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Preparation of $Ba_2NaNb_5O_{15}$ Thin Films by Pulsed Laser Ablation and Their Characterizations

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Abstract

$Ba_2NaNb_5O_{15}$ (BNN) thin films were prepared on Pt substrates by pulsed laser ablation method. We investigated O_2 gas pressure in the growth chamber effects on fabrication of BNN thin films in order to obtain good crystallinity and ferroelectric properties. The characterization of thin films were carried out by X-ray diffraction (XRD), electron probe micro-analyzer (EPMA) and observation of ferroelectric hysteresis loops. The thickness of all the BNN thin films were approximately 1·0 μm. All thin films prepared at various O_2 gas pressures showed single phase BNN with a prominent c*-axis orientation. The chemical composition of all thin films were nearly equal to the BNN stoichiometry. However, the remanent polarization* Pr *of BNN thin films was decreased from 0·96 to 0·43 μ C cm^{-2} with increasing O_2 gas pressure and could not be improved.* © *1999 Elsevier Science Limited. All rights reserved*

Keywords: $Ba_2NaNb_5O_{15}$(BNN), ferroelectric properties.

1 Introduction

Ferroelectric materials have been applied to many electronic and optical devices because they have excellent dielectric, piezoelectric and optical properties. Particularly in recent years, ferroelectrics have attracted much attention as materials for memory devices for capacitors of high density dynamic random access memories (DRAMs) and nonvolatile ferroelectric random access memories (FeRAMs) because of their high dielectric constants and polarization reversal upon the application of an external electric field.[1–3] The preparation of many ferroelectric thin films by various techniques has been actively investigated to make highly efficient FeRAMs and DRAMs in large-scale integrated (LS1) circuits.

$Ba_2NaNb_5O_{15}$ (BNN) which has a tetragonal tungsten bronze-type structure is well known to be an optic crystal and is expected to be applicable to optoelectronic devices such as optical modulation, nonlinear optics and second harmonic generation (SHG), because BNN crystals have a large refractive index, large electro-optic constant and nonlinear optical constant.[4–6] In addition to their good electro-optic properties, BNN crystals show remarkable ferroelectric properties such as spontaneous polarization of 40 μ C cm^{-2} and dielectric constant of 51 parallel to the *c* axis and suffer no optical damage to an intense laser beam in comparison with $LiNbO_3$.

With the appearance of solid-state lasers and the rapid progress of optical communication, optic crystals are required for the preparation of thin films due to miniaturization and integration of optical devices. Therefore, BNN crystals are required for the preparation of thin films to be applied in optical communications and optical information processing devices. In recent years, the preparation of polycrystaline and epitaxial BNN thin films by rf magnetron sputtering,[7] sol–gel method,[8] pulsed laser ablation[9] were reported. Recently, we prepared BNN thin films on Pt substrates by pulsed

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laser ablation and sol–gel techniques and obtained BNN thin films of very smooth surface with a single phase BNN and good ferroelectric properties.[10,11]

In this paper, we prepared BNN thin films on Pt substrates by pulsed laser ablation method at various O_2 gas pressures in the growth chamber and investigated the effects of the O_2 gas pressure on the fabrication of BNN thin films. The characterization of thin films were carried out by X-ray diffraction, scanning electron microscope, electron probe micro-analyzer and observation of ferroelectric hysteresis loops.

2 Experimental

2.1 Preparation of BNN thin films

BNN thin films were prepared by the pulsed laser ablation technique using a KrF excimer laser (COM Pex 102, Lambda-Physik Co.). The KrF excimer laser light beam (wavelength: 248 nm, pulse width: 2 ns) was focused by quartz lens and irradiated onto a rotating BNN ceramic target in the vacuum chamber. BNN ceramic targets required for the pulsed laser ablation technique were prepared by the cold press and sintering method. The starting raw materials were used powders of $BaCO_3$ (99·9%), $NaCO_3$ (99·5%) and Nb_2O_5 (99·9%) and were mixed with the cation molar ratio of Ba:Na:Nb = 2:1:5. The growth conditions of BNN thin films are shown in Table 1. To obtain the BNN thin films of 1·0 μm thickness, the deposition time was 100, 121, 167, 205 and 244 min at O_2 gas pressure of 0·1, 0·2, 0·3, 0·4 and 0·5 Torr, respectively. The size of Pt substrates was $10\times10\times0{\cdot}5\,mm^3$. The surface of Pt substrates were polished by a polishing machine using a diamond paste with the grain size of 0·25 μm. The film growth chamber was evacuated to a pressure below 10^{-7} Torr before O_2 gas was introduced at a pressure lower than 0·1∼0·5 Torr. After the deposition, oxygen annealing was carried out in the chamber for 20 min at the substrate temperature (600°C).

2.2 Characterization of BNN thin films

Crystallinity of BNN thin films were investigated by X-ray diffraction (XRD) using Cu-K_α radiation.

Table 1. The growth conditions of $Ba_2NaNb_5O_{15}$ thin films

Laser	KrF excimar laser (248 m)
Target	$Ba_2NaNb_5O_{15}$ ceramic
Substrate	Platinum (Pt)
Target–substrate distance	35 mm
Laser energy density	5·0 J cm^{-2}
Repetition frequency	7 Hz
Substrate temperature	600°C
Deposition time	100 min
O_2 gas pressure	0·1∼0·5 Torr

The chemical composition was determined by means of electron probe micro-analyzer (EPMA) and energy-dispersive X-ray micro-analyzer (EDX). Circular Au dots of 1 mm in diameter were deposited as top electrodes on the surface of the films by the vacuum evaporation. Dielectric constant was measured by a LCR meter, and D–E hysteresis loops were observed using a conventional Sawyer–Tower circuit with a sinusoidal field of 100 Hz.

3 Results and Discussions

Figure 1 shows the XRD patterns of BNN thin films deposited on Pt substrates at various O_2 gas pressures. The deposition time is 100 min (0·1 Torr), 121 min (0·2 Torr), 168 min (0·3 Torr), 205 min (0·4 Torr) and 244 min (0·5 Torr) in order to obtain the BNN thin films of the same thickness. It can be

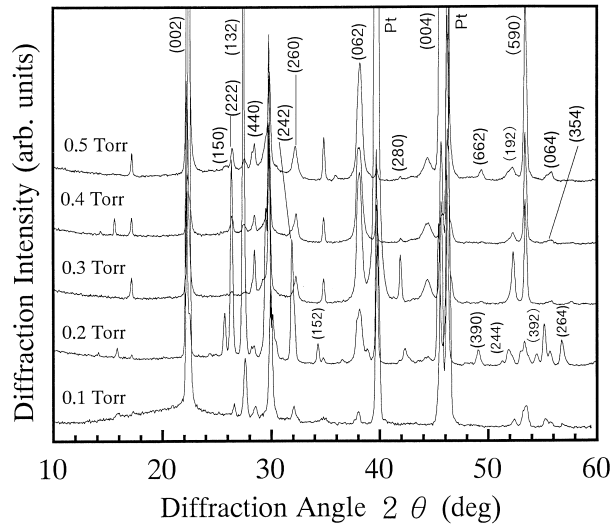

Fig. 1. XRD patterns of BNN thin films deposited on Pt substrates at the various O_2 gas pressures.

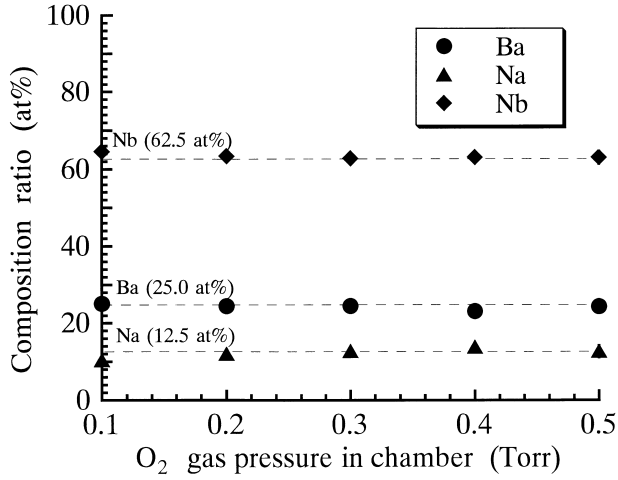

Fig. 2. The chemical composition of BNN thin films deposited on Pt substrates at laser energy density of 5·0 J cm^{-2} as a function of the O_2 gas pressures.

seen that all BNN thin films have single phase BNN and show similar with XRD patterns of strong (00ℓ) diffraction peaks such as (002) and (004). Recently, we prepared BNN thin films on Pt substrates at 0·1 Torr and various laser energy densities. From the results, we found that BNN thin films showed single phase BNN with a prominent *c*-axis orientation have stoichiometric BNN (content of cations).[11] Consequently, all BNN thin films prepared at various O_2 gas pressures are expected to show the BNN stoichiometric composition and ferroelectric properties because it gives *c*-axis oriented BNN thin films.

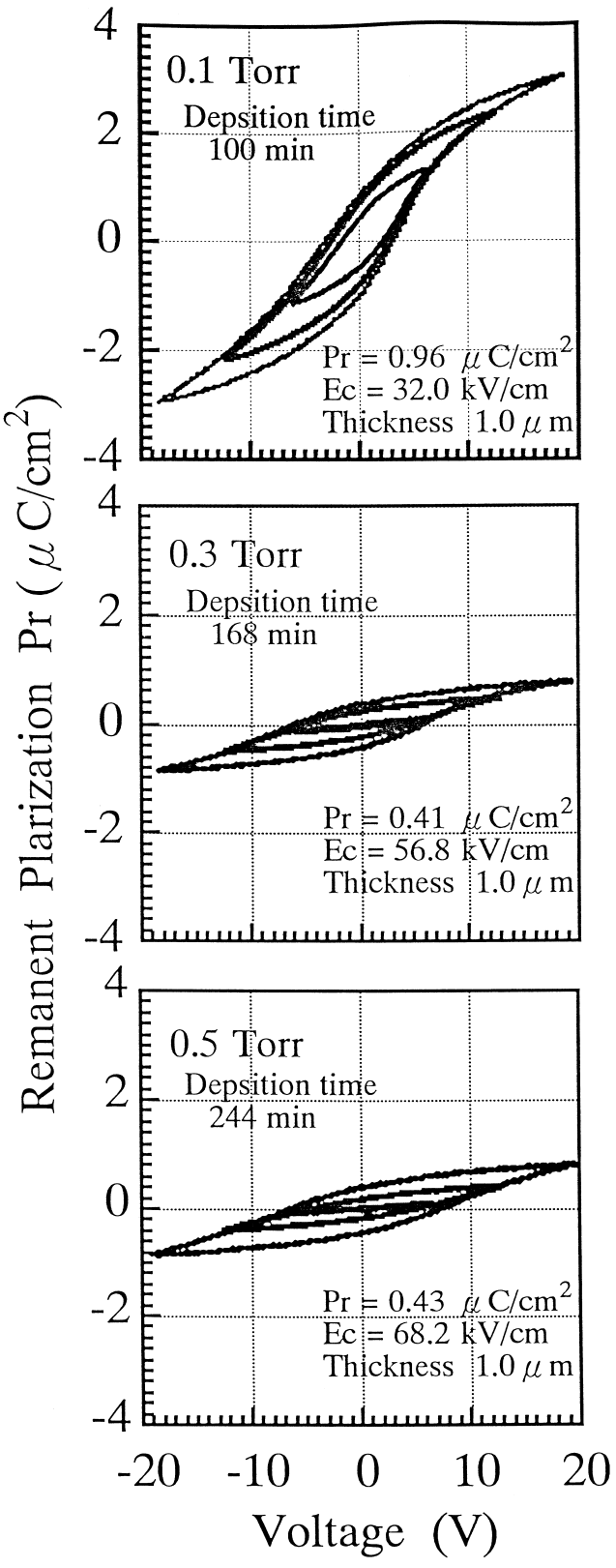

Fig. 3. The D–E hysteresis loops for BNN thin films deposited at various O_2 gas pressures of (a) 0·1 Torr, (b) 0·3 Torr (c) 0·5 Torr.

Figure 2 shows the dependence of chemical composition of thin films for various O_2 gas pressures. The broken lines in this figure shows the BNN stoichiometoric composition (Ba = 25·0 at%, Na = 12·5 at%, Nb = 62·5 at%). Incidentally, the chemical composition of BNN ceramic targets was Ba = 23.47 at%, Na = 15.90 at% and Nb = 60·36 a%. It can be seen that all thin films are nearly equal to the BNN stoichiometry. From the results of XRD patterns and the chemical composition analysis, it is confirmed that crystallinity and chemical composition of BNN thin films deposited at various O_2 gas pressures showed no dependence on the O_2 gas pressure.

Figure 3 shows the D–E hysteresis loops of BNN thin films prepared at various O_2 gas pressures. The remanent polarization *Pr* and the coercive field *Ec* were estimated from these D–E hysteresis loops and shown in the figure. The remanent polarization *Pr* decreased from 0·96 to 0·43 μ C cm^{-2} with increasing O_2 gas pressure. With increasing O_2 gas pressure, the coercive field *Ec* increases from 32 to 68·2 kV cm^{-1}.

Figure 4 shows the current–voltage (I–V) characteristics of BNN thin films deposited at various O_2 gas pressures. It can be seen that the leakage current density of BNN thin films deposited at 0·1 and 0·3 Torr keep stability and show tendency for a slightly increase with increasing O_2 gas pressure. On the other hand, the leakage current density of BNN thin films deposited at 0·5 Torr shows comparatively unstable and increase compared with BNN thin films deposited at 0·1 and 0·3 Torr.

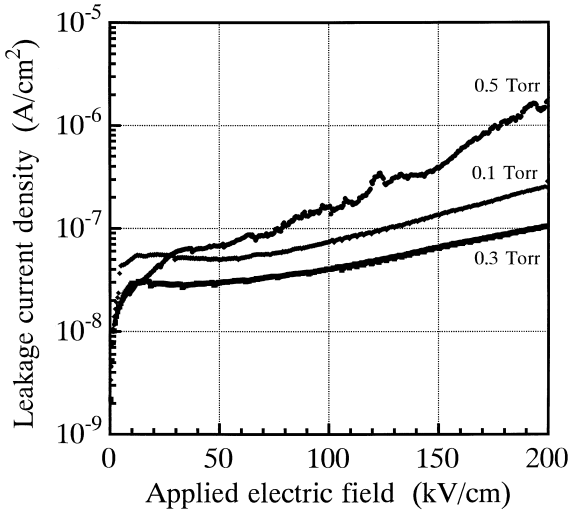

Fig. 4. The current–voltage (I–V) characteristics of BNN thin films deposited at various O_2 gas pressures.

Consequently, the remanent polarization and the leakage current density of BNN thin films became worse with increasing O_2 gas pressure. It is confirmed that, to obtain BNN thin films with a single phase, a stoichiometric composition and a good ferroelectric property one has to prepare the films at 0·1–0·3 Torr of O_2 gas pressure.

4 Conclusions

$Ba_2NaNb_5O_{15}$(BNN) thin films were prepared on Pt substrates by the pulsed laser ablation method using BNN ceramic targets. We examined the effects of the O_2 gas pressure on the fabrication of BNN thin films. All thin films prepared at various O_2 gas pressures obtained the BNN single phase with strongly *c*-axis orientation and nearly stoichiometric composition. Consequently, crystallinity and chemical composition of BNN thin films deposited at various O_2 gas pressures did not show a dependence on the O_2 gas pressure. However, the remanent polarization *Pr* of BNN thin films was decreased from 0·96 to 0·43 μ C cm^{-2} with increasing O_2 gas pressure and could not be improved.

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