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An Optoelectronic Sensor Configuration Using ZnO Thick Film for Detection of Methanol

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Abstract: In the present paper sensitivity of a nanocrystalline ZnO thick film to methanol vapors is reported. The sensing mechanism is the modulation in the intensity of light reflected from glass film interface. Modulation occurs due to the change in refractive index of ZnO film upon adsorption of vapor molecules. The film has been characterized by XRD, SEM, and optical transmission studies. XRD pattern reveals polycrystalline structure of the film with grain size 33.5 nm. *Copyright © 2007 IFSA.*

Keywords: **N**anocrystalline, Sensitivity, Physisorption, Chemisorption

1. Introduction

Increased industrial processes require low cost technology which can provide immediate onsite detection of products from inorganic or organic reactions, exhaust gases, leaks etc. Gas sensing devices are used for safety applications where combustible and toxic gases are present in comfort applications such as environmental control, good air quality, process control and lab analysis. New designs for gas sensors are continuously being reported [1-4]. Materials in film form are especially suitable for such sensors since they can be fabricated in small dimensions in large scale with low cost production and are compatible with microelectronic technology. Thick film sensors are comparatively more versatile and amenable for large scale production [5]. Metal oxide films are normally used due to their capability to adsorb gas molecules in a reversible manner. The two types of adsorption on the film surface - physical and chemical - can not be differentiated strictly in many cases. Chemisorption plays role in modulating electrical parameters of the film whereas for investigating modulation in the properties of a probe light beam physisorption is also important. Most of the sensors reported depend upon modulation in electrical parameters viz. resistance and capacitance of the film [6, 7]. Thus there are oxidizing gas (O_2 [8], Cl_2) sensors, reducing gas (H_2 [9], CO [10], NH_3 [11], CH_4 [9], NO_2 [12-13]) sensors, toxic gas (H_2S [14, 15], SO_2 [16], vapors of Hg) sensors, oxygen sensors [17], alcohol sensors [18-20], odor sensors and others. These sensors utilize films of In_2O_3, undoped and doped SnO_2 etc.

Now ZnO based films are being widely studied. Interestingly it has been one of the first materials used for studying gas sensing. Moreover ZnO is physically and chemically stable, has got high transparency in the visible region, good adherence to many substrates and can be used at high temperatures as well. Besides gases [21-23], it can also be used for sensing organic vapors [24, 25]. It has been used for sensing ethanol at an operating temperature of 332 °C [24] and at low temperature [5] also. ZnO nanowire gas sensor [26] with micro electromechanical technology is reported to show high sensitivity upon exposure to 1-200 ppm of ethanol at working temperature of 300 °C.

In the present work sensitivity of ZnO thick film to methanol is presented using coated prism as sensing element. Modulation in the emergent light intensity after being reflected from glass film interface is observed. Such modulation occurs due to the change in refractive index of the film upon chemisorption and physisorption of the vapor molecules on the film surface. The response and recovery time of the sensor element has been studied.

2. ZnO Thick Film

Zinc oxide powder (99.9% pure, Ranbaxy Chemicals, INDIA) is calcined at 800 °C for three hours and then milled along with 5wt% glass powder. Cellulose resin is added to the powder to form a thick paste. Few drops of n-butyl acetate are added in the paste for viscosity regulation. The substrates – glass slide and three right angled isosceles glass prisms (BK7) - are cleaned ultrasonically using methanol, acetone and deionised water. The paste is then printed on the slide and the base of the prisms using a screen. The films are dried and then annealed at 500 °C for four hours. The coated glass slide is used for structural, morphological and optical characterization while the coated prisms are used for sensing.

The XRD pattern has been recorded by X-ray powder diffractometer (Rigaku DMAX/JADE 6.0) using Cu-Kα_1 radiation (λ=1.54056À) and is shown in Fig.1. The pattern reveals polycrystalline structure of the film. Using Debye-Scherer formula, the average grain size is calculated to be 33.5 nm. The (hkl)-orientation parameter, γ_{hkl} is calculated from the relative heights of the (100), (002), (101) and (110) reflection peaks. The calculated values of γ corresponding to these orientations show that the orientation of the thick film is random.

Optical transmission is measured using UV-VIS spectrophotometer in the wavelength range 300 to 900 nm with glass slide taken as reference and is shown in Fig. 2. The transmission gradually increases from 53% at 360 nm to 61.8% at 900 nm.

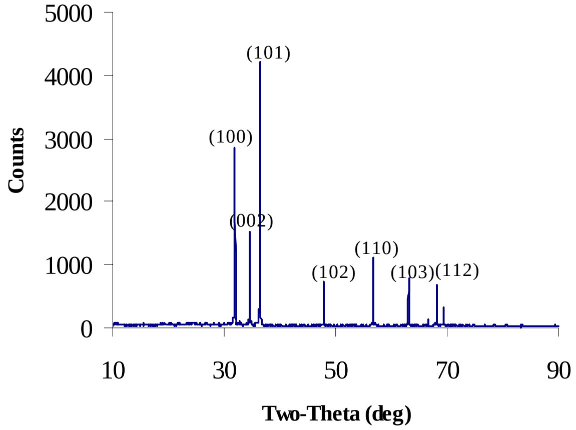

Fig. 1. XRD pattern of ZnO thick film.

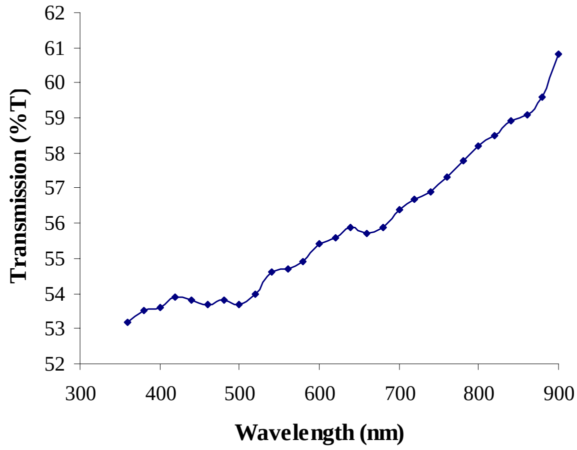

Fig. 2. Transmittance spectra of ZnO film.

3. Methanol Sensing Characteristics

The sensing element, a right angled isosceles glass prism with its base coated by ZnO thick film as mentioned in Sec. 2, is fixed in a rectangular chamber such that only the coated portion remains inside it. A small fan is fitted inside to facilitate uniform spreading of the vapors. Light from 4 mW polarized He-Ne laser (1101P, Uniphase, USA) falls, via the entry face, at the prism base - film interface at an angle θ_i = 54.82° gets reflected and then emerges out from the exit face. The emergent intensity is detected using a power meter from Newport USA. Throughout the experiment, the humidity of the chamber is maintained at 85 RH%.

25 ml of methanol is kept in a dish of 8cm diameter to facilitate slow evaporation, which in turn facilitates proper adsorption of methanol vapors on the surface of ZnO film. The effect taking place at surface of ZnO film is observed by noting the emergent intensity I_e with passage of time. With the passage of time, concentration of vapors inside the chamber increases and the emergent light intensity decreases. The variation is plotted in Fig. 3. After certain period of time, I_e becomes constant indicating a state of saturation.

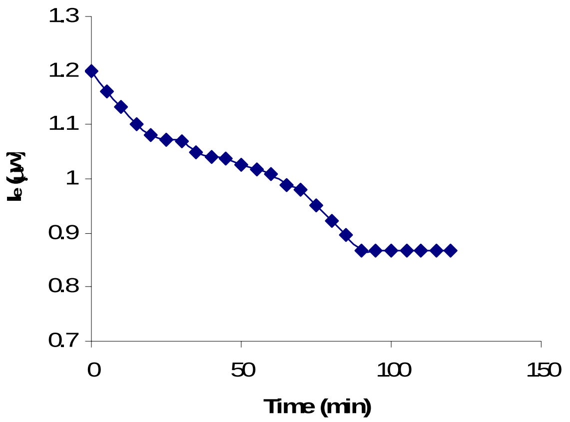

Fig. 3. Variation in the emergent light intensity from the sensing element as it is exposed to methanol vapors, pressure of which increases with passage of time.

Small volumes (270 ppm, 320 ppm and 380 ppm) of methanol are injected into the chamber which evaporate fast and vapors get adsorbed on the ZnO film. The variation in I_e with time for each concentration is plotted respectively as curves a, b and c of Fig. 4. For higher ppm of methanol , the time taken by sensing element to reach a constant value is higher The response time for detecting 270, 320 and 380 ppm of methanol is 52, 55 and 60 seconds respectively. Here the response time [27] is defined as the time taken by the sensor element to reach 75% of maximum response. The recovery time of the film is nearly 6 minutes.

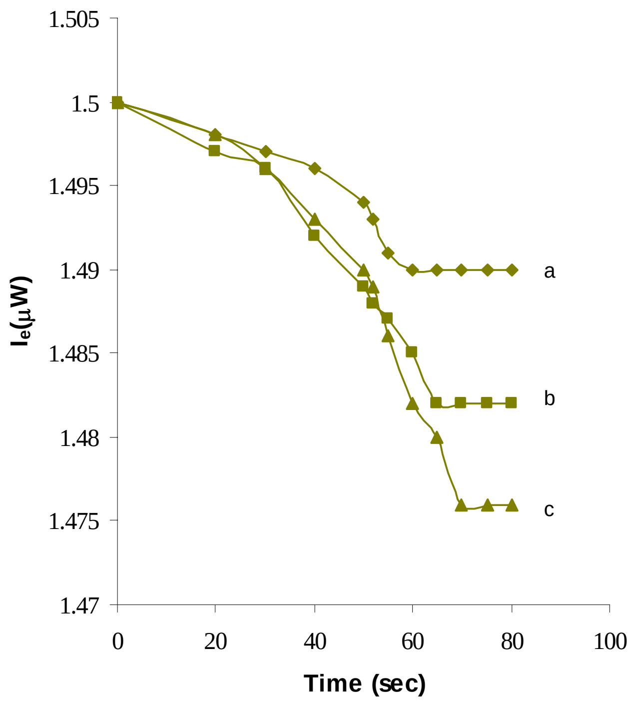

Fig. 4. Variation in the emergent light intensity from the sensor element with time as it is exposed to methanol vapors. Curves a, b and c respectively correspond to 270, 320 and 380 ppm.

The slow recovery time can be understood as occurrence of adsorption and desorption processes at different energy levels. Adsorption is an exothermic process, whereas desorption needs external energy for gas molecules to depart from the metal oxide film surface. So a relatively long time seems to be required to desorb the methanol vapor.

4. Surface Morphology

Fig. 5 shows the SEM of thick film of ZnO. Flakes of ZnO are scattered throughout the whole substrate forming a network of pores and flakes. These pores are expected to provide sites for facilitating adsorption sites and consequent sensing capability. Each flake is expected to have nanoparticles, as obtained by Debye - Scherer formula, and nanoporous structure.

Fig. 6 shows the surface structure of the ZnO film after its exposure to methanol. Comparison of Fig. 6 with Fig. 5 shows that most of the flakes seen in unexposed ZnO film have become smooth and the porosity has reduced.

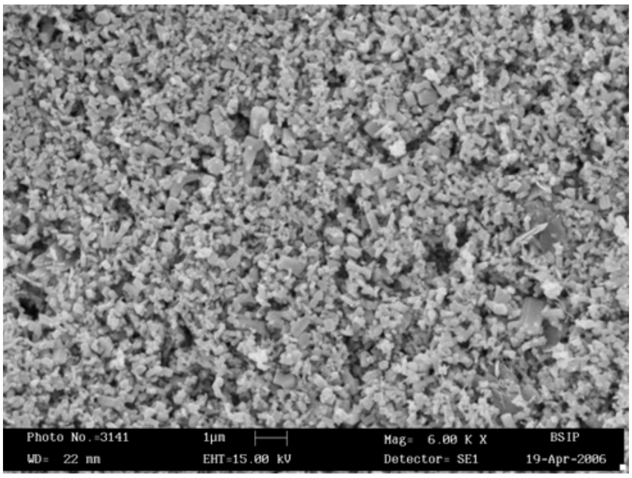

Fig. 5. SEM of ZnO film.

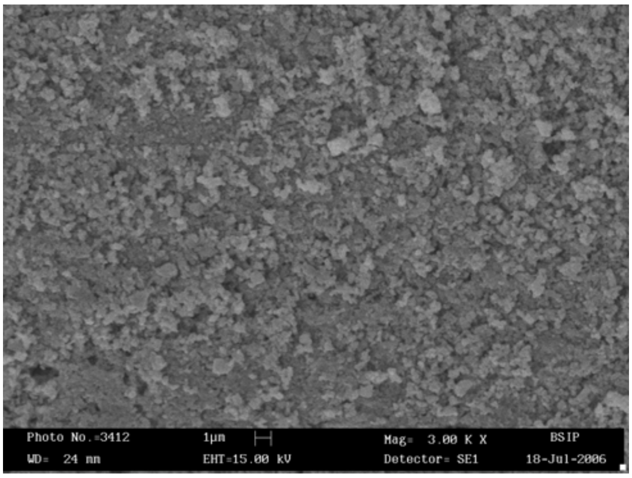

Fig. 6. SEM of ZnO thick film after its exposure to methanol vapors.

5. Discussion

The presence of methanol vapors inside the chamber leads to physisorption and chemisorption of vapor molecules. It is typical for the porous structure that the pores between the grains are connected to pores which reach to the film surface. As a result, films adsorb vapor molecules until they are saturated after reaching a state of equilibrium between adsorption and desorption. The surface retention of gas molecules changes the refractive index of the film. This leads to modulation in the intensity of the ray reflected from the glass - film interface. After certain period of time emitted light intensity becomes constant.

Thus the present optoelectronic sensor configuration using polycrystalline ZnO thick film having nano sized grains can be used for sensing methanol vapors.

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Sensors & Transducers Journal (ISSN 1726- 5479) provides an advanced forum for the science and technology of physical, chemical sensors and biosensors. It publishes state-of-the-art reviews, regular research and application specific papers, short notes, letters to Editor and sensors related books reviews as well as academic, practical and commercial information of interest to its readership. Because it is an open access, peer review international journal, papers rapidly published in *Sensors & Transducers Journal* will receive a very high publicity. The journal is published monthly as twelve issues per annual by International Frequency Association (IFSA). In additional, some special sponsored and conference issues published annually.

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Contributions are invited on all aspects of research, development and application of the science and technology of sensors, transducers and sensor instrumentations. Topics include, but are not restricted to:

- Physical, chemical and biosensors;
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- Theory, principles, effects, design, standardization and modeling;
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- Virtual instruments;
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