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Second-harmonic generation in highly textured LiNbO₃ films prepared by pulsed laser deposition

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LiNbO₃ films have been deposited on (001) sapphire substrates by pulsed laser deposition, in an oxygen environment. Films grown at substrate temperatures of 650 °C are crystalline, strongly textured, and show a degree of twining that is lower the higher the oxygen pressure is in the range of 0.5–1 Torr. Values of the nonlinear optical coefficients d_{33} and d_{31} of the films, measured via second-harmonic generation, are close to those for the bulk LiNbO₃ single crystal. The dependence of both the degree of twining and the nonlinear optical response on the film thickness suggests that the films become closer to single domain for larger thickness. © *2000 American Institute of Physics.* [S0021-8979(00)01519-X]

Lithium niobate (LN) has become widely used in optoelectronics. For nonlinear optical applications, the waveguide geometry offers high conversion efficiencies due to the large intensity-length factor associated with the tight confinement of the optical mode.

Several techniques have been used to produce LN waveguides. Among them, pulsed laser deposition (PLD) has recently shown its capability to produce highly textured LN films on a wide range of substrates, including Si,[1] SiO₂,[2] and sapphire.[3–7] Nevertheless, optimum growth conditions are not yet completely elucidated. Some authors have modified the stoichiometry of the target by using Li-enriched sintered targets[3,6,8] or changed the substrate-target distance.[7,9] The results show that oxygen pressures in the range $10^{-3}-10^{-2}$ Torr are enough to grow highly textured films from Li-enriched targets,[3,6] whereas higher pressures (>4×10^{-1} Torr) are required when using single crystal targets.[4,5] The latter produces a lower amount of droplets and/or roughness, generally leading to good results when substrate temperatures are in the range of 650–700 °C (apart from the work of one group reporting that the optimum substrate temperatures are in the 400–500 °C range[7,10]). To our knowledge there is only one report on second-harmonic generation (SHG) from LN films prepared by PLD.[7] The aim of this work is to investigate the optimum conditions for the growth of LN films on sapphire by PLD with high second-order nonlinear optical properties.

A rotating LN single crystal was ablated using a focused ArF excimer laser beam (pulse duration of 20 ns) incident at 45° and with an energy density of 2 J cm⁻². The deposition took place in a vacuum chamber (residual pressure of 5×10^{-7} Torr) upon an oxygen pressure in the range of 5×$10^{-2}-1$ Torr. The (001) sapphire substrates were placed at ≈30 mm in front of the target surface and parallel to it and were kept at a temperature in the range of 400–650 °C. After deposition, all the films were *in situ* cooled down in an oxygen pressure of 75 Torr.

The structure of the films was analyzed by normal incidence θ-2θ and ϕ x-ray diffraction. The θ-2θ scans of the films grown on substrates heated at 400 °C and at pressures of 5×10^{-2} and 4×10^{-1} Torr, and on substrates heated at 550 °C at a pressure of 5×10^{-2} Torr, showed no features thus suggesting they were amorphous. Table I summarizes the films investigated in this work that were grown on substrates heated at 650 °C. The θ-2θ scans of A500 and B500-1 samples are, respectively, shown in Figs. 1(a) and 1(b). The scans contain two significant peaks that correspond to the LN (006) reflection and to the sapphire substrate (*S*), thus indicating that both films are strongly textured along this axis. The scans of the other studied films show similar features except for the case of the thinner films (300 nm) that show an additional peak that might be related to the (220) reflection of the Li₃NbO₄ phase. The fact that films grown at 650 °C are strongly textured agrees quite well with the results reported in the literature using similar experimental conditions,[4,5] thus allowing us to conclude that temperatures in the range of 650–700 °C and oxygen pressures >10^{-1} Torr are required to grow highly textured LN films by PLD from single-crystal targets. The reasons why one group has achieved highly textured LN films at substrates temperatures close to 500 °C, for which we obtain amorphous films, is still unclear.[7,10] The only significant difference between their work and the present one is the use of a shadow mask to improve surface quality, while reducing the deposition rate (0.02 nm/s compared to 0.08 nm/s in our work). Since it has been reported that a reduced growth rate of 0.03–0.05 nm/s improves the crystallinity of LN films deposited by metalorganic chemical vapor deposition at 500 °C compared to the 0.08 nm/s that are required for sub-

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TABLE I. Maximum SH signal and effective nonlinear coefficients $d_{33,\text{eff}}$ and $d_{31,\text{eff}}$ determined in LN films grown by PLD at 650 °C and 1 Torr of oxygen pressure except A500 that was grown at 0.5 Torr for different film thickness (L).

Sample	L(nm)	$W_{2\omega}$ (a.u.)	$d_{33,\text{eff}}$ (pm/V)	$d_{31,\text{eff}}$ (pm/V)
Bulk	⋯	⋯	27.0	4.3
A500	500	1170	22.0	3.5
B700	700	1400	17.6	2.8
B500-1	500	700	17.2	2.7
B500-2	500	860	18.9	3
B300-1	300	160	13.5	2.1
B300-2	300	100	10.7	1.7

strates heated to 700 °C, the reduced rate used in Refs. 7 and 10 might explain the success reported using low substrate temperature.

The insets in Fig. 1 shows the corresponding ϕ-scan patterns that exhibit peaks when the films are rotated by 60° around their normal axis. This indicates that both films have two structural variants (twined crystals) which will be named α_1 and α_2. The corresponding peak intensity ratio is slightly higher (2 compared to 1.4) for the film grown at the highest oxygen pressure, thus indicating smaller twinning. The comparison of the ϕ scans from the substrate and the film shows that the variant α_1 exhibiting the more intense peaks is aligned with the substrate and thus the epitaxial growth is favored by increasing the oxygen pressure. This twining has often been reported in the literature and related to the large lattice mismatch between LN and sapphire.[12]

The second-order nonlinear optical properties were measured via SHG using a Q-switched and mode-locked Nd:YAG laser, operating at a wavelength λ of 1.064 μm.
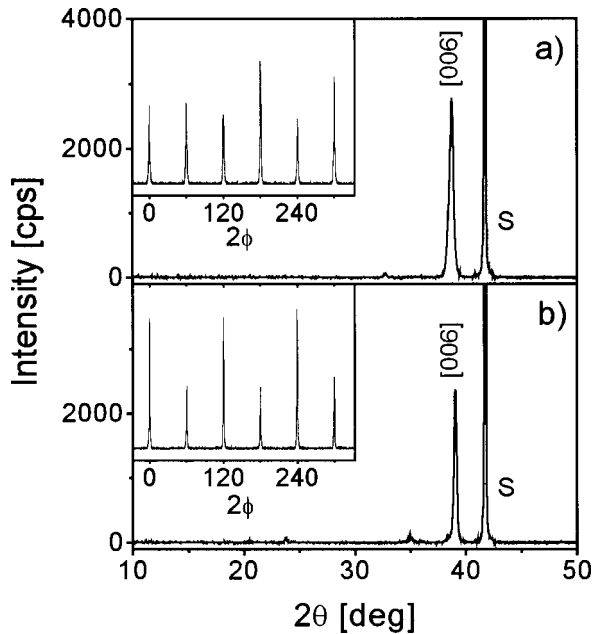

FIG. 1. θ-2θ scans of LN films grown at a substrate temperature of 650 °C and oxygen pressures of (a) 0.5 Torr and (b) 1 Torr. The peaks labeled (006) and S correspond to LiNbO₃ and the sapphire substrate, respectively. The insets show the corresponding ϕ scans.
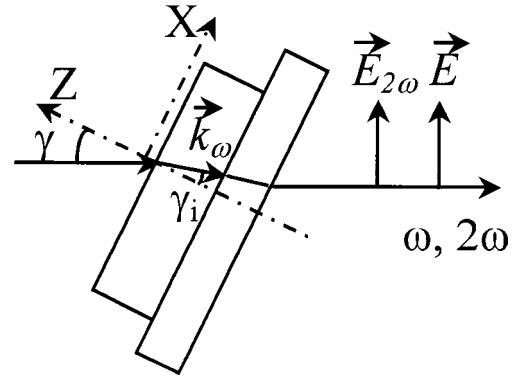

FIG. 2. Experimental configuration for the SH measurements. The input fundamental (ω) and detected output SH (2ω) beams are polarized in the plane of incidence. The z axis, perpendicular to the film (film texture axis), defines the plane of incidence with the x axis which is assumed parallel to one of the in-plane crystal twin variants.

Since the films are textured along the direction perpendicular to the substrate, we can assume that they are formed by domains oriented along this direction in the up (parallel P) or down (antiparallel $-P$) orientations. For each structural variant, two domain orientations are thus possible that lead to a total of four groups. The effective values for the nonlinear tensor components (effective nonlinear coefficients $d_{33,\text{eff}}$, $d_{31,\text{eff}}$) can be calculated[13]

$$d_{3i,\text{eff}} = [(\alpha_{1,P} + \alpha_{2,P}) - (\alpha_{1,-P} + \alpha_{2,-P})]d_{3i} \quad i=1,3 \quad (1)$$

where $\alpha_{j,P}$ and $\alpha_{j,-P}$ are, respectively, the volume fractions of domains up and down in variant j (j being 1 or 2) and d_{33}, and d_{31}, the nonlinear coefficients for single crystal bulk LN.[14]

The layout for the SHG experiment is shown in Fig. 2. The fundamental beam is linearly polarized in the plane of incidence [transverse magnetic (TM) polarized] and the SH beam is detected TM polarized. The z axis is parallel to the texture axis and thus all the domains are along it. Let us assume that the x axis, contained in the plane of incidence, is along the in-plane axis of one of the two crystal variants. In any case, it was experimentally found a weak dependence of the SH signal as a function of the rotation around the z axis. Assuming the fundamental and SH beams propagate parallel inside the film ($\vec{k}_w // \vec{k}_{2w}$) and neglecting multiple reflections, the normalized internal SH power for the TM(ω)→TM(2ω) as a function of the internal angle of propagation (γ_i) is given by[15]

$$W_{2w,\text{TM}-\text{TM}}(\gamma_i)$$

$$= C\left[\frac{1}{n_{\text{ex}}(\gamma_i,\lambda)^2 n_{\text{ex}}(\gamma_i,\lambda/2)}\frac{1}{\Delta k_{\text{ex}}(\gamma_i,\lambda)^2}\right]$$

$$\times\left[\frac{1-n_{\text{ex}}(\gamma_i,\lambda)^2 \sin^2\gamma_i}{1-\sin^2\gamma_i}\right]^{1/2}$$

$$\times d_{\text{eff}}(\gamma_i)^2 \sin^2\left(\frac{\Delta k_{\text{ex}}(\gamma_i,\lambda)L}{2\cos\gamma_i}\right), \quad (2)$$

where $C = 8\,\omega^2/\epsilon_0 c_0^3\,\pi w_0^2$, c_0 is the speed of light in vacuum, w_0 is the spot size ($1/e^2$ intensity radius) of the
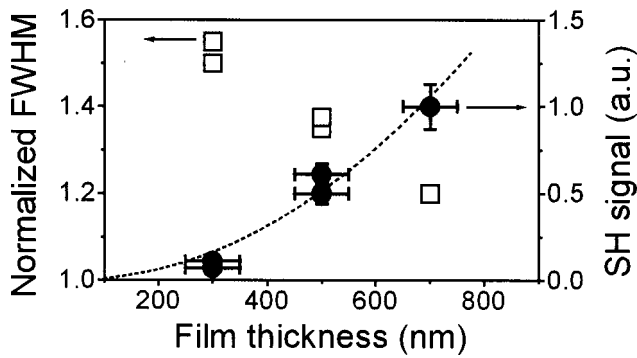
FIG. 3. (●) SH signal and (□) full width half maximum (FWHM) of the (006) reflection of LN measured in films grown at 1 Torr of pressure as a function of film thickness. The SH signal and FWHM are, respectively, normalized to the highest SH response (i.e., 700 nm thick) and to the value for the sapphire substrate. The dashed line is the best quadratic fit.

fundamental beam, ϵ_0 is the dielectric constant of vacuum $d_{\text{eff}}(\gamma_i) = 3 d_{31,\text{eff}} \sin \gamma_i \cos^2 \gamma_i + d_{33,\text{eff}} \sin^3 \gamma_i$ is an effective nonlinear coefficient which includes the interaction with all the four groups. L is the film thickness, $n_{\text{ex}}(\gamma_i, \lambda) = [n_e(\lambda) n_o(\lambda)] / [(n_o(\lambda) \sin \gamma_i)^2 + (n_e(\lambda) \cos \gamma_i)^2]^{1/2}$ is the refractive index as a function of $n_e(\lambda)$ and $n_o(\lambda)$ that, respectively, are the extraordinary and ordinary refractive indexes, and $\Delta k_{\text{ex}}(\gamma_i, \lambda) = 4 \pi [n_{\text{ex}}(\gamma_i, \lambda/2) - n_{\text{ex}}(\gamma_i, \lambda)] / \lambda$ is the wave-vector mismatch between fundamental and SH waves. Using a quartz sample as reference, the SH response provides d_{eff} and since $(d_{33,\text{eff}}/d_{33}) = (d_{31,\text{eff}}/d_{31})$, the values of $d_{33,\text{eff}}$ and $d_{31,\text{eff}}$ are easily determined. The obtained coefficient values together with those of $W_{2\omega,\text{TM-TM}}(\gamma_i)$ are included in Table I, the former being close to d_{33} and d_{31} measured in single domain crystals.[14]

From the ϕ-scans of the B500-1 film, the ratio α_1/α_2 between variants 1 and 2 is found to be about 2 and thus $\alpha_1 = \alpha_{1,P} + \alpha_{1,-P} = 0.66$ and $\alpha_2 = \alpha_{2,P} + \alpha_{2,-P} = 0.34$ (being $\alpha_1 + \alpha_2 = 1$). In addition, from the SHG measurements, $[(\alpha_{1,P} + \alpha_{2,P}) - (\alpha_{1,-P} + \alpha_{2,-P})] = (d_{3i,\text{eff}}/d_{3i}) = 0.64$ (for $i = 1,3$). Assuming that $(\alpha_{1,P}/\alpha_{1,-P}) = (\alpha_{2,P}/\alpha_{2,-P})$, the values of the volume fractions of the four groups are as follows: $\alpha_{1,P} \approx 0.54$, $\alpha_{2,P} \approx 0.27$, $\alpha_{1,-P} \approx 0.12$, $\alpha_{2,-P} \approx 0.06$. This result shows that $\geqslant 80\%$ of the volume is oriented in the same direction and thus the film is a ''quasisingle'' domain structure. Sample A500 shows greater SH signal than B500-1 although the ratio $\alpha_1/\alpha_2 = 1.4$ is closer to 1. This can be due to both a higher degree of domain orientation along the Z axis and/or a contribution from domains oriented parallel to the substrate. Since the last hypothesis is not likely because we observed no significant SHG response for normal incidence (i.e., $\gamma_i = 0$), we can infer that $\geqslant 90\%$ of the volume of the A500 film points in the same direction. The reason why the domains are more aligned in this film where there is less epitaxial growth is still unclear.

If the films were single-domain structures, the maximum SH signal would follow a quadratically increase [see Eq. (2)] when, as in our case, $\Delta k L \ll \pi$. The good agreement between the experimental data and the quadratic fit in Fig. 3 indicates that the structure maintains its quasisingle domain

structure for films with a thickness $\leqslant 700$ nm. A closer analysis suggests that the experimental data for the 300 nm films are below the fit which better match the experimental data for 500 and 700 nm films. This is consistent with the nonlinear coefficients values shown in Table I, where one can see that d_{33} and d_{31} for 300 nm thick films are significantly lower than those for 500 and 700 nm. These results suggest that the α_P/α_{-P} ratio increases as the thickness increases. This is probably related to strains originated during growth by the mismatch of lattice parameters between film and substrate, the thinner the film the more significant the mismatch effect and the poorer the crystalline quality.[11,16] This explanation is supported by the evolution of the width of the (006) reflection peak in the θ-2θ scans as a function of the film thickness (see Fig. 3) since it becomes narrower (crystalline quality improves) for increasing thickness.

In conclusion, highly textured LiNbO$_3$ films have been successfully grown on sapphire substrates, using the PLD technique with oxygen pressures of ~ 0.5–1 Torr and a substrate temperature of $\sim 650 \,^\circ\text{C}$. The second-order nonlinear response of the films is consistent with a quasisingle domain structure and leads to nonlinear coefficients comparable to those for single-crystal structures. Both the crystalline quality and the quasisingle domain character of the films increase as the film thickness increases and a similar improvement is observed for the nonlinear coefficients d_{33} and d_{31}, that approach those of the bulk for thickness $\geqslant 500$ nm.

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