

Introduction

1.1 Semi-conducting metal oxide (SMO) nano-structures

Metal oxide semiconductors in nanometer scale (nano-structured) have attracted a wide scale attention as they can promote a frontier area of research in the field of nanotechnology which may extend the device physics to one- (quantum wells), two- (quantum wires) or three-dimensional (quantum dots) confinements. In addition, the properties at the nanometer length scale are significantly different from their bulk materials [1] and the modern growth techniques make it possible to grow various oxide nano-structures down to a nanometer scale. Hence, self-organized formation of SMO nano-structures has perspective applications in quantum device physics and a detailed understanding of their growth mechanisms is of high practical importance [2]. Apart from the quantum device applications, complex and tunable nature of electrical properties makes SMO based nano-structures an interesting and attractive material for a wide range of applications in the field of optoelectronics [3], photo catalysis [4] and gas sensors [5] and solar cells [6]. In general, SMO based nano-structures are largely classified with different surface morphologies makes them as potential candidates for sensor and catalytic applications. In this aspect, growth mechanism of the SMO based nano-materials, their structure, morphology and chemistry can have a very significant impact on the gas sensing ability as well as the catalytic behaviour.

In recent days, the environmental safety is one of the most important and challenging issue faced by the human being. In one way it is extremely crucial to detect any toxic or dangerous materials, more precisely when it is invisible gas phase, in an early stage [7]. On other hand, it is equally necessary to recycle/remove any environmental pollutant such as industrial dyes through a proper degradation process [8]. In both aspects, SMO based nanostructures can play a significant role as they are widely used as gas sensing materials as well as various photo-catalytic activities. Moreover,

there photo-electrochemical and photo-voltaic properties can also be used as green energy sources through water splitting and solar cells [9].

1.1.1 Copper oxide nano-structures

In general, copper has two principal types of oxide: **cuprous** oxide (Cu_2O , cuprite) and **cupric** oxide (CuO , tenorite). More precisely, Cu_2O shows a cubic structure ($a = 4.27 \text{ \AA}$) and exhibits a direct band gap of $\sim 2.1 \text{ eV}$ [10] whereas CuO appears in monoclinic structure ($a = 0.4684 \text{ nm}$, $b = 0.3423 \text{ nm}$, $c = 0.5128 \text{ nm}$ and $\beta = 99.54^\circ$) with an indirect band gap in the range of $1.21 - 1.50 \text{ eV}$ [11]. As Cu_2O exhibits a direct band gap lying in the visible light wavelength range, it is a potential candidate for the absorber layer in solar cells [12-13]. Moreover, it shows an excellent photo-catalytic activity such as the degradation of the organic pollutants towards solving the environmental problems related to water splitting and anti-microbial applications [14]. In addition, its outstanding excitonic properties including a large exaction binding energy ($\sim 140 \text{ MeV}$) have also attracted many fundamental researches [15]. It has also been reported that the photo-catalytic performance of Cu oxides is very much controlled by the recombination of the photo-excited electrons and holes [16]. On the other hand, CuO appears having indirect band-gap in the range of $1.21 - 1.50 \text{ eV}$ [17]. CuO is suitable applicant for the gas sensor applications and several reports based on CuO nano-structures gas sensing for various gases have already been reported [18 - 20], including carbon monoxide gas [21]. In addition, various types of CuO nano-structures are also used for anode material in Li^+ batteries [22], infrared photo-detectors [23] and field emitting devices [24].

1.1.2 Zinc oxide nano-structures

ZnO is an n-type semiconductor having a direct band gap in the ultra violate regime of $\sim 3.5 \text{ eV}$ [25]. The crystal structures of ZnO may have two different phases such as **hexagonal** wurtzite structure as well as **cubic** zinblende structure. Among these, the wurtzite phase is the most common and a stable structure at ambient conditions [26]. Wurtzite ZnO crystal appears in hexagonal symmetry with $a = 0.3296 \text{ nm}$, $c = 0.52065 \text{ nm}$, which can be explain as alternating planes O^{2-} and Zn^{2+} ions, mounted along the c axis. The zinblende phase is not very common and only found when ZnO grows on a

substrate having a cubic crystal structure [27]. In any case, the most exciting features of ZnO is that it may appear in a variety surface morphologies in nano-scale [28-32], which is very appropriate for any gas sensing application. In recent days, ZnO based nano-structures are one of the most widely used materials in the field of gas sensor applications. Similar to copper oxide, ZnO based nanostructures also suffer from an unintentional doping effect which make it n-type in nature. Here it appears with oxygen vacancy whereas for copper oxide it was Cu vacancy. This unintentional doping/vacancy in ZnO lead to a stoichiometry issues, which finally limits/controls its electronic performances. However, p-type doping is found to be a very difficult task for ZnO and only a few acceptors elements are available [33]. The wide energy band gap of ZnO makes it a potential candidate with possible applications in the fields of blue light LEDs [34], UV laser [35] and UV detector [36-37]. However, ZnO thin films mostly appear to be transparent to visible light, which makes it also useful for solar cell application as a transparent conducting electrode in flat panel display and window layer for visible lights [38-40]. Piezo and pyroelectric behaviors are the unique property of ZnO based materials [10, 15]. Due to its piezoelectric properties and bio-degradability, it is capable to be utilized in the ceramics industry as well as in field of biomedicine [41]. Moreover, it is also having excellent mechanical and thermal stability at room temperature [42]. These entire properties make ZnO based nano-structures one of the most widely used materials with numerous applications.

1.2 Impact of Carbon monoxide (CO) on human health

In recent years, the most common air pollutants are CO, SO₂, NO₂ and O₃. Among which CO is known as a silent killer as it is colorless, odorless, tasteless and non-irritating. Breathing in CO environment for long period of time may cause severe health hazards such as headache, unconscious, vomiting, as well as dizziness, increased risk of any existing heart disease and even death. Even for a very low concentration (30ppm) of CO inhalation for a long duration may have an unrecoverable impact on human health. A graphical representation of CO impact on human health for different concentration and exposure time is also shown in Figure 1.1. Hence, an early detection CO for a low concentration is of high practical importance. In general, CO is being formed from the incomplete combustion of carbon-containing fuels. A major amount of CO is produced

from motor vehicles, gas appliances, wood stoves and cigarettes [3]. According to the United States (US) National Institute of Occupational Safety and Health (NIOSH), 35ppm of CO exposure for 8 hrs is the maximum limit for survival of any human body [7]. The sensing the CO gas through human body is very difficult and it can easily slow up the blood's ability to carry oxygen to vital organs. Inhaled CO gas will combine with the oxygen and form carboxyhemoglobin (*COHb*), which does not support to carry the oxygen in human body and leading to causes of human death. Hence, a prior precaution against any CO exposure for even low concentration is highly desirable which demands a highly sensitive CO sensor.

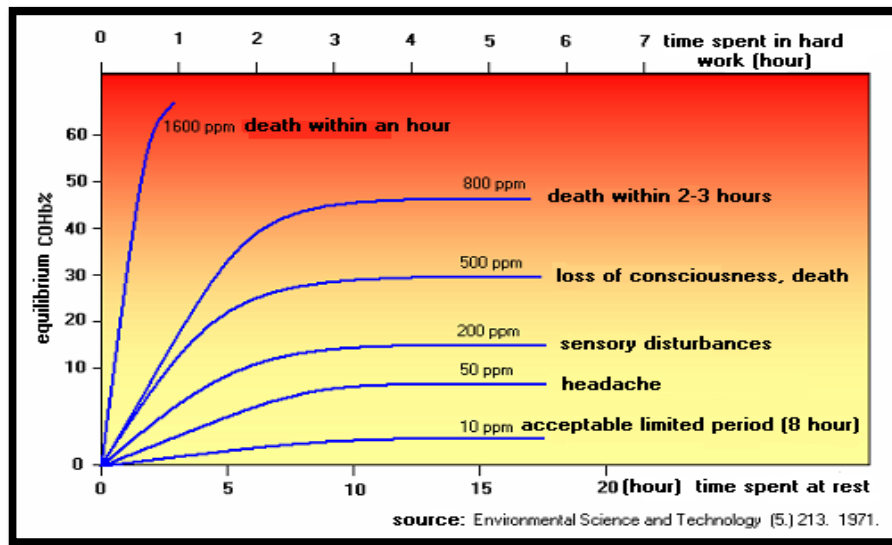


Figure 1.1: Schematic graphical representation of CO impact on human health for different concentration and exposure [43].

1.3 Impact of Ethanol vapour

Sensing and monitoring of ethanol (in vapour form) is also very important. Ethanol is also colorless, volatile and highly flammable liquid that has a minor odor. It is part of the hydroxyl group, which makes it a substructure of the water molecule. It is incredible and versatility material because it can easily mixed with water, chlorides and hydrocarbons and some other solvents. Ethanol is widely used in various daily products used for household cleaning , window cleaning solutions, nail polish remover, perfumes, liquid detergents, inks, paints and varnishes, flavorings and deicing sprays, etc. The effects of ethanol on human health those who drink extremely high level of alcoholic beverages are the following: nausea, vomiting, dizziness, even respiratory paralysis, etc, Liver

cirrhosis, cancers and nervous system disorders are the most serious pathologies caused by excessive use of alcoholic beverages. However, it is useful in many applications such as alcoholic beverages, hygiene products, preservative for biochemical samples, medicines, bio-fuel and gasoline additive. The exposure to ethanol can be in the form of vapor (breathing), body contact and ingestion. It has also been recognized that inhalation or the skin contact with ethanol vapours can be a source of localized irritation. In the vapors form ethanol has been used to test the alcohol levels of a driver, as well as in the field of chemical synthesis.

1.4 SMO nano-structures based gas sensors

Over the last few decades, enormous research efforts have been directed toward the development of suitable gas sensing devices for a number of important fields, including industrial process control, safety measurements, disease diagnoses, and environmental monitoring. Currently three types of solid state gas sensors are in large scale use based on: (a) resistance modulation of semiconducting surface, (b) solid electrolytes (electrochemical) and (c) catalytic combustion (pellistors) [44]. However, metal oxide (MO_x) based semiconductor gas sensors are the most popular as they offer low cost, high sensitivity and operational simplicity along with the compatibility of combining with other electronic devices. Metal oxides have played a key role as active materials for gas sensor for many years due to their unique combination of *redox* chemistry, optical, electrical and semiconductor properties. Currently, SMO based solid state gas sensors are the most popular type as they offer low cost, high sensitivity and operational simplicity along with their device compatibility. Particularly, nano-structures are extensively been investigated due to their large surface to volume ratio enhancing the adsorption capability as well as for improved stability [45]. The active part of a semiconductor gas sensor consists of metal-oxide nanostructures with high surface-to-volume ratio which is exposed to the gas molecules to be detected. The adsorbed gas species can significantly alter the electrical properties (conductivity) of the semiconducting surface by changing the free charge carrier density which finally leads to the detection/monitoring process. Moreover, faster response to the environmental gas as well as wide range of selectivity makes MO nanostructures promising candidates for gas sensing materials.

Among various semiconducting (MO_x) gas sensors, post-transition metal oxides with d^{10} electronic configuration such as SnO_2 and ZnO are the most widely used n-type semiconductors for gas sensor applications. From last few decades, TiO_2 nano-materials have also been used as health care products as well as gas sensors to detect the toxic and pollutant gasses from the environment [46-47]. According to recent research reviews, ZnO is found to be more prominent candidate for gas sensors and health care product, due to wide range of band gap (3.24 eV) and broader UV absorption spectrum (compare to TiO_2). Moreover, ZnO a very versatile and important material as it offers a variety of nanostructures formation. On the other hand, transition metal oxides such as copper oxide (CuO) and nickel oxide (NiO) are the most commonly used p-type sensor materials [48]. A schematic representation of the different metal oxide based gas sensor research is shown in Figure 1.2.

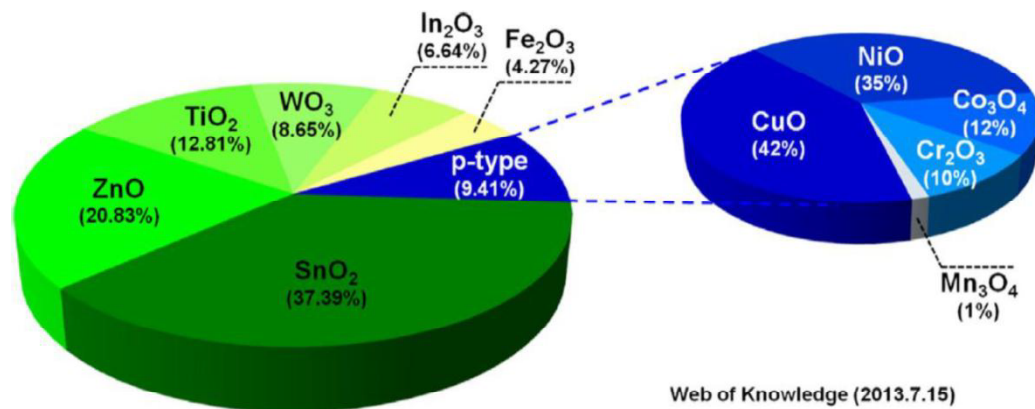


Figure 1.2: Schematic representation of various SMO based gas sensor research [48].

1.4.1 SMO nano-structures based CO sensors

Successful detection of CO using MOs based gas sensors were first reported by *Wiegleb et al.* [49] and *Barbi et al.* [50]. Thereafter, several researchers have reported CO sensing using both n- and p-type MOs nanostructures for CO sensing. Mostly, n-type semiconductors such as ZnO [25-26, 51], SnO_2 [33, 42], TiO_2 [52 -53], In_2O_3 [12-13], WO_3 [10] are used for CO sensing. However, p-type semiconductors such as NiO [14-15], CuO [16-18], and Co_3O_4 [19] are also used for successful sensing of CO. In principle, chemisorptions of surrounding gas molecules on semiconducting surface can

significantly alter the electrical transport property of the MOs layer, which effectively indicates the presence of the target gas molecules.

1.4.2 Recent gaps and possible approaches

In general, majority of the gas sensors are made up of n-type SnO₂ and ZnO. One of the greatest advantages of ZnO based nanostructures is that it may appear in a variety of shapes in nanometer scale which can potentially influence the gas sensing properties. Therefore a controlled growth and modulation of ZnO nanostructures are of great scientific as well as practical importance. In addition, another advantage of ZnO based nanostructures is that they can sense almost all kind of gas and volatile organic compounds (VOC). At the same time, it may appear as a major drawback of ZnO for the selective sensing of gas and VOCs. Hence, p-types, CuO nanostructures would also be a potential candidate to explore for CO sensing with improved sensitivity at lower operating temperature. In this aspect, oxide phase purity of the Cu film can play an important role towards its application in sensor devices. Moreover, a comparative study of p-type CuO and n-type ZnO based CO sensor will attracts much more attention to the scientific community for a better understanding of the gas sensing mechanism. Finally, a mutual doping or hetero-junction formation using these two types of SMOs may open a new pathway for both sensitive as well as selective CO sensing at a reasonably low operating temperature.

An important aspect of any resistive mode gas sensor device would be its operating temperature. It has been reported that the SMO based sensor generally suffers from a high operating temperatures, which eventually increases their power consumption. Hence, a lower operating temperature is one of the most desired criteria for any sensor to minimize the power consumption. In addition, a low operating temperature is also preferred for any sensor due to safety reason when it works in an open atmospheric ambient. Therefore, for a continuous monitoring process of any toxic gas such as CO, a highly sensitive sensor of a relatively lower operating temperature is of high technological demand.

In most cases pure metal oxides (semiconductor) show a significantly high operating temperature for CO sensing. In addition, selectivity is really a very challenging issue for any kind of SMO based gas sensors. A summary of different sensing materials

(MOs) with their operating temperatures are presented in Table 1. 1. From these reports it is quite obvious that lower operating temperature is a real challenge for any SMO based gas sensor. To overcome this issue, various approaches are widely been used such as doping with other metals [54-56], nano-particles decoration [57-58] and nano-composite formation [59-60]. At the same time, there is always a continuous race for searching of new materials with better sensing properties.

Table 1.1: Brief summary of the operating temperatures of MOs based CO sensors.

Material	CO Con.(ppm)	Performance (Response)	Optimum temp.(°C)	Author & Publications
ZnO	250	8	350	H. W. Ryu <i>et. al.</i> Sensors and Actuators B 96 (2003), 717.
	500	10	300	T. Krishnakumar <i>et. al.</i> Sensors and Actuators B 143 (2009)198.
	250	7.2		X. Pan <i>et. al.</i> Sensors 2015, 15, 8919-8930.
CuO	500	3	200	L. Liao <i>et. al.</i> Nanotechnology 20 (2009) 085203.
	Dry and humid	Humid effect performance	150	M. Hubner <i>et. al.</i> Sensors and Actuators B: Chemical 153 (2011), 347.
	100	5.5	175	L. Huo Talanta <i>et. al.</i> 188 (2018) 41 .
TiO ₂	5	84% (Sensitivity)	500	L. L. R. Rao <i>et. al.</i> IEEE Sensors J. 17 (2017) 22.
In ₂ O ₃	50	4	400	K. I. Choi <i>et. al.</i> Sensors Actuators B Chem. 138 (2009) 497.
SnO ₂	100	59% (Sensitivity)	270	C.Y Lee <i>et. al.</i> Sensors 10 (2010) 10701.
Co ₃ O ₄	100	6	130	Z. Wen <i>et. al.</i> Sensors Actuators B Chem. 203 (2014) 873.

In recent years, most of the gas sensing research is primarily focused on how to improve the sensitivity and selectivity issue by exploring new materials search [20-24] as well as modified designing of device fabrications [61-62]. However, much less has been reported on basic understanding of the materials properties and their formation mechanism which can further control the gas sensing mechanism [28-29]. Hence, more emphasize on the growth mechanism of MO nanostructures and their correlation with gas sensing behavior would be great scientific interest.

Another important issue of SMO based gas sensor studies is that most of the SMO nano-material are grown/synthesized using the chemical growth routes such as Sol-Gel technique, Hydro-thermal method, Wet chemical growth, Anodic oxidation etc. However, much less is done using the physical growth routes such as Pulsed laser deposition (PLD) [36], Magnetron sputtering [64-67], Molecular beam epitaxy (MBE)

[68] and Electron beam evaporation [69-70] etc. In general, chemical growth routes result in more variety of nanostructures with relatively higher gas sensitivity. At the same time, they largely suffer from the materials purity as well as thermal instability during the gas sensing operation. Moreover, it also has a disadvantage of poor adhesion to the substrate surface. Therefore, for the fabrication a robust gas sensor with better reproducibility, physical growth route is always preferable over the chemical route. In this aspect, a better understanding of the SMO growth mechanism may significantly help for the nanostructures formation and there sensitivity improvement issue.

1.5 SMO nano-structures based photo-catalyst

In the recent years, hazardous wastes and toxic water pollutant are becoming burning problems for the environmental safety as well for our ecosystem. The major sources of waste waters pollutants are organic dyes used in the food and textile industries. Due to their high toxicity and non-biodegradability, they have potential carcinogenic effects on human's health also [71]. These dyes are generally classified on the basics of their structure, source, color and method of application in color index. Among these variety of dyes, Methylene blue ($C_{16}H_{18}ClN_3S$) is widely used by the various textile industries such as a dye in silk and wool, leather, cotton, jute and paper as well as a food coloring additives [72-73]. Methylene blue (MB) is appear as a solid, odorless and a dark green powder at room temperature and also soluble in water which yields in blue solution. These dyes are stable and incompatible with bases, reducing agents as well as strong oxidizing agents. MB dyes have strong effects on the immune and reproductive systems of human body, if swallowed, inhaled and in contact with skin. A lot of methods such as biological treatment [74-75] adsorption [76] and photo catalysis [77] have been used for removal of these dyes from industrial effluents.

In the past few years, photo-catalysis has also become an important part of environmental research as it is widely used for the degradation of organic and inorganic pollutants in water. In this aspect, titanium oxide (TiO_2) is found to be one of the most promising catalysts for organic pollutants due to its strong oxidizing power, non-toxicity and long-term stability [78]. In addition, ZnO has been used as photo-catalyst to degrade and mineralize organic wastes in water [71]. However, both of the photo catalysts are only effective under UV light because of their wide band gap. The wide bad gap (3.2-3.5

eV), limits its application under the sunlight (visible light) as only 5% of solar spectrum lies in the ultra violet (UV) range. Therefore, it is consequently required to have highly efficient photo catalyst under the illumination of visible light to improve the absorption efficiency for the dye decomposition process. In this aspect, copper oxide (Cu_2O) is become one of the most promising photo-catalysts that is used in the visible light range. Cu_2O has a direct band gap (2.1 -2.5 eV) and a high optical absorption coefficient, which make it a promising candidate for the applications in various areas such as photo catalysis [79-80], general, the photo catalytic efficiency is limited due to slow interfacial electron transfer process. In this aspect, cuprous oxide (Cu_2O) would be a potential candidate as it has a direct optical band gap in the visible light regime. Recently, Cu_2O nano-particles exhibited excellent catalytic behaviour under visible light, which has already been used for water splitting (decompose the water into H_2 and O_2 molecules) [81]. Furthermore, Cu_2O performs as an excellent visible light active photo-catalyst for the destruction of dye pollutants with a high degree of mineralization [82].

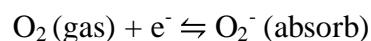
1.6 Gas sensing mechanism

The fundamental mechanism of gas sensing for SMO based nanostructures mainly depend the reaction between the surface atoms of SMO and target gas molecules (reducing or oxidizing gases). Typically, a gas sensor possesses three fundamental process of interaction between the sensor surface atoms and gas molecules, which can be divided in three types such as physical adsorption (physic-sorption), chemical adsorption (chemi-sorption) and non-reversible reactions (new compounds formation through chemical reaction, which is not expectable for any gas sensor). It is also important to understand that the gas sensing mechanism is not only depends upon the reactions between surface and target gas but also depends upon the ambient condition such as humidity level in the atmosphere as well as the sensors operating temperature. In case of dry air ambient oxygen molecules play the crucial role in the dry atmosphere and the ratio of active sites of O_2 molecules decide the adsorption mechanism. However, humidity can severely affect the sensing response of metal oxides and in most of cases high level of humidity in the atmosphere is greatly delays the sensor response [83-85]. Humidity effect can be described in terms of wet atmosphere where water molecules act as a major adsorption sites. In this thesis work, all gas sensing studies were performed

under dry air condition to remove the effect of the humidity. Hence, our main concern is based on dry atmosphere towards the adsorbed oxygen (O_2) molecules.

In dry atmosphere (less than 20% humidity level) oxygen molecules mostly decides the adsorption mechanism of any target gas. Apart from oxygen (O_2), nitrogen gas (N_2) may also have effect on interaction between the surface atoms and target gas molecules as it is one of the most abundant gases in atmosphere. However, N_2 is non-reactive to other gas molecules as well as SMO surface atoms and hence have very week interference on the adsorption process. Therefore, N_2 is generally used as a carrier gas to study the chemical kinetics of the interaction between a target gas and the metal oxide surface atoms [86]. Oxygen (O_2) plays a major role in the mechanism of surface gas interaction as it is having high electro-negativity (around 3.65) and lone pair of electrons. Diatomic oxygen is non-reactive in the gas phase, but when it interacts with the surface atom of SMO, it gets ionized [87] and forms a negatively charged ionic layer on the surface. This helps in sorption of other gas molecules on the surface of SMO.

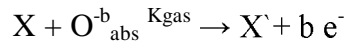
It is now accepted that chemisorbed oxygen molecules strongly influence the adsorption process in dry atmospheric condition [69]. In this process of chemi-sorption, oxygen molecules may have three different forms of ions such as O_2^- , O^- and O^{2-} , depending on the operating temperature range (100°C to 500°C). These oxygen ions are having different adsorption and desorption kinetics for the target gas molecules. Thus, the gas sensing mechanism of any metal oxide gas sensor under a dry ambient condition principally depends upon both the concentration of oxygen molecules as well the operating temperature. Initially, the rate of adsorption and desorption can be enhanced by increasing the operating temperature up to a certain temperature value and afterwards desorption process starts to dominate over the adsorption. *Barsan and Weimer* [88] and *Yamazoe et al.* [89] reported that at higher temperatures, oxygen molecules turn to oxygen ions of O^{2-} and O^- forms on the SMO surface whereas at lower operating temperature the adsorbed oxygen ion is in O_2^- form. In all cases, oxygen molecules trap the free surface electron from the conduction band of SMO to form the ions. For a relatively lower operating temperature of 100°C - 200°C , following reaction pathway is observed:



While, at higher operating temperature above 200°C, the oxygen molecules are dissociated into oxygen ions such as O^- and O^{2-} , by attracting another electron from the conduction band as shown here:



Here, K_{Oxy} is the reaction rater constant. These oxygen ions on the surface of SMO are extremely reactive to the target gas molecules. In contact with the target gas molecules they leave the SMO surface and transfer the trapped electrons back to the conduction band. The general reaction between gas molecule and oxygen ions is shown as:



Where, X, X' and b is target gas, out gas and number of electron respectively [88-89].

According to this reaction pathway, the carrier concentration of the SMO surface will alter upon absorption of the O_2 molecule, which consequently changes the surface electrical conductivity of gas sensor material. However, the change in surface resistance depends on both: (i) the type of SMO (p-type or n-type) as well as (ii) the type of target gas (oxidizing or reducing). SMO based resistive mode gas sensors are mainly classified into two broad categories, *n*-type (ZnO, SnO₂, WO₃ etc) and *p*-type (CuO_x and NiO etc) based on their majority charge carriers. However, the resistance for both type of metal oxides decreases when the temperature is increases, due to their semiconducting properties. The basic mechanism behind the gas sensing performance of both types of SMO based sensors are discussed below.

Schematic representations of the gas sensing mechanism for both p-type and n-type semiconductors for a reducing gas are depicted in Figure 1.3. In general, reducing gases act as electron donors when interact with oxygen pre-absorbed metal oxide surface. During the interaction, reducing gases remove the trapped surface electrons from the chemisorbed (oxygen ions) and physisorbed (hydroxyl ions) ions back to the metal oxide surface. This release of electron to SMO surface resultantly alters the surface electrical conductivity which is recorded as response of the sensor materials.

P-type materials: The majority carriers are holes in p-type materials. Under oxygen ambient, p-type MOS generates more effective holes by adsorption of oxygen molecules. These oxygen molecules turn to ions by capturing the surface free electrons which come either from minority carriers or dissociation of electro-hole pairs. This effect leads to the

formation of hole accumulation layer near the surface. As a result, the number of majority charge carrier (hole) effectively increases, which finally decreases the sensor resistance. However, during exposure of a reducing gas, the trapped surface free electrons are released back to surface and the effective hole concentration is again reduced due to electron-hole pair formation. Hence, the surface resistance of the sensor material increases upon exposure of any reducing gas. Figure 1.3(a) summarizes the various steps of the sensing mechanism of p-type semiconductor for a reducing gas. A completely reverse mechanism is also expected for an oxidizing gas exposure on a p-type sensor surface.

N-type metal oxide gas sensor: The majority carriers are electrons in n-type MOSs. In presence of oxygen ambient, the surface free electrons are trapped by the adsorbed oxygen molecules which then form the oxygen ions. This causes the formation of an electron depletion layer near the surface. The decrease in carrier concentration results in an increase of the surface resistance. During reducing gas exposure the trapped surface free electrons are released back to surface which effectively increase the majority carrier (free electron) concentration. As a result, the surface resistance of the sensor material decreases upon exposure of any reducing gas. Figure 1.3(b) summarizes the various steps of the sensing mechanism of n-type semiconductor for a reducing gas.

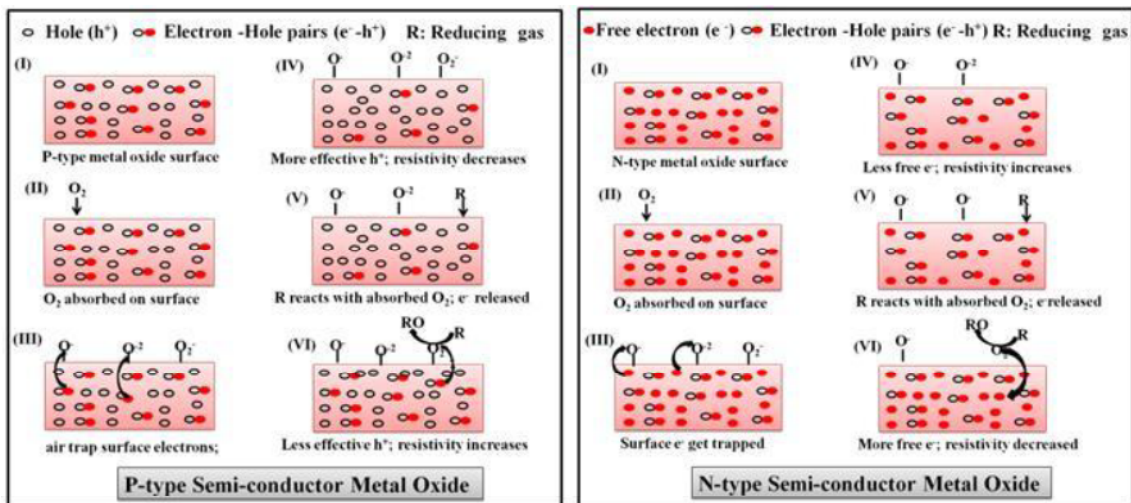


Figure 1.3: Schematic representations of gas sensing mechanism for reducing gas: (a) p-type semiconductor and (b) n-type semiconductor.

1.6.1 Basic characteristics of gas sensor

The surface redox chemistry of sensing material, during its exposure to any gas or vapour molecules, plays a very crucial role on the gas sensing mechanism. The electrical resistance of the sensor material drastically changes in presence of target gas molecules, which mainly depends on the material type (n-type or p-type) of the sensor and analyzing gas properties (reducing or oxidizing). A schematic response curve of the time dependent resistance variation during exposure and withdrawal of target gas (CO, a reducing gas) is shown in Figure 1.4. The response curve of any gas sensor is characterized by many parameters, which are briefly mentioned here.

Sensitivity: The sensitivity is defined as the ratio of the resistance of the sensors in the target gas to that in air. The sensitivity is highly dependent on surface morphology, thickness of film, operating temperature, crystallite size as well as electronic properties..

Selectivity: This characteristic is related to the discrimination capacity of a sensor towards a mixture of gases. Selectivity plays a major role in gas identification. Generally, a ‘fingerprinting’ method relies on its uniqueness.

Stability: It is a characteristic that takes into account the repeatability of device measurements after a long use. The success of the sensor will be limited if the sensor performance is not demonstrated as repeatable and stable over long-term testing. To avoid the effects of non-repeatability after repeated use, the sensor materials are submitted to a thermal pre-treatment, which would decrease posterior material instabilities.

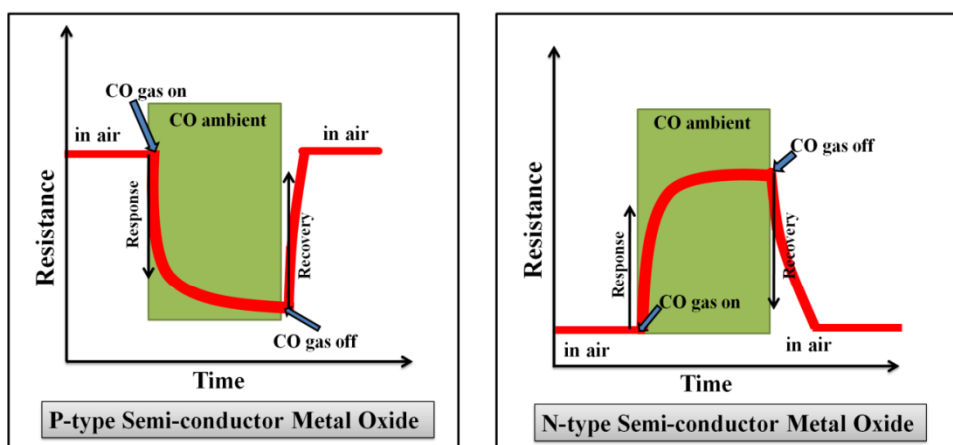


Figure 1.4: Schematic representation of response curve of (a) p-type and (b) n-type material for CO gas

Response Time: The response time is the time interval over which resistance attains a fixed percentage (typically 90%) of the final value when the sensor is exposed to full scale concentration of the gas. Time response is especially dependent on the sensor characteristics such as crystallite size, additives, electrode geometry, electrode position, diffusion rates. A small value of response time is indicating of a good sensor.

Recovery Time: This is the time interval over which the sensor resistance changes back to 10% of the initial value when the sensor is withdrawn from the exposure of target gas molecules and placed in a clean air ambient. A good sensor should have a small recovery time so that sensor can be used again.

1.7 Photo-Catalytic Dye Degradation Process

Photo-catalytic degradation is a promising method for the handling of wastewater, containing organic and inorganic pollutants. Photo-catalysis process is mainly depending on the catalytic ability of the nano-materials in presence of visible light to create electron-hole pairs. Under the illumination of light (photon), photo-catalyst materials produce electron-hole pairs which further results in generation of hydroxyl ions/radicals (OH) from water. These active radicals are capable of mineralizing most of the organic molecules in to very simple non-toxic elements such as carbon dioxide (CO₂) and water (H₂O) [90]. In case of water splitting applications, the majority charge carriers such as holes for copper oxides oxidize water to oxygen gas (O₂), while the photo-generated minority charge carriers (electrons) reduce water to hydrogen gas (H₂) [14]. The morphological texture such as high surface area as well as grain size of the SMO based nanostructures also strongly affects the photo-catalysis behavior of the nano-materials [77].

A schematic representation of MB dye degradation using Cu₂O thin film under the visible light illumination is depicted in Figure 1.5. The visible light itself cannot degrade the dye solution as shown in Figure 1.5(a). Similarly, Cu₂O film being a catalyst is not able to degrade the dye in absence of visible light photon Figure 1.5(b). For successful degradation of MB dye, both the catalytic Cu₂O film and visible light exposure are essential as shown in Figure 1.5(c).

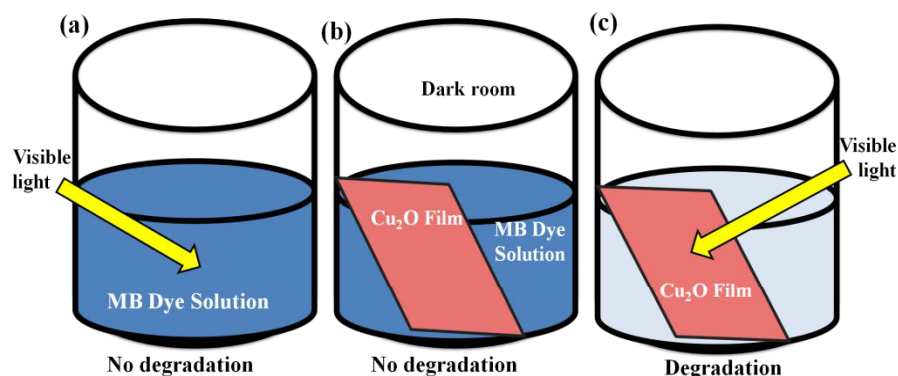


Figure 1.5: Schematic representation of photo-catalytic dye degradation process.

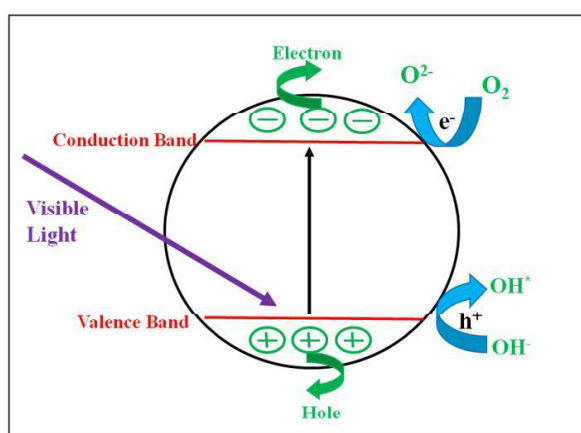


Figure 1.6: Schematic Representation for photo-generation of electron – hole pairs for Cu_2O , (b) MB dye photo-degradation under visible light.

Under a visible light illumination, the adsorbed dye molecules inject holes into the valence band (VB) of the semiconductor. Similarly, in the anodic processes the adsorbed dye molecule injects an electron into the conduction band (CB) of a semiconductor. The schematic representation of the charge transfer process is shown in Figure 1.6. In this dye degradation process, the semiconducting Cu_2O thin film deposited on glass substrate is dipped into the MB dye solution in the dark (absence of any visible light). The dye molecules are adsorbed on the surface of Cu_2O film and form a continuous layer. This Cu_2O thin film adsorbs the visible light and which excites the electrons within the adsorbed dye molecules. These excited electrons of dye molecules are then directly moved into the conduction band (CB) of the semiconductor (Cu_2O). This method is known as dye degradation process where dye molecules are chemically adsorbed on to the surface of photo-catalyst. The efficiency

and the rate of degradation are significantly influenced by the pH of the solution. The pH value of the solution can influence the surface charge density and thus the adsorption behavior of the impurity on to the surface. In addition, the type of catalyst as well as the type of semiconductor can also play an effective role on the degradation process.

1.8 Outline of the work

From all the above discussed information, it is quite clear that both the copper oxides (CuO_x) and zinc oxide (ZnO) materials are of high technological importance. Therefore, better understandings of their growth mechanism as well as its influences on various properties are highly desirable. Within this thesis, carbon monoxide sensing behaviour of SMO based nanostructures using both p-type copper oxides (CuO) and n-type zinc oxides (ZnO) are characterized, with a special focus on their growth mechanism, various analytical properties and their correlations with the gas sensing properties. Mostly, physical growth route is employed to form the SMO based nano-materials. SMO nano-structure based gas sensing mechanism is overall a complicated surface controlled process where grain size, lattice defects and surface adsorption/desorption kinetics can play significant roles for the gas response. Hence, a controlled formation of SMO nano-structures required more attention to systemically achieve a high surface to volume ratio as well as desired electronic properties to improve the overall sensitivity of any sensor material towards a lower operating temperature. In addition, photo-catalytic activity of copper oxide (Cu_2O and CuO) thin films towards the successful degradation of *Methylene blue* dye is also exploited. The catalytic activity of both type of copper oxides are compared where Cu_2O film appears to be superior over the CuO film. Finally, a growth mechanism of mixed oxides (CuO,ZnO) phase with possible doping and nano-composite formation is also discussed which is expected to significantly improve the gas sensing as well as catalytic properties of these SMO based nanostructures.

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