Nonlinear optical characteristics of sol-gel derived highly oriented ferroelectric strontium barium niobate films

Junmo Koo[*a], Eun-Seok Kang[b], Jae Hyeok Jang[b], and Byeong-Soo Bae[**b]
[a]Fiber Optic Div., Information & Communication Business, Samsung Electronics; [b]Laboratory of Optical Materials and Coating, Dept. of Materials Science and Engineering, Korea Advanced Institute of Science and Technology (KAIST)

ABSTRACT

Highly c-axis oriented SBN films with various compositions were obtained on MgO(100) substrates using sol-gel process. Although the sol-gel process has been developed for ferroelectric thin films, it is known as being hard to fabricate highly oriented films. Thus, the preferential orientation of the films was enhanced by two methods; (1) poling the film by a high dc electric field (>E_c), and (2) growing the film on an SBN seeded MgO substrate. The mechanisms of these methods were discussed. For their optical applications, second-harmonic generation (SHG) effect of SBN films was studied. Fundamental beam of Nd:YAG laser with 1064 nm was used as a pump beam. From Maker fringe measurements with a quartz reference, second-order nonlinear optical (NLO) coefficients d of the films were obtained. The second-order NLO coefficients of the films could be enhanced to considerable extents by applying the electric poling and using a self-seeds layer. These phenomena indicate that the SHG effect is sensitive to crystallographic structure as well as ferroelectric polarization. Mathematical equation was derived to correlate this microstructure to the SHG effect of SBN films.
Keywords: strontium barium niobate, film, sol-gel method, optical waveguide, nonlinear optic, SHG

1. Introduction

Nonlinear optical (NLO) phenomena have been the subject of intense researches in recent years for potential applications in blue light source, optical switches, filters, waveguides, and electro-optic devices.[1,2] For the large scale fabrication of NLO devices, it is crucial to have reliable, high-quality films with desirable NLO properties. To date, the majority of the works in these fields has focused on poled organic polymer films. However, the advantages of inorganic

* junmokoo@samsung.co.kr; phone 82 31 280-1854; fax 82 31 280-9639; Fiber Optics Division, Information & Communication Business, Samsung Electronics, Yongin-city, Kyungki-do, 449-900 Korea; ** bsbae@mail.kaist.ac.kr; phone 82 42 869-4119; fax 82 42 869-3310; http://mse.kaist.ac.kr/~lomc; Laboratory of Optical Materials and Coating (LOMC), Department of Materials Science and Engineering, Korea Advanced Institute of Science and Technology (KAIST), Taejon, 305-701, Korea

Materials and Devices for Photonic Circuits II, Mario N. Armenise, Editor,
Proceedings of SPIE Vol. 4453 (2001) © 2001 SPIE · 0277-786X/01/$15.00

films include improved structural and thermal stabilities, superior mechanical properties, and better impurity concentration control in device fabrication. Among potential inorganic NLO materials, strontium barium niobate [$Sr_xBa_{1-x}Nb_2O_6$ (denoted SBNx·100) where $0.25 \le x \le 0.75$] is a particularly promising candidate because of its high electro-optic coefficients.[3,4] 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.[1] SBN is a solid solution between $BaNb_2O_6$ and $SrNb_2O_6$ phases with a tetragonal tungsten bronze (TTB) structure, and its physical properties vary with its composition.[5] Its property and application have been investigated mainly for single crystals and polycrystalline ceramics. However, the demand for film processing has increased due to the development of electronic and optical integrated devices. SBN films, especially with highly c-axis orientation, are desired for optical applications such as electro-optic devices, photorefractive, and nonlinear optical applications because of taking full advantage of their ferroelectricity.

There are several kinds of fabrication techniques for the films such as rf-sputtering, metalorganic chemical vapor deposition (MOCVD), sol-gel method, and pulsed laser depositions.[6-8] Among these, the sol-gel process has been developed for ferroelectric film processes due to excellent homogeneity, ease of chemical composition control, high purity, low processing temperature, and film uniformity over large area. Therefore, many papers are reported on the synthesis of SBN films by using the sol-gel method, recently.[8] However, it was hard to obtain fully densified and oriented SBN films, and the quality of sol-gel derived films was not good due to being difficult to control the nucleation rate and the location of the nuclei during the crystallization of amorphous film. There are many methods to obtain the preferred oriented/epitaxial films, for example, using a lattice matching substrate, a seeded film growth method[9], modified drying conditions[10], and applying an electric field to a material[11]. Among these methods, it was used in this study to apply high dc electric field (larger than the coercive field of ferroelectrics) to the films with a self-seeds layer during heat-treatment for maximum ferroelectric properties which could make nonlinear optical applications including electro-optical devices. The crystallographic results of the seeds-layer effect was described in reference 12.

We report the investigation of the second-harmonic generation (SHG) of sol-gel derived SBN films with various compositions, and its enhancement with electric poling. The mechanism of this method is discussed.

2. Experiments

Four compositions were investigated in the present study with x = 0.25, 0.40, 0.60 and 0.75. Strontium metal, barium metal, and niobium ethoxide were used as the starting reagents. 2-methoxyethanol was used as a solvent to avoid precipitation. A precise procedure for preparing the precursor solution is presented in another paper.[12,13] The solution was spin-coated onto MgO(100) single crystal substrates at 2000 rpm for 30 secs. After drying in the air, the film was dried on a hot plate at 180°C for 10 mins and 360°C for 10 mins, to remove organic residues completely. These films were then heat-treated at 900°C by a modified heating schedule to enhance densification and crystallization.[13] Although SBN films on MgO substrate have highly c-axis orientation, the orientation quality of sol-gel derived film is generally not better than the films prepared by pulsed laser deposition (PLD) or metalorganic chemical vapor deposition (MOCVD) processes. Therefore, the preferential orientation of the films was enhanced by using MgO substrate with SBN seeds.[12] For preparing this seeds layer on MgO substrate, thinner film was prepared by a faster spin-coating at 3000 rpm, then heat-treated at 900°C for 1hr to form isolated islands. The SBN film with seeded substrate can be obtained by overcoating these islands using multi-coatings. SHG properties were measured using a Q-switched Nd:YAG laser at a wavelength of 1.064 μm. The pulse width is 10 ns with a repetition rate of 10 Hz. The second-harmonic wave of y-cut quartz (4.635 mm thickness) with NLO coefficient, $d_{11,Q}$ (≈ 0.34 pm/V) was used as reference signal. The SHG intensities of SBN films were measured using s- and p-polarized input beams, respectively by aligning the polarizer appropriately. Figure 1 shows the experimental setup for the electric poling of the films. The film was placed between two stainless steel plates as electrodes, and heat-treated at the crystallization temperature. When the cooling temperature after the crystallization was 300°C, the external dc electric field (a high voltage of up to 1 kV) which was higher than the coercive field E_c of the film, was applied to the normal direction of the surface of the film and still maintained to be constant until the sample cooled down to room temperature. Then, the preferential orientation of the films was investigated using by X-ray diffraction.

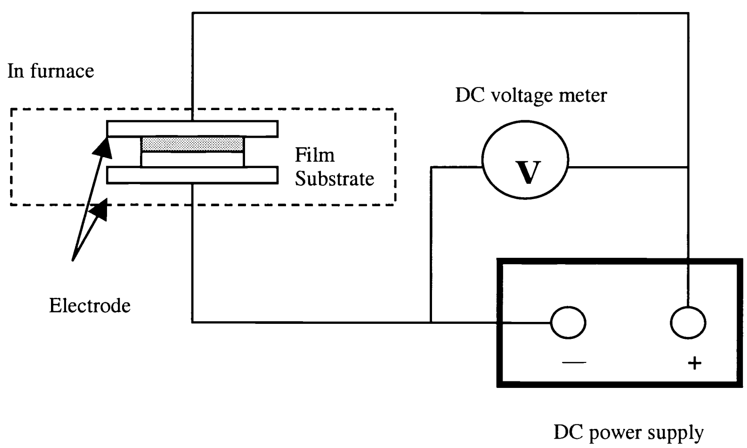

Figure 1. Experimental setup for dc electric poling during heat-treatment.

3. Results and Discussion

Figure 2 shows XRD patterns of SBN films (600 nm thickness) on seeded MgO substrate with an applied field (~ 100 kV/cm) at 300°C as a function of film composition. When the temperature where the field was applied was higher, the mixed orthorhombic and tetragonal phases were found in the film because of a large quantity of the movement of Sr and Ba cations in SBN unit cell. All the films in Figure 2 have c-axis orientation consisting of single TTB SBN phase, regardless of the film composition. However, the full width at half maximum (FWHM) values in 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 (00*l*) plane of SBN is perpendicular to c-axis, the applied field enhances the c-axis orientation of the film. The mechanism of poling effect by dc electric field is related to the sense of ferroelectric polarization. In the ferroelectric phase (below the phase transition temperature, T_C), all the cations (metals) are shifted from the nearest mean plane of oxygen ions. The shift of Nb atom from its plane in the c-axis is lager than the shifts of the other metals. Thus, the polar direction in the SBN is close to an octahedral O-Nb-O axis. The other Nb atom neighboring to this 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, the preferential domains are 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.

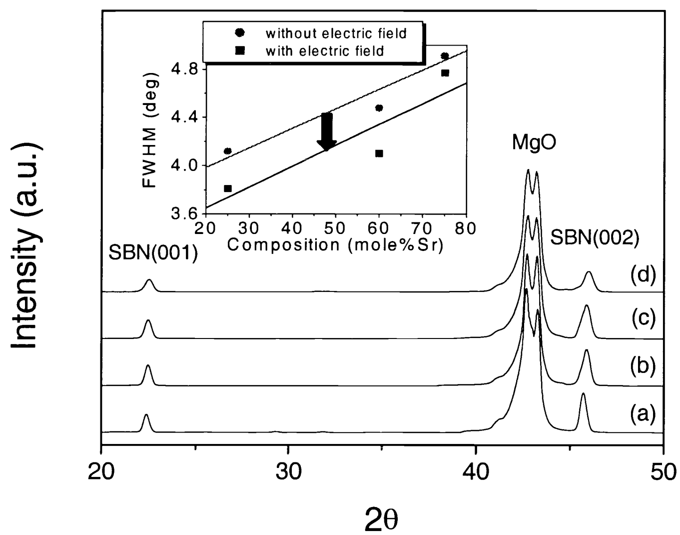

Figure 2. XRD patterns of SBN films on seeded MgO(100) substrates with an applied dc electric field at 300°C as a function of film composition; (a) SBN25, (b) SBN40, (c) SBN60, and (d) SBN75, where the inset is a plot of FWHM values of the rocking curves of the films.

Figure 3 shows Maker fringe patterns of SBN films on seeded MgO substrate with an applied field as a function of film composition. When the electric field was not applied to the film on MgO substrate, the SHG signal was not obtained. Since the film has random domains that mean a domain has a neighbor with opposite polar direction in the grain, net polarization contributed SHG effect has a little amount. This result indicates that the SHG effect is very sensitive polarizationally. For SHG measurements, $E_{in,s}^{\omega}$ - $E_{out,p}^{2\omega}$ means the polarization configuration of the input (s-polarization) and output (p-polarization) beams, whereas $E_{in,p}^{\omega}$ - $E_{out,p}^{2\omega}$ means the polarization configuration of the input (p-polarization) and output (p-polarization) beams, respectively. In case of $E_{in,s}^{\omega}$ - $E_{out,p}^{2\omega}$ combination, the effective nonlinear optical coefficient, d_{31}^{eff} of SBN25, 40, 60 and 75 films were measured as 6.25, 6.93, 9.09, and 11.93 × $d_{11,Q}$ (≈ 2.13, 2.35, 3.09 and 4.06 pm/V), respectively. Similarly, d_{33}^{eff} of SBN25, 40, 60 and 75 films were calculated as 18.18, 20.12, 23.30, and 30.82 × $d_{11,Q}$ (≈ 6.18, 6.84, 7.92, and 10.48 pm/V), respectively, at $E_{in,p}^{\omega}$ - $E_{out,p}^{2\omega}$ combination. The coefficient ratios of d_{33}/d_{31} for all compositions were estimated by ~ 3, which was in accord with a general assumption.[14] These values of the films increase with an increase of Sr content in the film, regardless of beam combinations, as shown in Figure 4. This behavior is similar with the linear electro-optic coefficients of SBN films, because the electro-optic effect is regarded as a special case of nonlinear optic effect.[15] It originates from the NLO coefficient which is dependent on the spontaneous polarization and the dielectric constant.[16] Both P_s and ε values of SBN films are known to increase as the Sr content increases.[13] Among these calculated values, the d_{31}^{eff} and d_{33}^{eff} coefficients for SBN films are comparable to those of $LiNbO_3$ films obtained by PLD technique ($d_{31} \approx -5.18$ and $d_{33} \approx -18.35$ pm/V).[17] Unfortunately, the comparison between the film and SBN single crystal was not carried out because the exactly measured values for the single crystal could not be found in the literature. Of course, there exist the theoretical calculated values of SBN75 single crystal by computing the electronic polarization of Nb-O bonds, which are $d_{31} = 5.0 \pm 3.0 \times d_{36,KDP}$ (2.5 ± 1.5 pm/V) and $d_{33} = 12.8 \pm 3.6 \times d_{36,KDP}$ (6.4 ± 1.8 pm/V).[18] The larger values of the SBN75 films measured in this study than the calculated values may be originated from the used model in the reference which took into account only electronic effects between Nb-O bonds neglecting the effects of the other bonds. Actually, the considerable differences between the measured d coefficients of $Ba_2NaNb_5O_{15}$ single crystal and the calculated values are found by 5 ~ 7 pm/V in the paper.[18]

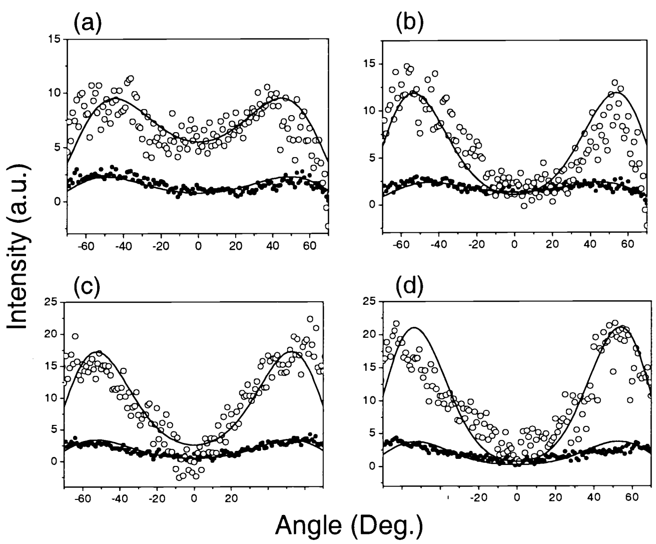

Figure 3. Maker fringe patterns of SBN films on seeded MgO(100) substrates with an applied dc electric field at 300°C as a function of film composition; (a) SBN25, (b) SBN40, (c) SBN60, and (d) SBN75, where s-p and p-p mean the input and output beams are either s- or p-polarized)

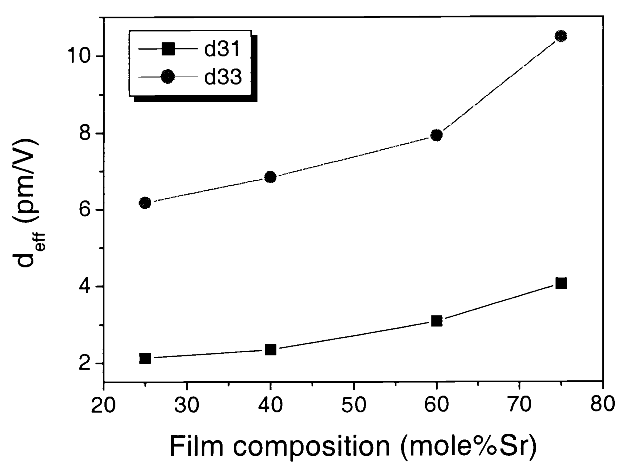

Figure 4. Plot of the effective nonlinear optical coefficients, d_{33} and d_{31} of SBN films on seeded MgO(100) substrates with an applied dc electric field at 300°C as a function of film composition.

The SHG effect of the SBN film is very sensitive crystallographiclly as well as polarizationally. Figure 5 shows Maker fringe patterns of SBN75 films on seeded and unseeded MgO (100) substrates, respectively. The SHG intensity of the film on seeded MgO substrate is higher than that of the film on unseeded substrate, regardless of beam configurations. As listed in Table 1, d_{33}^{eff} and d_{31}^{eff} coefficients of the film increase considerably by using a seeds layer. Thus, these results indicate that the nonlinear optical coefficients of SBN film can increase to a considerable extent by improving the epitaxial quality of the film.

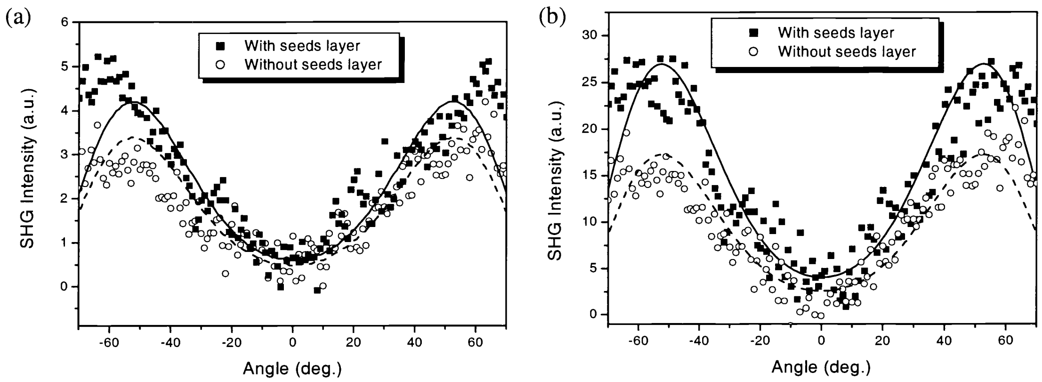

Figure 5. Maker fringe patterns of SBN75 films on SBN25 composition seeded and unseeded MgO (100) substrates, respectively, that all the films are applied with an applied dc electric field at 300°C; (a) input : s-pol., output : p-pol. and (b) input : p-pol., output : p-pol..

Table 1. Comparison of nonlinear optical coefficient, d for SBN75 films on unseeded and seeded MgO substrates.

d_{ij} ($\times 10^{-12}$ m/V)	Film on unseeded substrate	Film on seeded substrate
d_{33}	9.41	10.48
d_{31}	3.64	4.06

To understand the difference of Maker fringes shown in Figure 5, structural variants as well as ferroelectric spontaneous polarization directions should be taken into account. Two variants arise from the nucleation of a ferroelectric material (note that the film with the paraelectric phase was prepared in the heat-treatment). The first parameters, volume fractions of two types, are called $\alpha_{\pm p}$ related to ferroelectric polarization, whose subscript denotes the direction of spontaneous polarization. The second parameter is called D, corresponds to the degree of epitaxial growth. Considering all their contributions, the expressions of the effective nonlinear optical coefficients, d_{3i} (i = 1, 3) of SBN material are transformed by a following equation;

$$d_{3i}^{eff} = (\alpha_p - \alpha_{-p})D\, d_{3i} \quad (i = 1,3) \qquad (1)$$

where

$$\alpha_p + \alpha_{-p} = 1, \text{ and } 0 < D \leq 1$$

$(\alpha_p - \alpha_{-p})$ is equal to the net orientation of domains, and D means how much the film has grown epitaixally.

When the dc electric field was not applied to the film, the value of net orientation is a little ($\alpha_p \approx \alpha_{-p}$) and D is small because of random orientation of domains and rough lattice-matching. Thus, since the d_{eff}s of the film are closed to zero, the SHG effect did not occur (SH signals were not detected although SHG effect might be occur). However, when the dc electric field (higher than the coercive field, E_c) was applied to the film on an unseeded MgO substrate, the lattice dipoles of Nb-O octahedra align the direction parallel to the applied field along c-axis, according to the poling effect. Thus, the SH signals can be measured by the SHG effect in the film because $(\alpha_p - \alpha_{-p})$ was closed to 1, in spite of low value of D. Namely, $(\alpha_p - \alpha_{-p})$ describes the effectiveness of the electric poling. In case of the film on a seeded MgO substrate with an applied dc electric field, the NLO coefficients of the film on a seeded substrate has larger values than those of the film on an unseeded substrate as shown in Table 1 because $(\alpha_p - \alpha_{-p})$ and D are closed to 1 together by the effects of electric poling and seeded substrate. Thus, it is important to make a highly oriented film through applying the electric poling and using a seeds layer for the enhancement of the SHG effect.

4. Conclusions

Highly oriented sol-gel SBN films with various compositions have been prepared on SBN seeded MgO(100) substrates by applying dc electric field. The composition dependence for nonlinear optical property was observed from such SBN films. The second-order nonlinear optical coefficients increased as the Sr content increased and improved by applying the electric poling and using a seeds layer. The d_{33} and d_{31} coefficients of SBN75 films were comparable to those of $LiNbO_3$ single crystals. Thus, the sol-gel derived SBN films can be regarded as a promising medium for blue laser operation by second-harmonic generation (SHG) of commercially available GaAs/(Al,Ga)As diode laser because of their large nonlinear optical coefficients, if the other technological problems such as optical damage threshold and quasi-phase matching properties in the fabrication of devices will be overcome.

ACKNOWLEDGMENTS

This work has been financially supported by Korea Science and Engineering Foundation (Grant No. 981-0803-019-2), and partly by the Brain Korea 21 project.

REFERENCES

1. Y. Xu, *Ferroelectric Materials and Their Application*, pp. 37-100, Elsevier Science Publisher, Amsterdam, 1991.
2. A. M. Glass, "Investigation of the electrical properties of $Sr_{1-x}Ba_xNb_2O_6$ with special reference to pyroelectric detection," *J. Appl. Phys.* **40**, p. 4699, 1969.
3. P. V. Lenzo, E. G. Spencer, and A. A. Ballman, "Electro-optic coefficients of ferroelectric strontium barium niobate," *Appl. Phys. Lett.*, **11**, p. 23-25, 1967.
4. S. Sakamoto and T. Yazaki, "Anomalous electro-optic properties of ferroelectric strontium barium niobate and their device applications," *Appl. Phys. Lett.*, **22**, pp. 429-431, 1973.
5. N. S. VanDamme, A. E. Sutherland, L. Jones, K. Bridger, and S. R. Winzer, "Fabrication of optically transparent and electrooptic strontium barium niobate ceramics," *J. Am. Ceram. Soc.*, **74**, p. 1785, 1991.
6. S. S. Thöny, K. E. Youden, J. S. Harris, Jr., and L. Hesselink, "Growth of epitaxial strontium barium niobate thin films by pulsed laser deposition," *Appl. Phys. Lett.*, **65**, pp. 2018-2020, 1994.
7. M. J. Nystrom, B. W. Wessels, W. P. Lin, G. K. Wong, D. A. Neumayer, and T. J. Marks, "Nonlinear optical properties of textured strontium barium niobate thin films prepared by metalorganic chemical vapor deposition," *Appl. Phys. Lett.*, **66**, pp.1726-1728, 1995.
8. C. J. Chen, Y. Xu, R. Xu, and J. D. Mackenzie, "Ferroelectric and pyroelectric properties of strontium barium niobate films prepared by the sol-gel method," *J. Appl. Phys.*, **69**, p. 1763, 1991.
9. K. T. Miller, F. F. Lange, and D. B. Marshall, "The instability of polycrystalline thin films: Experiment and theory," *J. Mater. Res.*, **5**, p. 151, 1990.
10. C. J. Kim, D. S. Yoon, J. S. Lee, C. G. Choi, W. J. Lee, and K. No, "Electrical characteristics of (100), (111), and randomly aligned lead zirconate titanate thin films," *J. Appl. Phy.*, **76**, pp. 7478-7482, 1994.
11. K. Tanaka, A. Narazaki, K. Hirao, and N. Soga, "Optical second harmonic generation in poled MgO-ZnO-TeO_2 and B_2O_3-TeO_2 glasses," *J. Non-Crystal. Solids*, **203**, pp. 49-54, 1996.
12. J. Koo, J.H. Jang, and B.S. Bae, "Preparation and characteristics of seeded epitaxial $(Sr,Ba)Nb_2O_2$ optical waveguide thin films using sol-gel method," *J. Mater. Res.*, **16**, pp. 430-436, 2001.
13. J. Koo, J.H. Jang, and B.S. Bae, "Crystallization behavior of sol-gel-derived strontium barium niobate thin films," *J. Am. Ceram. Soc.*, **84**, pp. 193-199, 2001.
14. W. N. Herman and L. M. Hayden, "Maker fringes revisited: second-harmonic generation from birefringent or absorbing materials," *J. Opt. Soc. Am. B*, **12**, p. 416, 1995.
15. J. Koo, C. Lee, J.H. Jang, K. No, and B.S. Bae, "Measurement of the linear electro-optic coefficients of sol-gel derived strontium barium niobate thin films using two-beam polarization interferometer," *Appl. Phys. Lett.*, **76**, pp. 2671-2673, 2000.
16. P. Gunter, *Electro-Optic and Photo-refractive Materials*, p. 175, Spinger-Verlag, New York, 1991.
17. D-W. Kim, S-H. Lee, and T. W. Noh, "Structural and nonlinear optical properties of epitaxial $LiNbO_3$ films grown by

pulsed laser deposition," *Mater. Sci. & Eng. B*, **56**, pp. 251-255, 1998.

18. C. R. Jeggo and G. D. Boyd, "Nonlinear optical polarizability of the niobium-oxygen bond," *J. Appl. Phys.*, **41**, p. 2741, 1970.