Preparation of Ba$_2$NaNb$_5$O$_{15}$ Thin Films by the Sol-Gel Method

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Ba$_2$NaNb$_5$O$_{15}$ thin films were prepared on Pt and quartz substrates by the sol-gel method using Ba(CH$_3$COO)$_2$, NaNO$_3$ and Nb(O-n-Bu)$_5$. Very smooth surface films with a single phase of Ba$_2$NaNb$_5$O$_{15}$ were obtained by heat treatment at 800°C for 1 h. The remanent polarization and coercive field estimated from the ferroelectric hysteresis loop were 3.5 μC/cm$^2$ and 21.6 kV/cm, respectively. The dielectric constant and tanδ at room temperature were 176 and 0.03, respectively. The thin films on quartz substrates were optically transparent in the visible to ultraviolet region. It is expected that Ba$_2$NaNb$_5$O$_{15}$ thin films will be applied to ferroelectric memories and optoelectronic devices. [Received November 11, 1996; Accepted April 1, 1997]

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1. Introduction

Ferroelectric materials have been applied to actuators, SAW filters and sensors due to their piezoelectric and pyroelectric properties. In recent years, ferroelectric thin films have attracted a great deal of attention for use on memory devices in large-scale integrated circuits (high density DRAM and nonvolatile memories) and/or optoelectronic devices. Fabrication of perovskite and Bi-layer-structure ferroelectric thin films have been extensively studied for application to memory devices, for example, (Ba, Sr)TiO$_3$, (Pb, Zr)TiO$_3$, Bi$_4$Ti$_3$O$_{12}$ and SrBi$_2$Ta$_2$O$_9$.

Ferroelectric barium sodium niobate, Ba$_2$NaNb$_5$O$_{15}$ (BNN), has a tetragonal tungsten bronze structure, which belongs to the point group of mm2 at room temperature. The spontaneous polarization and dielectric constant parallel to the c-axis are 40 μC/cm$^2$ and 40, respectively. These large spontaneous polarization and low dielectric constant are advantageous for application to nonvolatile memories. Furthermore, the nonlinear optical coefficients of BNN are twice as large as those of LiNbO$_3$ and 20 times higher than those of KH$_2$PO$_4$. BNN is resistant to UV irradiation and does not exhibit any optically induced inhomogeneities of the refractive index that occur in LiNbO$_3$.

Thus, the combination of good ferroelectric, electro-optic and nonlinear optic properties enables BNN thin films to be used both in electronic memory devices and for laser communication. The preparation of BNN thin films is very important for integrated circuits. Recently, BNN thin films were prepared by the rf magnetron sputtering method. However, the chemical composition of the obtained films deviated from that of the BNN ceramic target. As a result, the ferroelectric properties were poor. However, the sol-gel process is one of the best methods of preparing thin films from the viewpoints of precise composition control, low-temperature heat treatment and simplicity.

In this paper, preparation of BNN thin films by the sol-gel process is reported.

2. Experimental

Figure 1 shows the preparation process of the BNN precursor solution. Barium acetate [Ba(CH$_3$COO)$_2$], sodium nitrate [NaNO$_3$] and niobium penta-n-butoxide [Nb (O-n-Bu)$_5$] were used as starting materials. Barium acetate (5.0 × 10$^{-3}$ mol) was dissolved at 80°C in acetic acid [CH$_3$COOH] (5 ml). The solution was dehydrated at 110°C for 6 h and cooled to room temperature. The solution was stirred for 4 h, then sodium nitrate (2.5 × 10$^{-3}$ mol) was added. The solution was stirred for an additional 4 h at room temperature.

[Fig. 1 Preparation process for BNN sol-gel solution]
The barium acetate solution and the niobium penta-n-butoxide solution with added sodium nitrate were mixed and stirred for 4 h at room temperature. The final concentration of the BNN precursor solution was 0.4 mol/l. Thermal analysis of the BNN precursor solution was performed by thermogravimetry-differential thermal analysis (TG-DTA) in order to determine the conditions to prepare BNN thin films.

Precursor thin films were prepared by spin-coating at 4000 rpm for 10 s onto Pt and fused quartz substrates. The preparation process for thin films is shown in Fig. 2. After spin-coating, the BNN precursor films were dried on an electric hot plate at 200°C for 10 min in air and then calcined at 600°C for 5 min using an infrared lamp. The above processes were repeated 20 times to obtain the 500 nm-thick BNN films. Finally, those thin films were heat-treated in O2 gas at 600, 700 and 800°C for 1 h to determine the effects of heat on the crystallization.

Measurement of the crystallinity of the obtained thin films was performed by X-ray diffraction (XRD) using monochromatized Cu Kα radiation. Surface morphology was observed using a scanning electron microscope (SEM). The dielectric constant, \( \varepsilon_r \), and dielectric loss, tan δ, were measured using an LCR meter. D-E hysteresis loops were observed using a Sawyer-Tower bridge with a triangular field of 100 Hz. The transparency of thin films was measured by a spectrometer.

3. Results and discussion

3.1 TG-DTA of the BNN precursor solution

TG-DTA curves of the BNN precursor solution were shown in Fig. 3. Weight loss with endothermal anomaly up to 190°C is due to the evaporation of CH3COOH and HOC2H4OC2H5. The exothermal anomaly apparent at around 250°C shows the combustion of organic components. After thermal decomposition of the solution at about 400°C, no additional thermal anomalies or weight loss were recognized. Thus, we determined preparation conditions such as drying at 200°C for 10 min and calcination at 600°C for 5 min, as shown in Fig. 2.

3.2 Characterization of BNN thin films

XRD patterns of thin films prepared on Pt substrates by heat treatments at 600, 700 and 800°C in O2 gas were shown in Fig. 4. It is apparent that the thin films obtained at 600 and 700°C include a BNN phase together with a small amount of the BaNb2O6 phase. The tungsten-bronze BNN single phase could be identified if the precursor films were heated at 800°C. The lattice constants were estimated to be \( a = 1.764 \) nm and \( c = 0.794 \) nm. In the case of the thin films prepared on quartz plates, we obtained similar XRD patterns as those of the thin films on Pt plates.

SEM micrographs of the surface morphology of the resultant thin films are shown in Fig. 5. It is clear that the grain growth was not significant in films heated at 600 and 700°C. The surface microstructure of BNN thin films obtained at 800°C shows dense, fine grains with an average size of 500 nm.

A 500 nm-thick BNN film prepared on a Pt plate at 800°C for 1 h shows a ferroelectric hysteresis loop, as shown in Fig. 6. The remanent polarization \( P_r \) and coercive field \( E_c \) estimated from the hysteresis loop were 3.5 \( \mu C/cm^2 \) and 21.6 kV/cm, respectively, at room temperature. It is considered that the remanent polarization is relatively small due to the random orientation of the BNN grains in the thin film. The dielectric constant, \( \varepsilon_r \), was 176 at 1 kHz.

The BNN thin films were optically transparent from 350 nm to the visible region. Although the optical transmission depends on the film thickness and grain size, it is clear that transmission over 60% is obtained even in BNN thin films.
4. Summary

Ba$_2$NaNb$_5$O$_{15}$ (BNN) thin films were prepared on Pt and fused quartz substrates using the sol-gel process with Ba(CH$_3$COO)$_2$, NaNO$_3$ and Nb(O(CH$_2$)$_3$CH)$_5$ as starting materials and CH$_3$COOH and CH$_3$OC$_2$H$_4$OC$_2$H$_4$OH as solvents.

BNN single-phase thin films, prepared using the heat treatment at 800°C for 1 h, were optically transparent down to 30 nm. A relatively good ferroelectric hysteresis loop was observed, from which the remanent polarization of 3.5 $\mu$C/cm$^2$ and the coercive field of 21.6 kV/cm were estimated.

Study of the electrical and optical properties of the BNN thin films is now in progress.

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