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Ba_2TiO_4 and $Ba_4Ti_{13}O_{30}$ Thick Films Prepared by Laser Chemical Vapor Deposition and Their Microstructure

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Abstract. Ba_2TiO_4 and $Ba_4Ti_{13}O_{30}$ thick films were prepared by laser chemical vapor deposition using Ba- and Ti-dipivaloylmethanate precursors. Single-phase Ba_2TiO_4 thick films were obtained at 845–946 K and Ba/Ti source molar ratio 2.4. Single-phase $Ba_4Ti_{13}O_{30}$ films were obtained at 944–1011 K and Ba/Ti source molar ratio 0.38. Ba_2TiO_4 thick films consisted of truncated grains, while $Ba_4Ti_{13}O_{30}$ thick films had shellfish-like grains. Ba_2TiO_4 and $Ba_4Ti_{13}O_{30}$ thick films showed a columnar growth and their deposition rates were 72 and 132 μm h^{-1}, respectively.

Introduction

$BaO\text{-}TiO_2$ quasi-binary system has many useful dielectric compounds. $BaTiO_3$ has been most widely studied as a lead-free ferroelectric material for broad applications such as ferroelectric memories, capacitors and piezoelectric actuators [1]. In Ba-rich side, Ba_2TiO_4 has recently been attracted much attention as a CO_2 gas absorber to reduce the greenhouse effect [2]. In Ti-rich side, on the other hand, $Ba_4Ti_{13}O_{30}$ is expected as a dielectric material having high-Q factor for microwave devices [3]. However, these Ba-Ti-O compounds have not been prepared in a single phase using a conventional chemical vapor deposition (CVD) because Ba-rich and Ti-rich source vapors are likely to form carbonate and TiO_2, respectively [4].

Laser CVD is advantageous to control the stoichiometric composition of deposits because precursor vapors are significantly activated by laser and thus the chemical composition in the vapor tends to close to that in the deposit. We have demonstrated the preparations of various complex oxide films, such as Y_2SiO_5 and $YBa_2Cu_3O_{7-x}$, using laser CVD [5–7]. Therefore, laser CVD would be possible to prepare the various Ba-Ti-O compounds by changing Ba to Ti ratio in the source vapor.

In the present study, Ba_2TiO_5 and $Ba_4Ti_{13}O_{30}$ thick films were prepared by laser CVD. The effects of deposition condition on phase, orientation and microstructure were investigated.

Experimental procedure

Table 1 lists deposition conditions for preparation of Ba_2TiO_4 and $Ba_4Ti_{13}O_{30}$ thick films by laser CVD. Details of the laser CVD apparatus have been reported elsewhere [5,6]. Pt-coated (100) Si single crystal wafer was used as a substrate. The substrate was placed on a hot stage, and a thermocouple was inserted near the substrate to measure the deposition temperature. The substrate was heated on a hot stage at a pre-heating temperature of 773 K. A continuous-wave mode Nd:YAG was used as a laser source. A laser beam 20 mm in diameter was introduced through a quartz window to irradiate the entire substrate. As the laser power increased from 53 to 93 W, deposition temperature increased from 845 to 1069 K. Ba-dipivaloylmethanate ($Ba(dpm)_2$) was heated at 563 K. Ti-diisopropoxy-dipivaloylmethanate ($Ti(O\mathit{i}Pr)_2(dpm)_2$) were for preparing Ba_2TiO_4 and $Ba_4Ti_{13}O_{30}$ at 419 and 446 K, respectively. Their vapors were carried into the chamber with Ar gas, and O_2 gas was separately introduced into the chamber through a double-tube gas nozzle. The total pressure in the chamber was maintained at 400 Pa. Deposition was conducted for 600 s.

The crystal structure of the films was studied by X-ray diffraction (XRD, Rigaku RAD-2C) using Cu Kα X-ray radiation. The surface and cross-sectional microstructure of these films was observed by a scanning electron microscope (SEM, Hitachi S-3100H).

Table 1. Deposition conditions for prepration of Ba_2TiO_4 and $Ba_4Ti_{13}O_{30}$ thick films.

Deposition parameter	Ba_2TiO_4	$Ba_4Ti_{13}O_{30}$
Substrate	(111) Pt-coated (100) Si single crystal wafer	
Substrate preheating temperature	773 K	
Laser	Nd:YAG laser (cw mode; wavelength: 1064 nm)	
Laser power	53–93 W	
Deposition temperature	845–946 K	944–1069 K
Ba precursor	$Ba(dpm)_2$	
Evaporation temp. for Ba precursor	563 K	
Ti precursor	$Ti(OiPr)_2(dpm)_2$	
Evaporation temp. for Ti precursor	419 K	446 K
Ba/Ti molar ratio in a source vapor	2.4	0.38
Total chamber pressure	400 Pa	
Gas flow rate for Ar carrier gas	8.45×10^{-2} Pa m^3 s^{-1}	
Gas flow rate for O_2 gas	1.69×10^{-1} Pa m^3 s^{-1}	
Nozzle temperature	623 K	
Deposition time	600 s	

Results and discussion

Figure 1 shows the XRD patterns of the Ba_2TiO_4 and $Ba_4Ti_{13}O_{30}$ thick films prepared at deposition temperature and Ba/Ti molar ratio at 894 K and 2.4, and 997 K and 0.38. Ba/Ti molar ratio in a supplied source vapor was estimated by mass change of precursor containers before and after deposition. At Ba/Ti molar ratio 2.4, single-phase Ba_2TiO_4 thick films were obtained at deposition temperatures 845–946 K (Fig. 1(a)). Ba_2TiO_4 has an orthorhombic structure (space group: $P2_1nb$; a = 0.6107 nm, b = 2.2952 nm and c = 1.054 nm; JCPDS #75-0677) [8]. The Ba_2TiO_4 thick films had a (100) and (091) co-orientation at s 865–931 K, and (161) orientation at 937–946 K.

At Ba/Ti molar ratio 0.38, single-phase $Ba_4Ti_{13}O_{30}$ thick films were obtained at 944–1011 K (Fig. 1(b)). $Ba_4Ti_{13}O_{30}$ also has an orthorhombic structure (space group: $Cmca$; a = 1.7063 nm, b = 0.9864 nm and c = 1.4053 nm; JCPDS #73-1188) [9]. $Ba_4Ti_{13}O_{30}$ thick films showed a strong (012) orientation at 944–1022 K. At 1022–1069 K, $BaTi_4O_9$ was co-deposited with $Ba_4Ti_{13}O_{30}$.

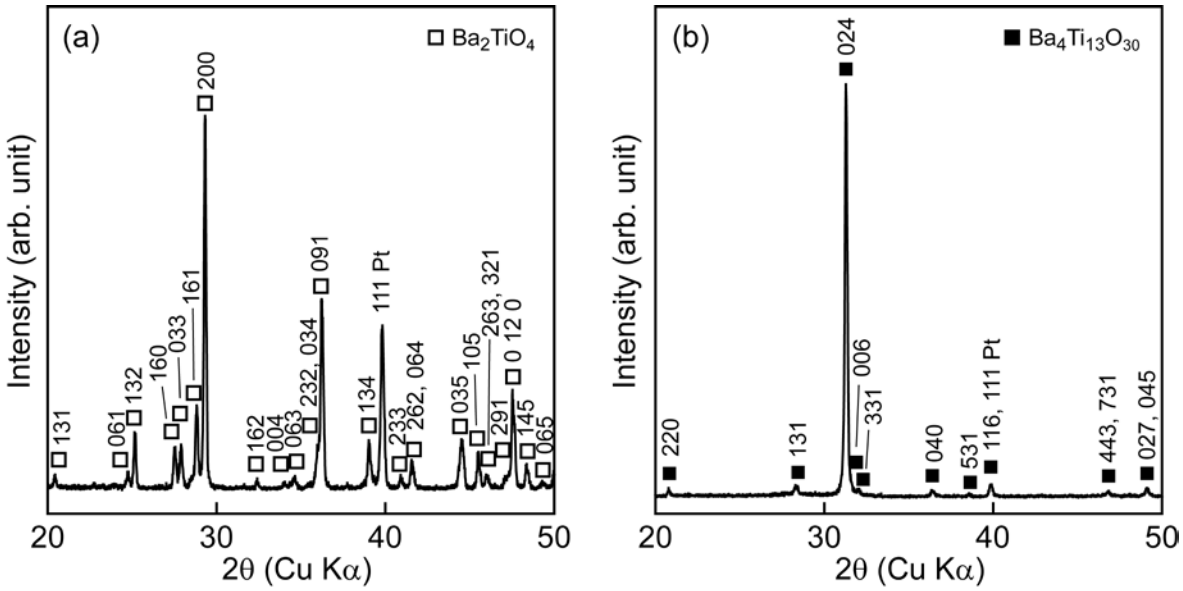

Figure 1. XRD patterns of the Ba_2TiO_4 thick film prepared at 894 K (a) and $Ba_4Ti_{13}O_{30}$ thick film at 997 K (b).

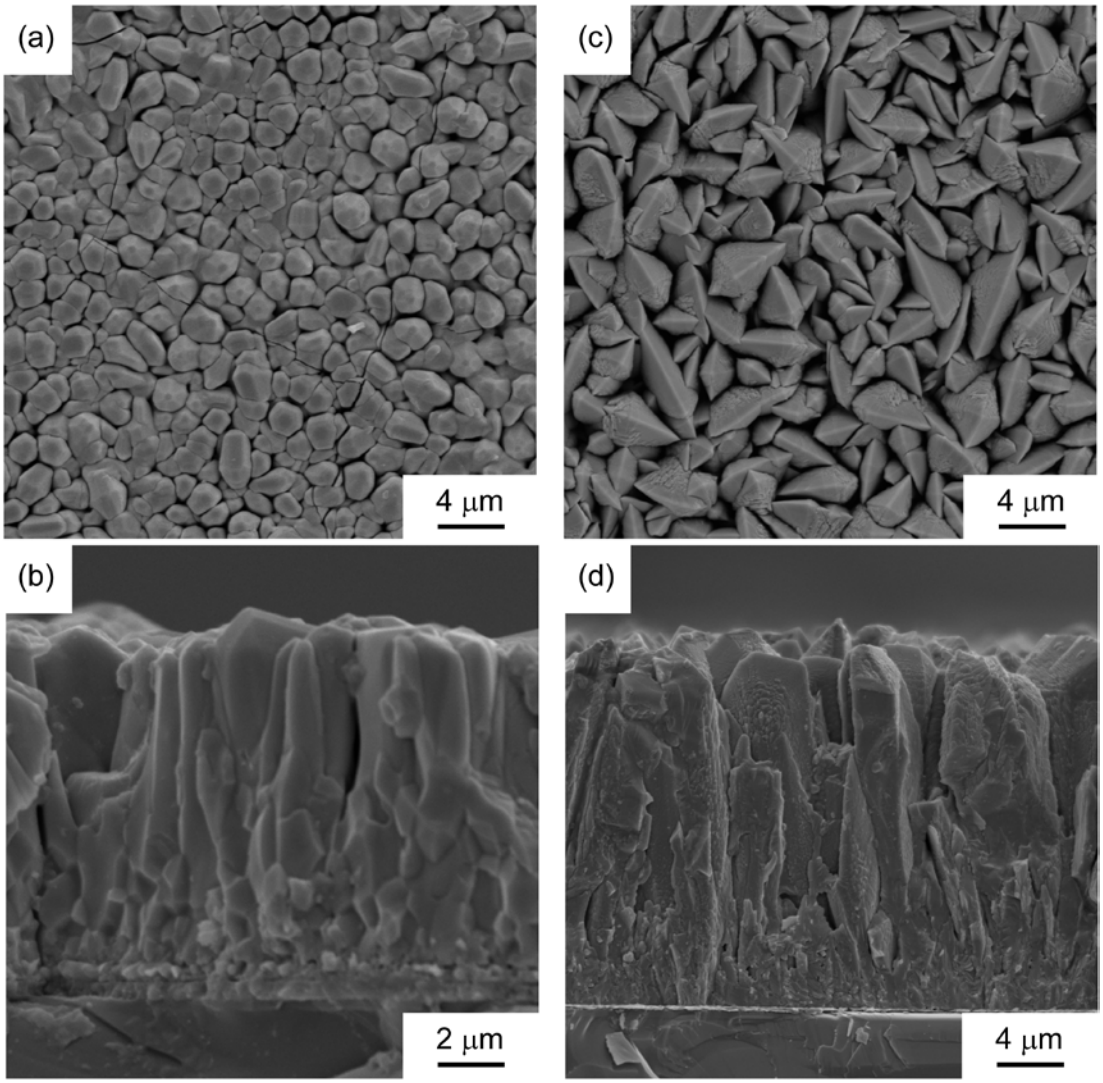

Figure 2. Surface (a, c) and cross-sectional (b, d) SEM images of the Ba_2TiO_4 thick film prepared at 894 K (a, b) and $Ba_4Ti_{13}O_{30}$ thick film at 997 K (c, d).

Figure 2 shows the surface and cross-sectional SEM images of the Ba_2TiO_4 and $Ba_4Ti_{13}O_{30}$ thick films prepared at deposition temperature and Ba/Ti molar ratio at 894 K and 2.4, and 997 K and 0.38. Ba_2TiO_4 thick film consisted of truncated grains about 2 μm in width and 4 μm in longer direction (Fig. 2(a)). $Ba_4Ti_{13}O30$ thick film had a shellfish-like grains 4–8 μm in longer direction (Fig. 2(c)). Both Ba_2TiO_4 and $Ba_4Ti_{13}O_{30}$ thick films showed a columnar growth 12 and 22 μm in thickness (Fig. 2(b), 2(d)), and their deposition rates were 72 and 132 μm h^{-1} respectively.

Summary

Single-phase Ba_2TiO_4 thick films were obtained at 845–946 K and Ba/Ti source molar ratio 2.4. Ba_2TiO_4 thick films had a (100) and (091) co-orientation at 865–931 K, and (161) orientation at 937–946 K. Single-phase $Ba_4Ti_{13}O_{30}$ films were obtained at 944–1011 K. $Ba_4Ti_{13}O_{30}$ thick films showed a strong (012) orientation at 944–1022 K. Deposition rates of Ba_2TiO_4 and $Ba_4Ti_{13}O_{30}$ thick films were 72 and 132 μm h^{-1}, respectively.

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References

[1] P.P. Phule and S.H. Risbud: J. Mater. Sci. Vol. 25 (1990), p. 1169–1183

[2] Y. Saito, H. Sato and Y. Sakabe: J. Chem. Eng. Jpn. Vol. 41 (2008), p. 441–446

[3] B. Y. Jang, Y. H. Jeong, S. J. Lee, K. J. Lee, S. Nahm, H. J. Sun and H. J. Lee: J. Eur. Cerm. Soc. Vol. 26 (2006), p. 1913–1916

[4] T. Tohma, H. Masumoto and T. Goto: Mater. Trans. Vol. 43 (2002), p. 2880–2884

[5] A. Ito, H. Kadokura, T. Kimura and T. Goto: J. Alloys Compd. Vol. 489 (2010), p. 469–474

[6] A. Ito, J. Endo, T. Kimura and T. Goto: Surf. Coat. Technol. Vol. 204 (2010), p. 3846–3850

[7] P. Zhao, A. Ito, R. Tu and T. Goto: Mater. Lett. Vol. 64 (2010), p. 102–104

[8] J. R. Guenter and G. B. Jameson: Acta Crystallogr. C Vol. 40 (1984), p. 207–210

[9] E. Tillmanns: Cryst. Struct. Comm. Vol. 11 (1982), p. 2087–2092