

Varied Sensing characteristics of In- doped ZnO Films Prepared by Sol Gel Spin Coating Technique

Sonik Bhatia, Neha Verma, R. K. Bedi

Abstract— Nowadays, for environmental protection, the use of portable gas sensor is essential to detect toxic gases. To control this problem of hazardous gases, metal oxide based sensors plays a vital role. These sensors enhanced charge transport and catalytic properties. In this recent study, Indium doped ZnO films were prepared by sol gel spin coating technique on glass substrate for the host of ethanol gas. To enhance the sensing properties, different concentrations of Indium (1.0at.wt%, 1.5 at.wt%, 2.0 at.wt%, 2.5 at.wt%) was used as dopant. XRD revealed hexagonal wurtzite structure highly oriented along (101) plane and well crystalline. FESEM images of prepared films permits the grain size was of the order of 40-75 nm. Optical properties confirmed the band gap lies in the range of 3.00-3.20eV. The detailed characterization studies revealed that the prepared In-doped ZnO films are well-crystalline which are used for fabrication of optoelectronic devices. Thus, at optimum In concentration (2.0 at.wt%) the prepared films are exhibiting highest response and sensitivity towards 6% volume of ethanol gas at different temperature. These films have fast response and recovery time in the range of 14-27 sec and 67-63 sec. This quick response and recovery time of gas sensor was explained by valence ion mechanism.

Index Terms—Ethanol, Gas sensor, In-ZnO films, Spin coating

I. INTRODUCTION

IN In the present scenario, growing population growth, Industrialization and leakage of toxic gases has led to increase the environmental pollution. In the biosphere, it is an alarming threat to ecosystem. For the security of environment, detection of these poisonous and hazardous gases is required. To detect toxic gases different types of sensors has been developed such as polymer sensor, electrochemical sensor and metal oxide semiconductor sensor [1-3]. Researchers around the globe are trying their best to develop novel variety of chemical sensors. A sensor is a component of electronic

circuit which sense changes on its surface due to adsorption and desorption of test gas molecules. Adsorption is a surface effect; it can be increased by using different type of modifiers (dopants) that has stronger chemical affinity for specific gas molecule. Till date most of the gas sensor facing difficulty in getting high response and recovery time at room temperature. To obtain good sensing properties at room temperature researchers are adopting different approaches such as doping, annealing temperature, synthesis techniques [4-6]. Doping element can create defects and these defects play an important role as adsorption sites for gas molecules, which can sense toxic gases at lower temperature [7]. In order to improve optoelectronic properties various researchers have studied that response of sensors can be improved by adding various type of dopants such as In, Ga, Au [8-10].

Ethanol is flammable, colorless, volatile liquid having structural formula $\text{CH}_3\text{CH}_2\text{OH}$. It is commonly called alcohol. Discharge of excess concentration of ethanol in atmosphere may cause skin and eye irritation, central nervous system depression, nausea. Therefore it is necessary to find the effective methods to control issue related to human health. Many techniques such as spray pyrolysis, sol gel with spin and dip coating, simple heat treatment and thermal evaporation were used [11-15]. Among these, sol gel spin coating technique is one of the best techniques for gas sensing application.

Nanotechnology played a heroic role in the field of physical, chemical, biological and other applied science domains. Transparent conductive oxide (TCO) is attracted a lot of attention to create smart, versatile and functional devices. ZnO based films plays a vital role for fast response and exquisite sensitivity to the surrounding environment. According to Junjie Qi et.al [16] very fast response (10s) and recovery time (23s) was observed at 450 ppm ethanol. Sen Liu [17] reported high performance of gas sensor using graphene based material.

In the present study, Indium (In) doped ZnO films were synthesized by sol gel spin coating technique. Herein different concentration of In (1.0at.wt%, 1.5 at.wt%, 2.0 at.wt%, 2.5 at.wt%) was used as dopant for preparation of In- doped ZnO films and their gas sensing applications towards ethanol gas is studied.

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II. MATERIALS AND METHODS

Synthesis of In- doped ZnO Films

Glass substrates (40x40 mm²) were cleaned ultrasonically in deionised water, acetone and isopropyl alcohol for 15 min each to remove impurities and then dry this substrate in hot air oven at 60°C for 5-10 min.

“Fig 1(a)” shows experimental procedure of spin coating technique. The source solution contained 0.4M of Zn acetate dihydrate, dissolved into ethanol (as solvent) and the mixture were stirred at 60°C for an hour to complete dissolve solute into solvent. When the solution turned into milky state, add Mono ethanol amine (MEA) as stabilizer slowly into the solution. In was doped by adding indium nitrate into the solution by varying In/Zn ratio (1.0at.wt%, 1.5 at.wt%, 2.0 at.wt%, 2.5 at.wt%). and the solution was stirred until completely dissolved, an equimolar concentration of MEA was added drop by drop. After preparing the solution was slowly dropped on a glass substrate. The spin coating time was 30 seconds, in the beginning 10 sec speed was 1500 rpm and in the later 20 seconds speed has 3000 rpm. After seven coatings, dry the substrate in hot air oven at 100°C for 20 min and then anneal these prepared films at different temperatures (600°C) for an hour was named as IZ1, IZ2, IZ3 and IZ4 respectively.

Gas sensing application

To prepare ZnO based films for gas sensor application, sol gel spin coating technique is used. Gas sensing properties of the prepared film is investigated from the static gas sensing set up. The concentration of the gas is achieved by injection of measured quantity of ethanol inside the chamber. The sensor response is calculated by using the relation $S = R_a/R_g$. Where R_a is resistance in air and R_g is resistance in gas. Systematic set up is shown in “fig 1(b)”. Gas sensing result shows In doped ZnO films has high sensitivity towards ethanol at low operating temperature. The obtained films were characterized in detail by using various analytical techniques.

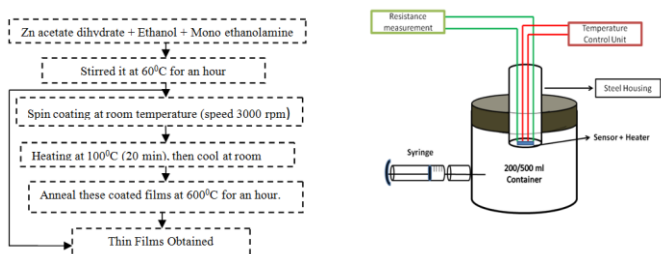


Fig. 1. Systematic diagram of experimental procedure (a) Sol gel spin coating technique (b) Gas sensing set up.

The various properties of ZnO films were prepared by sol gel spin coating technique. Crystallinity of ZnO nanoparticles was analyzed by X Ray Diffractometer, by use of analytical, Xpert Pro with CuK α_1 , nickel metal is used as beta filter, radiation source in the range 20-80°.

Surface morphology was observed from field emission Scanning Electron Microscope (FESEM- JSM6100 (Jeol)). Fourier Transformation Infrared Spectra (FTIR) was obtained from the KBr pellets using FTIR spectrometer (FTIR 8400S, IR Prestige 21) obtained from Shimadzu, it gives the information about organic, inorganic compound and vibrational modes. For the optical measurements (absorbance and optical band gap) a double beam spectrophotometer (UV-Vis 2600/2700) Shimadzu with the wavelength range 200-700 nm were employed. Gas sensing properties of the prepared films were investigated from the static gas sensing set up. The concentration of the gas is achieved by injection of measured quantity of ethanol inside the chamber. The sensor response was calculated by using the relation $S = R_a/R_g$.

III RESULTS AND DISCUSSIONS

Structural, morphological and optical Properties of In-doped ZnO films

“Fig. 2” shows X Ray Diffraction (XRD) spectra of In-doped ZnO. Different peaks of samples corresponds to hexagonal crystalline structure. Observed XRD pattern exhibits well reflections at $2\theta = 31.78^\circ, 34.40^\circ, 36.20^\circ, 47.54^\circ, 56.60^\circ, 62.91^\circ, 66.46^\circ, 68.20^\circ, 69.08^\circ$ corresponding to hexagonal phase of In- ZnO plane (100), (002), (101), (102), (110), (103), (200), (112), (201) respectively. These observed diffraction planes are well matched with standard card number (JCPDS 36-1451). The presence of most prominent peak at (101) shows polycrystalline nature. Intense and sharp peak highly demonstrates that the obtained films are well crystalline.

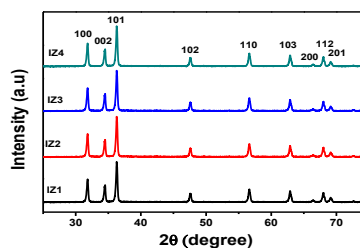


Fig. 2. Typical XRD pattern for (a) IZ1, (b) IZ2, (c) IZ3 (d) IZ4 Indium- doped ZnO films.

The lattice spacing was calculated from Bragg’s formula

$$2d \sin\theta = n\lambda$$

Where d is lattice spacing and θ is angle of incidence, λ is wavelength and n is the diffraction.

Crystal size can be found from scherrer’s formula

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

Where D is the crystalline size, K is constant i.e 0.89, λ = 0.154 nm, mean wavelength of CuK α_1 radiation, β is full width half maxima and θ is Bragg’s angle in radians. Interplanar distance (d) and strain (S) was calculated as follows [18]

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

$$S = \frac{\beta}{\tan\theta}$$

Where β is FWHM in radian. These all parameters are calculated with respect to most intense plane (101). Table 1 shows XRD parameters of prepared films. Observed crystal size lies in the range of 20-27 nm. It is clear that there is improvement in structural properties with variation in In concentrations [18,19]. Interplanar distance shows a very small change because there is very small variation in angle of peak.

Sample	Plane	Crystal size (nm)	Int. planar dist.(nm)	Strain(%)
IZ1	(101)	26.25	0.12	0.14
IZ2	(101)	26.25	0.12	0.14
IZ3	(101)	26.25	0.12	0.14
IZ4	(101)	26.25	0.12	0.14

Table1. Structural parameters of In-doped ZnO films

“Fig 3” shows the FESEM images of In-doped ZnO films prepared by sol gel spin coating technique. Promiscuous small grains are the main cause of mobility of nanoparticles which attributes size that can be activated by increased energy due to variation in concentration of doping elements. “Fig 3 (a)” shows rough and non uniform grains. However, roughness decreases with increase in indium concentration. It is clear from “fig 3” that doped ZnO nanoparticles produce almost non uniformly distributed Spherical, hexagonal and other morphologies [19]. This shows that the different morphology determined the outcome of gas sensing property. Aggregated sphere shaped nanoparticles were observed with average diameter 50-110 nm. The average width and length of In-doped ZnO nanoparticles are found to be 18.6 nm and 20.8 nm for IZ3 sample. This characterization technique reveals that with the variation in concentration of indium doping, the quality of prepared films is improved [20].

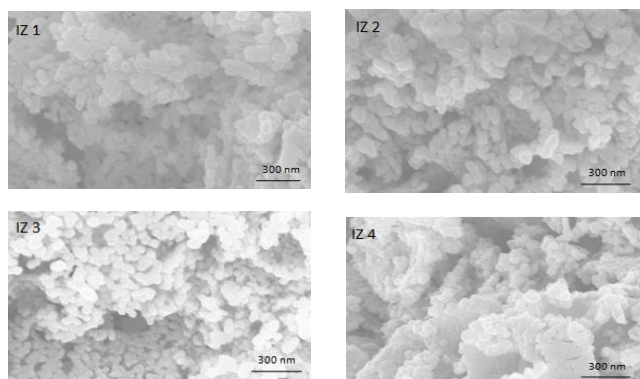
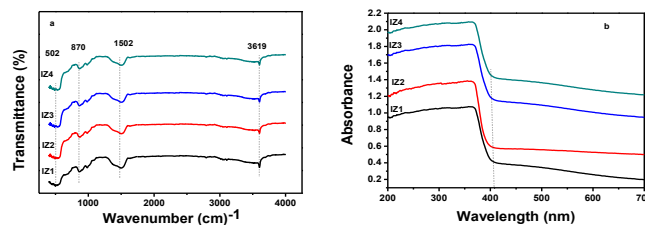


Fig. 3. Typical FESEM images of In-doped ZnO films for IZ1-IZ4 respectively.

“Fig4(a)” shows Fourier Transformation infrared Spectroscopy for In-doped ZnO films. The broad band near 3619 cm^{-1} is due to OH stretching mode of vibration for doped ZnO films and another strong band near 502 cm^{-1} indicating the stretching

mode of ZnO [21]. This indicates the presence of ZnO. The band near 1200-1550 cm^{-1} indicates COO^- group. The absorption bands at 900-1000 cm^{-1} appearing in IR spectrum indicates the stretching and bending vibrations of C=O



species.

Fig. 4. (a) FTIR spectra (b) UV Vis spectra of In- doped ZnO films for IZ1-IZ4 respectively.

“Fig 4(b)” shows absorbance spectra of In-ZnO films lies in the range of 200-700 nm is observed from UV Vis spectrophotometer at room temperature. UV Vis spectra give the information about the excitonic and inter transition of nanomaterials. The transmittance of the sample is defined as the ratio of photons that pass through the sample over the incident number of photons [22].

The UV absorption peak shift from 402 nm to 405 nm which is due to size difference [23]. In-doped ZnO films exhibits a well-defined absorption band which corresponds to wurtzite hexagonal phase of ZnO as reported in the literature [24]. The shift in peak towards higher wavelength correspond decrease in band gap. Single absorbance peak in UV spectrum reveals good optical properties of doped ZnO films. Based upon the absorbance spectra, optical band gap of the prepared films can be calculated by using energy and wavelength relation.

It has observed that the optical band gap lies in the range of 3.00 -3.20 eV and less band gap was observed in case of IZ3 sample. The decrease in band gap may be due to the influence of various factors such as presence of impurity, structural parameter, grain size and carrier concentration or it may be because of removal of oxygen vacancies [21,25].

Gas sensing property

The gas sensing property of In -ZnO films is studied in static gas sensing set up. In order to measure the sensor resistance in selected volume of ethanol was injected through microsyringe. To measure the response of sensor 6 % vol of test gas was injected into the chamber. Sensitivity of the active layer upon selected gas exposure is measured in terms of the ratio $S = R_{\text{gas}}/R_{\text{air}}$. Where R_{gas} is resistance in presence of gas and R_{air} is resistance before introduction of gas. Sensitivity of the sensor for temperature dependent was studied in the range of 100-280°C. It was observed that it is very difficult to measure sensing characteristics at room temperature due to sluggish recovery kinetics.

Sensitivity to In-doped ZnO films to Ethanol

“Fig 5(a)” shows the sensitivity of In-doped ZnO film towards ethanol (6% vol) at different operating temperature. Sensitivity of In-doped film reaches to maximum value of 85 at 210°C for ethanol. Which is around 2.5 times higher than sensitivity of Sn-Ga codoped ZnO towards 400 ppm ethanol [26].

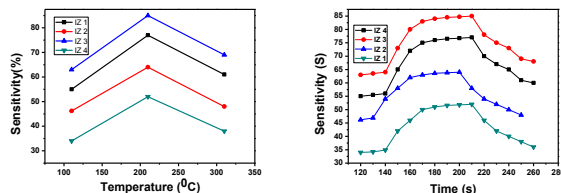


Fig.5. Gas sensing properties of In- ZnO films (a) at different operating temperatures (b) at various time.

Thus the optimum working temperature for sensor is 210 °C. In order to further clarification of sensing property of In-doped ZnO films, figure 5 (b) shows time dependence response towards ethanol for different indium doped ZnO films which was measured at 210°C. The sensitivity of the sensors abruptly increased with increase in concentration of indium. The gas sensing value is 77.04, 63.90, 85.5 and 74.85 corresponding to different concentration of indium (1.0at.wt%, 1.5 at.wt%, 2.0 at.wt%, 2.5 at.wt%) respectively. These films have fast response and recovery time in the range of 14-27 sec and 67-63 sec.

IV Conclusions

To conclude, well crystalline In-doped ZnO films prepared by sol gel spin coating technique and were used for gas sensing application towards ethanol gas. The synthesized films are well crystalline and have good optical properties. Gas sensing experiment confirmed that sensitivity of sensor increases with increase in indium concentration upto 2.0at.wt% (IZ3) and thereafter it decreases. Maximum sensitivity (85.5) was observed for ethanol at 210°C for IZ3. These properties reveal that In-doped ZnO films exhibit good sensing properties. These films have fast response and recovery time in the range of 14-27 sec and 67-63 sec. Quick response and recovery time of gas sensor are explained by oxygen space effect and valence ion mechanism.

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