Growth of highly *c-axis* oriented SBN thin films on Si(100) with/without MgO buffer layer by the sol-gel method*

XIAO-YAN CAO, HUI YE, ZHI-RU SHEN, NIAN-HUI DENG, BING GUO, GU-PEPOST
Instrumentation, Zhejiang University, Hangzhou 310027, People's Republic of China
E-mail: cswallowprc@hotmail.com
http://www46.mail.sohu.com/control/attac

Bulk strontium barium niobate ($Sr_xBa_{1-2x}Nb_2O_6$, or SBN:x) possesses the largest diagonal electro-optic coefficient and piezoelectricity among all electro-optic crystals reported to date. With the electro-optic coefficient r_{33} in the range of (4–13.5) $\times$ 10^{-10} m/V (x = 0.25–0.75), it compares quite favorably with industry standard $LiNbO_3$ where r_{33} is 0.3 $\times$ 10^{-10} m/V [1, 2]. But the growth of bulk, striation-free SBN crystals has proven to be difficult and expensive, the heteroepitaxial growth of thin and highly ordered SBN film, which is expected to allow integrated wave-guiding voltages about 1000 times lower than that required in SBN bulk crystals, is an effective alternative. However, the realization of the excellent electro-optic properties of SBN requires a successful heteroepitaxial growth of the film with the (001) SBN direction perpendicular to the lattice-matched substrate plane.

Si (100) or MgO (100) is commonly used as the substrate material for the hetero-growth of SBN thin films. The lattice mismatch between MgO(100) and SBN is Ma = Mb = 1.64%, Mc = 6.34%, and the mismatching of Si(100) and SBN is Ma = Mb = 12.6%, Mc = 37.1% [3]. The experiments have already proven that the preferred c-axis orientation of MgO-based SBN film is obviously better than that of the Silicon-based SBN film [4, 5] under the same condition. However, with the perfect development of silicon micro fabrication technology, the combination of ferroelectric films and silicon technology can construct a sort of ferroelectric-silicon integrated system which not only exert the ferroelectric films' excellent performance but also makes use of advanced silicon process technology. The growth of high-quality optoelectronic films on the semiconductor (such as Si and GaAs) substrates has proved to be practical in some fields. As a result, a number of researchers have attempted to prepare SBN thin film on the (100)Si substrate since the 1990s using various techniques. But the c-axis orientation of the SBN films was not very good [6, 7]. Considering the crystal constant's matching among MgO, semiconductor substrate and ferroelectric film, MgO film was usually introduced as a buffer layer sandwiched between them [8, 9]. But until now the growth of epitaxial SBN film on the Si substrate with MgO buffer layer has not been reported.

The sol-gel method was chosen to prepare the ferroelectric thin films, because it can offers many advantages such as excellent homogeneity, ease of precise composition control, high purity, and film uniformity over a large area [10]. In this paper we report a sol-gel method of growing highly c-axis-oriented SBN thin film on (100)Si with/without MgO buffer layer. SBN films with preferred c-axis orientation can be easily obtained under optimal annealing temperature, appropriate precursor solution and buffer-layer.

SBN thin films studied here were fabricated by the sol-gel method using metal alkoxides. Mg, Sr, Ba, $NbCl_5$ were used as raw materials and 2-methoxyethanol ($CH_3OC_2H_4OH$) was used as a common solvent. Mg, Sr, Ba metal alkoxide were obtained through dissolving Mg, Sr, Ba into the 2-methoxyethanol in a dry argon atmosphere. Niobium alkoxides are more complicated and difficult to prepare and was obtained by first reacting KOH and $NbCl_5$ in $CH_3OC_2H_4OH$ and then filtering out the KCl precipitate. The mixture of Sr, Ba and Nb alkoxides in a certain ratio formed the SBN ($Sr_xBa_{1-x}Nb_2O_6$) precursor solution, which was spin-coated onto the Si substrate at 1000 rpm for 3 s and 3000 rpm for 30 s and then heat-treated in a home-made rapid thermal annealing chamber (RTP-500) with a two-step heating process (ramping rate of 40 °C/s, 350 °C for 2 min, 1000 °C for 4 min) to crystallize the films. The two-step heating process can avoid strains and other defects at the interface between film and substrate [11]. The procedure was repeated until a desired thickness was obtained. Introducing of MgO buffer layer was accomplished by coating the Mg alkoxide on the Si substrate in the same way before depositing SBN thin film.

The epitaxial relationship between these films and substrate was analyzed by X-ray diffraction (XRD), which was affected by annealing temperature and MgO buffer layer. Fig. 1illustrates XRD patterns of the SBN60 films annealed at different temperatures. At 900 °C, the tungsten bronze structure of SBN phase was found to be not completely formed, and SN phase and SBN phase co-existed, the former represented higher diffraction intensity. Whereas at 1000 °C (001) and (002) peak intensity of SBN phase became much higher than the other orientations (such as(121), etc.), and the

* Supported by the National Natural Science Foundation and the Natural Science Foundation of Zhejiang Province of China, under Grant Nos. 60008005 and 500077.

0022–2461 © 2004 Kluwer Academic Publishers

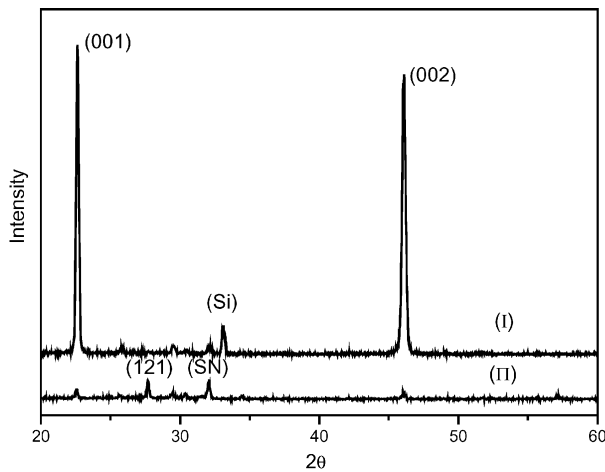

Figure 1 XRD diffraction patterns of the SBN60 thin films on Si(100) substrates with different crystallization temperature: (I) 900 °C and (II) 1000 °C.

corresponding intensity of SN phase was nearly negligible. This proves that the TTB SBN has already been completely formed. Therefore, annealing temperature is the considerable important factor for the growth of TTB SBN phase, only higher temperature can transform orthorhombic SN and BN to TTB SBN phase which has preferred *c*-axis orientation.

Fig. 2 showedthe XRD patterns of the SBN60 thin films on Si(100) substrates with different temperature

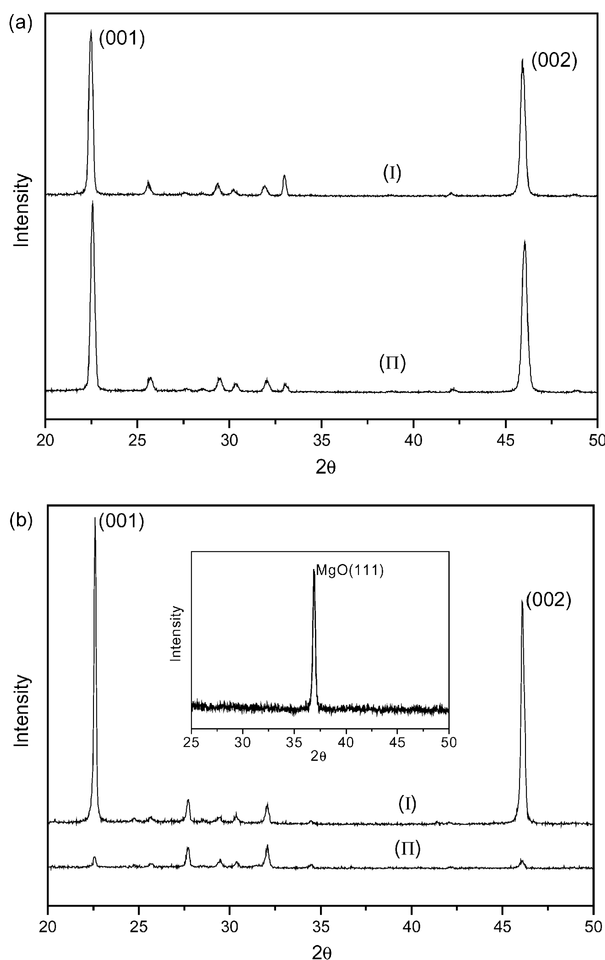

Figure 2 XRD patterns of the SBN60 thin films on Si(100) substrates at (a) 900 °C and (b) 1000 °C. (I) with MgO and (II) without MgO.

(a) 900 °C, (b) 1000 °C and with/without MgO buffer layer. Fig. 2b clearly indicates that SBN thin film with MgO buffer layer has the much higher preferred *c*-axis orientation on Si substrate. As expected, introducing the MgO buffer layer can effectively promote the formation of TTB SBN phase from SN and BN phases at lower temperature. However, the high temperature has already transformed SN and BN to TTB SBN phase sufficiently and increased the diffusion between the film and MgO buffer layer simultaneously. Accordingly, at 1000 °C all the films were found exhibiting strong (001) and (002) reflection of TTB SBN regardless of the MgO buffer layer. Distinctive diffraction peaks corresponding to the MgO layer could not be observed, probably due to its thin thickness (∼50 nm). It is concluded that MgO bufferlayer can decrease the crystalline temperature effectively, which appears favorable (111)—the oriented diffraction peak is clearly shown in the inset of Fig. 2b.

The thickness of the MgO buffer layer also strongly affected the quality of the films. Fig. 3 showsthe XRD patterns of SBN60 thin films with different thickness of MgO buffer layer under the annealed temperature of 900 °C. It is shown that thin films' preferred orientation in the (001) direction decreased as the layer number of MgO buffer layer increased. Randomly oriented polycrystalline SBN films with visible defects were obtained under the same process conditions when the MgO buffer layer was thicker (5 layer). It suggests that the structural endurance limit of the buffer layer under the strains of MgO/Si and SBN/MgO should be considered in processing. During the thermal process preparation of MgO thin films, strain was induced between the layers, the more the number of layers, the greater the strain induced. The distortion of the MgO lattice increased, so the lattice mismatch between the MgO layer and the SBN layer become larger. Therefore, highly preferred (001) direction SBN thin films are difficult to gain when the MgO buffer layer is thicker.

Fig. 4a andb shows images of AFM taken from the SBN60 films without/with MgO buffer layer at 900 °C. The film without MgO buffer layer consisted of 200 nm

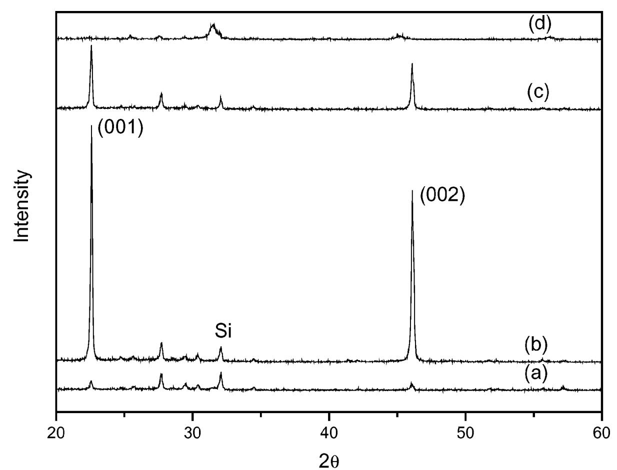

Figure 3 XRD diffraction patterns of the SBN60 thin films on Si(100) substrates with MgO buffer layer: (a): no, (b): 1 layer, (c): 2 layers and (d): 5 layers.

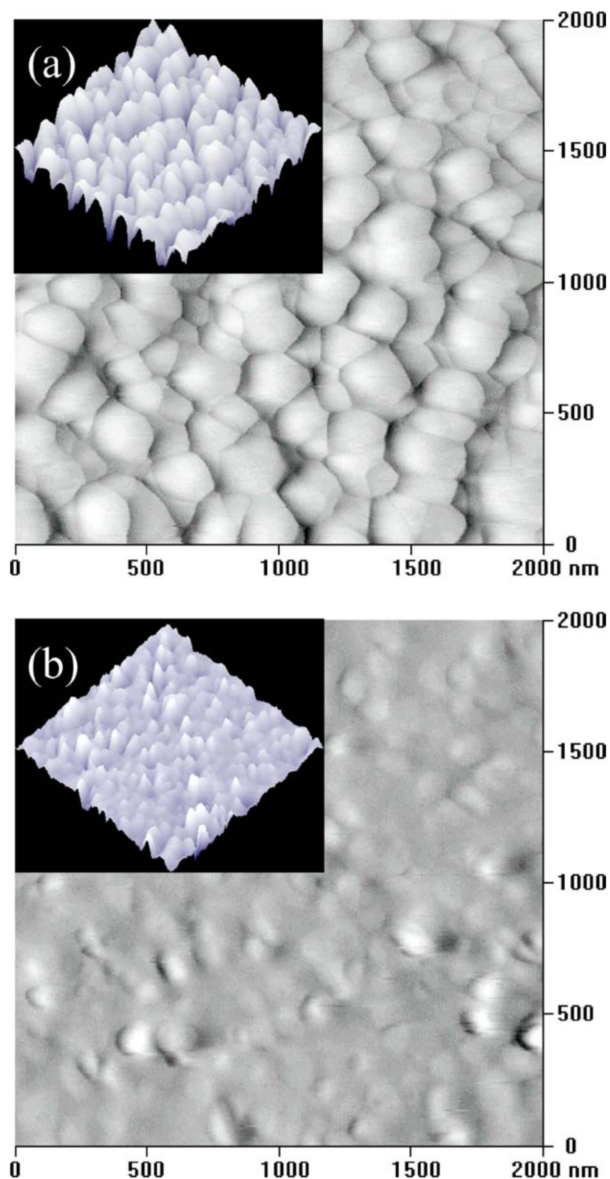

Figure 4 AFM images of the surface morphology of SBN60 thin films on Si(100) substrate without (a)/with (b) MgO buffer layer The images are 2 μm square, the mean grains are 200 and 400 nm and Ra are 12 and 4 nm respectively.

mean global grains uniformly distributed with the surface roughness (Ra) of 12 nm. Comparatively, the surface morphology of the film with MgO buffer layer are smoother and more uniform, the mean grains and Ra obviously decreased (100 and 4 nm respectively). Indeed, the good surface morphology is due to the smaller mismatch between the MgO layers and the substrate, and the MgO buffer layer acted as a self-template of SBN film, and played an important role on the growth of epitaxial films.

In summary, dense and crack-free SBN thin films with the preferred *c*-axis orientation were successfully obtained by the sol-gel method on Si(100) substrates without/with MgO buffer layer at different temperatures. Effects of annealing temperature and MgO buffer layer on the structural and morphological properties of SBN thin films were investigated. Experiments show that the temperature is the key factor for obtaining selectively superior orientation of SBN. The orthorhombic phases such as SN and BN appeared at lower temperatures and were transformed to single-phase TTB SBN, while introducing MgO buffer layer. The film with MgO buffer layer showed excellent epitaxy and densely packed grain morphology.

References

1. Y. H. XU, "Ferroelectric Materials and Their Applications" (Elsevier Science Publishers, Amsterdam, 1991) Chap. 6, p. 82.
2. D. TRIVEDI, P. TAYEBATI and M. TABAT, *Appl. Phys. Lett.* **68** (1996) 3227.
3. K. NISHIO, N. SEKI, J. THONGRUENG, Y. WATANABE and T. TSUCHIYA, *J. Sol-Gel Sci. Technol.* **16** (1999) 37.
4. H. YE and H. MINDE, *Opt. Instr.* **23** (2001) 193.
5. H. YE and M. T. MELANIE, *Ho, Act Optica Sinica.* **22** (2002) 1170.
6. J. KOO, J. H. JANG and B. S. BAE, *J. Amer. Ceram. Soc.* **84** (2001) 193.
7. H. F. CHENG and G. S. CHJOU, *Appl. Surf. Sci.* **113/114** (1997) 217.
8. D. K. FORK and G. B. ANDERSON, *Appl. Phys. Lett.* **63** (1993) 1029.
9. H. ROU, T. M. GRAETTINGER, A. F. CHOW, C. N. SOBLE, D. J. LICHTENWALNER, O. AUCIELLO and A. I. KINGON, *Mater. Res. Soc. Symp. Proc.* **81** (1992) 243.
10. Y. HU, *J. Mater. Sci.* **31** (1996) 4255.
11. J. KOO, J. H. JANG and B. S. BAE, *J. Sol-Gel Sci. Technol.* **19** (2000) 611.

Received 27 August 2003
and accepted 29 April 2004