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Ternary phase relation on preparation of $YBa_2Cu_3O_{7-\delta}$ films by laser CVD

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Abstract. *c*-axis-oriented $YBa_2Cu_3O_{7-\delta}$ films were prepared by laser chemical vapor deposition (laser CVD) using $Y(DPM)_3$, $Ba(DPM)_2$/$Ba(TMOD)_2$ and $Cu(DPM)_2$ as precursors with enhancement by a continuous wave Nd:YAG laser. $YBa_2Cu_3O_{7-\delta}$ film almost in a single phase and that with different second phases of $BaCuO_2$, $CuBaO_2$, BaY_2O_4, $CuYO_2$, Y_2O_3 and CuO were obtained by varying evaporation temperature of precursors. Ternary phase diagram as a function of evaporation amount of three precursors were obtained. The deposition rate of the *c*-axis-oriented YBCO film was 60 μm h^{-1}, about 60–600 times higher than those of conventional CVD.

Introduction

The preparation process of $YBa_2Cu_3O_{7-\delta}$ (YBCO) film has attracted great attention since the discovery of high-temperature superconductor YBCO with a high T_c of about 93 K in 1987 [1–3]. YBCO film has been prepared by various processes, *i.e.*, sol-gel [4], metalorganic deposition using trifluoroacetates (TFA-MOD) [5], multilayer evaporation [6], thermal evaporation [7], pulsed laser deposition [8], sputtering [9–10], molecular beam deposition [11] and metalorganic chemical vapor deposition (MOCVD) [12]. MOCVD is a promising process for the preparation of YBCO film due to the high controllability on orientation, deposition for large area and complex shape and relatively high deposition rate (R_{dep}) [12–20]. In MOCVD, however, YBCO film should be prepared at more higher R_{dep} and lower deposition temperature for practical applications in particular on metal tape substrate.

Several enhanced MOCVD such as magnetic-field, plasma and photo-enhanced MOCVD processes have been developed for the preparation of YBCO film. A high magnetic field enhanced MOCVD has been used to prepare YBCO film, which showed a high T_C of 88 K and a high J_C of 1.1 $\times 10^5$ A cm^{-2}. The R_{dep} of 0.3 μm h^{-1}, however, was not effectively improved [21-22]. Although YBCO film with high T_c = 90 K and $J_c = 3.3\times10^6$ A cm^{-2} (at 77 K) has been obtained by plasma-enhanced MOCVD, the R_{dep} was scarcely improved to 1.1 μm h^{-1} [23].

Laser is also able to enhance MOCVD process (termed laser CVD), yielding significant high deposition rate and orientation. We have prepared various oxide and non-oxide films, such as yttria stabilized zirconia (YSZ) [24], Al_2O_3 [25] and YBCO [26] by laser CVD. In the present study, we investigate a ternary phase relation on preparation of YBCO films on Al_2O_3 polycrystalline substrate by laser CVD.

Experimental

YBCO films were prepared on polycrystalline Al_2O_3 substrates (10 mm × 10 mm × 2.5 mm) by

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laser CVD using $Y(DPM)_3$, $Ba(DPM)_2$/$Ba(TMOD)_2$ and $Cu(DPM)_2$ (DPM; dipivaloy methanate and TMOD; 2,2,6,6-tetramethy1-3,5-octanedionato) as precursors. A mixture of $Ba(DPM)_2$ and $Ba(TMOD)_2$ with a molar ratio of 4 to 1 was used to suppress the decomposition of $Ba(DPM)_2$ at the temperatures over their eutectic point and to vaporize at a constant rate. A schematic of the laser CVD apparatus has been reported elsewhere [26]. A continuous wave Nd:YAG laser (wavelength: 1064 nm) with laser power (P_L) from 50 to 200 W was employed. The laser beam was defocused up to 20 mm in diameter to irradiate the whole substrate and was introduced through a quartz window at an incident angle of 30º to the substrate. The Al_2O_3 substrate was heated on a heating stage at pre-heating temperatures (T_{pre}) of 673–873 K. The deposition temperature (T_{dep}) was measured with a thermocouple inserted into a slot 1.5 mm in depth at the back side of the substrate. The flow rates of Ar and O_2 gases were 8.3 × 10^{-7} and 3.3 × 10^{-6} m^3 s^{-1}, respectively. The composition of the YBCO film was controlled by the vaporization temperature (T_{vap}) of the Y (T_Y), Ba (T_{Ba}), and Cu (T_{Cu}) precursor at the range of T_Y = 450–493 K, T_{Ba} = 580–623 K and T_{Cu} = 490– 533 K, respectively. The temperature of all the gas lines was maintained at 623 K to prevent the condensation of precursor. The total pressure was held at 1 kPa. The deposition was conducted for 600 s. The distance between the nozzle and the substrate was 28 mm. The crystal phase was identified by X-ray diffraction (XRD; Rigaku RAD-2C) and the microstructure was observed by a scanning electron microscope (SEM; Hitachi S-3100H). The composition was investigated by an electron probe micro analyzer (EPMA).

Results and discussion

Figure 1 shows the XRD patterns of the as-deposited films. At T_Y = 473 K, T_{Ba} = 583K and T_{Cu} = 533 K, $CuYO_2$ film with a little amount of CuO was obtained (Fig. 1(a)). *c*-axis-oriented YBCO film with second phases of Y_2O_3, CuO and $BaCuO_2$ was obtained at T_Y = 473 K, T_{Ba} = 613 K and T_{Cu} = 516 K (Fig. 1(b)) and at T_Y = 453 K, T_{Ba} = 603 K and T_{Cu} = 513 K (Fig. 1(c)). At at T_Y = 453 K, T_{Ba} = 613 K and T_{Cu} = 513 K, film with a mixture phase of BaY_2O_4 and $BaCuO_2$ was obtained (Fig. 1(d)). YBCO film almost entirely in a single phase was obtained at T_Y = 473 K, T_{Ba} = 600 K and T_{Cu}

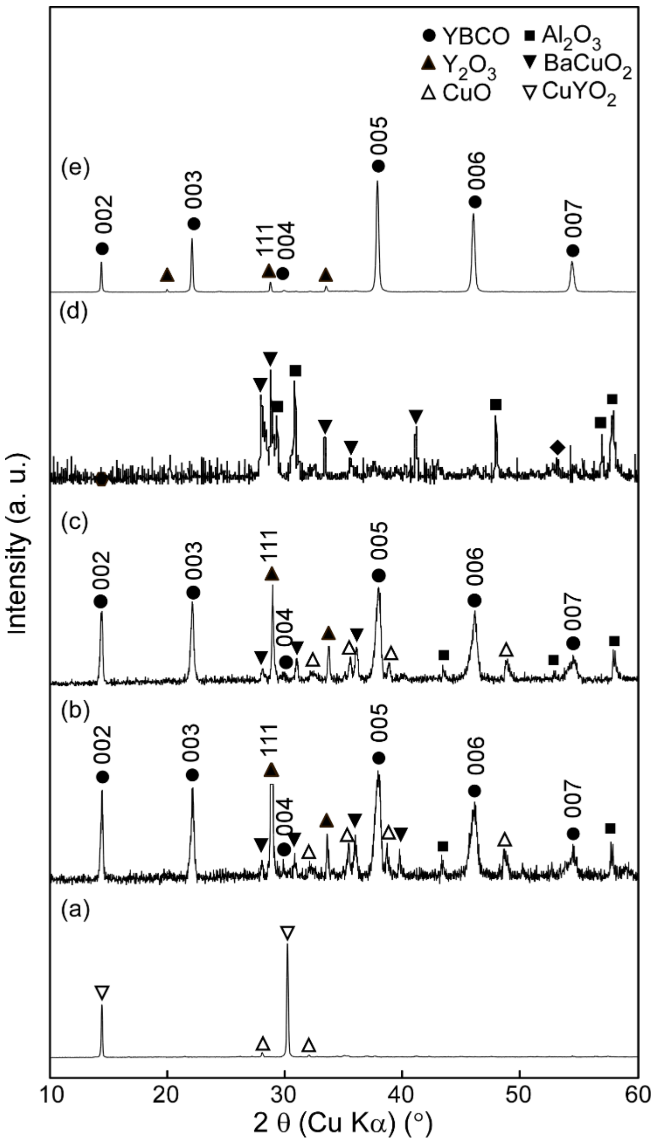

Fig. 1 XRD patterns of the YBCO film prepared at T_Y = 473 K, T_{Ba} = 583K and T_{Cu} = 533 K (a), T_Y = 473 K, T_{Ba} = 613 K and T_{Cu} = 516 K (b), T_Y = 453 K, T_{Ba} = 603 K and T_{Cu} = 513 K (c) T_Y = 453 K, T_{Ba} = 613 K and T_{Cu} = 513 K (d), and T_Y = 473 K, T_{Ba} = 600 K and T_{Cu} = 528 K (e).

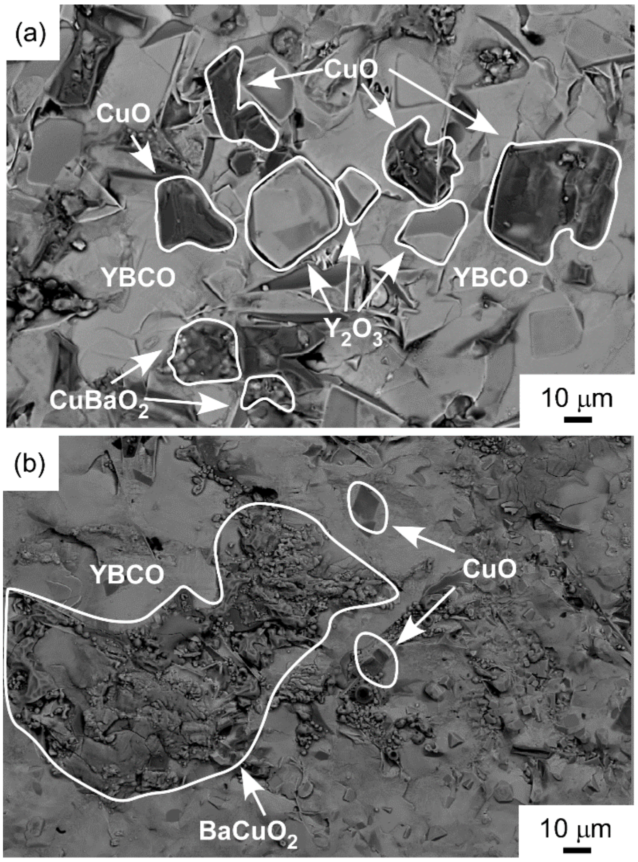

Fig.2 Surface BSE image of Y-B-C-O film prepared at T_Y= 473 K, T_{Ba} = 613 K and T_{Cu} = 516 K (a) and T_Y = 453 K, T_{Ba} = 603 K and T_{Cu} = 513 K (b).

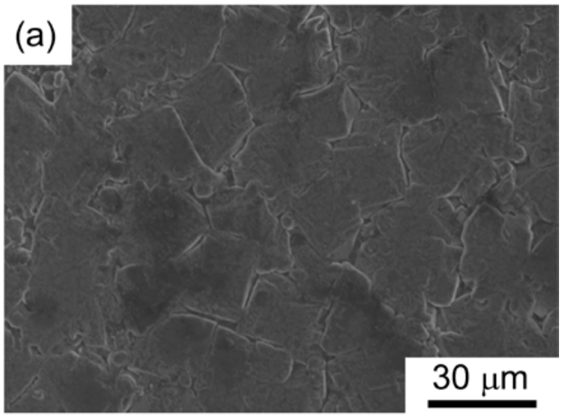

Fig. 3 Surface SEM image of *c*-axis oriented YBCO film prepared at T_Y = 473 K, T_{Ba} = 600 K and T_{Cu} =528 K.

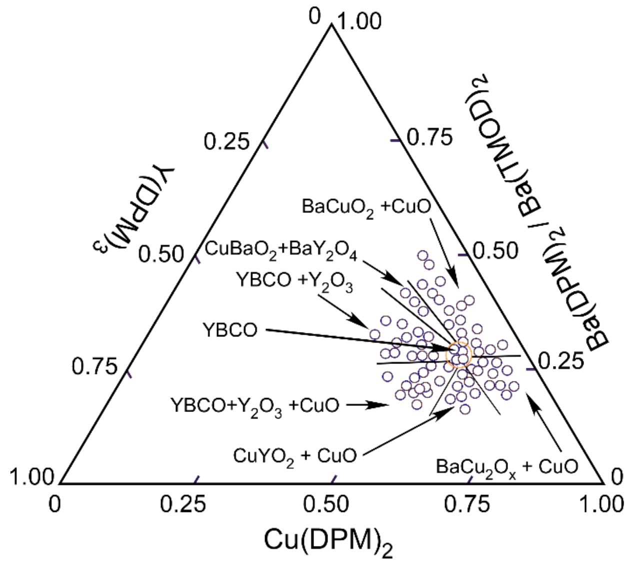

Fig. 4 Ternary phase relation as a function of evaporation amount ratio of each precursor.

= 528 K (Fig.1 (e)).

Figure 2 shows surface backscattering electron (BSE) image of YBCO film prepared at T_Y = 473 K, T_{Ba} = 613 K and T_{Cu} = 516 K (a) and that prepared at T_Y = 453 K, T_{Ba} = 603 K and T_{Cu} = 513 K (b). BSE image of the film showed a dense microstructure with some particles distributing in the surface (Fig. 2(a)). YBCO and Y_2O_3 grains showed gray color and the $CuBaO_2$ and CuO grains showed dark color in the BSE image (Fig. 2(a)). The Y_2O_3 grains showed hexangular or pyramid shape. $CuBaO_2$ and CuO grains showed no regular shape. $CuBaO_2$ grains showed melted feature, which was owing to the higher deposition temperature than melting point of $CuBaO_2$ (Fig. 2(a)). Dense microstructure was observed in the YBCO film prepared at T_Y= 453 K, T_{Ba}= 603 K and T_{Cu} = 513 K (Fig. 2(b)). $BaCuO_2$ phase exhibited cracked microstructure and the CuO grains showed rhombic and rectangular shapes. Both $BaCuO_2$ and CuO phases exhibited dark color in the BSE image (Fig. 1).

Figure 3 shows surface and SEM image of *c*-axis oriented YBCO film prepared at T_Y = 473 K, T_{Ba} = 600 K and T_{Cu} = 528 K. The surface of *c*-axis oriented YBCO film consisted of rectangular grains about 30 μm in size, which were flat and attributed to *c*-plane of YBCO. The deposition rate of present film was 60 μm h^{-1}, which is about 60–600 times higher than those of conventional MOCVD.

Figure 4 summarizes a ternary phase relation as a function of evaporation amount ratio of Y, Ba and Cu precursors. YBCO with different phases of $BaCuO_2$, $CuBaO_2$, BaY_2O_4, $CuYO_2$, Y_2O_3 and CuO were obtained by changing the vaporization temperature of the Y, Ba and Cu precursors in the range of 450–493 K, 580–623 K and 490–533 K, respectively. YBCO film almost in a single phase can be prepared at T_Y = 473 K, T_{Ba} = 600 K and T_{Cu} = 528 K.

Summary

A ternary phase relation as a function of evaporated amount ratio of precursors was obtained by optimizing evaporation temperature of precursors. A highly *c*-axis-oriented YBCO film almost in single phase was obtained at T_Y = 473 K, T_{Ba} = 600 K and T_{Cu} = 528 K. YBCO film had relatively large, rectangular-shaped grains about 30 μm in size. The R_{dep} of the *c*-axis-oriented YBCO film was 60 μm h^{-1}, about 60–600 times higher than those of conventional MOCVD.

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