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Lead-free piezoelectric thin films of Mn-doped $NaNbO_3$–$BaTiO_3$ fabricated by chemical solution deposition

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ABSTRACT

Lead-free piezoelectric thin films of $NaNbO_3$–$BaTiO_3$ were fabricated on Pt/TiO_x/SiO_2/Si substrates by chemical solution deposition. Perovskite $NaNbO_3$–$BaTiO_3$ single-phase thin films with improved leakage-current and ferroelectric properties were prepared at 650 °C by doping with a small amount of Mn. The 1.0 and 3.0 mol% Mn-doped $0.95NaNbO_3$–$0.05BaTiO_3$ thin films showed slim ferroelectric *P*–*E* hysteresis and field-induced strain loops at room temperature. The 1.0 and 3.0 mol% Mn-doped $0.95NaNbO_3$–$0.05BaTiO_3$ films showed remanent polarization values of 6.3 and 6.2 μC/cm^2, and coercive field of 41 and 55 kV/cm, respectively. From the slope of the field-induced strain loop, the effective piezoelectric coefficient (d_{33}) was found to be 40–60 pm/V.

1. Introduction

Piezoelectric materials are important in the electronics industry. In particular, Pb(Zr,Ti)O_3 (PZT)-based ceramics are widely used for piezoelectric devices because of their excellent electrical properties [1]. However, Pb is well known as a harmful element; therefore, lead-free piezoelectric materials are in high demand for environmental reasons. Among several lead-free piezoelectric materials, alkali niobate-based compounds, such as (K,Na)NbO_3, have been extensively studied as PZT alternatives [2–4]. Recently, $NaNbO_3$–$BaTiO_3$ (NN-BT) ceramics have been reported [5] and are expected to be promising candidates for lead-free piezoelectric materials. This solid solution system does not contain the volatile element potassium, so its properties are more easily controlled. At a composition of $0.9NaNbO_3$–$0.1BaTiO_3$, this system has *Tc* and d_{33} values of approximately 230 °C and 147 pC/N, respectively, which are relatively high compared with other lead-free piezoelectric materials [5].

Furthermore, thin-film processing is becoming increasingly important for microelectromechanical system (MEMS) applications. Chemical solution deposition (CSD), a promising thin-film processing method, offers high homogeneity, low-temperature fabrication, precise control of chemical composition, and reduced equipment cost. Several research groups have utilized CSD to fabricate piezoelectric MEMS devices [6–8]. In these studies, piezoelectric thin films containing heavy metal ion, such as Pb or Bi, are applied mainly. Therefore, alkali niobate-based piezoelectric thin films are very attractive. Moreover, piezoelectric thin films of NN-BT have never been reported. However, in general, it is difficult to achieve good ferroelectric properties for alkali niobate-based thin films because of their low electrical resistivity (relatively large leakage current) [9]. Thus, improvement in ferroelectric properties is strongly required for realizing piezoelectric alkali niobate-based, such as NN-BT, thin films.

In this study, NN-BT thin films were fabricated on Si-based substrates by CSD and their electrical properties were evaluated. Furthermore, they were Mn-doped to improve their ferroelectric properties.

2. Experimental procedure

For thin film preparation, the chemical compositions of the precursor solutions of NN-BT and Mn-doped NN-BT were set at $Na_{1-x}Ba_xNb_{1-x}Ti_xO_3$ [$x=0.05$, 0.1, 0.15; NN-BT100$(1-x)$], and $Na_{0.95}Ba_{0.05}(Nb_{0.95}Ti_{0.05})_{1-y}Mn_yO_3$ ($y=0$, 0.01, 0.03; Mn100y% NN-BT95). Appropriate amounts of $NaOC_2H_5$, $Nb(OC_2H_5)_5$, $Ba(OC_2H_5)_2$, $Ti(O^iC_3H_7)_4$, and $Mn(O^iC_3H_7)_2$ (Kojundo Chemical, Japan) with 10 at.% excess Na were dissolved in absolute 2-methoxyethanol and then refluxed for 20 h to yield a 0.3 M homogeneous solution. Since the starting materials are extremely sensitive to moisture, 2-methoxyethanol was dried over molecular sieves and distilled before use. Moreover, the entire procedure was conducted in a dry nitrogen atmosphere.

Thin films were fabricated using the precursor solution by spin coating on Pt (200 nm)/TiO_x (50 nm)/SiO_2 (500 nm)/Si (500 μm) substrates. As-deposited precursor films were dried at 150 °C for 5 min and calcined at 400 °C at a rate of 10 °C/min for 30 min in an

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oxygen flow. After two spin-coating and calcining cycles, the calcined layers were crystallized at 650 °C for 10 min in an oxygen flow. These cycles were repeated five times until the film thickness reached approximately 700 nm. The film thickness was evaluated by observing the cross-section of the films using a scanning electron microscopy (SEM).

The crystallographic phases of the prepared NN-BT thin films were identified by X-ray diffraction (XRD; Rigaku RAD RC) analysis using CuKα radiation with a monochromater. To evaluate the electrical properties of the films, 0.2-mm-diameter Pt top electrodes were deposited by DC sputtering on the films, and then annealed at 400 °C for 30 min. The Pt layer of the Pt/TiO_x/SiO_2/Si substrate acted as the bottom electrode. Ferroelectric properties were evaluated using a ferroelectric test system (Toyo FCE-1) at 83 and 298 K under vacuum. Current density–electric field (*J*–*E*) characteristics were examined using an electrometer/high-resistance meter (Keithley Instruments Model 6517A). Piezoelectric properties were evaluated from the electric-field-induced displacement of the films, using a combination of scanning-probe microscopy (SPM; Seiko SPI3800N) and a ferroelectric tester (aixACCT TF2000) at room temperature. A bipolar triangular wave with 15–20 V amplitude and 200 ms period drove the piezoelectric capacitor, and the SPM tip displacement above the top electrode was recorded. The conducting tips were prepared by deposition of Rh onto Si tips. The force constant of the tips was approximately 2.5 N/m. *X*-cut crystalline quartz was used as a piezoelectric standard.

3. Results and discussion

Homogeneous and stable $NaNbO_3$–$BaTiO_3$ (NN-BT) precursor solutions with various $BaTiO_3$ concentrations were prepared by optimizing the reacting conditions of starting metal-alkoxide compounds in a 2-methoxyethanol solution. Crystalline NN-BT thin films were fabricated by a heat treatment of NN-BT precursor films. XRD patterns of NN-BT100$(1-x)$ ($x=0.05$, 0.1, 0.15) thin films that crystallized at 650 °C are shown in Fig. 1. Although the diffraction pattern was similar to that of randomly oriented cubic (pseudo cubic) perovskite dielectrics, all the films were crystallized in the perovskite single phase with random orientation. As the $BaTiO_3$ content increased, each diffraction peak slightly shifted to the lower 2θ region. This result indicates assured preparation of the solid solution of $NaNbO_3$ and $BaTiO_3$, and is mainly ascribed to substitution of the larger cation Ba^{2+} (0.161 nm) at Na^+ (0.139 nm) sites, which increases the lattice parameter of perovskite NN-BT. On the contrary, from atomic force microscopy (AFM) images, the grain size as well as the surface roughness did not depend on the $BaTiO_3$ concentration, and the root mean square (RMS) values of the NN-BT thin films in a 1×1 μm^2 area were around 5 nm.

Fig. 2 shows polarization–electric field (*P*–*E*) hysteresis loops of NN-BT100$(1-x)$ ($x=0.05$, 0.1, 0.15) thin films measured at 83 and 298 K (1000 Hz). Although all the films showed typical *P*–*E* ferroelectric hysteresis loops, higher electric fields could not be applied to the films at 298 K because they have poor insulating resistance. Therefore, *P*–*E* behaviors at low temperature (83 K) were also characterized; the result is shown in Fig. 2. All the films showed relatively saturated *P*–*E* hysteresis loops containing few leakage components. The *P*–*E* curves are considerably slim compared with NN-BT bulk ceramics [5]. It may be mainly ascribed to fine-grained microstructure (less than 100 nm: confirmed by AFM) of the resultant thin films. As the $BaTiO_3$ content decreased, the remanent polarization (P_r) increased. This result is consistent with that of Zeng et al. [5]. Among the synthesized films, NN-BT95 thin film showed the highest

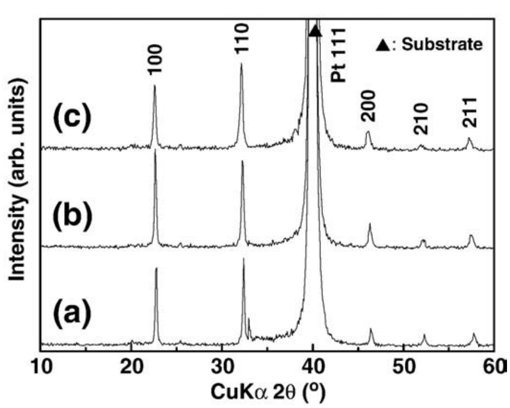

Fig. 1. XRD patterns of $Na_{1-x}Ba_xNb_{1-x}Ti_xO_3$ [NN-BT100$(1-x)$] thin films: (a) NN-BT95 ($x=0.05$), (b) NN-BT90 ($x=0.1$), and (c) NN-BT85 ($x=0.15$) fabricated at 650 °C on Pt/TiO_x/SiO_2/Si substrates.

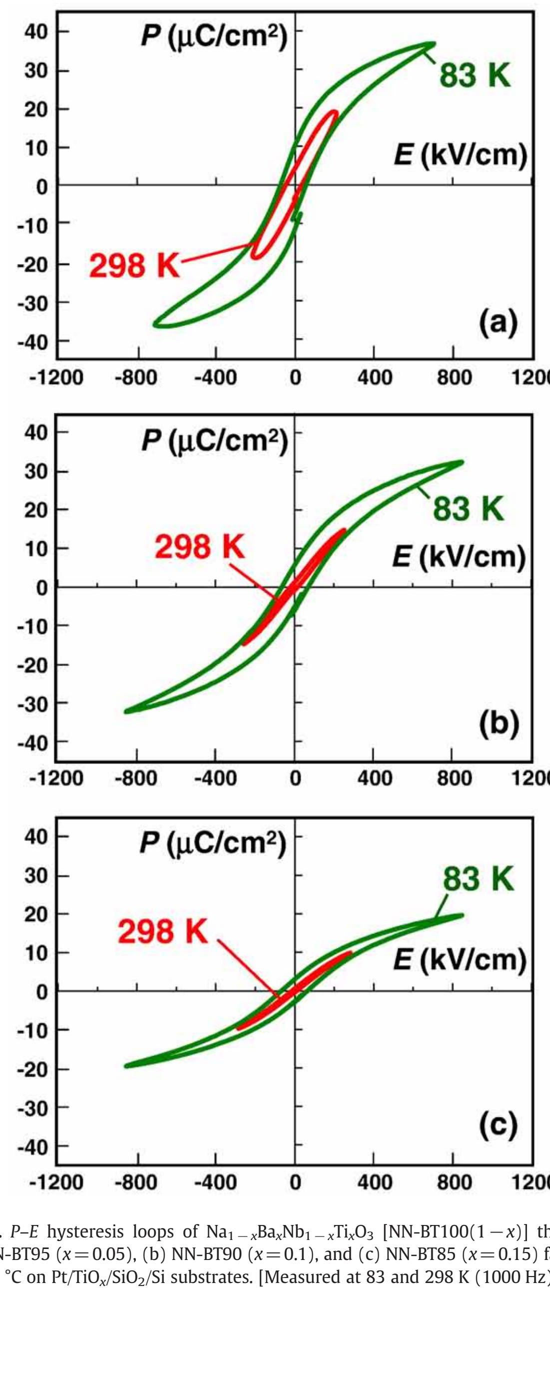

Fig. 2. *P*–*E* hysteresis loops of $Na_{1-x}Ba_xNb_{1-x}Ti_xO_3$ [NN-BT100$(1-x)$] thin films: (a) NN-BT95 ($x=0.05$), (b) NN-BT90 ($x=0.1$), and (c) NN-BT85 ($x=0.15$) fabricated at 650 °C on Pt/TiO_x/SiO_2/Si substrates. [Measured at 83 and 298 K (1000 Hz)].