Optical Properties of Lithium Niobate (LiNbO$_3$) Thin Film Doped with Ruthenium Oxide

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Abstract. We have succeeded in growing thin film of lithium niobate with variation of ruthenium oxide impurity (0, 2, 4, 6%) doped on pure silicon substrate (100) p-type with chemical solution deposition (CSD) method assisted with spin coating method. Lithium niobate thin films with variations of ruthenium oxide impurity and MESA surfactant precursors (methyl ester Sulfonat acid) with 2 M solubility was made using spin coating at a rotational speed of 8000 rpm for 30 seconds with three repeated coatings. The growth of thin film was carried out with an 850°C annealing temperature which is held for 8 hours under atmospheric conditions in the Furnace. The optical properties test was performed with the VIS-NIR Spectrophotometer tool and obtained energy gap values in the range of 2 to 3 eV using Kubelka method. The optical properties of thin films indicate that thin films of lithium niobate with variations of ruthenium oxide impurity (0, 2, 4, 6%) have the potential to become the embryo of light sensor materials.

Keywords: Optical properties, lithium niobate doped with ruthenium oxide, chemical solution deposition, Kubelka method, energy gap

1. Introduction
Mastery of basic science and thin film technology is essential in the development of materials science for the future. The role of ferroelectric/pyroelectric materials LiNbO$_3$, LiTaO$_3$, BTST, PZT and MCT, HgCdTe, GaAs/AlGaAs photon sensor materials are very interesting to study because they can be applied to DRAMs, temperature sensors and solar cells. The pyroelectric and piezoelectric materials are subgroups of ferroelectric materials. Because of these properties, the ferroelectric material, through hysteresis and high dielectric values, can be applied to dynamic random access memory (DRAM) [1-3], non-volatile random access memory (NVRAM) [4], and solar cells [5]. While the operating area of the ferroelectric sensor (which is also pyroelectric) is around the room temperature as long as below the Curie temperature (T$_c$ = 490°C) [6]. Therefore, in this study, ferroelectric material is selected as materials for temperature sensors and photovoltaic solar cell assisted with photonic crystals. In addition, the way of making this ferroelectric material is easier than MCT. Although the manufacture of thin films of ferroelectric materials with CSD and spin coating methods has disadvantages such as the response time is not as fast as the photovoltaic sensor, but has advantages in the environment that does not require cooling, meaning that making is easy to do in Indonesia campus laboratory.
The most widely used ferroelectric materials are LiNbO$_3$, LaTiO$_3$, PbTiO$_3$, PbZrO$_3$, BaxSr$_{1-x}$TiO$_3$ (BST) and BST with metal oxide impurity (BST derivatives) [1,3]. The thin films of LiNbO$_3$, BST and derivatives can be prepared by various methods such as \textit{sputtering} [4,7], \textit{chemical solution deposition} (CSD) processes [3,8,9], \textit{pulsed laser deposition} (PLD) [10], \textit{chemical vapor deposition} (CVD) [11,12], CSD and spin coating method is relatively cheap and easy compared to sputtering method, PLD, and CVD, so the proposer in this research using CSD method [3].

The objectives of this study are: (i) growth of thin film LRN with addition of RuO$_2$ (0, 2, 4, 6%) on Si (100) p-type substrate with CSD and spin coating method, (ii) analyzing the optical properties and surface morphology test.

\section{Materials and Methods}

LiNbO$_3$ thin films manufacturing was conducted in two stages. In the first stage, substrate was prepared by cutting the P-type Si (100) with the size of 8 mm and 8 mm then cleaned by aqua bidest and dried. In the next stage, the LiNbO$_3$ powder (precursor) was manufactured. Precursors were obtained by mixing LiCH$_3$COO powder, Nb$_2$O$_5$, and lanthanum and then dissolved in 1.875 ml acetate acid and 0.625 ml methyl ester soulfonat acid (MESA). The mixing process was conducted using ultrasonic of Branson 2210 for 90 minutes and then deposited on the substrate by using spin coating at speed of 3000 rpm, 2 times. The next step was annealing process using the furnace of VulcanTM3–130. The annealing process for each substrate was started from room temperature with the increasing rate of 1.7$^\circ$C/min to temperature of 850$^\circ$C and than held constantly for 8 hours. After that, cooled until room temperature [3]. The novelty from this research is there were four prepared precursors i.e undoped precursor, 2% ruthenium doped precursor, 4% ruthenium doped precursor and 6% ruthenium doped precursor.

The optical properties of thin films were characterized by using USB 2000 spectrometer and SEM model Hitachi SU3500 (investigate surface morphology of samples on magnitude of 20,000 times).

\section{Results and Discussion}

\subsection{Optical Properties Test}

The optical properties test data uses reflected (R) data on wavelength and is processed to obtain refractive index data and energy gap. It can be seen in Figs. 1 to 4 that there is an effect of giving RuO$_2$ impurity on LiNbO$_3$ thin films to the refractive index values and the largest refractive index occurring at wavelengths of 934 to 950 nm (near infra red spectrum).

![Figure 1. Relationship between refractive index to wavelength on thin film LiNbO$_3$ without RuO$_2$ impurities](image-url)
Figure 2. Relationship between refractive index to wavelength on thin film LiNbO$_3$ with 2\% RuO$_2$ impurity

Figure 3. Relationship between refractive index to wavelength on thin film LiNbO$_3$ with 4\% RuO$_2$ impurity
Figure 4. Relationship between refractive index to wavelength on thin film LiNbO$_3$ with 6% RuO$_2$ impurity

Figure 5. Relationship between Energy Gap Kubelka Munk Method to energy (eV) on thin film LiNbO$_3$ without RuO$_2$ impurities

It can be seen in Figs. 5 to 8 that there is an effect of giving RuO$_2$ impurity on LiNbO$_3$ thin films to the energy gap value by Kubelka Munk method in the range of 1.9 to 2.7 eV
Figure 6. Relationship between Energy Gap Kubelka Munk Method to energy (eV) on thin film LiNbO$_3$ with 2% RuO$_2$ impurity

Figure 7. Relationship between Energy Gap Kubelka Munk Method to energy (eV) on thin film LiNbO$_3$ with 4% RuO$_2$ impurity
Figure 8. Relationship between Energy Gap Kubelka Munk Method to energy (eV) on thin film LiNbO$_3$ with 6% RuO$_2$ impurity.

Figure 9. Scanning Electron Microscopy (SEM) image on thin film LiNbO$_3$ without RuO$_2$ impurities and 20,000 times magnification.
**Figure 10.** Scanning Electron Microscopy (SEM) image on thin film LiNbO$_3$ with 2% RuO$_2$ impurity and 20,000 times magnification.

**Figure 11.** Scanning Electron Microscopy (SEM) image on thin film LiNbO$_3$ with 4% RuO$_2$ impurity and 20,000 times magnification.
Figure 12. Scanning Electron Microscopy (SEM) image on thin film LiNbO$_3$ with 6% RuO$_2$ impurity and 20,000 times magnification.

It can be seen in Figs. 9-12 that based on SEM image data, there is an effect of giving RuO$_2$ impurity on the size of the thin film grain LiNbO$_3$. The optical properties and SEM of thin films indicate that thin films of lithium niobate with variations of ruthenium oxide impurity (0, 2, 4, 6%) have the potential to become the embryo of light sensor materials.

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