Optical properties doped RuO$_2$ (0, 2, 4, 6%) of thin film LiNbO$_3$

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Abstract. Lithium Niobate (LiNbO3) can be applied as a thin film coating because it has superior piezoelectric, optoelectronic, pyroelectric, and photorefractive properties. The growth of LiNbO$_3$ thin film using Chemical Solution Deposition (CSD) method with spin coating technique speed of 8000 rpm for 30 seconds on a p-type silicon substrate (100) with variations in concentration of RuO$_2$ container (0%, 2%, 4%, 6%) and annealing temperature (750 °C, 800 °C, 850 °C). The annealing temperature is kept on hold for 8 hours with an increase of 1.67 °C/minute. The result of LiNbO3 bandgap energy film is 2.55 eV to 3.18 eV with a refractive index ranging from 1.15 to 1.65.

1. Introduction
The development of increasingly rapid science and technology especially in the field of physics can produce functional materials that can be used as electronic devices because they have ferroelectric properties. A ferroelectric material is a material that has electric polarisation due to the presence of an external electric field [1]. Initially, this ferroelectric material was made in bulk, but the development of science and technology in this material began to be made in the form of thin films that have a thickness reaching nano. The thin layer is a fragile layer of organic, inorganic, metal and metal-organic mixtures that have the properties of conductors, semiconductors, superconductors and insulators [2].

LiNbO$_3$ is a ferroelectric material that has pyroelectric, piezoelectric, refractive, electro-optical and nonlinear optical properties. LiNbO$_3$ is suitable for application to non-linear optics, integrated optics, acoustic wave devices, and holography optics. In this paper, a thin film of lithium drug (LiNbO$_3$) was made by adding ruthenium oxide (RuO$_2$) receptacle. The substrate used is p-type silicon material (100), using the CSD method (Chemical Solution Deposition). A CSD method is a method of making thin films by depositing chemical solutions on the substrate, then preparing using spin coating at a certain rotational speed [3]. In this paper, the spin coating is rotated with a rotating speed of 8000 rpm. Based on the literature shows that at this speed thin films formed are thinner (in micrometre order) [4]. The CSD method has several advantages, such as stoichiometric control, homogeneity, temperature and relatively low costs [5].

2. Research Objective
This research objective is to determining the effect of variations in the concentration of RuO$_2$ receptacle and annealing temperature on thin films of LiNbO$_3$ on optical properties include reflectance, bandgap energy, and a refractive index of the film.
3. Methods

3.1. Tools and Materials
The materials used in this study were lithium acetate (Li$_2$C$_2$H$_3$O$_2$) 99.6% powder, niobium oxide (Nb2O5) 99.9%, dopant ruthenium oxide (RuO2), methyl ester sulfonic acid (MESA) surfactant, a p-type silicon substrate (100), and double distilled water. While the tools used are analytic balance, spin coater reactor, Vulcan TM-3000 brand furnace, and UV Opt-Opt Ocean USB Optical Spectroscopy.

3.2. Substrate Preparation
The substrate used is the p-type silicon substrate (100). The substrate was cut to a square size of 1 cm x 1 cm using a diamond eye knife. The substrate is then cleaned by dipping in double distilled water using tweezers for half a minute.

3.3. Making LiNbO$_3$ solution
The LiNbO$_3$ solution was made by mixing lithium acetate (Li$_2$C$_2$H$_3$O$_2$) powder, niobium pentoxide (Nb2O5), and ruthenium oxide (RuO2) into 2.5 ml of acetic acid solvent and MESA surfactant. Then stirred using a magnetic stirrer stirrer with a rotating speed of 600 rpm for 30 minutes which produced a solution of 2 M LiNbO$_3$.

3.4. The growth of thin films
The LiNbO$_3$ film was grown on p-type silicon substrate 1 cm x 1 cm using the chemical solution deposition (CSD) method. Deposition of film on the substrate is done by spin coating. Spin coating reactor playback is set with a rotating speed of 8000 rpm for 30 seconds and a 60-second pause for each drop. The penetration process is done three times to obtain three layers on the substrate. Then the film is annealed using a furnace.

3.5. Annealing process
The annealing process on the substrate starts from the room temperature which is then raised to the desired annealing temperature with an adjusted heating temperature increase of 1.67 °C / minute. After reaching the annealing temperature then the heating temperature is held constant for 8 hours. Then the cooling furnace is carried out until room temperature is recovered. Annealing is carried out with three temperature variations namely 750 °C, 800 °C, and 850 °C with the same holding time of 8 hours.

3.6. Determine thin film thickness
The thickness of the film can be calculated using the volumetric method by comparing the mass of the film deposited on the substrate with the area of the film and the density of the film. Calculation of film thickness in this method uses equation (1) [6,7].

\[ d = \frac{m_2 - m_1}{\rho_{film} \times A} \]

\( d \) is film thickness (m),
\( m_1 \) is substrate mass (gram),
\( m_2 \) is substrate mass after annealing (gram),
\( A \) is film surface area (m$^2$), and
\( \rho \) film is film density (gram / cm$^3$).

3.7. Determine the bandgap energy of the film
Bandgap energy is obtained by the reflectance method, which is to make a plotting of the relationship between (2) to the energy of the tv photon. Extrapolation is done on a curve that has the highest gradient and intersects the hv axis [8].
\[
\left[ \ln \left( \frac{R_{\text{max}} - R_{\text{min}}}{R - R_{\text{min}}} \right) \right]^2
\]  

(2)

3.8. Determine the refractive index of the film
The refractive index is obtained using equation (3) [9,10]

\[
n = \frac{1 + \sqrt{R}}{1 - \sqrt{R}}
\]

(3)

With R is the reflectance level of the film and n is the refractive index value of the film.

4. Results and Discussions

4.1. Reflectance
Figure 1 shows the reflectance relationship with the wavelength of the film that has passed the annealing process. Reflectance values of films at annealing temperatures of 750 ºC, 800 ºC, and 850 ºC with concentrations of 0%, 2%, 4% and 6% respectively show different values. This difference indicates the influence of the annealing temperature and the addition of dopant to the LiNbO3 film. The reflectance value for the same wavelength will be greater in films with a smaller thickness. The reflectance value difference is because the thicker the film, the more it contains LiNbO3 molecules involved in the light reflection process. The size of the reflected photon energy is influenced by the size of the atom making up the film.

![Reflectance graph of wavelength (nm) at annealing temperature](a) 750 ºC, (b) 800 ºC, (c) 850 ºC.

Figure 1. Reflectance graph of wavelength (nm) at annealing temperature (a) 750 ºC, (b) 800 ºC, (c) 850 ºC.

4.2. The bandgap energy of the LiNbO3 film
Figure 2, Figure 3, and Figure 4 shows the bandgap energy values of LiNbO3 films at different annealing temperatures and dopant concentrations. The values shown are different for each film. Figures indicate that there is an influence of annealing temperature and dopant concentration on bandgap energy and refractive index. We can see that the bandgap energy is inversely proportional to the annealing temperature and the amount of the dopant concentration used. The addition of dopant can increase the donor atom in the semiconductor until the energy level reaches the conduction band, causing the bandgap energy value to decrease with the addition of the dopant concentration.
Figure 2. Energy value of film gap (a) LiNb$_1$Ru$_0$O$_3$ (b) LiNb$_{0.98}$Ru$_{0.02}$O$_3$ (c) LiNb$_{0.96}$Ru$_{0.04}$O$_3$ (d) LiNb$_{0.94}$Ru$_{0.06}$O$_3$ annealed at 750 $^\circ$C

Figure 3. Energy value of film gap (a) LiNb$_1$Ru$_0$O$_3$ (b) LiNb$_{0.98}$Ru$_{0.02}$O$_3$ (c) LiNb$_{0.96}$Ru$_{0.04}$O$_3$ (d) LiNb$_{0.94}$Ru$_{0.06}$O$_3$ annealed at 800 $^\circ$C
Figure 4. Energy value of film gap (a) LiNb$_{1}$Ru$_{0}$O$_{3}$ (b) LiNb$_{0.98}$Ru$_{0.02}$O$_{3}$ (c) LiNb$_{0.96}$Ru$_{0.04}$O$_{3}$ (d) LiNb$_{0.94}$Ru$_{0.06}$O$_{3}$ annealed at 850 °C

4.3. Refractive index

Figure 5-7, the lowest refractive index value is in the LiNbO$_3$ film without dopant which is burned at an annealing temperature of 850 °C. The refractive index obtained is 1.15 which is at a wavelength of 443.7 nm with bandgap energy of 2.80 eV. Meanwhile, the highest refractive index is in the LiNbO$_3$ film plus 6% of doped RuO$_2$ which is burned at an annealing temperature of 750 °C. The refractive index obtained is 1.65 which is at wavelength 390.6 nm with bandgap energy 3.18 eV.

Figure 5. Refractive index value (a) LiNb$_{1}$Ru$_{0}$O$_{3}$ (b) LiNb$_{0.98}$Ru$_{0.02}$O$_{3}$ (c) LiNb$_{0.96}$Ru$_{0.04}$O$_{3}$ (d) LiNb$_{0.94}$Ru$_{0.06}$O$_{3}$ annealed at 750 °C
5. Conclusions

LiNbO₃ thin films were grown on a p-type silicon substrate using the CSD method using 0%, 2%, 4%, 6% pendants and annealing with temperatures of 750 °C, 800 °C, and 850 °C successfully made.
results of the analysis using the reflectance method show that in the wavelength range of 380 nm to 500 nm the refractive index ranges between 1.15 to 1.65 and bandgap energy 2.55 eV to 3.18 eV.

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