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## Gas Sensing Studies on Nanocrystalline ZnO Thin Films Prepared by Dip Coating

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### ABSTRACT

Nano crystalline zinc oxide (ZnO) films were fabricated by dip coating of ZnO hydrogel. Zinc nitrate hexahydrate and sodium carboxymethyl cellulose were used to prepare the hydrogel. The dip coated samples were annealed at 400°C to obtain the high quality thin films. The films were characterized by X-Ray Diffraction (XRD) which indicated that the films are single phase with the wurtzite structure. Surface morphology of the nanoparticles were studied by Field Emission Secondary Electron Microscopy (FESEM) and optical properties were studied by photo luminescence spectroscopy. Further, gas sensing behaviour were checked for the coated films for ammonia and acetaldehyde vapours at room temperature.

**Key words:** Hydrogel, dip coating, ZnO thin films

### INTRODUCTION

Semiconducting metal-oxides such as ZnO, TiO<sub>2</sub>, SnO<sub>2</sub>, WO<sub>3</sub>, V<sub>2</sub>O<sub>5</sub> are promising candidates for gas sensing applications because of their high sensitivity towards many target gases in conjunction with easy fabrication methods, low cost and high compatibility with other parts and processes. Among various metal oxide semiconductors, ZnO which is widely known as a kind of wide-band gap semiconductor, has been proven to be an excellent gas sensing material for both oxidizing and reducing gas. Usually, the gas sensing properties of metal oxide semiconductors depend on the surface state and morphology of these materials (Rai *et al.*, 2013). Thus the nanostructured gas sensors are expected to be able to detect gas molecules at lower concentration and exhibit better sensing properties than gas sensors based on bulk material.

Variety of techniques such as Molecular Beam Epitaxy (MBE) (Kim *et al.*, 2012a), Pulsed Laser Deposition (PLD) (Mosnier *et al.*, 2009), Atomic Layer Deposition (ALD) (Godlewski *et al.*, 2009), Radio Frequency (RF) magnetron sputtering (Sundaram and Khan, 1997), Chemical Vapor Deposition (CVD) (Jain *et al.*, 1998), hydrothermal method (Kim *et al.*, 2012b), spin-coating (Kim *et al.*, 2011) and dip-coating (Lee *et al.*, 2012) have been used to prepare sensing films. Among which dip coating is an inexpensive, simple and fast coating technique. It is more suitable for large scale production when compared with spin coating (Thongsuriwong *et al.*, 2013). Formation of dip coated film strongly depends on the viscosity of the solution. Structure of the films depends on factors such as sizes and structure of the precursors, the capillary pressure and speed at which the substrate is withdrawn from the solution. In our work, we have coated ZnO hydrogel

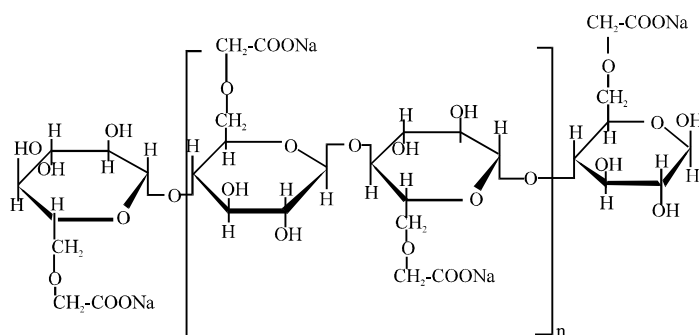


Fig. 1: Chemical structure of NaCMC

formed by mixing zinc nitrate and NaCMC on a glass substrate. Hydrogel is a polymer network chain, sometimes in the form of colloidal gel (Hashem *et al.*, 2013).

Cellulose is a polymer chain composed of repeating cellobiose units which in turn are composed of two anhydro glucose units. If hydrogen in each anhydro unit is replaced with CH<sub>2</sub>COONa it gives sodium carboxymethyl cellulose (NaCMC). The chemical structure of NaCMC is shown in Fig. 1 where n-represents the degree of polymerization. Characteristic of CMC depends on degree of substitution. It acts as stabilizer, binder, lubricant, gelling agent etc. (Shao *et al.*, 2008).

In work, CMC is used as a capping agent in order to reduce agglomeration. The main aim of this work is to report the sensing behavior of ZnO thin films prepared from the hydrogel by simple and efficient dip coating technique for ammonia and acetaldehyde vapours at room temperature.

## MATERIALS AND METHODS

The thin films of ZnO were prepared by dip coating method on a glass substrate. Glass substrates were cleaned with deionized water, acetone and ethanol before depositing the films. Zinc nitrate hexahydrate was taken as a precursor and sodium carboxymethyl cellulose was used as a capping agent.

The molar ratio of NaCMC to Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O was 1:3. Initially 6.338 g of precursor was dissolved in 100 mL deionized water with constant stirring. 100 mL deionized water was stirred and heated in a separate beaker into which 1.56 g of NaCMC was added at the temperature of 70°C which yields a viscous solution. Now the addition of precursor solution to the viscous solution results in the formation of white color solution. The solution was kept under constant stirring during the entire process. Now 1 mL of diluted hydrochloric acid was added to the milky white solution. It resulted in the formation of colourless viscous solution. Once the process was completed the solution was kept undisturbed for 24 h, hence viscosity get increased. This highly viscous solution was dip coated on a cleaned glass substrate using motorized dip coating unit. Five cycles of dipping were done on the substrate with drying (80°C) rate of 5 min. Then the films were dried in air atmosphere for 24 h. The dried films were finally annealed at 400°C for 1 h.

The crystallographic structures of samples was determined using a X-Ray Diffractometer (XRD) equipped with Cu K $\alpha$  radiation ( $\lambda = 0.15405$  nm). The particle morphology was examined using Field Emission Secondary Electron Microscope (FESEM). Photoluminescence (PL) spectroscopy property was studied at excitation wavelength of 325 nm. The gas sensing property of the films were analysed with ammonia and acetaldehyde vapour at room temperature and the change in electrical resistance of ZnO films were measured using electrometer (Keithley 6517A, Germany).

## RESULTS AND DISCUSSION

The XRD analysis was conducted for the films in order to reveal the crystalline nature of the ZnO nanoparticles. The traces of the XRD analysis are shown in Fig. 2. X-Ray diffraction studies confirmed that the synthesized materials were ZnO with wurtzite structure and all the diffraction peaks agreed with the JCPDS data (Kim *et al.*, 2010). Figure 3 shows the FESEM image of ZnO thin film. It revealed that the particles have spherical morphology with almost uniform distribution. The average size of the particles was in the range of 15-17 nm.

The room temperature photoluminescence (PL) spectra of ZnO thin film at excitation wavelength of 325 nm is shown in Fig. 4. The spectrum shows emission at 395 nm which is due to electron hole recombination and the emission in visible region is due to oxygen vacancies (Talam *et al.*, 2012).

The characteristic behaviour of n type semiconductor oxide gas sensors is that decrease of resistance upon detecting reducing gases. It has been reported that the gas sensing mechanism of most oxide semiconductor gas sensors was based on gas adsorption on the sensor surface

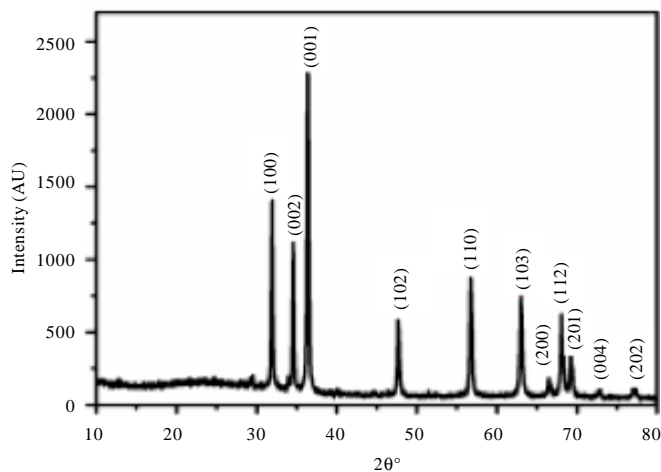


Fig. 2: XRD trace of ZnO nanoparticle deposited on a glass substrate

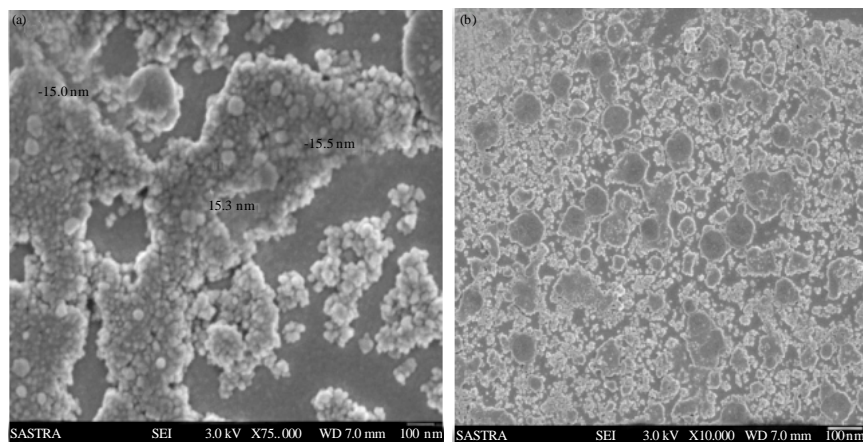


Fig. 3(a-b): FESEM image of ZnO nanoparticle at two different magnification

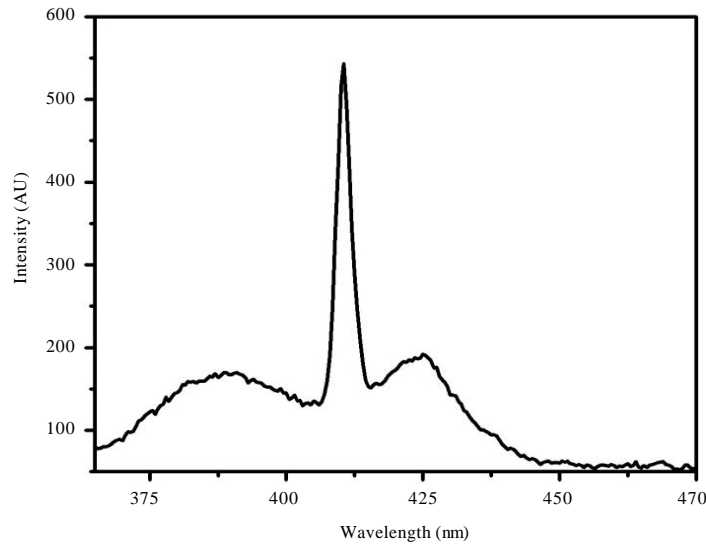


Fig. 4: PL spectra of ZnO thin films at the excitation wavelength of 325 nm

(Wang, 2004; Wan *et al.*, 2004). When the ZnO gas sensor is exposed to air, an oxygen ion molecule is adsorbed onto the surface of the film. By attracting an electron from the conduction band of the ZnO an  $O^-$ ,  $O^{2-}$ , or  $O_2^-$  ion is formed (Gergintschew *et al.*, 1995), thus the resistance is high. When the sensor is exposed to reduced gas, the exposed gas reacts with the adsorbed oxygen ion on the surface and donates electrons back into the conduction band from the surface of sensor. As a result there is increase in conductivity due to decrease in the resistance (Choopun *et al.*, 2007; Zeng *et al.*, 2009). The sensitivity (S) of the ZnO sensor towards reducing gas was calculated using the following equation:

$$S = \frac{R_g - R_0}{R_0} \times 100 \quad (1)$$

where,  $R_0$  and  $R_g$  are the sensor resistance in the absence and presence of reducing gas.

Sensitivity of ZnO thin films towards 100ppm of ammonia and acetaldehyde vapours at room temperature is shown in Fig. 5. For a comparison a film with single dipping is prepared. Figure 5a shows the sensing behaviour of ZnO thin films with single dipping. The sensitivity of the film towards acetaldehyde was 83%. Figure 5b represents the sensing behaviour of ZnO thin film with five dippings and its sensitivity towards acetaldehyde was 93%. Figure 5c shows that the ZnO film has no response towards ammonia.

From the above results it is observed that the ZnO thin films obtained from the hydrogel of zinc nitrate hexahydrate and NaCMC showed high sensing for acetaldehyde among ammonia and acetaldehyde vapours. In addition to that the sensitivity increases with increasing number of dipping cycles. The response and recovery time is in the order of seconds and minutes. Further work is in progress to develop ZnO sensor with enhanced sensing towards acetaldehyde at various concentration and temperature with better response and recovery time.

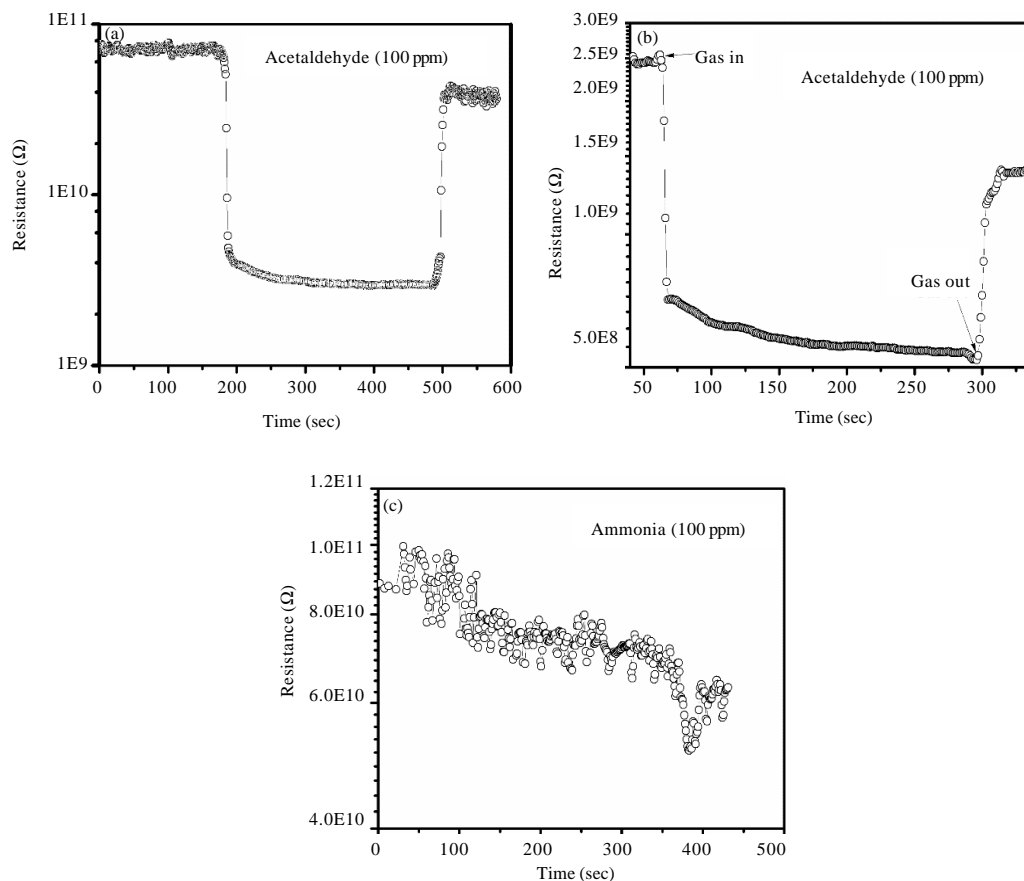


Fig. 5(a-c): Sensing response of ZnO thin films for (a and b) Acetaldehyde and (c) Ammonia vapours at room temperature

## CONCLUSION

Dip coated ZnO thin films was successfully obtained from the hydrogel of zinc nitrate and NaCMC. The high intense peaks of XRD pattern confirmed the crystallinity. FESEM image revealed that the particles had spherical morphology with the particle size in the range of 15-17 nm. The emission of the film for the excitation wavelength of 325 nm is obtained from the results of Photoluminescence spectrum. From the sensing characteristics it was observed that the hydrogel dip coated thin films had better sensing for acetaldehyde vapour at room temperature and the sensitivity increased with increase in number of dippings.

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