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Effect of laser power on orientation and microstructure of Ba_2TiO_4 film prepared by laser chemical vapor deposition

Dongyun Guo [a,b,*], Takashi Goto [b], Chuanbin Wang [a], Qiang Shen [a], Lianmeng Zhang [a]

[a] State Key Laboratory of Advanced Technology for Materials Synthesis and Processing, and School of Materials Science and Engineering, Wuhan University of Technology, Wuhan 430070, China

[b] Institute for Materials Research, Tohoku University, Sendai 980-8577, Japan

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ABSTRACT

Ba_2TiO_4 films were prepared on $Pt/Ti/SiO_2/Si$ substrates by laser chemical vapor deposition method. The effect of laser power (P_L) on orientation and microstructure was investigated. With increasing P_L from 52 to 93 W, the deposition temperature (T_{dep}) increased from 845 to 946 K. With increasing T_{dep} from 845 to 927 K, the preferred orientation of Ba_2TiO_4 films changed from (0 9 1) to (1 0 3), the surface morphologies changed from faceted to rectangular, and the columnar cross-section became thicker. The films prepared at high T_{dep} (931–946 K) had the porous cross-section consisted of powder-like grains. Ba_2TiO_4 film prepared at 881 K had high deposition rate (R_{dep}) of 51.4 $\mu m\,h^{-1}$, which was advantageous to industrial production.

1. Introduction

Ba_2TiO_4 is the only stable Ba-rich compound with TiO_4 tetrahedral in the BaO–TiO_2 system, which has two structures, the low-temperature monoclinic phase (β-form, space-group $P2_1/n$) and the high-temperature orthorhombic phase (α-form, space-group $P2_1nb$) [1–3]. The latter is a superstructure of the monoclinic cell. There were a few literature reported on preparation and property of the single-phase Ba_2TiO_4 ceramics or nano-particles. Pfaff prepared Ba_2TiO_4 ceramics by solid reaction and it had high dielectric constant about 950 at 1 MHz [4]. Van de Craats et al. investigated the luminescence of Ba_2TiO_4 ceramics [5]. Ahmad et al. synthesized nanometer-sized Ba_2TiO_4 particles with dielectric constant about 40 (at 100 kHz) [6]. Recently Saito et al. applied Ba_2TiO_4 powder to absorb CO_2 from flue gases [7]. However, due to the requirement of device miniaturization, it is necessary to be prepared in film form for practical applications.

Laser chemical vapor deposition (LCVD) is advantageous to prepare films at high deposition rate (R_{dep}) with controllability of orientation and microstructure [8–13]. The $Pt/Ti/SiO_2/Si$ substrate is widely used to prepare dielectric films due to its good thermal stability. In the previous work, we prepared the single-phase Ba_2TiO_4 film with (1 0 3) preferred orientation by LCVD [14]. For the LCVD process, the chemical reaction is affected by mainly laser power (P_L). In the present study, Ba_2TiO_4 films were prepared on $Pt/Ti/SiO_2/Si$ substrate by LCVD. The effect of P_L on orientation, morphologies and R_{dep} was investigated.

2. Experimental

Ba_2TiO_4 films were prepared on $Pt/Ti/SiO_2/Si$ substrate by LCVD with a continuous-wave Nd:YAG laser (wavelength: 1064 nm). The schematic diagram of LCVD apparatus was introduced elsewhere [14]. The substrate was pre-heated on a hot stage at temperature (T_{pre}) of 773 K before starting laser irradiation. A thermocouple was inserted at the bottom side of the substrate to measure the deposition temperature (T_{dep}). A laser beam 15 mm in diameter was introduced through a quartz window to irradiate the whole substrate. The P_L was changed from 52 to 93 W. The barium dipivaloylmethanate ($Ba(DPM)_2$) and titanium diisopropoxy-dipivaloylmethanate ($Ti(Oi\text{-}Pr)_2(DPM)_2$) precursors were heated at 563 K and 419 K, respectively, and their vapors were carried into the chamber with Ar gas. O_2 gas was separately introduced into the chamber through a double-tube gas nozzle. The total pressure (P_{tot}) in the CVD chamber was held at 400 Pa. The deposition was conducted for 600 s. Details of the deposition conditions are listed in Table 1.

* Corresponding author at: Institute for Materials Research, Tohoku University, Sendai 980-8577, Japan. Tel.: +81 80 3336 0912.
E-mail address: guodongyun@gmail.com (D. Guo).

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Table 1
Deposition conditions of Ba_2TiO_4 film.

$Ba(DPM)_2$ evaporation temperature (T_{Ba})	563 K
$Ti(Oi\text{-}Pr)_2(DPM)_2$ evaporation temperature (T_{Ti})	419 K
Substrate pre-heating temperature (T_{pre})	773 K
Total chamber pressure (P_{tot})	400 Pa
Gas flow rate	
Ar gas (FR_{Ar})	8.3×10^{-7} m^3 s^{-1}
O_2 gas (FR_{O_2})	1.7×10^{-6} m^3 s^{-1}
Laser power (P_L)	52–93 W
Deposition time (t)	600 s
Substrate-nozzle distance	25 mm
Substrate	Pt/Ti/SiO_2/Si (10 mm × 10 mm × 0.5 mm)

The crystal structure was analyzed by X-ray diffraction (XRD, Rigaku RAD – 2C) using CuKα X-ray radiation. The surface and cross-sectional microstructures were observed by a scanning electron microscope (SEM, Hitachi S-3100H).

3. Results and discussion

In the LCVD process, the T_{dep} can be determined for various parameters, such as P_L, P_{tot}, T_{pre} and precursor evaporation temperature. Fig. 1 shows the effect of P_L on T_{dep}. With increasing P_L from 52 to 93 W, T_{dep} increased from 845 to 946 K.

Fig. 2 depicts the XRD result of Ba_2TiO_4 film prepared at different T_{dep}. The XRD patterns could be indexed to the orthorhombic phase (JCPDS 75-0677). The single-phase Ba_2TiO_4 films were obtained. The preferred orientation was changed with increasing T_{dep}. At T_{dep} = 845 K, the intensity of (0 9 1) peak was the strongest. With increasing T_{dep} (865–931 K), the intensity of (1 0 3) peak became the strongest. At higher T_{dep} (937–946 K), the strongest peak changed to (1 6 1).

The typical morphologies of Ba_2TiO_4 films prepared at different T_{dep} were shown in Fig. 3. The film prepared at T_{dep} = 845 K consisted of faceted grains (Fig. 3(a)) and there was some cone-

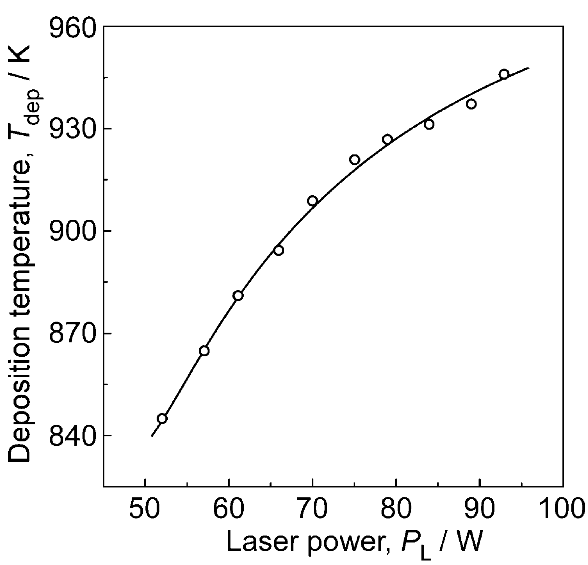

Fig. 1. Effect of P_L on T_{dep} of Ba_2TiO_4 films.

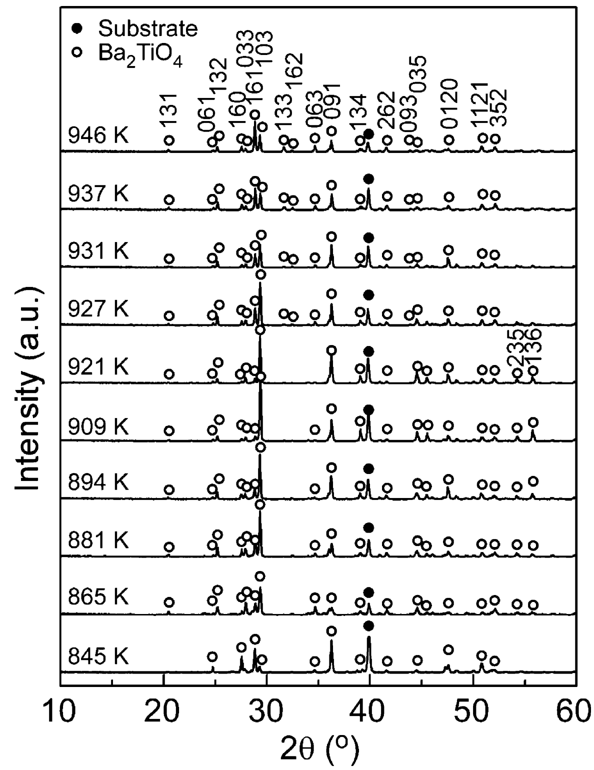

Fig. 2. XRD pattern of Ba_2TiO_4 film prepared at different T_{dep}.

like grains. Ba_2TiO_4 film prepared at 894 K had rectangular grains, which corresponded to (1 0 3)-oriented grains. There were the faceted and rhombic grains in Ba_2TiO_4 film prepared at 946 K. With increasing T_{dep}, the grain size became larger. The films prepared at low T_{dep} (845–927 K) showed columnar cross-section as shown in Fig. 3(b) and (d). The grains were regularly arranged along the perpendicular direction to the substrate and the microstructure of columnar grains near the substrate interface consisted of fine grains which grew into larger columnar grains, as commonly observed in conventional CVD [15]. With increasing T_{dep}, the column became thicker. However, as shown in Fig. 3(f), the Ba_2TiO_4 films prepared at high T_{dep} (931–946 K) had porous cross-section due to the powders formed in the gas phase near the substrate surface.

Fig. 4 demonstrates the relationship between R_{dep} and T_{dep} in the Arrhenius format. In the present study, the R_{dep} ranged from 30.8 to 51.4 μm h^{-1}. The high R_{dep} was owing to the relatively high supply rate of precursor gases and the enhancement of chemical reaction by laser irradiation of the film and the precursor gases [16]. As shown in Fig. 4, the plot could be divided into three regions labeled A, B and C. The A region represented the R_{dep} controlled by a reaction occurring at or near the substrate surface, the B region corresponded to the R_{dep} controlled by mass transport in the gas stream, and the C region characterized the R_{dep} limitation due to homogeneous gas phase nucleation of product, respectively [15].

4. Conclusions

The single-phase Ba_2TiO_4 films were prepared on Pt/Ti/SiO_2/Si substrate by LCVD. The orientation and microstructures of Ba_2TiO_4 films were affected by P_L. With increasing P_L from 52 to 93 W, T_{dep} increased from 845 to 946 K. With increasing T_{dep} from