PULSED LASER DEPOSITION OF LiNbO$_3$ THIN FILMS FROM Li-RICH TARGETS

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LiNbO$_3$ thin films were synthesized by pulsed KrF* (λ=248 nm, τ_{FWHM}~20 ns, ν = 1 Hz) laser ablation of Li-rich ceramic targets on (001) Al$_2$O$_3$ substrates. The crystalline state and composition of the as-grown films were studied by X-ray diffraction (XRD), Rutherford backscattering spectroscopy (RBS) and nuclear reaction analyses (NRA). The laser fluence proved essential for the improvement of the structure and optical properties of the deposited films. The X-ray diffractograms showed that the films consist prevalently of LiNbO$_3$ with preferred (006) orientation. The Li/Nb atomic ratio of about 1.0 was confirmed by the RBS and the NRA results. The ordinary refractive index at 632.8 nm of the film was found to be approximately 2.2, which is close to that of the bulk single-crystalline LiNbO$_3$. The films wave-guide losses measured at the same wavelength were about 18 dB/cm.

Lithium niobate (LiNbO$_3$) is a well known ferroelectric material. Moreover, because of its attractive piezoelectric, acoustooptical, electrooptical and non-linear optical properties is used in optical devices such as wave-guides, optical switches, modulators, nonlinear wavelength converters, including second harmonic generation, and surface acoustic wave filters [1]. These applications have been implemented mainly on single crystal bulk materials. However, LiNbO$_3$ thin films have several potential advantages from technological or commercial point of view of integrated optical devices.

Therefore, LiNbO$_3$ thin films have been grown by several techniques including molecular beam epitaxy [2], liquid phase epitaxy [3], sol-gel processes [4, 5], rf sputtering [6], thermal plasma spray chemical vapor deposition [7], or pulsed laser deposition (PLD) [8, 9]. Stoichiometric multicomponent oxide films have been successfully grown by PLD [10]. Indeed, PLD is considered to be one of the most promising techniques for thin films synthesis, due to its unique advantages as high reproducibility, control of the films growth rate, low impurity concentration in the composition of deposited films and possibility to use different substrate materials [11-13]. Moreover, in case of multicomponent targets the PLD technique allows for a stoichiometric material transfer from the target towards the substrates surfaces.

In the present work we investigated the effect of incident laser fluence value on the growth of LiNbO$_3$ thin films on Al$_2$O$_3$ substrates. The crystalline status and composition of the films was studied by X-ray diffraction (XRD), Rutherford backscattering spectroscopy (RBS) and nuclear reaction analysis (NRA). Special interest was focused also on the study of the optical properties of

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the obtained thin films. We used in our experiments Li-rich targets, with Li/Nb ratio up to 1.5 in order to compensate the loss of volatile Li and to promote the synthesis and the deposition on the collectors' surfaces of films with the desired $LiNbO_3$ stoichiometry.

The irradiations were performed in a stainless steel vacuum chamber evacuated down to a residual pressure of 5×10^{-4} Pa before each deposition. We used the pulses generated by a KrF* (λ=248 nm, τ_{FWHM}~20 ns, ν = 1 Hz) laser. The laser beam incidence angle onto the target surface was approximately 45°. The laser fluence values were chosen in the 1.0 - 3.0 J/cm^2 range.

The Li-enriched lithium niobate ceramic targets were prepared from powder mixtures of Li_2NbO_3 (99% purity) and $LiNbO_3$ (99.9% purity) with Li/Nb ratio of 1.5, and pressed at 7 MPa. The obtained targets were sintered for their mechanical integrity at $650°C$ for 3 h in air. Rutherford backscattering spectroscopy investigations before and after the sintering process showed that the Li/Nb ratio decreased with 72 % after sintering. The targets were mounted in a rotating holder and placed in the vacuum chamber.

Single-crystal c-cut Al_2O_3 (001) (sapphire) was chosen as a substrate material placed parallel to the target at a distance of 4.0 cm. During the depositions the substrates were heated up to $550°C$ by a resistive heater. After the initial evacuation, the vacuum chamber was filled with oxygen at a dynamic pressure value of 6 Pa. These growing conditions were chosen as optimum after several other attempts.

After the deposition the films were annealed at $550°C$ for 2 h in oxygen at a pressure value of 14 Pa in order to be reduced their oxygen deficiency. Then, the films were cooled down slowly with a step of 5 $°C$/min to avoid mechanical stresses due to the mismatch between the thermal expansion coefficients of the films and the substrates.

The crystal structure of the films was investigated by XRD in Bragg-Brentano geometry using the Cu Kα (λ = 0.154 nm) radiation. The ratios of oxygen to niobium and of lithium to niobium were determined by RBS and NRA, respectively. The refractive index and the thickness of the films were investigated by mode spectroscopy using the film-prism coupling. The wave-guide propagation is measured at a wavelength of 632.8 using a He-Ne laser.

Fig. 1 shows the θ - 2θ X-ray diffractograms of thin films obtained at (a) 1.5 J/cm^2 and (b) 2.0 J/cm^2 laser fluence values. Besides the pattern characteristic or the sapphire substrate, the diffraction patterns contain an intense peak at 38.94° and a less intense peak at 34.80° corresponding to the (006) and (110) lattice plane reflections of $LiNbO_3$ [14]. The weak $LiNbO_3$ (110) peak suggests that some $LiNbO_3$ grains of the film are a-axis oriented. In addition, the small peaks at 36.52° and 38.06° indicate the potential presence of lithium deficient $LiNb_3O_8$ phase.

With the increase of the laser fluence the intensity of the peak corresponding to the Li-deficient phase and that of the peaks corresponding to the (110) lattice plane reflection of $LiNbO_3$ decrease. Moreover, the strong (006) $LiNbO_3$ peak indicates that the film deposited at this higher laser fluence is textured with the c-axis normal to the sapphire substrate. We note that similar X-ray diffractograms were recorded also for the films deposited at higher laser fluences (up to 3.0 J/cm^2). These behaviors could be associated with the dynamics of the Li species in the plasma plume. Indeed, according to previous investigations the laser fluence determines the velocity distribution of Li species in the laser generated ablation plasma, i.e. higher laser fluence leads to larger velocity values [15]. This in turn results in the increase of the arrival rate of Li as compared to Nb atoms at the substrate surface.

RBS investigations were performed to determine the chemical composition as well as the thickness of the deposited thin films. We present in Fig. 2 the RBS spectra of the film obtained at 2.0 J/cm^2 incident laser fluence. For the RBS data we calculated an O/Nb ratio of about 3.0. This indicates that the thin film stoichiometry was close to that of single-crystal $LiNbO_3$. The film thickness was evaluated to be 260 nm.
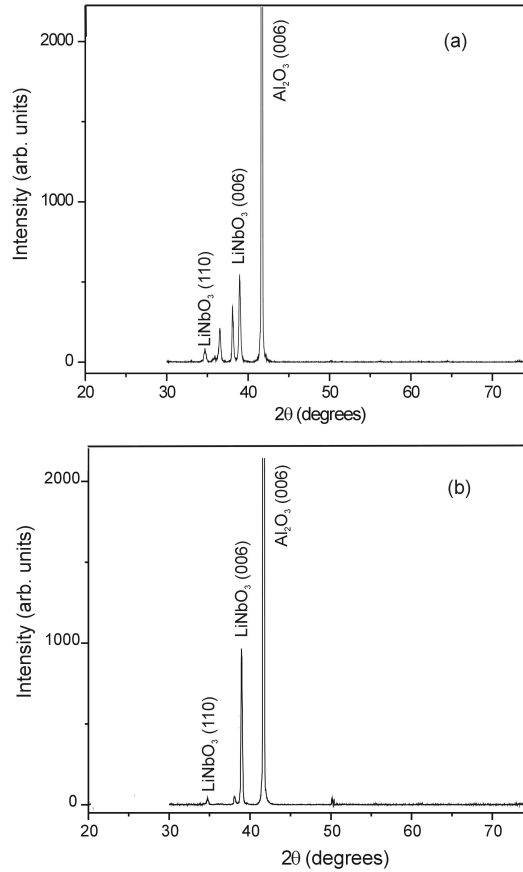
Fig. 1. X-ray diffractograms of the thin films prepared on c-cut sapphire substrates at 550°C substrate temperature, 6 Pa oxygen pressure, and (a) 1.5 J/cm^2 as well as (b) 2.0 J/cm^2 laser fluence
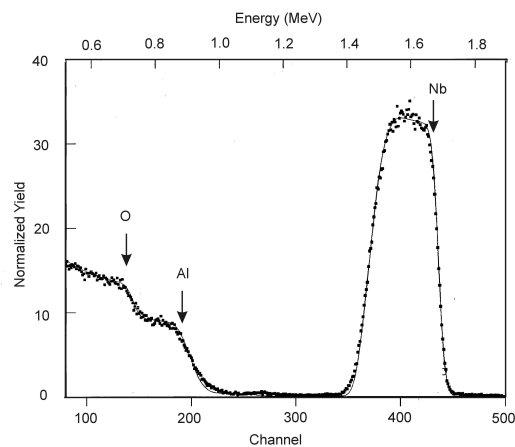

Fig. 2. RBS spectrum of the film grown on c-cut sapphire substrates at 550°C substrate temperature, 6 Pa oxygen pressure, and 2.0 J/cm^2 laser fluence.

The preferential growth of LiNbO$_3$ film on c-cut sapphire at a laser fluence of 2.0 J/cm^2 was confirmed also by NRA. Indeed, we calculated from the NRA data Li/Nb and O/Nb ratios of about 1.0 and 3.0, respectively.

The ordinary refractive index of the as-grown films at 632.8 nm wavelength was found to be approximately 2.20. This value is close to that of bulk single-crystal lithium niobate (2.28) [16]. The film wave-guide losses measured at the same 632.8 nm wavelength were higher that 20 dB/cm for the film deposited at 1.5 J/cm^2. This value decreases to approximately 18 dB/cm in case of the film deposited at 2.0 J/cm^2.

In conclusion we first reported the deposition of LiNbO$_3$ thin films by pulsed laser irradiation of Li-enriched ceramic targets in 6 Pa oxygen pressure. The c-cut sapphire substrates were heated at 550°C during the thin film deposition process. We studied the evolution of thin films stoichiometry as well as crystallographic orientation with the increase of the incident laser fluence. We clearly demonstrated by X-ray diffraction analyses that the increase of the fluence results in the growth of LiNbO$_3$ films with preferential (006) orientatd, following the crystal structure of the c-cut sapphire substrate. The stoichiometric LiNbO$_3$ composition of the films was independently confirmed by nuclear reaction analyses and Rutherford backscattering spectroscopy investigations. The value of the ordinary refractive index of the films was estimated to be close to that of the bulk single-crystalline lithium niobate. As a consequence the losses of the best thin film was reduced to 18 dB/cm.

Acknowledgements

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