DOI: https://doi.org/10.33103/uot.ijccce.20.1.2

Optical and Structural investigations of $LiNbO_3$ thin films by PLD

Sarah M. Taleb [1], Makram A. Fakhri[2], Salah Aldeen Adnan [3]
Laser and Optoelectronic Department, University of Technology, Baghdad, Iraq
mokaram_76@yahoo.com, 140017@uotechnology.edu.iq

Abstract— *Lithium niobate ($LiNbO_3$) nanostructure thin film was prepared and deposited on the substrates made of quartz by utilizing pulse laser deposition (PLD) technique. The effect of substrate temperature changing on the optical and structural properties of $LiNbO_3$ films was investigated and studied. The chemical mixture was prepared by mixing the raw material (Li_2CO_3, Nb_2O_5) with Ethanol liquid without any further purification, at the stirrer time 3hrs without heating, then the formed material was overexposed to annealing process at 1000°C for 4hrs. $LiNbO_3$ nanostructure thin film was characterized and analyzed by utilizing the Ultra-Violet visible (UV-vis) and X-Ray Diffraction (XRD). The UV-vis results showed that the increase in the substrate temperature to 300°C leads to decrease in the values of transmission (T%), absorption (A) and optical energy gap (Eg) and increase in the values of reflection (R%) and refractive index (n). While, the XRD results explained that the $LiNbO_3$ structure became more pure and crystalline with increase the substrate temperature, because the intensity of the phase 2θ at the value of 34.8°, 40.06° and 48.48° correspond to (110), (113) and (024) planes disappeared at the substrate temperature 300°C. So, all presented results give a good indication to use $LiNbO_3$ nanostructure thin film prepared at the substrate temperature 300°C for manufacturing the optical waveguide to give the best results.*

Index Terms— *$LiNbO_3$, thin film, PLD deposition, Waveguide, Optical properties.*

I. INTRODUCTION

Lithium Niobate ($LiNbO_3$) nano crystalline structure represents optical material extremely important because of it's an excellent electro-optical and acousto-optical properties [1]. It is widely utilized as an essential and effective material for photonic and optoelectronic applications [2]. Lithium niobate is an indirect band-gap material and is widely used in the applications of photonic [3]. $LiNbO_3$ represent a suitable choice for many optical and electrical applications due to its excellent optical and electrical properties. Therefore, $LiNbO_3$ is considered one of the most promising materials to fabricate the integrated optical devices [3]. $LiNbO_3$ nano photonic thin films have several special advantages compared with the bulk $LiNbO_3$, such as the possibility of producing step index, selectively introducing dopants and the fabrication of multilayer structures [4]. For the photonic device the optical waveguide is considered very essential, which is utilized to change the light spot size in order to have an excellent coupling efficiency and less loss between the two sections which have different refractive index and different cross sections [3]. In past years, nano $LiNbO_3$ optical waveguides are already widely used in many functional acousto-optic and electro-optic devices, where the structures of the waveguides are very important for several integrated-optical devices [5]. There are strict requirements

Received 29 April 2019; Accepted 8 October 2019

 ISSN (Print) 1811-9212 *ISSN (Online) 2617-3352*

enjoined on the waveguide films imperfections for waveguide application which represent porosity, refractive-index inhomogeneity, and the surface roughness, these requirements play an important role in the device performance [6]. $LiNbO_3$ represents one of the key materials to fabricate the technologies which are based on optical, due to the large second-order nonlinearities also $LiNbO_3$ single crystal represents the excellent material for a many applications such as the non- linear optics, electro-optics [7]. The crystals of $LiNbO_3$ are widely used for sensors and other piezoelectric applications [7]. There are many techniques which are used to prepare $LiNbO_3$ thin films such as sputtering, liquid phase epitaxial (LPE), hydrothermal methods, metal organic chemical vapor deposition (MOCVD) [8] also RF magnetron sputtering, soft- chemistry, and pulsed laser deposition [9]. Pulse laser deposition technique is widely used in the deposition of the several materials such as oxides, nitrides, superconductors, etc [10]. PLD represents a very important technique to install and deposit the thin films, because of several excellent advantages such as a possibility to use different substrate materials, low impurity concentration in the composition of deposited thin films and control of the films growth rate [11] also simplicity, low cost and others advantages than other techniques [12]. In this work, the change in the optical and structure properties has been studeied for $LiNbO_3$ nanostructure thin films which prepared by PLD technique on the quartz substrate due to the effect of changing the substrate temperature.

II. EPERIMENTAL PROCEDURE

$LiNbO_3$ nanostructure thin films were prepared by using pulsed laser deposition (PLD) technique on the quartz substrates. Before performing the deposition process , the quartz substrates are cleaned and sterilized. These steps of cleaning are very important to get rid of impurities and fingerprints which are located on the surface of quartz substrates. Furthermore, the quartz were immeresed into solution of water and soap for 10mins with hand cleaning, after that it has been rinsed with water several times to remove the soap, then immersed again into Ethanol liquid for 5mins, and finally the quartz substrates are dried under hot air. By using the chemical method , the $LiNbO_3$ target is prepared by mixing equal weights (5gm) of the raw materials ultra-purity which are: Lithium carbonate (Li_2CO_3), Niobium oxide (Nb_2O_5) together and dissolved them in the 30ml Ethanol liquid (C_2H_5OH) without heating but with stirrer time for 3hrs by the Magnetic stirrer device. Through solid-state interaction between Li_2CO_3 and Nb_2O_5, $LiNbO_3$ particles are traditionally synthesized, according to equation (1)

$$Li_2CO_3 + Nb_2O_5 \rightarrow\rightarrow\rightarrow 2LiNbO_3 + CO_2 \quad (1)$$

In order to maximize the formation of the stoichiometry of $LiNbO_3$ phase , the molar ratio is kept between the main raw materials (Li_2CO_3, Nb_2O_5) 1:1. After finishing the mixing process, the mixture is kept at room temperature for 48hrs for drying purposes. After 48hrs, the mixture is observed separately where the material was deposited at the bottom and the liquid at the top as shown in Fig.1.a due to the difficulty of dissolving these materials in the liquids. Then, the formed material was overexposed to annealing process for 4hrs at a temperature of 1000°C. The next step is grinding the result material by the manual method to convert it into a powder as shown in Fig.1.b. Finally, a pressure of 15 tons is applied into the powder to produce a pellet with 2cm diameter and 1cm height as shown in Fig.1.c. Finally, all these steps are summarized as a flow chart (Fig. 2).

By using double-beam Ultr–Violet (UV–vis) spectrophotometer (Shimadzu UV–Vis 1800, Japan) in wavelength range (200–1٢00) nm , a calculation by the spectrum of transmission (T%) of the optical

Received 29 April 2019; Accepted 8 October 2019

 ISSN (Print) 1811-9212 ISSN (Online) 2617-3352

properties of thin film has been done and it includes the absorption (A), optical energy gap (Eg), the reflectance (R%), refractive index (n). And by using X-ray diffraction (XRD), (X'Pert Pro MRD PW3040 system diffractometer, PANalytical Company, Netherlands) system equipped with Cu-K a-radiation of wavelength k = 0.15418 nm, at 40 kV and 30 mA we analyzed the crystal structure for the prepared films.

FIG. 1. LITHIUM NIOBATE $LiNbO_3$: A- AFTER THE DRYING PROCESS. B- POWDER. C- TARGET.

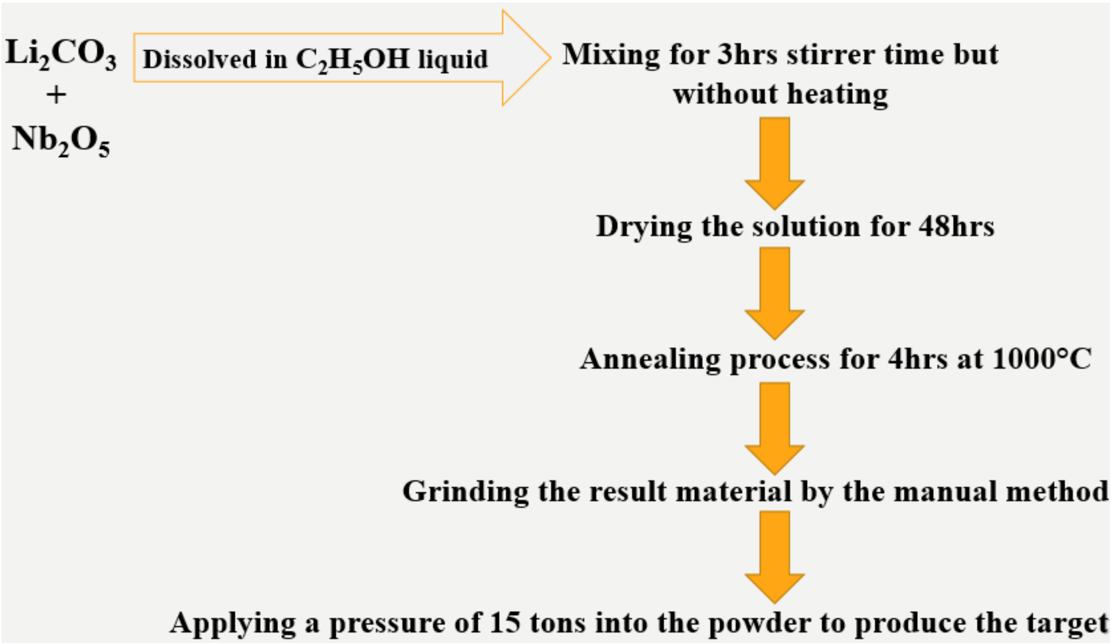

FIG. 2. THE FLOW CHART OF $LiNbO_3$ TARGET PREPARATION PROCESS.

III. RESULTS AND DISCUSSION

The optical properties of $LiNbO_3$ nanostructure thin films were calculated from the transmission spectrum in the wavelength range (200-1200) nm. Fig. 3 shows the optical transmission (T%) of $LiNbO_3$ films at substrate temperature (250°C-300°C), where it can be seen that the values of T% decreased with increasing the substrate temperature, these values are about (88-78) % corresponding to substrate temperatures (250°C-300°C) respectively. The high value of transmittance is attributed to the excessive ($LiNbO_3$) ions at interstitial site that increased its transparency level. Optical absorption (A) achieved the same result, where the absorption values also decreased when the substrate temperature increased as shown in Fig. 4, these values of absorption are about (3.3-2.7) at substrate temperature (250C°- 300C°). As a function of photon energy ,the optical energy gap (Eg) is established which is found by plotting the curve between $(\alpha h\nu)^2$ and (hv) as shown in Fig. 5, the Eg which calculated is about (4.7-4.4) eV corresponding to the (250°C-300°C) substrate temperature respectively, that means the increase in the substrate temperature leads to a decrease in Eg value and vice versa. From the transmission and absorption spectrums and according to the relation; R+T+A = 1, the decrease in two

Received 29 April 2019; Accepted 8 October 2019

 ISSN (Print) 1811-9212 ISSN (Online) 2617-3352

parameters leads to increase in the third parameter, so the decrease in the transmission and absorption values with substrate temperature leads to increase in the reflection values (R%) as shown in Fig. 6. Where this figure shows the R% of $LiNbO_3$ films at the different substrate temperature. It has been observed that the value of R% increased when the substrate temperature increased. To give more illustration, these values are about (11-20) % corresponding to the substrate temperature (250°C-300°C). Finally, based on the optical reflection values, the refractive index values (n) are measured. It has been found that there is an increase in the refractive index value when the substrate temperature increased, these values are about (2.49-2.63) at the substrate temperature (250C° -300C°) respectively as shown in Fig. 7. Where the high value of refractive index is more suitable for manufacture the optical waveguides to ensure access to total internal reflection to give the best result for this application.

Fig. 8 shows the effect of substrate temperature on the structural properties of $LiNbO_3$ films. With the lattice parameters a = 0.5147nm, c = 1.3862nm, it was found that the crystalline structure of $LiNbO_3$ films have a hexagonal structure. The XRD results ensured the formation of $LiNbO_3$ thin films successfully on the quartz substrates which have diffraction peaks appeared at 2θ= 23.66°, 32.66°, 34.8°, 38.94°, 40.06°, 42.52°, 48.48°, 53.22° and 62.38° correspond to (012), (104), (110), (006), (113) (202), (024), (116), and (300) planes. Also, it is observed in all films the peak with (012) orientation represents the preferred and the main peak. When studying the effect of substrate temperature on the $LiNbO_3$ films structural properties, it is found that the increase in the substrate temperature from 250°C to 300°C leads to an increase in the intensity of each peak. But the intensity of peak at 2θ= 34.8°, 40.06° and 48.48° corresponds to (110), (113) and (024) planes disappear when the substrate temperature increased. Also, when the substrate temperature increased to 300°C the intensity of the main and preferred peak (012) increased also from 720 a.u to 1640 a.u. So, it is clear that with increasing the substrate temperature, the nanophotonic $LiNbO_3$ film becomes more crystallized and high purity. That means, the improvement in the crystal structure of $LiNbO_3$ thin film was obtained when using the substrate temperature 300°C through the deposition process. Accordingly, the optical waveguide manufacturing will be better when using thin film prepared at the substrate temperature 300°C.

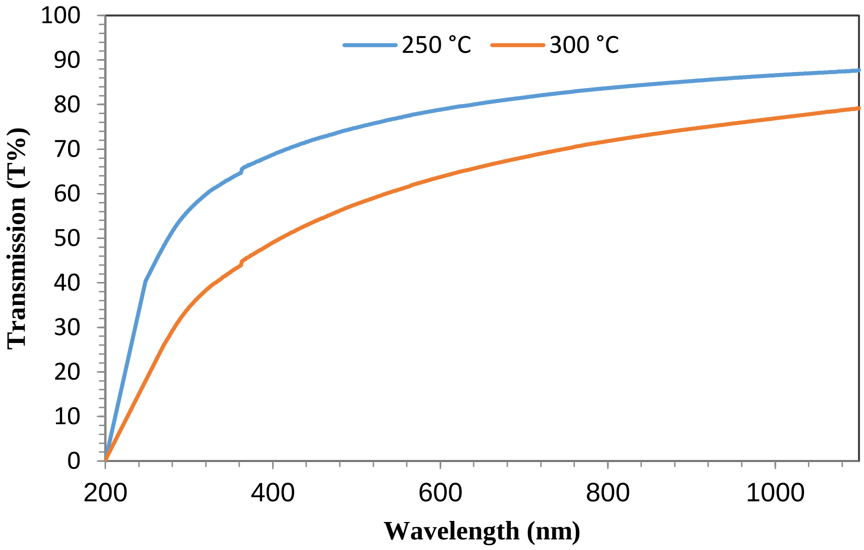

FIG. 3. THE OPTICAL TRANSMISSION OF $LiNbO_3$ THIN FILM AT DIFFERENT SUBSTRATE TEMPERATURE.

Received 29 April 2019; Accepted 8 October 2019

 ISSN (Print) 1811-9212 ISSN (Online) 2617-3352

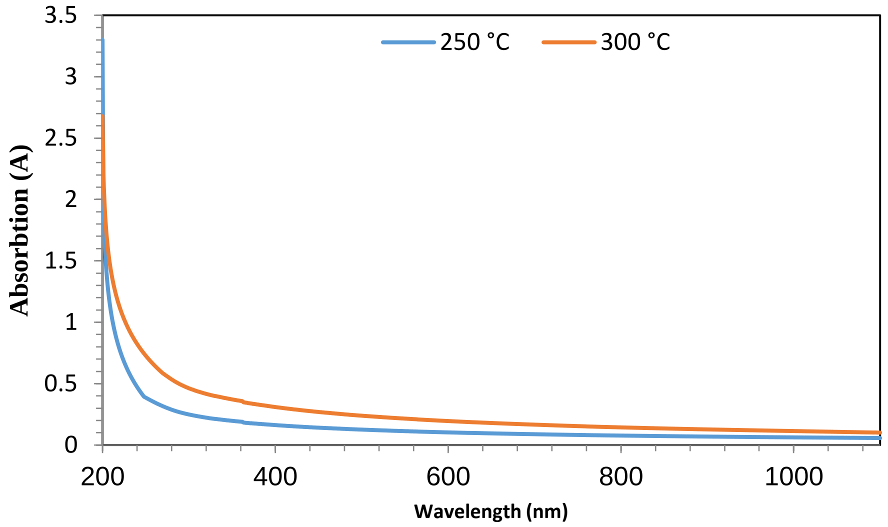

FIG. 4. THE OPTICAL ABSORPTION OF $LiNbO_3$ THIN FILM AT DIFFERENT SUBSTRATE TEMPERATURE.

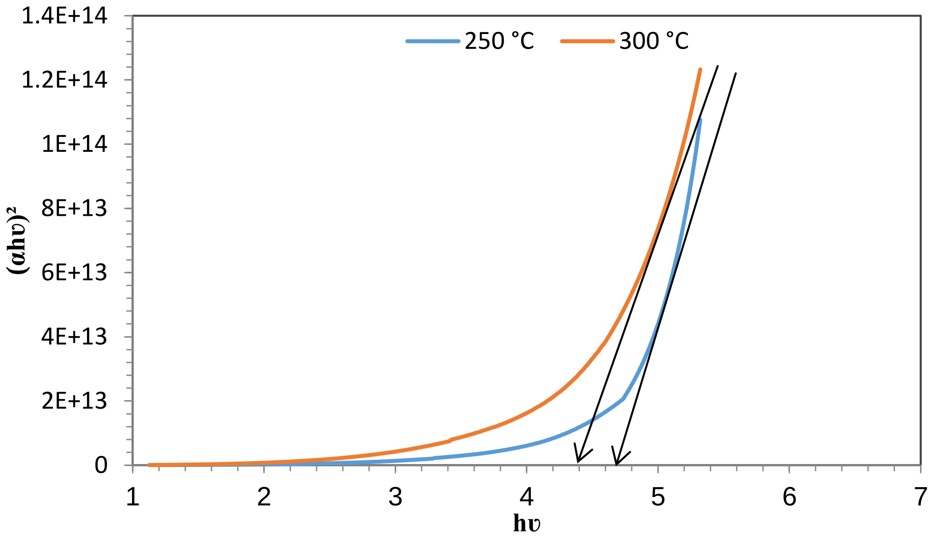

FIG. 5. THE OPTICAL ENERGY GAP OF $LiNbO_3$ THIN FILM AT DIFFERENT SUBSTRATE TEMPERATURE.

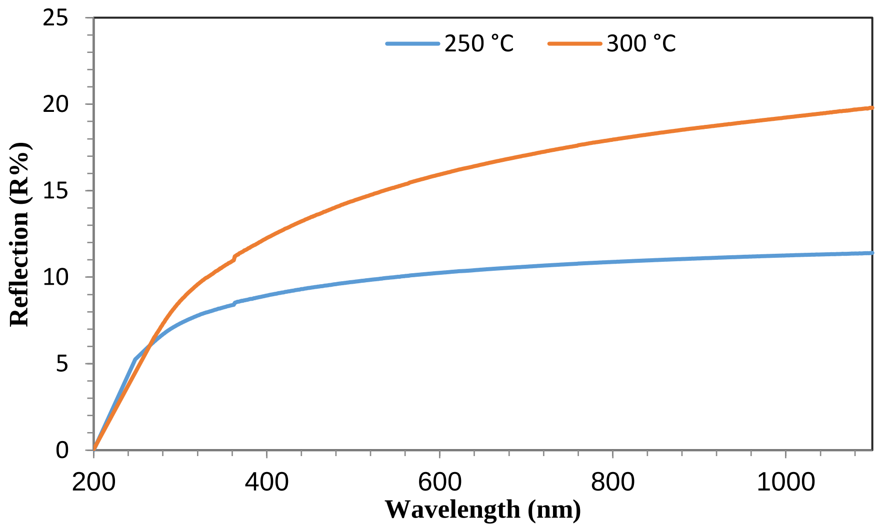

FIG. 6. THE OPTICAL REFLECTION OF $LiNbO_3$ THIN FILM AT DIFFERENT SUBSTRATE TEMPERATURE.

Received 29 April 2019; Accepted 8 October 2019

 ISSN (Print) 1811-9212 *ISSN (Online) 2617-3352*

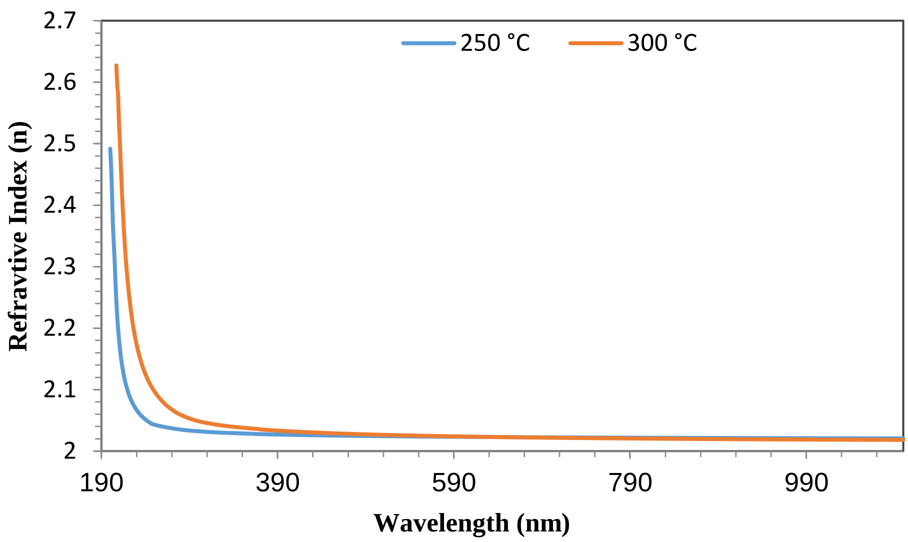

FIG. 7. REFRACTIVE INDEX OF $LiNbO_3$ THIN FILM AT DIFFERENT SUBSTRATE TEMPERATURE.

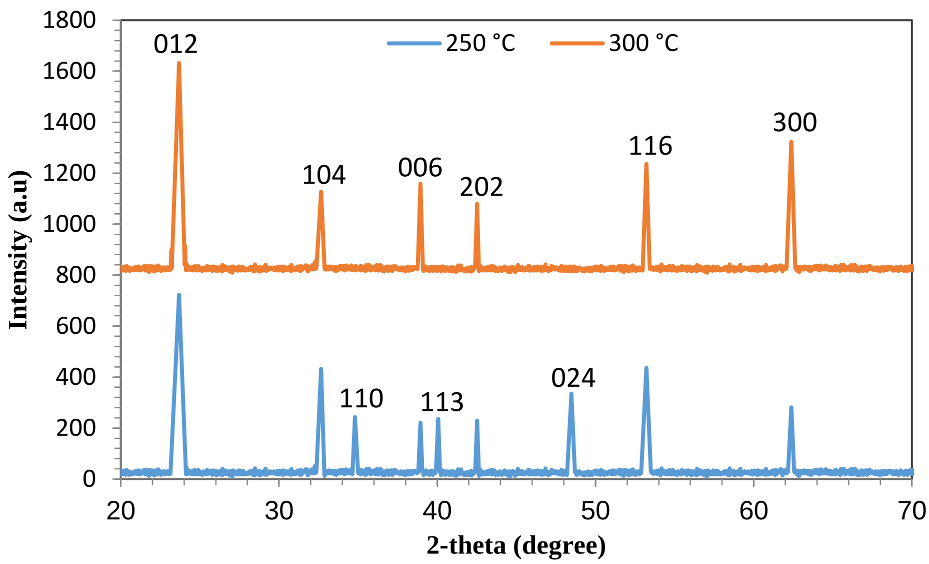

FIG. 8. XRD PATTERNS OF $LiNbO_3$ THIN FILM AT DIFFERENT SUBSTRATE TEMPERATURE.

IV. CONCLUSION

Nanostructure thin films of $LiNbO_3$ was prepared and deposited by PLD technique using a Q-switched Nd:YAG laser (532nm) on the quartz substrates with two different substrate temperature (250°C-300°C). It has been noticed from the UV-vis results that the increase in the substrate temperature has a negative effect on the values of transmission (T%), absorption (A) and optical energy gap (Eg), but it has a positive effect on the values of reflection (R%) and refractive index (n). While,it has been found from XRD results that the $LiNbO_3$ have a polycrystalline structure in nature due to having various peaks in various plane orientations. And, the film structure becomes more purity and more crystalline with increasing the substrate temperature. Also, the crystallization increases significantly at the substrate temperature 300°C due to increasing the peaks intensity. Therefore, the improvement in the crystal structure of $LiNbO_3$ film was obtained when the substrate temperature increased to 300°C through the deposition process. So, it can be concluded from these results that the substrate temperature 300°C represents the optimum substrate temperature to prepared $LiNbO_3$ nanostructure thin film.

Received 29 April 2019; Accepted 8 October 2019

 ISSN (Print) 1811-9212 ISSN (Online) 2617-3352

REFERENCES

[1] Makram A. Fakhri, Y. Al‑Douri, U. Hashim, Evan T. Salim, Deo Prakash and K. D. Verma, "Optical investigation of nanophotonic lithium niobate‑based optical waveguide," Appl. Phys. B, vol. 121, pp. 107-116, 2015.

[2] Makram A Fakhri, Evan T. Salim, U. Hashim and Zaid T. Salim, , "Effects of Different Parameters on XRD Properties of Nano and Micro LiNbO3 Using Chemical Method," Adv Nano Energy, vol. 1, pp. 98-106, 2017.

[3] Makram A. Fakhri, Y. Al-Douri and U. Hashim, "Fabricated Optical Strip Waveguide of Nanophotonics Lithium Niobate," IEEE Photonics Journal, vol. 8, no. 2, pp. 1-10, 2016.

[4] Makram A. Fakhri, U. Hashim, Evan T. Salim and Zaid T. Salim, "Preparation and charactrization of photonic LiNbO3 generated from mixing of new raw materials using spry pyrolysis method," Journal of Materials Science: Materials in Electronics, vol. 27, no. 12, pp. 13105-13112, 2016.

[5] Makram. A. Fakhri, Y. Al-Douri, Uda. Hashim and Evan. T. Salim, "Annealing Temperature Effects on Morphological and Optical Studies of Nano and Micro Photonics Lithium Niobate using for Optical Waveguide Applications, " Australian Journal of Basic and Applied Sciences, vol. 9, no. 12, pp. 128-133, 2015.

[6] Makram. A. Fakhri, Y. Al-Douri, Evan. T. Salim , Uda. Hashim and Yushamdan Yusof, "Effects of Chemical Stirring Time on the Physical Properties for LiNbO3 Photonic Film Using of Optical Waveguide Applications," Procedia Chemistry, vol. 19, pp. 531-538, 2016.

[7] MAKRAM. A. Fakhri, Y. AL-Douri , UDA Hashim and EVAN T. Salim, "XRD Analysis and Morphological Studies of Spin Coated LiNbO3 Nano Photonic Crystal Prepared for Optical Waveguide Application," Advanced Materials Research, vol. 1133, pp. 457-461, 2016.

[8] Y. Al-Douri, M.A. Fakhri, N. Badi and C.H. Voon, "Effect of stirring time on the structural parameters of nanophotonic LiNbO 3 deposited by spin-coating technique," Optik, vol. 156, pp. 886-890, 2018.

[9] Makram A. Fakhri, M.Halim A. Wahid, Ban A. Badr, Suad M. Kadhim, Evan T. Salim, Uda Hashim and Zaid T. Salim, "Enhancement of Lithium Niobate nanophotonic structures via spin-coating technique for optical waveguides application," EPJ Web of Conferences, vol. 162, pp. 01004, 2017.

[10] Mukkaram. A Fakhry, Farah A. Hattab and Esraa K. Hamed, "Laser Energy Effects on Optical Properties of Titanium Di-Oxide Prepared by Reactive Pulsed Laser Deposition," Eng.& Tech. Journal, vol. 30, no. 17, pp. 3104-3111, 2012.

[11] N. E. Stankova, S. H. Tonchev, E. Gyorgy, G. Socol and I. Mihailescu, "PULSED LASER DEPOSITION OF LiNbO3 THIN FILMS FROM Li-RICH TARGETS," Journal of Optoelectronics and Advanced Materials, vol. 6, no. 4, pp. 1345 - 1348, 2004.

[12] Farah Hattab and Makram Fakhry, "Optical and structure properties for nano titanium oxide thin film prepared by PLD," First National Conference for Engineering Sciences (FNCES 2012), 2012.

Received 29 April 2019; Accepted 8 October 2019

 ISSN (Print) 1811-9212 ISSN (Online) 2617-3352