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Surface Activated Hybrid Structured ZnO Films by CuO, Bi_2O_3 and MnO_2 on the Detection of NH_3 at Room Temperature

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Abstract

Zinc oxide (ZnO) thick film gas sensors typically require elevated operating temperatures to achieve adequate sensitivity toward ammonia (NH_3). In the present work, the effect of CuO, Bi_2O_3 and MnO_2 surface activation on the NH_3 sensing performance of ZnO thick films operable at room temperature is systematically investigated. ZnO thick films were fabricated using a conventional screen printing technique. Surface activation was carried out by incorporating trace amounts of CuO, Bi_2O_3 and MnO_2 separately on the surface of the pure ZnO thick films. Structural and morphological characterizations confirmed the polycrystalline nature of the films with enhanced surface roughness and increased density of active sites after activation. Gas sensing studies revealed a remarkable enhancement in NH_3 response for the activated ZnO films compared to pristine ZnO at room temperature. The improvement is attributed to synergistic effects of the activators, including catalytic activity, increased oxygen adsorption and modulation of the depletion layer at the ZnO surface. The activated films exhibit crucial response, faster response–recovery characteristics and good repeatability toward NH_3 at low concentrations. The proposed Cu–Bi–Mn activated ZnO thick films demonstrate strong potential for the development of low power, room temperature ammonia sensors for environmental monitoring and industrial safety applications.

Keywords: *Hybrid Structured ZnO; NH_3 gas sensor; Room temperature, etc.*

1. Introduction

The continuous growth of industrial activities has resulted in increased emission of toxic and hazardous gases, leading to serious environmental and health concerns. Ammonia (NH_3) is one of the most commonly used industrial gases in fertilizer manufacturing, refrigeration systems, chemical processing and medical diagnostics. Exposure to NH_3 even at low concentrations can cause irritation to the eyes, skin and respiratory system, while higher concentrations may result in severe pulmonary damage or fatality [1-2]. Therefore, the development of sensitive, reliable and low power ammonia gas sensors capable of operating at room temperature is of significant importance.

Metal oxide semiconductor (MOS) based gas sensors are widely studied due to their simple fabrication process, low cost, portable size and crucial gas response [3]. Among various MOS materials, ZnO has attracted considerable attention owing to its wide band gap (~3.37 eV), high exciton binding energy, excellent chemical stability, easy to handle and strong surface adsorption properties [4-6]. ZnO is an n-type semiconductor whose gas sensing mechanism primarily depends on surface adsorption and desorption of oxygen species, resulting in modulation of electrical resistance upon exposure to target gases [7]. However, pristine ZnO-based gas sensors typically require high operating temperatures in the range from 200°C to 400°C, to achieve sufficient response, which increases power consumption and restricts its application in portable and low-energy devices [8].

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To address these limitations, various approaches such as physico-chemical doping, surface activation, catalytic loading and composite formation have been employed to enhance the sensing performance of ZnO at lower operating temperatures [9-10]. Activation using suitable metal additives is an effective strategy to improve the gas response, selective nature, response–recovery profile and long-term stability of the sensor. The incorporation of dopant elements in the base materials, can alter the electronic structure of ZnO, increases oxygen vacancy concentrations and enhance catalytic activity, thereby promoting stronger interaction between the sensing material and target gas molecules [11].

Oxides of Copper (Cu), bismuth (Bi) and manganese (Mn) have individually shown promising effects in improving the gas sensing characteristics of metal oxide semiconductors. Cu acts as an efficient catalytic activator, which facilitates the oxidation of reducing gases (viz. NH_3) by enhancing surface reaction kinetics [12]. Bi incorporation is known to introduce defect states and improve charge carrier modulation due to its high oxygen affinity and large ionic radius [13]. Mn, a transition metal with multiple oxidation states, enhances surface reactivity and electron exchange processes during gas adsorption, leading to improve the sensing performance of the sensor [14]. The combined activation of ZnO using Cu, Bi and Mn is expected to produce a synergistic effect, resulting in enhanced ammonia sensing performance at room temperature through improved catalytic activity, increased defect density and efficient charge transfer mechanisms.

Thick film fabrication techniques, particularly screen printing, are widely used for gas sensor development due to their simplicity, reproducibility, mechanical robustness and suitability for large-scale production [15-17]. Thick films provide high porosity and large effective surface area, which are crucial for efficient gas adsorption and surface reactions [18-19]. Despite extensive research on doped ZnO-based ammonia gas sensors, studies focusing on the combined Cu–Bi–Mn activation of ZnO thick films for room-temperature NH_3 sensing remain limited.

In the present work, the activated ZnO thick films were systematically investigated for ammonia gas sensing at room temperature. The effect of Cu–Bi–Mn activation on sensor response, selectivity, response and recovery times, and stability toward NH_3 gas was studied. The results demonstrate that multi-element activation is a promising approach for developing low-power, room-temperature ammonia gas sensors suitable for environmental monitoring and industrial safety applications.

2. Experimental

2.1 Synthesis of Nanostructured ZnO

Hybrid-structured dry powder of zinc oxide (ZnO) was synthesized by using a microwave-assisted ultrasonication technique combined with centrifugation. The synthesis process utilized the following equipment: a charcoal convection microwave oven (LG, 32 L), a homemade disc-type ultrasonicator (40 KHz, 695 W), a box-type ultrasonic cleaner (BTI 48, 24 KHz, 400 W) and a research centrifuge (Remi R-23, 6900 rpm). Additional instruments used during the process included a digital table pH meter (range 0 - 14), muffle furnace (1200ºC) and a magnetic stirrer with hotplate (5MLH). Initially, the distilled water was added in propylene glycol in 1:1 proportion and 0.1 M aqueous solution of zinc chloride was added to the previously prepared aqueous alcohol solution. Ammonium hydroxide was added drop by drop slowly as 1 ml / min. in the above solution and kept on a hotplate under constant stirring till precipitate of zinc hydroxide was formed. Then the solution containing precipitate was washed 4 to 5 times followed by centrifugation and thereafter, kept it in a microwave oven for 10 minutes with continuous on-off cycles, repeatedly, then it was allowed for calcination at 500ºC for 3 hrs in high power muffle furnace. The dried precipitate was ground by agate pestle-mortar to ensure sufficiently fine particle size and re-calcined in a muffle furnace at 500ºC for 2 hrs, to eliminate the organic impurities, if present any.

2.2 Fabrication of Thick Films and Surface Activation

Thixotropic paste preparation and the screen-printing process constitute the key steps in thick-film fabrication. By mixing the synthesized powder of pure ZnO along with ethyl cellulose solution in the mixture of organic solvents, such as butyl carbitol acetate, butyl cellulose, terpineol and thixotropic paste was formulated. Thixotropic paste was screen printed on the glass substrates in desired patterns of 9 mm × 4 mm in size. Accordingly, the fabricated thick films were first dried at 80°C under an IR lamp and subsequently fired at 450°C for 30 min in an air atmosphere. After this, the prepared pure ZnO thick films were dipped in aqueous solution (0.01M) of copper chloride, bismuth nitrate and manganese chloride for different activation time. Silver contacts were made on the sensor elements for electrical measurements.

2.3 Characterizations

The XRD patterns of thick films are monitored using X-ray diffractometer D8 Advance (Bruker AXS GmbH, Germany) with CuK$_{\alpha 1}$(λ=1.54056Å) radiation in the 2θ range 20°-80°, with 0.5°/min scanning speed, to confirm the crystalline nature and size. The morphology of the thick film was recorded using Hitachi field emission scanning electron microscope (FE-SEM, S4800 TypeII). The E-DAX was carried out using X-Flash 5030 detector (Bruker AXS GmbH, Germany).

3. Results and Discussion

3.1 X-ray Diffraction Studies

Fig. 1 depicts the X-Ray diffraction patterns of the pure and activated ZnO. The XRD spectra reveal that, the pure and activated materials are polycrystalline in nature. The XRD pattern of the pure ZnO powder perfectly matches with that of hexagonal wurtzite structure with space group P 63 mc (186) having JCPDS number 036-1451. The lattice parameters of pure ZnO were found to be a = b = 3.2466 Å and c = 5.2029 Å and unit cell volume V = 47.4921 Å. It is estimated from Fig. 1 that, the average crystallite sizes of pure ZnO, CuO activated ZnO, CuO-Bi_2O_3 activated ZnO and MnO_2 activated ZnO samples were observed to be 29.65 nm, 27.35 nm, 25.05 nm and 31.64 nm, respectively.

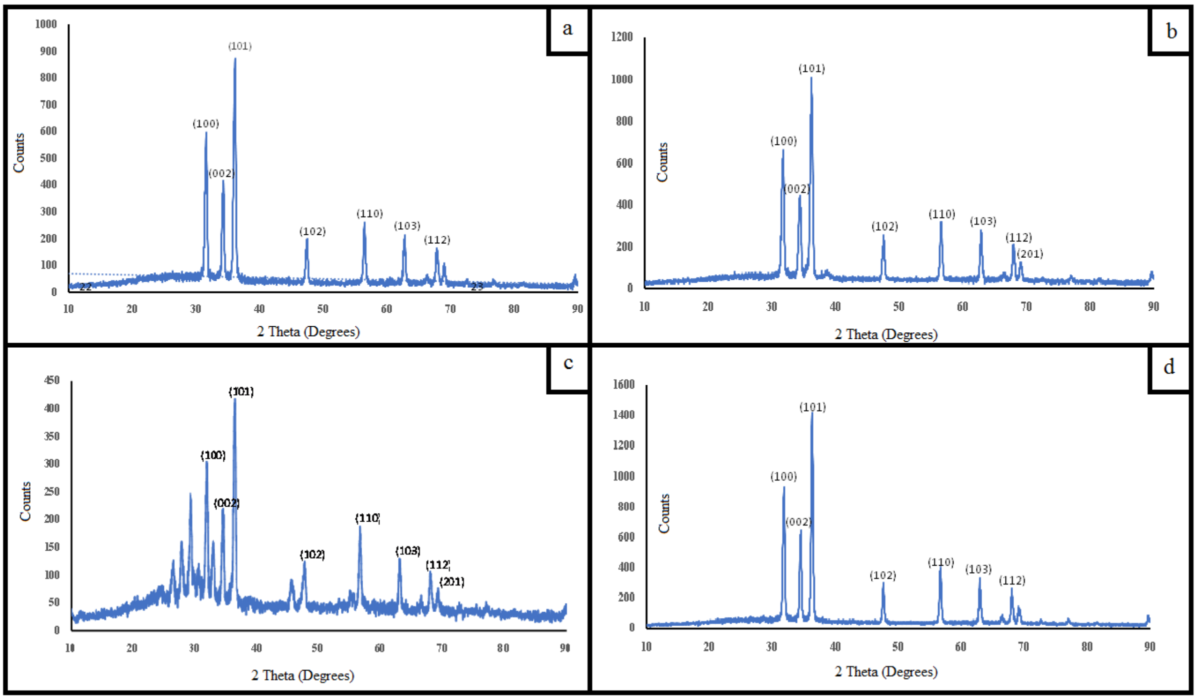


Fig. 1: XRD patterns of (a) Pure ZnO, and ZnO activated (10 min) by (b) CuO, (c) Bi_2O_3 - CuO and (d) MnO_2

3.2 Elemental Analysis E-DAX

Table 1: Elemental analysis of pure ZnO and surface activated ZnO

Materials		Elements (mass%)								
		Zn	O	ZnO	Cu	CuO	Bi	Bi_2O_3	Mn	MnO_2
	Expected	80.34	19.66	---	---	---	---	---	---	---

Pure ZnO	Observed	80.90	19.10	---	---	---	---	---	---	---
CuO-Act(ZnO)		65.50	13.60	79.10	16.70	20.90	---	---	---	---
MnO_2-Act(ZnO)		79.40	20.13	99.53	---	---	---	---	0.30	0.48
CuO+Bi_2O_3-Act(ZnO)		72.50	16.08	88.58	4.40	5.51	5.3	5.91	---	---

Table 1 depicts the estimation of constituent elements of the materials of thick films. All the films are activated for 10 min. The stoichiometric proportion of Zn and O in ZnO is 80.34 and 19.66 mass %. However, mass % of Zn and O elements (in ZnO) is found to be 80.90 and 19.10 respectively, indicating that the pure ZnO is deficient in oxygen or excess in zinc. Hence, the materials exhibit the semiconducting nature. As the synthesized material is oxygen deficient, very few electrons from the conduction band are captured by oxygen atoms and large number of free electrons is available to carry the current, thus, the material exhibits more n typeness characteristics. Table 1 depicts that, MnO_2 activated ZnO is excess in oxygen resulting in decrease in n typeness. Also, the grains of MnO_2 present on the surface activate the film and oxidize the NH_3 gas quickly by the bulk oxygen atoms. This may be one of the reasons of exhibiting the crucial response to NH_3 at room temperature.

3.3 Microstructural Analysis (SEM)

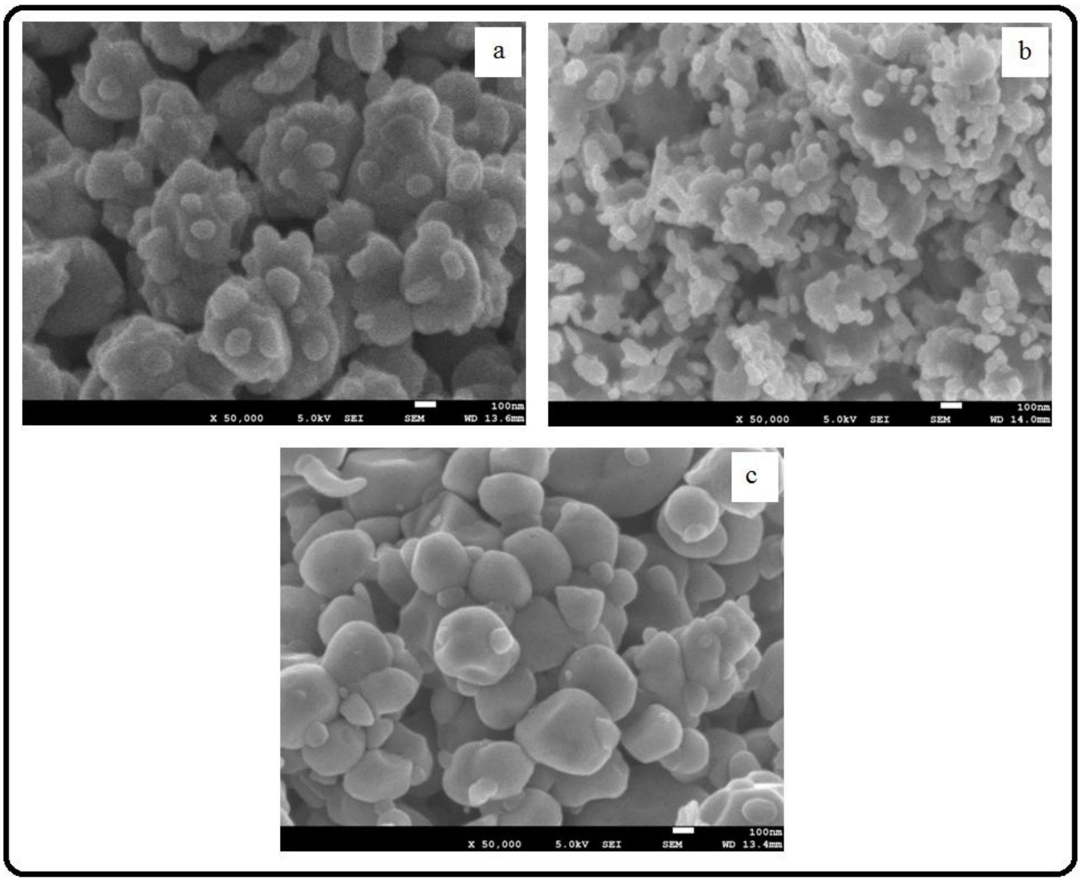


Fig. 2: SEM Micrographs of (a) Pure ZnO, and ZnO activated (10 min) by (b) CuO, and (c) MnO_2

Figs. 2 (a-c) depict the scanning electron micrographs of pure ZnO and ZnO activated by CuO and MnO_2. Thick films of hybrid structured ZnO was surface activated by CuO and MnO_2 for 10 min. to enhance the ammonia sensing performance of the films. The ZnO material has been synthesized by microwave-assisted ultrasonication technique combined with centrifugation is the composition of micro-grains and nano-grains, exhibiting the hybrid structured nature. We can tailor the electronic properties of the hybrid structured materials as compared with homostructured materials (viz. nanostructured, microstructured, bulk, etc.). It is observed from Fig. 2 (b) that the smaller grains of CuO were dispersed on the surface of the pure ZnO thick film, which decreases the porosity of the film surface. Less number of pores results in decreasing the surface active sites and hence lowers the gas response. However, in Fig. 2 (c) larger grains of MnO_2 were dispersed on the surface of ZnO thick film. These larger grains would create large number of pores on the surface of the film, which enhances the effective surface active sites and favours the ammonia gas response, crucially. This film exhibits crucial response to 50 ppm NH_3 gas at room temperature (25°C). The surface activation tunes the properties and hence the surface reactivity of the film. Each film has different texture.

4. Electrical Behaviour of Sensor

4.1 I-V Characteristics

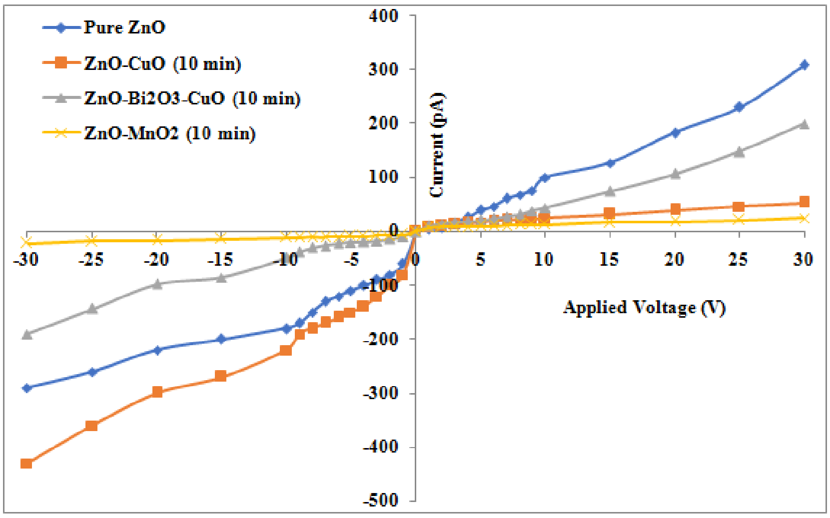


Fig. 3: I-V characteristics of Pure ZnO and activated ZnO

Nearly symmetrical nature of I-V characteristics of pure ZnO and activated ZnO thick films (Fig. 3) proved the ohmic (resistive) nature of both, the material of the film as well as the silver electrodes. So, the material is also referred as a resistor. Some non-linearity in Fig. 3 was observed due to the presence of hybrid nature of the materials in the film, i. e. the crystallite size may vary in large scale (from few nm to few µm).

4.2 Arrhenius Behaviour: NTC Nature of Materials

Electrical conductivity of pure ZnO and activated ZnO films as a function of the reciprocal of operating temperature is depicted as Arrhenius plot in Fig. 4. It was observed from figure that, the logarithms of conductivities of all the samples are decreasing with decrease in operating temperature. So, the films exhibit negative temperature coefficient of resistance (NTC) this confirms the semiconducting nature of all the materials.

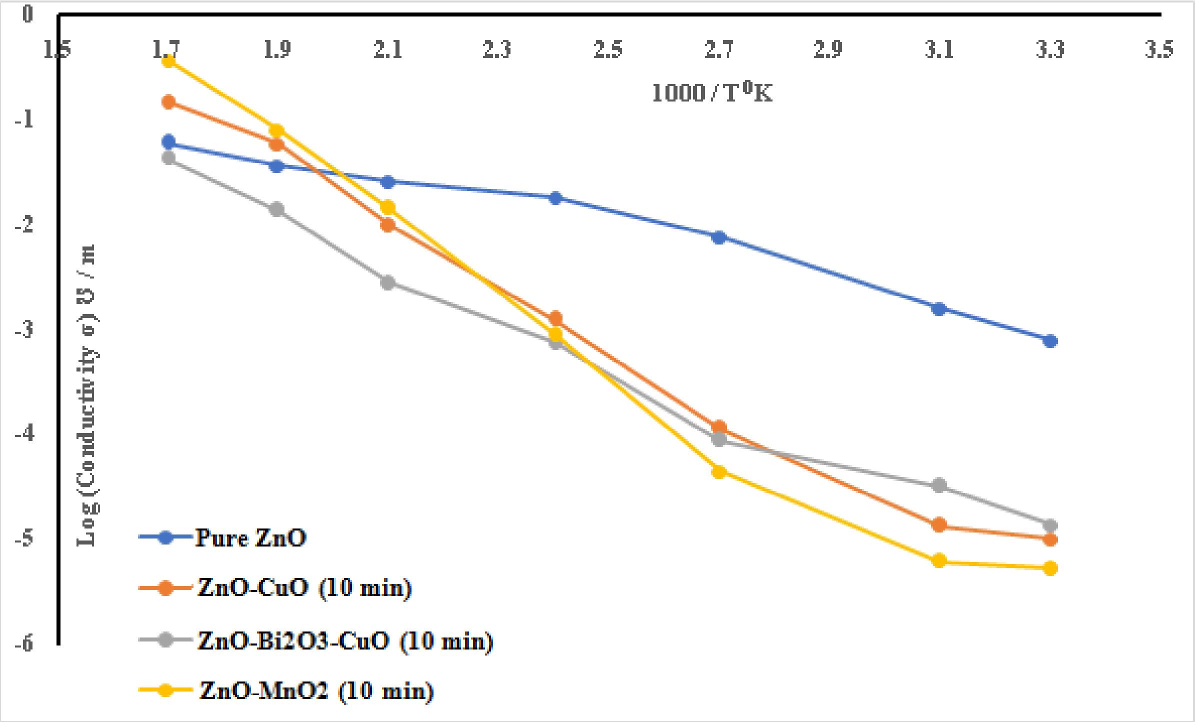


Fig. 4: Arrhenius variations of pure ZnO and Activated ZnO

5. Sensing Performance of Sensor

5.1 Temperature Dependent Response

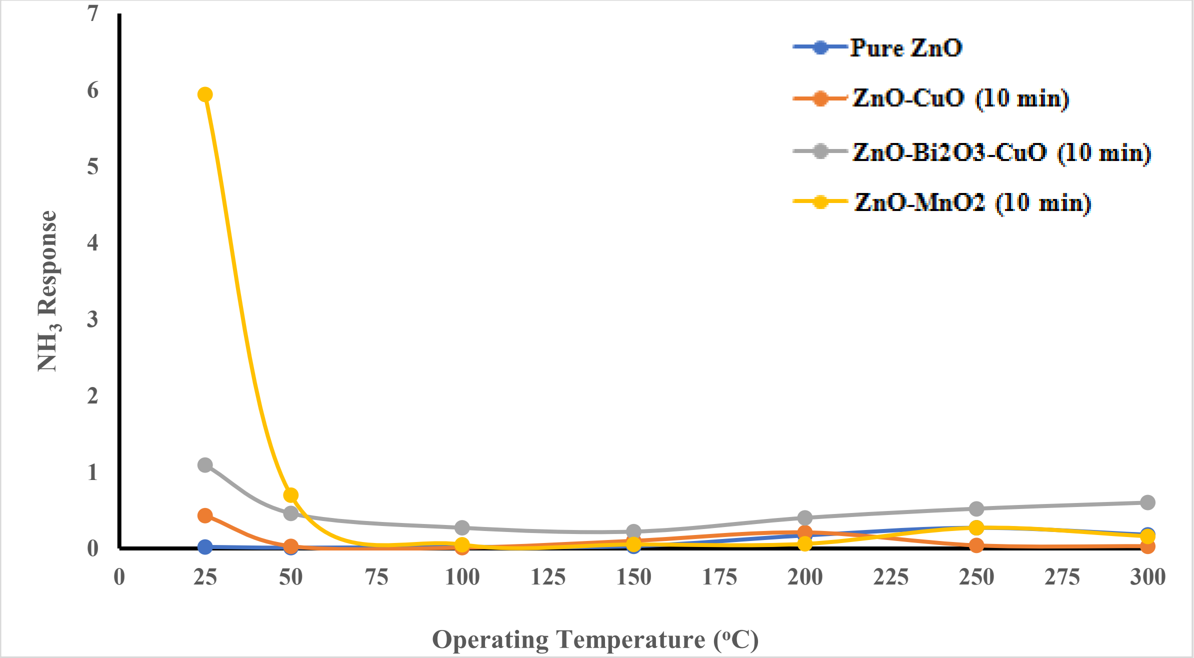
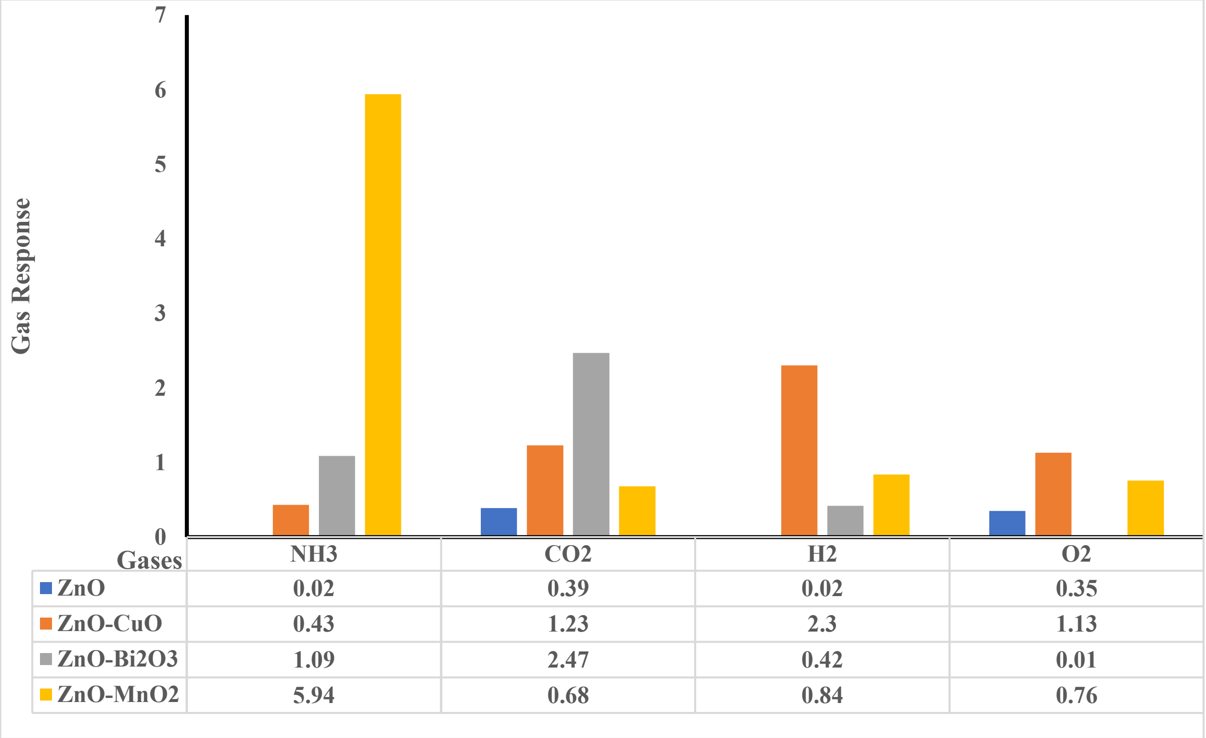


Fig. 5: NH_3 response as a function of operating temperature

From Fig. 5, it is cleared that, the thick film of MnO_2 activated ZnO (10 min) exhibits crucial response to 50 ppm NH_3 at room temperature (25°C), whereas, that of all other films is nearly negligible even with high operating temperature range.

5.2 Selectivity of the Sensor

Fig. 6 describes that, the MnO_2 activated ZnO (10 min) sensor offers crucial response to 50 ppm NH_3 at room temperature (25°C). The sensors exhibit high selective nature to NH_3 among O_2, H_2, CO_2, etc.



Gases	NH3	CO2	H2	O2
🟦 ZnO	0.02	0.39	0.02	0.35
🟧 ZnO-CuO	0.43	1.23	2.3	1.13
⬜ ZnO-Bi2O3	1.09	2.47	0.42	0.01
🟨 ZnO-MnO2	5.94	0.68	0.84	0.76

Fig. 6: Selectivity of sensor to NH_3 among different gases

5.3 Ammonia Sensing Mechanism

Ammonia can be monitored at room temperature is mainly by direct reaction of lattice oxygen or interstitial oxygen with NH_3. The surface reaction processes can explain the selective ammonia response of the sensor at room temperature. The hybrid structured and activated materials form of intergrain boundaries of the constituent grains. At room temperature, the molecules of exposed NH_3 interact with the interstitial oxygen from the bulk or the surface of the film. The ammonia get oxidized in to NO_x and H_2O and evaporate in the form of gases. This would lead to eject oxygen from the materials and trapping behind the free electrons in the conduction band of the materials. Thus, conductivity of the materials of the film increases crucially. The increase in the conductivity of the film could be attributed to the charge-carrier generation mechanism resulted from the electronic defects due to hybrid-structure of the materials.

6. Conclusions

Thick film of pure hybrid structured ZnO offers less response to 100 ppm NH_3 at room temperature (25°C). However, MnO_2 activated ZnO for activation time 10 min. offers crucial response to 50 ppm NH_3 at room temperature. Also, NH_3 gas should be detected either below or nearly upto TLV to avoid disastrous defects on human health, when in contact. The efforts are made in the direction and MnO_2 activated ZnO (10 min) was found to be sensitive to 25 ppm NH_3 (though less) at room temperature and exhibits excellent selectivity to NH_3 against other gases.

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