Surface Morphology Properties Doped RuO₂ (0, 2, 4, 6%) of Thin Film LiNbO₃

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Abstract. Successful LiNbO₃ film was prepared with the variation of 0%, 2%, 4%, and 6% RuO₂ concentration and annealing temperature variation above the p-type silicon substrate (100), using the CSD method with the spin coating at 8000 rpm for 30 seconds in solubility 2 M. Films in annealing at 850 °C for 8 hours with a temperature increase of 1.67 °C/min. Samples were characterised using SEM and EDX spectrometer. We have obtained the morphology nonhomogenous surface and element stoichiometry. LiNbO₃ thin film is a potential material for light sensors.

1. Introduction

The increasingly rapid development of 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, producers have made this ferroelectric material in bulk, but along with the development of science and technology, producers have begun to make this material 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].

LiNbO₃ is a ferroelectric material that has pyroelectric, piezoelectric, refractive, electro-optical and nonlinear optical properties. LiNbO₃ is suitable for application to non-linear optics, integrated optics, acoustic wave devices, and holography optics [3,4]. In this paper, we have made a thin film of lithium drug (LiNbO₃) by adding ruthenium oxide (RuO₂) 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, we have done the spin coating with a rotating speed of 8000 rpm. Based on the literature shows that at this speed thin films formed are thinner (in micrometer order) [4]. The CSD method has several advantages, such as stoichiometric control, homogeneity, temperature and relatively low costs [5].

SEM is a microscope that uses the principle of electrons emitted on a sample. While energy dispersion X-ray spectroscopy (EDS or EDX) is an analytical technique used to analyse elements or chemical characterisation of LiNbO₃ thin films. SEM is one variant of spectroscopic X-ray fluorescence that relies on sample investigations through interactions between electromagnetic and
material radiation. EDX is used to determine the atomic composition contained in the sample. SEM is used to determine the surface morphology of the film, crystal grain size, structural defects and impurity composition of the material [6].

**Research Objective**
This research objective is to look at the surface morphology of lithium-thin film with variations of doping 0%, 2%, 4% and 6%.

2. Methods

2.1. Tools and Materials
The materials used in this study were lithium acetate (Li₂C₂H₃O₂) 99.6% powder, niobium oxide (Nb₂O₅) 99.9%, with ruthenium oxide (RuO₂) dopant, methyl ester sulfonic acid (MESA) surfactant, a p-type silicon substrate (100), and double distilled water. While the tools used are an analytic balance, spin coater reactor, Vulcan TM-3000 brand furnace, and UV Opt-Opt Ocean USB Optical Spectroscopy.

2.2. 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. We have cleaned the substrate by dipping in double distilled water using tweezers for half a minute.

2.3. Making LiNbO₃ solution
We have made The LiNbO₃ solution by mixing lithium acetate (Li₂C₂H₃O₂) 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 with a rotating speed of 600 rpm for 30 minutes which solved 2 M of LiNbO₃.

2.4. The growth of thin films
The LiNbO₃ film was grown on a p-type silicon substrate 1 cm x 1 cm using the chemical solution deposition (CSD) method. We have done the deposition of films on the substrate by spin coating. We have set the spin coating reactor playback 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.

2.5. Annealing process
The annealing process on the substrate starts from the room temperature which we have 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 it has returned to the room temperature. Annealing is carried out at 850 °C with the same holding time of 8 hours.

2.6. 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].

\[
d = \frac{m_2 - m_1}{1/p_{film} \times A}
\]

*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

$p_{film}$ is film density (gram / cm$^3$).

3. Results and Discussions

We have obtained the morphology and composition of film elements from the results of SEM and EDX analysis in this study using Analytical Scanning Electron Microscope, and Energy Dispersed X-ray Spectroscopy (EDX) JEOL Brand JSM-6510LA. Four films were characterised using SEM and EDX namely LiNbO$_3$ (Figure 1), LiNb$_{0.98}$Ru$_{0.02}$O$_3$ (Figure 2), LiNb$_{0.96}$Ru$_{0.04}$O$_3$ (Figure 3), and LiNb$_{0.94}$Ru$_{0.06}$O$_3$ (Figure 4) films which we have annealed them at 850 °C for 8 hours.

![Figure 1. SEM image of a LiNbO$_3$ film with annealing temperature of 850°C](image1)

![Figure 2. SEM image of a LiNb$_{0.98}$Ru$_{0.02}$O$_3$ film with annealing temperature of 850°C](image2)

![Figure 3. SEM image of a LiNb$_{0.96}$Ru$_{0.04}$O$_3$ film with annealing temperature of 850°C](image3)
Figure 4. SEM image of a LiNb$_{0.94}$Ru$_{0.06}$O$_3$ film with an annealing temperature of 850$^0$C.

The overall average crystal size obtained was 0.327$\mu$m for LiNbO$_3$ films, 0.367 $\mu$m for LiNb$_{0.98}$Ru$_{0.02}$O$_3$ films, 0.353 $\mu$m for LiNb$_{0.96}$Ru$_{0.04}$O$_3$, and 0.330 $\mu$m for LiNb$_{0.94}$Ru$_{0.06}$O$_3$ films.

Table 1. Atomic composition of LiNbO$_3$ films

| Thin Film | Atomic % | O  | Nb   | Ru  | Li  |
|-----------|----------|----|------|-----|-----|
| LiNbO$_3$ |          | 69.12 | 30.88 | 0   | Not detected |
| LiNb$_{0.98}$Ru$_{0.02}$O$_3$ | | 71.39 | 28.59 | 0.03 | |
| Li$_{0.96}$Ru$_{0.04}$NbO$_3$ | | 75.62 | 24.33 | 0.05 | |
| Li$_{0.94}$Ru$_{0.06}$NbO$_3$ | | 71.73 | 28.13 | 0.04 | |

The atomic composition of the LiNbO$_3$ film was obtained from the EDX test results using Energy Dispersive X-ray Spectroscopy JEOL JSM-6510LA Brand. Table 1 has shown that Li atoms cannot be detected by EDX characterisation because Li atoms have a small atomic number and energy so that a wave of fluorination cannot capture them (Figure 5, Figure 6, Figure 7, and Figure 8).

Figure 5. EDX spectrum of a LiNbO$_3$ film with an annealing temperature of 850 $^0$C.
Figure 6. EDX spectrum of a LiNb$_{0.98}$Ru$_{0.02}$O$_3$ film with an annealing temperature of 850 °C.

Figure 7. EDX spectrum of a Li$_{0.98}$Ru$_{0.02}$NbO$_3$ film with an annealing temperature of 850 °C.
Figure 8. EDX spectrum of a Li$_{0.94}$Ru$_{0.06}$NbO$_3$ film with an annealing temperature of 850 °C

4. Conclusion
We have successfully made LiNbO$_3$ thin films grown on p-type silicon substrates using the CSD method with 0%, 2%, 4%, 6% pellets and 850 °C annealing. The results of surface morphology analysis have shown the evenly distributed thin film surface. The average crystal size of the films is 0.327 μm to 0.367 μm.

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