Sensors and Materials, Vol. 33, No. 7 (2021) 2531–2535
MYU Tokyo

LETTER

S & M 2636

Preparation of (511)-oriented $BaTi_2O_5$ Thick Film on Pt/MgO(111) Substrate by Laser Chemical Vapor Deposition

Xiaojie Yang[1] and Dongyun Guo[2*]

[1]Faculty of Building Materials, Kunming Metallurgy College, Kunming 650033, China
[2]School of Materials Science and Engineering, Wuhan University of Technology, Wuhan 430070, China

(Received May 26, 2021; accepted June 22, 2021)

Keywords: $BaTi_2O_5$ thick film, laser chemical vapor deposition, orientation, dielectric property

A $BaTi_2O_5$ film was deposited on a Pt-coated MgO(111) single-crystal substrate by laser chemical vapor deposition. The crystal structure, morphologies, and dielectric properties of the film were investigated. A single-phase $BaTi_2O_5$ thick film with (511) orientation was obtained at a high deposition rate of 65.1 μm/h and consisted of rhombic grains with a columnar cross section. The (511)-oriented $BaTi_2O_5$ thick film had a dielectric constant of 75 and a dielectric loss of 0.015 at 300 K and 1 MHz, and its Curie temperature (T_C) was approximately 720 K, indicating its potential application in capacitors.

1. Introduction

Ferroelectric materials have many applications as storage capacitors, micro-actuators, infrared sensors, and ferroelectric memory, where a lead-free ferroelectric material with a high Curie temperature (T_C) is needed.(1–5) Akashi *et al.*(6,7) synthesized a $BaTi_2O_5$ single crystal with a high T_C (750 K) and a remnant polarization (P_r) of 1.92×10^{-2} C/m^2 along the *b*-axis direction. A first-principles calculation showed that the piezoelectric response of $BaTi_2O_5$ is comparable to that of $PbTiO_3$, indicating that $BaTi_2O_5$ is a promising new lead-free ferroelectric material.(8)

With the growing demand for the miniaturization of electronic devices, $BaTi_2O_5$ should be applied in the form of a film. $BaTi_2O_5$ films have been prepared by many deposition methods, such as metal-organic chemical vapor deposition (MOCVD), pulsed laser deposition, the sol-gel method, and laser chemical vapor deposition (CVD). Gorbenko *et al.*(9) reported the preparation of epitaxial $BaTiO_3$ films by aerosol MOCVD. As the Ba/Ti molar ratio in the diglyme solution they used in the preparation was 0.65, they deposited a pure *b*-oriented $BaTi_2O_5$ film on a MgO(100) single-crystal substrate. However, details of the preparation of the *b*-oriented $BaTi_2O_5$ film were not reported. Wang *et al.*(10) prepared (020)-oriented $BaTi_2O_5$ thin films on MgO(100) single-crystal substrates by pulsed laser deposition. The (020)-oriented $BaTi_2O_5$ thin films had a significant peak of the dielectric constant (ε') at T_C of 750 K, in agreement with that of $BaTi_2O_5$ single crystal. Ito *et al.*(11) deposited (020)-oriented $BaTi_2O_5$ thick films on $Pt/Ti/SiO_2/Si$ substrates by laser CVD at a high deposition rate of about 90 μm/h. The (020)-oriented $BaTi_2O_5$

*Corresponding author: e-mail: guody@whut.edu.cn
https://doi.org/10.18494/SAM.2021.3442

ISSN 0914-4935
https://myukk.org/

thick films had a maximum ε' of 653 at T_C of 759 K, and their T_C was close to that of the $BaTi_2O_5$ single crystal. Since the $BaTi_2O_5$ single crystal shows anisotropic dielectric properties, it is necessary to investigate the dielectric properties of $BaTi_2O_5$ films with different orientations. In our previous study, randomly oriented $BaTi_2O_5$ thin films with ε' of 55 were prepared on Pt/Ti/SiO_2/Si substrates by the sol-gel method.(12) The (112)-oriented $BaTi_2O_5$ thick films were deposited on Pt/MgO(110) substrates by laser CVD. These films exhibited ε' of 67 and a dielectric loss (tanδ) of 0.015 at room temperature and a measurement frequency of 1 MHz.(13) $BaTi_2O_5$ films with different orientations were prepared on MgO(100), (110), and (111) single-crystal substrates by laser CVD, and it was found that the orientation of the films was seriously affected by the substrate and deposition temperature.(14) In this study, a $BaTi_2O_5$ film was prepared on a Pt-coated MgO(111) single-crystal substrate by laser CVD, and the crystal structure, microstructure, and dielectric properties of the $BaTi_2O_5$ film on the Pt/MgO(111) substrate were investigated.

2. Experimental Details

The $BaTi_2O_5$ film was 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.(15,16) Details of the deposition conditions are summarized in Table 1. The Pt/MgO(111) substrate was placed on a hot stage and heated at a pre-heating temperature of 773 K. A laser beam of 14 mm diameter was introduced through a quartz window to irradiate the whole substrate. The laser power was 135 W. The barium dipivaloylmethanate [$Ba(DPM)_2$] and titanium diisopropoxy-dipivaloylmethanate [$Ti(Oi\text{-}Pr)_2(DPM)_2$] precursors were kept in reservoirs and heated at 563 and 445 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 kept at 600 Pa. The deposition was conducted for 420 s.

The crystal structure of the film was analyzed by X-ray diffraction (XRD, Rigaku RAD-2C) using CuKα X-ray radiation at 30 kV and 20 mA. The surface and cross-sectional microstructures

Table 1
Deposition conditions of $BaTi_2O_5$ thick film.

$Ba(DPM)_2$ evaporation temperature (T_{Ba})	563 K
$Ti(Oi\text{-}Pr)_2(DPM)_2$ evaporation temperature (T_{Ti})	445 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} m^3/s
O_2 gas (FR_{O2})	1.7×10^{-6} m^3/s
Laser power (P_L)	135 W
Deposition time (t)	420 s
Substrate–nozzle distance	30 mm
Substrate	Pt/MgO (10 × 10 × 0.5 mm^3)

of the film were characterized using a scanning electron microscope (SEM, Hitachi S-3100H). Au paste was deposited on the film and heated at 300 ºC to form a top electrode. The dielectric properties of the film were measured using an impedance spectroscope (Hewlett-Packard HP4194) in air from 300 to 900 K.

3. Results and Discussion

Figure 1 shows the XRD pattern of the film. The XRD pattern was indexed to the monoclinic $BaTi_2O_5$ phase with the space group of *C*2 and lattice parameters of a = 1.6908(9) nm, b = 0.3937(1) nm, c = 0.9418(4) nm, and β = 103.12(5)º.[6] The (112), (−313), and (511) peaks of the monoclinic $BaTi_2O_5$ phase were observed, which indicated that a single-phase $BaTi_2O_5$ film was obtained within the detection limit of the XRD apparatus. The (511) peak had the strongest intensity, which meant that the $BaTi_2O_5$ film had (511) orientation.

Figure 2 shows surface and cross-sectional SEM images of the (511)-oriented $BaTi_2O_5$ film. The $BaTi_2O_5$ film consisted of rhombic grains and had a columnar cross section. According to the cross-sectional SEM image of the $BaTi_2O_5$ film [Fig. 2(b)], the film thickness was approximately 7.59 µm, which indicated that the R_{dep} of the film was 65.1 µm/h. This value of R_{dep} was more than 100 times higher than those reported for $BaTi_2O_5$ films prepared by pulsed laser deposition and MOCVD,[9,10] and such a high R_{dep} is advantageous for preparing films with high efficiency.

The temperature dependences of ε' and tanδ for the (511)-oriented $BaTi_2O_5$ thick film at 1 MHz are shown in Fig. 3. The $BaTi_2O_5$ thick film exhibited ε' of 75 and tanδ of 0.015 at 300 K. With increasing temperature, ε' increased and reached a maximum of 605 at 720 K, which indicated that T_C of the (511)-oriented $BaTi_2O_5$ thick film was approximately 720 K. As the

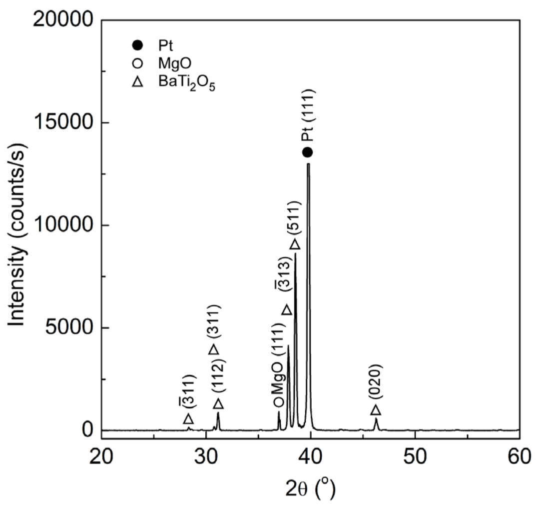
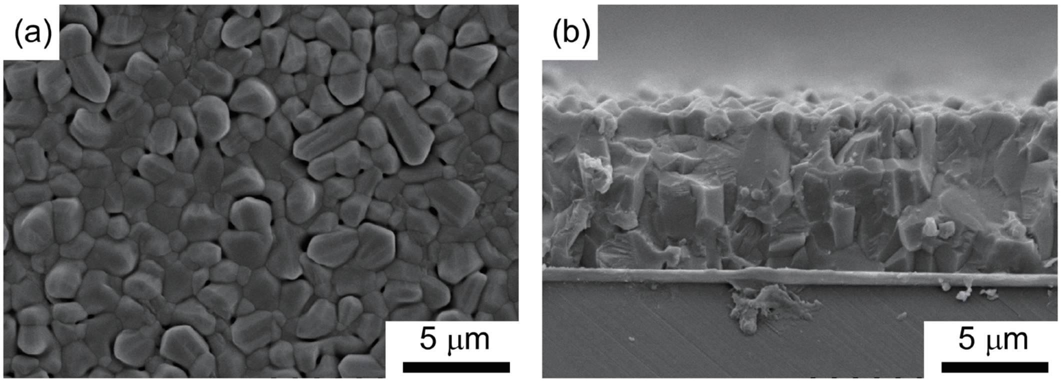


Fig. 1 XRD pattern of $BaTi_2O_5$ film.



(a) (b)

Fig. 2 Morphologies of $BaTi_2O_5$ film: (a) surface and (b) cross section.

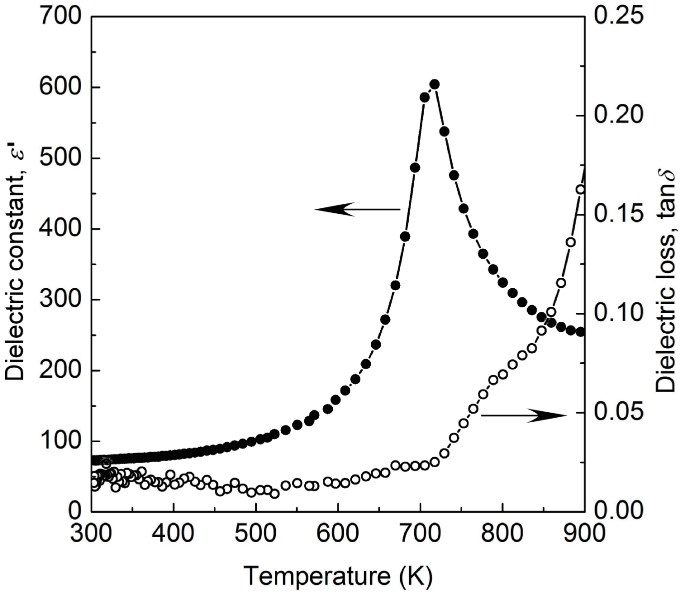


Fig. 3 Temperature dependences of dielectric properties for (511)-oriented $BaTi_2O_5$ thick film.

temperature increased from 300 to 720 K, tanδ showed little temperature dependence. However, when the temperature increased to more than 720 K, tanδ abruptly increased. Akashi *et al.*[6,7] synthesized a $BaTi_2O_5$ single crystal with an anisotropic dielectric property. ε' perpendicular to the (010) plane reached a maximum of 20500 at 748 K, and ε' values perpendicular to the (100) and (001) planes were about 140 and 70, respectively. Randomly oriented $BaTi_2O_5$ thin films have been prepared on $Pt/Ti/SiO_2/Si$ substrates by the sol-gel method, and the values of ε' and tanδ were 55 and 0.063, respectively, at 300 K and 1 MHz.[12] A (112)-oriented $BaTi_2O_5$ thick film prepared by laser CVD on a Pt/MgO(110) substrate exhibited ε' of 67 and tanδ of 0.015.[13] At room temperature (300 K), the ε' value of the (511)-oriented $BaTi_2O_5$ thick film in the present study was close to that of the (112)-oriented $BaTi_2O_5$ thick film, while it was larger than that of randomly oriented $BaTi_2O_5$ films.

4. Conclusions

A (511)-oriented $BaTi_2O_5$ thick film with a high R_{dep} of 65.1 μm/h was deposited on a Pt/MgO(111) substrate by laser CVD. The $BaTi_2O_5$ thick film consisted of rhombic grains and had a columnar cross section. The $BaTi_2O_5$ thick film exhibited ε' of 75 and tanδ of 0.015 at 300 K and 1 MHz. At T_C of 720 K, ε' reached a maximum of 605.

Acknowledgments

This work was supported by the National Natural Science Foundation of China (Grant No. 50902108).

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