

LITAO3 CHARACTERIZATION OF RUBIDIUM ON TEMPERATURE VARIATIONS

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Abstract. One of the studies that recently attracted the attention of physicists is research on ferroelectric material because this material is very promising for the development of new generation devices in connection with the unique properties it has. Ferroelectric materials, especially those based on a mixture of lithium tantalite (LiTaO₃), are expected to be applied to the infrared sensor. Lithium tantalate (LiTaO₃) is a ferroelectric material that is unique in terms of pyroelectric and piezoelectric properties that are integrated with good mechanical and chemical stability. Therefore LiTaO₃ is often used for several applications such as electro-optical modulators and pyroelectric detectors. LiTaO₃ is a non-hygroscopic crystal, colorless, soluble in water, has a high transmission rate and does not easily damage its optical properties. LiTaO₃ is a material that has a high dielectric constant and a high load storage capacity. This research has succeeded in determining the band gap energy of the LiTaO₃ film in the rubidium chamber obtained in the range of values 2.02-2.98 eV as shown in figure 4. The LiTaO₃ film after the annealing process at a temperature of 650 °C, has the highest band gap energy of 2.98 eV. Large energy is needed on the electrons to be excited from the valence band to the conduction band. Whereas in the LiTaO₃ film after an annealing process of 800 °C, the band gap energy obtained is 2.02 eV. This makes it easier for electrons to be excited from the valence band to the conduction band because the energy needed is not too large.

Keywords: absorbance, energy gap, Lithium Tantalate (LiTaO₃)

I. INTRODUCTION

Semiconductors are materials with an electrical conductivity between insulators and conductors. These materials are very useful in the electronics field because their electrical conductivity can be changed by injecting other materials (commonly called doped materials). Semiconductors are basic elements of electronic components such as diodes, transistors, and integrated circuits (IC). They are very widely used, especially since the invention of transistors in the late 1940s. The well-known semiconductor materials are silicon (Si), germanium (Ge), and Gallium Arsenide (GaAs). Lately, silicon has become famous after it was discovered how to extract silicon material from nature. Silicon is the second largest ingredient on earth after oxygen. Sand, glass, and other rocks are natural materials which contain many elements of silicon (Irzaman [1]).

Semiconductors that have been contaminated (not pure anymore) by atoms of other types of band structure and electrical resistivity will change. Impurities in semiconductors can donate electrons and holes in energy bands. Thus, the electron concentration cannot be the same as the hole concentration, but each depends on the concentration and type of impurity material. In the application, sometimes only material with an electron-carrying carrier or only a hole is needed. This is done by storing impurities into the semiconductor.

To get a high-quality semiconductor device, what must be considered is "purity" and "single crystal perfection" of semiconductors that are used as materials for making these tools. Generally, the addition of a little impurity affects the carrier of the charge, therefore affecting the components to be made. On the contrary, the more perfect of the crystal, which has very little damage to the crystal layer, the more perfection of the crystal determine the characteristics of the components.

Intrinsic semiconductors are semiconductors consisting of only one element, for example, Si or Ge only. In Si semiconductor crystals, 1 Si atom has 4 valence electrons attached to 4 other Si atoms. In Si intrinsic semiconductor crystals, the primitive cell is cuboid. Bonds that occur between adjacent atoms are covalent bonds. This is due to the use of 1 electron along with two adjacent Si atoms. According to the energy band theory, at $T = 0$ K the semiconductor valence band is filled with electrons, while the conduction band is empty. The two bands are separated by a small energy gap, which is in the range of 0.18 - 3.7 eV. At room temperature, Si and Ge each have an energy gap of 1.11 eV and 0.66 eV (Sutrisno, [2]).

When the material gets enough energy, for example from heat energy, electrons can escape from covalent and excited bonds across the energy gap. The valence electrons in the Ge atom are more easily excited to be free electrons rather than valence electrons on Si atoms because the Si energy gap is greater than the Ge energy gap. These electrons are free

to move between atoms. Whereas the electron void is called a hole. Thus the conduction band base is inhabited by electrons, and the valence band peaks are occupied by holes. When the two bands are partially filled, it will cause a net current when subjected to an electric field. If on a dielectric material is subject to an electric field, then certain atoms experience a shift and cause an electric dipole moment. This dipole moment causes polarization. The moment of dipole per unit volume is called dielectric polarization. Polarization occurs in the dielectric as a result of an external electric field and symmetry in the crystallographic structure in the unit cell. Ferroelectric shows that groups of dielectric material can be polarized electrically internally over a certain temperature range (Seo [3]).

One of the studies that recently attracted the attention of physicists is research on ferroelectric material because this material is very promising for the development of new generation devices in connection with the unique properties it has. Ferroelectric materials, especially those based on a mixture of lithium tantalate (LiTaO₃), are expected to be applied to infrared sensors, the nature of polarizability can be applied as Non-Volatile Ferroelectric Random Access Memory (NVRAM), and electro-optic properties can be used in thermal infrared switches (Irzaman [4]).

The nature of a ferroelectric material is used for the needs of electronic devices. The role of LiTaO₃ ferroelectric materials is very interesting to study because in its application it can be used as an infrared sensor. LiTaO₃ is an object that has been studied intensively over the past few years because it has unique properties. LiTaO₃ is ferroelectric at room temperature. From the results of several studies, LiTaO₃ is an optical, pyroelectric and piezoelectric material. LiTaO₃ has a high dielectric constant and a high load storage capacity as well (Uchino [5]). In addition, LiTaO₃ is a non-hygroscopic crystal which does not easily damage its optical properties, this property makes the LiTaO₃ material superior to other materials (Seo [3]).

Ferroelectric Materials

Ferroelectric thin films are widely used in applications for electronic and electronic devices. Pyroelectric and piezoelectric materials are subgroups of ferroelectric materials. Ferroelectric materials (embedded in pyroelectric) such as LiTaO₃. Ferroelectric shows that a group of dielectric materials can be polarized internally within a certain temperature range. Polarization occurs in the dielectric as a result of an external electric field and symmetry in the crystallographic structure in the unit cell. If the ferroelectric material is subject to an electric field, then certain atoms experience a shift and cause an electric dipole moment. This dipole moment causes polarization. The moment of dipole per unit volume is called dielectric polarisation (Seo[3]).

Ferroelectric is a symptom of spontaneous changes in electrical polarization of material without interference from the external electric field. Ferroelectricity is a phenomenon shown spontaneously by crystals with a polarization and hysteresis effect. It is related to dielectric changes in response to the application of an electric field. High hysteresis properties and dielectric constants can be applied to Dynamic Random Access Memory (DRAM) memory cells with a storage capacity exceeding 1 Gbit in which semiconductor dielectric layers are required to reduce the size of the cell which is considered impractical. Piezoelectric properties can be used as microactuators and sensors and they can be applied to infrared thermal switches. The nature of polarizability can be applied as Non Volatile Ferroelectric Random Access Memory (NVRAM) (Irzaman [4]).

Substrat Silikon (Si)

Silicon is a chemical element that has the Si symbol and atomic number 14. Si is the second most abundant element on earth and elements from group IVA in the periodic system of elements. Most Si free elements are not found in nature. Therefore Si is produced by reducing quartz and sand with high-quality carbon. Silicon for the use of semiconductors is further purified by the czochralski crystalline melting method. This Si crystal has metallic luster and crystallizes with diamond structure (Saito [6]).

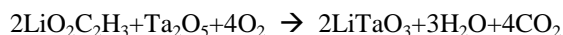
Silicon is a substitute for germanium semiconductors. An isolated Si atom has 14 protons and 14 electrons (Malvino [7]). Each Si atom has four valence electrons. The Si atom occupies the lattice in the crystal. Each Si atom is bound by four atoms. The other Si forms covalent bonds. Si crystals are intrinsic semiconductors, namely pure semiconductors that have not been mixed or contaminated with other atoms. At 0 ° K, Si crystals are insulators because they have an empty conduction band. But when heated electrons get energy, this results in the transfer of electrons to the conduction band so that it can be a conductor (Sutrisno [2]).

Lithium Tantalate (LiTaO₃)

Lithium tantalate (LiTaO₃) is a ferroelectric material that is unique in terms of pyroelectric and piezoelectric properties that are integrated with good mechanical and chemical stability. Therefore LiTaO₃ is often used for several applications such as electro-optical modulators and pyroelectric detectors. LiTaO₃ is a non-hygroscopic crystal, colorless, soluble in water, has a high transmission rate and does not easily damage its optical properties. LiTaO₃ is a material that has a high dielectric constant and a high load storage capacity (Seo [3]).

The manufacture of LiTaO₃ uses equipment that is quite simple, low cost and carried out in a relatively short time. LiTaO₃ is a mixture of reaction results between lithium acetate [(LiO₂C₂H₃), 99.9%]

and tantalum oxide [(Ta₂O₅), 99.9%]. Following is the reaction equation that produces LiTaO₃:



LiTaO₃ is a ferroelectric crystal which experiences a high currie temperature process of (601 ± 5.5) °C (Paula [8]). The mass of LiTaO₃ of 7.45 g / cm³ is used to calculate film thickness. (Irzaman [9]). LiTaO₃ is an object that has been studied intensively over the past few years because it has unique properties. Based on the research, LiTaO₃ material is an n-type semiconductor because the electron concentration of the LiTaO₃ material is greater than the concentration of the hole.

P-N Junction

The workings of most semiconductor devices are based on the nature of the connection between n-type and p-type materials. Such connections can be made in several ways, for example, diffuse impurities in the form of steam into semiconductor wafers. An important property of the p-n semiconductor connection is that the electric current can pass through it more easily in a certain direction than in the opposite direction to that direction. P-type semiconductor materials consist of elements in group IVA on a periodic system such as Si. N-type semiconductor material consists of elements in group V and group III in the periodic system.

P-N junctions are meeting areas that occur when p-type and n-type semiconductors are reunited. Another name for p-type semiconductor linkages and n-type semiconductors that form crystals is diodes (Kwok, [10]). A diode is an electronic component that can pass current in one direction only. Diodes play an important role in electronics, among others, to produce a directional voltage from alternating voltage, to make various signal waveforms, to regulate unidirectional voltage so that it does not change with load or with voltage changes, for electronic switches, LEDs, semiconductor lasers (Sutrisno [2]).

Teknik chemical solution deposition (CSD)

Chemical Process

The Chemical Solution Deposition (CSD) technique consists of a sol-gel process and Metalorganic Deposition which is used to produce thin layers of perovskite ceramics, especially for lithium tantalate (LiTaO₃) thin films. This method is more economical not only for scientific research but also used in the manufacture of modern ceramics and technologies that require high purity and control of microstructure and composition. Since the chemical reactants for CSD can be purified by distillation and crystallization, high purity films can be fabricated. The most important CSD advantage is the element that can be made, resulting in the final mixture composition at the molecular level, which means the diffusion time in inorganic films after pyrolysis to achieve

thermodynamic conditions, the stable phase is quite short, which can eventually produce a homogeneous mixture (Irzaman [1]).

In CSD principle prepares a solution of a solvent mixture in the spin coating on the surface of the substrate. The solution polymerized form a gel and heat to eliminate inorganic oxidation.

Spin Coating

The deposition of thin layers using the spin coating method has been used for decades. The spin coating process can be understood by the behavior of solution flow on a rotating substrate disk. The volumetric flow of fluid with a radial direction on the surface of the substrate is minimized, ie there is no vibration, no dry stains, etc. Then the disk is accelerated with a specific rotational speed which causes the liquid to be evenly distributed. There are four steps in the spin coating process. The first step is a deposition of the coating solution on the substrate surface. This can be done by using a pipette, dripping a coating solution on the substrate. The second step is to accelerate substrate with a high rotational speed of 3000 rpm of thinning coating liquid. In this step, the coating fluid is usually out of the substrate surface because the rotational motion makes the inertia of the upper layer solution cannot be maintained when the substrate rotates faster. The third step is when the substrate is at a constant speed (as desired), which is characterized by a gradual thinning of the coating solution so that the thickness of the coating solution is homogeneous. Sometimes it is also seen on the edge of the substrate which is thickened with a coating solution. The fourth step is when the substrate is rotated at constant speed and solvent evaporation occurs. The thickness of the layer and other properties depend on the type of fluid (viscosity, drying speed and molarity) and the parameters selected during the spin coating process include rotating speed, acceleration, and vacuum. Generally, high rotating speed and rotating time produce thinner layers.

II. RESEARCH METHODS

his research was carried out at the Material and Spectroscopy Physics Laboratory, Department of Physics, Faculty of Mathematics and Natural Sciences, Bogor Agricultural University. The research was conducted from August 2017 to March 2018. The materials used in this study were Lithium Acetate powder [LiO₂C₂H₃], Tantalum Oxide powder [Ta₂O₅], Rubidium [Rb₂O], 2- methoxyethanol [C₃H₈O₂], Si substrate (100) p-type, deionized water, acetone PA [CH₃COCH₃, 58.06 g / mol], methanol PA [CH₃OH, 32.04 g / mol], fluoride acid (HF), preparatory glass, silver paste, fine copper wire, and aluminum foil.

In this study, thin films of LiTaO₃ were made using the chemical solution deposition (CSD) method which had long been developed for the growth of perovskite thin films. This method has the advantage that the procedure is easy, the costs are relatively economical and get good results. The chemical solution deposition (CSD) method is a film-making method by depositing a chemical solution on the surface of the substrate, then preparing it with the spin coating at a speed of 3000 rpm for 30 seconds each penetration of the LiTaO₃ solution.

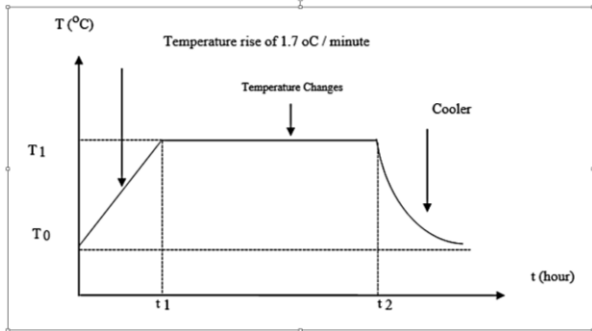


Figure 1 Annealing Process

The annealing process is carried out in stages using the Vulcan™ 3-130 furnace. Annealing functions to diffuse LiTaO₃ solution with a silicon substrate which starts from room temperature then increases to the annealing temperature of 650 °C, 700 °C, 750 °C and 800 °C with a temperature rise of 1.7 °C / minute and held constant for 8 hours at the annealing temperature. Then the cooling process is carried out until it returns to room temperature cooling down.

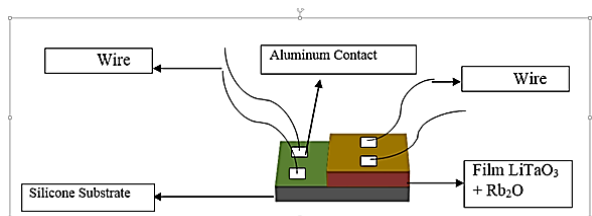


Figure 2 Film Design LiTaO₃ Didadah Rb₂O Ferroelektrik

Characterization of Optical Properties

Characterization of optical properties of thin films was carried out at the Physics Laboratory of IPB from an ocean optics program which has wavelengths from 339 nm to 1022 nm. Absorption spectroscopy has five main components: namely radiation sources, monochromators, samples, detectors, and recorders. The source of radiation used is xenon lamps which are commonly used in spectroscopy, while the monochromator serves to produce a radiation beam with one wavelength. If radiation or white light passed through a solution, radiation with a certain wavelength will be absorbed selectively and other radiation will be

transmitted or reflected. Then the device is connected to the software of the ocean optics program so that an absorptive curve of the wavelength and reflection of the wavelength is obtained. The curves can be analyzed by the optical properties of thin films

A spectrophotometer is an analytical method based on the absorption of electromagnetic radiation. Light consists of radiation to the sensitivity of the human eye, different wavelengths will cause different light while the mixture of light with a wavelength will arrange white light. White light covers the entire visible spectrum of 400-780 nm while infrared light in the spectrum above the wavelength is 780 nm.



Figure 3. Oceanopic Tools

Spectrophotometry is an analytical method based on measuring monochromatic light absorption by a colored solution lane at a specific wavelength using a prism monochromator or diffraction lattice and a phototube vacuum detector or hollow photon tube. The tool used is a spectrophotometer, which is a device used to determine a compound both quantitatively and qualitatively by measuring absorption or reflection.

The spectrophotometer produces light from a spectrum with a certain wavelength. In a wavelength spectrophotometer, white light can be more selected and this is obtained by decomposers such as prisms, gratings or optical gaps. A spectrophotometer is composed of a continuous visible spectrum source, monochromator, and absorbing cell for the sample solution. It only occurs when electrons move from a low energy level to a higher energy level. Electron displacement is not followed by changes in spin direction, this is known as an excited singlet (Paula [8]).

$$\alpha h\nu = A(h\nu - E_g)^n$$

$$2\alpha d = [\ln (R_{max}-R_{min})/(R-R_{min})]^2$$

Description: α is the absorbance coefficient (cm⁻¹), h is the Planck constant (4.135669 x 10⁻¹⁵ eV · s), ν is the light frequency (Hz), E_g is the bandgap energy (eV),

R is the reflectance value (%), and d is the film thickness (cm).

III. RESULTS AND DISCUSSION

Optic Characteristic

The energy gap is the energy needed by electrons to break covalent bonds so that they can move from the valence band to the conduction band. In semiconductor materials, because the energy gap is narrow if the temperature rises, some electrons in the valence band rise to the conduction band by leaving a hole in the valence band. Electrons that have been in the conduction band as well holes in the valence band will act as load carriers for electric current.

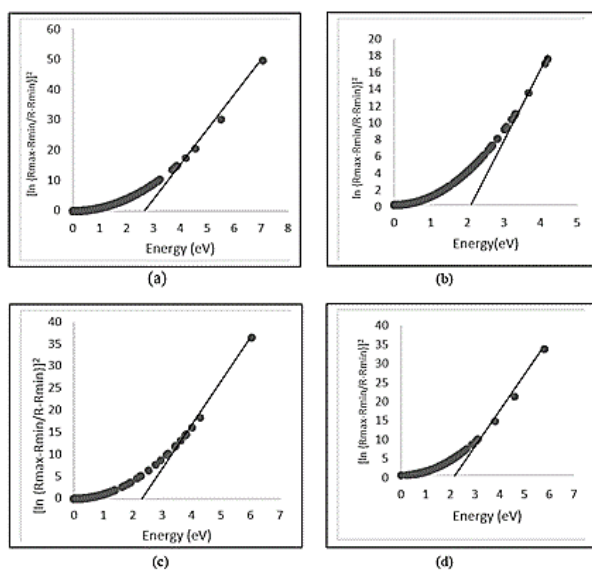


Figure 4 Band gap film energy LiTaO3 proceeded by Rb2O on annealing temperature (a) 650 °C, (b) 700 °C, (c) 750 °C, (d) 800 °C

Calculation of bandgap energy values is done by the reflectance method which uses equation. Bandgap energy obtained from reflectance calculations uses extrapolation $\left[\ln \left(\frac{R_{max}-R_{min}}{R-R_{min}} \right) \right]^2$. The thickness of the LiTaO3 film will vary. This is caused by several factors. First the temperature factor of the substrate. The process of the film caused by atoms diffusing around the substrate which is affected by the temperature of the substrate. When the substrate temperature reaches the optimum temperature, the atoms formed spread evenly on the surface of the substrate thereby increasing the rate of growth of the film. Whereas when the substrate temperature passes the optimum temperature, the atoms formed can be separated from the surface of the substrate (evaporation) which results in the film's growth rate decreasing. Secondly, the CSD method relies on the solution penetration skills on the surface of the spin coating. Third, from the results of the research conducted, there are several parts of the film that

become dry and detach from the substrate thereby reducing the thickness of the film.

The thickness of the film greatly affects the amount of bandgap energy. The variation in annealing temperature also affects the amount of bandgap energy from the LiTaO3 film. The bandgap energy of the LiTaO3 film in this study was obtained in the range of values 2.02-2.98 eV as shown in figure 4. The LiTaO3 film after the annealing process at a temperature of 650 °C, has the highest bandgap energy of 2.98 eV. Large energy is needed on the electrons to be excited from the valence band to the conduction band. Whereas in the LiTaO3 film after an annealing process of 800 °C, the bandgap energy obtained is 2.02 eV. This makes it easier for electrons to be excited from the valence band to the conduction band because the energy needed is not too large.

IV. CONCLUSION

The results shows that the bandgap energy of the LiTaO3 film in the rubidium chamber was obtained in the range of values 2.02-2.98 eV as shown in figure 4. The LiTaO3 film after the annealing process at a temperature of 650 °C, has the highest bandgap energy of 2.98 eV. Large energy is needed on the electrons to be excited from the valence band to the conduction band. Whereas in the LiTaO3 film after an annealing process of 800 °C, the bandgap energy obtained is 2.02 eV. It is easier for electrons to be excited from the valence band to the conduction band because the energy needed is not too large.

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REFERENCES

- [1] Irzaman, A. Fuad, and M. Barmawi. 2001. Spectral Response of Al/Si Photodiodes for IR Sensor. Proceeding Instrumentation, Measurement, and Communications for the Future, Indonesian German Conference (IGC), Bandung: 340 – 342.
- [2] Sutrisno. 1986. Elektronika Teori dan Penerapannya. Bandung: Institut Teknologi Bandung.
- [3] Seo, J.Y, Park S.W. 2004. Chemical Mechanical Planarization Characteristic of Ferroelectric Film for FRAM Applications. *International Journal of Korean Physics society* 45: 769-772.
- [4] Irzaman, Maddu A, Syafutra H dan Ismangil A. 2010. Uji konduktivitas listrik dan dielektrik film tipis lithium tantalate (LiTaO3) yang didadah niobium pentaoksida (Nb2O5) menggunakan metode chemical solution

- deposition. Prosiding Seminar Nasional Fisika, Bandung: 175-183.
- [5] Uchino K. 2000. Ferroelectric Devices. New York: Marcel Dekker, Inc.
- [6] Saito, T, I. 1996. Kimia Anorganik. Permiission of Iwanami Shaten Publisher.
- [7] Malvino A V. 1990. Prinsip-prinsip Elektronika. Jakarta: Salemba Teknika.
- [8] Paula M.V, Nathalie B, Sebastian Z, Pedro F, Maria H.F. 2014. Are lithium niobate (LiNbO₃) and lithium tantalate (LiTaO₃) ferroelectrics bioactive. *Journal Materials Science and Engineering* 39:395-402.
- [9] Irzaman, Darvina Y, Fuad A, Arifin P, Budiman M dan Barmawi M. 2003. Physical and pyroelectric properties of tantalum oxide doped lead zirconium titanate [Pb_{0.9950} (Zr_{0.525} Ti_{0.465} Ta_{0.010}) O₃] thin films and its applications for IR sensor. *Physica Status Solidi (a) Germany* 199: 416-424.
- [10] Kwok, K. N. 1995. Complete Guide to Semiconductor Device. McGraw-Hill, inc. Liu X. 2005. Nanoscale chemical etching of near-stoichiometric lithium tantalite. *Journal Material sains* 97(1):30-38.