AIP Applied Physics Letters

# Low-temperature growth of epitaxial LiNbO3 films on sapphire (0001) substrates using pulsed laser deposition

See-Hyung Lee, Tae Kwon Song, T. W. Noh, and Jai-Hyung Lee

Citation: Applied Physics Letters **67**, 43 (1995); doi: 10.1063/1.115486
View online: http://dx.doi.org/10.1063/1.115486
View Table of Contents: http://scitation.aip.org/content/aip/journal/apl/67/1?ver=pdfcov
Published by the AIP Publishing

# Low-temperature growth of epitaxial $LiNbO_3$ films on sapphire (0001) substrates using pulsed laser deposition

See-Hyung Lee, Tae Kwon Song, T. W. Noh,[a] and Jai-Hyung Lee
*Department of Physics, Seoul National University, Seoul 151-742, Korea*

(Received 12 August 1994; accepted for publication 13 April 1995)

Epitaxial $LiNbO_3$ films were grown on sapphire (0001) substrates using pulsed laser deposition. A single-crystal $LiNbO_3$ was used as a target. Growth behaviors of the $LiNbO_3$ films deposited at various deposition conditions such as temperature, oxygen pressure, and annealing condition were studied. Deposition temperature is found to be an important parameter which enables us to grow $LiNbO_3$ films without the $LiNb_3O_8$ phase: formation of the Li deficient phase can be suppressed by depositing the films at temperature below 500 °C. Oxygen pressure during deposition influences crystallographic orientations of the films. An x-ray pole figure shows that epitaxial $LiNbO_3$ film was grown, but with twin boundaries. The ordinary refractive index of the film was found to be 2.28, which is in good agreement with the bulk value. © *1995 American Institute of Physics.*

Lithium niobate ($LiNbO_3$) thin films have interesting electro-optic and nonlinear optical properties, which are suitable for various applications, such as electro-optic modulators, frequency doubling devices, and optical waveguides. Therefore, $LiNbO_3$ films have been studied with various deposition techniques, including rf sputtering,[1,2] molecular beam epitaxy,[3] liquid phase epitaxy,[4] and sol–gel process.[5] Recently, high quality epitaxial $LiNbO_3$ films were fabricated using pulsed laser deposition (PLD).[6–8]

Various oxide films have successfully been grown epitaxially using the PLD technique. However, even with the PLD technique, it has been found to be difficult to get epitaxial $LiNbO_3$ films since Li is highly volatile. Most workers used deposition temperatures of 650–800 °C, where Li deficient phases, such as $LiNb_3O_8$, were often formed.[6,7] Therefore, they had to use Li-rich targets which had the Li/Nb ratio up to 2.0 in order to grow epitaxial $LiNbO_3$ films. This technique of changing target composition is rather difficult, since a proper Li/Nb ratio of a target strongly depends on the film growth conditions. Recently, we found that it is possible to grow high quality thin films on **c**-cut sapphire substrates from a $LiNbO_3$ single-crystal target, which has the congruent-melting composition (~ 48.4 mol % $Li_2O$). In this letter, we report our efforts to obtain epitaxial $LiNbO_3$ thin films at a low deposition temperature of 400–450 °C.

Third harmonics (wavelength: 355 nm) of a *Q*-switched Nd:YAG laser were used in this study instead of commonly used excimer lasers. The laser was pulsed at a rate of 10 Hz and its pulse width was ~5–6 ns. The laser beam was focused with an UV-quality quartz lens onto a single-crystal $LiNbO_3$ target. The target-to-substrate distance was ~35–40 mm and the base pressure was $1 \times 10^{-5}$ Torr. (For a wide range of laser fluence, i.e., 1.4–10 J/cm$^2$, it was possible to grow epitaxial $LiNbO_3$ films. Since laser fluence is not an important deposition parameter, detailed results related to laser fluence will not be presented in this letter.)

$LiNbO_3$ films were grown on single-crystal **c**-cut sapphires which were maintained at a deposition temperature ($T_d$) of 350–550 °C and in an oxygen atmosphere $[P_d(O_2)]$ of 2–400 mTorr. The $LiNbO_3$ films were *in situ* annealed at 400 °C for 30 min in an oxygen pressure $[P_a(O_2)]$ of 10–400 Torr. After the deposition, their structural properties were characterized using x-ray diffractometry (XRD) methods, such as $\theta$-$2\theta$ scan and pole figure measurements. The stoichiometry and the refractive indices of the films were determined using the Rutherford backscattering spectrometry (RBS) and ellipsometry, respectively.

Figure 1 shows XRD patterns of $LiNbO_3$ films obtained at various deposition temperatures. All films in this figure were grown with $P_d(O_2) = 50$ mTorr and *in situ* annealed with $P_a(O_2) = 400$ Torr. As shown in Figs. 1(a) and 1(b), the films deposited at 550 and 500 °C show peaks of a Li deficient phase $LiNb_3O_8$, which are marked with solid triangles.

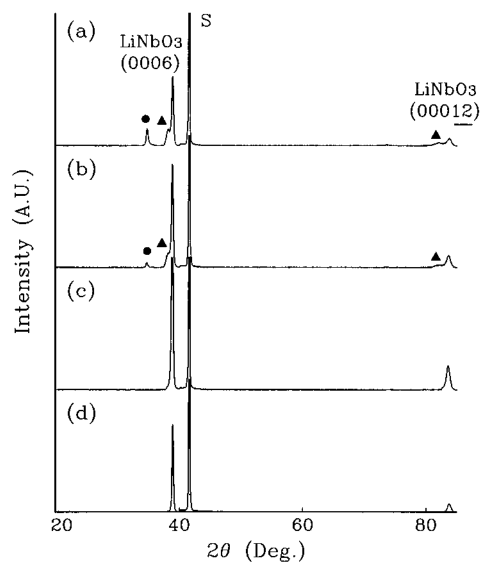


FIG. 1. XRD $\theta$-$2\theta$ patterns of $LiNbO_3$ films deposited at (a) 550 °C, (b) 500 °C, (c) 450 °C, and (d) 400 °C on sapphire (0001) substrate. The oxygen pressure during deposition of these samples is 50 mTorr. The solid triangles and circles correspond to peaks of $LiNb_3O_8$ phase and $LiNbO_3(11\bar{2}0)$ planes, respectively. "S" represents the substrate (0006) peak.

[a]Electronic mail: twnoh@phya.snu.ac.kr

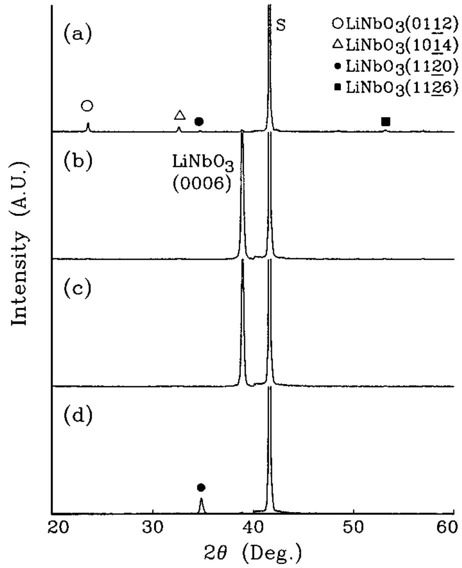


FIG. 2. XRD $\theta$-$2\theta$ patterns of the $LiNbO_3$ films deposited at various oxygen pressure: (a) 400 mTorr, (b) 100 mTorr, (c) 50 mTorr, and (d) 2 mTorr. These samples are deposited at 400 °C.

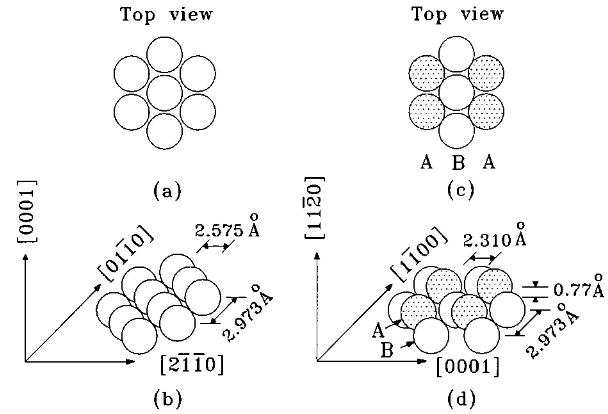


FIG. 3. Oxygen arrangements in $LiNbO_3$ crystal structure: (a) a top view and (b) a perspective view of the **c**-cut $LiNbO_3$ plane, and (c) a top view, and (d) a perspective view of the **a**-cut $LiNbO_3$ plane. Both white and dotted circles represent O ions, but they have different relative positions along the [11$\underline{2}$0] direction.

The solid circles in these figures correspond to $LiNbO_3$(11$\underline{2}$0) peaks, indicating that some $LiNbO_3$ grains of the films are **a**-axis oriented. As $T_d$ becomes lower, the Li deficient phase disappears. As shown in Figs. 1(c) and 1(d), thin films deposited at 450 and 400 °C show only $LiNbO_3$(0006) and (000$\underline{12}$) peaks. The film deposited at 350 °C does not show any XRD peaks except those of substrate. Therefore, in order to get good quality films from a single-crystal $LiNbO_3$ target, a low deposition temperature between 400 and 450 °C should be used. (In order to develop integrated optics circuits based on semiconductor wafers such as GaAs, a low growth temperature is required to prevent degradation of substrate and interdiffusion between film and substrate. The temperature used in this work might be low enough to overcome such difficulties.)

Figure 2 shows x-ray $\theta$-$2\theta$ results of $LiNbO_3$ films deposited at various oxygen pressures $P_d(O_2)$. All films in this figure were deposited at $T_d$=400 °C and annealed with $P_a(O_2)$=400 Torr. Oxygen pressure during deposition $P_d(O_2)$, is found to be an important parameter which influences the crystalline growth behaviors significantly. As $P_d(O_2)$ decreases, the films become highly oriented. In Fig. 2(a), the $LiNbO_3$ film deposited with $P_d(O_2)$=400 mTorr shows weak (11$\underline{2}$0) and (0006) peaks as well as strong (01$\underline{1}$2), (10$\underline{1}$4), and (11$\underline{2}$6) peaks. The relative intensities are similar to those of $LiNbO_3$ powder patterns,[9] indicating that grains in this film are randomly oriented. As shown in Figs. 2(b) and 2(c), $LiNbO_3$ films deposited with $P_d(O_2)$ =20–100 mTorr have only $LiNbO_3$(0006) peaks, indicating that these films are composed of highly oriented grains. For the films deposited with a lower value of $P_d(O_2)$, i.e., 2 mTorr, a strong (11$\underline{2}$0) peak appears, as shown in Fig. 2(d).

It should be noted that all films deposited at $T_d$=400 °C do not have any Li deficient phase. This result is different from the report of Shibata *et al.*,[6] where the $LiNb_3O_8$ phase strongly appears at high values of $P_d(O_2)$ when $LiNbO_3$ films are deposited at $T_d$=750 °C. Our study shows that the oxygen pressure during deposition is not an important parameter to obtain $LiNbO_3$ films at low deposition temperature.

The appearance of the (11$\underline{2}$0) peak at a low oxygen pressure, as shown in Fig. 2(d), might be due to the differences in $LiNbO_3$(0006) and (11$\underline{2}$0) planes. Figure 3 shows positions of the oxygen ions in the $LiNbO_3$(0006) and (11$\underline{2}$0) planes. As shown in Figs. 3(a) and 3(c), their top views are very similar. However, the positions of the oxygen ions are different: all oxygen ions in Fig. 3(b) are closed packed on a plane perpendicular to [0001], but the oxygen ions shown in Fig. 3(d) are rather loosely packed on two planes perpendicular to [11$\underline{2}$0]. At a low value of $P_d(O_2)$, the loosely packed oxygen surface might be easier to grow initially on a **c**-cut sapphire substrate. More detailed studies are required.

When films are deposited at low $T_d$'s, is likely that most crystallization processes occur during the *in situ* annealing process, then the oxygen pressure during the annealing process, $P_a(O_2)$, might be an important deposition parameter to get high quality films. In Table I the ratios of the $LiNbO_3$(0006) to sapphire(0006) peak intensities are shown at various values of $P_a(O_2)$. As $P_a(O_2)$ increases, the ratio becomes larger.

The $LiNbO_3$ film grown with $T_d$=400 °C, $P_d(O_2)$=50 mTorr, and $P_a(O_2)$=400 Torr was found to be epitaxial. Lateral registry between crystal axes of the film and in-plane vectors of the substrate was analyzed by an x-ray pole measurement of Shultz reflection method. Figure 4 shows two

TABLE I. Ratio of the $LiNbO_3$(0006) to $Al_2O_3$(0006) XRD peak intensities.

| Oxygen pressure (Torr) | XRD peak intensity ratio of the $LiNbO_3$(0006) to $Al_2O_3$(0006) |
|---|---|
| Not annealed | <0.02 |
| 10 | 0.02 |
| 100 | 0.08 |
| 400 | 0.32 |

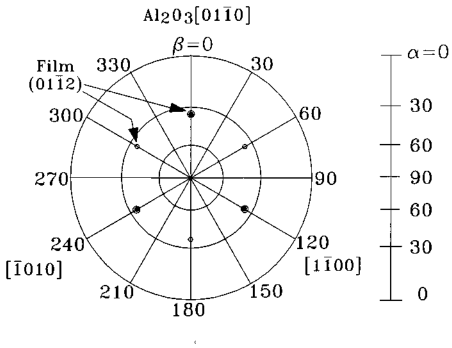


FIG. 4. X-ray pole figure of $LiNbO_3$ (01$\bar{1}$2) poles for the epitaxial film.

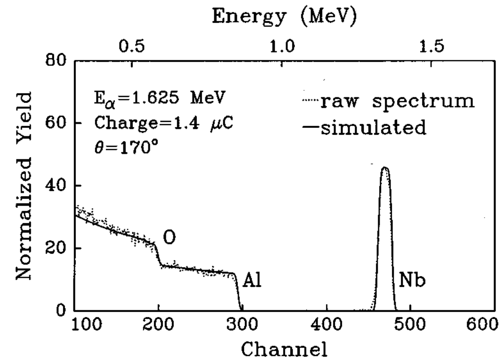


FIG. 5. RBS spectrum obtained from the epitaxial $LiNbO_3$ film.

groups of $LiNbO_3$ (01$\bar{1}$2) poles, each of them having three-fold symmetry. One group of the poles is located at $\beta$=0°, 120°, and 240°, and the other at $\beta$=60°, 180°, and 300°. The relative intensity ratio between these two groups is about 3:2. This pole figure suggests the presence of twins of grains which are rotated by 60° above the film normal with one another in the epitaxial $LiNbO_3$ film.

RBS and ellipsometry measurements were taken on the epitaxial sample. In RBS measurements, niobium and oxygen concentrations of $LiNbO_3$ film were determined with 1.65 MeV He ions. Lithium absorbs so much energy from the particles that its concentration cannot be measured with this technique. From the RBS data in Fig. 5, the oxygen to niobium in the film was found to be 3.00±0.15. It supports that our film has a stoichiometry close to that of single-crystal $LiNbO_3$, although we did not use a Li-rich target. From the ellipsometry measurement using a He–Ne laser, the ordinary refractive index of the $LiNbO_3$ film was determined to be $n_0 = 2.28$, in good agreement with its bulk value,[10] $n_0 = 2.2866$.

In summary, we have grown epitaxial $LiNbO_3$ films on sapphire(0001) substrates using pulsed laser deposition. It is found that the high quality films can be grown from a single-crystal $LiNbO_3$ target with a low deposition temperature between 400–450 °C. The oxygen pressure during the deposition is also found to be an important parameter which influences crystalline orientations significantly.

We would like to thank Joon-Kon Kim of KIGAM for his assistance in the RBS measurements. This work was financially supported by the Korea Telecom Research Center and the Korea Science and Engineering Foundation through the RCDAMP at Pusan National Univeristy.

[1] T. Kanata, Y. Kobayashi, and K. Kubota, J. Appl. Phys. **62**, 2989 (1987).
[2] T. A. Rost, T. A. Rabson, B. A. Stone, D. L. Callahan, and R. C. Baumann, IEEE Trans. Ultrason. Ferroelectr. Freq. Control **38**, 640 (1991).
[3] R. A. Betts and C. W. Pitt, Electron. Lett. **21**, 960 (1985).
[4] A. Yamada, H. Tamada, and M. Saitoh, Appl. Phys. Lett. **61**, 2848 (1992).
[5] A. A. Wernberg, H. J. Gysling, A. J. Filo, and T. N. Blanton, Appl. Phys. Lett. **62**, 946 (1993).
[6] Y. Shibata, K. Kaya, K. Akashi, M. Kanai, T. Kawai, and S. Kawai, Appl. Phys. Lett. **61**, 1000 (1992).
[7] D. K. Fork and G. B. Anderson, Appl. Phys. Lett. **63**, 1029 (1993).
[8] A. M. Marsh, S. D. Harkness, F. Qian , and R. K. Singh, Appl. Phys. Lett. **62**, 952 (1993).
[9] The Joint Committee on Power Diffraction Standards, Card No. 20-631.
[10] R. S. Weis and T. K. Gaylord, Appl. Phys. Lett. **37**, 191 (1985).