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STUDY ON ALCOHOL SENSING APPLICATION OF EDL DILECTRIC POLYMER GATED/NON-GATED, ZnO/AZO CHANNELED THIN FILM AND TRANSISTOR

--Manuscript Draft--

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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 DILECTRIC POLYMER GATED/NON-GATED, ZnO/AZO CHANNELED 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

STUDY ON ALCOHOL SENSING APPLICATION OF EDL DILECTRIC POLYMER GATED/NON-GATED, ZnO/AZO CHANNELED 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_2, TiO_2, WO_3, CuO, and Fe_2O_3 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

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 [2-5].

For over 40 years, in electrochemical sensors, Field effect transistors (FET) have been significantly used as transducers because of their enhanced sensitivity, resolution, low power, portability, and fabrication compatibility. They have been used to detect ions and biomolecules, and sense DNA sequencing and mobile diagnostics. The sensing surface (or receptor) which interacts with the target analyte (gas in our case) and the transducer which converts this interaction into a legible electronic signal are the two basic components of the sensor upon which the performance characteristics of the sensor depend. Since the target analyte interacts only with the receptor, sensor selectivity and predilection towards the target analyte depends exclusively on the receptor whereas the sensor sensitivity, resolution, and calibration are found to be influenced by both the components [6].

Nowadays, conventional oxide-based gate dielectrics in such devices have been superseded by electric double layer (EDL) gate dielectrics because of its relevancy in FET with nanostructured channel where the control of grain boundary (interface between two crystallites) charges substantially controls charge transport in the channel. EDL 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 [7]. 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].

In this research work, we will dop various concentrations (1-5% Vol.) of Aluminum on Zinc Oxide films and construct Field Effect Transistor (FET) using $LiClO_4$ casted Polyethylene Oxide (PEO) as Electric Double Layer (EDL) gate and study its gas sensing properties. The doping concentration can change gas sensing properties and transparency as well. The aim of the research is to provide a high quality of FET for gas sensing application that can monitor the alcohol.

II. Methodology

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

Deposition of thin film:

Among various methods for deposition of thin film, spin coating was found budget and labframe-feasible because of its plainness, cost-efficiency, facile doping, low operating temperature, and regulative spin and film thickness. The substrate is rotated at high speed after drop-casting a very few amounts of coating material over it to distribute the material uniformly all over it then annealed for the evaporation of the unwanted solvent and continued until the desired thickness or resistance of the film is achieved [5, 6].

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^{o}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 ^{o}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^3; 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

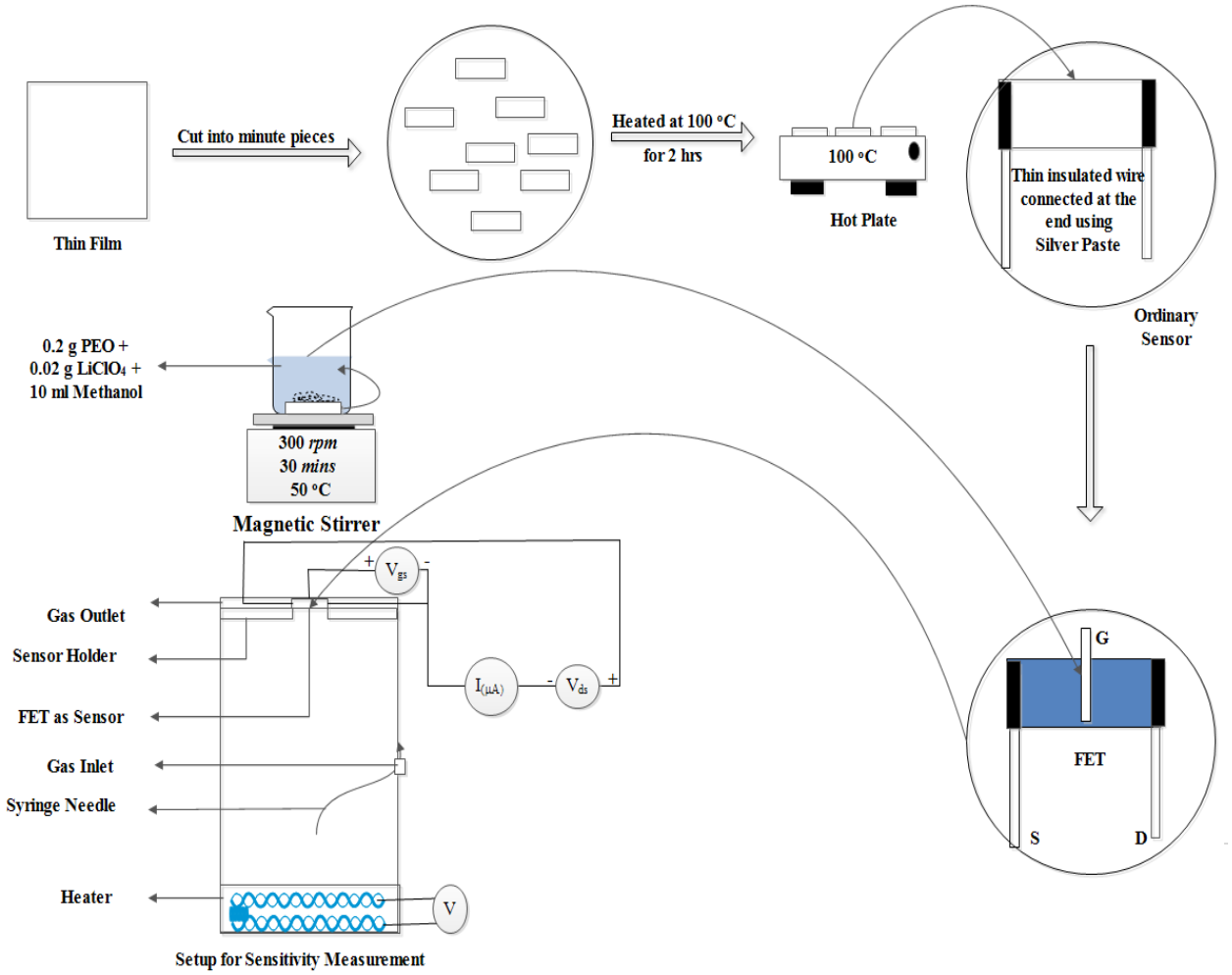


Figure 1: Fabrication of FET as a Sensor and Setup for Sensitivity Measurement.

($LiClO_4$) 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_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.

$$2C_2H_5OH \rightarrow 2CH_3CHO + H_2 \quad (1)$$

$$2CH_3CHO\ (ad) + 5O_2^{2-}\ (ad) \rightarrow 4CO_2 + 4H_2O + 10e^- \quad (2)$$

$$2C_2H_5OH\ (ad) + O_2^{2-}\ (ad) \rightarrow 2C_2H_4O^-\ (ad) + 2H_2O \quad (3)$$

$$C_2H_4O^-\ (ad) \rightarrow CH_3CHO\ (ad) + e^- \quad (4)$$

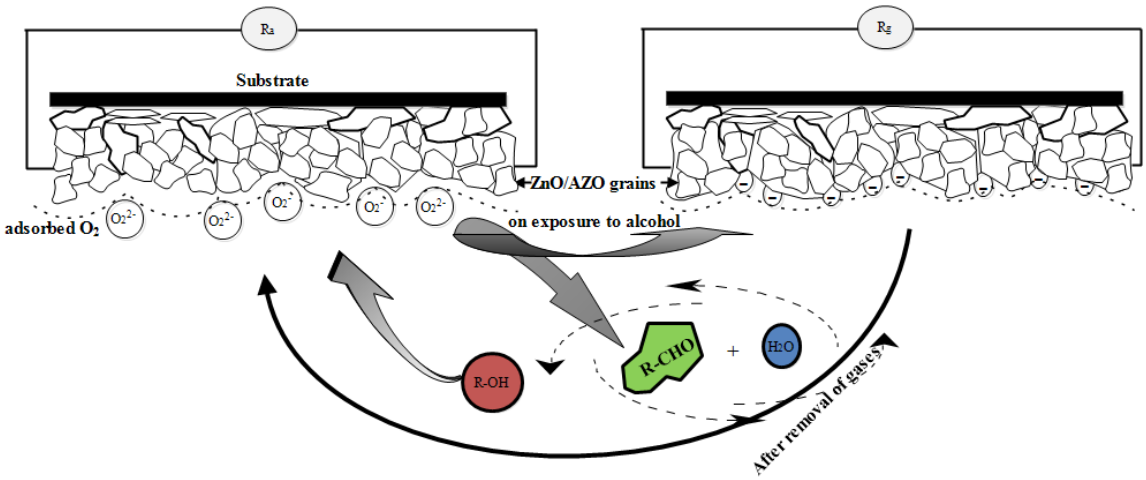


Figure 2: Sensing Mechanism of ZnO/AZO thin Film.

$$CH_3OH\ (g) \rightarrow CH_3OH\ (ad) \rightarrow CH_3O\ (ad) + H(ad) \quad (5)$$

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

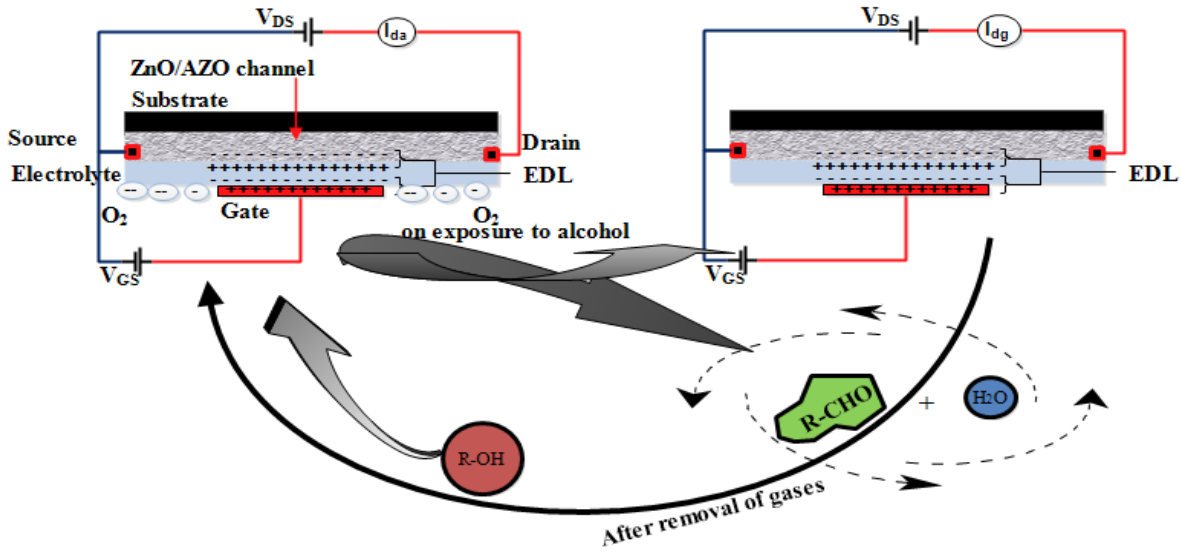


Figure 3: Sensing Mechanism of EDL gated TFT.

[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 α 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.

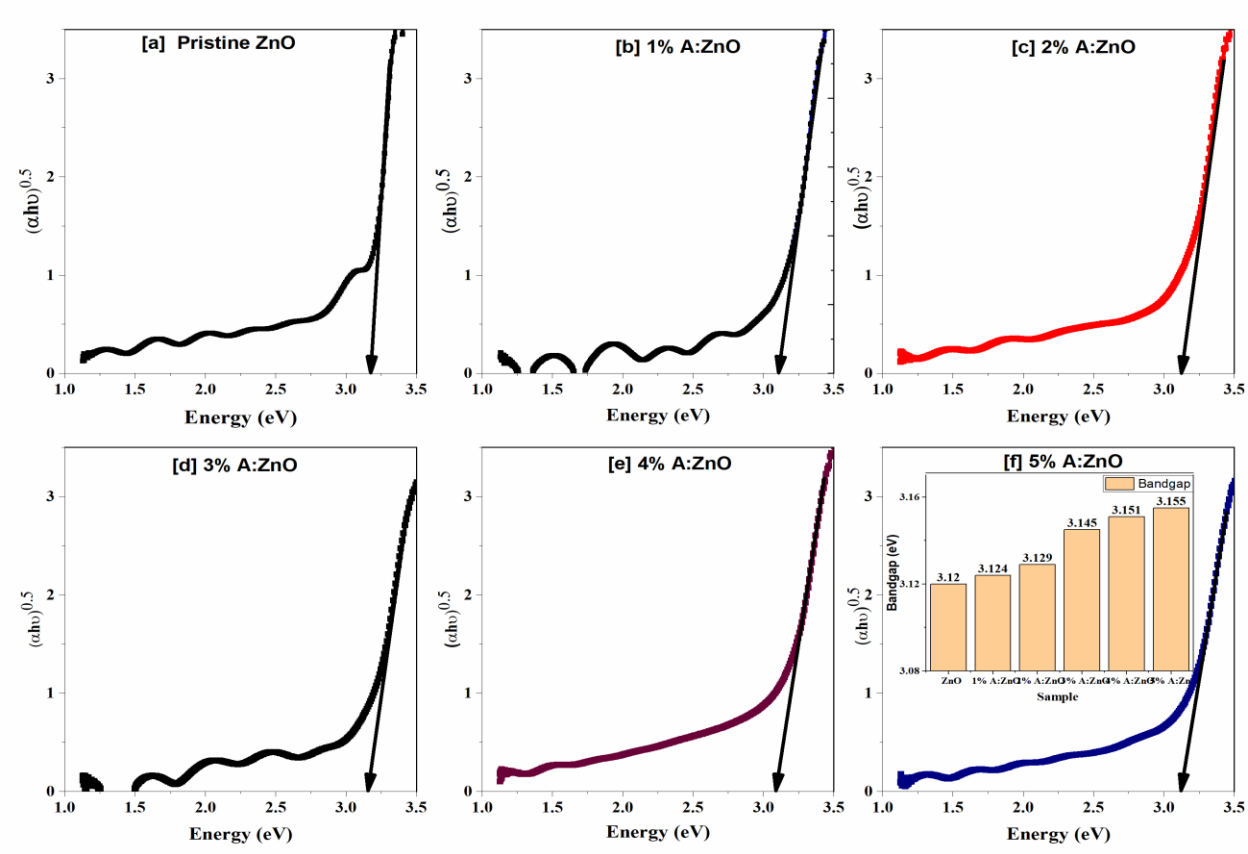


Figure 4: Calculation and Comparison of Bandgap Energy of pristine [a] ZnO thin film and [b-f] various concentrations of Al-doped ZnO films using Absorbance.

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 CuKα radiation (wavelength: 1.54184 Å)] at 40 KV of operating voltage and current of 40 mA in the 2θ range of 20° - 80° at scanning rate of 15° per minute at NAST, Khumaltar, Lalitpur, Nepal. The Debye Scherrer's formula used to calculate the average grain size 'D' is given by,

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

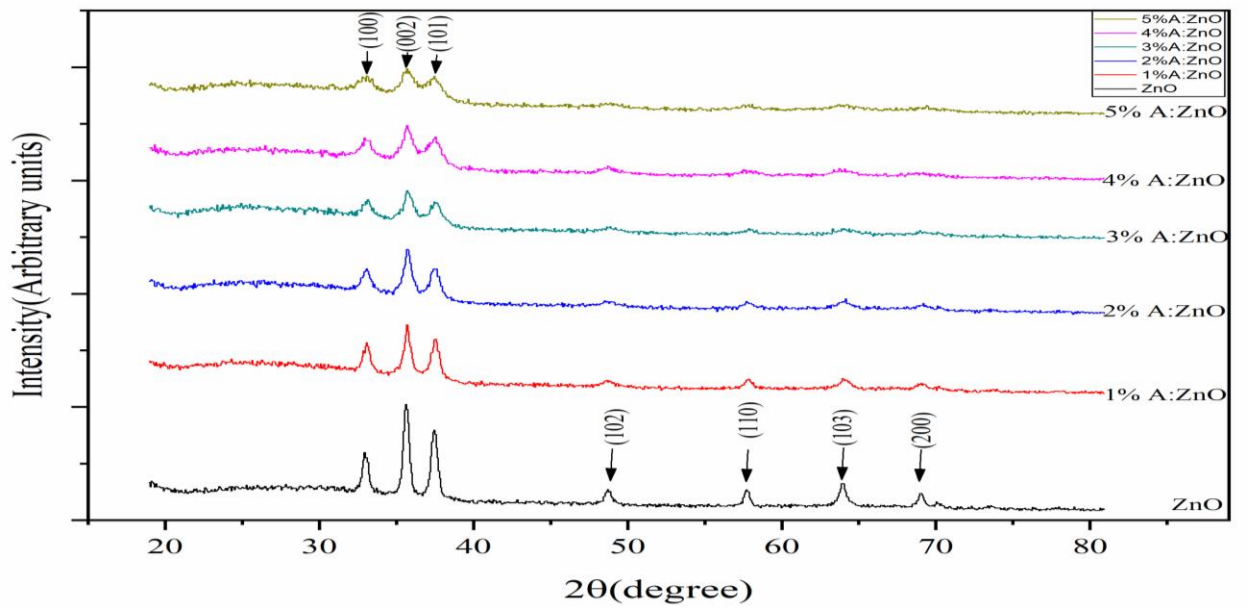


Figure 5: XRD pattern of undoped and Al-doped ZnO thin films labelled in legends.

(Eq. 2)

where, 0.9 is the correction factor, λ is the wavelength of the x-radiation, β is the full width at half maximum (FWHM) of the observed peak and θ is the Bragg's angle. 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,

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

(Eq. 3)

where k is the shape factor, λ is the incident wavelength, β is the FWHM measured in radians, D is the average grain size, ϒ is the lattice strain and θ is the Bragg angle of diffraction peak.

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

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

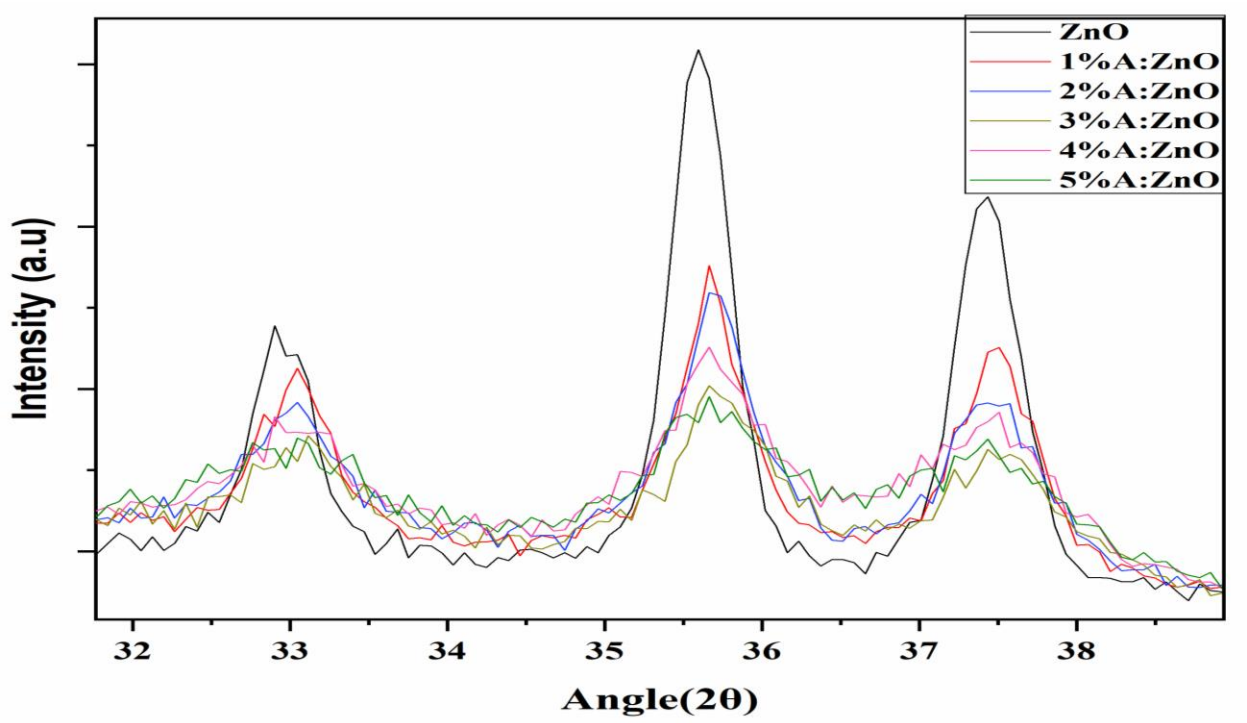


Figure 6: XRD Pattern of ZnO and Al-doped ZnO corresponding to (100), (002) and (101).

(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

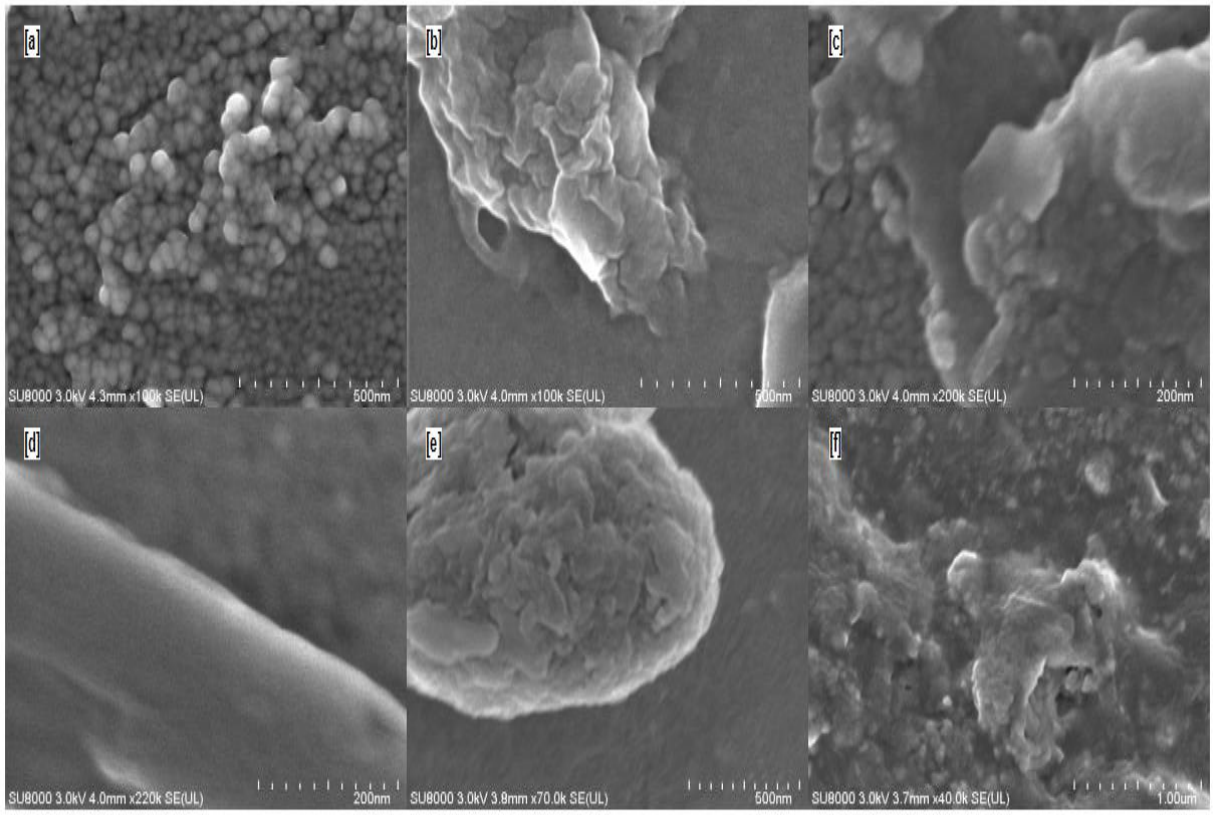
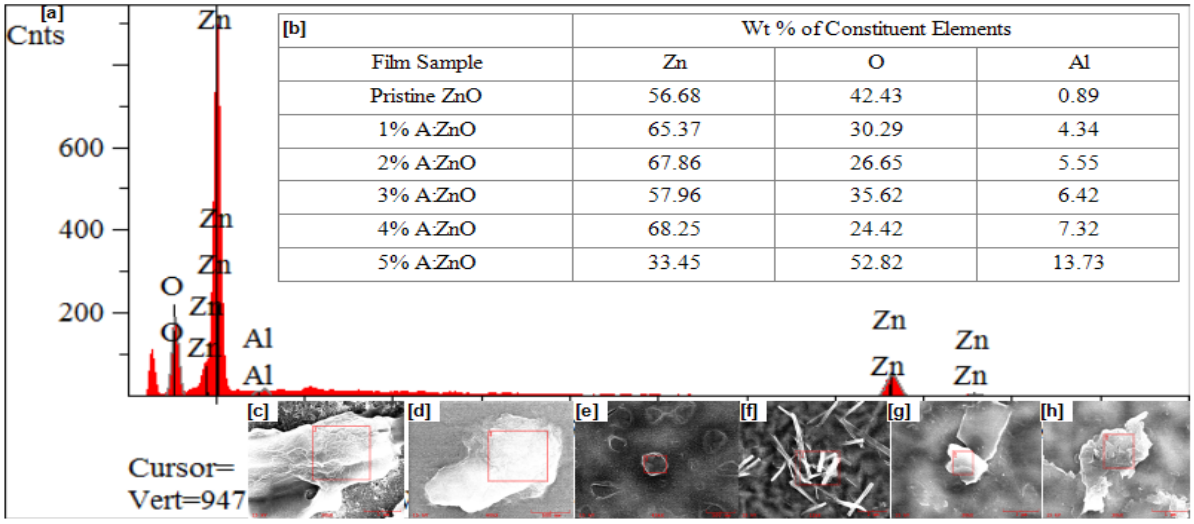


Figure 7: SEM Images of [a] Pristine ZnO thin film and [b-f] 1% - 5% Al-doped ZnO thin films respectively.

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.



[b]

Film Sample	Wt % of Constituent Elements		
	Zn	O	Al
Pristine ZnO	56.68	42.43	0.89
1% A:ZnO	65.37	30.29	4.34
2% A:ZnO	67.86	26.65	5.55
3% A:ZnO	57.96	35.62	6.42
4% A:ZnO	68.25	24.42	7.32
5% A:ZnO	33.45	52.82	13.73

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 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:

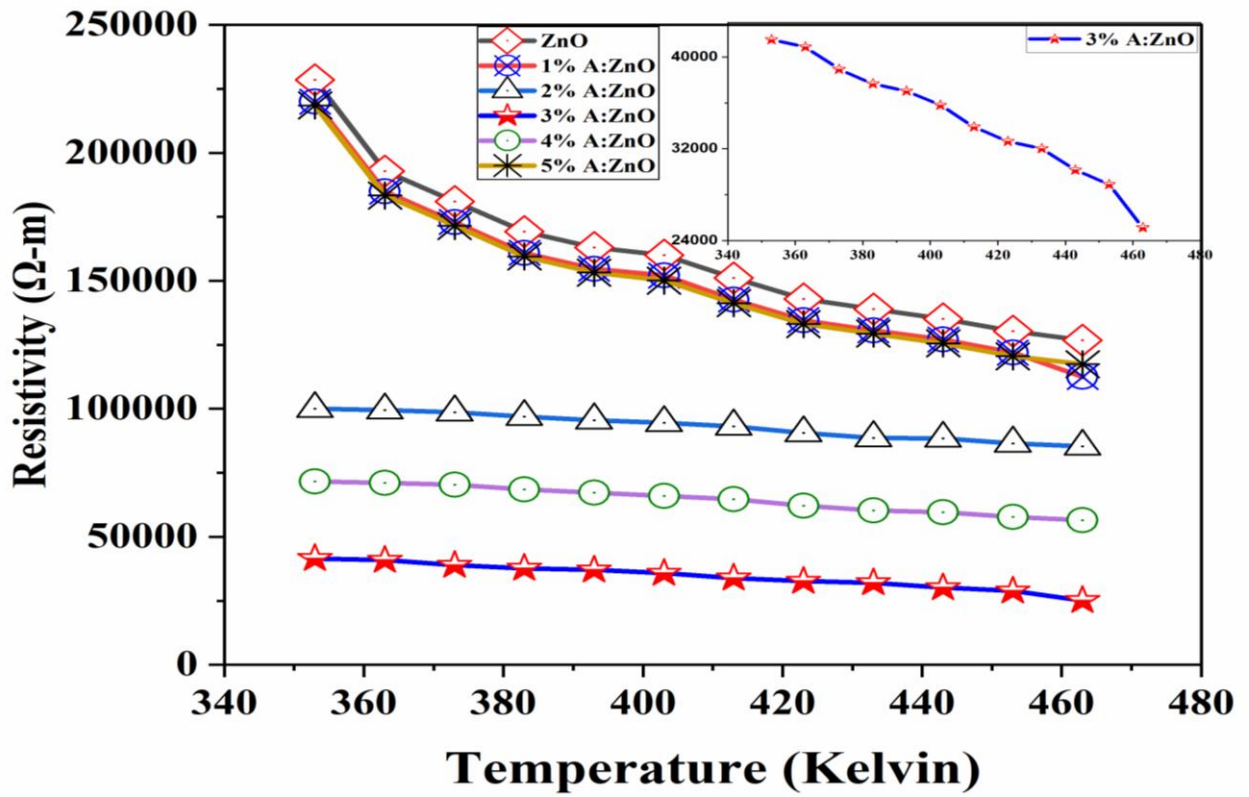


Figure 9: Resistivity of pristine ZnO and various concentration of Al doped ZnO varying with temperature.

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 Al^{3+} and replaces 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})

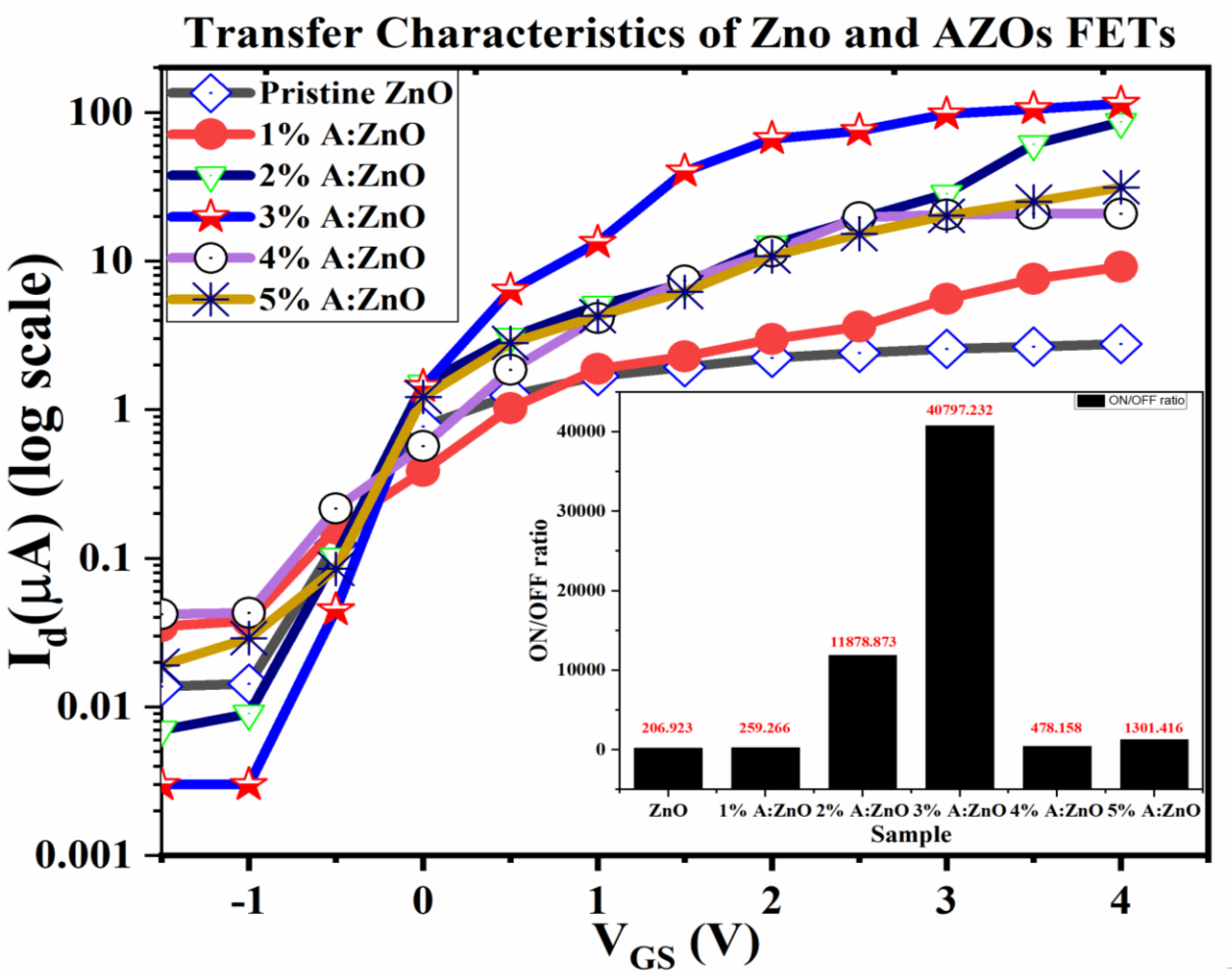


Figure 10: Transfer Characteristics of ZnO and AZOs channeled, EDL gated TFTs.

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 x 10^{-4} µA and maximum stable current i.e. drain current of ON-state is found approximately 115 µA. 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:

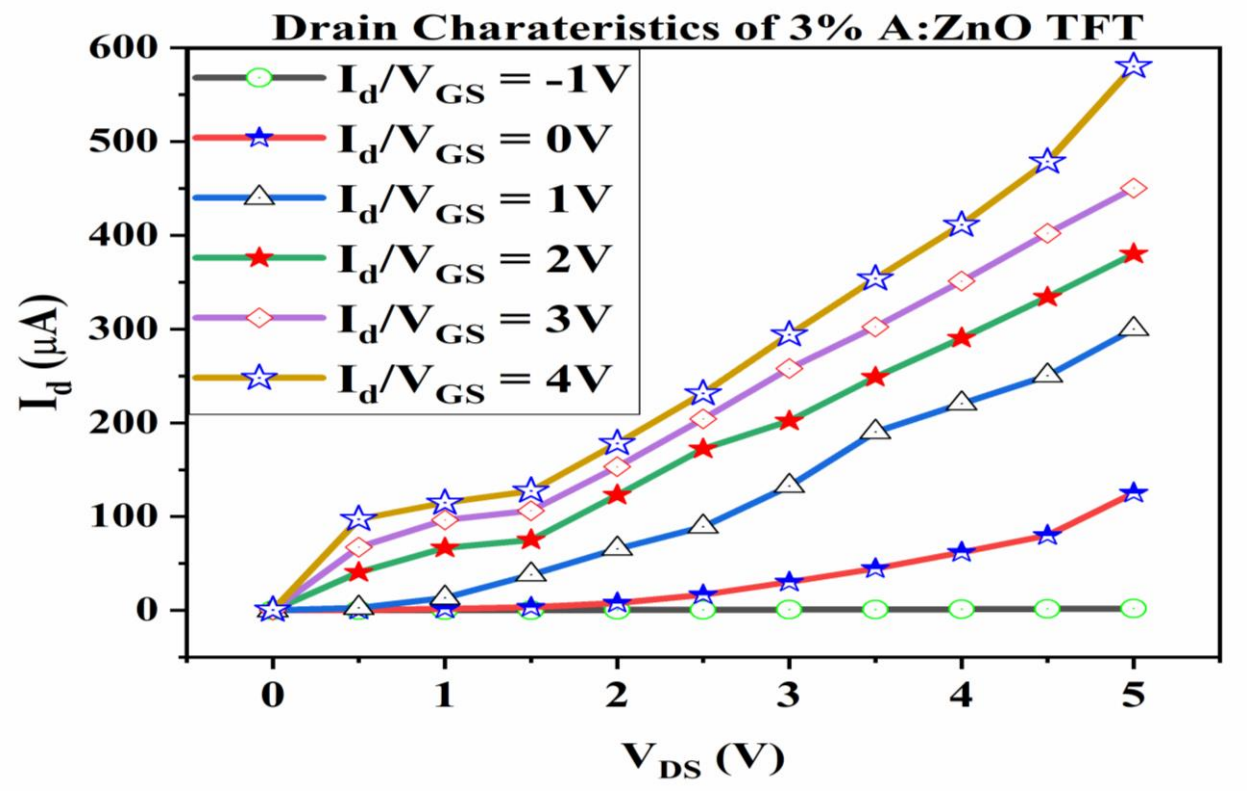


Figure 11: Drain Characteristics of 3% Al-doped ZnO channeled, EDL gated TFT at various Gate-Source Voltages.

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.

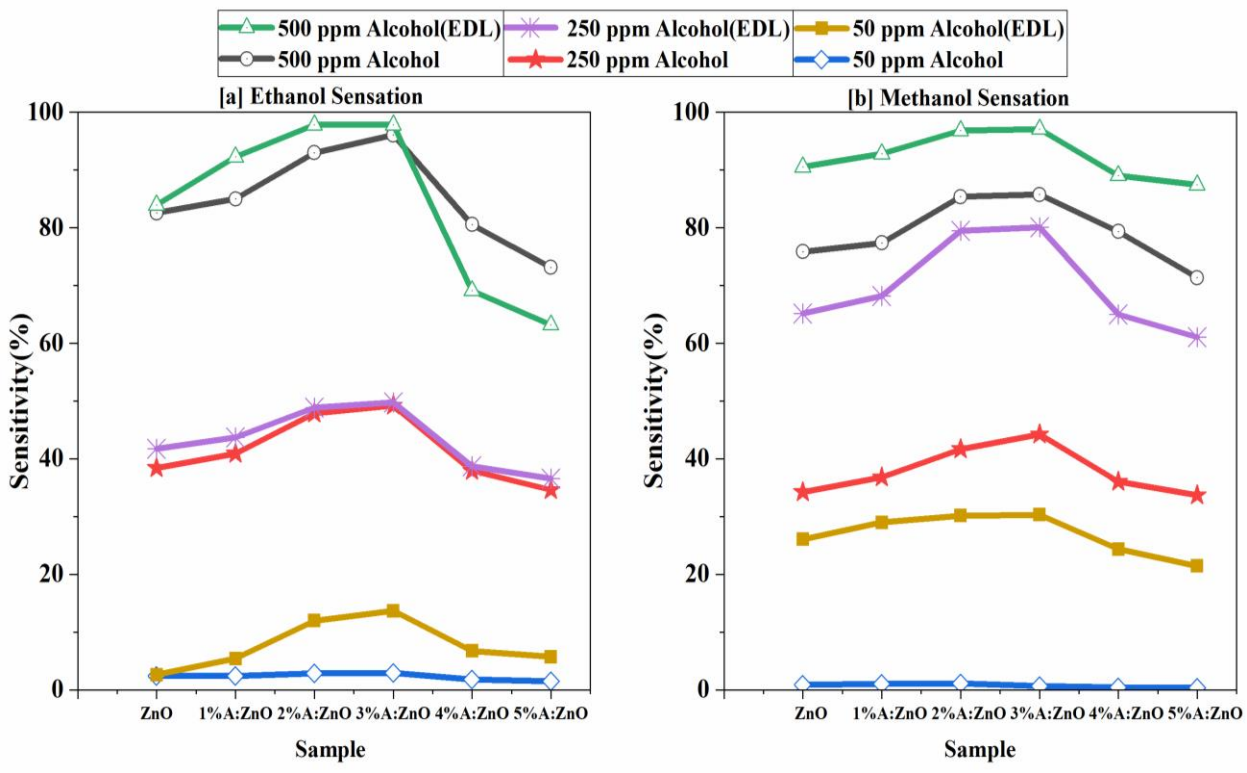


Figure 12: Sensitivity of Bare and EDL layered Two-Terminal Sensors in response to [a] Ethanol and [b] Methanol Vapors.

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

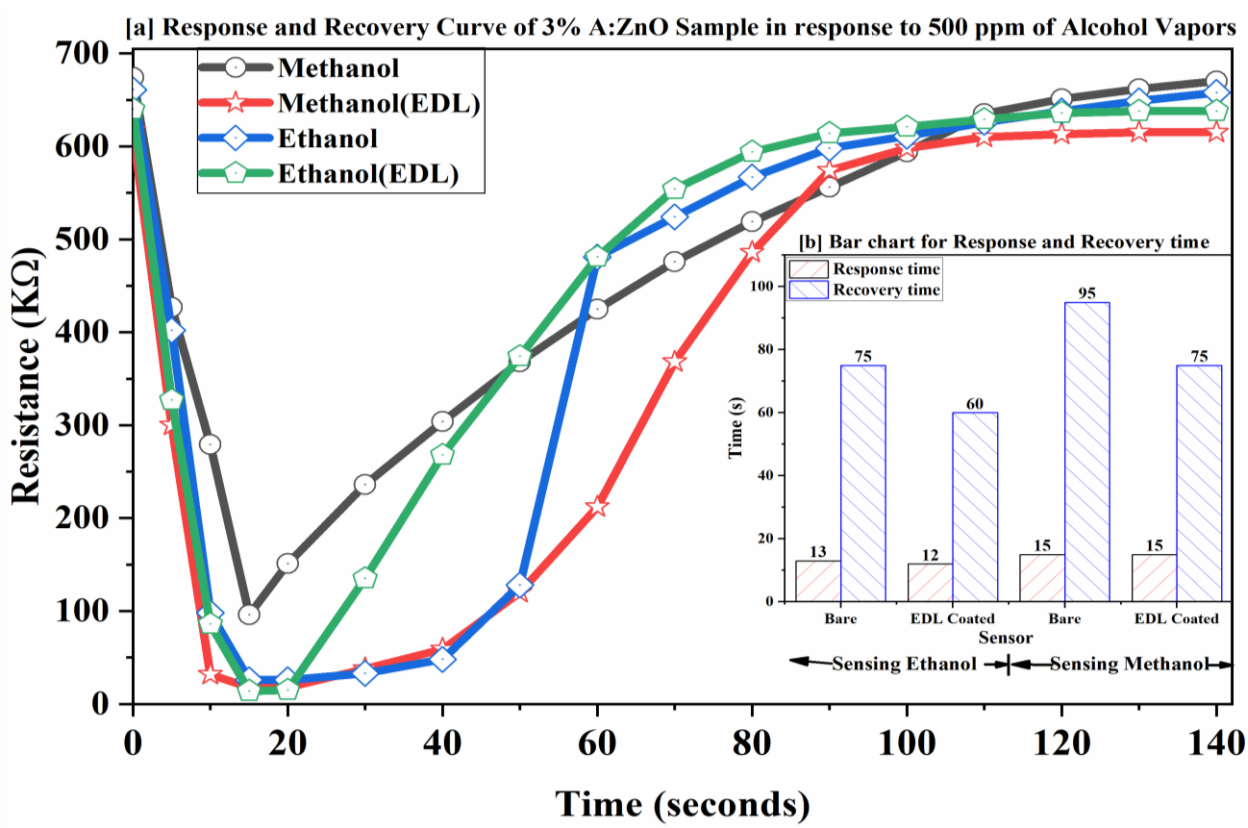


Figure 13: [a] Variation in Resistances of Bare and EDL Layered 3% A:ZnO films with respect to time in response to Ethanol and Methanol Vapors [b] Bar chart for response and recovery time of Bare and EDL coated 3% A:ZnO thin-film sensors.

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.

Sensitivity of Three Terminal Sensors

The sensitivity of the three-terminal sensors i.e. FETs are calculated using relation 1.2 and their corresponding graphs are shown.

The sensitivities of pristine ZnO and 1 to 5% Al-doped ZnO channeled, EDL dielectric polymer gated thin-film 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 ethanol, 18.98% to 49.70% in response to 250 ppm of methanol, 24.35% to 53.82% in response to 250 ppm of 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% A:ZnO channeled thin-film FET sensor is found approaching the sensitivity of 3% A:ZnO 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

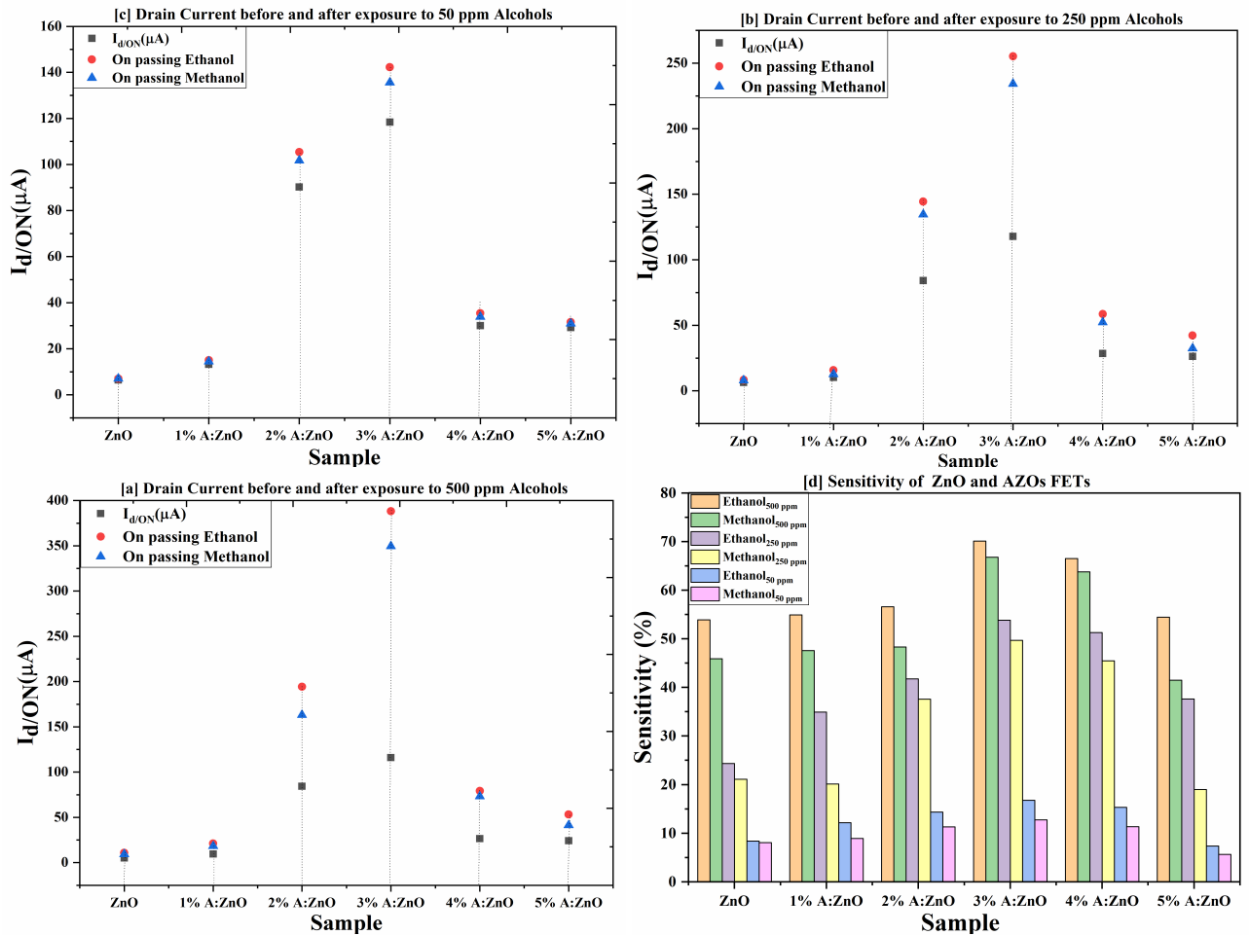


Figure 14: [a-c] Drain current, [d] Sensitivity of ZnO and AZOs channeled FETs before and after exposure to various concentration of alcohols.

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

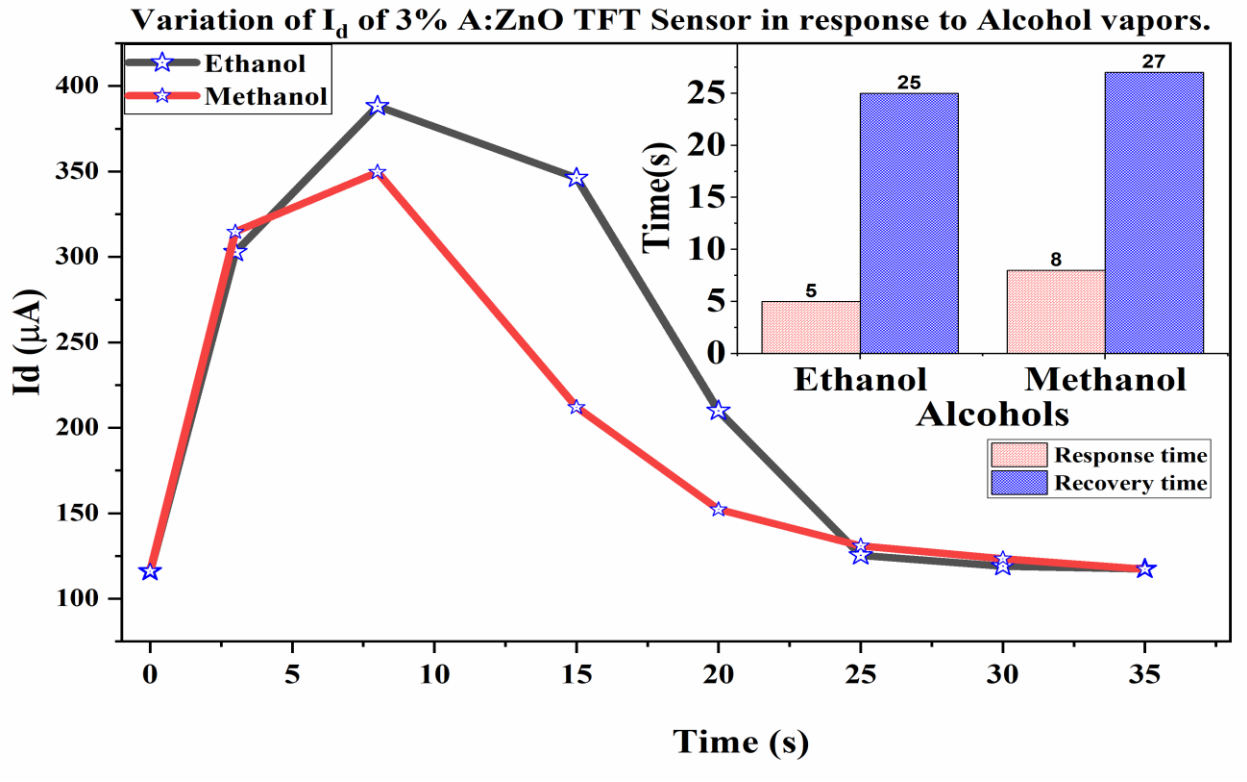


Figure 15: Variation of Drain Curent of 3% A:ZnO channeled EDL dielectric polymer gated TFT in response to 500 ppm of Ethanol and Methanol Vapors, and Bar chart showing Response and Recovery time of respective TFT embeded.

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 Al^{3+} and replaces 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-1), 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

responsible for such a biasing response. The response and recovery time for bare as well as EDL dielectric polymer coated 3% Al-doped ZnO sample in response to 500 ppm of alcohol vapors is found excellent (~13 s and ~70 s) compared to other samples of the sensors. The drain current of OFF-state of EDL gated 3% Al-doped ZnO TFT is found 6 x 10^{-4} µA and drain current of ON-state is found approximately 115 µA with an ON/OFF ratio of around 40800 (maximum of all) approves fantabulous transfer characteristic of 3% Al-doped ZnO among the rest of the TFTs which is the responsible factor for its higher sensitivity towards the alcohol vapors. The response and recovery time (~6 s and ~25 s) of 3% EDL electrolyte polymer gated TFT are seen promisingly small compared to rest samples of the TFT sensors and two terminal sensors.

Thus, we would like to suggest that 3% vol. is the optimum concentration of doping for the excellent performance of thin-film in sensing ethanol and methanol. Furthermore, though the sensitivities of two-terminal sensors seem higher than that of TFTs, 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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Conflicts of Interest Statement

Manuscript title: **STUDY ON ALCOHOL SENSING APPLICATION OF EDL DILECTRIC POLYMER GATED/NON-GATED, ZnO/AZO CHANNELED THIN FILM AND TRANSISTOR**

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

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

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