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Growth and microstructure of Ba β-alumina films by laser chemical vapor deposition

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Abstract

Ba β-alumina films were prepared by laser chemical vapor deposition. Mostly single-phase Ba β-alumina films were obtained at 1125–1200 K and for an Al/Ba molar ratio of 12.4–16.6. $BaAl_2O_4$ and α-Al_2O_3 were codeposited with Ba β-alumina under Ba- and Al-rich conditions, respectively. The Ba β-alumina films consisted of hexagonal grains, and the (1 1 0)-oriented Ba β-alumina films had a fin-like columnar structure. The highest deposition rate reached 120 $\mu m\,h^{-1}$ at around 1200 K. A thin layer of Ba-rich superstructure was formed on the surface of the (1 1 0)-oriented columnar grains.

Keywords: Ba β-alumina; Laser CVD; Oriented growth; Microstructure

1. Introduction

Barium hexaaluminate (Ba β-alumina) is a promising phosphor and solid electrolyte material because of its high transparency, moderate ionic conductivity, and high-temperature stability. Hexaaluminate of alkali and alkaline earth elements (M) has two family structures: magnetoplumbite-type ($MAl_{12}O_{19}$) and β-alumina-type ($MAl_{11}O_{17}$) structures.[1–3] Both structures have hexagonal symmetry with the Al spinel blocks stacked with a mirror plane along the c-axis. Ba hexaaluminate was considered to exhibit the magnetoplumbite structure with $BaAl_{12}O_{19}$ stoichiometry, similar to Ca and Sr systems; however, subsequent studies revealed that the large ionic radius of Ba^{2+} favors only the β-alumina-type structure. In addition, two nonstoichiometic phases have been reported for Ba β-alumina, namely Ba-poor phase I (typically $Ba_{0.79}Al_{10.9}O_{17.14}$) and Ba-rich phase II (typically $Ba_{2.34}Al_{21.0}O_{33.84}$).[1] Phase I is a defective β-alumina structure, while phase II has a superstructure exhibiting ordering of the excess Ba–O layers.

Ba β-alumina single crystals and polycrystals have been prepared by the Czochralski method,[4] floating-zone method,[2,5–7] and solid-state sintering.[8–12] To date, Ba β-alumina in film form has never been reported. Although a 15 nm thick Na β-alumina thin film was prepared as transistor gate dielectrics on zinc–tin oxide and indium–tin oxide substrates by the sol–gel technique,[13] it is difficult to prepare β-alumina films by a dry process because of the high vapor pressure and chemical reactivity of the alkali and alkaline earth metals. Chemical vapor deposition (CVD) has been widely adopted to prepare various oxide films but never used to make β-alumina films. In the CVD process, we employed a high-power laser to activate the precursors and demonstrated that laser CVD can be used to prepare highly oriented films of α-Al_2O_3,[14,15] as well as Ba complex oxides, $YBa_2Cu_3O_{7-\delta}$[16] and $BaTi_2O_5$.[17,18]

In the present study, we prepared Ba β-alumina films by laser CVD and investigated the effects of deposition temperature and Al/Ba supply molar ratio on the composition, microstructure, and orientation of Ba β-alumina films.

2. Experimental procedures

Details of the laser CVD apparatus have been reported elsewhere.[14,15] $Al(acac)_3$ (acac: acetylacetonate) and $Ba(dpm)_2$ (dpm: dipivaloylmethanate) precursors were heated at 543–553 and 423–440 K, respectively. The Al to Ba molar ratio in the source vapor ($R_{Al/Ba}$) was controlled between 2 and 6 by changing the evaporation temperature. $R_{Al/Ba}$ was calculated from

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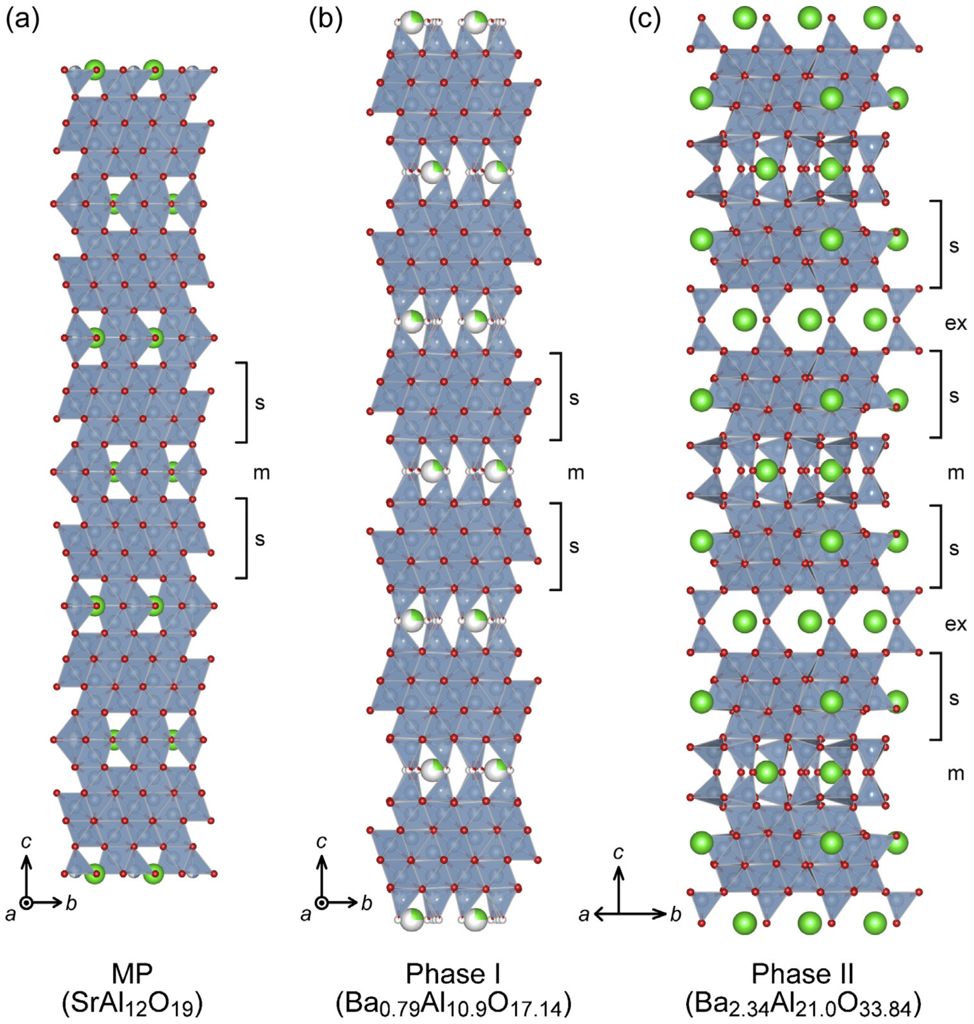

Fig. 1. A schematic of crystal structure of magnetoplumbite (MP) as $SrAl_{12}O_{19}$, Ba β-alumina phase I as $Ba_{0.79}Al_{10.9}O_{17.14}$ and Ba β-alumina phase II as $Ba_{2.34}Al_{21.0}O_{33.84}$. Symbols s, m, ex denote Al spinel block, mirror plane and Ba–O excess layer, respectively.

the mass change in each precursor. The precursor vapors were transported into the chamber with Ar carrier gas. O_2 gas was introduced into the chamber through a double-tube nozzle. The total pressure in the chamber was maintained at 400 Pa.

An continuous-wave mode InGaAlAs diode laser beam (wavelength: 808 nm) was expanded by lenses to irradiate the whole substrate area and introduced in the CVD chamber through a quartz glass window. The AlN substrate (8 mm × 8 mm × 1 mm) was preheated on a hot stage at 673 K. The deposition temperature increased from 1072 to 1240 K by increasing the laser power from 100 to 180 W. The deposition temperature was defined by a measured value using a thermocouple inserted into a 0.5 mm-deep slot at the backside of the substrate. The deposition rate was calculated from the thickness and deposition time (0.6 Ks).

Phase was studied by X-ray diffraction with Cu Kα radiation (θ–2θ XRD; scanning rate of 4° min^{-1}; Rigaku, RAD-2C). The composition of the film was evaluated by Rutherford backscattering spectrometry (RBS) at room temperature using He^{2+} ions accelerated at 2 MeV. The RBS detector was positioned at an angle of 170° to the beam direction. 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). A schematic crystal structure was drawn by VESTA.[19]

3. Results and discussion

Fig. 1 illustrates the typical crystal structures of hexaaluminate. Hexaaluminates consist of layered structure of $Al_{11}O_{16}$ spinel block and the mirror plane of MAlO$_3$ or M–O in the magnetoplumbite-type or β-alumina-type structure, respectively. Because of the large ionic radius of Ba^{2+}, the β-alumina-type structure is feasible for Ba hexaaluminate. Ba β-alumina (stoichiometrically $BaAl_{11}O_{17}$) has two nonstoichiometic phases: Ba-poor phase I ($Ba_{0.79}Al_{10.9}O_{17.14}$; ICSD #49525) and Ba-rich phase II ($Ba_{2.34}Al_{21.0}O_{33.84}$; ICSD #81999). Phase I is a defective β-alumina structure; the M and O sites on the M–O mirror plane are partially occupied (Fig. 1(b)). In the phase II structure, the excess Ba ions are located in the spinel block and the Ba–O layer (Fig. 1(c)).