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Fabrication and properties of Er-substituted $BaNb_2O_6$ thin films through a chemical route

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Abstract

Tungsten bronze $(Ba,Er)Nb_2O_6$ thin films have been fabricated by chemical solution deposition. Homogeneous and stable precursor solutions were prepared by controlling the reaction of starting metal-alkoxide sources in 2-ethoxyethanol. Tungsten bronze $Ba_{0.66}Er_{0.22}Nb_2O_6$ (BEN66) thin films were successfully fabricated by optimizing the several processing conditions, such as amount of Er substitution. The synthesized BEN66 thin films on Pt/MgO(1 0 0) and Pt/MgO/Si(1 0 0) substrates were found to have *c*-axis (direction of polarization) preferred orientation and to exhibit ferroelectric P–E hysteresis loops. The BEN66 thin films underwent a gradual and frequency dependent phase transition, which is the characteristic behavior along *c*-axis of tetragonal tungsten bronze niobate single crystals.

Keywords: $(Ba,Er)Nb_2O_6$; Tungsten bronze; Thin film; Preferred orientation; Chemical solution deposition; Electrical properties

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1. Introduction

Tungsten bronze niobate crystals are very attractive because of their several excellent properties [1,2]. Ferroelectric tungsten bronze niobate thin films are also expected for applications in several electronic thin film devices. Therefore, the establishment of processing routes for tungsten bronze niobate thin films with desired property is very important. For several ferroelectric applications, tungsten bronze niobate thin films with *c*-axis preferred orientation are strongly required, because the *c*-axis is the direction of polarization of these substances. The advantage of these tungsten bronze niobates over other ferroelectric materials is easy to control the orientation along the direction of polarization. The authors have reported that the preparation and properties of tungsten bronze $(Sr,Ba)Nb_2O_6$- and $(Pb,Ba)Nb_2O_6$-based ferroelectric thin films with *c*-axis preferred orientation on MgO(1 0 0) and Pt/MgO(1 0 0) substrates using metal-organic precursor solutions [3–5].

Recently, rare-earth-substituted barium niobate ($BaNb_2O_6$)-based compounds are receiving great attention as a new ferroelectric tungsten bronze niobate material. $BaNb_2O_6$ does not show any ferroelectric properties, because its crystal structure is not the tungsten bronze type. $BaNb_2O_6$ is reported to consist of two phases, the orthorhombic and the hexagonal metastable phase (low-temperature phase) [6]. On the other hand, rare-earth-ion-modified $BaNb_2O_6$ has the tetragonal tungsten bronze structure, according to the literature [7]. Various $Ba_{3.75}Ln_{0.833}Nb_{10}O_{30}$ [Ln: La–Er, Y]-type bulk ceramics were prepared by the solid-state reaction. However, further investigations to optimize the selection of rare earth elements and the amount of rare-earth-ion substitution into the $BaNb_2O_6$ structure were required to design new ferroelectric compositions leading to a stable ferroelectric tungsten bronze phase and higher Curie temperatures for ferroelectric thin film applications [8–10]. Also, the fabrication of ferroelectric thin films on Si-based

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substrates is indispensable for practical applications to combine with the semiconductor device processes.

We describe the fabrication of highly oriented Er-substituted $BaNb_2O_6$ thin films of the ferroelectric tungsten bronze phase by chemical solution deposition (CSD), because the CSD process has several advantages, such as precise control of composition. In this study, Er ion is chosen as a substituent, because rare-earth-ions of relatively small radii are reported to have high Curie temperatures [7]. The effects of the Er content and substrate on the crystallization of tungsten bronze phase and the electrical properties are examined in order to synthesize tungsten bronze films with the desired crystal orientation and ferroelectric properties.

2. Experimental procedure

Ba metal, $Er(O^iPr)_3$ and $Nb(OEt)_5$ were used as starting materials for preparing a $(Ba,Er)Nb_2O_6$ precursor solution. 2-Ethoxyethanol was selected as a solvent, which was dried over molecular sieves and distilled before use. Ba metal and $Er(O^iPr)_3$ corresponding to a $(Ba_{0.75}Er_{0.167})Nb_2O_6$ (BEN75) or $(Ba_{0.66}Er_{0.22})Nb_2O_6$ (BEN66) composition were dissolved in absolute 2-ethoxyethanol. The solution was refluxed for 18 h and then mixed with $Nb(OEt)_5$ solution. The mixed solution was reacted again at a reflux temperature for 18 h. All the procedures were conducted in a dry N_2 atmosphere. Then, the solution was condensed to approximately 0.2 M by removing the solvent by vacuum evaporation.

Films were fabricated using the precursor solution by spin-coating onto Pt(200 nm)/MgO(1 0 0), Pt(200 nm)/Ir(50 nm)/Ti(50 nm)/SiO_2/Si(1 0 0) and Pt(200 nm)/MgO(50 nm)/Si(1 0 0) substrates. The rotation rate of the substrate and time for spin-coating of the precursor film were set to be 3000 rpm and 30 s, respectively. After the film was heated at 300 °C for 1 h in an O_2 flow at a rate of 1 °C/min, it was heated to a crystallization temperature for 1 h, and then cooled in an O_2 flow at a rate of 5 °C/min. The coating-crystallization process was repeated several times to adjust the thickness of the film.

In order to enhance the orientation growth of films, a thin layer was prepared as a buffer layer on a substrate using a 0.01 M precursor solution under the same coating and heating conditions as described above. The precursor film was then coated onto the precrystallized buffer layer using a 0.2 M precursor solution.

Precursor powder was also prepared from the precursor solution to study the crystallographic phase after heat treatment. The solvent was removed from the precursor solution by vacuum evaporation. The precursor was dried at 100 °C, yielding a brown solid, which was then heat-treated between 600 and 1200 °C in an O_2 flow for 1 h.

The prepared powders and films were characterized by X-ray diffraction (XRD) analysis using Cu Kα radiation with a monochromator and by Raman microprobe spectroscopy. The electrical properties of the films were measured using a Pt top electrode deposited by dc sputtering onto the films and a Pt layer of substrates as a bottom electrode. Measurement of the dielectric properties of the films was conducted in a wafer cryostat using an LCR meter, and the temperature was varied from −190 to 190 °C under vacuum. The P–E hysteresis loops of the films were also evaluated with a ferroelectric test system at a room temperature.

3. Results and discussion

3.1. Crystallization of $(Ba,Er)Nb_2O_6$ precursor powder

Homogeneous and stable $(Ba_{0.75}Er_{0.167})Nb_2O_6$ (BEN75) and $(Ba_{0.66}Er_{0.22})Nb_2O_6$ (BEN66) precursor solutions with sufficient long-term stability were successfully prepared by optimizing the preparation conditions of precursor solutions. The determination of the amount of Er substitution in $BaNb_2O_6$ is important for the synthesis of tungsten bronze $(Ba,Er)Nb_2O_6$ (BEN) thin films. Therefore, prior to the fabrication of thin films, the crystallographic phase of precursor powders after heat treatment was mainly investigated by XRD.

Fig. 1 illustrates the XRD profiles of BEN75 and BEN66 precursor powders heat-treated at 800 °C. These powders were amorphous below 600 °C. In the case of BEN75 powder, a mixture of low-temperature phase similar to that of hexagonal $BaNb_2O_6$ and tetragonal tungsten bronze BEN was formed at 800 °C, and then the sample completely transformed into the single-phase tungsten bronze BEN above 1200 °C. Additionally, Raman spectra of BEN75 powders prepared below 1200 °C contained the scattering modes of hexagonal $BaNb_2O_6$ phase. The crystallization of the hexagonal $BaNb_2O_6$ phase has already been reported by the authors for the alkoxy-derived $BaNb_2O_6$ powders [8]. It revealed that a tetragonal tungsten bronze BEN phase was difficult to obtain in alkoxy-derived BEN75 with relatively small rare

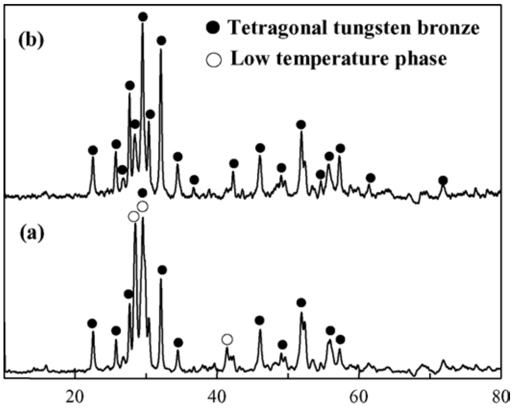

Fig. 1. XRD profiles of (a) $Ba_{0.75}Er_{0.167}Nb_2O_6$ (BEN75) and (b) $Ba_{0.66}Er_{0.22}Nb_2O_6$ (BEN66) precursor powders after heat treatment at 800 °C.

earth ions such as Er. On the other hand, BEN66 precursor powder crystallized in the tetragonal tungsten bronze phase of BEN at around 800 °C, as shown in Fig. 1(b), which was about 400 °C lower than the crystallization temperature of BEN75. This is a result of adopting an appropriate stabilization condition of the optimal amount of Er substitution for the formation of tetragonal tungsten bronze BEN. The composition ratio of Ba and Er was considered to be optimized when the composition of (Ba,Er)Nb_2O_6 was set to be BEN66.

3.2. Fabrication of (Ba,Er)Nb_2O_6 thin films on substrates

In this study, thin film fabrication was performed using a BEN66 composition on the basis of the crystallization behavior of BEN75 and BEN66 precursor powders described in the previous section. Fig. 2 illustrates the XRD profile of BEN66 thin film on a Pt/MgO(1 0 0) substrate heat-treated at 800 °C. This film has strong 0 0 1 and 0 0 2 reflections, as shown in Fig. 2. The BEN66 thin films on Pt/MgO(1 0 0) substrates crystallized into the desired tetragonal tungsten bronze phase with 0 0 *l* preferred orientation. The lattice parameters of BEN66 was calculated from the XRD data of powder sample to be $a = 12.439$ Å and $c = 3.934$ Å, respectively. The crystallization of BEN66 films with *c*-axis preferred orientation results from the crystallographic matching of the *c*-plane of BEN66 to Pt/MgO(1 0 0), similar to the cases of other alkoxy-derived tungsten bronze niobate thin films reported by the authors [3–5]. Furthermore, Raman spectrum of the BEN66 thin film revealed that the synthesized film crystallized into the tetragonal tungsten bronze phase confirmed by the comparison with that of tetragonal tungsten bronze BEN66 powder.

For practical integrated device applications, the fabrication of thin films on Si-based substrate is strongly required. Therefore, BEN66 thin films were also prepared on Pt/Ir/Ti/SiO_2/Si(1 0 0) and Pt/MgO/Si(1 0 0) substrates. Fig. 3 illustrates the XRD profiles of BEN66 thin films on Pt/Ir/Ti/SiO_2/Si and Pt/MgO/Si substrates after heat treatment. In the case of BEN66 thin film on Pt/Ir/Ti/SiO_2/Si, synthesized films were polycrystalline having relatively low 0 0 *l* preferred orientation, as shown in Fig. 3(a). On the other hand, BEN66 thin film on Pt/MgO/Si crystallized into the desired tungsten bronze phase having 0 0 *l* preferred orientation. These results indicate that MgO layer between Pt and Si is effective in obtaining 0 0 *l*-oriented tungsten bronze films as in the case of BEN66 films on Pt/MgO(1 0 0). Although the growth mechanism of the MgO layer is not clear now, (1 0 0)-oriented MgO may be grown on Si(1 0 0) as reported by Senzaki et al. [11]

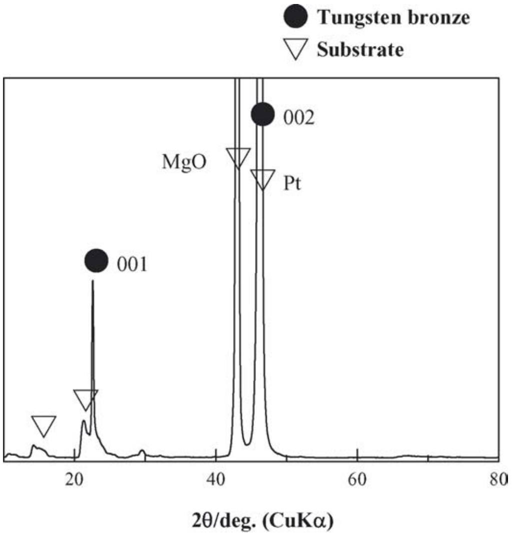

Fig. 2. XRD profile of BEN66 thin films on a Pt/MgO(1 0 0) substrate heat-treated at 800 °C.

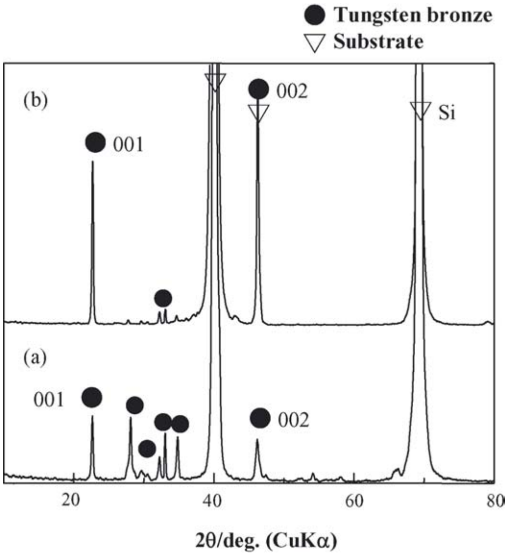

Fig. 3. XRD profiles of BEN66 thin films on (a) Pt/Ir/Ti/SiO_2/Si(1 0 0) and (b) Pt/MgO/Si(1 0 0) substrates heat-treated at 800 °C.

According to the SEM observation, the synthesized films appeared crack free and dense and had a smooth surface with uniform thickness. The quality of the films was found to be sufficient for the characterization of electrical properties.

3.3. Dielectric and ferroelectric properties of (Ba,Er)Nb_2O_6 thin films

Fig. 4 shows the temperature dependence of the dielectric constant for BEN66 thin film on Pt/MgO/Si(1 0 0) substrate in the comparison with the data of BEN66 thin film on Pt/MgO(1 0 0). The thickness of the films was 0.6 μm. In the case of BEN66 thin film on Pt/MgO/Si, the maximum dielectric constants of approximately 400 were observed at 170 °C at 10 kHz. Also, for both BEN66 thin films on Pt/MgO(1 0 0) and Pt/MgO/Si, the values of dielectric constant depend upon the frequency of measurement, as shown in Fig. 4. In addition, since the peaks of the ε–T curves were broad, the BEN66 films were found to exhibit diffuse phase transition. This behavior is a characteristic property of tungsten bronze niobate single

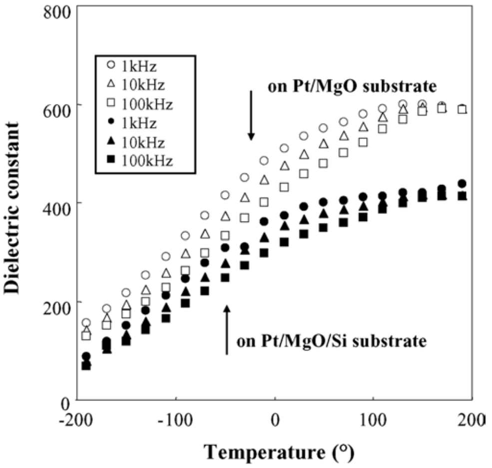

Fig. 4. Temperature dependence of dielectric constants of $Ba_{0.66}Er_{0.22}Nb_2O_6$ thin films on Pt/MgO(1 0 0) and Pt/MgO/Si(1 0 0) substrates crystallized at 800 °C.

crystal along the *c*-axis [12]. The grain size of the BEN66 thin films was confirmed to be about 80–100 nm from atomic force microscope (AFM) images. The small grain size is considered to be responsible not only for the broadening of ε–T curves but also for the lower Curie temperature compared with reported data of $(Ba,Er)Nb_2O_6$ bulk ceramics [7].

On the other hand, the low dielectric constants of approximately 30–60 were observed at 1–100 kHz in the case of the BEN66 films on $Pt/Ir/Ti/SiO_2/Si$ substrates. Also, the dielectric constant did not depend upon the temperature of measurement so much. This behavior is mainly due to the low 0 0 *l* preferred orientation of the BEN66 film on $Pt/Ir/Ti/SiO_2/Si$ and the large anisotropy of dielectric properties of tungsten bronze niobate crystals reported by Huang et al. [12]

Fig. 5 shows the P–E hysteresis loop of BEN66 thin film on Pt/MgO(1 0 0) measured at room temperature. The hysteresis loop of the BEN66 film showed a remanent polarization (P_r) of 3.2 μC/cm^2 and a coercive field (E_c) of 30 kV/cm. Therefore, the BEN66 thin film was ferroelectric at room temperature.

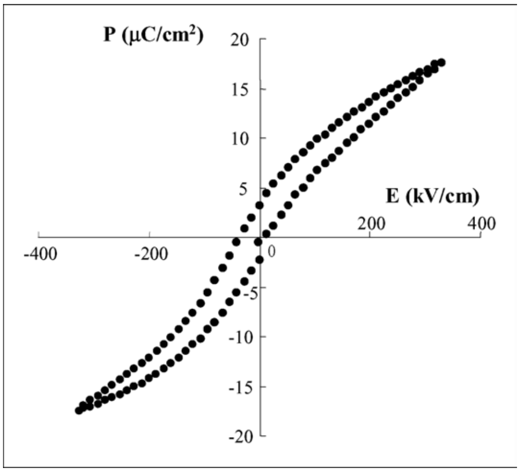

Fig. 5. P–E hysteresis loop of BEN66 thin film on a Pt/MgO(1 0 0) substrate measured at room temperature.

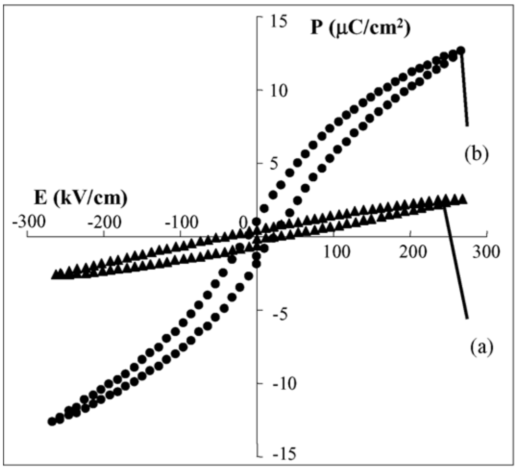

Fig. 6. P–E hysteresis loops of BEN66 thin films on (a) $Pt/Ir/Ti/SiO_2/Si(1\,0\,0)$ and (b) Pt/MgO/Si(1 0 0) substrates measured at room temperature.

Fig. 6 shows the P–E hysteresis loops of BEN66 thin films on $Pt/Ir/Ti/SiO_2/Si(1\,0\,0)$ and Pt/MgO/Si(1 0 0) substrates measured at room temperature. It can be seen from Fig. 6 that the synthesized BEN66 film on $Pt/Ir/Ti/SiO_2/Si$ did not show sufficient ferroelectricity at room temperature, because the degree of *c*-axis (direction of polarization) orientation of the film was low, as shown in Fig. 3. On the other hand, the BEN66 thin film on Pt/MgO/Si showed a typical P–E hysteresis loop at room temperature, as shown in Fig. 6(b), because the Curie temperature of the film was clearly observed approximately 170 °C at 10 kHz, as shown in Fig. 4. The P_r and E_c values of the BEN66 film on Pt/MgO/Si were found to be about 1.3 μC/cm^2 and 20 kV/cm, respectively. Although the values of dielectric constant and P_r were relatively low, the dielectric and ferroelectric behaviors of the BEN66 thin film on Pt/MgO/Si were similar to those of BEN66 on Pt/MgO(1 0 0). The current $(Ba,Er)Nb_2O_6$ films also require further optimization of the processing conditions in order to improve their dielectric and ferroelectric properties. Synthesis of BEN films at lower temperatures on Si-based substrates is also now in progress.

4. Conclusions

Highly oriented Er-substituted $BaNb_2O_6$ thin films with a tungsten bronze structure were successfully synthesized on Pt/MgO(1 0 0) and Pt/MgO/Si(1 0 0) substrates from a metal-organic precursor solution. The substitution of the Ba^{2+} site in $BaNb_2O_6$ by Er in the appropriate amount was quite effective in fabricating the tetragonal tungsten bronze film. The tungsten bronze $Ba_{0.66}Er_{0.22}Nb_2O_6$ (BEN66) thin films with preferred orientation along the direction of polarization exhibited the diffuse phase transition and the ferroelectric P–E hysteresis loops at room temperature. The ferroelectric

BEN thin films developed in this study open the avenue to various thin film device applications.

Acknowledgement

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References

[1] M.H. Francombe, Acta Crystallogr. 13 (1960) 131–140.

[2] B. Jaffe, W.R. Cook Jr., H. Jaffe, Piezoelectric Ceramics, Academic Press Limited, New York, 1971, pp. 213–235.

[3] W. Sakamoto, T. Yogo, A. Kawase, S. Hirano, J. Am. Ceram. Soc. 81 (1998) 2692–2698.

[4] W. Sakamoto, K. Kosugi, T. Yogo, S. Hirano, Jpn. J. Appl. Phys. 37 (1998) 5215–5219.

[5] W. Sakamoto, K. Kosugi, T. Arimoto, T. Yogo, S. Hirano, J. Sol–Gel Sci. Tech. 16 (1999) 65–75.

[6] O. Yamaguchi, K. Matsui, K. Shimizu, J. Am. Ceram. Soc. 68 (1985) C-173–C-175.

[7] N. Wakiya, J.-K. Wang, A. Saiki, K. Shinozaki, N. Mizutani, J. Eur. Ceram. Soc. 19 (1999) 1071–1075.

[8] W. Sakamoto, Y. Horie, T. Yogo, S. Hirano, Integr. Ferroelectr. 36 (2001) 191–200.

[9] W. Sakamoto, M. Mizuno, Y. Horie, T. Yogo, S. Hirano, Jpn. J. Appl. Phys. 41 (2002) 6647–6652.

[10] W. Sakamoto, M. Mizuno, T. Yamaguchi, K. Kikuta, S. Hirano, Jpn. J. Appl. Phys. 42 (2003) 5913–5917.

[11] J. Senzaki, O. Mitsunaga, T. Uchida, T. Ueno, K. Kuroiwa, Jpn. J. Appl. Phys. 35 (1996) 4195–4198.

[12] W.-H. Huang, D. Viehland, R.R. Neurgaonkar, J. Appl. Phys. 76 (1994) 490–496.