Comparative studies of Pure and Mn doped ZnO thin film for gas sensor and Magnetic applications

[a] Pankaj Varshney, [a] Dr.Sandip Mahajan, [a] Dr.Ramphal Sharma*
[a] Thin Film and Nanotechnology Laboratory, Department of Physics and Nanotechnology, Dr. Babasaheb Ambedkar Marathwada University, Aurangabad-431004, (M.S.), India.

Abstract

Pure ZnO and Mn doped thin films were fabricated on glass substrates by DC co-sputtering method for magnetic and gas sensor applications. Pure and doped thin films were analyzed by X-ray diffraction (XRD) and scanning electron microscopy (SEM). The results of pure and doped thin films were also compared to investigate for improvement of magnetic and gas sensing properties. Pure and Mn doped ZnO both thin films had a hexagonal wurtzite structure with a (0 0 2) preferred orientation. From SEM results, it was seen that Mn doped ZnO thin film shows circular morphology. The Mn doped ZnO thin film exhibits enhancement in sensing properties towards the ammonia gas compared to pure ZnO through the whole detection range (20-1000 ppm). The proposed sensor is capable to detect the ammonia gas down to 20 ppm level at working temperature of 250 °C. The Mn doped ZnO sensor displays a considerably high sensing response (S.R ~23 %) towards ammonia gas at 200 ppm level with a very fast response and recovery times of few seconds. The working principle and sensing mechanism of the proposed sensor was also studied in detail. Furthermore, we have demonstrated the variation in the response for ammonia gas under different humidity conditions (0-60% RH) at the optimum temperature (250 ºC). Therefore, the present work opens a new possibility to design the remarkable ammonia gas sensor at low temperatures. The ferromagnetic behavior is presented in both pure and doped samples.

Keywords: DC sputtering; doped; ammonia sensor, ferromagnetic

Introduction

The past decade, the ZnO is one of the most tuneable and technologically semiconductor materials due to its numerous applications. Properties tuned by different ways such as doping, annealing and radiation to

improved applications in magnetic, laser and gas sensor etc. The chemical, transportation and process control industries have attracted the attention of researchers to a great extent towards monitoring of certain toxic gases such as NH_3, CO, CO_2, and NOx which are being regularly contributed to the environment in significant quantities and deteriorating the atmosphere in a number of ways [1]. Safety and security measures are also hinge upon sensing of trace elements of chemical agents. Some of these pollutants are extremely hazardous, and hence sensing them at ppm level is more important for the compatible survival of living beings. Ammonia is a common reagent and colorless toxic ingredient with a pungent odour and most dangerous and toxic gas among all the pollutants [2].Thus, the detection of dangerous and toxic gases in environment, industry or household using miniaturized devices has become a significant task. One of the most dangerous gases is ammonia. In comparison to high-power-consumption and high-temperature-operated sensors, the low-temperature-operated sensors are associated with many problems to be solved.Therefore, the highly sensitive, selective and reproducible gas sensor is requisite for detection of trace amount of ammonia at low temperatures.

Now a days, most of the researchers in the field of nanoscience and nanotechnology have been focused on the wide band gap (WBG) semiconducting materials such as hafnium oxide, titanium oxide, tungsten oxide, tin oxide and zinc oxide as these semiconductors allow the device to be operated at higher voltages with high switching speed and the radiation rich environment than the conventional (Si, Ge etc.) semiconducting materials. Among them, zinc oxide is a very encouraging material due to its remarkable physical and chemical properties such as large direct band gap (~3.2 eV), good resistivity (1.5×10^{-4} Ω-cm) [3], non-toxicity, excellent thermal & chemical stability with enhanced biocompatibility [4]. Basically, it is n-type semiconductor with stable wurtzite structure at room temperature (RT). Therefore, it is recently being used for wide range of scientific and technological applications such as gas sensor [5] , UV detectors [6], biosensors [7], neuromorphic sensors [8] and solar cells [9].

Different materials and detection schemes have been adopted in this context to achieve high responsivity combined with less response/recovery time, which are key quality factors that define the sensor performance. Literature reveals that the ZnO thin films were prepared by a variety of deposition techniques,

such as RF magnetron sputtering [10], chemical vapour deposition [11], pulsed laser deposition [12], chemical vapor deposition, [13] and sol–gel process[14], etc. Among them, the DC sputtering method offers the eco-friendly, highly uniform and large scale production for technological development.

In this work, we report the *in situ* synthesis of pure ZnO and Mn doped ZnO nanostructured thin films on glass substrates using DC sputtering method. The surface morphological and gas sensing properties of as prepared thin film samplesunder low detection limit (20-1000 ppm) were studied in detail. Since, reducing the operating temperature with improving the response has become the great challenge for the scientific community. Thus, we suppose that the Mn doping recognised the enhancement in sensivity towards ammonia and create an encouraging approach to manufacture the sensor at relatively low temperature regime for cost effective device applications. The magnetic properties were studied using M-H curve to confirm ferromagnetic behaviour.

Experimental work

2.1. Synthesis of ammonia sensor:

The method for the synthesis of thin films was performed in a custom designed chamber using high purity (99.98 %) Zn and Mn sputtering targets. Prior to deposition, the glass substrates were rinsed in deionized water for 10 min and then inserted into the custom built co-sputter chamber at fix distance of 6 cm from the high purity manganese and zinc targets. Initially, the chamber was evacuated to 8×10^{-6} Torr using turbo molecular pump backed by rotary oil pump. Thereafter, Ar gas was inserted into the sputtering chamber using mass flow controller (MKS). During all thin film fabrication, the working pressure of the sputtering chamber was kept constant at 10 mTorr with constant flow rate of $Ar:O_2$ (8:2). The nanostructured thin film samples were directly sputtered on the glass substrates at room temperature. A direct current (DC) power supply was used to fabricate the Mn doped ZnOthin films from the Mn and Zn targets at a power of ~10 W and 60 W respectively for a period of 15 minutes. It may be so far the most promising synthesis method to fabricate thin films on the large scale in contamination free environment.

2.3 Instrumentation

The structural characterization has studied X-ray diffractometer Bruker A8 advanced instrument. Surface morphologies of pure and doped samples has characterized by ZEISS scanning electron microscopy. For gas sensing applications, all the measurements were performed for as deposited samples in a custom made testing chamber. The change in electrical resistance of the samples was monitored using Keithley 6221 source-meter. The sensor response is defined as the ratio of the device resistance in synthetic air (R_a) to the resistance (R_g) after exposure to ammonia gas molecules. The response and recovery time is defined as the elapsed time to extent the signal up to 90 % change of the maximum saturated signal during adsorption and desorption process respectively. Furthermore, the entire CO sensing characterizations were repeated three times and about 2% variation in the sensing properties was detected so far. Magnetic measurements at room temperature were performed by using a standard Quantum Design superconducting quantum interference device (SQUID) MPMS magnetometer with maximum field of 10kOe.

3. Result and discussion

3.1The film morphology

Figure 2(a) show SEM micrographs of pure ZnO thin film has irregular circular shapes of grain synthesized by DC sputtering method and (b) shows cross section image. Figure 3(a) Mn doped ZnO samples shows regular shapes in circular morphology and little porous morphology to enhanced gas sensing results [15].

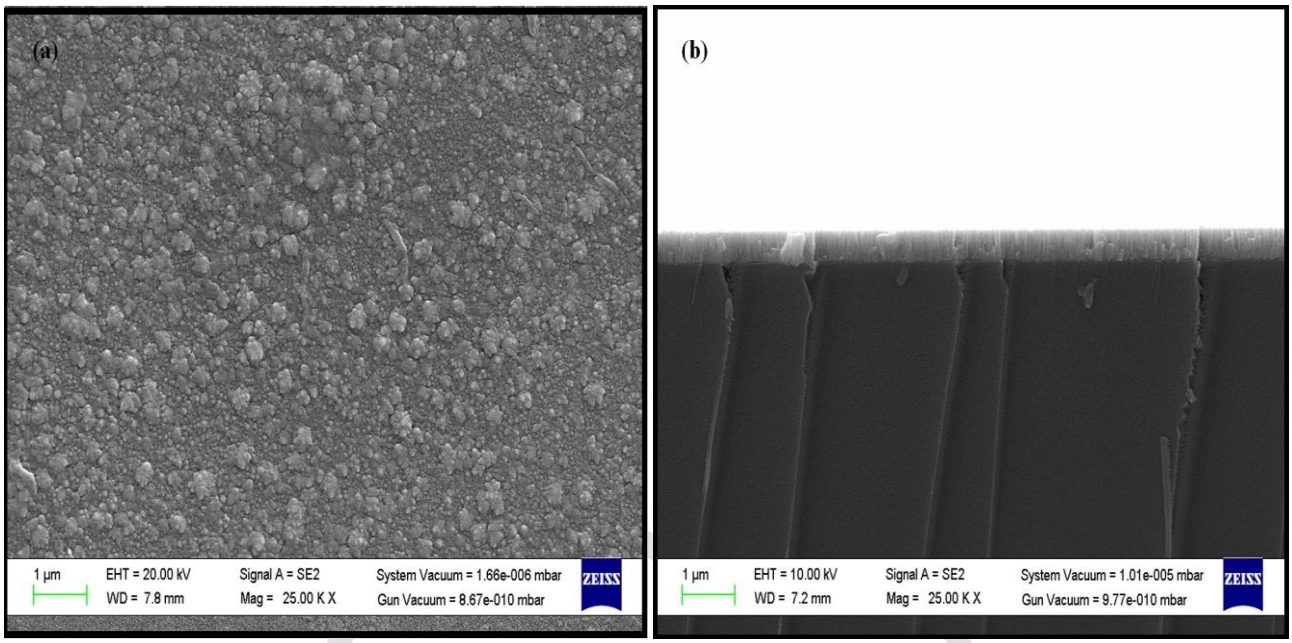

Figure: 2(a) SEM micrographs of pure ZnO thin film and 2(b) Cross section image.

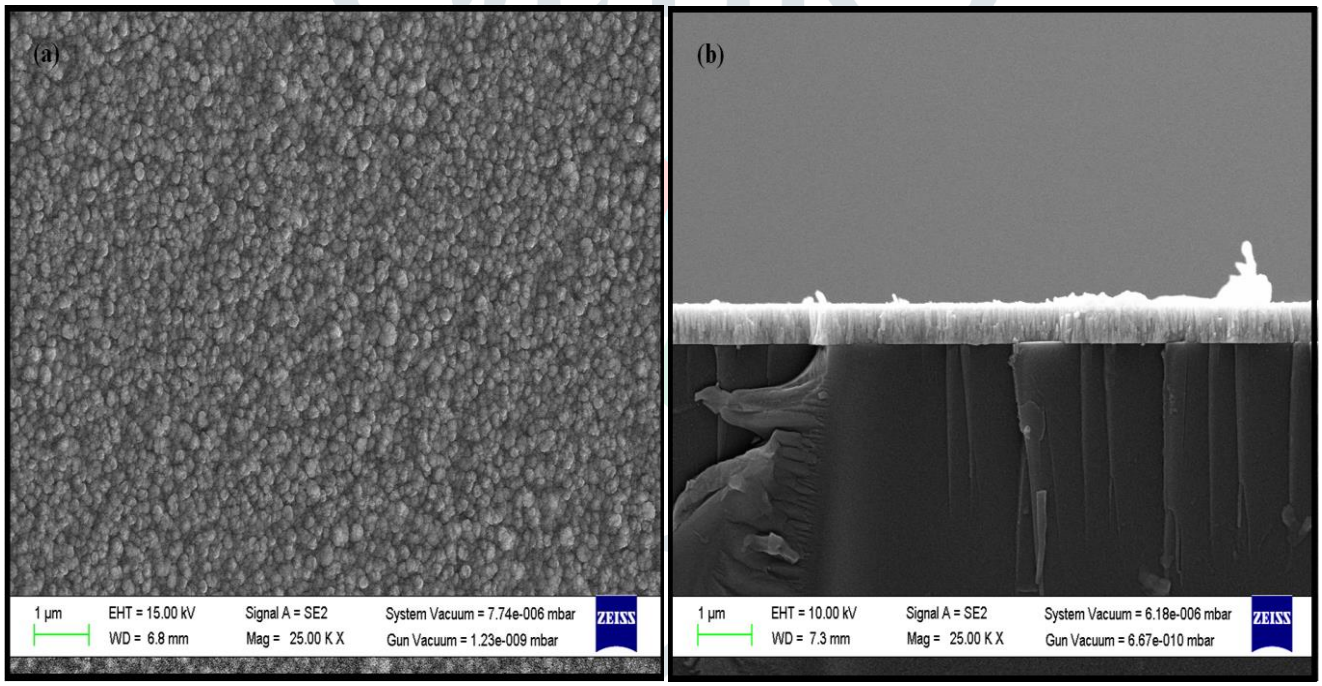

Figure 3(a) SEM micrographs Mn doped ZnO and 3(b) Cross section image.

3.2 Structural properties

Fig.1 show the XRD patterns of pure and Mn doped ZnO thin films were prepared by DC sputtering method. In both cases a dominant peak at 34.04^{O} is seen, corresponding to the ZnO (002) reflection match with JCPDS card 36-1451. These peaks confirming the deposit as ZnO thin film with the normal hexagonal

wurtzite structure. No another peaks found by Mn doping. After Mn doping was seen in XRD studies suggesting that Mn substituated for Zn in the ZnO host matrix without varying the wurtzite structure. The average particles size has calculated of pure ZnO and Mn doped ZnO are 10 nm and 11 nm respectively.

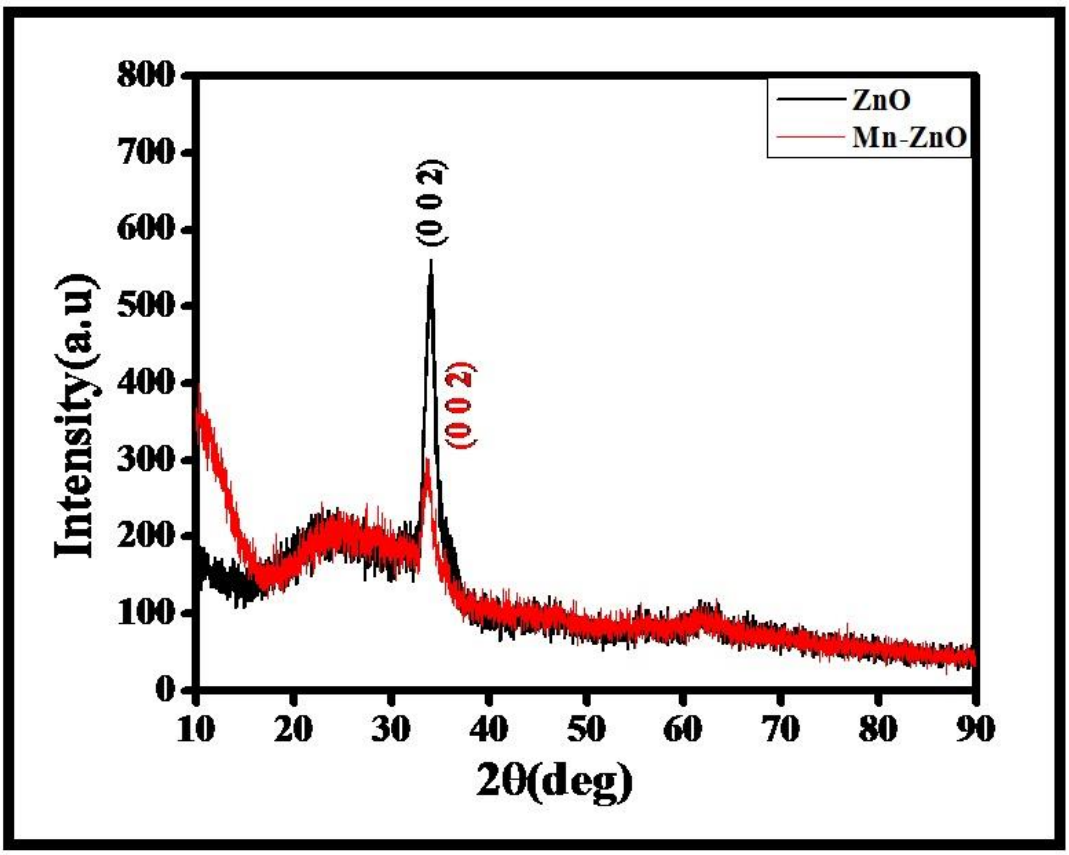

Figure 1: the XRD patterns of pure and Mn doped ZnO thin films

3.2 Gas sensing properties

The performance of resistive gas sensor can be estimated by value of its sensing response and response/recovery time. The oxidizing gases acts as acceptor for n type materials so that decrease the electron concentration which results to significantly enhance the initial resistance. On the other hand, the reducing gases behave like donors which causes to decline the resistance of sensing layer for n-type materials and contrary is true for p-type materials. Here, pure ZnO and Mn doped ZnO gas sensors exhibit

the n-type behavior. Therefore, the sensor response is defined as the ratio of resistance in reducing gas atmosphere to that of in dry air. The sensor response of the sensor is defined by the following equation [16].

$$Sensor Response\ (\%) = \frac{R_a - R_g}{R_a} \times 100 \qquad (1)$$

where R_a and R_g are the resistance in air and target gas environment respectively.

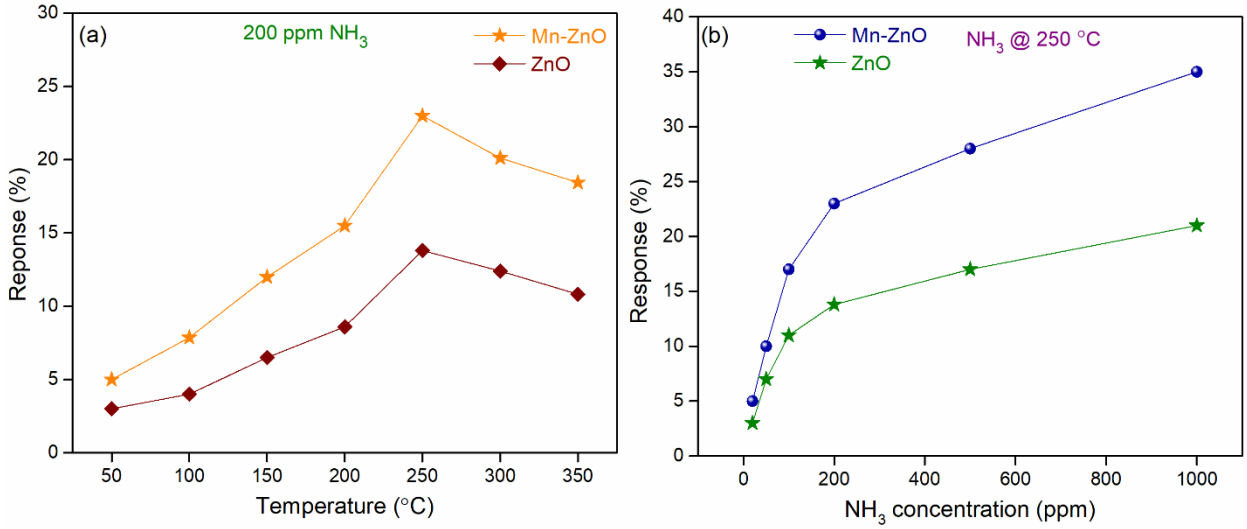

Fig. 4 (a) Gas response behavior of pure ZnO and Mn doped ZnO sensors versus operating temperatures to 200 ppm ammonia, **(b)** Gas response curve for both the sensors as a function of the ammonia gas concentration (20-1000 ppm) at 250 °C.

Fig 4a shows the gas sensing response curves of both the sensors investigated at various operating temperatures between 50 and 300°C upon exposure to 200 ppm highly pure ammonia in synthetic air. These results revel that for both the sensors the sensor response follows the rising trend with increasing the operating temperature up to some critical value upon exposure to 200 ppm NH_3 gas. Thereafter, the response starts to decline with further increasing the temperature beyond the critical limit. Because at high operating temperatures, the adsorbed analyte gas molecules may escaped from the sensor surface before reaction takes place and hence the sensor response deteriorates [17]. It can be seen that, the Mn-ZnO sensor exhibits greater response as compared to pure ZnO in whole temperature range. This hike in response can be recognized to the presence of high surface area (large number of active sites) in Mn-ZnO thin film sensor. Thus, these nanostructures may deliver a path for transfer of mobile charge carriers and dynamic sites for

the adsorption and desorption of ammonia on the top of the sensor surface. It might be possible due to appropriate substitution of Mn declines the crystallite size and rise the active surface area and surface reactivity of the proposed sensing layer. Based on these measurements, the maximum response for pure ZnO and Mn-ZnO sensors was recognized at 250°C.

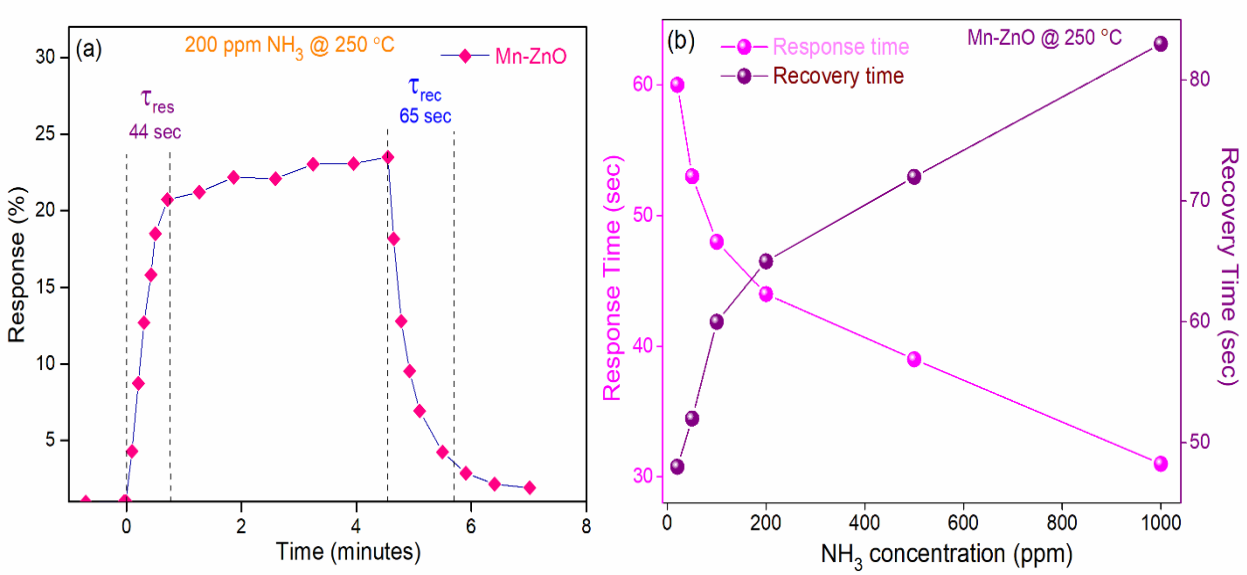

Fig. 5(a) gas response versus time curve of the Mn doped ZnO sensor towards 200 ppm ammonia at 250 °C and **(b)** Response-recovery time curve versus ammonia gas concentrations in dry air at 250 °C.

The variation in the sensor response for Mn-ZnO sensors was observed at different concentrations from 20 to 1000 ppm ammonia in synthetic air (Fig. 5b). It indicates that the proposed sensor is able to detect the trace amount of ammonia down to 20 ppm level at 250 °C.Hence, these measurements depicts that the ammonia sensing properties for Mn doped ZnO sensor were found to be remarkable enhanced. The sensor response versus time characteristic is shownat 250 °C for 200 ppm ammonia gasin synthetic dry air (Fig. 5a). It can be seen that the response and recovery time for Mn doped ZnO sensor was found to be 44 sec and 65 sec respectively. The variation in response and recovery time with different concentration of ammonia gas at 250 °C is depicted in Fig 5b. The result reveals that the response time falls and recovery time rises with improving the analyte (ammonia) gas concentration. This can be observed due to diffusion limited kinetics at relatively low ammonia gas concentration [18].

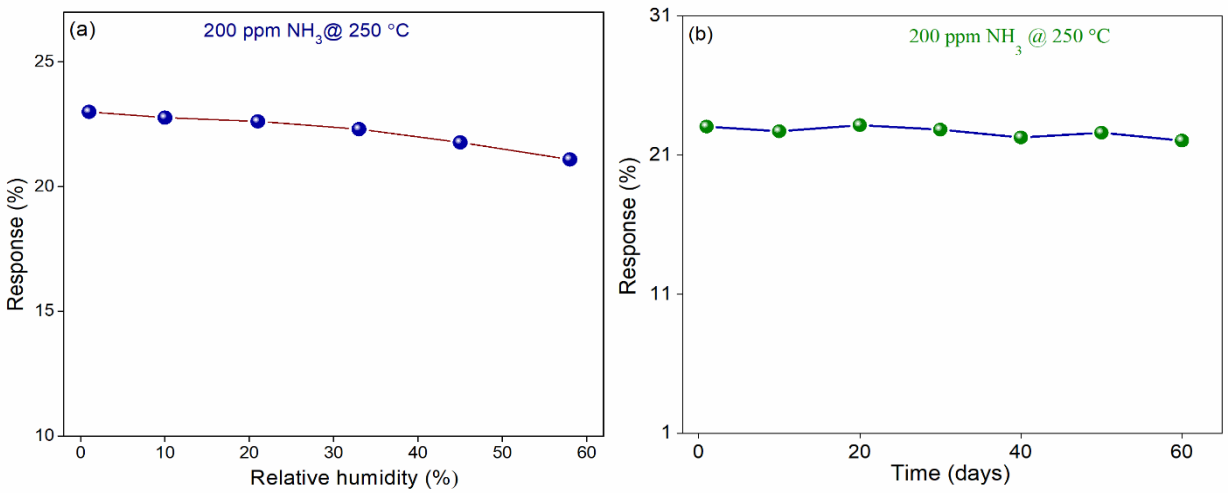

Fig. 6(a) Gas response curve of given sensor as a function of the relative humidity up to 60 % at 2000 ppm ammonia concentration level in dry air, **(b)** The response versus time behavior for 60 days, indicating the long-term stability of the proposed sensor.

Fig. 6a, shows the effect of moisture on the performance of Mn doped ZnO thin film sensor towards 200 ppm ammonia with different relative humidity conditions at 250 °C. The decay in the sensor response of approximately 8 % was detected for proposed sensor under the high humidity (60 % RH) conditions. The decay in response is mostly accredited to the water molecules present in humid air, which preventing the adsorption of target gas molecules on the sensor surface and hence reduce the base line resistance of the sensing layer [19, 20].Thereafter, the stability test of Mn doped ZnO gas sensor was also performed at 250 °C towards ammonia gas at 200 ppm level.

Fig. 6b depicts the stability test of the given sensor performed at 250 °C for 60 days. Here, we observed that the proposed sensor reveals almost constant response signal (~7 % changes) after 60 days, demonstrating the long term reproducibility of the sensing layer. Thus, these outcomes exhibits that the Mn doped ZnO layer can be used as a potential candidate for detection of trace amount of ammonia gas in our environment at low working temperatures.

3.4 Sensing mechanism

The most fundamental reaction mechanism of chemiresistive gas sensors has been well recognized using depletion layer or space charge model [21, 22]. Basically, the role of changing the electrical resistance of sensor device during the adsorption and desorption process of target gas molecules on the sensor surface is noteworthy. Thus, the basic working principle of bare Mn doped ZnO sensor towards ammonia gas comprises the following steps: Firstly, when the oxygen molecules presented in our atmosphere adsorbed on top surface of the sensing layer then they extract the electrons from the conduction band of ZnO, caused to decline the charge carrier concentration which leads to significantly enhance the initial resistance of the sensing layer [23].

$$O_{(adsorbed)} + e^-_{(fromZnO)} \rightarrow O^- \quad (2)$$

$$2NH_3 + 3O^- \rightarrow 3H_2O + N_2 + e^-_{(to\ ZnO)} \quad (3)$$

In beginning, the oxygen molecules present in air can adsorb on top surface of sensing layer and it will extract the free electrons from the conduction band of ZnO, which leads to decline the conduction band electrons and hence the initial resistance starts to increase [22]. In this step we observed the chemisorbed oxygen species on the sensor surface. Secondly, when these oxygen species react with ammonia gas molecules then transferring the electron back to the conduction band, hence reduce in resistance of sensing layer (see Eq. 1 and 2).

3.5 Magnetic Properties

Figure 7 reveals the dependence of magnetization (M) with applied magnetic field (H) for pure and Mn doped Zno thin films [24]. The field dependence of magnetization at room temperature for pure and Mn doped ZnO thin films is studied in the magnetic field range of 0-3000G. The M-H curve shows the paramagnetic phase is dominant. The doping samples shows ferromagnetic signal is solely due to the presence of Mn ions in ZnO host matrix [24-25]. The shapes of M-H curve of both samples are suggesting

the presence of weak ferromagnetism behavior. The intrinsic point defect of ZnO has the main contribution toward the ferromagnetism in ZnO:Mn thin films [24-25].

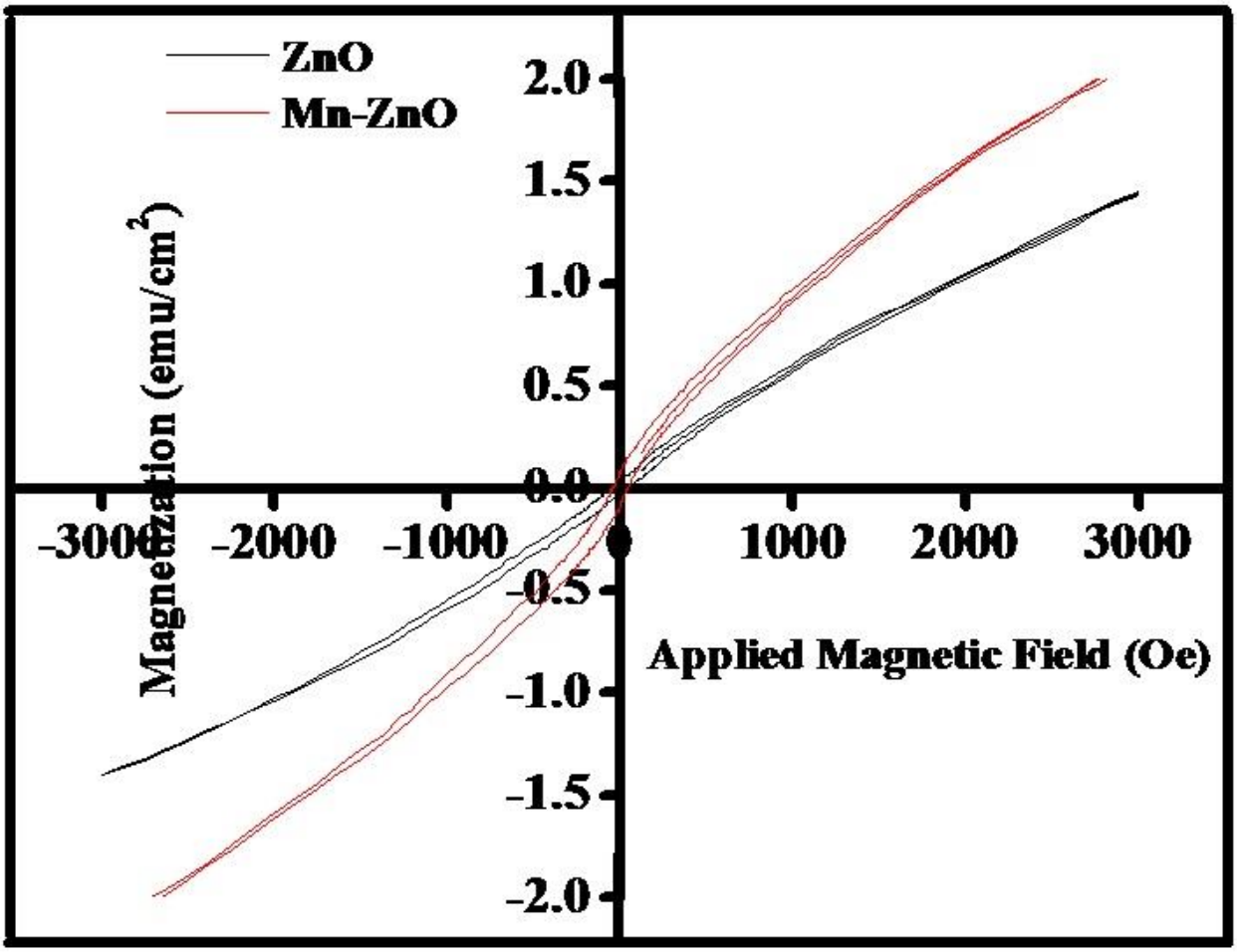

Figure 7: the dependence of magnetization (M) with applied magnetic field (H) for pure and Mn doped Zno thin films

4. Conclusion

We have developed a very sensitive and selective ammonia gas sensor based on nanostructured Mn-ZnO thin film. The sensing properties of the given thin film samples were studied using, Keithley source meter. The proposed sensor shows a considerably high sensing response to ammonia gas under low (20-1000 ppm) detection level. It display very fast response and recovery time of 44 sec and 66 sec respectively at 200 ppm level of ammonia in dry air. The fast sensing response (S.R~ 23 %), good reproducibility and stability at low temperature make this sensor implausible. Therefore, the application of Mn doped ZnO sensor becomes

very promising as simple and low cost sensor for detection of low concentration of ammonia gas in our environment. The working principle and role of Mn doping behind their excellent performance were also studied. Therefore, the proposed sensing layer fabricated on the glass substrates can be used as promising material for detection of trace amount of ammonia gas in our environment.

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