Research Article

Preparation of TiO$_2$-rich Ba–Ti–O thick films by laser chemical vapor deposition method

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Abstract: TiO$_2$-rich Ba–Ti–O films were prepared on Pt/Ti/SiO$_2$/Si substrate by laser chemical vapor deposition (LCVD). Their phase relationship and microstructure were investigated. The single-phase BaTi$_2$O$_5$, Ba$_4$Ti$_{13}$O$_{30}$ and BaTi$_5$O$_{11}$ films were prepared at Ti/Ba molar ratios $m_{Ti/Ba}$ = 1.84–1.90, 2.83 and 4.49–4.55, respectively. The high deposition rate of TiO$_2$-rich Ba–Ti–O films ranged from 54.0 μm/h to 177.6 μm/h. The permittivity of BaTi$_2$O$_5$ film (prepared at $m_{Ti/Ba}$ = 1.84 and deposition temperature T_{dep} = 877 K), Ba$_4$Ti$_{13}$O$_{30}$ film (prepared at $m_{Ti/Ba}$ = 2.83 and T_{dep} = 914 K) and BaTi$_5$O$_{11}$ film (prepared at $m_{Ti/Ba}$ = 4.49 and T_{dep} = 955 K) were 50, 40 and 21, respectively.

Keywords: laser chemical vapor deposition (LCVD); TiO$_2$-rich Ba–Ti–O film; microstructure; deposition temperature; dielectric properties

1 Introduction

TiO$_2$-rich BaO–TiO$_2$ system has been widely investigated, since this system has several compounds that are useful for a number of electronic device applications [1–3]. BaTi$_2$O$_5$ (BT$_2$), a new lead-free ferroelectric, has potential high-temperature application due to high Curie temperature (T_C = 750 K) [4]. Ba$_6$Ti$_{17}$O$_{40}$ (B$_6$T$_{17}$), Ba$_4$Ti$_{13}$O$_{30}$ (B$_4$T$_{13}$), Ba$_2$Ti$_9$O$_{20}$ (B$_2$T$_9$), BaTi$_4$O$_9$ (BT$_4$) and BaTi$_5$O$_{11}$ (BT$_5$) compounds can be applied to the microwave dielectric devices [5–10]. Laser chemical vapor deposition (LCVD) is considered to be a promising process to prepare high-quality films at high deposition rate (R_{dep}) with

controllability of microstructure and orientation [11–13]. In our previous research, LCVD was used to prepare Ba$_2$TiO$_4$, BaTiO$_3$, BT$_2$, B$_4$T$_{13}$ and BT$_4$ single-phase films by varying Ti/Ba molar ratio ($m_{Ti/Ba}$) in a precursor gas at high R_{dep} (30–144 μm/h) [14]. However, in the TiO$_2$-rich region of BaO–TiO$_2$ system, there are many compounds and their phase relationship is still not clear in our previous research. It is necessary to re-investigate the phase relationship in the TiO$_2$-rich region of Ba–Ti–O films prepared by LCVD. In this paper, we report that TiO$_2$-rich Ba–Ti–O films are prepared on Pt/Ti/SiO$_2$/Si substrate by LCVD. The effects of $m_{Ti/Ba}$ and deposition temperature (T_{dep}) on the phase relationship of TiO$_2$-rich Ba–Ti–O films are investigated.

2 Experiment

TiO$_2$-rich Ba–Ti–O films were prepared on Pt/Ti/SiO$_2$/

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Si substrate by LCVD with a continuous-wave Nd:YAG laser (wavelength = 1064 nm). A schematic of LCVD apparatus has been reported elsewhere [15]. Details of the deposition conditions are summarized in Table 1. The Pt/Ti/SiO₂/Si(100) substrate was placed on a hot stage, and a thermocouple was inserted at the bottom side of the substrate to measure T_{dep}. The substrate was heated at a pre-heating temperature (T_{pre}) of 773 K. A laser beam, 14 mm in diameter, was introduced into the chamber through a quartz window to irradiate the whole area of the substrate. The laser power (P_L) was changed from 48 W to 116 W. The barium dipivaloylmethanate (Ba(DPM)₂) and titanium diisopropoxy-dipivaloylmethanate (Ti(Oi-Pr)₂(DPM)₂) precursors were evaporated by heating. The evaporation temperature of Ba source (T_{Ba}) was fixed at 563 K and that of Ti source (T_{Ti}) was changed from 443 K to 460 K to change $m_{Ti/Ba}$ in the precursor gases. The evaporated amounts of Ba and Ti precursors were calculated from the mass change of the precursor containers before and after the deposition experiment. The precursor gases were carried into LCVD chamber with Ar gas. O₂ gas was separately introduced through a double-tube gas nozzle. The total chamber pressure (p_{tot}) was held at 600 Pa. The deposition was conducted for 300 s.

The crystal phase was determined by X-ray diffraction (XRD, Rigaku RAD-2C). The morphologies were observed by a scanning electron microscope (SEM, Hitachi S-3100H). The dielectric properties were measured by an impedance spectroscope (Hewlett-Packard HP4194) at 1 MHz using an AC driving voltage of 10 mV.

Table 1 Deposition conditions of Ba−Ti−O films by LCVD

Ba(DPM)₂ evaporation temperature (T_{Ba})	563 K
Ti(Oi-Pr)₂(DPM)₂ evaporation temperature (T_{Ti})	443–460 K
Substrate pre-heating temperature (T_{pre})	773 K
Total chamber pressure (p_{tot})	600 Pa
Gas flow rate	
Ar gas (FR_{Ar})	8.3×10^{-7} m³/s
O₂ gas (FR_{O_2})	1.7×10^{-6} m³/s
Laser power (P_L)	48–116 W
Deposition time (t)	300 s
Substrate–nozzle distance	30 mm
Substrate	Pt/Ti/SiO₂/Si (10 mm × 10 mm × 0.5 mm)

3 Results and discussion

Figure 1 shows the relationship between T_{Ti} and $m_{Ti/Ba}$. As T_{Ti} is changed from 443 K to 460 K, the evaporation amount of Ti precursor increases, which results in the increase of $m_{Ti/Ba}$ from 1.84 to 4.55. The composition of Ba–Ti–O film is controlled by changing $m_{Ti/Ba}$. In LCVD process, T_{dep} is mainly affected by P_L and precursor content. Figure 2 depicts the typical relationship between P_L and T_{dep} under various $m_{Ti/Ba}$. The increase of P_L results in an accompanying increase of T_{dep}. For example, at $m_{Ti/Ba} = 1.84$, with increasing P_L from 48 W to 98 W, T_{dep} increases from 877 K to 982 K. With increasing $m_{Ti/Ba}$, T_{dep} decreases due to the increase of precursor supply, which shows the similar trend as our previous report [14].
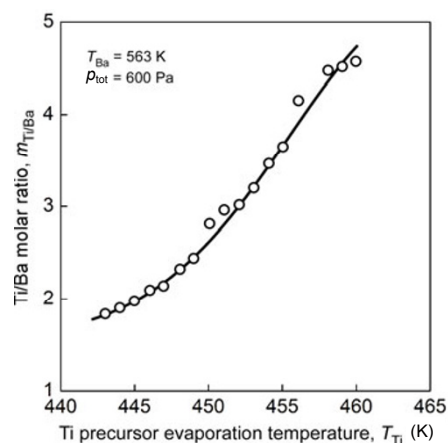

Fig. 1 Ti/Ba precursor molar ratio ($m_{Ti/Ba}$) as a function of T_{Ti} at $T_{Ba} = 563$ K.
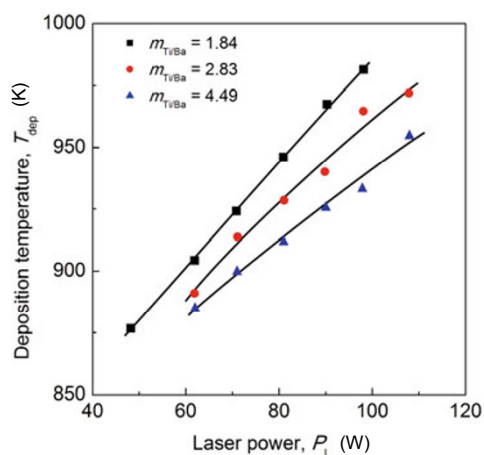

Fig. 2 Effect of P_L on T_{dep} for Ba–Ti–O films prepared at various $m_{Ti/Ba}$.

The typical XRD patterns of TiO_2-rich Ba–Ti–O films prepared at various $m_{Ti/Ba}$ and T_{dep} are shown in Fig. 3. The single-phase BT_2 film is obtained at $m_{Ti/Ba} = 1.84$ and $T_{dep} = 877$ K (JCPDS 34-0133, Fig. 3(a)). As $m_{Ti/Ba}$ increases to 2.83, the single-phase B_4T_{13} film is obtained at $T_{dep} = 914$ K (JCPDS 35-0750, Fig. 3(b)). At high $m_{Ti/Ba}$ (4.49), the single-phase BT_5 film is prepared at $T_{dep} = 955$ K (JCPDS 35-0805, Fig. 3(c)).
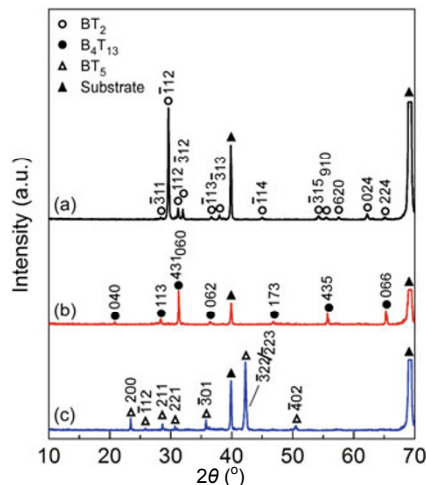

Fig. 3 XRD patterns of Ba−Ti−O films prepared at various $m_{Ti/Ba}$ and T_{dep}: (a) 1.84 and 877 K, (b) 2.83 and 914 K, and (c) 4.49 and 955 K.

The phase relationships in the TiO_2-rich region of Ba–Ti–O films are shown in Fig. 4(a). The single-phase BT_2 films are obtained at $m_{Ti/Ba} = 1.84$ and 1.90. And the single-phase BT_2 film is also obtained at $m_{Ti/Ba} = 1.98$ and $T_{dep} = 869$ K. At $m_{Ti/Ba} = 1.98$, with increasing T_{dep}, B_6T_{17} phase is co-deposited with BT_2 phase. In the $m_{Ti/Ba}$ range of 2.11–2.44, a mixture of BT_2 and B_6T_{17} phases is deposited. At $m_{Ti/Ba} = 2.34$ and $T_{dep} = 975$ K, and $m_{Ti/Ba} = 2.44$ and $T_{dep} = 962$ K, B_4T_{13} phase is co-deposited with BT_2 and B_6T_{17} phases. At $m_{Ti/Ba} = 2.83$, below $T_{dep} = 929$ K, the single-phase B_4T_{13} films are obtained, while a mixture of B_4T_{13} and B_6T_{17} phases is deposited above $T_{dep} = 940$ K. In the $m_{Ti/Ba}$ range of 2.97–3.66, a mixture of B_4T_{13} and BT_4 phases is deposited. At $m_{Ti/Ba} = 3.21$ and $T_{dep} = 940$ K, B_2T_9 phase is co-deposited with B_4T_{13} and BT_4 phases, while BT_5 phase is also co-deposited with B_2T_9, B_4T_{13} and BT_4 phases above $T_{dep} = 948$ K. At $m_{Ti/Ba} = 3.47$ and $T_{dep} = 932$ K, B_2T_9 phase is co-deposited with B_4T_{13} and BT_4 phases, while BT_5 phase is also co-deposited with B_2T_9, B_4T_{13} and BT_4 phases above $T_{dep} = 948$ K. At $m_{Ti/Ba} = 3.66$, a mixture of B_4T_{13}, BT_4, B_2T_9 and BT_5 phases is obtained. At $m_{Ti/Ba} = 4.17$, a

mixture of BT_4, B_2T_9 and BT_5 phases is obtained. At $m_{Ti/Ba} = 4.49$, below $T_{dep} = 900$ K, BT_5 phase is co-deposited with BT_4 phase, while the single-phase BT_5 films are obtained above $T_{dep} = 912$ K. In the $m_{Ti/Ba}$ range of 4.52–4.55, the single-phase BT_5 films are obtained. Figure 4(b) shows our previous phase relationship diagram of Ba–Ti–O films prepared by LCVD [14], and Fig. 4(c) shows an equilibrium phase
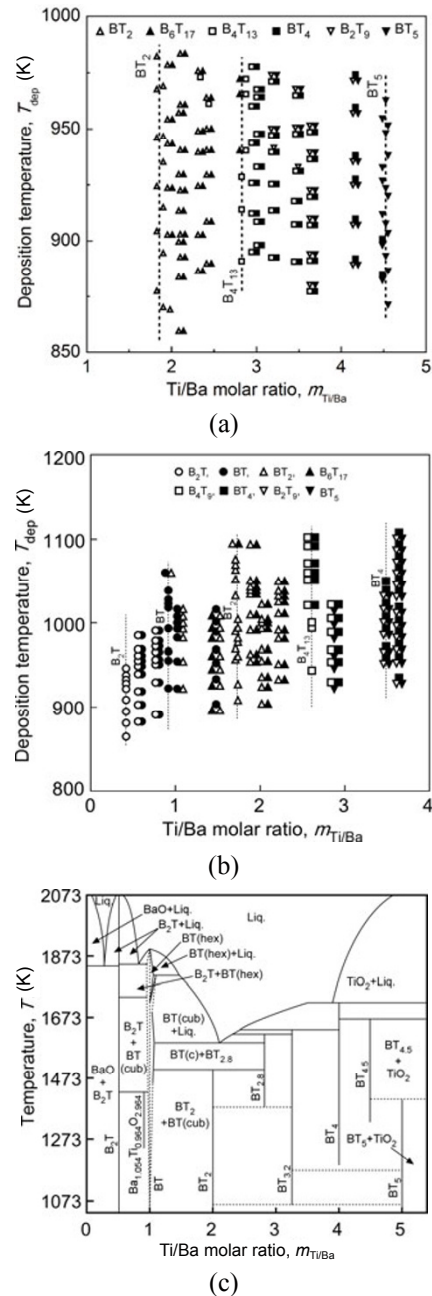

(a)

(b)

(c)

Fig. 4 (a) Phase relationship diagram of TiO_2-rich Ba–Ti–O films prepared at various $m_{Ti/Ba}$ and T_{dep}; (b) our previous phase relationship diagram of Ba–Ti–O films [14]; (c) the equilibrium phase diagram of BaO–TiO_2 bulk reported by Lee *et al*. [10].

diagram of BaO–TiO$_2$ bulk system reported by Lee *et al.* [10]. The $m_{Ti/Ba}$ to obtain the single-phase BT$_2$, B$_4$T$_{13}$ and BT$_5$ films is approximately consistent with the $m_{Ti/Ba}$ of each phase reported in Fig. 4(c). The $m_{Ti/Ba}$ to obtain the single-phase BT$_2$, B$_4$T$_{13}$ and BT$_5$ films is slightly smaller than those of the corresponding molecular formula of each phase (e.g., the single-phase BT$_2$ film is obtained at $m_{Ti/Ba} = 1.84$). Since Ba(DPM)$_2$ could be partly decomposed at high temperature, a little of Ba precursor is depleted in the container, which results in the smaller $m_{Ti/Ba}$. Compared with our previous phase relationship diagram (Fig. 4(b)), the $m_{Ti/Ba}$ to obtain the single-phase BT$_2$ and B$_4$T$_{13}$ films in the present study is slightly larger than the previous $m_{Ti/Ba}$. In the present study, the deposition time (300 s) is only half of the deposition time (600 s) in our previous study [14]. As the deposition time increases, more Ba(DPM)$_2$ precursor is decomposed in the container to result in the smaller $m_{Ti/Ba}$. This result indicates that the enough supply of Ba(DPM)$_2$ and Ti(Oi-Pr)$_2$(DPM)$_2$ precursors is very important for the reproducibility of crystalline phases prepared by LCVD. The single-phase BT$_5$ film is also obtained due to the higher $m_{Ti/Ba}$.

Figure 5 illustrates the typical surface microstructures of TiO$_2$-rich Ba–Ti–O films. BT$_2$ film prepared at $m_{Ti/Ba} = 1.84$ and $T_{dep} = 877$ K consists of fine grains (Fig. 5(a)). With increasing T_{dep}, the grain size increases and the rectangular-faceted grains form (Fig. 5(b)). With increasing $m_{Ti/Ba}$ to 2.83, B$_4$T$_{13}$ film prepared at $T_{dep} = 914$ K has the triangular-faceted grains (Fig. 5(c)), and the film prepared at $T_{dep} = 972$ K mainly consists of the rectangular-faceted grains co-deposited with the pinecone-like grains (Fig. 5(d)). At $m_{Ti/Ba} = 4.49$, BT$_5$ film prepared at $T_{dep} = 885$ K has the shellfish-like structure (Fig. 5(e)), which consists of fine grains, and the film prepared at $T_{dep} = 955$ K has the pinecone-like grains (Fig. 5(f)) due to growth of the fine grains in the shellfish-like structure. All TiO$_2$-rich Ba–Ti–O films have columnar growth as shown in their cross-sectional morphologies (Fig. 6). With increasing T_{dep}, the column becomes wider.

Figure 7 displays the relationship between R_{dep} and T_{dep} of TiO$_2$-rich Ba–Ti–O films in Arrhenius format. As $m_{Ti/Ba}$ increases, R_{dep} increases due to the increase of precursor supply. R_{dep} of TiO$_2$-rich Ba–Ti–O films ranges from 54.0 μm/h to 177.6 μm/h. With increasing T_{dep}, R_{dep} slightly changes. In the present study, the laser irradiation enhances the reactivity of high-rate-supply precursor vapors and accelerates the surface
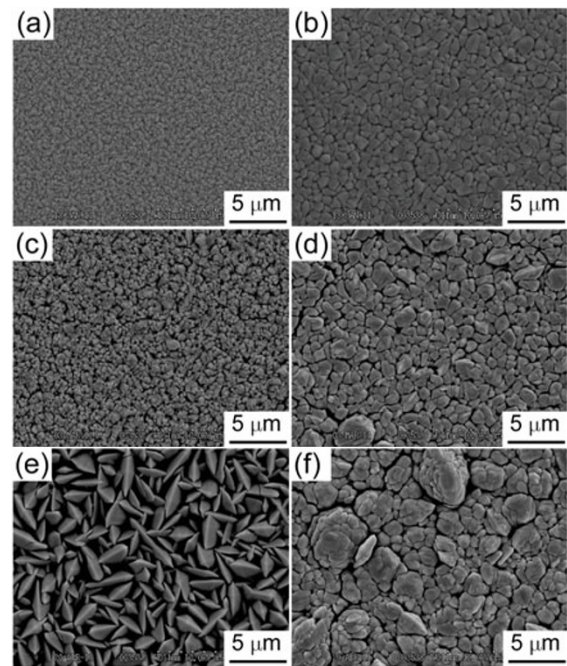

Fig. 5   Surface morphologies of Ba–Ti–O films prepared under various conditions: (a) and (b) BT$_2$ films ($m_{Ti/Ba} = 1.84$, $T_{dep} = 877$ K and 982 K respectively); (c) and (d) B$_4$T$_{13}$ films ($m_{Ti/Ba} = 2.83$, $T_{dep} = 914$ K and 972 K respectively); (e) and (f) BT$_5$ films ($m_{Ti/Ba} = 4.49$, $T_{dep} = 885$ K and 955 K respectively).
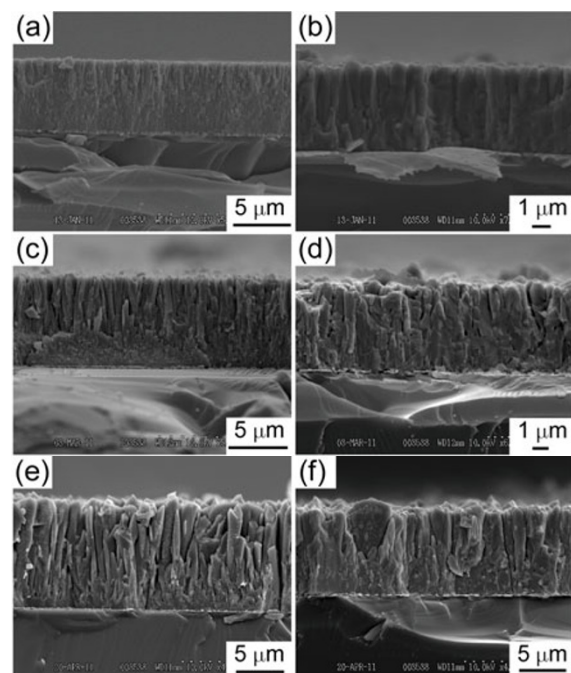

Fig. 6   Cross-sectional morphologies of Ba–Ti–O films prepared under various conditions: (a) and (b) BT$_2$ films ($m_{Ti/Ba} = 1.84$, $T_{dep} = 877$ K and 982 K respectively); (c) and (d) B$_4$T$_{13}$ films ($m_{Ti/Ba} = 2.83$, $T_{dep} = 914$ K and 972 K respectively); (e) and (f) BT$_5$ films ($m_{Ti/Ba} = 4.49$, $T_{dep} = 885$ K and 955 K respectively).

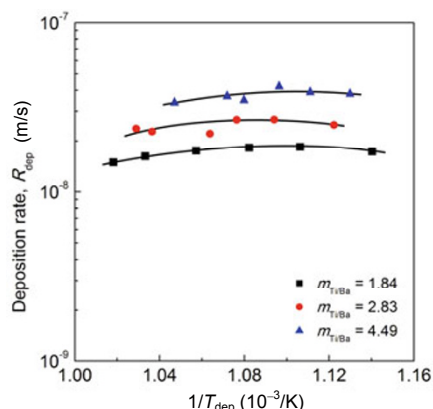mobility of chemical species, which results in the preparation of TiO_2-rich Ba–Ti–O films at high R_{dep}.

Fig. 7 Relationship between R_{dep} and T_{dep} of Ba–Ti–O films in Arrhenius format.

The effect of temperature on permittivity (ε') of TiO_2-rich Ba–Ti–O films measured at 1 MHz is shown in Fig. 8. The ε' values of BT_2 film (prepared at $m_{Ti/Ba} =$ 1.84 and $T_{dep} = 877$ K), B_4T_{13} film (prepared at $m_{Ti/Ba} =$ 2.83 and $T_{dep} = 914$ K), and BT_5 film (prepared at $m_{Ti/Ba} = 4.49$ and $T_{dep} = 955$ K) are 50, 40 and 21, respectively. To the best of our knowledge, there is no literature reporting on the dielectric property of single-phase B_4T_{13} ceramic and film. The ε' value of BT_2 single crystalline is anisotropic, and has values of 140 along the *a*-axis direction and 70 along the *c*-axis direction [4]. The ε' value of BT_5 ceramic is about 41 reported by Ritter *et al.* [5]. The ε' values of BT_2 and BT_5 films in this work are smaller than those of BT_2 and BT_5 ceramics due to the orientation. These results indicate that these films might be applied to the microwave devices.

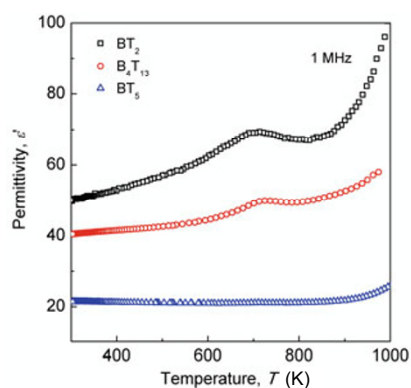
Fig. 8 Effect of temperature on permittivity of Ba–Ti–O films (measured at 1 MHz) prepared under various conditions: BT_2 film ($m_{Ti/Ba} = 1.84$, $T_{dep} =$ 877 K), B_4T_{13} film ($m_{Ti/Ba} = 2.83$, $T_{dep} = 914$ K), and BT_5 film ($m_{Ti/Ba} = 4.49$, $T_{dep} = 955$ K).

4 Conclusions

The TiO_2-rich Ba–Ti–O films were prepared on Pt/Ti/SiO$_2$/Si substrate by LCVD. The single-phase BT_2, B_4T_{13} and BT_5 films were prepared at $m_{Ti/Ba} =$ 1.84–1.90, 2.83 and 4.49–4.55, respectively. The high R_{dep} of TiO_2-rich Ba–Ti–O films ranged from 54.0 μm/h to 177.6 μm/h. The ε' values of BT_2 film (prepared at $m_{Ti/Ba} = 1.84$ and $T_{dep} = 877$ K), B_4T_{13} film (prepared at $m_{Ti/Ba} = 2.83$ and $T_{dep} = 914$ K) and BT_5 film (prepared at $m_{Ti/Ba} = 4.49$ and $T_{dep} = 955$ K) were 50, 40 and 21, respectively.

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