

TEA CONCENTRATION EFFECT ON THE OPTICAL, STRUCTURAL, AND SURFACE ROUGHNESS OF Ag₂O THIN FILMS

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This work presents, the effect of the TEA concentration on the structural, optical and surface roughness of Ag₂O films prepared using the chemical bath deposition method. The structural properties ensure the formation of simple cubic crystal structure. The estimated energy gap value finds to range between (1.62-1.9eV) with TEA concentration. Surface roughness has it minimum value of (0.714nm) at specific TEA value of about (2.5ml)

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1. Introduction

Silver oxide could be found in multiple forms, it contains different amounts of Ag and O, for example (Ag₄O₃, Ag₃O₄, Ag₂O, AgO, Ag₂O₃). These phases have a various crystalline structures Produce different optical, electrochemical and photochemical characteristics [1, 2]. Ag₂O more stable than other phases. The most important characteristics of silver oxide films are high thermal conductivity, thermal stability, low quality resistance, cost of making inexpensive and high-grade symmetry on the substrate surface [3, 4].

There are different deposition techniques to prepare Ag₂O thin films such as chemical bath deposition, thermal evaporation, electron beam evaporation, RF sputtering, chemical vapor deposition, DC sputtering, electro-deposition and pulsed laser deposition. Many studies show that silver oxide films have a range of energy band gap from 1.2 to 3.4eV. Various crystalline phases could be obtained depending on the techniques that used in deposition process [5, 6]. The Fermi level of Ag₂O thin film was found from 4.8eV to 5.1eV with ionization energy (E_i) about (1.0eV). It's also one of the P-type semiconductors. NWanya et al (2013) reported the optical energy gap of (Ag₂O) thin films (1.64 eV to 1.95 eV). The XRD showed the moderate of (200) and (211) phases, while the Particle size found at range 31.52 to 67.54nm (Saroja et al. 2013). Ezenwai et al (2015) on the other hand fabricated (Ag₂O) thin film by deposition in a chemical bath (CBD) method at various concentration of complexing (TEA). They estimated energy band gap attained a value of about (1.62). In (2016) Elfadel et al. found The (Ag₂O) thin films gave relatively high transmittance in near IR region and high absorption in visible region.

Ag₂O thin film used in many applications such as photovoltaic cells, high density optical storage devices, Organic light-emitting diodes, gas sensors and as contacts in microelectronic devices and photo diodes [7, 8]. Silver oxide is used in modern medicine fields as an antibacterial coating [9, 10].

2. Experimental

Ag₂O thin films were deposited on glass slide (2x1.5) and p-type silicon as a substrates using chemical bath deposition (CDB). Before deposition glass slide cleaned with methanol, distilled water and dried in air. 0.2 g of silver nitrate (AgNO₃) solid added to 10 ml distilled water. Then added different consternation (2.5ml, 5ml, 7.5ml and 10ml) from triethanolamine (Known as TEA) (C₆H₁₅NO₃) solution as a complexing agent with constant stirred until the brown color

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disappears[11-15]. The final volume mixture (150 ml) by addition distilled water in beaker. After (60 min) from stirred solution with constant temperature 50C ° immersed vertically glass slid in solution. All above chemical reactions take the following chemical formulas [16-18].



After deposition thin films, the structural characterization of the films were examined using X-ray diffraction instrument. UV-visible (shimatzu) double beam spectrophotometer using to measurements the optical properties. Morphological properties of (Ag₂O) were achieved using atomic force microscope.

3. Results and discussion

Figure (1) presents the X-rays diffraction peaks of the samples at different TEA concentration (2.5, 5, 7.5 and 10ml), the figure reveals its crystal structure and orientation. These results ensure the complete desolation of the raw material. The obtained diffraction pattern for (2.5-7.5) TEA concentration respectively show the formation of two diffraction peaks at (200) and (211) diffraction plane at $2\theta = (38.7, 45)$ diffraction angle which is related to Ag₂O crystals as matches with (00-001-1041) standard cards. The sample prepared at 10ml of TEA concentration shows the demonstrated of just one peak at (112) diffraction plane at $2\theta = (50.6)$ which reveals the formation of AgO crystal, the last result is coincident with the (01-073-6645) standard card. However, silver oxide (Ag₂O) is the dominated one at (200) diffraction plane. A clear improve in the films crystalline formation at 2.5 TEA concentrations could be recognized, other works presents similar results [3, 19-23].

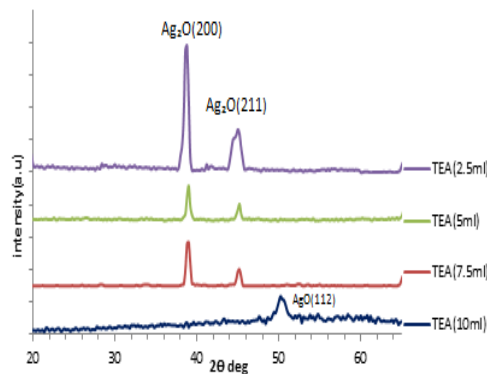


Fig. 1. (Ag) and (Ag₂O) X-ray diffraction peak.

The parameters which distinguish the structure of the deposited films were characterized by analyzing of (XRD) result by using the following equations [9, 10]:

$$D = \frac{K\lambda}{\beta(\cos\theta)} \quad (4)$$

$$\delta = \frac{1}{D^2} \quad (5)$$

$$\varepsilon = \frac{\beta}{4 \tan \theta} \quad (6)$$

β = full width at half maximum in radius, D (nm) represents the grain size, K is constant value called shape factor depended on wavelength used, Θ is Bragg angle, δ represents the dislocation density, ϵ is the strain and the wavelength of X-ray is λ . The estimated values of crystallite size, the strain and density of dislocation for silver oxide film have been tabulated in table (1). It is seen that as the TEA decrease, (Ag_2O) peak appear to be the dominating diffraction peak. This may be related to the chemical reaction of AgO that take placed with the (OH^-) or due to the chemical reaction of Ag raw metal with (OH^-) , This could attributed to its conversion into (Ag_2O) [1, 24-28].



The results also revealed that the average grains sizes decreases as the TEA concentration increased except at the (7.5ml) concentration the deposited film was out of trend, similar results could be found else were. The obtained results also show that the strain and the density of dislocation increased with increase the TEA which resulting in reducing the particle size as shown in other work also[1, 11, 29, 30].

Figure 2(a-d) shows the relation between the film's absorption and the incident wavelength as a function of TEA concentration (2.5- 10ml) respectively.

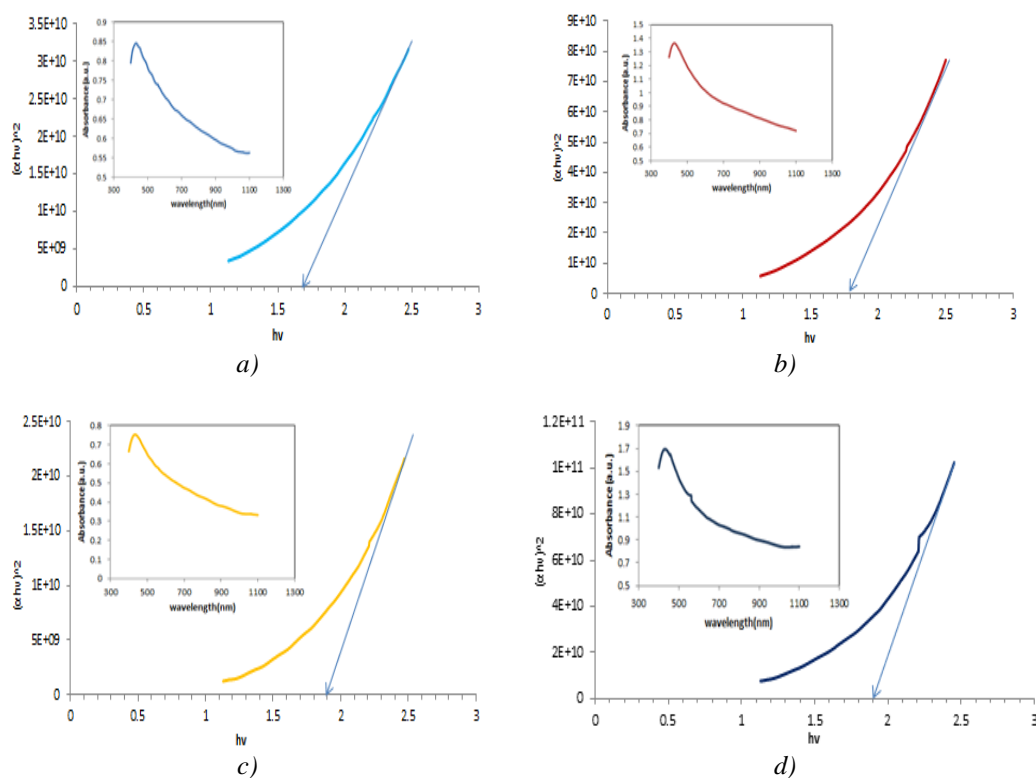


Fig. 2. the plots of $(ahv)^2$ versus $(h\nu)$ for (Ag_2O) thin films prepared at different TEA solution (A)2.5ml,(B)5ml and (c) 7.5ml (d) (c) 10ml.

It is obvious that the absorbance intensity was high in the UV-VIS region of the electromagnetic spectrum and low in the (NIR-IR) region. This is due to the slightly conversion of the Ag metal films to its oxide form with (Ag_2O) structure which has a semiconductor properties similar to other TCO's material, this shows a good agreement with other work [1,3,15, 31]. Using Tauc equation [7], the energy gap of the deposited film could be estimated depending on the absorption spectrum

$$\alpha = \frac{A(h\nu - E_g)^n}{h\nu} \quad (9)$$

where α is the absorption coefficient, A is constant, h is the Planck's constant, E_g is the energy band gap, ν is the photon frequency, n depends on the type of transition For $n=2$ indirect or $n=1/2$ direct [11, 32, 33].

In The relation between $(\alpha h\nu)^2$ versus $(h\nu)$ is called Tauc plot, the extrapolation to the linear region would give the value of E_g as shown in the same figure. The estimated optical band gap (E_g) values are (1.62, 1.8, 1.85 and 1.9 eV) at different concentration (2.5ml, 5ml, 7.5ml and 10ml) respectively. There is a slight increase in optical band gap as the TEA increases, this might be related to the light change in the film composition, also may be attributed to the quantum confinement effect [34-37].

The estimations of n (Refractive index), k (extinction coefficient), α = optical conductivity, ϵ_r and ϵ_i (real and imaginary parts in dielectric constant) was done depend on the optical properties using the equations (7 to 11).

$$K = \frac{\alpha\lambda}{4\pi} \quad (10)$$

$$n = \frac{1+R}{1-R} \sqrt{4R/(1-R)^2 - K^2} \quad (11)$$

$$\sigma = \frac{\alpha n}{4} \quad (12)$$

$$\epsilon_r = n - K \quad (13)$$

$$\epsilon_i = 2nK \quad (14)$$

(λ) Is the wavelength of the incident photon [38-41].

The relation between the incident wavelength (nm) and the refractive index and the extinction coefficient is shown in figure 3 (a, and b). It is clear that the absorbance decreased with the incident wave length and it is obvious that variation was observed in both (n) and (k) with the TEA solution. The observed decreasing may be due to the increase of the absorption showing a normal dispersion of the thin film. While the increase of (K) is related to the variation in the polarization of the thin films as shown in other works [1, 12, and 42].

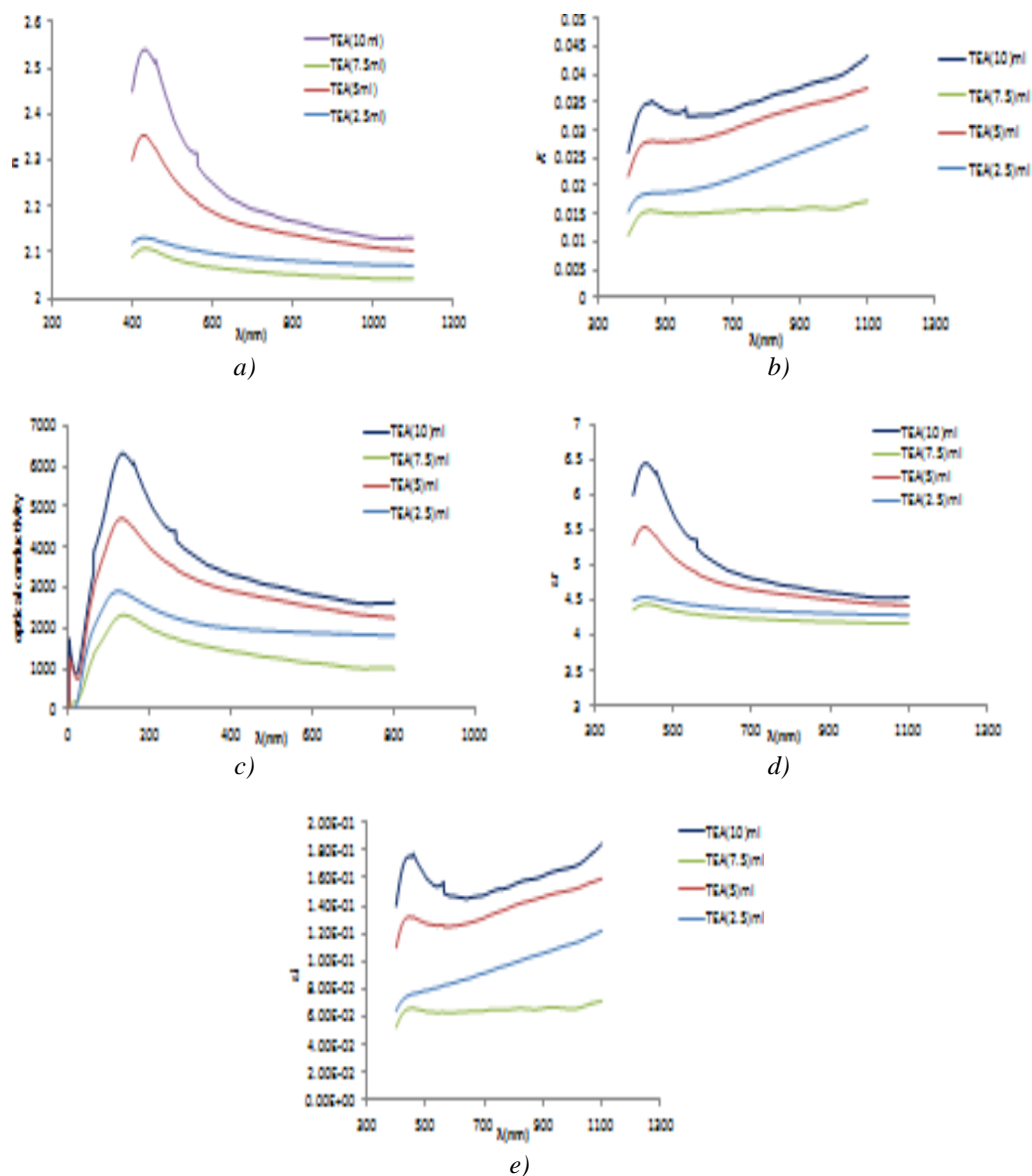


Fig. 3. Wavelength(nm) Vs (a) refractive index, (b)extinction coefficient, (c)optical conductivity, (d) real and (e) imaginary dielectric coefficient.

The variation of optical conductivity with wave length is shown in figure (3 -c), from this figure, it's obvious that the optical conductivity increased with the increase of the wave length for the different volume of TEA solution. This increasing may be due to the increase in the density of state in the band gap as shown in other work [15, 43].

The relation of both (ϵ_r) and (ϵ_i) with (λ) for films under consideration could be shown in Figure 5 (d-e) for thin films at different volume TEA solution. It's notes that real (ϵ_r) part of the dielectric constant was decreases with the increase of the wavelength and this is associated with how much the velocity of the photon retard inside the material and gives the indication about the losing of energy of a charged particle which passed through the material. While we were found the (ϵ_i) imaginary part the similarity between this relation and extinction coefficient(K) curve due to it independent on extinction coefficient with great degree as in relation (11) [11,33, 44].

Figure 4(a-d) shows the atomic force microscopic analysis of the prepared (Ag_2O) films at various triethanolamine concentration (2.5- 10) ml, respectively. It's clear that by increasing the TEA concentration the crystalline size is decrease, these results are coincide with the results obtained from the XRD analysis. The obtained results also show that all samples insure the

formation of uniform surface formed of large islands spread on the substrate; this may be related to the quantum size effect predominant on the thin films surface. The surface roughness of silver oxide films also increased with increase the (TEA) concentration; the obtained results are tabulated in Table (2). In order to determine the optimum volume of (TEA), it should be favorite to obtain thin films with low roughness so as to reduce the scattering losses, so that the lower volume of (TEA) appears to be the optimum choice [3, 45, and 46].

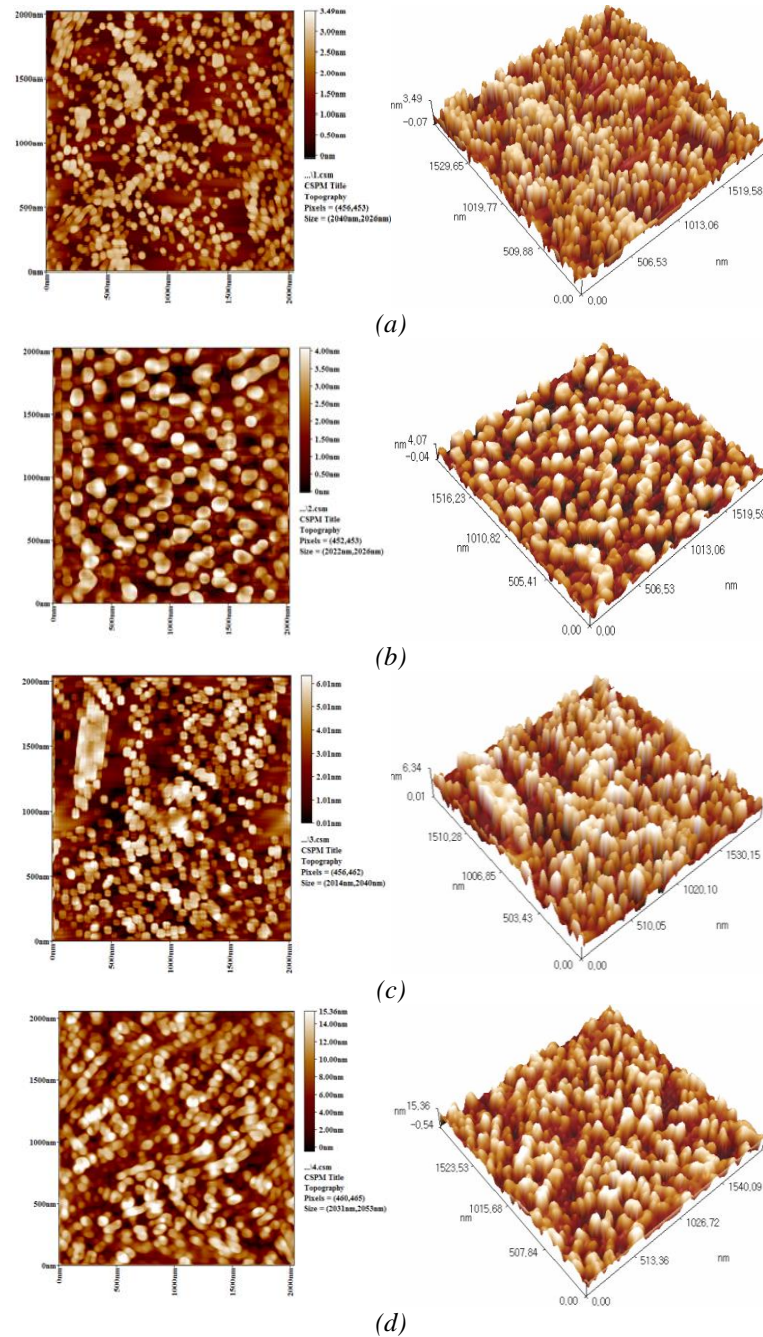


Fig. 4. AFM image of silver oxide films prepared at different TEA solution (A)2.5ml, (B)5ml and (c) 7.5ml (d) (c) 10ml.

Table 1. Structural parameters of samples extracted from x-ray diffraction technique.

TEA(ml)	2 θ (deg)	d-spacing (Å)	hkl	B (deg)	D (nm)	(δ) *10 ⁻³ (lines/m ²)	ϵ *10 ⁻³
2.5	38.7	2.326	200	0.524	16.07	3.86	2.1
5	38.8	2.320	200	0.578	14.57	4.7	2.3
7.5	38.8	2.326	200	0.542	15.53	4.14	2.2
10	50.68	1.801	112	0.759	11.58	7.44	2.9

Table 2. Data obtained from the (AFM) analyses of silver oxide films.

TEA(ml)	Roughness Average (nm)	Root mean square(nm)
2.5	0.719	0.819
5	0.928	1.08
7.5	1.46	1.7
10	3.05	3.65

4. Conclusions

After studied the obtained results in this work we could conclude that TEA concentration has an effected rule on the formation and construction of Ag₂O₃ thin films. 2.5ml TEA concentrations reflect the formation of optimum films properties with the respect to other concentration. Good quality silver oxide film with minimum surface roughness and semiconductor energy gab could be obtained at 2.5ml TEA. Other optical constants such as permeability and optical conductivity also found to vary with TEA concentration.

References

- [1] A. C. Nwanya, P. E. Ugwuoke, B. A. Ezekoye, R. U. Osuji, F. I. Ezema, *Advances in Materials Science and Engineering* **8**, 450820 (2013).
- [2] Makram A. Fakhri, *Int. J. Nanoelectronics and Materials* **9**, 93 (2016).
- [3] Evan tareq Salim, Raid A Ismail, Halemah T Halbos, *Materials Research Express*, **6(11)**, 116429 (2019) (2019).
- [4] S. M. Taleb, M. A. Fakhri, S. A. Adnan, *Journal of Ovonic Research* **15(4)**, 261 – 269 (2019).
- [5] Esben Lund, Augustinas Galeckas, Alexander Azarov, Edouard V. Monakhov, Bengt G. Svensson, *Thin Solid Films* **536**, 156 (2013).
- [6] Marwa Abdul Muhsiena, Haidar H. Hamdanb. *Energy Procedia* **18**, 300 (2012).
- [7] Salim, E.T., Halboos, H.T, *Materials Research Express* **6(6)**, 066401 (2019).
- [8] Badr, B.A., Mohammed, Q.Q., Numan, N.H., Fakhri, M.A., Abdul Wahhab, A.W., *International Journal of Nanoelectronics and Materials* **12(3)**, 283-290 (2019).
- [9] Rita Rebelo, S. V. Calderon, Raul Fangueiro, Mariana Henriques, Sandra Carvalho, *Surface & Coatings Technology* **305**, 1 (2016).
- [10] Ifeanyichukwu Chinedu Amaechi, *Chemistry and Materials Research* **8**, 2224 (2015).
- [11] Evan T Salim, Azhar I Hassan, Saif A Naaes, *Materials Research Express* **6(8)**, 086416 (2019).
- [12] Bader, B.A., Numan, N.H., Khalid, F.G., Fakhri, M.A., Abdulwahhab, A.W., *Journal of Ovonic Research* **15(2)**, 127-133 (2019).
- [13] Mahima Ranjan Das, Partha Mitra, *Journal of Physical Science* **28(2)**, 127 (2017).

- [14] M Abood, ET Salim, JA Saimon, Journal of Ovonic Research, **15(2)**, 109 – 115 (2019).
- [15] Makram A Fakhri, Ahmed W Abdulwahhab, Suad M Kadhim, Marwa S Alwazni, Salah A Adnan, Materials Research Express, **6(2)**, 026429 (2018).
- [16] I. A. Ezenwa, P. O. Obiagauzo, L. N. Ebeh, (IJITR) International Journal of Innovative Technology and Research **3**, 2220 (2015).
- [17] Z. T. Salim, U. Hashim, M. K. M. Arshad, M. A. Fakhri, Int. J. Appl. Eng. Res. **11**, 8785 (2016).
- [18] Nadir F. Habubi, Ahmed N. Abd, Mohammed, O. Dawood, A. H. Reshak, Silicon **8**, 371 (2018).
- [19] Gao Xiao-Yong, Feng Hong-Liang, Ma Jiao-Min, Zhang Zeng Yuan, Lu Jing-Xiao, Chen Yong-Shenga, YangShi-E, Gu Jin-Hua, Physica B **405**, 1922 (2010).
- [20] Naayi, S.A., Hassan, A.I., Salim, E.T., International Journal of Nanoelectronics and Materials **11**, 1-6 (2018).
- [21] AS Ibraheam, JM Rzaiz, Makram A Fakhri, AW Abdulwahhab, Materials Research Express **6(5)**, 055916 (2019).
- [22] Gandhimathinathan Saroja, Veerapandy Vasu, Nagayasamy Nagarani, Open Journal of Metal. **3**, 57 (2013).
- [23] Raid A. Ismail, Khalid Z. Yahya, Omar A. Abdulrazaq, Surface Review and Letters **12**, 299 (2005).
- [24] Ban A. Badr, Najwan H. Numan, Farah G. Khalid, Makram A. Fakhri, Ahmed W. Abdulwahhab, Journal of Ovonic Research **15(2)**, 127-133 (2019).
- [25] M. K. Abood, E. T. Salim, and J. A. Saimon, International Journal of Nanoelectronics and Materials **11(2)**, 127-134 (2018).
- [26] M. Sangappa, Padma Thiagarajan, Indian J. pharm. Sci. **77**, 151 (2015).
- [27] M. A. Muhsien, E. T. Salem, I. R. Agool, H. H. Hamdan, Appl. Nanosci. **4**, 719 (2014).
- [28] Hattab, F., Fakhry, M., 2012 First National Conference for Engineering Sciences (FNCES 2012).
- [29] M. K. Abood, M Halim A Wahid, E. T. Salim, Jehan Admon, The European Physical Journal Conferences **162**, 01058 (2017).
- [30] Dalya A Mohammed, Abdulhadi Kadhim, Makram A Fakhri, AIP Conference Proceedings **2045(1)**, 020014 (2018).
- [31] E. T. Salim, M. A. Fakhri, H. Hasan, Int. J. Nanoelectron. Mater. **6**, 121 (2013).
- [32] Israa H. Hilal, Waffaa K. Salman, Zahrra H. Hila, Baghdad Science Journal **11(2)**, 2014.
- [33] Y. Jayasree, U. Chalapathi, P. Uday Bhaskar, V. Sundara Raja, Applied Surface Science **258**, 2732 (2012).
- [34] Abood, M.K., Salim, E.T., Saimon, J.A., International Journal of Nanoelectronics and Materials **11**, 55-64 (2018).
- [35] Ban A. Badr, Najwan H. Numan, Farah G. Khalid, Makram A. Fakhri, Ahmed W. Abdulwahhab, Journal of Ovonic Research **15(1)**, 53-59 (2019).
- [36] K. Manikandana, P. Mani, C. Surendra Dilip, S. Valli, P. Fermi Hilbert Inbaraj, J. Joseph Prince, Applied Surface Science **288**, 76 (2014).
- [37] Subramaniyam Ravichandran, Veeranna Paluri, Gaurav Kumar, Karthik Loganathan, Bhaskara Rao Kokati Venkataa, Journal of Experimental Nanoscience **11**, 445 (2016).
- [38] Abood, M.K., Wahid, M.H.A., Saimon, J.A., Salim, E.T., International Journal of Nanoelectronics and Materials **11**, 237-244 (2018).
- [39] Mariam M Hassan, Makram A Fakhri, Salah Aldeen Adnan, IOP Conf. Series: Materials Science and Engineering **454(1)**, 012172 (2018).
- [40] Qamar Q. Mohameed, Farah A. Hattab, Mukkaram A. Fakhry, IJAP **11**, 33 (2015).
- [41] P. Narayana Reddy et al., ISRN Optics, 684317 (2014).
- [42] Salim, E.T., Halboos, H.T., Materials Research Express **6(6)**, 066401 (2019).
- [43] Makram A. Fakhri, Najwan H. Numan, Qamar Q. Mohammed, Mustafa S. Abdulla, Omer S. Hassan, Saad A. Abduljabar and Abdulrahman A. Ahmed, International Journal of Nanoelectronics and Materials **11** (2018) 109-114
- [44] H.-L. Feng et al., J. Korean Phys. Soc. **56(4)**, 1176 (2010).

- [45] Haleemah T. Halboos, Evan Tareq Salim, IOP Conference Series Materials Science and Engineering **454(1)**, 012174 (2018).
- [46] Marwa A Dawood, Makram A Fakhri, Farah G Khalid, Omer S Hassan, Mustafa S Abdulla, Abdulrahman A Ahmed, Saad A Abduljabar, IOP Conference Series: Materials Science and Engineering **454(1)**, 012161 (2018).