

Spectroscopy, Optical Properties of NiFe₂O₄ Nanoparticles Prepared by Co-Sputtering Technique in Different Gasses Mixture Ratio

Baha T. Chiad, Ruaa A. Mohammed

Abstract— We report the optical properties of the inverse spinel ferrite NiFe₂O₄. All the films were deposited on Si (100) substrate by co-sputtering technique. We carried out variable gasses mixture argon to oxygen for transmittance measurements on the thin films to investigate the optical properties. Thicknesses of the films determined by x-ray reflectivity vary from 73nm to 176nm as the varies of gas mixture from 30:70 to 10:90 (Ar:O₂) respectively. The films were characterized by Fourier transform infrared (FTIR), Optical properties were studied by UV-vis reflectance spectra. The value of optical indirect band gap ranging between (1.779-1.785eV) was found to be independent of thickness of the film. The absorption spectra of NiFe₂O₄ nanoparticles for the prepared sample in the spectral uv- visible region 400-700 was obtained.

Index Terms— Nickel Ferrite, Co-Sputtering, FTIR, UV-vis spectroscopy.

I. INTRODUCTION

Ferrites are a very important group of magnetic materials due to their extensive use in a wide range of applications, such as ferrofluids, radar absorbing coatings, waveguides in the gigahertz region, biomedical and clinical devices, magnetic resonance imaging, oxyfuel technology, gas sensors, for the fabrication of magnetic cores of read/write heads for high-speed digital tapes or for disc recording [1-5]. NFO is one of the most attracting material of spinel ferrite due to their interesting and important properties such as high electrical resistivity, large expansion coefficient, high saturation magnetization, high permeability and low eddy current loss, etc. In view of these properties, it is used as one of the best microwave absorber materials. This type of ferrites is also used in various forms such as nanoparticles, nanowires, nanotubes, thin films and so on [6-7]. Several techniques are used for the preparation of ferrite particles, such as citric acid combustion method, sol-gel method, organic gel thermal decomposition method, hydrothermal method, co-precipitation method [8-9]. Sol-gel is a simple method that has advantages, such as simple preparation route, with precisely controlled relative stoichiometric ratios, which produces ultrafine and homogeneous powders [9]. Spinel ferrites are a large important class of

materials with the general formula MFe₂O₄, where M is a divalent cation. Nickel ferrite, NiFe₂O₄ (NFO), is an inverse spinel in which the tetrahedral sites (A) are occupied by Fe²⁺ and Ni²⁺ ions [10,11].

There are various growth parameters that affect the microstructure of the film such as substrate temperature during deposition, thermal expansion coefficient and lattice mismatch between the film and substrate, deposition time, distance between the target and substrate, gasses mixture etc. Size and surface effects lead to strong deviations from bulk properties, which additionally depend on the sample thickness and stoichiometry [10]. The thin films of these inverse ferrites display relatively weaker physical properties compare to the bulk counterparts [12,13].

In this study, highly crystalline nanosized nickel ferrite thin film was prepared by spray co-sputtering techniques, (NiFe₂O₄) nanostructures at low pressures with employment of concentric Ni and Fe targets. The structural characteristics of the prepared nanostructures are studied.

II. EXPERIMENT

The dc plasma sputtering system used in this work contains of a vacuum chamber, two discharge electrodes, vacuum pumps, and cooling and heating facilities.

The chamber could be evacuated down to 10⁻³ mbar by a rotary pump and to 10⁻⁵ mbar by a diffusion pump. The base vacuum was determined by the purpose of the discharge process. The inter-electrode distance was 4cm. The two targets of highly pure nickel (Ni, 0.9999) and iron (Fe, 0.999) were mounted on the cathode with some geometrical arrangement suitable for the work, as shown in Fig. (1) while the substrate on the anode, the gasses mixture was controlled by mixture unit before enter to the chambers. Highly-pure oxygen gas was flowing to the chamber throughout needle valve to represent the reactive gas required to form the compound of nickel ferrite. Thickness measurements on the prepared film samples were performed by the laser interference method. The films thickness was measured and characterized by Fourier-Transform Infrared (FTIR) Spectroscopy. Then the spectral measurement for the prepared sample was measured to obtain the value of the optical energy band gap.

Baha T. Chiad science of physics, Baghdad/ science / dr. baha, Baghdad Iraq).

Ruua A. Mohammed, science of physics, Baghdad/ science / mr.s ruua Baghdad Iraq).

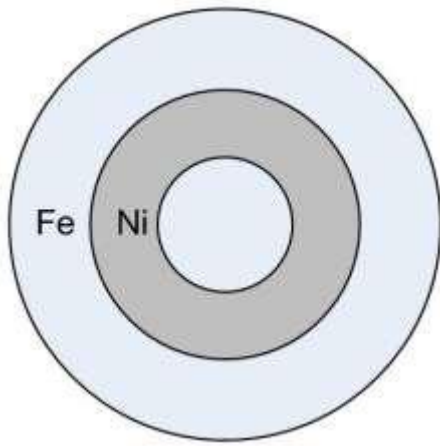


fig.1

III. RESULT AND DISSECTION :

The film thickness was measured as a function of gas mixture, The minimum thickness was ~73nm for the film sample prepared using Ar:O₂ gas mixture of 10:90, while the maximum thickness of ~176nm was measured for the sample prepared using Ar:O₂ gas mixture of 30:70 for the same deposition time. This can be attributed to the increase in argon content in the gas mixture, which lead to increase the density of argon atoms – and hence Ar⁺ ions – generated by the electric discharge ,In the FTIR transmission spectrum of the prepared nanostructured NiFe₂O₄ thin film in Fig. (2), two distinct peaks are observed around 430 and 590 cm⁻¹. They are attributed to the octahedral metal stretching vibration (Ni-O) and the tetrahedral metalintrinsic stretching vibration (Fe-O), respectively. Other peaks observed in the range 2800-3600 cm⁻¹ are assigned to the stretching modes of the free or adsorbed water. Figure (3) shows the absorption spectra in the spectral region 400-800nm at room temperature. It is clear that the absorbance decreases with decreasing argon content (i.e., increasing oxygen content) in the gas mixture. This behavior is in accordance to the increase in film thickness with decreasing argon content in the gas mixture as the absorption coefficient and hence the absorbance (A) increases with increasing film thickness. These spectra are very important to determine and study the energy band gap of the prepared nanostructures fig (4) show the Absorption spectra of the prepared NiFe₂O₄ film samples using different ratios of Ar:O₂ gas mixtures, A common way to extract the direct (*E_gdirect*) and indirect (*E_gindirect*) energy band gaps from optical absorption spectra is the Tauc plot, The value of optical energy band gap is calculated by extrapolating straight line portion of $(\alpha h\nu)^2$ versus photon energy (hν). The intercept on the horizontal axis gives the value of indirect energy gap one can see that the optical energy band gap decreases with increasing oxygen content in the gas mixture. This may be due to the increase in the film thickness with increasing oxygen content. The increase in film thickness leads to increase the defects in crystal structure which causes an increase in localized states inside the energy gap and then decrease in its value (*E_g*). There is another possible reason for such behavior that may originate from the increase in grain size, as mentioned above, as a red shift was observed from the absorption edge.[14]. The values of indirect energy band gaps (*E_gindirect*) of the prepared

samples were ranging in 1.779-1.785eV, respectively as shown in fig (5)

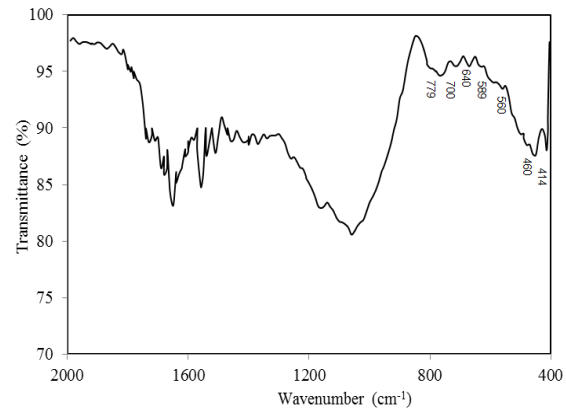
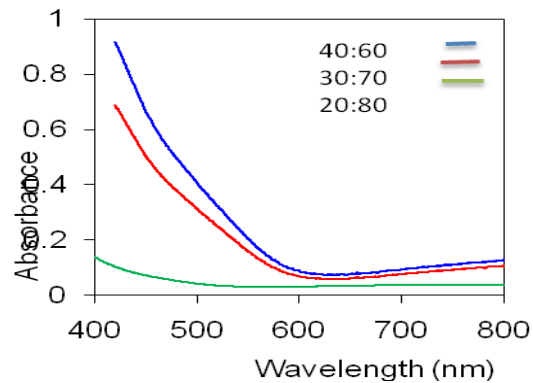


FIG. (2) FTIR SPECTRA FOR NiFe₂O₄ THIN FILMS PREPARED



Fig(3)Absorption spectra of the prepared NiFe₂O₄ film samples using different ratios of Ar:O₂ gas mixtures

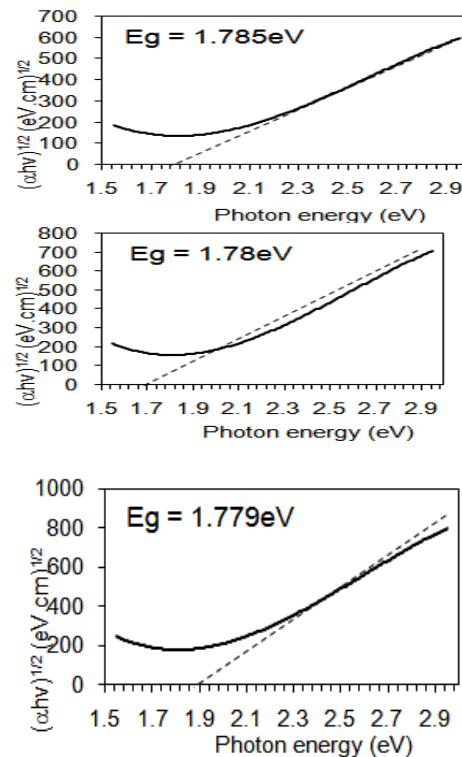


Fig. (4) Determination of indirect optical energy gap (*E_g*) for the NiFe₂O₄ samples prepared using different mixing ratios Ar and O₂ gases

IV. CONCLUSION

According to the obtained results The gas mixing ratio (Ar/O_2) is very important parameter to control and determine the phases of final Nickel Ferrite sample. The gas mixing ratio and inter-electrode distance have reasonable effects on the particle size of the prepared Nickel Ferrite. The average particle size of the sample prepared using gas mixture of 30:70 and inter-electrode distance of 4cm was greater than the sample prepared using gas mixture of 10:90 and the same inter-electrode distance. The value of optical energy band gap OF Nickel Ferrite was decreasing with increasing the oxygen content in the gas mixture, that may originate from the increase in grain size, as mentioned above, as a red shift was observed from the absorption edge.

ACKNOWLEDGMENT

Authors would like to thank Dr. Baha T. chiad for their assistance and support during the experimental part of this work. Also would like to thanks the department of physics in science of college, university of Baghdad to use the labs and help us with some work instruments

REFERENCES

- [1] J.A. Paiva, M.P. Graça, J. Monteiro, M.A. Macedo, and M.A. Valente, "Spectroscopy studies of NiFe₂O₄ nanosized powders obtained using coconut water," *J. Alloys and Compounds*, vol. 485, pp. 637–641, 2009.
- [2] M.M. Krupa and I.V. Sharay, "Magnetic and magneto optical properties of Fe₃O₄ and NiFe₂O₄ nanoparticles," *Function. Mater.* vol. 21, pp. 15, 2014.
- [3] A.T. Nelson, J.T. White, D.A. Andersson, J. A. Aguiar, K.J. McClellan, D.D. Byler, and C.R. Stanek, "Thermal Expansion, Heat Capacity, and Thermal Conductivity of Nickel Ferrite (NiFe₂O₄)," *J. Amer. Ceramic Soc.* vol. 97, pp. 1559–1565, 2014.
- [4] Z. Shi, J. Zhang, D. Gao, Z. Zhu, Z. Yang, Z. Zhang, and D. Xue, "Magnetic resonance of the NiFe₂O₄ nanoparticles in the gigahertz range," *Nanoscale Research Lett.* vol. 8, pp. 1–5, 2013.
- [5] M. Balaguer, J.G. Fayos, C. Solis, and J.M. Serra, "Fast Oxygen Separation Through SO₂- and CO₂- Stable Dual-Phase Membrane Based on NiFe₂O₄-Ce_{0.8}Tb_{0.2}O_{2-δ}," *Chem. Mater.* vol. 25, pp. 4986–4993, 2013.
- [6] Z. Shi, J. Zhang, D. Gao, Z. Zhu, Z. Yang, Z. Zhang, and D. Xue, "Magnetic resonance of the NiFe₂O₄ nanoparticles in the gigahertz range," *Nanoscale Research Lett.* vol. 8, pp. 1–5, 2013
- [7] C. Solis, S. Somacescu, E. Palafox, M. Balaguer, and J.M. Serra, "Particular Transport Properties of NiFe₂O₄ Thin Films at High Temperatures," *J. Phys. Chem. C*, vol. 118, pp. 24266–24273, 2014
- [8] A. Ahlawat, V.G. Sathe, V.R. Reddy, and A. Gupta, "Mossbauer, Raman and X-ray diffraction studies of superparamagnetic NiFe₂O₄ nanoparticles prepared by sol-gel auto-combustion method," *J. Magnetism and Magnetic Mater.*, vol. 323, pp. 2049–2054, 2011.
- [9] P. Sivakumar, R. Ramesh, A. Ramanand, S. Ponnusamy, and C. Muthamizchelvan, "Preparation and properties of nickel ferrite (NiFe₂O₄) nanoparticles via sol-gel auto-combustion method," *Mater. Research Bulletin*, vol. 46, pp. 2204–2207, 2011.

- [10] S.A. Abdel-Hameed and F.H. Margha, "Preparation, crystallization behavior and magnetic properties of nanoparticles magnetic glass-ceramics in the systems Fe₂O₃-CoO- MnO₂, Fe₂O₃-NiO-MoO₃ and Fe₂O₃-CoO- V₂O₅," *J. Non-Crystalline Solids*, vol. 358, pp. 832–838, 2012.
- [11] B. Senthilkumar, R. KalaiSelvan, P. Vinothbabu, I. Perelshtein, and A. Gedanken, "Structural, magnetic, electrical and electrochemical properties of NiFe₂O₄ synthesized by the molten salt technique," *Mater. Chem. Phys.* vol. 130, pp. 285–292, 2011
- [12] Gagan Dixit¹, J.P. Singh, R.C. Srivastava, H.M. Agrawal, R.J. Chaudhary' Structural, magnetic and optical studies of nickel ferrite thin films' *ADVANCED MATERIALS Letters*, Lett. 2012, 3(1), 21-28.
- [13] G. Hu, J.H. Choi, C.B. Eom, V.G. Harris, Y. Suzuki, *Phys. Rev. B* 62, R779 (2000)
- [14] S. Venzke, R.B. van Dover, J.M. Phillips, E.M. Gyorgy, T. Siegrist, C.-H. Chen, D. Werder, R.M. Fleming, R.J. Felder, E. Coleman, R. Opila, *J. Mater. Res.* 11, 1187 (1996).
- [15] W.A. Goddard, D.W. Brenner, S.E. Lyshevski and G.J. Iafrate, *handbook of Nanoscience, Engineering and Technology*, CRC Press LLC (2003), Ch. 13.W. Demtröder, *Molecular Physics*, Wiley-VCH (2003), p. 263