

Modeling of Gas Sensor based on Zinc Oxide Thin Films by Feedback Loop using Operational Amplifier

--Manuscript Draft--

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Abstract:	Gas sensing is seeking the attention of both industries and academia because of its wide-ranging application and intrinsic limitations of sensing technologies. Mostly, the gases are sensed due to variation in electrical, optical, acoustic, chromatographic, and calorimetric properties of sensing materials in the influence of various gases but in case of zinc oxide thin film, its resistance varies in influence to reducing gases [1, 2]. Particularly, this article is concerned in modeling durable sensing device using Zinc oxide thin film at low cost and operating within the low potential. To eliminate the temperature dependency for higher sensitivity of the sensor and fabricate cheap, portable, precise, less energy-consuming and durable sensing device, a new electronic model of the sensor was self-designed and analyzed. Monitoring the change in film's resistance, a perfect gas sensor was built. Zinc oxide thin film was synthesized by using the Sol-gel method (Spin coating) and was characterized by XRD and SEM which revealed wurtzite polycrystalline nature of Zinc oxide film with average grain size 17-25 nm. The fabricated film showed a fabulous response to ethanol and methanol vapors. It's the noble electronic model of gas sensing in the current time.
Opposed Reviewers:	
Additional Information:	
Question	Response
Publication ethics	I confirm
Please confirm that you have reviewed our guidelines for Ethics in Publishing as well as Heliyon's Ethics and Editorial Policies .	

Christian Schulz
Editorial Director
Cell Press Heliyon

Dear Schulz,

Warm greeting from Patan Multiple Campus and Nepal Academy of Science and Technology (NAST), Nepal. We would like to submit the manuscript entitled “Modeling of Gas Sensor based on Zinc Oxide Thin Films by Feedback Loop using Operational Amplifier” to be considered for publication as an original article in Sensors and Actuators.

Our research is concerned in modeling of gas sensor and we designed an unaccustomed electronic circuit, modeled it theoretically, and then experimentally verified that the circuit performs well by using Zinc oxide thin film as sensing material in the circuit.

We declare that our findings are completely novel till date and no such articles have been published in any of the journals before. Furthermore, we would like to apprise that this manuscript is original, has not been published before and is not currently being considered for publication elsewhere.

We are known that this publication has no conflicts of interest associated and there hasn't been any financial support for this research that could influence its outcomes. As a corresponding Author, I would like to confirm that the manuscript has been read and approved for submission by all the authors.

Sincerely,
Raju Bhattarai

Conflicts of Interest Statement

Manuscript title: MODELLING OF GAS SENSOR BASED ON ZINC OXIDE THIN FILMS BY FEEDBACK LOOP USING OPERATIONAL AMPLIFIER

The authors whose names are listed immediately below certify that they have **NO** affiliations with or involvement in any organization or entity with any financial interest (such as honoraria; educational grants; participation in speakers' bureaus; membership, employment, consultancies, stock ownership, or other equity interest; and expert testimony or patent-licensing arrangements), or non-financial interest (such as personal or professional relationships, affiliations, knowledge or beliefs) in the subject matter or materials discussed in this manuscript.

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This statement is signed by all the authors to indicate agreement that the above information is true and correct.

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Date

1 Sep 2023

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3 Sep 2023

Ram Bahadur Thapa



2 Sep 2023

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3 Sep 2023

About the revision

Christian Schulz
Editorial Director
Cell Press Heliyon

Dear Schulz,

Manuscript entitled "**Modeling of Gas Sensor based on Zinc Oxide Thin Films by Feedback Loop using Operational Amplifier**" had been sent back for revision. We want to greet heartily the reviewers for their valuable reviews and apologies for inconvenience and commend the following edition as per the reviewer's suggestion for the publication of the article.

1. Data will be made available whenever asked.

2. Reviewer #1:

(a) The authors of the study claimed that their sensor was better, but failed to provide a comparative analysis. It would be useful to compare their work with the widely used chemi-resistive gas sensors, like MQ sensors, which are based on potential divider networks. This would allow readers to better understand the effectiveness of the sensor fabricated in the study.

Replied: As suggested, we have compared our sensor with MQ-sensors referencing concerned article. MQ sensor uses heating mechanism to heat its sensing material around 300 °C but we do not need to heat the film to sense the gases. (P2 last paragraph)

(b) In Figure 3, connections are not proper.

Replied: All the connections are proper. It is obvious that the amplifier should be connected to Vcc and ground.

(c) In order to ensure transparency and reproducibility, authors are advised to include the code number of the amplifier used in their research.

Replied: Most of the amplifier fits well in the circuit. We have not included the code here so as to save the article and findings from being copied. After publication, it can be made available if asked.

(d) If possible, merge Figure 8 with Table 2 for clarity.

Replied: Figure 8 and Table 2 have been merged as per suggestion.

(e) Repeatability is an important parameter for the gas sensing device. It is recommended that authors include repeatability measurements for a minimum of three cycles.

Replied: We have passed different concentrations of alcohol vapors (Ethanol and Methanol) through the same sample of thin film and have stated the response and recovery time too. We have conducted multiple experiments and noted the similar data. Presenting same or similar data for multiple times may not look good. So we represented the data of various concentrations of Ethanol and Methanol once.

(f) It is recommended that the authors make some corrections to their manuscript, specifically addressing errors such as the following:

In P2L41, provide a space in "Solutionwas"

In P2L42, change 'ml' to 'mL'

In P7L48, do not capitalize the first alphabet of trigonometric functions.

Replied: All of these are corrected.

3. Reviewer #2:

The manuscript deals with the elimination of the temperature dependency for higher sensitivity of the metal oxide gas sensor and fabrication of a cheap, portable and durable sensing devices and a new electronic circuit, a perfect gas sensor. Zinc oxide thin film was synthesized by using the Sol-gel method (Spin coating) and was characterized by XRD and SEM which revealed wurtzite polycrystalline nature of Zinc oxide film with average grain size 17-25 nm.

Please explain what does it mean?

Replied: As these been stated in an abstract, we have explained all these in introductory, characterization, result and discussion section. For example, in last paragraph of "Introduction" Section, we have discussed dependency of sensing material of MQ-sensor in temperature for sensing the gases.

4. Editor comment: This work presents a design of an electronic circuit made specifically for a sensor system. In order to be acceptable as a scientific article the manuscript needs to go beyond a technical report of a sensor, reporting scientific advances in sensor science (not only development of a circuit). Please revise the manuscript and make sure that it goes beyond a technical report of a sensor circuit and emphasize the contribution to scientific advance.

Replied: The manuscript has been revised. It is not just a technical report. It has described the way to synthesize the ZnO thin film in a unique way and has characterized it. It explains the use of ZnO as a thin film sensor. It claims the sensor performs better than other and verifies experimentally. Thus, it is scientific work.

Sincerely,

Raju Bhattacharai

About the revision

Jordi Faraudo

Section Editor

Cell Press Heliyon

Dear Schulz,

Manuscript entitled "**Modeling of Gas Sensor based on Zinc Oxide Thin Films by Feedback Loop using Operational Amplifier**" had been sent back for second revision. We want to greet heartily the reviewers for their valuable reviews and apologies for inconvenience and commend the following edition as per the reviewer's suggestion for the publication of the article.

1. Data have been made publicly available by linking the Google drive. Reviewer can easily access the data and revised manuscript here.

https://drive.google.com/drive/folders/1pOSLycaa9S-5fXB9wiAPMWMq_ADDM512?usp=sharing

2. Reviewer #1:

Major corrections have been made by the authors. However, some of the issues are still there.

Reviewer #3: The revised manuscript contains required information. So I recommend the manuscript to accept for publication.

Replied: We are thankful to the reviewers. Reviewer-1st has addressed the major revisions made but has not pointed the remaining issues particularly. Therefore, we proceed to address the next reviewer.

3. Reviewer #4:

- (1) In most of the lines author had used (,) before "and", so kindly make changes in the given page no and line numbers:

Page no 1 - Line 39, Line 42, Line 45, Line 47, Line 54

Page no 2 - Line 17, Line 29, Line 33

Page no 3 - Line 56

Page no 5 - Line 35

Page no 6 - Line 37

Page no 8 - Line 46

Page no10- Line 15

Replied: We had reviewed the article published in Heliyon and found that (,) has been used before "and", so we followed the same. But, as it's a minor issue, we kindly followed the reviewer and edited as per suggestion.

(2) In Page no 2 - Line 23, High energy ball milling is not a thin film fabricating technique.

Replied: We wanted to mention it as a nanopowder fabrication technique but underlying reviewer's comment we have removed it.

(3) In Page no 3 - Fig 2, in the designed circuit part, in amp 1, + connection is incomplete and in amp 2 the - connection is wrong.

Replied: We have completed the connection in amp1 and would like to confirm that the connection in amp 2 is in accordance to the circuit that we have designed and worked with.

(4) In Page no 4 - Line 5 to 9, sentence was not in proper form

Replied: We have corrected it by using simple sentences as:

Page 4: Line 4-12

The positive input terminal of first amplifier was connected to the junction of R_1 and R_2 and the negative input terminal was joined to the junction of feedback resistor (R_f) and film resistor (R_x). The output terminal was connected to its negative input terminal through a feedback resistor and to non-inverting input terminal of second amplifier as shown as in the figure 3. In case of second amplifier, its inverting input terminal was connected to positive terminal of the battery, positive input terminal was connected to output terminal of first amplifier. Two light emitting diodes (LEDs; one red and another green) held anti-parallel (anode of red joined to cathode of green and vice-versa) were connected between the outputs of first and second amplifiers (cathode of red LED connected to output of first amplifier).

(5) In Page no 4 - Fig 3, give the battery voltage

Replied: We have given the battery voltage as suggested. It was not necessary to mention because the circuits works well even when different voltages other than 3 V is supplied.

(6) In Page no 10 - Table 3, by which formula author arrived the critical point value, film resistance range and minimum sensitivity. Provide the formulas.

Replied: Here we have not used any formulae to evaluate those values. We analyzed all these in values using CircuitMod 2.7. We have presented these data so that it would ease to choose the feedback resistor and other components of the circuit on accordance to the resistance of fabricated thin film. These are empirical data. We mentioned it as:

Page 10: Line 10-18

Here we present some particular values of these components and the critical point value of the film resistance (value of film resistance beyond which the output voltage of the circuit changes its polarity or the LEDs switch) for the particular configuration of the circuit. We analyzed the circuit fixing the feedback resistance and the ratio ($R_1: R_2$) and manually changing the value of film resistance unless we obtained critical value.

The film resistance of quite higher value than the critical value should be used for better sensing. Considering this, best range of the film was estimated and their corresponding sensitivity was calculated using the relation:

$$S = \frac{R_x - R_g}{R_x} \quad (\text{Eq. 4})$$

Where, S is sensitivity, R_x is film resistance before exposure to gas and R_g is the value resistance of film after exposure to gas.

- (7) In Page no 11 - Fig 9 (a,b and c) - What is the parameter represented by the value given in top of graph. Kindly specify.
- (8) In Page no 11 - Fig 9, By which formula author arrived the sensitivity percentage and why difference in sensitivity percentage in 1:10 ratio.

Replied: We have specified it. It is the resistance of the film used to analyze. We have written the formula to calculate the sensitivity in relation (4). Since film resistances of different values varying from several Ω to $M\Omega$ are analyzed, their sensitivity on the basis of ratio $R_1:R_2$ is quite difficult to compare and we do not find necessary to compare such a way. Hope this could justify.

Page 11-12

In the sensitivity stacked chart for different ratio $R_1:R_2$ and different feedback resistance above, film resistance from which sensitivity is measured, is mentioned at the top of it. If we use the film with above mentioned resistance as sensor, and corresponding values of feedback resistance and ratio $R_1:R_2$, the sensitivity of the film on exposure to gas must be as indicated on green block so as to sense it. In other words, the exposure to gas should reduce the film resistance by indicated values to detect the gas. These suggest that for higher film resistance, we should use higher value of feedback resistor or large $R_1:R_2$ for more sensitive sensor and for film resistance with low resistance, comparably small values of the components can be used.

- (9) In Page no 13 - Line 33, spelling mistake in (got)

Replied: We have corrected it.

- 4. Editor comment:** This work presents a design of an electronic circuit made specifically for a sensor system. In order to be acceptable as a scientific article the manuscript needs to go beyond a technical report of a sensor, reporting scientific advances in sensor science (not only development of a circuit). Please revise the manuscript and make sure that it goes beyond a technical report of a sensor circuit and emphasize the contribution to scientific advance.

Replied: The manuscript has been revised. It is not just a technical report. It has described the way to synthesize the ZnO thin film in a unique way and has characterized it. It explains the use of ZnO as a thin film sensor. It claims the sensor performs better than other and verifies experimentally. Thus, it is scientific work. Further, to design such electronic circuit for sensing is nobel. It has reduced temperature dependency of sensing materials and can easily conduct in room temperature. We have experimentally verified and presented the data along with the response and recovery time. This has emphasized the contribution to scientific advance.

Sincerely,

Raju Bhattacharai

Modeling of Gas Sensor based on Zinc Oxide Thin Films by Feedback Loop using Operational Amplifier.

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Abstract: Gas sensing is seeking the attention of both industries and academia because of its wide-ranging application and intrinsic limitations of sensing technologies. Mostly, the gases are sensed due to variation in electrical, optical, acoustic, chromatographic, and calorimetric properties of sensing materials in the influence of various gases but in case of zinc oxide thin film, its resistance varies in influence to reducing gases [1, 2]. Particularly, this article is concerned in modeling durable sensing device using Zinc oxide thin film at low cost and operating within the low potential. To eliminate the temperature dependency for higher sensitivity of the sensor and fabricate cheap, portable, precise, less energy-consuming and durable sensing device, a new electronic model of the sensor was self-designed and analyzed. Monitoring the change in film's resistance, a perfect gas sensor was built. Zinc oxide thin film was synthesized by using the Sol-gel method (Spin coating) and was characterized by XRD and SEM which revealed wurtzite polycrystalline nature of Zinc oxide film with average grain size 17-25 nm. The fabricated film showed a fabulous response to ethanol and methanol vapors. It's the noble electronic model of gas sensing in the current time.

Keywords: Miniatured sensing device, less energy consuming, noble electronic model.

I. Introduction

Currently, gas sensing is tugging the attention of both industries and academia because of its wide-ranging application in the areas like industrial production (e.g., detection of methane in mines), automotive industry (e.g., detection of pollutant gases from vehicles), medical applications (e.g., electronic noses simulating the human olfactory system), supervision of indoor air quality (e.g., carbon monoxide detection), environmental studies (e.g., monitoring greenhouse gas). Since the last sixty years, researches have been focused on investigation of different types of sensing materials, sensing mechanism and, fabrication techniques of sensing materials. Those researches revealed various fabrication techniques, introduced several sensing materials (e.g., different metal-oxides, polymers), and different approaches of sensing mechanism [1].

Mostly, the gases are sensed by the particular materials due to variation in electrical, optical, acoustic, chromatographic, and calorimetric properties of sensing materials in influence of various gases. In context of metal oxide semiconductor thin films, nanotubes, and polymers electrical property, i.e. resistance of the film varies due influence of respective gases [2]. Monitoring this change in value of resistance of the film, a perfect gas sensor can be built.

The way that the traffic police takes a breathalyzer test in Nepal (going closer to the subject and asking to blow air from mouth then smelling it) has motivated us to conduct research on the gas sensing device so that we could contribute to our nation. So, particularly this article is concerned in modeling durable sensing device at low cost, and operating within the low potential. Most of the metal oxide-based gas sensors are too expensive and need to be maintained at a certain value of operating temperature for higher sensitivity. For instance MQ-sensors use their inbuilt heating system to heat the reducing gases around the sensing material in the range of 200 °C - 300 °C for

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4 sensing. It alone cannot sense the gases, rather it should be connected with Aurdino UNO and cannot be operated
5 with small battery source. It requires huge warm up time to work well [3]. To eliminate this temperature
6 dependency for higher sensitivity of the sensor and to fabricate cheap, portable, precise, less energy consuming and
7 durable sensing device, new model of sensor is designed and analyzed. It's one of the emerging and demanding
8 techniques of gas sensing in the current time.
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13 II. Methodology

14 Gas sensing properties of various metal oxide semiconductors were studied through published journals and
15 variation in resistance of different materials were noted. Different electronic circuits were designed using
16 CircuitMod 2.7 and Online Circuit Simulator and Schematic Editor-Circuit Lab. Then the variation in output of the
17 designed circuit due to change in resistance of the variable resistor (Thin Film) was tabulated and analyzed. For the
18 experimental verification, single coated Zinc Oxide thin films were fabricated using spin coating method.
19
20

21 Fabrication of thin film:

22 There are more than dozens of methods: Laser ablation, High energy ball milling, Physical vapour
23 decomposition, Melt mixing, Sputter deposition, Electric arc deposition, Ion implantation, Precipitation method, Co-
24 precipitation method, Colloidal methods, Sol-gel processing (Spin coating, Dip coating, and Spray pyrolysis),
25 Water-oil micro-emulsion method, Hydrothermal synthesis, Solvothermal, Sono-chemical synthesis, Polyol
26 methods, Vapour phase fabrication, etc for thin film fabrication [4, 5]. Because of its simplicity, reliability, and
27 accessibility, we found Spin Coating method being feasible within our budget and lab frame too.
28
29

30 Spin Coating is the most preferred technique for the thin film deposition on the flat substrate due to its plainness,
31 low cost, easy doping, low operating temperature, and spin and film thickness controllability. A very small amount
32 of coating material is dropped at the centre of the substrate spinning at a constant speed or at rest, then is rotated
33 at high speed to spread the material uniformly all over the substrate. As soon as, the coating is completed, the
34 substrate is annealed for the evaporation of the unwanted solvent and deposition of the film. The process is
35 continued until the desired thickness or resistance of the film is achieved [6, 7].
36
37

38 Glass substrates were cut into square pieces (2.5cm x 2.5cm), washed with distilled water then sonicated for 15
39 minutes with distilled water and Acetone at 70°C then dried in a hot air oven at 100°C. For 0.5 M precursor solution
40 (Solution for pure ZnO thin film), 13.3872 g of Zinc Acetate Dihydrate (ZAD) and 6mL of Diethyl Amine (DEA)
41 added to 120 mL of Ethanol was stirred at 300 rpm for an hour at room temperature. 0.1 mL of precursor solution
42 was spread over the spinning (at 3000 rpm for 30 seconds) substrate in a spin coater and was annealed over the hot
43 plate at 550°C for 15 minutes.
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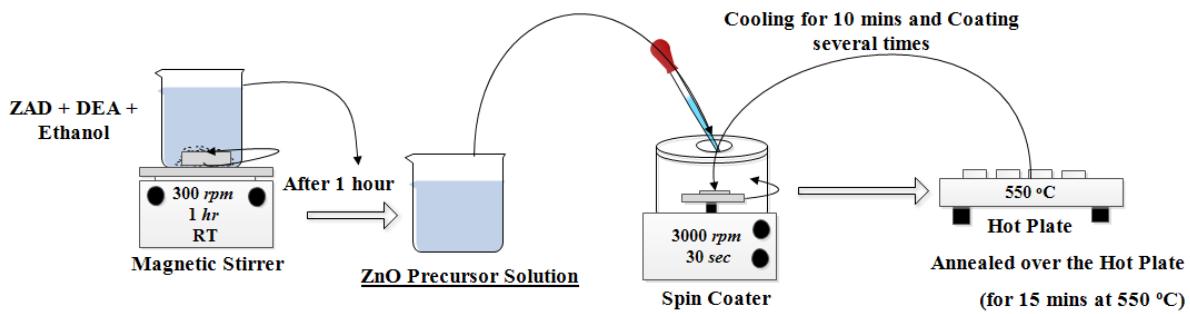


Figure 1: Preparation of ZnO thin film by Spin Coating Method.

The films fabricated were further cut into minute pieces (4 mm x 7 mm) and heated at 100°C for 2 hours. As soon as the film gets heated, thin insulated wires-conducting at the ends were connected to both the ends of the film using Silver paste. Two heating system was adjusted at the ends of a cylinder of the volume of about 300 cm³; heater at the top was to monitor the temperature of the film (if necessary) and heater at the bottom was to evaporate liquid (if necessary). The needle of the syringe was adjusted as shown as in the figure below so as to pass gas or drop liquid over the heater. This is the way, how we built a setup for the exposure of thin film to gas for sensing purpose.

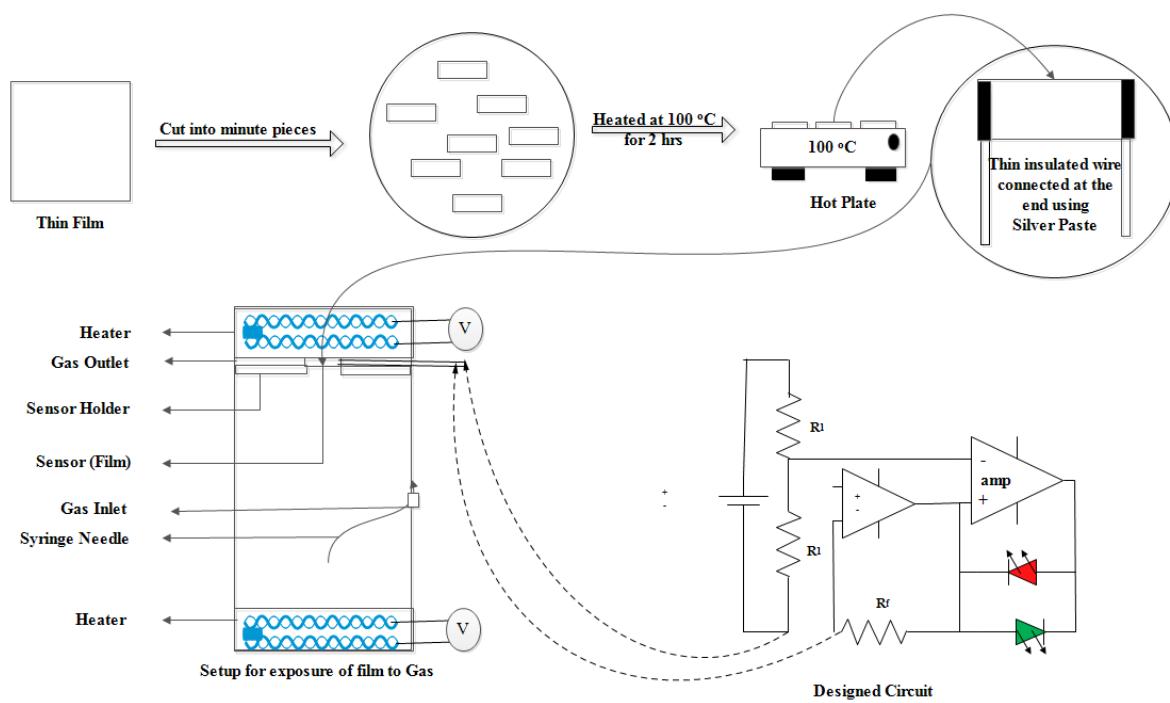


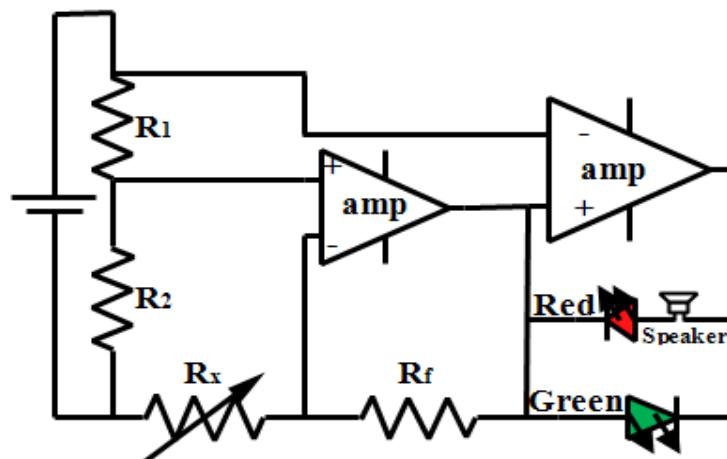
Figure 2: Entire setup for sensing.

Different concentration of ethanol and methanol was passed into the chamber, and corresponding response of the circuit was observed and noted.

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4 **Circuit (Sensor) Designing:**

5 Several electronic circuits were designed using CircuitMod 2.7 and Online Circuit Simulator and
6 Schematic Editor-Circuit Lab, and variation of outputs due to variation in resistance of thin film used in the circuit
7 was analyzed. Then the necessary electronic components were fixed in the PCB board.

8 Two resistors (R_1 and R_2) were connected in series with 3 V battery. The positive input terminal of first amplifier
9 was connected to R_2 , negative input terminal was grounded through film and output terminal was connected to its
10 negative input terminal through a feedback resistor (R_f). In case of second amplifier, its negative input terminal was
11 connected to R_1 , positive input terminal was connected to output terminal of first amplifier and its output terminal
12 was connected to its positive input terminal through two light emitting diodes (LEDs; one red and another green) in
13 parallel and opposite configuration (positive end of red LED connected to negative end of green LED and vice-
14 versa). The seventh pins of both amplifiers were connected to positive terminal of source; fourth pins were
15 grounded, whereas first and eighth pins were left floating. Also, a bugger was connected in series with red LED.



40 **Figure 3:** Designed Sensor Circuit where R_x is film resistance.

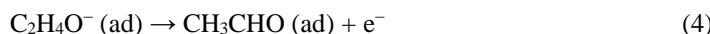
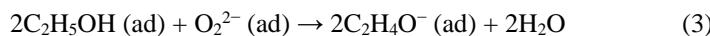
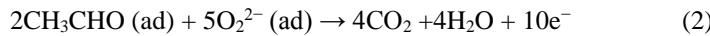
41 Also, the configuration works if the both amplifiers and LEDs are flipped in respect to polarity.

42
43 **Sensing Mechanism:**

44 The detection mechanism of Semiconductor Metal Oxide (SMO) as a sensor is complex and not yet fully
45 understood. Adsorption ability, electrophysical and chemical properties, catalytic activity, thermodynamic stability
46 and the adsorption/desorption properties of the surface of SMO as well yields this complexity [1]. ZnO (n-type
47 semiconductor) thin film surface, when exposed to air, adsorb oxygen molecules to form molecular type adsorbate
48 (O_2 , O_2^-) and dissociative type (O_2^{2-}) adsorbate ions forfeiting electrons from the conduction band, yielding electron-
49 depleted space-charge layer in the grain boundary region which leads to large surface potential barrier and large
50 resistance. The target gas (ethanol/methanol) may undergo dehydration and dehydrogenation and successively
51 oxidized to CO, CO_2 , and H_2O , but ZnO being basic oxide, dehydrogenation is favored. The response of the film
52 towards alcohol vapors is dependent on the conversion of alcohol into aldehydes [7, 8].



(1)



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10 The release of electrons back to the film enhances the conductivity of the film and deduces the resistance [8]. When
11 oxygen adsorbed onto the film surface which traps electrons from the bulk of material forming a potential barrier is
12 replaced by reducing gas molecules the barrier at the grain boundaries decreases and thus reduces the electrical
13 resistance of the film [1]. This reduces potential at the negative input terminal of the first amplifier which yielding
14 change in its output and potential at the positive input terminal of the second amplifier. This change in the value of
15 positive input of the second amplifier changes the polarity of its output from negative to positive and current flows
16 through red LED only. So, only red LED glows and bugger beeps.

17
18 In the former case (when the film is not exposed to reducing gas), the circuit yields negative output so red LED
19 being reverse biased blocks electron to flow through it and only green LED being forward biased allows flowing
20 current through it and glows. As soon as the vapor passes away, the film undue starts adsorption of atmospheric
21 oxygen and tends to achieve its former state [8]. And, again the circuit glows Green as soon as the film recovers.

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31 **III. Results and Discussion**

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33 **UV-Vis Spectroscopy:**

34 The optical characterization of the samples was performed in Nepal Academy of Science and Technology
35 (NAST) using UV-Vis spectrophotometer (Carry 60 spectrophotometer, Agilent Technology). The absorbance, and
36 transmittance of the films were measured which were further analyzed to calculate the band gap and thickness of the
37 films. For indirect transition, the variation in absorption coefficient with the photon energy obey Tauc's plot method,

38
39 $(\alpha h\nu)^{0.5} = A(h\nu - E_g)$ (Eq. 1)

40 Where A is a constant, E_g is the optical band gap, h is the plank constant and α is the absorption coefficient.
41
42 Extrapolation of $(\alpha h\nu)^{0.5} = 0$ yields the optical bandgap energy of the films [9].

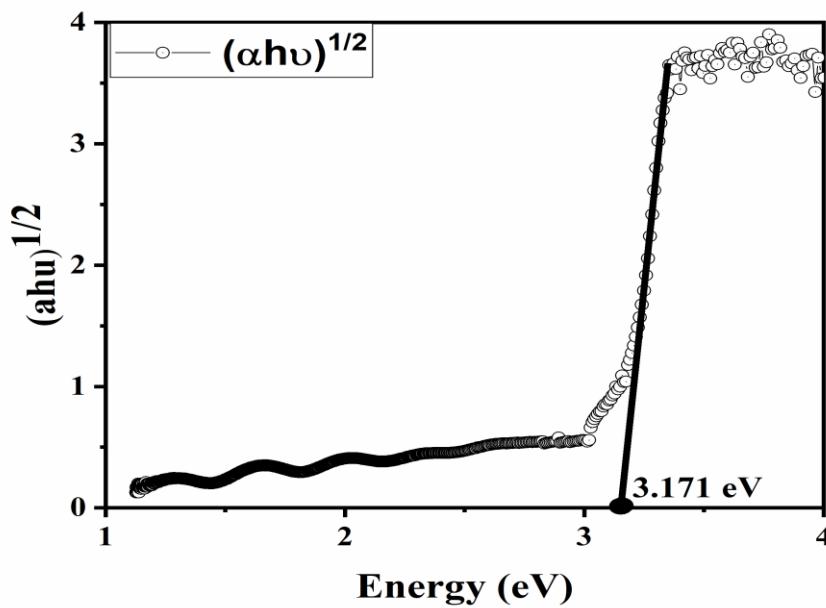


Figure 4: Tauc's Plot for calculation of Energy Bandgap

The bandgap of thin film fabricated by us was found to be 3.171 eV.

X-ray Diffraction (XRD):

The dual natured (behaving as both particle and wave) electromagnetic radiation having high penetration power⁶, photon energy within 100 eV- 100 KeV is termed as X-ray. It is a non-destructive technique used for characterizing crystalline substance. This helps in the identification and quantification of the crystalline phase, structure, orientation, composition, and defects. Further, it is used to measure the size, strain or micro-strain effects, transparency and electron mobility in thin-films [10]. The structural characterizations of fabricated thin films were analyzed using XRD [Bruker D2 Phaser X-ray diffractometer of CuK α radiation (wavelength: 1.54184 Å)] at 40 KV of operating voltage and current of 40 mA in the 2θ range of 20° - 80° at scanning rate of 15° per minute at NAST, Khumaltar, Lalitpur, Nepal. The Debye Scherrer's formula used to calculate the average grain size 'D' is given by,

$$D = \frac{0.9\lambda}{\beta \cos\theta} \quad (\text{Eq. 2})$$

where, 0.9 is the correction factor, λ is the wavelength of the x-radiation, β is the full width at half maximum (FWHM) of the observed peak and θ is the Bragg's angle [10]. Comparing calculated d-spacings with the standard JCPDS values of card number 36-1451, the observed peaks were indexed. The average crystallite size of ZnO was found to be 20.068 nm using Scherrer's method.

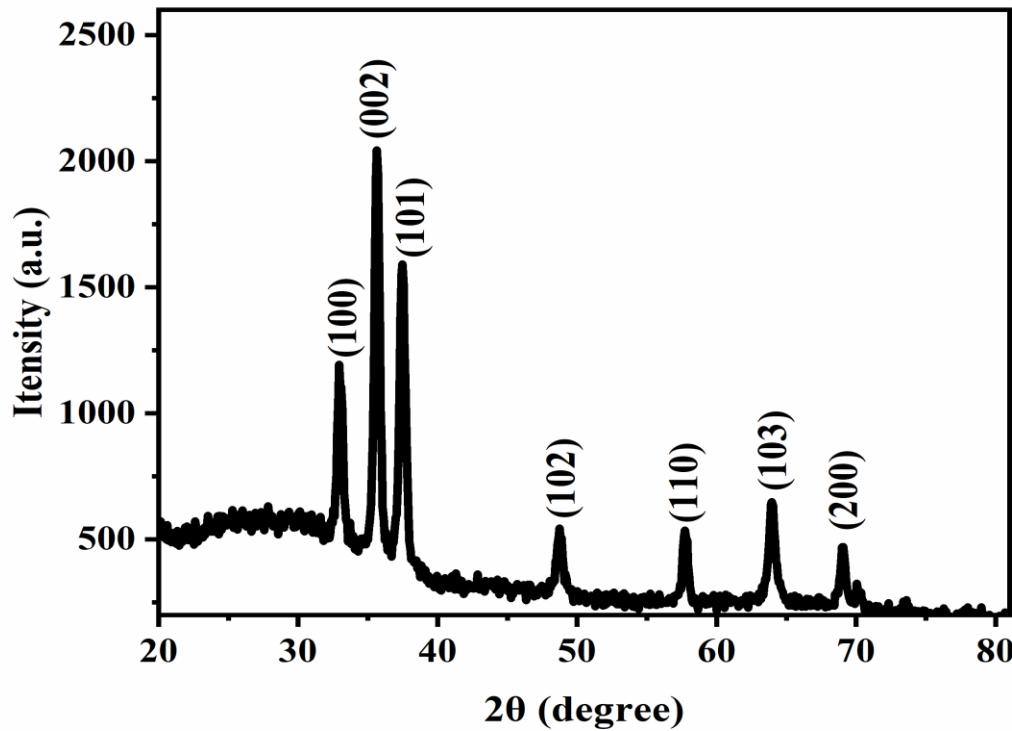


Figure 5: XRD pattern of Pristine ZnO thin film.

The crystallite size of as deposited ZnO thin films were also calculated using W-H plot method using prominent XRD planes then compared with that obtained from Scherrer's formula. The W-H plot is related with the full width half maxima (FWHMs) (β) of XRD peaks and crystallite size(D) through the relation,

$$\frac{\beta \cos \theta}{\lambda} = \frac{1}{D} + \frac{4\epsilon \sin \theta}{\lambda} \quad (\text{Eq. 3})$$

Where, ϵ is the amount of residual strain, θ is the angle of diffraction, λ is the wavelength of X-ray [10]. A graph between $\beta \cos \theta / \lambda$ versus $4 \sin \theta / \lambda$ when plotted and fitted linearly, the reciprocal of the x-intercept gives the average crystallite size [11] and was found to be 17.345 nm.

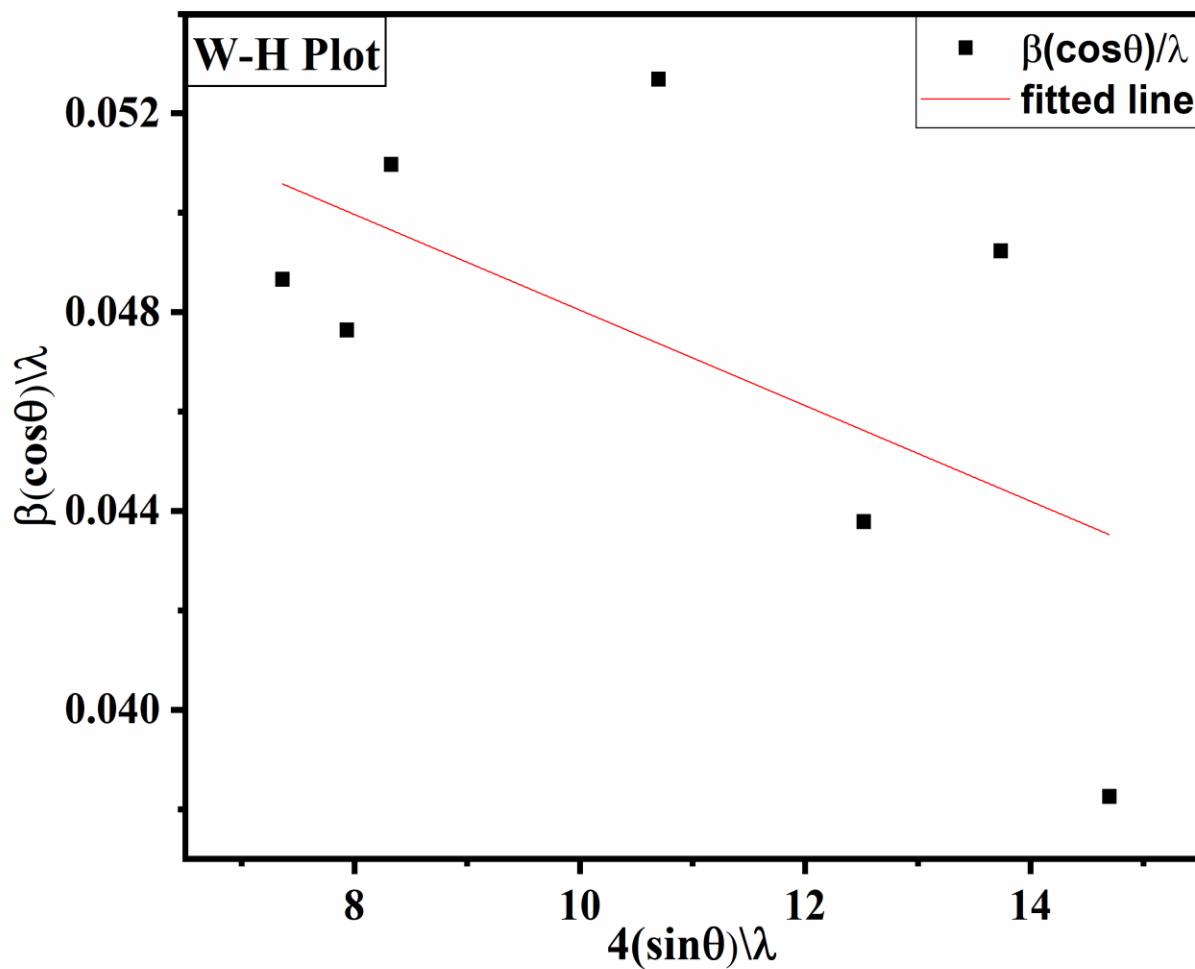


Figure 6: William-Hall (W-H) plots of pristine ZnO.

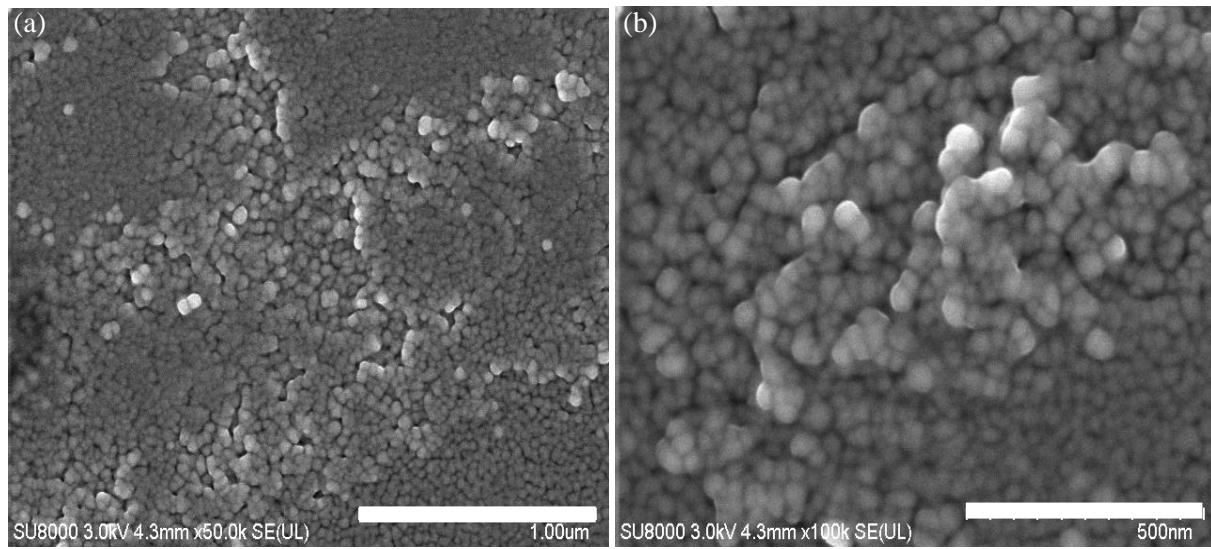
The crystallite size of the fabricated film calculated from the W-H plot was found consistent with that as calculated from Scherrer's method.

Table no 1: Shows XRD analysis for miller indices, d-spacing, and grain size of the deposited ZnO thin film.

S.N.	Miller Indices	Angle 2θ	Calculated d (\AA)	JCPDS(36-1451) d (\AA)	Crystallite Size D(nm)	
					Scherrer's Method	W-H plot
1.	(100)	32.95075	2.7172	2.8142	19.31788	20.0678 17.3445
2.	(002)	35.60633	2.5204	2.6033	19.73324	
3.	(101)	37.42934	2.4018	2.4759	18.44347	
4.	(102)	48.69692	1.8692	1.9111	17.84351	
5.	(110)	57.69607	1.5972	1.6247	21.46739	
6.	(103)	63.92009	1.4559	1.4771	19.09518	
7.	(200)	69.00289	1.3605	1.4072	24.57326	

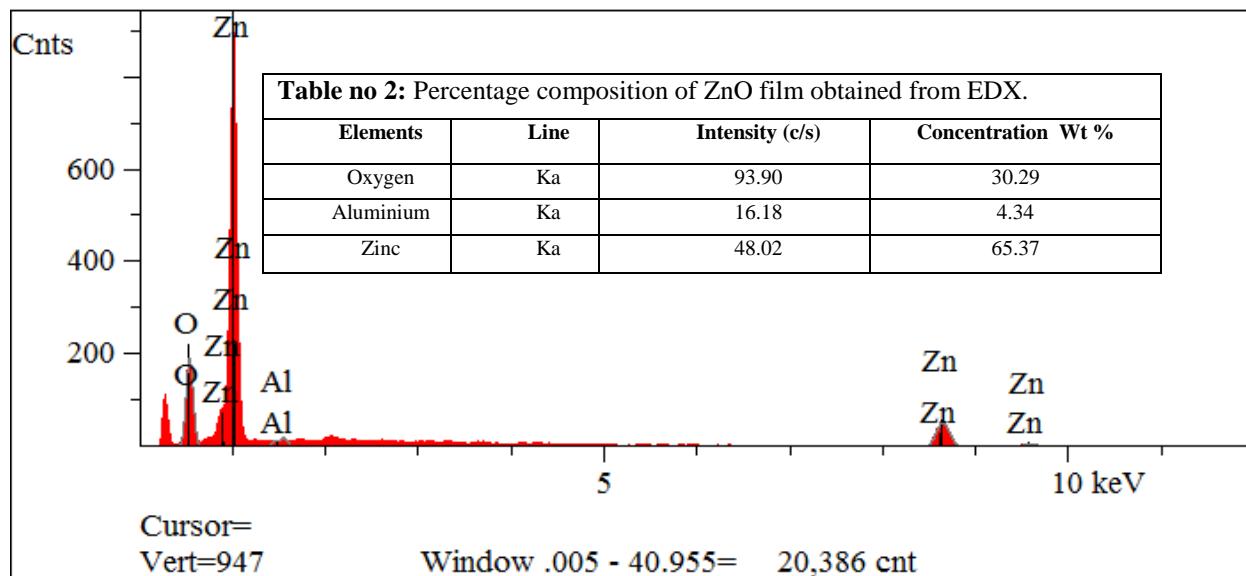
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Scanning Electron Microscope (SEM) and EDX analysis:

6 The surface morphology of ZnO thin films were performed using Scanning Electron Microscope at Research Centre
7 for Eco-Environment Sciences, Chinese Academy of Sciences, Beijing, China.
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30 **Figure 7:** SEM images of ZnO thin film with scale (a) 1 μ m and (b) 500nm
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37 Figure 7(a) and 7(b), shows the SEM images of undoped ZnO with scale 1 μ m and 500nm and magnification of 50K
38 and 100K respectively. The SEM image depicts grainy structure of film. The average grain size of ZnO was found to
39 be around 25 nm which is quite corresponding to results obtained from XRD analysis.
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66 **Figure 8:** Energy Dispersive X-ray image of Pristine ZnO film.
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Figure 8 shows the EDX spectra which assure that the film is of Zinc oxide. Very small peak of Aluminium is detected which may be due to Aluminium silicate (glass) substrate. The EDX spectrum of ZnO sample shows the high content i.e. 65.37 wt. % of Zinc, 32.29 wt. % of Oxygen and 4.34 wt. % of Aluminium which is almost negligible compared to oxygen and Zinc.

Circuital Analysis:

The circuit designed is the novel concept in sensing gas. Since the resistance of the film is influenced by material used for depositing thin film, the number of coating done, doping in film, and aging of the film, the values of the resistors used in the circuit must be different for different value of film resistance at the ordinary condition. These values of the components must be appropriate to determine or sense the selected reducing gas. Here we present some particular values of these components and the critical point value of film resistance for the particular configuration of the circuit. The critical point value is the value of film resistance beyond which the output voltage of the circuit changes its polarity or the LEDs switch.

Table no 3: Shows the values of Components to be used in accordance to film resistances and selected gas.

S.N.	Feedback Resistance R_f (KΩ)	Ratio $(R_1: R_2)$	Critical Point Value (KΩ)	Best Range of Film Resistance R_x	Minimum Sensitivity S (%)
1.	560	1:3	1679	(2-1.7) MΩ	(15-1.24)
	560	1:10	5999	(50-6) MΩ	(22-0.02)
	560	1:100	55899	(200-56) MΩ	(72-0.18)
2.	470	1:3	1410	(2-1.5) MΩ	(30-5)
	470	1:10	4759	(15-5) MΩ	(67-4.82)
	470	1:100	46899	(200-47) MΩ	(77-0.22)
3.	100	1:3	298.99	(400-300) KΩ	(25-0.34)
	100	1:10	999.79	(2-1) MΩ	(50-0.021)
	100	1:100	9982.56	(40-10) MΩ	(75-0.174)
4.	10	1:3	44.98	(80-45) KΩ	(44-0.04)
	10	1:10	99.98	(300-100) KΩ	(67-0.02)
	10	1:100	997.92	(3-1) MΩ	(67-0.02)
5.	1	1:3	2.999	(5-3) KΩ	(40-0.03)
	1	1:10	9.998	(30-10) KΩ	(67-0.02)
	1	1:100	99.82	(300-100) KΩ	(67-0.18)

Table no 3 represents the theoretical values for the circuital components for sensing the selected gas to approximate the appropriate value of feedback resistor, the ratio of R_1 and R_2 to be used in the circuit for sensing particular gas within a limited range of sensitivity.

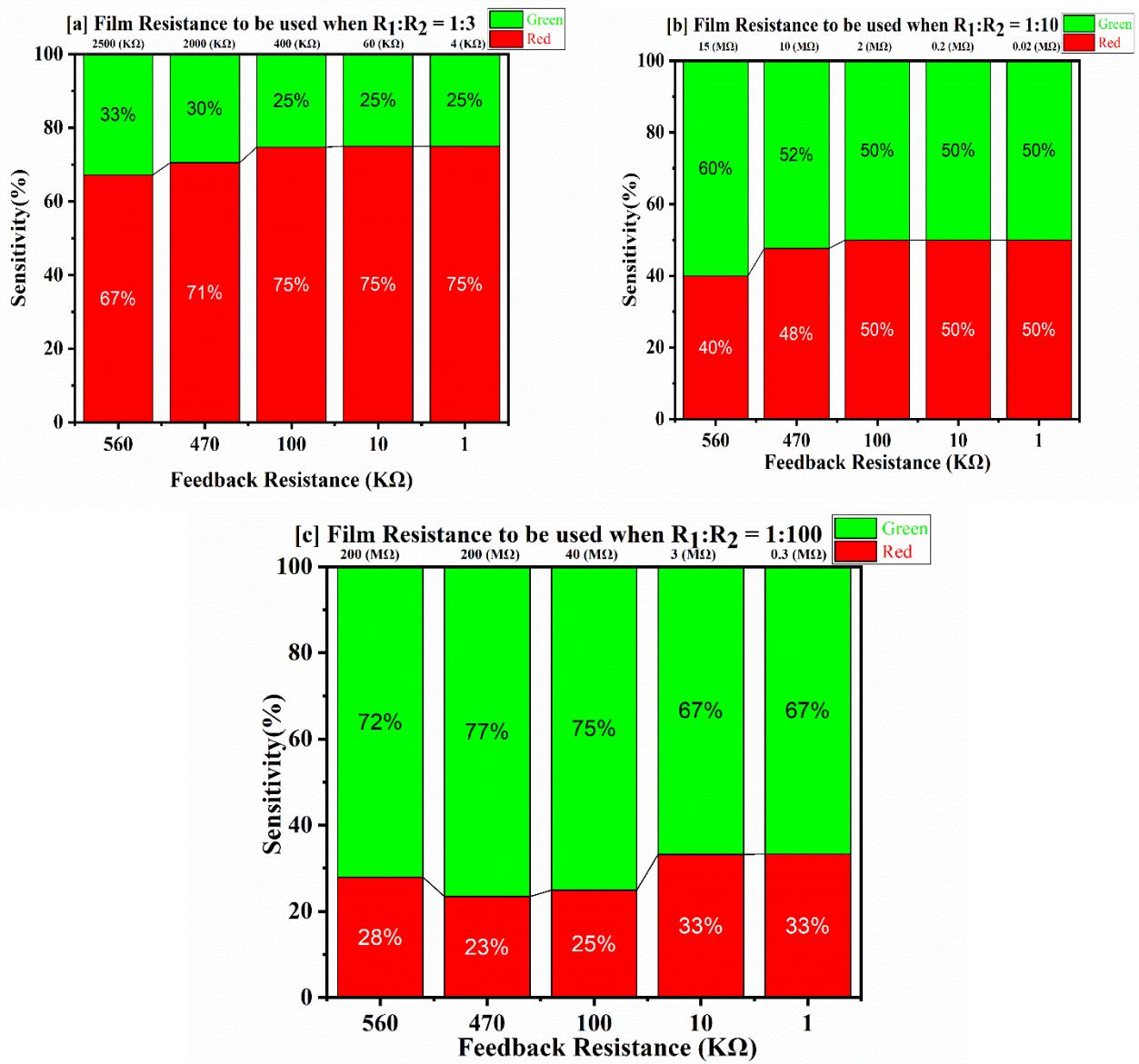


Figure 9: Sensitivity Stacked Chart for different ratio of R_1 and R_2 (a) 1:3, (b) 1:10 and (c) 1:100 and different values of Film and Feedback Resistances.

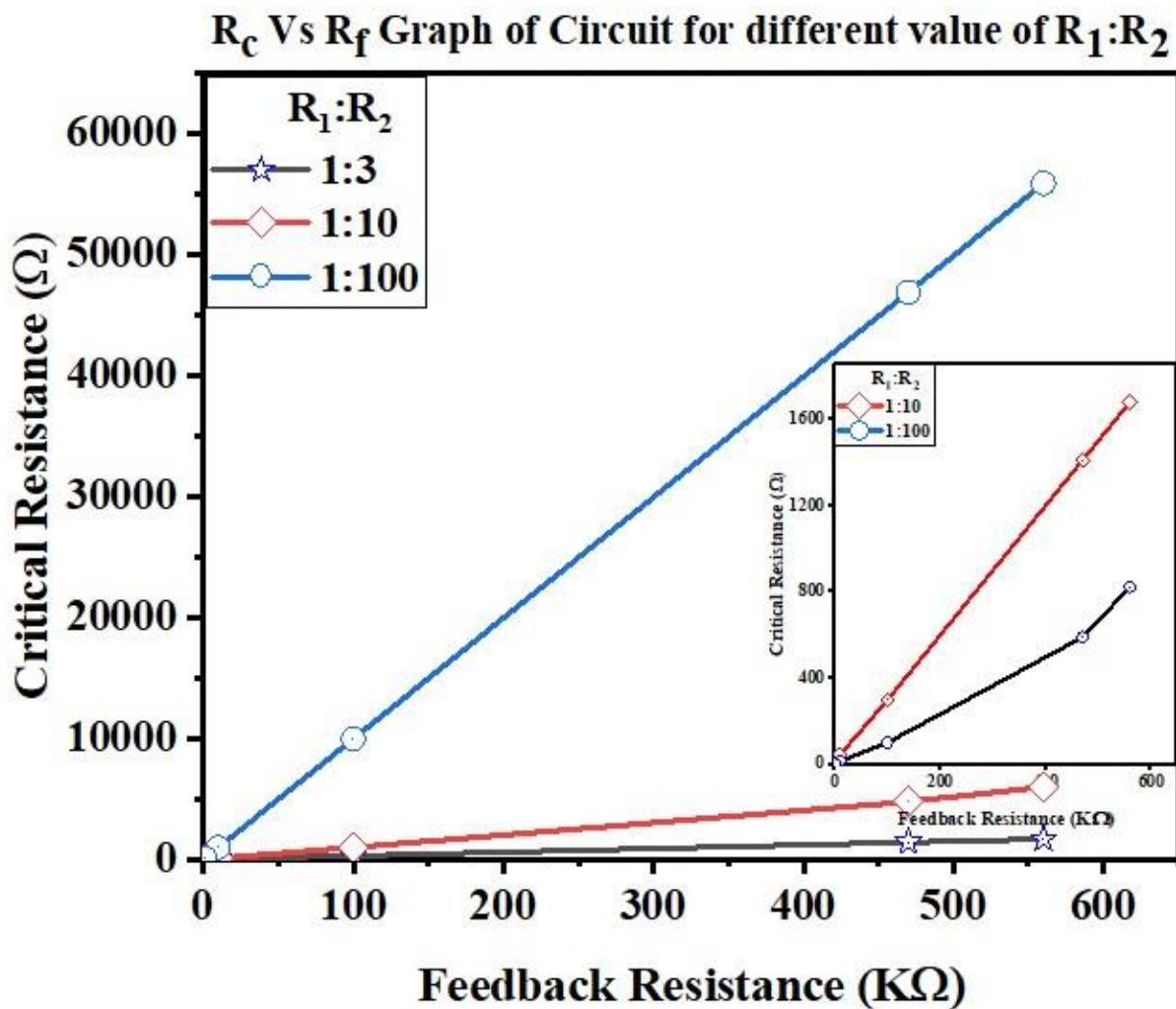


Figure 10: Critical vs feedback resistance graph at different ratio of R_1 and R_2 .

Figure 10 clearly depicts that critical point value or the critical resistance of the film is linearly dependent on the feedback resistance used in the circuit for same $R_1:R_2$. The critical resistance is such value of the film above which the circuit glows Green and below which results glowing Red. Also, it suggests that increment in the ratio $R_1:R_2$ yields higher value of critical resistance which will be very efficient for using highly resistive film as a sensor. Lower value of $R_1:R_2$ gives lower value of critical resistance which will be more effective if used with less resistive film. Furthermore, highly resistive film can be used as sensor along with lower value of $R_1:R_2$ if the target gas highly reduces the film below critical value. The mechanism is same for feedback resistor. Thus, appropriate value of $R_1:R_2$ and feedback resistor can let us sense reducing gas of any concentration.

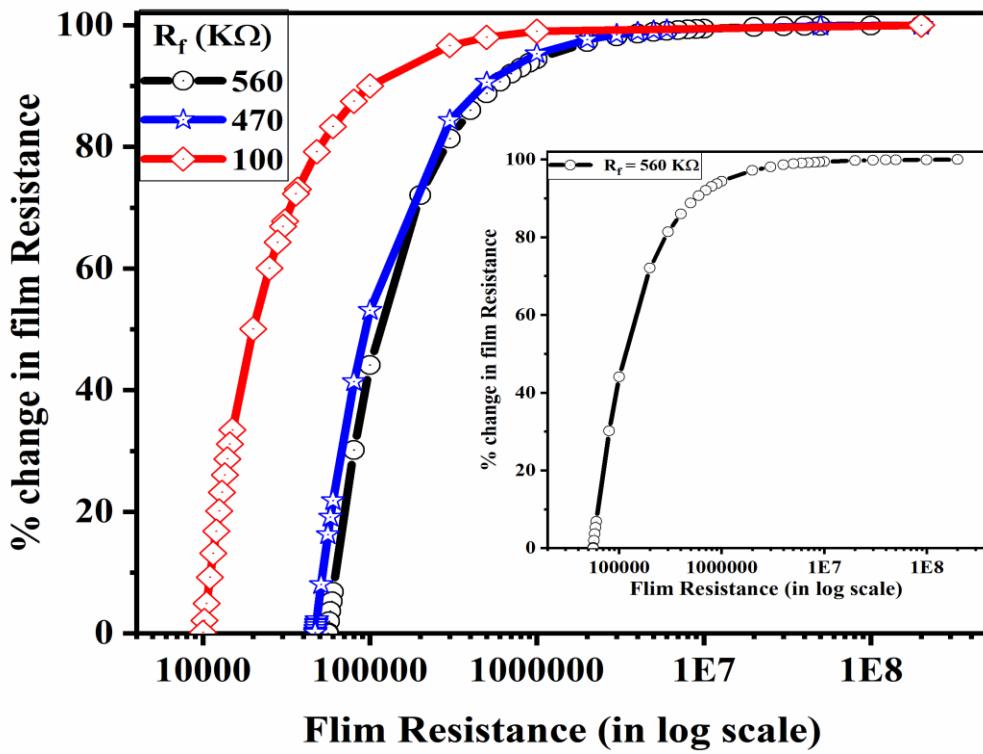


Figure 11: Least percentage change of Film Resistance required for sensing vs Film resistance graph for different value of R_f .

Figure 11 is the plot of film resistance (in log scale) vs least percentage change required for sensing the target gas at different value of feedback resistance for $R_1:R_2$ equals 1:100. The graph clearly shows that highly resistive film needs more than 90% change in their film resistance for sensing (RED glow in circuit) in above mentioned configuration. But Film resistance closer to the critical value of resistance can sense well within less percentage change in its former value. This circuit best suits for sensing even if the target gas increases the film resistance. But selecting appropriate and accurate $R_1:R_2$, feedback resistor and remaining circuital components is most for excellence performance.

Thus, analyzing Figure 10 and Figure 11, we can conclude that sensitivity of the circuit is dependent on the value of critical resistance of the film but not on the film resistance. This is the most fantabulous characteristics of the circuit which overcomes the dependency of the available ordinary sensors on film resistance. Furthermore, the critical value of the film is controllable. It depends upon the components used in the circuit. The film resistance may vary from few $\text{K}\Omega$ to hundreds of $\text{M}\Omega$ and no chemical synthesis yields film of desired resistance with accuracy which has brought complexion in sensing with desired accuracy. Thus, the noble circuit designed is the ultimate way to eradicate this drawback of the ordinary sensor. Finally, designation of sensor can be summed up as:

- (i) Measuring film resistance after fabrication R_x .
- (ii) Choosing sensitivity (S).
- (iii) Calculating Critical Resistance using selected sensitivity and Film Resistance as:

$$R_c = R_x - \frac{S \times R_x}{100} \quad (\text{Eq. 4})$$

(iv) Choosing appropriate value of $R_1:R_2$, R_f and other circuital components and fabricating sensor.

Experimental Verification:

This was experimentally verified using alcohol (ethanol and methanol) vapors as reducing gas and ZnO as sensing material in the film. The value of the fabricated film resistance was more than $200\text{ M}\Omega$, ratio ($R_1: R_2$) was 1: 3, the value of feedback resistance was $560\text{ K}\Omega$ and two eight pins chips (UA741CN) were used as amplifiers. Two LEDs (one red and another green) were fixed as shown in the circuit. 9 Volt battery was used as a source for two amplifier chips and another 3 Volt battery was conned in series with R_1 , and R_2 . The film was exposed to different concentrations of gas (alcohol vapors) and corresponding change was noted. The table below represents the experimental values.

Table no 4: Value of Input and Output Voltages of Circuit before and after exposure to alcohol vapors.

S.N.	Gas	Concentration (ppm)	Potential (V)			
			Before passing gas		After passing gas	
			Input	Output	Input	Output
1.	Ethanol	500	0.35	-4.15	6.27	2.56
		250	0.36	-4.15	5.11	2.28
		50	0.35	-4.14	4.12	2.13
2.	Methanol	500	0.36	-4.14	5.56	2.52
		250	0.34	-4.15	4.92	2.23
		50	0.36	-4.13	3.98	2.06

The table above clearly shows the switching of potential at output of circuit due to exposure of alcohol vapors. This confirms that the designed circuit senses alcohol vapor (reducing gas) using pristine zinc oxide thin film.

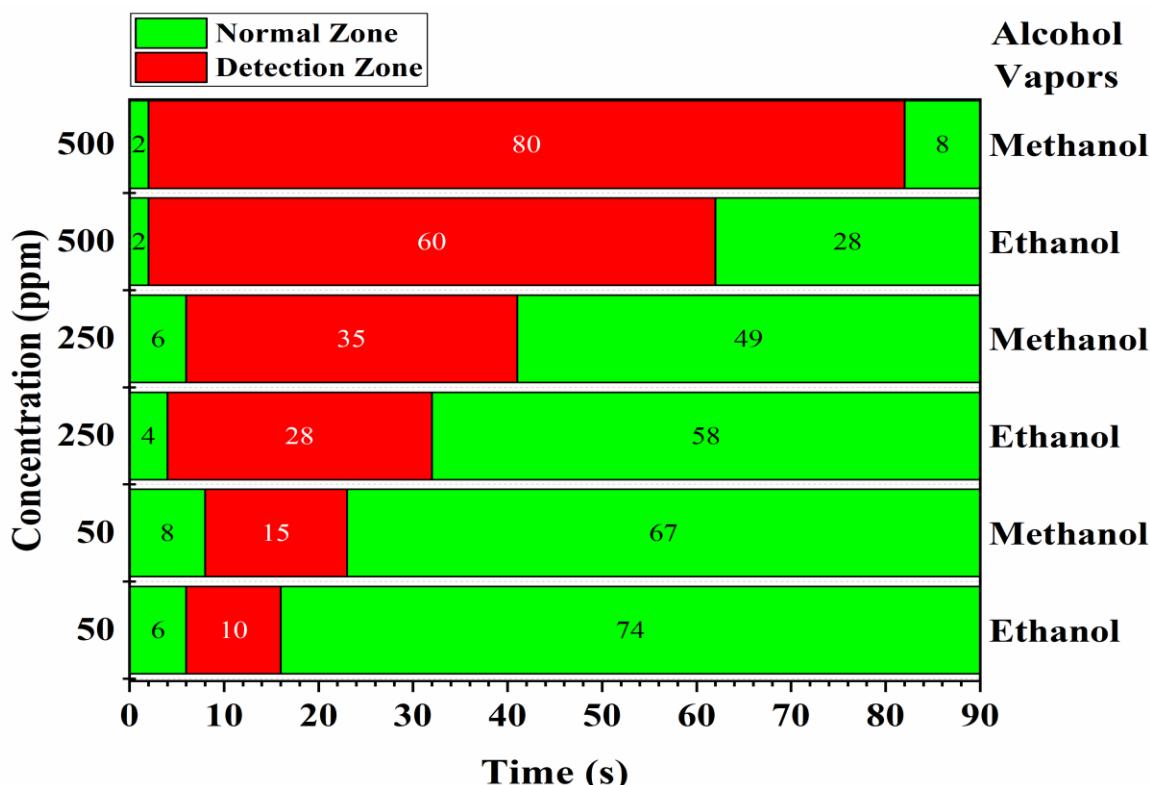
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4 **Response and Recovery:**

5 Response and recovery time are another indispensable factor for determining whether or not a sensor is reliable.
6
7 Here we have tabulated response and recovery time of our circuital sensor after exposure to different concentration
8 of ethanol and methanol vapors.
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10 **Table no 5:** Response and Recovery time of ZnO thin-film varying with concentration and types of alcohol.

S.N.	Alcohol	Concentration (ppm)	Response Time (s)	Recovery Time (s)
1.	Ethanol	500	2	60
		250	4	28
		50	6	10
2.	Methanol	500	2	80
		250	5	35
		50	8	15

20 The circuit remains in either normal state/zone (glowing Green) or in detection zone (glowing Red). When the target
21 gas is passed, sooner the film resistance decreases and reaches the critical resistance, the circuit changes its state
22 from normal and when the gas passes by, film resistance starts increasing again. As soon as it exceeds R_c , it changes
23 its state back to normal. The time for which the circuit remains in either state while responding to different
24 concentrations of Ethanol and Methanol vapors is shown below in Figure 12 :



54 **Figure 12:** Time for which the circuit remains in either state in response to different concentration of alcohol vapors.
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56 The figure above clearly depicts that higher the concentration, longer it stays in detection zone. Further, for same
57 concentration, circuit responds faster to ethanol than methanol.
58

The vapors were passed simultaneously into the sensor setup and were free to escape at any time. The variation in film resistance in response to 50, 250 and 500 ppm of Ethanol and Methanol vapors were observed and are graphed as shown in Figure 13. The graph reflects that the resistance of the film while responding reducing gases decreases rapidly for few seconds then slows down and reaches its minimum value. The minimum value is attained when the

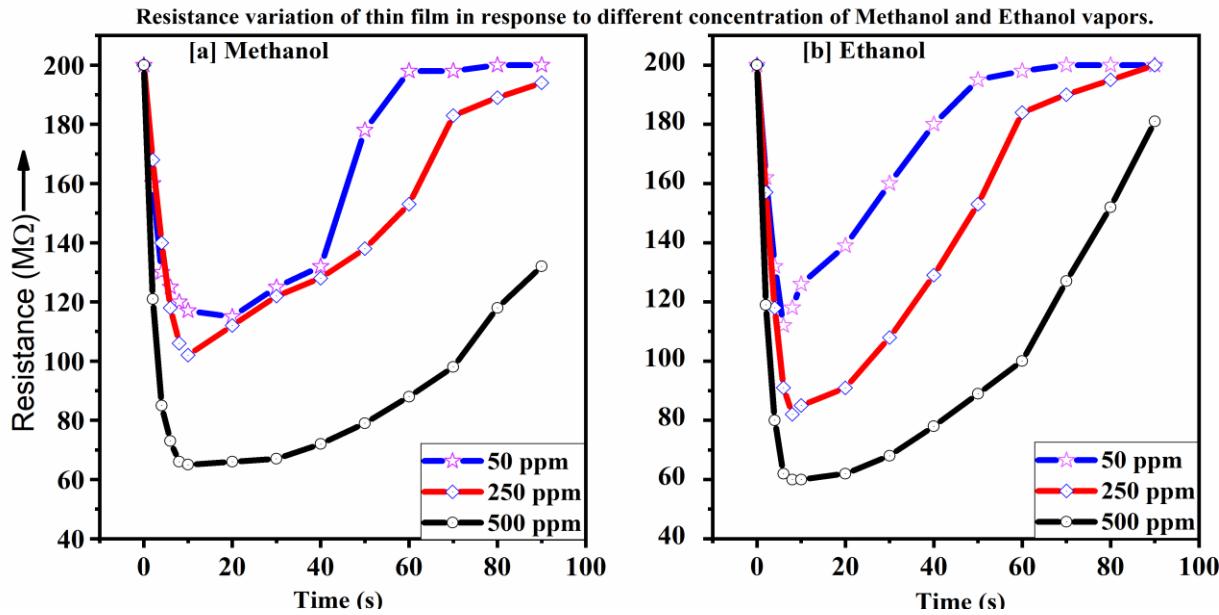


Figure 13: Variation of film resistance in response to various concentrations of Alcohol vapors.

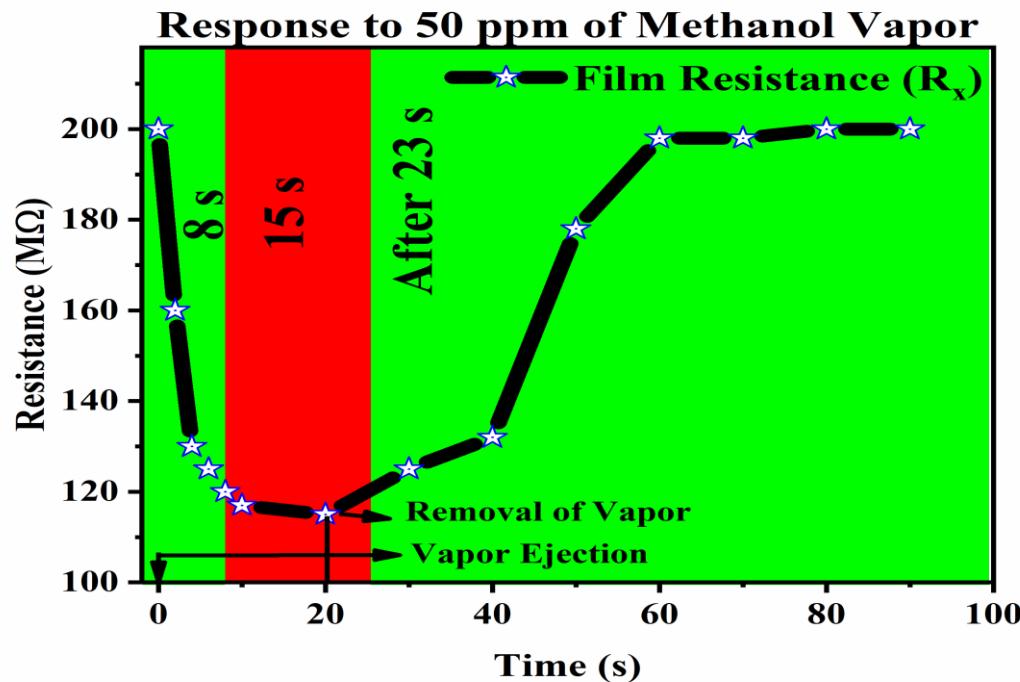


Figure 14: Film response to 50 ppm of Methanol Vapors.

target gases replace maximum number of reduced oxygen molecules in the grain boundary of film. As soon as the impact of the gas diminishes, the oxygen molecules in reduced form starts gathering at the grain boundary region and the film resistance starts increasing again. Its obvious that lower the concentration, less is the impact on film resistance.

Clearly, the experimental result shows that the film is sustainable and is very sensitive to reducing gases. The longevity of recovery time may be due to poor ventilation for gas outlet in our experimental setup.

IV. Conclusions

The novel circuit introduced for gas sensing approach can sense any reducing gases using zinc oxide thin film. After the fabrication of thin-film, film resistance will be known and analyzing table no 3, Figure 10 and Figure 11, we will be able to find the appropriate value of feedback resistor, the ratio of R_1 and R_2 to be used in the circuit for sensing particular gas within limited sensitivity range. Furthermore, the electrical components used are available in variable small size in the market, so we will be able to fabricate portable miniaturized sensing device or sensor of the desired size at low cost and consuming less energy, simply using zinc oxide thin film. Also, the circuit can be used for simple breathalyzer testing.

Acknowledgments

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References

- [1] Liu X, Cheng S, Liu H, Hu S, Zhang D, Ning H. A survey on gas sensing technology. Sensors. 2012;12(7):9635-65.
- [2] Kanan S, El-Kadri O, Abu-Yousef I, Kanan M. Semiconducting metal oxide-based sensors for selective gas pollutant detection. Sensors. 2009;9(10):8158-96.
- [3] Yu Z, Fang L, Deqin L and Bingqian G. Monitoring the spontaneous combustion of coal stack based on ZigBee and Lab view. Journal of Physics: Conf. Series. **1303**; 2019.
- [4] Naveed Ul Haq A, Nadhman A, Ullah I, Mustafa G, Yasinzai M, Khan I. Synthesis approaches of zinc oxide nanoparticles: the dilemma of ecotoxicity. Journal of Nanomaterials. 2017;2017.
- [5] Mohammed A, Naik PS, Suryavanshi SS, Nadaf LI. Design and fabrication of low cost and miniaturized setup for gas sensor. IOSR Journal of Applied Physics. 2015; 7(2):2278-4861.
- [6] Unalan HE, Hiralal P, Rupesinghe N, Dalal S, Milne WI, Amaratunga GA. Rapid synthesis of aligned zinc oxide nanowires. Nanotechnology. 2008;19(25):255608.
- [7] Jiaqiang X, Jianjun H, Yuan Z, Yu'an S, Bing X, Studies on alcohol sensing mechanism of ZnO based gas sensors. Sensors and Actuators B: Chemical. 2008; 132:334-339.
- [8] S.C Navale, V.R.S. Mulla, S.W. Gosavi, and S.K. Kulkarni, *Sensors and Actuators B: Chemical*, **126**(2), 382-386(2007).
- [9] Mulmi DD, Dahal B, Kim H-Y, Nakarmi ML, Panthi G. Optical and photocatalytic properties of lysozyme mediated titanium dioxide nanoparticles. Optik. 2018;154:769-76.
- [10] F Garcés F, Budini N, Koropecki R, Arce R. Structural analysis of ZnO (: Al, Mg) thin films by X-ray diffraction. Procedia Materials Science. 2015;8:551-60.
- [11] Chaki SH, Chaudhary MD, Deshpande M. SnS thin films deposited by chemical bath deposition, dip coating and SILAR techniques. Journal of Semiconductors. 2016;37(5):053001.

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9 **Modeling of Gas Sensor based on Zinc Oxide Thin Films by**
10 **Feedback Loop using Operational Amplifier.**

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14 Thapa¹

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17 **Abstract:** Gas sensing is seeking the attention of both industries and academia because of its wide-ranging
18 application and intrinsic limitations of sensing technologies. Mostly, the gases are sensed due to variation in
19 electrical, optical, acoustic, chromatographic and calorimetric properties of sensing materials in the influence of
20 various gases but in case of zinc oxide thin film, its resistance varies in influence to reducing gases [1, 2].
21 Particularly, this article is concerned in modeling durable sensing device using Zinc oxide thin film at low cost and
22 operating within the low potential. To eliminate the temperature dependency for higher sensitivity of the sensor and
23 fabricate cheap, portable, precise, less energy-consuming and durable sensing device, a new electronic model of the
24 sensor was self-designed and analyzed. Monitoring the change in film's resistance, a perfect gas sensor was built.
25 Zinc oxide thin film was synthesized by using the Sol-gel method (Spin coating) and was characterized by XRD and
26 SEM which revealed wurtzite polycrystalline nature of Zinc oxide film with average grain size 17-25 nm. The
27 fabricated film showed a fabulous response to ethanol and methanol vapors. It's the noble electronic model of gas
28 sensing in the current time.

29 Keywords: Miniatured sensing device, less energy consuming, noble electronic model.

30 **I. Introduction**

31 Currently, gas sensing is tugging the attention of both industries and academia because of its wide-ranging
32 application in the areas like industrial production (e.g., detection of methane in mines), automotive industry (e.g.,
33 detection of pollutant gases from vehicles), medical applications (e.g., electronic noses simulating the human
34 olfactory system), supervision of indoor air quality (e.g., carbon monoxide detection), environmental studies (e.g.,
35 monitoring greenhouse gas). Since the last sixty years, researches have been focused on investigation of different
36 types of sensing materials, sensing mechanism and, fabrication techniques of sensing materials. Those researches
37 revealed various fabrication techniques, introduced several sensing materials (e.g., different metal-oxides, polymers)
38 and different approaches of sensing mechanism [1].

39 Mostly, the gases are sensed by the particular materials due to variation in electrical, optical, acoustic,
40 chromatographic and calorimetric properties of sensing materials in influence of various gases. In context of metal
41 oxide semiconductor thin films, nanotubes and polymers electrical property, i.e. resistance of the film varies due
42 influence of respective gases [2]. Monitoring this change in value of resistance of the film, a perfect gas sensor can
43 be built.

44 The way that the traffic police takes a breathalyzer test in Nepal (going closer to the subject and asking to blow air
45 from mouth then smelling it) has motivated us to conduct research on the gas sensing device so that we could
46 contribute to our nation. So, particularly this article is concerned in modeling durable sensing device at low cost and
47 operating within the low potential. Most of the metal oxide-based gas sensors are too expensive and need to be
48 maintained at a certain value of operating temperature for higher sensitivity. For instance, MQ-sensors use their
49 inbuilt heating system to heat the reducing gases around the sensing material in the range of 200 °C - 300 °C for

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4 sensing. It alone cannot sense the gases, rather it should be connected with Aurdino UNO and cannot be operated
5 with small battery source. It requires huge warm up time to work well [3]. To eliminate this temperature
6 dependency for higher sensitivity of the sensor and to fabricate cheap, portable, precise, less energy consuming and
7 durable sensing device, new model of sensor is designed and analyzed. It's one of the emerging and demanding
8 techniques of gas sensing in the current time.
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11 II. Methodology

12 Gas sensing properties of various metal oxide semiconductors were studied through published journals and
13 variation in resistance of different materials were noted. Different electronic circuits were designed using
14 CircuitMod 2.7 and Online Circuit Simulator and Schematic Editor-Circuit Lab. Then the variation in output of the
15 designed circuit due to change in resistance of the variable resistor (Thin Film) was tabulated and analyzed. For the
16 experimental verification, single coated Zinc Oxide thin films were fabricated using spin coating method.
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19 Fabrication of thin film:

20 There are more than dozens of methods: Laser ablation, Physical vapour decomposition, Melt mixing,
21 Sputter deposition, Electric arc deposition, Ion implantation, Precipitation method, Co-precipitation method,
22 Colloidal methods, Sol-gel processing (Spin coating, Dip coating and Spray pyrolysis), Water-oil micro-emulsion
23 method, Hydrothermal synthesis, Solvothermal, Sono-chemical synthesis, Polyol methods, Vapour phase
24 fabrication, etc for thin film fabrication [4, 5]. Because of its simplicity, reliability and accessibility, we found Spin
25 Coating method being feasible within our budget and lab frame too.

26 Spin Coating is the most preferred technique for the thin film deposition on the flat substrate due to its plainness,
27 low cost, easy doping, low operating temperature and spin and film thickness controllability. A very small amount
28 of coating material is dropped at the centre of the substrate spinning at a constant speed or at rest, then is rotated
29 at high speed to spread the material uniformly all over the substrate. As soon as, the coating is completed, the
30 substrate is annealed for the evaporation of the unwanted solvent and deposition of the film. The process is
31 continued until the desired thickness or resistance of the film is achieved [6, 7].
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33 Glass substrates were cut into square pieces (2.5cm x 2.5cm), washed with distilled water then sonicated for 15
34 minutes with distilled water and Acetone at 70°C then dried in a hot air oven at 100°C. For 0.5 M precursor solution
35 (Solution for pure ZnO thin film), 13.3872 g of Zinc Acetate Dihydrate (ZAD) and 6mL of Diethyl Amine (DEA)
36 added to 120 mL of Ethanol was stirred at 300 rpm for an hour at room temperature. 0.1 mL of precursor solution
37 was spread over the spinning (at 3000 rpm for 30 seconds) substrate in a spin coater and was annealed over the hot
38 plate at 550°C for 15 minutes.
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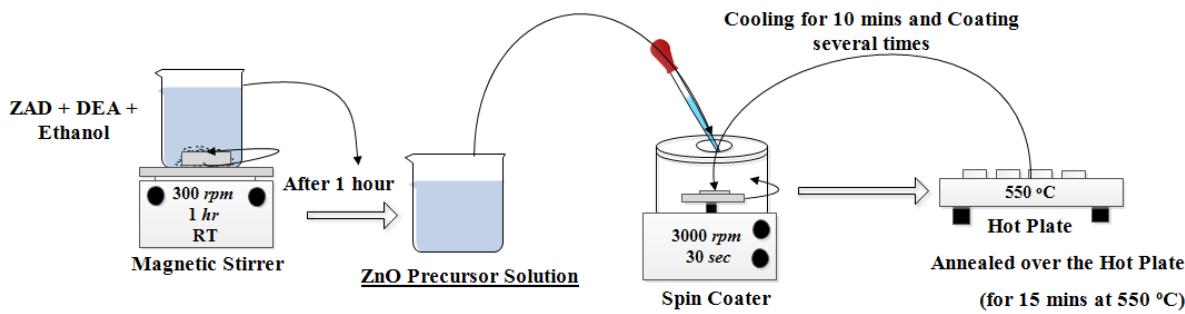


Figure 1: Preparation of ZnO thin film by Spin Coating Method.

The films fabricated were further cut into minute pieces (4 mm x 7 mm) and heated at 100°C for 2 hours. As soon as the film gets heated, thin insulated wires-conducting at the ends were connected to both the ends of the film using Silver paste. Two heating system was adjusted at the ends of a cylinder of the volume of about 300 cm³; heater at the top was to monitor the temperature of the film (if necessary) and heater at the bottom was to evaporate liquid (if necessary). The needle of the syringe was adjusted as shown as in the figure below so as to pass gas or drop liquid over the heater. This is the way, how we built a setup for the exposure of thin film to gas for sensing purpose.

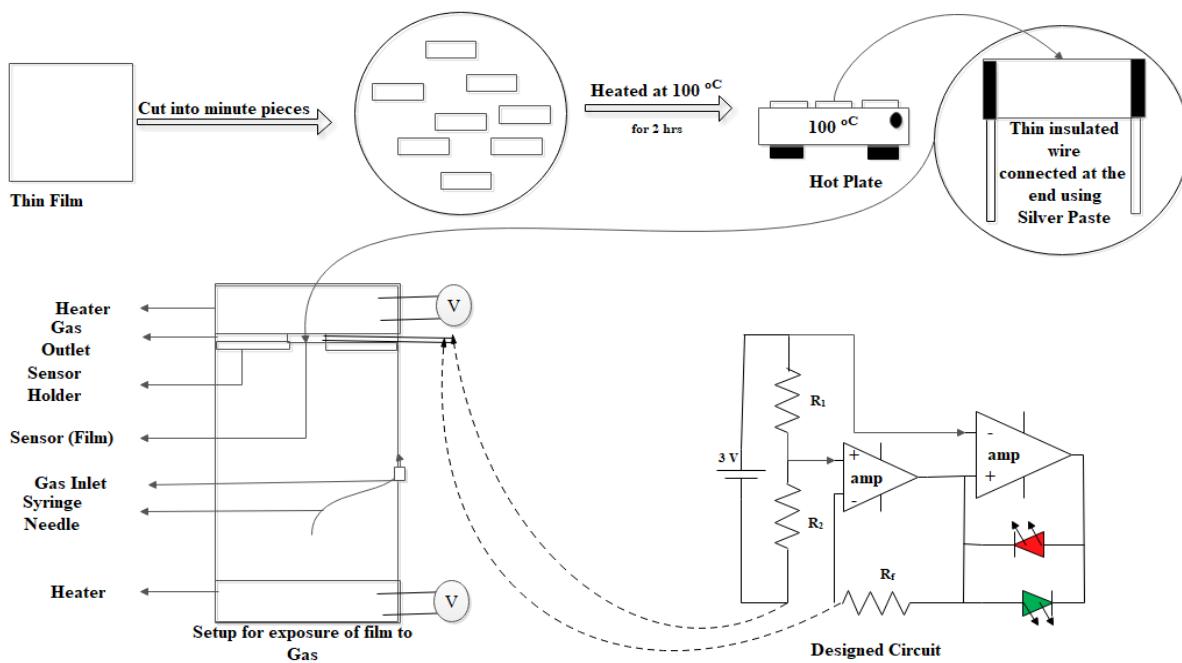


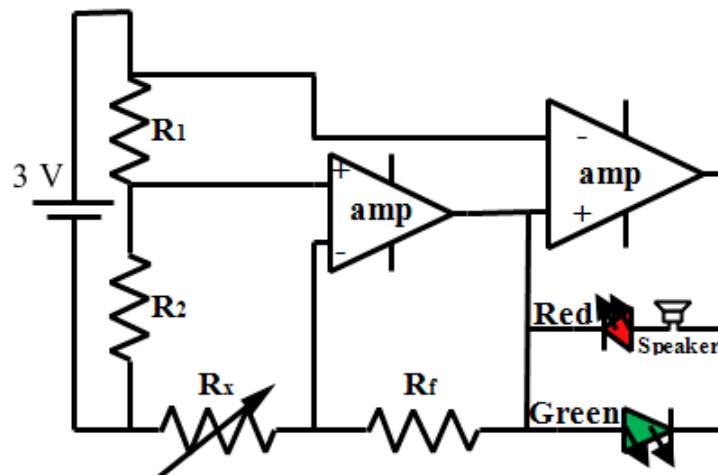
Figure 2: Entire setup for sensing.

Different concentration of ethanol and methanol was passed into the chamber and corresponding response of the circuit was observed and noted.

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4 **Circuit (Sensor) Designing:**

5 Several electronic circuits were designed using CircuitMod 2.7 and Online Circuit Simulator and
6 Schematic Editor-Circuit Lab and variation of outputs due to variation in resistance of thin film used in the circuit
7 was analyzed. Then the necessary electronic components were fixed in the PCB board.

8 Two resistors (R_1 and R_2) were connected in series with 3 V battery. The positive input terminal of first amplifier
9 was connected to the junction of R_1 and R_2 and the negative input terminal was joined to the junction of feedback
10 resistor (R_f) and film resistor (R_x). The output terminal was connected to its negative input terminal through a
11 feedback resistor and to non-inverting input terminal of second amplifier as shown as in the figure 3. In case of
12 second amplifier, its inverting input terminal was connected to positive terminal of the battery, positive input
13 terminal was connected to output terminal of first amplifier. Two light emitting diodes (LEDs; one red and another
14 green) held anti-parallel (anode of red joined to cathode of green and vice-versa) were connected between the
15 outputs of first and second amplifiers (cathode of red LED connected to output of first amplifier). The seventh pins
16 of both amplifiers were connected to positive terminal of source; fourth pins were grounded, whereas first and
17 eighth pins were left floating. Also, a bugger was connected in series with red LED.

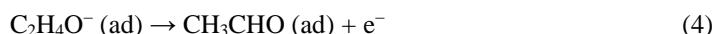


43 **Figure 3:** Designed Sensor Circuit where R_x is film resistance.
44 Also, the configuration works if the both amplifiers and LEDs are flipped in respect to polarity.

45 **Sensing Mechanism:**

46 The detection mechanism of Semiconductor Metal Oxide (SMO) as a sensor is complex and not yet fully
47 understood. Adsorption ability, electrophysical and chemical properties, catalytic activity, thermodynamic stability
48 and the adsorption/desorption properties of the surface of SMO as well yields this complexity [1]. ZnO (n-type
49 semiconductor) thin film surface, when exposed to air, adsorb oxygen molecules to form molecular type adsorbate
50 (O_2 , O_2^-) and dissociative type (O_2^{2-}) adsorbate ions forfeiting electrons from the conduction band, yielding electron-
51 depleted space-charge layer in the grain boundary region which leads to large surface potential barrier and large
52 resistance. The target gas (ethanol/methanol) may undergo dehydration and dehydrogenation and successively
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oxidized to CO, CO₂ and H₂O, but ZnO being basic oxide, dehydrogenation is favored. The response of the film towards alcohol vapors is dependent on the conversion of alcohol into aldehydes [7, 8].



The release of electrons back to the film enhances the conductivity of the film and deduces the resistance [8]. When oxygen adsorbed onto the film surface which traps electrons from the bulk of material forming a potential barrier is replaced by reducing gas molecules the barrier at the grain boundaries decreases and thus reduces the electrical resistance of the film [1]. This reduces potential at the negative input terminal of the first amplifier which yielding change in its output and potential at the positive input terminal of the second amplifier. This change in the value of positive input of the second amplifier changes the polarity of its output from negative to positive and current flows through red LED only. So, only red LED glows and buger beeps.

In the former case (when the film is not exposed to reducing gas), the circuit yields negative output so red LED being reverse biased blocks electron to flow through it and only green LED being forward biased allows flowing current through it and glows. As soon as the vapor passes away, the film undue starts adsorption of atmospheric oxygen and tends to achieve its former state [8]. And, again the circuit glows Green as soon as the film recovers.

III. Results and Discussion

UV-Vis Spectroscopy:

The optical characterization of the samples was performed in Nepal Academy of Science and Technology (NAST) using UV-Vis spectrophotometer (Carry 60 spectrophotometer, Agilent Technology). The absorbance and transmittance of the films were measured which were further analyzed to calculate the band gap and thickness of the films. For indirect transition, the variation in absorption coefficient with the photon energy obey Tauc's plot method,

$$(\alpha h\nu)^{0.5} = A(h\nu - E_g) \quad (\text{Eq. 1})$$

Where A is a constant, E_g is the optical band gap, h is the plank constant and α is the absorption coefficient. Extrapolation of $(\alpha h\nu)^{0.5} = 0$ yields the optical bandgap energy of the films [9].

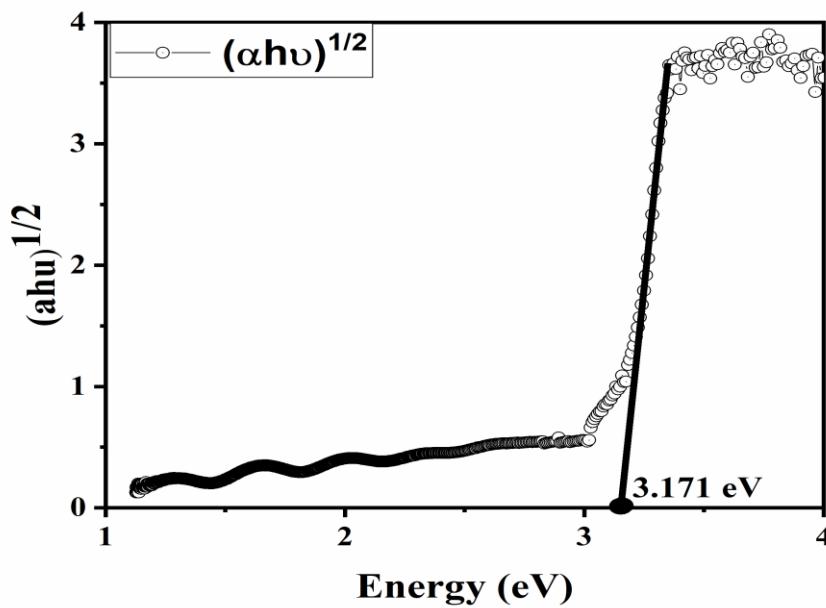


Figure 4: Tauc's Plot for calculation of Energy Bandgap

The bandgap of thin film fabricated by us was found to be 3.171 eV.

X-ray Diffraction (XRD):

The dual natured (behaving as both particle and wave) electromagnetic radiation having high penetration power⁶, photon energy within 100 eV- 100 KeV is termed as X-ray. It is a non-destructive technique used for characterizing crystalline substance. This helps in the identification and quantification of the crystalline phase, structure, orientation, composition and defects. Further, it is used to measure the size, strain or micro-strain effects, transparency and electron mobility in thin-films [10]. The structural characterizations of fabricated thin films were analyzed using XRD [Bruker D2 Phaser X-ray diffractometer of CuK α radiation (wavelength: 1.54184 Å)] at 40 KV of operating voltage and current of 40 mA in the 2θ range of 20° - 80° at scanning rate of 15° per minute at NAST, Khumaltar, Lalitpur, Nepal. The Debye Scherrer's formula used to calculate the average grain size 'D' is given by,

$$D = \frac{0.9\lambda}{\beta \cos\theta} \quad (\text{Eq. 2})$$

Where, 0.9 is the correction factor, λ is the wavelength of the x-radiation, β is the full width at half maximum (FWHM) of the observed peak and θ is the Bragg's angle [10]. Comparing calculated d-spacings with the standard JCPDS values of card number 36-1451, the observed peaks were indexed. The average crystallite size of ZnO was found to be 20.068 nm using Scherrer's method.

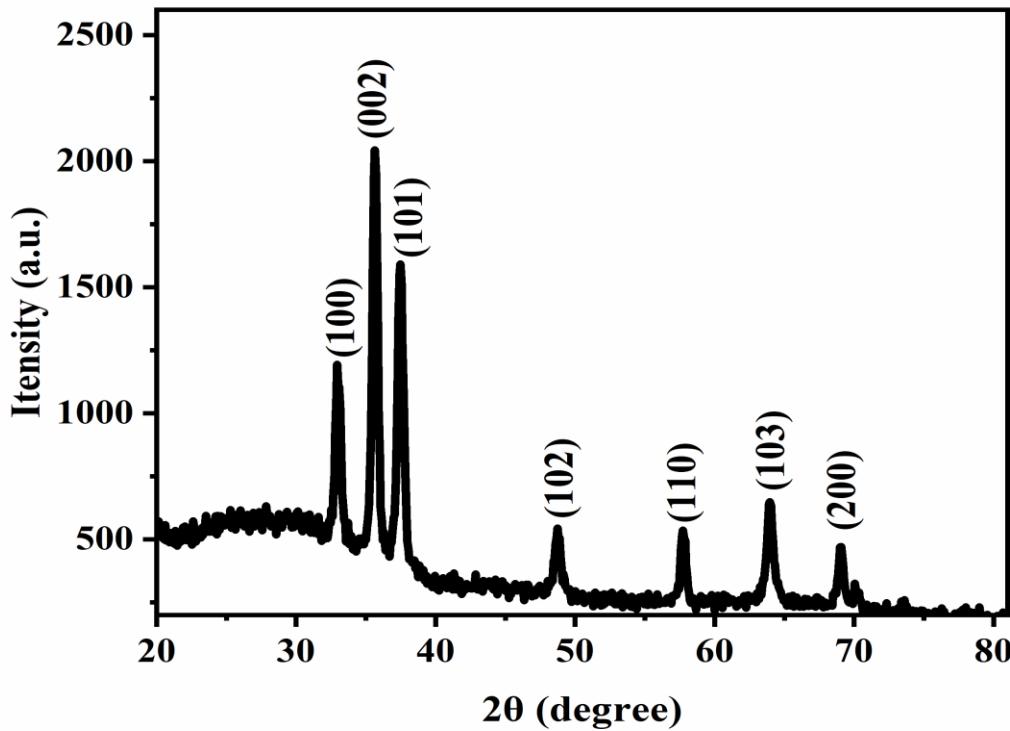


Figure 5: XRD pattern of Pristine ZnO thin film.

The crystallite size of as deposited ZnO thin films were also calculated using W-H plot method using prominent XRD planes then compared with that obtained from Scherrer's formula. The W-H plot is related with the full width half maxima (FWHMs) (β) of XRD peaks and crystallite size (D) through the relation,

$$\frac{\beta \cos \theta}{\lambda} = \frac{1}{D} + \frac{4\epsilon \sin \theta}{\lambda} \quad (\text{Eq. 3})$$

Where, ϵ is the amount of residual strain, θ is the angle of diffraction, λ is the wavelength of X-ray [10]. A graph between $\beta \cos \theta / \lambda$ versus $4\sin \theta / \lambda$ when plotted and fitted linearly, the reciprocal of the x-intercept gives the average crystallite size [11] and was found to be 17.345 nm.

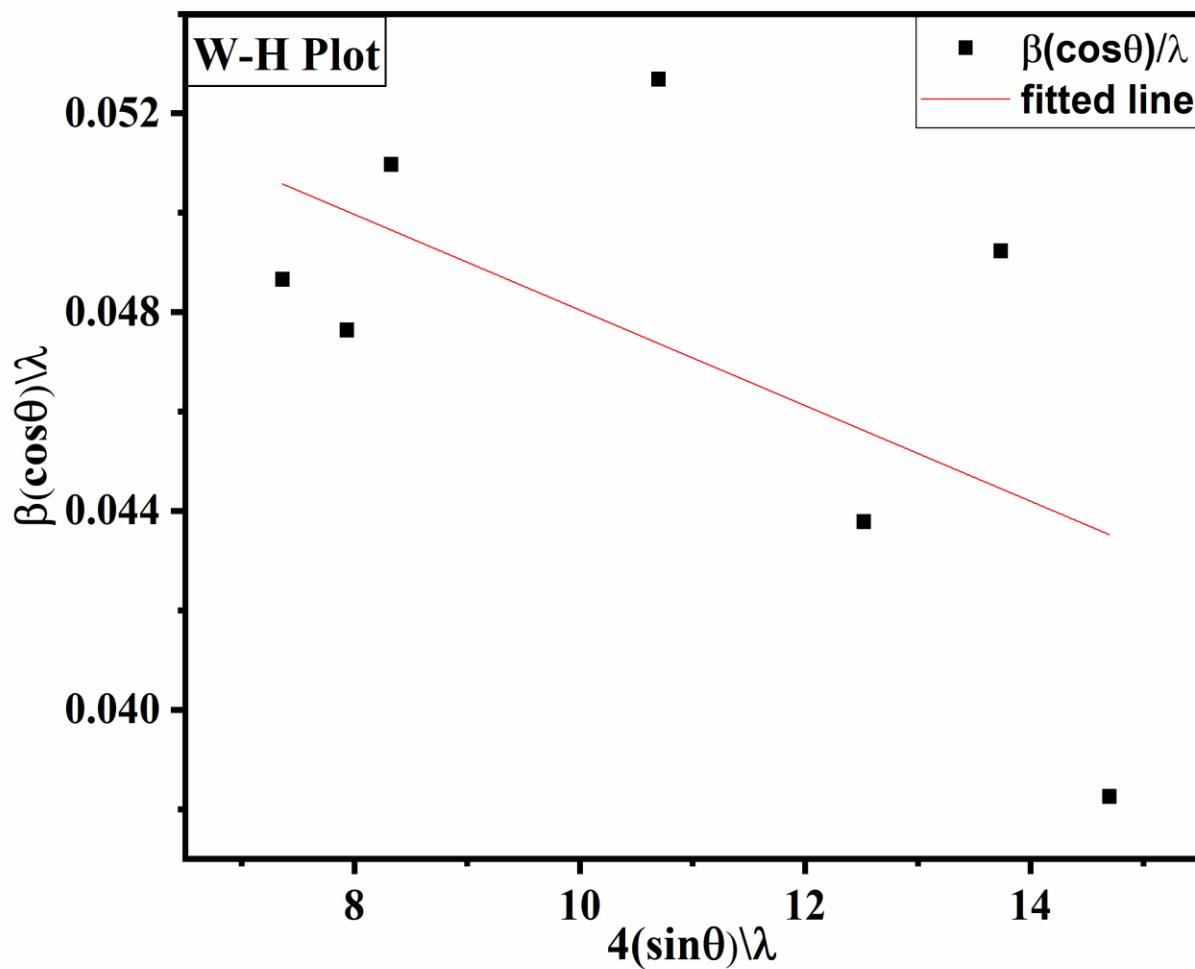


Figure 6: William-Hall (W-H) plots of pristine ZnO.

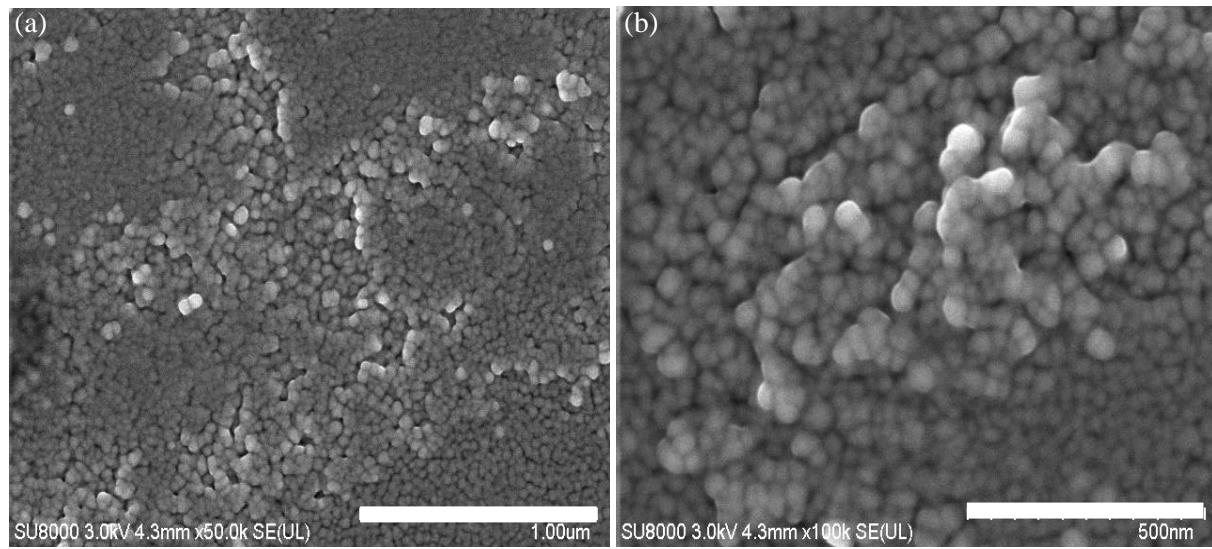
The crystallite size of the fabricated film calculated from the W-H plot was found consistent with that as calculated from Scherrer's method.

Table no 1: Shows XRD analysis for miller indices, d-spacing and grain size of the deposited ZnO thin film.

S.N.	Miller Indices	Angle 2θ	Calculated d (\AA)	JCPDS(36-1451) d (\AA)	Crystallite Size D(nm)	
					Scherrer's Method	Average
1.	(100)	32.95075	2.7172	2.8142	19.31788	20.0678
2.	(002)	35.60633	2.5204	2.6033	19.73324	
3.	(101)	37.42934	2.4018	2.4759	18.44347	
4.	(102)	48.69692	1.8692	1.9111	17.84351	
5.	(110)	57.69607	1.5972	1.6247	21.46739	
6.	(103)	63.92009	1.4559	1.4771	19.09518	
7.	(200)	69.00289	1.3605	1.4072	24.57326	

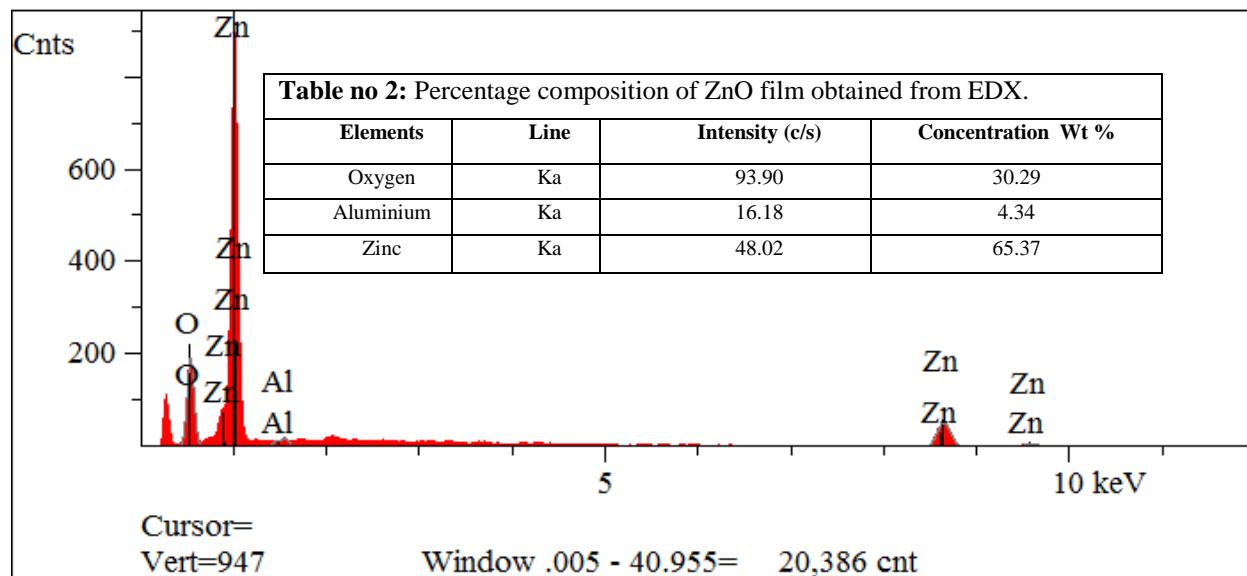
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Scanning Electron Microscope (SEM) and EDX analysis:

6 The surface morphology of ZnO thin films were performed using Scanning Electron Microscope at Research Centre
7 for Eco-Environment Sciences, Chinese Academy of Sciences, Beijing, China.
8
9



30 **Figure 7:** SEM images of ZnO thin film with scale (a) $1\mu\text{m}$ and (b) 500nm
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35 Figure 7(a) and 7(b), shows the SEM images of undoped ZnO with scale $1\mu\text{m}$ and 500nm and magnification of 50K
36 and 100K respectively. The SEM image depicts grainy structure of film. The average grain size of ZnO was found to
37 be around 25 nm which is quite corresponding to results obtained from XRD analysis.
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57 **Figure 8:** Energy Dispersive X-ray image of Pristine ZnO film.
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Figure 8 shows the EDX spectra which assure that the film is of Zinc oxide. Very small peak of Aluminium is detected which may be due to Aluminium silicate (glass) substrate. The EDX spectrum of ZnO sample shows the high content i.e. 65.37 wt. % of Zinc, 32.29 wt. % of Oxygen and 4.34 wt. % of Aluminium which is almost negligible compared to oxygen and Zinc.

Circuital Analysis:

The circuit designed is the novel concept in sensing gas. Since the resistance of the film is influenced by material used for depositing thin film, the number of coating done, doping in film and aging of the film, the values of the resistors used in the circuit must be different for different value of film resistance at the ordinary condition. These values of the components must be appropriate to determine or sense the selected reducing gas. Here we present some particular values of these components and the critical point value of the film resistance (value of film resistance beyond which the output voltage of the circuit changes its polarity or the LEDs switch) for the particular configuration of the circuit. We analyzed the circuit fixing the feedback resistance and the ratio ($R_1: R_2$) and manually changing the value of film resistance unless we obtained critical value.

The film resistance of quite higher value than the critical value should be used for better sensing. Considering this, best range of the film was estimated and their corresponding sensitivity was calculated using the relation:

$$S = \frac{R_x - R_g}{R_x} \quad (\text{Eq. 4})$$

Where, S is sensitivity, R_x is film resistance before exposure to gas and R_g is the value resistance of film after exposure to gas.

Table no 3: Shows the values of Components to be used in accordance to film resistances and selected gas.

S.N.	Feedback Resistance R_f (KΩ)	Ratio ($R_1: R_2$)	Critical Point Value (KΩ)	Best Range of Film Resistance R_x	Minimum Sensitivity S (%)
1.	560	1:3	1679	(2-1.7) MΩ	(15-1.24)
	560	1:10	5999	(10-6) MΩ	(40-0.02)
	560	1:100	55899	(200-56) MΩ	(72-0.18)
2.	470	1:3	1410	(2-1.5) MΩ	(30-5)
	470	1:10	4759	(15-5) MΩ	(67-4.82)
	470	1:100	46899	(200-47) MΩ	(77-0.22)
3.	100	1:3	298.99	(400-300) KΩ	(25-0.34)
	100	1:10	999.79	(2-1) MΩ	(50-0.021)
	100	1:100	9982.56	(40-10) MΩ	(75-0.174)
4.	10	1:3	44.98	(80-45) KΩ	(44-0.04)
	10	1:10	99.98	(300-100) KΩ	(67-0.02)
	10	1:100	997.92	(3-1) MΩ	(67-0.02)
5.	1	1:3	2.999	(5-3) KΩ	(40-0.03)
	1	1:10	9.998	(30-10) KΩ	(67-0.02)
	1	1:100	99.82	(300-100) KΩ	(67-0.18)

Table no 3 represents the theoretical values for the circualt components for sensing the selected gas to approximate the appropriate value of feedback resistor, the ratio of R_1 and R_2 to be used in the circuit for sensing particular gas within a limited range of sensitivity. Further the tables, eases to choose the sensor components accordance to resistance of fabricated film. We need to select the sensitivity within which we are willing to work with. This helps finding the critical value using relation (4) and helps to approximate the feedback resistance and ratio $R_1:R_2$. Clearly, ratio of feedback resistance and critical value seems roughly equal to ratio $R_1:R_2$.

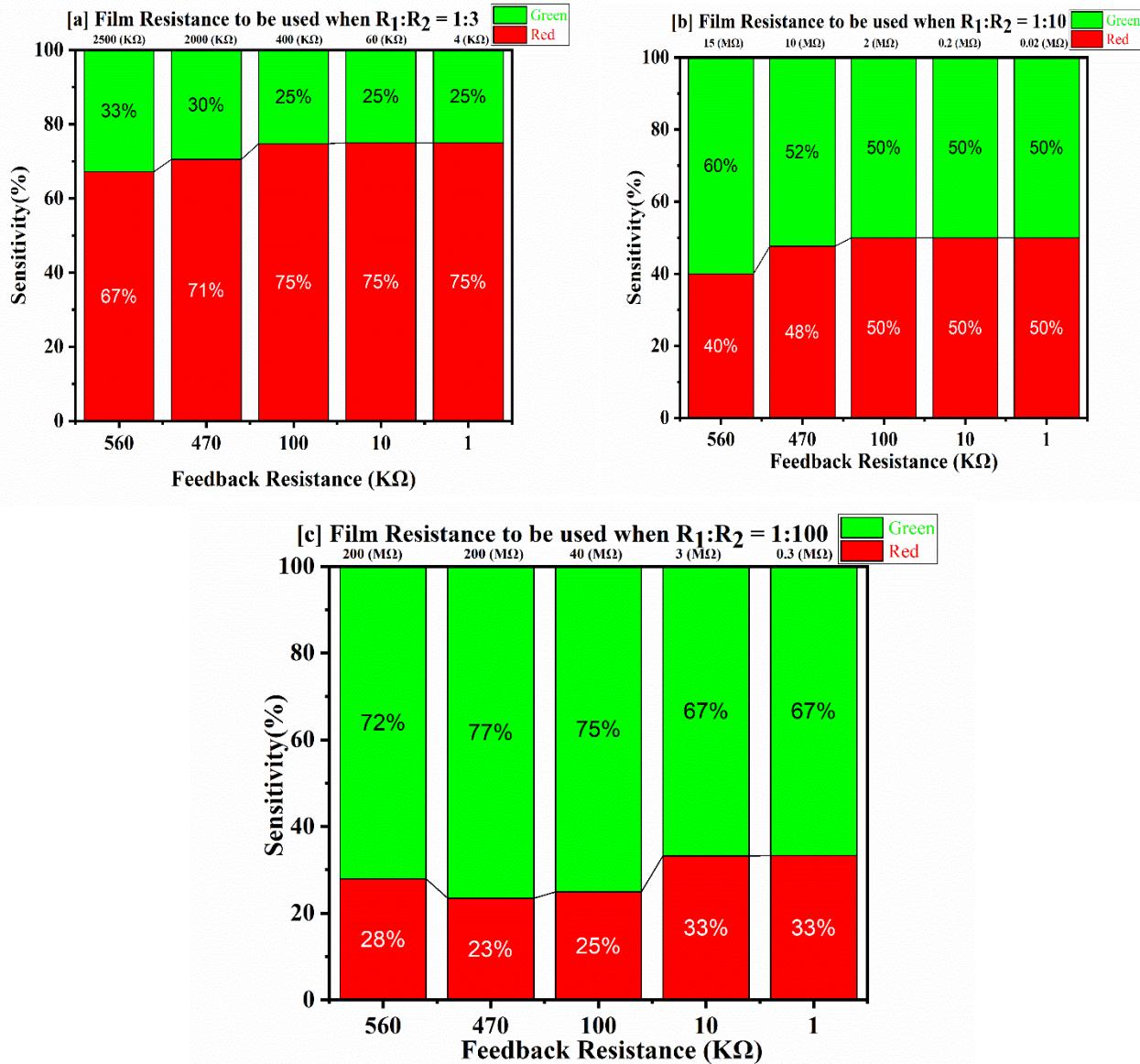


Figure 9: Sensitivity Stacked Chart for different ratio of R_1 and R_2 (a) 1:3, (b) 1:10 and (c) 1:100 and different values of Film and Feedback Resistances.

In the sensitivity stacked chart for different ratio $R_1:R_2$ and different feedback resistance above, film resistance from which sensitivity is measured, is mentioned at the top of it. If we use the film of above mentioned resistance as sensor, and corresponding values of feedback resistance and ratio $R_1:R_2$, the sensitivity of the film on exposure to gas

must be as indicated on green block so as to sense it. In other words, the exposure to gas should reduce the film resistance by indicated values to detect the gas. These suggest that for higher film resistance, we should use higher value of feedback resistor or large $R_1:R_2$ for more sensitive sensor and for film resistance with low resistance, comparably small values of the components can be used.

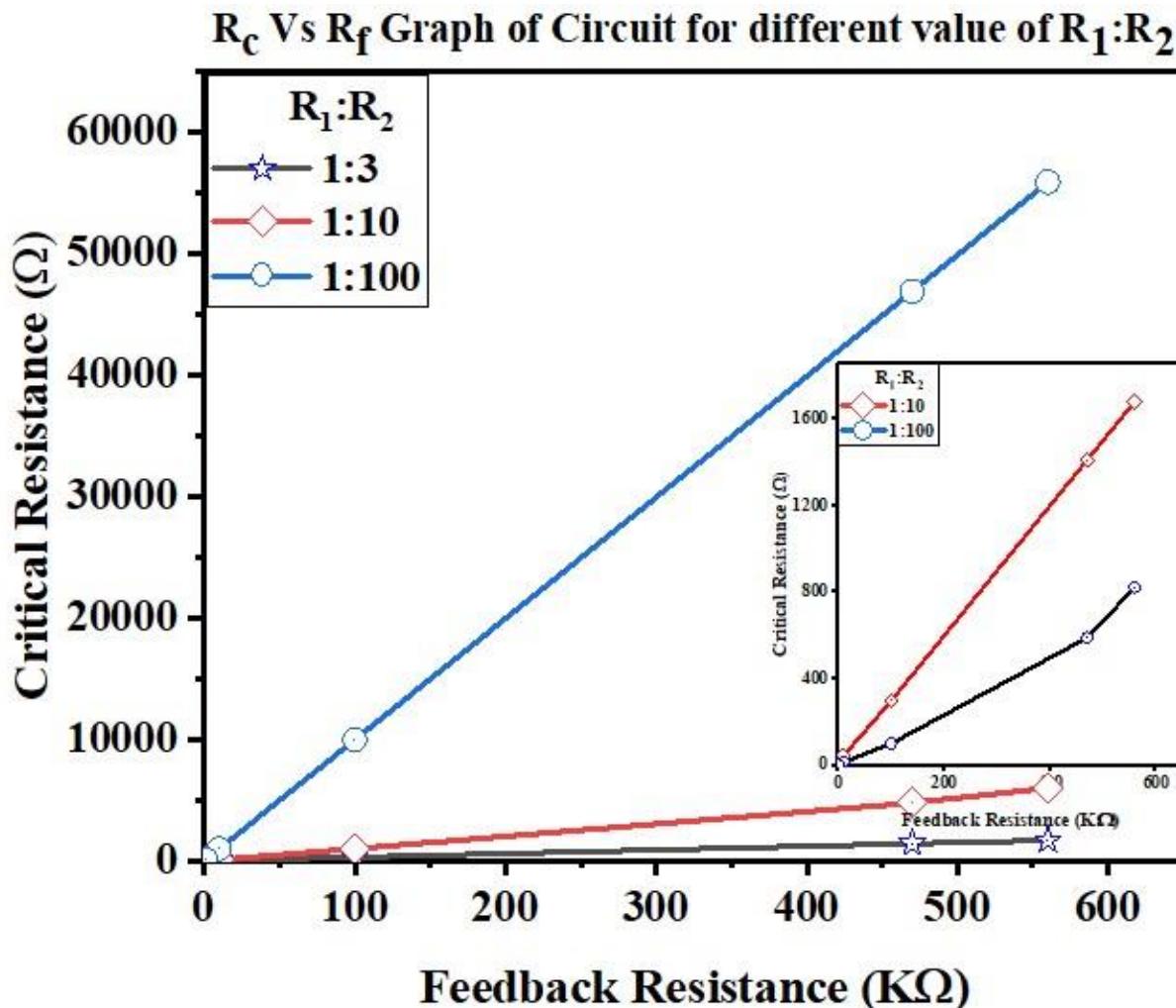


Figure 10: Critical vs feedback resistance graph at different ratio of R_1 and R_2 .

Figure 10 clearly depicts that critical point value or the critical resistance of the film is linearly dependent on the feedback resistance used in the circuit for same $R_1:R_2$. The critical resistance is such value of the film above which the circuit glows Green and below which results glowing Red. Also, it suggests that increment in the ratio $R_1:R_2$ yields higher value of critical resistance which will be very efficient for using highly resistive film as a sensor. Lower value of $R_1:R_2$ gives lower value of critical resistance which will be more effective if used with less resistive film. Furthermore, highly resistive film can be used as sensor along with lower value of $R_1:R_2$ if the target gas highly reduces the film below critical value. The mechanism is same for feedback resistor. Thus, appropriate value of $R_1:R_2$ and feedback resistor can let us sense reducing gas of any concentration.

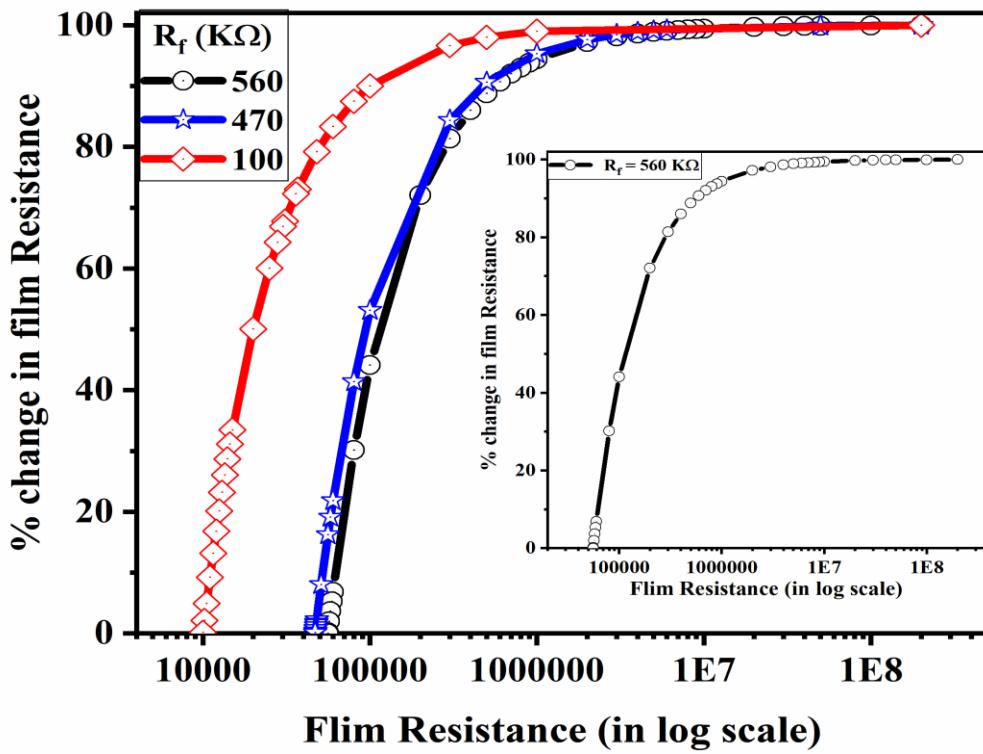


Figure 11: Least percentage change of Film Resistance required for sensing vs Film resistance graph for different value of R_f .

Figure 11 is the plot of film resistance (in log scale) vs least percentage change required for sensing the target gas at different value of feedback resistance for $R_1:R_2$ equals 1:100. The graph clearly shows that highly resistive film needs more than 90% change in their film resistance for sensing (RED glow in circuit) in above mentioned configuration. But Film resistance closer to the critical value of resistance can sense well within less percentage change in its former value. This circuit best suits for sensing even if the target gas increases the film resistance. But selecting appropriate and accurate $R_1:R_2$, feedback resistor and remaining circuital components is most for excellence performance.

Thus, analyzing Figure 10 and Figure 11, we can conclude that sensitivity of the circuit is dependent on the value of critical resistance of the film but not on the film resistance. This is the most fantabulous characteristics of the circuit which overcomes the dependency of the available ordinary sensors on film resistance. Furthermore, the critical value of the film is controllable. It depends upon the components used in the circuit. The film resistance may vary from few K Ω to hundreds of M Ω and no chemical synthesis yields film of desired resistance with accuracy which has brought complexion in sensing with desired accuracy. Thus, the noble circuit designed is the ultimate way to eradicate this drawback of the ordinary sensor. Finally, designation of sensor can be summed up as:

- (i) Measuring film resistance after fabrication R_x .
- (ii) Choosing sensitivity (S).
- (iii) Calculating Critical Resistance using selected sensitivity and Film Resistance as:

$$R_c = R_x - \frac{S \times R_x}{100} \quad (\text{Eq. 5})$$

(iv) Choosing appropriate value of $R_1:R_2$, R_f and other circuital components and fabricating sensor.

Experimental Verification:

This was experimentally verified using alcohol (ethanol and methanol) vapors as reducing gas and ZnO as sensing material in the film. The value of the fabricated film resistance was more than $200\text{ M}\Omega$, ratio ($R_1: R_2$) was 1: 3, the value of feedback resistance was $560\text{ K}\Omega$ and two eight pins chips (UA741CN) were used as amplifiers. Two LEDs (one red and another green) were fixed as shown in the circuit. 9 Volt battery was used as a source for two amplifier chips and another 3 Volt battery was conned in series with R_1 and R_2 . The film was exposed to different concentrations of gas (alcohol vapors) and corresponding change was noted. The table below represents the experimental values.

Table no 4: Value of Input and Output Voltages of Circuit before and after exposure to alcohol vapors.

S.N.	Gas	Concentration (ppm)	Potential (V)			
			Before passing gas		After passing gas	
			Input	Output	Input	Output
1.	Ethanol	500	0.35	-4.15	6.27	2.56
		250	0.36	-4.15	5.11	2.28
		50	0.35	-4.14	4.12	2.13
2.	Methanol	500	0.36	-4.14	5.56	2.52
		250	0.34	-4.15	4.92	2.23
		50	0.36	-4.13	3.98	2.06

The table above clearly shows the switching of potential at output of circuit due to exposure of alcohol vapors. This confirms that the designed circuit senses alcohol vapor (reducing gas) using pristine zinc oxide thin film.

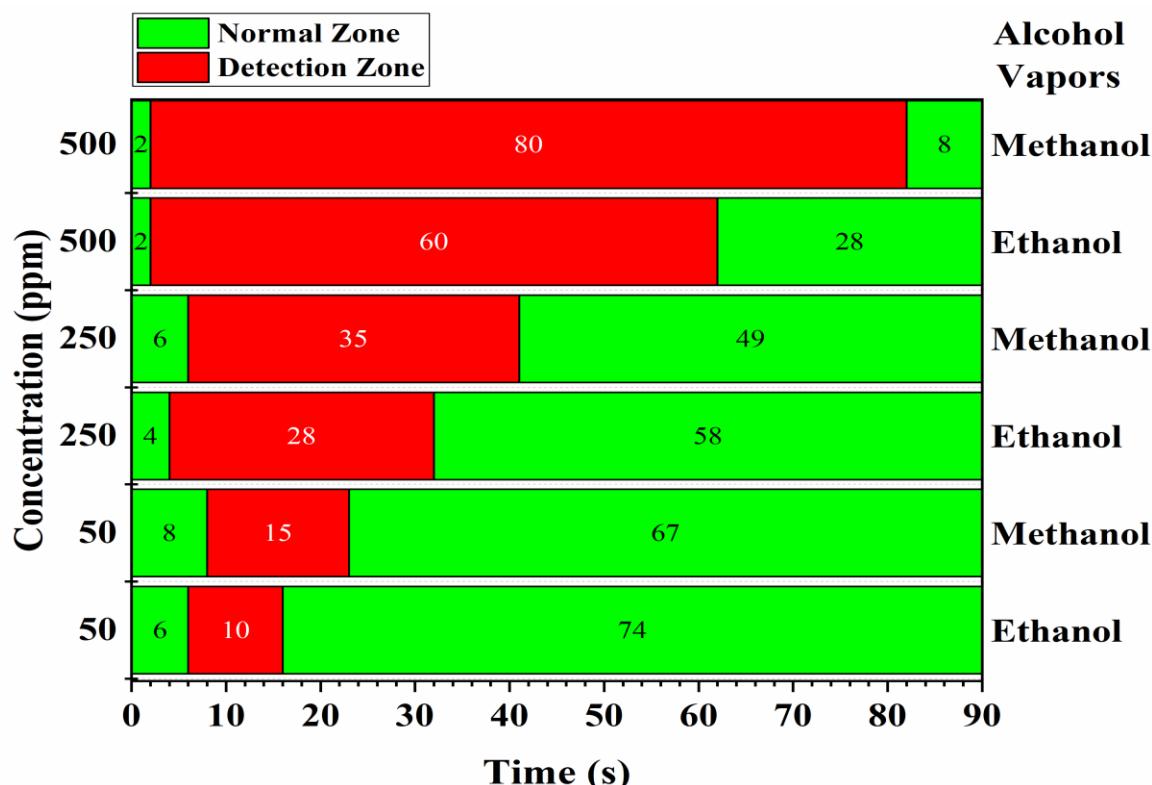
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4 **Response and Recovery:**

5 Response and recovery time are another indispensable factor for determining whether or not a sensor is reliable.
6
7 Here we have tabulated response and recovery time of our circuital sensor after exposure to different concentration
8 of ethanol and methanol vapors.
9

10 **Table no 5:** Response and Recovery time of ZnO thin-film varying with concentration and types of alcohol.

S.N.	Alcohol	Concentration (ppm)	Response Time (s)	Recovery Time (s)
1.	Ethanol	500	2	60
		250	4	28
		50	6	10
2.	Methanol	500	2	80
		250	5	35
		50	8	15

20 The circuit remains in either normal state/zone (glowing Green) or in detection zone (glowing Red). When the target
21 gas is passed, sooner the film resistance decreases and reaches the critical resistance, the circuit changes its state
22 from normal and when the gas passes by, film resistance starts increasing again. As soon as it exceeds R_c , it changes
23 its state back to normal. The time for which the circuit remains in either state while responding to different
24 concentrations of Ethanol and Methanol vapors is shown below in Figure 12 :



54 **Figure 12:** Time for which the circuit remains in either state in response to different concentration of alcohol vapors.
55

56 The figure above clearly depicts that higher the concentration, longer it stays in detection zone. Further, for same
57 concentration, circuit responds faster to ethanol than methanol.
58

The vapors were passed simultaneously into the sensor setup and were free to escape at any time. The variation in film resistance in response to 50, 250 and 500 ppm of Ethanol and Methanol vapors were observed and are graphed as shown in Figure 13. The graph reflects that the resistance of the film while responding reducing gases decreases rapidly for few seconds then slows down and reaches its minimum value. The minimum value is attained when the

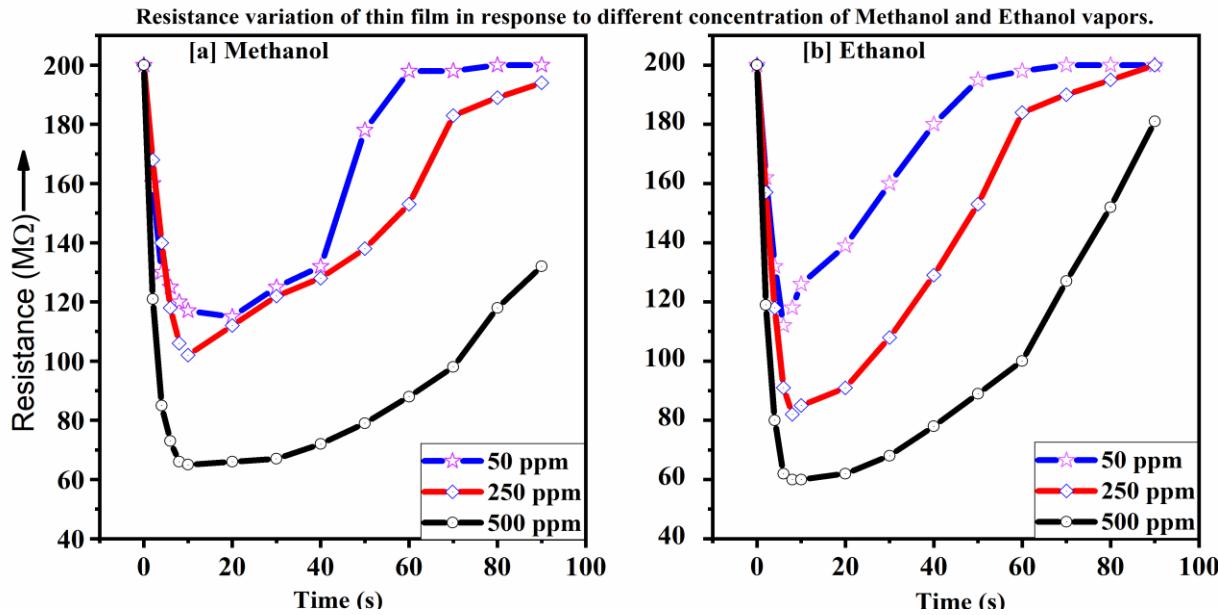


Figure 13: Variation of film resistance in response to various concentrations of Alcohol vapors.

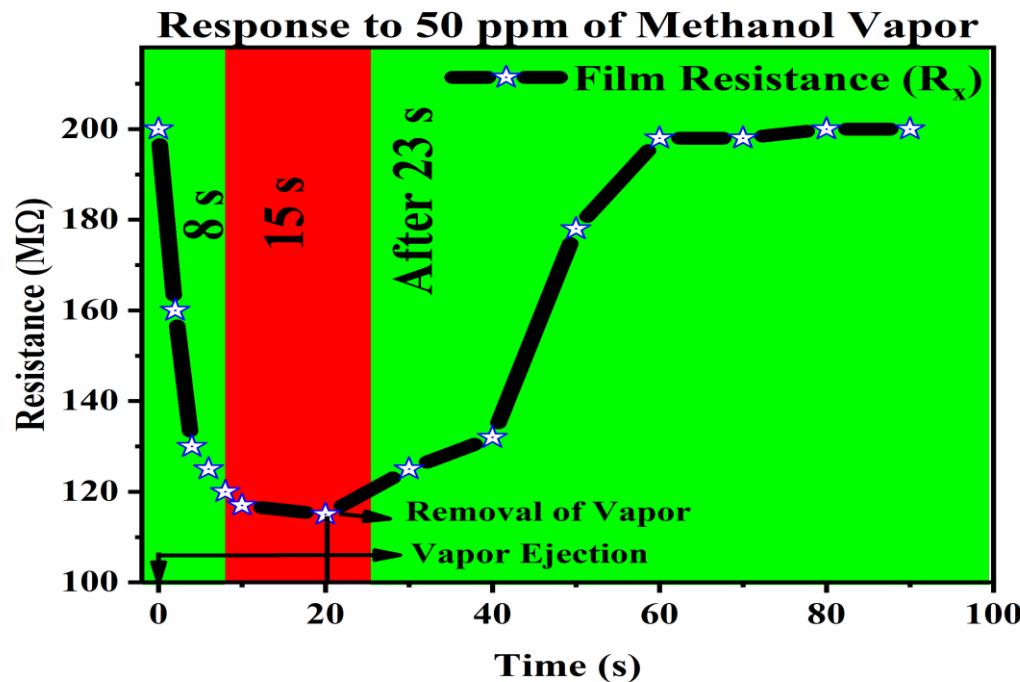


Figure 14: Film response to 50 ppm of Methanol Vapors.

target gases replace maximum number of reduced oxygen molecules in the grain boundary of film. As soon as the impact of the gas diminishes, the oxygen molecules in reduced form starts gathering at the grain boundary region and the film resistance starts increasing again. Its obvious that lower the concentration, less is the impact on film resistance.

Clearly, the experimental result shows that the film is sustainable and is very sensitive to reducing gases. The longevity of recovery time may be due to poor ventilation for gas outlet in our experimental setup.

IV. Conclusions

The novel circuit introduced for gas sensing approach can sense any reducing gases using zinc oxide thin film. After the fabrication of thin-film, film resistance will be known and analyzing table no 3, Figure 10 and Figure 11, we will be able to find the appropriate value of feedback resistor, the ratio of R_1 and R_2 to be used in the circuit for sensing particular gas within limited sensitivity range. Furthermore, the electrical components used are available in variable small size in the market, so we will be able to fabricate portable miniaturized sensing device or sensor of the desired size at low cost and consuming less energy, simply using zinc oxide thin film. Also, the circuit can be used for simple breathalyzer testing.

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Acknowledgments
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17 **References**
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- 20 [1] Liu X, Cheng S, Liu H, Hu S, Zhang D, Ning H. A survey on gas sensing technology. Sensors.
21 2012;12(7):9635-65.
22 [2] Kanan S, El-Kadri O, Abu-Yousef I, Kanan M. Semiconducting metal oxide-based sensors for selective gas
23 pollutant detection. Sensors. 2009;9(10):8158-96.
24 [3] Yu Z, Fang L, Deqin L and Bingqian G. Monitoring the spontaneous combustion of coal stack based on ZigBee
25 and Lab view. Journal of Physics: Conf. Series. **1303**; 2019.
26 [4] Naveed Ul Haq A, Nadhman A, Ullah I, Mustafa G, Yasinzai M, Khan I. Synthesis approaches of zinc oxide
27 nanoparticles: the dilemma of ecotoxicity. Journal of Nanomaterials. 2017;2017.
28 [5] Mohammed A, Naik PS, Suryavanshi SS, Nadaf LI. Design and fabrication of low cost and miniaturized setup
29 for gas sensor. IOSR Journal of Applied Physics. 2015; 7(2):2278-4861.
30 [6] Unalan HE, Hiralal P, Rupesinghe N, Dalal S, Milne WI, Amaratunga GA. Rapid synthesis of aligned zinc oxide
31 nanowires. Nanotechnology. 2008;19(25):255608.
32 [7] Jiaqiang X, Jianjun H, Yuan Z, Yu'an S, Bing X, Studies on alcohol sensing mechanism of ZnO based gas
33 sensors. Sensors and Actuators B: Chemical. 2008; 132:334-339.
34 [8] S.C Navale, V.R.S. Mulla, S.W. Gosavi and S.K. Kulkarni, *Sensors and Actuators B: Chemical*, **126**(2), 382-
35 386(2007).
36 [9] Mulmi DD, Dahal B, Kim H-Y, Nakarmi ML, Panthi G. Optical and photocatalytic properties of lysozyme
37 mediated titanium dioxide nanoparticles. Optik. 2018;154:769-76.
38 [10] F Garcés F, Budini N, Koropecki R, Arce R. Structural analysis of ZnO (: Al, Mg) thin films by X-ray
39 diffraction. Procedia Materials Science. 2015;8:551-60.
40 [11] Chaki SH, Chaudhary MD, Deshpande M. SnS thin films deposited by chemical bath deposition, dip coating and
41 SILAR techniques. Journal of Semiconductors. 2016;37(5):053001.
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