

## Fabrication of alcohol sensor using undoped and Al doped ZnO nanostructure film with polymer electrolyte gating

--Manuscript Draft--

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<b>Abstract:</b>	We report the fabrication of two terminal and three terminal gas sensor using Al-doped ZnO thin films and polymer electrolyte gate dielectric on glass substrate by vacuum free chemical method. The Al doped ZnO films are characterized by XRD, SEM, EDX, and UV-vis Spectrometer. The characterization results have revealed the polycrystalline structure of both undoped and doped ZnO; with loosely packed, porous, and spherical grain nanostructure with mean grain size 20–10 nm and bandgap of the films is within the range of 3.12–3.16 eV. The conductivity of the ZnO film is tuned by Al concentration and the maximum value of conductivity was observed in 3% Al doped ZnO films. Similarly, the best performance index of TFT such as current ON/OFF ratio, high transconductance and low threshold voltage was observed in 3% Al doping concentration. The ordinary (two-terminal) sensor and three-terminal(FET) sensors' responses towards three different concentrations 50, 250, 500 ppm of ethanol and methanol vapors have been studied. The sensitivity of the film is modulated by Al concentration and higher value of sensitivity was achieved at 3% Al doped ZnO films. The use of polymer electrolyte enhanced the sensitivity of the device which is more effective in methanol vapor. The response and recovery time of gas sensor is significantly improved in three terminal devices than the two terminal devices.
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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 “STUDY ON ALCOHOL SENSING APPLICATION OF EDL DIELECTRIC POLYMER GATED/NON-GATED, ZnO/AZO CHANNELLED THIN FILM AND TRANSISTOR” to be considered for publication as an original article in Sensors and Actuators.

Our research is concerned in study of alcohol sensing properties of zinc-oxide thin film, Aluminium doped zinc oxide thin films, electric double layer dielectric polymer gated zinc-oxide and Al-doped zinc-oxide thin film transistors.

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:** STUDY ON ALCOHOL SENSING APPLICATION OF EDL DIELECTRIC POLYMER GATED/NON-GATED, ZnO/AZO CHANNELLED THIN FILM AND TRANSISTOR

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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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# STUDY ON ALCOHOL SENSING APPLICATION OF EDL DIELECTRIC POLYMER GATED/NON-GATED, ZnO/AZO CHANNELLED THIN FILM AND TRANSISTOR

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**Abstract:** In this research, undoped and various concentrations of Al-doped ZnO thin films have been fabricated by the spin coating method and characterized by XRD, SEM, EDX, and UV-vis Spectrometer. The characterization results have revealed the wurtzite polycrystalline structure of both undoped and doped ZnO; loosely packed, porous, spherical and homogeneously arranged granny nanostructure with mean grain size 20–10 nm and bandgap 3.12–3.16 eV. The ordinary (two-terminal) sensor and three-terminal sensor; EDL electrolyte polymer gated TFT and their responses towards three different concentrations; 50, 250, 500 ppm of ethanol and methanol vapors have been studied. This concludes that gas sensing mechanism of ZnO to alcohol, strongly modulated by the appropriate concentration of dopant; is simply the chemisorption of adsorbed oxygen at the grain boundary of the sensing material. The response of deposited thin-films with appropriate doping of Al has significantly increased the response of ZnO to alcohol. The 3% Al-doped ZnO thin-film sensor shows extremely outstanding gas responses to all concentrations and momentously to 500 ppm of both ethanol and methanol with sensitivity around 70%.

**Keywords:** EDL Polymer Gated, Field Effect Transistor Sensor, 3% Al-doped ZnO.

## I. Introduction

Gas sensing technologies have attracted much more attention of the scientific community, industry, and academia with increasing applications of industrial productions, medicines, automotive, indoor air quality control, environmental monitoring, etc. Due to the different applicability and inherent limitations of various gases, researchers have been working on different scenarios with enhanced gas sensor calibration [1]. Semiconducting metal oxides such as ZnO, SnO<sub>2</sub>, TiO<sub>2</sub>, WO<sub>3</sub>, CuO, and Fe<sub>2</sub>O<sub>3</sub> are strong and well-researched material for gas sensing applications. Different types of oxide-based nanostructures such as nanoparticles, thin films, nanorods, and nanowires have been synthesized and employed in the fabrication of gas sensors. It was found that chemical components, surface states, morphology, and microstructure play an important role in gas sensing performance. Among the various oxide semiconductors, ZnO, a wide direct-band gap(~3.2eV) semiconductor with wurtzite structure, is a promising candidate due to its strong shape, size, and surface tenability. It is non-toxic, eco-friendly, cost-effective and easy to synthesize [2]. The surface of ZnO is depleted due to the absorption of gases from the environment. Thus, the electrical conductivity of ZnO can be drastically changed in the presence of reactive gases present in the environment. The doping of foreign elements like Al, Cu, Ag, etc. in ZnO increases its conductivity

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4 and sensitivity by changing the shape and surface morphologies of ZnO. The defect states of ZnO may change with  
5 doping concentration, which has a higher role in carrier transport phenomena. Also, doping Aluminum makes the  
6 film more transparent [2-5].  
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10 For over 40 years, in electrochemical sensors, Field effect transistors (FET) have been significantly used as  
11 transducers because of their enhanced sensitivity, resolution, low power, portability, and fabrication  
12 compatibility. They have been used to detect ions and biomolecules, and sense DNA sequencing and mobile  
13 diagnostics. The sensing surface (or receptor) which interacts with the target analyte (gas in our case) and the  
14 transducer which converts this interaction into a legible electronic signal are the two basic components of the  
15 sensor upon which the performance characteristics of the sensor depend. Since the target analyte interacts only  
16 with the receptor, sensor selectivity and predilection towards the target analyte depends exclusively on the  
17 receptor whereas the sensor sensitivity, resolution, and calibration are found to be influenced by both the  
18 components [6].  
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21 Nowadays, conventional oxide-based gate dielectrics in such devices have been superseded by electric double layer  
22 (EDL) gate dielectrics because of its relevancy in FET with nanostructured channel where the control of grain  
23 boundary (interface between two crystallites) charges substantially controls charge transport in the channel. EDL  
24 induces huge surface charges which enhance the mobility and the drain current (current through the semiconductor  
25 channel) by passivating the charge defects and changing the occupancy of defect states [7]. Whenever the target  
26 analyte (gas) interacts with polymeric dielectric, it proliferate electrons as freebie to the EDL dielectric polymer  
27 which leads to an immense enhancement in drain current. As soon as the gas is removed, atmospheric Oxygen  
28 molecules are further adsorbed and supplied Gate-Source voltage begins to stabilize the charge in the EDL  
29 minifying the drain current back to its former value [8].  
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32 In this research work, we will dop various concentrations (1-5% Vol.) of Aluminum on Zinc Oxide films and  
33 construct Field Effect Transistor (FET) using LiClO<sub>4</sub> casted Polyethylene Oxide (PEO) as Electric Double Layer  
34 (EDL) gate and study its gas sensing properties. The doping concentration can change gas sensing properties and  
35 transparency as well. The aim of the research is to provide a high quality of FET for gas sensing application that can  
36 monitor the alcohol.  
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## 46           II.     Methodology

47       The approaches that have been taken for the entire fabrication of sensor and its application process can be  
48 summed up in following steps:  
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### 51       **Deposition of thin film:**

52       Among various methods for deposition of thin film, spin coating was found budget and labframe-feasible  
53 because of its plainness, cost-efficiency, facile doping, low operating temperature, and regulative spin and film  
54 thickness. The substrate is rotated at high speed after drop-casting a very few amounts of coating material over it to  
55 distribute the material uniformly all over it then annealed for the evaporation of the unwanted solvent and continued  
56 until the desired thickness or resistance of the film is achieved [5, 6].  
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For 0.5 M precursor solution (Solution for pure ZnO thin film), 13.3872 g of Zinc Acetate Dihydrate (ZAD) and 6ml of Diethyl Amine (DEA) added to 120 ml of Ethanol was stirred at 300 rpm for an hour at room temperature. For 0.5 M dopant solution, 1.91 g Aluminium Nitrate in 20 ml Ethanol is stirred at 300 rpm for an hour at room temperature. Then, 0.2 ml, 0.4 ml, 0.6 ml, 0.8 ml, and 1.0 ml of dopant solution is added to 19.8 ml, 19.6 ml, 19.4 ml, 19.2 ml, and 19.0 ml of precursor solution for doping 1%, 2%, 3%, 4%, and 5% of Aluminium by volume respectively and stirred at 300 rpm for an hour at room temperature.

0.1ml of precursor solution was spread over the spinning (at 3000 rpm for 30 seconds) substrate in a spin coater and was annealed over the hot plate at 550°C for 15 minutes.

#### Fabrication of Sensor:

The films fabricated are further cut into minute pieces (3 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 are connected to both the ends of the film using Silver paste; these are then ready to use as an ordinary sensor. Two heating system is adjusted at the ends of a cylinder of the volume of about 300 cm<sup>3</sup>; heater at the top is to monitor the temperature of the film (sensor) and heater at the bottom is to evaporate liquid (if necessary). The needle of the syringe is adjusted as shown as in the figure below so as to pass gas or drop liquid over the heater. This is the way, how ordinary sensors are constructed using fabricated thin films.

The EDL gate electrolyte is prepared by stirring 0.2 g of Polyethylene Oxide (PEO) and 0.02 g of Lithiumchlorate

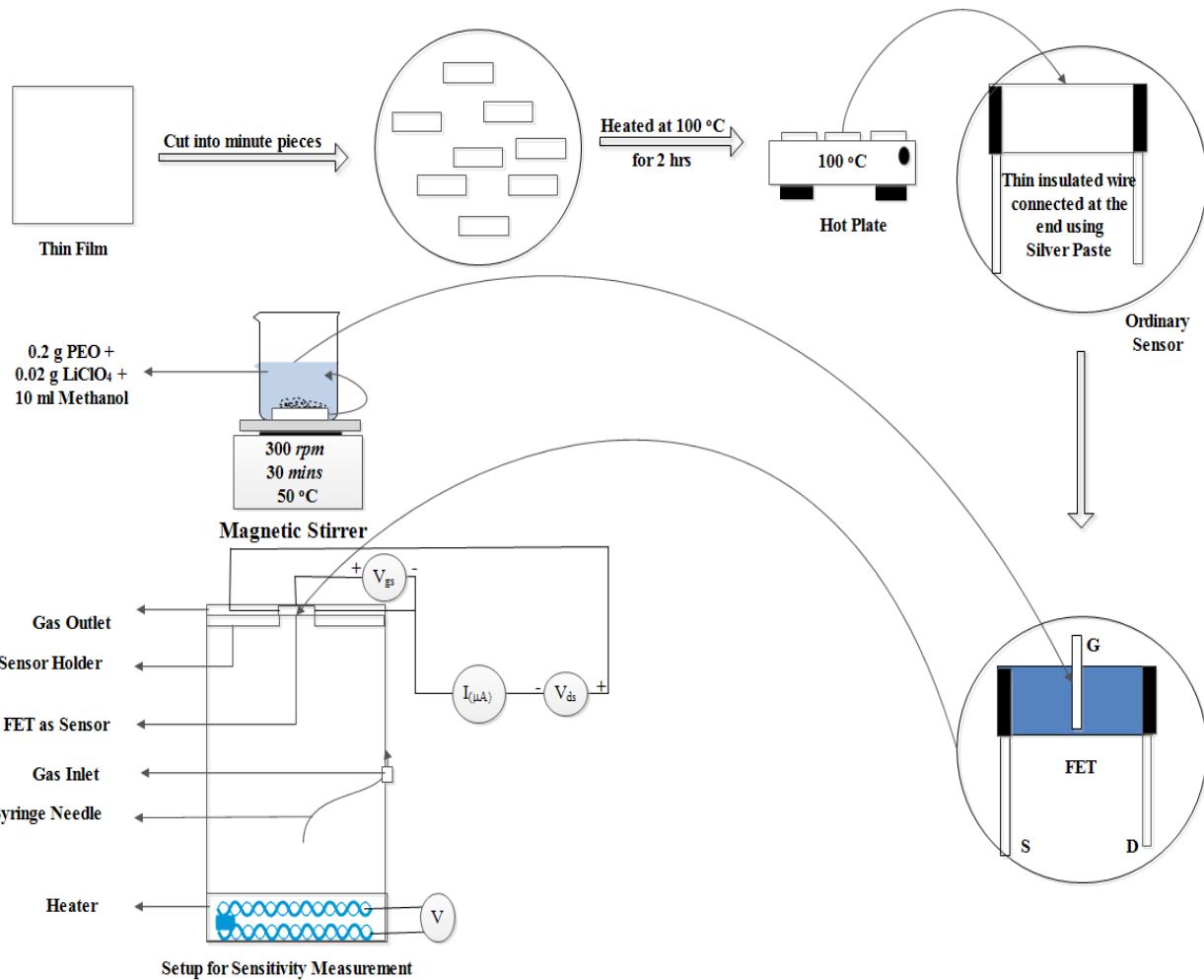


Figure 1: Fabrication of FET as a Sensor and Setup for Sensitivity Measurement.

(LiClO<sub>4</sub>) in 10 ml of Methanol at 300 rpm, and 50 °C for 30 minutes. The same procedure of constructing an ordinary sensor is followed then the contacts between the wire and film are insulated using glue and a single drop of electrolyte is drop cast and spread over the channel. Soon, an insulated thin wire-conducting at the ends is placed gently over the electrolyte and the device is allowed to dry. As soon as the electrolyte dries, for the stability of the device, source and drain wires across the channel and gate wire over the electrolyte are fixed over Printed Circuit Board (PCB) by soldering and substrate is glued. These are the procedure followed to construct the Thin Film Transistor (TFT). Then the device is ready for further characterization and application. As shown in figure 2, for the sensitivity measurement, the heater at the top of the former setup is removed, the ordinary sensor is replaced by fabricated FET.

### Sensing Mechanism:

ZnO (n-type semiconductor) thin film surface, when exposed to air, adsorb oxygen molecules to form molecular type adsorbate (O<sub>2</sub>, O<sub>2</sub><sup>·</sup>) and dissociative type (O<sub>2</sub><sup>2-</sup>) adsorbate ions forfeiting electrons from the conduction band, yielding electron-depleted space-charge layer in the grain boundary region which leads to large surface potential barrier and large resistance. The target gas (ethanol/methanol) may undergo dehydration and dehydrogenation and successively oxidized to CO, CO<sub>2</sub>, and H<sub>2</sub>O, 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.

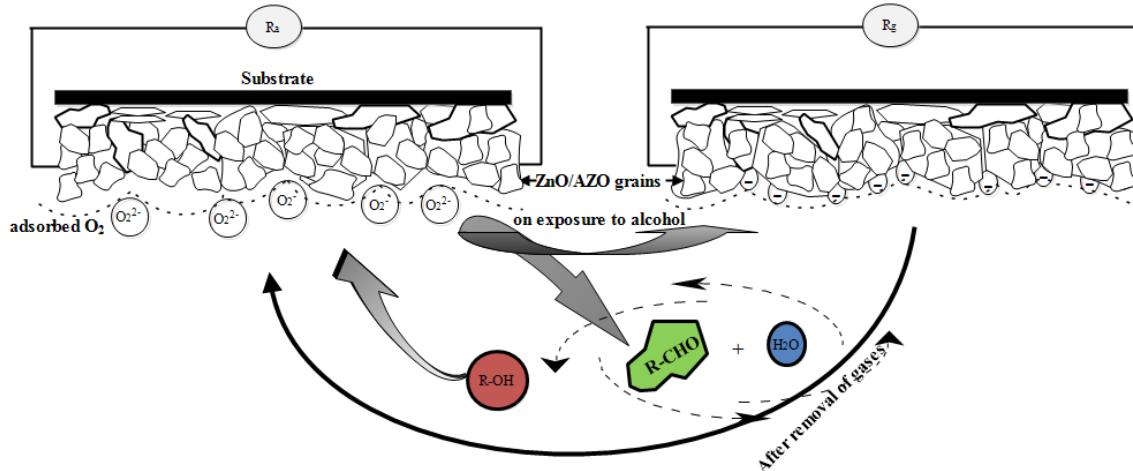
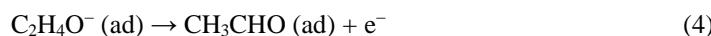
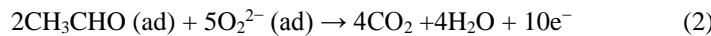
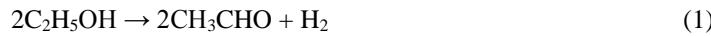


Figure 2: Sensing Mechanism of ZnO/AZO thin Film.



The release of electron back to the film enhances the conductivity of the film and deduce the resistance. As soon as the vapor passes away, the film undue starts adsorption of atmospheric oxygen and tends to achieve its former state

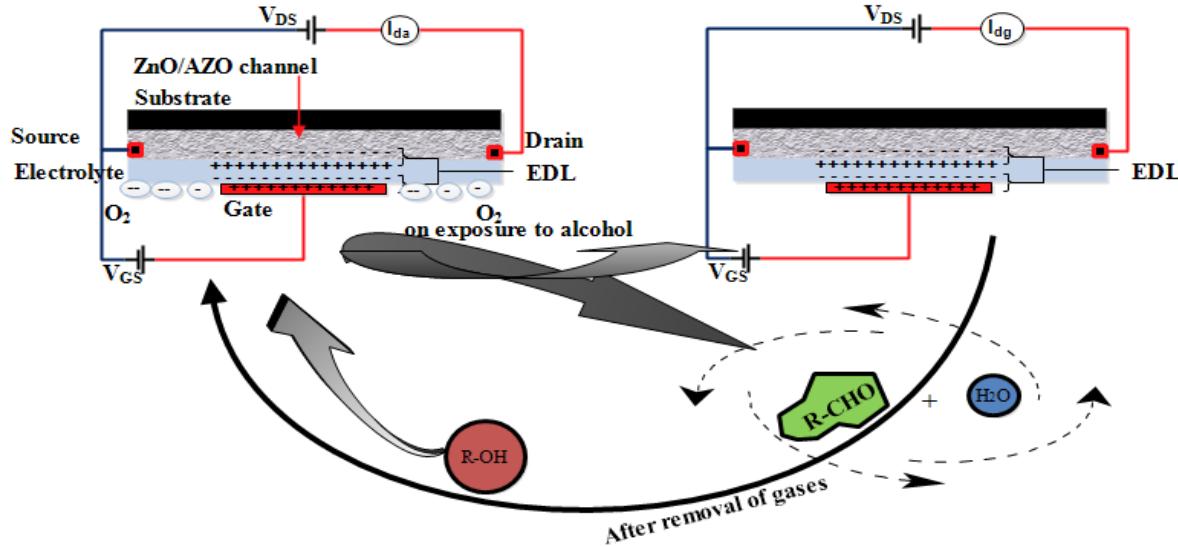


Figure 3: Sensing Mechanism of EDL gated TFT.

[11]. Electric double-layer (EDL) gated thin-film transistor as a roseate candidate has attracted profound attention due to its huge ion-induced capacitance at semiconductor/electrolyte interface, sensitive interfacial features, low voltage operation and vehement gating effect strong enough to modulate the carrier density of the semiconductor channel.

The conversion of alcohol vapors into aldehydes due to adsorption of Oxygen at the grain boundary region is similar to bare films but its effect is quite alike as the adsorption here, affects the interfacial potential and enhances the channel current by an EDL capacitive coupling effect [8].

### 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. 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  $\alpha$  is the absorption coefficient. Extrapolation of  $(\alpha h\nu)^{0.5} = 0$  yields the optical bandgap energy of the films [7, 8].

The Tauc's Plot of Pristine ZnO and various concentration of Al-doped ZnO thin films are plotted and corresponding bandgaps were evaluated as shown in figure 4.

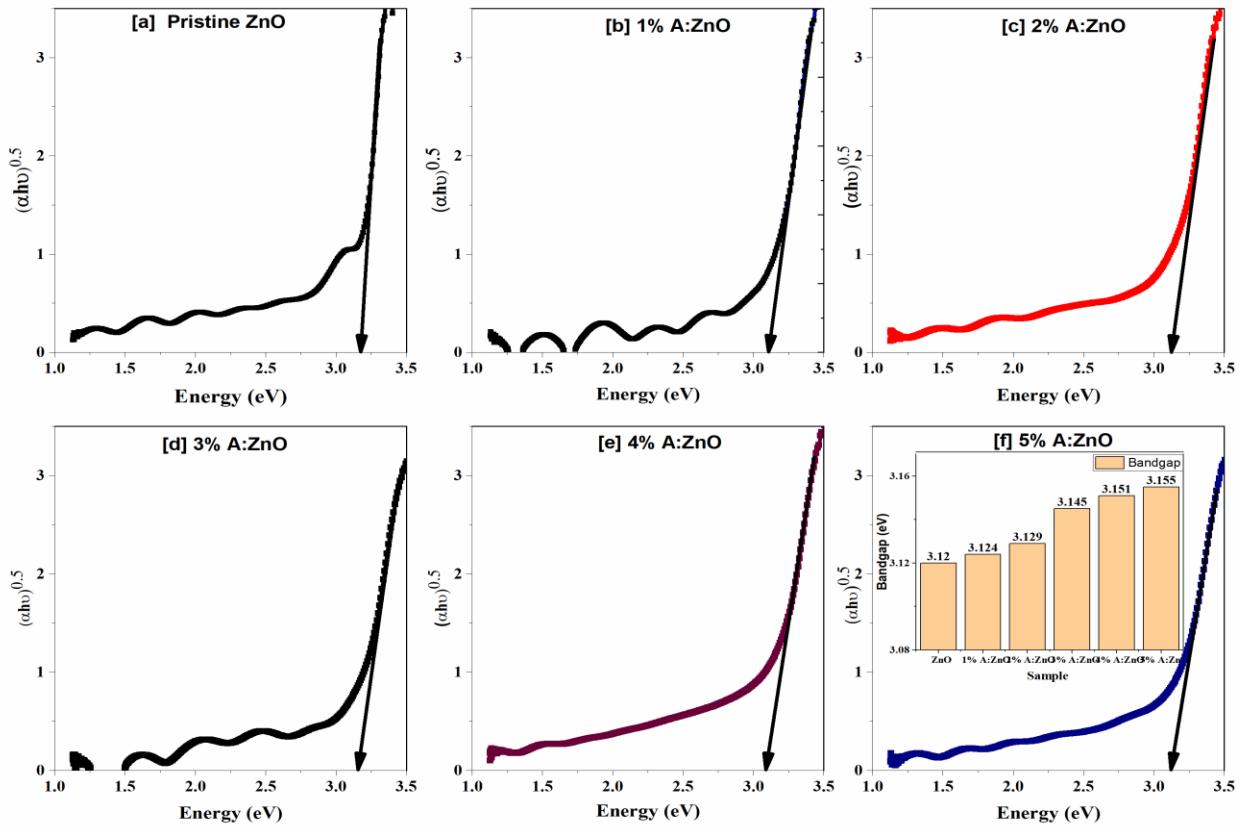


Figure 4: Calculation and Comparison of Bandgap Energy of pristine [a] ZnO thin film and [b-f] various concentrations of Al-doped ZnO films using Absorbance.

It is obvious that the direct bandgap of the AZO films increases with increasing Al content due to the fact that Al ions tend to occupy among ZnO lattice planes yielding the increase of the transport path of charge carriers into ZnO lattice and a significant decrease in grain size. Furthermore, when Al is doped in ZnO, donor electrons accumulated at the lower edge of the conduction band get excited to the higher energy levels in the conduction band with required extra energy which in fact broadens the optical bandgap of the film [4]. Here, the bandgap of pristine ZnO is found 3.120 eV, 1% Al-doped ZnO thin film is found to be 3.124 eV and the optical bandgaps are found gradually increasing to 3.155 eV on increasing the concentrations of the dopant.

#### X-ray Diffraction (XRD):

The structural characterizations of fabricated thin films are analyzed using XRD [Bruker D2 Phaser X-ray diffractometer of CuK $\alpha$  radiation (wavelength: 1.54184 Å)] at 40 KV of operating voltage and current of 40 mA in the 2 $\theta$  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,

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

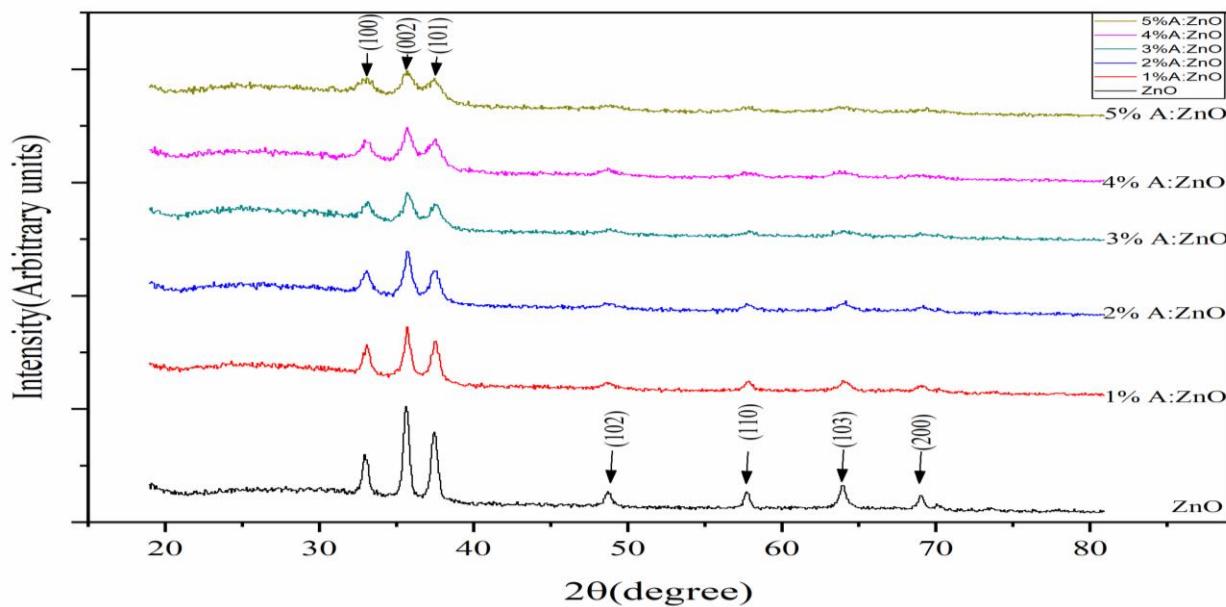


Figure 5: XRD pattern of undoped and Al-doped ZnO thin films labelled in legends.

(Eq. 2)

where, 0.9 is the correction factor,  $\lambda$  is the wavelength of the x-radiation,  $\beta$  is the full width at half maximum (FWHM) of the observed peak and  $\theta$  is the Bragg's angle. Comparing calculated d-spacings with the standard JCPDS values of card number 36-1451, the observed peaks are indexed.

Figure 6, shows that all the diffraction peaks are observed around 33.01°, 35.61°, 37.43°, 48.70°, 57.70°, 63.92°, and 69.01° corresponding to (100), (002), (101), (102), (110), (103) and (112) respectively, which depicts the films to be hexagonal crystallite in structure or polycrystalline in nature. In addition, no significant shift in XRD peaks are observed in Al-doped ZnO films compared to ZnO film with the exception of the peaks of (100), (002), and (101). Increasing doping concentration changed the peaks intensity and width, and minor peaks (102, 110, 103, 200) are seemed disappearing, whereas the three major peaks (100, 002, 101) are seen significantly decreasing due to the incorporation of Al in ZnO lattice [25].

The reason for the shift of (100), (002), and (101) peaks seen in figure 6, is substitution of zinc ions by Aluminium ions into hexagonal lattice of ZnO film [26].

Also, the average grain size can be calculated using Williamson Hall method, whose equation is given by,

$$\beta \cos\theta = \frac{k\lambda}{D} + \frac{\gamma}{2}\sin\theta$$

(Eq. 3)

where  $k$  is the shape factor,  $\lambda$  is the incident wavelength,  $\beta$  is the FWHM measured in radians,  $D$  is the average grain size,  $\gamma$  is the lattice strain and  $\theta$  is the Bragg angle of diffraction peak.

The lattice spacing parameter ‘d’ was calculated using relation:

$$d = \frac{\lambda}{2\sin\theta}$$

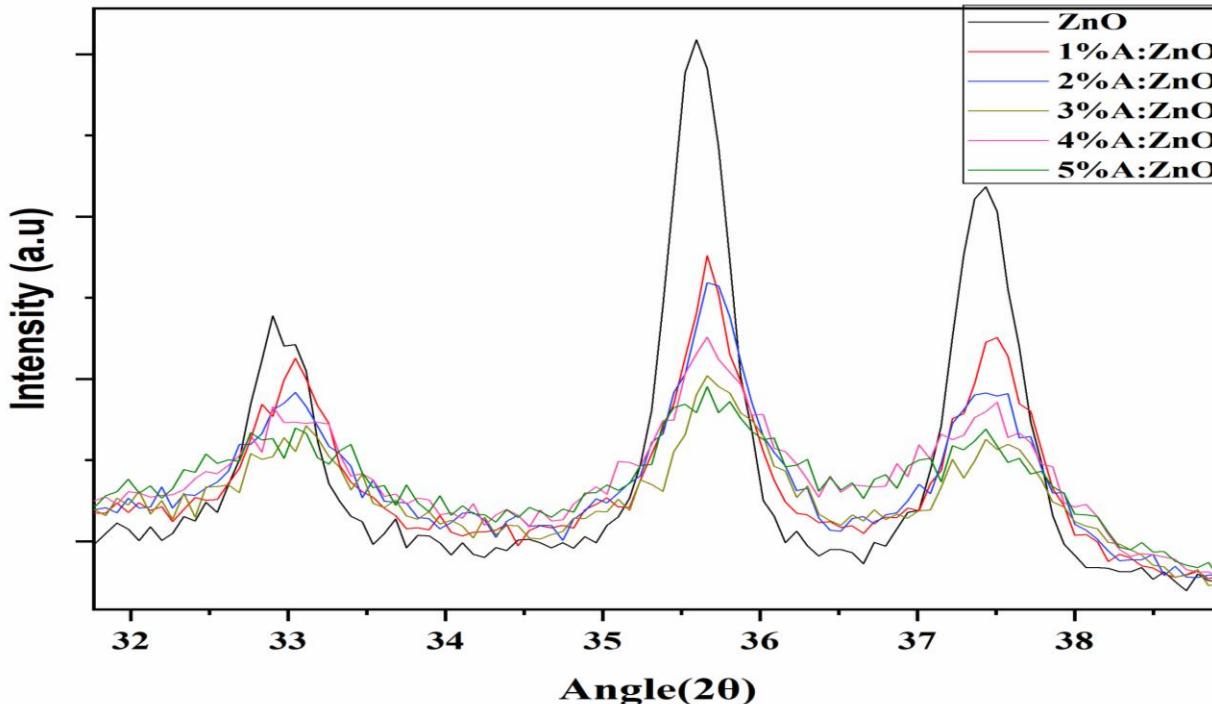


Figure 6: XRD Pattern of ZnO and Al-doped ZnO corresponding to (100), (002) and (101).

(Eq. 4)

Further, for the hexagonal crystal structure, the lattice spacing ‘d’ can be calculated using the relation:

$$\frac{1}{d^2} = \frac{4(h^2 + hk + k^2)}{3a^2} + \frac{l^2}{c^2}$$

(EqIII. 5)

where ‘h’, ‘k’, and ‘l’ are miller indices, and ‘a’, and ‘c’ are lattice constants.

The particle size is determined from Sherrer’s equation (Eq. 2), and is found around 20 nm, 16 nm, 15 nm, 13 nm, 12 nm and 11 nm respectively. This significant decrease in particle size on doping and increasing the doping concentration is due to incorporation of Aluminium atom in place of Zinc atom in the lattice site [25].

#### Scanning Electron Microscope (SEM) and EDX analysis:

The surface morphology of ZnO thin films were performed using Scanning Electron Microscope at Research Centre for Eco-Environment Sciences, Chinese Academy of Sciences, Beijing, China. The surface morphology of undoped ZnO thin film and various concentrations of Al-doped ZnO thin films is studied using Scanning Electron Microscope at Research Center for Eco-Environmental Science, Chinese Academy Science, Beijing, China. The SEM images of ZnO thin film and various concentration of Al-doped ZnO thin films are attached herewith. These SEM images depict loosely packed, porous, spherical and homogeneously arranged granny

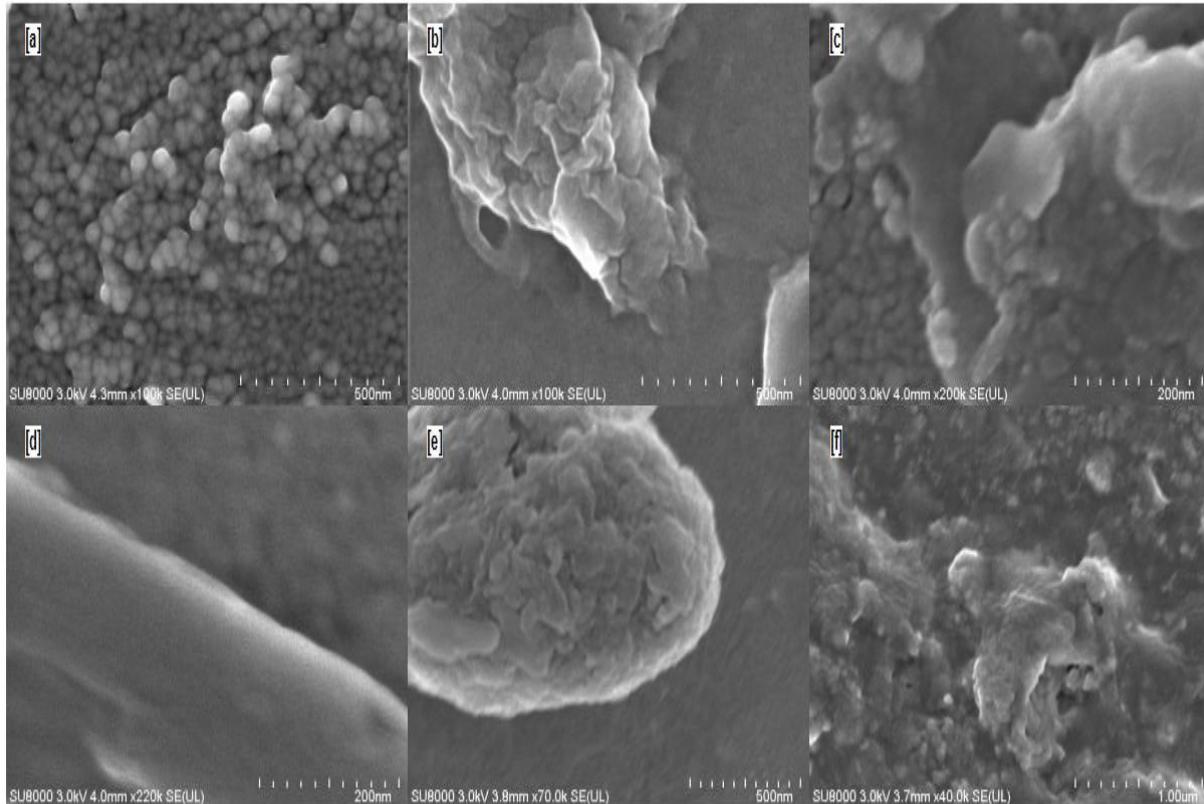


Figure 7: SEM Images of [a] Pristine ZnO thin film and [b-f] 1% - 5% Al-doped ZnO thin films respectively.

nanostructure. The porosity and surface roughness seem to be decreased on doping Al and again, increase in the dopant concentration has increased the roughness of the films too. The morphology of the sensing films has significant role in gas detection. Thus, porous surface with small grain size is considered to possess better gas sensitivity [30].

The EDX analysis was also performed in Research Center for Eco-Environmental Science, Chinese Academy of Science, Beijing, China along with SEM imaging.

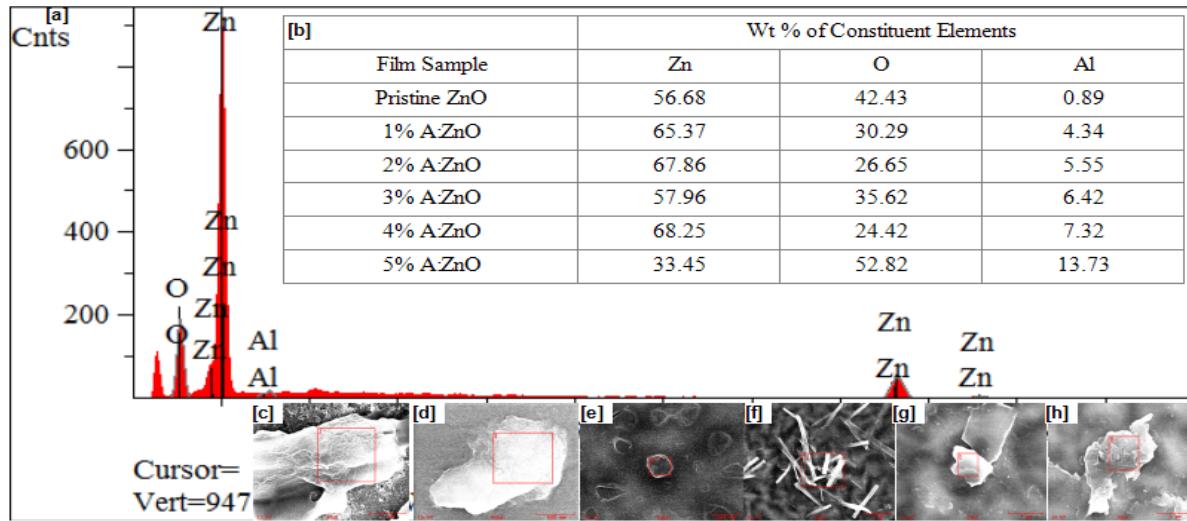


Figure 8: [a] EDX analysis image of 3% A:ZnO, [b] table representing wt. % of constituent elements in undoped and various concentration of Al-doped thin films, [c-h] SEM images of selected area of ZnO and various concentrations of Al-doped ZnO thin films over which EDX analysis was done.

The EDX data above confirms that the film composition is of elements zinc and oxygen in pristine ZnO film and Zinc, Oxygen and Aluminum in AZO films without any other impurities. Negligible wt. % of Al is found in the film of pristine ZnO too which may be due to Aluminium Silicate substrate. Increasing doping concentration has increased wt. %, but it does not resemble doping by volume concentration anymore which may be due to inhomogeneity in distribution of Al in the precursor during its preparation. Also, it may be due to the fact that EDX analysis is done by selecting a very little area of about  $100\text{ nm}^2$  which is one out of 400 billion parts of the film prepared. So, the data of wt. % of Zinc and Oxygen seem quite erratic. Though the data, in overall, convince the film being homogeneous.

#### Resistivity of thin films

The value of resistivity of the film is found decreasing when the temperature of the specimen is raised. This is due to the fact that when temperature of the specimen rises, the electrons in the specimen get thermally excited and move towards the conduction band increasing carrier mobility. The resistivity of ZnO and AZO films calculated from e (3.7) at various temperature is graphed below:

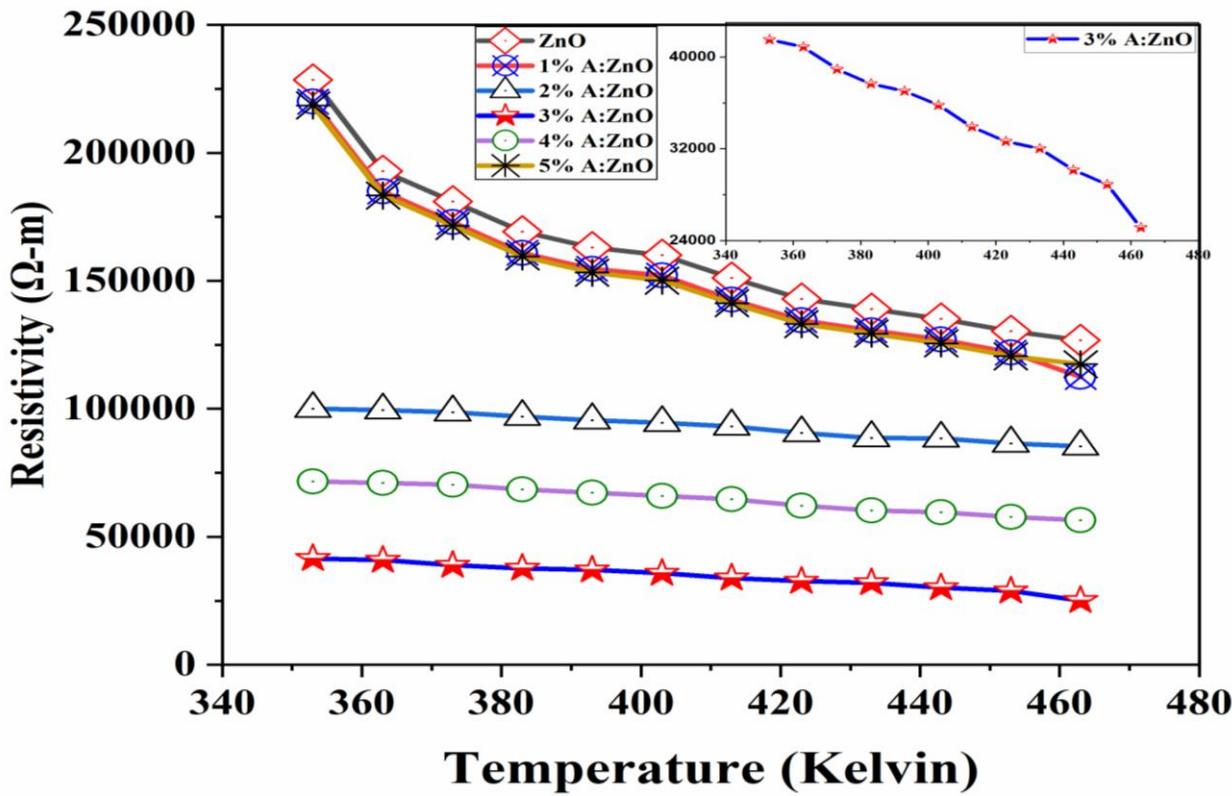


Figure 9: Resistivity of pristine ZnO and various concentration of Al doped ZnO varying with temperature.

The value of resistivity is found minimum for 3% Al-doped ZnO film at all temperatures and is found maximum for pristine ZnO sample at all temperatures. However, with an increase in the Al doping concentration above 3% by volume, the resistivity is found increasing significantly. When a small amount of Al is pioneered as dopant, Al ionizes to  $\text{Al}^{3+}$  and replaces  $\text{Zn}^{2+}$  yielding one free electron responsible for the increment of carrier concentration. Therefore, carrier concentration increases or resistivity decreases with increasing Al concentration at first up to 3 vol% doping. Further, on increasing Al concentrations, increasing Al dopant atom may form neutral defects and do not contribute free electron and the number of electrically active dopant atoms reduces in the film. This is the reason for the further decrement of the carrier concentration and resistivity increment [31].

## Field Effect Transistor (FET) Characteristics

The principal of transfer characteristics is the most important factor in evaluation of performance of TFTs. In this section, we will present transfer characteristics of ZnO and AZOs channeled, EDL gated TFTs and discuss about the findings. The transfer characteristics of pristine ZnO thin film and various concentrations of Al-doped ZnO thin films are studied keeping drain-source voltage ( $V_{DS}$ ) equals 1 Volt and varying gate-source voltage ( $V_{GS}$ )

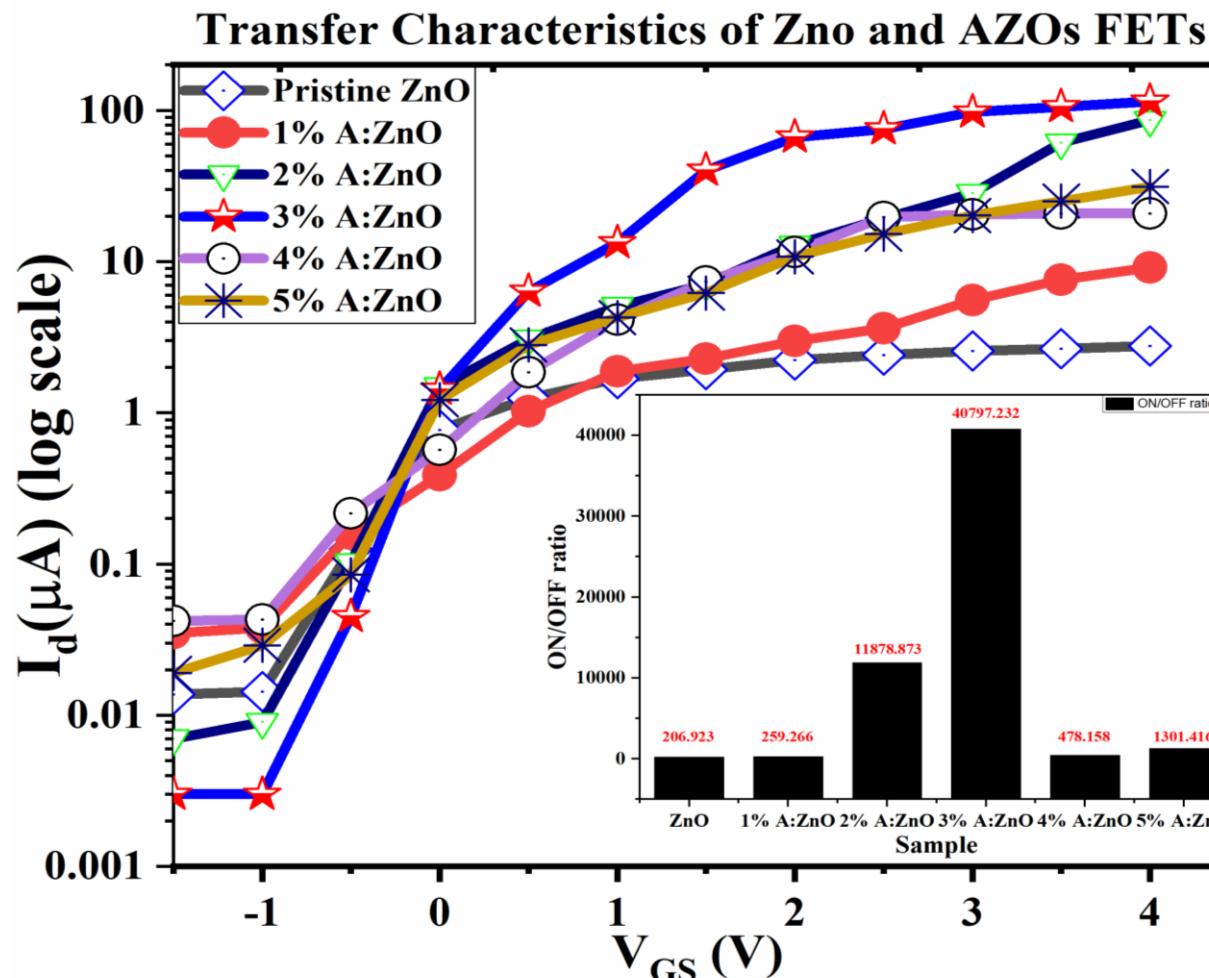


Figure 10: Transfer Characteristics of ZnO and AZOs channelled, EDL gated TFTs.

from negative of 3 Volts to positive 4 Volts and the corresponding changes in drain current ( $I_d$ ) are noted.  $I_d$  versus  $V_{GS}$  graph "termed as Transfer characteristics" is plotted and respective ON-OFF ratios i.e. ratio of maximum stable drain current to minimum stable drain current are calculated. The minimum stable current i.e. drain current of OFF-state of EDL gated 3% Al-doped ZnO TFT is found  $6 \times 10^{-4} \mu\text{A}$  and maximum stable current i.e. drain current of ON-state is found approximately  $115 \mu\text{A}$ . The transfer characteristic of 3% Al-doped ZnO is found fantabulous as expected as its ON-OFF ratio is found to be maximum (~40800) among the rest of the films which may endow the higher sensitivity. So, its drain characteristics were further studied keeping  $V_{GS}$  constant (-1 V, 0 V, 1 V, 2 V, 3 V, 4 V) and varying drain-source voltage from 0 V to 5 V and noting the corresponding changes in drain current.

The drain characteristic of the concerned sample is too found conspicuous which is as shown in figure 4.6 below:

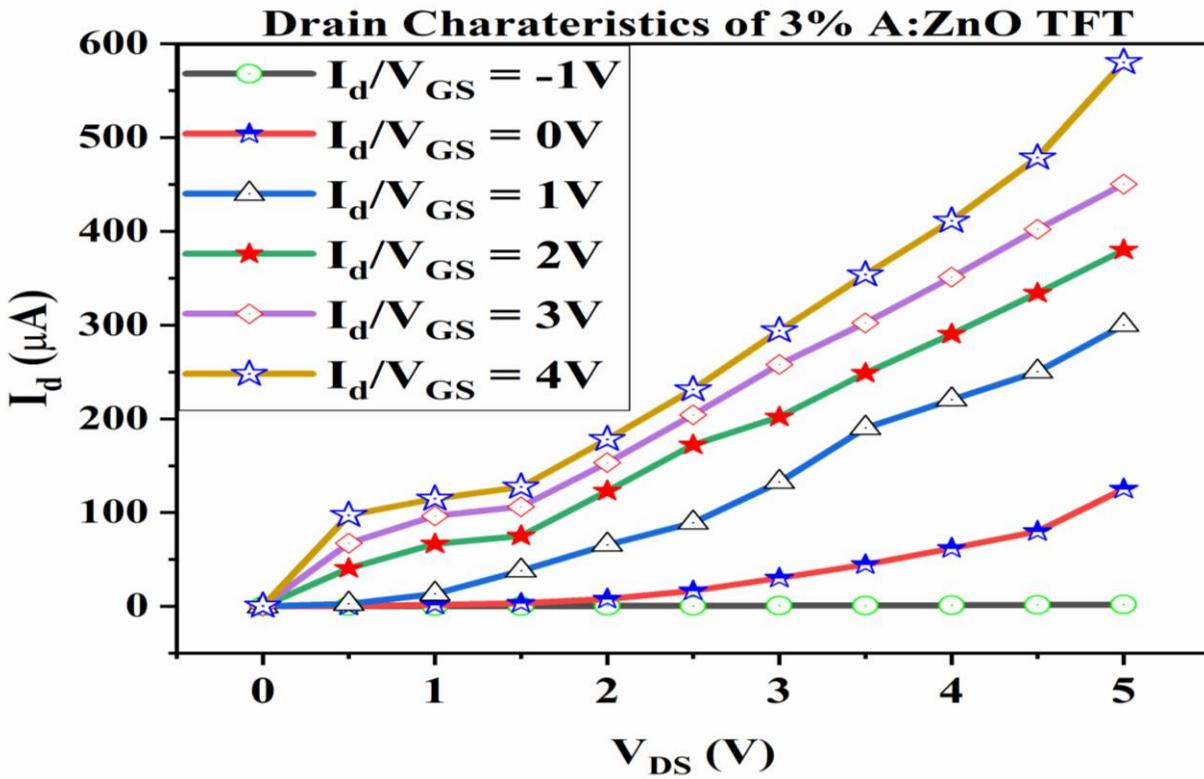


Figure 11: Drain Characteristics of 3% Al-doped ZnO channeled, EDL gated TFT at various Gate-Source Voltages.

### Sensitivity of Two Terminal Sensors

Three different concentrations (50 ppm, 250 ppm, 500 ppm) of alcohol vapors are passed into the setup shown in figure 3.2, and the response and recovery time, and the corresponding decrease in the values of resistances are noted. The sensitivity of the two-terminal sensors i.e. bare films and EDL coated films at room temperature are calculated using relation 1.1 and their corresponding graphs are shown in figure 9.

Sensing within room temperature is one of the challenges that we have faced and overcome. The sensitivities of bare pristine ZnO and 1 to 5% Al-doped ZnO thin films range from 0.33% to 1.13% in response to 50 ppm of methanol, 1.5% to 2.9% in response to 50 ppm of ethanol, 33.69% to 44.22% in response to 250 ppm of methanol, 34.60% to 49.24% in response to 250 ppm of ethanol and 71.36% to 85.75% in response to 500 ppm of methanol, 73.13% to 96.06% in response to 500 ppm of ethanol; sensitivity in 3% Al-doped ZnO always succeeding and sensitivity in 5% Al-doped ZnO always preceding.

Furthermore, sensitivities of EDL coated pristine ZnO and 1 to 5% Al-doped ZnO thin films range from 21.46% to 30.32% in response to 50 ppm of methanol, 2.60% to 13.67% in response to 50 ppm of ethanol, 61.06% to 80.06% in response to 250 ppm of methanol, 36.59% to 49.74% in response to 250 ppm of ethanol and 87.43% to 97.08% in response to 500 ppm of methanol, 63.19% to 97.81% in response to 500 ppm of ethanol; sensitivity in 3% Al-doped ZnO always succeeding.

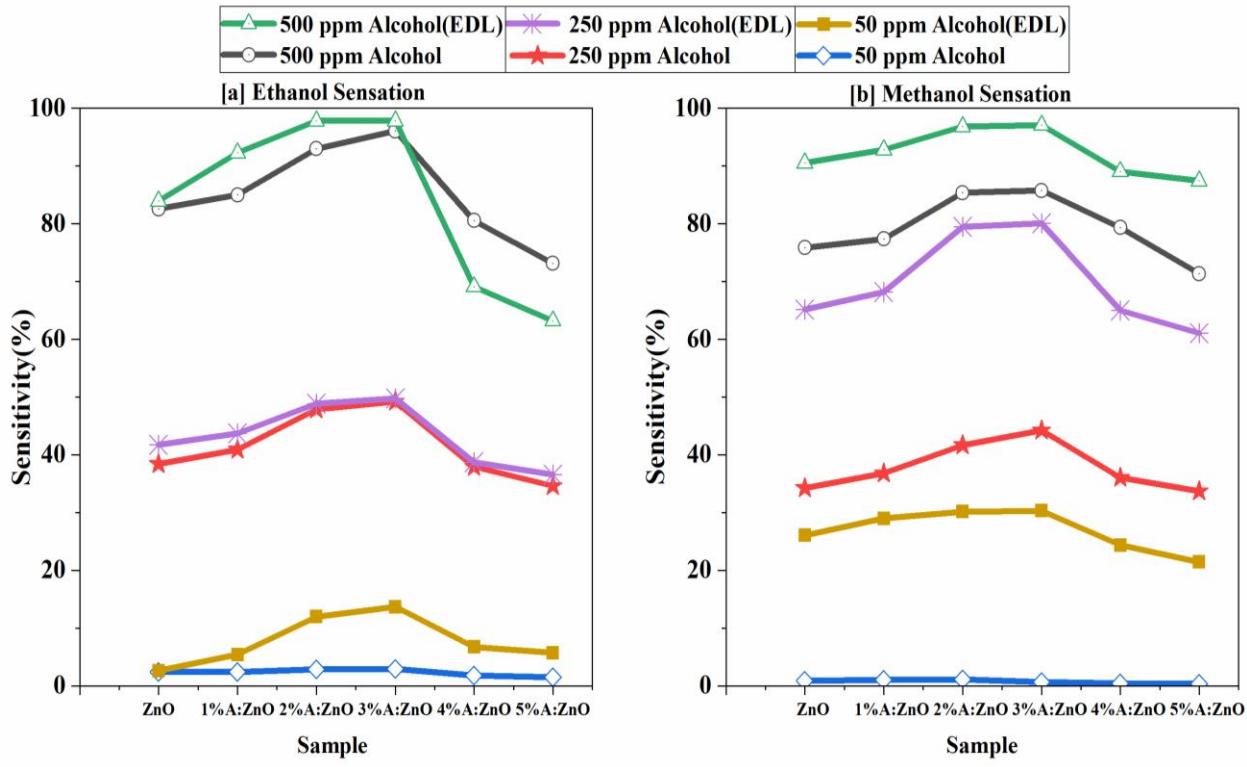


Figure 12: Sensitivity of Bare and EDL layered Two-Terminal Sensors in response to [a] Ethanol and [b] Methanol Vapors.

The sensitivity of films in response to higher concentrations of alcohol vapors is found higher. Higher concentrations of alcohol vapors mean a higher number of alcohol molecules. More, the number of reducing molecules, the more is the number of Oxygen reduced from the grain boundary of the film yielding an abrupt reduction in resistance of the film. This is the reason for such an upshot. The sensitivity of the bare film in response to ethanol is always found greater than methanol. This is due to the fact that the oxidation potential of ethanol (-0.66 V) is less than that of methanol (-0.55 V) and higher the electrooxidation potential, it's more difficult to get oxidized [32]. Also, the sensitivity of 3% Al-doped ZnO thin film is always found succeeding sensitivities of the rest of the films. The smallest value of resistivity, smaller grain size, and its rough surface may have made it favorable for this result. The EDL electrolyte coated over the bare pristine ZnO and various concentrations of Al-doped ZnO sensors has enhanced the sensitivity of the film significantly but quite erratically. It shows the marvelous response to methanol than to ethanol vapors in enhancing the sensitivity. The use of methanol for the preparation of electrolyte polymer may be responsible for such a biasing response.

#### Response and Recovery of Two Terminal Sensors

The time interval within which the film achieves its minimum value of resistance due to exposure of reducing gas is considered to be the response time while the time interval within which the film regains 90% of its initial value of resistance after removal of gas is considered to be the recovery time. Experiments for determination

of response and recovery time of all sensors are performed. The change in resistances of the bare and EDL dielectric polymer coated ZnO and AZOs films in response to Ethanol and Methanol Vapors with respect to time are noted, graphed and response and recovery time are calculated. The response time of the sensor is found always shorter than the recovery time. Since the performance of 3% Al-doped ZnO sample is found excellent compared to the rest of the samples, so its response to both 500 ppm of ethanol and methanol vapors are graphed and shown in figure 10.

### Sensitivity, Response and Recovery of Three Terminal Sensors

The response time for bare and EDL dielectric polymer coated 3% Al-doped ZnO sample is found to be 13 s and 12 s in response to 500 ppm of ethanol vapors, 15 s and 15 s in response to 500 ppm of methanol vapors and the recovery time for the concerned sample is found to be 75 s and 60 s in response to 500 ppm of ethanol vapors and 95

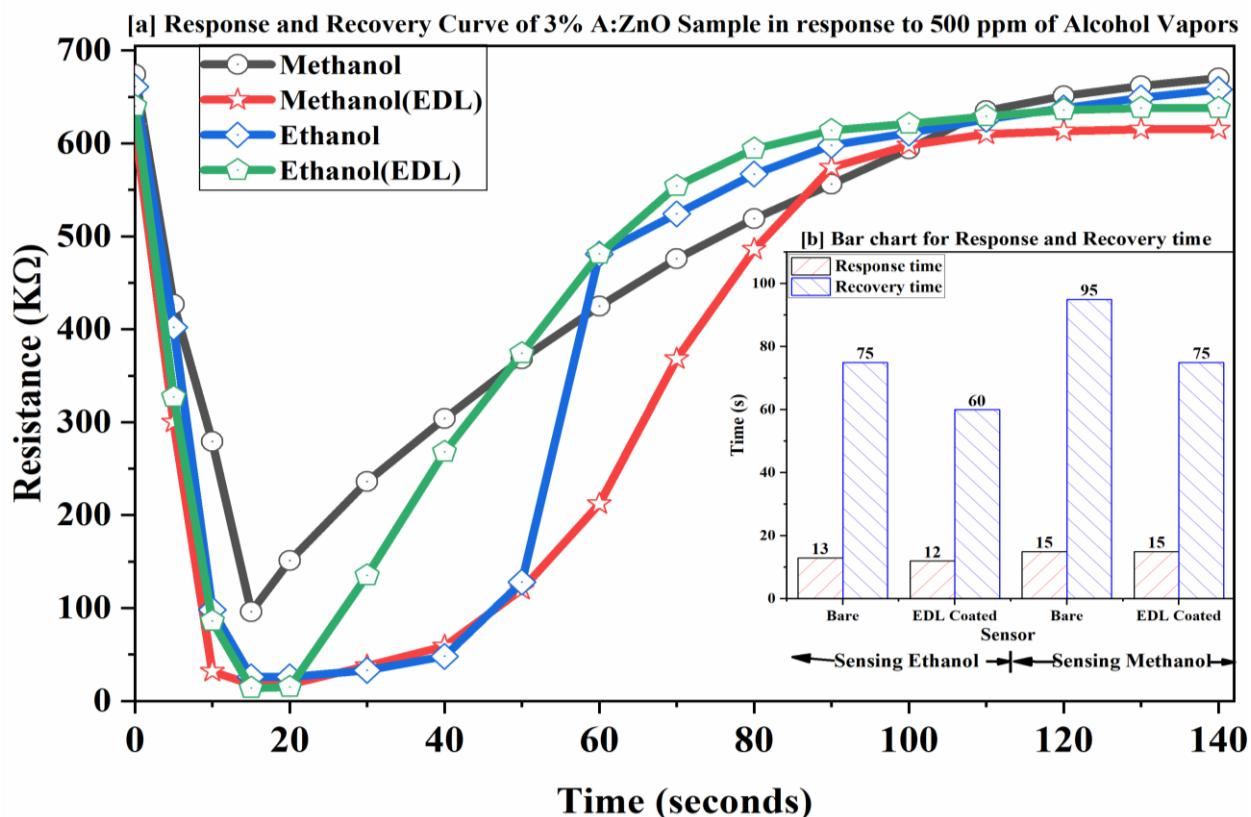


Figure 13: [a] Variation in Resistances of Bare and EDL Layered 3% A:ZnO films with respect to time in response to Ethanol and Methanol Vapors [b] Bar chart for response and recovery time of Bare and EDL coated 3% A:ZnO thin-film sensors.

s and 75 s in response to 500 ppm of methanol vapors respectively. Response and recovery time for ethanol vapors is always shorter than for methanol vapors which may be due to less oxidation potential of ethanol.

Various concentrations of alcohol vapors are passed into the setup shown in figure 3.3 keeping the FETs at ON state, and the response and recovery time, and the corresponding increase in the values of drain current are noted.

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4 **Sensitivity of Three Terminal Sensors**  
5 The sensitivity of the three-terminal sensors i.e. FETs are calculated using relation 1.2 and their  
6 corresponding graphs are shown.  
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8 The sensitivities of pristine ZnO and 1 to 5% Al-doped ZnO channeled, EDL dielectric polymer gated thin-film  
9 FETs range from 5.65% to 12.75% in response to 50 ppm of methanol, 7.36% to 16.79% in response to 50 ppm of  
10 ethanol, 18.98% to 49.70% in response to 250 ppm of methanol, 24.35% to 53.82% in response to 250 ppm of  
11 ethanol and 41.49% to 66.81% in response to 500 ppm of methanol, 53.91% to 70.11% in response to 500 ppm of  
12 ethanol; sensitivity in 3% Al-doped ZnO always succeeding the sensitivities of the rest of the samples. The  
13 sensitivity of 4% A:ZnO channeled thin-film FET sensor is found approaching the sensitivity of 3% A:ZnO  
14 channeled thin-film FET sensor.  
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is due to less oxidation potential of ethanol vapor. The sensitivities of TFTs sensors in response to higher

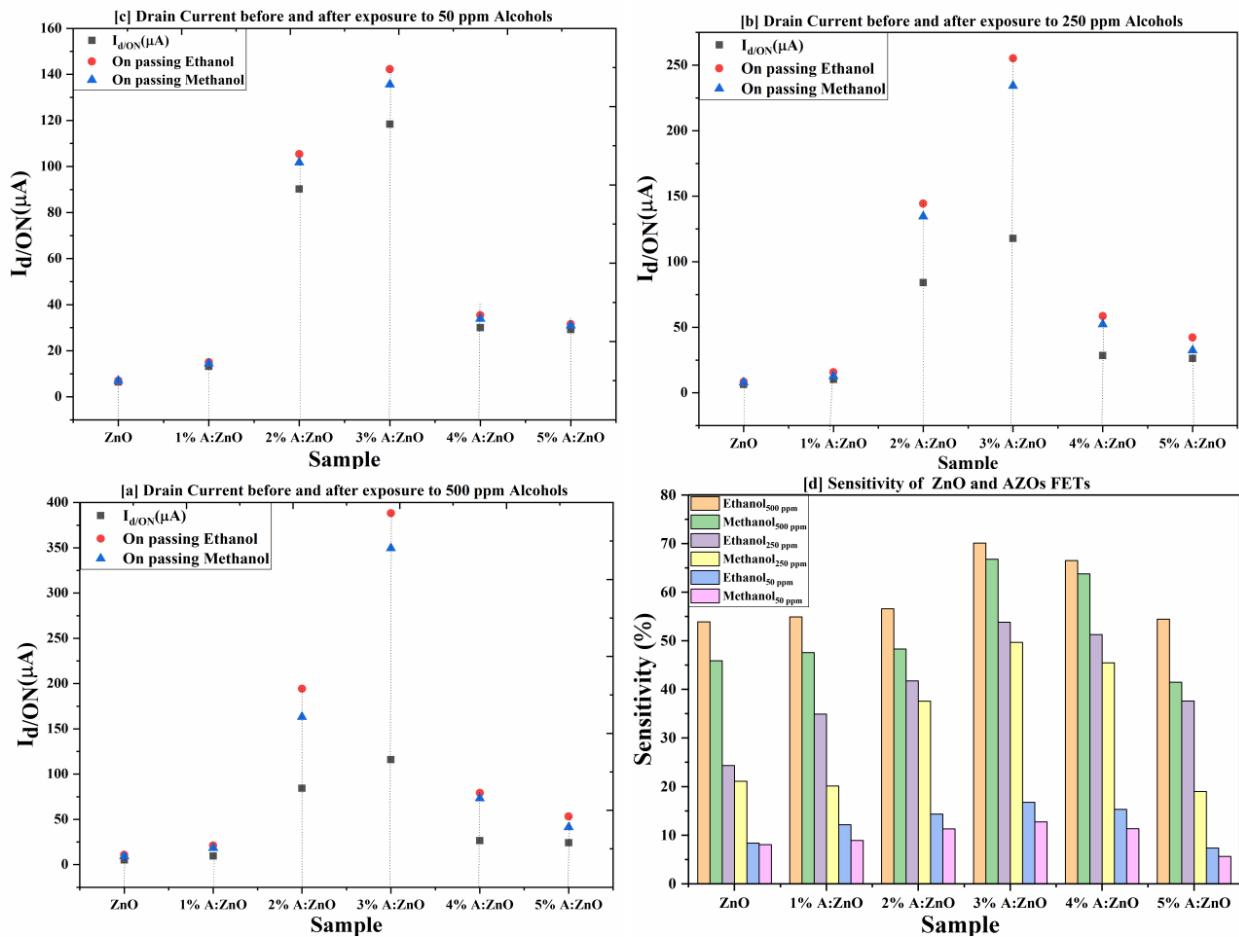


Figure 14: [a-c] Drain current, [d] Sensitivity of ZnO and AZOs channelled FETs before and after exposure to various concentration of alcohols.

concentrations of alcohol vapors are found higher. This is because higher concentrations of alcohol vapors have a

higher number of alcohol molecules which reduces a huge number of oxygen molecules from the grain boundary of the polymer yielding an abrupt enhancement in channel current of the film. The low value of resistivity and sufficiently large value of the ON-OFF ratio of around 40800 ( $>10^3$ ) in 3% Al-doped ZnO channeled EDL electrolyte polymer gated TFT sensor is responsible for its higher sensitivity.

### Response and Recovery of Three Terminal Sensors

The time interval within which the film achieves its maximum value of drain current due to exposure of reducing gas is considered to be the response time while the time interval within which the film regains its initial value of drain current (+5% for our convenience) after removal of gas is considered to be the recovery time. Experiments for determination of response and recovery time of all sensors are performed. The significant change in channel current of the EDL dielectric polymer gated, ZnO and AZOs channeled thin-films in response to Ethanol and Methanol

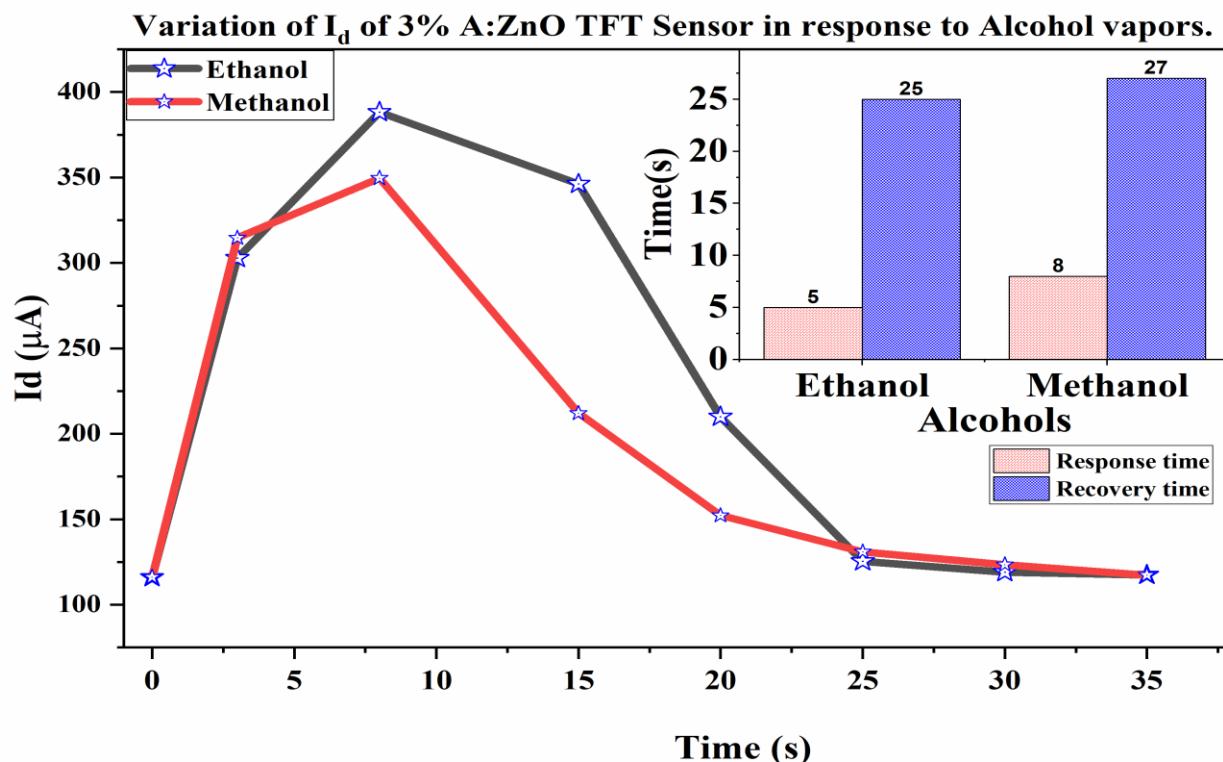


Figure 15: Variation of Drain Current of 3% A:ZnO channeled EDL dielectric polymer gated TFT in response to 500 ppm of Ethanol and Methanol Vapors, and Bar chart showing Response and Recovery time of respective TFT embedded.

Vapors with respect to time are noted, graphed and response and recovery time are calculated. The response time of the sensor is found always shorter than the recovery time. Since the performance of 3% Al-doped ZnO sample is found excellent compared to the rest of the samples, so its response to both 500 ppm of ethanol and methanol vapors are graphed as shown in figure 12.

The response and recovery time for 3% Al-doped ZnO channeled EDL gated TFT sample is found to be 5 s and 25 s in response to 500 ppm of ethanol vapors and 8 s and 27 s in response to 500 ppm of methanol vapors respectively. Response and recovery time for ethanol vapors is always shorter than for methanol vapors which may be due to less oxidation potential of ethanol. Also, it is obvious that response time is always shorter than the recovery time. The water vapor is produced during oxidation of alcohol vapors when they interact with EDL polymer which may take few more seconds to evaporate. This may be the reason for such upshot.

#### IV. Conclusions

Undoped and 1-5% Al-doped ZnO nanostructured thin films are synthesized using the spin coating method, two-terminal sensors (bare and EDL electrolyte polymer coated), and three-terminal sensors (TFT) are fabricated and the sensing properties have been studied by investigating their electrical response towards different concentrations of ethanol and methanol vapors. The wurtzite polycrystalline nature of ZnO and AZOs films is confirmed by the XRD pattern. The peaks have been shifted, and the intensity of the three major peaks (100, 002, 101) have significantly decreased whereas minor peaks (102, 110, 103, 200) are seen disappearing due to the incorporation of Al into the hexagonal lattice of ZnO film. The grain size of the film is seen significantly decreasing (20-10 nm) on increasing the doping concentration of Al and the SEM images confirm the same. Also, the SEM images depict loosely packed, porous, spherical and homogeneously arranged granny nanostructure of the film. The porosity and surface roughness seem to be decreased on doping Al but again, an increase in the dopant concentration has increased the roughness of the films too. EDX results have revealed the incorporation of Al in the lattice and wt.% of Zinc decreases with the increase in the doping concentration of Al. The analysis of optical results obtained from the UV-vis spectrometer has confirmed the increase in the bandgap of the film (3.12-3.16 eV), redshift (shift towards longer wavelength) of absorbance edge in the visible range of wavelength due to increment in incorporated Al in ZnO lattice. A small amount (3% by volume as optimum) of Al pioneered as dopant ionizes to  $\text{Al}^{3+}$  and replaces  $\text{Zn}^{2+}$  yielding one free electron responsible for the increment of carrier concentration (decrement in resistivity) whereas further increment of dopant gives rise to neutral defect, reduces the number of electrically active Al and give rise to further resistivity increment.

The sensitivities of films in response to higher concentrations of alcohol vapors are higher because huge number of Oxygen in the grain boundary region is reduced by a large number of alcohol molecules present in them. The low electrooxidation potential of ethanol (-0.66 V) always supports ethanol to be more sensitive to the sensor than the methanol. The smallest value of resistivity (~40 Kohmm<sup>-1</sup>), smaller grain size (~13 nm), and rough surface have made 3% Al-doped ZnO thin film more efficient than the rest of the films favorable for this result. The EDL electrolyte coated over the bare pristine ZnO and various concentrations of Al-doped ZnO sensors has enhanced the sensitivity of the film significantly but quite erratically. It shows the marvelous response to methanol than to ethanol vapors in enhancing the sensitivity. The use of methanol for the preparation of electrolyte polymer may be

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4 responsible for such a biasing response. The response and recovery time for bare as well as EDL dielectric polymer  
5 coated 3% Al-doped ZnO sample in response to 500 ppm of alcohol vapors is found excellent (~13 s and ~70 s)  
6 compared to other samples of the sensors. The drain current of OFF-state of EDL gated 3% Al-doped ZnO TFT is  
7 found  $6 \times 10^{-4}$   $\mu$ A and drain current of ON-state is found approximately 115  $\mu$ A with an ON/OFF ratio of around  
8 40800 (maximum of all) approves fantabulous transfer characteristic of 3% Al-doped ZnO among the rest of the  
9 TFTs which is the responsible factor for its higher sensitivity towards the alcohol vapors. The response and recovery  
10 time (~6 s and ~25 s) of 3% EDL electrolyte polymer gated TFT are seen promisingly small compared to rest  
11 samples of the TFT sensors and two terminal sensors.  
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14 Thus, we would like to suggest that 3% vol. is the optimum concentration of doping for the excellent performance of  
15 thin-film in sensing ethanol and methanol. Furthermore, though the sensitivities of two-terminal sensors seem higher  
16 than that of TFTs, TFTs are the promising candidate for sensing applications compared to two-terminal sensors  
17 because of their significant variation in drain current due response to alcohol vapors and shorter response and  
18 recovery time and controllability of channel current applying suitable gate-source voltage bias.  
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## 24 25 Acknowledgments

26 We will always be grateful to Nepal Academy of Science and Technology (NAST) for providing us a  
27 platform to our research work.  
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## About the revision

Christian Schulz

Editorial Director

Cell Press Heliyon

Dear Schulz,

Manuscript entitled "STUDY ON ALCOHOL SENSING APPLICATION OF EDL DIELECTRIC POLYMER GATED/NON-GATED, ZNO/AZO CHANNELLED THIN FILM AND TRANSISTOR" 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.

Further we would like to change the title of the article too as the later title better suits the article than former one.

**Title: "Fabrication of alcohol sensor using undoped and Al doped ZnO nanostructure film with polymer electrolyte gating".**

1. Data will be made available whenever asked.

2. **Reviewer #1:**

i. From Figure 5, it can be seen that the diffraction peaks of both pure ZnO thin film and Al doped ZnO thin films shift significantly towards a larger angle direction. For example, as is well known, the (002) peak of undoped ZnO should be around  $34.5^\circ$ , while the (002) peak of undoped ZnO in Figure 5 has moved to  $35.6^\circ$ . Why is this?

**Addressed:**

The reason for the shift of (100), (002), and (101) peaks of AZO films towards larger angle direction as seen in figure 5 and 6, is substitution of zinc ions by Aluminium ions into hexagonal lattice of ZnO film and even it shifts in pristine ZnO films because of the presence of Aluminium as impurity in glass substrate which is revealed by EDX results in Figure 8.

**ii.** From Figure 7, it can be seen that the uniformity of the ZnO films is very poor. They should not be suitable for preparing high-performance optoelectronic and microelectronic devices.

**Addressed:**

We agree with reviewer comments. The uniformity of ZnO film has significant impact in optoelectronic application. But in our case the variation of resistance of similar film synthesized in different time in different glass substrate is almost stable and within the value of certain range. And there is no obstacle for the fabrication of 2 terminal and three terminal gas sensor which is our principal motivation. To overcome such limitation of sample inhomogeneity we have used the EDL gated dielectric which controls the sample resistance in its own way and it works to some extent to overcome the drawbacks of the poor quality of films.

**iii.** In Figure 13, (b) does not need to be inserted into (a).

**Addressed:**

May it not be necessary, but it helps observing the variation in resistance in response to alcohol along with the response and recovery time at a glance which will be beneficial to the reader.

**iv.** The conclusion section is too verbose; it needs to be compressed into a paragraph of text.

**Addressed:**

We have rewritten the conclusion and addressed the reviewer comments.

**v.** I suggest that the authors update the references.

**Addressed:**

As per your suggestion, the references have been completely revised and updated.

**vi.** Al doped ZnO film is an important multifunctional material. In recent years, some novel properties of Al doped ZnO thin films prepared by sol-gel method have also been reported. It is recommended that the authors add appropriate discussion in this area in the introduction section to enhance the scientific validity of the paper.

**Addressed:**

As per the suggestion, the article has been completely re-edited and revised. Thus we have included that you have suggested in the '**Introduction**' portion.

### **3. Reviewer #2:**

**i.** The references jump from 8 to 11, from there to 25 and 26, then to 30. There are expressions such as figure 3.2 and relation 1.1 in the text.

#### **Addressed:**

As per the reviewer suggestions the article is fully revised and these typing errors have been completely eradicated.

**ii.** The exact purpose and objectives of the study and its results are not fully stated.

#### **Addressed:**

We have revised the introduction and point out the motivation as well as objective with scientific validation.

Nowadays, conventional oxide-based gate dielectrics in field effect devices have been superseded by polymeric electrolyte gate dielectrics because of its high carrier accumulation strength especially in oxide material and relevancy in field effect transistor (FET) with nanostructured channel where the control of grain boundary (interface between two crystallites) charges substantially controls charge transport in the channel. The electric double layer (EDL) formed by polymer electrolyte with ZnO surface induces huge surface charges which enhance the mobility and the drain current (current through the semiconductor channel) by passivating the charge defects and changing the occupancy of defect states [6]. Filed effect transistor configuration is a popular electrochemical sensor used as a transducer for over 40 years. In many reports conventional oxide materials are used as gate dielectric which requires high vacuum technology. Here we have used the polymer electrolyte in gel form and drop cast on ZnO surface which is simple cost-effective vacuum free method and have high performance index even used for flexible electronic [5]. In this work the transducer has two major components one is ZnO channel which generate the electrical signal after imposing analyte gas and another is the polymer electrolyte which is also sensitive to the analyte. The polymer electrolyte surface directly interacts with target analyte and the ZnO channel converts this interaction to electrical signal. Whenever the target analyte (gas) interacts with polymeric dielectric, it proliferate electrons as freebie to the EDL dielectric polymer which leads to an immense enhancement in drain current. As soon as the gas is removed, atmospheric oxygen molecules are further adsorbed and supplied Gate-Source voltage begins to stabilize the charge in the EDL minifying the drain current back to its former value [7]. The control of the sensor is directly linked with applied gate bias.

In this work, we will dop various concentrations (1-5% Vol.) of Aluminum on Zinc Oxide films. Among them 3% concentration of Al doped ZnO film showed high value of conductivity and appropriate for the fabrication of TFT using LiClO<sub>4</sub> and Polyethylene Oxide (PEO) as gate dielectric. Use of polymer electrolyte dielectric in two terminal device fabricated by 3% AZO film interestingly enhanced the sensitivity for methanol vapor and fast response and recovery time is achieved in three terminal (Polymer electrolyte gating) devices. Thus this vacuum free, cost effective solution method is a promising alternative for the fabrication of alcohol sensor in future.

The aim of the research is to provide a high quality of FET for gas sensing application that can monitor the alcohol.

**iii.** Gas detection results for alcohol, ethanol and methanol should be re-evaluated and their advantages should be revealed.

**Addressed:**

Experiments were conducted multiple times and the most recurring data are considered and then evaluated. Their advantages are revealed in **Conclusions**.

**iv.** The article needs to be completely re-edited.

**Addressed:**

Being thankful for your suggestion, the article has been completely revised and re-edited.

We have considered all the recommendation of the reviewers as far as possible being hopeful that the research will be published.

Sincerely,

Raju Bhattacharai

## About the revision

Christian Schulz

Editorial Director

Cell Press Heliyon

Dear Schulz,

Manuscript entitled "**FABRICATION OF ALCOHOL SENSOR USING UNDOPED AND AL DOPED ZNO NANOSTRUCTURE FILM WITH POLYMER ELECTROLYTE GATING**" had been sent back for minor 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 by linking the drive.

**2. Reviewer #1:**

Al-doped ZnO film is an important multifunctional material. In recent years, some novel properties of Al-doped ZnO thin films prepared by sol-gel method have also been reported. The authors should make in-depth analysis and comments in the introduction part based on those Al-doped ZnO films deposited by sol-gel method reported in recent years. However, the reviewer found that in the revised manuscript, the authors not only did not add relevant references in the introduction section, but also greatly reduced the number of references. This cannot improve the quality of this manuscript, but rather lower its quality. Authors need to carefully revise it.

**Addressed:**

Agreeing with the reviewer, we added two more references which are recently published and based on experiment on Al-doped ZnO in the year 2022 and 2023. We are agreed with the reviewer that the quality of the article degrades on reduction of relevant references but in our first revised manuscript, we discarded some irrelevant and similar type of references. The reviewers also had suggested to revise the manuscript especially in introduction section. And some of the references are not validated by Heliyon's cross reference checker so we had removed such references. These are the reasons behind the reduction of references. Therefore, we believe that the quality of the article will

not be reduced in this context. If reviewers point out specific phrases to be cited, we are ready for that too.

Further, our research work is novel on fabrication procedure and its findings. Thus we concluded that the reference articles that we have cited are enough for our manuscript.

### **3. Question 1:** Are the objectives and the rationale of the study clearly stated?

**Our response to reviewer 1<sup>st</sup> :** We have clearly stated the objective and rationale of our research in the last two paragraphs of **Introduction** portion.

In many reports conventional oxide materials are used as gate dielectric which requires high vacuum technology. Here we have used the polymer electrolyte in gel form and drop cast on ZnO surface which is simple cost-effective vacuum free method and have high performance index even used for flexible electronic [8]. Though there are several reports on fabrication of gas sensor using ZnO material, but there is no reports on gas sensor using polymer electrolyte as a gate dielectric till date. In this work the transducer has two major components one is ZnO channel which generate the electrical signal after imposing analyte gas and another is the polymer electrolyte which is also sensitive to the analyte. The polymer electrolyte surface directly interacts with target analyte and the ZnO channel converts this interaction to electrical signal. Whenever the target analyte (gas) interacts with polymeric dielectric, it proliferate electrons as freebie to the EDL dielectric polymer which leads to an immense enhancement in drain current. As soon as the gas is removed, atmospheric oxygen molecules are further adsorbed and supplied Gate-Source voltage begins to stabilize the charge in the EDL minifying the drain current back to its former value [9]. The control of the sensor is directly linked with applied gate bias [10]. In this work, we doped various concentrations (1-5% Vol.) of Aluminum on Zinc Oxide films. Among them 3% concentration of Al doped ZnO film showed high value of conductivity and appropriate for the fabrication of TFT using LiClO<sub>4</sub> and Polyethylene Oxide (PEO) as gate dielectric. Use of polymer electrolyte dielectric in two terminal device fabricated by 3% AZO film interestingly enhanced the sensitivity for methanol vapor and fast response and recovery time is achieved in three terminal (Polymer electrolyte gating) devices. Thus this vacuum free, cost effective solution method is a promising alternative for the fabrication of alcohol sensor in future.

The aim of the research is to provide a high quality of FET for gas sensing application that can monitor the alcohol.

### **4. Question 6:** Have the authors clearly emphasized the strengths of their study/theory/methods/argument?

### **Question 7:** Have the authors clearly stated the limitations of their study/theory/methods/argument?

**Our Response:** For these questions, Reviewer 3<sup>rd</sup> have agreed with our manuscript and reviewer 1<sup>st</sup> has marked for improvement, but he has not clearly mentioned or suggested and numbered the limitations where we have to improve.

Sincerely,  
Rishi Ram Ghimire

# Fabrication of alcohol sensor using undoped and Al doped ZnO nanostructure film with polymer electrolyte gating

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**Abstract:** We report the fabrication of two terminal and three terminal gas sensor using Al-doped ZnO thin films and polymer electrolyte gate dielectric on glass substrate by vacuum free chemical method. The Al doped ZnO films are characterized by XRD, SEM, EDX, and UV-vis Spectrometer. The characterization results have revealed the polycrystalline structure of both undoped and doped ZnO; with loosely packed, porous, and spherical granary nanostructure with mean grain size 20–10 nm and bandgap of the films is within the range of 3.12–3.16 eV. The conductivity of the ZnO film is tuned by Al concentration and the maximum value of conductivity was observed in 3% Al doped ZnO films. Similarly, the best performance index of TFT such as current ON/OFF ratio, high transconductance and low threshold voltage was observed in 3% Al doping concentration. The ordinary (two-terminal) sensor and three-terminal(FET) sensors' responses towards three different concentrations 50, 250, 500 ppm of ethanol and methanol vapors have been studied. The sensitivity of the film is modulated by Al concentration and higher value of sensitivity was achieved at 3% Al doped ZnO films. The use of polymer electrolyte enhanced the sensitivity of the device which is more effective in methanol vapor. The response and recovery time of gas sensor is significantly improved in three terminal devices than the two terminal devices.

**Keywords:** EDL gate dielectric, Field effect transistor sensor, Al doped ZnO, Polymer electrolyte.

## I. Introduction

Gas sensing technologies have attracted much more attention of the scientific community, industry, and academia with increasing applications of industrial productions, medicines, automotive, indoor air quality control, environmental monitoring, etc. Due to the different applicability and inherent limitations of various gases, researchers have been working on different scenarios with enhanced gas sensor calibration [1]. Semiconducting metal oxides such as ZnO, SnO<sub>2</sub>, TiO<sub>2</sub>, WO<sub>3</sub>, CuO, and Fe<sub>2</sub>O<sub>3</sub> are strong and well-researched material for gas sensing applications. Different types of oxide-based nanostructures such as nanoparticles, thin films, nanorods, and nanowires have been synthesized and employed in the fabrication of gas sensors. It was found that chemical components, surface states, morphology, and microstructure play an important role in gas sensing performance. Among the various oxide semiconductors, ZnO, a wide direct-band gap (~3.2eV) semiconductor with wurtzite structure, is a promising candidate due to its strong shape, size, and surface tenability. It is non-toxic, eco-friendly, cost-effective and easy to synthesize [2]. The surface of ZnO is depleted due to the absorption of gases from the

environment. Thus, the electrical conductivity of ZnO can be drastically changed in the presence of reactive gases present in the environment [3]. The doping of foreign elements like Al, Cu, Ag, etc. in ZnO increases its conductivity and sensitivity by changing the shape and surface morphologies of ZnO. The defect states of ZnO may change with doping concentration, which has a higher role in carrier transport phenomena. Also, doping Aluminum makes the film more transparent and has huge application in fabrication of optical detector [4].

The moderately high carrier mobility, surface and shape tenability, easy functionalization and doping are the major strength of ZnO. Though the numerous significance of nanostructure ZnO are listed for electronic, optoelectronic and sensing applications, it has serious drawback because of slow response, sample inhomogeneity and lack of reproducibility, especially for chemically grown nanostructured films. These drawbacks of ZnO films are reduced by doping, functionalization and surface treatment and improve the performance index in electronic and optoelectronic applications [5]. In this report, we have used an alternative method to control the ZnO channel resistance using polymer electrolyte which aids surface modification to the film without changing its stoichiometry. The effect of polymer electrolyte on ZnO surface is purely electrostatic and it can control by applied bias voltage in there terminal device [5]. In this study we compare the two terminal and three terminal ZnO based gas sensor using polymer electrolyte. The objective of this study is to elaborate and establish the significance enhancement of sensitivity and quick response of gas sensor using polymer electrolyte.

Nowadays, conventional oxide-based gate dielectrics in field effect devices have been superseded by polymeric electrolyte gate dielectrics because of its high carrier accumulation strength especially in oxide material and relevancy in field effect transistor (FET) with nanostructured channel where the control of grain boundary (interface between two crystallites) charges substantially controls charge transport in the channel. The electric double layer (EDL) formed by polymer electrolyte with ZnO surface induces huge surface charges which enhance the mobility and the drain current (current through the semiconductor channel) by passivizing the charge defects and changing the occupancy of defect states [6]. Filed effect transistor configuration is a popular electrochemical sensor used as a transducer for over 40 years. In many reports conventional oxide materials are used as gate dielectric which requires high vacuum technology. Here we have used the polymer electrolyte in gel form and drop cast on ZnO surface which is simple cost-effective vacuum free method and have high performance index even used for flexible electronic [7]. In this work the transducer has two major components one is ZnO channel which generate the electrical signal after imposing analyte gas and another is the polymer electrolyte which is also sensitive to the analyte. The polymer electrolyte surface directly interacts with target analyte and the ZnO channel converts this interaction to electrical signal. Whenever the target analyte (gas) interacts with polymeric dielectric, it proliferate electrons as freebie to the EDL dielectric polymer which leads to an immense enhancement in drain current. As soon as the gas is removed, atmospheric oxygen molecules are further adsorbed and supplied Gate-Source voltage begins to stabilize the charge in the EDL minifying the drain current back to its former value [8]. The control of the sensor is directly linked with applied gate bias.

In this work, we will dop various concentrations (1-5% Vol.) of Aluminum on Zinc Oxide films. Among them 3% concentration of Al doped ZnO film showed high value of conductivity and appropriate for the fabrication of TFT

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4 using LiClO<sub>4</sub> and Polyethylene Oxide (PEO) as gate dielectric. Use of polymer electrolyte dielectric in two terminal  
5 device fabricated by 3% AZO film interestingly enhanced the sensitivity for methanol vapor and fast response and  
6 recovery time is achieved in three terminal (Polymer electrolyte gating) devices. Thus this vacuum free, cost  
7 effective solution method is a promising alternative for the fabrication of alcohol sensor in future.  
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10 The aim of the research is to provide a high quality of FET for gas sensing application that can monitor the alcohol.  
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## II. Methodology

17 The approaches that have been taken for the entire fabrication of sensor and its application process can be  
18 summed up in following steps:  
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### Deposition of thin film:

21 Among various methods for deposition of thin film, spin coating was found budget and labframe-feasible  
22 because of its plainness, cost-efficiency, facile doping, low operating temperature, and regulative spin and film  
23 thickness. The substrate is rotated at high speed after drop-casting a very few amounts of coating material over it to  
24 distribute the material uniformly all over it then annealed for the evaporation of the unwanted solvent and continued  
25 until the desired thickness or resistance of the film is achieved [7, 9].  
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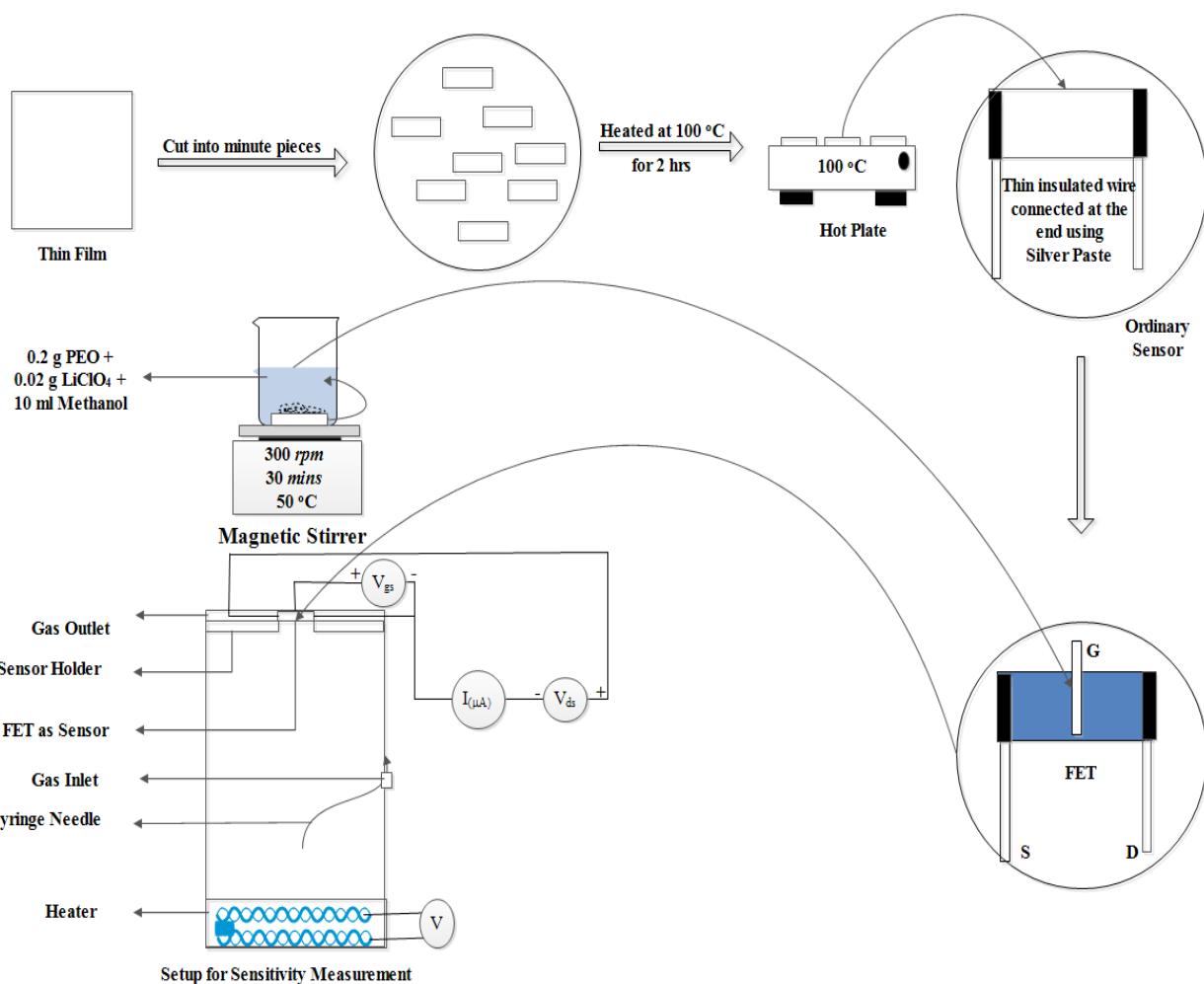
29 For 0.5 M precursor solution (Solution for pure ZnO thin film), 13.3872 g of Zinc Acetate Dihydrate (ZAD) and 6ml  
30 of Diethyl Amine (DEA) added to 120 ml of Ethanol was stirred at 300 rpm for an hour at room temperature.  
31 For 0.5 M dopant solution, 1.91 g Aluminium Nitrate in 20 ml Ethanol is stirred at 300 rpm for an hour at room  
32 temperature. Then, 0.2 ml, 0.4 ml, 0.6 ml, 0.8 ml, and 1.0 ml of dopant solution is added to 19.8 ml, 19.6 ml, 19.4  
33 ml, 19.2 ml, and 19.0 ml of precursor solution for doping 1%, 2%, 3%, 4%, and 5% of Aluminium by volume  
34 respectively and stirred at 300 rpm for an hour at room temperature.  
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38 0.1ml of precursor solution was spread over the spinning (at 3000 rpm for 30 seconds) substrate in a spin coater and  
39 was annealed over the hot plate at 550°C for 15 minutes.  
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4 **Fabrication of Sensor:**

5 The films fabricated are further cut into minute pieces (3 mm x 7 mm) and heated at 100 °C for 2 hours. As  
6 soon as the film gets heated, thin insulated wires-conducting at the ends are connected to both the ends of the film  
7 using Silver paste; these are then ready to use as an ordinary sensor. Two heating system is adjusted at the ends of a  
8 cylinder of the volume of about 300 cm<sup>3</sup>; heater at the top is to monitor the temperature of the film (sensor) and  
9 heater at the bottom is to evaporate liquid (if necessary). The needle of the syringe is adjusted as shown as in the  
10 figure below so as to pass gas or drop liquid over the heater. This is the way, how ordinary sensors are constructed  
11 using fabricated thin films.  
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14 The EDL gate electrolyte is prepared by stirring 0.2 g of Polyethylene Oxide (PEO) and 0.02 g of Lithiumchlorate  
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54 Figure 1: Fabrication of FET as a Sensor and Setup for Sensitivity Measurement.  
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56 (LiClO<sub>4</sub>) in 10 ml of Methanol at 300 rpm, and 50 °C for 30 minutes. The same procedure of constructing an  
57 ordinary sensor is followed then the contacts between the wire and film are insulated using glue and a single drop of  
58 electrolyte is drop cast and spread over the channel. Soon, an insulated thin wire-conducting at the ends is placed  
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gently over the electrolyte and the device is allowed to dry. As soon as the electrolyte dries, for the stability of the device, source and drain wires across the channel and gate wire over the electrolyte are fixed over Printed Circuit Board (PCB) by soldering and substrate is glued. These are the procedure followed to construct the Thin Film Transistor (TFT). Then the device is ready for further characterization and application. As shown in figure 1, for the sensitivity measurement by FET, the ordinary sensor at the top of the former setup replaced by fabricated FET.

### Sensing Mechanism:

ZnO (n-type semiconductor) thin film surface, when exposed to air, adsorb oxygen molecules to form molecular type adsorbate ( $O_2$ ,  $O_2^-$ ) and dissociative type ( $O_2^{2-}$ ) adsorbate ions forfeiting electrons from the conduction band, yielding electron-depleted space-charge layer in the grain boundary region which leads to large surface potential barrier and large resistance. The target gas (ethanol/methanol) may undergo dehydration and dehydrogenation and successively oxidized to CO,  $CO_2$ , and  $H_2O$ , 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.

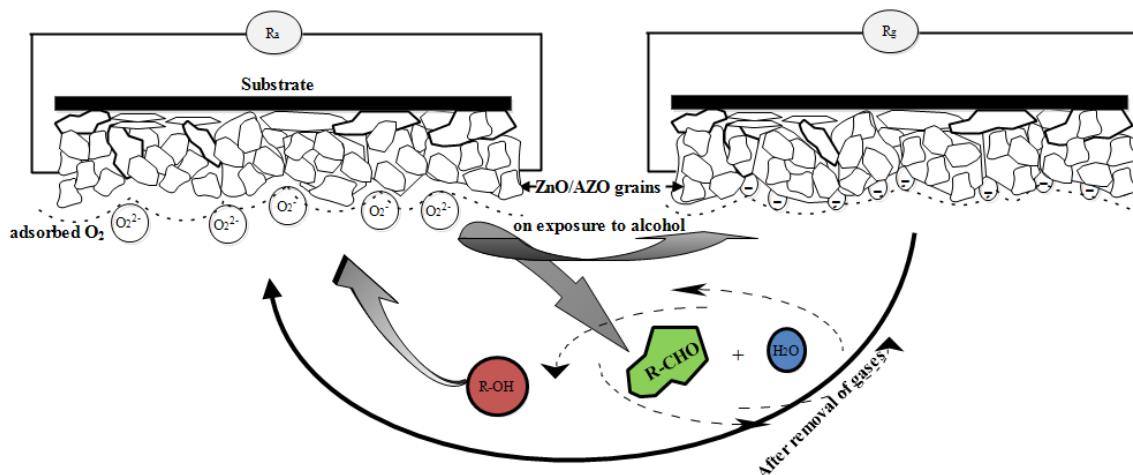
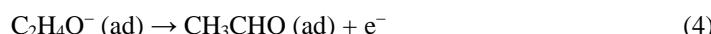
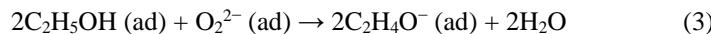
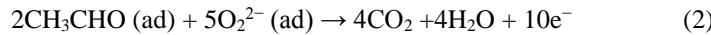


Figure 2: Sensing Mechanism of ZnO/AZO thin Film.

The release of electrons back to the film enhances the conductivity of the film and deduces the resistance. As soon as the vapor passes away, the film undue starts adsorption of atmospheric oxygen and tends to achieve its former

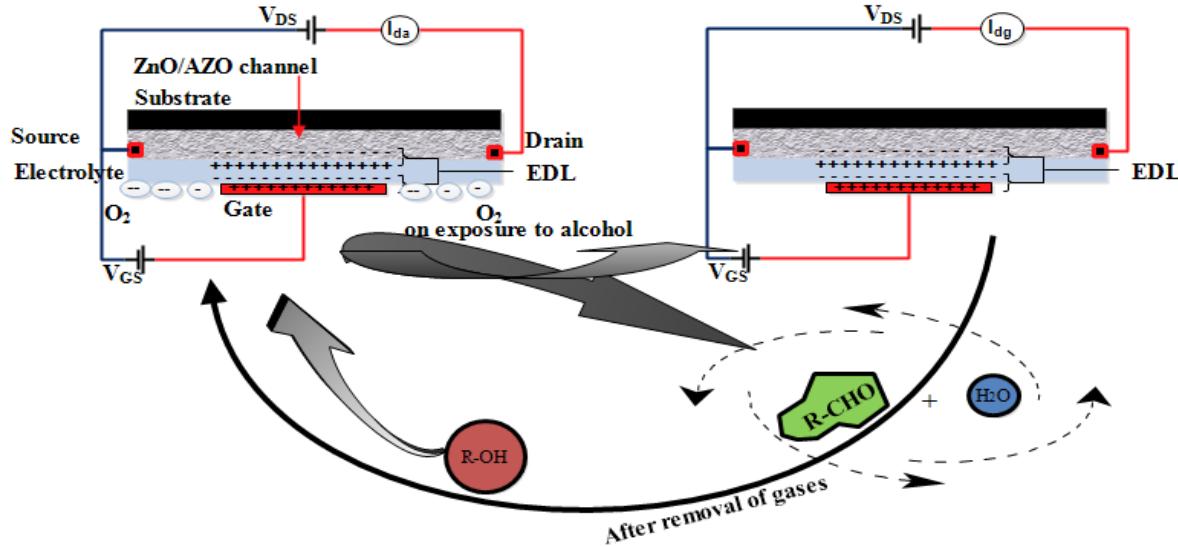


Figure 3: Sensing Mechanism of EDL gated TFT.

state [9]. Electric double-layer (EDL) gated thin-film transistor as a roseate candidate has attracted profound attention due to its huge ion-induced capacitance at semiconductor/electrolyte interface, sensitive interfacial features, low voltage operation and vehement gating effect strong enough to modulate the carrier density of the semiconductor channel.

The conversion of alcohol vapors into aldehydes due to adsorption of Oxygen at the grain boundary region is similar to bare films but its effect is quite alike as the adsorption here, affects the interfacial potential and enhances the channel current by an EDL capacitive coupling effect [8].

### 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. For indirect transition, the variation in absorption coefficient with the photon energy obey Tauc's plot method,

$$(\alpha h\nu)^{0.5} = A(h\nu - E_g)$$

(Eq. 1)

Where A is a constant,  $E_g$  is the optical band gap, h is the plank constant and  $\alpha$  is the absorption coefficient. Extrapolation of  $(\alpha h\nu)^{0.5} = 0$  yields the optical bandgap energy of the films [11].

The Tauc's Plot of Pristine ZnO and various concentrations of Al-doped ZnO thin films are plotted and corresponding bandgaps were evaluated as shown in figure 4.

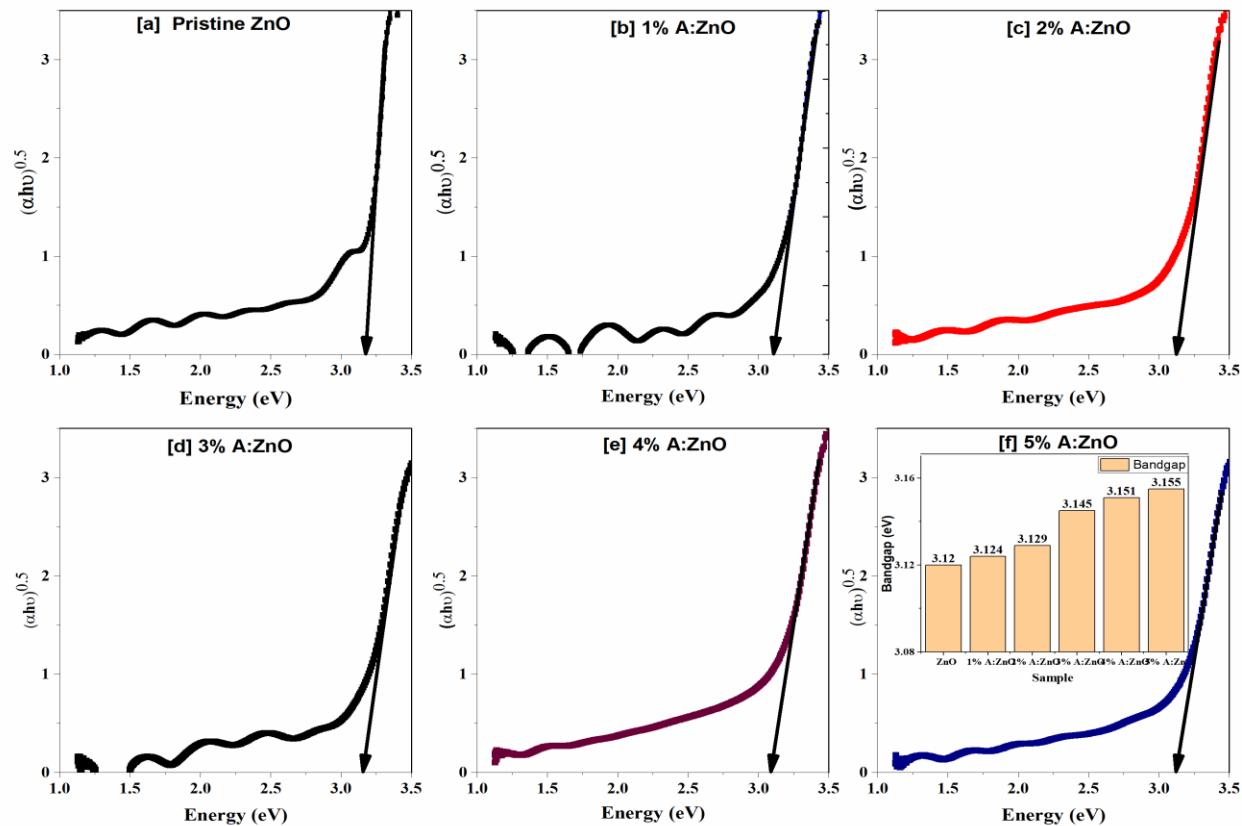


Figure 4: Calculation and Comparison of Bandgap Energy of pristine [a] ZnO thin film and [b-f] various concentrations of Al-doped ZnO films using Absorbance.

It is obvious that the direct bandgap of the AZO films increases with increasing Al content due to the fact that Al ions tend to occupy among ZnO lattice planes yielding the increase of the transport path of charge carriers into ZnO lattice and a significant decrease in grain size. Furthermore, when Al is doped in ZnO, donor electrons accumulated at the lower edge of the conduction band get excited to the higher energy levels in the conduction band with required extra energy which in fact broadens the optical bandgap of the film [4]. Here, the bandgap of pristine ZnO is found 3.120 eV, 1% Al-doped ZnO thin film is found to be 3.124 eV and the optical bandgaps are found gradually increasing to 3.155 eV on increasing the concentrations of the dopant.

### X-ray Diffraction (XRD):

The structural characterizations of fabricated thin films are analyzed using XRD [Bruker D2 Phaser X-ray diffractometer of CuK $\alpha$  radiation (wavelength: 1.54184 Å)] at 40 KV of operating voltage and current of 40 mA in the 2 $\theta$  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,  $\lambda$  is the wavelength of the x-radiation,  $\beta$  is the full width at half maximum (FWHM) of the observed peak and  $\theta$  is the Bragg's angle. Comparing calculated d-spacings with the standard JCPDS values of card number 36-1451, the observed peaks are indexed.

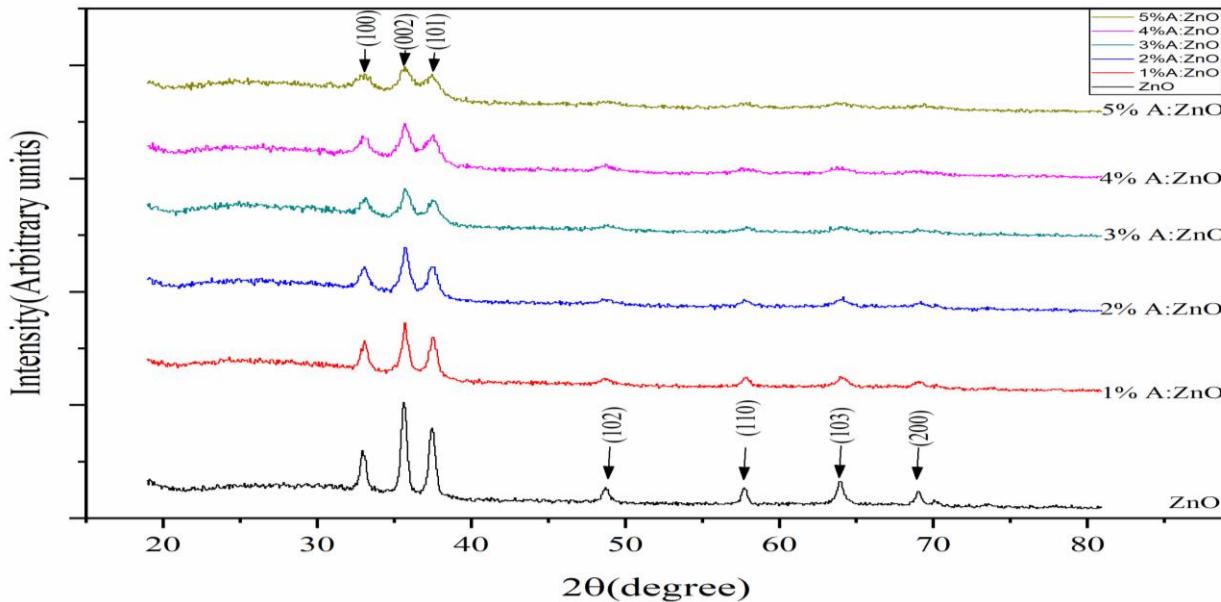


Figure 5: XRD pattern of undoped and Al-doped ZnO thin films labelled in legends.

Figure 5 and 6, significantly shows that all the diffraction peaks are observed around  $33.01^\circ$ ,  $35.61^\circ$ ,  $37.43^\circ$ ,  $48.70^\circ$ ,  $57.70^\circ$ ,  $63.92^\circ$ , and  $69.01^\circ$  corresponding to (100), (002), (101), (102), (110), (103) and (112) respectively, which depicts the films to be hexagonal crystallite in structure or polycrystalline in nature. In addition, no significant shift in XRD peaks are observed in Al-doped ZnO films compared to ZnO film with the exception of the peaks of (100), (002), and (101). Increasing doping concentration changed the peaks intensity and width, and minor peaks (102, 110, 103, 200) are seemed disappearing, whereas the three major peaks (100, 002, 101) are seen significantly decreasing due to the incorporation of Al in ZnO lattice [4].

The reason for the shift of (100), (002), and (101) peaks of AZO films towards larger angle direction as seen in figure 5 and 6, is substitution of zinc ions by Aluminium ions into hexagonal lattice of ZnO film and shifts in ZnO films are due to presence of Aluminium as impurity from its glass substrate [12].

Also, the average grain size can be calculated using Williamson Hall method, whose equation is given by,

$$\beta \cos\theta = \frac{k\lambda}{D} + \gamma \sin\theta$$

(Eq. 3)

Where,  $k$  is the shape factor,  $\lambda$  is the incident wavelength,  $\beta$  is the FWHM measured in radians,  $D$  is the average grain size,  $\gamma$  is the lattice strain and  $\theta$  is the Bragg angle of diffraction peak.

The lattice spacing parameter 'd' was calculated using relation:

$$d = \frac{\lambda}{2 \sin\theta}$$

(Eq. 4)

Further, for the hexagonal crystal structure, the lattice spacing 'd' can be calculated using the relation:

$$\frac{1}{d^2} = \frac{4(h^2 + hk + k^2)}{3a^2} + \frac{l^2}{c^2}$$

(Eq. 5)

where 'h', 'k', and 'l' are miller indices, and 'a', and 'c' are lattice constants.

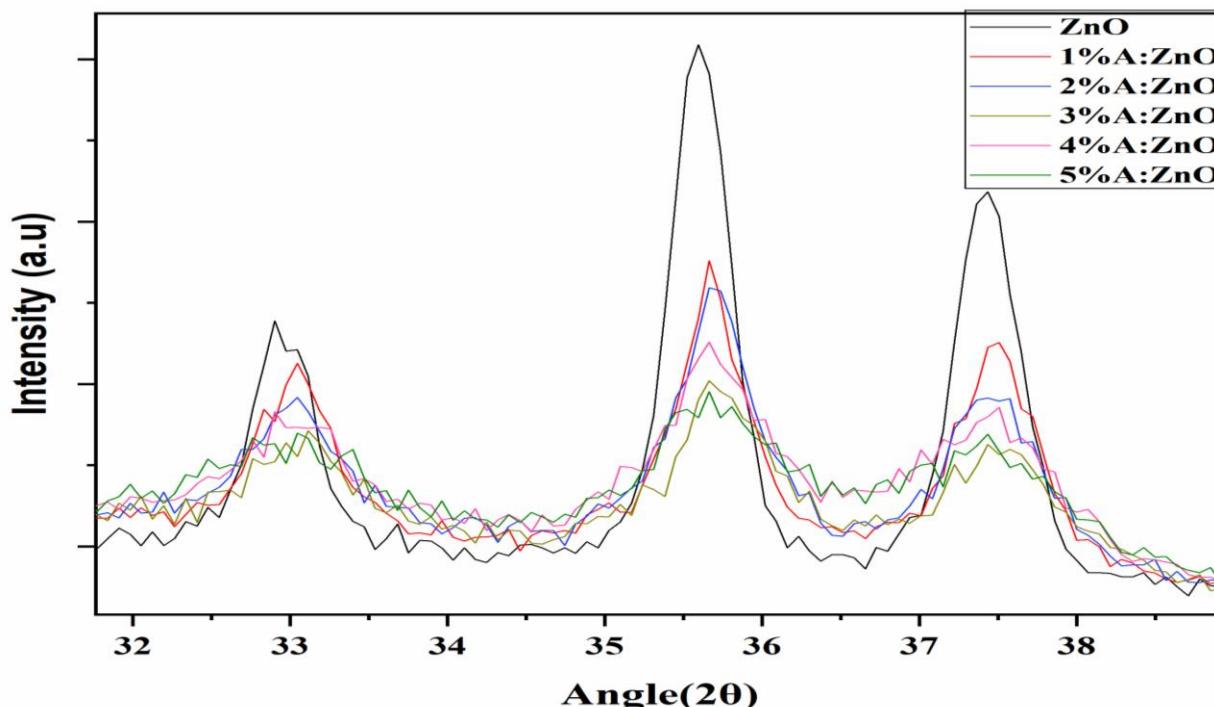
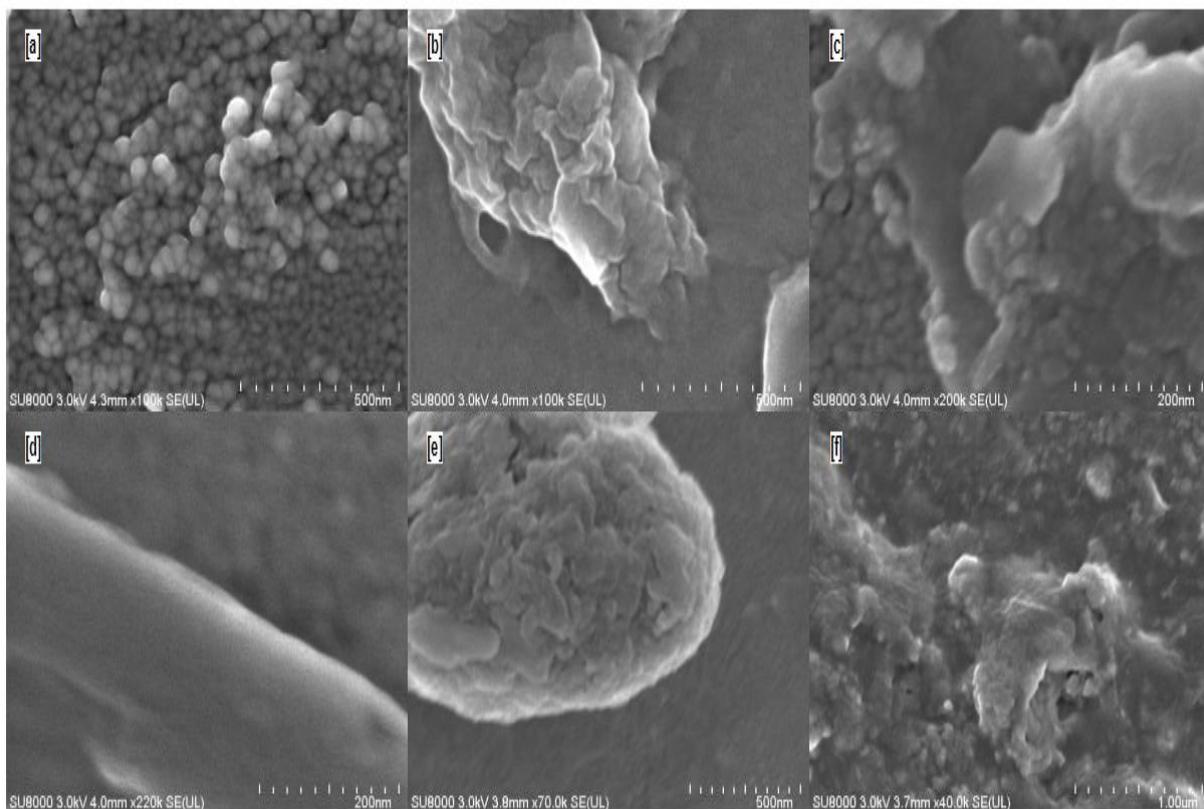


Figure 6: XRD Pattern of ZnO and Al-doped ZnO corresponding to (100), (002) and (101).

The particle size is determined from Sherrer's equation (Eq. 2), and is found around 20 nm, 16 nm, 15 nm, 13 nm, 12 nm and 11 nm respectively. This significant decrease in particle size on doping and increasing the doping concentration is due to incorporation of Aluminium atom in place of Zinc atom in the lattice site [4].

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4 **Scanning Electron Microscope (SEM) and EDX analysis:**

5 The surface morphology of ZnO thin films were performed using Scanning Electron Microscope at  
6 Research Centre for Eco-Environment Sciences, Chinese Academy of Sciences, Beijing, China. The surface  
7 morphology of undoped ZnO thin film and various concentrations of Al-doped ZnO thin films is studied using  
8 Scanning Electron Microscope at Research Center for Eco-Environmental Science, Chinese Academy Science,  
9 Beijing, China. The SEM images of ZnO thin film and various concentrations of Al-doped ZnO thin films are  
10 attached herewith. These SEM images depict loosely packed, porous, spherical and homogeneously arranged granny  
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45 Figure 7: SEM Images of [a] Pristine ZnO thin film and [b-f] 1% - 5% Al-doped ZnO thin films respectively.  
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47 nanostructure. The porosity and surface roughness seem to be decreased on doping Al and again, increase in the  
48 dopant concentration has increased the roughness of the films too. The morphology of the sensing films has  
49 significant role in gas detection. Thus, porous surface with small grain size is considered to possess better gas  
50 sensitivity [13]. The uniformity of the film seems poor and may not be suitable for optoelectronic devices [14] but it  
51 has less impact in gas detection, thus can be used as gas sensor.  
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The EDX analysis was also performed in Research Center for Eco-Environmental Science, Chinese Academy of Science, Beijing, China along with SEM imaging.

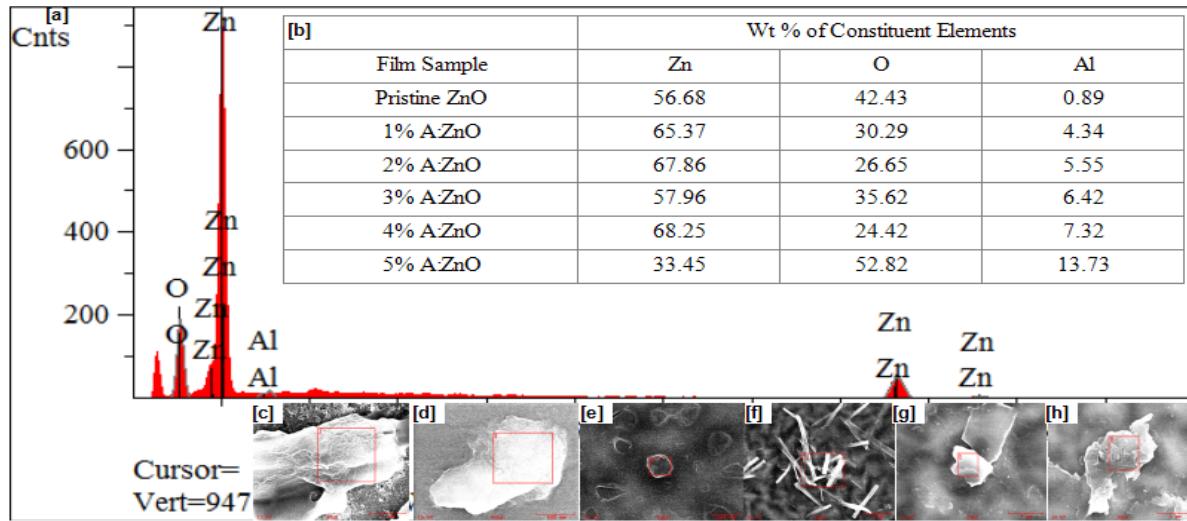


Figure 8: [a] EDX analysis image of 3% A:ZnO, [b] table representing wt. % of constituent elements in undoped and various concentration of Al-doped thin films, [c-h] SEM images of selected area of ZnO and various concentrations of Al-doped ZnO thin films over which EDX analysis was done.

The EDX data above confirms that the film composition is of elements zinc and oxygen in pristine ZnO film and Zinc, Oxygen and Aluminum in AZO films without any other impurities. Negligible wt. % of Al is found in the film of pristine ZnO too which may be due to Aluminium Silicate substrate. Increasing doping concentration has increased wt. %, but it does not resemble doping by volume concentration anymore which may be due to inhomogeneity in distribution of Al in the precursor during its preparation. Also, it may be due to the fact that EDX analysis is done by selecting a very little area of about  $100 \text{ nm}^2$  which is one out of 400 billion parts of the film prepared. So, the data of wt. % of Zinc and Oxygen seem quite erratic. Though the data, in overall, convince the film is homogeneous.

#### Resistivity of thin films

The electrical resistivity of ZnO and AZO is calculated using four probe technique using the relation

$$\rho = \frac{2\pi s V_{ds}}{I} \quad (\text{Eq. 6})$$

Here, constant current ( $I$ ) is passed through two outer probes and potential ( $V_{ds}$ ) developed across two inner probes is measured given that the distance ( $s$ ) between all the four probes is equal [15]. The value of resistivity of the film is found decreasing when the temperature of the specimen is raised. This is due to the fact that when temperature of the specimen rises, the electrons in the specimen get thermally excited and move towards the conduction band increasing carrier mobility. The resistivity of ZnO and AZO films calculated from eq (6) at various temperatures is graphed below:

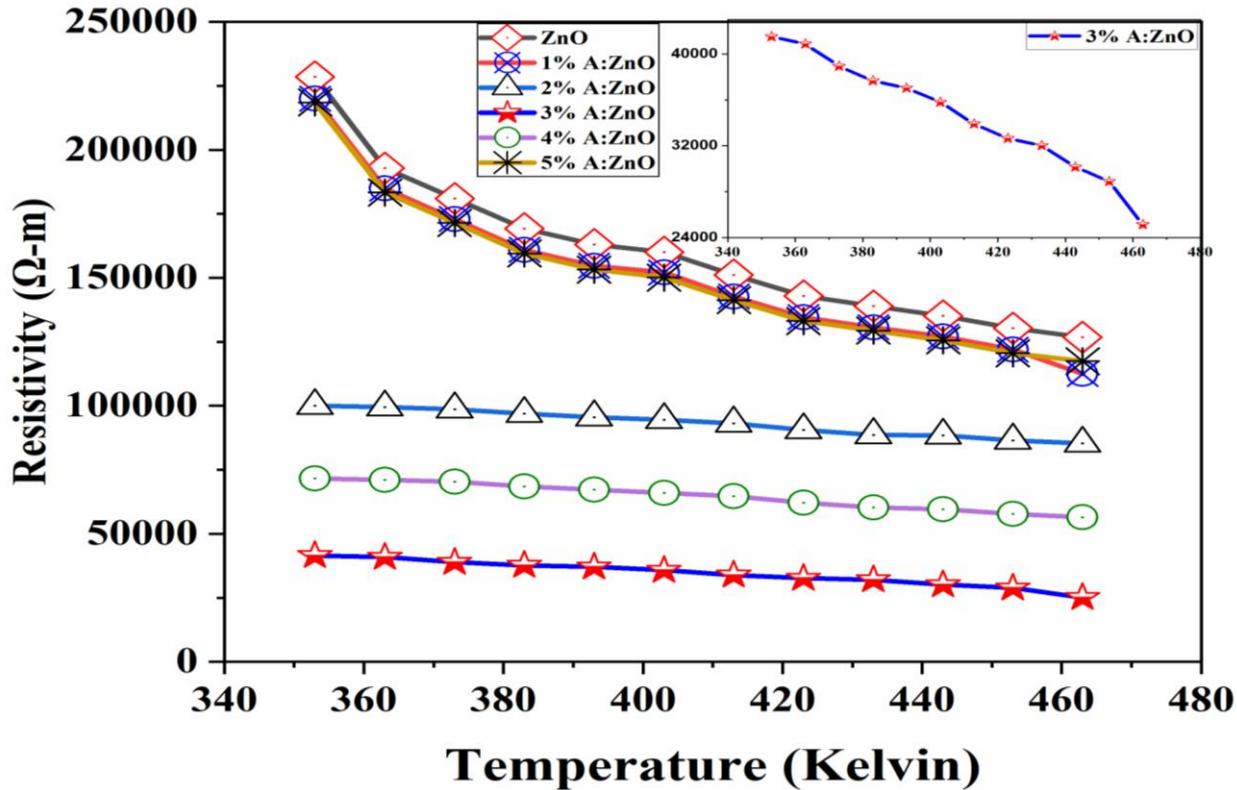
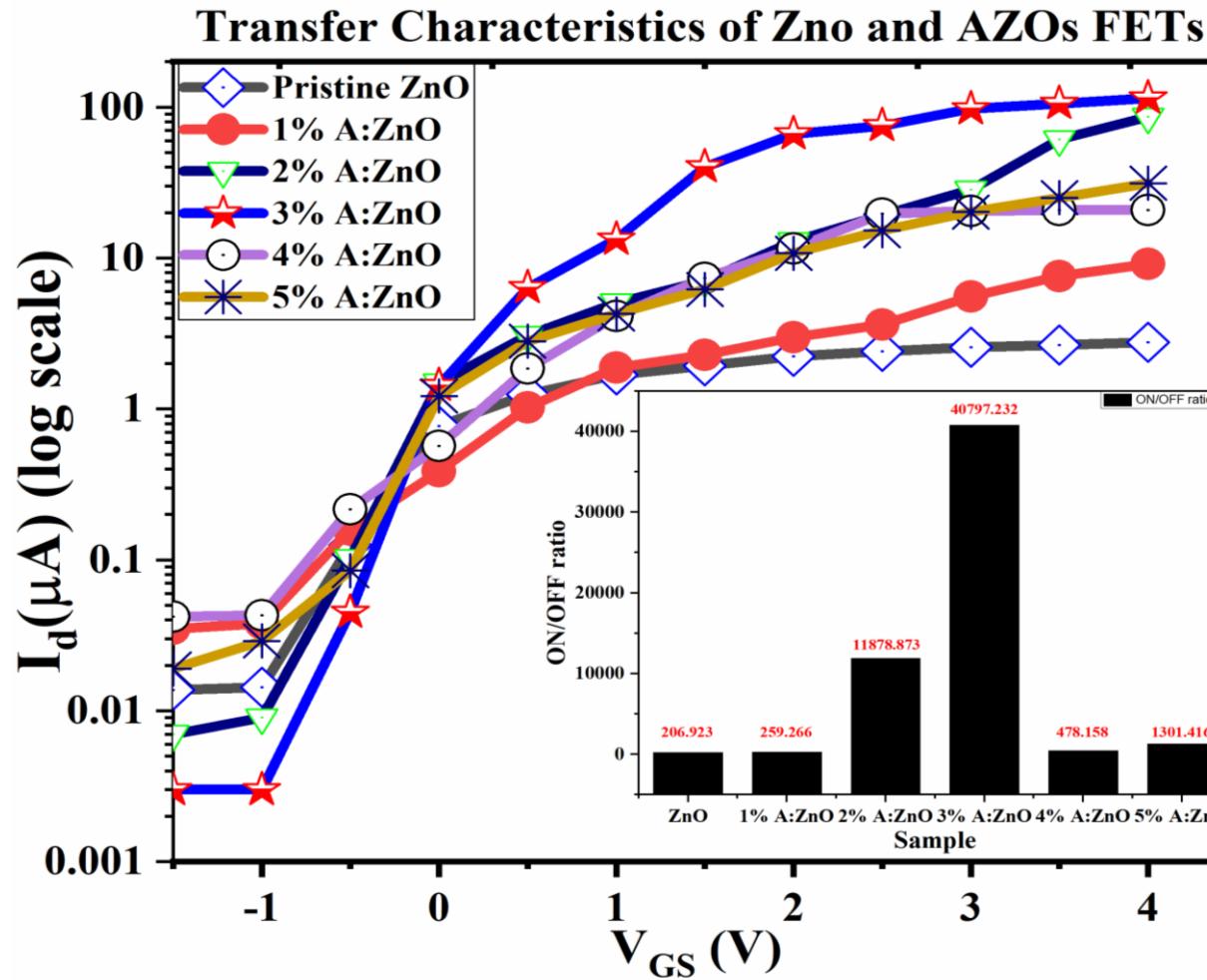


Figure 9: Resistivity of pristine ZnO and various concentration of Al doped ZnO varying with temperature.

The value of resistivity is found minimum for 3% Al-doped ZnO film at all temperatures and is found maximum for pristine ZnO sample at all temperatures. However, with an increase in the Al doping concentration above 3% by volume, the resistivity is found increasing significantly. When a small amount of Al is pioneered as dopant, Al ionizes to  $\text{Al}^{3+}$  and replaces  $\text{Zn}^{2+}$  yielding one free electron responsible for the increment of carrier concentration. Therefore, carrier concentration increases or resistivity decreases with increasing Al concentration at first up to 3 vol% doping. Further, on increasing Al concentrations, increasing Al dopant atom may form neutral defects and do not contribute free electron and the number of electrically active dopant atoms reduces in the film. This is the reason for the further decrement of the carrier concentration and resistivity increment [16].

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**Field Effect Transistor (FET) Characteristics**

5 The principal of transfer characteristics is the most important factor in evaluation of performance of TFTs.  
6 In this section, we will present transfer characteristics of ZnO and AZOs channeled, EDL gated TFTs and discuss  
7 about the findings. The transfer characteristics of pristine ZnO thin film and various concentrations of Al-doped  
8 ZnO thin films are studied keeping drain-source voltage ( $V_{DS}$ ) equals 1 Volt and varying gate-source voltage ( $V_{GS}$ )  
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45 Figure 10: Transfer Characteristics of ZnO and AZOs channelled, EDL gated TFTs.  
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47 from negative of 3 Volts to positive 4 Volts and the corresponding changes in drain current ( $I_d$ ) are noted.  $I_d$  versus  
48  $V_{GS}$  graph termed as "Transfer characteristics" is plotted and respective ON-OFF ratios i.e. ratio of maximum stable  
49 drain current to minimum stable drain current are calculated. The minimum stable current i.e. drain current of OFF-  
50 state of EDL gated 3% Al-doped ZnO TFT is found  $6 \times 10^{-4} \mu\text{A}$  and maximum stable current i.e. drain current of  
51 ON-state is found approximately  $115 \mu\text{A}$ . The transfer characteristic of 3% Al-doped ZnO is found fantabulous as  
52 expected as its ON-OFF ratio is found to be maximum (~40800) among the rest of the films which may endow the  
53 higher sensitivity. So, its drain characteristics were further studied keeping  $V_{GS}$  constant (-1 V, 0 V, 1 V, 2 V, 3 V, 4  
54 V) and varying drain-source voltage from 0 V to 5 V and noting the corresponding changes in drain current.  
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The drain characteristic of the concerned sample is too found conspicuous which is as shown in figure 11 below:

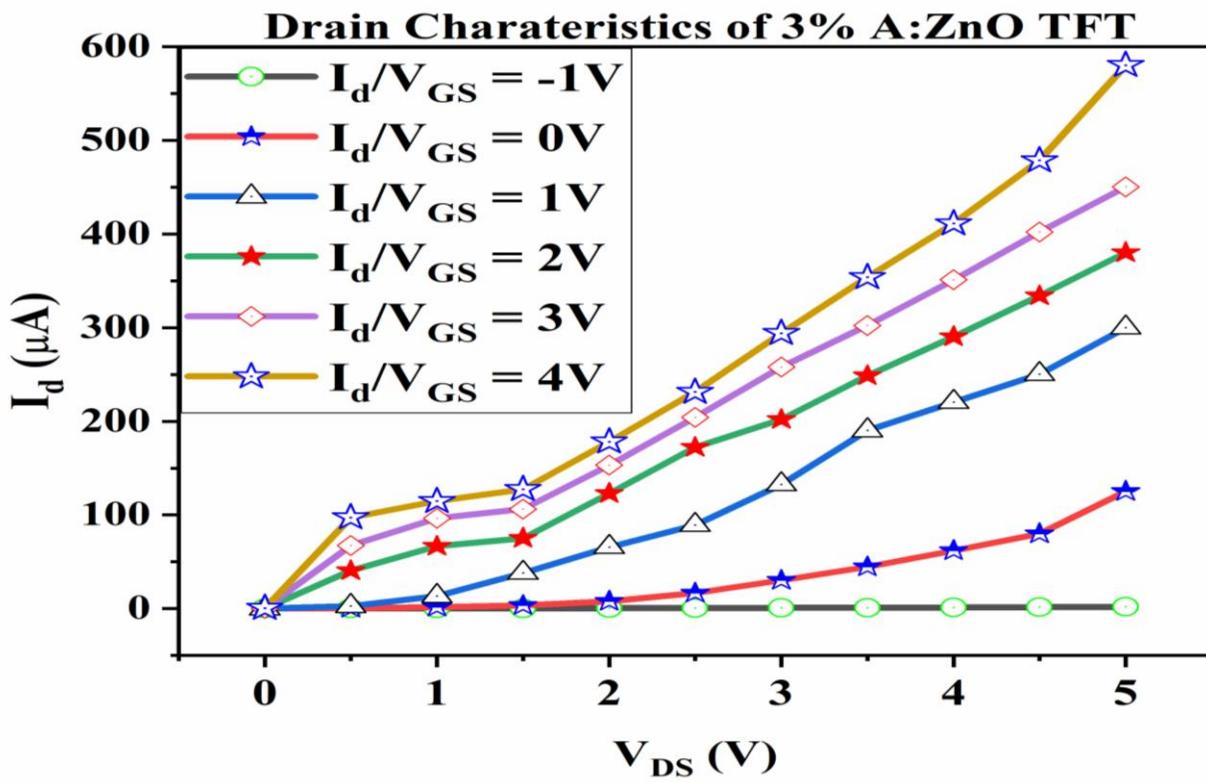


Figure 11: Drain Characteristics of 3% Al-doped ZnO channelled, EDL gated TFT at various Gate-Source Voltages.

### Sensitivity of the Sensors

The attenuation of film-resistance is prominent in two-terminal sensors and variation of channel current is kenspeckle in three-terminal sensors, so the sensitivity of the two-terminal sensor is calculated using the relation:

$$s = \frac{R_a - R_g}{R_a} \times 100\% \quad (\text{Eq. 7})$$

Where, 's' stands for sensitivity,  $R_a$  and  $R_g$  are resistances of the two-terminal sensors before and after exposure to alcohol vapors [8].

For the three-terminal sensor, slight modification i.e. resistances are expressed in terms of current in relation (7) is done and calculated as:

$$s = \frac{I_g - I_a}{I_g} \times 100\% \quad (\text{Eq. 8})$$

where 's' stands for sensitivity,  $I_a$  and  $I_g$  are channel current of the EDL electrolytic polymer gated TFT sensors before and after exposure to alcohol vapors. Here,  $R_a$  is replaced by  $I_g$  so as to obtain the sensitivity within the range of 0-100%. Else, sensitivity more than 150% would have been obtained which seems quite impractical.

Three different concentrations (50 ppm, 250 ppm, 500 ppm) of alcohol vapors are passed into the setup shown in figure 1, and the response and recovery time, and the corresponding decrease in the values of resistances are noted. The sensitivity of the two-terminal sensors i.e. bare films and EDL coated films at room temperature are calculated using relations 7 and 8 and their corresponding graphs are shown in figure 12.

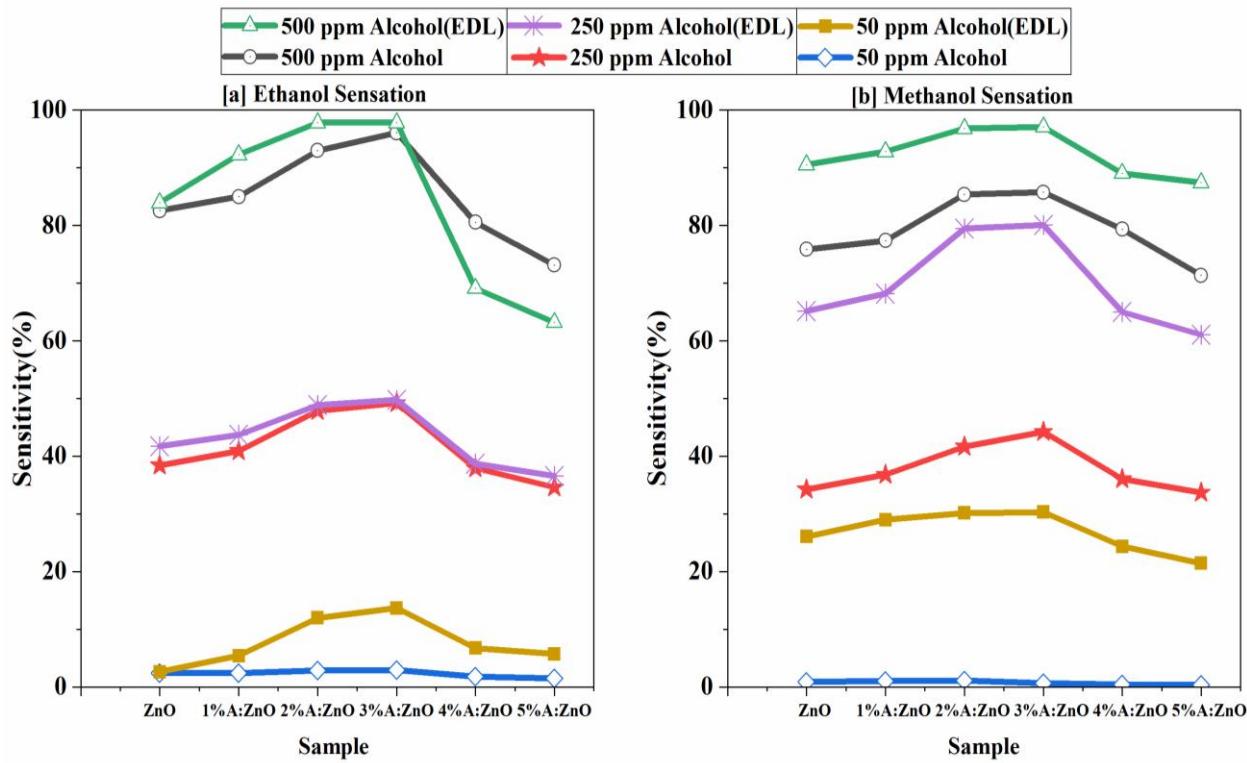


Figure 12: Sensitivity of Bare and EDL layered Two-Terminal Sensors in response to [a] Ethanol and [b] Methanol Vapors.

Sensing within room temperature is one of the challenges that we have faced and overcomed. The sensitivities of bare pristine ZnO and 1 to 5% Al-doped ZnO thin films range from 0.33% to 1.13% in response to 50 ppm of methanol, 1.5% to 2.9% in response to 50 ppm of ethanol, 33.69% to 44.22% in response to 250 ppm of methanol, 34.60% to 49.24% in response to 250 ppm of ethanol and 71.36% to 85.75% in response to 500 ppm of methanol, 73.13% to 96.06% in response to 500 ppm of ethanol; sensitivity in 3% Al-doped ZnO always succeeding and sensitivity in 5% Al-doped ZnO always preceding.

Furthermore, sensitivities of EDL coated pristine ZnO and 1 to 5% Al-doped ZnO thin films range from 21.46% to 30.32% in response to 50 ppm of methanol, 2.60% to 13.67% in response to 50 ppm of ethanol, 61.06% to 80.06% in response to 250 ppm of methanol, 36.59% to 49.74% in response to 250 ppm of ethanol and 87.43% to 97.08% in response to 500 ppm of methanol, 63.19% to 97.81% in response to 500 ppm of ethanol; sensitivity in 3% Al-doped ZnO always succeeding.

The sensitivity of films in response to higher concentrations of alcohol vapors is found higher. Higher concentrations of alcohol vapors mean a higher number of alcohol molecules. More, the number of reducing molecules, the more is the number of Oxygen reduced from the grain boundary of the film yielding an abrupt reduction in resistance of the film. This is the reason for such an upshot. The sensitivity of the bare film in response

to ethanol is always found greater than methanol. This is due to the fact that the oxidation potential of ethanol (-0.66 V) is less than that of methanol (-0.55 V) and higher the electrooxidation potential, it's more difficult to get oxidized [17]. Also, the sensitivity of 3% Al-doped ZnO thin film is always found succeeding sensitivities of the rest of the films. The smallest value of resistivity, smaller grain size, and its rough surface may have made it favorable for this result. The EDL electrolyte coated over the bare pristine ZnO and various concentrations of Al-doped ZnO sensors has enhanced the sensitivity of the film significantly but quite erratically. It shows the marvelous response to methanol than to ethanol vapors in enhancing the sensitivity. The use of methanol for the preparation of electrolyte polymer may be responsible for such a biasing response.

### Response and Recovery of Two Terminal Sensors

The time interval within which the film achieves its minimum value of resistance due to exposure of reducing gas is considered to be the response time while the time interval within which the film regains 90% of its initial value of resistance after removal of gas is considered to be the recovery time. Experiments for determination of response and recovery time of all sensors are performed. The change in resistances of the bare and EDL dielectric polymer coated ZnO and AZOs films in response to Ethanol and Methanol Vapors with respect to time are noted, graphed and response and recovery time are calculated. The response time of the sensor is found always shorter than the recovery time. Since the performance of 3% Al-doped ZnO sample is found excellent compared to the rest of the samples, so its response to both 500 ppm of ethanol and methanol vapors are graphed and shown in figure 13.

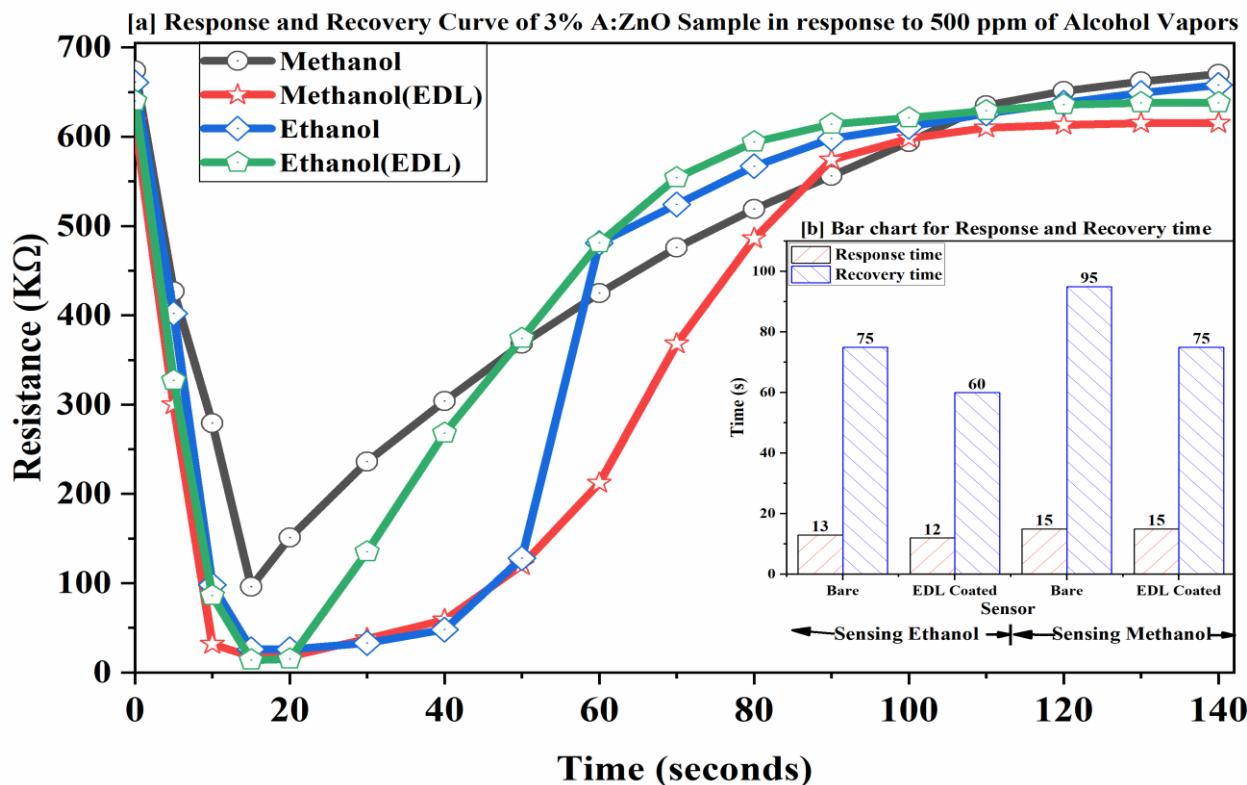


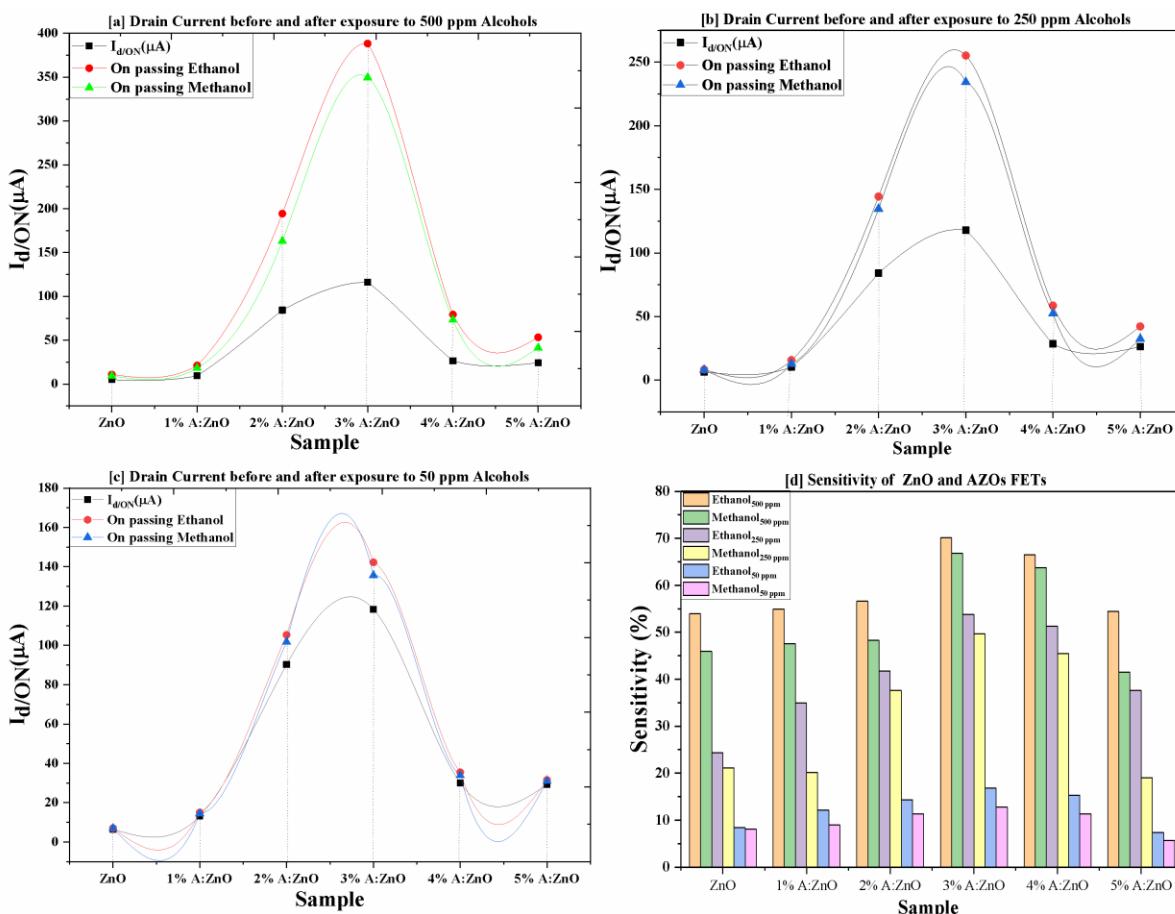
Figure 13: [a] Variation in Resistances of Bare and EDL Layered 3% A:ZnO films with respect to time in response to Ethanol and Methanol Vapors [b] Bar chart for response and recovery time of Bare and EDL coated 3% A:ZnO thin-film sensors.

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**Sensitivity, Response and Recovery of Three Terminal Sensors**  
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6 The response time for bare and EDL dielectric polymer coated 3% Al-doped ZnO sample is found to be 13  
7 s and 12 s in response to 500 ppm of ethanol vapors, 15 s and 15 s in response to 500 ppm of methanol vapors and  
8 the recovery time for the concerned sample is found to be 75 s and 60 s in response to 500 ppm of ethanol vapors  
9 and 95 s and 75 s in response to 500 ppm of methanol vapors respectively. Response and recovery time for ethanol  
10 vapors is always shorter than for methanol vapors which may be due to less oxidation potential of ethanol.  
11 Various concentrations of alcohol vapors are passed into the setup shown in figure 1 keeping the FETs at ON state,  
12 and the response and recovery time, and the corresponding increase in the values of drain current are noted.  
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**Sensitivity of Three Terminal Sensors**  
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18 The sensitivity of the three-terminal sensors i.e. FETs are calculated using relation 8 and their  
19 corresponding graphs are shown.  
20



53 **Figure 14: [a-c] Drain current, [d] Sensitivity of ZnO and AZOs channelled FETs before and after exposure to  
54 various concentrations of alcohols.**

55 The sensitivities of pristine ZnO and 1 to 5% Al-doped ZnO channelled, EDL dielectric polymer gated thin-film  
56 FETs range from 5.65% to 12.75% in response to 50 ppm of methanol, 7.36% to 16.79% in response to 50 ppm of  
57 ethanol, 18.98% to 49.70% in response to 250 ppm of methanol, 24.35% to 53.82% in response to 250 ppm of  
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ethanol and 41.49% to 66.81% in response to 500 ppm of methanol, 53.91% to 70.11% in response to 500 ppm of ethanol; sensitivity in 3% Al-doped ZnO always succeeding the sensitivities of the rest of the samples. The sensitivity of 4% AZO channeled thin-film FET sensor is found approaching the sensitivity of 3% AZO channeled thin-film FET sensor.

The sensitivity in response to ethanol is found higher than in response to methanol for all equal concentration which is due to less oxidation potential of ethanol vapor. The sensitivities of TFTs sensors in response to higher concentrations of alcohol vapors are found higher. This is because higher concentrations of alcohol vapors have a higher number of alcohol molecules which reduces a huge number of oxygen molecules from the grain boundary of the polymer yielding an abrupt enhancement in channel current of the film. The low value of resistivity and sufficiently large value of the ON-OFF ratio of around 40800 ( $>10^3$ ) in 3% Al-doped ZnO channeled EDL electrolyte polymer gated TFT sensor is responsible for its higher sensitivity.

### Response and Recovery of Three Terminal Sensors

The time interval within which the film achieves its maximum value of drain current due to exposure of reducing gas is considered to be the response time while the time interval within which the film regains its initial value of drain current (+5% for our convenience) after removal of gas is considered to be the recovery time. Experiments for determination of response and recovery time of all sensors are performed. The significant change in channel current of the EDL dielectric polymer gated, ZnO and AZOs channeled thin-films in response to Ethanol and Methanol

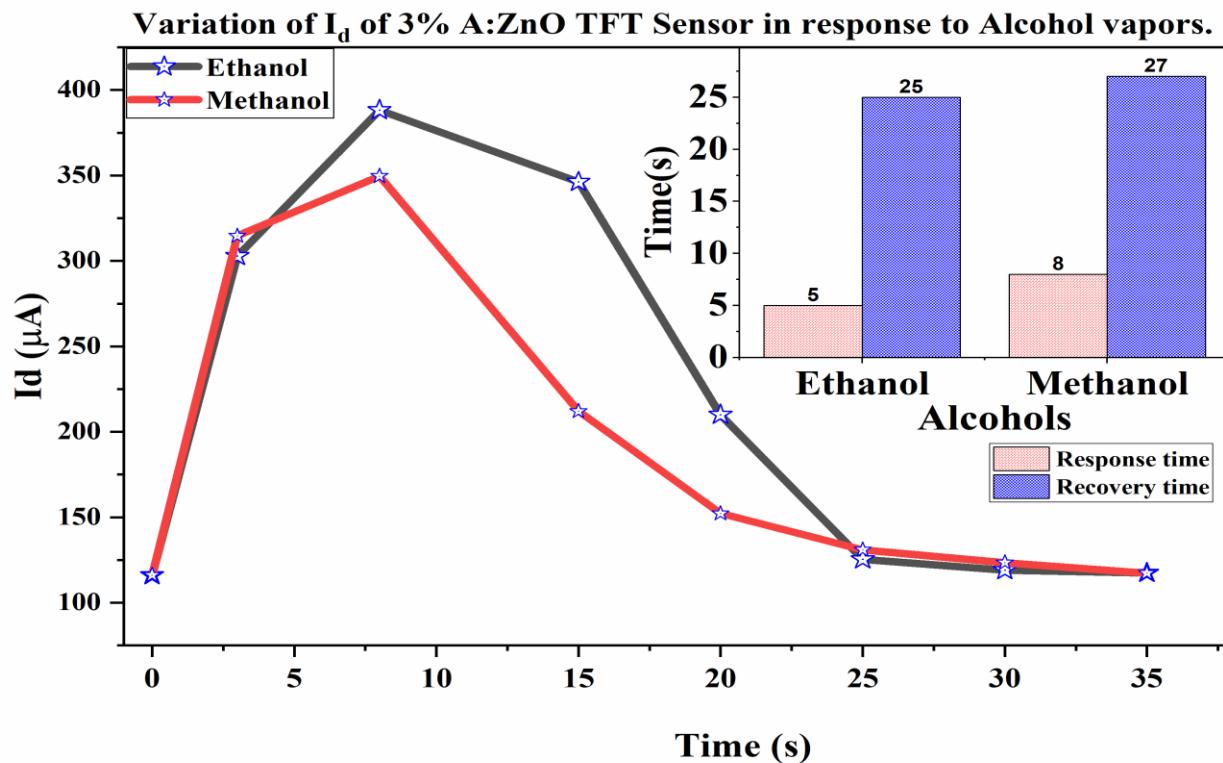


Figure 15: Variation of Drain Current of 3% A:ZnO channeled EDL dielectric polymer gated TFT in response to 500 ppm of Ethanol and Methanol Vapors, and Bar chart showing Response and Recovery time of respective TFT embedded.

Vapors with respect to time are noted, graphed and response and recovery time are calculated. The response time of the sensor is found always shorter than the recovery time. Since the performance of 3% Al-doped ZnO sample is found excellent compared to the rest of the samples, so its response to both 500 ppm of ethanol and methanol vapors are graphed as shown in figure 12.

The response and recovery time for 3% Al-doped ZnO channeled EDL gated TFT sample is found to be 5 s and 25 s in response to 500 ppm of ethanol vapors and 8 s and 27 s in response to 500 ppm of methanol vapors respectively. Response and recovery time for ethanol vapors is always shorter than for methanol vapors which may be due to less oxidation potential of ethanol. Also, it is obvious that response time is always shorter than the recovery time. The water vapor is produced during oxidation of alcohol vapors when they interact with EDL polymer which may take few more seconds to evaporate. This may be the reason for such upshot.

#### IV. Conclusions

Undoped and 1-5% Al-doped ZnO nanostructured thin films are synthesized using spin coating chemical method on glass substrates. The polycrystalline性质 of ZnO and AZOs films is confirmed by the XRD pattern and the SEM images. The films consists with loosely packed, porous and spherically arranged granny nanostructure with grain boundary. The analysis of optical results obtained from the UV-vis spectrometer has confirmed the increase in the bandgap of the film (3.12-3.16 eV). A small amount (3% by volume as optimum) of Al pioneered as dopant ionizes to  $\text{Al}^{3+}$  and replaces  $\text{Zn}^{2+}$  yielding one free electron responsible for the increment of carrier concentration (decrement in resistivity) whereas further increment of dopant gives rise to neutral defect, reduces the number of electrically active Al and give rise to further resistivity increment.

Among the grown films, the best conductive 3% Al doped ZnO film was used as a channel material to fabricate two terminal and three terminal gas sensor. Polymer electrolyte was used as gate dielectric for TFT application which can induce ultra-high charge carrier on surface of the Al:ZnO channel and enhance the performance index of TFT sensor. The sensitivity of two terminal device towards methanol vapor using polymer electrolyte is remarkable enhance in comparison to ethanol vapor. This means the polymer electrolyte is more sensitive to methanol vapor. Similarly, the sensitivity and the response and recovery time is improved in three terminal gate controlled field effect device.

Thus, this report suggests that 3% Al vol. is the optimum concentration of doping for the excellent performance of thin-film in sensing for ethanol and methanol. Furthermore, though the sensitivities of three terminal device is comparable to two terminal devices but TFTs are the promising candidate for sensing applications compared to two-terminal sensors because of their significant variation in drain current due response to alcohol vapors and shorter response and recovery time and controllability of channel current applying suitable gate-source voltage bias.

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# Fabrication of alcohol sensor using undoped and Al doped ZnO nanostructure film with polymer electrolyte gating

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**Abstract:** We report the fabrication of two terminal and three terminal gas sensor using Al-doped ZnO thin films and polymer electrolyte gate dielectric on glass substrate by vacuum free chemical method. The Al doped ZnO films are characterized by XRD, SEM, EDX, and UV-vis Spectrometer. The characterization results have revealed the polycrystalline structure of both undoped and doped ZnO; with loosely packed, porous, and spherical granular nanostructure with mean grain size 20–10 nm and bandgap of the films is within the range of 3.12-3.16 eV. The conductivity of the ZnO film is tuned by Al concentration and the maximum value of conductivity was observed in 3% Al doped ZnO films. Similarly, the best performance index of TFT such as current ON/OFF ratio, high transconductance and low threshold voltage was observed in 3% Al doping concentration. The ordinary (two-terminal) sensor and three-terminal(FET) sensors' responses towards three different concentrations 50, 250, 500 ppm of ethanol and methanol vapors have been studied. The sensitivity of the film is modulated by Al concentration and higher value of sensitivity was achieved at 3% Al doped ZnO films. The use of polymer electrolyte enhanced the sensitivity of the device which is more effective in methanol vapor. The response and recovery time of gas sensor is significantly improved in three terminal devices than the two terminal devices.

**Keywords:** EDL gate dielectric, Field effect transistor sensor, Al doped ZnO, Polymer electrolyte.

## I. Introduction

Gas sensing technologies have attracted much more attention of the scientific community, industry, and academia with increasing applications of industrial productions, medicines, automotive, indoor air quality control, environmental monitoring, etc. Due to the different applicability and inherent limitations of various gases, researchers have been working on different scenarios with enhanced gas sensor calibration [1]. Semiconducting metal oxides such as ZnO, SnO<sub>2</sub>, TiO<sub>2</sub>, WO<sub>3</sub>, CuO, and Fe<sub>2</sub>O<sub>3</sub> are strong and well-researched material for gas sensing applications. Different types of oxide-based nanostructures such as nanoparticles, thin films, nanorods [2], and nanowires have been synthesized and employed in the fabrication of gas sensors. It was found that chemical components, surface states, morphology, and microstructure play an important role in gas sensing performance. Among the various oxide semiconductors, ZnO, a wide direct-band gap(~3.2eV) semiconductor with wurtzite structure, is a promising candidate due to its strong shape, size, and surface tenability. It is non-toxic, eco-friendly, cost-effective and easy to synthesize [2,3]. The surface of ZnO is depleted due to the absorption of gases from the

environment. Thus, the electrical conductivity of ZnO can be drastically changed in the presence of reactive gases present in the environment [4]. The doping of foreign elements like Al, Cu, Ag, etc. in ZnO increases its conductivity and sensitivity by changing the shape and surface morphologies of ZnO. The defect states of ZnO may change with doping concentration, which has a higher role in carrier transport phenomena. Also, doping Aluminum makes the film more transparent and has huge application in fabrication of optical detector [5].

The moderately high carrier mobility, surface and shape tenability, easy functionalization and doping are the major strength of ZnO. Though the numerous significance of nanostructure ZnO are listed for electronic, optoelectronic and sensing applications, it has serious drawback because of slow response, sample inhomogeneity and lack of reproducibility, especially for chemically grown nanostructured films. These drawbacks of ZnO films are reduced by doping, functionalization and surface treatment and improve the performance index in electronic and optoelectronic applications [6]. In this report, we have used an alternative method to control the ZnO channel resistance using polymer electrolyte which aids surface modification to the film without changing its stoichiometry. The effect of polymer electrolyte on ZnO surface is purely electrostatic and it can control by applied bias voltage in there terminal device [6]. In this study we compare the two terminal and three terminal ZnO based gas sensor using polymer electrolyte. The objective of this study is to elaborate and establish the significance enhancement of sensitivity and quick response of gas sensor using polymer electrolyte.

Nowadays, conventional oxide-based gate dielectrics in field effect devices have been superseded by polymeric electrolyte gate dielectrics because of its high carrier accumulation strength especially in oxide material and relevancy in field effect transistor (FET) with nanostructured channel where the control of grain boundary (interface between two crystallites) charges substantially controls charge transport in the channel. The electric double layer (EDL) formed by polymer electrolyte with ZnO surface induces huge surface charges which enhance the mobility and the drain current (current through the semiconductor channel) by passivizing the charge defects and changing the occupancy of defect states [7]. Filed effect transistor configuration is a popular electrochemical sensor used as a transducer for over 40 years. In many reports conventional oxide materials are used as gate dielectric which requires high vacuum technology. Here we have used the polymer electrolyte in gel form and drop cast on ZnO surface which is simple cost-effective vacuum free method and have high performance index even used for flexible electronic [8]. Though there are several reports on fabrication of gas sensor using ZnO material, but there is no reports on gas sensor using polymer electrolyte as a gate dielectric till date. In this work the transducer has two major components one is ZnO channel which generate the electrical signal after imposing analyte gas and another is the polymer electrolyte which is also sensitive to the analyte. The polymer electrolyte surface directly interacts with target analyte and the ZnO channel converts this interaction to electrical signal. Whenever the target analyte (gas) interacts with polymeric dielectric, it proliferate electrons as freebie to the EDL dielectric polymer which leads to an immense enhancement in drain current. As soon as the gas is removed, atmospheric oxygen molecules are further adsorbed and supplied Gate-Source voltage begins to stabilize the charge in the EDL minifying the drain current back to its former value [9]. The control of the sensor is directly linked with applied gate bias [10].

In this work, we doped various concentrations (1-5% Vol.) of Aluminum on Zinc Oxide films. Among them 3% concentration of Al doped ZnO film showed high value of conductivity and appropriate for the fabrication of TFT

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4 using LiClO<sub>4</sub> and Polyethylene Oxide (PEO) as gate dielectric. Use of polymer electrolyte dielectric in two terminal  
5 device fabricated by 3% AZO film interestingly enhanced the sensitivity for methanol vapor and fast response and  
6 recovery time is achieved in three terminal (Polymer electrolyte gating) devices. Thus this vacuum free, cost  
7 effective solution method is a promising alternative for the fabrication of alcohol sensor in future.  
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10 The aim of the research is to provide a high quality of FET for gas sensing application that can monitor the alcohol.  
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## 16 II. Methodology

17 The approaches that have been taken for the entire fabrication of sensor and its application process can be  
18 summed up in following steps:  
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### 20 Deposition of thin film:

21 Among various methods for deposition of thin film like electro-chemical deposition method, spray  
22 pyrolysis, chemical vapor deposition, molecular beam epitaxy[11] and so on, spin coating was found budget and  
23 labframe-feasible because of its plainness, cost-efficiency, facile doping, low operating temperature, and regulative  
24 spin and film thickness. The substrate is rotated at high speed after drop-casting a very few amounts of coating  
25 material over it to distribute the material uniformly all over it then annealed for the evaporation of the unwanted  
26 solvent and continued until the desired thickness or resistance of the film is achieved [8-11].  
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29 For 0.5 M precursor solution (Solution for pure ZnO thin film), 13.3872 g of Zinc Acetate Dihydrate (ZAD) and 6ml  
30 of Diethyl Amine (DEA) added to 120 ml of Ethanol was stirred at 300 rpm for an hour at room temperature.  
31 For 0.5 M dopant solution, 1.91 g Aluminium Nitrate in 20 ml Ethanol is stirred at 300 rpm for an hour at room  
32 temperature. Then, 0.2 ml, 0.4 ml, 0.6 ml, 0.8 ml, and 1.0 ml of dopant solution is added to 19.8 ml, 19.6 ml, 19.4  
33 ml, 19.2 ml, and 19.0 ml of precursor solution for doping 1%, 2%, 3%, 4%, and 5% of Aluminium by volume  
34 respectively and stirred at 300 rpm for an hour at room temperature.  
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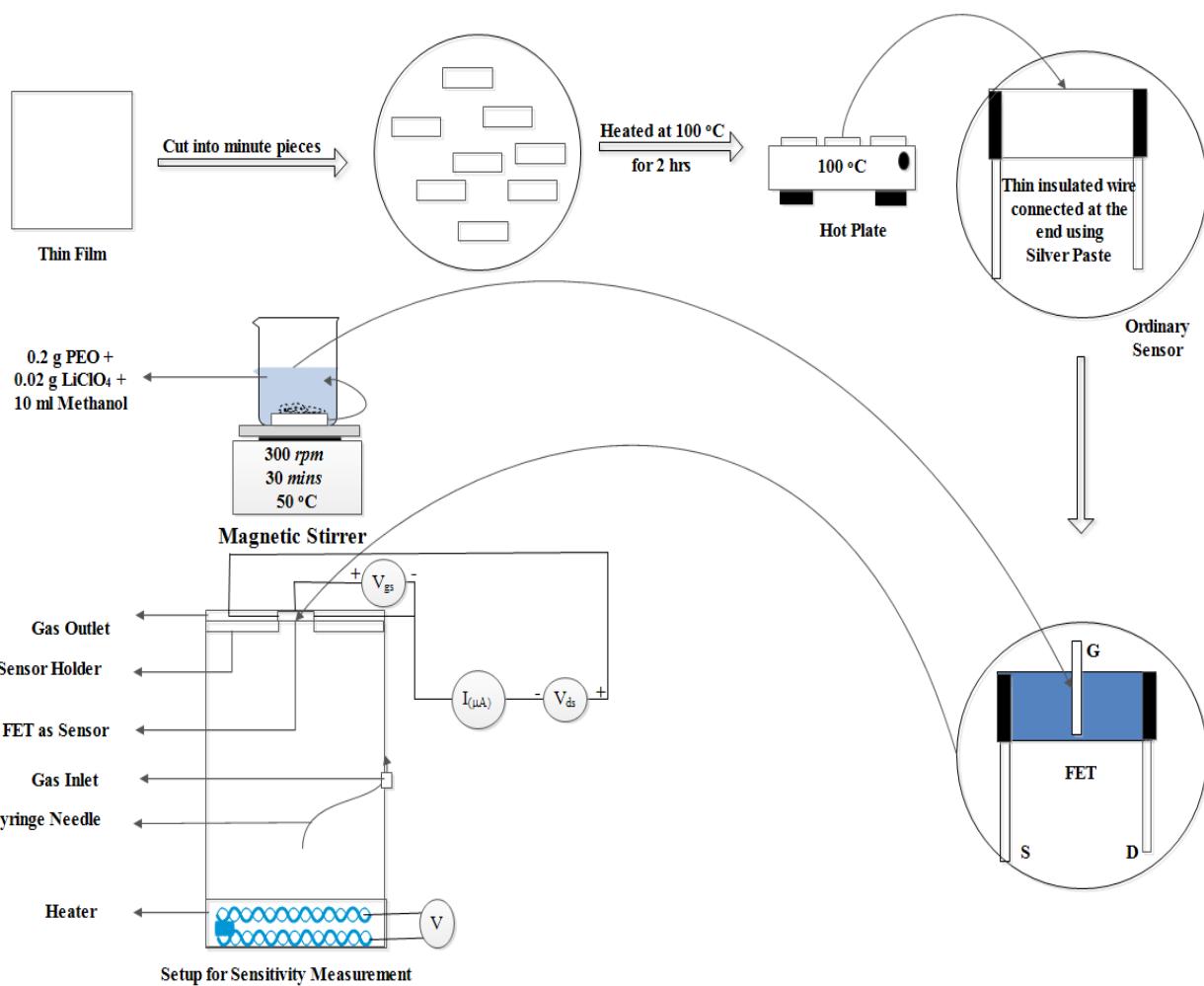
37 0.1ml of precursor solution was spread over the spinning (at 3000 rpm for 30 seconds) substrate in a spin coater and  
38 was annealed over the hot plate at 550°C for 15 minutes.  
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4 **Fabrication of Sensor:**

5 The films fabricated are further cut into minute pieces (3 mm x 7 mm) and heated at 100 °C for 2 hours. As  
6 soon as the film gets heated, thin insulated wires-conducting at the ends are connected to both the ends of the film  
7 using Silver paste; these are then ready to use as an ordinary sensor. Two heating system is adjusted at the ends of a  
8 cylinder of the volume of about 300 cm<sup>3</sup>; heater at the top is to monitor the temperature of the film (sensor) and  
9 heater at the bottom is to evaporate liquid (if necessary). The needle of the syringe is adjusted as shown as in the  
10 figure below so as to pass gas or drop liquid over the heater. This is the way, how ordinary sensors are constructed  
11 using fabricated thin films.  
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14 The EDL gate electrolyte is prepared by stirring 0.2 g of Polyethylene Oxide (PEO) and 0.02 g of Lithiumchlorate  
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54 Figure 1: Fabrication of FET as a Sensor and Setup for Sensitivity Measurement.  
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56 (LiClO<sub>4</sub>) in 10 ml of Methanol at 300 rpm, and 50 °C for 30 minutes. The same procedure of constructing an  
57 ordinary sensor is followed then the contacts between the wire and film are insulated using glue and a single drop of  
58 electrolyte is drop cast and spread over the channel. Soon, an insulated thin wire-conducting at the ends is placed  
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gently over the electrolyte and the device is allowed to dry. As soon as the electrolyte dries, for the stability of the device, source and drain wires across the channel and gate wire over the electrolyte are fixed over Printed Circuit Board (PCB) by soldering and substrate is glued. These are the procedure followed to construct the Thin Film Transistor (TFT). Then the device is ready for further characterization and application. As shown in figure 1, for the sensitivity measurement by FET, the ordinary sensor at the top of the former setup replaced by fabricated FET.

### Sensing Mechanism:

ZnO (n-type semiconductor) thin film surface, when exposed to air, adsorb oxygen molecules to form molecular type adsorbate ( $O_2$ ,  $O_2^-$ ) and dissociative type ( $O_2^{2-}$ ) adsorbate ions forfeiting electrons from the conduction band, yielding electron-depleted space-charge layer in the grain boundary region which leads to large surface potential barrier and large resistance. The target gas (ethanol/methanol) may undergo dehydration and dehydrogenation and successively oxidized to CO,  $CO_2$ , and  $H_2O$ , 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.

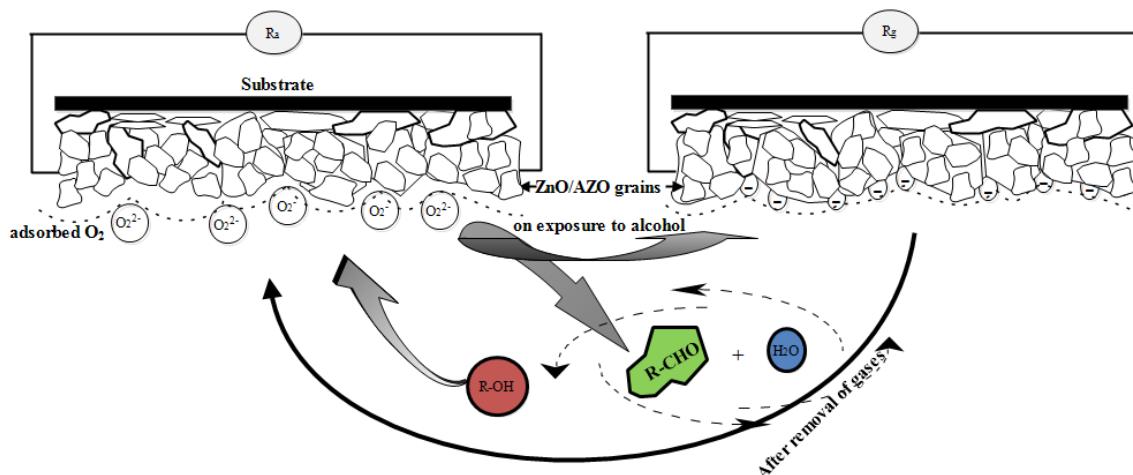
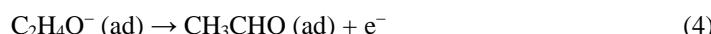
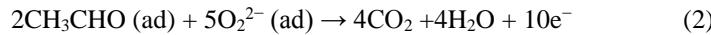


Figure 2: Sensing Mechanism of ZnO/AZO thin Film.

The release of electrons back to the film enhances the conductivity of the film and deduces the resistance. As soon as the vapor passes away, the film undue starts adsorption of atmospheric oxygen and tends to achieve its former

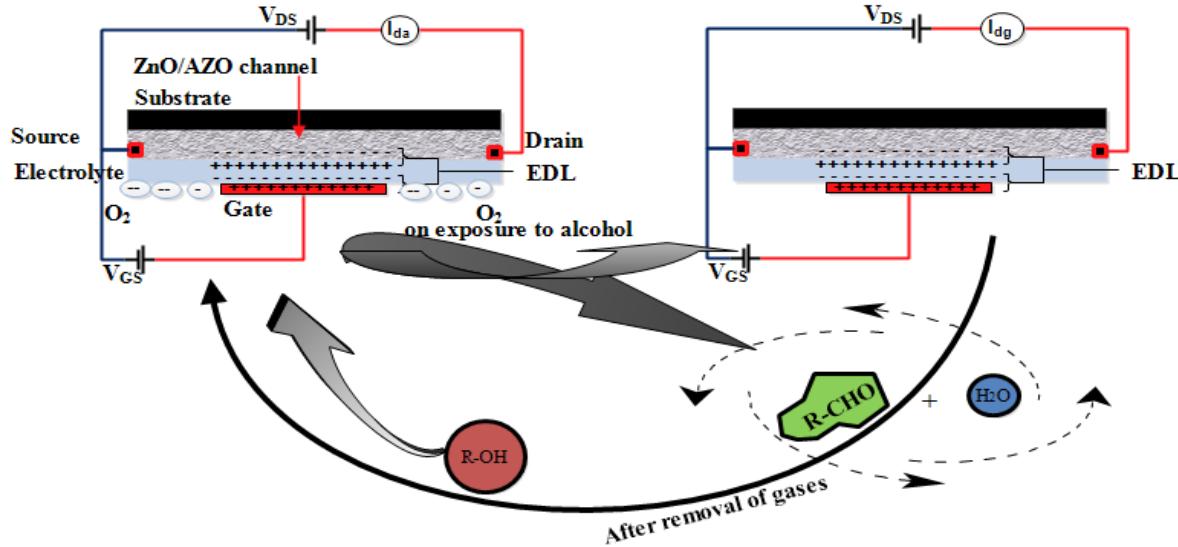


Figure 3: Sensing Mechanism of EDL gated TFT.

state [10]. Electric double-layer (EDL) gated thin-film transistor as a roseate candidate has attracted profound attention due to its huge ion-induced capacitance at semiconductor/electrolyte interface, sensitive interfacial features, low voltage operation and vehement gating effect strong enough to modulate the carrier density of the semiconductor channel.

The conversion of alcohol vapors into aldehydes due to adsorption of Oxygen at the grain boundary region [11, 12] is similar to bare films but its effect is quite alike as the adsorption here, affects the interfacial potential and enhances the channel current by an EDL capacitive coupling effect [9].

### 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. For indirect transition, the variation in absorption coefficient with the photon energy obey Tauc's plot method,

$$(\alpha h\nu)^{0.5} = A(h\nu - E_g)$$

(Eq. 1)

Where A is a constant,  $E_g$  is the optical band gap, h is the plank constant and  $\alpha$  is the absorption coefficient. Extrapolation of  $(\alpha h\nu)^{0.5} = 0$  yields the optical bandgap energy of the films [13].

The Tauc's Plot of Pristine ZnO and various concentrations of Al-doped ZnO thin films are plotted and corresponding bandgaps were evaluated as shown in figure 4.

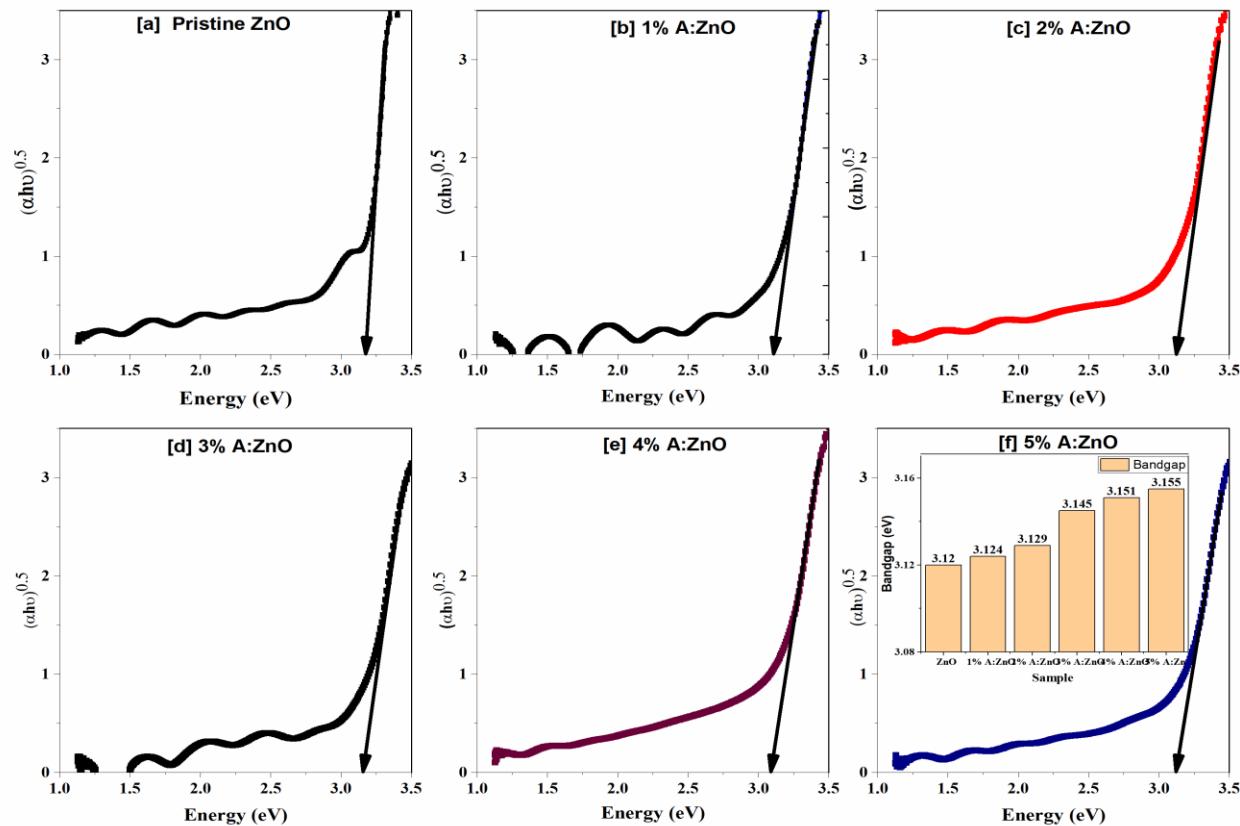


Figure 4: Calculation and Comparison of Bandgap Energy of pristine [a] ZnO thin film and [b-f] various concentrations of Al-doped ZnO films using Absorbance.

It is obvious that the direct bandgap of the AZO films increases with increasing Al content due to the fact that Al ions tend to occupy among ZnO lattice planes yielding the increase of the transport path of charge carriers into ZnO lattice and a significant decrease in grain size. Furthermore, when Al is doped in ZnO, donor electrons accumulated at the lower edge of the conduction band get excited to the higher energy levels in the conduction band with required extra energy which in fact broadens the optical bandgap of the film [5]. Here, the bandgap of pristine ZnO is found 3.120 eV, 1% Al-doped ZnO thin film is found to be 3.124 eV and the optical bandgaps are found gradually increasing to 3.155 eV on increasing, the concentrations of the dopant.

### X-ray Diffraction (XRD):

The structural characterizations of fabricated thin films are analyzed using XRD [Bruker D2 Phaser X-ray diffractometer of CuK $\alpha$  radiation (wavelength: 1.54184 Å)] at 40 KV of operating voltage and current of 40 mA in the 2 $\theta$  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,  $\lambda$  is the wavelength of the x-radiation,  $\beta$  is the full width at half maximum (FWHM) of the observed peak and  $\theta$  is the Bragg's angle. Comparing calculated d-spacings with the standard JCPDS values of card number 36-1451, the observed peaks are indexed.

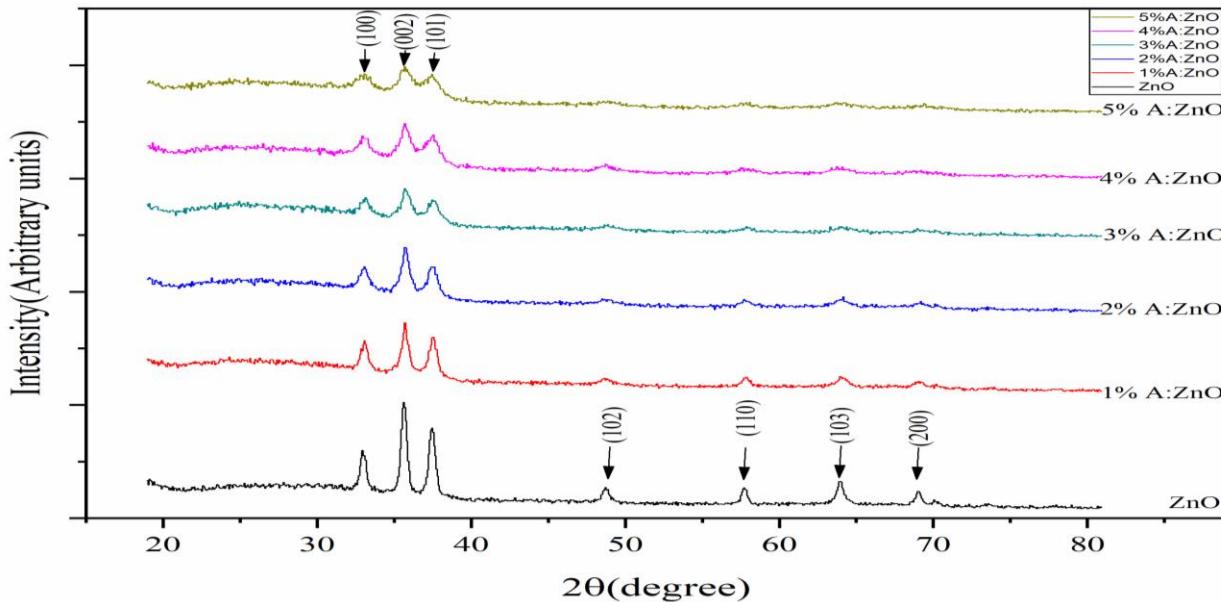


Figure 5: XRD pattern of undoped and Al-doped ZnO thin films labelled in legends.

Figure 5 and 6, significantly shows that all the diffraction peaks are observed around  $33.01^\circ$ ,  $35.61^\circ$ ,  $37.43^\circ$ ,  $48.70^\circ$ ,  $57.70^\circ$ ,  $63.92^\circ$ , and  $69.01^\circ$  corresponding to (100), (002), (101), (102), (110), (103) and (112) respectively, which depicts the films to be hexagonal crystallite in structure or polycrystalline in nature. In addition, no significant shift in XRD peaks are observed in Al-doped ZnO films compared to ZnO film with the exception of the peaks of (100), (002), and (101). Increasing doping concentration changed the peaks intensity and width, and minor peaks (102, 110, 103, 200) are seemed disappearing, whereas the three major peaks (100, 002, 101) are seen significantly decreasing due to the incorporation of Al in ZnO lattice [5].

The reason for the shift of (100), (002), and (101) peaks of AZO films towards larger angle direction as seen in figure 5 and 6, is substitution of zinc ions by Aluminium ions into hexagonal lattice of ZnO film and shifts in ZnO films are due to presence of Aluminium as impurity from its glass substrate [14].

Also, the average grain size can be calculated using Williamson Hall method, whose equation is given by,

$$\beta \cos\theta = \frac{k\lambda}{D} + \gamma \sin\theta$$

(Eq. 3)

Where,  $k$  is the shape factor,  $\lambda$  is the incident wavelength,  $\beta$  is the FWHM measured in radians,  $D$  is the average grain size,  $\gamma$  is the lattice strain and  $\theta$  is the Bragg angle of diffraction peak.

The lattice spacing parameter ‘d’ was calculated using relation:

$$d = \frac{\lambda}{2 \sin\theta}$$

(Eq. 4)

Further, for the hexagonal crystal structure, the lattice spacing ‘d’ can be calculated using the relation:

$$\frac{1}{d^2} = \frac{4(h^2 + hk + k^2)}{3a^2} + \frac{l^2}{c^2}$$

(Eq. 5)

where ‘h’, ‘k’, and ‘l’ are miller indices, and ‘a’, and ‘c’ are lattice constants.

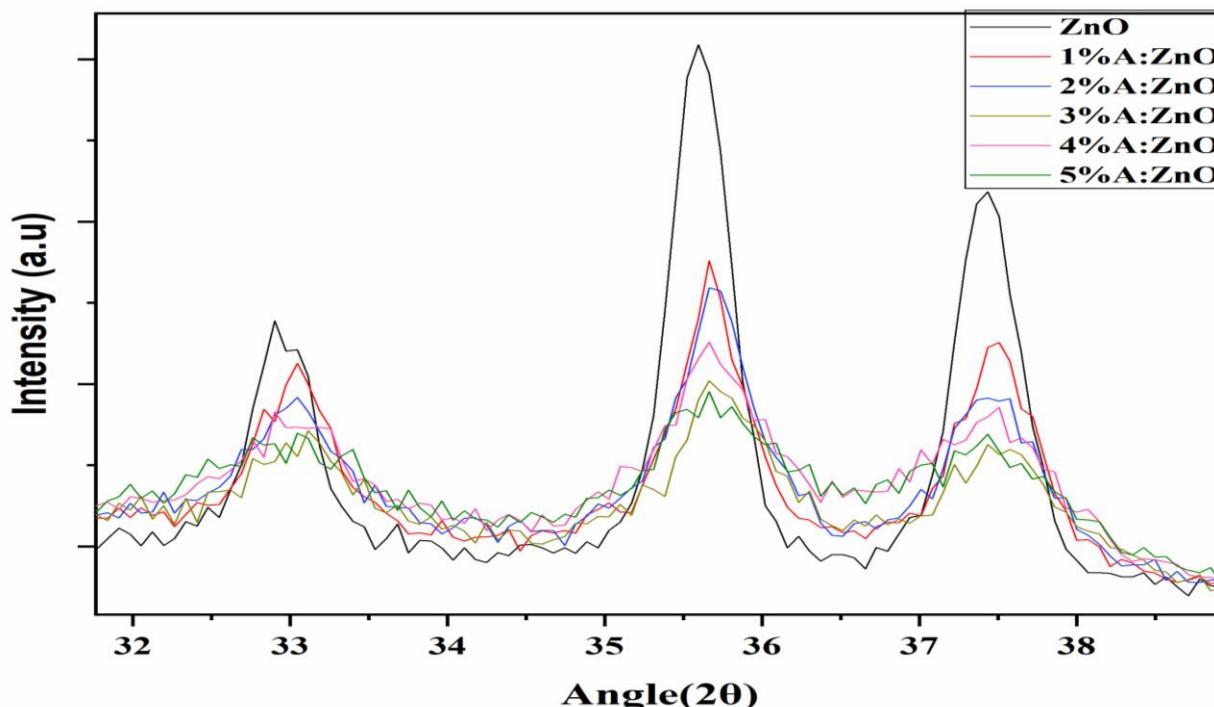
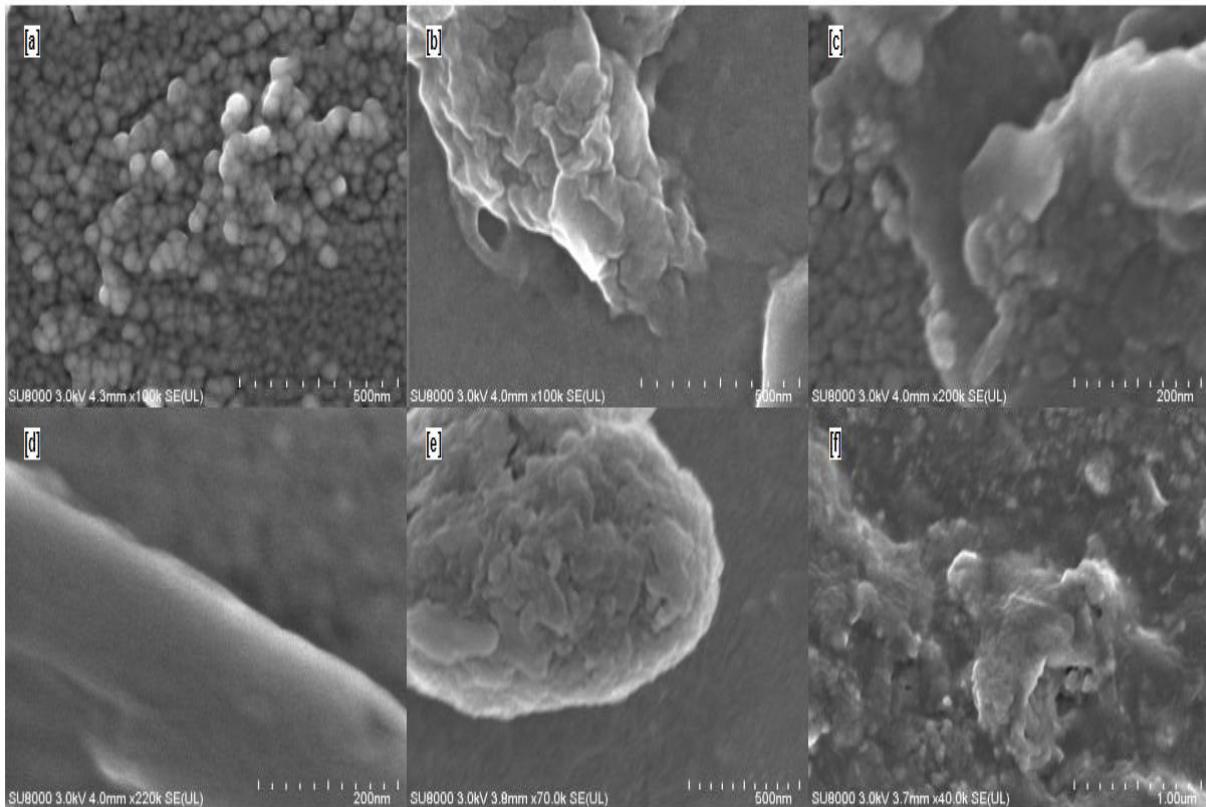


Figure 6: XRD Pattern of ZnO and Al-doped ZnO corresponding to (100), (002) and (101).

The particle size is determined from Sherrer’s equation (Eq. 2), and is found around 20 nm, 16 nm, 15 nm, 13 nm, 12 nm and 11 nm respectively. This significant decrease in particle size on doping and increasing the doping concentration is due to incorporation of Aluminium atom in place of Zinc atom in the lattice site [5].

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4 **Scanning Electron Microscope (SEM) and EDX analysis:**

5 The surface morphology of ZnO thin films were performed using Scanning Electron Microscope at  
6 Research Centre for Eco-Environment Sciences, Chinese Academy of Sciences, Beijing, China. The surface  
7 morphology of undoped ZnO thin film and various concentrations of Al-doped ZnO thin films **are** studied using  
8 Scanning Electron Microscope at Research Center for Eco-Environmental Science, Chinese Academy Science,  
9 Beijing, China. The SEM images of ZnO thin film and various concentrations of Al-doped ZnO thin films are  
10 attached herewith. These SEM images depict loosely packed, porous, spherical and homogeneously arranged granny  
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45 Figure 7: SEM Images of [a] Pristine ZnO thin film and [b-f] 1% - 5% Al-doped ZnO thin films respectively.  
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47 nanostructure. The porosity and surface roughness seem to be decreased on doping Al and again, increase in the  
48 dopant concentration has increased the roughness of the films too. The morphology of the sensing films has  
49 significant role in gas detection. Thus, porous surface with small grain size is considered to possess better gas  
50 sensitivity [15]. The uniformity of the film seems poor and may not be suitable for optoelectronic devices [16] but it  
51 has less impact in gas detection, thus can be used as gas sensor.  
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The EDX analysis was also performed in Research Center for Eco-Environmental Science, Chinese Academy of Science, Beijing, China along with SEM imaging.

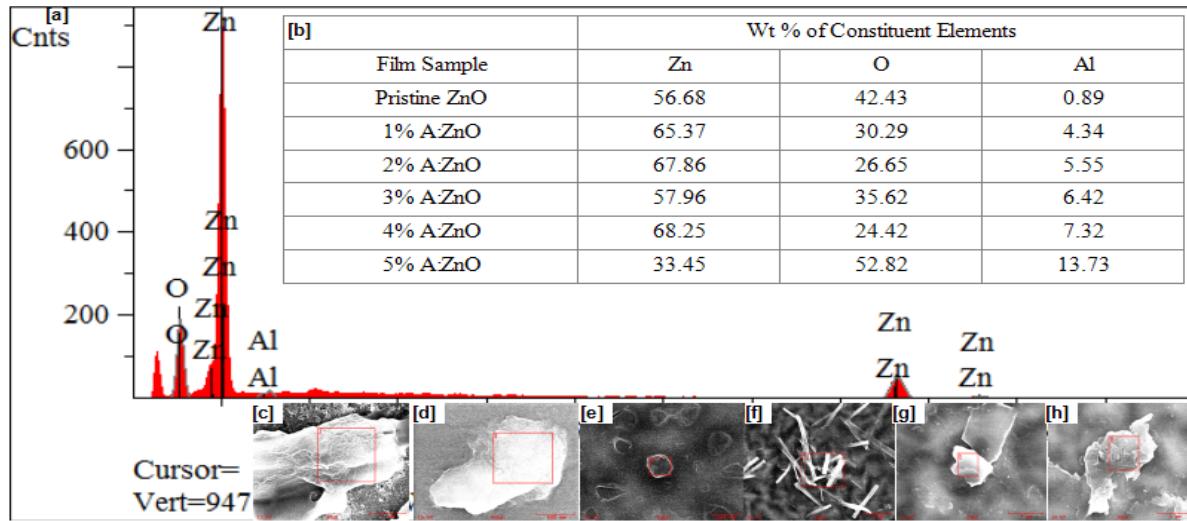


Figure 8: [a] EDX analysis image of 3% A:ZnO, [b] table representing wt. % of constituent elements in undoped and various concentration of Al-doped thin films, [c-h] SEM images of selected area of ZnO and various concentrations of Al-doped ZnO thin films over which EDX analysis was done.

The EDX data above confirms that the film composition is of elements zinc and oxygen in pristine ZnO film and Zinc, Oxygen and Aluminum in AZO films without any other impurities. Negligible wt. % of Al is found in the film of pristine ZnO too which may be due to Aluminium Silicate substrate. Increasing doping concentration has increased wt. %, but it does not resemble doping by volume concentration anymore which may be due to inhomogeneity in distribution of Al in the precursor during its preparation. Also, it may be due to the fact that EDX analysis is done by selecting a very little area of about  $100 \text{ nm}^2$  which is one out of 400 billion parts of the film prepared. So, the data of wt. % of Zinc and Oxygen seem quite erratic. Though the data, in overall, convince the film is homogeneous.

#### Resistivity of thin films

The electrical resistivity of ZnO and AZO is calculated using four probe technique using the relation

$$\rho = \frac{2\pi s V_{ds}}{I} \quad (\text{Eq. 6})$$

Here, constant current ( $I$ ) is passed through two outer probes and potential ( $V_{ds}$ ) developed across two inner probes is measured given that the distance ( $s$ ) between all the four probes is equal [17]. The value of resistivity of the film is found decreasing when the temperature of the specimen is raised. This is due to the fact that when temperature of the specimen rises, the electrons in the specimen get thermally excited and move towards the conduction band increasing carrier mobility. The resistivity of ZnO and AZO films calculated from eq (6) at various temperatures is graphed below:

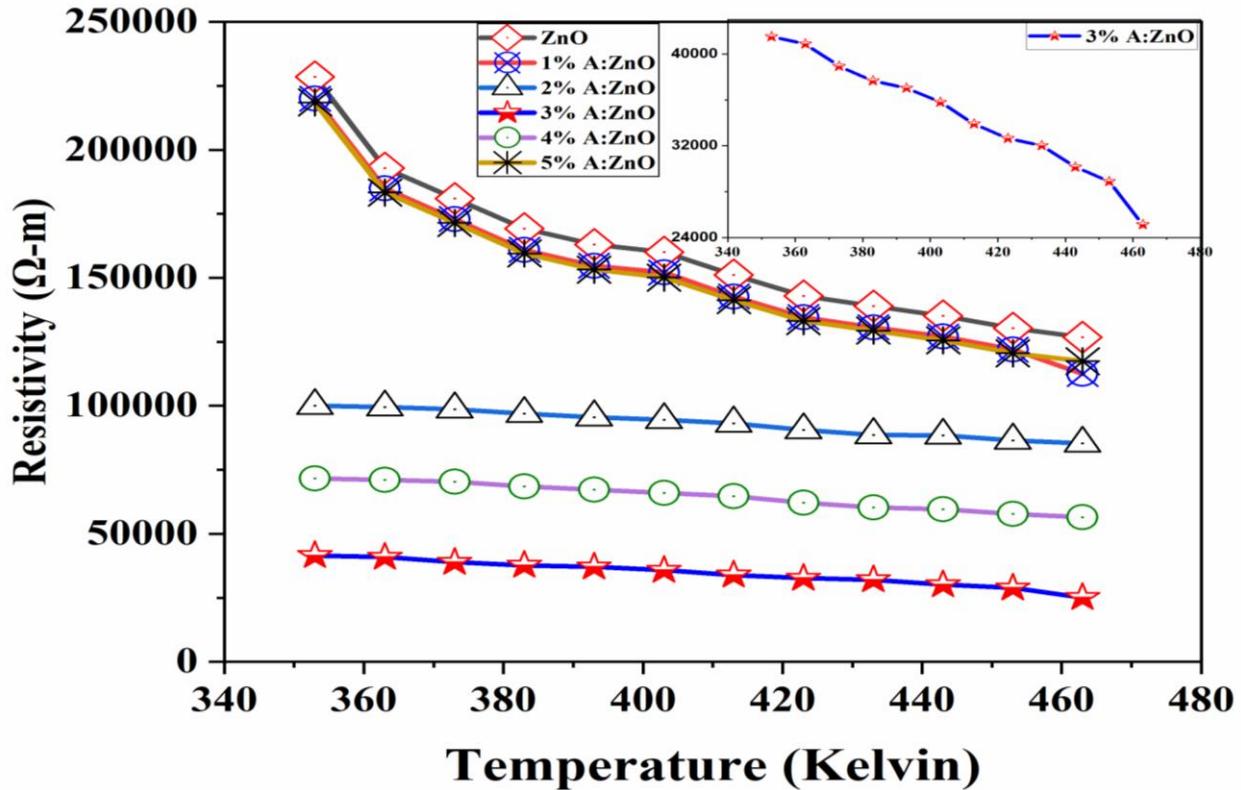
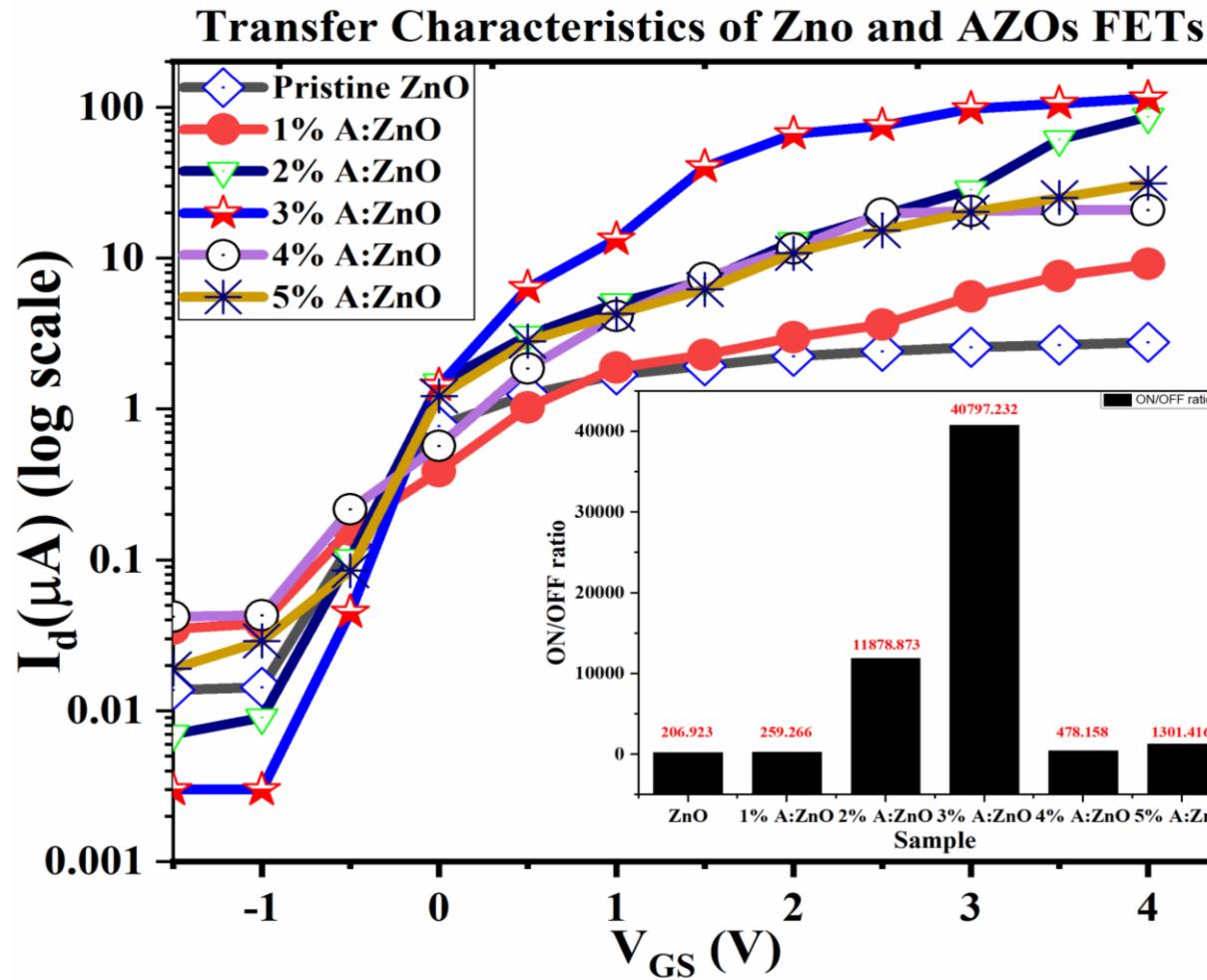


Figure 9: Resistivity of pristine ZnO and various concentration of Al doped ZnO varying with temperature.

The value of resistivity is found minimum for 3% Al-doped ZnO film at all temperatures and is found maximum for pristine ZnO sample at all temperatures. However, with an increase in the Al doping concentration above 3% by volume, the resistivity is found increasing significantly. When a small amount of Al is pioneered as dopant, Al ionizes to  $\text{Al}^{3+}$  and replaces  $\text{Zn}^{2+}$  yielding one free electron responsible for the increment of carrier concentration. Therefore, carrier concentration increases or resistivity decreases with increasing Al concentration at first up to 3 vol% doping. Further, on increasing Al concentrations, increasing Al dopant atom may form neutral defects and do not contribute free electron and the number of electrically active dopant atoms reduces in the film [2, 18]. This is the reason for the further decrement of the carrier concentration and resistivity increment.

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**Field Effect Transistor (FET) Characteristics**

5 The principal of transfer characteristics is the most important factor in evaluation of performance of TFTs.  
6 In this section, we will present transfer characteristics of ZnO and AZOs channeled, EDL gated TFTs and discuss  
7 about the findings. The transfer characteristics of pristine ZnO thin film and various concentrations of Al-doped  
8 ZnO thin films are studied keeping drain-source voltage ( $V_{DS}$ ) equals 1 Volt and varying gate-source voltage ( $V_{GS}$ )  
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45 Figure 10: Transfer Characteristics of ZnO and AZOs channelled, EDL gated TFTs.  
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47 from negative of 3 Volts to positive 4 Volts and the corresponding changes in drain current ( $I_d$ ) are noted.  $I_d$  versus  
48  $V_{GS}$  graph termed as "Transfer characteristics" is plotted and respective ON-OFF ratios i.e. ratio of maximum stable  
49 drain current to minimum stable drain current are calculated. The minimum stable current i.e. drain current of OFF-  
50 state of EDL gated 3% Al-doped ZnO TFT is found  $6 \times 10^{-4} \mu\text{A}$  and maximum stable current i.e. drain current of  
51 ON-state is found approximately  $115 \mu\text{A}$ . The transfer characteristic of 3% Al-doped ZnO is found fantabulous as  
52 expected as its ON-OFF ratio is found to be maximum (~40800) among the rest of the films which may endow the  
53 higher sensitivity. So, its drain characteristics were further studied keeping  $V_{GS}$  constant (-1 V, 0 V, 1 V, 2 V, 3 V, 4  
54 V) and varying drain-source voltage from 0 V to 5 V and noting the corresponding changes in drain current.  
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The drain characteristic of the concerned sample is too found conspicuous which is as shown in figure 11 below:

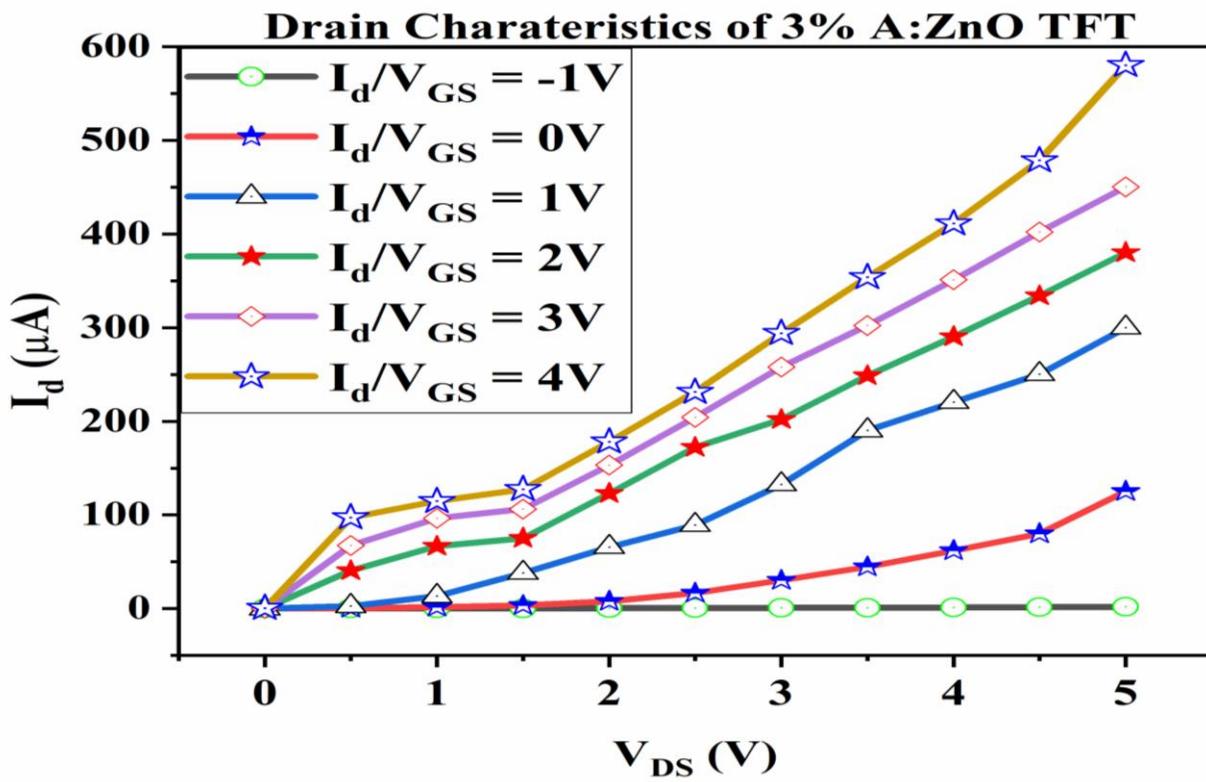


Figure 11: Drain Characteristics of 3% Al-doped ZnO channelled, EDL gated TFT at various Gate-Source Voltages.

### Sensitivity of the Sensors

The attenuation of film-resistance is prominent in two-terminal sensors and variation of channel current is kenspeckle in three-terminal sensors, so the sensitivity of the two-terminal sensor is calculated using the relation:

$$s = \frac{R_a - R_g}{R_a} \times 100\% \quad (\text{Eq. 7})$$

Where, 's' stands for sensitivity, R<sub>a</sub> and R<sub>g</sub> are resistances of the two-terminal sensors before and after exposure to alcohol vapors [9].

For the three-terminal sensor, slight modification i.e. resistances are expressed in terms of current in relation (7) is done and calculated as:

$$s = \frac{I_g - I_a}{I_g} \times 100\% \quad (\text{Eq. 8})$$

where 's' stands for sensitivity, I<sub>a</sub> and I<sub>g</sub> are channel current of the EDL electrolytic polymer gated TFT sensors before and after exposure to alcohol vapors. Here, R<sub>a</sub> is replaced by I<sub>g</sub> so as to obtain the sensitivity within the range of 0-100%. Else, sensitivity more than 150% would have been obtained which seems quite impractical.

Three different concentrations (50 ppm, 250 ppm, 500 ppm) of alcohol vapors are passed into the setup shown in figure 1, and the response and recovery time, and the corresponding decrease in the values of resistances are noted. The sensitivity of the two-terminal sensors i.e. bare films and EDL coated films at room temperature are calculated using relations 7 and 8 and their corresponding graphs are shown in figure 12.

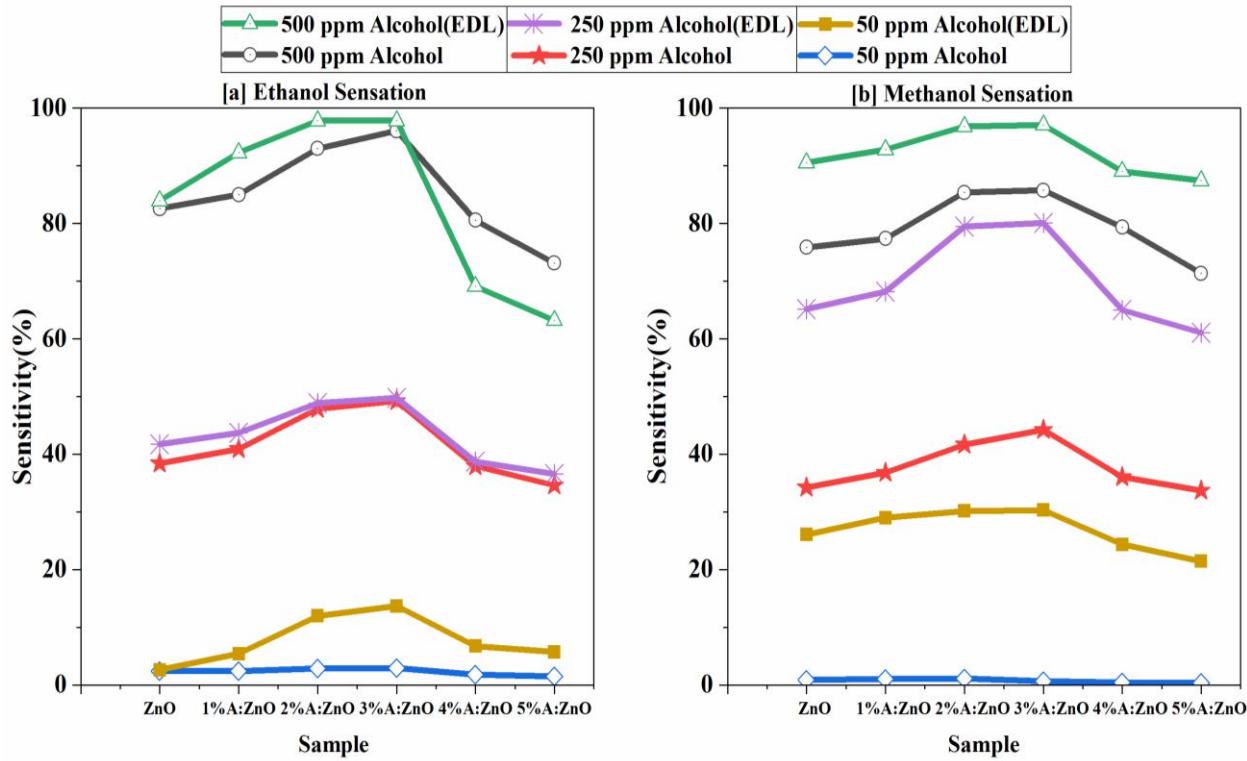


Figure 12: Sensitivity of Bare and EDL layered Two-Terminal Sensors in response to [a] Ethanol and [b] Methanol Vapors.

Sensing within room temperature is one of the challenges that we have faced and overcomed. The sensitivities of bare pristine ZnO and 1 to 5% Al-doped ZnO thin films range from 0.33% to 1.13% in response to 50 ppm of methanol, 1.5% to 2.9% in response to 50 ppm of ethanol, 33.69% to 44.22% in response to 250 ppm of methanol, 34.60% to 49.24% in response to 250 ppm of ethanol and 71.36% to 85.75% in response to 500 ppm of methanol, 73.13% to 96.06% in response to 500 ppm of ethanol; sensitivity in 3% Al-doped ZnO always succeeding and sensitivity in 5% Al-doped ZnO always preceding.

Furthermore, sensitivities of EDL coated pristine ZnO and 1 to 5% Al-doped ZnO thin films range from 21.46% to 30.32% in response to 50 ppm of methanol, 2.60% to 13.67% in response to 50 ppm of ethanol, 61.06% to 80.06% in response to 250 ppm of methanol, 36.59% to 49.74% in response to 250 ppm of ethanol and 87.43% to 97.08% in response to 500 ppm of methanol, 63.19% to 97.81% in response to 500 ppm of ethanol; sensitivity in 3% Al-doped ZnO always succeeding.

The sensitivity of films in response to higher concentrations of alcohol vapors is found higher. Higher concentrations of alcohol vapors mean a higher number of alcohol molecules. More, the number of reducing molecules, the more is the number of Oxygen reduced from the grain boundary of the film yielding an abrupt reduction in resistance of the film. This is the reason for such an upshot. The sensitivity of the bare film in response

to ethanol is always found greater than methanol. This is due to the fact that the oxidation potential of ethanol (-0.66 V) is less than that of methanol (-0.55 V) and higher the electrooxidation potential, it's more difficult to get oxidized [19]. Also, the sensitivity of 3% Al-doped ZnO thin film is always found succeeding sensitivities of the rest of the films. The smallest value of resistivity, smaller grain size, and its rough surface may have made it favorable for this result. The EDL electrolyte coated over the bare pristine ZnO and various concentrations of Al-doped ZnO sensors has enhanced the sensitivity of the film significantly but quite erratically. It shows the marvelous response to methanol than to ethanol vapors in enhancing the sensitivity. The use of methanol for the preparation of electrolyte polymer may be responsible for such a biasing response.

### Response and Recovery of Two Terminal Sensors

The time interval within which the film achieves its minimum value of resistance due to exposure of reducing gas is considered to be the response time while the time interval within which the film regains 90% of its initial value of resistance after removal of gas is considered to be the recovery time. Experiments for determination of response and recovery time of all sensors are performed. The change in resistances of the bare and EDL dielectric polymer coated ZnO and AZOs films in response to Ethanol and Methanol Vapors with respect to time are noted, graphed and response and recovery time are calculated. The response time of the sensor is found always shorter than the recovery time. Since the performance of 3% Al-doped ZnO sample is found excellent compared to the rest of the samples, so its response to both 500 ppm of ethanol and methanol vapors are graphed and shown in figure 13.

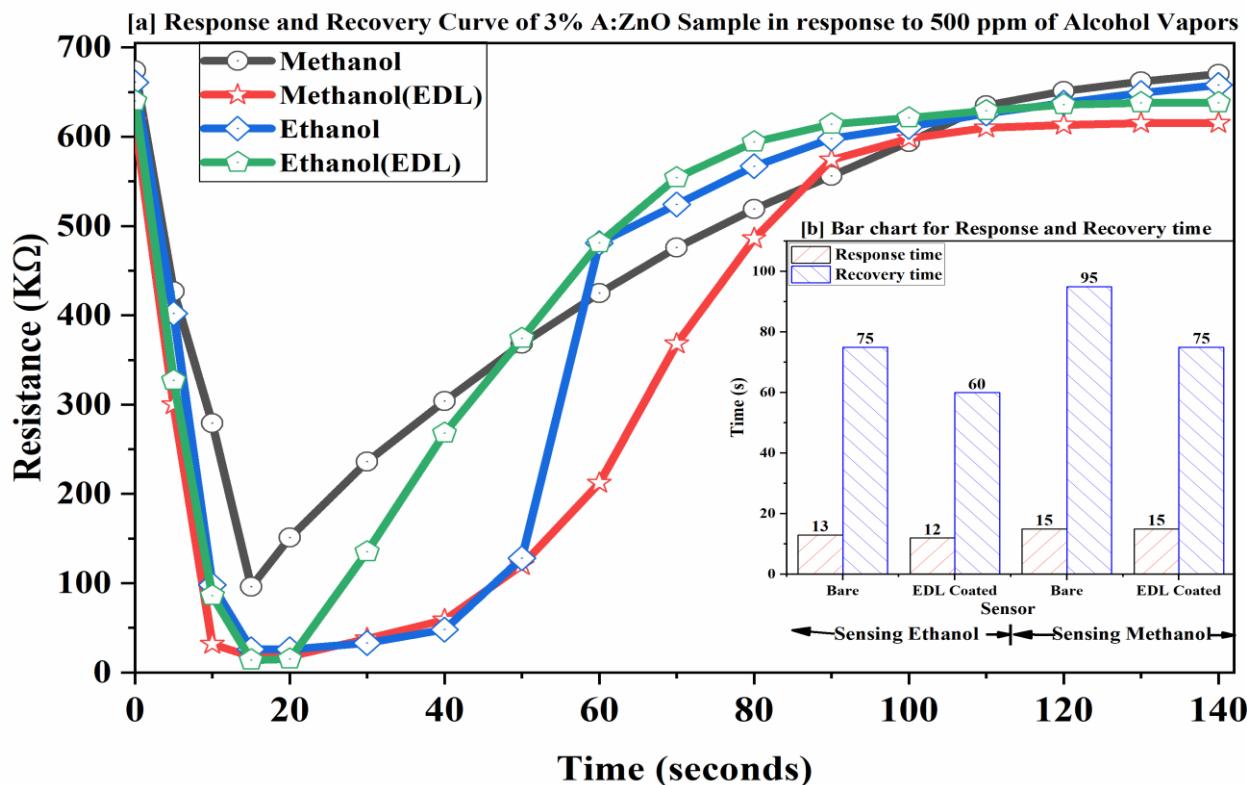


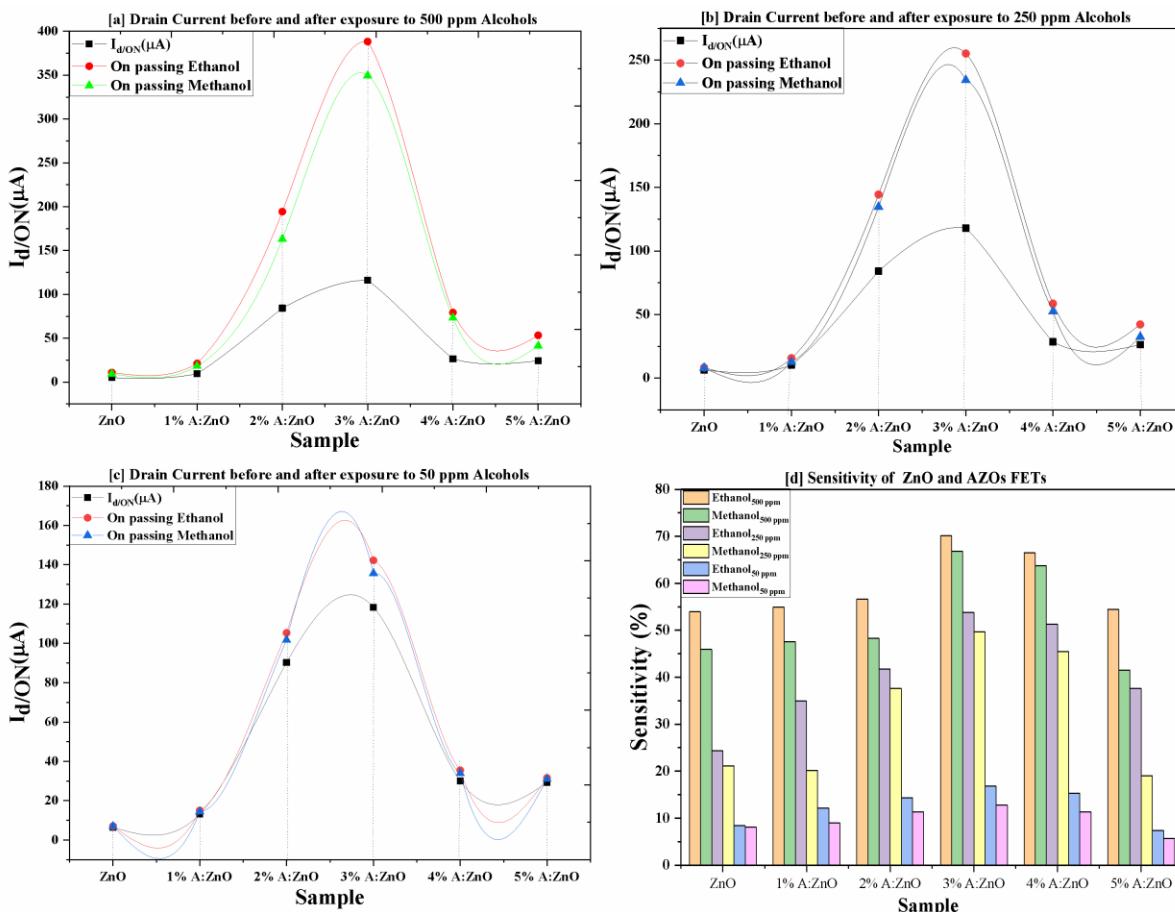
Figure 13: [a] Variation in Resistances of Bare and EDL Layered 3% A:ZnO films with respect to time in response to Ethanol and Methanol Vapors [b] Bar chart for response and recovery time of Bare and EDL coated 3% A:ZnO thin-film sensors.

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**Sensitivity, Response and Recovery of Three Terminal Sensors**  
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6 The response time for bare and EDL dielectric polymer coated 3% Al-doped ZnO sample is found to be 13  
7 s and 12 s in response to 500 ppm of ethanol vapors, 15 s and 15 s in response to 500 ppm of methanol vapors and  
8 the recovery time for the concerned sample is found to be 75 s and 60 s in response to 500 ppm of ethanol vapors  
9 and 95 s and 75 s in response to 500 ppm of methanol vapors respectively. Response and recovery time for ethanol  
10 vapors is always shorter than for methanol vapors which may be due to less oxidation potential of ethanol.  
11 Various concentrations of alcohol vapors are passed into the setup shown in figure 1 keeping the FETs at ON state,  
12 and the response and recovery time, and the corresponding increase in the values of drain current are noted.  
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**Sensitivity of Three Terminal Sensors**  
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18 The sensitivity of the three-terminal sensors i.e. FETs are calculated using relation 8 and their  
19 corresponding graphs are shown.  
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53 Figure 14: [a-c] Drain current, [d] Sensitivity of ZnO and AZOs channelled FETs before and after exposure to  
54 various concentrations of alcohol.  
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56 The sensitivities of pristine ZnO and 1 to 5% Al-doped ZnO channelled, EDL dielectric polymer gated thin-film  
57 FETs range from 5.65% to 12.75% in response to 50 ppm of methanol, 7.36% to 16.79% in response to 50 ppm of  
58 ethanol, 18.98% to 49.70% in response to 250 ppm of methanol, 24.35% to 53.82% in response to 250 ppm of  
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ethanol and 41.49% to 66.81% in response to 500 ppm of methanol, 53.91% to 70.11% in response to 500 ppm of ethanol; sensitivity in 3% Al-doped ZnO always succeeding the sensitivities of the rest of the samples. The sensitivity of 4% AZO channeled thin-film FET sensor is found approaching the sensitivity of 3% AZO channeled thin-film FET sensor.

The sensitivity in response to ethanol is found higher than in response to methanol for all equal concentration which is due to less oxidation potential of ethanol vapor. The sensitivities of TFTs sensors in response to higher concentrations of alcohol vapors are found higher. This is because higher concentrations of alcohol vapors have a higher number of alcohol molecules which reduces a huge number of oxygen molecules from the grain boundary of the polymer yielding an abrupt enhancement in channel current of the film. The low value of resistivity and sufficiently large value of the ON-OFF ratio of around 40800 ( $>10^3$ ) in 3% Al-doped ZnO channeled EDL electrolyte polymer gated TFT sensor is responsible for its higher sensitivity.

### **Response and Recovery of Three Terminal Sensors**

The time interval within which the film achieves its maximum value of drain current due to exposure of reducing gas is considered to be the response time while the time interval within which the film regains its initial value of drain current (+5% for our convenience) after removal of gas is considered to be the recovery time. Experiments for determination of response and recovery time of all sensors are performed. The significant change in channel current of the EDL dielectric polymer gated, ZnO and AZOs channeled thin-films in response to Ethanol and Methanol

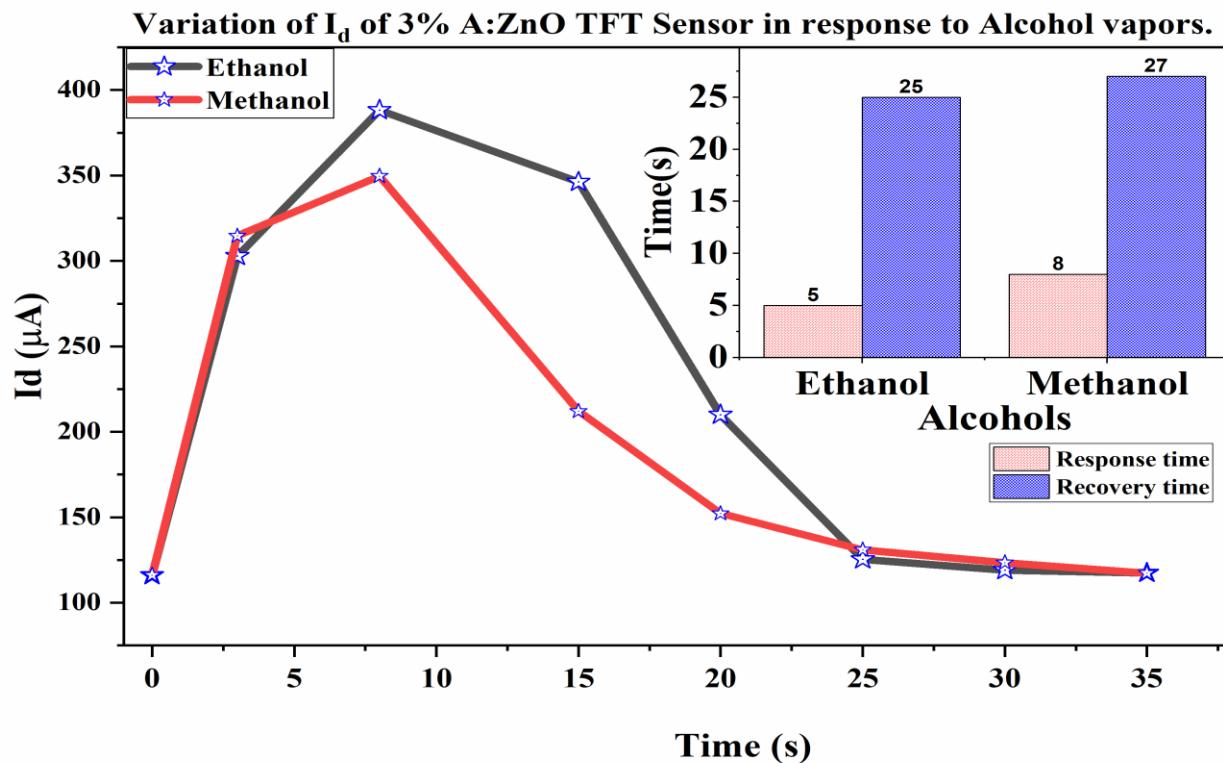


Figure 15: Variation of Drain Current of 3% A:ZnO channeled EDL dielectric polymer gated TFT in response to 500 ppm of Ethanol and Methanol Vapors, and Bar chart showing Response and Recovery time of respective TFT embedded.

Vapors with respect to time are noted, graphed and response and recovery time are calculated. The response time of the sensor is found always shorter than the recovery time. Since the performance of 3% Al-doped ZnO sample is found excellent compared to the rest of the samples, so its response to both 500 ppm of ethanol and methanol vapors are graphed as shown in figure 12.

The response and recovery time for 3% Al-doped ZnO channeled EDL gated TFT sample is found to be 5 s and 25 s in response to 500 ppm of ethanol vapors and 8 s and 27 s in response to 500 ppm of methanol vapors respectively. Response and recovery time for ethanol vapors is always shorter than for methanol vapors which may be due to less oxidation potential of ethanol. Also, it is obvious that response time is always shorter than the recovery time. The water vapor is produced during oxidation of alcohol vapors when they interact with EDL polymer which may take few more seconds to evaporate. This may be the reason for such upshot.

#### IV. Conclusions

Undoped and 1-5% Al-doped ZnO nanostructured thin films are synthesized using spin coating chemical method on glass substrates. The polycrystalline性质 of ZnO and AZOs films is confirmed by the XRD pattern and the SEM images. The films consists with loosely packed, porous and spherically arranged granny nanostructure with grain boundary. The analysis of optical results obtained from the UV-vis spectrometer has confirmed the increase in the bandgap of the film (3.12-3.16 eV). A small amount (3% by volume as optimum) of Al pioneered as dopant ionizes to  $\text{Al}^{3+}$  and replaces  $\text{Zn}^{2+}$  yielding one free electron responsible for the increment of carrier concentration (decrement in resistivity) whereas further increment of dopant gives rise to neutral defect, reduces the number of electrically active Al and give rise to further resistivity increment.

Among the grown films, the best conductive 3% Al doped ZnO film was used as a channel material to fabricate two terminal and three terminal gas sensor. Polymer electrolyte was used as gate dielectric for TFT application which can induce ultra-high charge carrier on surface of the Al:ZnO channel and enhance the performance index of TFT sensor. The sensitivity of two terminal device towards methanol vapor using polymer electrolyte is remarkable enhance in comparison to ethanol vapor. This means the polymer electrolyte is more sensitive to methanol vapor. Similarly, the sensitivity and the response and recovery time is improved in three terminal gate controlled field effect device.

Thus, this report suggests that 3% Al vol. is the optimum concentration of doping for the excellent performance of thin-film in sensing for ethanol and methanol. Furthermore, though the sensitivities of three terminal device is comparable to two terminal devices but TFTs are the promising candidate for sensing applications compared to two-terminal sensors because of their significant variation in drain current due response to alcohol vapors and shorter response and recovery time and controllability of channel current applying suitable gate-source voltage bias.

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**Acknowledgments**  
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