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SYNTHESIS OF ZnO NANORODS ON ALUMINUM FOIL FOR ETHANOL SENSING AT LOW TEMPERATURE

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In the current research, zinc oxide (ZnO) nanorods and nano-walls are prepared which credibly shows high sensitivity to ethanol gas detection at room temperature. ZnO nanorods were synthesized by chemical method using liquid solution method on aluminum foil as a substrate. Its sensitivity for ethanol gas detection at low temperature was investigated. X-ray diffraction shows the crystal arrangement that is hexagonal wutzite and FE-SEM investigates the surface morphology is hexagonal wutzite. Sensing response was measured against different parameters such as time, temperature, gas concentration and metal catalyst. The working temperatures varies from 20-300^{o}C for ethanol sensing. We investigated percentage sensitivity and response versus time (s) on various substrates at 150^{o}C working temperature. We had also investigated that resistivity decreased with metal catalyst. Photoluminescence spectra show that ZnO is good absorber. Sensing response versus gas concentrations in ppm (10-1000ppm) ethanol shows that its sensitivity increases with gas concentration. The experimental results show that response is excellent at low temperature and increase gradually with temperature.

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Keywords: Ethanol sensing, Sensitivity, Aqueous solution, ZnO nanorods, Aluminum foil

1. Introduction

In the current work, we investigate the ethanol sensing as its demand in fermentation manufacturing for different procedures in chemical industries, observing wine and food excellence. At present we require to synthesize cheap, capable and steady ethanol sensor. So, various semiconductor oxides have been explored and synthesized as ethanol detectors [1, 2]. In the case of sensors enhancing response is a critical issue. Consequently, it becomes vital to take up appropriate procedure for enhancing the sensing response. Thus, different methods have been suggested by scientists to increase the sensing response of gas detectors such as improve structure [3], control temperature, time and proper substrate for fabrication of nanostructures [4].

We have increase sensitivity of a sensor with thin layer of gold coating and conducting substrate (aluminum foil) in the current experimental work. Additionally, sensitivity of the sensor can also be increase by controlling the structure of zinc oxide nanorods by a suitable strategy [5].

Reducing gas detectors that are made from semiconductor are appealing for scientists by its viable applications since 1968 [6-7]. The manufacturing methods of such detectors are flexible.

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The probable appliances have set them in a type of extremely explored sensors [8-10]. Conductance or resistance of detectors varies with flow of oxidizing gases [11-13]. Sensors made from semiconductor metal oxide have operating temperature range from 200 to 300^{o}C [14] that is high enough. High temperature is essential for creation of reaction mechanism. As the response time decreases selectivity attains high value [15]. The sensing response increases with humidity effect. But the humidity cause decreased at a temperature higher 100^{o}C [16]. Toxic and hazardous gases are being polluting the environment that released from industries and vehicles [17]. So we need reliable and inexpensive sensing devices. To detect the dangerous gases and control the pollution level, an alarm system in industries and vehicles must be installed. Sensors are manufactured from different materials and techniques. Usually gas sensors constructed from ZnO, WO_3 and SnO_2 that are n-type metal oxides. In these sensors reducing or oxidizing gas molecules are adsorbed as ions in grains. So resistivity enriched by reduces in electrical mobility. Sensing technique depends on pre-adsorbed oxygen gas ions on active layer of the detector for reducing gases. Ions are absorbed with gas molecules and hence the conductivity enhanced in the detectors. ZnO recognized as magic material for manufacturing gas sensors. As it have numerous potential applications like large charge density and thermal stability. Such characteristics are associated with working situations of the detector. Nanostructures comprise of large charge mobility [18]. Due to these characteristics they are very important in research. Nanostructures are used in solar cells, sensors and in piezoelectric mechanism [19-21]. ZnO nanostructures have been fabricated by different techniques [22-23]. "Major techniques are hydrothermal [24], sol gel [25], thermal evaporation [26] and spray pyrolysis [27]". The exterior vicinity increased in nanostructures due to reduce in grain size. In this technique the decrease in grain size surface activity increased. Sensing response can be increased by coating a thin layer of noble metals like gold. Hence the nanorods can be fabricated at low temperature on conducting substrate [28-29].

The fabrication of gas sensor is necessary because of safety measurements in industries to detect explosive and poisonous gases that contaminate the environment. The demand of Zinc oxide is high due to its adaptable characteristics. It has good gas sensing response, high solidity, inexpensive and non-flame able that made it attractive element for detectors [30- 32].

Sensing response in oxide detectors is mainly increased by sputtering a thin layer of Au, Pt and Pd, etc. Thin gold layer behaves like metal catalyst that increases the surface activation for detection. A number of results show that stability and sensing response can be enhanced by sputter and dope with metal catalysts [33- 36]. Pt coated ZnO nanorods detect hydrogen gas at room temperature was investigated by Tien et al.

We fabricate gas sensor with economical substrate such as aluminum foil that increase the surface activation as nanorods grow are very thin [37- 42]. In this experimental work zinc-oxide nanorods synthesized hydrothermally that used for ethanol vapors detection.

2. Growth of semiconductor metal oxide nanorods

Zinc oxide nanorods were synthesized from analytical grade chemicals. We have purchased from Sigma Aldrich United Kingdom with 99.9% pure. Substrates are of Aluminum foil. For this propose Al tape was pasted on simple glass slides. Contamination were removed with the typical technique and then dehydrated in an electric oven. Substrates (with aluminum foil) were drop in 1% solution of dode-canethiol [$(CH_3(CH_2)_{10}CH_2SH)$] prepare in ethanol for adhesion of seed layer. Dipped the slides for 4 hours and dried out in an electric oven at 60^{o}C. We prepared zinc acetate di-hydrate 8 mM solution in alcohol for seeding layer. Drop a thin layer of $Zn(CH_3COO)_2.2H_2O$ on substrate by means of spin-coater and dry it at 60^{o}C. Repeat the process 6 times to add the mandatory width 300 nm.

For fabrication substrates were drop in zinc nitrate hexahydrate ($Zn(NO_3)_2.6H_2O$) with hexamethylene tetramine ($(CH_2)_6N_4$) 15 mM solution. A bowl with substrates was positioned in a furnace for 12 h at 90^{o}C temperature. Change the solution after every 4-hours. Post annealing do away with volatile compounds and impurities from the surface at 120^{o}C for 2 h. Sensitivity increases with a substantial gold thin film of 4 nm. Au layer was sputtered with EMITECH K-550

sputter-coater. Au layer act as catalyst so enhance the surface activation energy. The gold target has dimension 60mm × 0.1mm × 1 and operated at 12 V dc voltages. Sputter-coater gains a pressure 2×10^{-1} mbar prior to sputtering and current was 30 mA (1 mbar=0.75 torr=10 Pa). During sputtering current attains a value of 40 mA. Sputtering produces a 100 nm thick gold layer in 4 minutes. Sputtering process was repeated to gain the requisite thickness.

3. Results and discussion

The analysis of energy dispersive X-ray of ZnO nanorods shows in Fig. 1 with Au-coating. Oxygen, Zn, Al and gold is here in the pattern. EDX peaks are present at 0.265 KeV, 1.0 KeV, 1.5 KeV and 2.1 KeV for oxygen, zinc, aluminum and gold (O, Zn Al and Au). Within typical structure SiO_2 gives O, Al_2O_3 emits Al and Zn comes from Zn.

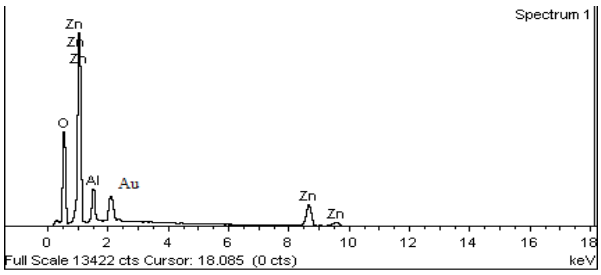

Fig.1. EDX spectra of ZnO nanorods with a thin layer of gold f on fabricated on aluminum foil at < 100^oC temperature.

Au, Zn and oxygen elements are investigated in the EDX pattern. EDX peaks communicate the required elements. We study the quantitative analysis of EDX. The compositional ratios of investigated elements are 1:1 that correspond to Zn: O. At an energy level 2.1 KeV, the gold singles are detected. The peaks energy dispersive x-ray spectroscopy (EDX) pattern that communicates with energy intensity level M_α cannot be investigated. This is due to the reason that sputter and doping layer thickness should greater than 1% for EDX pattern. As the reflection range for EDX detection must be ≥ 1% wt. Thus if the coating/doping layer thickness of the elements < 1%, then EDX pattern cannot identify the said element.

Fig. 2 shows the XRD analysis of nanorods fabricated on a conducting substrate like Aluminum foil by hydrothermal procedure. We used the Aluminum foil as an active layer. The presence of piercing and well determined peaks was compared by laboratory measurements (ref-code 01-079-2205). X-ray diffraction analysis shows hexagonal wurtzite pattern and aliened aluminum peaks in analysis.

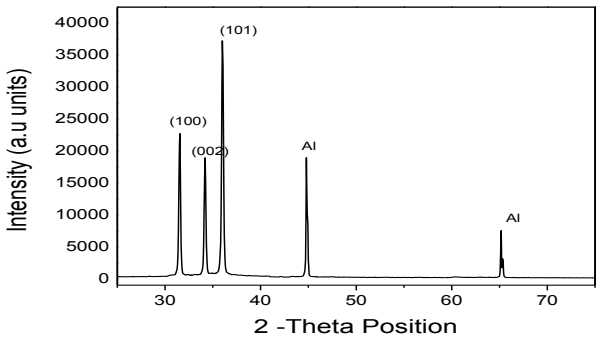

Fig. 2. X-ray diffraction analysis of ZnO fabricated on Al-foil

Intensity versus 2θ position is plot in X-ray diffraction analysis. In X-ray diffraction analysis 2θ changes from 25-75. Analysis was done with a step size (2θ): 0.049. X-ray diffraction pattern was taken at 25°C temperature. In machine anode was of Cu material and radiations were CuKα. with λ= 1.54060A^o. Current was 40 mA with accelerating voltage 40 KeV was kept through the scaaning process. In X-ray diffraction peak with highest intensity appears at 36.2049 with indices (1 0 1). The 2nd peak has 2θ position at 31.7327 and indices (1 0 0). The 3rd highest peak has 2θ position at 34.3788 with indices (0 0 2). The aluminum peaks appears at 45, 65 on 2θ position. The Au layer does not appear in XRD analysis due its small thickness. The crystal array is hexagonal wurtizite (space group: P63mc, Space group number: 186). The 2-lattice parameters are equal and investigated at a (A^o) = b (A^o) = 3.2488 and the third parameter is located at c (A^o) = 5.2054. The two measuring angles have the same values that are α = β = 90^o and γ=120^o is the third angle.

We have investigated the surface of as developed ZnO nanorods with a machine FESEM (JEOL-6340F). The surface is smooth of the as fabricated nanorods. The images show in fig-3 as measured by FESEM has hexagonal wurtizite structure with high density. Nanorods have diameter in the range 100–400nm are more than 1μm high. SEM images are investigated by 30 kV accelerating voltage. The images are taken with secondary electron images (SEI). We used the standard approach and working distance (WD) that vary from 9 mm to 10 mm. The magnification of the machine has different values ×16,000, ×6,000, ×19,000, and ×3,000, ×5,500 and ×3,700. SEM images of the nanorods and nano-walls show in fig-3 are hexagonal wurtzite. We use different magnifications.

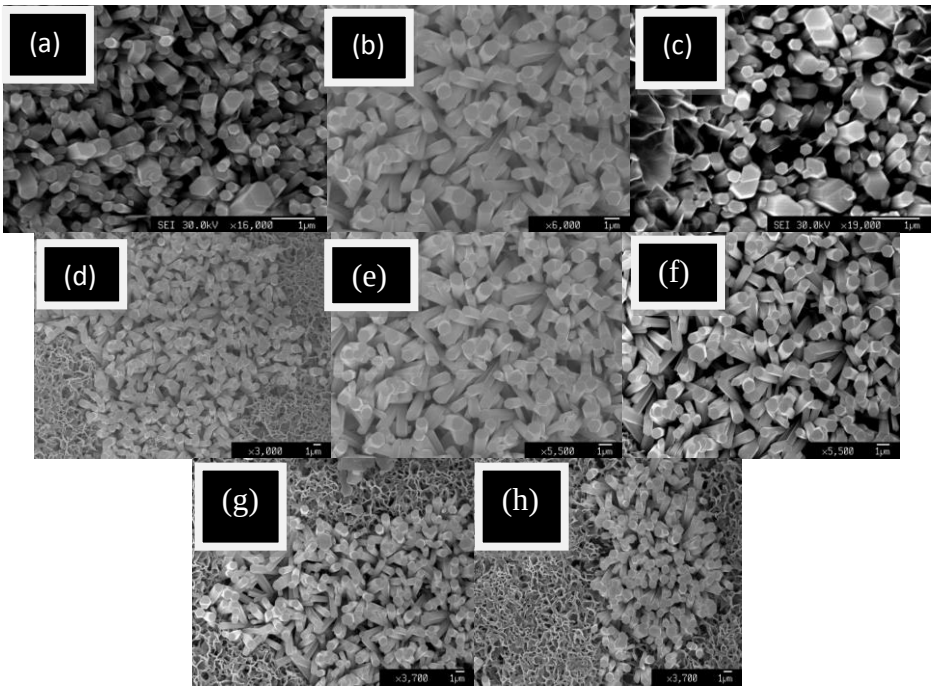

Fig. 3. SEM images at ×16,000, ×6,000, ×19,000, ×3,000, ×5500 and ×3700 magnifications ZnO nanorods and nano-walls have hexagonal wurtzite structure on aluminum foil as substrate.

Scanning electron microscope operated at different magnifications and images are taken as 16,000×, 6,000×, 3,000× 19,000×, 5500×, 3,700×. We have investigated the surface with JEOL/EO format. The instrument was of model JSM-6340F. The images were taken by secondary electron emission (SEI) signals. The machine was used in standard mode with WD=10 mm. The absorption process of ethanol molecules on the active layer of the detector is high. Absorption of the gas molecules is done at low temperature as the thickness of nano-walls and nano-rods is very small on the aluminum foil.

Sensing of ZnO nanostructures for oxidizing/reducing ethanol can be investigated by simple laboratory made device that is known as resistance sensor [43]. Contacts are applied on the active layer of the sensor with a sputter coating machine. Here we have used Pt as target in the sputtering machine. Secondly we can also use silver paste for contacts. Resistance was calculated precisely with Keithley-614 electrometer.

Fig. 4 shows the sensing behavior of manufactured detector at various temperatures. The best possible temperature is 150^{o}C as investigated from the experimental data. The changeable temperature was providing with a hotplate to the detector. The gas sensing process needs a specific quantity of thermal energy. The thermal energy required for crossing potential barrier and to unite with adsorbed oxygen gas molecules. Several gas molecules necessitate a critical amount of energy at the best probable working temperature and react with oxygen species that are absorbed in active layer of the detector. Necessarily high change in conductance of sensing elements occur that high resistivity and less conduction characteristics. By such situations charge leakage from the surface of nanorods avoided. Edge effect is the source of presence of such atoms in ZnO nanorods surface. So sensitivity enhanced by sputtering of noble metal coating. Sensing response also increases by using a sensor have small diameter of nanorods as its sensing surface as of "Edge Effects"

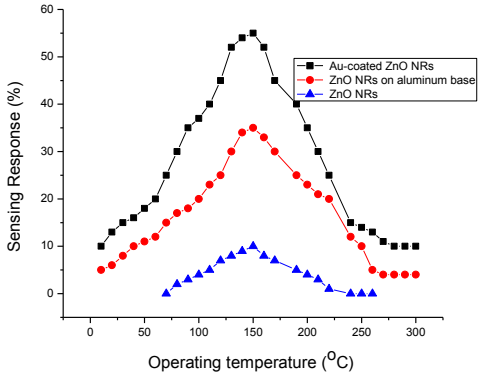

Fig. 4. Sensing response to ethanol for zinc oxide nanorods at different temperatures.

Nanorods have large number of atoms at the periphery as compared with inner side of the nanorods, so high resistivity and poor conductivity exists in the internal region of nanorods. This prevents the leakage of charges from NRs. These atoms are present due to edge effects in ZnO NRs. So, the sputtered layer increases the gas response. Sensitivity also enhanced with thin NRs because of "Edge Effects"

At a temperature higher than 150^{o}C, the adsorbed O_2 molecules on the surface of the sensor reduce as a result smaller quantity of gas species ingest. Hence the sensing response reduces beyond 150^{o}C.

Fig. 5 shows that the sensor response to ethanol vapors continuously enhances with the increase in gold sputtered layer. As reducing gas molecules disassociate at lower temperature due to Au coating.

The sensor response improves significantly with exterior activation. The ethanol sensing response enhanced more than eight times after activation with 4 nm thin gold sputter layer. Research was repeated on a set of three samples to positively confirm the reproducibility of outcomes. Further investigation shows the response time (5–10 s) and recovery time (15–20 s) of all the samples was small.

Investigations shows that the most favorable working temperature for the sensor was 150^{o}C that is much lower than reported in the literature *(Wang, L et al. 2012).*

Hence, the sensing decreased beyond 150^{o}C. Sensitivity to 300 ppm ethanol at 150^{o}C versus time shows in fig.5. The above graph shows the sensing response verses time (s) at different substrates condition and at fixed temperature 150^{o}C. The sensing response enhanced with time and attains a saturation value after that it gradually decreased and gains the original value. Graph

represents the maximum response at 150°C to the gold coated active layer, which means that the sensor response increased if the target gas flows on the surface of the sensor for longer time at higher temperature.

Gas sensing mechanism based on reactions that taking place on the surface sandwiched between ZnO nanorods and the ethanol molecules. Oxygen (O_2) molecules As the temperature increases and becomes greater than 150°C, the number of adsorbed oxygen species decreased on the active layer of the sensor. Consequently, a small quantity of O_2 gas species absorbed on the surface. By such mechanics sensitivity of the gas molecules decreased when temperature increases further than 150°C.

Fig 5 shows the sensitivity of ethanol gas vapors. Sensitivity is maximum with the Au thin coated film. In the presence of gold thin layer the ethanol a reducing gas its species disassociate at low temperature.

Sensitivity of the sensor enhances crucially by improving the activation layer. Gas sensing response of ethanol can be increased more than eight times by coating 4 nm thin gold thin films. Experiment was done three times with different samples for confirmation of reproducibility of the results. The results show that the sensor response time varies from 5–10 s and its recovery time 15–20 s. The sensor has small values of response and recovery time for each of the samples.

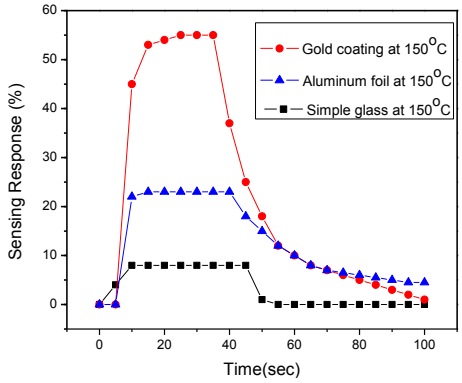

Fig. 5. Graph between sensing behavior versus time of Au-coated ZnO NRs for various values of temperatures to ethanol gas at 300 ppm.

Experimental result shows that the suitable operating temperature for ZnO nanorods detector was 150°C. Hence its value is far below as compared to reported temperatures in the literature [44].

Consequently, sensitivity reduced further than 150°C. Sensing response versus time to 300 ppm ethanol gas at 150°C temperature investigated in fig-5. The investigation shows the sensitivity against time (s) for various substrates and at flat 150°C temperature. The above graph shows that sensitivity increased with time and gains the saturation condition. After the saturation value steadily reduced and attains the initial value. The sensitivity has a maximum for Au coating sample at 150°C. It concludes that the detector sensitivity has a larger value at high temperature.

The gas detection procedure depends on reactions that happened on the surface of the sensor that are sandwiched among nanorods and the ethanol gas species. The instant when ZnO nanorods (n-type semiconductor metal oxide) open to the elements in air oxygen gas species absorbed in the surface. Additionally, response and recovery time of the detector also varies [45]. Disassociate the oxygen into ions likes O^{2-}, O_2^{2-} that capture electrons from the active layer of the sensor. Hence a space charge layer generates on the active surface of the detector that constituted by depleted electrons. Oxygen molecules (O_2, O^{2-}) absorbed, O_2^{2-} dissociates and oxygen exists in the form O^{2-} on the surface. The amount of oxygen that adsorbed organized to desorbed species.

The adsorbed oxygen species on the surface of the sensor modify themselves to oxygen ions (e.g., O_2^-, O− or O^{2-}). This process depends on temperature. The ion formation is done through catching free available electrons having in conduction band of zinc oxide nanorods. Equations (1) – (4) show the required process [46].

$$O_{2\,(g)} \leftrightarrow O_{2\,(ads)} \quad (1)$$

$$O_{2\,(ads)} + e^- \leftrightarrow O^-_{2(ads)} \quad (2)$$

$$O_{2\,(ads)} - + e^- \leftrightarrow 2\,O^-_{(ads)} \quad (3)$$

$$2\,O^-_{(ads)} + e^- \leftrightarrow O^{-2}_{(ads)} \quad (4)$$

A charge carrier area becomes at the face by positively charged nanorods. Negative charge of adsorbed oxygen ions is explained in equations (2 - 4). The distinctive thickness of nano-walls is very small usually less than its Debye length that (50 nm) [47]. The depletion area expands to the complete dimensions of nanorods. After detector is open to the target-gas, due to oxidizing / reducing character of the gas, two processes can be occur: (a) entire depletion of charge barrier from the conduction-band creates an insulating behavior. (b) entire removal of adsorbed oxygen molecules from the sensor produce a conducting behavior. Hence the gas molecules quickly modify the conductivity of the sensor by change in resistance, hence show large sensitivity and quick response and recovery time.

In this experimental work the best operating temperature of the sensor was 150^{o}C and the oxygen species O^{2-} are imperative than any other adsorbents. The target gas has to undergo different reaction mechanisms and then de-composes either by dehydration or dehydrogenation.

$$C_2H_5OH \leftrightarrow C_2H_4 + H_2O \quad \text{(acidic-oxide)} \quad (5)$$

$$2C_2H_5OH \leftrightarrow 2CH_3CHO + H_2 \quad \text{(basic-oxide)} \quad (6)$$

These essentials successively oxidized to carbon dioxide (CO_2), carbon monoxide (CO) and water (H_2O).

$$C_2H_4 + 3O_2^{2-} \leftrightarrow 2CO_2 + 2H2O + 6e^- \quad (7)$$

$$2CH_3CHO + 5O_2^{2-} \leftrightarrow 4CO_2 + 4H_2O + 10e \quad (8)$$

The De-hydrogenation process is probable in only basic-oxide such as ZnO. On the surface of sensor, oxidation of alcohol agrees-well with the above mentioned reactions simply CH_3CHO was found. The change of C_2H_5OH and its sensitivity improved with working temperature. The conversion ratio of C_2H_5OH determines the response. The conversion ratio of CH_3CHO increased the sensitivity of alcohol. Therefore, acetaldehyde plays a vital role in the detection.

$$2C_2H_5OH + O_2^{2-} \leftrightarrow 2C_2H_4O^- + 2H_2O \quad (9)$$

$$C_2H_4O^- \leftrightarrow CH_3CHO + e^- \quad (10)$$

Xu, J has showed that ZnO NRs sensing to C_2H_5OH is chemisorbed process of negative charge of oxygen [48]. The growth temperature and seeding layer determine the aspect-ratio and porosity of NRs. The thin gold layer increases the sensitivity of detector. At low temperature the surface activity was increased by gold coating. Oxygen molecules disassociate at low temperature conditions.

In semiconductors like ZnO the crystallography grow various energy shells in surface states and active sites. The quantity of oxygen adsorbed on the surface was improved and ethanol oxidation increased. Due to variation in resistance conductance and sensitivity of the sensor amplified significantly. The stability and reproducibility were periodical as shown by experimental results. At constant temperature, resistance of the sensor decreased by target gas flow as show in fig-5. Sensing increased with working temperature and flow of target gas. Thus resistance steadily reduces with the increase in sensitivity, and gain a maximum value 150^{o}C. As a result when the gas flow was stopped up the resistance reduced and attains the initial value.

It was investigated that resistance decreased with ethanol flow due to ethanol adsorption on the active layer of the sensor [49].

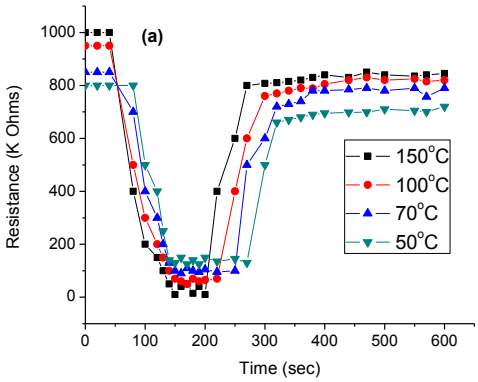

Fig. 6a. Resistance versus time of Au-coated ZnO nanorod with 1000 ppm ethanol at various temperatures from 50-150°C

The molecules of ethanol interact with oxygen species in the sensing film. Then electrons are emitted back into the conduction band. Resistance decreased by the detector. Au coated ZnO nanorods show lees resistance than ZnO nanorods sensor as mentioned in graph (Fig-6). As gold (Au) is a noble metal. So in the presence of thin gold coating gas molecules disassociates at less temperature. Consequently, sensor detect at less temperature conditions.

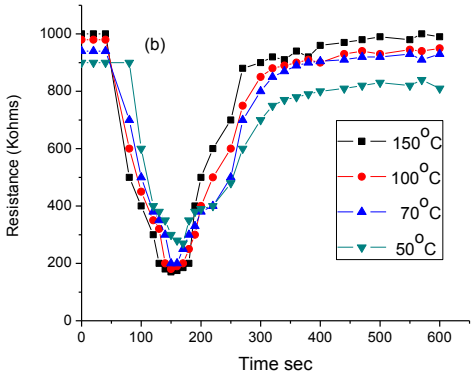

Fig.6b. Resistance versus time of un-coated Au ZnO nanorods with 1000 ppm ethanol gas at 50-150°C.

The resistance reduces up to 50 Kohms with gold coating while it was 200 Kohms without gold coating. So the gold thin layer increased the sensing response as the resistance decreased. Au thin coating film behaves like catalyst that decomposes the target-gas at less temperature. So sensitivity increases of the ZnO detector.

4. Photoluminescence (PL) measurements

The active performance of sensors was calculated through photo-luminescence spectra. UV photo-luminescence spectra are well built and have centered at 390 nm as shows in fig-7. The spectrum certified the near band-edge shift of wide band gap metal-oxide semiconductor [50]. It is memorable that not any wavelength peak shifts or band-profile dissimilarity was determined. Maximum absorption intensity attains (45000 a.u) except for successive spectral appearance. Graph shows absorption versus wavelength of ZnO that is an excellent absorber.

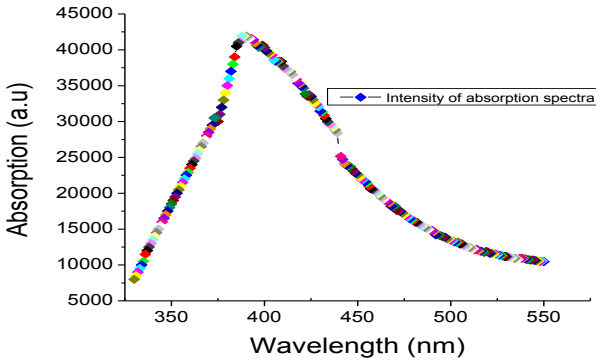

Fig. 7. Photoluminescence spectrum of ZnO nanorods at room temperature.

Absorption pattern versus wavelength for concentration 10-1000 ppm shows in the graph (fig. 7). The absorption increases with ethanol efficiently. It gains the same initial limit when target gas cut-off from the active surface of the detector. This result was repetitive with various ethanol gas concentrations.

Consequently it was established from the experimental results that sensitivity increases with different values of target gas (ethanol) concentration. Lager crystallite-size results in less recovery time. Consequently corresponds to small scattering in the electron transmit process. These consequences in fast and efficient diffusion of gas molecules from the active layer of the sensor [51].

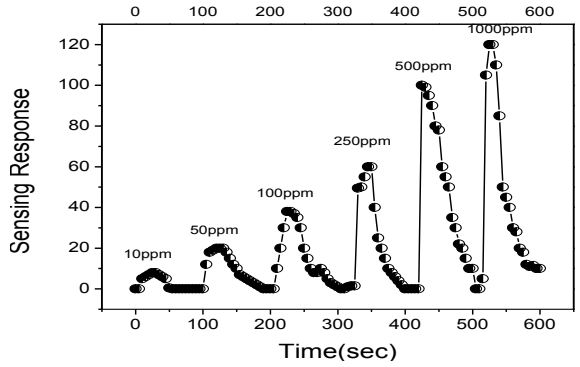

Fig. 8. Sensing response versus time at 10-1000 ppm ethanol at 150^{o}C.

The graph shows sensing response versus time at 150^{o}C with gas concentration varies from 10-1000 ppm. Figure.8 shows that the gas response increase with gas concentration and attains the initial level zero sensing response when gas is discharge from the surface of nanorods. The detected gases show fast response and recovery time as detected by ZnO nanorods based sensor. Sensitivity, quick response and recovery time of the detector is effected from its design. It is concluded from the target gas diffusion features [52]. During sensing mechanism defects are exist on the surface of the sensor and play a crucial part. Sensing is being proceeded by absorbing/desorbing the gas species by holes and channels [53].

A variation in arrangement, can be occur at <200^{o}C temperature. At the structural change the grain-size is less than 50–100 nm. Generally the thermal stability of the detector can be lower by reduce in grain size of nanostructures. The ethanol gas detection was done at different operating temperatures by ZnO nanorods sensor. Sensor has fast and reversible response to the reducible gas such as ethanol. Thus play a crucial part in potential application like detectors [52].

In this experimental research we have determined the gas sensing response at low temperature conditions. By Au (noble metal) coating, temperature, time and increase in ethanol gas concentration the gas sensing enhanced.

5. Conclusions

ZnO nanostructures were synthesized by hydrothermal technique. We have fabricate the nanorods on conducting substrate like aluminum foil and investigate that the conducting substrate enhance porous quality of the surface and the aspect ratio. The customized surface increased the sensitivity crucially. The best possible operating temperature of the sensor was investigated in this research is 150^{o}C. The maximum value of sensitivity was investigated in the experimental data is 55 that is increased with temperature. The surface morphology was improved by the surface activation. The activated surface has no effect on the bulk characteristics of ZnO surface. At recovery time (~5-10 s) and (~15-20 s) a quick response was investigated. The sensitivity increased with the ethanol concentrations. The ethanol sensing can also be improved with the help of conducting substrate that improve the quality of ZnO nanorods. The reversible behavior of the sensor is investigated with different time and nanorods samples.

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