Analysis of Crystal Structure of Fe$_3$O$_4$ Thin Films Based on Iron Sand Growth by Spin Coating Method

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Abstract. Recently, iron sand used as one of base materials in the steel industry. However, the content of iron sand can be used as starting materials in sensor technology in the form of thin films. In this paper, we report the analysis of crystal structure of magnetite thin film based on iron sand from Tiram’s Beach. The magnetic content of sand separated by a permanent magnet, then it was milled at 30 hours milling time. In order to increase the purity of magnetite, it washed after milling using aquades under magnetic separation by a magnet permanent. The thin film has been prepared using iron (III) nitrate by sol–gel technique. The precursor is resulted by dissolving magnetite in oxalic acid and nitric acid. Then, solution of iron (III) nitrate dissolved in ethylene glycol was applied on glass substrates by spin coating. The X-Ray Diffraction is operated thin film characterization. The structure of magnetite has been studied based on X-Ray Peaks that correspond to magnetite content of thin films.

1. Introduction
Iron is the second most plentiful metal in the ground and present in sediment form. The sediment of iron contained in sedimentary rocks in form of sand, known as iron sand. Distribution of iron sand in Indonesia have encountered in various islands began the West Coast of Sumatra, Kalimantan, Sulawesi, region of Nusatenggara, Maluku Islands and South Beach of Java [1].

The iron sand is commonly called as black sands due to its own colour. The colour is affected by the iron oxides content like magnetite (Fe$_3$O$_4$), maghemite ($\gamma$-Fe$_2$O$_3$) and hematite ($\alpha$-Fe$_2$O$_3$). Magnetite (Fe$_3$O$_4$) has become a priority in research activities because it has more much advantages compared with the other mineral compounds. The structure of Fe$_3$O$_4$ formed in cubic inverse spinel. According to ICDD with the code 01-089-0688known that Fe$_3$O$_4$ has a space group F d-3m with No. 227 and the same lattice parameter $a = b = c$ of 8.396 Å and the angle $\alpha = \beta = \gamma = 90^\circ$ [2]. Detail of the structure of Fe$_3$O$_4$ is shown in Figure 1.

Recently, Research on magnetic oxide has progressed rapidly. Nanostructure of oxide magnetic is important in development of advance and new functional materials [3]. Magnetic characteristic of magnetite is superior in respond external magnetic field compared to the other magnetic compounds contained in the iron sands [4]. Magnetite is a potential candidate as materials for ceramics, energy storage, magnetic data storage, ferofluids, and magnetic sensor.

Thin film is a layer made from organic, inorganic, metal, or a compound of an organic metal material which can have physical properties as conductors, semiconductors, superconductors, and insulator. The film is made using atomic or particle deposition technique. The thickness of film can be
obtained in micrometer even nanometer scale. The common characteristic of thin film is different with powder or bulk materials, it caused by the differences of preparation process, composition, morphology and structure. Various materials have potential as semiconductors, photo-catalyst, magnetic storage and the dielectric have been studied. The magnetite film can be used as a data storage memory, magnetic sensors for mitigation of earthquake disaster and for DNA detection [5].

The following physical thin film growth method: sputtering [2], DC magnetron sputtering [6], spray pyrolysis [7] slip casting [8], electrophoresis [9], and screen printing [10] have disadvantage like lack of deposition areas, requiring sophisticated instruments, high operating costs, and complicated cleaning systems [11]. Chemical method such as chemical vapour deposition has inadequate for film production on a large scale because it requires complicated additional tools [12].

The coating method is the simplest and easiest method in thin film deposition. Different properties of thin film obtained in difference type of coating methods. Spin coating is one of the coating methods in which deposition done over the substrate at a certain rotary speed. Solution or gel that dropped above the substrate flow toward the edge cause of centripetal force that resulted by rotation. Then the solvent evaporated in which condensation reaction take place. These processes will result solid thin film above the substrate. Spin coating disc sketched in Figure 2. The coated gel is produced using sol-gel technique involving chemical process such as hydrolysis and condensation reactions. In addition, the sol-gel technique is easy to produce homogenous materials and the composition of materials can be controlled as desired [13]. Spin coating process conducted in four steps consisting of deposition, spin-up and spin-off and evaporation. These steps will determine the thickness of thin film [14]. Spin coating process can be explained using Figure 3.
The first step of coating is dripping or flowing of the gel on the substrate. At the deposition step, the substrate has not been rotated. Then at the next step the substrate begins to rotate. Since centrifugal force resulted from circular motion the liquid become dispersed out of the disc centre toward the edge. At this step the substrate accelerates and the next two steps the rotation rate begins to be constant, meaning no angular acceleration on the substrate. At the spin-off step an amount of excess liquid or gel will go to the edge and eventually detached. The thinner film deposited the less droplets are wasted. This affected by the addition of flow resistance and viscosity when the layer gets thinner. The last step is evaporation as the significant process of depletion film [15].

One of important things in film deposition is thickness caused it will affect the quality of crystal, different thickness will produce different crystal quality. Thin film thickness determined by coated angular velocity used. The velocity is one of the most important factors in the coating process. The velocity will affect the angle of the centrifugal force on the liquid. For more specific, the angular velocity will determine the crystal structure [16]. In this paper will discuss the influence of the coated angular velocity on crystal structure of Fe₃O₄ thin films.

2. Experimental
The iron sand is taken from Tiram’s Beach, Padang Pariaman West Sumatra, which then separate using magnetic stick for 30 times, this process aims to sort out the iron content from impurities. Then it washed using aquades, dried and retracted using a permanent magnet for 20 times. The iron sand 6 gr is milled using HEM-E3D for 30 hours. Then it washed using distilled water to purge or eliminate impurities. Drying introduced as final purification process.
In this study, \( \text{Fe}_3\text{O}_4 \) thin film is prepared using sol-gel techniques with precursor iron (III) nitrate \( (\text{Fe(NO}_3)_3.9\text{H}_2\text{O}) \). The precursor resulted by dissolving 17.4 gr magnetite in oxalic acid 4.5 gr \( (\text{C}_2\text{H}_2\text{O}_4) \) and nitric acid \( (\text{HNO}_3) \) 42 mL, at \( 110^\circ\text{C} \). Then, solution of \( (\text{Fe(NO}_3)_3.9\text{H}_2\text{O}) \) dissolved in ethylene glycol at \( 80^\circ\text{C} \) for 2 h under constant stirring. The coating solution was dropped onto glass substrate, which was rotated at 1000 rpm, 1500 rpm, 2000 rpm, 2500 rpm and 3000 rpm. The coating process conducted in 60 s. After deposition by spin coating, the film was dried at \( 110^\circ\text{C} \) for 15 minutes and followed annealing process at \( 300^\circ\text{C} \), for 3.5 hours. Magnetite thin films then characterized using X-Ray Diffraction (XRD) to analyze the crystal structure of magnetite. The results then compared with standard ICDD for magnetite.

3. Result and discussion

The peak intensity of XRD graph at plane (311) is more dominant than the other planes of \( \text{Fe}_3\text{O}_4 \) crystals (see Fig. 4). According to ICDD standards (International Center of Diffraction Data), the orientation intensity of the crystal plane (311) is higher than the other orientations of magnetite crystal. The XRD data also give information that magnetite phase lattice parameters ranged from 0.8366 nm to 0.8367 nm, slightly lower than standard value of 0.84045 nm. The graph also show the presence of a peak that correspond to nitric acid \( (\text{HNO}_3) \) at \( 2\theta = 27.90^\circ \) at almost of XRD Graphs except at 200 rpm. Nitric acid \( (\text{HNO}_3) \) used as reagent in synthesis of precursors \( (\text{Fe(NO}_3)_3.9\text{H}_2\text{O}) \). An amount of nitric acid does not react completely with magnetite powder so it still leaves in the solution. Although thin films have been given heat processes such as drying and annealing, but not enough to evaporate all of the nitric acid.

The XRD results show the magnetite films grown in polycrystalline crystal indicated by three until six magnetite peaks at each X-Ray pattern with variation of angular velocity. Yet the crystal of thin films at 2000 rpm having three magnetite peaks less than the others. This mean that order of crystal orientation at 2000 rpm is more uniform than the others. The film deposited at 2000 rpm also has higher purity rate compared to the others. This statement is supported by XRD data showing no peak \( \text{HNO}_3 \) at 2000 rpm. So it can be conclude that magnetite thin film that deposited at 2000 rpm has a better quality of crystal compared to the other thin films.

![Figure 4. X-Ray Diffraction Pattern of magnetite thin films.](image)

Effect of coating velocity on \( \text{Fe}_3\text{O}_4 \) crystal structure can be explained from the diffraction pattern produced at each variation of angular velocity. The results of XRD (Figure 4) show that number of
orientation intensity of the Fe₃O₄ crystal planes decreases as increasing the angular velocity, 1000 rpm up to 1500 rpm and 2500 rpm up to 3000 rpm. Similar results were also found in the PZT thin film study [17], that found decreasing the orientation intensity of the crystal planes of PZT thin film. The decrease in the intensity of the crystal orientation of the thin film is due to the higher angular velocity rate resulting high magnitude of centrifugal force. So amount of gel scattered out the substrate. This means that the number atoms in film-deposition decreased, so the probability of crystalline formation decreases that affects the intensity of XRD results[9].

XRD graphs for certain angular velocity indicate an increase of intensity value. The increasing intensity, 1500 rpm up to 2500 rpm, caused by mass of gel dropped is not the same (due to difficulty in microgram scale) so that the number of Fe₃O₄ atoms dropped is different for each coating process. Increasing of Fe₃O₄ gel mass make more gel attached to the substrate in the coating process. As a result, the number of the atoms making up the crystalline plane of the Fe₃O₄ thin films increases, so the probability of Fe₃O₄ formation also increases and directly affects the peak intensity. There are factors that cause the result of thin films characterization is not obey to theory: homogeneity of thin films, flatness of thin films that is uneven, and the difference in the mass of dropped gel[18].

Not only the velocity effect the intensity of the crystal orientation, but also it caused change of FWHM at each diffraction peak. FWHM is a function of the particle size. So difference of FWHM gives different crystallite size. Diameter of crystallite (D) expressed in the following Scherrer equation [19].

\[
D = \frac{\lambda}{B \cos \theta_B}
\]  

(1)

The microstrain (e) satisfies the equation [18],

\[
e = \frac{b}{4 \tan \theta_B}
\]  

(2)

\(\lambda\) (lambda) is the wavelength 1.54 Å, \(\theta_B\) is the Bragg angle, B is FWHM of the selected peak, and K is the material constant that value is less than one, Commonly K ~ 0.9. The FWHM value determines the size of the crystals and the value of the microstrain of the magnetite crystals formed. These changes can be seen in the graph of the relation of the angular velocity to the crystallite size and the microstrain in Figure 5.

![Figure 5. Effect angular velocity of spin coating on crystallite size and microstrain of magnetite thin film.](image)
The average magnetite crystallite size decreases at 1000 rpm up to 1500 rpm and at 2500 rpm and 3000 rpm. Decreased crystal size correlates with decreasing film thickness. Study of Cobalt Ferrite [3] also found that the crystalline size becomes decrease by depletion of film thickness from 48 to 40 nm.

The change in FWHM values also affects the value of the microstrains. The microstrain of the magnetite thin films shows an increase in value at 1000 rpm up to 1500 rpm and at 2500 rpm and 3000 rpm. This is due to the diffraction peaks marked by the increase of the FWHM value. On the other hand, the angular velocity of 1500 rpm to 2500 rpm indicates a decrease in the value of microstrains caused by the FWHM value is getting smaller.

4. Conclusion
The results of this study indicate that at angular velocity of 1000 rpm to 1500 rpm and at 2500 rpm to 3000 rpm there is a decrease in the XRD peak intensity value of crystal field. On the other hand, the microstrains have increased in that range. The XRD graph also shows a thin film grown at 2000 rpm has better crystal quality compared to other thin layers.

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