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Optical and Electrical Properties of Ferroelectric SBN Thin Films Prepared by Sol-Gel Process

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Abstract. Strontium barium niobate thin films were prepared by sol-gel method on various substrates using an improved process, two-step heating process. The two-step heating process applies an additive heat-treatment before crystallization for enhancement of the densification and the nucleation of films. Also, highly *c*-axis oriented SBN thin films with various compositions were obtained on MgO(100) and Pt(100)/MgO(100) substrates. Their optical and electrical properties such as optical propagation loss, refractive index, P-E hysteresis, and dielectric constant, were characterized as a function of the film composition.

Keywords: sol-gel, strontium barium niobate, thin film, ferroelectric material, optical waveguide

1. Introduction

Strontium barium niobate ($Sr_xBa_{1-x}Nb_2O_6$, where $0.25 \leq x \leq 0.75$) is currently investigated as a potential material for such many micro-electric device applications as pyroelectric infrared detectors, piezoelectrics, electro-optic modulators, holographic storage, and beam steering [1]. Also, the SBN is a ferroelectric solid solution between $BaNb_2O_6$ and $SrNb_2O_6$ with a tetragonal tungsten bronze (TTB) structure, and physical properties vary depending on its composition [2].

Recently, the demand for thin film processing has increased because of miniaturization of electric and optical components for integrated devices and lower fabrication cost compared to single crystals. The SBN thin films, especially highly *c*-axis oriented SBN thin films, are expected to be better for optical applications such as electro-optic properties, photorefractive, and nonlinear optical applications [3, 4].

In the present study, the SBN thin films with various compositions were prepared on various substrates by the sol-gel process. Optical and electrical properties such as optical propagation loss, surface roughness, refractive index, P-E hysteresis, and dielectric constant, of these films are characterized as a function of the film composition for optical waveguide applications.

2. Experimental Procedure

Three compositions were investigated in the present study with $x = 0.25, 0.60$ and 0.75 in the general chemical formula, $Sr_xBa_{1-x}Nb_2O_6$ (which is denoted SBN$x \cdot 100$). A precise procedure for preparing the precursor solution was presented elsewhere [5].

The solution was spin-coated onto various substrates such as fused silica glass, silicon(100), and MgO(100) single crystal, at 2000 rpm for 30 sec. After air drying for 5 min, the film was dried at 180°C for 10 min and 360°C for 10 min, to remove organic residues completely. A coating yields about 60 nm film-thickness. This procedure was repeated until a desired thickness was obtained. These green films were heat-treated by a new heating schedule, two-step heating process, to enhance the densification and the crystallization of the films. In the two-step heating process, the films were first heated from room temperature to 550°C with slow

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heating rate (=2°C/min) and maintained at 550°C for 5 h. The temperature is then raised up to the crystallization temperature (≈1000°C) by the heating process with same heating rate. The effect of the two-step heating process was described in another paper [5].

Crystallographic orientation as well as crystalline phase of the films was characterized using X-ray diffraction. The measurements of refractive indices and film-thicknesses were performed by a prism-coupler. The surface roughness of films was measured by AFM (atomic force microscopy). For the measurement of electric properties, P-E (polarization-electric field) curve of the films was measured using the charge mode in a standard ferroelectric test-system (RT66A). Dielectric constant of the films was calculated from the capacitance measured by an impedance analyzer.

3. Results and Discussion

3.1. Preparation of Polycrystalline and Highly Oriented SBN Thin Films

The SBN film on a fused silica substrate studied previously was rarely crystallized at 700°C although the film on a silicon substrate could be crystallized at this temperature [6]. This phenomenon is caused that a crystalline substrate comparing with an amorphous substrate, easily provides nucleation sites for the crystallization of SBN phase. Thus, the SBN thin films on amorphous substrate such as a fused silica glass, should be crystallized at higher temperature with a special heating process i.e. two-step heating process to enhance the crystallization, which was described previously. Figure 1 shows XRD patterns of the SBN60 films on fused silica and silicon substrates that crystallized at 1000°C with a conventional process which applies single heating, and two-step heating process, respectively. The film on a fused silica substrate heat-treated with single heating process is not crystallized even at 1000°C, while the film with two-step heating process shows crystalline peaks relatively. In case of the films on silicon substrates, all the films are crystallized with only tetragonal phase, regardless of heating processes. However, the film heat-treated with two-step heating is more crystallized. The additive heating at 550°C for 5 h promotes the nucleation so that enhances the crystallization. In addition, tiny pores in the film become to collapse during this heating, so the densification of a film is enhanced. Thus, it is found that the two-step heating process is more effective to the crystallization of the films. All the SBN thin films in this study were prepared by the two-step heating process.

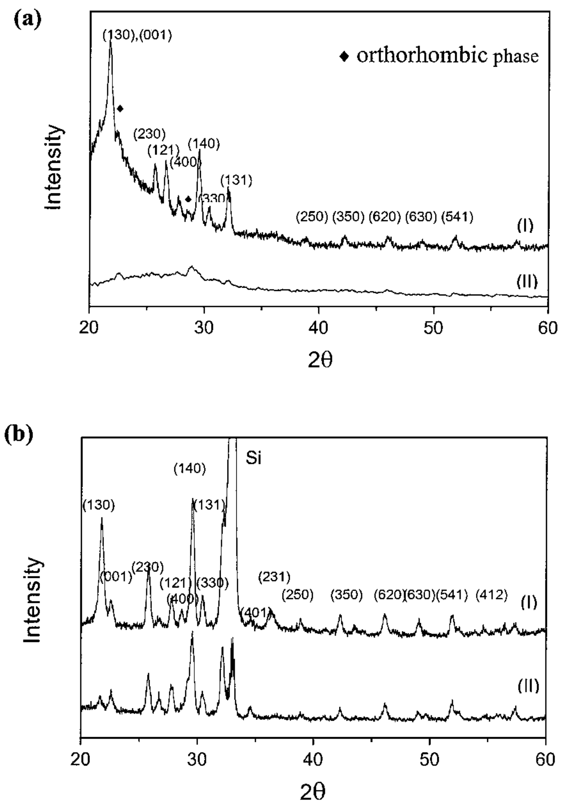

Figure 1. XRD patterns of SBN60 films (600 nm thickness) on (a) fused silica substrates and (b) silicon substrates crystallized at 1000°C by different heating processes; (I) two-step heating process and (II) single heating process.

The selection of substrate is very important for the epitaxial growth of films because the lattice parameter and the crystal structure matching between the film and the substrate strongly affect the crystal growth behavior of the films. Further more, the refractive index of a substrate should be lower than that of a film for optical waveguide applications. Thus, MgO(100) substrate was used as a substrate for the oriented crystallization of SBN films in this study. Figure 2(a) shows XRD patterns of the SBN thin films on MgO(100) substrates as a function of film composition. All the films crystallized at 1000°C by the two-step heating process have the *c*-axis preferred orientation, regardless of the film composition. SBN thin films on Pt(100)/MgO(100) substrates prepared for the measurements of electric and ferroelectric properties, also exhibit the *c*-axis preferred orientation regardless of composition as shown as Fig. 2(b), because the lattice parameter of Pt unit cell is similar to that of MgO [4, 5].

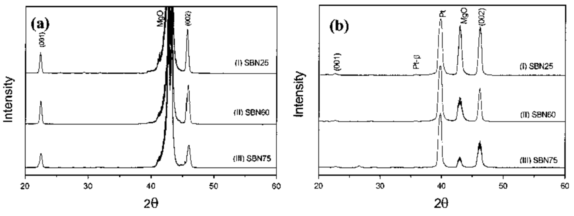

Figure 2. XRD patterns of SBN thin films (600 nm thickness) on (a) MgO(100) and (b) Pt(100)/MgO(100) substrates heat-treated at 1000°C as a function of the film composition.

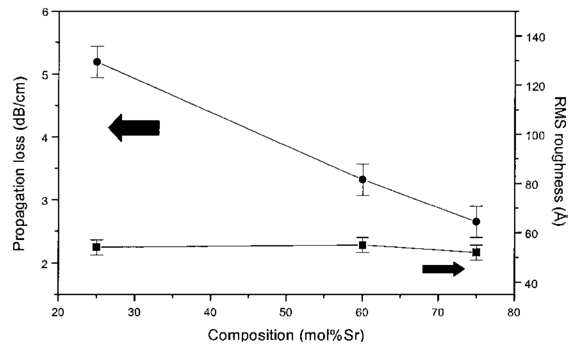

Figure 4. Optical propagation loss and RMS surface roughness of SBN thin films (600 nm thickness) on MgO(100) substrates as a function of film composition.

3.2. *Optical and Electrical (Ferroelectric) Properties of the Oriented SBN Films*

Figure 3 shows the refractive indices of SBN films having the different composition on MgO(100) substrates. This figure exhibits SBN is optically uniaxial negative material ($n_o > n_e$). The ordinary refractive index, n_o decreases as the Sr content decreases due to an increase of barium oxides having higher index. However, the extraordinary index, n_e is more sensitive to the change of film composition than the ordinary index, n_o since n_e is affected by electronic and ionic polarization, the change of lattice parameter and structure, whereas n_o is affected only by electronic polarization [2]. In addition, it is found that the birefringence, Δn ($=n_o - n_e$) of the film decreases as the Sr content decreases.

Figure 4 is the plot of optical propagation loss and RMS (root-mean-square) surface roughness of SBN thin films on MgO(100) substrates. The optical propagation loss of the films decreases with an increase of Sr content although the RMS surface roughness of the films is not varied. This phenomenon is caused by lower birefringence of the SBN film having higher Sr content prevents the optical scattering from the anisotropic refractive indices. Generally, the optical scattering in the material is due to the variations in refractive index either through material inhomogeneities or by grain misorientation in a thin film of birefringent material. And, the surface roughness of the film produces a large variation in refractive index [7]. Therefore, the degree of birefringence becomes the cause of the optical propagation loss in the SBN films which have uniform surface roughness, regardless of composition.

P-E hysteresis loops were obtained for SBN thin films with different compositions on Pt(100)/MgO(100) substrates having MIM (metal-insulator-metal) structure. Figure 5 shows that the remnant polarizations (P_r) and the coercive fields (E_c) of the films having *c*-axis orientation. Both P_r and E_c values of the films increase as the Sr content increases, regardless of the film orientation. The increase of E_c values

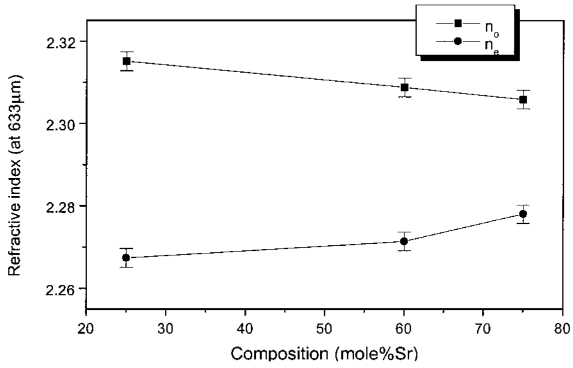

Figure 3. Refractive index of SBN thin film (600 nm thickness) on MgO(100) substrate as a function of the film composition.

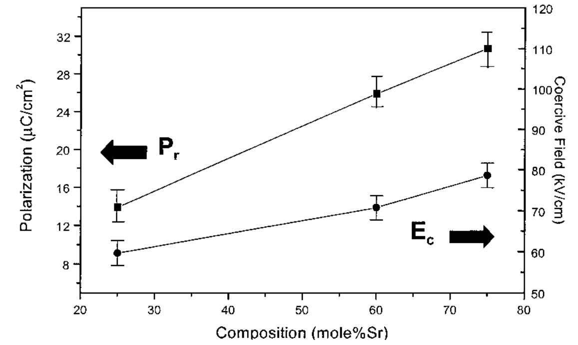

Figure 5. Remnant polarization and coercive electric field in *c*-axis orientated SBN thin films (600 nm thickness) on Pt(100)/MgO(100) substrates a function of film composition.

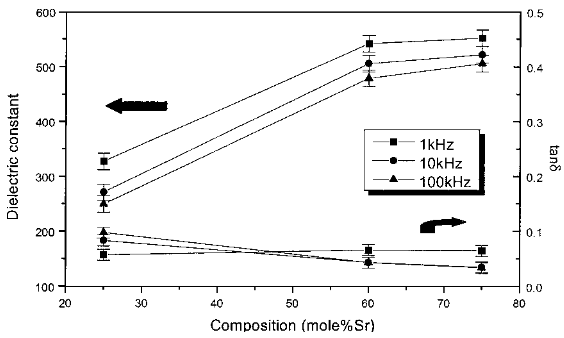

Figure 6. Dielectric constants of *c*-axis oriented SBN thin films (600 nm thickness) on Pt(100)/MgO(100) substrates applied various frequencies of electric field as a function of film composition.

with increasing Sr content might be correlated with an increase of lattice distortion in the tungsten bronze structure as the Sr content is raised in the SBN composition [8]. The more distorted lattice with more Sr^{2+} ion content would be difficult to change the direction of permanent dipoles along the applied electric field.

The dielectric constants (ε), taken from C-V (capacitance-applied voltage) curves, of SBN thin films with various composition having *c*-axis orientation as a function of applied frequency are shown in Fig. 6. The dielectric constants of the films decreases with an increase of applied frequency from 1 kHz to 0.1 MHz, while the dielectric losses are maintained as a level of below 0.1, independently of the film composition. In addition, the dielectric constants also increase as the Sr content increases.

4. Conclusion

Polycrystalline SBN films on fused silica, silicon, and MgO(100) substrates are prepared by sol-gel method using two-step heating process. The *c*-axis preferred orientation is observed for SBN films on MgO(100) and Pt(100)/MgO(100) substrates. The anisotropy of refractive indices (n_o and n_e) of the oriented films on MgO(100) substrates decreases fairly as the Sr content in the film composition increases. Optical propagation loss of the film decreases with an increase of Sr content though the RMS surface roughness is constant regardless of the film composition because low birefringence suppresses the optical scattering by the anisotropy of refractive indices. For ferroelectric properties of the films, both remnant polarization and the coercive filed of the SBN films as well as the dielectric constants increase as the Sr content increases.

Acknowledgments

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