Stirrer time effect on optical properties of nanophotonic LiNbO₃

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HIGHLIGHTS
- Prepare nanophotonic LiNbO₃ via feasible method.
- Analyze the optical and structural properties of nanophotonic LiNbO₃ under stirrer time.
- Characterize the nanophotonic LiNbO₃ under stirrer time.
- Elaborate the refractive index of nanophotonic LiNbO₃ for optical applications.

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ABSTRACT
Lithium niobate (LiNbO₃) nanostructures are synthesized on n-silicon substrate by spin coating technique with stirrer times: 8 h, 24 h and 48 h. LiNbO₃ is characterized and analyzed by Scanning Electron Microscope (SEM), Atomic Force Microscopy (AFM), X-ray diffraction (XRD) and UV-visible and Photoluminescence (PL). The measurements show that as stirrer time increases, the structures start to crystallize to become more regular distribution, which helps to apply in optical waveguides. In addition, the calculated refractive index and optical dielectric constant are in agreement with experimental data.

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1. Introduction

Lithium niobate (LiNbO₃) is a very important optical material which is widely used by the photonics industry due to its excellent electro/acousto-optical properties [1,2]. LiNbO₃ is an important ferroelectric material because of its excellent piezoelectric, electro-optical, pyroelectrical and photo-refractive properties [3–6]. It is widely used as polar material for photonic applications [7–9]. In addition, it is employed in nonlinear optics for frequent conversion in telecommunication for electro-optic modulation [10–12]. It is very attractive material for fabrication of optical wave-guide devices [13,14]. This crystal plays an important role as a high quality source material with low optical loss [15] due to their mechanical robustness, good availability, optical homogeneity [16], integrated optics with lasers, modulators [17] and filters on a single LiNbO₃ wafer [18]. Thin films of nanophotonic LiNbO₃ have been studied in integrated form with unique pyroelectric, piezoelectric and nonlinear optical properties, which would made it an ideal material for fabrication of surface acoustic wave (SAW) [19] and optoelectronic devices [20]. LiNbO₃ was prepared using various experimental techniques such as sputtering [21,22], liquid phase epitaxial (LPE) [23], metal organic chemical vapor deposition (MOCVD) [24–26], soft-chemistry [27], hydrothermal methods [28] and pulsed laser deposition (PLD) [29,30].

Bartasyte et al. [31] have deposited LiNbO₃ films of high epitaxial quality and with thicknesses of 120–500 nm at 650 °C on C-sapphire by atmospheric pressure metal-organic chemical vapor deposition. They have investigated Li nonstoichiometry, residual stresses, twinning, and thermal expansion of the films as a function...
of the film thickness and by means of Raman spectroscopy and X-ray diffraction, and studied the relaxation of residual stresses, Li2O loss, inelastic deformation and elastic hysteresis during cycles of heating up to 860 °C and cooling down to room temperature, as well. The residual stresses and thermal expansion of films were highly thickness dependent. It was shown that the (01T2) twinning contributed to the stress relaxation in the thick LiNbO3 films. While, Lim and Lee [32] have investigated the effects of poly(-lysine) as a biomolecular additive on the synthesis of LiNbO3. The addition of PLL to a LiNbO3 precursor solution enhanced the aggregation of the produced LiNbO3 nanoparticles. This aggregation was induced by the electrical attraction of PLL with LiNbO3 nanoparticles, and was enhanced with increasing PLL molecular weight. Furthermore, the association of PLL with LiNbO3 nanoparticles was increased by the addition of methanol, which enhanced the miscibility of PLL with the precursor solution working as a co-solvent. The LiNbO3 nanoparticles generated with PLL exhibited piezoelectric properties without post-thermal treatment, suggesting that PLL contributes to the piezoelectricity. Their results are intriguing in terms of the potential for diverse engineering nanomaterials synthesis through a biomolecule that can also improve the physicochemical properties. Furthermore, Nozawa et al. [33] have noticed that the cs-MgO:LN (Li2O:Nb2O5:MgO) ionic species. In this case, the equilibrium partition coefficient for giving better (cEMF) structure of LiNbO3 nanostructures is found to have hexagonal structure as shown in Fig. 1. It is observed that the peaks at 2θ = 23.634, 32.637, 34.674, 48.355, 53.106, and 55.879 correspond to (012), (104), (110), (1024), (116) and (122) planes. All the mentioned peaks are exactly matched with the crystalline structure of LiNbO3 nanostructures that corresponding to the standard (ICDD PDF2008, 00-029-0537). Therefore, the crystalline structure will be crystalline and more purity for LiNbO3 with increasing stirrer time due to increasing the peak intensity. The measured structural properties of LiNbO3 nanostructures are listed in Table 1. Crystallite size (D) was calculated using Scherrer’s formula [34].

\[ \frac{D}{\beta \cos \theta} = \frac{K \lambda}{\beta \cos \theta} \]

where K is a constant taken to be 0.94, λ is the wavelength of X-ray used (λ = 1.54 Å), β is the full width at half maximum of XRD pattern and θ is Bragg’s angle, around 26.41°.

In addition, the dislocation density (δ) and strain (ε) of LiNbO3 nanostructures were determined using the following relations [35].

\[ \delta = \frac{1}{D^2} \]

\[ \epsilon = \frac{D}{\beta \cos \theta} \]

Fig. 1. XRD patterns of LiNbO3 nanostructures at different stirrer times (a) 8 h, (b) 24 h and (c) 48 h.
lithium niobate could be recognized, a mixture. It is found at peaks 2\(^{0}\) and 4\(^{0}\) planes at high stirrer time, and at peak 35.981 were very close to the reported data\[37\]. The thin structure with lattice constants \(a = 5.1566\) and \(c = 13.85\) corresponds to (212) plane at low stirrer time. This is attributed to annealing effect in static air, oxygen atmosphere and total interaction between the chemicals. There is no impurities like Nb\(_2\)O\(_5\), were detected in high stirrer time because of increased hours of mixing, but in low stirrer time we find Nb\(_2\)O\(_5\) at peaks 2\(^0\) = 24.433 and 31.623 correspond to (105) and (014) planes as raw material.

### Table 1

<table>
<thead>
<tr>
<th>Stirrer time (h)</th>
<th>Orientation hkl</th>
<th>Peak (°)</th>
<th>Particle size (nm)</th>
<th>Dislocation density ((10^{15})lines/m(^2))</th>
<th>Strain (10(^{-3}))</th>
<th>(d_{\text{hkl}}) (Å)</th>
<th>Lattice constants (Å)</th>
<th>Roughness (nm)</th>
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\(a\) Ref. [35] exp.  
\(b\) Ref. [36] exp.

\[ e = \beta/4\tan\theta. \]  
\[ d = h\lambda/2\sin\theta. \]  
\[ \frac{1}{d^2} = \frac{4}{a^2} \left( \frac{h^2 + 2hk + k^2}{a^2} \right) + \frac{P^2}{c^2} \]  
\(\epsilon\) The interplanar distance \(d\) is calculated for all set of LiNbO\(_3\) nanostructures using Bragg’s formula [35].

\(\beta\) The optical reflectance of surface with wavelength of LiNbO\(_3\) nanostructure. The optical band gaps were determined with the help of reflection spectra [38,39]. Almost all the II–VI compounds are direct band gap semiconductors. According to Tauc relation [39,40], the absorption coefficient for direct band gap material is given by:  
\[ a = \frac{\alpha}{h\nu} \left( \frac{\nu}{E_g} \right)^{\frac{2}{3}} \]
Absorption coefficient can be related to the band gap of the material and the refractive index. The refractive index can be found from the extrapolation of straight line to a reference point (Fig. 2c). The extrapolation gives the value of direct band gap. From this graph, the value of energy band gap comes out to be 3.97 eV (Table 2).

The refractive index \( n \) was determined from a transmittance spectrum as a function of the wavelength in the range 300–700 nm. There is a decreasing in the refractive index may be attributed to invisible range; it was estimated 2.26–2.58 at 330 nm as shown in Fig. 2c and given in Table 2. The refractive index changes slightly and steadily after 330 nm–700 nm as shown in Fig. 2c. We can notice from that, the refractive index increases as stirrer time increases. This behavior may be attributed to increasing of thickness due to multilayer deposition (Table 2). The highest values of refractive index are suitable for optical waveguide. Intuitive, increasing stirrer time leads to increase thickness of synthesized LiNbO3 nanostructures that correlate directly with refractive index as confirmed in Fig. 2c.

The photoluminescence (PL) spectra of LiNbO3 nanostructures are grown on n-Si substrate at 25 °C as shown in Fig. 3, where emissions are appeared in 313 (3.961 eV) within 48 h, 325 (3.815 eV) within 24 h and 336 (3.691 eV) within 8 h. The peak at 313 nm is more intense. A central factor of this discussion is the nature of the characterized samples. It must be pointed out that the LiNbO3 nanostructures used to study PL behavior are usually synthesized with distinct method. Furthermore, the relative peak intensities of each peak depend also on the corresponding radiative recombination efficiency. Thus, PL spectra of LiNbO3 nanostructures demonstrate that the produced material has enough quality to be used in the research of semiconductor devices and optoelectronics. This trend can be understood that surface-to-volume ratio becomes smaller with increasing grain size, and the larger grains have smaller nonradiative relaxation rates over the surface states resulting in the enhancement of PL intensity. On the other hand, it is noted clearly a blue shift in PL and UV-vis, where the band gap values increase from 3.6 to 3.9 eV with increasing of stirrer times, that can be attributed to improvement of nanostructures demonstrate that the produced material has enough quality to be used in the research of semiconductor devices and optoelectronics. This trend can be understood that surface-to-volume ratio becomes smaller with increasing grain size, and the larger grains have smaller nonradiative relaxation rates over the surface states resulting in the enhancement of PL intensity. On the other hand, it is noted clearly a blue shift in PL and UV-vis, where the band gap values increase from 3.6 to 3.9 eV with increasing of stirrer times, that can be attributed to improvement of nanostructures demonstrate that the produced material has enough quality to be used in the research of semiconductor devices and optoelectronics.

\[ n = \alpha + \beta E_g, \]  
(7)

where \( \alpha = 4.048 \) and \( \beta = -0.62 \text{ eV}^{-1} \).

Inspired by simple physics of light refraction and dispersion, Herve and Vandamme [45] have proposed an empirical relation as:

\[ n = \sqrt{1 + \left(\frac{A}{E_g + B}\right)^2}, \]  
(8)

where \( A = 13.6 \text{ eV} \) and \( B = 3.4 \text{ eV} \).

Ghosh et al. [46] had taken a different approach by considering the band structural and quantum-dielectric formulations of Penn [52] and Van Vechten [53]. Introducing, A (contribution from the valence electrons) and B (constant additive to the lowest band gap \( E_g \)), the expression was written as:

\[ n^2 - 1 = A / (E_g + B)^2, \]  
(9)

where \( A = 25E_g + 212, B = 0.21E_g + 4.25 \) and \( (E_g + B) \) refers to an appropriate average energy gap of the material.
corresponds to (012) at 2θ = 23.634. As expected, the structure is more crystalline as the time of stirrer increases. In addition, SEM shows diameter of gain size from 18 to 92 nm, and AFM shows roughness ranging between 5 and 20 nm. Optical properties give explanations the prepared LiNbO₃ to be embodied as stirrer time in-


H.K. Lam, J.V. Dai, H.H.W. Chan, Orientation controllable deposition of LiNbO₃ nanostructures based on XRD results, the LiNbO₃ nanostructures have polycrystalline in nature. The intensity is 900 a.u. and corresponds to (012) at 2θ = 23.634. As expected, the structure is more crystalline as the time of stirrer increases. AFM shows diameter of gain size from 18 to 92 nm, and roughness ranging between 5 and 20 nm. Optical properties give values of reflection that is about 21–33% and the measured energy band gaps are between 3.61 and 3.97 eV. We found an approximated matching between the energy gaps values calculated using UV-vis and PL. The highest value of n is an appropriate for optical waveguide. Refractive index determined from speciﬁc empirical models revealed that the highest value and Ghosh et al. model is more appropriate for optical waveguide.

Thus, these three models for variation of n with energy gap have been tried. In addition, the calculated values of the optical dielectric constant (ε∞) were obtained using the relation ε∞ = n² [54]. The calculated refractive index and optical dielectric constant are given in Table 2. This is showing that the Ghosh et al. model is an appropriate model for solar cells applications due to its agreement with experimental refractive index value [58].

4. Conclusions

The LiNbO₃ nanostructures have been chemically prepared by spin-coating technique. Based on XRD results, the LiNbO₃ nanostructures have polycrystalline in nature. The intensity is 900 a.u. and corresponds to (012) at 2θ = 23.634. As expected, the structure is more crystalline as the time of stirrer increases. AFM shows diameter of gain size from 18 to 92 nm, and roughness ranging between 5 and 20 nm. Optical properties give values of reflection that is about 21–33% and the measured energy band gaps are between 3.61 and 3.97 eV. We found an approximated matching between the energy gaps values calculated using UV-vis and PL. The highest value of n is an appropriate for optical waveguide. Refractive index determined from specific empirical models revealed that the highest value and Ghosh et al. model is more appropriate for optical waveguide.

References


