Available online at www.sciencedirect.com
ScienceDirect
Thin Solid Films 515 (2007) 3475 – 3479
www.elsevier.com/locate/tsf

# Fabrication of *c*-axis oriented potassium-doped $Sr_{0.6}B_{a0.4}Nb_2O_6$ thin films on Si substrates by pulsed laser deposition method

Z.R. Shen [a,b], H. Ye [a,b], C.L. Mak [a,*], T.Y. Yum [a], K.H. Wong [a]

[a] *Department of Applied Physics and Materials Research Centre, The Hong Kong Polytechnic University, Hung Hom, Kowloon, Hong Kong, China*
[b] *State Key Laboratory of Modern Optical Instrumentation, Zhejiang University, Hangzhou 310027, People's Republic of China*

Received 10 October 2005; received in revised form 9 October 2006; accepted 18 October 2006
Available online 1 December 2006

**Abstract**

Potassium-doped strontium barium niobate (SBN) thin films have been fabricated directly on p-type (100)Si substrates using pulsed laser deposition method. The presence of potassium ions and the use of appropriate oxygen pressure help to produce *c*-axis oriented SBN films. Post-annealing at high temperature also enhances the formation of tetragonal tungsten-bronze phase SBN. Excellent guided mode propagation for 632 nm wavelength radiation has been demonstrated. On the basis of our studies, we have shown that highly *c*-axis oriented SBN films grown directly on (100)Si substrates can be achieved and SBN is a suitable material for developing integrated electro-optic devices.


*Keywords:* Orientation; Potassium ion; Oxygen pressure; Post-annealing process

## 1. Introduction

Ferroelectric strontium barium niobate (SBN, $Sr_xBa_{1-x}Nb_2O_6$, $0.2<x<0.8$) has many remarkable properties such as large pyroelectric coefficient [1], excellent linear electro-optic characteristics [2] and unusually large photorefractive effects [3]. Its lead-free composition also makes it environmental friendly. Therefore, SBN is an attractive material being widely considered very useful in diverse device applications [4]. It has been shown that by doping rare-earth and alkali ions into SBN crystals, substantially enhanced electro-optic and photorefractive coefficients can be obtained [5,6]. For this reason there is a big interest in fabricating high quality rare-earth/alkali ions doped SBN crystalline films.

Due to the anisotropic properties of SBN, it is desirable to obtained oriented SBN films. A number of studies have been demonstrated *c*-axis oriented SBN films grown on (100)MgO substrates [7,8]. However, pure *c*-axis oriented SBN films prepared directly on silicon substrates have rarely been reported [9]. Indeed, an important step to elevate SBN films to future industrial applications is to integrate them onto Si substrates. Unfortunately the large lattice mismatch between Si (0.543 nm) and SBN ($a=b=1.25$ nm and $c=0.395$ nm) renders the deposition of *c*-axis oriented SBN films directly on silicon substrates a rather difficult task. Various techniques including radio-frequency magnetron sputtering [10], metal-organic chemical vapor deposition [11], sol–gel method [12] and pulsed laser deposition (PLD) [7,9] have been attempted to fabricate oriented crystalline SBN thin films. The aim of this paper is to fabricate preferred *c*-axis oriented potassium-doped SBN films directly on (100)Si substrates by PLD method. The effects of target material composition, oxygen ambient pressure and post-annealing temperature on the microstructure as well as the optical properties of the SBN60 thin films are investigated.

## 2. Experimental procedures

The potassium-doped SBN60 target was prepared by conventional mixed-oxide process using analysis grade $SrCO_3$, $BaCO_3$, $Nb_2O_5$ and $K_2CO_3$ powders (99.9%) as the starting materials. These powders were weighted according to a molar ratio of 0.6: 0.4: 1.0: 0.67, respectively. The powders were ball-milled with de-ionized water inside a Teflon jar for

* Corresponding author.
*E-mail address:* apaclmak@polyu.edu.hk (C.L. Mak).

0040-6090/$ - see front matter © 2006 Elsevier B.V. All rights reserved.
doi:10.1016/j.tsf.2006.10.103

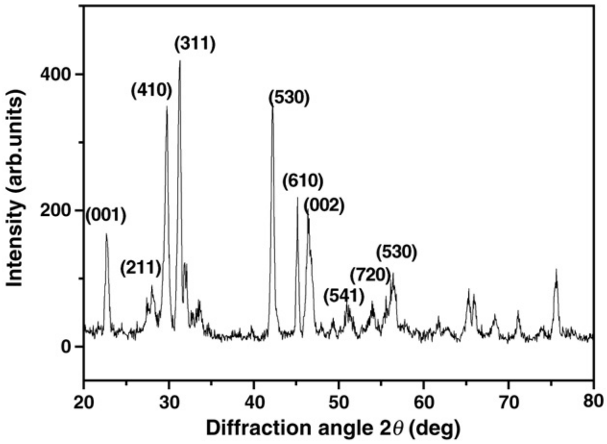


Fig. 1. XRD pattern of potassium-doped SBN target sintered at 1300 °C for 2 h.

24 h. The mixture was then calcined at 1200 °C for 10 h. It was re-milled and pressed in a die of around 20 mm diameter and 5 mm thickness under a pressure of 4 MPa. The pellet was sintered at 1300 °C in air for 2 h. Then, it was naturally cooled down to room temperature. All as-prepared targets showed prominent SBN crystalline phases as revealed by X-ray diffraction (XRD). In our PLD process, ablation of the solid target was induced by 248 nm wavelength laser pulses emitted from a KrF excimer laser (Lambda Physik COMPEX 200). The laser energy density and repetition rate were 1 J/cm$^2$ and 10 Hz, respectively. Before mounting on the sample holder, the p-type (100)Si substrates were etched with 10% HF solution for 15 min in order to remove the native $SiO_2$ layer. The distance between the etched Si substrate and the target was fixed at 4 cm. All SBN films were deposited at a substrate temperature of 750 °C. Various ambient oxygen pressures (from 0 Pa to 50 Pa) during film growth have been attempted. Immediately after the deposition, the films were in-situ post-annealed at 900 °C for 30 min before they were naturally cooled down to room temperature.

The crystal structures of the SBN60 films were characterized by a four-circle XRD (Philips X′ pert) with Cu $K_{\acute{a}}$ radiation

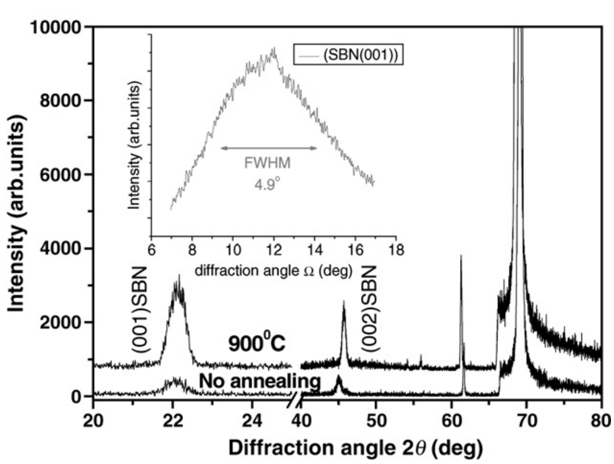


Fig. 2. XRD patterns of SBN films with different post-annealing temperatures. Inset shows the rocking curve of SBN film post annealed at 900 °C.

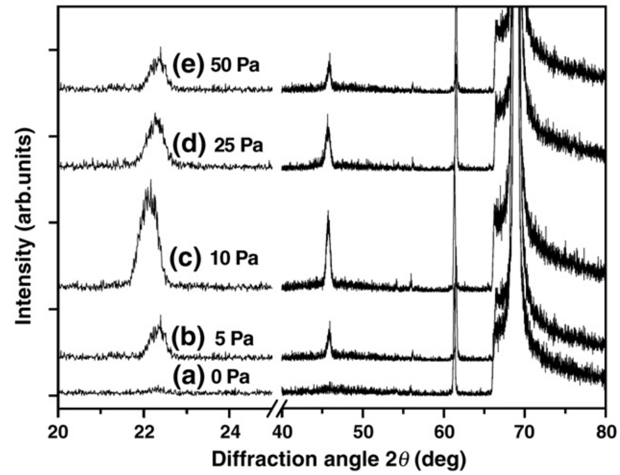


Fig. 3. XRD patterns of SBN thin films with different oxygen pressure deposited at 750 °C with post-annealing at 900 °C.

operated at an acceleration voltage of 50 kV. The orientation of the films was characterized by studying X-ray rocking curves of (001)SBN. The tetragonal tungsten bronze (TTB) phase of the SBN films was also revealed by Raman microprobe spectroscopy (Renishaw Ramascope 3000). In the Raman measurements, the samples were excited by a 10 mW He–Ne laser with an output wavelength of 632.8 nm. The laser was focused to a spot size of ~4 μm$^2$ at the sample surface using a microscope. The room temperature Raman spectra were recorded by a charge-coupled device detector. A scanning electron microscope (SEM, Leica Stereoscan 440) operated at 20 kV was employed to examine the surface morphology and the cross-section profile of the SBN films. Optical properties of the SBN60 films were measured using a prism coupling technique (Model 2010 prism, Metricon, USA). In this method, a rutile

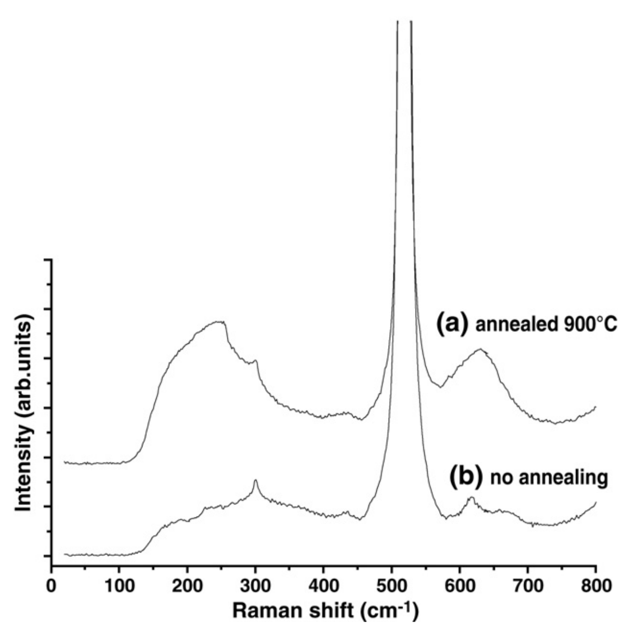


Fig. 4. Raman spectra of SBN films fabricated at 750 °C with oxygen pressure of 10 Pa (a) without and (b) with the post annealing process.