DOI: 10.24996/ijs.2019.60.9.14

ISSN: 0067-2904

Optical Properties of Mixed ZnO: Fe_2O_3 Grown via Pulsed laser deposition

S. M. Hanfoosh*, N. K. Hassan
Department of Physics, College of Education for Pure Science, Tikrit University, Tikrit, Iraq

Abstract
In this study, mixing of zinc oxide (ZnO) nanoparticles with iron oxide(Fe_2O_3) at (0, 0.1, 0.3, 0.5 and 1)%wt., are deposited on glass substrates by pulsed laser deposition (PLD) technique for study characterization ZnO:Fe_2O_3 as solar cell electrode. The profound effect of mixed film on the structural and optical of ZnO: Fe_2O_3 thin films was observed. Meanwhile, the films have polycrystalline Hexagonal structures for ZnO, Rhombohedra and cubic structure for Fe_2O_3, and as indicated by the X-ray diffraction patterns of the films. The mean crystallite size of ZnO increase with increasing mixed ratio. The direct energy gap (Eg) of ZnO is 3.36 eV and decreasing with increasing mixed ratio.

Keywords: Zinc Oxide, Iron Oxide, Pulsed-laser deposition, structure properties.

الخصائص البصرية لخليط ZnO:Fe_2O_3 المنمى بواسطة الترسيب بالليزر النبضي

سيف الدين محمد حنفوش*، نديم خالد حسن
قسم الفيزياء ، كلية التربية للعلوم الصرفة ، جامعة تكريت

الخلاصة
في هذه الدراسة ، خلط جزيئات أكسيد الزنك (ZnO) مع أكسيد الحديد (Fe2O3) عند %(0 ، 0.1، 0.3 ، 0.5 و 1) ، على ركائز زجاجية بواسطة تقنية ترسب الليزر النبضي (PLD). لتوصيف دراسة ZnO:Fe_2o_3 استخدامها في الخلايا الشمسية. وقد لوحظ التأثير الكبير لاغشية الخليط على الخصائص الهيكلية والبصرية للأغشية الرقيقة ZnO: Fe_2O_3 وفي الوقت نفسه ، تحتوي الاغشية على هياكل سداسية متعددة البلورات بالنسبة ل اوكسيد الخارصين وهيكيلية مختلطة Rhombohedra و مكعبي لFe_2O_3,وكما يتضح من أنماط حيود الأشعة السينية للأغشية. فجوة الطاقة البصرية لاغشية اوكسيد الخارصين بحدود 3.37 eV وتتناقص مع زيادة نسبة الخلط.

1. Introduction

Recently, crystalline nanoparticle oxides have taken the researchers attention because of the increasing the surface area of the active and important in absorbing the largest amount of radiation falling on the material, which in turn is converted into an electric current, as in solar cells. Among them zinc oxide (ZnO) and iron oxide (Fe_2O_3), regarded one of semiconductor materials which have many physical properties that make them suitable for thin-film applications. such as, good electrical conductivity, inexpensive material, and chemical stability[1-2]. ZnO semiconductors were widely used as photoelectrode in solar cell [3]. n-type II–VI ZnO is a thermally and chemically stable compound semiconductor with large exaction binding energy (60 meV), and wide band energy about (3.37 eV)[4]. ZnO is promising material for application to window layers of hetero junction solar cells, UV light emitting/receiving devices, transparent electrodes, piezoelectric nanogenerators photocatalysts and antibacterial activities[5-7]. ZnO doped with transition metals such as Fe, Co, and

*Email: saef_aldeen2002@yahoo.com

Ni have many advantages for their appropriate optical and electronic properties required for optoelectronic devices[8]. Fe_2O_3 is one of the most materials used as photoelectrochemical and photocatalytic applications due to its have narrow band gap (2.0–2.2 eV), which could collect up to 40 % of the solar spectrum energy. Fe_2O_3 nanoparticles exhibit great stability in aqueous solutions. The crystal structure of Fe_2O_3 is rhombohedra , and has attracted biggest interest because of their potential applications in solar cell, catalysis, gas sensors, pigments, medicine applications, optical devices and it used as an anode material[9-10]. The technique of preparation of the semiconductor electrode plays an active role in the performance of such solar cells[1]. Many methods can be utilized to prepare ZnO and Fe_2O_3 electrodes such as pulse laser deposition, chemical vapor deposition, spray pyrolysis, sol–gel method, hydrothermal [11-14]. In this work we focused attention on iron doped ZnO, Iron is also the most common in recent years.

2. Experimental

Nano powder ZnO from (US research nanomatrials, Inc, USA) mixed with nano powder Fe_2O_3 were deposited on glass substrate using PLD technique. ZnO powders doping with 0, 0.1, 0.3, 0.5, 1(Fe_2O_3) were mixed using a Mixar(METUCHEN, N.J. Q8B40 U.S.A) and then pressed under 6ton to form targets with 2cm diameter and 0.3 cm thickness. The target were ensured to be homogeneous and dense as possible to prepared good quality ZnO:Fe_2O_3 billet, which would be deposited by the PLD technique. Film deposition was carried out inside a 10^{-3} Torr evacuated chamber. The focused Q-switched Nd:YAG laser beam was incident at an angle of 45° on the target surface, and the energy of the laser was 900 mJ. the glass was cut into square-shape pieces $(2.5\times 2.5)cm^2$ and were ultrasonically cleaned in distilled water. The structure of the films were examined by X-ray diffraction (XRD-6000-shemadzu with CuKα, wavelength =1.54 A˚). The UV-Visible optical transmission spectra of the thin films were recorded by (Shemadzu UV-160/UV-Visible recorder spectrophotometer).

3. Result and Discussion

3.1 Structure

The result of the XRD scan of ZnO thin films mixed with Fe_2O_3 deposited on the glass substrate at RT temperature illustrated in Figure-1. XRD pattern shows that all mixed films are polycrystalline in nature. The XRD pattern ZnO exhibits many peaks at 2θ of 31.75, 34.42, 36.22, 47.57, 56.61, and 62.89, which are referred to (100) , (002), (101),(102),(110) and (103) planes of the Hexagonal structure of ZnO, respectively, according to the file (card no.36-1451. This is good agreement with that of [15]. when add a thin Fe2O3 as matrix material, many peaks referring to Fe_2O_3 at 2θ of 24.138, 27.50, , 33.15, 40.85, 43.28, 50.0 are observed and refer to the (012), (022), (104), (113), (400), (421) planes of the Rhombohedra and cubic structure of Fe2O3, respectively, from the Diffraction (card no. 33-0664, 39-1346). also notice decrease in the peak of diffraction when increasing in the ratio at (0, 0.1, 0.3, 0.5, 1)wt%. The mean crystallite size(D) was calculated via Sherrer's formula[16]

$$D = \frac{k\lambda}{\beta cos\theta} \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (1)$$

where λ is wavelength ($\lambda = 1.5406$ A˚) , k is a constant equals 0.94 and β is Full Width at Half Maximum (FWHM). The crystal size of ZnO be 18.5 nm and increases when mixed ratio increased, to be 19.7, 20.3, 22.1, 23.4 and 25.0 nm with mixed ration (0, 0.1, 0.3, 0.5, 1), and FWHM increases.

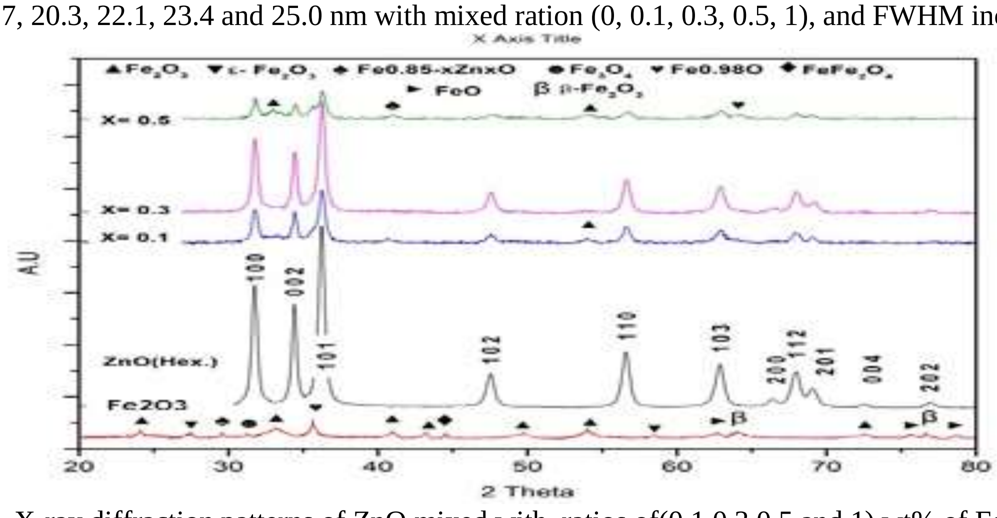

Figure 1-X-ray diffraction patterns of ZnO mixed with ratios of(0.1,0.3,0.5 and 1) wt% of Fe_2O_3**.**

2. Atomic Force Microscope (AFM)

The three and two-dimensional (3D,2D) topographic image has been used to study the surface morphologies of the $ZnO:Fe_2O_3$ thin film with (0, 0.1, 0.3 , 0.5 and 1) % wt are shown in Figure-2. The average diameter, roughness, surface thickness and root mean square (R.M.S) are deduced from AFM images. The AFM images appear and all samples are granular structure and good uniformity revealing a uniform growth of the films. The average diameter increased with increasing of mixed ratio with Fe_2O_3. Also increasing in roughness with increasing in mixed ratio, this may be attributed to grain growth and some structure densification of the deposition processes. The average diameter, roughness, peak-peak and root mean square (R.M.S) are shown in Table-1.

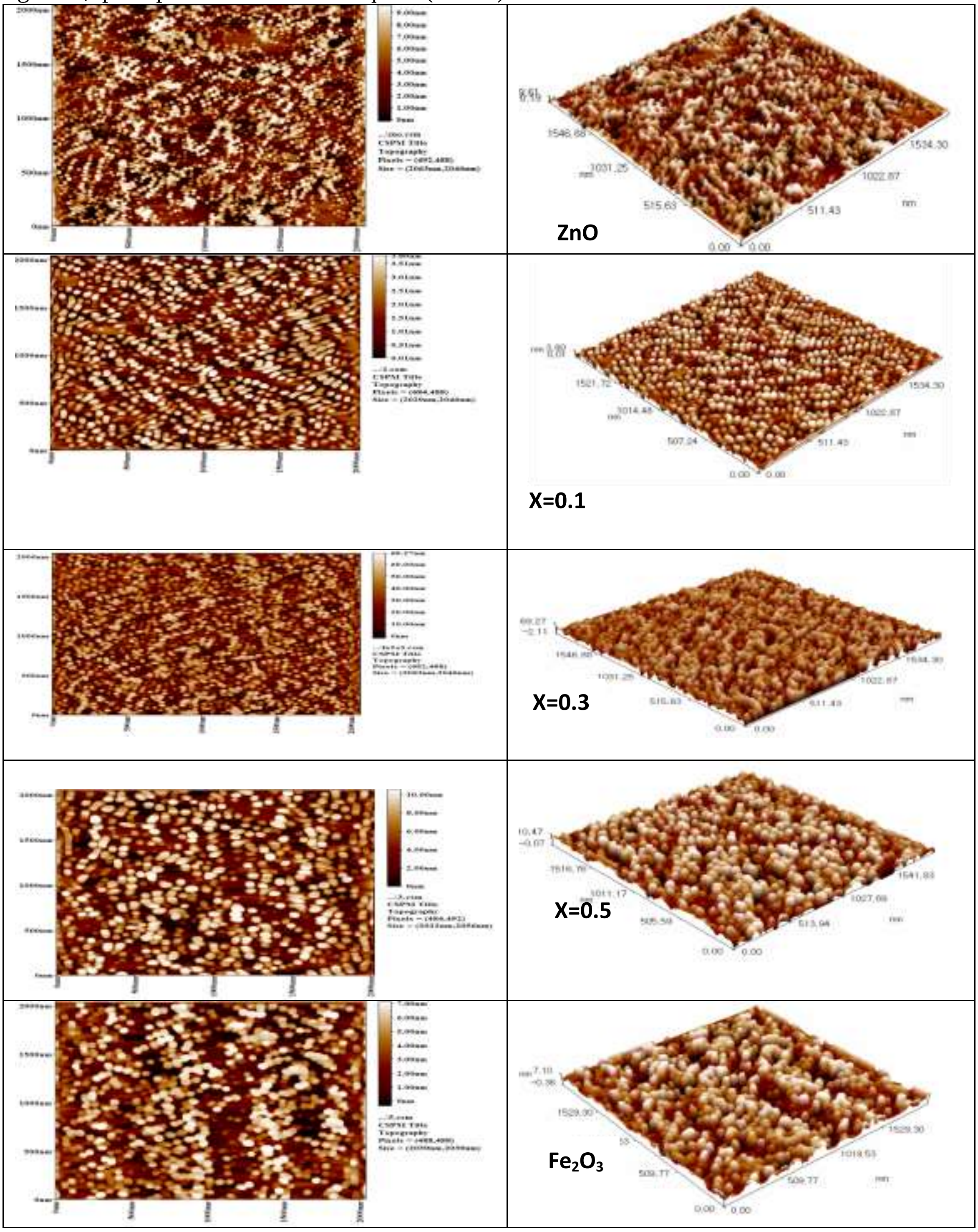

Figure 2-2 and 3-D AFM micrographs of ZnO mixed with ratios of(0.1,0.3,0.5 and 1) wt% of Fe_2O_3

Table 1-AFM parameter of ZnO mixed with ratios of(0.1,0.3,0.5 and 1) wt% of Fe_2O_3

Sample	Ave. diameter (nm)	Roughness (nm)	R.M.S (nm)	peak-peak (nm)
ZnO	47.19	2.45	2.83	9.8
X=0.1	55.91	0.947	1.09	3.79
X=0.3	58.84	1.86	2.15	7.46
X=0.5	64.96	2.64	3.04	10.5
Fe_2O_3	76.74	14.0	16.2	57.5

3. Optical properties

The optical absorption coefficient (α) is important parameter in the design of calculations of the electronic and optoelectronic device. where this factor changes according to the semiconductor materials and affects the amount of light absorbed by the films and is a function of the wavelength of the light incident. The absorption coefficient changed of ZnO and doped with Fe_2O_3 at (0, 0.1, 0.3 , 0.5 and 1)%wt., concentration as shown in Figure-3 from the relation between absorption coefficient(α) and wave length (λ) . High absorption coefficient values for all films, were found to be (> 104 cm^{-1}), this is good evidence that all films had a direct energy gap. The spectral in the region about (500-1100) nm showed the high stability of absorption coefficient with increasing wavelength, this is because of the relative stability of the rate of increase in transmittance within this spectral. The absorption coefficient increase with increased of Fe_2O_3 concentration, as Table-2 and it may be attributed to the increase of crystallite size with increasing mixed concentration as shown in XRD result.

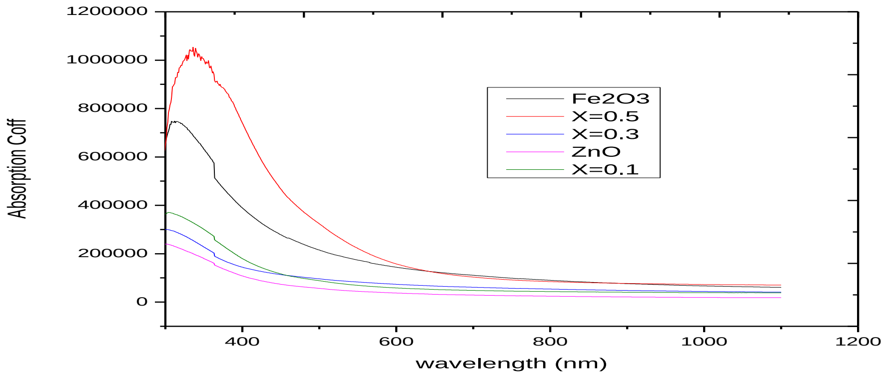

Figure 3-Absorption coefficient spectra of ZnO mixed with ratios of(0.1,0.3,0.5 and 1) wt% of Fe_2O_3

From the relationship between transmission (T) and wave length(λ), the UV–Vis transmission is shown in Figure-4. Transmittance of ZnO increased with increasing the wavelength and at wave length 500nm about 60%. When adding Fe_2O_3, with concentration (0, 0.1, 0.3, 0.5, 1) wt%., the transmittance is decreasing, this may be attributed to the increase in the absorbance within ultraviolet-visible region of spectrum. all prepared films exhibit a low transmittance in the UV region.

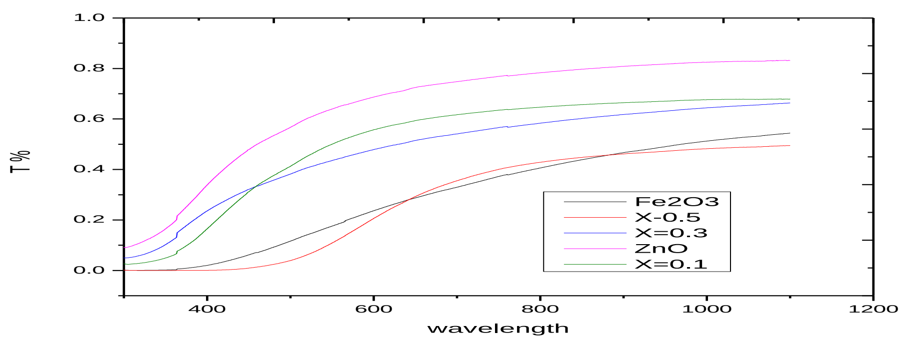

Figure 4-Transmittances spectra of of ZnO mixed with ratios of(0.1,0.3,0.5 and 1) wt% of Fe_2O_3

Optical energy gap can be used to estimate the difference between the valence and conduction bands, which can help determine the thermoelectric and electronic properties of the materials[17]. The photon energy(hν) versus the variation ($\alpha h\nu^2$) for ZnO thin films which mixed at different concentration of Fe_2O_3 (0, 0.1, 0.3,0.5 and 1) %wt. is shown in Figure-5. the optical energy gap is evaluated via extrapolating the linear portion to zero absorption coefficient (α=0)[18].The energy band gap of ZnO at a thickness of 200 nm is found to be 3.36 eV, this good agreement with A. Kaphle1 and P. Hari[19]. in which at mixed with Iron Oxide the band gap energy decrease as shown in Table-2 to reach to 2.78eV. This trend shifted toward low energy (blue shift) as a result of the increasing of grain size[20].

Table 2-optical parameter of ZnO mixed with ratios of(0.1,0.3,0.5 and 1) wt% of Fe_2O_3at (λ=500 nm).

Sample	Transmittances T %	Absorption α (cm^{-1})	Energy gap E.g (eV)
ZnO	60	0.9×10^{-5}	3.36
0.1	48	1.2×10^{-5}	3.04
0.3	42	1.3×10^{-5}	2.996
0.5	9	3.0×10^{-5}	2.93
Fe_2O_3	12	2.15×10^{-5}	2.78

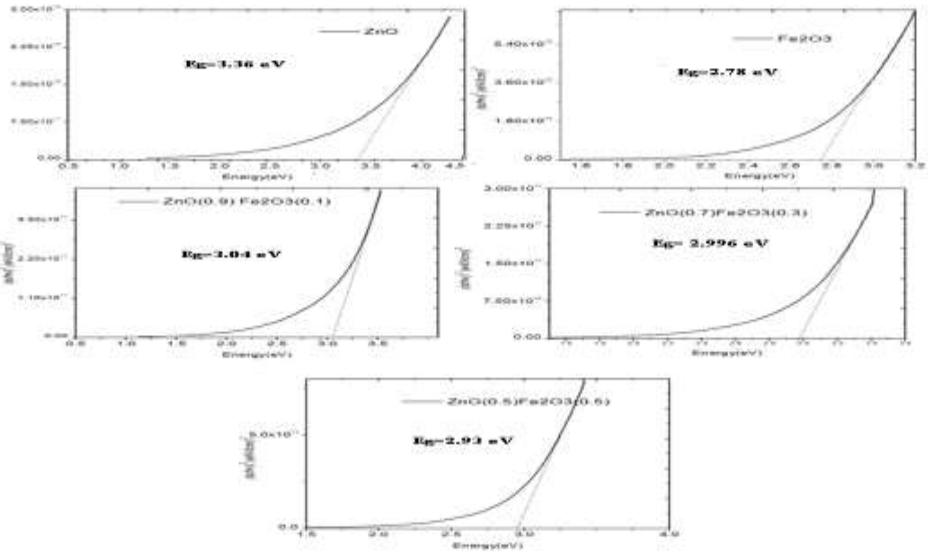

Figure 5-The variation of ($\alpha h\upsilon^2$)versus photon energy (hυ) of ZnO mixed with ratios of(0.1,0.3,0.5 and 1) wt% of Fe_2O_3

4. Conclusion

The effects of mixed ratio Fe_2O_3 on the performance of ZnO/glass as electrode are examined. The results of structure, morphological, and optical properties have been achieved. The X-ray pattern of ZnO demonstrates that increasing the mixed ratio leads to broadening in diffraction peaks and increasing in crystal size. The AFM images appear that all samples are granular structure and good uniformity revealing a uniform growth of the films. The band gap energy decrease with increasing Fe_2O_3, this trend shifted toward low energy (blue shift) as a result of the increasing of grain size.

Reference

1. Reda, S.M. **2010**. "Synthesis of ZnO and Fe_2O_3 nanoparticles by sol–gel method and their application in dye-sensitized solar cells", *Materials Science in Semiconductor Processing*, 417–425, 13.

2. Aslan, MH., Oral AY, Mens-ur E, Gul A, Bas ¨ -aran E. **2004**. Preparation of c-axis orientation zinic- oxide thin films and the study of their microstructure and optical properties. Solar Energy Materials and Solar Cells; **82**: 543–52(2004).

3. Hongsitha, K. Niyom, B., Hongsithb, C., Duangmanee Wongratanaphisana, B., Atcharawon Gardchareona, B., Surachet Phadungdhitidhadaa, b, Supab Choopun. **2015**." Efficiency

Enhancement of ZnO Dye-sensitized Solar Cells by Modifying Photoelectrode and Counterelectrode", *Energy Procedia*, **79**: 360 – 365.

4. Xiaojuan Wu, 1,2 Zhiqiang Wei,1,2 Lingling Zhang,2 Xuan Wang,2 Hua Yang,1,2 and Jinlong Jiang. **2014**. " Optical and Magnetic Properties of Fe Doped ZnO Nanoparticles Obtained by Hydrothermal Synthesis", Hindawi Publishing Corporation *Journal of Nanomaterials* Volume (2014).
5. Azuma, M. and Ichimura, M. **2008**. *Materials Research Bulletin* 3537, 43.
6. Song, J., Zhou, J. and Wang, Z.L. **2006.** *Nano Lett*. 1656, 6.
7. Kaneva, N.V., Dushkin, C.D. **2011.** *Bulgarian Chemical Communications* 259, 43.
8. Salaken, S.M., Farzana, E. and Podder, J. **2013.** *Journal of Semiconductors* 073003-1-6, 34.
9. Alagiri, M. **2014.** Sharifah Bee Abdul Hamid" Green synthesis of a-Fe_2O_3 nanoparticles for photocatalytic application" *J Mater Sci*: *Mater Electron* 3572-3577.
10. Zhong, Z., Lin, J., The, S.P., Teo, J., Dautzenberg, F.M**. 2007.** *Adv. Funct. Mater*. **17**: 1402.
11. Trang Minh Nguyen Thai · Seong-Ryoung Kim · Heon-Jung Kim. **2014**. " Synthesis of Fe_2O_3 Polymorph Thin Films via a Pulsed Laser Deposition Technique", New Physics: Sae Mulli, **64**(3): 252-255(2014).
12. ozer N, Tepehan F. **1999**. Optical and electrochemical characteristics of ¨ sol–gel deposited iron oxide films. Solar Energy Materials and Solar Cells; **65**: 141–52(1999).
13. Ghosh R, Paul GK, Basak D. Effect of thermal annealing treatment on structural electrical and optical properties of transparent sol–gel ZnO thin films. *Materials Research Bullet*, **40**: 1905 – 14(2005).
14. Siberaa, D., Jędrzejewskia, R., Mizerackib, J., Preszb, A., Narkiewicza, U. and Łojkowski, V. **2009**. "Synthesis and Characterization of ZnO Doped with Fe_2O_3 — Hydrothermal Synthesis and Calcination Process" *Acta Physica Polonica A*, **116** (2009).
15. Kumar, p., Khatri, T., Bawa, H. and deep, J. **2017.** "ZnO-Fe_2O_3 Heterojunction for Photocatalytic Degradation of Victoria Blue Dye" *American Institute of Physics*, 020065-1–020065-7.
16. Ibraheam, A.S., Al-Douri, Y., Abubaker S. Mohammed , Deo Prakash , U. Hashim , K.D. Verma. **2018**. "Electrical, Optical and Structural Properties of $Cu_2Zn_{0.8}Cd_{0.2}SnS_4$ Quinternary Alloy Nanostructures Synthesized by Spin Coating Technique" *Int. J. Electrochem. Sci*., **10**: 9863-9876, (2015).
17. Ibrahim, M., Abubaker S. and Asmiet R. **2018.** "Energy Band Diagram of NiO: Lu2 O3/n-Si heterojunction Isam" *Iraqi Journal of Science*, **59**(1B): 287-293(2018).
18. Iibrahima, I.M., A. S. Mohammed, A.S., Ramizy, A. **2018.** "Responsivity Enhancement Of Lutetium Oxide Doped –Nio Thin Films", *Journal of Ovonic Research*, **14**(1) January – February: 17 – 25 (2018).
19. Kaphle1, A. and Hari, P. **2016**. "Characterization of Aluminum Doped Nanostructured ZnO/p-Si Heterojunctions" *IJES*, **5**(10): 41-51.
20. Karpinski, A., Ouldhamadouche, N., Ferrec, A., Cattin, L., Plouet, M.R., Brohan, L., Djouadi, M.A., Jouan, P.Y. **2011.***Thin Solid Films*. **519**(17): 5767.