Preparation of Ba–Ti–O films by laser chemical vapor deposition

Akihiko Ito *, Dongyun Guo, Rong Tu, Takashi Goto

Institute for Materials Research, Tohoku University, 2-1-1 Katahira, Aoba-ku, Sendai 980-8577, Japan

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ABSTRACT

Ba–Ti–O films were prepared on Pt-coated Si substrate by laser chemical vapor deposition, and their orientations and microstructures were compared. Ba_2TiO_4, $BaTiO_3$, $BaTi_2O_5$, $Ba_4Ti_{13}O_{30}$ and $BaTi_4O_9$ single-phase films were prepared at Ti to Ba molar ratio from 0.41 to 3.49. The α'-Ba_2TiO_4 film showed (0 1 0) and (0 9 1) co-orientation with elongated, truncated columnar grains. The $BaTiO_3$ film was composed of triangular and hexagonal grains with slight (1 1 1) orientation. The $BaTi_2O_5$ film had (0 1 0) orientation and faceted columnar grains. The $Ba_4Ti_{13}O_{40}$ film showed (1 0 0) and (0 1 2) co-orientation with shellfish-like grains. The $BaTi_4O_9$ film showed (0 1 0) orientation with slightly rounded faceted columnar grains. The deposition rates of Ba–Ti–O films ranged from 30 to 144 μm h^{-1}.

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1. Introduction

The barium oxide (BaO)–titanium dioxide (TiO_2) quasi-binary system has been extensively studied for application in dielectric materials such as $BaTi_5O_{11}$ (BT_5), $Ba_2Ti_9O_{20}$ (B_2T_9), $BaTi_4O_9$ (BT_4), $Ba_4Ti_{13}O_{30}$ (B_4T_{13}), $Ba_6Ti_{17}O_{40}$ (B_6T_{17}), $BaTi_2O_5$ (BT_2), $BaTiO_3$ (BT) and Ba_2TiO_4 (B_2T) [1–4]. The TiO_2-rich compounds such as BT_5, B_2T_9, BT_4, B_4T_{13} and B_6T_{17} have microwave applications [5,6], and the BaO-rich phase of B_2T is a CO_2 gas absorber [7]. BT has been extensively studied as a lead-free ferroelectric compound for application in memory and piezoelectric actuators. BT_2 has recently been attracting much attention as a new ferroelectric compound having a high Curie temperature (T_C = 740 K) for high temperature applications [8,9].

The Ba–Ti–O compounds can be prepared in thin or thick film forms for diverse applications. Yet, only BT films have been intensively studied and widely used [10–22]. Other types of Ba–Ti–O films are scarcely prepared and are infrequently used in manufacturing despite unique dielectric properties and considerable promise [5,7–9]. A limited number of studies on BT_2 films prepared by physical vapor deposition (PVD) techniques such as sputtering and laser ablation have been reported [23–26]. In case of chemical vapor deposition (CVD) technique, although we used metal–organic chemical vapor deposition across a wide range of Ba/Ti ratios (from 0.1 to 1), only TiO_2 and BT phases were identified in the films [21]. This result implied that formation of TiO_2 is kinetically favorable in thermal CVD process. So far, the

TiO_2-rich compounds have not been synthesized in a single phase by conventional CVD.

We have applied intense laser field in CVD process to enhance chemical reactions and have reported the successful application of laser CVD to prepare complex oxide films such as Y_2O_3–ZrO_2, Al_2O_3, Y_2SiO_5 and $YBa_2Cu_3O_{7-\delta}$ thick films at high deposition rates (several hundred micrometers per hour) [27–30]. Therefore, laser CVD would prepare the TiO_2-rich compounds, such as BT_2, B_6T_{17}, B_4T_{13} and BT_4, under highly activated chemical reaction conditions by varying Ti to Ba molar ratio in a source gas. In the present study, we investigate the effects of supplied Ti/Ba molar ratio and deposition temperature on phase relationship and demonstrate that laser CVD can be employed to prepare various Ba–Ti–O thick films.

2. Experimental

Ba–Ti–O films were prepared by laser CVD with a continuous-wave Nd:YAG laser (wavelength: 1064 nm). A schematic of the laser CVD apparatus has been reported elsewhere [30] and the deposition conditions are summarized in Table 1. The (1 1 1)-oriented Pt-coated (1 1 1) Si substrate with Ti and SiO_2 buffer layers (Pt/Ti/SiO_2/Si) was used. The substrate was placed on a hot stage, and a thermocouple was inserted at the bottom side to measure the deposition temperature (T_{dep}) and was pre-heated to 773 K. A laser beam was introduced into the CVD chamber through a quartz window to irradiate the whole area of the substrate and the laser power (P_L) was increased from 57 to 93 W. The barium dipivaloylmethanate (Ba(dpm)$_2$) and titanium diisopropoxy-dipivaloylmethanate (Ti(OiPr)$_2$(dpm)$_2$) precursors were evaporated by heating. The evaporation temperature of the Ba source (T_{Ba}) was fixed at 563 K and the Ti source (T_{Ti}) was changed

* Corresponding author. Tel.: +81 22 215 2106; fax: +81 22 215 2107.
E-mail address: itonium@imr.tohoku.ac.jp (A. Ito).

Table 1
Deposition conditions of Ba–Ti–O films by laser CVD.

Ba(dpm)$_2$ evaporation temperature (T_{Ba})	563 K
Ti(OiPr)$_2$(dpm)$_2$ evaporation temperature (T_{Ti})	419–454 K
Substrate pre-heating temperature (T_{pre})	773 K
Total chamber pressure (P_{tot})	400 Pa
Ar gas flow rate (FR_{Ar})	8.3×10^{-7} m^3 s^{-1}
O$_2$ gas flow rate (FR_{O_2})	1.7×10^{-6} m^3 s^{-1}
Laser power (P_L)	57–93 W
Deposition time (t)	600 s
Substrate–nozzle distance	25 mm
Substrate	Pt/Ti/SiO$_2$/Si
	(10 mm × 10 mm × 0.5 mm)

from 419 to 454 K to change the Ti to Ba molar ratio ($m_{Ti/Ba}$) in a source gas. The evaporated amounts of Ba and Ti precursors were calculated from the mass change of the precursor container before and after the deposition measured by an electronic balance. The precursor gases were delivered to the CVD chamber in an Ar carrier. O$_2$ gas was introduced separately through a double-tube gas nozzle. The total chamber pressure (P_{tot}) was held at 400 Pa and deposition was conducted for 600 s.

The crystal phase was determined by X-ray diffraction (XRD, Rigaku RAD-2C). The cross-section and surface morphology were observed by a scanning electron microscope (SEM, Hitachi S-3100H). A schematic of the crystal structures of Ba–Ti–O compounds was constructed using VESTA, a three-dimensional visualization system [31].

3. Results and discussion

3.1. Preparation of Ba–Ti–O films

Fig. 1 shows $m_{Ti/Ba}$ as a function of T_{Ti} at T_{Ba} = 563 K. The $m_{Ti/Ba}$ was estimated from the evaporation amounts of Ba and Ti precursors. By increasing T_{Ti} from 419 to 454 K, $m_{Ti/Ba}$ increased from 0.41 to 3.61. Fig. 2 depicts the effect of P_L on T_{dep} at various $m_{Ti/Ba}$. Increasing P_L from 57 to 93 W results in a concomitant increase in T_{dep}, e.g., from 865 to 946 K at $m_{Ti/Ba}$ = 0.41.

Fig. 3 shows the XRD patterns of Ba–Ti–O films prepared at various $m_{Ti/Ba}$. The single-phase α′-B$_2$T film was formed at $m_{Ti/Ba}$ = 0.41 and T_{dep} = 894 K (Fig. 3(a)). Relative intensities of (0 1 2 0) and (0 9 1) peaks were higher than those reported in the JCPDF #75-0677, whereas the relative intensities of (1 0 1), (1 3 1), (1 6 1) and
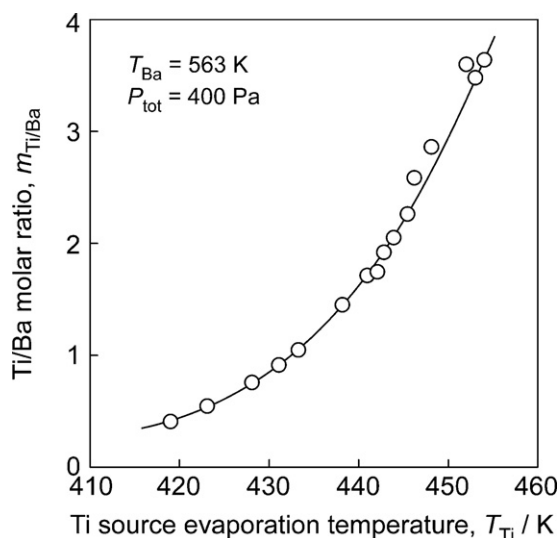
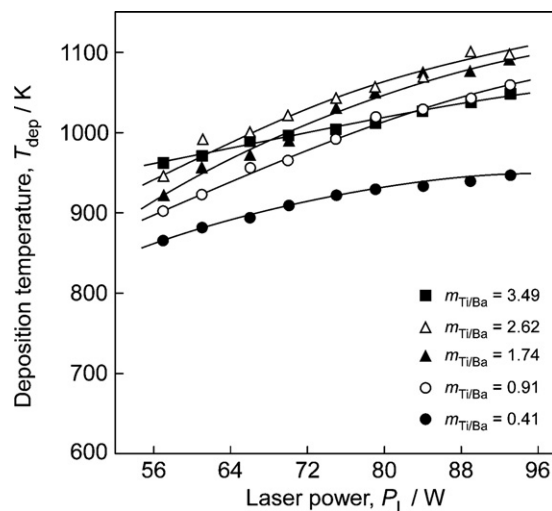**Fig. 2.** Effects of P_L on T_{dep} for Ba–Ti–O film deposition at various $m_{Ti/Ba}$.

(0 6 3) peaks were lower than those in the JCPDF, implying (0 1 0) preferred orientation of α′-B$_2$T film. Both the BT and B$_2$T phases appeared with B$_2$T phase at $m_{Ti/Ba}$ ratios from 0.58 to 0.79 and T_{dep} = 883–991 K. At a $m_{Ti/Ba}$ of 0.91 and a T_{dep} of 957 K, a single-phase BT film was obtained (Fig. 3(b)). A relative intensity of (1 1 1) peak was slightly higher than that of the JCPDF #79-2264, whereas those of (1 0 0) and (0 0 1) peaks were weak, suggesting (1 1 1)-orientation growth of BT film. The single-phase BT$_2$ film was obtained at $m_{Ti/Ba}$ = 1.72 and T_{dep} = 978 K (Fig. 3(c)), and a significant (0 1 0) orientation was identified in comparison to the JCPDF #72-3812. At T_{dep} = 997 K and $m_{Ti/Ba}$ = 2.62, a single-phase B$_4$T$_{13}$ film was formed (Fig. 3(d)). A significant (0 1 2) and (1 0 0) co-orientation was identified in this B$_4$T$_{13}$ film in comparison to JCPDF #73-1188. A single-phase BT$_4$ film was prepared at $m_{Ti/Ba}$ = 3.49 and T_{dep} = 1049 K (Fig. 3(e)). For this product, relative intensity of (0 2 0) peak was slightly higher than that reported in JCPDF #77-1565, whereas relative intensities of (1 0 0) and (0 0 1) peaks were lower than those of the JCPDF, implying b-axis orientation growth of BT$_4$ film.

3.2. Phase relation of Ba–Ti–O films and bulks

Fig. 4(a) shows the effect of $m_{Ti/Ba}$ and T_{dep} on phase relationships for Ba–Ti–O films. Single-phase B$_2$T films were obtained at $m_{Ti/Ba}$ = 0.41. Increasing the $m_{Ti/Ba}$ ratio to a range 0.58–0.79 resulted in the BT phase being co-deposited with the B$_2$T phase. Up to T_{dep} = 1037 K and $m_{Ti/Ba}$ = 0.91, single-phase BT films were obtained. A further increase in $m_{Ti/Ba}$ to 1.06 resulted in the co-deposition of both the BT$_2$ and BT phases. At $m_{Ti/Ba}$ = 1.48, the BT$_2$ and B$_6$T$_{17}$ phases were co-deposited with the BT phase. The single-phase BT$_2$ film was obtained below T_{dep} = 1074 K at $m_{Ti/Ba}$ = 1.72. A mixture of BT$_2$ and B$_6$T$_{17}$ were deposited at $m_{Ti/Ba}$ = 1.72 and T_{dep} = 1092 K in the $m_{Ti/Ba}$ range 1.94–2.27. Single-phase B$_4$T$_{13}$ was obtained at $m_{Ti/Ba}$ = 2.62 below T_{dep} = 1000 K, while a mixture of B$_4$T$_{13}$ and BT$_4$ was deposited above T_{dep} = 1000 K. At $m_{Ti/Ba}$ = 2.89, a mixture phase of B$_4$T$_{13}$, BT$_4$ and BT$_5$ was obtained. A single-phase BT$_4$ was obtained at $m_{Ti/Ba}$ = 3.49 and T_{dep} = 1050 K, while the B$_2$T$_9$ and BT$_5$ phases were co-deposited with the BT$_4$ phase below T_{dep} = 1050 K. A mixed phase of BT$_4$, B$_2$T$_9$ and BT$_5$ was obtained in the range $m_{Ti/Ba}$ = 3.63–3.65.

Fig. 4(b) shows an equilibrium phase diagram of the BaO–TiO$_2$ bulk system [32]. $m_{Ti/Ba}$ for preparing single-phase B$_2$T, BT, BT$_2$, B$_4$T$_{13}$ and BT$_4$ films (Fig. 4(a)) was largely consistent with the Ti/Ba molar ratio of each phase reported in the diagram. $m_{Ti/Ba}$

Fig. 1. Ti/Ba supply molar ratio ($m_{Ti/Ba}$) as a function of T_{Ti} at T_{Ba} = 563 K.