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Effect of Deposition Temperature on the Growth of $Y_1Ba_2Cu_3O_{7-x}$ Thin Film by Aerosol Assisted Chemical Vapor Deposition Using Liquid Solution Sources

Bo-Ryoun Kim, Shafeeque G. Ansari, Young-Soon Kim, Gil-Sung Kim, Sang-Chul Hwang,
Hee-Gyoun Lee* and Hyung-Shik Shin[†]

Thin Film Technology Lab., Department of Chemical Engineering, Chonbuk National University, Chonju 561-756, Korea
*IGC Super-power, Schenectady, NY 12304, U.S.A.
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Abstract−We have investigated the effect of the deposition temperature on the growth of $Y_1Ba_2Cu_3O_{7-x}$ (YBCO) thin film using liquid solution sources on MgO (100) single crystalline substrate and have characterized the superconducting properties. The YBCO films were prepared by aerosol assisted chemical vapor deposition (AACVD). Single solution source of Y, Ba, and Cu β-diketonates dissolved in tetrahydrofuran (THF) was used as precursor. This precursor was passed through an ultrasonic aerosol generator and transported into a hot-wall CVD reactor using Ar as reactant gas (400 sccm). The substrate was placed normal to the gas stream and the substrate temperature was varied from 760 to 860 °C. Deposition was carried out in oxygen atmosphere maintaining total pressure of 3.2 Torr inside the chamber. Deposition time was also varied from 10 to 30 min. The grown YBCO thin films were highly oriented to (001) orientation perpendicular to the substrate. The film deposited at 815 °C had a sharp transition to superconducting state about 87 K. The activation energy estimated from the Arrhenius plot is ~19.14 kJ/mol at the deposition temperature of 815 °C.

Key words: Y-Ba-Cu-O Thin Film, AACVD, Liquid Source, Deposition Temperature

INTRODUCTION

In order to obtain high quality epitaxial $Y_1Ba_2Cu_3O_{7-x}$ (YBCO) thin films which are suitable for electronic devices, it is important to understand details of the crystal growth mechanism of the films. Since the discovery of oxide superconductors, such investigations have been performed by growing HTS films using various deposition techniques. Chemical Vapor deposition (CVD) and physical vapor deposition (PVD) techniques have been successfully applied to grow such films meeting most of the superconducting properties with critical current in excess of 10^6 A/cm^2 on single crystal substrate. Among these, CVD is a promising technique for the fabrication of HTS films, having special merits, such as high deposition rate, the possibility of a long time deposition, no limitation of shape and the scale, and so on. Although CVD technique possesses many kinds of merits, various problems still need to be addressed because of the lack of easy handling, stable precursors [Yoshida et al., 1996], particularly for alkaline earth metals such as barium, a relatively high processing temperature and a large number of parameters that must be controlled to maintain stoichiometry during the period of deposition. An important demand on the deposition process is a very good stability of growth rate and film stoichiometry over long deposition periods.

Until now, hydrocarbon based β-diketone chelate precursors such as Ba(thd)$_2$ (thd=2,2,6,6-tetramethyl-3,5-heptanedionate) have been used for fabrication of HTS films by CVD. The barium derivative, Ba(thd)$_2$ has been found to have an irreproducible and variable transport rate because of gas phase and solid-state oligomerization and/or hydrolysis reaction. Because of the long residence time in the sublimation vessel and plumbing, the stability of the precursor is critical in maintaining deposition rate and stoichiometry control. An attempt is made to ease the problems associated with the thermal decomposition of the source material over a long time, that the Ba(thd)$_2$ appears to have, by developing a new precursor with sufficient and stable volatility. We refer to as aerosol-assisted CVD (AACVD), which uses a single liquid solution source for the fabrication of YBCO films. This technique minimizes the residence time at high temperature that any of the precursor must survive before deposition [Salazar et al., 1992; Kim et al., 2000]. In AACVD of YBCO, the precursors need to be dissolved in suitable solvent without reacting with it and at the same time must have a sufficiently high vapor pressure to evaporate completely at the temperature of the preheating zone [Klippe and Wahl, 1997]. The solution is then introduced into an ultrasonic aerosol generator. The aerosol is transported into the preheated zone of the reactor and then it is held at temperature sufficient to vaporize the compound.

In our earlier publication, we reported a detailed procedure for the preparation of HTS YBCO thin film by AACVD using liquid solution source and presented the effect of various parameters, viz. oxygen pressure, substrate preheating temperature and distance between evaporating source (nozzle) and substrate [Kim et al., 2000].

We now report the effect of deposition temperature on the film growth, superconducting properties and deposition rate using AACVD and single source technique. The superconducting properties of the grown films are studied by using AC four point probe technique and structural and morphological studies are carried out by X-ray diffraction and scanning microscopic techniques. The results are compared and discussed with the reported work elsewhere.

EXPERIMENTATION

[†] To whom correspondence should be addressed.
E-mail: hsshin@chonbuk.ac.kr

The deposition of YBCO by the AACVD process was carried out using THF (tetrahydrofuran) mixed single solution of β-diketone chelates of $Y(thd)_3$, $Ba(thd)_2$ $Cu(thd)_2$, (thd=2,2,6,6-tetramethyl-3,5-heptanedionate), purchased from Strem Co. Ltd., USA, on single crystalline MgO (100) substrate. The experimental setup and procedures used were similar to the earlier reported work [Kim et al., 2000]. Mass flow controllers were used to control the flow of the precursor vapours to the deposition chamber. The molar ratio of the precursors, Y : Ba : Cu was 1 : 1.8 : 2.7 and the precursor solution was transformed into a mist by an aerosol generator at a constant rate of 0.2 ml/min. The mist was then transported, with Ar as carrier gas (600 sccm), to the preheating zone kept at 380 °C (optimized temperature), prior to entering the deposition area [Kim et al., 2000]. Oxygen gas was used as the reactant gas with a constant flow rate of 400 sccm. The deposition was carried out at fixed oxygen partial pressure of 3.2 Torr and the deposition temperature and time was varied from 760 °C to 860 °C and 10-30 min, respectively. The samples are hereafter referred to as 'a', 'b', 'c' and 'd' with deposition temperature of 760 °C, 800 °C, 815 °C and 860 °C, respectively. After deposition, films were cooled to 200 °C at 15 °C/min in oxygen atmosphere. No further post-annealing treatment was applied.

In the case of depositing YBCO films by AACVD process using single precursor solution, the following reaction is expected to occur [Kim et al., 2000].

$$Y(thd)_3+2Ba(thd)_2+Cu(thd)_3+2THF+206O_2$$
$$\rightarrow Y_1Ba_2Cu_3O_{7-x}+119CO_2+123.5H_2O$$

X-ray diffraction patterns (III-A Rigaku, Japan) of the films deposited at various deposition temperatures were recorded in the Bragg angle ranging from 5 to 60° with a step scan of 1°/min and using Cu-Kα as radiation source. Zero resistance temperature (T_{czero}) was measured by AC four probe method. Surface morphological study of the film was carried out using scanning electron microscopy (X-650, Hitachi, Japan).

RESULTS AND DISCUSSION

The structural changes can be seen in the X-ray diffraction patterns of the films presented in Fig. 1 as a function of Bragg angle and deposition temperature (760 °C, 800 °C, 815 °C and 860 °C) for 20 min. It can be seen that crystallinity and number of peak increases with increasing deposition temperature. The diffraction patterns mainly consist of strong c-axis peaks from YBCO (001) in addition to slight a- or b-axis peaks and a small CuO peaks. A good c-axis oriented YBCO film was obtained at a deposition temperature of 815 °C. When film deposited above this temperature (i.e., at 860 °C) a shoulder of CuO peak was found in the diffraction pattern.

The scanning electron microscopic images of the films grown at various deposition temperatures are shown in Fig. 2. It is seen that the film grown at 760 °C appears partly amorphous and partly crystalline confirming the X-ray diffraction results with smaller particles. An improved crystallinity and increase in particle size was observed when grown at 800 °C. The film grown at 815 °C shows a smooth ground surface of c-axis oriented YBCO with faceted small plate-like YBCO crystallites about 2 μm size with very small precipitates. This morphology resembles the surface of the films grown by liquid phase epitaxy [Yamada et al., 1995]. Thus the surface mor-

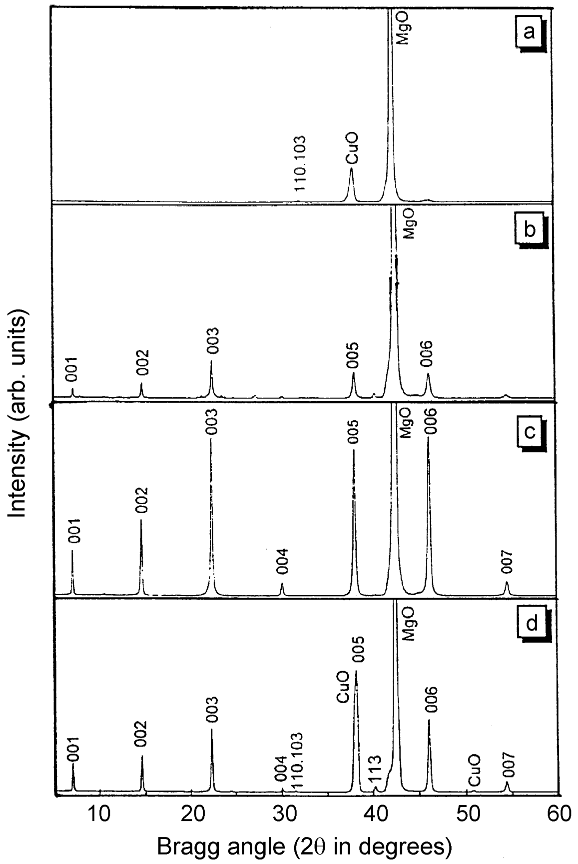

Fig. 1. X-ray diffraction patterns of the film deposited at (a) 760 °C, (b) 800 °C, (C) 815 °C and (d) 860 °C for 20 min with O_2 partial pressure of 3.2 Torr and preheating zone temperature of 380 C.

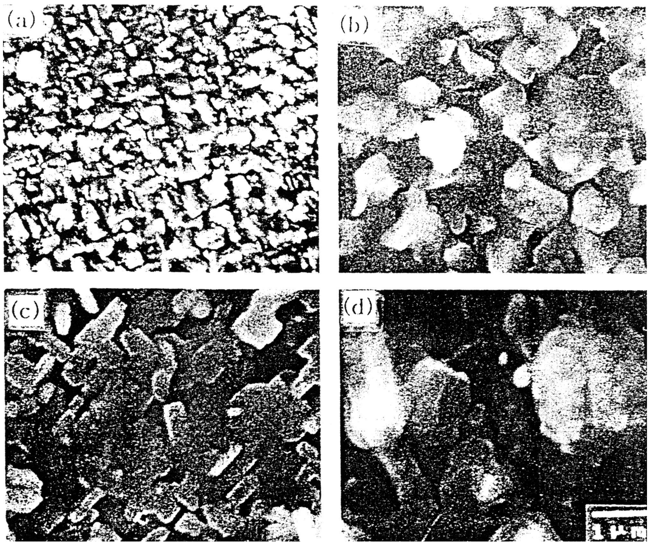

Fig. 2. Scanning electron microscopic images of the films grown at (a) 760 °C, (b) 800 °C, (c) 815 °C and (d) 860 °C for 20 min with O_2 partial pressure of 3.2 Torr and preheating zone temperature of 380 °C.

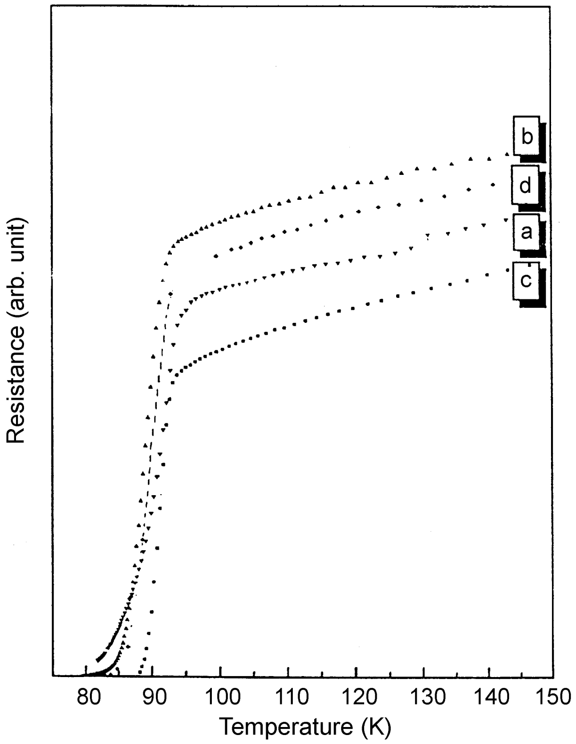

Fig. 3. The variation in the resistance of the sample, measured using AC four-probe technique, with operating temperature of the films deposited at (a) 760 °C, (b) 800 °C, (C) 815 °C and (d) 860 °C for 20 min with O_2 partial pressure of 3.2 Torr and preheating zone temperature of 380 °C.

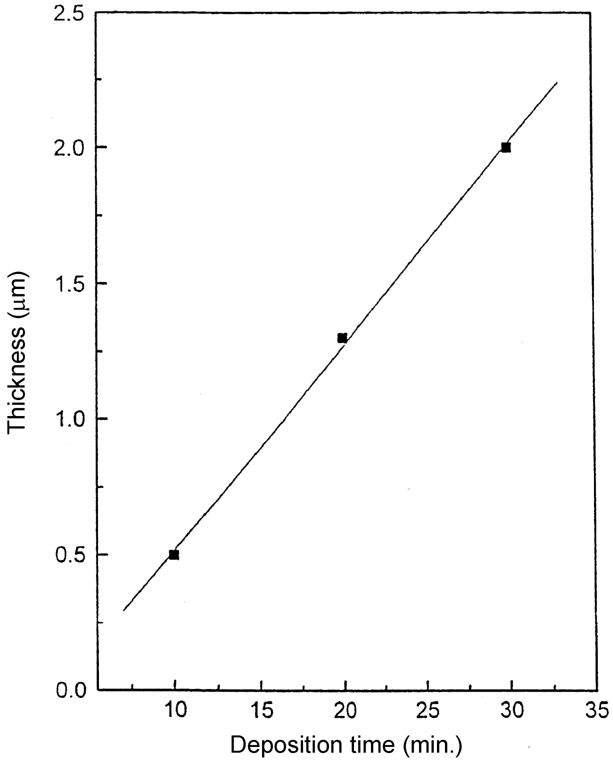

Fig. 5. Variations in film thickness with deposition time when film grown at 815 °C with O_2 partial pressure of 3.2 Torr and preheating zone temperature of 380 °C.

phology is drastically changed at a temperature above 800 °C. In order to find the temperature window for such morphological changes, the film was also grown at 830 °C, and it was observed that the phenomenon remains the same (and hence not presented). The film grown at 860 °C shows large crystallites with precipitation on the surface and appears like agglomerated crystallites.

It is reported by Yoshida et al. that the surface morphology changes drastically with deposition temperature. They studied the deposition upto 800 °C and found that when deposited above 750 °C, the surface morphology changes to a plate-like structure and the terrace width (when studied with AFM) increase with increasing temperature above 750 °C to 850 °C and it remains almost same below 750 °C [Yoshida et al., 1996]. It is also reported that change of growth temperature above 850 °C may require adjusting the flow of individual source gas (precursor vapors) in order to maintain the stoichiometric 1 : 2 : 3 compositions. Similar phenomenon is also observed in the present studies. Therefore, it can be said that the suggested method can produce good HTS film. Further studies are required to optimize the source gas flow rate for the growth of film above 815 °C. This requires the understanding of the efficiencies of Y, Ba and Cu incorporation in the growth of YBCO film.

The variation in the resistance of the sample, measured using AC four-probe technique, with operating temperature is shown in Fig. 3. Sample 'c' (with deposition temperature as 815 °C, O_2 pressure as 3.2 Torr and preheating temperature as 380 °C) exhibits the highest transition temperature (T_c=87 K) with an onset transition temperature ($T_{c,onset}$) above 90 K, and the transition width ($\Delta T=T_{c,onset}-T_{c,zero}$) of about 3 °C. Samples 'a', 'b' and 'd' (i.e., 760 °C, 800 °C and 850 °C deposition temperatures) show broad transition width of about

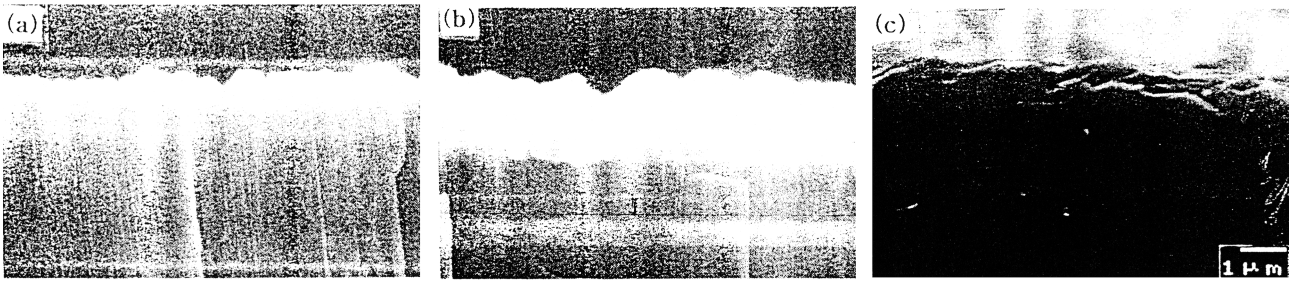

Fig. 4. The cross sectional SEM image of the film grown at 815 °C for (a) 10 min, (b) 20 min and (c) 30 min with O_2 partial pressure of 3.2 Torr and preheating zone temperature of 380 °C.

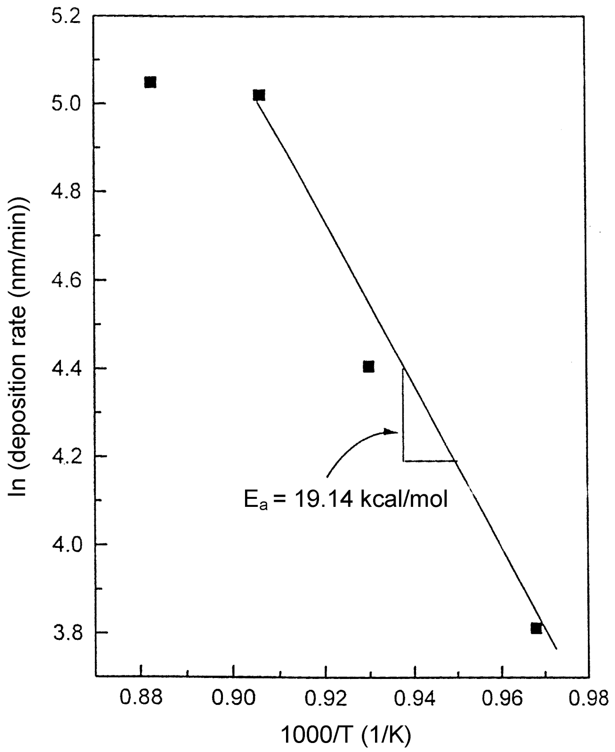

Fig. 6. The Arrhenius plot of the film grown at 815 °C with O_2 partial pressure of 3.2 Torr and preheating zone temperature of 380 °C.

6 °C with transition temperature of ~81, 83 and 85 °C, respectively. The variation in the transition width might be due to factors related to poor interconnectivity of the grains and voids, which can be seen in SEM images of the sample 'a', 'b' and 'd' (Fig. 2).

In order to study the growth rate, YBCO thin films were grown with the best obtained deposition conditions (at deposition temperature of 815 °C, O_2 pressure 3.2 Torr and preheating at 380 °C) at different deposition times, i.e., 10 min, 20 min and 30 min. The cross sectional SEM images of the film grown at these times are shown in Fig. 4. It can be seen that with increasing time, the thickness of the film increases. The growth rate estimated from these images was found to be about 75 nm/min. A plot of variation in thickness with deposition time can be seen in Fig. 5. It is realized that the thickness increases linearly with increasing deposition time.

The activation energy of the grown film as deduced from the Arrhenius plot (Fig. 6) is about 19.14 kJ/mol for the film grown at the best deposition conditions.

CONCLUSION

We have grown $Y_1Ba_2Cu_3O_{7-x}$ (YBCO) thin film using liquid solution sources and AACVD technique on MgO (100) single crystalline substrate at various deposition temperature from 760 °C to 860 °C and have found the superconducting properties similar to the reported work. Single solution source of Y, Ba, and Cu β-diketonates dissolved in tetrahydrofuran (THF) was used as precursor. Deposition was carried out in oxygen atmosphere maintaining total pressure of 3.2 Torr inside the chamber. Deposition time was also varied from 10 to 30 min. The grown YBCO thin films were highly oriented to (001) orientation perpendicular to the substrate. The film deposited at 815 °C had a sharp transition to superconducting state about 87 K with a transition width of ~3 °C. X-ray diffraction patterns mainly consist of strong c-axis peaks from YBCO (001). SEM images shows that the film grown at 815 °C has a smooth ground surface of c-axis oriented YBCO with faceted small plate-like YBCO crystallites and growth rate estimated to be ~75 nm/min. The activation energy estimated from the Arrhenius plot is ~19.14 kJ/mol at the deposition temperature of 815 °C.

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REFERENCES

Cho, I. J. and Shin, H. S., "The Preparation of Y-Ba-Cu-O High Tc Superconducting Thin Film by CVD and Property Change Induced by Heat Treatment," *HWAHAK KONGHAK*, **31**, 9 (1993).

Kim, B. R., Hwang, S. C., Lee, H. G. and Shin, H. S., "Preparation of Superconducting Y-Ba-Cu-O Films by Aerosol Assisted Chemical Vapour Deposition Using Liquid Source Solution," *Korean J. Chem. Eng.*, **17**, 524 (2000).

Klippe, L. and Wahl, G., "Single Source MOCVD of Y-, Ba- and Cu-oxide from thd-Precursors," *J. Alloys and Compounds*, **251**, 249 (1997).

Salzar, K. V., Otto, K. C., Dye, R. C., Hubbars, K. M., Peterson, E. J., Coulter, J. Y. and Kodas, T. T., "Aerosol Assisted Chemical Vapour Deposition of Superconducting $YBa_2Cu_3O_{7-y}$," *Physica C*, **198**, 303 (1992).

Yoshida, Y., Ito, Y., Hirabayashi, I., Nagai, H. and Takai, Y., "Surface Morphology and Growth Mechanism of $YBa_2Cu_3O_{7-y}$ Films by Metalorganic Chemical Vapour Deposition Using Liquid Sources," *Appl. Phys. Lett.*, **69**, 845 (1996).