Chapter 1

Introduction

Nowadays, technology is witnessing a tremendous transformation that appears to be equally inspiring and productive as well as ominous and disruptive. On the one hand, where technology is helping human beings in their social and economic progress by use of modern gadgets, advanced transportation, improved diagnosis techniques, etc., but on the other hand, rapid industrialization has led to many serious-environment issues like emission of toxic and unsafe gases including volatile organic compounds (VOCs). According to a report by World Health Organization (WHO), in 2016, 91% of the total world's population did not breathe clean air and approximately 7 million deaths were caused due to indoor and outdoor pollution [1]. This implies that one in eight deaths has occurred due to the severe effects of air pollution on the human body.

VOCs are one of the most dominant by-products emitted by industries, motor vehicles, etc. and these compounds are defined as those organic chemicals which have a low boiling point and high vapor pressure which makes them volatile in nature [2]. VOCs can enter very easily in the human body and many of these VOCs possess harmful effect on human health which include nausea, dizziness, allergy, and even death. Common list of VOCs includes methanol, ethanol, acetone, benzene, formaldehyde, n-butanol, xylene, toluene, etc. and their detection is important for (i.) environment safety, (ii.) medical purpose, (iii.) food quality monitoring, (iv.) road safety, etc. These VOCs are also used in various commercial and household applications, e.g. ethanol is used as a fuel, solvent in chemical industries, and the base component of many alcoholic beverages [3]. Since drunk-driving cases are one of the most common reasons for road accidents in many countries, and thus a reliable detection of ethanol is essential to ensure the safety of road traffic. Acetone, being a bio-marker, has been widely studied in the medical field and a very high concentration

of acetone in breath is an indication of diabetic disease [4]. Methanol is another popular VOC that has been widely used in fuel cells, waste water denitrification, biodiesel preparation, as a solvent in dyes, drugs, colors, etc. [5]. However, methanol is dangerous to the human body as methanol decomposes into toxic formaldehyde and formic acid which causes health problems like headache, fatigue, nausea, blurred vision and even death [6,7]. Therefore, various countries and health agencies established a certain range of concentrations for different VOCs in human consumable products and permissible exposure limits of harmful VOCs in the environment [8]. Thus, it is important to note that the ultimate goal of all technological developments is to keep the planet with human beings, plants, and animals in a prosperous state. Thus, in the context of making the technology as positive as possible, the implementation of sensing devices that can detect different VOCs has been attracted great interest in the past for improving the quality of the environment and human health [9-13].

1. 1 Solid-state gas sensors

A solid-state gas sensor is defined as a device that changes its physical properties like mass, resistance, dielectric properties, etc. upon exposure to any gaseous species. These changes are further converted into an electrical signal having a magnitude that is proportional to the concentration of the target gas. At present, gas sensors have found applications in many important areas like air quality monitoring, medical diagnosis, health care, detection of hazardous gases in mines, gas leakage monitoring, food packaging, weather stations, etc. [14-21]. Also, various nanomaterials based solid-state gas sensors have been reported in the past which include metal nanoparticles, metal complexes, metal oxides, polymers, polymer-based composites, carbon-based nanostructures, etc. [22]. However, metal oxide-based nanostructures have a strong market presence and attracted great research interest due to their impressive physical, chemical and electrical properties [23-24]. Metal oxide-based sensors have demonstrated a huge potential because of their following versatile properties: (i.) high

sensitivity to a wide range of gases and VOCs, (ii.) cost- effective, (iii.) long lifetime, (iv.) lightweight, and (v.) simple fabrication techniques [23-25].

The evolution of metal oxide-based gas sensors has been started from the early 1900s. In 1938, Wagner and Hauffe discovered that interaction of certain type of atoms and molecules with semiconductor resulted in a change in surface properties of the semiconductor [26]. In 1953, Brattain and Bardeen discovered that resistance of the semiconductors gets changed to a large amount upon adsorption of gas molecules on their surface [27]. From this onwards, around the world, a detailed study of gas adsorption phenomenon on semiconductor was carried out to realize a commercial sensor. In 1962, the first chemo-resistive gas sensor was proposed by Seiyama et al. [28]. In 1970, Taguchi (Figaro) identified SnO_2 as the first metal oxide for gas sensing and developed sensors for commercial usage [29]. Since then, a number of industries are offering metal oxide-based sensors like Figaro, Paragon, MICS, FIS, UST, CityTech, Hanwei Electronics, Microsens, etc. Fig. 1.1 (a-d) shows the images of different gas sensors fabricated by different research groups around the world.

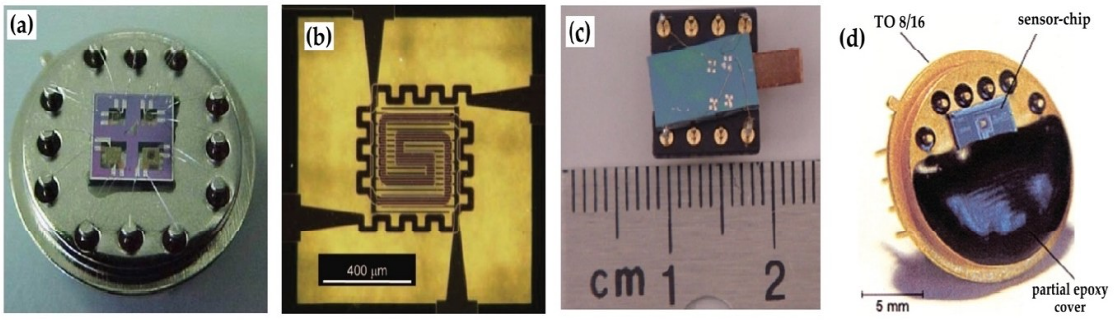

Fig. 1.1 Images of gas sensors: (a) SnO_2 nanoparticles-based gas sensor for detecting ethylene [30], (b) A micro hot plate sensor with interdigitated electrodes layered over heater leads [31], (c) Single-layer $MoSe_2$ based NH_3 sensor [32], and (d) Packed chip of the sensor based on nanocrystalline SnO_2 [33].

In general, several parameters are used to characterize a sensor and the definitions of majorly used parameters in accordance with their measurable quantities are discussed as follows:

- *Sensitivity or response magnitude* is defined as the ratio of change in the magnitude of measured electrical signal upon exposure to target gas relative to the original measured electrical signal (baseline value).
- *Selectivity* of the sensor corresponds to the ratio of sensitivity of the sensor for target analyte relative to sensitivity of the sensor for any other analyte. This value determines the ability of the sensor to recognize only one type of gas from a group of other existing gases.
- *Stability* is the measure of the baseline electrical signal of the sensor over a certain interval of time. This value determines the reproducibility parameter of sensor.
- *Response time* is defined as the time required by the sensor to reach 90% of its maximum response magnitude value upon exposure to the target gas. This value determines how fast a sensor can respond to a particular gas.
- *Recovery time* is the time required by the sensor signal to recover 90% of its maximum response magnitude value after the target gas is cut off. This value determines how fast a sensor can reach to its baseline value.

In gas sensing research, a considerable amount of work has been carried out to improve above-mentioned parameters but some elementary problems are still unsolved which hinders the commercial growth of gas sensors [34]. One of the most fundamental problems is of selectivity which always remains a major barrier for metal oxide-based sensors [35, 36]. As an example, all commonly used metal oxide-based sensors respond to a wide variety of gases and this would become problematic when one needs to detect only a particular type of gas. Thus, a sensor with a high response magnitude for only a particular gas or VOC is highly desirable. Various approaches that were implemented by the researchers in the past for enhancing selectivity of the sensor and these techniques are discussed in sec 1.5 of this chapter. These techniques involved the usage of nanostructured metal oxides for developing a highly selective sensor. Hence, the basic knowledge of metal oxide nanomaterials is essential for designing a selective sensor; therefore, the next section discusses the basics of nanostructured metal oxides.

1. 2 Nanostructured metal oxides

Nanomaterials, the materials that are having at least one of its length in the range of 1-100 nm, have received an appreciable growing interest because of their peculiar physical and chemical properties with respect to their bulk counterparts. Nanotechnology is a branch of technology that deals with synthesis of various nanomaterials and fabrication of different types of devices based on nanomaterials. The idea of nanotechnology first came into picture when Richard Feynman delivered a famous talk on "There is plenty of room at bottom" at the annual meeting of American Physical Society in 1959 [37]. However, the word "nanotechnology" was first suggested by Norio Taniguchi in 1974 [38]. Since then, advancement in different areas like synthesis methods, analytical tools, and processing techniques, etc. have enabled researchers to obtain well-characterized nanomaterials with well-defined production steps [39]. As an example, development of sophisticated characterization tools like Field Emission Secondary Emission Microscopy (FESEM), Transmission Electron Microscopy (TEM), Atomic Force Microscopy (AFM), X-ray Photoelectron Spectroscopy (XPS), etc. facilitate the investigation of nanomaterials at the atomic level, and hence materials can be manipulated at the nanoscale level for achieving desired physical and chemical properties of nanomaterials.

Nanostructures of metal oxides have attracted increasing interest in gas sensing applications because of their complex crystal and electronic properties [40-47]. Metal oxides are usually represented as M_xO_y, where M represents a metal such as Sn, W, Fe, Zn, Ti, etc. and O represents oxygen. Metal and oxygen exist as ionic compounds in metal oxide having positive (x) and negative (y) charges, respectively. The electrostatic interaction between these ions resulted in strong solid ionic bonds. In general, metal oxide has good thermal and chemical stability due to its filled s-shells. However, due to partially filled d-shells, a wide variety of vital properties are observed in metal oxides such as wide band gaps, good electrical, optical and thermodynamic properties, high dielectric constants, etc. [48]. Other unique properties exhibited by

metal oxides nanostructures are due to the presence of different oxidation states, symmetry, phases, density, coordination numbers, and stoichiometry. Nanostructured metal oxides are usually grown by either chemical or physical techniques. Chemical techniques involve electrochemical anodization method, sol-gel process, solvothermal, hydrothermal process, etc. [49]. Physical techniques involve chemical vapor deposition, atomic layer deposition, thermal evaporation sputtering, etc. [50-52]. These techniques are highly controllable and different morphologies of nanostructures can be synthesized with the implementation of these sophisticated synthesis methods. One of the salient features that make nanostructures popular in the gas sensing area is that these structures offer high surface energy and surface-to-volume ratio. Fig. 1.2 demonstrates the importance of reducing the size of the material where the surface to volume (SVR) increases with the reduction of size. A higher surface to volume means that a large number of atoms in these structures can be regarded as surface atoms, and thus effective adsorption/desorption sites get increased. Thus, more target gas/vapor molecules can interact with the surface of nanomaterials which enhances the response/sensitivity of nanostructures.

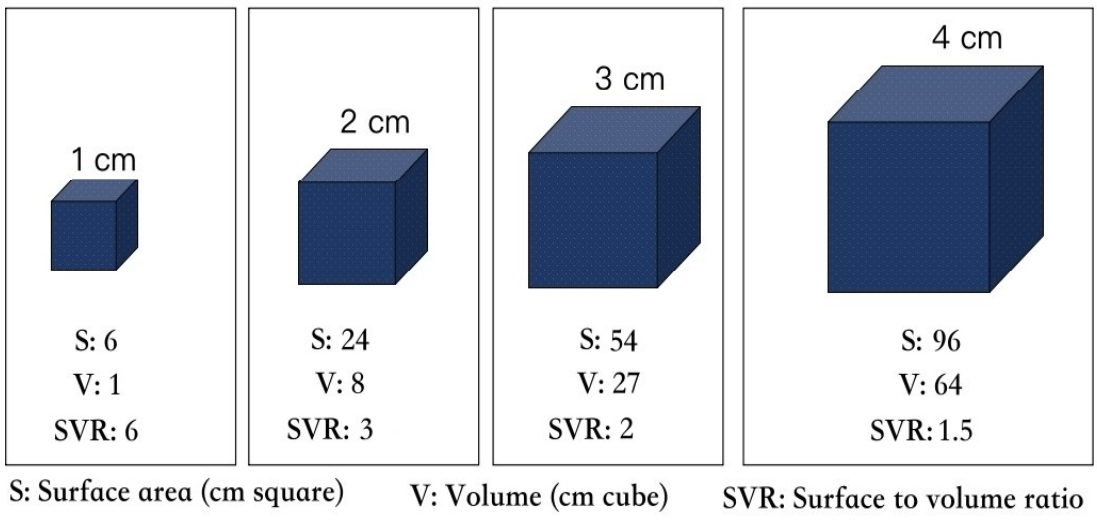

Fig. 1.2 A schematic showing the effect of dimensions on surface area, volume, and surface to volume ratio of the material [53].

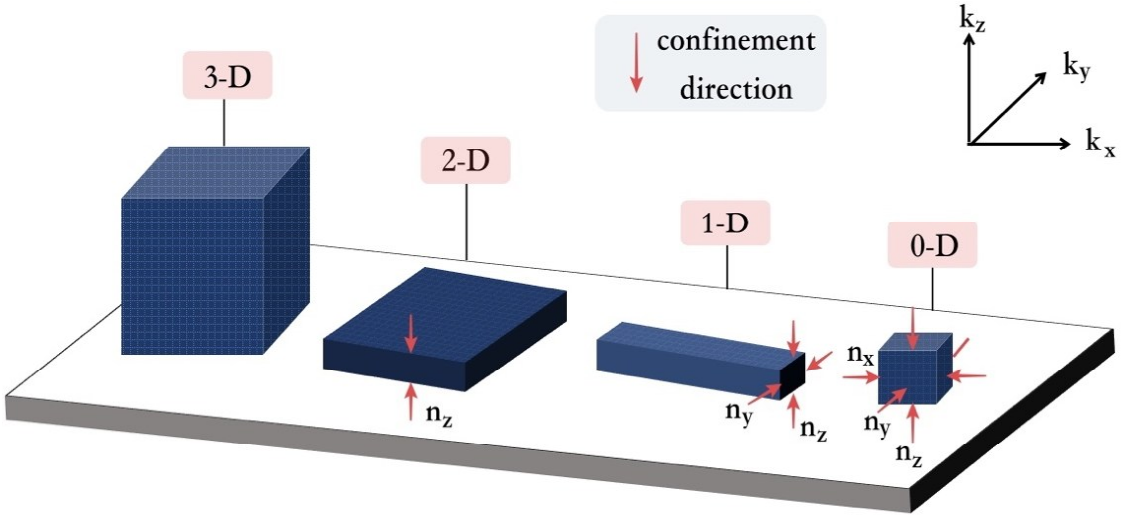

Fig. 1.3 A schematic showing classification of nanomaterials based on their dimensionality [54].

A major feature that can discriminate various types of nanostructures is the number of dimensions that are in the nanoscale range (1-100 nm). Typically, nanostructures based on their dimensionality can be classified into following four different groups (Ref. Fig. 1.3) [54]:

i. 0-D nanomaterials: 0-D nanomaterials have nanoscale sizes in three dimensions like quantum dots. Electrons in these materials exhibit no delocalization and are confined in all three directions (x, y, and z).

ii. 1-D nanomaterials: 1-D nanomaterials have nanoscale sizes in two dimensions only like nanowire, nanorods, nanotubes. In these materials, electrons can move freely or delocalized in one direction (x) and are confined in two directions (y, and z).

iii. 2-D nanomaterials: 2-D nanomaterials have nanoscale size in one dimension only like quantum wells, thin films. In these materials, electrons can move freely or delocalized in two directions (x, and y) and are confined in one direction (z).

iv. Bulk/3-D nanomaterials: Bulk nanomaterials have no nanoscale sizes in any of the three dimensions like nanocomposites. In these materials, electrons can move freely or delocalized in all three spatial directions (x, y, and z).

Among all of these different types of nanostructures, 1-D metal oxide nanostructures gained significant attention in gas sensing because of the following reasons [55-59]:

i. 1- D nanostructures correspond to the confinement of charge carriers in two dimensions. This means that Debye length in these structures is in comparison with their radius. Thus, the electronic properties of these structures become highly dependent on their surface properties.

ii. 1-D nanostructures of different shapes like nanotubes, nanorods, nanowires, etc. can be easily synthesized with controlled stoichiometry and crystallinity which enhances the stability of the device. The higher aspect ratio of 1-D nanostructures (length in the order of micrometers and diameter in the order of nanometers) eases fabrication of different device structures like Field Effect Transistors (FETs), capacitive type devices, etc. A capacitive type of structure essentially has two metal electrodes which are separated by a dielectric medium. However, 1-D nanostructures can be also be placed in between two electrodes which can act as a sensing layer. The fabrication of capacitive sensor using other types of nanostructures are relatively difficult and complex. A thin layer of 0-D nanostructures in between two electrodes may short circuit the sensor for a small voltage. 2-D nanostructures may be used for capacitive structure but it would offer less SVR and an additional barrier to electron transport. Thus, 1-D nanostructures seems to be the best suited structure for developing a capacitive type of sensors.

iii. Metal-oxide nanostructures offer large charge carrier concentration as they exhibit either electron or hole conductivity and no external impurity is required to increase the conductivity of the materials. 1-D geometry further enhances the conductivity as less scattering of charge carriers is observed, and hence results in better mobility of the charge carriers.

The above discussion shows the potentiality of 1-D metal oxide nanostructures in gas sensing area. However, to develop an efficient gas sensor, further investigations on the

properties of metal oxide nanostructures is essential. Thus, the next section discusses the sensing properties of various reported metal oxide nanostructures-based sensors.

1. 3 Nanostructured metal oxides-based sensors

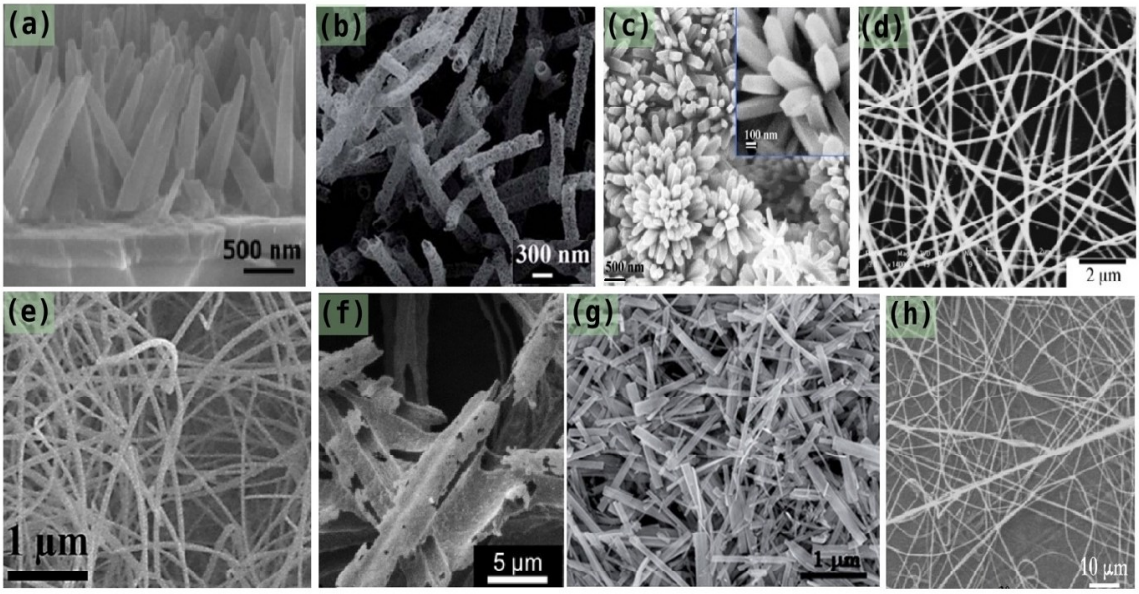

Fig. 1.4 FESEM images of various reported metal oxide nanostructures: (a) ZnO nanorods [70], (b) SnO_2/SnS_2 nanotubes [77], (c) SnO_2 nanoflowers [79], (d) SnO_2 nanofibers [83], (e) WO_3 nanorods [86], (f) WO_3 nanotubes [88], (g) WO_3 nanorods [89], and (h) In_2O_3 nanoribbons [96].

In past few decades, a number of nanostructured metal oxides like ZnO [60-72], SnO_2 [73-83], WO_3 [84-93], In_2O_3 [94-99] and TiO_2 [100-111] were reported for sensing a wide range of gases, like volatile organic compounds (VOCs), H_2, NH_3, CO, NO_2, H_2S, and CH_4, etc. Essentially, a gas sensor has an element that converts the concentration of adsorbed gas/vapor molecules into an electronic signal. These sensors have different categories including resistive type that tracks the change in resistance of sensing layer, capacitive type that monitors the change in dielectric property of sensing layer, and mechanical type that detects the change in mass of sensor [112-114]. This section reviews the performance of resistive and capacitive type sensors having different metal oxides as its sensing layer.

1. 3. 1 Resistive sensing

Table 1.1 lists various metal oxide nanostructures-based gas sensors working in resistive mode. The sensing mechanism in resistive type of sensor relies on the free electron theory of chemisorption on semiconductor surface [115]. Surface reactions that take place between adsorbed oxygen molecules and the target gas/vapor result in the change of electron concentration of sensing layer, and hence the resistivity [116]. Conventionally, resistive mode of sensing has a planar electrode configuration where two electrodes are placed on same plane either below or above the sensing layer. For example, M.W. Ahn et al synthesized ZnO nanowires on SiO_2/Si with carbothermal reduction route and studied its sensing properties for detecting NO_2 gas at 225 °C [69]. Y.J. Li et al synthesized Co-doped ZnO nanorods on ITO substrate which were 700-800 nm long with 50-60 nm of diameter and sensing properties of the sensor were tested for CO at 350 °C. For 750 ppm of CO, they found that ZnO nanorods exhibited 45 % of response magnitude [70]. A WO_3 nanorods based NO_2 sensor was reported by M. Horprathum et al where they found sensitivity of 28 for 2 ppm of NO_2 at 400 °C [90]. Highly sensitive WO_3 nanorods was synthesized by D.D. Nguyen et al which showed a response magnitude of 192 for 250 ppm of NH_3 at 50 °C [93]. Q.Q. Jia et al [92] reported a WO_3 nanorods based acetone selective sensor with detection limit of 0.25 ppm, response of 3.53 for 1 ppm of acetone at 230 °C with response and recovery time of 9 and 14 s, respectively. S.S. Shendage et al [91] prepared WO_3 nanoplates by hydrothermal method and its NO_2 sensing properties were tested at 100 °C. The sensor exhibited a response of 10 and 131.75 for 5 and 100 ppm of NO_2, respectively. Y.Y. He et al fabricated In_2O_3 nanospheres based sensor for NO_2 sensing [97]. In_2O_3 nanospheres were synthesized using two-step method involving solvothermal and calcination processes. The sensor was operated at 140 °C and responses of 163, 220 and 375 were measured towards 100 ppm of nitro-methane, nitro-ethane and nitro-propane, respectively.

Table 1.1 Various metal oxide nanostructures-based gas sensors working in resistive mode.

S. No.	*Metal oxide*	*Nanostructure*	*Substrate*	*Synthesis*	*Sensitivity[a/b], ppm*	*Analyte*	*Temp. (°C)*	*Ref.*
1	ZnO	Nanowires	SiO_2/Si	Carbothermal reduction	98 [a] , 20	NO_2	225	69
2	Co-ZnO	Nanorods	ITO	Electrodeposition	45 [b] , 750	CO	350	70
3	Pd/ZnO	Nanorods	Si	RF sputtering	38.7 [b] , 7	H_2	50	71
4	ZnO	Nanorods	Sapphire	Hydrothermal	80.6 [b] , 1000	NH_3	300	72
5	WO_3	Nanorods	Alumina	DC magnetron sputtering	28 [a] , 2	NO_2	400	90
6	WO_3	Nanoplates	Glass	Hydrothermal	10 [a], 5	NO_2	100	91
7	WO_3	Nanorods	Alumina	Hydrothermal	3.53 [a] , 1	Acetone	230	92
8	WO_3	Nanorods	SiO_2/Si	Hydrothermal	192 [a] , 250	NH_3	50	93
9	SnO_2	Nanoflowers	ITO	Hydrothermal	49.5 [a] , 100 ppm	n-butanol	320	79
10	Pt/SnO_2	Nanoflowers	Alumina	Dipping-precipitation	44 [a] , 50	n-butanol	100	80
11	SnO_2	Nanosheets	Alumina	Hydrothermal	207.7 [a] , 200	HCHO	200	81
12	SnO_2	Nanowires	Ceramic	Hydrothermal	18 [a] , 100	Ethanol	380	82
13	Co-SnO_2	Nanofibers	Ceramic	Electrospinning	24 [a], 100	H_2	330	83
14	In_2O_3	Nanoribbons	Alumina	Hydrothermal	19.4 [a] , 0.05	NO_2	125	95
15	In_2O_3	Nanoribbons	Alumina	Electrospinning	70 [a] , 12	NO_2	200	96
16	In_2O_3	Nanospheres	Ceramic	Solvothermal	375 [a] , 100	Nitropropane	140	97
17	WO_x/In_2O_3	Nanosheets	Ceramic	Impregnating	10 [a] , 100	HCHO	170	98
18	Au/In_2O_3	Nanospheres	Ceramic	Hydrothermal	26.3 [a] , 100	1-butylamine	340	99
19	Pd-TiO_2	Nanofibers	SiO_2/Si	Anodization	55 [a] , 2.8	NO_2	180	100
20	TiO_2	Nanoporous	Alumina	Hydrothermal	25.97 [a] , 500	Acetone	370	101
21	TiO_2	Nanotubes	Si	Anodization	74 [b] , 1000	Acetone	27	102
22	TiO_2	Nanotubes	Ti	Anodization	239.4 [b] , 100	H_2	27	103
23	TiO_2	Nanotubes	Ti	Anodization	300 [b] , 5000	2-propanol	200	104

It is apparent from Table 1.1 that metal oxides offer a wide variety of morphology and different types of gases can be detected by them. Resistive mode sensing majorly relies on the surface adsorption–desorption property where resistance of the sensing material gets changed upon exposure to target gas. This type of sensing is simple and popular from measurement aspect. However, resistive mode sensing suffers from high operating temperature, long-term stability and selectivity issues. Also, resistive sensors rely on the transfer of charges between sensing layer and contact electrodes; thus, it is susceptible to flicker (1/f) noise and incomplete recovery of charges [117].

1. 3. 2 Capacitive sensing

Capacitive mode of sensing involves monitoring the change in dielectric constant value of device in different ambient [113]. Usually, the capacitive mode of sensing has a vertical electrode configuration where sensing layer is placed in between two electrodes. Also, this configuration is highly appropriate for 1-D nanostructures-based sensors where faster response/recovery at relatively low operating temperature can be achieved [118]. Z. Wang et al [119] successfully synthesized ZnO nanorods on Si nanowire using chemical bath deposition for sensing relative humidity (RH) at room temperature. Capacitance of the sensor was reported to change 0.69 nF/%RH. The sensor exhibited good stability with 2.93 % of standard deviation from its baseline capacitance value. K. Narimani et al [120] tested different sensors based on ZnO nanorods with variable density and found that response of the sensor towards RH gets increased with the decrease in density of nanorods. The maximum sensitivity of 61.23 % was recorded at 95% RH. X. Zhou et al [121] fabricated ZnO nanorods based capacitive ethanol sensor. Capacitance of the sensor increased by 122% when exposed to 20 ppm ethanol at room temperature. K. Dutta et al reported a Pd/ZnO nanorods/Si based sensor having MIS type structure. The sensor showed excellent capacitive sensitivity of 7200% towards 700 ppm ethanol at 275 °C [122]. L. L. Wang et al [123] obtained a SnO_2/Sn type

composite thin film on Si nanoporous pillar array by using a vapor–liquid–solid (VLS) growth method. Using this material, a capacitive sensor for humidity sensing was fabricated and Ag electrodes was deposited over thin film using sputtering. The sensor showed a capacitive sensitivity of 265% at 1 kHz when RH level changed from 11-95 %. Response and recovery time of the sensor were reported below 20 s. K. Dutta et al [115] established a facile electrochemical method to synthesize TiO_2 nanotubes over Ti substrate and a capacitive sensor was fabricated by depositing Ti over TiO_2 nanotubes using electron beam evaporation technique. The sensor was successfully tested for sensing non-polar VOCs like benzene, toluene and xylene at 150 °C and exhibited sensitivity of 14.33%, 9.86% and 8.93% for benzene, toluene and xylene, respectively.

It is apparent from the above discussion that capacitive mode of sensing relies on the dielectric properties of the target vapor. The literature review confirmed that metal oxides-based sensors for VOC detection in capacitive mode are less explored as compared to other nanomaterials like Si, C, polymers etc. [124-131]. Also, most of the reported capacitive sensors were used for humidity sensing as a high capacitive change can be obtained for the analyte having high value of dielectric constant. Capacitive sensors are more popular for humidity sensing as water exhibits a very high dielectric constant value ($\mathcal{E}_r$ =81). Capacitive mode sensing consumes no static power; thus, are very much in demand in energy constrained environment [132]. Also, the detection mechanism in a capacitive sensor does not involve any transportation of charges unlike resistive sensing. Thus, it provides more sensitivity, improved selectivity and reliability for chemical detection [117, 132].

1. 4 TiO_2 nanostructures for sensing application

Among various metal-oxide nanostructures discussed above, TiO_2 nanostructures offer the following advantages for sensing application:

i. TiO_2 is a highly stable (both chemically and thermally), non-toxic, corrosion-resistant, and biodegradable material which makes it a promising material for gas

sensing applications [133].

ii. TiO_2 has three crystalline phases: anatase (tetragonal), rutile (tetragonal) and brookite (orthorhombic). TiO_2 has a wide and indirect optical band gap (3 eV for rutile and 3.2 eV for anatase) which enhances the lifetime of electron-hole pairs. Also, anatase TiO_2 is a relatively more active structure than their counterparts like rutile and brookite [134]. A large number of charge carriers are available on the surface of anatase TiO_2 which results in the reduction of activation energy required by the target molecules to react on the surface. Thus, it makes anatase TiO_2 as a perfect sensing element where low/room temperature of sensing operation is required [135].

iii. TiO_2 in anatase phase has an excellent lattice matching with Si and SiO_2 that makes it a suitable candidate to be used as a sensing element in Complementary Metal Oxide Semiconductor (CMOS) compatible processes [136].

iv. For metal oxide-based sensors (like ZnO, SnO_2, WO_3, etc.), nanostructures were placed over foreign substrates like ITO, alumina, ceramic, SiO_2, etc. (Refer Table 1.1). This degrades the overall stability of the sensor as grown metal oxide nanostructures have poor lattice matching with these substrates. However, TiO_2 nanostructures grow over the metallic Ti substrate which increases the overall stability of material as TiO_2 has an excellent lattice matching with Ti metal.

v. TiO_2 offers a wide variety of nanostructures like nanorods, nanotubes, nanofibers, nanowires [100-111]. These morphologies are highly tunable and can be easily reproducible by well-defined and facile synthesis methods.

vi. Most of the metal oxide nanostructures do not have highly ordered and well defined 1-D nanostructures as evident from Fig. 1.4 where nanostructures were placed random in space with no symmetry. However, TiO_2 nanotubes are highly ordered and directional in 1-D [134].

vii. TiO_2 is a highly non-stoichiometric transition metal oxide which has two types of ionic lattice defects, namely, oxygen vacancies (donor defects) and Ti (acceptor

defects) [137]. The nature of conductivity is governed by the defect that have the dominant density. TiO_2, in its stable phase, exhibits n-type conductivity due to the presence of higher oxygen vacancies. However, the nature of conductivity of TiO_2 can be changed from n- to p-type if the concentration of Ti vacancies gets increased with respect to oxygen vacancies. Thus, the type and magnitude of conductivity of TiO_2 can be changed by controlling these defect densities.

From above discussion, 1-D TiO_2 nanostructures can be considered as a promising material for gas sensing applications. Also, if a vertical type structure was chosen for fabricating sensors then 1-D TiO_2 nanostructures can be placed with an ease in between two metal electrodes. This type of structure can be used to explore the gas sensing properties of the sensor in both resistive and capacitive modes. Therefore, in this thesis, an attempt is made to enhance gas sensing performance of 1-D TiO_2 nanostructures by studying their physical, chemical and electrical properties.

1. 5 Selectivity issue in nanostructured metal oxides-based sensors

As discussed in the above section, nanostructured metal oxides based sensors using different metal oxides like TiO_2, ZnO, WO_3, SnO_2 to name a few have been successfully used for detecting different types of gases. These types of sensors exhibited excellent performance concerning cost [138], sensitivity [139], and reliability [140] but usually suffer from inherent poor selectivity issues [36]. As these types of materials respond to a wide range of gases; thus, making the sensor difficult to sense a particular gas/vapor from the mixture of other gases present in ambient.

The most popular sensing mechanism for these types of sensors is based on the change of electrical resistance in air and target gas ambient [141-143]. In air ambient, adsorption of oxygen molecules extracts free electrons from the conduction band of metal oxide (for n-type) surface and hence a depletion layer is formed [144]. In any reducing gas ambient, the adsorbed negatively charged oxygen ions oxidize the reducing gas and refill the conduction band with electrons. The adsorption/desorption

of target gas on metal oxide significantly changes the resistance of sensor and this change is measured to determine the target gas. However, the same amount of change in resistance may occur for any other vapor at different concentrations. As an example, x ppm of vapor A may have the same response magnitude as of y ppm of vapor B. Thus, the same response may correspond to different vapors and hence the problem of cross-sensitivity or selectivity arises in metal oxide-based resistive sensors. Another popular mode of operation for gas sensors is measuring of the capacitive change of sensor upon exposure of a particular concentration of vapor [145-147]. This type of response can also be the same for different vapors at a different concentration, and hence the similar issue of cross-sensitivity arises in the capacitive type of sensors also.

To achieve the required selectivity in metal oxide-based sensors, the following different strategies have been used by the researchers (i) use of temperature cycling [148-150], (ii) doping in nanomaterials [151-155], (iii) use of multi-composite materials [156-59], (iv) surface modification with functionalized materials and noble metals [160-163], (v) use of multi-sensor array and pattern recognition [164]. A summary of the sensors which were fabricated to achieve high selectivity using all the above techniques is given in Table 1.2. These reported methods have its own drawbacks considering the sophistication of the steps involved to achieve the selectivity and the following shortcomings are found from these methods:

i. Selectivity of the sensor get changed from one gas/vapor to another gas/vapor if operating temperature get changed. Kang et al [148] reported that the same Pt-doped SnO_2 is selective towards both toluene and formaldehyde at different operating temperatures. Similarly, [149] reported CuO doped SnO_2-ZnO based sensor which was selective towards CO and H_2 when operated at 150-250 °C and 310-440 °C, respectively. Thus, changing the operating temperature of sensor for detecting different gases may become difficult in real-time environment sensing. Also, the operating temperature of metal oxide-based sensor has been reported quite high. [152] reported Mn-doped ZnO sensor which

Table 1.2 Summary of various sensors reported for detecting VOCs with high selectivity.

S. No.	*Material*	*Morphology*	*Target gas*	*Other tested gases*	*Temp. (°C)*	*Ref.*
1	Pt doped SnO_2	Thin film	Toluene	HCHO, CO	325	148
2	Pt doped SnO_2	Thin film	HCHO	Toluene, CO	440	148
3	CuO doped SnO_2/ZnO composite	Microspheres	CO	H_2	150-250	149
4	CuO doped SnO_2/ZnO composite	Microspheres	H_2	CO	310-440	149
5	WO_3/SnO_2 composite	Nanoplates	Ammonia	Acetone, hexane, toluene, ethanol, $CHCl_3$	200	150
6	Fe and C doped WO_3	Nanospheres	NH_3	Toluene, methanol, ethanol, CO, NO	300	151
7	Mn doped ZnO	Nanoparticles	Ethanol	Acetone, benzene, HCHO	340	152
8	Ni-doped ZnO	Nanowire	p-xylene	Benzene, trimethylamine, H_2, CO, HCHO	400	153
9	Cr-doped TiO_2	Nanotubes	NO_2	CO	500	154
10	Nb doped TiO_2	Nanorods	Ethanol	LPG, H_2	500	155
11	$SnSO_4$/ZnO composite	Nanoparticles	HCHO	Ethanol, benzene, NH_3, H_2, CO	27	156
15	PbS QD/TiO_2 composite	Nanotubes	NH_3	Methanol, ethanol, acetone, toluene	27	157
16	NiO/TiO_2 composite	Microspheres	NH_3	Methanol, ethanol, acetone, HCHO	27	158
17	ZnO/SnO_2 composite	Microrods	H_2	Methane, CO	150	159
18	WO_3/SnO_2 composite	Nanoplates	Ethanol	Ammonia, hexane, toluene, acetone, $CHCl_3$	300	159
19	WO_3/SnO_2 composite	Nanoplates	Acetone	Ammonia, hexane, toluene, ethanol, $CHCl_3$	350	159
20	Pt functionalized In_2O_3	Nanocubes	H_2	CO	27	160
21	rGO functionalized TiO_2	Thin film	NH_3	H_2S, H_2, CO_2, SO_2, CO, NO_2	27	161
22	Pd functionalized ZnO	Nanowires	H_2	Methane, ethanol, acetone, CO	200	162
23	rGO functionalized TiO_2	Thin film	HCHO	Ethanol, acetone, CO, H_2S, H_2	27	163

was operated at 340 °C. Similarly, B. Mondal et al [159] reported ZnO-SnO_2 based sensor which was operated at 150 °C.

ii. Most of the sensors have been tested for selectivity where the physical and chemical properties of test and interfering gases/vapors are quite different. Liu et al [157] reported NH_3 selective sensor using PbS/TiO_2 composites where all the interfering components were organic vapor like methanol, ethanol, acetone, and toluene. [151] used Fe and C doped WO_3 sensor for selective detection of ammonia with respect to other tested gases like CO, NO, toluene, methanol, and ethanol. Y. Yang et al [158] tested the selectivity towards ammonia using NiO/TiO_2 sensor where other tested gases were formaldehyde, methanol, ethanol, and acetone. Thus, these studies did not compare the sensitivity of the sensor for similar kind of VOCs while studying its selectivity performance.

iii. Selectivity of the sensor towards a particular gas/vapor usually shows very random selection when the surface of sensor gets modified. Also, there is no systematic approach to explain the selective detection of a particular gas/vapor [161,163]. As an example, Z. Ye et al [161] used rGO functionalized TiO_2 nanoparticles for detecting ammonia. However, Z. Ye et al [163] used the same material for detecting formaldehyde (HCHO) in another report. Thus, the same material was reported for selective sensing of different types of analytes and it would be difficult to differentiate by the sensor if both ammonia and formaldehyde are present in the environment.

From the above discussion, it is quite evident that selectivity is a critical issue with regards to metal oxide-based sensors which obstruct their practical use. High operating temperature and poor stability further limit the application of these types of sensors. Thus, the main objective of this thesis is to study TiO_2 based 1-D nanostructures-based sensor for selective detection of VOCs. An in-depth analysis of electrical parameters of TiO_2 nanostructures is the key to explore new solutions to the problem of inadequate selectivity in metal oxide-based sensor.

1. 6 Objectives

The above literature review demonstrates the versatile capabilities of gas sensors based on nanostructured metal oxides. As discussed, these types of sensors usually suffers from issues like poor selectivity, high operating temperature and less stability. Also, to achieve the required selectivity in these sensors, different strategies have been used by the researchers but all these techniques required some sort of chemical modifications in the metal oxide material which hampers the intrinsic properties of the sensing layer. However, in this work, new methods were explored from the prospective of device structure of 1-D TiO_2 nanostructures for enhancing the selectivity of the sensor. In a nutshell, this thesis attempts to achieve the following objectives :

i. To develop VOC sensors based on 1-D TiO_2 nanostructures with high sensitivity, selectivity, stability, and low operating temperature.
ii. To model an equivalent electrical circuit of a sandwich structured sensor having 1-D TiO_2 nanostructures as its sensing layer.
iii. To develop a new measurement technique for selective detection of various VOCs like methanol, ethanol, acetone, etc. by using a single sensor.
iv. To develop a portable, low cost, and energy-efficient sensor system that can detect methanol contamination in alcoholic beverages.

To achieve the above objectives, the basic flow of work was planned as follows:
Firstly, different 1-D nanostructures of TiO_2 were synthesized over Ti substrate using different techniques like electrochemical anodization and hydrothermal method. The grown TiO_2 nanostructures were characterized thoroughly using XRD, FESEM, TEM, XPS, etc. Afterward, different sandwich structure sensors having different 1-D TiO_2 nanostructures as its sensing layer were fabricated. The resistive and capacitive sensing properties of these sensors were measured upon exposure to different VOCs and these sensing results were used to address the issue of selectivity. Finally, to show the application of the sensor in real-time environment, a prototype of the sensor system was demonstrated for detecting methanol contamination in alcoholic beverages.

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