INTRODUCTION

Carbon dioxide is one of the most frequently found nontoxic gases in atmosphere. The CO₂ gas is odorless & cannot be detected without measuring instruments. CO₂ is harmless in small quantity because it is naturally consumed by the soil, trees and the ocean. However, the concentration of CO₂ is increasing in the atmosphere due to industrial revolution, combustion process and green house effect. This increase in concentration may lead to problems in future as in high concentrations it is fatal & insidious. Therefore, demand for the detection of carbon dioxide gas is increasing for global environmental surveillance and in several key fields such as indoor and outdoor air quality monitoring, biogas, smoke systems, process control in fermentation, medical field and vegetable intelligent packaging. Variety of materials like semiconductors, polymers, and zeolite based materials are being used as CO₂ gas sensors. Most of the recently available carbon dioxide sensors work on optical principles and are usually bulky and expensive. Therefore, there is a need of an alternative sensor for CO₂ monitoring which is not only cheap but also efficient. In this context, use of semiconductor metal oxides for carbon dioxide detection is an excellent option due to their low power consumption, cost effectiveness, efficiency, ability to integrate into electronic and control devices and response to gases after exposure.

Zinc oxide (ZnO) is one of the unique and promising metal oxide semiconducting materials with attractive optical and electrical properties. It is an n-type semiconductor of wurtzite structure with a direct energy wide-band gap of about 3.37 eV and a relatively large excitation binding energy of 60 meV at room temperature. It can be used as a transparent electrode in solar cells and flat panel displays as well as for the fabrication of gratings in optoelectronic devices, as a window material in antireflection coatings and in optical filter. Furthermore, ZnO is being widely used as a gas sensor due to its conductivity changes when exposed to gases because of its chemical sensitivity to gases, suitability to doping, non-toxicity, and low cost, high chemical and mechanical stability, eco-friendly nature, biocompatibility and abundance.
Review of literature reveals that lot of work has been carried out on ZnO material as a gas sensor for sensing ethanol, ammonia, hydrogen, methane, nitrogen, oxygen, carbon monoxide, & hydrogen sulphide gases\textsuperscript{12,14-30}. However, very meager work has been carried out on CO\textsubscript{2} gas sensor. Zinc oxide thin films, synthesized using reactive d.c. sputtering method, have been used for gas sensor applications and the sensitivity of the film synthesized at substrate temperature of 130°C is found to be 2-17 in the presence of CO\textsubscript{2} gas at a measuring temperature of 100°C\textsuperscript{31}. The study on the response of ZnO tetrapod-based sensor in various gas environments such as H\textsubscript{2}, CO, i-butane, CH\textsubscript{4}, CO\textsubscript{2}, and SO\textsubscript{2} at room temperature is also carried out\textsuperscript{29}. Nevertheless, the gas sensor based on pure ZnO can not cope up with current requirements for fast, continuous and trace detection. Attempts have been made to improve the properties of gas sensors by using additives like noble metals and transition metals\textsuperscript{32-34} and there is lot of scope and need for the improvement of gas sensitivity. From this point of view, swift heavy ion (SHI) irradiation is one of the effective techniques which can alter the material properties to a great extent. However, the interaction of an ion beam with a material depends on the ion energy, fluence and ion species\textsuperscript{35-36}. While traveling through the matter, swift heavy ions lose their energy due to interaction with target atoms through inelastic collision. This energy released in a very short duration of time leads to amorphisation, recrystallization or phase change. Moreover, it is reported in the literature that the H\textsubscript{2}S gas sensitivity of the ZnO nanowires could be modulated and enhanced by He\textsuperscript{+} implantation at an appropriate dose\textsuperscript{37}. Effect of 100 MeV O\textsuperscript{1+} ions irradiation on ethanol sensing response of nanostuctures of ZnO and SnO\textsubscript{2} has been carried out by R. C. Singh\textsuperscript{38}. K. Watanabe et al have developed and analyzed effect of UV irradiation on NO\textsubscript{2} desorption from ZnO thin films\textsuperscript{39}. Thus there is a hope that the gas sensing properties of ZnO-based gas sensors could be affected when exposed to highly energetic SHI radiations.

Therefore, this paper deals with the development of CO\textsubscript{2} gas sensor based on zinc oxide thick films and investigation of the effect of ion irradiation on the structural and gas sensing behavior of ZnO films prepared by sol gel spin coating method. The films are irradiated using Ag\textsuperscript{7+} ions with a fixed fluence of 3 \times 10\textsuperscript{11} ions/cm\textsuperscript{2} carrying energy 100 MeV. The pristine and irradiated ZnO films are characterized by means of XRD for structural identification. The effect of SHI irradiation is studied by carrying out detailed study on CO\textsubscript{2} gas sensing behavior of pure and modified films.

**MATERIAL AND METHODS**

**Film preparation**

Zinc acetate dihydrate, iso-propanol, ethanol amine, analytical grade reagents (Sigma Aldrich) are used as the precursors for the sol preparation. Initially, zinc acetate dihydrate (3.10 gm) is dissolved in iso-propanol (15 ml). Ethanol amine (0.86 ml) is then added to the zinc acetate solution with ethanol amine to zinc acetate molar ratio 1:1. The mixture is continuously stirred at 60°C for 60 minutes\textsuperscript{40-43}. The sol, thus obtained, is then aged for 24 hrs for gelation to occur. ZnO thick films are deposited on precleaned glass substrate by sol gel spin coating technique. Cleaned glass substrates are fixed on the spin coater and are spun at 2500 rpm for about 1 minute while aged gel is dropped onto a glass substrate. The obtained single layer film is then heat treated in air oven at 270°C for about 10 minutes for the decomposition of the precursor components & formation of metal-oxides. Thus, six layered film is deposited by spin coating, followed by baking at 270°C after deposition of each layer, resulting in a thick film. These six layered films are annealed at a temperature of 350°C and are used as sensors for further studies. Figure 1 gives flowchart of sol gel spin coating process of ZnO thick films.

**Film Modification**

The ZnO films, mounted on a ladder in high voltage irradiation chamber, are modified by exposing them to heavy ion beam with a fixed dose of 3\times 10\textsuperscript{11} ions / cm\textsuperscript{2}. Films of about 1 cm\textsuperscript{2} area are irradiated with 100 MeV Ag\textsuperscript{7+} ions using 15UD Pelletron tandem accelerator installed at Inter University Accelerator Centre, New Delhi. Beam current is maintained around 1 nano ampere. Ion beam, focused to a spot of 1 mm diameter, is then scanned over 1 cm \times 1 cm area using a magnetic scanner. Through out the experiment the vacuum...
of the order of $10^{-6}$ torr is maintained. In our experiment, high energy is selected to have the range of the ions up to few microns in the material so that no ions are implanted in the film and there will be only defects due to the irradiation. The SRIM analysis of the Ag$^{7+}$ with 100 MeV ions bombarded on the ZnO thick film has shown that electronic energy losses dominate the nuclear energy losses. Using SRIM, the projected range of the ion in ZnO is determined and it is found to be approximately 50 µm.

Characterization by X-ray diffraction

The pristine and irradiated sensors are subjected to XRD analysis. The crystalline phase of ZnO thin films is identified using Rigaku make X-ray powder diffractometer (Miniflex). The samples are irradiated with monochromatic CuK$_\alpha$ radiation having a wavelength of 1.542 Å and the XRD patterns are recorded over a 2$\theta$ range of 30$^\circ$ to 70$^\circ$.

Gas Sensing Study

The pristine and irradiated sensors are tested for sensing response to carbon dioxide. The CO$_2$ gas sensing study on pristine and ion beam irradiated ZnO films is carried out using static gas characterization system as shown in figure 2. The fabricated sensor is placed in the test chamber of known volume. For the measurement of gas response, a load resistor is connected in series with a gas sensor. The circuit voltage is set at 30 V, and the output voltage measured across load resistor. The working temperature of a sensor is varied through varying the heating voltage of the heater. The sensor film is initially heated from RT to 400 $^\circ$C and voltage drop (Vr) across resistor (Rr) in air atmosphere is measured at a selected interval of temperature. A known volume of the CO$_2$ gas is injected inside the system to establish required gas concentration using a doctor’s syringe followed by measurement of voltage drop across resistor (Rr) in gas environment as a function of temperature. The electrical resistance of the film in air (Ra) and in the presence of CO$_2$ gas (Rg) is determined by using the formula:

$$R_{sensor} = \left(\frac{V_{supply} - V_{reference}}{V_{reference}}\right) \cdot R_{reference}$$

$$V_{reference}$$

The change in resistance of the ZnO thick film, when exposed to a test gas, is determined to evaluate the gas response or sensitivity factor and the percentage sensitivity factor is calculated by using the following formula:

$$SF = \frac{R_{g} - R_{a}}{R_{a}} \times 100 = \left(\frac{\Delta R}{R_{a}}\right) \times 100$$

A graph of gas response as a function of temperature with a fixed gas concentration is plotted to determine the operating temperature of the sensor film. The operating temperature is defined as the temperature at which the sensor film has maximum gas response SF (%). The gas uptake capacity of the sensor film is optimized by exposing the virgin as well as irradiated films to a gas of variable concentration.

RESULTS AND DISCUSSION

XRD Analysis

Figure 3(A-B) represents the X-ray diffraction profiles ZnO thick films before and after SHI irradiation at a fixed fluence of 100 MeV Ag$^{7+}$ ions. The XRD analysis is carried out using the JCPDS card (36-1451) for ZnO by search/match method. Both the XRD patterns exhibit all the peaks corresponding to the standard wurtzite hexagonal structure. It has been observed that [101] reflections corresponding to 2$\theta$ = 36.17$^\circ$ are of maximum intensity for both the film samples. This indicates that virgin as well as SHI modified ZnO films have strong orientation in the direction of [101] plane. All these peaks are also found to be matching with standard data and literature. From the XRD profile of modified ZnO film it can be revealed that there is increase in intensity and sharpness. It can be concluded that irradiation leads to increase in crystallinity of the ZnO film. The crystallite sizes, estimated for (101) peaks of pure and modified XRD patterns using Scherrer’s formula, are found to be 35 nm and 20 nm respectively. It is observed that even after irradiation with 100 MeV Ag$^{7+}$ ions, the modified ZnO film shows the crystalline phase. Thus it can be concluded that the influence of ion irradiation do not lead to amorphisation in case of ZnO. This result is in consistence with literature.

Analysis of Gas Sensing Study

Figure 4 represents a typical variation of sensitivity factor for a pristine sample sintered at
Fig. 1: Flow chart of methodology used for preparation of sol gel deposited ZnO thick films

- Preparation of gel
- Heating at constant temperature and time with continuous stirring
- Spin coating on substrate for 1 min
- Pre heating at 270°C during deposition for 10 min
- Final product 6-layered film
- Post heating of the films at 350°C, 450°C, and 550°C for 80 min
- Characterization by XRD
- Gas sensing study
- Modification by Ag⁺ ion irradiation

350°C as a function of temperature for 1000 ppm of CO₂. It is observed that sensitivity factor shows drastic change in the temperature range 90°C to 110°C. It reaches a maximum sensitivity value of 37.3 at 100°C & then decreases with further increase in temperature. This behavior indicates that optimum operating temperature of a six layered pure ZnO film is 100°C.

Figure 5 depicts the temperature dependence of gas response of modified ZnO thick film. Similar kind of behavior is shown by the modified ZnO film wherein the sensitivity factor initially increases with temperature, shows a maxima at 150°C & then decreases further at higher temperatures. The modified sensor displays the maximum highest sensitivity of the order of 73.8 at 150°C for 1000ppm CO₂ gas. However, it is worth to note that in both the films after every cycle decrease in response is observed.

Figure 6 shows the effect of SHI irradiation on operating temperature and sensitivity. It can be concluded that irradiation effect leads to shift in operating temperature and enhancement in sensitivity factor compared to that for pure sample.

The sensor response in the range 1000 to 14000 ppm, for pristine and modified ZnO films when operated at 100°C and 150°C, is presented in figure 7. It can be concluded that gas uptake capacity is not affected by the SHI irradiation because both films show saturation at 8000 ppm.

Fig. 2: Static gas sensor unit showing various parts of the system
Fig. 3: XRD profiles of the ZnO sensor films deposited on glass substrate via sol gel spin coating technique and sintered at 350 °C; A) Pristine ZnO sensor, B) Modified ZnO sensor

Fig. 4: CO₂ gas response of the virgin ZnO film sintered at 300 °C for a fixed concentration of 1000ppm as a function of temperature
Further increase in CO₂ gas concentration does not show any significant change. This reveals that the active region of the sensors is up to 8000 ppm.

The electronic behavior of the semiconductor material plays a major role in the sensor applications. In semiconducting oxide based gas sensor like ZnO, the sensing mechanism is considered as the adsorption phenomenon. Upon the adsorption of gases the electrical conductance of semiconductor changes and can be correlated to the gas present in the ambient atmosphere.

The adsorption process can be grouped as physiosorption, chemisorption and ionosorption. Ionosorption process, dominant in metal oxide semiconductors, involves capture of holes or of electrons or give up electrons.

The surface of ZnO is ionic in nature. Its surface metal ion can capture electron and the surface oxygen ions give up an electron. At room temperature donor levels near to the conduction band are completely ionized. But below conduction band, donor levels are not completely ionized. Thus the density of donor level in conduction band can be increased with increasing temperature or by exposing to gases.

The gas sensing mechanism is either by adsorption of atmosphere oxygen of the surface and/ or by direct reaction of the lattice oxygen or interstitial oxygen with the test gases.

When the atmospheric oxygen adsorbs on the surface, it extracts an electron from the conduction band, and formation of oxides or peroxides takes place. They are mainly responsible for the detection of the test gases.

\[
O₂ + e^- \rightarrow 2O^-
\]

This adsorbed oxygen ion decreases the electrical conductance of the semiconductor.

Whereas the reducing gases R, present in the ambient, react with the oxygen ions by trapping the electrons and liberating into the conduction bond. This leads to the increase in conductance in semiconductor.

\[
R + O^· \rightarrow RO + e^-
\]

This reaction of the conductance of the semiconductor due to this reaction can be accelerated by the presence of suitable catalyst or doping.

Thus the gaseous molecules split into ions and spread over the semiconductor surface and reacts with the lattice oxygen ion. If sensor material is with sufficient activation energy then the ionized reducing gas itself get spread over the surface of the semiconductor.

In addition to this defect structure consisting of oxygen of vacancies and interstitial oxygen ions also contribute to this mechanism. In such situation the reactions can be written in terms of krogervink notations.

\[
O_0 \rightarrow V_{0}^{++} + O_{1}^{-}
\]

\[
R + O_{1}^{-} \rightarrow RO + 2e^-
\]

Where,

\[O_0\] = The lattice oxygen.

\[V_{0}^{++}\] = The oxygen vacancy in the lattice.

\[O_{1}^{-}\] = The interstitial oxygen.

Reaction of the reducing gas with the interstitial oxygen provides two electrons to the sensor material and there by the conductance increases.

Thus, ZnO sensor works on the adsorption of oxygen on the available surface site and the reaction between adsorbed oxygen and the test gas (CO₂) is the cause of change in resistance of the sensor material. The decrease in sensitivity factor (R) at higher temperature may be due to desorption of pre-adsorbed oxygen ions from the surface of the sensor.

The ZnO thick films are prepared successfully using sol gel spin coating technique. The ZnO films are modified by the use of 100 MeV Ag³⁺ ion beam. Both, the virgin and irradiated ZnO films possess hexagonal wurtzite structure with \(c = 5.271Å\) and \(a = 3.285Å\). The crystallite size, estimated using Debye – Scherer formula, for as deposited ZnO films and modified film are 35 nm and 20 nm respectively. Irradiation leads to increase
Fig. 5: Change in sensitivity as a function of temperature in SHI irradiated ZnO film for 1000 ppm CO₂ gas

Fig. 6: Typical CO₂ gas response of the virgin and modified films showing the effect of SHI irradiation on operating temperature and sensitivity

Fig. 7: Typical change in gas response as a function of CO₂ gas concentration depicting the active region and saturation limit of the sensor
in crystallinity and reduction in average crystal size for modified ZnO films. The optimum operating temperatures for pure & modified ZnO films are found to be 100°C & 150°C respectively. The change in operating temperature is due to swift heavy ion irradiation effect. Sensitivity factor of sol gel prepared ZnO film towards CO2 has been improved by modifying it with Ag+7 irradiation. There is no effect of SHI irradiation on saturation in terms of concentration. Modified as well as unmodified ZnO have the working range of 8000 ppm.

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REFERENCES

16. References and further reading may be available for this article. To view references and further reading you must purchase this article.
24. References and further reading may be available for this article. To view references and further reading you must purchase this article.
25. Suchea M., Christoulakis S., Moschovis K.,


