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Vapour sensing property of metal oxide thin films at ambient condition: Influencing factors: A Review.

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ABSTRACT

The paper critically reviews the vapour sensing property of metal oxides semiconductor based sensing elements operated at ambient temperature with focus on various influencing factor. Metal oxides such as Fe_2O_3, Bi_2O_3 and ZrO_2 prepared by spray pyrolysis methods were selected in the present study and their ambient temperature operated vapour sensing property were analyzed and reported.

Keywords: Metal Oxide; Thin films; Nanocrystallites; VOC's; Vapour Sensor; Chemiresistor

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INTRODUCTION

Gas sensing technology has a long history and different methods were used to detect the gases or vapours from surroundings. Since, coal mines had combustible and toxic gases like carbon monoxide and methane with low level of oxygen, first attempt to detect the toxic gases were executed there with canary bird in early 20th century [1]. The canary birds are singing birds which are more susceptible than human to low oxygen, methane or carbon monoxide gas environment, because of its highly sensitive nature towards gases. These birds would stop singing or even die when they are exposed to toxic gases environment, thereby signaling the miners to exit the mine quickly. Later, Davey's flame lamps [2] served as one of the first detection systems in detection of various gases and vapours present in atmosphere. The flame height was calibrated with reference to the concentration of the gas present in the ambient. Low oxygen environment would cause the flame to burn low or extinguished. On the other hand, atmosphere rich in combustible gases would cause the flame to burn more brightly. In 1920's, a number of significant advancement have been made in the field of gas detection. In 1925, Jiro Tsuji [3] developed a method to detect combustible gases using light-wave interference method. In 1927, Oliver Johnson [4] has developed a method to detect combustible gases, using a platinum catalyst in a Wheatstone bridge electronic circuit. Around 1953, the idea of using semiconductor as gas sensitive device was introduce by Brattain and Bardeen [5], who first reported the sensing effect of germanium (Ge). Later, metal oxides were identified as most possible sensitive materials by Heiland [6], Bielanski et al. [7] and Seiyama et al. [8]. In 1968, Taguchi [9] revolutionized the gas sensing field by identifying the metal oxide materials as gas sensing elements and brought as an industrial product. By using the resistive type sensing device, Taguchi has invented a gas leakage alarm to prevent domestic accidents. About 1970, the semiconductor gas sensors were further subjected to several revisions including the addition noble metals like Pt, Pd as sensitizers to increase the sensitivity, selectivity and stability of the material.

Gas sensor started playing a decisive role and allows us to detect the presence of toxic and combustible gases in the atmosphere; therefore, the use of these devices can prevent disastrous consequences for people [10]. Furthermore, a gas or vapour sensor is a diagnostic tool for identifying diseases in early stages by analyzing the volatile organic compounds (VOCs) from human exhaled breath [11]. Due to the huge application range of the gas sensors, there is a demand and need of cheap, small, low power consuming and reliable solid state gas sensors, has aroused over the years and triggered a huge research worldwide to overcome sensors drawbacks and also summed up in improving the well known "3S" : Sensitivity, Selectivity and Stability. The multidimensional nature of the interaction between function and composition, preparation method, and end use conditions of sensing materials often make them a rational design choice for real world applications. Furthermore, the world of sensing material is broad and practically all well known materials can be used as chemical sensors. Hence, the selection of optimal sensing materials for a particular application is necessary [12]. This review article is focused on selection of suitable metal oxide semiconductor materials for gas / vapour sensor applications.

Materials for gas / vapour sensor applications

Various materials such as covalent semiconductor, semiconducting metal oxides, solid electrolytes, polymers, ionic membranes, organic semiconductors, carbon based materials, moisture absorbing material, ionic salts etc. [13] were used for detecting plenty of gases and vapours. Amongst, metal oxide semiconductors, polymers, carbon based materials and moisture absorbing materials are mainly used as vapour / humidity sensing materials. The selection of optimal sensing material is the major requirement in both designing and manufacturing of gas or vapour sensor with optimal operation conditions.

Metal oxides semiconductors for chemiresistor

Conductometric sensor or chemi-resistor has a simple structure and their operating principle is based on the fact that their electrical conductivity or electrical conductance can be modulated by the presence or absence of chemical species that comes in contact with the device [12]. A chemiresistor comprises of three elements. They are sensitive conducting layer, heater and contact electrodes. The electrodes are interdigitated and embedded in the sensitive layer. The DC voltage is applied to the device, and the current flow through the electrode is monitored as the response. The simple operating principle of chemi resistive sensor is "Change in the electrical resistance due to the effect of reactions (diffusion, adsorption, chemical reaction) takes place on

the surface and in the bulk region of the sensing layer" [12]**.** The reactions that control the rate of sensor response and are involved in gas / vapour detection [14] are given in the following Table 1.

Table 1. Diffusion and surface reaction types

Diffusion	Surface reactions
Intercrystallite oxygen diffusion	Adsorption / Desorption
Bulk oxygen diffusion in crystallites	Reduction/Reoxidation
Gas diffusion inside the metal oxide	Catalysis and chemical reactions (chemical transformation)
Surface diffusion of adsorbed species	Charge transfer between adsorbed species and bulk

Metal oxide semiconductor based sensors are more advantageous owing to their low cost, simple function, high sensitivity, ease of combining with external measuring devices. Moreover, the sensor device comprising the sensitive element, signal converter and controlled electronics, make the device simple and portable, which are the main advantages of chemiresistive type sensors over other devices [15]. Hence, the present work focuses on the various semiconductor metal oxides thin film based chemical sensors for exhaled breath applications.

Gas / vapour sensing mechanism

In chemi-resistive sensors, the interaction between gas / vapour with semiconductor metal oxide surface occurs at crystallites boundaries of the crystalline film. The gas sensing mechanism may involve any of the following mechanism [16]

1. Direct adsorption of chemical species on to the semiconductor surface
2. Adsorption by reaction with surface states associated with pre-adsorbed ambient oxygen

When the metal oxide semiconductor is operated at low temperature (< 150 °C), oxygen molecules in the atmosphere are adsorbed on its surface to form molecular oxygen ionic species by extracting an electron from the conduction band of the metal oxide semiconductors as given in the Eq. (1) [16]

At higher temperature, the ionic oxygen molecules are dissociated into the oxygen ion with singly or doubly negative electric charges by extracting an electron again from the conduction band as given in Eqs. (2) and (3) [16].

$$O_{2(gas)} + e^- \Leftrightarrow O^-_{2\,(adsorb)} \quad \text{----------} \quad (1)$$

$$\frac{1}{2}O_{2(gas)} + e^- \xleftrightarrow{k_{Oxy}} O^-_{(adsorb)} \quad \text{----------} \quad (2)$$

$$\frac{1}{2}O_{2(gas)} + 2e^- \xleftrightarrow{k_{Oxy}} O^{2-}_{(adsorb)} \quad \text{----------} \quad (3)$$

where k_{Oxy} is the reaction rate constant. The oxygen ions on the surface of the metal oxide semiconductor are extremely active with the target-gas molecules and return the electrons from the surface to the conduction band of the metal oxide. The general chemical reaction between the gas molecules and oxygen ions is given in Eq. (4) [17].

where X and X' are the target gas / vapour and by products respectively. The k_{gas} is the reaction rate constant of the gas reaction and 'b' represents the number of electrons. The chemical reaction causes changes to the carrier concentration in the conductivity, which leads to changes in sensor resistance. These electrical resistance changes depend on the type of metal oxide semiconductors and type of interacting gas / vapour. A schematic diagram of change in the sensor electrical resistance upon exposure to the target gas / vapour (reducing nature) in the cases of n-type and p-type metal oxide semiconductor sensors are illustrated in Fig. 1.

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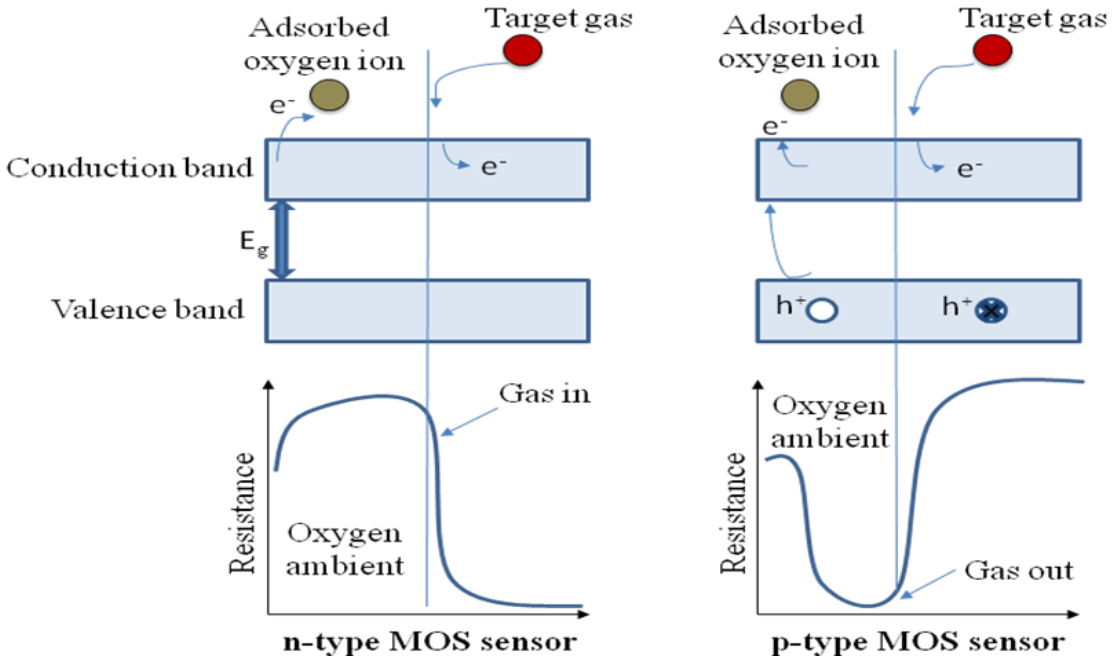

Fig. 1. Electrical Resistance variation based on its semiconducting properties

There are four possible combination of sensing mechanism as shown in the Table 2. In the case of n-type semiconductor towards reducing vapour or p-type semiconductor towards oxidizing vapour, the sensing response is estimated using the following relation;

$$X + O^{b-}_{adsorb} \xrightarrow{k_{gas}} X' + be^{-} \text{ ----------(4)}$$

$$\%S = \left(\frac{R_o - R_g}{R_g} \right) \times 100 \text{ ----------(5)}$$

whereas n-type semiconductors towards oxidizing vapour or p-type semiconductors towards reducing vapour, the sensing response is estimated using the following relation;

$$\%S = \left(\frac{R_g - R_o}{R_o} \right) \times 100 \text{ ----------(6)}$$

where, R_o is the baseline resistance and R_g is the saturated resistance of the sensor.

Table 2. Electrical resistance variation of n- and p-type semiconductor towards oxidizing and reducing gas / vapour.

Semiconductor type	Oxidizing gas / vapour	Reducing gas / vapour
n-type	Electrical resistance increases	Electrical resistance decreases
p-type	Electrical resistance decreases	Electrical resistance increases

Factors influencing the gas / vapour sensing property of metal oxide semiconductors

The major influencing factors of metal oxide semiconductor based sensing element towards various gas / vapours are represented in Fig. 2. The detailed discussions about the influencing factor are as follows;

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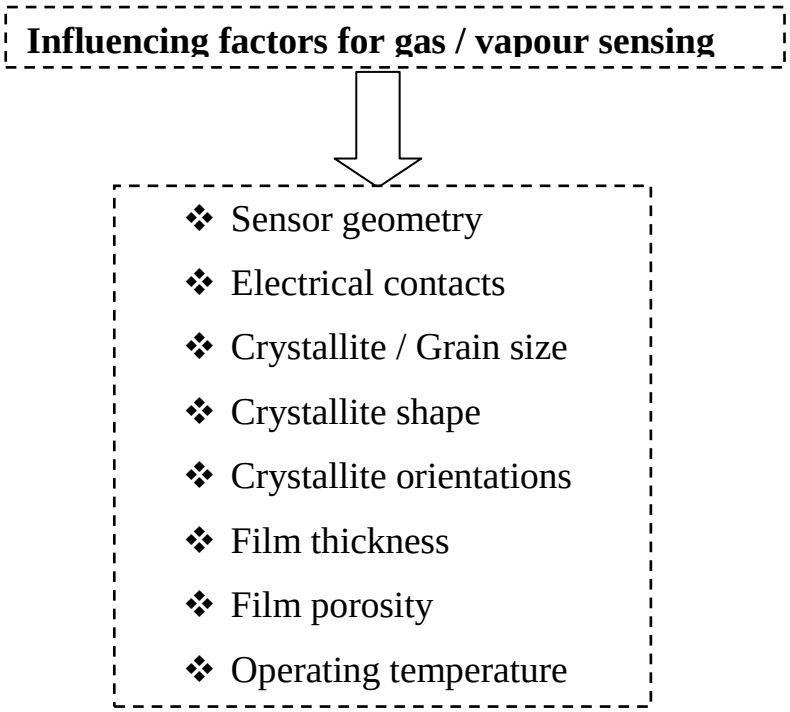

Fig. 2. Major influencing factors for gas / vapour sensing property

Sensor geometry and contacts

Based on sensor fabrications, a sensor can be classified into two type's namely ceramic and planar type sensor [18,19]. In ceramic type gas sensors, powdered metal oxide particles are deposited over the cylindrical surface and electrodes are developed on the sensor surface. In planar type gas sensors, the sensing material is deposited as a thin or thick film on a substrate. This kind of structure provides greater flexibility in the sensor fabrication process. The electrodes can be fabricated together on a substrate before or after the sensing film deposition. The sensor geometric effect plays an important role in the gas sensing response, because the film conductance does not change instantly, when the gas environment changes; the gas / vapour must diffuse through the film and react with the surface particles, which leads to variation in film conductance.

Vilanova et al. [20] reported that developed sensors show high sensitivity to target gas and that sensitivity increases when electrodes are designed underneath, whereas sensitivity decreases, when electrodes are deposited on top of the film. In thin film based sensors, the type of electrode has a strong influence on the sensing response. The electrode materials such as Pt, Pd, and Au act as active catalysts with specific catalytic properties, which enhance or affect the sensor response mainly in the area closer to contacts. Electrode materials act as catalysts and improve the gas sensing properties. Moreover, the sensing response towards the gas / vapour in a relative humid environment is affected by electrode materials. Capone et al. [21] reported that the influence of water on CO response of SnO_2 based sensors is greater in Au electrodes than in Pt electrodes. Tamaki et al. [22] studied the effect of micro gap electrodes of WO_3 sensors on NO_2 gas sensing. The gap size varies from 0.1 µm to 1.5 µm, when the gap size is less than 0.8 µm, the WO_3 sensors shows a greater response to NO_2 gas.

Film thickness

In ceramic and thick film sensors, grain / crystallite size is independent of film thickness whereas in thin film based sensors, grain / crystallite size strongly depends on film thickness. Korotcenkov et al. [23] reported the thickness effect of spray deposited In_2O_3 film towards ozone sensing characteristics. He observed a decreasing trend of ozone sensing response with an increase in film thickness from 20 nm to 400 nm, due to the formation of larger grains. Similarly, Chang et al. [24] investigated the influence of WO_3 film thickness towards NO_2 sensing and suggested that films with a lower thickness contain smaller crystallites. This leads to

a larger surface and in turn enhances the surface reaction with the target gas and provides a greater response. Salunkhe et al. [25] examined thickness effect of SILAR deposited CdO film towards LPG detection and concluded that the film thickness is directly proportional to LPG sensing response, because optimum film thickness provides uniform spherical nanocrystallites which will enhance the gas-solid interactions. Few reports suggested that, as film thickness increases the response and recovery time also increases [14].

Crystallite / grain size

The "grain model" represents dependency between the electro-physical properties of the polycrystalline materials and the microstructure [14]. Grain size and the Debye length or space charge layer are inter-dependent and influence the gas sensing properties of the materials. When the grain size is decreased, at least two effects play a role;

1. The number of surface sites available for gas adsorption increases with decreasing grain size because of the increase in the surface to volume ratio (s/v) as grain size decreases.
2. As the size of grains becomes comparable to the depletion layer or the Debye length, the sensitivity of gas detection is found to increase significantly. Moreover, the thickness of the space charge layer is in order of 1 nm to 100 nm and this displays a greater sensitivity and fast response time towards the gas or vapour.

Ogawa et al. [26] suggested that, when grain size becomes twice that of the Debye length, a space-charge region will develop over the whole grain and the maximum sensing response can be observed. Ansari et al. [27] investigated the effect of SnO_2 particle size towards hydrogen gas and reported that particles of size 20 nm are more hydrogen sensitive (nearly 10 times) than those of 25 - 45 nm. Lu et al. [28] investigated the influence of SnO_2 particle size towards carbon monoxide (CO) sensing behaviour and concluded that 8 nm to 10 nm SnO_2 nanoparticles yield a good carbon monoxide sensing response and lower response - recovery time compared with large particles. Fine nanoparticles may lag in structural stability at moderate or high operating temperature, which predicts the change in the surface and catalytic properties of the sensors [29]. Hence, an optimum grain or crystallite size is required to achieve good gas / vapour sensing at different operating temperatures.

Crystallite shape and orientations

The crystallite shape and faceting crystallites are related to the gas / vapour sensing properties of the materials. Based on the literature results, the following statements are framed, related to crystallite shape / faceting and the gas / vapour sensing properties of materials [30]

- Although, all the planes of nanocrystals have gas - solid interactions, only some planes decide the specific gas / vapour sensing properties of materials. The shape of nanocrystals determines some parameters such as crystallographic planes, inter-grain contact, area of inter-grain contacts, gas permeability and so on.
- Every crystallographic crystal has its own combination of crystallographic planes and every plane has its own combinations of surface electronic parameters such as surface state density, energetic position of the levels, adsorption and desorption energies of interacted gas molecules, the concentration of adsorption surface states, and activation energy for native point defects. Hence, the chemisorption changes are strongly dependent on crystal surface orientations.
- Activation energy is required for the adsorption and desorption process and these processes depends on orientations, crystal size and crystal shape. Moreover, the size and shape of the nanocrystals influence the concentration of adsorbed species and type of bonding to the material surface. The adsorption of some chemical species on the edges / corner sites or plane facets depends on the type of bonding.

Film porosity

Film porosity is one of the simplest ways to improve the sensing response of the film. In compact layer of sensing elements, the interaction with gases / vapours happens only at geometric surface, whereas, in porous materials, the whole volume of the sensing layer can be accessed by the interacting gases / vapours

and in turn the active surface area becomes more than the geometric area, which leads to higher sensing response [31]. Sberveglieri et al. [32] reported that the gas sensing characteristics of SnO_2 films with greater porosity enhances the gas sensing response. Also, Tian et al. [33] investigated the pore size dependent formaldehyde sensing characteristics of SnO_2 mesoporous microfibers and resulted in small crystallites with larger pores increases the active surface area for gas - solid interaction which improves the formaldehyde sensing response. Moreover, the pore diameter will also enhance the selectivity of the film. Shimizu et al. [34] reported the effects of gas diffusivity and reactivity on gas-sensing properties of porous SnO_2-based sensors. He reported that, when the pore diameter is less than 3 Å then it selectively detects H_2 gas instead of methane or ethanol. This is because methane (4.2 Å) and ethanol (6.1 Å) has more molecular diameter than pore size. Hence, these gases would not able to penetrate into the interior region which leads to selective detection towards H_2 gas.

Humidity

Environmental humidity is one of the major influencing factors that decreases the sensing performance of metal oxide semiconductor based gas / vapour sensor. The possible reasons are as follows: The reaction between surface oxygen and water molecules decreases the baseline resistance of the sensors, which in-turn decreases the gas / vapour sensing response. The adsorption of water molecules leads to less chemisorption of oxygen species on the metal oxide surface or water molecules act as a barrier against gas / vapour, hence less interaction exist between them. Therefore, less sensing response, lower sensitivity, slow response and recovery behaviour was obtained in relative humid environment [14].

Ling et al. [35] investigated the effect of relative humidity on NO_2 sensing characteristics of SnO_2 / WO_3 heterostructure based gas sensor and reported that NO_2 sensitivity linearly decreases with increase in relative humidity ranging from 0 % to 60 % and above 60 % of RH, heterostructure is almost insensitive to NO_2 gas at room temperature. Gong et al. [36] reported sol-gel spin-coated SnO_2 thin film and its H_2S sensing characteristics were studied in dry air and in various relative humid environments (7 % - 98 % of RH). The baseline resistance of the film and H_2S sensing response decreases as the relative humidity increases from 0 % to 98 %. Water molecules compete with H_2S and limit the oxygen ion - H_2S interactions which lead a decreasing trend of sensing response. Qi et al. [37] examined the undoped and Sm_2O_3-doped SnO_2 (different wt %) to acetylene vapour at different relative humid environment. Sm_2O_3-doped SnO_2 thin film showed decrease in both baseline resistance and acetylene sensing response at lower to higher relative humid environment.

Metal and noble metal dopant

The addition of dopant (either cationic or anionic) in metal oxides modifies the electrical conductivity and gas sensing response of the materials. Guan et al. [38] investigated the hydrothermally synthesized SnO_2 hierarchical architectures and its Zn dopant effect towards ethanol sensing characteristics. Addition of Zn in SnO_2 increases the number of adsorbed oxygen species over the surface, which leads to increase the ethanol sensing response. Zhao et al. [39] examined the undoped and Mg-doped In_2O_3 nanotubes towards H_2S sensing characteristics and pointed out that Mg-doped In_2O_3 nanotubes provides high sensing response towards H_2S than undoped In_2O_3 nanotubes. Lu et al. [40] investigated thermally evaporated Sn-Ga co-doped ZnO nanobelt and its ethanol gas sensing characteristics and reported that addition of Sn and Ga in ZnO forms a nanobelt structure which shows maximum sensitivity to ethanol vapour at 225 °C.

Bahadur et al. [41] investigated the selective gas sensing performance of different Ag loading in TiO_2 powder by sol-gel method. The different mol % loading of Ag in TiO_2, shows a selective response to different vapours (i.e) bare TiO_2 for acetone vapour, 0.05 mol % of Ag / TiO_2 for ethanol vapour and 0.5 mol % of Ag / TiO_2 for toluene vapour. The addition of Ag catalyst in TiO_2 improves the surface area, adsorption capacity and active sites which will enhance the sensing characteristics towards particular vapour. Jiao et al. [42] investigated ethanol sensing performance of bare SnO_2 and Pd modified (0 wt %, 0.3 wt %, 0.6 wt %, and 0.9 wt %) flower like SnO_2 nanopowders. Amongst, 0.3 wt % of Pd loaded in SnO_2 shows a good sensitivity, fast response-recovery time at lower temperature, due to the higher catalytic nature of palladium. Tian et al. [43] examined the bare ZnO and Au nanoparticles modified flower like ZnO structure with their acetone sensing properties and concluded that by the addition of Au in ZnO hybrid structure improves the catalytic activity towards acetone vapour.

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Even though these methods could improve the gas sensing properties, still it raise the structural instability related problem, complication in fabrication problems and also decreases the sensor life. Among various metal oxide semiconductors such as zinc oxide, tin oxide, cadmium oxide, indium oxides, etc., iron oxide, bismuth oxide, zirconium oxide were found to have significant physical, chemical and electronic properties. Those significant properties of the selected metal oxide semiconductors and sensing behaviour of these metal oxides were stated briefly through wide literature survey.

Iron oxide (Fe_2O_3)

In Fe-O system contains different polymorphic forms such as wustite (FeO), magnetite (Fe_3O_4) and Fe_2O_3 exist. Also, Fe_2O_3 has two typical modifications: α-Fe_2O_3 (hematite, corundum-type hexagonal lattice a=5.035 Å and c=13.750 Å) and β-Fe_2O_3 (maghaemite). Among different Fe-O system, several researchers have studied various properties and applications of α-Fe_2O_3 and β-Fe_2O_3 phases of iron oxide. The synthesis of high quality maghemite is difficult as it shows phase transition from ferrimagnetic β-Fe_2O_3 to antiferromagnetic hematite (α-Fe_2O_3) at higher temperature. α-Fe_2O_3 has a complex defect structure in which three type's defects species, namely, oxygen vacancies, Fe^{3+} interstitials and Fe^{2+} interstitials are present. The presence of these defects gives rise to semiconducting properties. Loss of oxygen leaves behind extra electrons and produces an n-type semiconductor; while extra oxygen (entering the lattice as O_2) creates a deficit of electrons (i.e. introduces electronic hole), which produces p-type behavior. Thus, in α-Fe_2O_3 a transition from n-type to p-type response or vice versa can be induced by the change in the gas concentration, by appropriate dopant and/or by the operating temperature. Fe_2O_3 is known to show high sensitivity towards organic gases [44]. However, n-type hematite (α-Fe_2O_3) is an attractive environmental friendly semiconductor material for photoelectrochemical and photocatalytic purposes due to its stability, benign nature and abundance. Also because of its low cost, high resistance to corrosion, good chemical stability, high refractive index and non-toxicity, it has been traditionally used as catalysts, pigments, gas and humidity sensors, solar filters, supercapacitors, as an electrode material, in water treatment, in magnetic storage devices and in solid state lithium batteries, etc. In addition to this, α-Fe_2O_3 shows biomedical applications such as drug delivery system, hyperthermia and magnetic resonance imaging.

Iron oxide thin film samples were deposited by chemical spray pyrolysis method and show a polycrystalline α-Fe_2O_3 phase and spherical morphology on film surface. It shows good characteristics towards acetaldehyde vapour at ambient temperature. The acetaldehyde sensing studies were carried out in the concentration range of 0.25 ppm to 100 ppm. Based on this study, the detection of α-Fe_2O_3 thin film was found to 0.25 ppm to 10 ppm. Below 0.25 pm, there is no measurable electrical resistance changes was observed and above 10 ppm saturated electrical resistance and acetaldehyde sensing response was observed due to the insufficient of adsorbed oxygen species over the film surface. Moreover, the linear sensing response (R^2= 0.97545) was observed in the range of 0.25 to 10 ppm is shown in Fig. 3.

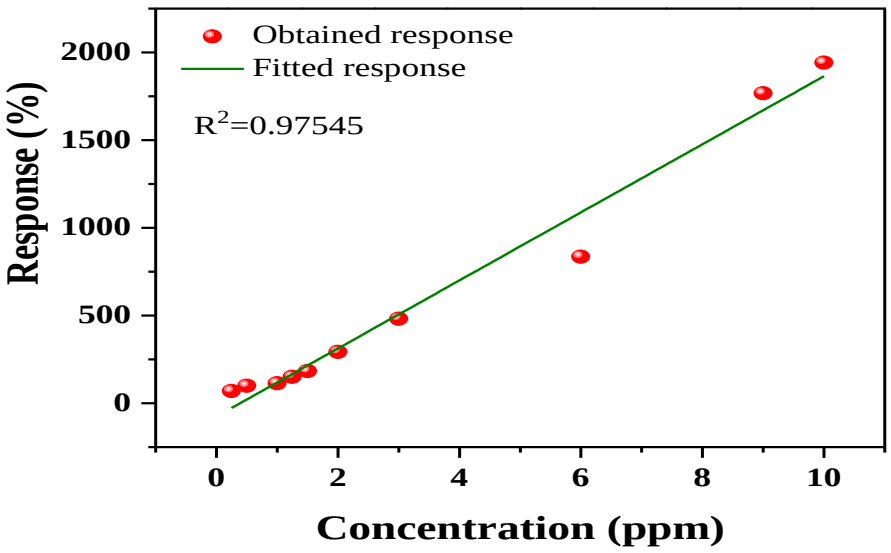

Fig. 3. Acetaldehyde vapour concentration dependent sensing response plot.

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Bismuth oxide (Bi_2O_3)

Bismuth oxide (Bi_2O_3) is versatile and technologically interesting material with wide band-gap, high refractive index, dielectric permittivity, high oxygen conductivity, remarkable photoconductivity and photoluminescence. These unique characteristics make Bi_2O_3 suitable for applications in solid oxide fuel cells, gas sensors, photoelectric materials, catalysts, glass manufacturing and functional ceramics, Schottky barrier solar cells, metal-insulator-semiconductor capacitors, microwave integrated circuits etc. Until now, at least seven polymorphs of Bi_2O_3 have been reported, including α, β, γ, δ, ε, ώ and high-pressure hexagonal phases. Among them, α, β, γ and δ-Bi_2O_3 are main polymorphic forms [45]. The monoclinic α-Bi_2O_3 phase and face-centered cubic δ-Bi_2O_3 phase are stable at room and high temperature (730–825 °C) respectively, while the tetragonal β-Bi_2O_3 phase and the body-centered cubic γ-Bi_2O_3 phase are high temperature metastable phases and usually transform into the monoclinic phase when temperature is reduced. Each polymorph possesses different crystal structures and various electrical, optical and mechanical properties. However, the characteristics of this film strongly depend on its crystal phases: its electrical conductivity may vary by over five orders of magnitude, while its energy gap may change from around 2–3.96 eV. Therefore, it is required to manufacture high-quality Bi_2O_3 films with a single phase.

Bismuth oxide thin films were deposited by chemical spray pyrolysis method and the deposited films have polycrystalline nature with α-Bi_2O_3 polymorphic phases. The dimethylamine sensing studies were carried out and important results are reported as follows; the sensing studies are done in the concentration of 0.5 ppm to 100 ppm. Amongst, 0.5 to 20 ppm of dimethylamine vapour shows linear sensing with the adjacent R^2 value is 0.9724, which is shown in Fig. 4 (a). Beyond 20 ppm saturated sensing response was observed, due to lack of oxygen adsorption sites over the film surface. Moreover, the dynamic selectivity study was carried out for various reducing vapours such as trimethylamine (TMA), monomethylamine (MMA), ammonia, acetaldehyde, formaldehyde, water vapour (75 % of RH), acetone, ethanol, diethanaolamine (DEA), toluene, xylene, benzene at ambient temperature (from Fig. 4 (b)) . From this study, we concluded that, spray deposited β-Bi_2O_3 thin film shows maximum electrical resistance variation in the presence of dimethylamine when compare to other vapour. However, the other amine group vapours such as TMA, MMA and ammonia may be influence the DMA sensing response. However, the reason behind for this DMA selective detection still under unanswerable.

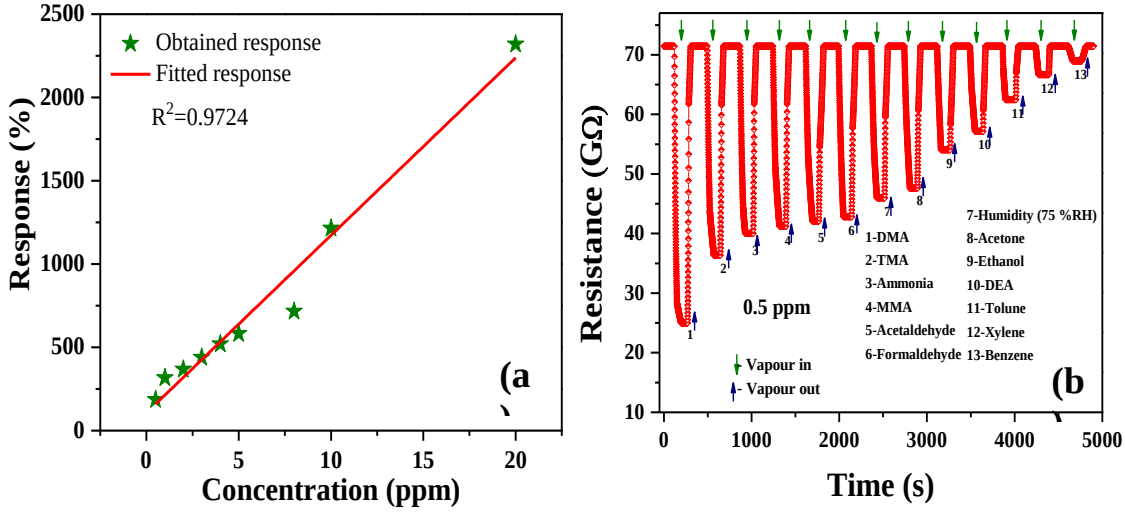

Fig. 4. (a) Linearity plot of α-Bi_2O_3 thin film towards dimethylamine vapour towards and (b) Transient plot of α-Bi_2O_3 thin film for various reducing vapours.

Zirconium oxide

Zirconium oxide (ZrO_2) contains three polymorphic phases such as monoclinic (m-ZrO_2), tetragonal (t-ZrO_2) and cubic (c-ZrO_2). The monoclinic m-ZrO_2 phase is thermodynamically stable from room temperature to 1170 °C. The tetragonal phase forms at 1170–2370 °C and it transforms to cubic phase at temperature over

2370°C [46]. The properties of the zirconium oxide are strongly depending on its crystalline phase. Even though monoclinic m-ZrO_2 is thermodynamically stable polymorphic phase at standard temperature and pressure, high temperature forms a tetragonal (t-ZrO_2) and cubic (c-ZrO_2) polymorphic phases are desirable for functional applications due to their excellent properties over m-ZrO_2. Zirconium oxide exhibits novel characteristics such as high hardness, high melting point, excellent chemical inertness, low thermal conductivity, ionic conductivity, high corrosion resistance, high dielectric constant value, high melting point, electrically insulating behaviour and so on. Hence, zirconia has multiple applications which include solid state fuel cells, adsorbent, oxygen sensors, catalysts, catalyst support, heavy duty membranes etc. The optical band gap of the zirconium oxide is in the range of 5 to 5.85 eV. The crystal structure, lattice defects and morphology of the ZrO_2 make significant effect on its catalytic activities. The zirconia have been found to be useful in oxygen pumps, sensors and fuel cells because of the good ionic conductivity, also used as thermal barriers because of their low thermal conductivity and high heat resistance. The ZrO_2 is one of the most important candidate materials for the replacement of SiO_2 as gate dielectric in microelectronic industry because of their high dielectric constant.

Zirconium oxide thin films were deposited onto the glass substrate by chemical spray pyrolysis method. The structural and morphological studies revealed that polycrystalline nature and formation of fine nanocrystallites over the film surface. The polycrystalline ZrO_2 thin film was tested towards monomethylamine vapour at the concentration of 0.25 ppm to 50 ppm. Up to 20 ppm, increasing trend of sensing response and beyond it saturated monomethylamine sensing response was observed. The linear sensing response was obtained in 0.25 ppm to 10 ppm and the adjusted R^2 value is found to be 0.95865, which is shown in Fig. 5 (a). The sensing response was estimated towards monomethylamine and other reducing vapours such as diethanaolamine, formaldehyde, ethanol, acetone, dimethylamine, xylene, ammonia, trimethylamine as displayed in Fig. 5 (b), which indicates selective detection towards monomethylamine.

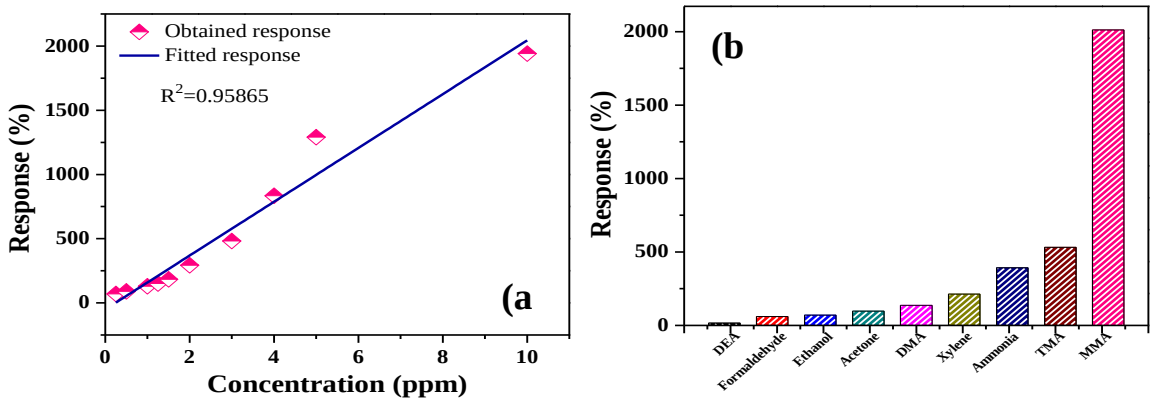

Fig. 5. (a) Monomethylamine concentration dependent sensing response of ZrO_2 thin films. (b) Sensing response of ZrO_2 thin films towards monomethylamine and other reducing vapours at ambient temperature.

Summary and outlook

The review articles discussed about the importance of metal oxide semiconductor based sensor elements, gas sensing mechanisms, selection of metal oxides based on its various properties and investigation of the factors influencing the sensing properties of various metal oxide semiconductors. Based on this knowledge, few metal oxides such as iron oxide, bismuth oxide, zirconium oxide were selected for vapour sensing studies. Furthermore, the selected metal oxides shows significant sensing characteristics towards different vapours at ambient temperature and important results were highlighted in this review article. Further studies can be made to these metal oxide thin film to fabricate sensing device for various applications

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