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1995 Jpn. J. Appl. Phys. 34 L625

(http://iopscience.iop.org/1347-4065/34/5B/L625)

Jpn. J. Appl. Phys. Vol. 34 (1995) pp. L 625–L 627
Part 2, No. 5B, 15 May 1995

Growth of Epitaxial-Like $(Sr_{0.5}Ba_{0.5})Nb_2O_6$ Ferroelectric Films

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(Received January 20, 1995; accepted for publication March 28, 1995)

Epitaxial-like $(Sr_{0.5}Ba_{0.5})Nb_2O_6$ (SBN) films were successfully grown on (100) silicon substrates, using [002] CeO_2 as the buffer layer and $[00l]YBa_2Cu_3O_{7-x}$ (YBCO) as the base electrode. The θ-2θ scan and ϕ-scan X-ray diffraction suggest that $[210]_{SBN}/\!/[100]_{YBCO}/\!/[110]CeO_2/\!/[110]_{Si}$. The ferroelectric hysteresis curves measured by the modified Sawyer-Tower technique show that the epitaxial-like SBN/YBCO/CeO_2/Si films possess substantially better ferroelectricity than the polycrystalline SBN/Pt(Ti)/Si films. The remanent polarization (P_r) and coercive field (E_c) are, respectively, $P_r=27.2\ \mu C/cm^2$ and $E_c=24.8$ kV/cm.

KEYWORDS: SBN, epitaxial, ferroelectric, hysteresis, thin films

1. Introduction

$Sr_xBa_{1-x}Nb_2O_6$ (SBN) materials are of tetragonal tungsten-bronze crystal structure forming a solid solution[1)] in the range of $0.25<x<0.75$. They exhibit very good ferroelectric properties, electrooptic characteristics[2)] and photorefractive effects.[3)] Moreover, the SBN films possess excellent pyroelectric properties with response time faster than 30 ns when the composition of the materials is in the range of $0.5<x<0.75$.[4)] The applications of SBN materials in these areas have been thoroughly investigated for single crystals[5)] and ceramics.[6–8)] However, thin films of SBN materials are required for fabrication of sensor elements compatible with silicon devices.

Physical vapor deposition techniques[9–12)] and the sol-gel method[13–15)] have been investigated for synthesizing SBN thin films. The laser ablation technique, however, possesses overwhelming advantages, since the stoichiometry of the films can be precisely controlled. It is therefore adopted in this research in order to synthesize textured SBN thin films and to correlate the electrical properties of thin films thus obtained with their preferred orientation.

2. Experimental

The $(Sr_{0.5}Ba_{0.5})Nb_2O_6$ target materials were prepared via the conventional mixed oxide route. The $SrCO_3$, $BaCO_3$ and Nb_2O_5 oxides with cationic ratio $Sr^{2+}:Ba^{2+}:Nb^{5+}=0.5:0.5:2$ were mixed with deionized water in a plastic jar, using ZrO_2 balls. The mixtures were calcined at 1150°C for 2 h, pulverized, pelletized and then sintered at 1135°C for 4 h to form SBN targets of diameter 30 mm and thichness 5 mm The SBN thin films were synthesized using the pulsed laser deposition (PLD) technique. The plume was induced from the target by 248 nm laser beams emitted from a KrF excimer laser (Lambda Physix LPX200) with pulse energy density 1.5 J/cm^2 and repetition rate 4 Hz. The substrate was located 6 cm from the target and was heated by a resistance heater.

The crystal structure and microstructure of films thus obtained were examined using X-ray diffractometry (Rigaku DMAX-IIB with Cu-Kα source) and atomic force microscopy (AFM) (Nanoscope III), respectively. The ferroelectric hysteresis curve of the thin films was obtained using the Sawyer-Tower method.

3. Results and Discussion

SBN films with good crystallinity can be obtained for substrate temperatures higher than 680°C and oxygen pressure higher than 0.1 mbar. The SBN films are generally polycrystalline when deposited on bare silicon or Pt-coated silicon, regardless of the deposition temperature or oxygen pressure. Typical X-ray diffraction patterns for the films deposited at 680°C (0.1 mbar) are shown in Figs. 1(a) and 1(b). However, SBN films which are highly textured in [00l]-orientation are required to optimize the ferroelectric properties of the films, since the c-axis is the orientation of spontaneous polarization. Several substrate materials have been tested for growth of [00l]-textured SBN films. Figure 1(c) indicates that when the [002] CeO_2 and [00l] $YBa_2Cu_3O_{7-x}$ (YBCO) layers were sequentially deposited on a Si substrate through appropriate control of the

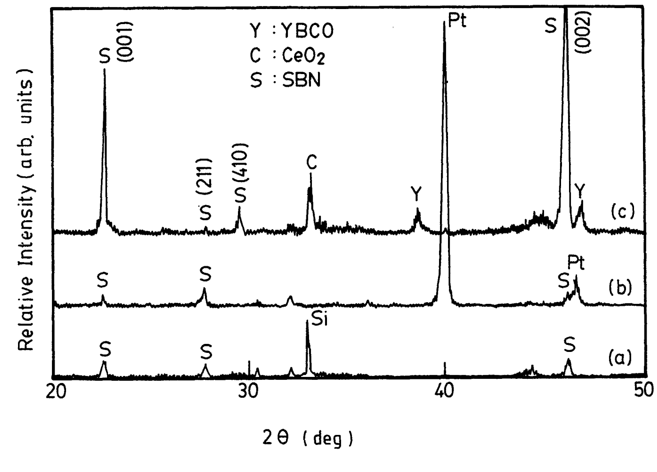

Fig. 1. The X-ray diffraction patterns of the SBN films deposited on (a) p-type silicon substrates, (b) Pt(Ti)/Si and (c) [00l]YBCO/[002]CeO_2/Si. The [00l]-textured SBN films were obtained only on YBCO/CeO_2/Si substrates (Si: silicon, Pt: platinum, C: [002]CeO_2, Y: [00l]YBCO and S: SBN).

deposition parameters, the subsequently grown SBN films (~390 nm) were highly preferentially oriented in [00*l*] directions. The [002]CeO_2 layer (~170 nm), which prevented reaction between the films and the substrate, was directly obtained on Si substrates by depositing the films at the substrate temperature of 700°C, under 0.1 mbar oxygen pressure. The [00*l*] YBCO layer (~250 nm), which was used as the base electrode, on the other hand, could be easily grown at 750°C and 0.6 mbar when the CeO_2 layer was [002]-textured.

The in-plane orientation of the a and b axes of these [00*l*]-textured films was examined by ϕ-scan of [211] SBN, [102]YBCO and [202]CeO_2 diffraction peaks. The results are shown in Fig. 2, and indicate that all three films are of 4-fold symmetry, which suggests that the a and b axes of the lattice are aligned in each film. In other words, the SBN, YBCO and CeO_2 films are all epitaxial-like. The orientation relationship between the films and substrate can be determined from the relative position of the diffraction peaks in the ϕ-scan plots. The YBCO [102] peaks shift 45° with respect to the CeO_2 [202] peaks, which implies that the a and b axes of the YBCO lattice are parallel to ⟨110⟩-orientation of the CeO_2 lattices. This is the orientation relationship reported previously.[16] Figure 2 also reveals that the SBN [211] peaks occur at the same ϕ-angle as the YBCO [102] peaks, suggesting that the [210] orientation of the (00*l*)SBN lattice plane is parallel to the a and b axes of the (00*l*)YBCO lattice plane. The [202]Si peaks coincide exactly with the [202]CeO_2 peaks. The crystal structure and lattice parameters of these materials are listed in Table I to indicate their correlation with orientation relationship.

The surface morphologies of these layers were examined using AFM and are shown in Figs. 3(a), 3(b) and 3(c) for CeO_2, YBCO and SBN films, respectively. The

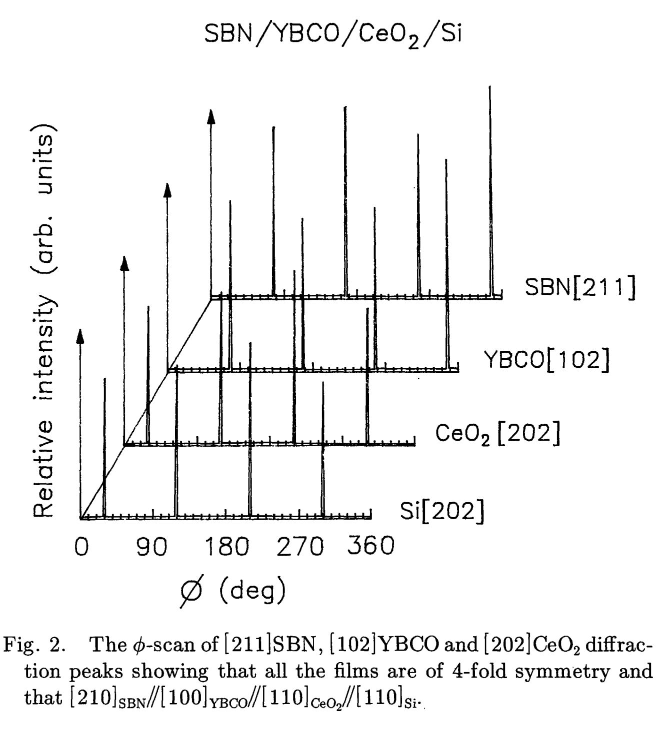

Fig. 2. The ϕ-scan of [211]SBN, [102]YBCO and [202]CeO_2 diffraction peaks showing that all the films are of 4-fold symmetry and that $[210]_{\mathrm{SBN}}/\!/[100]_{\mathrm{YBCO}}/\!/[110]_{\mathrm{CeO_2}}/\!/[110]_{\mathrm{Si}}$.

Table I. Crystal structure and lattice parameters of the Si, CeO_2, YBCO and SBN materials.

Materials	Crystal Structure	Lattice Parameters (nm)
Si	Diamond	a=0.5431
CeO_2	Fluorite	a=0.5411
YBCO	Perovskite	a=0.382, b=0.389, c=1.3
SBN50	Tungsten-bronze	a=1.2465, c=0.3952

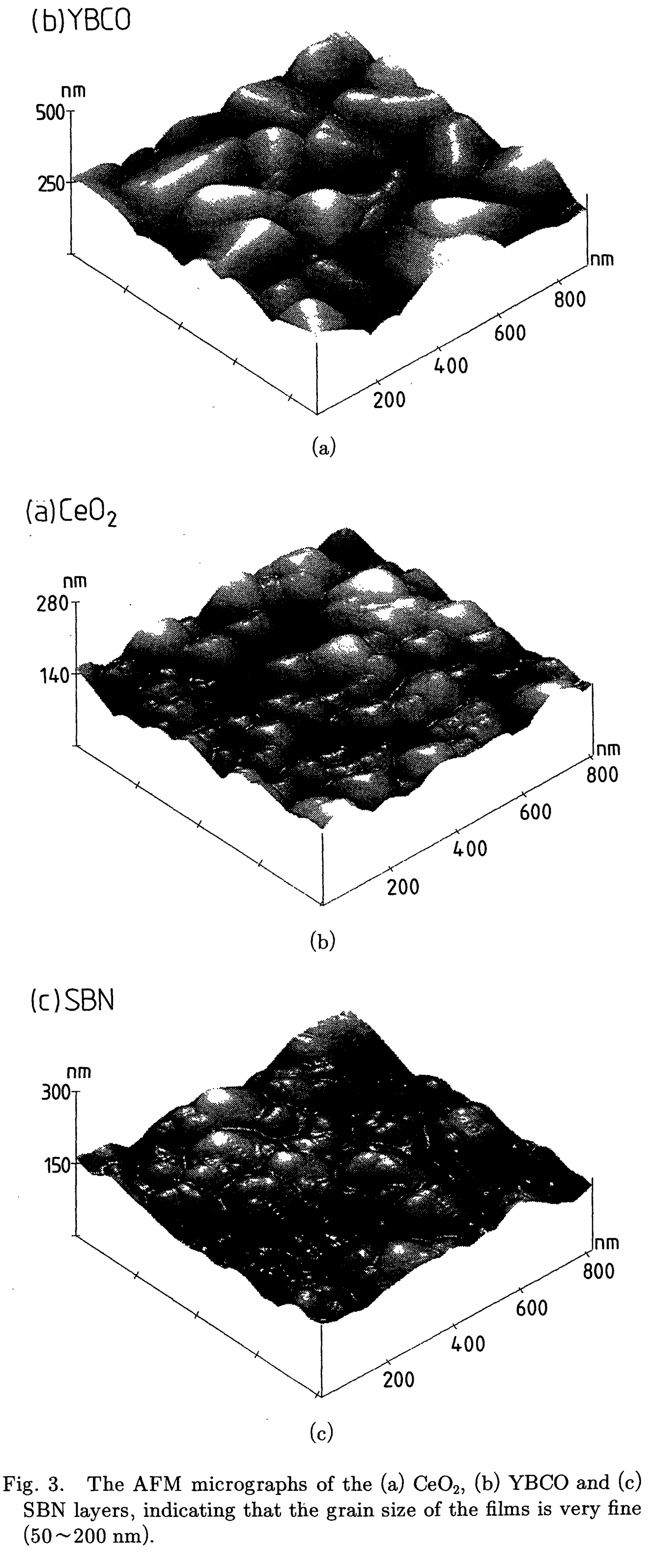

Fig. 3. The AFM micrographs of the (a) CeO_2, (b) YBCO and (c) SBN layers, indicating that the grain size of the films is very fine (50~200 nm).

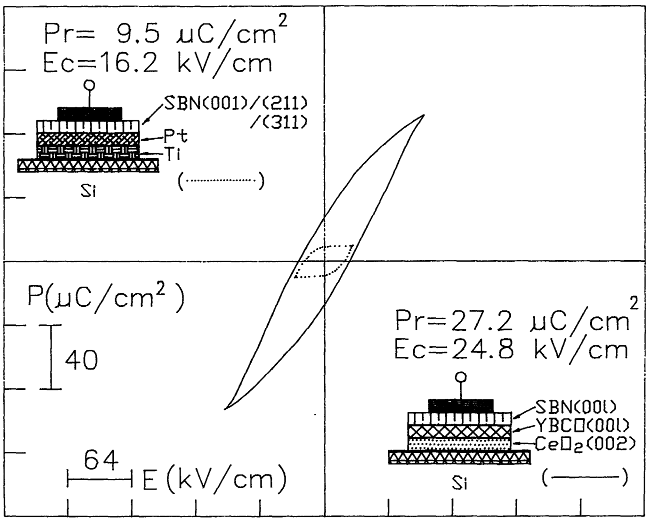

Fig. 4. The ferroelectric hysteresis loops (*P-E* curves) of the epitaxial-like (solid curve) and polycrystalline (dash-dotted curve) SBN films which were grown on YBCO/CeO_2/Si and Pt(Ti)/Si substrates, respectively.

CeO_2 grains are around 100 nm in size (Fig. 3(a)). The grains of the YBCO layer (Fig. 3(b)) are slightly larger (~200 nm). The subsequently grown SBN films (Fig. 3(c)) have very fine grains (50~100 nm) and the surface is very smooth, which is very important for device application.

The ferroelectric properties of the SBN films were measured using the modified Sawyer-Tower technique, where a resistance is connected in parallel with the reference capacitor to compensate for leakage current. The electrical polarization-electrical field (*P-E*) curves of the SBN/YBCO/CeO_2/Si and SBN/Pt(Ti)/Si films are shown in Fig. 4, and they demonstrate that the ferroelectricity of the epitaxial-like SBN films (solid curve) is overwhelmingly superior to that of the polycrystalline SBN films (dash-dotted curve) with randomly oriented grains. The remanent polarization (P_r) and coercive field (E_c) of these films are, respectively, $P_r=27.2\ \mu C/cm^2$ and $E_c=24.8$ kV/cm for epitaxial-like films and $P_r=9.5\ \mu C/cm^2$ and $E_c=16.2$ kV/cm for polycrystalline films. It shoud be noted that the P_r-value of the SBN films is much higher than that of the epitaxial-like $BaTiO_3$ (BTO) films ($P_r=4.0\ \mu C/cm^2$ for BTO/YBCO/STO films).[17] High remanent polarization of the SBN films makes these films particularly suitable for application to ferroelectric random access memory (FRAM).

4. Conclusions

SBN films were deposited using the pulsed laser deposition technique. The films grown on Pt(Ti)-coated or bare-silicon substrates are polycrystalline with grains of random orientation, while those grown on YBCO/CeO_2/Si substrates are highly [00*l*]-textured. The 4-fold symmetry of the ϕ-scan of selected diffraction peaks of each layer in SBN/YBCO/CeO_2/Si films suggests that these films are epitaxial-like and that $[210]_{SBN}//[100]_{YBCO}//[110]_{CeO_2}//[110]_{Si}$.

The electrical polarization-electric field (*P-E*) measurement shows that the epitaxial-like films (SBN/YBCO/CeO_2/Si) possess substantially better ferroelectric properties than the polycrystalline films (SBN/Pt(Ti)/Si). The remanent polarization (P_r) and coercive field (E_c) values are, respectively, $P_r=27.2\ \mu C/cm^2$, $E_c=24.8$ kV/cm for the former and $P_r=9.5\ \mu C/cm^2$, $E_c=16.2$ kV/cm for the latter. Properties in both cases are, however, superior to those of epitaxial-like $BaTiO_3$/YBCO/STO films and are concluded to be suitable for FRAM application.

Acknowledgement

This work is supported by the National Science Council of the Republic of China under contract No. NSC 83-0208-M009-052.

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