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NANOCRYSTALLINE ZINC OXIDE THIN FILM GAS SENSOR FOR DETECTION OF HYDROCHLORIC ACID, ETHANOLAMINE, AND CHLOROFORM

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ABSTRACT

Zinc oxide (ZnO) thin films and micro- and nanostructures are very promising candidates for novel applications in emerging thin-film transistors, solar cells, sensors and optoelectronic devices. In this paper, a low-cost sol–gel spin coating technique was used to fabricate ZnO films on ITO glass substrates. The sol–gel fabrication process of the ZnO films is described. The influence of different precursor on the material properties of the ZnO films was investigated. X-ray diffractometer showed the phase and the crystalline structure of the ZnO as wurtzite. UV-Vis absorption spectrum showed the absorption of ZnO at 340-360 nm. EDX showed the chemical composition of Zn in ZnO. Aluminium contacts were deposited on the ZnO thin films by the use of thermal evaporation method with turbo pressure at $5x10^{-5}$Torr. The gas sensor was prepared and was checked for various gases such as conc. HCI, ethanolamine, etc. and graphs were obtained with potential volt with respect to time.

Keywords: Thin Films, Sol-gel, Scanning Electron Microscope, X-ray Diffractometer, Atomic Force Microscopy, EDX.

I. INTRODUCTION

Zinc oxide is an inorganic compound, white powdery form, with the formula ZnO. It is insoluble in water, and used as additive for applications including ceramics, glass, cement, batteries, etc. [1]. Zinc oxide (ZnO) exhibits piezoelectric, semiconducting, and pyro electricproperties. These nanostructures are bio-safety, and finds applications in optoelectronics, sensors, transducers, etc. [2]. ZnO has wide direct band gap (3.37 eV or 375 nm at room temperature). ZnO has a larger excitonbinding energy, ~60 meV, 2.4 times of the room-temperature thermal energy. It is also stable towards high-energy radiation, which makes it a potential material for space applications [3].The I-V characteristic is nonlinear, similar to that of a Zener diode. ZnOvaristors are known by various names, such as nonlinear resistors, variable resistors, surge suppressors, surge protectors, and voltage limiters [4].

Gas monitoring devices are in demand for a rapidly growing range of applications. Metal oxide based chemical sensors have been used extensively for the detection of toxic pollutant gases, combustible gases and organic

vapours. Several techniques have been used to prepare doped ZnO films, such as RF magnetron sputtering, chemical vapour deposition, sol-gel, and spray pyrolysis. In this study, the Al doped ZnO (defined as ZnO: Al) thin film sensors deposited by RF magnetron sputtering using Pt as the electrode are reported. X-ray diffraction (XRD), scanning electron microscopy (SEM), and conductivity measurements were used to characterize the microstructure and electrical properties of ZnO: Al gas-sensing films that were deposited on Si substrate [5].B. B. Dhale, S. H. Mujawar, P. S. Patil worked on the preparation of zinc oxide thin films and their optical and electrical properties were studied [6]. Onkar Singh, NipinKohli, Manmeet Pal Singh, KanikaAnand and Ravi Chand Singh studied gas sensing properties of zinc oxide thin films prepared by spray pyrolysis. They used spray pyrolysis technique to obtain zinc oxide thin films on glass substrate. A 0.2 M solution of zinc acetate in a methanol was used for spray. The substrate temperature was fixed at 350°C [7].

Mohammad TaghiHosseinnejad et al. [8] prepared nano structured ZnO thin films using magnetron sputtering and gas sensing properties were studied. ZnO is one of the most promising transparent conducting oxide materials, which is widely used in thin film gas sensors. Obtained results from these analyses revealed that the surface topography of ZnO deposited samples strongly depend on thermal oxidation time. Also the effect of thermal oxidation time on the performance of ZnO gas sensors is investigated. The results indicated that the ethanol gas sensing properties of ZnO samples improve with decreasing the size of grains [8].Keh-moh Lin, Paijay Tsai did a parametric study on preparation and characterization of ZnO: Al by sol-gel method and studied its application in solar cells [9].N. V. Kaneva and C. D. Dushkin prepared Nanocrystalline thin film of ZnO by sol gel dip coating. In this paper nanocrystalline ZnO thin films were deposited from sol-gel of zinc acetate and using dip coating onto two different substrates: glass and aluminium foil [10].Rajesh Kumar, Girish Kumar, Ahmad Umar prepared ZnO nano structures for NO2 gas-sensor application. Further, the utilization of various ZnOnanomaterials such as nano rods, nanowires, nano-micro flowers, quantum dots, thin films and nano sheets, etc. for the fabrication of NO_2 gas sensors are also presented [11].

In this researchZnO nanoparticles were synthesized by chemical route and characterized by UV-Vis spectrophotometry, XRD, SEM, EDAX, and AFM. The fabricated gas sensing device is tested for its potentiality towards HCl, ethanolamine, and chloroform.

II. EXPERIMENTAL PROCEDURE

The chemicals employed in the present study are zinc acetate dihydrate(Merck, India), sodium hydroxide (Merck, India), mono ethanolamine (Merck, India),2-propanol (Merck, India), 2-methoxy ethanol (Merck, India), and acetone (Merck, India).

0.35 M of zinc acetate dihydrate ($C_4H_{10}O_6Zn$) was mixed in 100 mL of 2-methoxy ethanol as the solvent. Mono ethanolamine was added for maintaining the pH to 10. The solution was heating for 2 hours to remove all the excess mono ethanolamine present in the solution. The formation of gel was evident from the naked eye. The obtained ZnO nanoparticles were characterized by UV-Vis spectrophotometry, XRD, SEM, EDAX, and AFM. By the use of spin coater, the synthesized ZnO was coated on ITO glass slide, at 3000 rpm for 20 seconds. The slides were heated to 80°C for 5 minutes during each cycle of coating of the nano crystalline ZnO with a time interval of 5 minutes for 5 cycles. The ITO glass slide coated with nano crystalline ZnO were annealed at 200˚C.

Aluminium contacts were deposited on the prepared films by thermal evaporation method. The power source was connected to that of the film and the aluminium contacts. The voltmeter was connected to ZnO surface and the aluminium contact. The gas sensing property was tested for HCl, ethanolamine, and chloroform

III. RESULTS AND DISCUSSIONS

X-Ray diffraction analysis:

The XRD patterns of the ZnO films (after annealing) are plotted in Figure 1. These results showed that the films were polycrystalline. The highest intensity of the (1, 0, 1) peak appeared at T pre-heat = 200˚C. In order to further analyse the intensity changes of (1, 0, 1) peak, we calculated the crystallite size using Scherrer's formula. The XRD patterns were similar to those of the ZnO powder [12], i.e., the crystallite did not have any preferred orientation. As expected, the crystallite sizes were much smaller than those of the ZnO powder. Different from the growth conditions of the ZnO powder, the ZnO films were coated layer by layer. As the first layer was formed, the nucleation and crystallite growth were random. This grown surface restrained the crystallite growth in the following layers.

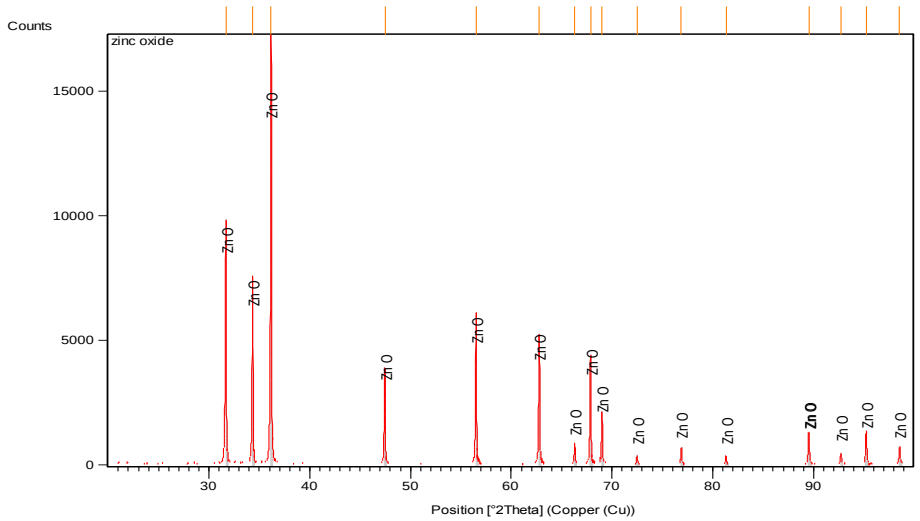

Figure 1: XRD peak of ZnO after annealing

XRD results can be used to study size, crystal structure etc. of the sample. Properties and parameters regarding the sample are studied using the XRD peaks. Table 1, and Table 2 show the entire peaks obtained from our sample, and pattern list, respectively.

Table 1: Peak list of XRD

Pos. [°2Th.]	Height [cts]	FWHM [°2Th.]	d-spacing [Å]	Rel. Int. [%]
31.6920	7814.86	0.0864	2.82106	59.24
34.3434	5634.99	0.0864	2.60909	42.71
36.1734	13192.16	0.0960	2.48119	100.00
47.4625	2743.66	0.0864	1.91404	20.80

56.5188	4230.58	0.0768	1.62694	32.07
62.7807	3529.04	0.0960	1.47888	26.75
66.3117	515.67	0.0864	1.40844	3.91
67.8722	2933.77	0.0864	1.37980	22.24
69.0099	1421.15	0.0960	1.35981	10.77
72.4693	213.80	0.0864	1.30318	1.62
76.8827	460.54	0.0576	1.23899	3.49
81.3095	202.79	0.0960	1.18235	1.54
89.5280	841.78	0.0480	1.09388	6.38
89.5591	797.99	0.0384	1.09358	6.05
92.7329	291.64	0.0960	1.06429	2.21
95.2152	842.70	0.0960	1.04300	6.39
98.5306	446.05	0.0672	1.01658	3.38

Table 2: Pattern list

Ref. Code	Score	Compound Name	Displacement [°2Th.]	Scale Factor	Chemical Formula
03-065-3411	45	Zinc Oxide	0.000	0.152	ZnO

UV-Vis Spectrophotometric studies:

The optical transmittance and absorption coefficient spectra of the thin films in the UV–Vis wavelength range are presented in Figure 2. It can be seen that the films have high transparency in the visible range (>92%). The first derivative of optical transmittance spectra are presented in Figure 2 correspond to the peaks for all of the films were 376 nm. The optical band gap with direct transition can be calculated from the following relationship, $(\alpha h\nu) = B(h\nu - E)^{1/2}$ where $h\nu$ is photon energy and B is a constant between 10^7 and 10^8 m^{-1}.

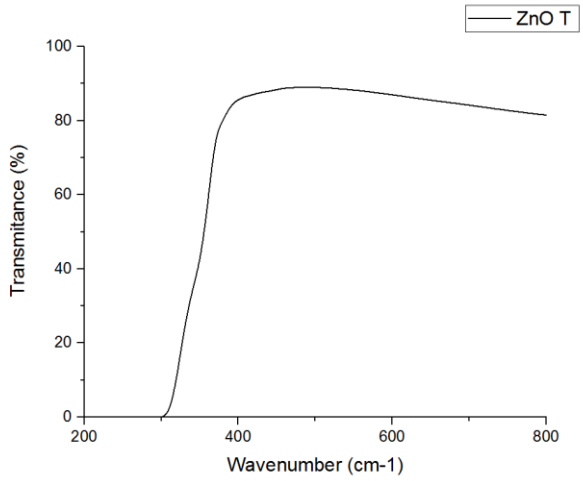

Figure 2: UV-Vis spectrophotometer transmittance graph for ZnO

Atomic force microscopic studies:

Atomic force microscope can be used to obtain optical image of thin film, topographical image, etc. AFM produces 3D topography of the sample. Figure 3 show the topography of the ZnO thin film. Y-axis in the figure shows the height of the obtained ZnO film. These images show the obtained thin is uniform throughout and the height of thin film was in the range of 20 -30 nm.

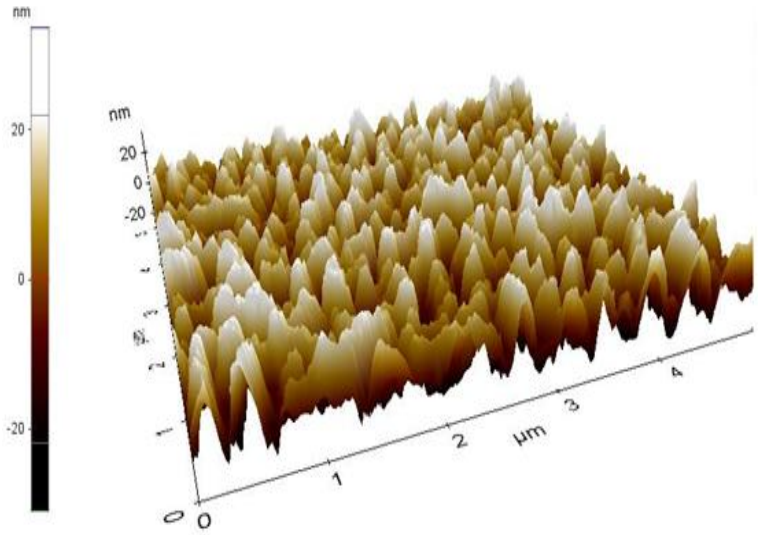

Figure 3: AFM results of ZnO thin film

Crystallites in thin films are normally referred as grains. They are small or even microscopic crystals and form during the cooling of materials. The orientation can be random with no preferred direction. Interface between two grains are known grain boundaries. It is a single phase interface, with crystals on each side of the boundary. Figure 4 show the grains in ZnO thin films. Table 3 show the grain boundary details.

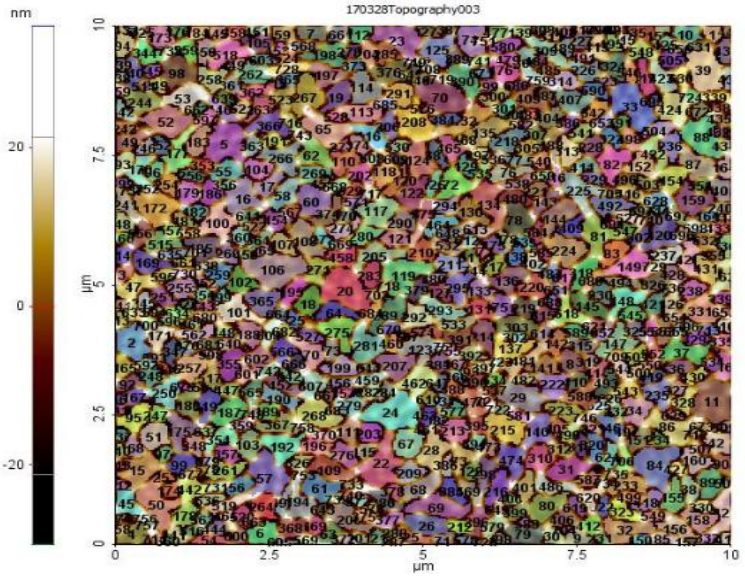

Figure 4: Grains in ZnO thin film

Table 3: Grain boundary details of ZnO thin film

Grain	Area(µm²)	Vol(µm³)	Length(µm)	Peri(µm)	Rpv(nm)
Mean	1.1E-1	5.088E-4	0.477	1.456	33.447
Std.	8.635E-2	3.828E-4	0.201	0.658	9.938
1	0.079	0.000	0.369	1.250	31.470
2	0.307	0.001	0.746	2.427	43.097
3	0.067	0.001	0.391	1.025	35.354
4	0.000	0.001	0.586	1.917	38.742
5	0.000	0.000	0.860	3.094	43.969
6	0.169	0.001	0.581	1.751	38.066
7	0.111	0.001	0.524	1.461	27.244
8	0.154	0.001	0.555	1.692	38.042
9	0.101	0.000	0.457	1.315	29.843
10	0.125	0.000	0.524	1.627	37.132
11	0.449	0.000	0.984	3.167	43.245
12	0.172	0.001	0.843	2.418	37.736
13	0.060	0.000	0.315	0.970	39.814
14	0.085	0.000	0.387	1.181	45.137
15	286865.234	0.000	0.754	2.570	37.339
16	0.299	0.000	0.767	2.795	47.015
17	0.157	0.000	0.664	2.105	39.476
18	0.183	0.001	0.630	1.968	35.061
19	0.191	0.001	0.758	2.193	31.355
20	0.500	0.001	1.019	3.388	47.026

Figure 5 show the graphical representation of average length, perimeter, area and volume of the grain boundary of ZnO thin film. It represents all the 759 grains found using atomic microscope.

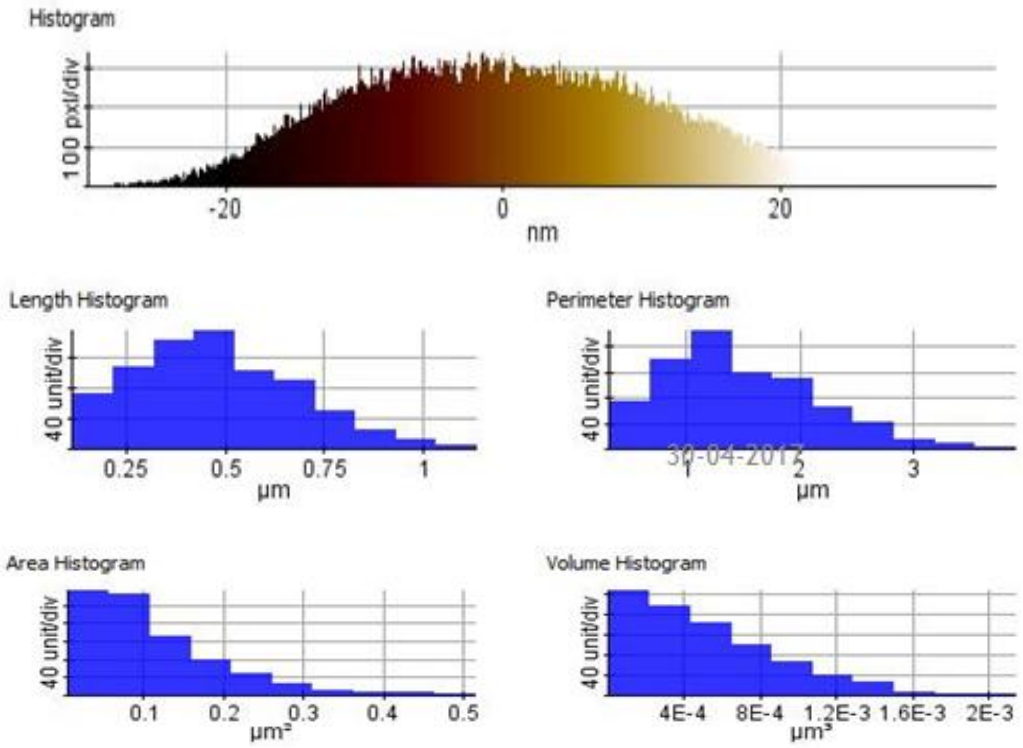

Figure 5: Histogram details of grains in ZnO thin film

Figure 6 (a, and b) show the optical image of ZnO thin film using AFM. Figure 6 (b) clearly show the coated and uncoated junction. Red colour area show the thin. The optical image was taken at 800X magnification.

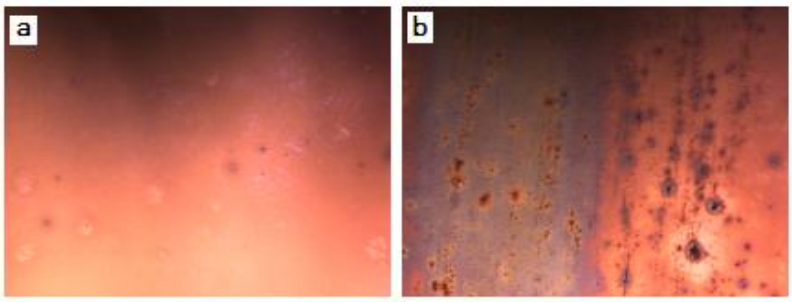

Figure 6: (a) AFM optical images showing thin film coated on ITO, (b) show the thin film coated and uncoated area

Scanning electron microscopic studies:

A scanning electron microscope (SEM) is a type of electron microscope that produces images of a sample by scanning the surface with a focused beam of electrons. The electrons interact with atoms in the sample, producing various signals that contain information about the sample's surface topography and composition. Figure 7 show the surface image obtained using scanning electron microscope.

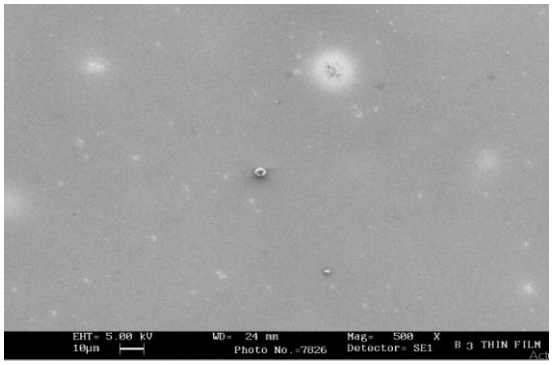

Figure 7: SEM image of ZnO thin film

Energy dispersive X-ray studies:

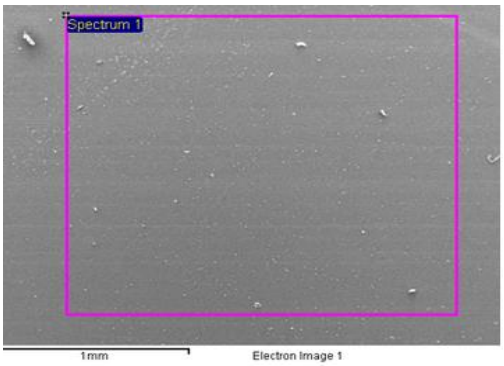

Figure 8: Electron image using EDAX

Energy dispersive X-ray is an analytical technique used for the elemental analysis or chemical characterization of a sample. It relies on an interaction of some source of X-ray excitation and a sample. Its characterization capabilities are due in large part to the fundamental principle that each element has a unique atomic structure

allowing a unique set of peaks on its electromagnetic emission spectrum. Figure 8 show the surface of ZnO coated substrate using EDX.

Figure 9 indicate the amount of chemical compounds present on the ZnO coated substrate. The weight percentage and atomic percentage of the compounds are mentioned in the Table 4.

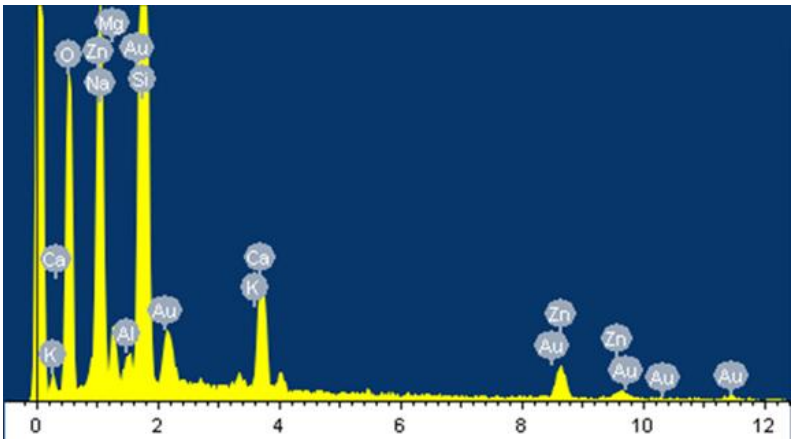

Figure 9: EDAX graph showing the presence of ZnO on substrate

Table 4: EDAX details showing presence of different compounds

Element	Weight %	Atomic %	Formula
Na K	10.67	10.01	Na_2O
Mg K	2.07	1.84	MgO
Al K	0.56	0.45	Al_2O_3
Si K	30.36	23.33	SiO_2
K K	0.53	0.29	K_2O
Ca K	4.49	2.42	CaO
Zn K	7.45	2.46	ZnO
O	43.88	59.2	--
Totals	100	--	--

Gas sensor measurement:

Keitheley power source was used for testing gas sensing property. It has two connectors through which the substrate is held. Now the gases are passed and the aluminium electrodes present on the substrate help in determining the potential changes. The voltage values were recorded for each gas. The values are given in Table 5, 6, and 7, respectively.

Table 5: Gas sensor response to concentrated HCl

Time (minutes)	Potential values of conc. HCl (In volts)
1	30
2	29
3	18
4	13

Table 6: Gas sensor response to ethanolamine

Time (minutes)	Potential values of ethanolamine (In Volts)
1	34.4
2	28.4
3	27.4
4	26.0
5	27.5

Table 7: Gas sensor response to chloroform

Time (minutes)	potential values of chloroform(In volts)
1	30.4
2	29.8
3	27.4
4	26.5
5	25.4

VI. CONCLUSION

This research work shows that zinc oxide thin film is a good candidate for gas sensors. The results obtained shows that they are capable of sensing different gases. A voltmeter was used to measure the change in electrical conductivity of zinc oxide thin film which indicates the presence of gas present in the surrounding. Varying voltage shows the presence of different gases in atmosphere. Zinc oxide precursor solution was prepared using sol-gel technique and was successfully deposited on to ITO glass using spin coating technique. It is then characterized using AFM, SEM, and XRD. AFM results showed the thickness of thin film at 20-30 nm range. Later aluminium contact was made on ITO glass to functionalize it as a gas sensor. In order to read the voltage changes in the gas sensor a voltmeter was used. Voltmeter output shows that zinc oxide nano structures are well suitable for gas sensors and has good quick recovery time and selectivity towards gases.

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