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Growth of highly orientated strontium barium niobate thin films on Si substrates through the sol–gel process using a K: SBN template layer

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Abstract We report the growth of highly *C*-axis orientation of $Sr_xBa_{1-x}Nb_2O_6$ (SBN) thin films on p-type (100) Si substrates by using a potassium-substituted SBN template layer with the sol–gel method. The crystallization of SBN thin films was found closely related to the potassium ion doping concentration and the postannealing temperature of the K-SBN template layer. Secondary ion mass spectrometry analysis showed that potassium elements were accumulated at the interface of the template layer and silicon substrate. SBN films postannealed at 750 °C with K-SBN template layer has a smaller full width at half maximum of X-ray rocking curve of 2.45° than that of 5.40° for the pure SBN films. By introducing a template layer, the surface morphologies of SBN films fabricated on silicon substrate were greatly improved.

Introduction

Strontium Barium Niobate ($Sr_xBa_{1-x}Nb_2O_6$, SBN100x, where $0.25 \le x \le 0.75$) thin film, with ferroelectric tungsten bronze structure, is currently being investigated as attractive materials for many applications such as pyroelectric infrared detectors, nonvolatile random access memories (NvRAMs), electrooptic modulators, holographic storage due to its extremely high pyroelectric coefficient, large electro-optic coefficient, excellent piezoelectric property, as well as strong photorefractive effect [1–4]. In particular, growth of heteroepitaxial or highly *C*-axis-orientated SBN thin films on substrates is desired to fabricate integrated devices with high opto-electronic properties and low optical loss. Recently, highly *C*-axis-orientated SBN thin films have been prepared on MgO(100) substrate by a variety of deposition methods, such as pulsed laser deposition (PLD) [5], RF sputtering[6], metal-organic chemical vapor deposition (MOCVD) [7] and sol–gel process [8], The epitaxial relationship between SBN unit cell and MgO unit cell was found to be (100)SBN// (310)MgO [9]. However, it has been proven difficult to deposit preferred *C*-axis orientated SBN thin films directly on Si substrates or with thin buffer layers due to the large lattice mismatch between the Si(100) and SBN(001) ($M_a = M_b = 12.6\%$, $M_c = 37.1\%$). 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 make use of advanced silicon process technology. Chiu [10] and coworkers prepared highly (001)-textured SBN thin films on Si(100) substrate with epitaxial $LaNiO_3$(100) electrode and a CeO_2/YSZ bi-buffer layer using PLD method. SBN thin films were also reported (001) epitaxial growth on Si(100) by the RF sputtering method [11], but the authors did not provide

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the detailed epitaxial relationship and interface properties between the SBN thin film and silicon substrate.

In this communication, we report the growth of highly *C*-axis orientated SBN thin films deposited on Si(100) substrate with the sol–gel process using a potassium-substituted SBN template layer. The microstructural and orientated characterizations, as well as a discussion of the related growth mechanism, will be presented.

Experiments

SBN/K-SBN heterostructures have been successfully grown on Si(100) substrates by sol–gel process. The sol–gel method was always chosen to prepare the ferroelectric thin films, because it can offer many advantages such as excellent homogeneity, ease of precise composition control, high purity, and film uniformity over a large area. Potassium-substituted SBN template thin films were fabricated by using metal alkoxide. Sr, Ba, $Nb(OEt)_5$, KOH (all from Acros Oranics, Belgium) were selected as starting materials and 2-methoxyethanol was used as common solvent and a stabilizing agent. Sr and Ba metal alkoxides were obtained by directly reacting Sr or Ba metal with 2-methoxyethanol in a dry argon atmosphere, and K alkoxide was made by reacting KOH with 2-methoxyethanol. The mixture of Sr, Ba, K alkoxides and $Nb(OEt)_5$ in a certain ratio formed the K-substituted $Sr_{0.6}Ba_{0.4}Nb_2O_6$ (SBN60) precusor solution, which was spin-coated onto the Si(100) substrate at 1,000 rpm for 6 s and 3,000 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, 1,000 °C for 4 min) to crystallize the films. The procedure was repeated until a desired thickness was obtained. The SBN60 thin films deposited onto the K-substituted SBN60 template layer were fabricated with the same procedure except that no potassium ion was introduced into the mixture solution, and the postannealing temperature was decreased to 750 °C. The crystallinity of the films was investigated by X-ray diffraction (XRD) with CuK_α radiation and Raman scattering. The Raman spectra were obtained by excitation with 514.5 nm laser light from a continuous wave (cw) argon gas laser. A 55 mm f/1.8 lens and a double grating spectrometer equipped with a cooled photomultiplier tube were used to collect and detect scatted light. The orientation quality of the SBN thin films was characterized by X-ray rocking curve. Atomic force microscopy (AFM) was used to examine the surface roughness and grain uniformity. The diffusion of constituent elements in a K-SBN/Si interface was analyzed by second ion mass spectrometry (SIMS).

Results and discussion

Figure 1 shows XRD patterns of 300 nm-thick potassium-substituted SBN60 thin films grown on (100) Si substrate with different K^+/Nb^{5+} molar ratio. The XRD pattern of the SBN60 film with zero potassium, shown in Fig. 1(a), was found to be polycrystalline with random orientation in spite of high annealing temperature. This indicates that the SBN thin films directly deposited on Si substrate have relatively poor crystallinity. The XRD patterns of the SBN60 films doped with different potassium ions were shown in Fig. 1(b)–(e), all the films were found exhibiting strong (001) and (002) peak reflection, and the film with the K^+/Nb^{5+} molar ration of 2/3 ($K_{2/3}$SBN60 afterwards) showed the strongest intensity of (001) plane reflection. This implies potassium-substituted SBN thin films fabricated with the sol–gel process have a highly *C*-axis preferred orientation perpendicular to the Si(100) substrate.

The inset of Fig. 1 is the relationship of the full width at half-maximum (FWHM) of X-ray rocking curves of (001) peak and the film composition of potassium-substituted SBN60 thin films. It is clearly seen that the potassium-substituted SBN thin film with the K^+ concentration of 2/3 of K^+:Nd^{5+} (molar ratio) has a smallest FWHM values of 3.38° than that of 5.40°

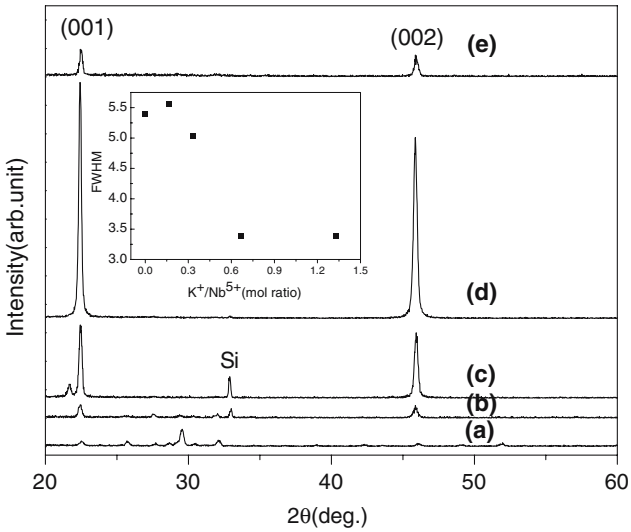

Fig. 1 XRD patterns of the K-substituted SBN thin films on (100) Si substrates postannealed at 1,000 °C with the K^+/Nb^{5+} molar ratio of (**a**) 0:3, (**b**) 1:6, (**c**) 1:3, (**d**) 2:3, (**e**) 4:3. Inset is the FWHM values of (001) peak X-ray rocking cure of K-SBN films as a function of film composition

for the pure SBN60 film, that means by introducing right proportional of potassium ions into the SBN structure, the crystalline quality of the sol–gel derived SBN thin film is improved. The FWHM data of 3.38° is even smaller than that of 4° [12] reported for the SBN film on MgO substrate prepared by the sol–gel method.

As XRD analysis is not a sufficient evidence to determine the tetragonal tungsten bronze (TTB) type of potassium-substituted SBN phase on silicon substrate, Raman scattering was always used to characterize the crystalline structure of the films. The Raman spectrum pattern of potassium-substituted SBN60 thin film, which has two broad A_1 (TO) photons at about 265 cm^{-1} and 630 cm^{-1}, was shown in Fig. 2, and the Raman spectrum pattern was found in good agreement with that of pure TTB SBN60 thin film.

In order to investigate the distribution and interdiffusion of K, Sr, Ba, Nb and Si elements at the interface of the potassium-substituted SBN60 thin film and the substrate, the depth profile of SIMS for the $K_{2/3}$SBN60 thin film was recorded in Fig. 3 on a semilogarithmic scale, the thickness of the film is approximately 300 nm. As the postannealed temperature of the samples is as high as 1,000 °C, the interdiffusion layer formed between ferroelectric thin film and semiconductor substrate was found very thick, as shown in Fig. 3. From the surface to 200 nm depth in the film, the concentrations of Sr, Nb, K elements were found constant, while the Ba concentration was highest in the vicinity of 150 nm depth in the film, indicating a nearly unchangeable composition in the bulk region of the K-SBN film. It was also found that the concentrations of Sr, Ba, Nb elements decreased from 200 nm to the interface (300 nm) of the K-SBN thin film and the silicon substrate, in contrast, the concentration of K increased, reached the highest in the vicinity of the

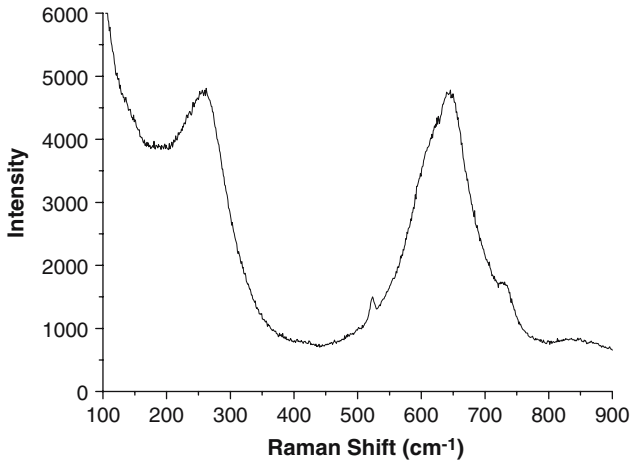

Fig. 2 Raman spectrum of K-SBN60 film on Si (100) substrate

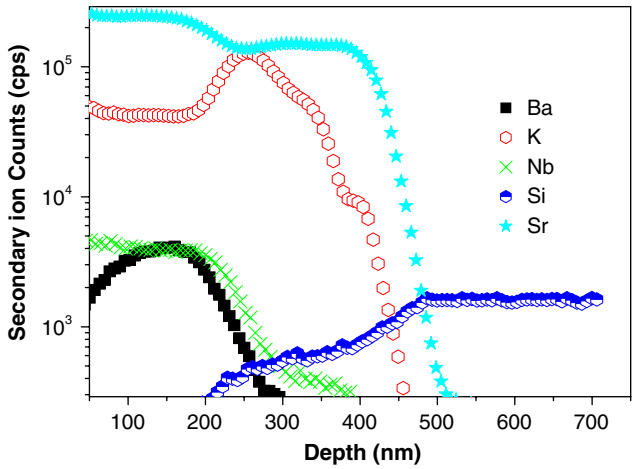

Fig. 3 SIMS depth profile for 300 nm-thick K-substituted SBN films postannealed at 1,000 °C, the K^+/Nb^{5+} molar ratio of the films is 2:3

interface, indicating the presence of a potassium-rich layer at the K-SBN/Si interface. In addition, silicon element was detected in the K-SBN thin film, this indicated that Si diffused toward the surface due to higher annealed temperature; the diffusion depth toward the silicon substrate of elements Sr and K was found thicker than that of Nb and Ba, this is probably due to the smaller atomic radius of Sr and K hence larger mobility compared to Ba elements. Niobium, though is not larger than Sr and K, possesses the lower mobility in the SBN crystal because it is located in the central site of the oxygen octahedral framework. Strontium, potassium, oxygen, as well as silicon interdiffused markedly at the interface and substrate to make the film composition different from the bulk region of the K-SBN film. The interdiffusion layer formed by SrO, K_2O and SiO_2 at high annealing temperature may therefore act as the buffer layer to improve the lattice mismatch of SBN thin film and silicon substrate through gradually adjusting the film lattice constant. Furthermore, we also fabricate SBN thin film and different amount of potassium ion doping K-SBN films on silicon substrate with the annealing temperature of 900 °C, no preferred *C*-axis orientation growth was found at the films annealed at lower temperature, this result implies that the quality of sol–gel derived K-SBN thin films is closely related to the Potassium doping concentration as well as the postannealing temperature.

As seen in Fig. 3, the concentration of K elements was constant from the surface to 200 nm depth in the film, that means apart from accumulating at the interface to form the interdiffusion layer, potassium will occupied the A or the C sites of incompletely filled

tungsten-bronze(TB) type SBN structure. The site occupancy formula of TB type structure can be written as $(A_1)_2(A_2)_4(C)_4(B_1)_2(B_2)_8O_{30}$, and the sites A1, A2 and C are occupied by either alkaline earth ions or alkali ions, in order to meet the requirements of cations size, valence match and electroneutrality, potassium ions may occupy the 1/6 unoccupied A sites and even C sites. Because the molar ratio of K/Nb is relatively high in our KSBN films, some residual potassium ions may therefore supposed to replace Sr^{2+} or Ba^{2+} at A sites of SBN structure. The lattice constants of K-SBN and SBN thin film, calculated from their XRD data, is C = 0.396 nm and C = 0.393 nm, respectively. Indeed, the lattice expansion of K-SBN is attributed to the A sites occupancy of potassium ions.

Many researchers reported that the interdiffusion layer formed at the interface of ferroelectric thin film and the substrate caused the deterioration of the crystalline and the epitaxial quality, our research reveals the adverse observation, the interdiffusion layer is considered to improve the lattice mismatch between the SBN and silicon. However, if the interfacial layer becomes too thicker due to higher postannealing temperature, the interface defects and traps between the SBN films and substrate would inevitably worsen the ferroelectric properties, E-O effects and even electric properties of SBN films, and in consequence, deteriorate the operation of the devices.

The K-substituted SBN60 ''thin films'' were therefore used as the template layer to improve the *C*-axis orientation growth of the pure SBN60 ''thick films'' on silicon substrate. In order to inhibit the Potassium ions diffusion into the upper SBN60 layer, the postannealing temperature of SBN films was decreased to 750 °C. Figure 4 presents the XRD patterns of 300 nm-thick SBN60 thin films grown on $K_{2/3}$SBN60 template layers with different thickness (25–100 nm), all the films were found exhibiting high (001) preferred orientation, and the FWHM value of the X-ray rocking curve of the SBN(001) peak with and without the K-SBN template layer were 2.45° and 5.40°, respectively. This indicates that K-substituted SBN layer acts as a useful template layer for growth of sol–gel derived SBN thin films, and the orientation characterization of SBN films are independent of the template thickness.

The surface morphologies of SBN films annealed at 750 °C with and without template layer were recorded by AFM, as shown in Fig. 5. It can be clear seen that

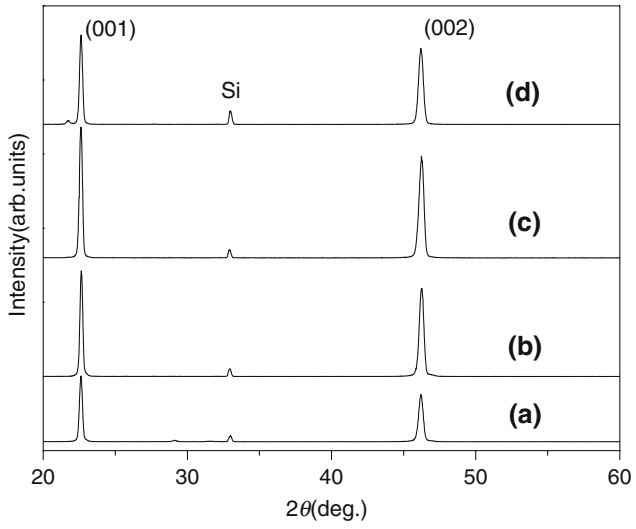

Fig. 4 XRD patterns of the SBN60 thin films fabricated on Si (100) substrates with a K-SBN60 template layer, where the thickness of the template layer is (**a**) 25 nm, (**b**) 50 nm, (**c**) 75 nm and (**d**) 100 nm, respectively

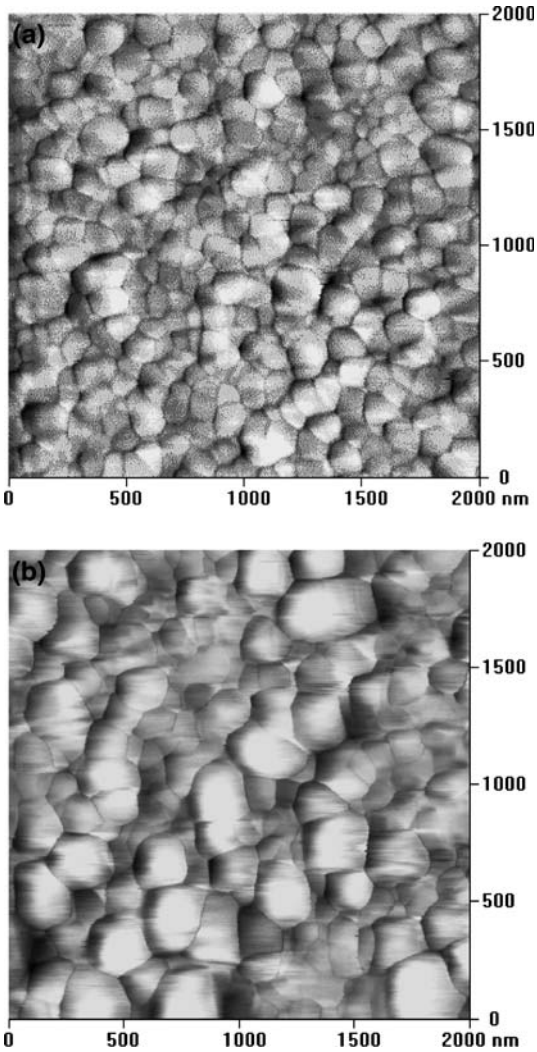

Fig. 5 AFM images of sol–gel-derived SBN thin films on Si(100) (**a**) with and (**b**) without a K-SBN template layer

grain size of the films with template layer is about a half of that of the films without template layer. The surface roughnesses of SBN films with and without the K-substituted SBN template layer are 3.8 nm and 12.3 nm, respectively. Apparently, the surface smoothness is improved by introducing the template layer.

Conclusions

In summary, we successfully fabricate c-axis oriented SBN60 thin films with K-substituted SBN template layer on p-type (100) silicon substrates by sol–gel process. The depth profile of SIMS of K-substituted SBN60 thin films reveals that Potassium element was accumulate near the interface of the substrate and thin film. SrO, K_2O and SiO_2 may form an interdiffusion layer at the interface to improve the lattice mismatch between the film and substrate, and SBN thin films deposited onto the K-SBN template layer presents the *C*-axis orientated growth. From the AFM images, the grain size of the sol–gel derived SBN thin films with the template layer was found decreased to one half of the film without template layer, and the surface smoothness of the SBN films was improved by introducing the template layer.

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