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Formation and Optical Characteristics of Sol-Gel Derived Highly Oriented Ferroelectric (Sr,Ba)Nb_2O_6 Optical Waveguide Thin Films

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Highly c-axis oriented SBN thin films with various compositions were obtained by sol-gel process. The preferential orientation of sol-gel derived film was enhanced by poling the film with high *dc* electric field, and growing the film on seeded MgO substrate. The mechanisms of these methods were discussed in this study. For their optical waveguide applications, the optical properties of SBN thin films were investigated. The anisotropy of refractive indices (n_o and n_e) of the oriented films decreased certainly as Sr content in the film composition increased.

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I. INTRODUCTION

Strontium barium niobate ($Sr_xBa_{1-x}Nb_2O_6$, it is called as SBN:100x, where $0.25 \leq x \leq 0.75$) is currently being investigated as potential ferroelectric material for many micro-device applications such as pyroelectric infrared detectors, electro-optic modulators, holographic storage, and beam steering because of its large pyroelectric coefficient, excellent piezo-electric and electro-optic properties, and photo-refractive sensitivity [1]. Compared with other well-known ferroelectric materials, SBN has an extremely high electro-optic coefficient, for example, the figure of merit is more than 50 times higher than that of $LiNbO_3$ offering the possibility of much smaller devices [2]. SBN is a solid solution between $BaNb_2O_6$ and $SrNb_2O_6$ phases with a tetragonal tung-sten bronze (TTB) structure, and its physical proper-ties vary with its composition [3]. These properties and their applications have been investigated mainly for single crystals and polycrystalline ceramics.

However, the demand for thin film processing has increased due to the developments of electronic and optical integrated devices. Thus, SBN thin films, especially highly c-axis oriented thin films are desired for optical applications because of taking full ad-vantage of their ferroelectricity. There are many processes to obtain the preferred oriented/epitaxial films, for example, using a lattice matching substrate, a seeded thin film growth method [4], modified drying conditions [5], dipped pyrolysis [6], CVD [7] and applying an electric field to a material. Among these methods, first, it was used for having preferential orientation domains to apply high *dc* electric field (larger than coercive field of ferroelectrics) during heat-treatment. Second, we enhanced the orientation of the films on MgO(100) substrates by using a seeds layer in the present study. In addition, their optical properties of these films were characterized as a function of the film composition for optical waveguide applications.

II. EXPERIMENTAL PROCEDURE

Three compositions of SBN films were investigated in the present study with $x = 0.25$, 0.60 and 0.75. Detailed procedure for preparing the films is presented in reference [8]. Single crystal silicon (p-type, (100) oriented wafer), and single crystal magnesium oxide (100) were used for substrates in this study. The SBN solution was spin-coated on these substrates using a spin coater. A single coating yields about 800 Å film-thickness. This procedure was repeated until a desired thickness was obtained. These green films were heat-treated by a two-step heating process, to enhance the densification and the crystallization of the films. The two-step heating process means that the films were first heated from room temperature to 550 °C with slow heating rate (≈ 2 °C/min) and maintained at 550 °C for 5 hr, the temperature is then raised up to the crystal-lization temperature (≈ 1000 °C) with

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same heating rate. The effect of the two-step heating process is described in another paper [9].

Crystallographic orientation as well as crystalline phase of the films was characterized using X-ray diffraction analyzer (Rigaku, D/MAX-RC). The measurements of refractive index and film-thickness were performed by a prism-coupler system using He-Ne laser (MELLES GRIOT, 5 mW) and rutile prism ($n_p = 2.584$ at 633 nm).

For observation of near-field pattern from SBN thin film waveguide, an end-fire coupling method was used in our experiment. The light source was a semiconductor laser with 1.5 μm of wavelength. The output beam was detected by a CCD camera.

III. RESULTS AND DISCUSSION

A preferentially oriented SBN thin film could be obtained by applying a *dc* electric field (about 100 kV/cm) as shown in Fig. 1, which is perpendicular to the surface of thin film during cooling step of the heat-treatment. The film was placed between two stainless steel plates as electrodes, and heat-treated at the crystallization temperature. When the temperature became decreased at the cooling step, the external electric field was applied to the normal direction of the surface of the film and still maintained to be constant until the film was cooled down to room temperature. In this process, it was important when the electric field was applied to the films. Because the applied electric field makes cations of SBN unit cell move easily along the direction of the field in high temperature, the stoichiometry of TTB SBN phase may be broken. Figure 2 shows XRD patterns of SBN60 thin films on silicon substrate, as a function of the temperature at which *dc* electric field was applied. When the temperature is higher, the film with an applied *dc* field shows that the intensities of planes perpendicular (or nearly perpendicular) to *c*-axis such as (211), (311), and (321) increase and those of planes parallel (or nearly parallel) to *c*-axis such as (220), (320), (210), (400), and (410) decrease slightly whereas the film without any *dc* electric field exhibits random orientations. In another word, the domains inside grains in the film were oriented with respect to the field direction. However, the mixed orthorhombic and tetragonal phases were found in the film applied the field at higher temperature because of a large quantity of the movement of Sr and Ba cations in SBN unit cell. In case of the film applied the field at 300 °C, it has only TTB SBN phase as well as a good orientation. These results indicate that the film has the preferential orientation without undesirable phase when the *dc* electric field is applied to the film at 300 °C. (of course, the temperature should be higher than Curie temperature, T_C of SBN) The mechanism of poling effect by *dc* electric field is related to the sense of ferroelectric polarization. In the ferroelectric phase, all the cations (metal ions) are shifted from the nearest mean plane of oxygen ions. The shift of Nb atoms from their planes in the *c*-axis is larger than the shifts of the other metals. Thus, a main polar direction in the SBN is close to an octahedral O-Nb-O axis of Nb. The other Nb atom neighboring to the Nb atom has polar direction opposite to that of the Nb atom. Namely, the *c*-axis of crystal phase in one grain does not coincide with that of the other grain. Therefore, in the view of whole film, it shows random domains. However, a preferential domain is formed, when a higher *dc* electric field than the coercive field E_c of the ferroelectrics, is applied to the ferroelectric films. In case of SBN, the Nb atoms move along *c*-axis and parallel (or almost parallel) to electric field direction. Thus, a single domain is formed in each grain. Finally, the whole film shows a preferred domain arrangement almost parallel to the electric field direction.

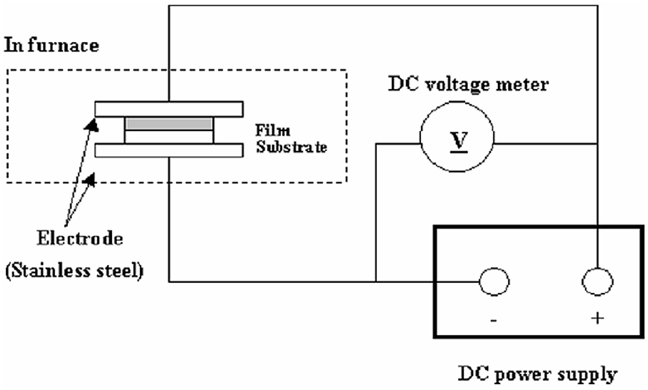

Fig. 1. Equipment for SBN thin film poled by *dc* electric field during heat-treatment.

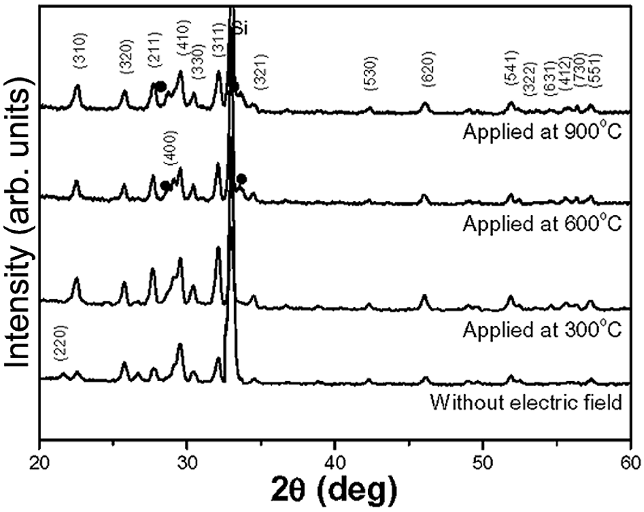

Fig. 2. XRD patterns of SBN60 thin films on silicon substrate as a function of the temperature at which *dc* electric field was applied. (●: orthorhombic phase)

To prepare SBN thin film having better *c*-axis orienta-

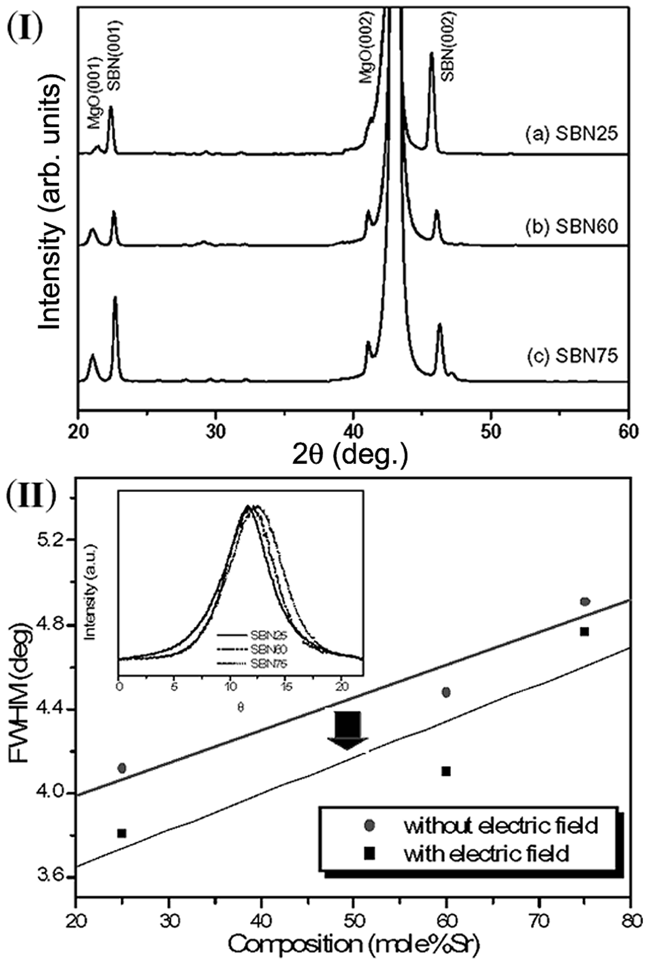

Fig. 3. (I) XRD patterns of SBN thin films on seeded MgO substrate with an applied *dc* electric field as a function of film composition; (a) SBN25, (b) SBN60, and (c) SBN75, (II) FWHM values from rocking curves of SBN thin films on seeded MgO substrates with and without an applied *dc* electric field as a function of film composition. The inset is the rocking curves of the films with the field.

tion, the *dc* electric field was applied to the film on seeded MgO(100) substrate. For preparing this SBN seeds layer on MgO substrate, thinner SBN film was first prepared by a faster spin-coating at 3000 rpm, then heat-treated at 900 °C for 1 hr to form isolated islands. The film on seeded substrate can be obtained by overcoating on these islands using multi-coatings.

The mechanism of highly oriented film by the seeded layer has been proposed that an epitaxial single-crystal thin film can be formed from the isolated epitaxial islands by the following procedures: (1) formation of a continuous and dense epitaxial thin film on single-crystal substrate; (2) growth of pre-existing holes and/or pores greater than a critical size when the film is thinner than the critical thickness; (3) breaking up the film into epitaxial single crystal islands; (4) epitaxial growth of the film by the seeds [4,8]. Figure 3 shows XRD patterns of SBN thin films on seeded MgO substrate with an applied field as a function of film composition. All the films have *c*-axis orientation consisting of single TTB SBN phase, regardless of the film composition. The full width at half maximum (FWHM) values of the inset increase slightly as Sr content in the film increases, and the values are lower than those of the films without the electric field. Since (00l) plane of SBN is perpendicular to *c*-axis, the applied field enhances the *c*-axis orientation of the film.

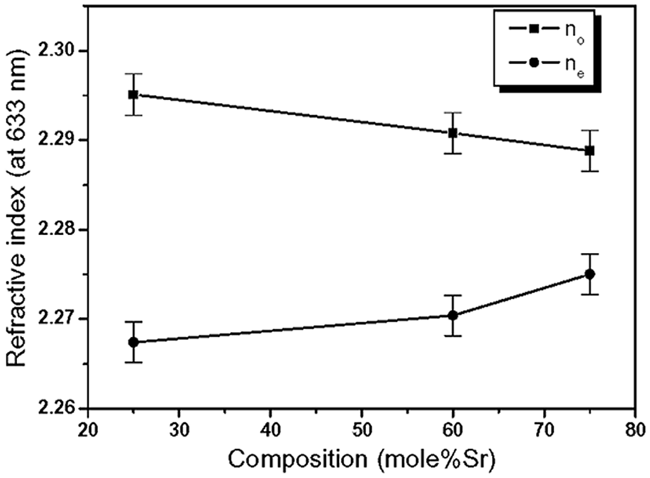

Fig. 4. Refractive indices of SBN thin films on seeded MgO substrate as a function of film composition.

Figure 4 shows the refractive indices of *c*-axis oriented SBN thin films on the seeded MgO substrates as a function of the composition. This result exhibits SBN is optically uniaxial negative material ($n_o > n_e$). The refractive indices of the films approach that of single crystal SBN, which reflects the films are fully densified [10]. In addition, a birefringence, Δn ($= n_o - n_e$) decreases when Sr content in the film composition decreases. The lower birefringence of the higher Sr content of SBN thin film

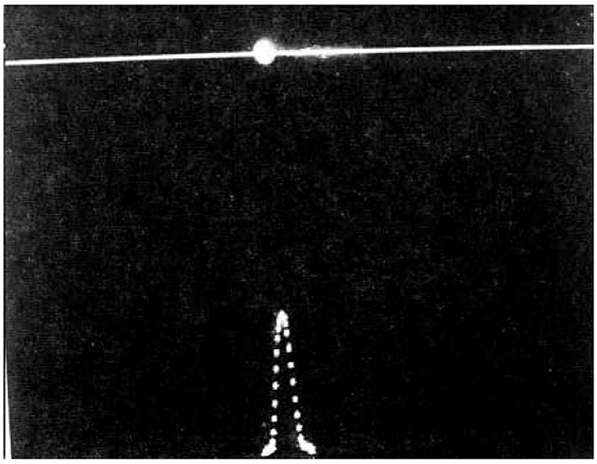

Fig. 5. Single mode optical near-field pattern and intensity profile of SBN slab waveguide on seeded MgO substrate.

prevents optical scattering by the anisotropic refractive indices [10].

For unpatterned slab waveguide, an optical near-field pattern was measured. Figure 5 shows the optical near-field pattern of the SBN75 thin film on seeded MgO substrate. The thickness of the waveguide was 0.5 μm, which admits only one mode. This pattern of a slab waveguide is a proof to realize optical guiding, demonstrating that there exists a total reflection between the core film and the cladding substrate.

IV. CONCLUSION

Highly oriented sol-gel SBN thin films with various compositions have been prepared on seeded MgO(100) substrates by applying *dc* electric field. The film on a seeded substrate has highly orientation because the number of epitaxial nuclei was increased at the interface between the film and the substrate. Also, the mechanism of *dc* electric poling is originated from that Nb atoms in SBN unit cell move along *c*-axis and parallel to electric field direction. Thus, the film shows a preferred domain arrangement almost parallel to the electric field direction. The anisotropy of the refractive indices of films decreases certainly as the Sr content in the film increases. Since the sol-gel process enables the fabrication of micro-devices with various and complex shapes, the sol-gel derived SBN thin films with excellent structural and optical properties could be important material for optical waveguide applications.

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