Optical Properties of Fe₃O₄ Thin Films Prepared from the Iron Sand by Spin Coating Method

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Abstract. Research on magnetic oxide is growing very rapidly. This magnetic oxide can be found in nature that is in iron sand. One of the beaches in Sumatera Barat containing iron sand is Tiram Beach, Padang Pariaman District, Sumatera Barat. The content of iron sand is generally in the form of magnetic minerals such as magnetite, hematite, and maghemite. Magnetite has superior properties that can be developed into thin films. The purpose of this research is to investigate the optical properties of transmittance, absorbance, reflectance and energy gap from Fe₃O₄ thin films. This type of research is an experimental research. The iron sand obtained from nature is first purified using a permanent magnet, then made in nanoparticle size using HEM-E3D with milling time for 30 hours. After that, the process of making thin film with sol-gel spin coating method. In this research, variation of rotation speed from spin coating is 1000 rpm, 2000 rpm and 3000 rpm. Based on XRD results indicated that the iron sand of Tiram beach contains magnetite minerals and the SEM results show that the thickness of the thin films formed is 25μm, 24μm and 11μm. The characterization tool used for characterizing optical properties is the UV-VIS Spectrophotometer. So it can be concluded that the greater the speed of rotation the thickness of the thin layer will be smaller, resulting in the transmittance and reflectance will be greater, while the absorbance will be smaller. Energy gap obtained from this research is 3,75eV, 3,75eV and 3,74eV. So the average energy gap obtained is 3,75eV.

1. Introduction
In the field of science and technology, one of the most rapidly growing researches today is the study of magnetic oxides. Magnetic oxide can be found in nature that is in iron sand. Magnetic minerals are the main compositions contained in iron sand such as magnetite (Fe₃O₄), hematite (α- Fe₂O₃), and maghemite (γ- Fe₂O₃) [1].

One of the beaches in West Sumatra containing iron sand is Tiram Beach in Padang Pariaman District of West Sumatera. Where based on the results of XRD characterization shows that iron sand Tiram beach mineral oxide containing iron in the form of magnetite in addition to other oxide minerals. Fe₃O₄ in the form of nano has superior properties so has a great opportunity in the field of industry and electronics for the manufacture of thin films, as semiconductor devices. The simplest and often used method of preparation for growing a thin films is the sol-gel method because it has the advantage of high homogeneity of the material [2].
To grow this thin film there are several methods such as DC magnetron sputtering [3], Screen printing [4], and pyrolysis spray [5]. But this method has the disadvantage of requiring sophisticated instruments, requiring high operating costs, and the small formation area of film produced [6].

Coating method such as spin coating is the easiest and simplest growth method. Because this method has advantages such as can produce a thin films that has a pretty good quality and also the cost of making a relatively cheap.

A thin films is a material of nanometer size formed from the arrangement and incorporation of the atomic properties. Growing technique is by way of growth of particles or atoms on the surface of the substrate with the magnitude of thickness in the order of micrometer. This thin layer is made of metal, inorganic, organic, or organic metal mixture and has the properties of semiconductors, insulators and conductors. The thin films has optical properties that are heavily dependent on the energy gap of the properties of the thin film material to be deposited.

The optical properties of the material are the response form of the material to the electromagnetic especially visible light. The UV-VIS spectrophotometer is used to look at the optical properties of the material, when light is passed on the material then some of this light will be reflected, some will be absorbed, transmitted and scattered, which is mathematically. The incoming light can be written in the equation:

\[ I_o = R_c + T + A_b + S = 100\% \]

With \( I_o \) is the intensity of light coming, \( R_c \) is reflectance, \( T \) is transmittance, \( A_b \) is absorbance and \( S \) is scattered. The energy gap is the amount of energy required to move from the valence band to the conduction band. The energy gap can be searched using UV-Vis diffuse reflectance spectrophotometry based on the intensity measurements that are reflected by the sample. To know the energy gap can be used Kubelka-Munk method. Energy gap is obtained from the graph of the intermediate relationship:

\[ h\nu \text{ (eV)} = (F(R'\infty)h\nu)^{1/2} \]

\( E_g \) is an energy gap (eV), \( h \) is planck constant (6,626x10^{-34} Js), \( c \) is the speed of light (3x10^8m/s) and \( \lambda \) is the wavelength (nm). The amount of \( h\nu \) at the moment \((F(R'\infty)h\nu)^{1/2} = 0\), Obtained from the linear regression equation is the amount of energy gap [7].

Fe\textsubscript{3}O\textsubscript{4} is a material with semiconductor material properties, reported by Ghandoor, H.E, et al, 2012 [8]. Semiconductor materials are materials having electrical conductivity between conductors and insulators with large energy gaps < 6 eV [9].

2. Experimental

This research is a type of experimental research, with the flow diagram shown in Figure 1. The sample used is iron sand samples taken from Tiram’s Beach in Padang Pariaman District, West Sumatra. In this research, the tools used are HEM-E3D, magnetic stirrer, spin coating, furnace, permanent magnet, digital scales, spatula, measuring cylinder, erlenmeyer tube, beaker, stirrer, drop pipette, glass substrate and UV-VIS spectrophotometer. While the material is iron sand, aquabidest, oxalic acid, nitric acid and ethylene glycol.

The shape of the iron sand of Tiram’s Beach is shown in Figure 2. Iron sand is then purified by pulling iron sand using permanent magnet 30 times to separate iron sand (ferrite) with other material mixed in iron sand (residue). After that iron sand washed using aquabidest. It is then dried and retracted using a permanent magnet 20 times. Then the sample is milling using HEM-E3D for 30 hours. Which shows that at milling time 30 hours visible loss of hematite phase so that only one phase left is Fe\textsubscript{3}O\textsubscript{4}.

After completion of the process of purification and manufacture of nanoparticles Fe\textsubscript{3}O\textsubscript{4}. Furthermore, the process of making a thin layer with spin coating is prepared using sol-gel method with precursor (Fe(NO\textsubscript{3})\textsubscript{3}·9H\textsubscript{2}O).
Precursor (Fe(NO$_3$)$_3$·9H$_2$O), prepared at a temperature of 110°C by reacting 17.4 gr Fe$_3$O$_4$ and 4.5 gr oxalic acid (C$_2$H$_2$O$_4$) with 42 mL of nitric acid (HNO$_3$). Furthermore, the process of sol-gel synthesis of magnetite as in [10], by dissolving 14 gr precursor produced with 55 gr ethylene glycol. The solution is then heated at a temperature of 80°C for 2 hours while stirring using a magnetic stirrer at a constant speed.

Then a thin films of Fe$_3$O$_4$ is grown using a spin coating on a glass substrate that has been using ethanol. The magnetite gel solution is dripped on the glass substrate and then rotated with a spin coating velocity variation. Variations of spin coating speed used are 1000 rpm, 2000 rpm and 3000 rpm with 60 seconds duration. The length of time the coatings were used according to previous research conducted by Eken, 2009 [10]. Furthermore, each thin films formed was dried at 110°C for 15 minutes, after which it was annealed at 300°C, then characterized by UV-VIS Spectrophotometer.
3. Result and discussion

Based on the result of characterization of Fe₃O₄ thin film using UV-VIS spectrophotometer, optical properties such as transmittance, absorbance and reflectance value can be obtained. The SEM results show that the thickness of the thin film for the rotation speed of 1000 rpm, 2000 rpm and 3000 rpm respectively is 25μm, 24μm and 11μm.

The results of the transmittance measurements of the Fe₃O₄ thin film at a rotation speed of 1000 rpm, 2000 rpm and 3000 rpm are respectively shown by Figure 3.

![Graph of wavelength relation to transmittance at thin films at speed (a) 1000 rpm (b) 2000 rpm (c) 3000 rpm.](image)

The most transmitted wavelength range is in the range 470-780 nm, with the highest transmittance percentage at 31.2%, 31.3% and 31.4% - 32.7%. The highest transmittance peaks were 34.5% at 600 nm, 35.5% at wavelength 650-640 nm, and 37.5% at wavelength 710 nm. The larger the rotational speed the transmittance value will increase. This is because the thickness is smaller.

The results of the absorbance measurements of the Fe₃O₄ thin films by Figure 4.

The amount of absorbance value successively in the wavelength range between 200-780 nm that is equal to 96.721% - 31.247%, 95.428% - 33.785% and 93.54% - 33.551%. The most abundant wavelength range is in the range of 200-280 nm, with the highest absorbance percentage of 96.721% - 100%, 95.428% - 95.207% and 93.54% - 93.109%. It can be seen that the absorbance will decrease with the reduced thickness of the thin film. This is in accordance with Beer’s Law which states that the...
magnitude of the absorbance value is proportional to the thickness of the material / medium penetrated by light. The result of the reflectance measurement of the Fe₃O₄ thin film is shown in Figure. 5.

**Figure 4.** Graph of wavelength relation to absorbance in thin film at speed (a) 1000 rpm (b) 2000 rpm (c) 3000 rpm

**Figure 5.** Graph of the wavelength relation to the reflectance at the thin film at a rate of (a) 1000 rpm (b) 2000 rpm (c) 3000 rpm.
The magnitude of the reflectance value in the wavelength range between 200-780 nm is 33.2%, 33.7% and 34.2%. The most reflected wavelength range is in the range 490-780 nm, with the highest percentage of transmission is 32.3% - 33.2%, 32.3% - 33.7% and 32.3% - 34.2%. The highest peak reflectance was 36.5% at 640 nm, 37% at 620 nm, 39.4% at 665 nm wavelength. Based on the above results indicate that if the spin coating rotation is greater then the reflectance value will also be greater. Because the rotational speed resulted in the smaller film thickness. So the value of reflectance will be greater.

The decrease of thickness of a thin films, then the absorbance is also greater, while the reflectance or the forwarded will be smaller and vice versa, the thinner the thickness the greater the light is transmitted and reflected, while the light absorbed will be smaller. The magnitude of the energy gap of the Fe$_3$O$_4$ thin film is shown in Figure 6.

![Figure 6](image-url)

**Figure 6.** Graph of energy gap at a thin films with speed (a) 1000 rpm (b) 2000 rpm (c) 3000 rpm

The purpose of analyzing the energy gap of a material serves to determine a material that is conductor, semiconductor or insulator. The smaller the energy gap value of a material the energy band gap (between the conduction band and the valence band) becomes smaller, so that the electrons in the valence band will be easier to jump (excitation) to the higher band of conduction band [11]. The magnitude of the Fe$_3$O$_4$ thin films energy gap value at 1000 rpm, 2000 rpm and 3000 rpm is 3.75 eV,
3.75 eV and 3.74 eV, respectively. So the average value of the energy gap in the Fe$_3$O$_4$ thin films is 3.75 eV.

4. Conclusion
Based on the research, the optical properties of the Fe$_3$O$_4$ thin films are transmittance, absorbance, reflectance and energy gap of Fe$_3$O$_4$. This shows that the rotational velocity affects the transmittance, absorbance and reflectance. The greater the rotational speed the transmittance and the reflectance will also be greater, while the absorbance will decrease. Because the thickness of the thin films will decrease with increasing rotational speed. While the amount of energy gap obtained is 3.75 eV, 3.75 eV and 3.74 eV. So the average value of energy gap on Fe$_3$O$_4$ thin films is 3.75 eV.

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