Tungsten-Bronze Ba$_2$NaNb$_5$O$_{15}$ and Layer-Structured Bi$_4$Ti$_3$O$_{12}$ Ferroelectric Thin Films

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INTRODUCTION

Recently, considerable attention has been centered on the development in film technologies of ferroelectric materials for many useful electronic and optical devices such as optical memory, display, non-linear, DRAM and nonvolatile memory devices (FRAM), because these materials have excellent dielectric, piezoelectric and optical properties. Presently, several attempts have been made to form layer structured ferroelectric Bi$_4$Ti$_3$O$_{12}$ (BIT) and tungsten bronze typed ferroelectric Ba$_2$NaNb$_5$O$_{15}$ (BNN) thin films by ECR and RF planar magnetron sputtering using a ceramic target. So far many electrical properties of the modified hot-forging BIT ceramics have been mainly studied. [1] It is known that RF sputtering enables the epitaxial growth of BIT film on single crystalline MgO substrates and the preferred orientation is c-axis on Si substrates. [2,3,4] The present paper describes the epitaxial growth of BIT films on sapphire substrates by the ECR plasma sputtering, deposition of BNN films on Pt/Al$_2$O$_3$ substrates by the RF magnetron sputtering method and dielectric, ferroelectric, optical and crystallographic properties.

EXPERIMENTAL PROCEDURE

An electron cyclotron resonance (ECR) plasma sputtering apparatus (Sumitomo Metal ES037) was used for BIT films. A ring shaped sintered Bi$_4$Ti$_3$O$_{12}$ was used as a target. The sapphire single-crystal substrates, having crystal planes of A, R and C planes, were used. For BIT film, the sapphire substrate was heated to 640 °C using an infrared lamp. The apparatus was evacuated with turbomolecular pump up to 5.1×10$^{-7}$Pa and 50% Ar, 50% O$_2$ mixture gas was introduced into its chamber. BNN films were deposited by a RF magnetron sputtering apparatus (ANELVA: SPF210A). For BNN films, the alumina substrate, having less than 1 μm surface roughness, was heated to 800 °C using a nichrom heater. The apparatus was evacuated with rotary and diffusion pumps up to 2×10$^{-5}$Pa and then 90% Ar, 10% O$_2$ mixture gas was introduced into its chamber. The chamber pressure was varied from 8×10$^{-2}$ to 8Pa.

The structures of BIT and BNN films were analyzed by X-ray diffraction (XRD)(Rigaku RAD-C system). The texture was observed by using a scanning electron microscope(SEM)(Akashi ALPHA 30). Furthermore, reflection high-energy electron diffraction (RHEED) patterns were also used in the film evaluation. The amount of metal elements (Ba,Na,Nb) of the BNN films was analyzed quantitatively by a fluorescence X-ray apparatus (Rigaku-3030, 40kV, 20mA). The dielectric constant was measured at 1kHz with a ADEX-221A LCR meter. Reflective coefficients of BIT films were observed by an optical system and refractive indices of the films were calculated from the measured Brewster angle $\theta_B=tan^{-1} (n_2/n_1)$, where $n_1$ and $n_2$ are refractive indices of
air and the BIT film, respectively. The remnant polarization and coercive field were obtained from the 50Hz D-E hysteresis loop, using a modified Sawyer-Tower circuit.

RESULTS AND DISCUSSIONS

Figure 1 shows the XRD pattern of the BIT films prepared at Tsub=400, 500 and 640 °C on the sapphire C plane. As seen in Fig.1 (c), the film deposited at 400°C consists of a pyrochlore type oxide, Bi2Ti2O7. The BIT films at temperatures above about 500°C are orientated to (104) [Fig.1(a) and (b)]. The line width of each peak becomes narrower with increasing the substrate temperature. The half-width of the rocking curve of the BIT film prepared at 640°C is about 0.3°.

This half width is almost the same as the half width (0.5°) of the PLZT film and AlN film with good crystallinity[5].

The diffraction patterns of BIT films are indexed with the pseudo-tetragonal system because of nearly equal length of the a- and b-axes (a=5.45 Å, b=5.41 Å and c=32.82 Å).

From RHEED and X-ray results, it is clear that thin films were epitaxially grown on (1120) Al2O3 || (001) BIT, (1102) Al2O3 || (001) BIT and (0001) Al2O3 || (104) BIT, respectively. These relationships were explained because of the nearness of the oxygen atoms in the crystals of sapphire and BIT.

Figure 2 shows the temperature dependence of the dielectric constant calculated from measured capacitance C of an interdigital electrode on the top of the film using the approximation proposed by Farnell et al.[6] The values of the dielectric constant and dielectric loss factor of the film at room temperature are 194 and 0.015, respectively.

No dielectric constant peak of the Curie point was not observed for the specimen in the range of 20 to 420°C. The angular dependence of the reflective coefficient is shown in Fig.3. Relationship between refractive index n1 and Brewster angle (θB) is expressed by n1=tan⁻²θB.

From this formula, θB and n1 are calculated to be 68.7° and 1.88, respectively. Open and closed symbols shown in Fig.3 are the maximum and the minimum values of reflective coefficient at two parts of the BIT film, respectively, and the solid line is the computer fitting result calculated from Snell’s and Fresnel’s laws. The differences between observed and calculated results are large in the vicinity of low incident angle. It appears that the phase difference of light occurs because of an interference phenomenon according to a multireflection of light. Since every light transmits at the Brewster angle, the difference is almost negligible. Furthermore, the difference between observed and
calculated values are small above the Brewster angle.

![Graph 1](image1)

**Figure 2.** Temperature dependence of dielectric constant and dielectric loss factor.

![Graph 2](image2)

**Figure 3.** Angular dependence of dielectric coefficient.

The sputtering time dependence of the chemical compositions and deposited amount of BNN films are shown in Fig. 4, under the substrate temperature 800°C and input RF power 150W. When the sputtering time is shorter than 4 hours, the BNN film chemical composition deviates largely from the chemical composition of the BNN ceramic target. However, with increasing sputtering time to 6 or 8 hours, the deposited film composition comes close to the target composition. The deposited weight and film thickness are linearly proportional to the sputtering time. In this case, the deposited weight and the film growth rate are about 13.5μg/min and 5.42nm/min, respectively. It is considered that the sputtering rate depends on materials and, respectively, the deposited rate of Nb element is slower than that of Ba and Na.

The time constant (τ) of the deposited curve may be assumed as the inverse of reaction rate and, these values for Ba, Na and Nb are determined 155×10^{-6}, 210×10^{-6} and 140×10^{-6} (S), respectively. At the beginning, a tungsten-bronze type compound was not obtained but, owing to increasing the sputtering time (therefore, increasing the deposited amount of Nb), the tungsten-bronze structured BNN compound was synthesized.

The chemical compositions of samples deposited for 2 and 8 hours are Ba_{3.12}Na_{1.318}Nb_{5.276}O_{1.156} and Ba_{1.426}Na_{0.867}Nb_{5.046}O_{14.485}, respectively. These results are in good agreement with the phase diagram of BaNb_{2}O_{6}-NaNb_{2}O_{5} system reported by B.A. Scott et al. [7] BNN tungsten-bronze compounds are synthesized with broad composition of BaNb_{2}O_{6} from 67 to 80% similar to single crystal compositions.

From the X-ray diffraction result of BNN film, as the sputtering time is longer, the chemical composition of deposited films shows a tendency to become similar to that of the BNN ceramic target. The deposited sample sputtered for 2 hours is not shown to be crystallized.

It seems that Ba, Na and Nb ions sputtered in plasma are deposited amorphously on the substrate and, as the sputtering time is longer from 4 to 8 hours, the deposited film thickness is increased and the amorphous film changes to NaNb_{2}O_{5}, Ba_{2}Nb_{2}O_{6} and Ba_{2}NaNb_{4}O_{15} complex compounds by chemical reactions. The lattice parameters are a=17.628 Å, b=17.732 Å and...
c=7.966Å calculated from (600), (420) and (004) planes, respectively.

The lattice constants are consistent with values reported by Van Uitert et al.[8] The orientation along the c-axis is stronger under the lower gas pressure.

The dependence of dielectric constant on temperature is shown in Fig. 5. The dielectric constant and the loss factor (tan\(\delta\)) increase sharply with increasing temperature over the temperature from 300 to 400°C, therefore the Curie temperature of the film is not detected. The loss factor curve changes weakly in the vicinity of 200°C. This peak is believed to be the transition point between orthorhombic and tetragonal ferroelectric phases. The dielectric constant and loss factor are 141 and 0.02 at room temperature, respectively.

To examine the ferroelectric behavior of this film, the polarization switching was observed using a Sawyer-Tower circuit at 50Hz. As seen in the hysteresis loop of this film, the polarization is not saturated. The remnant polarization \(P_r\) is 32\(\mu\)C/cm\(^2\) and coercive field \(E_c\) is 576V/mm.

The electrical resistivity decreases sharply in the vicinities of 250 and 450°C. This electrical conducting behavior is similar to the temperature dependence of dielectric loss factor. The leakage current density at 8kV/cm is \(1.706 \times 10^{-6}\)A/cm\(^2\).

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**References**


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