Epitaxial $Sr_{1.8}Ca_{0.2}NaNb_5O_{15}$ thin film waveguides grown by pulsed laser deposition: Optical properties and microstructure

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Epitaxial $Sr_{1.8}Ca_{0.2}NaNb_5O_{15}$ (SCNN) thin films slab waveguide structures that support several low-loss transverse electric (TE) and transverse magnetic (TM) modes were grown on MgO(100) substrates by pulsed laser deposition. To optimize the waveguiding properties, the relationship between film microstructure and deposition temperature was investigated by x-ray diffraction, atomic force microscopy, and scanning electron microscopy. The prism coupler technique provides for the refractive indices and structural anisotropy of the core SCNN films deposited at various temperatures. Characterization based on this technique is proposed as a mean to relate the surface morphology to optical features such as the full width at half maximum of the excited guide mode.

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I. INTRODUCTION

In the past several decades, lead-free tetragonal tungsten bronze structure (TTB) ferroelectric materials have attracted considerable attention for their potential applications in various electronic and optical devices due to their large spontaneous polarization, large piezoelectric, pyroelectric, and electro-optical (EO) coefficients.[1–4] Among these TTB niobates, calcium-modified strontium sodium niobate, $Sr_{2-x}Ca_xNaNb_5O_{15}$ (SCNN, $0.05 \leq x \leq 0.35$), is a new material developed by Neurgaonkar *et al.*[5,6] in 1987 which is reputed to have a huge EO coefficient ($r_{33} \sim 1325$ pm/V), large refractive index (~2.3), good optic figure of merit (~8.9 pm/V), and high Curie temperature (279–297 °C).[5–7] All of these properties make SCNN an attractive candidate for waveguide-based devices where the inherent optical confinement allows for significant improvement in the efficiency of EO and nonlinear-optical applications. A high refractive index SCNN core layer when coupled with a low index cladding layer will lead to strong confinement that can lead to large nonlinear effects within the high quality SCNN structures. Although the dielectric, ferroelectric, piezoelectric, and EO properties of SCNN crystals[5,6] and ceramics[7,8] have been well studied, reports of their response as optical thin film waveguides are still limited.

It is now well known that the optical properties of ferroelectric films are very sensitive to their crystallographic microstructure. To ensure high photon confinement and low losses for waveguide applications, high quality SCNN epitaxial films grown with superior crystalline properties as well as high optical index are required. One aim of the current work is to search for the optimum deposition conditions for the fabrication of epitaxial crystalline $Sr_{1.8}Ca_{0.2}NaNb_5O_{15}$ (SCNN) film waveguides using pulsed laser deposition (PLD) technique. We investigate light guiding parameters as the refractive index and optical anisotropy and their dependence on the deposition temperature, film microstructure, and surface roughness.

II. EXPERIMENT

A. Fabrication of SCNN thin films

SCNN thin films have been grown on MgO(001) substrates by PLD using ceramic targets. The laser used for the PLD process was a KrF excimer laser (Lambda Physik, COMPex205, 248 nm, 20 ns) with a repetition rate of 10 Hz. The distance between the substrate and the target was fixed at 3.5 cm. The on-target laser energy density was ~ 5 J cm^{-2}. In order to optimize the deposition parameter, the SCNN films were deposited at substrate temperatures T_{sub} ranging from room temperature to 750 °C under a fixed oxygen pressure of 180 mTorr. The films were postannealed *in situ* at the growth temperature with an ambient oxygen pressure of 10 Torr for 10 min before they were naturally cooled to room temperature to minimize oxygen deficiency.

B. Structural and optical characterization

The crystalline quality and crystallographic orientations of these deposited films were investigated by x-ray diffraction (XRD) analysis using a four-circle diffractometer (Philips, X'pert system) with a monochromated Cu $K\alpha$ radiation. Their surface morphologies were investigated by atomic force microscope (AFM, Nanoscope IV, Digital Instruments) and scanning electron microscope (SEM, Leica, Stereoscan 440). The optical waveguiding properties were examined by a prism coupler technique (Model 2010 prism, Metricon, USA) using a 632.8 nm laser.

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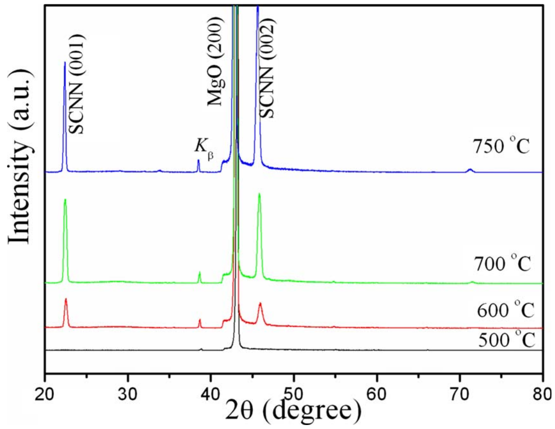


FIG. 1. (Color online) XRD θ-2θ scan patterns of SCNN thin films deposited on MgO(100) substrates at different substrate temperatures.

III. RESULTS AND DISCUSSION

A. Structural and crystallographic properties

For the PLD process, the substrate temperature (T_{sub}) has a significant effect on the crystalline growth of ferroelectric oxide thin films. We investigated the structure of SCNN thin films deposited at T_{sub} ranging from room temperature to 750 °C. The XRD θ-2θ scan profiles in Fig. 1 for T_{sub} lower than 600 °C shows no peaks from the films indicating that these as-grown SCNN films were amorphous. For T_{sub} >600 °C, the SCNN films were crystalline with only the (001) peaks evident, revealing that the SCNN films deposited on MgO were highly c-axis oriented. The intensity and sharpness of the SCNN (002) peaks increased with T_{sub}, indicating better crystalline quality at higher substrate temperature.

Since grain orientation is a key factor, which is known to correlate with the optical loss of thin film waveguides,[9,10] its alignment must be controlled in order to avoid high optical losses due to light scattering at grain boundaries. The degree of grain orientation in our SCNN thin films was evaluated by measuring the full width at half maximum (FWHM) of the XRD ω-scan of (002) diffraction peaks, as shown in Fig. 2. It is evident that the FWHM drops substantially at higher substrate temperatures. The highest degree of grain orientation

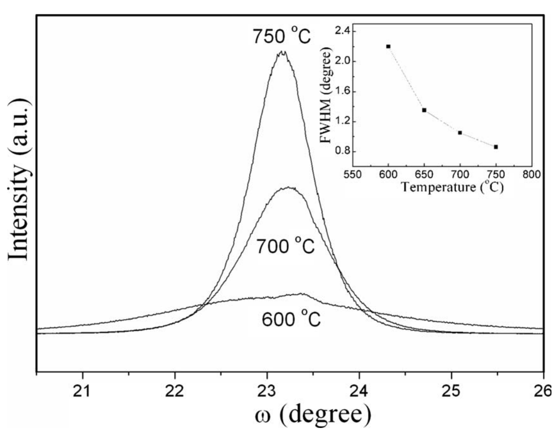


FIG. 2. Rocking curves of the (002) diffraction peak for SCNN thin films grown on MgO (001) substrate at different substrate temperatures. Inset plots the variation of FWHM as a function of substrate temperature.

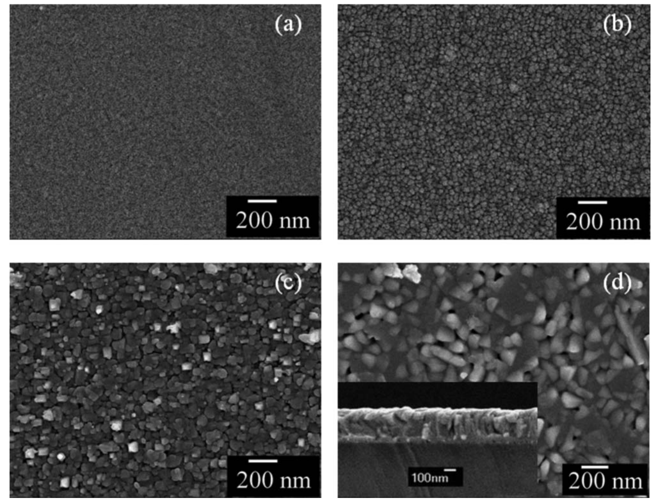


FIG. 3. SEM micrographs showing the surface morphologies of SCNN films deposited at substrate temperatures of (a) 400 °C, (b) 500 °C, (c) 600 °C, and (d) 700 °C. The inset of (d) is the SEM cross section of the SCNN deposited at 700 °C.

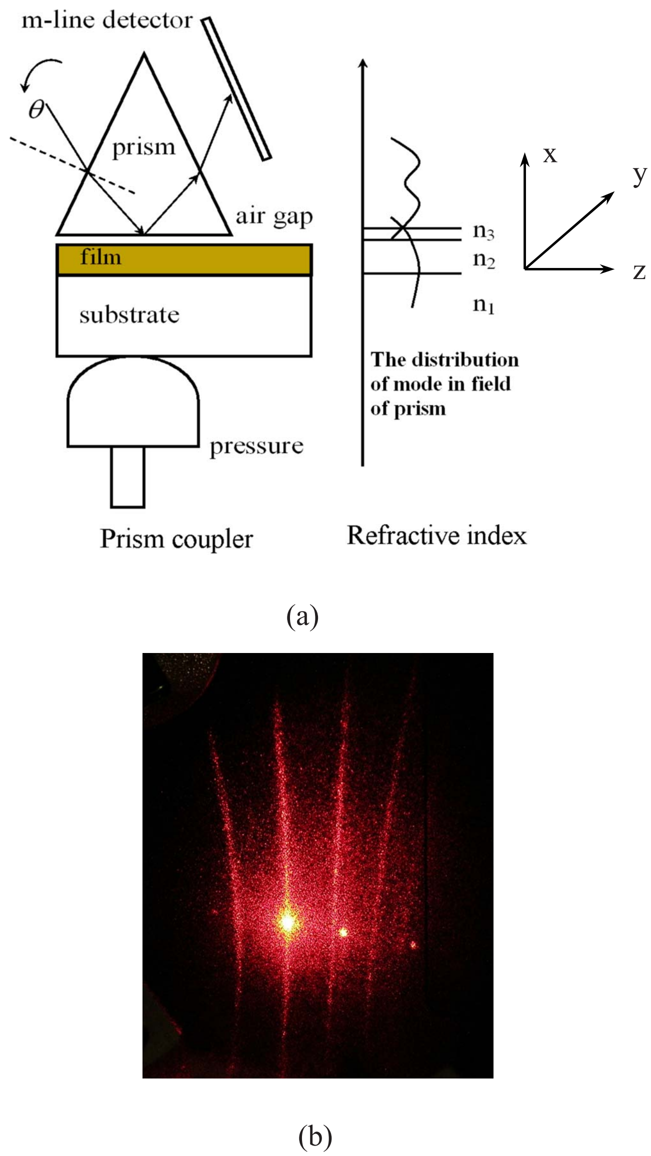


FIG. 4. (Color online) (a) The principal components and principle of the m line measurement setup. (b) Photograph of a screen image of m lines of confined TE multimodes of the SCNN film deposited at 600 °C.

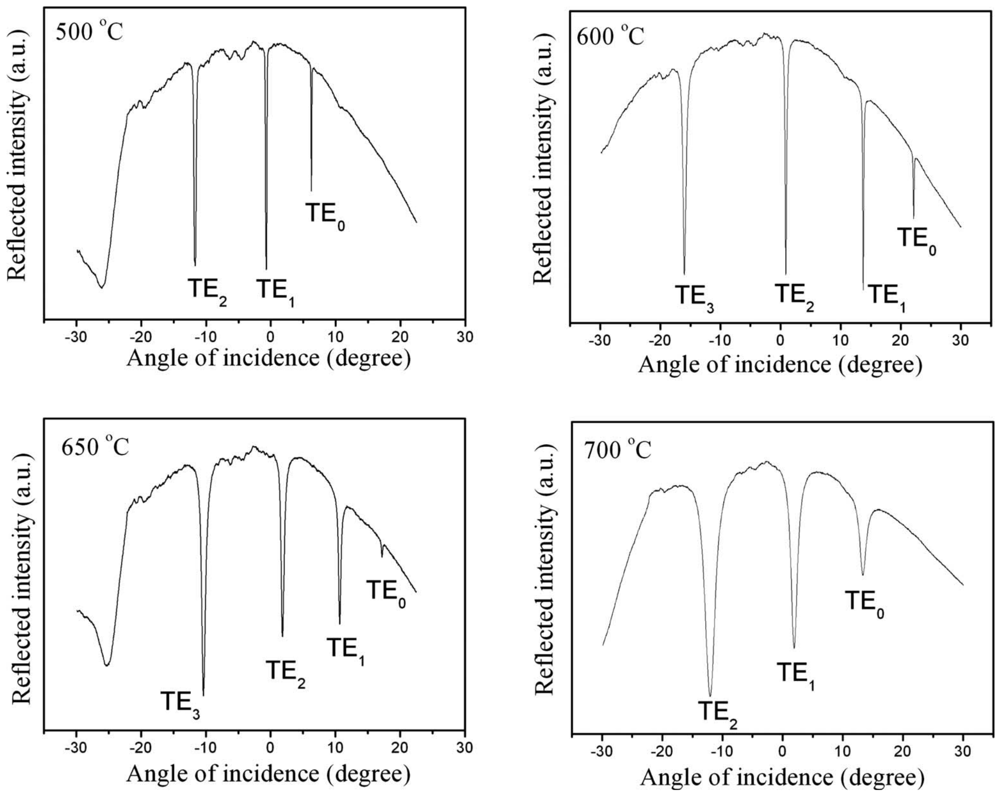


FIG. 5. TE mode spectra of SCNN films deposited at different substrate temperatures.

with the smallest FWHM value (0.86°) was achieved in the SCNN film deposited at 750 °C. Since the crystalline qualities of ferroelectric thin films degrade at $T_{sub} > 800$ °C due to the nonuniform strain originating from point defects, such as oxygen vacancies,[11] we selected 750 °C as the "optimized" substrate temperature for SCNN film growth.

Figure 3 shows the surface morphologies of SCNN films deposited at different temperatures. Films grown below 500 °C were amorphous with very smooth surfaces. Fine grains with an average size of 20 nm appeared at $T_{sub} > 500$ °C, and grain growth was evident at higher substrate temperatures. Films grown at 700 °C were well crystallized with an average grain size of 100 nm. Consistent with the XRD patterns, the SEM micrographs indicate the films crystallized at 500–600 °C. The optimal substrate temperature for high quality SCNN film growth lies within the 550–750 °C window that is known for high quality ferroelectric film growth.[12] Besides SEM, AFM was employed to measure surface roughness of these films. The root mean square roughness increased from 1.3 to 13.0 nm while the deposition temperature increased from 400 to 750 °C.

B. Optical properties

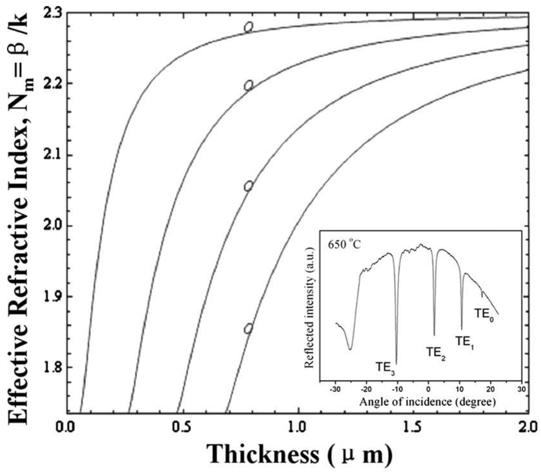
The waveguide properties of the SCNN films were investigated using a prism coupler technique, which is a well-developed method to evaluate dielectric and ferroelectric waveguide structures. This nondestructive technique retains the original surface of the sample and characterization of optical devices based on this technique is simple, direct, and accurate. The model 2010 prism coupler experimental setup, whose principles are described elsewhere,[13] to monitor the mode lines (m line) is shown in Fig. 4(a). In this method, at certain discrete incident angles (mode angles), photons tunnel across the air gap to form an optical propagation waveguide mode. The resulting narrow bright m lines cause sharp drop in the intensity of light reaching the detector. As shown in Fig. 4(b), the m lines of confined TE modes were distinct and sharp, implying that the SCNN thin films on MgO substrates are of good optical waveguide quality. Figure 5 shows the m lines of TE modes guided within SCNN films grown at different temperatures. Following Ulrich and Torge,[14] the refractive index and thickness of the waveguide films were calculated using intrinsic waveguide equation and the angle at which the modes were excited.

The waveguide geometry is a three-layer air/SCNN/MgO structure shown in Fig. 4(a). Assuming that the x axis is normal to the film plane and that the waveguide is infinitely wide along the y axis, E and H are both independent of y. Moreover, these fields vary along the propagation direction z as $\exp(i\beta z)$ and are given by $\tilde{E}=E(x,y)e^{-i(\beta z-\omega t)}$, $\tilde{H}=H(x)e^{-i(\beta z-\omega t)}$, where β is the complex propagation constant. The dispersion for the TE and TM modes are generated by numerically solving the respective transcendental equations:[15]

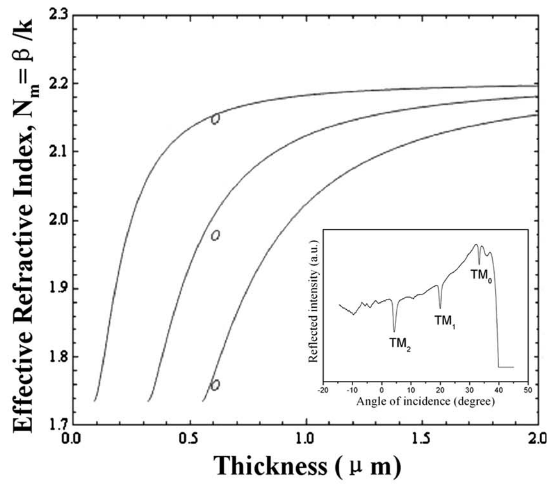
$$\tan(ht) = \frac{h(p+q)}{h^2 - pq},$$

$$\tan(ht) = \frac{n_2^2 h(n_3^2 p + n_1^2 q)}{n_1^2 n_3^2 h^2 - n_2^4 pq},$$

where $p=(\beta^2-k^2n_3^2)^{1/2}$, $h=(k^2n_2^2-\beta^2)^{1/2}$, $q=(\beta^2-k^2n_1^2)^{1/2}$, t is the thickness of waveguide layer and n_3 is the refractive



(a)



(b)

FIG. 6. (a) TE and (b) TM modes effective index dispersion curves for the SCNN/MgO waveguide deposited at 650 °C. The individual data (open circles) are experimental values obtained using the prism-coupling method. Insets are respective TE and TM mode spectra measured by the prism-coupler technique.

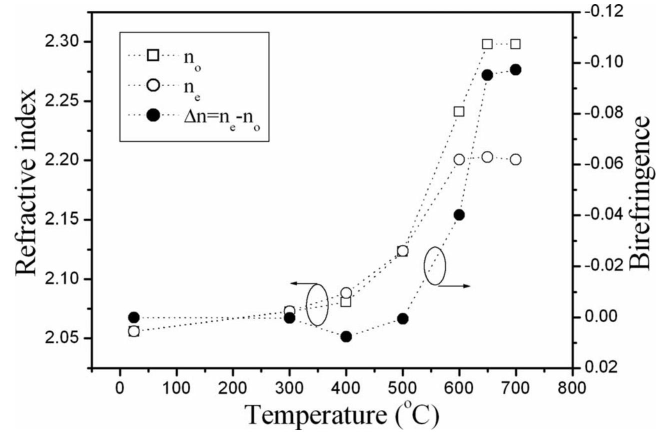


FIG. 7. Refractive indices and birefringence for SCNN films deposited at different substrate temperatures.

index of the air gap. Solutions are found by iterating the effective refractive index N_m between n_1 and n_2, the indices of the substrate and film; the resulting dispersion for the waveguide fabricated at 650 °C is illustrated by the solid curves in Fig. 6. Experimental values for the equivalent index $N_m = \beta/k$ are obtained using the prism coupler method introduced in previous studies,[14] and plotted in Fig. 6 as open circles. Good agreement is achieved between the measured TE as well as TM modes and the numerical solutions of the three-layer mode equations.

SCNN is a uniaxial crystal with the *c*-axis as its optical axis. In our studies, the SCNN films were *c*-axis epitaxially grown on MgO(100) substrates. The measured n_{TE} and n_{TM} thus, respectively, represented the ordinary (n_o) and the extraordinary (n_e) refractive index of the SCNN layers. Figure 7 shows the variation of n_o and n_e as well as birefringence ($\Delta n = n_e - n_o$) as a function of the deposition temperature. The refractive indices increased slowly for $T_{sub} < 500$ °C, and then rapidly increased and remain almost constant above 600 °C with values of $n_o \sim 2.29$ and $n_e \sim 2.19$, in very close agreement to that of SCNN single crystals.[5] Generally, the refractive index is sensitive to the change in microstructure and crystallinity of the films. These differences in the refractive indices are intrinsic to the amorphous and crystalline state of the films. Due to random packing of individual molecules in amorphous films, the density is reduced relative to epitaxial crystalline films. Since, as revealed by the SEM cross-sectional micrographs, our epitaxial films are composed of small columnar crystallites [inset of Fig. 3(d)], they were not as dense as SCNN single crystal. The rapid increase in the refractive index is directly related to the microstructure, which is greatly improved when $T_{sub} > 500$ °C. These results suggest that a transition from an amorphous phase to TTB crystalline phase occurs in the 500–600 °C range. Therefore, a temperature as low as 600 °C might be sufficient to prepare epitaxial SCNN films on MgO with properties suitable for optical applications. These findings on the refractive index are consistent with the evolution of the microstructure as observed by XRD. The birefringence increases dramatically beyond the amorphous to crystalline transition range after being nearly zero for temperature below 500 °C where the SCNN films are amorphous and isotropic. Above 650 °C, Δn remains constant at around -0.10. At higher substrate temperatures, the SCNN films generally develop enhanced anisotropy from further *c*-orientation alignment (Fig. 2) leading to greater differences of refractive indices in *a* and *c* axes (birefringence) with substrate temperature T_{sub}. Similar dependence of the refractive index and birefringence on the microstructure and substrate temperature was also observed in PLD deposited TiO_2 films.[16]

The increasing need for nondestructive surface and interface characterization in waveguide structures has stimulated interest in seeking suitable surface characterization methods. AFM is one of the most popular methods to characterize surface morphology and surface roughness of samples. In this paper, we characterized SCNN film surfaces using the prism coupler technique. As shown in Fig. 5, dips of reflected optical intensity indicate the excitation of specific modes whose sharpness is a good indicator of light confinement within the SCNN waveguide and to the morphology of films. Optical characterization based on the prism coupler technique was undertaken in this study to carefully

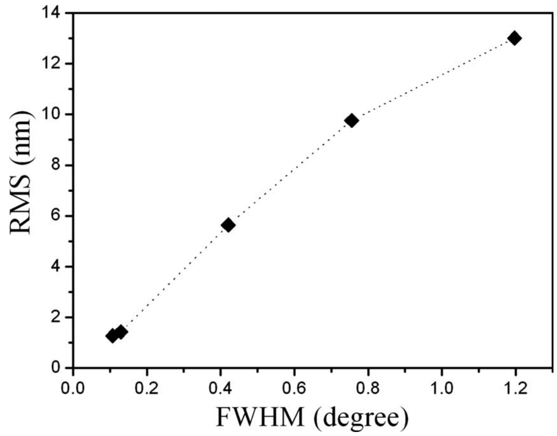


FIG. 8. Correlation of the FWHM of the TE_0 excited guided mode and surface roughness of SCNN films.

establish a relationship between the surface morphology and the optical characteristics of guided modes. Figure 8 shows the evolution of the surface roughness measured by AFM as a function of the FWHM of the TE modes. With increased surface roughness light scattering by roughness of the SCNN films modify the FWHM of the TE modes. Since our findings indicated that the FWHM of the TE modes are linearly proportional to the data obtained from the AFM studies, we suggest that the prism coupler technique can thus be another useful sensitive surface probe of optical waveguide structures.

IV. CONCLUSION

We have successfully grown *c*-axis epitaxial SCNN thin films on MgO(100) substrates by PLD at various T_{sub} ranging from room temperature to 750 °C. Films grown below 500 °C are amorphous with lower refractive indices, whereas those grown at 600 °C or above are highly *c*-axis oriented with higher refractive indices. Optical measurements by a prism coupler technique yield a refractive index value of 2.29, which is close to the bulk SCNN refractive index. The correlation between optical, structural, and crystallographic properties is established through variation of the growth temperature. Our results indicate that the degree of film orientation increases with the substrate temperature up to 750 °C. A rapid increase in refractive index and birefringence is obtained at high substrate temperature due to the transition from amorphous to an oriented crystalline phase in the film, and a concomitant symmetry transformation from isotropic to anisotropic. Finally, the sharpness of the dips of the excited TE modes has a close relationship to the surface roughness of the SCNN thin films. Based on our results, we demonstrate that the prism coupler technique can be used as an alternative probe for the surface roughness of such thin films.

ACKNOWLEDGMENTS

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