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Journal of Applied Physics

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Cite as: J. Appl. Phys. **102**, 093106 (2007); https://doi.org/10.1063/1.2809400
Submitted: 13 April 2007 • Accepted: 19 September 2007 • Published Online: 15 November 2007

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Growth and optical properties of $KTa_{1-x}Nb_xO_3$ thin films grown by pulsed laser deposition on MgO substrates

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(Received 13 April 2007; accepted 19 September 2007; published online 15 November 2007)

Perovskitelike $KTa_{1-x}Nb_xO_3$ (KTN, x ranging from 0 to 1) thin films were grown on (100)MgO substrates using pulsed laser deposition. X-ray diffraction analyses evidenced the epitaxial growth of the films along the (100) orientation. The optical properties of KTN planar waveguides were characterized by prism coupling for determination of ordinary and extraordinary refractive indices n_{TE} and n_{TM} (transverse electric and transverse magnetic). The influence of Nb content was also investigated relative to the films' indices. The film behavior and the substrate-to-layer interface were directly qualified from the measured optical data using the experimental and theoretical approach (*i*WKB) (inverse Wentzel-Kramers-Brillouin). The results showed a change in the refractive index profile at the interface, which may be related to the existence of structural defects. [DOI: 10.1063/1.2809400]

I. INTRODUCTION

Ferroelectric thin films are attractive materials for integrated optics applications, such as electro-optic waveguide modulators[1] and frequency-doubling second-harmonic generation.[2] Among the various compounds investigated in this field, besides $LiNbO_3$,[1–5] the perovskitelike $KTa_{1-x}Nb_xO_3$ (KTN) compound is of prime interest.[6,7] The development of guided-wave applications has concentrated on the fabrication of materials in thin-film form performing the same function as bulk (with higher speeds and smaller applied voltage), taking advantage of the geometrical flexibility and possible integration with semiconductors integrated circuits as reported by Knauss *et al.*,[8] which proposed potential applications in integrated optics using potassium-based materials deposited on GaAs semiconductors. Until recently, most of the optical research on oxide thin films has been focused on the optimization of the growth process and the comprehensive study of the relationship between microstructures and optical properties. Thus, it is important to characterize the optical properties of such thin-film materials in order to provide feedback information for growth process optimization. To perform such an analysis, a single measurement technique, i.e., the prism coupling technique, capable of determining the film thickness, the composition, the refractive index, the interface properties, and the surface roughness with a quick turnaround time is extremely valuable to any growth program.

II. EXPERIMENT

In the KTN compound, the Curie temperature, T_c, can be monitored by choosing a selected composition in the solid solution $KTaO_3$-$KNbO_3$:[9] T_c is expected to vary continuously according to the formula T_c [K]$=676x+32$ (for $x \geq 4.5\%$).[9,10] Adjustment of T_c to a value close to the temperature of experiment gives access to high values of permittivity (maximum to $T \sim T_c$) and broad effects into electro-optical and nonlinear optics.[8,11] Thus, KTN is an attractive material for applications in various fields.[12–14] Many studies showed the difficulty in preserving the metal atoms ratio according to the pseudobinary phase diagram established for KTN single crystals[10,15,16] or ceramics.[9,17,18] Indeed, one of the main difficulties of KTN thin-film synthesis is to preserve the potassium content and to avoid any pyrochlore-type phase. Various methods were carried out for KTN thin-films deposition like liquid phase epitaxy (LPE),[15] metalorganic chemical vapor deposition (MOCVD),[19,20] sol-gel method,[21–25] rf sputtering,[26,27] and pulsed laser deposition (PLD).[8,28–34] In this paper, we report on optical waveguide measurements in pulsed laser deposited $KTa_{1-x}Nb_xO_3$ thin films epitaxially grown on (100) MgO single-crystal substrates.

$KTa_{1-x}Nb_xO_3$ thin films, ~500 nm thick, for various compositions x were grown *in situ* by PLD using a KrF excimer laser (Tuilaser Excistar, pulse duration of 20 ns, $\lambda = 248$ nm), with a fluence of ~1.5 J/cm^2, operating at 2 Hz. KTN films were deposited from homemade sintered targets prepared by solid-state reaction. An excess of potassium (50 at %) was added as KNO_3 to a mixture of $KNbO_3$ and $KTaO_3$ in proportion to x, before sintering in order to avoid K deficiency in the films.[34] Thin films were grown at 700 °C under an oxygen pressure of 0.3 mbar

III. RESULTS AND DISCUSSION

Epitaxial films were analyzed by x-ray diffraction (XRD) using a four-circle texture diffractometer (Brüker

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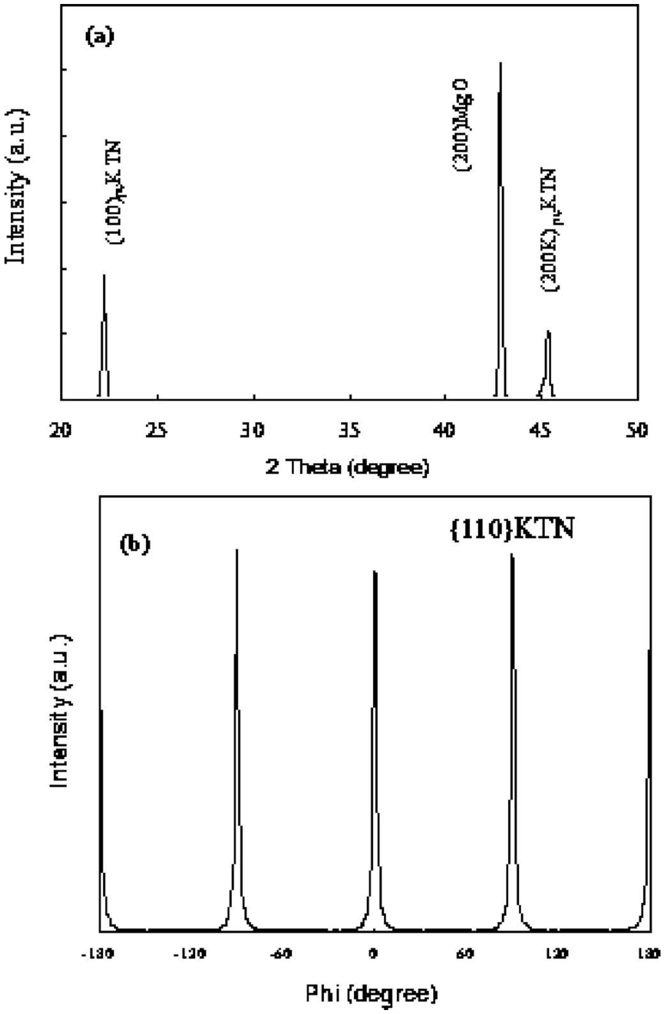

FIG. 1. (a) Typical θ-2θ XRD pattern of KTN (here $x=0.4$) films grown on (100)MgO. (b) XRD patterns in φ scan mode performed on the 110 reflection of KTN.

AXS D8 Discover) operated with Cu $K\alpha_1$ radiation in θ-2θ, ω-scan, and φ-scan modes. Thin-film surface morphology was observed with a field effect emission scanning electron microscope (SEM, JEOL F-6301) operated at low voltage (typically 9 kV) in order to limit charge effects and to achieve a high resolution without the need of surface metallization. As-deposited KTN films are (100) oriented as revealed by the θ-2θ XRD represented in Fig. 1(a), which exhibits only h00 peaks of KTN on (100)MgO, referring to the pseudocubic subcell.[35] The full width at half maximum, $\Delta\omega$, of the ω-scan of 100_{pc} peak ranges between 0.8° and 1.5°, close to previous values reported on this substrate.[36] This ω-scans width is in agreement with a high crystalline quality, although higher than the corresponding value measured on films grown on $SrTiO_3$ ($\Delta\omega \sim 0.3°$). This difference of crystalline quality can be related to the difference of lattice mismatch between KTN and the substrate (~−5% on MgO to be compared to ~+2% on $SrTiO_3$). In spite of this mismatch, MgO was chosen as the substrate for its optical index far enough from the one of KTN in view of this optical study. Indeed, thin films grown on (100)MgO, are epitaxial-like as shown by the typical φ-scan XRD patterns [Fig. 1(b)] performed on the 110 reflection of KTN. As expected, structural characteristics strongly influence the films, which exhibit a quite dense and well-organized in-plane microstructure (Fig. 2), in agreement with the in-plane structural ordering. Moreover, Rutherford backscattering (RBS) measurements performed on films deposited from the different targets showed that $K/(Nb+Ta)=1.00\pm0.05$, and that the Nb/Ta ratio was quite the same in the films as in the starting targets.

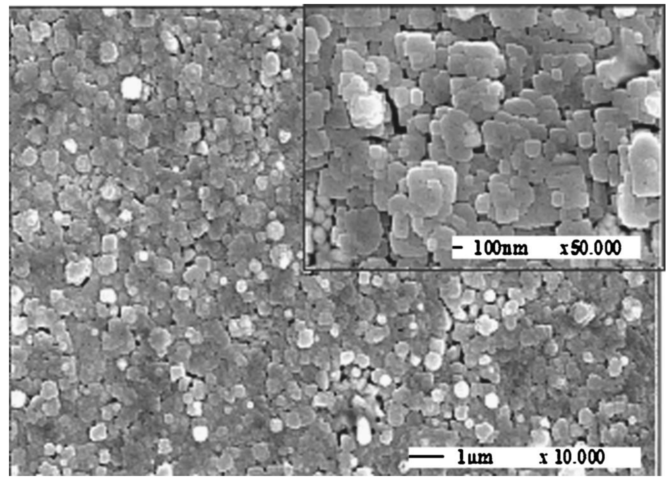

FIG. 2. Typical morphology observed by scanning electron microscopy for KTN films grown on MgO,—: 1 μm, inset–100 nm.

In this work, we chose to apply the nondestructive prism-coupling method to study the material's optical waveguide properties of the KTN films. This technique is based on the principle of the coupling evanescent waves between a rutile (TiO_2) prism of high index and samples via an air gap that is created between the two media. The latter is pressed against the base of a right-angle prism. The experimental details involved in the prism coupler method are discussed in Refs. 3 and 37. By measuring the reflected intensity versus the angle of incidence, we draw the guided mode spectrum of the sample. Reflectivity dips at certain angles of incidence correspond to the excitation of guided modes. Two He-Ne lasers (632.8 and 543.5 nm) were used as the light sources. The low refractive index of MgO ($n_{MgO}=1.706$ @ 632.8 nm) allows the guided wave within the proposed structure. For our samples with the optical axis perpendicular to the surface, the ordinary and the extraordinary guided modes are, respectively, studied by using light of TE (transverse electric) and TM (transverse magnetic) polarization. As an example, Table I details the results for TE and TM modes experimentally determined in the case of $KTa_{0.4}Nb_{0.6}O_3$ films. It could be obtained similarly for other films' composition. All of the modes are sharp and distinguishable, indicating that the films are of high optical quality. For 500 nm thick KTN samples, three TE and two TM modes are excited within the structure. From the angular position of the guided modes ($\theta_{TE0}=+13.280°$, $\theta_{TE1}=+0.810°$, and $\theta_{TE2}=-17.420°$), we computed the corresponding effective indices as reported in Table I. The refractive indices n_{TE} and n_{TM} were determined from the TE modes to be $n_{TE}=2.220\pm0.001$ and $n_{TM}=2.106\pm0.001$ @ 632.8 nm, which is lower than the refractive indices of the KTN single crystal of

TABLE I. Effective indices for TM (extraordinary excitation) and TE (ordinary excitation) waveguided modes (sample $KTa_{1-x}Nb_xO_3$, $x=0.6$). The experimental values (N_m expt) are compared to the theoretical ones (N_m th).

Wavelength	Polarization	Mode	Angle θ(°)	N_m expt	N_m th	Deviation
λ_1	TM	0	+14.31	1.972	1.997	0.024
		1	−5.26	1.740	1.746	0.005
	TE	0	+13.28	2.181	2.171	0.010
		1	+0.81	2.036	2.023	0.013
		2	−17.42	1.803	1.777	0.026
λ_2	TM	0	+16.57	2.066	2.072	0.006
		1	+0.94	1.886	1.9075	0.020
	TE	0	+12.55	2.2396	2.220	0.019
		1	+2.65	2.1240	2.072	0.052
		2	−11.34	1.9479	1.822	0.120

the same composition $n_{TE}=2.318$ reported by Van Raalte[38] and $n_{TE}=2.350$ by Gunter *et al.*[39] This difference is mainly related to the material quality and, based on our optical results and using the Bragg-Pippart model,[40] the packing density was estimated to be 97%. Such a study also has been reported recently.[8] Figure 3 describes the evolution of the ordinary refractive index as a function of the film composition x, i.e., Nb content (from $x=0.2$ to 0.8) for TE polarizations, at $\lambda_1=543.5$ nm and $\lambda_2=632.8$ nm. We have related the evolution of the refractive index with the x content in the KTN composition. The thickness value is found to be 550 nm±10 nm, in good agreement with the value determined from SEM observation performed on cross sections.

In this study, we have reconstructed the refractive index profiles directly from the measured effective indices by using an improved version of the inverse Wentzel–Kramer–Brillouin (iWKB) method. This method only depends on the refractive index distributions within the guiding layer. More details of the calculation are given by Dogheche *et al.*[41] Using a polynomial interpolation of the measured effective indices, we computed the refractive index profiles as a smooth function of the thickness. As shown in Fig. 4, the refractive index remains constant within the guiding region, and the interface containing defects manifests itself through the changes of the optical properties of samples. As a consequence, the diminution of refraction index toward the substrate can be attributed to film/substrate interface effects, such as chemical interdiffusion that was evidenced by the profile composition obtained by secondary neutral mass spectrometry on a KTN film grown on MgO. On the other hand, such profiles confirmed the KTN composition homogeneity along the thickness far from the film/substrate interface area. For comparison, some measurements were also performed on films grown on (100)$LaAlO_3$ substrates. The results were quite similar, suggesting no clear influence of the substrate on the growth process impacting the optical properties.

IV. CONCLUSIONS

To summarize, we present the results of investigation of potassium niobium ($KTa_{1-x}Nb_xO_3$) films grown on (100)MgO substrates by the pulsed laser deposition technique. To assess the structural quality of the films, we performed x-ray diffraction. The results revealed that the epitaxial structure is verified whatever the film thickness. Based on our studies, we concluded that the proposed process leads to a good controlled epitaxy of quite thick $KTa_{1-x}Nb_xO_3$ samples. Using the well-known prism-coupling technique, we have characterized the optical properties of the deposited

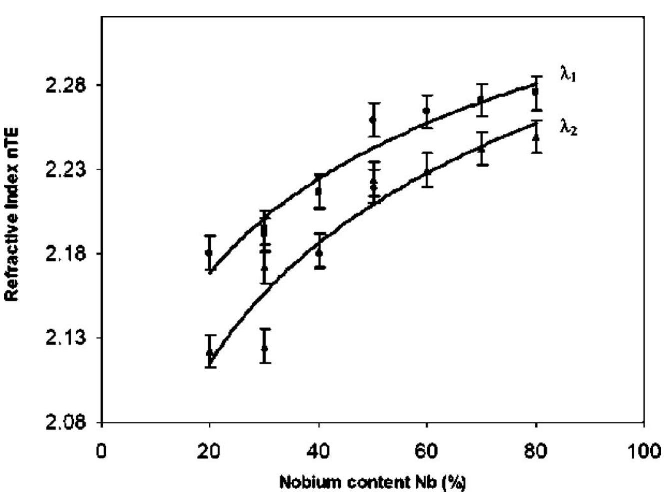

FIG. 3. Influence of niobium content (x) on the refractive index of KTN films on MgO for $\lambda_1=543.5$ nm and $\lambda_2=632.8$ nm.

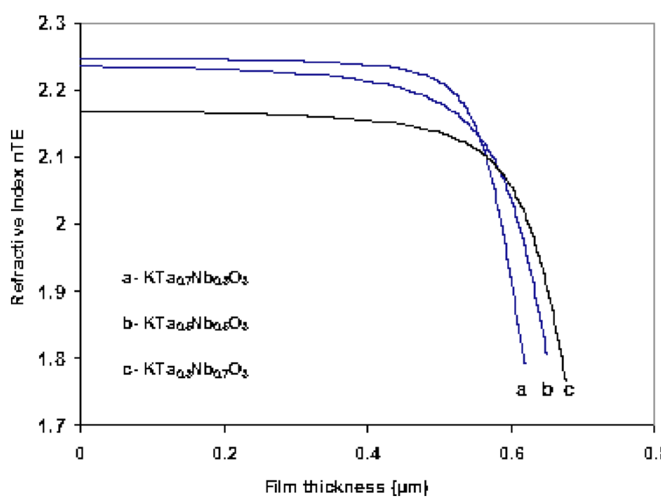

FIG. 4. (Color online) Typical iWKB refractive index reconstruction from optical analysis ($\lambda_2=632.8$ nm) for $KTa_{1-x}Nb_xO_3$ with $x=0.3$, 0.5, and 0.7.

layers. For $KTa_{1-x}Nb_xO_3$ samples, the ordinary (n_{TE}) and extraordinary (n_{TM}) refractive indices are, respectively, determined for various film composition x. In addition, we have qualified the properties of the film prepared under optimized process conditions. Reconstruction of index profiles for the KTN/MgO structure is proposed, and revealed an index evolution near the interface. The sharp decrease of the refraction indices suggests the presence of a low density of defects near the film-substrate interface.

ACKNOWLEDGMENTS

The authors would like to acknowledge CMEBA at University of Rennes 1 for scanning electron microscopy observations. F. Lalu and S. Henry at CSNSM in Orsay are warmly acknowledged for RBS analyses. One of the authors (A. Rousseau) received a grant from Region Bretagne (under Contract CACET No. A2CA33).

[1]H. Robinson, C. W. Pitt, and R. A. Gibson, Appl. Opt. **32**, 3981 (1993).
[2]G. D. Boyd, R. C. Miller, K. Nassau, W. L. Bond, and A. Savage, Appl. Phys. Lett. **5**, 234 (1964).
[3]X. Lansiaux, E. Dogheche, D. Rèmiens, M. Guilloux-Viry, A. Perrin, and P. Ruterana, J. Appl. Phys. **90**, 5274 (2001).
[4]V. Bouquet, M. I. B. Bernardi, S. M. Zanetti, E. R. Leite, E. Longo, J. A. Varela, M. Guilloux-Viry, and A. Perrin, J. Mater. Res. **15**, 2446 (2000).
[5]P. Aubert, G. Garry, R. Bisaro, and J. Garcia Lopez, Appl. Surf. Sci. **86**, 144 (1995).
[6]J. E. Geusic, S. K. Kurtz, T. J. Nelson, and S. H. Wemple, Appl. Phys. Lett. **2**, 185 (1963).
[7]K. Fujiara and K. Nakamura, Proc. SPIE **5623**, 518 (2005).
[8]L. A. Knauss, K. S. Harshavardhan, H. M. Christen, H. Y. Zhang, X. H. He, Y. H. Shih, K. S. Grabowski, and D. L. Knies, Appl. Phys. Lett. **73**, 3806 (1998).
[9]S. Triebwasser, Phys. Rev. **114**, 63 (1959).
[10]D. Rytz and H. J. Scheel, J. Cryst. Growth **59**, 468 (1982).
[11]H. J. Scheel and P. Günter, in *Crystal Growth of Electronic Materials*, edited by E. Kaldis (Elsevier, Amsterdam, 1985), p.149.
[12]H. Khemakhem, J. Ravez, and A. Daoud, Phys. Status Solidi A **161**, 557 (1997).
[13]F. S. Chen, J. E. Geusic, S. K. Kurtz, J. G. Skinner, and S. H. Wemple, J. Appl. Phys. **37**, 388 (1966).
[14]M. J. Lancaster, J. Powell, and A. Porch, Supercond. Sci. Technol. **11**, 1323 (1998).
[15]M. Sasaura, T. Imai, H. Kohda, S. Tohno, M. Shimokozono, H. Fushimi, K. Fujiura, S. Toyoda, K. Enbutsu, A. Tate, K. Manabe, T. Matsuura, and T. Kurihara, J. Cryst. Growth **275**, e2099 (2005).
[16]V. A. Kallur and R. K. Pandey, Ferroelectrics **158**, 55 (1994).
[17]H. Khemakhem, J. Ravez, and A. Daoud, Ferroelectrics **188**, 41 (1996).
[18]A. Reisman, S. Triebwasser, and F. Holtzbzerg, J. Am. Chem. Soc. **77**, 4228 (1955).
[19]A. Onoe, A. Yoshida, and K. Chikuma, Appl. Phys. Lett. **78**, 49 (2001).
[20]B. M. Nichols, B. H. Hoerman, J.-H. Hwang, T. O. Mason, and B. W. Wessels, J. Mater. Res. **18**, 106 (2003).
[21]S. Wang, T. Zhon, L. Wang, and A. Kuang, Ferroelectrics **195**, 259 (1997).
[22]A. Nazeri and M. Kahn, J. Am. Ceram. Soc. **75**, 2125 (1992).
[23]J. Buršík, I. Drbohlav, P. Vaněk, and V. Železný, J. Eur. Ceram. Soc. **24**, 455 (2004).
[24]C. J. Lu and A. X. Kuang, J. Math. Sci. **32**, 4421 (1997).
[25]I. T. Weber, M. Garel, V. Bouquet, A. Rousseau, M. Guilloux-Viry, E. Longo, and A. Perrin, Thin Solid Films **493**, 139 (2005).
[26]S. R. Sashital, S. Krisnakumar, and S. Esener, Appl. Phys. Lett. **62**, 2917 (1993).
[27]B. Tunaboylu, S. R. Sashital, P. Harvey, and S. C. Esener, Ferroelectr., Lett. Sect. **28**, 75 (2001).
[28]A. C. Carter, J. S. Horwitz, D. B. Chrisey, J. M. Pond, S. W. Kirchoefer, and W. Chang, Integr. Ferroelectr. **17**, 273 (1997).
[29]S. Yilmaz, T. Venkatesan, and R. Gerhard-Multhaupt, Appl. Phys. Lett. **58**, 2479 (1991).
[30]H. M. Christen, D. P. Norton, L. A. Géa, and L. A. Boatner, Thin Solid Films **312**, 156 (1998).
[31]F. E. Fernandez, M. Pumarol, P. Marrero, E. Rodriguez, and H. A. Mourad, Mater. Res. Soc. Symp. Proc. **493**, 365 (1998).
[32]W. D. Ma, Z. S. Zhao, S. M. Wang, D. M. Zhang, D. S. Zu, X. D. Wang, and Z. J. Chen, Phys. Status Solidi A **176**, 985 (1999).
[33]A. Perrin, A. Rousseau, J. R. Duclère, and M. Guilloux-Viry, Ferroelectrics **316**, 71 (2005).
[34]A. Rousseau, V. Laur, M. Guilloux-Viry, G. Tanné, F. Huret, S. Députier, A. Perrin, F. Lalu, and P. Laurent, Thin Solid Films **515**, 2353 (2006).
[35]V. Gopalan and R. Raj, J. Am. Ceram. Soc. **78**, 1825 (1995).
[36]W. Chang, A. C. Carter, J. S. Horwitz, S. W. Kirshoefer, J. M. Pond, K. S. Grabowski, and D. B. Chrisey, Mater. Res. Soc. Symp. Proc. **493**, 353 (1988).
[37]P. K. Tien, R. Ulrich, and J. R. Martin, Appl. Phys. Lett. **14**, 291 (1969).
[38]J. A. van Raalte, J. Opt. Soc. Am. **57**, 671 (1967).
[39]P. Gunter, Phys. Rep. **93**, 199 (1982).
[40]W. L. Bragg and A. B. Pippard, Acta Crystallogr. **6**, 865 (1953).
[41]E. Dogheche, B. Belgacem, D. Rèmiens, P. Ruterana, and F. Omnes, Appl. Phys. Lett. **75**, 3324 (1999).