

# Novel route for the epitaxial growth of (SrBa)Nb<sub>2</sub>O<sub>6</sub> thick films by the sol-gel method using a self-template layer

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A novel sol-gel processing method has been developed to fabricate epitaxial (SrBa)Nb<sub>2</sub>O<sub>6</sub> (SBN) thin films on MgO substrates. It involves the introduction of a SBN self-template layer on MgO by pulsed laser deposition (PLD). Effects of the SBN self-template layer on the structural and morphological properties of the sol-gel-derived SBN films were investigated. Compared to the sol-gel-derived SBN films without a self-template layer, our new technique produces SBN films of excellent epitaxy and more dense grains with uniform distribution. This can be explained by the self-template-layer-induced homoepitaxial growth. The innovative processing method with combination of PLD and sol-gel is a promising technique in preparing high-quality, thick epitaxial SBN films for electro-optics device applications.

## I. INTRODUCTION

The need for various opto-electronic devices, including electro-optic, spatial light modulators, pyroelectric detectors, and many others has greatly stimulated the investigation on the growth of ferroelectric tungsten bronze.<sup>1-3</sup> Strontium barium niobate with tetragonal tungsten bronze (TTB) structure (Sr<sub>x</sub>Ba<sub>1-x</sub>Nb<sub>2</sub>O<sub>6</sub>, SBN) possesses extremely high linear electro-optical ( $r_{33} = 1340$  pm/V), nonlinear optical coefficients ( $d_{33} = 12.8$  pm/V), strong photorefractive effect, and excellent pyroelectric property. The TTB-type SBN composition can also be continuously varied over a wide range ( $x = 0.25$  to  $0.75$ ) to tailor and optimize certain properties for use in various devices.<sup>4,5</sup> However, the growth of bulk SBN crystals is difficult.<sup>6</sup> Recently, the demand for thin-film processing has increased due to the development of integrated devices. Heteroepitaxial or highly *c*-axis-oriented growth of SBN thin films of several micrometers thick is viewed as an

alternative solution for electro-optic, photorefractive, and pyroelectric applications. For example, the desired SBN orientation for waveguide applications is with its optical axis (*c*-axis for SBN) orthogonal to the plane of the interface, so that the largest electro-optic and nonlinear optical coefficients can be accessed. In addition, to decrease the propagation optical loss, epitaxial SBN films with adequate surface smoothness are required. Therefore, technique to fabricate epitaxial thick SBN films is of paramount importance to engineers and designers.

To date, epitaxial SBN films have been prepared by pulse laser deposition (PLD), radio-frequency sputtering, and liquid-phase epitaxy,<sup>7-9</sup> whereas only *c*-axis-oriented SBN grains were produced by sol-gel<sup>3,10,11</sup> and metalorganic chemical vapor deposition (MOCVD).<sup>12</sup> Among them, the sol-gel method offers many advantages such as excellent homogeneity over large area, ease of precise composition control, low equipment cost, and large-scale reproduction for giant commercial prospects.<sup>13</sup> At the same time, films with thickness above 1 μm can be easily fabricated by the sol-gel process. However, it is usually very difficult to obtain epitaxial films by the sol-gel method. Great efforts have been attempted to adjust the film orientation in sol-gel processing.<sup>14-16</sup> Ishikawa *et al.* reported the role of PbTiO<sub>3</sub>

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seeding layer on texture and microstructure of sol-gel-derived (PbZr)TiO<sub>3</sub> thin films. In the work of Osaka *et al.*, a Bi–Ta multi-seeding layer system was demonstrated to improve the orientation and ferroelectric properties of SrBi<sub>2</sub>Ta<sub>2</sub>O<sub>9</sub> thin films. However, until now little effort has been made to control the orientation of sol-gel-derived SBN thin films. As is known, PLD has been shown to be ideally suited to the epitaxial growth of multicomponent oxides.<sup>17</sup> So in this paper, a novel technique, combining the PLD and sol-gel methods, has been developed to prepare epitaxial SBN thick films. Firstly, a thin self-template layer of epitaxial Sr<sub>0.6</sub>Ba<sub>0.4</sub>Nb<sub>2</sub>O<sub>6</sub> (SBN60) was deposited on MgO using the PLD method. Then SBN thick films were deposited on this self-template layer by sol-gel method. Our experimental results indicate high-quality epitaxial SBN films have successfully fabricated on MgO substrates. The innovative processing technique thus incorporates the advantages of both the PLD and sol-gel methods.

## II. EXPERIMENTAL

SBN60 self-template layers were prepared using a typical PLD set-up. A KrF excimer laser operating at 248 nm and 10 ns pulse width was employed. The average energy density irradiated on the target was maintained around 4 J/cm<sup>2</sup>, and a laser repetition rate of 10 Hz was used. The SBN60 target was prepared by conventional ceramic processing. The (100) MgO was chosen as growth substrate from crystallinity and optical considerations. Deposition was carried out with substrate temperature at 700–750 °C in an oxygen partial pressure of 200 mtorr for 3 to 12 min. *In situ* postanneal was performed at the deposition temperature for 15 min with oxygen pressure > 10 torr. Under these conditions, the typical growth rate was in the vicinity of 0.04 nm/pulse. The self-template layer thickness was about 100–300 nm.

Sol-gel-derived SBN60 thick films were deposited on the self-template SBN layer by the spin-coating technique. The precursors used were strontium metal, barium metal, and niobium chloride with 2-methoxyethanol as the solvent and stabilizing agent.<sup>18</sup> As-deposited wet films were baked at 260 °C on a hot plate and then heat treated at 700–750 °C for 10 min. SBN films of single-layer deposition were around 40 nm thick according to observation of scanning electron microscope (SEM) cross-section samples. A prescribed film thickness of 0.5–1.2 μm was produced by multiple repetitions of the process. Final annealing was performed at 700–750 °C for 60 min in air. To make a comparative investigation, sol-gel SBN films with similar thickness without template layer were also prepared.

The crystallinity of SBN films was determined by x-ray diffraction (XRD) with Cu K<sub>α</sub> radiation and Raman scattering. The epitaxial quality of the SBN films was

characterized by x-ray rocking curve and pole figure measurements. SEM and atomic force microscopy (AFM) were used to examine the surface roughness and grain uniformity. Film roughness is represented by the root mean square value (RMS), measured by AFM in a 10 × 10 μm<sup>2</sup> area.

## III. RESULTS AND DISCUSSION

Figure 1 shows θ–2θ scans of sol-gel-derived SBN films approximately 1.2 μm thick prepared at 750 °C on MgO with and without a self-template layer. The XRD profiles were obtained with alignment optimized for MgO substrate. The PLD-derived self-template layer thickness is approximately 100 nm. Both SBN films exhibit strong (001) and (002) reflections. However, with the same thickness, SBN films with template layer show a much higher intensity of (001) plane reflections than the one without template layer. This implies SBN films with template layer have a better *c*-axis preferred orientation perpendicular to the substrate.

Because sometimes XRD analysis is not a sufficient method to determine the TTB-type SBN phase on MgO,<sup>3</sup> Raman scattering was often employed to characterize the crystalline structure of the films. In SBN films with a self-template layer, two broad A<sub>1</sub>(TO) phonons at about 240 and 630 cm<sup>-1</sup> are basically similar to that in the TTB phase single crystal, except for the weaker intensity and the frequency downshift of Raman modes due to the stress effect in the film.<sup>18</sup> In contrast, the Raman peak in sol-gel directly derived SBN films can hardly be recognized. This indicates SBN films without a template layer have relatively poor crystallinity, which is in reasonably good agreement with the XRD result.

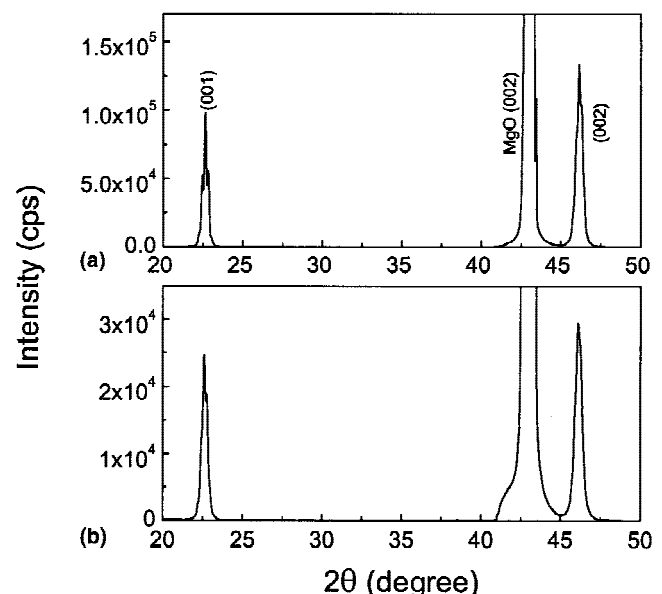


FIG. 1. XRD profiles of sol-gel-derived SBN thin films on (100) MgO (a) with and (b) without a self-template layer at 750 °C anneal.

The x-ray rocking curves of the SBN (002) peak with and without a template layer were measured to identify the epitaxial quality, as illustrated in Fig. 2. It is clearly seen that the SBN film prepared at 750 °C by combination of PLD and sol-gel has a smaller full width at half-maximum (FWHM) of 0.71° than that of 2.30° for the pure sol-gel film. By introducing an additional SBN template layer, the quality of the sol-gel-derived SBN film is markedly improved. The FWHM value of sol-gel-derived SBN film with template layer is comparable to that of SBN films obtained by PLD method. To our knowledge, this is by far the best FWHM result for sol-gel-derived SBN films. Indeed most reports on highly *c*-axis-oriented SBN films or KSNB films prepared by the sol-gel method did not even provide the FWHM data.

To investigate the in-plane crystallographic alignment of SBN thin films on MgO (100) substrates, the x-ray pole-figure measurement was performed. Figures 3(a) and 3(b) displays the result for the (311) planes of the sol-gel-derived SBN films with and without SBN template layer.  $\beta$  is the rotation axis orthogonal to the film plane, and  $\alpha$  is the rotation axis perpendicular to  $\beta$  and  $\theta$ . In Fig. 3(a), orderly distribution of 12 spots is clearly observed, among which the intensity of four dark spots with 90° intervals is about twice of that of eight bright spots with 15° interval each other. It is consistent with the theoretical calculation and the other groups' reports using PLD,<sup>7,10</sup> suggesting that the two crystal lattice planes of SBN are intergrown at an orientation of 18.5° on the MgO (100) substrate. In comparison, pure sol-gel-derived SBN film shows an ambiguous pattern. No definite relation can be determined, which is similar to that of sol-gel-deposited SBN films reported by Sakamoto *et al.*<sup>3</sup> The analyses for the (211) and (221) planes of SBN films with and without a self-template layer draw the same conclusion.

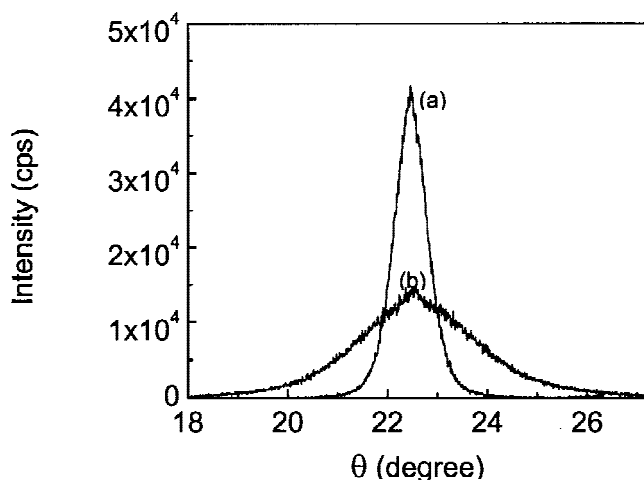


FIG. 2. X-ray rocking curves of sol-gel-derived SBN thin films on (100) MgO (a) with and (b) without a self-template layer at 750 °C anneal.

The surface morphologies of SBN films annealed at 700 °C with and without template layer were recorded by SEM, as shown in Fig. 4. Obviously, films with template layer reveal better crystallinity and higher density with uniform global grains. Similar results were obtained by AFM studies. The surface roughnesses of SBN films with and without a template layer are 4.9 and 10.1 nm, respectively. Apparently, the surface smoothness is improved by introducing the PLD template layer. Figure 5 gives the cross-sectional views of the above films. Evident columnar structure can be clearly seen in SBN film with template layer, corresponding to the preferred direction of crystal growth, namely the *c*-axis direction whereas no similar feature is observed in films without template layer.

Based on our experiments, it is found that PLD-derived SBN self-template layer acts as a useful seeding layer for growth of sol-gel derived SBN films. Indeed, when the SBN self-template layer on MgO was a randomly oriented SBN thin layer, the sol-gel-derived SBN film grown on the self-template layer exhibited polycrystalline characteristics. If the PLD-derived SBN template layer had a large FWHM and surface roughness, the subsequent deposited SBN sol-gel films also showed similar values. Our results thus confirm that the quality of sol-gel-derived SBN films is closely related to orientation and microstructure of SBN self-template layer.

The x-ray phi scan confirmed that the unit cell of SBN rotated in the plane of the film by  $\pm 18.4^\circ$  with respect to the MgO substrate unit cell. Thus, the epitaxial

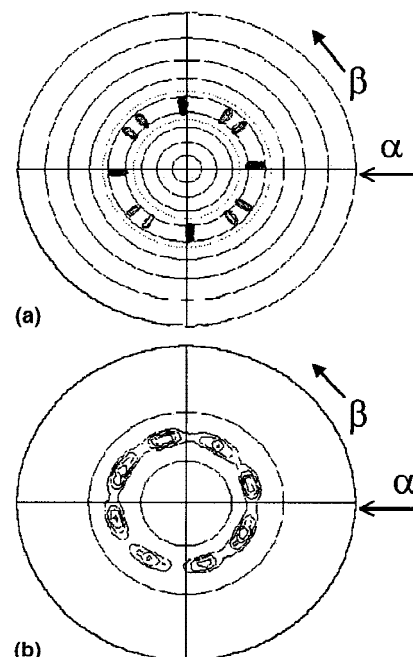


FIG. 3. X-ray pole figures of sol-gel-derived SBN thin films on (100) MgO (a) with and (b) without a self-template layer at 750 °C anneal.

relationship of (100)SBN/(310)MgO implies a 7% lattice mismatch. If SBN film is directly deposited on MgO substrate by the sol-gel method, the larger lattice mismatch means the heteroepitaxial growth from amorphous

to crystalline needs to overcome a larger nucleation barrier and produces a larger strain. This easily leads to a harmful influence on the orientation and microstructure of SBN film. An introduction of a SBN self-template

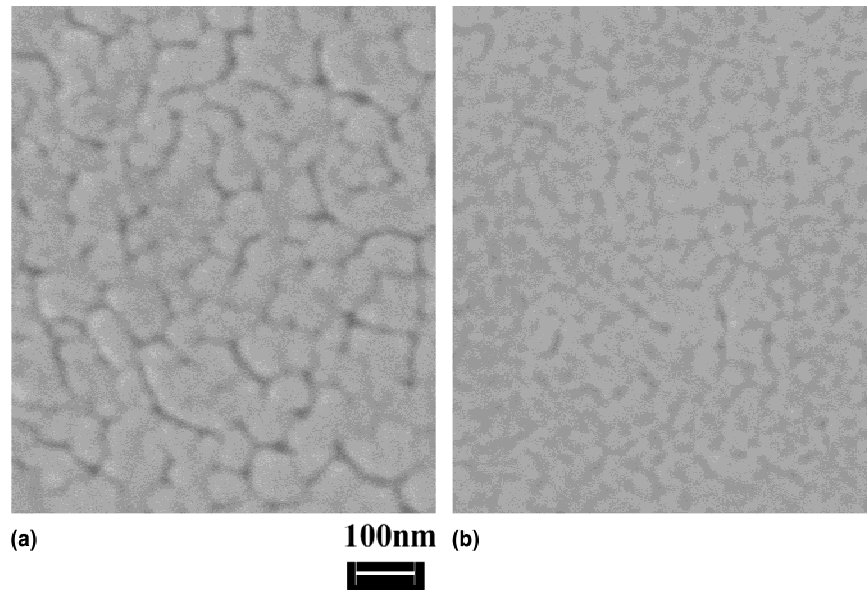


FIG. 4. Surface SEM images of sol-gel-derived SBN thin films on (100) MgO (a) with and (b) without a self-template layer at 700 °C anneal.

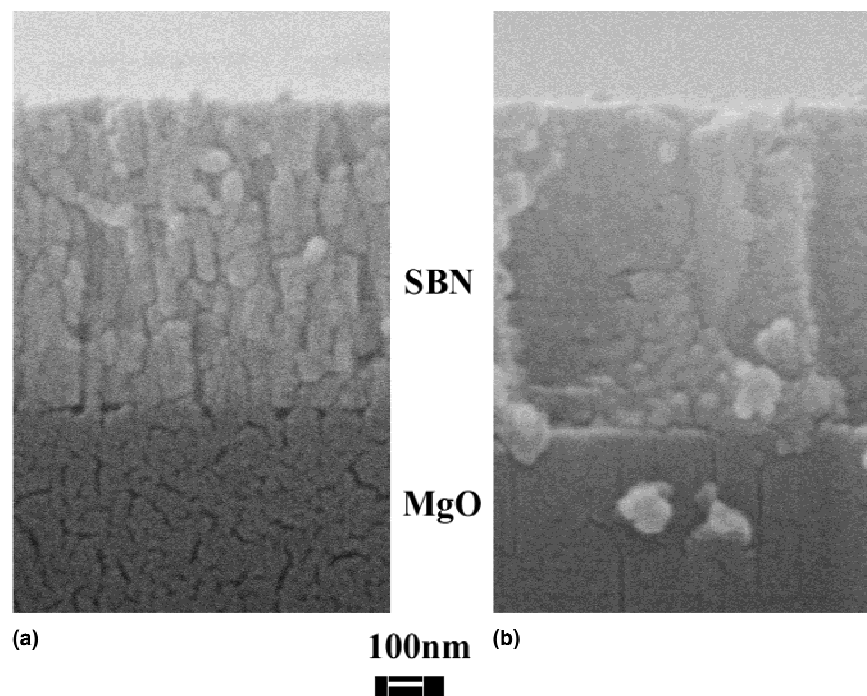


FIG. 5. Cross-sectional SEM images of sol-gel-derived SBN thin films on (100) MgO (a) with and (b) without a self-template layer at 700 °C anneal.

layer as seeding layer solves this problem by greatly decreasing the nucleation energy due to the homoepitaxial growth.

#### IV. CONCLUSION

In summary, epitaxial ferroelectric Sr<sub>0.6</sub>Ba<sub>0.4</sub>Nb<sub>2</sub>O<sub>6</sub> (SBN) thin films were successfully fabricated on MgO substrates using a self-template layer by sol-gel method. Effects of the PLD-deposited SBN self-template layer on the structural and morphological properties of sol-gel derived SBN films were investigated. The films with a self-template layer showed excellent epitaxy and densely packed grain morphology. This indicated that the template layer plays a key role on adjusting the orientation and microstructure of sol-gel derived films. Therefore, this novel processing method incorporates the advantages of both sol-gel and PLD methods. It is expected that this new technique can be applied to preparation of other high-quality multicomponent oxide films for electro-optic device applications.

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