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Growth of *b*-axis-oriented $BaTi_2O_5$ Nanopillars by Laser Chemical Vapor Deposition

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Abstract. *b*-axis-oriented $BaTi_2O_5$ nanopillars were prepared on (100) MgO single crystal substrate by laser chemical vapor deposition using Ba and Ti dipivaloylmethanate precursors. *b*-axis-oriented $BaTi_2O_5$ nanopillars were approximately 250–400 nm in width and 2.5 μm in height. Deposition rate of $BaTi_2O_5$ nanopillar arrays was about 75 μm h^{-1}.

Introduction

We have first prepared ferroelectric $BaTi_2O_5$ single crystal and reported its high permittivity along the *b*-axis (ε' = 20000) and high Curie temperature (T_C = 750 K) [1,2]. Since the first-principle calculation implies that the piezoelectric response of $BaTi_2O_5$ can be comparable to that of $PbTiO_3$ [3], $BaTi_2O_5$ can be a promising new lead-free ferroelectric material.

One-dimensional ferroelectric materials, such as nanowires and nanopillars, have recently attracted extensive interest for potential applications in piezoelectric, dielectric and electro-optic devices. Nanostructured $BaTi_2O_5$ would be a great candidate as nanoscale sensors and actuators. $BaTi_2O_5$ nanowires have been prepared using solution techniques, such as hydrothermal reaction [4] and molten salt method [5,6]. However, these routes required a prolonged process time (5–84 h). $BaTi_2O_5$ has a spontaneous polarization along *b*-axis direction; however, nano-sized Bai_2O_5 with *b*-axis orientation has not been prepared [5,6].

Chemical vapor deposition (CVD) is a versatile technique to prepare nano-sized materials such as nanopillars, nanodots and nanowires of Si, GaP and ZnO with controlled orientation [7,8]. However, nano-sized complex oxides have been hardly prepared with controlling orientation and composition. Although $BaTi_2O_5$ would be unstable decomposing $BaTiO_3$ and $Ba_4Ti_{13}O_{30}$ below 1480 K or above 1600 K [9,10], $BaTi_2O_5$ films has been prepared by laser CVD [11]. We have reported that laser CVD can prepare nano-sized Y-Si-O film with fur-like microstructure [12], and laser CVD is advantageous to prepare unique nano-sized complex oxides.

In the present study, *b*-axis oriented $BaTi_2O_5$ nanopillars were prepared by laser CVD and their nanostructure was investigated.

Experimental procedure

Details of the laser CVD apparatus have been reported elsewhere [13]. Barium dipivaloylmethanate ($Ba(dpm)_2$) and titanium diisopropoxy-dipivaloylmethanate ($Ti(OiPr)_2(dpm)_2$) precursors were heated at 567 K and 441 K, respectively. Their vapors were carried into a 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 held at 0.4 kPa. (100) MgO single crystal plate was used as a substrate. The substrate was preheated on a hot stage at 773 K, and a thermocouple was inserted near the substrate to measure the deposition temperature. A continuous-wave mode Nd:YAG laser beam (wavelength: 1064 nm; diameter: 20 mm) was introduced through a quartz window to irradiate the whole substrate. Deposition was conducted for 120 s.

The crystal phase was analyzed by X-ray diffraction (XRD, Rigaku RAD-2C) using Cu Kα X-ray radiation. The surface and cross-sectional microstructures were observed by a scanning electron microscope (SEM, Hitachi S-3100H) and a transmission electron microscope (TEM, Topcon EM-002B). TEM specimen was prepared on a Cu mesh by a scratch method.

Results and discussion

Figure 1 shows the XRD pattern of $BaTi_2O_5$ nanopillars prepared on (100) MgO substrate at 1373 K. $BaTi_2O_5$ has an orthorhombic structure (space group: *C*2; a = 1.6899 nm, b = 0.3935 nm, c = 0.9410 nm, β = 103.0°; ICSD #281548; JCPDS #72-3812) [2]. $BaTi_2O_5$ film prepared at 1373 K showed a strong (020) orientation with minor peaks of $BaTi_2O_5$, implying that *b*-axi-oriented $BaTi_2O_5$ film grew epitaxially on (100) MgO substrate [16].

Figure 2 shows the cross-sectional and surface SEM images of $BaTi_2O_5$ nanopillars. $BaTi_2O_5$ nanopillar grains about 250–400 nm in width and 2.5 μm in height grew on the film. Deposition rate of $BaTi_2O_5$ nanopillars was approximately 75 μm h^{-1}.

Figure 3 shows the TEM bright-field image and selected-area electron diffraction (SAED) pattern of a $BaTi_2O_5$ nanopillars. The $BaTi_2O_5$ nanopillar had 275 nm in width (Fig. 3(a)). The SAED pattern taken from [310] zone indicated that $BaTi_2O_5$ nanopillar was a single crystal and grew along *b*-axis direction (Fig. 3(b)).

$BaTi_2O_5$ nanowires were prepared by using solution technique, such as hydrothermal reaction [4] and molten salt method as listed in Table 1 [4–6]. In these studies, $BaTi_2O_5$ nanowires were oriented perpendicularly to (100) or (011) planes, and these methods required a prolonged process time (5–84 h). Since $BaTi_2O_5$ has a spontaneous polarization and high permittivity perpendicular to (010) plane, *b*-axis-oriented $BaTi_2O_5$ nanowires or nanopillars should be prepared. In the present study, we demonstrated high-speed preparation of *b*-axis-oriented $BaTi_2O_5$ nanopilars by laser CVD.

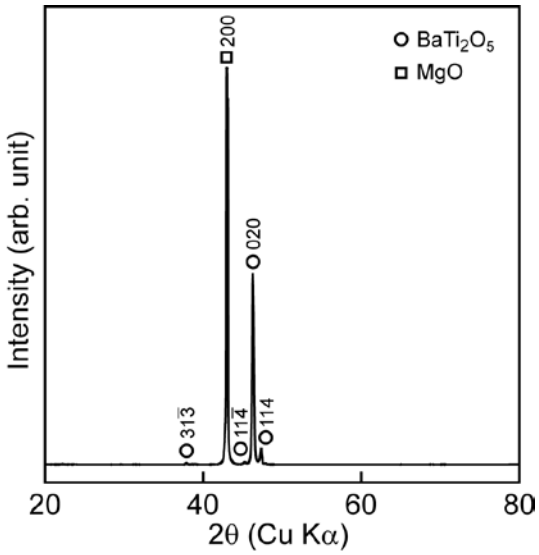

Fig. 1 XRD pattern of the $BaTi_2O_5$ nanopillars prepared on (100) MgO substrate at 1373 K.

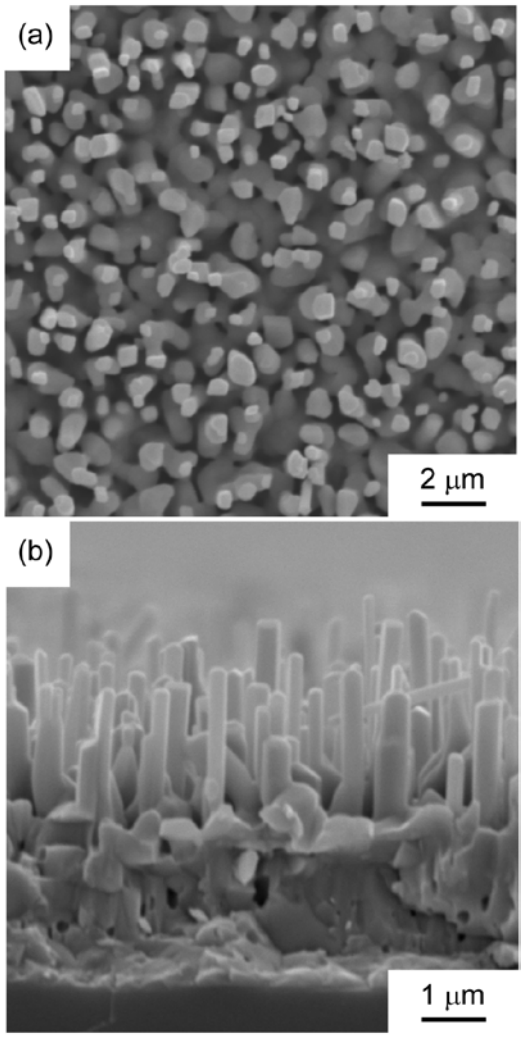

Fig. 2 Surface (a) and cross-sectional (b) SEM images of the *b*-axis-oriented $BaTi_2O_5$ nanopillars prepared on (100) MgO substrate at 1373 K.

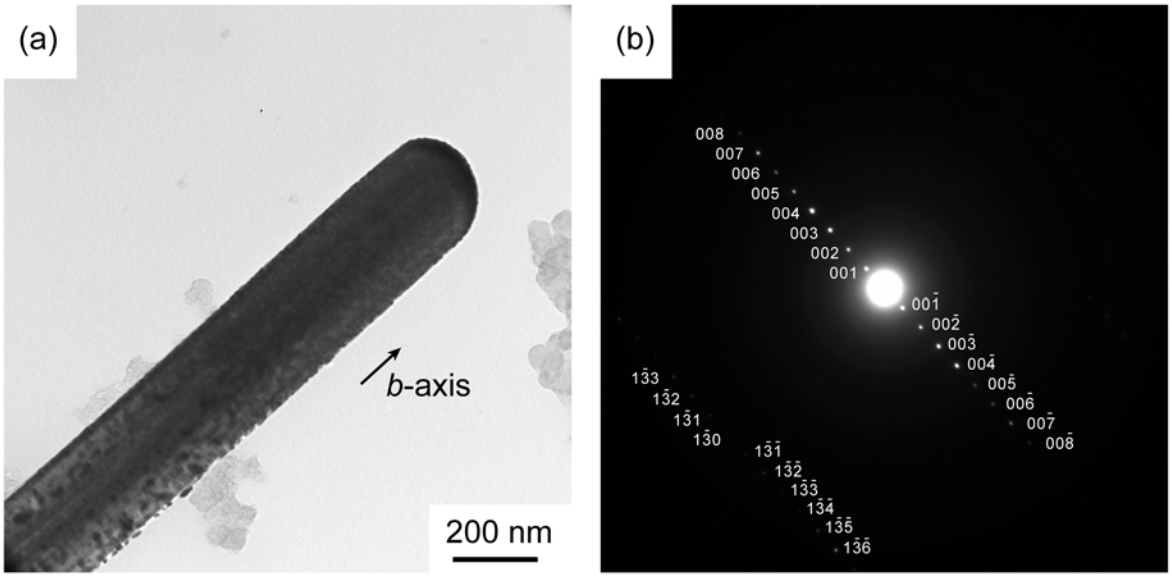

Fig 3. TEM bright-field image (a) and selected-area electron diffraction pattern (b) of a *b*-axis-oriented $BaTi_2O_5$ nanopillar.

Table 1. Preparation methods for $BaTi_2O_5$ nanowires [4–6] and nanopillars.

Method	Synthsis temperature	Process time	Dimmension*	Orientation
Hydrothermal reaction [4]	453 K	84 h	200−300 nm (W) several μm (H)	Not studied
Molten salt [5]	1233 K	5 h	30–500 nm (W) several hundred μm (H)	(100)
Molten salt [6]	1143 K	12.5–21 h	80–200 nm (W) 10 μm (H)	(011)
Laser CVD**	1373 K	120 s	250–400 nm (W) 2.5 μm (H)	(010)

* W: width, H: height (longitudinal direction); ** Present study

Summary

b-axis-oriented $BaTi_2O_5$ nanopillars were prepared on (100) MgO single crystal substrate by laser CVD. $BaTi_2O_5$ nanopillars were approximately 250–400 nm in width and 2.5 μm in height. Deposition rate of $BaTi_2O_5$ nanopillars were about 75 μm h^{-1}.

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