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Light-Assisted Ethanol Sensor at Ambient Temperature Using Spray Deposited ZnO Thin Films

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Abstract : ZnO thin film was deposited on to the preheated glass substrates by spray pyrolysis technique. The polycrystalinity and the hexagonal structures were observed from the X-ray diffraction pattern and the variation in lattice constant was also being reported. The average crystallite size was found to be 30 nm to 35 nm. The morphological studies confirmed the formation of ZnO nanorods. From optical studies, the band gap was found to be ~3.32 eV. The room temperature vapour response was studied for different volatile vapours by chemiresistor method. It was observed that the film had a good response towards ethanol vapour under the exposure of light. The sensing mechanism, sensitivity and response-recovery profile as a function of ethanol concentration were studied and reported.

Introduction

Ethanol is widely seen in alcoholic beverages which are inflammable, colorless compound. It finds its importance in many places like food industries, chemical industries, and wine quality testing. It plays vital role in many applications especially in safety control even though it is slightly toxic in nature[1]. According to Occupational safety and health administration (OSHA) the human permissible exposure limits of ethanol gas is 1000 ppm as eight hour time weighted average (TWA)[2]. Once this human permissible limits exceeds it will leads to neurobehavioral toxicity and even also affects the immunity level. Several works have been done to control and monitor the ethanol vapour. For the past few years metal oxide semiconductors such as ZnO, SnO_2, TiO_2 and V_2O_5 have been extensively used as ethanol sensors[3]. Out of which ZnO find its trademark due to their unique properties like, direct band gap typically about ~3.34 eV, high electron mobility, good optical transparency, high photo electric response and low working temperature[4].The sensing with the visible light irradiation have been used to improve the photocurrent response. Visible-light induced formaldehyde gas sensing by using CdS/ZnO heterostructures were already reported[5]. In this work, the room temperature visible light induced ethanol sensing by spray deposited ZnO thin films were reported. The structural and morphological studies were carried out through X-ray diffraction (XRD) and scanning electron microscope (SEM) and reported. The optical studies were carried out in order to determine the optical band gap and also reported. The photoelectric response of prepared ZnO films were also studied and reported.

Experimental

ZnO thin films were prepared by home-build spray pyrolysis technique[6]. Initially 0.1 M of zinc acetate dihydrate (Zn $(CH_3COO)_2$.) $2H_2O$, 99.99% purity, Sigma -Aldrich) was taken as a precursor salt and allowed to dissolve in 50 mL of deionized water. The glass slides were cut in to 25 mm x 25 mm in dimensions and pre-heated at 523 K. The different spray parameters were listed in the Table 1. The solution was sprayed on the pre-heated substrate with the help of pressurized carrier gas which was converting the solution in to aerosols and sprayed through the spray nozzles. The appropriate distance between the spray nozzle and the pre-heated substrate should be maintained and the angle of the spray gun also should be optimized to avoid spilling of precursor solution. The spray time was maintained at 5 s and 25 s interval were maintained for each successive deposition for the nucleation and growth process of the films. The spray deposited films were obtained through the following pyrolytic reaction[7].

$$Zn(CH_3COO)_{2(solid\ near\ substrate)} \rightarrow 4Zn(CH_3COO)_{2(solid\ near\ substrate)} + H_2O \rightarrow$$
$$Zn_4O(CH_3COO)_{6(adsorbed/substrate)} + 2CH_3COOH_{(gas\ near\ substrate)}\ and \uparrow Zn_4O(CH_3COO)_{6(adsorbed/substrate)}$$
$$+3H_2O \rightarrow 4ZnO_{(film/substrate)} + 6CH_3COOH_{(gas)} \uparrow ------------------------ \quad (1)$$

Table 1. Different spray parameters in spray pyrolysis technique

Spray parameters	
Precursor salt	Zinc acetate dihydrate (Zn $(CH_3COO)_2).2H_2O$
Concentration of precursor salt	0.1M
Dissolving agent	50 mL of deionized water
Deposition temperature	523K
Angle of spray gun	45 °
Distance between the spray nozzle and the preheated substrate	40 cm
Solution flow rate	4 mL/min
Interval between each successive sprays	25s

Results and Discussion:

Structural studies

The structural properties of prepared films were carried out through X' Pert PRO Diffraction system (XRD) at the scanning angle of 20° to 80°. Fig 1. Shows the X-Ray diffraction pattern of spray deposited ZnO thin film. The observed peaks were compared with the JCPDS [card 36-1451]. The observed peaks revealed that material exhibit polycrystallinity and it also confirmed the formation of hexagonal wurtzite structure.

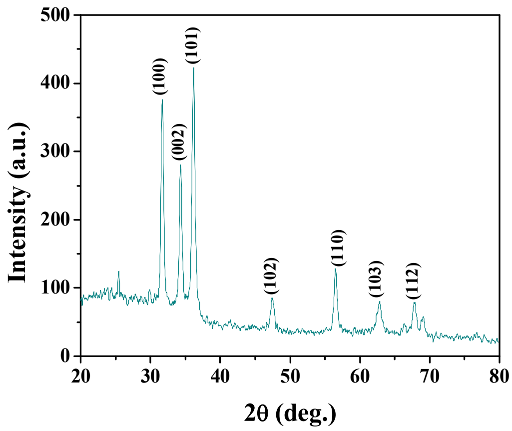

Fig. 1. X-ray diffraction pattern of spray deposited ZnO thin film.

Table 2. Comparison of lattice constant d in (Å) and corresponding crystallite size for standard and observed values.

2θ (obs.)	2θ (std.)	d(Å) (obs.)	d(Å) (std.)	D(nm) (obs.)	D(nm) (std.)	(h kl)
31.703	31.770	2.820	2.814	38.59	38.60	(100)
34.380	34.442	2.606	2.601	36.09	36.09	(002)
36.204	36.253	2.479	2.475	33.12	33.12	(101)
47.503	47.539	1.912	1.911	31.64	31.64	(102)
56.520	56.603	1.626	1.624	32.88	32.89	(110)
62.834	62.864	1.477	1.477	16.97	16.97	(103)
67.825	67.963	1.380	1.378	17.45	17.46	(112)

Table 2. Shows the variation in the lattice constant of ZnO for various observed and standard 2θ values. For the larger 2θ, the lattice constant had the greater influence and on the other hand the insignificant variation were observed for lower diffraction angle. The significant peaks obtained as (100), (002), (101) and its corresponding crystallite size D (nm) were found using Debye-Scherrer formula [8] and listed in Table 2 for observed and standard 2θ values. The average crystallite size was varied from 30 nm to 35 nm.

$$D = \frac{S\lambda}{\beta \cdot \cos\theta} \text{ - - - - - - - - } \quad (2)$$

Where S is the shape factor (0.94) and λ is the wavelength of Cu-Kα_1 (1.5406 Å) which is source of X-ray, β is the full width at half maxima (FWHM) and θ is the diffraction angle.

Morphological studies

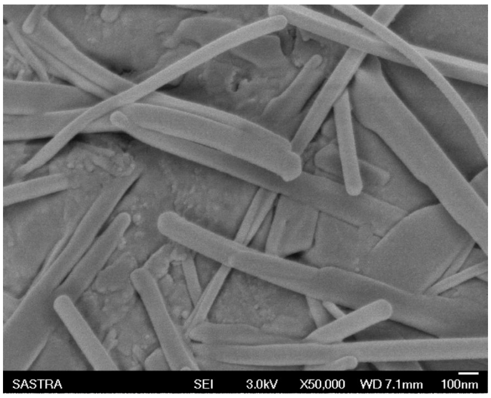

Fig. 2. Scanning electron microscope image of ZnO thin film

Morphological studies of the prepared thin films were realized through field-emission scanning electron microscopy (JSM - 6701FFE-SEM). Fig 2. Shows the scanning electron microscope image of ZnO and it confirms the formation of hexagonal pillar shaped nanorods. The spherical shaped nanoparticles were also formed due to the agglomeration of nanorods. The grain size distribution was observed in the range of 35 nm to 45 nm.

Optical studies

The optical studies of prepared ZnO thin film was carried out using UV-Vis Spectrophotometer (Lambda 35 with scan speed of 480.00 nm/min). Fig 3. shows the optical absorbance characteristics as a function of wavelength and it was observed that ZnO absorbed all the light below 400 nm and as expected the maximum absorption occurred within the visible region. The maximum absorption occurred at 381 nm. Their corresponding band gap and the grain size of ZnO nanoparticles was calculated from the below formulas[9] and obtained values were ~3.29 eV and ~37 nm respectively.

$$E = \frac{hc}{\lambda} \quad \text{------------------} \quad (3)$$

Where h is the Planck's constant, c is the velocity of light and λ is the absorption wavelength.

$$r(nm) = \frac{-0.3049 + \sqrt{-0.3049 + \dfrac{10240.72}{\lambda_p\ (nm)}}}{-0.63829 + \dfrac{2483.2}{\lambda_p\ (nm)}} \text{--------} \quad (4)$$

Where λ_p is the peak absorbance wavelength (381 nm) and r is the radius of ZnO nanoparticles. The observed grain size of the ZnO nanoparticles matches with the grain size distribution obtained from the morphological studies. The ZnO film also shows good optical transparency in the visible region. Optical band gap E_g was calculated from the Tauc's plot by relating the incident photon energy (hν) with absorption coefficient (α) as [10],

$$(\alpha h\upsilon)^{1/n} = A\,(h\upsilon - E_g) \text{---------------} \quad (5)$$

where A is a constant, E_g is the band gap of the material and for different values of n different type of transition will occur. For n=1/2, 2, 3/2 and 3 the transition will be of direct, allowed indirect, forbidden direct and forbidden indirect respectively. Absorption coefficient (α) is calculated from Lamberts law.

$$\alpha = \frac{(2.303\ A)}{t} \text{-----------------} \quad (6)$$

Where A is the optical absorbance and t is the thickness of the films. By relating the photon energy (hν) and $(\alpha h\nu)^2$ and extrapolating the linear portion of the curve, the optical band gap was determined as shown in Fig 4. The optical band gap obtained as ~3.32 eV which matches with the theoretical band gap value.

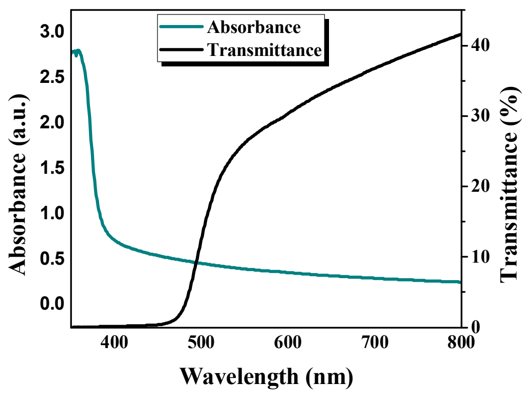

Fig 3. Optical absorption and transmission spectrum of ZnO thin film.

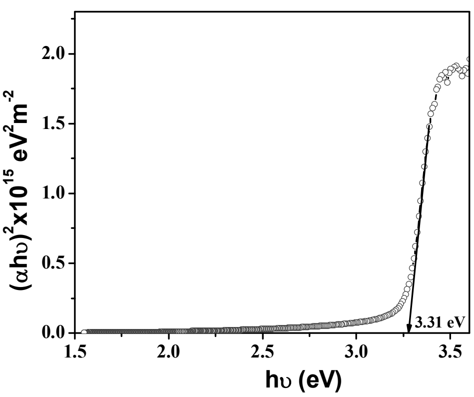

Fig. 4. (hν) versus $(\alpha h\nu)^2$ plot showing the optical band gap of ZnO thin film.

Ethanol sensing studies

Photoelectric characteristics

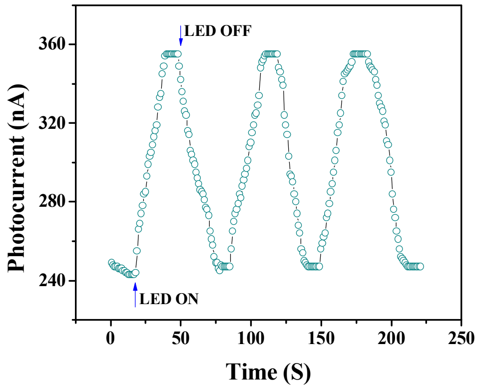

Fig 5. Photoelectric characteristics of ZnO thin film.

Fig. 5 indicates the photoelectric characteristics of the prepared ZnO thin film. The photoelectric characteristic were done by keeping the thin film in air atmosphere and results were noted down. Under the illumination of LED light (normally UV-LED) the current intensity of the sample increased rapidly due to the increase in carrier concentration which induced the photo-generated electrons and holes tends to decrease in the potential barrier height. In the absence of LED light, current intensity decreases sharply due to the recombination of photo activated electrons and holes[11].

Selectivity

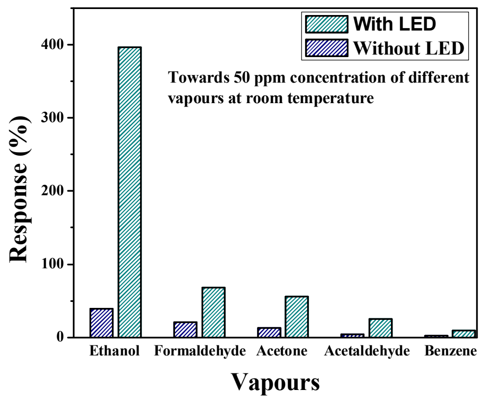

Fig 6. Selectivity of ZnO thin film with and without LED

Selectivity of the sensor is defined as ability of the sensor to discriminate the particular vapour when a mixture of vapour is present[12]. The selectivity plot is shown in Fig 6 in which 50 ppm of different vapours starting from ethanol, formaldehyde, acetone, acetaldehyde and benzene were taken. The selectivity of ethanol vapour is maximum when illuminated with the LED. Formaldehyde and acetone also shows appreciable response under the illumination of LED.

Room temperature ethanol sensing

Room temperature gas sensing was done by using homemade sensing setup[13]. Fig 7(a) shows the response towards ethanol vapour of 50 ppm concentration. The response of the sensor is given as ratio of difference in resistance in air atmosphere and resistance in targeted gas atmosphere to the resistance change in targeted gas atmosphere[14].

$$S = \frac{(R_a - R_g)}{R_g} \times 100 ---------------------- \quad (7)$$

Where R_a is the electrical resistance of the film before injecting the targeted vapour and R_g is the electrical resistance of the film after injecting the targeted vapour.

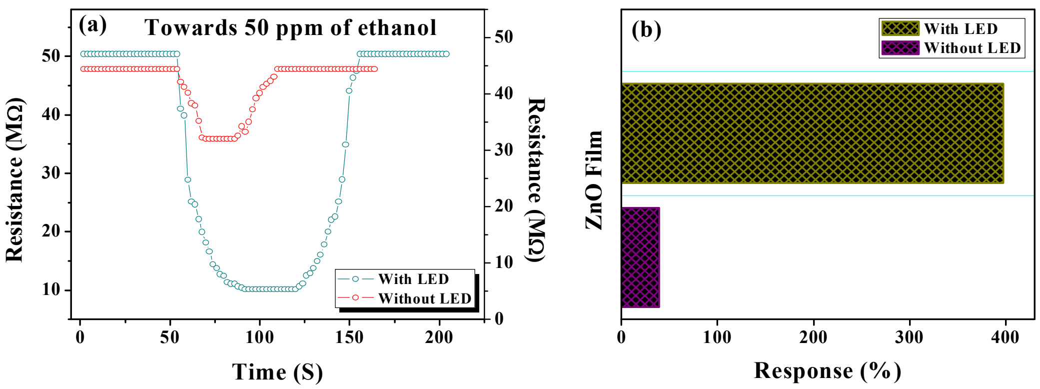

Fig 7 (a) Room temperature ethanol sensing of ZnO thin film with and without LED (b) the corresponding response of ZnO thin film at 50ppm concentration of ethanol

The response of the ethanol vapour under the illumination of LED has significant when compared to the response without LED. Due to the intervention of LED photo activated electron and holes were generated within ZnO in which turns increase in carrier concentration and it react with the photo activated ethanol molecules. The rapid change in the photoconductivity is due to the following aspects. The amount of photo generated holes is more than photo generated electrons, due to the decrease in oxygen adsorbed, amount of trapped electrons reduces on the surface[11]. From Fig 7 (b) it shows the corresponding response value of ZnO film with and without LED which reveals that the response of the ethanol increased more than ten times when the film illuminated with LED.

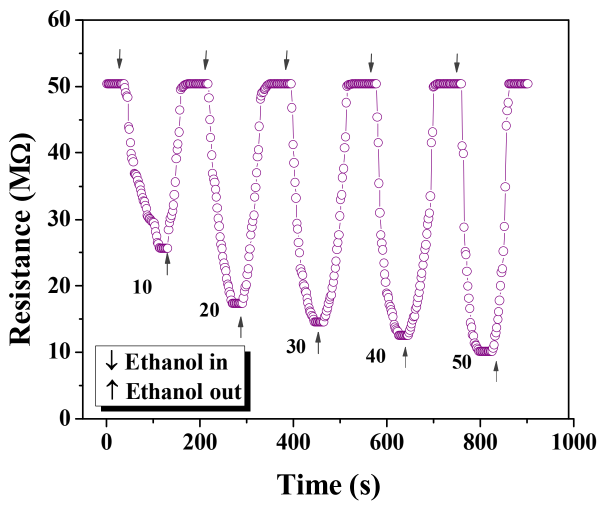

Fig. 7. Transient response of different concentration of ethanol vapour.

The transient response of resistance change versus time at different concentration of ethanol was plotted in Fig 7. The curve shows that increase in the response on increasing the concentration of ethanol. This is due to monolayer of oxygen molecules expected to form at lower concentration. At higher concentration multilayer of oxygen molecules were expected to adsorb on the surface of ZnO leads to saturation in response[12].

Response and recovery Profile

The response and recovery profile as a function of concentration of ethanol as plotted in Fig. 8. The response and recovery time increasing linearly as increase in ethanol concentration. The corresponding response and recovery time for each concentration of ethanol is shown in Table 3. The response time shortens as the concentration increases and recovery time increases as shown in Fig 8 (b).

Table 3. Characteristics of concentration versus response time and recovery time.

Concentration (ppm)	Response %	(Response*90)/100 %	(Response*10)/100 %	Response time (S)	Recovery time (S)
10	96.72546	87.05292	9.672546	9	84
20	191.1838	172.0654	19.11838	8	86
30	247.3522	222.6197	24.73552	6	96
40	302.7707	272.4936	30.27707	5	102
50	397.9847	358.1863	39.79847	4	108

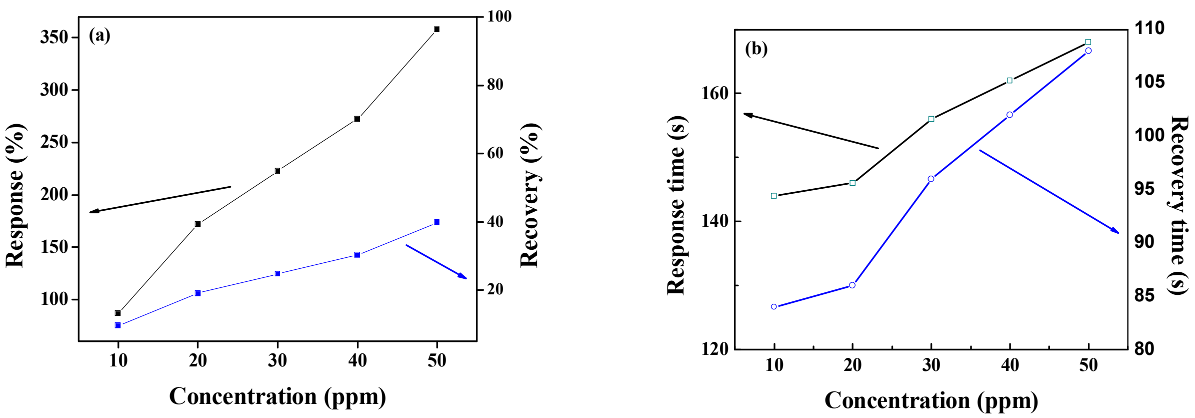

Fig 8 (a) Response and recovery characteristics as a function of concentration (b) response and recovery times of ZnO thin film at different concentration of ethanol.

Conclusion

The ZnO thin films were deposited onto the pre-heated glass substrates using spray pyrolysis technique. The XRD pattern confirmed the polycrystalline nature and hexagonal wurtzite structure. Field-emission scanning electron micrograph shows the formation of hexagonal pillar shaped ZnO nanorods and the average crystallite size was obtained in the range of 30 nm - 35 nm. The band gap of the ZnO thin film was observed from the Tauc's plot as ~3.32 eV which matches with the theoretical band gap value of ZnO and film had good optical transmittance in visible region. The photoelectric response of ZnO thin films were also reported and it shows rapid increase in photocurrent under LED light illumination. The room temperature vapour sensing characteristics were done using home-build gas/vapour sensing setup and it shows good response towards ethanol. The response and recovery profile as a function of varying concentration were also reported. Hence, ZnO acts as a suitable candidate for detecting ethanol vapour under the light assistance.

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