ZnO/Ti Thin Film: Synthesis, Characterization and Methane Gas Sensing Property

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Abstract. Thin films of ZnO were synthesised on glass substrate by dc sputtering technique at a system pressure of 10⁻⁴ Torr. A layer of TiO₂ was deposited onto the above ZnO films by high pressure sputtering technique. The composite structure was then subjected to rapid thermal annealing at a pressure of 10⁻² Torr in argon ambience. Microstructural and compositional analyses were carried out by SEM, EADX and XRD studies. The optical band gap pure ZnO (~3.45 eV) was found to shift to higher energy (~3.54 eV) for the ZnO/Ti structures. FTIR measurement indicated the presence of a prominent absorption peak at ~490 cm⁻¹ due to ZnO stretching mode. Methane gas sensing measurement was carried out at 353K, indicated that the highest sensitivity was nearly 60% with a response time ~52 min when the film were exposed to 10% vol. of methane gas.

1. Introduction
The detection of different kinds of explosives and hazardous gases in the atmosphere is generally made by using metal oxides and porous silicon based sensors. These sensors are quite expensive and are not readily available in the market. Hence, it is of prime interest to the researchers to synthesize new materials which would allow developing sensors of low cost, high sensitivity, selectivity, short response and recovery times as well as of small dimensions to enhance their portability and use.

The current day gas sensors, generally made of thin film structures of different metal oxides (SnO₂, TiO₂, ZnO, etc.), are being studied widely [1-6]. Most of them have the ability to transform the change in gas concentration to electrical signal immediately (i.e. electrical resistance or change in conductivity of these materials), which allow using rationally simple scheme for implementing the final equipment. Besides, thin film sensors using less electrical input have also been manufactured. Among these, zinc oxide (ZnO) is one such material which has been studied in various forms for the detection of different gases (Table 1). However, as can be seen from Table 1, the sensors made of ZnO have high working temperatures.

ZnO is also a multifunctional material. Because of its high chemical stability, low dielectric constant, large electrochemical coupling coefficient and high luminous transmittance, ZnO materials have been widely used as dielectric ceramic, pigment, catalyst and sensing material. It is sensitive to many sorts of gases, and has satisfactory stability. Its gas selectivity can be improved by doping additives and catalysts. However, the working temperature of these sensors is rather high, normally 400-500°C and their gaseous
selectivity, comparatively poor. Studies on gas sensing materials by improving their preparation method and decreasing their working temperature are currently one of the major research topics [13].

| Sensor                | Gas               | °C  | K   | Ref  |
|-----------------------|-------------------|-----|-----|------|
| ZnO nanorods          | ethanol, H₂       | 350 | 623 | [7]  |
| ZnO nanowire          | ethanol           | 300 | 573 | [8]  |
| Al-doped ZnONOₓ       |                   | 100-300 | 373-573 | [9]  |
| ZnO thin films        | CH₄               | 150-350 | 423-623 | [10] |
| SnO₂-ZnO              | ethanol, acetone  | 300 | 573 | [11] |
| Fe₂O₃-ZnO             | NH₃               | 350 | 623 | [12] |

In this connection methane sensor made of nanocrystalline Ti/ZnO composite films has been reported. The films show good sensing behaviour at a temperature ~353K, quite low as compared to the other methane sensors reported before.

2. Experimental

ZnO/Ti composite thin films were deposited on cleaned glass substrates. ZnO films were deposited by d.c. sputtering technique. The substrate was maintained at room temperature and the argon gas pressure during deposition was kept constant at ~0.3 mbar. The deposition was carried out for 3 hours at a constant power (~60 W). Subsequently, titanium was sputtered at room temperature at an argon pressure of ~0.3 mbar at a constant power of ~75 W. The deposition was carried out for 10 minutes and a very thin layer of Ti was deposited. The base pressure was maintained better than ~10⁻⁵ mbar. The ZnO/Ti composite structures so obtained were subjected to rapid thermal annealing inside a quartz chamber. Annealing was carried out for 3 minutes at temperature ~573K in partial argon gas pressure (~10⁻⁴ Torr). Gold contacts were deposited on the ZnO/Ti thin films for sensitivity measurements.

Optical studies were performed by measuring transmittance in the wavelength range λ=200-2500 nm using a spectrophotometer (Hitachi-U3410) at room temperature. The spectra were recorded with a resolution of λ ~ 0.07 nm along with a photometric accuracy of ±0.3% for transmittance measurements. Compositional information was obtained by EDAX (Oxford Instruments' INCA Energy 250 Microanalysis System), which indicated that the films were nearly stoichiometric. The surface morphology of the films was studied by Field Emission Scanning Electron Microscope (FESEM) (Carl Zeiss SUPRA® 55 with GEMINI® Technology with resolution ~0.8 nm @ 15 kV). AFM pictures were recorded by using a Nanosurf Easy Scan 2 in contact mode while X-Ray Diffraction (XRD) studies were carried out by Rigaku MiniFlex using Cu Kα line (0.154 nm). FTIR spectra were recorded in the range of 400-4000 cm⁻¹ by using a Nicolet™-380 FTIR.

3. Results and Discussion

3.1. Microstructural Studies.

3.2.1. SEM studies

The SEM micrograph of pure ZnO on the glass substrate sputtered for 3 hrs is shown in Fig. 1(a). It is clearly identified that the ZnO particles form a cluster over the surface of the glass substrate. As seen from the micrograph, the film is compact and quite homogeneous in nature. Fig 1(b) shows the micrograph of a ZnO/Ti film subjected to RTA 3 minutes at ~573 K. Cracks have developed on the surface of the film.
3.1.2. EDAX Studies.
Energy Dispersive X-Ray method was used to determine the qualitative and quantitative composition of the surface of the film. Fig. 2 shows the EDX spectrum of a ZnO/Ti film. The spectrum is dominated by the peaks of zinc (Zn), oxygen (O₂), gold (Au) and with suppressive peaks of titanium (Ti). The percentage weight of the elements present as obtained from the analysis of the spectra are oxygen (18.22%), titanium (0.76%) and zinc (81.03%). The gold peaks have been excluded from the analysis.

Fig. 2. EDAX spectrum of a representative ZnO/Ti film

Fig. 3. XRD traces of: a) pure ZnO sample and b) ZnO/Ti sample
3.1.3. XRD Studies.
X-Ray diffraction pattern was obtained from Rigaku Miniflex. Diffraction pattern of pure ZnO is shown in Fig. 3a. XRD peaks at $2\theta \sim 31^\circ, 34^\circ, 36^\circ, 47^\circ$ and $62^\circ$ are due to the reflections from the (100), (002), (101), (102) and (103) planes of ZnO, respectively and the XRD pattern of ZnO/Ti (Fig. 4b) depicts that peaks at $2\theta \sim 31^\circ, 35^\circ, 56^\circ$ and $76^\circ$ correspond to the reflections from (100), (101), (110) and (202) planes of ZnO, respectively. There was no observable peak for reflection from Ti.

3.2. Optical Studies.
The band gap of ZnO was found by the optical procedure, in which the transmittance vs. wavelength was obtained by UV-VIS-NIR Spectrometer. The band gap was determined by extrapolating the linear portion of the plot of $(\alpha h\nu)^2$ versus $h\nu$ (Fig. 4c, d). The band-gap of pure ZnO was $\sim 3.45$ eV and ZnO/Ti was shifted to $\sim 3.54$ eV due to Burnsten Moss Shift.

![Fig. 4](image_url)

Fig. 4. Transmittance vs. wavelength plot of a) pure ZnO thin film, b) ZnO/Ti thin film. $(\alpha h\nu)^2$ vs. $h\nu$ plot; c) pure ZnO thin film, b) ZnO/Ti thin film

![Fig. 5](image_url)

Fig. 5. FTIR spectra of: a) ZnO and b) ZnO/Ti film
3.3. FTIR Studies.
FTIR absorbance spectrum was recorded in the range of 400 to 4000 cm\(^{-1}\) of the pure ZnO and ZnO/Ti is shown in the Fig. 5. The spectral region encompasses every stretching and bending mode. It may be observed that FTIR spectra for both pure ZnO and ZnO/Ti film (Fig.6) show a prominent peak at ~488 cm\(^{-1}\) due to Zn-O stretching mode. Peak at ~1701 cm\(^{-1}\) (Fig. 5(b)) is due to OH bending of water.

4. Sensitivity Studies.
After characterising the material, the sensitivity tests of the material towards methane gas was carried out. For this, the sample was mounted on a platform. Electrical contacts were made to an ammeter and a voltmeter through the gold contacts which was deposited by the evaporation technique on the corners of the sample. The chamber was isolated using a glass bell jar.

Before injecting the gas into the chamber, the sensor was heated to ~60\(^\circ\) C. It was observed that as the temperature was increased, the resistance of the sensor material decreased with increasing temperature. The temperature was maintained at 60\(^\circ\) C for gas sensing experiment. Resistance remained all most steady [Fig (6)] at the controlled temperature of 60\(^\circ\) C. Then at this temperature, at a steady value of resistance, methane gas (10% volume concentration) was injected into the chamber. The change in the electrical resistance of the sensor was calculated by studying the change of current. The sensitivity(S) of the material was calculated based on the following formula:

\[
S = \left(\frac{R_{\text{air}} - (R_{\text{gas}) \text{ eq}}}{R_{\text{air}}}\right) \times 100
\]

Where, the sensor’s resistance in presence of the target gas (i.e. R\(_{\text{gas}}\)) and that in air (i.e. R\(_{\text{air}}\)) [14]

Fig (7) shows the plot of the sensitivity versus time interval. It is found that S is less than unity for reducing gases. The percent sensitivity i.e. the percent reduction of sensor resistance is given by [14]:

![Fig. 6. Resistance vs. Temperature](image1)

![Fig. 7. Sensitivity vs. time](image2)

5. Conclusion.
In this work deposition and characterization of de-sputtered ZnO/Ti thin film and its use for detecting methane gas was carried out. The sensitivity measurement of the film was carried out at ~330K in presence of 10%vol. concentration of the methane gas. Its sensitivity may be increased by increasing uniformly deposition of titanium (Ti) over ZnO layer or by using other catalyst like palladium or by using multiple layers. Experiments in these directions are in progress. Also the selectivity and stability of the sensors are to be examined. The above result may be utilized to design a methane gas sensor for environment health and safety.
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