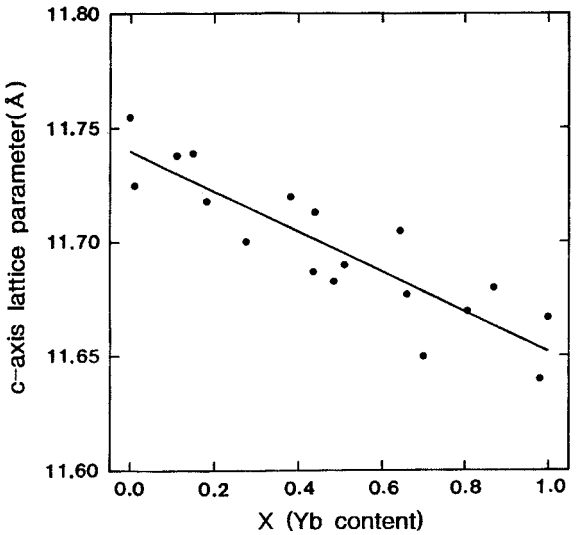

Fig. 3. The c-axis lattice parameter of the $Y_{1-x}Yb_xBa_2Cu_3O_{7-y}$ (x= 01.0) thin films on $SrTiO_3$(100) at substrate temperature 750 °C and Po_2=0.0248 torr as a function of x.

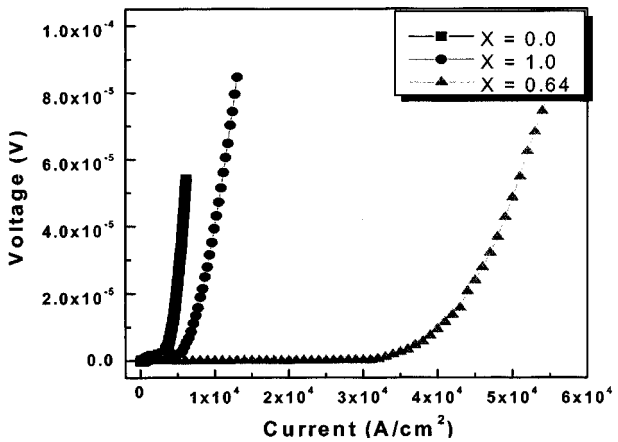

Fig. 4. Current-voltage curves of $Y_{1-x}Yb_xBa_2Cu_3O_{7-y}$ thin films on $SrTiO_3$(100) at substrate temperature 750 °C and Po_2= 0.0248 torr.

Fig. 3 reveals the variation of c-axis lattice parameter of $Y_{1-x}Yb_xBa_2Cu_3O_{7-y}$ films. The c-axis lattice parameter tends to decrease linearly when the Yb amount increases. These results coincide well with those obtained for bulk $Y_{1-x}Yb_xBa_2Cu_3O_{7-y}$ specimens [Kim, 1994]. The linear change of lattice parameter indicates that the Yb was substituted for Y in full range.

Fig. 4 shows current-voltage curves for $Y_{1-x}Yb_xBa_2Cu_3O_{7-y}$ thin films with x=0, 0.64 and 1. $Y_{1-x}Yb_xBa_2Cu_3O_{7-y}$ thin film (x=0.64) shows a higher critical current density than $Y_1Ba_2Cu_3O_{7-y}$, or $Yb_1Ba_2Cu_3O_{7-y}$ thin film that appears due to more second phases uniformly distributed in it.

SUMMARY

The $Y_{1-x}Yb_xBa_2Cu_3O_{7-y}$ thin film was successfully manufactured by CVD method. As the substituted content of Yb for Y increased, the c-axis lattice parameter linearly decreased and the Tc also decreased upto 1.5 K. Microstructure analysis indicated that more fine and uniformly distributed second phases such as Y_2O_3, 211 and $Yb_2Cu_2O_5$ etc. grow in the presence both Y and Yb because of their mutual material inhibition effects from crystalline growth. $Y_{1-x}Yb_xBa_2Cu_3O_{7-y}$ (x=0.64) film turned out to have a higher critical current density than $Y_1Ba_2Cu_3O_{7-y}$ or $Yb_1Ba_2Cu_3O_{7-y}$ films, because of the fine and uniformly distributed second phases that act as flux pinning centers in $Y_{1-x}Yb_xBa_2Cu_3O_{7-y}$ films.

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