Ba$_2$NaNb$_5$O$_{15}$ thin film formed by electron cyclotron resonance plasma sputtering

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Abstract. Ba$_2$NaNb$_5$O$_{15}$ (BNN) thin films were formed on sapphire (0001) substrates and magnesium oxide substrates using electron cyclotron resonance plasma sputtering. The BNN films were 7.2-8.4 µm thick and had atomic ratio compositions of Ba=2.0-2.1/5Nb and Na=0.9-1.1/5Nb. The films had no cracks. Single-phase BNN and (001)-oriented BNN films on sapphire (0001) were obtained at 823 K and 923 K. An in-plane-oriented BNN film on sapphire (0001) was formed at 923 K. The films were transparent and had the ability of second harmonic generation. The films on magnesium oxide (100) were also single-phase BNN, and (001)-oriented BNN films were obtained at 823 K, 873 K, and 923 K. An in-plane-oriented BNN film on magnesium oxide (100) was formed at 823 K. The films were transparent.

1. Introduction

Ba$_2$NaNb$_5$O$_{15}$ (BNN) with a tungsten bronze structure has large nonlinear optical and Pockels coefficients [1,2,3]. Optical damage is less likely to occur in BNN compared to LiNbO$_3$ [4]. Therefore, BNN is a useful material for optical IC, piezoelectric devices, and other optical devices [5]. However, single BNN crystals tend to become cracked because of a sharp change in the coefficient of thermal expansion of the c-axis around 800-850 K during cooling from the melting temperature, and it is difficult to form single crystals with high transmittance by melting [6,7]. Application of BNN to optical IC requires the formation of thin films, preferably crystalline films. Even so, when preparing thin films by, for example, RF sputtering, cracks develop, and it becomes difficult to form BNN thin films with high transmittance or high levels of other optical abilities.

BNN thin films were prepared without cracking on sapphire (1120) and (012) substrates using electron cyclotron resonance (ECR) plasma sputtering (ES037; Sumitomo Metal Industries, Ltd.) in our previous studies [7-9]. This system generates ECR plasma with high electron density, so the substrate temperature is low during film formation and compositional deviation is not likely [10]. There is compositional deviation in BNN film deposition because Na has high vapor pressure; we reported on the amount of deviation and a method for controlling deviation [7,8]. In this study, we report on various BNN films formed by ECR plasma sputtering on sapphire (0001) of hexagonal crystal structure and magnesium oxide (MgO) single-crystal substrates of cubic crystal structure, crystal

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orientations of resulting BNN films. In addition, second harmonic generation (SHG) waves were measured for the BNN films on sapphire (0001).

2. Experimental Procedures
In ECR plasma sputtering, microwaves (2.45 GHz, 800 W) were introduced into a plasma chamber through a rectangular waveguide, and a magnetic field (87.5 mT) for ECR was applied to generate ECR plasma, as shown in Figure 1. Target raw materials were BaCO₃ (99% pure, Wako Pure Chemical Industries, Ltd.), Na₂CO₃ (JIS primary standard, Wako), and Nb₂O₅ (99.9% pure, Wako). The materials were mixed in an agate mortar, calcined for 12 h at 1073 K in the air, mixed again, and then sintered for 12 h at 1373 K [7,8]. Then, 10 mm×10 mm substrates with Pt film or no Pt film (for transmittance measurement) were heated with an infrared lamp to 773-923 K. After the film formation chamber was evacuated to 1×10⁻⁴ Pa, 2.5×10⁻⁵ m³/min argon gas and 2.5×10⁻⁵ m³/min oxygen gas were introduced into the plasma chamber to form film at 0.1 Pa. In the case of the formation of multimodal films, the experiment was halted every 2 h to cool the system, dividing the experiment into 13 periods. The BNN films obtained were several microns thick. To avoid film discontinuity caused by dividing the experiment, we pre-sputtered the films for 5 min before each cycle for activation during film growth. The consistency of the film’s thickness was evaluated based on the film’s composition and texture. The BNN films were 7.2-8.4 µm thick and had atomic ratio compositions of Ba=2.0-2.1/5Nb and Na=0.9-1.1/5Nb. The samples were checked by eye and by scanning electron microscopy (SEM). Crystal structures and orientations of the films were measured by X-ray diffraction (XRD, RAD-C, Rigaku). In-plane orientations of the films were measured by pole figure (RAD-C, Rigaku) using BNN (402) peaks. Transmittances of the films were measured by a spectrophotometer (UV-31010PC, Shimadzu). SHG waves were measured using a Nd³⁺: YAG laser of 1.06 µm wavelength. The laser was applied at a 45° angle with respect to the BNN film surface, and the spectrometer was located in another 45° direction.

3. Results and Discussion
3.1 Ba₂NaNb₅O₁₅ thin films on sapphire (0001) plane substrates
None of the surfaces of the films formed at the substrate temperature of 823 K, 873 K, or 923 K had any cracks, and all were transparent by visual observation. As shown in the SEM photograph in Fig. 2, the films had no cracks in their surfaces or their interiors. Formation temperatures of the films were lower than those of typical melting processes, such as BNN single crystal formation by the Czochralski method [6,7], and therefore no cracks were formed on the BNN films during the decrease of temperature from the deposition temperature to room temperature. Though the formation of each film needed 13 periods of deposition by ECR plasma sputtering, discontinuous interaction was not observed in the cross sections of the films and the films were formed uniformly, as occurred in our previous study [8]. A BNN thin film formed at 773 K had a smooth surface in our previous study [8],
but angular shapes were observed on the surface of the BNN films in the present study. The XRD patterns of the films had peaks only of BNN, as shown in Fig. 3. This indicated that single-phase BNN was deposited on sapphire (0001) without cracking using the low-temperature process of the ECR plasma sputtering method. The film formed at 873 K had lower (00l)-orientation, which might have

Fig. 2 SEM photographs of BNN films formed on sapphire (0001) substrates at (a) 923 K, (b) 873 K, (c) 823 K.

Fig. 3 XRD patterns of BNN films formed on sapphire (0001) substrates at 823-923 K. (Index numbers are BNN.)

Fig. 4 Pole figure of BNN films formed on sapphire (0001) substrates at 823 K.

Fig. 5 Pole figure of BNN films formed on sapphire (0001) substrates at 923 K.
caused the formation of the jagged structure of the surface of the film. The BNN thin films formed at 823 K and 923 K were (00l)-oriented films. Pole figures of BNN films are shown in Figs. 4 and 5. The BNN film formed at 823 K had no in-plane orientation, but that formed at 923 K did have in-plane orientation of sapphire <100> // BNN <010>, sapphire (0001) // BNN (001). BNN single crystal had a sharp change in the coefficient of thermal expansion of the c-axis around 800-850 K [6,7]; thus, the BNN film formed at 823 K might not have in-plane orientation. A cause of the 3-direction in-plane orientation might have been that sapphire has a hexagonal crystal structure and 11 times the A-O distance of the a-axis in sapphire (0001) is an 0.8% mismatch of the BNN b-axis. Transmittances of the BNN films are shown in Fig. 6. The BNN films had lower transmittances than those formed at 823 K, but the BNN films in this work had high transmittances at high wavelengths. The transmittance of the polycrystalline BNN film formed at 823 K was the lowest. SHG measurement results of BNN films are shown in Fig. 7. All BNN films formed at 823-923 K showed 532-nm SHG waves, and the BNN film with low transmittance had a high SHG peak. The BNN film with the highest SHG ability was formed at 873 K and was polycrystalline. A laser with one direction might form SHG waves with the polycrystalline BNN film effectively because the nonlinear optical coefficients of BNN are anisotropic; $d_{31}=-13.2\times10^{-12}$, $d_{32}=-13.22\times10^{-12}$, and $d_{33}=-18.2\times10^{-12}$ m/V [4].

![Fig. 6 Transmittances of BNN films formed on sapphire (0001) substrates at 823-923 K.](image)

![Fig. 7 SHG using a Nd$^{3+}$: YAG laser (1.06 µm wavelength) and BNN films formed on sapphire (0001) substrates at 873 K.](image)

3.2 Ba$_2$NaNb$_5$O$_{15}$ thin films on sapphire MgO substrates
The XRD patterns of the samples had only peaks of BNN, as shown in Fig. 8. Single-phase BNN was also deposited on MgO substrates. The BNN thin films formed at 823 K, 873 K, and 923 K were (00l)-oriented films. A pole figure of the BNN film formed at 823 K is shown in Fig. 9. The BNN thin film had in-plane orientation at a lower substrate temperature than the deposition temperature of in-plane-oriented BNN on sapphire (0001). The BNN single crystal had a sharp change in the coefficient of thermal expansion of the c-axis around 800-850 K [6,7], and the BNN film on sapphire (012) was also not in-plane oriented [8]. MgO might be more congenial to BNN than sapphire at 823 K. The films formed at 823 K on MgO (100) substrate had 2 patterns of 4-direction in-plane orientation, and the direction pattern of in-plane orientation was different from the 3-direction in-plane orientations of the films on sapphire (0001). Though matching positions of atoms between BNN and MgO were not clear, the cause of 4-direction in-plane orientations might be that MgO had a cubic crystal structure of 4-times rotational symmetry.
4. Summary

By the ECR plasma sputtering method, we formed BNN single-phase thin films without any cracks on sapphire (0001) substrates and MgO (100) substrates. The crystal orientations of the films on sapphire (0001) were different from those of the films on MgO (100) substrates. The in-plane-oriented BNN thin film was formed at 923 K. The films had second harmonic generation ability. BNN single-phase thin films were also formed on MgO (100) substrates, in which case the in-plane-oriented BNN thin film was formed at 823 K. SHG waves were observed by the films on sapphire (0001) using a Nd<sup>3+</sup>-YAG laser. These results indicate that the ECR plasma sputtering method is useful for forming single-mode thin BNN film and multimodal BNN film, and this method is expected to be useful for preparing optical BNN films for optical and piezoelectric IC.

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