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Structure and Electrical Properties of $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ Ferroelectric Thick Films Derived From a Polymer Modified Sol-Gel Method

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Abstract

Lead-free $\text{Na}_{0.5}\text{Bi}_{0.5}\text{TiO}_3$ (NBT) ferroelectric thick films were prepared by a poly(vinylpyrrolidone) (PVP) modified sol-gel method. The NBT thick films annealed from 500°C to 750°C exhibit a perovskite structure. The relationship between annealing temperature, thickness, and electrical properties of the thick films has been investigated. The dielectric constants and remnant polarizations of the thick films increase with annealing temperature. The electrical properties of the NBT films show strong thickness dependence. As thickness increases from 1.0 to 4.8 μm , the dielectric constant of the NBT films increases from 620 to 848, whereas

the dielectric loss is nearly independent of the thickness. The remnant polarization of the NBT thick films also increases with increasing thickness. The leakage current density first decreases and then increases with film thickness.

I. Introduction

Thus far, the most widely used piezoelectric materials have been lead-based materials, because of their excellent ferroelectric and piezoelectric properties. However, materials containing lead are considered to be a serious threat to the environment and human health. As a result, studies on lead-free piezoelectric films have become important in recent years. Potassium sodium niobate [(K,Na)NbO₃ (KNN)] is a promising candidate for lead-free piezoelectric materials because of its excellent piezoelectric properties, high Curie temperature (T_C) and low anisotropy [1]. Meanwhile, bismuth sodium titanate [(Na_{0.5}Bi_{0.5})TiO₃ (NBT)] is also considered to be an excellent candidate because of its strong ferroelectricity with relatively large remnant polarization ($P_r = 38 \mu\text{C}/\text{cm}^2$) at room temperature [2]. Because of the high cost of KNN films prepared using the precursor solution-based sol-gel process (i.e., niobium ethoxide) [3]–[5], NBT thick films prepared from a low-cost precursor solution are an attractive alternative. At present, the research on NBT-based films is concentrated on thin films. Several methods have been used to prepare NBT thin films, including pulsed laser deposition [6], [7], radio-frequency magnetron sputtering [8], and sol-gel [9]–[12]. However, there are few reports on NBT thick films [13]. The sol-gel process has several advantages over other techniques, such as low cost and low annealing temperature to limit volatilization of compositions. Polymers used in a sol-gel process can help to achieve the desired viscosity of precursor solutions and act as binding agents to metal precursors [14], [15]. By proper control and optimization of processing parameters such as sol concentration, spin coating parameters, heat treatment, and repeat times, thick films with desired thickness and minimum defects can be obtained. In our previous work, fine KNN ceramic powder and NBT precursor solution had been used to prepare 0–3 KNN/NBT composite thick films. A high-frequency ultrasonic transducer with a center frequency of 193 MHz and –6-dB bandwidth of 34% has been successfully fabricated using the composite thick films [16].

In this study, lead-free Na_{0.5}Bi_{0.5}TiO₃ (NBT) ferroelectric thick films were prepared by a poly(vinylpyrrolidone) (PVP)-modified sol-gel method. The effect of annealing temperature and thickness on structures, morphologies, and electrical properties of the resulting NBT thick films has been investigated.

II. Experimental

NBT thick films were prepared by a PVP-modified solgel method using bismuth nitrate pentahydrate, sodium acetate, and tetrabutyl titanate as the raw materials. 2-methoxyethanol and acetylacetone were used as the solvent and the chelating agent, respectively. To compensate for the evaporation of sodium and bismuth during the thermal treatment [3]–[6], 10 mol% excess sodium acetate and 2 mol% excess bismuth nitrate pentahydrate were added to the precursor solution. PVP with an average molecular weight of 30 000 was added to the precursor solution. The molar ratio of PVP monomer to tetrabutyl titanate is 1:1 in the experiment [3], [14], [15], [17]. The concentration of the precursor solution was adjusted to 0.45 M. The solution was deposited on (111) Pt/TiO₂/SiO₂/Si substrates by a spin coating method. Each layer was pyrolyzed in two steps, first at 150°C for 3 min and then at 410°C for 10 min in a rapid thermal process furnace. Then, the deposited films were annealed in the range of 500°C to 750°C for 3 min in air. This procedure was repeated until the desired thickness was reached.

Thermal analyses including differential scanning calorimetry (DSC) and thermogravimetric analysis (TG) for the NBT dry gel were characterized by TA SDT Q600 thermal analyzer in air from room temperature to 800°C with a heating rate of 20°C/min. The phase structures were examined using an X-ray diffractometer (XRD, Rigaku D/Max-2400, Tokyo, Japan) with Cu K α radiation. The surface and cross-sectional morphologies of the NBT thick films were examined by a field-emission scanning electron microscope (FESEM, JEOL JSM-7000F, Tokyo, Japan). To measure the electrical properties, 0.5-mm-diameter top Au electrodes were sputtered on the surfaces of the films. Polarization-electric field (P - E) hysteresis loops were measured using a ferroelectric standard testing system with an FE module (aixACC T TF analyzer 2000, aixACC T Systems GmbH, Aachen, Germany) at room temperature. The dielectric constant and loss tangent were measured by a precision impedance analyzer (Agilent 4294A, Agilent Technologies Inc., Santa Clara, CA) at an ac oscillation level of 500 mV. The leakage currents were measured using a semiconductor characterization system (4200-SCS/F, Keithley Instruments Inc., Cleveland, OH). The thickness of the films was measured by a stylus surface profiler (Dektak 6M, Veeco Instruments Inc., Plainview, NY).

III. Results and Discussion

The thermal analyses were used to investigate the decomposition and crystallization process of the NBT gel from the precursor solution dried at 80°C in air. Fig. 1 gives the DSC-TG curve of dried NBT gel. There is an endothermic peak at 155.9°C which corresponds to vaporization of residual organic solvents, accompanied by 4.12% weight loss. The three peaks at 263.6°C, 305.4°C, and 345.9°C resulted from combustion of the remaining solvent and organic ligands which are either from the precursor or from the by-product of the decomposition and polycondensation [11]. Subsequently, another exothermic peak at 464.2°C is related to the formation of the perovskite structure, accompanied by 32.85% weight loss to 500°C. There is no significant new peak appearance in the DSC curve as the temperature increases to 800°C. This indicates that the perovskite structure can be formed once the sintering temperature is higher than 465°C. According to the thermal analysis of the NBT dry gel, the pyrolysis temperature was set at 410°C, and the annealing temperature was set in a range of 500°C to 750°C.

Fig. 2(a) shows the XRD patterns of NBT films annealed at various temperatures ranging from 500°C to 750°C. It is found that the NBT films show a rhombohedral perovskite phase. The crystallization is improved by increasing the annealing temperature because the intensity of the XRD peaks increases with annealing temperature. The NBT thick films prepared by a modified sol-gel process exhibit relatively low crystallization temperatures. The full-width at half-maximum (FWHM) of the (110) peaks decreases with increasing annealing temperature. The average crystallite size is evaluated by a Scherer formula [$d = 0.89 \cdot \lambda / (B \cos \theta)$] using the XRD data. The calculated crystallite size increases from 23 to 37 nm as the annealing temperature increases from 500°C to 750°C, as shown in Fig. 2(b).

Because higher annealing temperature can promote the crystallization of the NBT thick films, the films with thickness between 1.0 and 4.8 μm were annealed at 750°C for 3 min. The FESEM morphologies of the surfaces and cross-sections of the NBT films are shown in Fig. 3. The thicknesses of NBT thick films are 1.0, 2.0, 3.4, and 4.8 μm . The surface morphologies indicate that the surfaces of the thick films with various thicknesses are smooth and compact, and the cross-sectional morphologies indicate that the NBT thick films exhibit very dense columnar structures. The grain nucleation starts from the bottom electrode interface. The decomposition of the PVP polymer during the thermal treatment promotes structural relaxation and prevents cracking in the films [14], [15]; however, some cracks in the films can be observed in the FESEM pictures with larger scales (not shown).

here). The cracks lead to the increase of the leakage currents and deterioration of the electrical properties. Generally, cracking became more serious with increasing film thickness. The particle size of thick films annealed at 750°C is between 50 and 80 nm, and shows no significant change with the film thickness. The particles are clusters of even smaller crystal grains in size of ~37 nm.

The dielectric properties of the NBT thick films annealed at various temperatures are shown in Fig. 4. The dielectric constant of the NBT films with thickness between 3.1 and 3.4 μm increases from 650 to 900, whereas the dielectric loss slightly decreases when the annealing temperature increases from 650°C to 750°C. The results indicate that the NBT thick films annealed at high temperature exhibit improved dielectric properties because of better crystallization at high annealing temperature [18], [19].

As shown in Fig. 5(a), the dielectric constant slightly decreases with increasing frequency, whereas the dielectric loss slightly increases. The thickness dependence of the dielectric constant and dielectric loss at 1 kHz are given in Fig. 5(b). When the thickness increases from 1.0 to 4.8 μm , the corresponding dielectric constant increases from 680 to 1050 at 1 kHz, whereas the dielectric loss is nearly independent of the thickness. A similar thickness effect is also reported in ferroelectric PZT thick films [20]–[22].

The decrease of the dielectric constant with decreasing film thickness is often attributed to the low dielectric constant of the interface layers between the electrodes and the films [23], [24]. The NBT film sample can be treated as a simple two-capacitor-in-series circuit: one represents the thick films layer and the other represents the interface layer. The measured dielectric constant ϵ_r can be expressed as: $1/\epsilon_r = (d_i/\epsilon_{ri}) \cdot (1/d) + (1/\epsilon_{rf})$, where d is the film thickness, d_i is the thickness of the interface layer. ϵ_r , ϵ_{ri} , and ϵ_{rf} are measured dielectric constant, dielectric constant of the interface layer, and dielectric constant of the NBT thick film, respectively. There should be a linear relationship between $1/\epsilon_r$ and $1/d$; however, there is an obvious difference between the experimental data and the linear relationship, as shown in Fig. 6. This means that, except for the electrode-film interface layer, other factors such as stress [25], [26] and domain structure effect [27] may also strongly affect the thickness dependence of the dielectric constant in the NBT films [28].

The influence of annealing temperature on the ferroelectric properties of the NBT films is shown in Fig. 7. The voltage available from the ferroelectric test system is not high enough to measure the saturation polarization for the NBT films thicker than 2 μm . However, the values of polarization do increase from 7.3 to 17.5 $\mu\text{C}/\text{cm}^2$ with annealing temperature increasing from 650°C to 750°C at the same applied electric field of 350 kV/cm (below saturation). This indicates that the NBT films annealed at higher temperature exhibit improved ferroelectric properties resulting from the improved crystallization of the films [29]. The results are consistent with the XRD results. It can be seen in Fig. 7(b) that the coercive field also increases with annealing temperature. The grain size of the films increases with increasing annealing temperature. This decreases the volume fraction of the grain boundaries and domain walls, resulting in the increase of the domain alignment and the remanent polarization [30]. However, the volatility of Bi and Na also increases with annealing temperature; hence, the concentration of the charged carriers such as bismuth vacancies, sodium vacancies and oxygen vacancies increases. These charged carriers would act as pinning centers to pin domains nearby [31]. Thus, P_r and E_c of the films increase with annealing temperature.

The polarization-electric field (P - E) response was measured with a variable applied field for NBT thick films with different thickness, however, the available maximum voltage from the ferroelectric test system is 120 V—not high enough to measure the saturation polarization

for NBT films thicker than 2 μm . Therefore, Figs. 8(a)–8(c) present the P - E hysteresis loops under different applied fields for the NBT thick films with different thickness. For NBT films of thicknesses 1.0, 2.0, 3.4, and 4.8 μm , the values of remnant polarization, P_r , are 18.0, 17.8, 17.5, and 14.6 $\mu\text{C}/\text{cm}^2$, respectively. The corresponding coercive fields, E_c , are 99.5, 96.7, 73.6, and 59.0 kV/cm , respectively, as shown in Fig. 8(a). It can be seen in Figs. 8(b) and 8(c) that the remnant polarization increases with film thickness, but the P_r value of the 4.8- μm -thick films decreases because of the lower electric field on the film. It is well known that many factors affect the ferroelectric properties of the films, such as interfacial layer [32], residual stress, substrate pinning, domain wall motion [33], and depolarization field.

The relationship between the current density and the applied electric field of NBT thick films with various thicknesses ranging from 1.0 to 4.8 μm is shown in Fig. 9. The leakage current density first decreases with increasing film thickness because the effect of substrate on the electric properties of NBT films [34], then it increases as the film thickness increases from 2.0 to 4.8 μm , because the defects increase with thickness. The 2.0- μm -thick NBT film has the minimum leakage current density, which is less than $1.0 \times 10^{-10} \text{ A}/\text{cm}^2$ at zero field. As the electric field increases to 60 kV/cm , the leakage current density increases to $10^{-8} \text{ A}/\text{cm}^2$. As the film thickness further increases to 4.8 μm , the leakage current densities of the film increase to $10^{-7} \text{ A}/\text{cm}^2$ at 0 kV/cm and $10^{-4} \text{ A}/\text{cm}^2$ at 60 kV/cm , respectively. An asymmetric current behavior between the negative field region and the positive field region, as shown in Fig. 9, is contributed by the interfaces between the different electrodes and the films [35], [36].

The fabrication of high-frequency ultrasonic transducers using the NBT thick films is under way and will be reported elsewhere.

IV. Conclusions

NBT thick films have been successfully prepared on (111) Pt/TiO₂/SiO₂/Si substrates by a PVP-modified solgel method. The thick films annealed between 500°C and 750°C exhibit a pure perovskite structure. The crystallite size increases with annealing temperature. The NBT thick films with thicknesses in the range of 1.0 to 4.8 μm show compact and smooth structure. The particle size of the films annealed at 750°C is between 50 and 80 nm. As the film thickness increases from 1.0 to 4.8 μm , the dielectric constant of the NBT thick films increases from 620 to 848, whereas the dielectric loss is nearly independent of the thickness and less than 6%. The remnant polarization increases with film thickness. I - V characteristics indicate that the leakage current of the thick films first decreases and then increases as the film thickness increases from 1.0 to 4.8 μm .

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Fig. 1.
Differential scanning calorimetry (DSC) and thermogravimetric analysis (TG) thermographs of NBT dry gel.

Fig. 2.
X-ray diffraction patterns of NBT thick films annealed at different annealing temperatures.

Fig. 3. Field-emission scanning electron microscope morphologies of surfaces and cross sections of NBT thick films annealed at 750°C with various thicknesses.

Fig. 4. Dielectric constant and loss tangent as functions of frequency and annealing temperature for NBT thick films.

Fig. 5. Frequency dependence of dielectric constant and loss tangent of NBT thick films annealed at 750°C with thickness from 1.0 to 4.8 μm .

Fig. 6.
Reciprocal of dielectric constant as a function of reciprocal of thickness for NBT thick films.

Fig. 7. Ferroelectric properties as a function of annealing temperature for NBT thick films.

Fig. 8.

(a) Ferroelectric E - P loops of NBT thick films with various thicknesses at different electric fields. (b) Ferroelectric E - P loops of NBT thick films with various thickness at approximately 280 kV/cm. (c) Thickness dependence of the polarization and coercive field of NBT thick films with the electric field at about 280 kV/cm.

Fig. 9.
J-E characteristics of NBT thick films annealed at 750°C with thickness from 1.0 to 4.8 μm .