ISSN: 0974-5823 Vol. 7 No. 2 February, 2022

International Journal of Mechanical Engineering

Elaboration and characterization of NiO thin films for sensing H_2S gas

Radhiyah M. Aljarrah[1,*] , Nawar Raheem[1], Ali l- Jawdah[2]

[1] Department of Physics, Faculty of Science, University of Kufa, Najaf, Iraq

[2] Department of Physics, Faculty of Science, University of Babylon, Al Hillah, Iraq

Abstract

Nickel oxide is considered a p-type semiconductor has a wide range of applications. Recent trends have focused on employing it as a gas-sensor element. In this work, nickel oxide thin films have been prepared to produce a film with sensitizing properties suitable for working as a gas sensor application, by using a spray system. Several concentrations of nickel nitrate salt solution were used to investigate the effect of the salt solution concentration on the structure, and sensing properties of the films. The structure and morphology of the NiO films were investigated and confirmed by x-ray diffraction and field-emission scanning electron microscopy (FE SEM). X-ray patterns, and SEM images test results have confirmed that all films have a good consistency, uniform structure, and well adherent to the substrates. The results also showed that the structure of the films are a polycrystalline cubic and having a preferential orientation along the (111) plane. The gas sensing properties of the films were tested via a dynamic gas testing system wherein the target gas was H_2S at different temperature (50,100, 200, 250, 300 and 350 ^{O}C). The experimental data shows that at 200°C the system possessed, short response and recovery times, and better longer-term stability to H_2S than the others operating temperature.

Keywords: Operating temperature, Response time, Recovery time, rock salt, Sensitivity , Spray pyrolysis.

Introduction

Metal oxides are a widely used material for the sensor and biosensor applications. Metal oxide in a form of nano and normal scale structure has a lot of applications in ranges of fields of applied technology. Earlier, the scientists interested in the bulk form of these oxides, then they extended to the its thin film applications. (ZnO, SnO_2, TiO_2, WO_3, Cu_2O and CdO) are considered the most important of this kind of oxides. Nowadays, several a new kind of metallic-oxides thin films have been appearing and starts getting attentions. Nickel oxide films, which is one of these materials have a wide range of application, such as optoelectronic, semiconductor, and magnetic devices [1-5].

Metal oxides thin film can be created by using many proper deposition techniques, such as chemical deposition, dc-magnetron sputtering, electron beam evaporation, etc.[6-17]. Spray pyrolysis method is the most suitable technique to coat large areas due to its feature in terms of low cost, proper to deal with mass production, and its ability to produce high purity metallic and non metallic thin films [18,19]. In this work, NiO thin films have been created using the spray pyrolysis method, and investigate its structure and sensing properties. Keeping the environment, safety from these dangers requires providing proper detector for these chemicals. Moreover, in industrial applications and research there are still demand to improve these detectors. Particularly in terms of sensitivity, detection limitation, and selectivity [20-22].

Experimental procedure

NiO thin films have been realized on (25mm x 25mm x 1mm) glass substrate using the spray pyrolysis technique.A different concentrations of NiO solution was prepared by dissolving NO in distilled water, with a continuous stirring for 1 hour in room tempruture to obtain complete mixing using Magnetic Stirrer (IKA® C-MAG HS 7). Weighs of 0.29079gm, 0.87238 gm, 1.445397gm, 2.03555 gm, and 2.9079 gm of ($Ni(NO_3)_2.6H_2O$), each weight has been solved in 100 ml to produce (0.01, 0.03, 0.05, 0.07 and 0.1M) concentration respectively.The weight of of ($Ni(NO_3)_2.6H_2O$) that required for each concentration has been determined by use the following equation :

$$M = \frac{W}{M_W} \times \frac{1000}{V}$$

where: M represents the concentration in molars, W, Material Weight, M_W: molecular weight equal to 74.6928 gm/mol, V: distilled-water volume (100 ml).

The thin film depositing process has been performed by fixing the nozzle at 30 cm distance from the substrate, which was placed in contact with heater to avoid decreasing of substratum temperature, and keep it at 420±8 °C. The deposition was carried on by approximately 11-sec intervals, followed by two minutes with 5 ml/h of air flow rate. The film thickness was determined by use the relation: [23]

$$t = \frac{\Delta m}{A.\rho}$$

where A is representing the actual area of the film, Δm is the weight difference before and after deposition process, ρ is the density of NiO which is equal to 6.67 gm / cm3. The thickness of the prepared films ranged between 250-350 nm.

Results and Discussion

The crystal structure of NiO films has been identified via a Philips X-ray diffractometer device with Cu (kα) radiation source, with a wavelength of λ=1.54059292 Å, Maximum rated output 1.2 kW, a Tube current of 30 mA, and Tube voltage 40 kV. The results which are scattered intensity as a function of the outgoing direction was presented graphically. The angular positions of the peaks of energies have confirmed that the structure of the prepared NiO films had polycrystalline structures, with face-centered cubic (FCC), and the phase with bulk lattice constants a= 4.17382 Å. Figure (1) shows are three peaks at 38.51o , 44.73o, and 65.19o which corresponds to (111), (200) and (220) planes, respectively. On the other hand, no diffraction peaks were observed belong to the impurities or metallic Ni. The weak peaks means there is textured, the degree of the texturing depends on the kind of sprayed solution. While the strong peaks confirm that the dominant phase is crystalline phase.

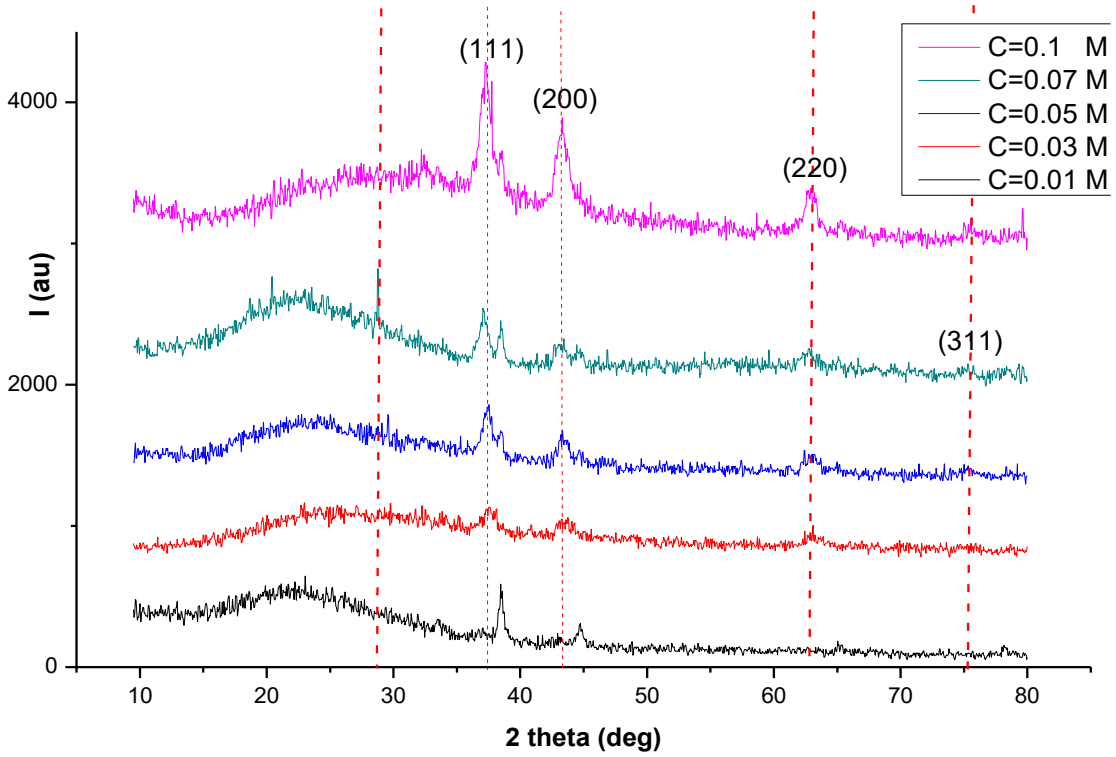


Fig.1: XRD patterns of NiO thin films at different precursor molarity

The crystallite size D has been calculated from the highest peak (111) at 2θ = 38.5 using Scherrer formula: [24]

$$D = \frac{0.9\lambda}{\beta \cos\theta}$$

where (β) represents the half maximum of full width (FWHM) for the peak diffraction at an angle (θ)), λ= wavelength of the X-Ray beam.

The structural parameters involving lattice constants (a), mean strain (ε), dislocation density (δ), and the space (d) have been calculated using the following equations [25-27] and the data in table (1).

$n\lambda=2d\sin\theta$,

$$d_{hkl} = \frac{a_{hkl}}{\sqrt{h^2 + k^2 + l^2}}. ,$$

$$\varepsilon = \frac{a_{\exp} - a_{bulk}}{a_{bulk}} ,$$

$$\delta = \frac{1}{D^2}\left(lines/m^2\right).$$

The lattice parameter values for all studied films look smaller than for the standard lattice parameter (a=4.17382 Å) of NiO, this difference can be interpreted because of the existence of internal strain, defects and impurities in the films, similar results are also reported by other researchers [28, 29].

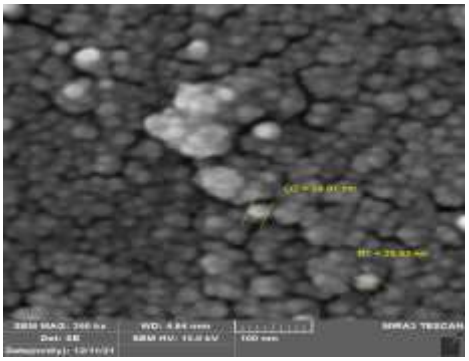
The negative sign in the mean strain expression means that the strain is a compressive strain. It is noticed that average crystal sizes are increasing from 9.7834 nm to 28.5314 nm with raising the solution concentration, which can be attributed to the increment of the defects and empty spaces in the crystalline structure with increasing the concentration of solutions. Also, it can be noticed that the film with the best structural properties possess the smallest mean straing value which effects on the crystallization level.

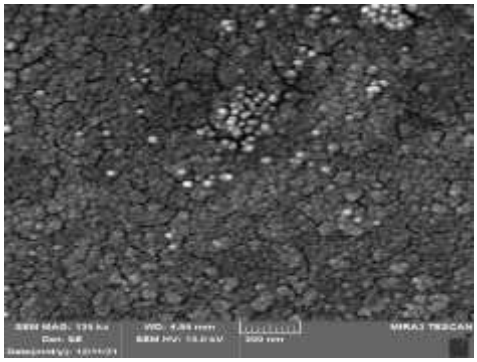
Table1: Structural parameters of NiO thin film at different precursor molarity

Precursor molarity (mol/ L)	2Ɵ (deg)	d(Å) exp	a(Å) exp	D(nm)	δ 10^{16} (lines/m2)	ε(%)	Miller Indies' s
0.01	38.5110	2.33578	4.045	9.7834	104,38	- 0.1461	(111)
0.03	37.7076	2.38367	4.128	10.66988	87.83777	-0.1286	(111)
0.05	37.4932	2.39681	4.151	12.18642	67.3361	-0.1238	(111)
0.07	38.4850	2.33729	4.195	21.38948	21.85746	-0.1456	(111)
0.1	38.6250	2.32914	4.173	28.53139	12.2844	-0.1485	(111)

The surface morphology was observed by (SEM) using a (Hitachi S-4160 SEM device). Figures (2, 3, 4, 5, and 6), shows the SEM topographic of nano-crystalline NiO thin film with EDX measurements for a different concentrations.The images show a homogeneous, uniform distribution of NiO nano-crystallites over a scanned area, and the grains shaped of different sizes.

The micro-structural details resolved by SEM show the grain size differ from the size which estimation from XRD data. This difference could be due to the grain in SEM is possibly formed by several crystallites of different crystallographic orientations whereas XRD gives the mean. X-ray data indicate and SEM images also there is textured development in nano scale. The existence of contrasting locations in the respective images denotes different density of particles which was related to the grain size. The aggregate elemental composition of the phases in the sample is determined using EDX attached to the SEM instrument as in figures (2, 3, 4, 5, and 6) and table (2).





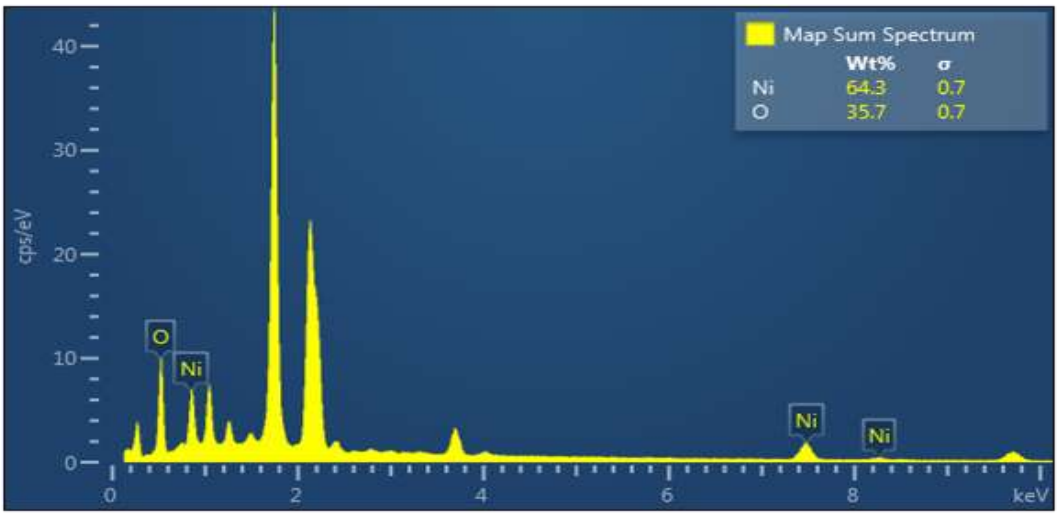
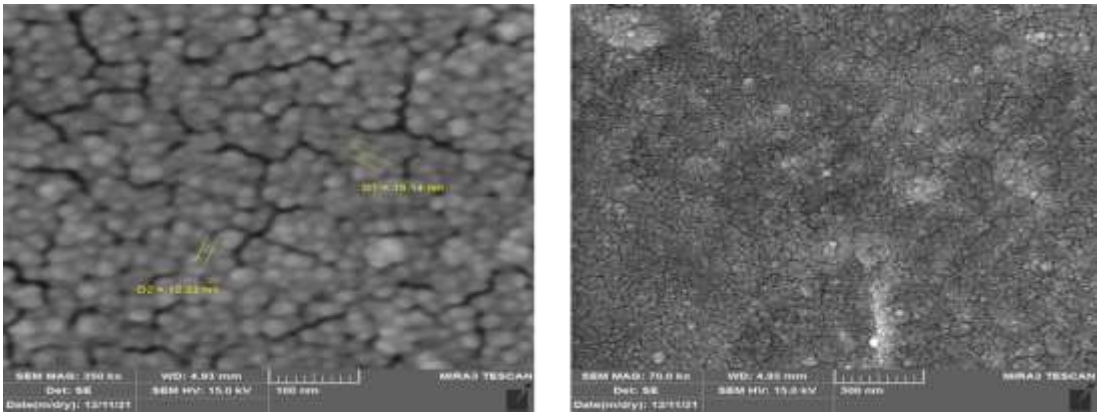


Fig.2 : SEM images of NiO nanostructure for 0.01M concentration and EDX spectrum .



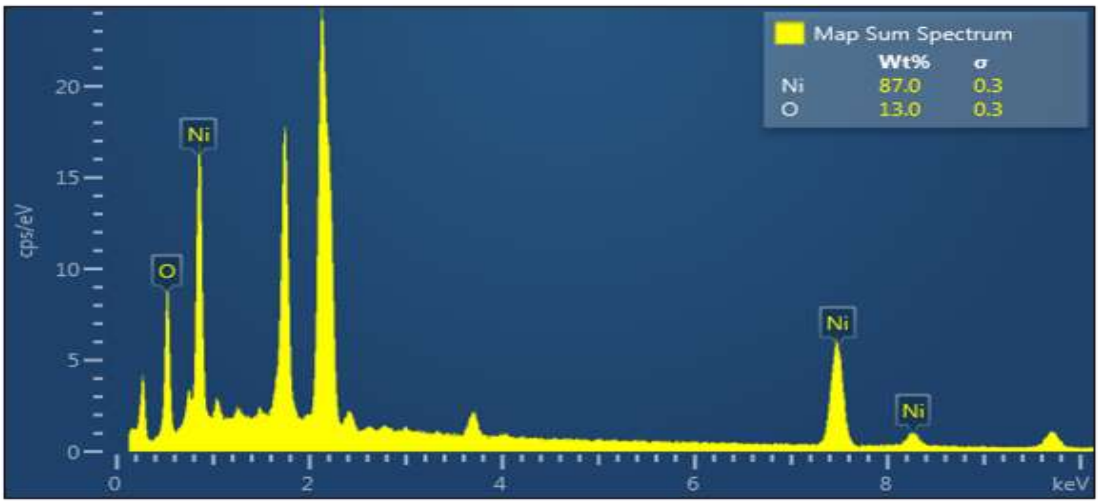


Fig.3 : SEM images of NiO nanostructure for 0.03 M concentration and EDX spectrum.

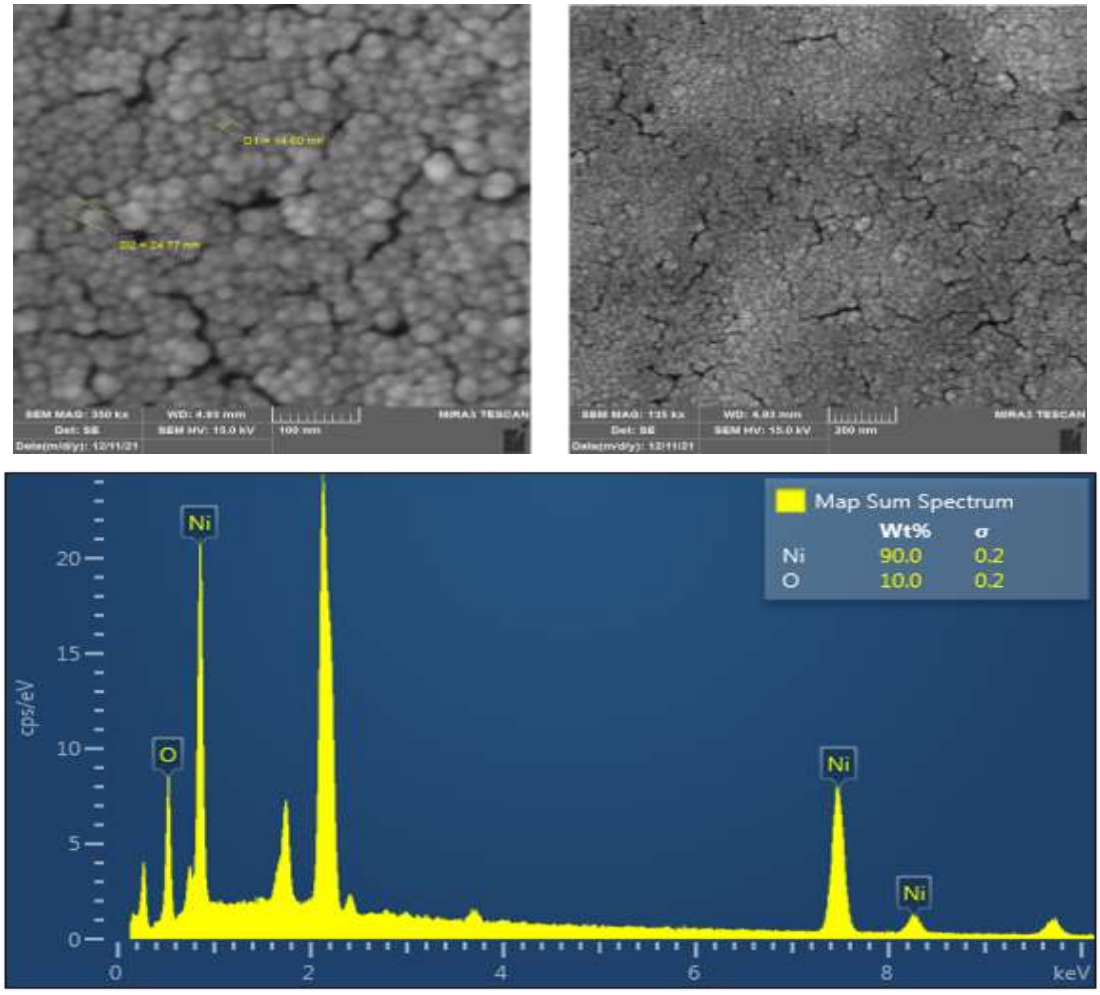
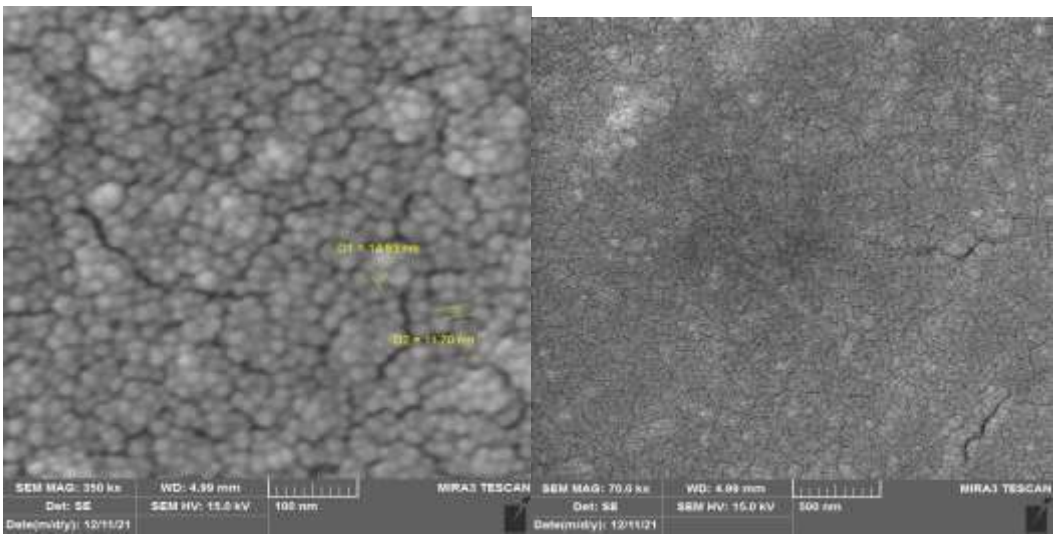


Fig.4 : SEM images of NiO nanostructure for 0.05 M concentration and EDX spectrum.



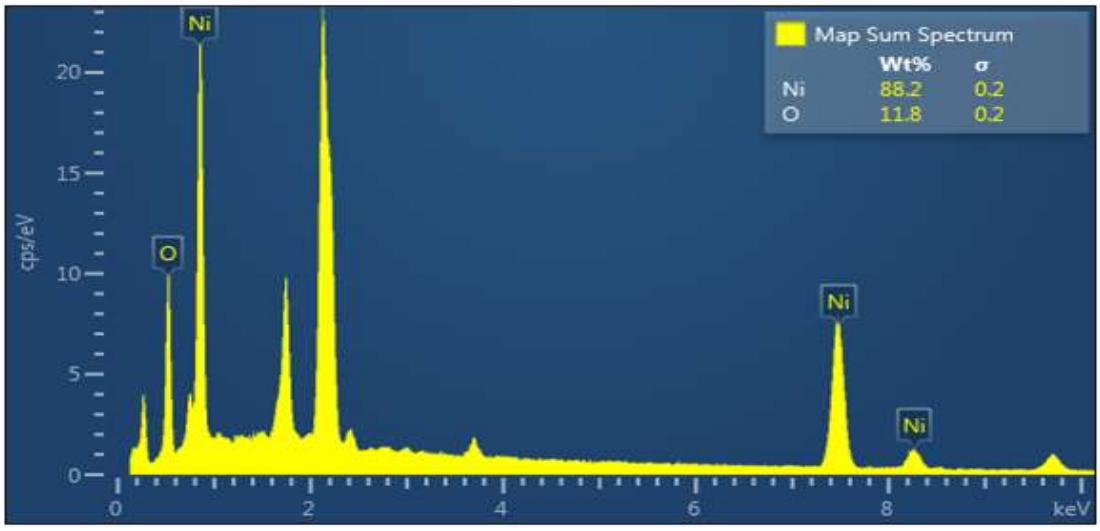


Fig.5 : SEM images of NiO nanostructure for 0.07 M concentration and EDX spectrum .

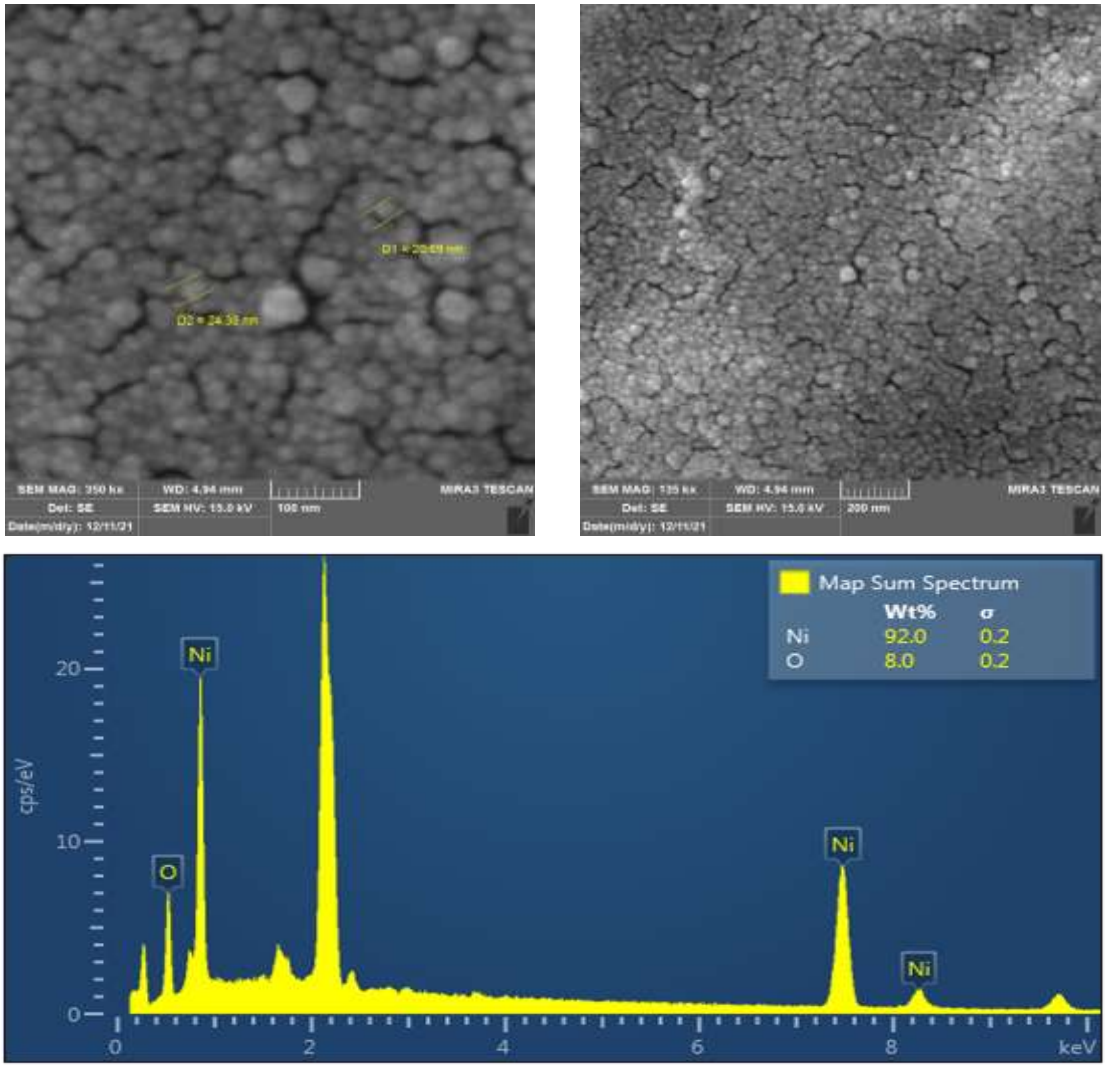


Fig.6: SEM images of NiO nanostructure for 0.1M concentration and EDX spectrum.

Table 2: EDX measurements of NiO nanostructure thin films at different concentration

Element	0.01 M	0.03 M	0.05 M	0.07 M	0.1 M	Standard Label
O	35.66	12.97	9.95	11.85	8.01	SiO2
Ni	64.34	87.03	90.05	88.15	91.99	Ni
Total:	100.00	100.00	100.00	100.00	100.00	

Gas sensing properties

For gas sensing tests, an acrylic plastic chamber equipped with 500-watt electric ceramic heater with computerized control has been installed. The chamber is supplied by mixtures of target gas (H_2S) and air in controlled proportions via two mass flow/control valves was set at a 1000 sccm during the test. A current source (2400 Source Meter, Keithley, Cleveland, Ohio, USA) was used to follow and record the changes in electrical resistance of the samples during the sensing exam.

The change of NiO film resistance in the resulting from adsorption of targeted gas molecules was translated into an electrical signal by the sensor and could be used to detect or calculate the target gas concentration, The measurement set-up is shown in Figure 7.

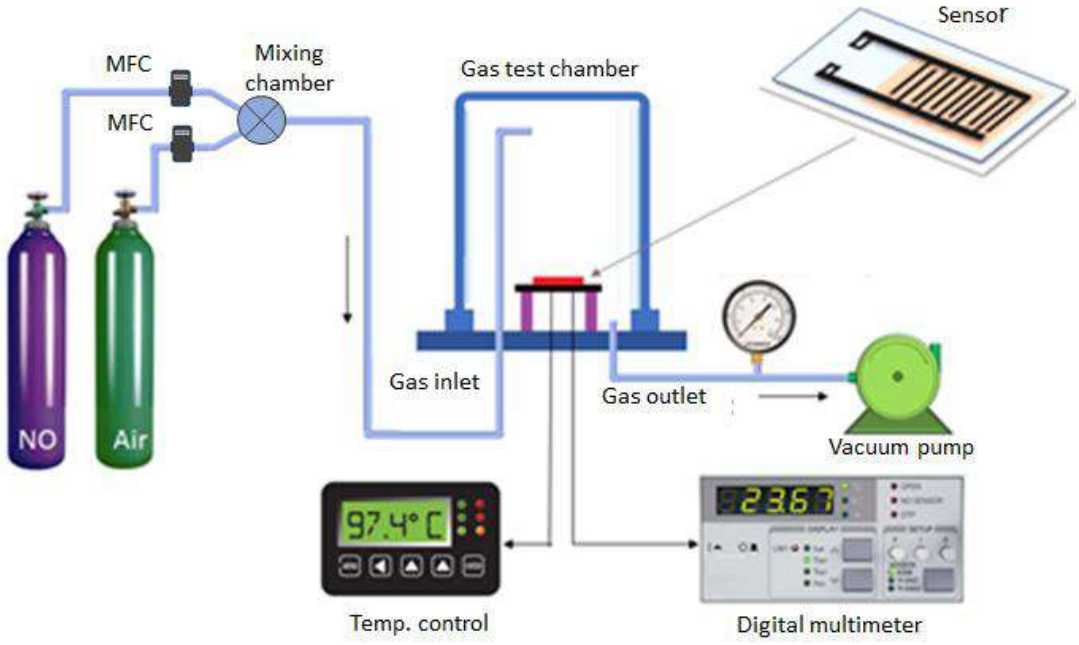


Fig. 7: Experiment setup, gas sensor testing system

The sensitivity of p-type semiconductor (NiO) film for H_2S gas estimated by:

$$S = \frac{R_a - R_g}{R_a} \times 100\%.$$

where R represents the electrical resistance of the film [30-32]. The testing results show that the sensitivity changing with the temperature (25-350 C) for all studied concentration as shown in figure 8. The increasing in the operating temperature was led to boost the sensitivity, so it peaks at operating temperature 200 ºC, then the rising stops, because increasing the temperature more, will begin to impede the oxidation process. Therefore, the optimal operating temperature for this kind of sensor is a 200 ºC. The maximum sensitivity value toward H_2S gas gets 154 % for 0.01 M. Table (3) shows the sensitivity and operating temperature. The reaction of the system in optimum temperature with 90 pp concentration of H_2S gas in terms of response and recovery time is

shown in Figure 9. To find out the effect of gas concentration on the response time, they listed in Table 4. , the data indicates that the response time increases with the concentration and the shorter time was 2.68 s for 0.03 M concentration.

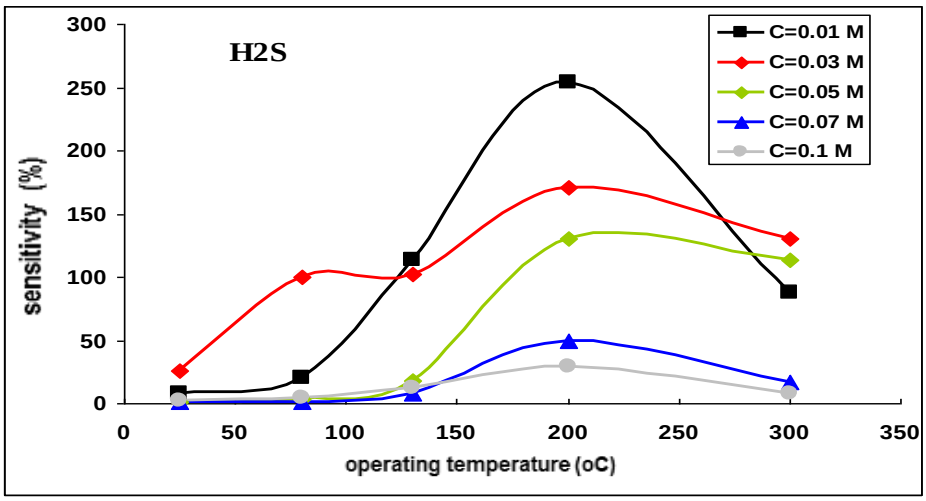
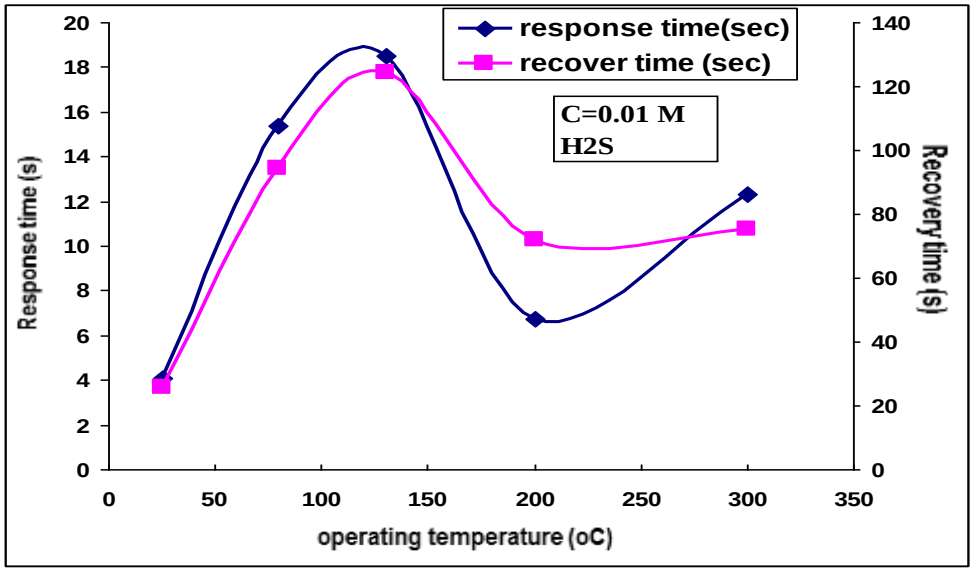
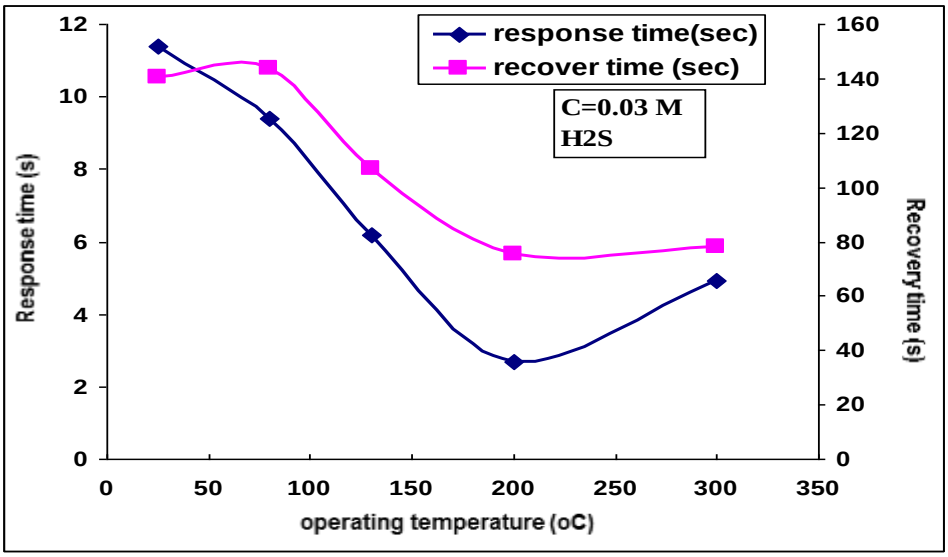
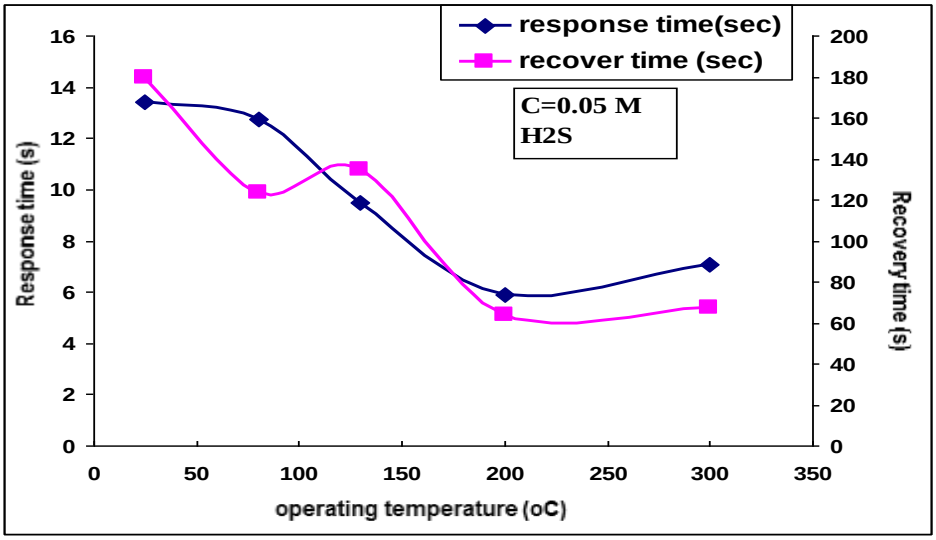
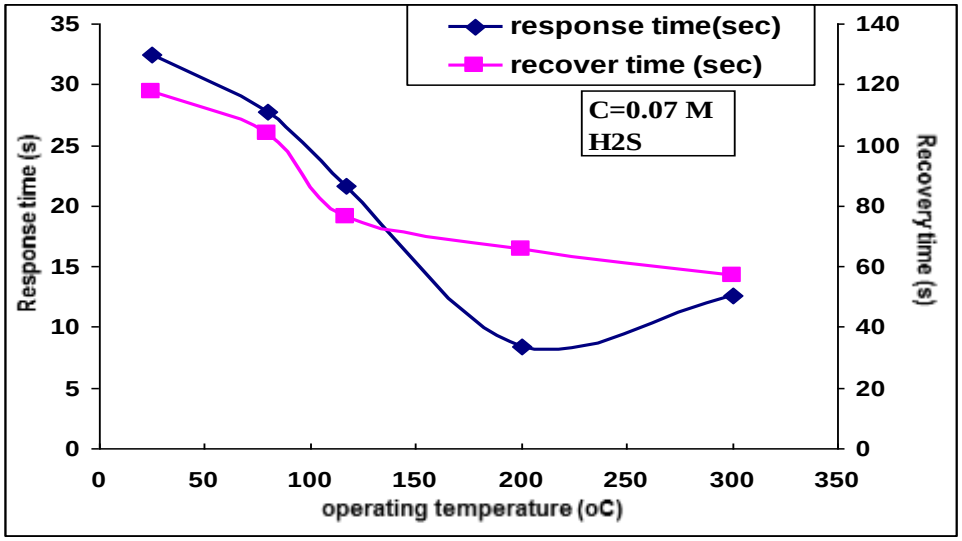


Fig. 8: The variation of the sensitivity for H_2S gas with operating temperature for films at different concentration.









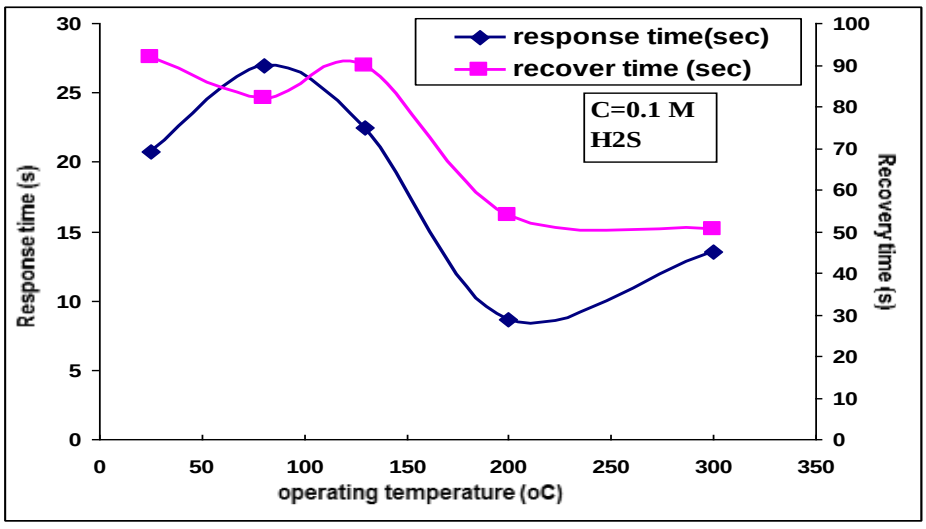


Fig. 9: The variation of Response time and Recovery time with concentration at optimum operating temperature(200 ºC).

Table 3: The sensor parameters for NiO films when exposed to H_2S gas.

Conce	Sensitivity %	Operating temperature	Response time	Recovery time
0.01	**254**	**190**	**6.71**	**72**
0.03	**171**	**200**	**2.68**	**75.6**
0.05	**135**	**200**	**5.9**	**64**
0.07	**50**	**200**	**8.4**	**65.9**
0.1	**29**	**200**	**8.6**	**54**

Conclusion:

In summary, high sensitive gas sensor system was realized by deposit tin oxide thin film on glass substrate. X-ray and SEM screening has indicated that the structure of NiO films ware a polycrystalline, and the crystallite size was 9.7834 – 28.53139 nm. As for gas sensing performance to H_2S, gas sensing tests have been done using of varying concentration of the target gas (H_2S), nickel oxide films (NiO) (1-10 wt%). The maximum sensitivity about 254 % at 200 ºC as an optimum working temperature and NiO films optimum concentration of 0.01 M. The NiO gas sensor shows an excellent response and recover time, which is 2.68 and 75.6 s, respectively at optimum temperature 200 ºC. It was shown that by the chosen parameters, it is possible to establish an outstanding performance for detection of H_2S gas.

References

1. I. D. Farrukh, R. M. Kevin and E. S. Mohammed, "Morphology and property control of NiO nanostructures for supercapacitor applications", Nanoscale Research Letters, Vol. 8, No. 1, (2013),p.p 1-7.
2. J. S. Anandh, M. Haris and P. Immanuel, "Structural and Optical Properties of Pure Nio and Li-Doped Nickel Oxide Thin Films by Sol-Gel Spin Coating Method", International Journal of Science and Research, Vol. 23, (2014), p.p58-87.
3. A. A. G. Attieh, M. S. A. Wahabab, A. A. Farghalibc and P. M. Z. Hasana, "Structural optical and photo-catalytic activity of nanocrystalline NiO thin films", Materials Research Bulletin, Vol. 7, (2016), p.p71-75.

[5] Zengjun Chen a, Tatjana Dedova a, Ilona Oja Acik a, Mati Danilson b, Malle Krunks, Nickel oxide films by chemical spray: Effect of deposition temperature and

solvent type on structural, optical, and surface properties", Applied Surface Science, Vol.548, (2021), p. 149118 .

[6] D. G. Enrico and M.Alessandro, "Sol-Gel Thin Films for Plasmonic Gas Sensors", Sensors, Vol. 15, No. 7, (2015),p.p 16910-16928.

[7] G. Williams and G. S. V. Coles, "The Gas-Sensing Potential of Nanocrystalline Tin Dioxide Produced by a Laser Ablation Technique", MRS Bulletin, Vol. 24, No. 6, (1999), p.p 25-29.

[8] David C. Look, D. C. Reynolds, C. W. Litton, R. L. Jones, D. B. Eason, and G. Cantwell, "Characterization of homoepitaxial p-type ZnO grown by molecular beam epitaxy", Applied Physics Letter, Vol. 81, No. 10, (2002), p.p1830-1832.

[9] A. M. Reddya, A. S. Reddyb and P. S. Reddya, "Annealing effect on the physical properties of dc reactive magnetron sputtered nickel oxide thin films", Physics Procedia, Vol. 49, (2013), p.p 9-14.

[10] P.J. Kelly and R.D. Arnell, "Magnetron sputtering: a review of recent developments and applications", Vacuum, Vol. 56, (2000), p.p 159-172.

[11] Yingming Zhao a , Xiang Zhang a , ∗, Xi Chen a , Wenjie Li b , Lebin Wang a , Zitong Li a , Jiupeng Zhao b , Frank Endres c , Yao Li aPreparation of Sn-NiO films and all-solid-state devices with enhanced electrochromic properties by magnetron sputtering method, Electrochimica Acta 367, (2021), p. 137457.

[12] D. Perednis and L. J. Gauckler, "Thin film deposition using spray pyrolysis", Journal of Electroceramics, Vol. 14, (2005), p.p103-111.

[13] S. A. Mahmoud, S. Alshomer and M. A. Tarawnh, "Structural and optical dispersion characterization of sprayed Nickel Oxide thin films", Journal of Modern Physics, Vol. 2, (2011), p.p1178-1186.

[14] R. C. Korošec and P. Bukovec, "Sol-Gel Prepared NiO thin films for electrochromic applications", Acta Chim. Slov, Vol. 53, (2006),p.p 136-147.

[15] F. Y. Yang, Kai Liu, Kimin Hong, D. H. Reich, P. C. Searson and C. L. Chien" Large magnetoresistance of electrodeposited Single-Crystal Bismuth thin films", Science, Vol. 284, No. 5418, (1999),p.p 1335-1337.

[16] J. C. Osuwa and G. I. Onyejiuwa, "Structural and electrical properties of annealed Nickel Oxide (NiO) Thin Films preapared by chemical bath deposition", Journal of Ovonic Research, Vol. 9, No. 1, (2013),p.p 9-15.

[17] Y.Z. Liu, C.C. Wang and M. Chu, "Low threshold 1.3-μm InGaAsP/InP lasers prepared by a single-step liquid-phase epitaxy", Journal of Applied Physics, Vol. 63, (1988), p.p2151-2151.

[18] L. Filipovic et al, "Methods of simulating thin film deposition using spray pyrolysis techniques", Microelectronic Engineering, Vol. 117, (2014),p.p 57-66.

[19] Tang-Yu Lai, Te-Hua Fang, Yu-Jen Hsiao, Ching-An Chan, "Characteristics of Au-doped SnO2–ZnO heteronanostructures for gas sensing applications." Vacuum, Vol.166, (2019): p.p155-161.

[20] Maziarz, Wojciech. "TiO2/SnO2 and TiO2/CuO thin film nano-heterostructures as gas sensors." Applied Surface Science, Vol.480, (2019): p.p 361-370.

[21] Dilip L.Kambleab, Namdev S.Haralec, Vithoba L.Patilc, Pramod S.Patilc, Laxman D.Kadam , "Characterization and NO2 gas sensing properties of spray pyrolyzed SnO2 thin films." Journal of Analytical and Applied Pyrolysis, Vol. 127, (2017):p.p 38-46.

[22] M.M. Gomaaa,, M.H. Sayeda, V.L. Patilb, M. Boshtaa, P.S. Patilb"Gas sensing performance of sprayed NiO thin films toward NO2 gas." Journal of Alloys and Compounds 885, (2021), p. 160908.

[23] Jarrah, Radhiyah Mahdi Shaker. "Synthesis and characterization of ZnO nanocrystal line for gas sensor application." Journal of Physics: Conference Series. Vol. 1279. No. 1. IOP Publishing, 2019, p..012064

[24] D. Callister, Materials science and engineering an introduction, John Wiley and Sons, New York, (1997) , p.p 174–207.

[25] C Ricbard Brundle Charles A. Evans, Jr. ,Sbaun Wihon and Lee E.Fitzpatrick, "Encyclopedia of Materials Characterization: Surfaces, Interfaces, Thin Films", Publishing by Butterworth- Heinemann, a division of Reed CUSA Inc, (1992).

[26] Y. Shao, D. Tang, J. Sun, Y. Lee, W. Xiong, China Part. Vol.2, (2004) , p.p119 –123.

[27] John J. Quinn and Kyung-Soo Yi," Solid State Physics Principles and Modern Applications", Springer-Verlag Berlin Heidelberg, (2009).

[28] R. Barir, B. Benhaoua, S. Benhamida, A. Rahal, T. Sahraoui and R. Gheriani, "Effect of precursor concentration on structural optical and electrical properties of NiO thin films prepared by spray pyrolysis", Journal of Nanomaterials, Vol. 2017, (2017), p.p1-10.

[29] S. Joishy, and B. V. Rajendra, "Effect of substrate temperature and molarity on optical and electrical properties of mixed structured Zn0.80Cd0.20O thin films", Journal of Electronic Materials, Vol. 47, No. 11, (2018),p.p 6681-6690.

[30] Aljarrah, Radhyah Mahdy, and Ali M. Aljawdah. "Concentration Effects on Characteristics of Gas Sensors Based on SnO2: Sb2O3 Thin Films." Materials Science Forum. Vol. 1039. Trans Tech Publications Ltd, 2021,.p.p 416-425

[31] Jarrah, Radhiyah M. Sal, and Iman Muslim Alessa. "The effect of annealing temperature on the structural and optical properties of nanostructure ZnO." International Journal of Energy and Environment 10.3, (2019): p.p163-168.

[32] A. S Garde, "Gas Sensing Properties of WO3 Thick Film Resistors Prepared by Screen Printing Technique, International Journal of Chemical and Physical Sciences", Vol. 5, No. 3, (2016),p.p 1-13.