Preparation and characterization of thin film CoFe$_2$O$_4$/Zn/CoFe$_2$O$_4$ by using spin-coating method

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Abstract. Research has been conducted on the manufacture of CoFe$_2$O$_4$/Zn/CoFe$_2$O$_4$ thin films using sol gel-spin coating method. This study aims to look at the effect of rotational speed on optical properties and electrical properties, and to find the highest GMR ratio. Making CoFe$_2$O$_4$ uses Co$^{2+}$ precursors and Fe$^{3+}$ precursors with a mole ratio of 1: 2, dissolved with ethyl alcohol. The Zn precursor was made with a concentration of 0.5 M from Powder (CH$_3$COO)$_2$Zn. 2H$_2$O dissolved with ethyl alcohol. The rotation speed variations used are at 2000 rpm, 2500 rpm, 3000 rpm, 3500 rpm and 4000 rpm. The thin layer of GMR is made with a sandwich structure. CoFe$_2$O$_4$/Zn/CoFe$_2$O$_4$ thin films with variations in rotational speed were tested for electrical properties using the 4-point probe system method and characterized using X-Ray Diffraction, Scanning Electron Microscopy (SEM), and UV-Vis Specrophotometer. Based on the testing of the electrical properties obtained the lowest resistance and resistivity values at 2000 rpm rotation speed, where the faster the rotational speed is used, the greater the resistance and resistivity values. The highest GMR ratio obtained was 53.5%. Measurement results with Scanning Electron Microscopy (SEM) obtained layer thickness of 3.5 μm.

1. Introduction

Ferrite nanoparticles have attracted the attention of many researchers because of their wide application in various fields such as biomedicine, wastewater treatment, catalysts and electronic devices (Kafeni et al, 2017). One of the most widely studied Ferrite nanoparticles currently being studied is cobalt ferrite nanoparticles (CoFe$_2$O$_4$) nanoparticles have the potential to be developed in various technology applications such as catalysts, soft magnets, biosensors, and magnetic fluids (Siswanto et al, 2014), this is because they have a higher anisotropy constant than Fe$_3$O$_4$ (magnetite) and γ- Fe$_2$O$_3$ (maghemite) (Castillo, 2005). By controlling the material size, CoFe$_2$O$_4$ will have superparamagnetic properties that have high magnetization when given an external magnetic field, even though it has zero average magnetization without an external field (Mattei et al, 2007).

There are several techniques in the manufacture of CoFe$_2$O$_4$ nanoparticles which include (1) Co-precipitation, (2) thermal decomposition, (3) hydrothermal, (4) sol gel, (5) solvothermal, (6) sonochemistry, (7) vapor deposition, where the first 4 are more popular (Kafeni et al., 2017). Making
CoFe$_2$O$_4$ using the sol gel method has several advantages, including operating at low temperatures, low costs and does not require special instruments. The sol gel method consists of several coating techniques, namely spin coating, dip-coating, and spray coating. Spin coating method is a method of growing thin layers on the substrate by dripping liquid into the center of the rotating substrate (Huang, 2003). This method is often used by researchers because the process is easy, the resulting thin layer has a fairly high homogeneity and thickness of the coating, desired can be controlled based on the time and rotation speed of the spin coater device.

The thickness of CoFe$_2$O$_4$ thin layer can be controlled based on the time and rotation speed of the spin coater device. Rotational speed is one of the most important factors in the spin coating process (Doyle, 2003). Generally a high rotational speed and a longer turnaround time produce a thinner layer. Based on this theory, the authors will use the parameters of spin coating speed variation to see the changes that occur in the thin layer of CoFe$_2$O$_4$. CoFe$_2$O$_4$ is one of the materials for the manufacture of a thin layer of Giant-Magnetoresistance (GMR). The basic principle of Giant magnetoresistance is the change in resistance in the multilayer layer which when given an external magnetic field is the effect of quantum mechanics which depends on the scattering spin phenomenon. The thickness of GMR material layers must be made in nanometer order (Djamal and Yulkifli, 2009).

There are 3 types of structures for GMR thin layers, namely: (1) sandwich structure, (2) spin valve structure, and (3) multilayer structure. Each structure has a different magnetoresistance (MR) effect. Sandwich structure is the basic structure of GMR which consists of three layers with ferromagnetic / nonmagnetic / ferromagnetic material arrangement (FM-NM-FM). Previously, GMR research on sandwich structure using CoFe$_2$O$_4$ as ferromagnetic material has been done by Ramli et al, where the method used is DC magnetron sputtering and the maximum GMR ratio at room temperature obtained is 70% (Ramli et al, 2016). Based on what the authors know, there is no research on GMR production with the composition of CoFe$_2$O$_4$/Zn/CoFe$_2$O$_4$ using sol gel spin coating method. Based on the description above, the writer conducted a study entitled "Preparation and Characterization of Thin Film CoFe$_2$O$_4$/Zn/CoFe$_2$O$_4$ By Using Spin-Coating Method".

2. Method

The preparation of CoFe$_2$O$_4$/Zn/CoFe$_2$O$_4$ thin film was carried out using sol gel-spin coating method. The research procedure was started by making CoFe$_2$O$_4$ 0.25 M precursor with the ratio of Co$^{2+}$ (Co(NO$_3$)$_2$·6H$_2$O precursors and Fe$^{2+}$ (Fe(NO$_3$)$_2$·9H$_2$O precursors) is 1:2, dissolved with ethyl alcohol. Then made of 0.5 M Zn precursor from Powder (CH$_3$COO)$_2$Zn·2H$_2$O and dissolved with ethyl alcohol. The glass plate will be coated with the above material cleaned first using acetone. Nano Particles CoFe$_2$O$_4$ is coated into a glass plate through spin coating method with coating rotation variations: 2000 rpm, 2500 rpm, 3000 rpm, 3500 rpm, 400 rpm for 30 seconds, then oven at 100°C for 1 hour, calcined at 300°C for 3 clock (post-annealing) and at 500°C for 1 hour (post-annealing). A thin layer of Giant Magnetoresistance (GMR) with sandwich structure is made by means of a glass plate coated with CoFe$_2$O$_4$ coated again with ZnO precursor and then oven at 100°C for 1 hour, calcined at 300°C for 3 hours (pre-annealing) and at a temperature 500°C (post-annealing) for 1 hour. Next, it was coated again with CoFe$_2$O$_4$ on top and calcined with the same temperature variation. Furthermore it was characterized by XRD, SEM, and electrical properties.

3. Result And Discussion

CoFe2O4/ Zn / CoFe2O4 thin layer has been successfully grown on glass substrate using the spin-coating technique through a sol-gel process. Rotational speed variations were carried out to obtain optimum results in making CoFe2O4/ Zn / CoFe2O4 thin layers. CoFe2O4/ Zn / CoFe2O4 thin layer samples were characterized using XRD to determine the structure and size of crystals, SEM to determine the surface morphology and thickness of the layers, and the electrical properties using method of 4-point probe systems to find the resistance and resistivity.

3.1. X-Ray Difraction Characterization
The spectrum XRD of thin layer of CoFe$_2$O$_4$/Zn/CoFe$_2$O$_4$ can be seen in Figure 1.

**Figure 1.** Spectrum XRD Thin Layer of CoFe$_2$O$_4$/Zn/CoFe$_2$O$_4$

Figure 1 shows the XRD results of CoFe$_2$O$_4$/Zn/CoFe$_2$O$_4$ thin film in the form of CoFe$_2$O$_4$ characteristic peaks with the highest intensity at an angle of $2\theta = 62.4156^\circ$ with a diffraction pattern (440), while the highest intensity of ZnO characteristic peaks is at angle $2\theta = 35.9672^\circ$ with diffraction pattern (101). In Figure 4 it also shows that no other peaks such as cobalt oxide or iron oxide appear which indicates that pure CoFe$_2$O$_4$/Zn/CoFe$_2$O$_4$ crystals have been formed. Overall data from the XRD CoFe$_2$O$_4$ and ZnO test results can be seen in tables 1 and 2.

**Table 1.** Data on XRD CoFe$_2$O$_4$ Test results

| No | $2\theta$   | FWHM  | Rel. Int (%) | Crystal Size | hkl |
|----|-------------|-------|--------------|--------------|-----|
| 1. | 29.7467     | 0.3070| 20.43        | 27.85 nm     | 220 |
| 2. | 47.2760     | 0.4093| 14.31        | 22.28 nm     | 331 |
| 3. | 62.4156     | 0.5628| 22.78        | 17.24 nm     | 440 |

**Table 2.** Data on XRD ZnO Test Results

| No | $2\theta$   | FWHM  | Rel. Int (%) | Crystal Size | hkl |
|----|-------------|-------|--------------|--------------|-----|
| 1. | 31.3985     | 0.3070| 53.77        | 27.85 nm     | 110 |
| 2. | 34.1412     | 0.2047| 52.85        | 42.59 nm     | 002 |
| 3. | 35.9672     | 0.2303| 100.0        | 38.11 nm     | 101 |
| 4. | 47.2760     | 0.4093| 14.31        | 22.28 nm     | 102 |
| 5. | 56.4094     | 0.4093| 27.44        | 22.28 nm     | 110 |
| 6. | 62.4156     | 0.5628| 22.78        | 17.24 nm     | 103 |
| 7. | 67.6031     | 0.6140| 9.97         | 10.27 nm     | 112 |
| 8. | 68.9067     | 0.4093| 8.71         | 24.54 nm     | 201 |
| 9. | 72.6050     | 0.3070| 20.6         | 32.91 nm     | 004 |

Based on the results obtained, the detected peak can be known as CoFe$_2$O$_4$ crystals with the formation of a single phase with spinel ferrite structures that have cubic crystal structure with Fd3m group space, this is in accordance with the existing theory (Yadav et al., 2016). ZnO peaks that are detected form a hexagonal structure with group space P63mc.

3.2. **SEM Characterization**

To find out the surface morphology and thickness of CoFe$_2$O$_4$/Zn/CoFe$_2$O$_4$ thin layer it can be seen using a SEM (Scanning Electron Microscope) instrument. The thickness of the CoFe$_2$O$_4$/Zn/CoFe$_2$O$_4$ thin layer is one of the factors that affect the quality of the thin layer.
Figure 2. SEM Photos of Surface CoFe2O4/Zn/CoFe2O4 Thin Layer with 10,000 x Magnification

Figure 2 is a surface morphological form of CoFe2O4 / Zn / CoFe2O4 thin layer with various magnifications grown at 2500 rpm. In the picture it can be seen that the magnetic gel phase has formed on glass substrates, but there are several points of the imaging that have not completely transformed magnetic powder form to gel form. The thickness of the CoFe2O4 / Zn / CoFe2O4 thin layer can be seen in Figure 3.

Figure 3. Imaging results of cross section CoFe2O4/Zn/CoFe2O4 thin layer

Figure 3 shows the results of cross section imaging CoFe2O4/Zn/CoFe2O4 thin layer which shows a change in the size of the layer thickness produced. The average thickness of CoFe2O4 / Zn / CoFe2O4 thin film which was successfully coated on the surface of the glass substrate was 3.5 μm.

4. UV-Vis Characterization

The results of the graph measuring the absorbance of wavelengths in the CoFe2O4 / Zn / CoFe2O4 thin layer can be seen in Figure 4.
In Figure 4, we can see that the absorbance is at λ 292 nm with an absorptive value of 2.3631 A. Absorbance causes the excitation of electrons from the valence band of the conduction band. Where when a light with a certain wavelength about a material, then light at a certain wavelength that will be absorbed. After absorbing the light there will be an electron transfer from the ground state to the excited state. This absorbance is related to energy gap. Because absorbance shows the amount of light that can be absorbed by a material used for electrons can move from the conduction band to the valence band, this is also called the energy gap.

5. Electrical Properties Characterization

The following is a graph of the relationship between rotational speed and resistance and the relationship between rotational speed and resistivity without the provision of a magnetic field which can be seen in Figure 5.

Based on the results obtained, the resistance and resistivity values of the lowest CoFe2O4 / Zn / CoFe2O4 thin layer were obtained at 2000 rpm rotation speed and the higher the rotational speed, the greater the resistance value. This result can be caused by the influence of the viscosity of the solution used is low, so that at high speeds the thin layer will become less uniform and more solution will be lost. Characterization of electricity in a thin layer of GMR using the 4-point probe system method is used to find the resistance and resistivity values of the sample. In this study, samples were used with 5 variations of rotation speed measured by 2 conditions, namely without the provision of an external magnetic field to obtain ρ (H = 0) and by providing an external magnetic field to obtain ρ (H). From the experiments it was found that the resistance and resistivity values ρ (H) were smaller than ρ (H = 0). This is due to the existence of superparamagnetic properties in samples that will have high magnetization when given an external magnetic field, but have zero average magnetization without
6. Conclusion
In this study, a CoFe2O4 / Zn / CoFe2O4 thin layer was successfully made using the Sol Gel-Spin Coating method, this was proven by XRD, SEM, and electrical properties. 2000 rpm, where the higher the rotation speed, the greater the resistance and resistivity values. The highest GMR ratio obtained was 53.5% (negative magnetoresistance).

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