Study of Characterization of Cupper Ferrites Thin Film Prepared by Pulse Laser

Abstract- In this work, it has been used two methods to prepare ferrite thin film: festival “Auto combustion “and secondly “Pulse laser deposition” to synthesis copper ferrite as powder and thin film respectively. Different physical properties have been studied. XRD results indicated that synthesized ferrite as powder and thin film with two different energy (700-800) mJ prepared, where single cubic phase with spinel structure have. SEM photographs showed the spherical shape of particles with average size in range (88-109μm) and how these particles would create a uniform shape of film via laser with energy 800 mJ. Transmittance results showed that thin films prepared with low energy (i.e. 700 mJ) has higher transmittance as compared with that prepared via high energy. Furthermore more thin films band gap recorded increment from 3.8eV - 3.97 eV as laser energy increased from 700 mJ to 800mJ.

Keywords- cu-ferrites, PLD technical, energy gap, XRD diffraction.

1. Introduction

Ferromagnetic ceramic can be electrically defined as compound materials, consisting of different compositions of iron oxides for example “Hematite (Fe₂O₃)” or “Magnetite (Fe₃O₄)” and other metals oxides such as (NiO, CuO, ZnO, MnO,CoO). Ferrite is ceramic polycrystalline material with magnetic properties that used in different types of electronics. Ferrites considered hard, brittle material with iron containing and have gray or black color. Spinel type may be considered as the simplest type of ferrites, generally its chemical formula (M₂+ Fe₂3+O₄2-). The Cu-Fe-O system has outstanding interest in different fields of solid state physics, metallurgy, mineralogy, ceramics and electronic industry because it exhibits interesting physical, magnetic and electrical properties with chemical and thermal stabilities [1-3]. There were different methods for preparation such as chemical methods, electro deposition, sol-gel, co- precipitation, hydrothermal methods and micro emulsion technique [4]. In this work, it has been selected sol-gel technique to form nano crystalline ferrites with controlled stoichiometry and narrow particle size distribution. Moreover, this process is simple, low cost, required short time of production and the most important is that final product has high purity and homogeneity [5, 6]. Technology of thin films has great accelerating fields in research can be used as a replacement to the bulk material since it plays a vital role in the technology development in particular integrated circuit field [7].Particular Pulsed Laser Deposition (PLD) participated in improved the efficiency of obtaining ferromagnetic oxides thin films [8]. PLD technique depends on various parameters including wavelength, width of the pulse, repetition rate, energy density (fluence), background gas pressure, substrate temperature and the distance between target and substrate[9, 10]. The aim of present work is preparation thin film from Cu-ferrites powder and studies some physical properties.

2. Experimental Work

Cu-ferrites prepared in two ways:- festival as powder and secondly as thin film by using PLD technique.

I. Powder formation via Auto- combustion method

Ferrites powders have been prepared using auto combustion method, which is chemical method. High purity cupric nitrate hydrate Cu (NO₃)₂·6H₂O Cu (NO₃)₂·6H₂O, ferric nitrate monohydrate Fe (NO₃)₃·9H₂O used as outset materials. The mixture added to citric acid (C₆H₅O)₆·H₂O 2M, in molar ratio 3:1 (acid: nitrates). Mixed solution of these

How to cite this article: G.K. Salman, S.S. Shaker and A.H. Abd alsalam, “Study of Characterization of Cupper Ferrites Thin Film Prepared by Pulse Laser,” Engineering and Technology Journal, Vol. 35, Part B, No. 1, pp. 57-62, 2017.

https://doi.org/10.30684/etj.35.1B.12
2412-0758/University of Technology-Iraq, Baghdad, Iraq
This is an open access article under the CC BY 4.0 license http://creativecommons.org/licenses/by/4.0
materials were prepared in deionized water with vigorous stirring until the solution being a gal (2 hour). The resultant powder was ground and pressed under less than 10-ton pressure to form a target with 3 cm diameter and 0.5 cm thickness.

II. Thin Films preparation via Pulse laser deposition method

Ferrite films were synthesized by PLD using double frequency Nd:YAG laser different laser energy 700 mJ and 800 mJ of 532 nm laser light. Glass and Si (111) substrates baked out in vacuum at 350°C were used for depositions. The thin films were grown in an oxygen pressure of 10⁻² mbar.

III. Physical Characterization

Scanning electron microscope (SEM, the VEGA Easy Probe) analysis (SEM) have been used to study the structure and morphology. X-ray diffraction apparatus using Philips PW 1050 X-ray diffract meter has been used. The optical transmittance properties was measured by using (Double–beam UV-IR 210A Spectrophotometer). The parameters of these processes determined from the spectral based on the absorption coefficient α. The dependence of α on the wavelength λ can be correlated between, the reflection Rs and absorption coefficient α.

\[ T = (1 - R_s)^2 \exp(-\alpha d) \]  
(1)

\[ \alpha = \frac{1}{d} \ln \left( \frac{1}{T} \right) \]  
(2)

At which: d is the film thickness and T is the transmission in % percentage the curves of the absorption. [11]

The variation in α with photon energy (in electron volts) was found to obey a relation of the form. [12]

\[ \alpha(h\nu) = A(h\nu - E_g)^{1/2} \]  
(3)

(FT-IR) from (SHIMADZO IRAFFINITY) probes has been used.

3. Results and Discussion

Figure 1 shows the SEM images of Cu-ferrites powder. The surface morphology of has shown different shapes of nano sphere of Cu-ferrites powder with average size (88-109) nm. Figures (2 a and b) show surface morphology of Cu-ferrites thin films deposited under 5×10⁻¹ mbar oxygen gas at substrate temperature 400°C at laser energy 700mJ and 800mJ respectively. Results showed that Cu-ferrites thin films have nanostructure and varied significantly with deposition laser energy. Ferrite films deposited at laser energy 700-mJ exhibit an asymmetric fine XRD pattern of CuFe₂O₄ nano powder is shown in Figure 3. Results confirmed spinel structure formation of ferrite. Inter planar spacing (d) agrees with Bragg’s law and the average lattice parameter ‘a’ using Eq.4 equal to (8.312Å).

The grain size of the bulk sample (12.223 nm) was estimated by performing Debye Scherer equation (Eq.5), for a cubic system of most intensity peak (311).

To collected the lattice parameter (a);

\[ a^2 = (h^2 + k^2 + l^2) \]  
(4)

h,k,l= miler index, d= the inter planer spacing.

The Average particle size (Dₓ) calculated by using Debye-Scherer Formula:

\[ D_x = \frac{0.9 \lambda}{\beta \cos \theta} \]  
(5)

Λ: wave length of X-ray, β: broadening of the diffraction peak, θ : angle of diffraction, the calculated crystallite size of (311) XRD peak. grained nanostructure and as the laser energy is increased to 800mJ, the films exhibit Cu-ferrites aggregation with more uniform shape which strongly different as compared with films that formed at laser energy 700 mJ.

Figure 1: SEM image of Cu-ferrites powder in different magnification
The Crystalline thin films of ferrite growth were detected by x-ray diffraction technique as shown in Figure 4, the as-deposited spectra indicated the existence of spinel ferrite phase without any impurities. The lines can be indexed to the representative inter planar space (200), (311), (222), (400), and (440) of the structure spinel with cubic symmetry. The (hkl) peak location slight shift, in the direction normal to the plane of the film gives the strain in the film measure, whichever compressive or tensile, towards lower angle characteristic shift associated to ideal crystal indicates lattice expansion, variation in lattice parameter, the higher cell parameter (8.5Å) than in bulk. This difference can be interpreted to the local stresses emerged from atomic peening due to the strain presented in the film during deposition. [10], this strain may be produced because, counting cavities and film substrate incongruity. Absence of known peaks of spinel ferrites and the low intensity for some peaks goes to crystallographic structure [11, 12].
Finally, FTIR spectra have been registered for the copper ferrites and powder sample were recorded in the bands of (2000-500) cm\(^{-1}\) as shown in figure (5a). FTIR spectra of cu-ferrite thin films with different laser energy 700 mJ, and 800 mJ .cu-ferrite thin film structure were similar to mineral spinel crystalline structure that arises usually in cubic form or sometimes in tetragonal system depending upon the ions participating in the solicitous solid material. The FTIR spectra of as prepared samples in general below 1000 cm\(^{-1}\). common feature of FTIR spectra shows two main absorption band \(V_1\) and \(V_2\) as assembly, in identity to Waldron [13] the band \(v_1\) around 578 cm\(^{-1}\) was attributed to stretching vibration of tetrahedral complexes and the band \(v_2\) at 408cm\(^{-1}\) according to the result show in Figures 5(b)–5(c).Where the ferrites band performing at the higher wave number (500–600 cm\(^{-1}\)) were assign to tetrahedral compounds, while octahedral complexes assigned at (406–456cm\(^{-1}\)). \(\text{Fe}^{3+}\)-O\(^2-\) vibration in sub lattice site A represents higher wave number \(v_1\), while the lower wave number band \(v_2\) represents the trivalent metal oxygen vibration at the octahedral B-sites. In spite of different in laser energy, note that Minor changes in band of wave number. In addition, it is clear present band wave number of Si substrate there is a peak present at about 1000cm\(^{-1}\).

Figure 6 shows that the optical transmittance of thin films formed on glass substrate at 700 mJ laser density was higher than that deposited at 800 mJ. Moreover transmittance analysis results shown that the optical transmittance decreases with raising laser energy and this may be due to the increase in film and crystallinity revealed in the SEM and XRD, in addition the increase in the surface homogeneity belongs to the increase in light scattering [14].

Figure 7 shows realtion of \((\alpha h\nu)^2\) against photon energy (hv) used to determine band gap energy of the films using a relation (3).The extrapolation of the straight line to zero absorption indicates to the direct band gap of the films [15] that increases from 3.8eV - 3.97 eV as laser energy increased from 700 mJ to 800mJ. This shift in the band gap can be interpreted by the Burstein–Moss effect at which the absorption edge moves towards the higher energy ones with an increase of carrier concentration [16-18].
4. Conclusion
Cu-ferrites powder produced by sol-gel auto combustion method is suitable for thin films formation by pulse laser deposition (PLD) at different laser energy at which Cu-ferrites is the target. Morphological SEM results showed the uniform shape of Cu-ferrites thin films at laser energy 800 mJ. Optical properties of Cu-ferrites thin films at 800mJ is transparent more than 86% with optical band gap of the films 3.97 eV.

References
[1] S.D. Sartale, C.D. Lokhande, M. Muller, “Electrochemical synthesis of nanocrystalline CuFe₂O₄ thin films from non-aqueous (ethylene glycol) medium,” Mater. Chem. Phys., 80, pp.120–128, 2003.
[2] Z. Sun, L. Liu, D.z. Jia, W. Pan, “Simple synthesis of CuFe₂O₄ nanoparticles as gas sensing materials,” Sens. Actuators, B: Chem. 125, pp. 144–148, 2007.
[3] K.-S. Kang, C.-H. Kim, W.-C. Cho, K.-K. Bae, S.-W. Woo, C.-S. Park, “Reduction characteristics of CuFe₂O₄ and Fe₂O₃ by methane; CuFe₂O₄ as an oxidant for two-step thermochemical methane reforming,” Int. J. Hydrogen Energy, 33, pp.4560–4568, 2008.
[4] S. Gubbala, H. Nathani, K. Koizol and R. D. K. Misra, “Magnetic Properties of Nanocrystalline Ni-Zn, Zn-Mn, and Ni-Mn Ferrites Synthesized by Reverse Micelle Technique,” Physica B, 348. (1-4), pp. 317-328, 2004.
[5] S. Sahi, A.R. Daud and M. Hashim, “A Comparative Study of Nickel-Zinc Ferrites by Sol-Gel Route and Solid-State Reaction,” Materials Chemistry and Physics, (106), (2-3), pp. 452-456, 2007.
[6] A. Saberi, F. Golestani-Fard, H. Sarpoalak, M. Willert-Porada, T. Gerdes and R. Simon, “Chemical Synthesis of Nano crystalline Magnesium Aluminate Spinel (MgAl₂O₄) via Nitrate-Citrte Combustion,” Journal of Alloys and Compounds, 462, (1-2), pp. 142-146, 2008.
[7] Physics and technology of thin films, IWTF, Proceedings of the International Workshop, Tehran, Iran, 22 February – 6 March 2003.

[8] S. B. Ogale, K. Ghosh, R. P. Sharma, R. L. Green, R. Ra- mesh and T. Venkatesan, “Magnetotransport Anisotropy Effects in Epitaxial Magnetite (Fe3O4) Thin Films,” Physical Review B, (57), (13), pp. 7823-7828, 1998.

[9] A.K. Yousif, “Characterization of ZnO Film Grown on Different Substrates Using PLD,” Ph.D. Thesis, University of Technology, 2010.

[10] D.B. Fahad, “Structural, Electrical and Optical Properties of CuLa2Fe3yFerrite System,” MSc. Thesis, College of Science, University of Baghdad, 2014.

[11] A. Lisfi and C.M. Williams, “Magnetic anisotropy and domain structure in epitaxial CoFe2O4 thin films”. J. Appl. Phys. 93, 8143, 2003.

[12] A. Lisfi, J.C. Lodder, E.G. Keim, and C.M. Williams, "Reorientation of magnetic anisotropy in epitaxial cobalt ferrite thin films", Appl. Phys. Lett. 82, 76, 2003.

[13] J. Joseph, R.B. Tangsali, R.J. Choudhary, D.M. Phase and V. Ganeshan, “Magnetic properties of textured nanocrystalline manganese-zinc ferrite thin films fabricated by pulsed laser deposition.” Int. J. Thin Fil. Sci. Tec. 3, (3), 81-87, 2014.

[14] R.D. Waldron, “Infrared spectra of ferrites,” physical review, 99, 6, pp. 1727–1735, 1955.

[15] Suaad salim shaker" Ag -Doped SnO2 Sensor for H2S Gas, Prepared by PLD" M.Sc. Thesis, College of Science, University of Technology, 2013.

[16] F. R. Chowdhury, S. Choudhury, H. Firozhasan and T. Begum, “Optical Properties of Undoped and Indium-Doped Tin Oxide Thin Films,” Journal of Bangladesh Academy of Sciences, 35, 1, 99-111, 2011.

[17] M. Girtan, A. Bouteville, G.G. Rusu and M. Rusu, “Preparation and Properties of SnO2: F Thin Films,” Journal of Optoelectronics and Advanced Materials, (8), (1), P.P. 27 - 30, 2006.

[18] L.S. Roman, R. Valaski, C.D. Canestraro, E.C.S. Magalha’es, C. Persson, R. Ahuja, E.F. da Silva Jr., I. Pepe and A. F. Silva, “Optical and Edge Absorption of oxide compound SnO2”, Applied Surface Science, (252), PP. 5361–5364, 2006.

[19] H.M. Ahmed, “Structural, Electric and Dielectric Properties of Cadmium Doped Nickel-Cobalt Ferrite,” Journal of American Science, 2,11,8, 2015.