Optical and Structural Properties of (In_2O_3:ZnO:Au) Nanocomposite Thin Films Prepared by Spray Pyrolysis Method

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Received on: 18/6/2017
Accepted on: 12/10/2017

Abstract- *Indium Oxide (In_2O_3) and Zinc Oxide (ZnO) nanoparticles were mixed carefully with gold nanoparticles, which were synthesis, by turkevich method. By using the method of spray pyrolysis different concentrations (5:5:0 ml, 5:4:1 ml, 5:3:2 ml, 5:2:3 ml, 5:1:4 ml and 5:0:5 ml) from these chemical compounds were used to preformed nanocomposite thin films of thickness of (250-300) nm. The structural properties were studied for all nanocomposite thin film samples with different concentrations. The existence of Miller indices conforms to (211), (222), (400), (333), (440) and (622) major lattice planes of the cubic spinel phase of In_2O_3 at 2θ =20.17, 33, 44.66, 50.95, 59.02, 72.48 and 73.12. While secondary lattice planes of (100) and (002) of ZnO at 2θ = 31.5582 and 34.1617, also lattice planes of (111) and (200) of Au were found at 2θ = 38.5799 and 45.6016. The work also extended to study the optical properties, which included the transmission spectrum, absorption spectrum, absorption coefficient, attenuation coefficient and estimation of optical energy gap for all samples. The results of optical properties were clearly demonstrated that the increasing of gold concentration is decreasing the transmission, and decreasing the optical band gap from 3.10 to 3.05 eV, but increasing the absorption coefficient and attenuation coefficient. Finally The real and imaginary part of dielectric constant of (In_2O_3:ZnO:Au) nanocomposite thin film with different concentrations decrease with increasing of frequency, and increases with gold nanoparticles increasing.*

Keywords: *nanocomposite thin films spray pyrolysis, (In_2O_3) nanparticle.*

How to cite this article: A. Kadhim, F.T.M noori and N.D. Hamza, "Optical and Structural Properties of (In_2O_3:ZnO:Au) Nanocomposite Thin Films Prepared by Spray Pyrolysis Method," *Engineering and Technology Journal*, Vol. ٣٦, Part B, No. 1, pp. 53-58, 2018.

1. Introduction

Recently, many efforts in optical investigations of nanocomposite are promote the exploration of their optical, nonlinear optical, especially luminescent properties [1]. As a main transparent conducting metal oxides (TCOs) with a broad band gap of 3.55-3.75 eV, indium oxide (In_2O_3) has taken big attention because of its low electron effective mass, high electron affinity and increasingly considerably applications in sensors, fuel cells, etc [٢]. (In_2O_3:ZnO:Au) nanocomposite thin films were deposited by The process of spray pyrolysis , which is one of the most generally used methods for preparation, because its simplicity, it is cheap technique and vacuumless deposition system [3,4]. It is used for the layer deposition which transfers from an atomizer on glass substrate [5]. It is also gives a very simple method for any composition film preparing, spray pyrolysis does not need substrates with high-quality, the method has been utilized for the porous film deposition, thick films, and for the powder manufacture [6]. For structural properties, Law of Bragg's diffraction by using equation 1 was calculated the interplant distance and planes [7]. The full width at half maximum of the reflection and using Scherer's formula equation 2 evaluated Average crystallite sizes [8].

$$n\lambda = d \sin \theta \quad (1)$$

Scherer's formula is

$$t = \frac{0.9\,\lambda}{\beta \cos \theta} \quad (2)$$

The work extended to study the optical properties also, which included the absorption coefficient. Generally, it can be discovered that when gold concentration increases the absorption ratio increasing, which were calculated by using equation 3[9]:

$$\alpha = 2.302A'/t \quad (3)$$

The extinction coefficient (k) was studied. It related to the wave exponential degrade when it travels through the medium and it is defined as:

$$k = \alpha\lambda/4\pi \quad (4)$$

Where (λ) is the incident radiation wavelength.

https://doi.org/10.30684/etj.36.1B.9
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And the imaginary and real parts of dielectric constant of the films were also determined by the equation (5, 6) [10].

$$\varepsilon_1 = n^2 - k^2 \qquad (5)$$

$$\varepsilon_2 = 2nk \qquad (6)$$

Where $k=\alpha\lambda/4\pi$ and n are refractive index.

The thickness of the film (t) was determined by utilizing the technique of optical interferometer. This method is based on interference of light beam reflected from the surface of the film and the base of the substrate bottom. He-Ne laser (532nm) as a light source was utilized and the thickness was measured according to the formula 7 [11]:

$$t = \frac{\lambda}{2}\frac{\Delta x}{x} \qquad (7)$$

Where (Δx) and (x) are the shift between interference fringes and the fringe width respectively.

In the present work an attempt was being made to synthesis (In_2O_3:ZnO: Au) thin films with different concentrations deposited by spray pyrolysis technique. The structural and optical properties for all nanocomposite thin film samples with different concentrations were studied.

2. Experimental Details

The raw materials include the following compounds:

Indium Oxide nanoparticles (In_2O_3) of purity of 99.999 and particle size ranged of (82.07nm), Zinc Oxide nanoparticle (ZnO) of purity of 99.999 and particle size ranged of (53.63nm), gold nanoparticles of purity of 99.999 and particle size ranged of (73.74nm). All compounds were supplied from fluka company swiss product. Propanol solution ($CH_3.CH_2.CH_2OH$) of purity of 99.999 and double distilled deionized water.

Raw materials of (0.1 g In_2O_3 and 0.01 g ZnO) nanoparticle each of them dissolved in 20 ml propanol solution for 1 hour by using ultrasonic technique, Au nanoparticle prepared by turkevich method [12]. In_2O_3: Zno: Au thin films with different concentrations (5:5:0 ml, 5:4:1 ml, 5:3:2 ml, 5:2:3 ml, 5:1:4 ml and 5:0:5 l) were prepared by spray pyrolysis and the influence of substitution of ZnO and Au in In_2O_3 on structural and optical properties are investigated. The raw materials with different concentrations were mixed carefully by using ultrasonic device for one hour. The thin films were deposited on glass substrates placed on hot plate at 250 ^{0}C by spray pyrolysis technique. All samples placed in the furnace at 400 ^{0}C for one hour. The deposition set up involves the carrier air gas linked to a spray nozzle, precursor solution, reaction chamber in which heated and controlled substrate by a variac. Precursor spray solution was first inserted in a syringe with a metallic needle and then travelled to the hot substrate kept at temperature of 250±5°C using a thermocouple based digital temperature regulator. The pressure of carrier air gas was preserved at 1 bar. The distance between the nozzle of the spray and substrate and was fixed at 30 cm. The solution spray amount to the hot substrate was kept at (5 ml/min) during the experiment and the spray time was kept constant deposition, then the samples were allowed to cool unhurriedly at room temperature after 15 minutes [13].

The structural properties of all samples were measured by using X-ray diffraction techniques type (XRD-6000) a SHIMADZU product of Japanese – made with Cu kα radiation (λ=1.5405Å), currents of 30 mA and voltage of 40 kV. The optical measurements of thin films samples represent one of the important qualities of different optical applications. These measurements were carrying out by using a double –beam UV-VIS SP-80001 spectroscopy. The optical energy gaps (E_g) of the samples was determined through the Tauc plots.

3. Results and Discussion

I. Structural results

Figure 1 shows the XRD spectra of In_2O_3:ZnO:Au nanocomposite thin films at various concentrations (5:5:0 ml, 5:4:1 ml, 5:3:2, 5:2:3 ml, 5:1:4 ml and 5:0:5 ml). The existence of Miller indices conforms to (211), (222), (400), (333), (440) and (622) major lattice planes of the cubic spinel phase at 2θ =20.17, 33, 44.66, 50.95, 59.02, 72.48 and 73.12 which at is specified by the reference of In_2O_3 powder diffraction of card number (96-101-0342). Also, secondary lattice planes of (100) and (002) of ZnO at 2θ = 31.5582 and 34.1617, which is specified by the reference of ZnO powder diffraction of card number (96-901-1663), (111) and (200) of Au were found at 2θ = 38.5799 and 45.6016 by the reference of Au powder diffraction of card number (96-901-2431). The primary phase was cubic spinel structure for all samples. It is clear that the X-ray density and lattice parameter increases linearly with increasing gold concentrations. The lattice parameters for all samples are calculated for the most prominent peak (200). The XRD outcomes appear that the film were polycrystalline wurtzite hexagonal and cubic structure and have no distinguished orientation**.** Planes and Interplant distance are calculated by law of Bragg's diffraction and index method using equation1.

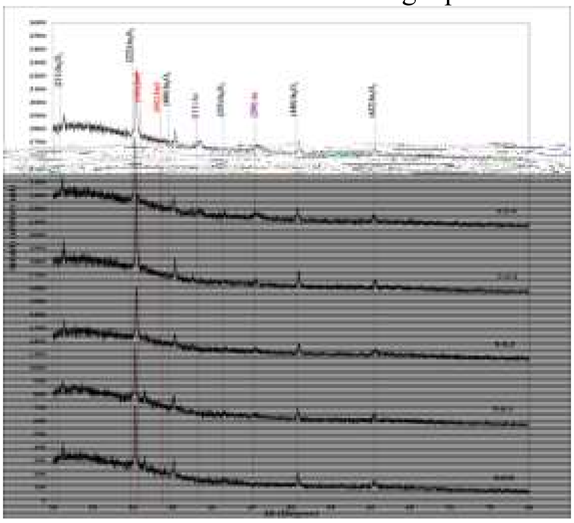

Figure 1: XRD pattern of (In_2O_3:ZnO:Au) nanocomposite thin films with different concentrations (5:5:0 ml, 5:4:1 ml, 5:3:2 ml, 5:2:3 ml, 5:1:4ml and 5:0:5ml).

II. Optical properties

1. Transmission Spectrum Results

Figure 2 show the optical transmissions of the (In_2O_3:ZnO:Au) nanocomposite thin films with different concentrations (5:5:0, 5:4:1, 5:3:2, 5:2:3, 5:4:1, 5:5:0) as a function of wavelength in the range from (300-1100 nm). One can notice that the transmissions for all specimens have less value at wavelengths of 325 nm (UV region) and it begins to increase at the visible region whose value reaches to (82.52%) at (gold concentration=0) in the wavelength (1100 nm). Generally, it can be observed from Figure 2 that the transmittance value decreases with increasing of gold content. It could be attributed to light reflection from the rough surface, because the decrease of transmittance at doping concentrations may be due to the enhancement of photon scattering by crystal defects which created by doping [13]. The spectral dependence shown in the Figure 2 reveals two main regions of interest: the fundamental absorption and the interference oscillation region. If the thickness (t) is not uniform or is slightly tapered, all interference effects will be smoothed out in the transmission curve, and the presence of these oscillations in the figure reflects an indication of good optical quality of the films this induces grain growth and agglomerations, which finally make the surface rough. The linear behavior of the graph at the absorption edge in transmission spectra confirms that the films are direct band gap semiconductors [14].

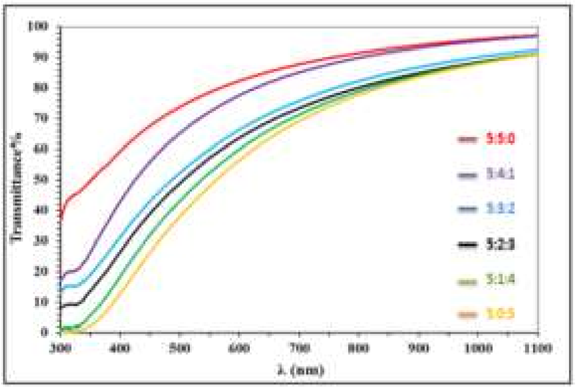

Figure 2: Transmittance pattern of (In_2O_3:ZnO:Au) nanocomposite thin films with different concentrations (5:5:0 ml, 5:4:1 ml, 5:3:2 ml, 5:2:3 ml, 5:1:4ml and 5:0:5 ml).

2. Absorption Coefficient

The variance of absorption coefficient with wavelength of (In_2O_3:ZnO:Au) ferrite thin films which were calculated by using equation 3 are shown in Figure 3. It could be discovered that the absorption factor decreases with increasing of wave length due to increases the transmittance. The maximum value of the absorption coefficient at 335nm wavelength at the UV region. The absorption coefficient begins to reduce at the visible region unfaithfully until its value reaches to 0 cm^{-1} at the wavelength of 1100 nm. Generally, it can be discovered that the absorption ratio increases when Au nanoparticle increasing.

Figure 4 shows the behavior of the extinction coefficient (k).Which was calculated by using equation 4. It is nearly similar to the corresponding absorption coefficient for (In_2O_3:ZnO:Au) nanocomposite thin films, which means that the extinction coefficient decreases with increasing of wavelength. The increasing in (k) values due to high absorption coefficient (i.e. increasing the density of localized state). In general, it may be observed that the extinction coefficient increases with increasing of Au nanoparticle.

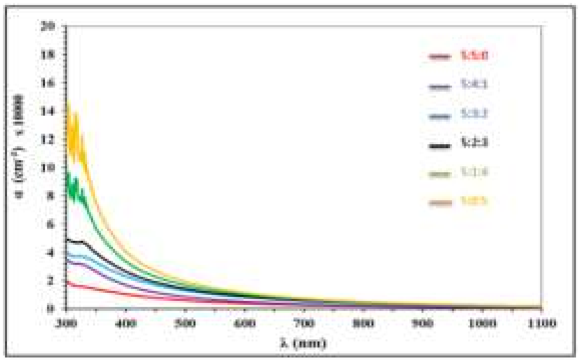

Figure 3: Absorption Coefficient pattern of (In_2O_3:ZnO:Au) nanocomposite thin films with

different concentrations (5:5:0 ml, 5:4:1 ml, 5:3:2 ml, 5:2:3 ml, 5:1:4ml and 5:0:5 ml).

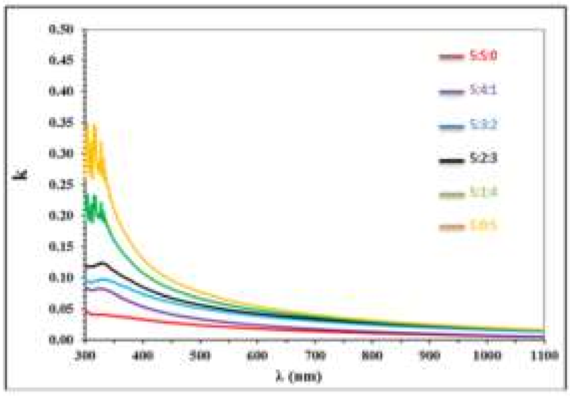

Figure 4: Extinction coefficient (k) versus wavelength for (In_2O_3:ZnO:Au) with different concentrations (5:5:0 ml, 5:4:1 ml, 5:3:2 ml, 5:2:3 ml, 5:1:4ml and 5:0:5 ml).

3. Dielectric Properties Results

The real parts of dielectric constant and imaginary parts of dielectric constant of the films were determined by the equations (5 and 6). The real and imaginary part dielectric constant alteration of all (In_2O_3:ZnO:Au) nanocomposite thin films samples at different concentrations is shown in Figures 5 and 6. From these figures can be observed that the real part dielectric constant and imaginary part dielectric constant of all trials decreases rapidly when the frequency increasing. The variant of the frequency with the constant of the dielectric appears the dispersion due to Maxwell - Wagner [15,16] type of interfacial polarization in accordance with Koops phenomenological theory [17]. The thin films of (In_2O_3:ZnO:Au) thin films exhibited the lowest dielectric constant and lowest dielectric loss tangent. The reduction in dielectric constant is due to the fact that polarization decreases with frequency and then remains constant. In accordance to Rabinkin and Novikova [18] the polarization mechanism is comparable to the conduction process.

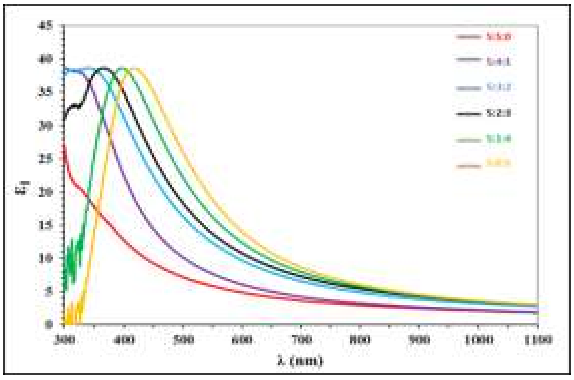

Figure 5: real part of dielectric constant versus frequency for (In_2O_3:ZnO:Au) nanocomposite thin films with different concentrations (5:5:0 ml, 5:4:1 ml, 5:3:2 ml, 5:2:3 ml, 5:1:4ml and 5:0:5 ml).

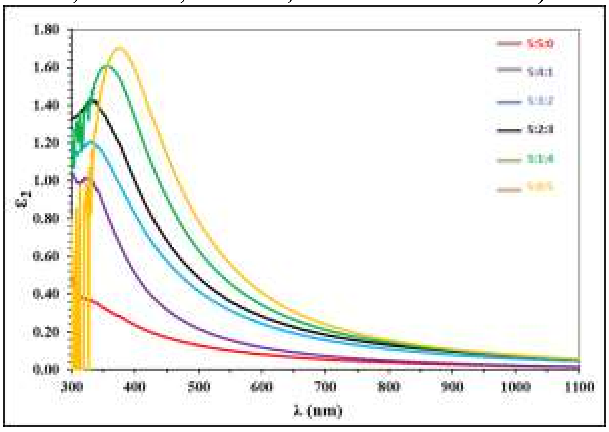

Figure 6: imaginary part dielectric constant versus frequency for (In_2O_3:ZnO:Au) nanocomposite thin films with different concentrations (5:5:0 ml, 5:4:1 ml, 5:3:2 ml, 5:2:3 ml, 5:1:4ml and 5:0:5 ml).

4. Refractive index

The refractive index variation of the (In_2O_3:ZnO:Au) nanocomposite thin films with wavelength in the range of 300-1100 nm are shown in Figure 7. It could be noticed that the refractive index rises with increasing the wavelength but begin to reduce in the visible region. Generally, it can be showed that the Au nanoparticles increasing lead to the refractive index increasing.

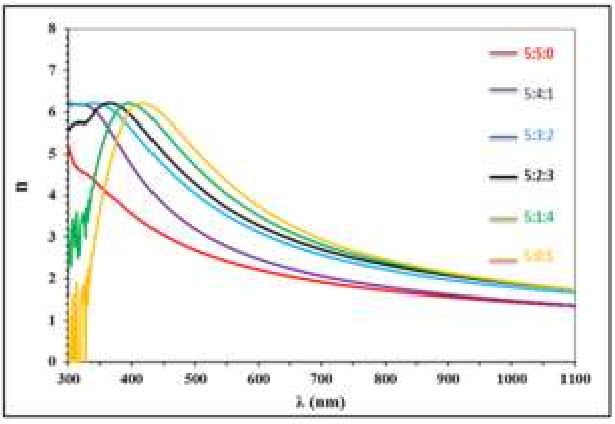

Figure 7: Refractive index versus wavelength for (In_2O_3:ZnO:Au) nanocomposite thin films with different concentrations (5:5:0 ml, 5:4:1 ml, 5:3:2 ml, 5:2:3 ml, 5:1:4ml and 5:0:5 ml).

5. Optical Energy Gap

Figure 8 show the optical energy gap. It appears the variation of $(\alpha h\upsilon)^2$ with photon energy ($h\upsilon$) for direct allowed transition of (In_2O_3:ZnO:Au) thin films with different concentration. Table (1) shows that Au nanoparticles concentration increasing lead to the optical energy gap decreasing from 3.10 to 3.05 eV. The decreasing in the optical energy gap may be because the

(In_2O_3:ZnO:Au) nanocompsite thin films structure modulation.

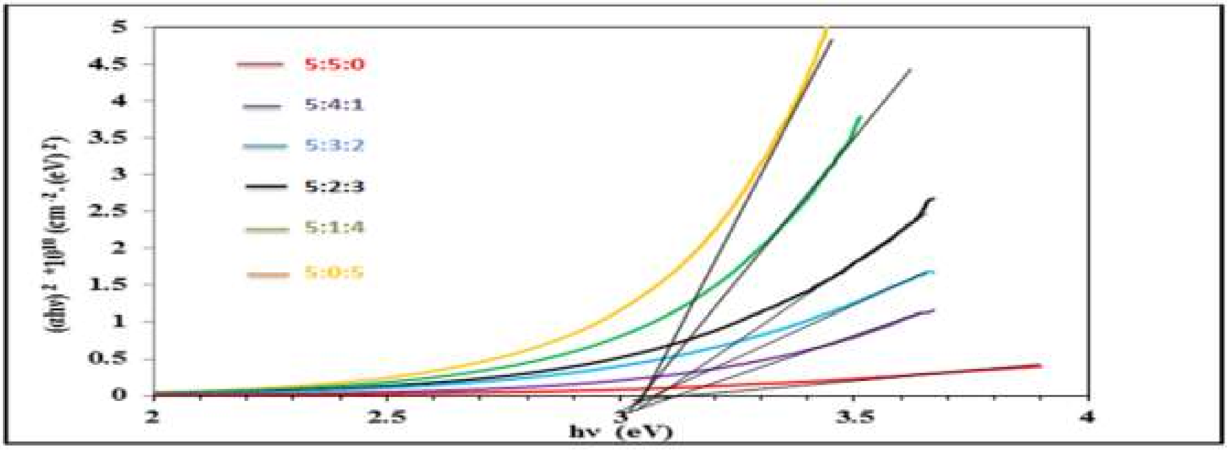

Figure 8: Energy band gap at R.T for (In_2O_3:ZnO:Au) nanocomposite thin films with different concentrations (5:5:0 ml, 5:4:1 ml, 5:3:2 ml, 5:2:3 ml, 5:1:4ml and 5:0:5 ml).

Table 1: optical properties data of (In_2O_3: ZnO: Au) nanocomposite thin films with different concentrations (5:5:0 ml, 5:4:1 ml, 5:3:2 ml, 5:2:3 ml, 5:1:4ml and 5:0:5 ml).

Sample	T%	α cm^{-1}	K	n	ε_2	ε_1	E_g
5:5:0	73.96	6034	0.024	2.677	7.165	0.129	3.10
5:4:1	65.31	8521	0.034	3.188	10.161	0.216	3.10
5:3:2	52.35	12943	0.052	4.043	16.339	0.417	3.08
5:2:3	48.95	14288	0.057	4.286	18.366	0.488	3.08
5:1:4	43.19	16793	0.067	4.712	22.197	0.630	3.05
5:0:5	38.10	19299	0.077	5.095	25.953	0.783	3.05

4. Conclusion

The (In_2O_3:ZnO:Au) nanocomposite thin film have been successfully synthesized by spray pyrolysis method. X-ray pattern for samples indicate the formations of the crystalline structure of (In_2O_3:ZnO:Au) nanocomposite thin film is cubic spinal structure phase of In_2O_3 and Au, and Hexagonal Structure phase of ZnO. When the gold content increases in concentration the lattice parameter increases. The transmittance and optical energy gap of (In_2O_3:ZnO:Au) nanocomposite thin film with different concentrations are decreased with increasing of gold nanoparticles content. The absorption coefficient, extinction coefficient, refractive index, real and imaginary dielectric constant of (In_2O_3:ZnO:Au) nanocomposite thin film with different concentrations increases with increasing of gold nanoparticles content. The optical band gap reduces with the increasing of gold concentration from. The high extinction coefficient and the high magnitude of optical conductivity promote the presence of very high samples photo response.

Acknowledgement

Thanks and high appreciation is given to Laser and Optoelectronics Engineering Department and department of science, university of Baghdad, University of Technology, Iraq, Baghdad for support this research.

References

[1] I. V. Kityk, J. Ebothe, S. Tkaczyk, R. Miedzinski, L. Nzoghe-Mendome, J. He, X. Sun, K. Sun, Q. Liu, Z. Sun, J. Lin and J. Fang, "Photoinduced Electrooptics in the In_2O_3 Nanocrystals Incorporated into PMMA Matrixes," J. Phys, Vol. 19, 1–10, 2007.

[2] G. Liu, "Synthesis, Characterization of In_2O_3 Nanocrystals and Their Photoluminescence Property", Int. J. Electrochem, Vol. 6, Pp.2162–2170, 2011.

[3] S.M. Rozati and Z. Bargbidi, "Formation of Transparent and Ohmic Nanostructure Thin Films of Fluorine-Doped Indium Oxide Prepared by Spray," World Renewable Energy Congress, 2795–2799, 2011.

[4] Sh. Sh. Batros, Investigation of pyrolysis method for preparing CdO:In_2O_3 thin films gas sensor for NO2 gas, Eng. &Tech. Journal, Vol. 33, 1134-1144, 2015.

[5] L. Filipovic, Member, IAENG,S. Selberherr, G.C. Mutinati, E. Brunet, S. Steinhauer, A. K¨ock, J. Teva, J. Kraft, J. Siegert, and F. Schrank, "Modeling Spray

Pyrolysis Deposition," Proceedings of the World Congress on Engineering, Vol. II, Pp.1–6 , 2013.

[6] D. Perednis & L.J. Gauckler, "Thin Film Deposition Using Spray Pyrolysis Journal of Electroceramics," Vol. 14, 103–111, 2005.

[7] G.R. Kumar, K.V. Kumar, Y.C. Venudhar, "Synthesis, Structural and Magnetic Properties of Copper Substituted Nickel Ferrites by Sol-Gel Method," Materials Sciences and Applications, Vol.3, 87–91, 2012.

[8] G. Nabiyouni, M. J. Fesharaki, M. Mozafariand and J.Amighian, "Characterization and Magnetic Properties of Nickel Ferrite Nanoparticles Prepared by Ball Milling Technique," Chin. Phys. Lett. Vol. 27, No. 12, 6401, 2010.

[9] D.A. Hashim, "Study the Effect of Thermal Annealing on Structural and Some Optical Properties of The $Znse_{1-X}$ Al_x Thin Film, Eng. & Tech. Journal, Vol. 33, 587-594, 2015.

[10] G. Sathishkumar, C. Venkataraju and K. Sivakumar, "Magnetic and Dielectric Properties of Cadmium Substituted Nickel Cobalt Nanoferrites," J.O Mater Science: Materials in Electronics, Vol. 24, Issue 3, 1057 –106, 2013.

[11] M.S. Majeed, M.K. Dhahir, Z.F. Mahdy, Studying the Structure and the Optical Properties of Pd Nanoparticles Affected by Precursor Concentration, Int. Journal of Engineering Research and Applications, Vol. 6, 12-17, 2015.

[12] Z. Yahia, R.M.S. Al-Haddad, "The effect of silica concentrations on the absorbance of gold nanoparticles, International Journal of Chem. Tech Research," Vol.10, 448-455, 2017.

[13] S.S. ROY and J. Podder, "Synthesis and Optical Characterization of Pure and Cu Doped SnO_2 Thin Films Deposited by Spray Pyrolysis," Journal of Optoelectronic And Advanced Materials, Vol. 12, No. 7, 1479 – 1484, 2010.

[14] A.J. Haider, S.D.S. Shaker and A.H. Mohammed, "A study of Morphological, Optical and Gas Sensing Properties for Pure and Ag Doped SnO_2 Prepared by Pulsed Laser Deposition (PLD)," Energy Procedia, Vol. 36, Pp.776 – 787, 2013.

[15] M. Abdullah, F.T. Mohammed Noori and A.H. Al-Khursan, "Millimeter Waves from Frequency Generation and Optical Rectification in Quantum dot Structure," Optical and Quantum Electronics, Vol.48, Pp.1–17, 2016.

[16] R.S. Devan, Y.D. Kolekar and B.K. Chougule, "Effect of Cobalt Substitution on the Properties of Nickel–Copper Ferrite," J. Phys: Condense.Matter, 18, 9809–9821, 2006.

[17] J.C. Maxwell, "Electricity and Magnetism", London Oxford University Press, 1873.

[18] M.H.M. Ahmed, S. Choudhury and A.K.M.A. Hossain, "AC Electric Transport Properties of Zn Substituted Li Ferrites," European Scientific Journal, Vol.10, 456–462, 2014.

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