UV-LED Photo-Activated Metal Oxide Semiconductors for Gas Sensing Application:

Fabrication and Performance Evaluation

by

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Abstract

The idea of functionalizing chemical gas sensors at room temperature as well as making them smaller and more efficient has initiated important progresses in the last few years among scientists worldwide. Ultraviolet Light Emitting Diode (UV-LED) technology has shown its capability to fulfill the gap between laboratorial and industrial production of room temperature gas sensors.

In this research, a review on the performances, preparation techniques, and most influential factors of several photo-activated metal oxide semiconductor gas sensors under UV-LED irradiation was conducted. Further, a comparative study on the development of sensitive gas sensors using ZnO and In$_2$O$_3$ semiconductors for NO$_2$ gas detection was performed. The results indicated that the sensitivity of In$_2$O$_3$ to NO$_2$ is approximately two times greater than that of ZnO for all the experimented irradiances. The highest sensitivities with complete recovery for the ZnO and In$_2$O$_3$ based sensors were obtained at 1.2 mW/cm$^2$ and 2.8 mW/cm$^2$ irradiances, respectively. In general, the In$_2$O$_3$ sensors required a higher UV irradiance compared to ZnO sensors, to prevent permanent adsorption of target gas molecules on the surface.

To further increase the sensitivity and reduce the response time, n-type semiconductor oxides of ZnO and In$_2$O$_3$ were coupled using co-precipitation method, to obtain nano-crystalline composite sensing materials. The composition, structure and optical properties of the prepared samples were characterized by EDS, XRD, SEM, XPS and UV-Vis analyses. The composite materials showed higher sensitivity towards NO$_2$ with a 200s decrease in response time compared to pristine samples. A favorable composition ratio of [In]:[Zn] was determined to be 1:2 for the nano-composite particles, with 2.21 sensitivity as the highest sensing performance to 5 ppm NO$_2$. The high sensitivity of this combination is attributed to the morphology and composite porous structure, as well as lower band-gap of the target composite. The irradiance of 1.7 mW/cm$^2$
provided the highest sensitivity, short response time and a complete recovery for the ZnO/In$_2$O$_3$ composite structures, within the experimented range. It’s believed that, ZnO favors the flow of charge carriers and increases the surface area, while In$_2$O$_3$ acts as active light absorption centers and enhances chemisorption ability in the composite.
Preface

This dissertation is original and unpublished and is co-authored with my research supervisor, Dr. Fariborz Taghipour. All of the work presented henceforth was conducted in the Photoreaction Laboratory in the Chemical and Biological Engineering Department, University of British Columbia, Vancouver campus. All hardware and software used in this research were designed, manufactured and programmed by the Author.

E. Espid was the contributor of preparation, characterization and analyzing the samples and writing of the manuscripts. Dr. Fariborz Taghipour largely contributed to the development of experimental plans, the discussion of the results, and the revision of the manuscript drafts.

By the time of submitting this thesis, two research papers have been presented in conferences:


The authors have also prepared several research reports related to chapter 2, chapter 3 and chapter 4 to be published at international scientific journals:


- Ehsan Espid, Fariborz Taghipour, “A comparative study on thin film ZnO and In2O3 properties in photo-activated gas sensing application”, expected to be submitted on Oct. 2015.

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<table>
<thead>
<tr>
<th>Acronym</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>BAW</td>
<td>bulk acoustic wave sensors</td>
</tr>
<tr>
<td>BET</td>
<td>Brunauer-Emmett-Teller</td>
</tr>
<tr>
<td>CVD</td>
<td>chemical vapor deposition</td>
</tr>
<tr>
<td>CB</td>
<td>conduction band</td>
</tr>
<tr>
<td>$E_g$</td>
<td>band-gap energy</td>
</tr>
<tr>
<td>eV</td>
<td>electron volt</td>
</tr>
<tr>
<td>EBPVD</td>
<td>e-Beam Physical Vapour Deposition</td>
</tr>
<tr>
<td>EDX</td>
<td>energy-dispersive X-ray spectroscopy</td>
</tr>
<tr>
<td>EPR</td>
<td>electron paramagnetic resonance</td>
</tr>
<tr>
<td>FE-SEM</td>
<td>field emission scanning electron microscope</td>
</tr>
<tr>
<td>FTIR</td>
<td>Fourier transform infrared spectroscopy</td>
</tr>
<tr>
<td>FWHM</td>
<td>full width at half maximum</td>
</tr>
<tr>
<td>GC</td>
<td>gas chromatography</td>
</tr>
<tr>
<td>LED</td>
<td>light emitting diode</td>
</tr>
<tr>
<td>LPG</td>
<td>liquefied petroleum gas</td>
</tr>
<tr>
<td>MOS</td>
<td>metal oxide semiconductor</td>
</tr>
<tr>
<td>PCB</td>
<td>printed circuit board</td>
</tr>
<tr>
<td>PECVD</td>
<td>plasma-Enhanced chemical vapor deposition</td>
</tr>
<tr>
<td>ppm</td>
<td>part per million</td>
</tr>
<tr>
<td>ppb</td>
<td>part per billion</td>
</tr>
<tr>
<td>RH</td>
<td>relative humidity</td>
</tr>
<tr>
<td>RGTO</td>
<td>rheotaxial Growth and Thermal Oxidation</td>
</tr>
<tr>
<td>SAM</td>
<td>self-assembled monolayer</td>
</tr>
<tr>
<td>SAW</td>
<td>surface acoustic wave sensors</td>
</tr>
<tr>
<td>SEM</td>
<td>scanning electron microscope</td>
</tr>
<tr>
<td>SWCNT</td>
<td>Single-walled carbon nanotubes</td>
</tr>
<tr>
<td>Acronym</td>
<td>Description</td>
</tr>
<tr>
<td>---------</td>
<td>--------------------------------------</td>
</tr>
<tr>
<td>TEC</td>
<td>thermos-electric cooler</td>
</tr>
<tr>
<td>TLV</td>
<td>threshold limit value</td>
</tr>
<tr>
<td>TPD</td>
<td>temperature Programmed Desorption</td>
</tr>
<tr>
<td>UV</td>
<td>ultraviolet</td>
</tr>
<tr>
<td>VB</td>
<td>valence band</td>
</tr>
<tr>
<td>VIS</td>
<td>visible</td>
</tr>
<tr>
<td>VOC</td>
<td>Volatile organic compound</td>
</tr>
<tr>
<td>XPS</td>
<td>X-ray photoelectron spectroscopy</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray diffraction</td>
</tr>
</tbody>
</table>
Glossary

- **Detection Limit**: The lowest concentration of the analyte that can be detected at any given condition.

- **Dynamic Range**: Total range changeable parameter in the sensor from the smallest possible values to largest quantity.

- **Light Intensity**: The quantity of light that is emitted in unit time per unit solid angle.

- **Light Irradiance**: The rate of light actually striking the surface of objects per unit area. It depends upon the intensity and distance of the light source.

- **Response Time**: The time that it takes for sensor to respond to ambient gas from 10% to 90% of its maximum value.

- **Recovery Time**: The time that it takes for the sensor signal to return from 90% to 10% of its maximum value.

- **Resolution**: The smallest change in concentration that can be distinguished by sensor.

- **Sensitivity**: The change in output resistance signal per measured resistance in pure air.

  **Selectivity**: The ability of the sensor to discriminate between various components of a gas mixture and provide signal for the component of interest.

- **Sensing Range**: The specified range which sensor is designed to work over.

- **Stability**: Describes the reproducibility of the sensor measurements for a certain period of time. This includes retaining the sensitivity, selectivity, response, and recovery time.

- **Working Temperature/irradiance**: The temperature/irradiance at which the sensor can operate in fully efficient mode.
Acknowledgements

First and foremost, I would like to express my deep gratitude to my supervisor, Dr. Fariborz Taghipour who has supported me to work in this field and appreciate his highly valued advices and constructive questions during the project. He kindly monitored my progress continuously, discussed my results and supported me with precise suggestions. I also greatly thank him for giving me the freedom to explore my ideas and define my own lines of research inquiry to become a mature researcher.

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Their sacrifices enabled me to have the privilege of a good upbringing, education, and opportunity to pursue my dreams. They owed more of the credit for the work presented than anyone else. I owe them a debt of gratitude that words cannot even begin to describe.

This work is dedicated to my family and to my dear uncle who left his academic careers and prestigious positions and was martyred in July 15, 1982 for his faith on choosing the right way in defense of his honor and country, in Iran-Iraq war. He has always been my role model and I have always looked up to find his philosophy and his approach towards life. He defined to me the pleasure of being sacrificed in the love of God, fading in faith and sinking into the world of meaning. He went to protect me and to serve me the opportunity to have a good education. His sincerity for the sake of God is greatly appreciated.
To my family:

All I have

&

To my beloved uncle:

Shahid GholamAli Espid
Chapter 1: Introduction

A gas sensor is a device that identifies the gases in its environment through conversion of a physical/chemical change into an electrical (visible or audible) signal. Gas sensors are produced to help people monitor and adjust their surrounding environments. More than 5 decades ago, it was revealed that the electrical conductivity of a metal oxide is dependent on its surrounding gas contents [1].

In 1962, Taguchi [2] built the first generation of metal oxide semiconductor (MOS) gas sensors based on thick films of SnO$_2$ and employed them in explosive gases (such as Methane and LPG) warning devices. This invention was very important for Japanese cities with densely built-up wooden houses, equipped with gas furnaces.

During the last decade, gas sensing technology has been significantly developed due to its major role in human’s life. In addition to control the outdoor harmful gases and monitor indoor air contents, gas sensors can be utilized in many other applications such as breath analysis and diagnosing, food quality control in food industry and storage, leakage detection in industrial plants and explosive vapors detection in security sites. Developed sensors should have several important criteria such as good performance, high stability, low power consumption, as well as low cost and small size in order to be integrated into arising microelectronic technology.

In this chapter, after a brief review on the importance of the research on gas sensing technology, the fundamental concepts of any gas sensor platform are presented.

1.1 Hazardous Gases

Increasing amounts of atmospheric pollutants, specifically in urban and industrial areas has been a major concern for human society. According to the health Canada Organization, there are three types of hazard classes, “physical hazard classes, which represent hazards relating to physical and chemical
properties, such as flammability; health hazard classes, which represent hazards to health arising from exposure to a substance and, environmental hazard classes which address environmentally harmful effects” (Health Canada, 2015).

From the chemical point of view, hazardous materials in the atmosphere include toxic gases such as H₂S, CO and NH₃, greenhouse gases such as CH₄ and CO₂ and some special gases such as NO₂ and NO which are both toxic and greenhouse gases. Hazardous gases can come from both natural and human sources. Natural sources include smoke from forest fires, volcanoes, bacteria and chemicals released by plants and animals, or pollutants attributed to the sources made by humans.

Among the released atmospheric pollutant gases, Nitrogen Dioxide which is produced greatly through chemical combustion plants and automobiles, significantly contributes to the human and environmental problems.

1.1.1 Nitrogen Dioxide (NO₂)

Nitrogen Dioxide which is a reddish-brown gas with low solubility in water is part of a highly reactive family known as “Oxides of Nitrogen” that includes a number of gases that are composed of oxygen and nitrogen.

Fuel combustion for energy production, home and industrial use, accounts for approximately 94% of the emissions of nitrogen oxides produced by human activities in Canada (Health Canada, 2015). In addition to its contribution to the formation of ground level ozone, it can cause severe damage to the respiratory system such as respiratory infection through lowering its resistance, and irritate and impair lung function. It can turn into nitric acid or nitrous acid which are the main components of acid rain.

Exposure to NO₂ from outdoor sources strongly depends on the proximity to source in space and time, given that mobile sources are the main contributors to ambient NO₂. Therefore, NO₂ levels vary
considerably between homes, due to differences in exterior and interior sources. However, for indoor environments, these emissions may become significant if the appliances are not vented or poorly vented.

The threshold limit value (TLV) is considered as the maximum concentration of a chemical allowed for long period of time of exposure without making health problems. The TLV of NOx compounds is 3 ppm and it could be harmful to human respiratory systems at concentrations above that. Taken from Health Canada Organization, the standard exposure limit for residential places considering risk management purposes are shown in table 1.1.

Table 1-1: Residential maximum exposure limit for NO2 (Health Canada, 2015)

<table>
<thead>
<tr>
<th>Exposure period</th>
<th>Concentration</th>
<th>Critical Effects</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>µg/m³/ppb</td>
<td></td>
</tr>
<tr>
<td>Short-term</td>
<td>170/90</td>
<td>Decreased lung function and increased airway responsiveness in asthmatics</td>
</tr>
<tr>
<td>Long-term</td>
<td>20/11</td>
<td>Higher frequency of days with respiratory symptoms and/or medication use in asthmatic children</td>
</tr>
</tbody>
</table>

Exposure to 50 ppm NO2 can cause pulmonary edema and it is fatal if being inhaled at concentrations above 100 ppm. Recently, epidemiological scientists have presented a correlation between the development of chronic lung disease and respiratory symptoms with long-term exposure to NO2. Although the effects of short-term exposure are still unclear, but long term exposure to concentrations that are higher than those normally found in the ambient may cause increased incidence of acute respiratory illness in children.

NO2 continuous monitoring may provide better indices of exposure over time. Gas sensing technology could be a useful protocol to invest on, in order to prevent unwanted, unpredicted disease both for human and environment.
1.2 Overview of Gas Sensors Technologies

The need for reliable sensor devices accompanied by the rapid development of information technology have initiated a large amount of both empirical and theoretical research worldwide to resolve drawbacks associated with every kind of gas sensors, and to improve the well-known “3S” parameters: sensitivity, selectivity, and stability. Depending on the sensing mechanism, gas sensors are classified into several categories. Optical sensors, piezoelectric sensors, electrochemical sensors and solid state resistive gas sensors are four of the commonly utilized classes. Every sensor has its own advantages and disadvantages, so depending on the sort of facility and conditions, one of the gas detection systems must be selected. In order to realize the difference in terms of mechanism and applicability, some of commercially manufactured gas sensors are briefly described.

1.2.1 Piezoelectric Gas Sensors

Piezoelectric sensors are divided into two categories, the surface acoustic wave sensors (SAW) and the bulk acoustic wave sensors (BAW). The sensing mechanism in SAW devices is based on producing a surface wave that is transferred along the surface while the mechanism in BAW sensors attributes to the waves that travel through the bulk of the sensor [4].

Generally, A change in the mass of the sensitive membrane due to the gas absorption caused by the interaction with target gas, results in a change in the resonant frequency of the produced wave that propagates along the surface or the bulk; this change in resonant frequency is therefore used for the gas detection [4,5]. Piezoelectric sensors can be used for a wide range of applications, for all types of gases at all ranges. However, they are very expensive and complex, which makes the maintenance requirements more difficult.
1.2.2 Optical Gas Sensors

Optical gas sensors are working based on the fact that each gas absorbs a very specific characteristic wavelength of the spectrum. Optical gas sensors offer fast responses (time constants below 1 s are possible), minimal drift and high gas selectivity, with zero cross response to other gases as long as their design is carefully considered [6]. They are typically used where a very high accuracy and selectivity is required, but this high level of precision meant they are somewhat expensive.

1.2.3 Electrochemical Gas Sensors

In an electrochemical gas sensor, target gas is oxidized or reduced on electrode, producing a specific current/potential through the cell, the concentration of the gas is determined by measuring the resulting current/potential. Since they have extremely low power consumption they can be used in portable instruments. However, they suffer from poor selectivity due to cross-responses emanate from close current/potential supplied in electrochemical reactions. Noble metals such as platinum or gold are normally chosen as the sensing electrode to catalyze the electrode reactions which apparently raises the cost [7].

1.2.4 Chemical Resistive Gas Sensors

Chemical resistive gas sensors are sensitive and effective gas sensors that are able to be used for detecting a broad range of gases including toxic and combustible vapors. There are wide variety of advantages for these gas sensors including simplicity, fast response and being very inexpensive. However, they have some issues in selectivity and stability. Solid-state chemical gas sensors are typically made of semiconductor metal oxides as the sensing material to detect pollutant gases. The detection principle of resistive sensors is based on the interaction of the surrounding gas to be detected with the
sensing layer, resulting in a change of the resistance of the thin film layer due to the change in the flow of electrons involved in the reactions. In conventional MOS sensors the sensing material is held in temperatures between 300 °C and 500 °C where main reactions proceed at sufficient rates. However new classes of MOS sensors are emerging that are able to operate at room temperature with good performance. More details will be presented in the next chapters.

1.3 Semiconductors

Semiconductor refers to a substance with electrical conductivity between metals and insulators at room temperature. They are more conductive at higher temperatures and will act as insulators at absolute zero. These behaviors are attributed to the electronic structure of semiconductors and the position of valence and conduction bands. Valence band (E_v) is the highest occupied band level by electrons while the conduction band (E_c) is the lowest unoccupied band level and the energy difference from the top of the valence band to the bottom of the conduction band is defined as the band-gap.

Contrary to metals, semiconductor conduction bands are sufficiently far from the valence band to prevent any significant population of excited electrons, and conduction orbital levels do not overlap each other; at the same time, the band gap is smaller than that of an insulator so electrons can possibly cross the band gap.

If a semiconductor receives a very small amount of energy from external sources, the electrons ascend to higher levels. When the electrons excite from the valence level to conduction level, a hole is created in the valence band. Holes and excited electrons are attributed to the electrical conductivity of the semiconductor.

Intrinsic semiconductor refers to those semiconductors that the electrical conductivity increases by providing external energy source. Generally, since a few of electrons in intrinsic semiconductors are able
to jump from the valence band and many of them cannot pass the whole band-gap, they don’t show much conductivity at all. However, the properties of semiconductors can be greatly changed by adding impurities into their crystal lattice which is called doping. Doped semiconductors are known as extrinsic semiconductors. If the impurity is an electron donor, then the electrons are the majority carriers and holes are the minority carriers, this improves the conductivity of the semiconductor that is known as an N-type semiconductor. If the added impurity is an electron acceptor, it can produce some holes somewhere closer to valence band, thus the holes are the majority carriers and electrons are the minority carriers in these materials that are known as the P-type semiconductors. By adding any impurity to the pure semiconductor, the electrical conductivity may vary by factors of thousands or millions.

Fermi level is considered to be a hypothetical energy level that has 50% probability of being occupied at any given time by electrons. In N-type semiconductors the Fermi level increases and lies closer to the conduction band while a reciprocal approach happens in P-type semiconductors meaning that the Fermi level decreases and sits somewhere closer to the valence band. For intrinsic semiconductors, Fermi level is at the middle of band-gap which means that there is an equal probability of finding an electron at the conduction band as there is of finding a hole at the valence band. In fact, Fermi level addresses the amount of surface potential needed to change the electrical properties of the material. The surface potential is measured based on the energy required to excite electron from Fermi level to vacuum.

Figure 1-1: Band levels for Intrinsic (A), N-type (B) and P-type (C) semiconductor
Figure 1-1 depicts a schematic illustration of the valence band, conduction band and fermi level of different semiconductor materials. Gas sensors are typically using N-type semiconductors such as ZnO, SnO₂, TiO₂, WO₃, Fe₂O₃ or In₂O₃ to detect various types of oxidizing and reducing gases.

1.4 The Sensing Mechanism of MOS Gas Sensors

The fundamental mechanism of any chemi-resistive gas sensor is based on the reaction of the generated electrons/holes with the ambient oxygen or surrounding gas. Electron hole pairs are generated through either thermal activation or photo-activation.

1.4.1 Oxygen Chemisorption

Adsorption of oxygen molecules on the surface of metal oxides is accompanied by an electron extraction from the conduction band, forming negative sites on the surface and positive holes in the conduction band. These stable displacements of negative/positive charges produce an electric field making a barrier for remaining electrons to excite, and leading to formation of an electron-depleted region. This formed potential barrier is usually between 0.5 to 1 eV [8]. The negative charges that are trapped in the adsorbed oxygen species can cause an upward band bending in the semiconductor structure resulting in reduced conductivity [9]. At lower temperatures, oxygen is adsorbed molecularly but as the temperature increases, it tends to be adsorbed in the form of O²⁻ and O⁻ atoms [10,11]. Figure 1-2 shows the electrical changes in conduction band incurred by oxygen adsorption process.

It should be noted that the mechanism in Figure 1-2 is only suitable for n-type semiconductors in which depletion regions are smaller than grain size [9]. Due to the high reactivity of the adsorbed oxygen ions, the most influential factor in any metal oxide resistive gas sensor is the interaction between oxygen and surface of sensing layer.
1.4.2 Target Gas Reaction

After adsorbing oxygen in the form of $\text{O}_2^-$ or $\text{O}^-$ ions, created depletion region would cause to increase the film resistance. In the presence of a reducing gas, adsorbed oxygen ions react with the gas molecules. Removing oxygen ions by their reaction with the surrounding gas or replacement of the adsorbed oxygen by other molecules can reverse the band bending, resulting in an increased conductivity [9]. However, oxidizing gases typically participate in the reactions that involve both electrons (or produce holes) and adsorbed oxygen ions, cause to enhance the film resistance.

1.5 Influencing Factors on MOS Gas Sensor Response

Sensing performance of any metal oxide resistive gas sensor is attributed to three major independent parts of the sensor platform: receptor function, transducer function and utility factor (Figure 1-3 and Figure 1-4) [12]. Receptor function refers to the ability of the solid surface to interact with target gas. Oxygen adsorption, water vapor adsorption and acid or basic properties of the surface greatly influence the receptor function. The main duty of transducer function in a sensor device belongs to the conversion of the signal produced by chemical interaction of the oxide surface into electrical signal. The utility factor
shows the accessibility of inner oxide grains to the target gas. If the rate of the reaction is much greater than the rate of the diffusion, then the gas molecules cannot diffuse to the inner grains and cannot utilize them, so the sensor efficiency would be lower [12].

Figure 1-3 : Receptor function, transducer function and utility factor[12]

Figure 1-4: Schematic diagram of the receptor, transducer and the utility functions of a semiconducting metal-oxide layer [13].
The sensing performance is directly related to the physical/chemical changes occur either on the surface or in the bulk of sensing layer. Controlling parameters are summarized in Figure 1-5.

![Diagram showing controlling parameters for MOS sensors](image)

Figure 1-5: Controlling parameters for the performance of MOS gas sensors (adopted from [14])

Indeed, reactivity, diffusivity or to be more accurate, difference in diffusivity between target gas and oxygen in sensing layer plays a significant role in determining the overall sensitivity of the sensor. For instance, Shimizu et al. [15] have investigated the effects of gas diffusivity and reactivity for SnO$_2$ for several kinds of target gases.

Structural properties of the prepared materials also greatly affect the sensing mechanism. Major influential parameters both structural and operational are listed in Figure 1-6 and demonstrated in next several sub-sections.
1.5.1 Oxygen and Water Vapor Adsorption

To proceed sensing reactions, oxygen should be ionosorbed either molecularly or atomic in the form of $O_2^-$, $O^-$ or $O^{2-}$ on the surface. The desorption of oxygen ions or their reaction with the surrounding gas will result in a decrease in film resistance. However, the reaction mechanism is different for any specific oxidizing or reducing gas. Figure 1-7 shows various states of adsorbed oxygen at different temperatures on the metal oxide surface.
There is also a possibility for other gaseous species in the environment that do not interfere in the surface reactions, to affect the electric resistance of the layer. The dissociative adsorption of water vapor and its effects on the performance of gas sensors is an example of such interferences. This phenomenon necessitates the interaction between water molecules and sensor surface. FTIR\textsuperscript{1} and TPD\textsuperscript{2} techniques are used to observe the adsorption states of water molecules on the surface. The observations show that the interaction of water-surface is strongly dependent on the operating temperature. Water molecules can be adsorbed through physisorption (hydrogen bonding) or chemisorption (creating hydroxyl groups) process\textsuperscript{10}.

\textsuperscript{1} Fourier transform infrared spectroscopy  
\textsuperscript{2} Temperature Programmed Desorption  
\textsuperscript{3} Electron paramagnetic resonance
The exact mechanism of water surface adsorption is still unclear but electrical measurements show that the surface conductivity is reversibly increased in the presence of water vapor, confirming the fact that hydroxyl groups are present on the surface, since water molecules cannot solely increase the conductivity [16]. Figure 1-8 shows the possible formations of adsorbed water species at different temperatures on SnO\(_2\) surface. At lower temperatures, water is physically adsorbed while at temperatures above 400 °C hydroxyl groups dominate on the surface.

![Diagram showing adsorbed water formations at different temperatures on SnO\(_2\) surfaces](image)

Figure 1-8: Adsorbed water formations at different temperatures on SnO\(_2\) surfaces [10]

So far, several mechanisms have been proposed in the literature to explain the detailed adsorption processes of water molecules on the surface, two main mechanisms are briefly summarized. In the first mechanism, water molecules react with adsorbed oxygen ions to form hydroxyl groups and release an electron to the conduction band (Figure 1-9A). In the second mechanism, as it has been shown in Figure
1-9B, two hydroxyl groups are generated, one from the water molecule dissociation and the other from the reaction between hydrogen and oxygen in the metal oxide structure.

![Diagram showing two different mechanisms for the interaction between water with the surface of a metal oxide sensor (here reduced SnO$_2$) [16]](image)

1.5.2 Sensor Geometry and Microstructure

Chemiresistive gas sensors are typically consisted of thin or thick film sensing layers deposited over gold or platinum electrodes on the ceramic or silica substrates using various commercially available techniques including sputtering, thermal evaporation and chemical vapor deposition. It has been demonstrated in literature that the geometrical design of the sensing layer and electrodes contribute greatly in the sensor performance since the whole film doesn’t go through a conformal variation in conductivity when it’s exposed to the target gas [17].

1.5.3 Grain Size

By the adsorption of the molecules on the surface of the sensing layer, electrons can either transfer from the molecule to the surface or travel from the surface to the molecule. This charge separation create
an electric field. A potential barrier between 0.5 to 1 eV is formed at the surface leading to a band bending and depletion region creation [8].

Additionally, formed negative surface sites prevent remaining excited electrons to move freely all over the surface. The distance that other electrons are not allowed to go closer to the stable negative sites is called Debye length. A Debye sphere is accordingly a volume whose radius is the Debye length. Equation 1 shows the expression used to measure the Debye length:

\[ L = \sqrt{\frac{\varepsilon k T}{q^2 n_c}} \]  

Equation 1-1

Where \( k \) is Boltzmann constant, \( \varepsilon \) is dielectric permittivity, \( T \) is operating temperature, \( q \) electron charge and \( n_c \) carrier per volume. To have a good sensitivity, the critical dimension of the nanostructure should be at most twice the Debye length for the material. It has been demonstrated in the literature that the sensitivity would increase dramatically if the grain size is smaller than the Debye length [5].

If the grain size is smaller than twice of depletion region, the whole grain will be depleted upon excitation, leading to a rapid variation in sensor response [13]. In the latter case, it has been assumed that the grain boundary potential (called double Schottky barrier) for electron transfer is constant in all grain sizes. Additionally, high surface to volume ratio can also increase the surface reactivity because of increasing surface disorders which provide more accessible active sites.

There is also a minimum value for the grain size. Very small particles increase the sensitivity to humidity and worsen the stability of the sensor response due to the lack of sufficient amounts of electrons and internal resistance. Figure 1-10 shows the influence of grain size on sensor response in SnO₂ sensors.

On the other hand, in larger grain sizes, the potential barriers at particle interfaces become determining factors in sensor response. If the grain size is much larger than the Debye length, then a minor change in
the grain size would not affect the response significantly. Many researches are devoted to find the critical grain size for any particular sensor materials which a great change would happen in the performance.

![Graph showing grain size effects on SnO₂ sensor response towards 800ppm H₂ and 800ppm CO in air at 300 °C]

**Figure 1-10:** Grain size effects on SnO₂ sensor response towards 800ppm H₂ and 800ppm CO in air at 300 °C [13]

### 1.5.4 Temperature

Temperature has a strong influence on physical properties of semiconductors and surface reactions. Increasing temperature would cause electrons to rescue from the surface and result in a decrease in resistance, this phenomenon is called “Thermionic Emission” [18]. Adsorption/Desorption processes, chemical dissociation and surface oxidations are dependent to the operating temperature. Sensitivity and
dynamic response time that are usually account for the sensor performance are greatly influenced by the operating temperature.

1.5.5 Additives

Controlling the catalytic activity of the gas sensor material is very effective in enhancing the performance of gas sensors. Usually noble metals such as Pd, Pt, Cd, Au and Ag are added to the sensing layer structure in order to increase the maximum sensitivity, shorten response time and lower the operating temperature. Generally, contribution of additives in medication of the surface properties is either through increasing the concentration of reactants at the surface or lowering the activation energy of the reaction, or both, but specifically, they increase the charge density in the bulk [9]. These effects mainly happen through promoting catalytic activity of the sensing material and reducing charge recombination rate.

1.6 State of the Art of Photo-Activated Gas Sensors

To summarize aforementioned influencing factors on the sensor performance, several important criteria in the performance of a chemical gas sensor are listed as follow:

- The smaller the crystallite size, the higher the sensitivity but there is a limit for minimum grain size.
- The activation energy of the chemisorption of the oxygen and target gas molecules should be smaller than the activation energy of the desorption of the species
- Catalytic noble metals can be added to promote the sensing performance.
- Many other factors such as the particle crystalline facets, porosity of the metal oxide, sensor configuration, etc., can influence the performance of gas sensor.
Although the above parameters can be controlled to enhance the performance of gas sensors, several issues related to the operating condition, stability and selectivity still remain.

Conventional MOS chemi-resistive gas sensors work at high temperatures, usually 200 °C to 500 °C to produce excited charges required for sensing reactions (thermal activation). At high temperature, the electrons gain adequate energy to jump from the valence band into the conduction band. Generated electrons then pave the way for either adsorption or direct gas phase reactions of the target gas. This physical/chemical processes will change the flow of surface electrons which is measured as film resistance.

Operating at high temperature dictates many limitations including gas sensor applicability in environments containing flammable gases, since high temperature may result in an explosion. It will also lower the useful lifetime of the sensor and affects the stability and the cost needed to meet power consumption requirements.

The main idea of having photo-activated gas sensors was initiated from the fact that irradiating UV to the surface of the sensor film could change the resistance of the semiconductor, indicating the generation of electron hole pairs in the layer. Since the electrons/holes are the main components participating in the sensing reactions, what if we use UV to activate the sensor rather than increasing the temperature?

UV illumination can lower the temperature and produce sufficient amounts of electrons/holes at room temperature. Indeed, the semiconductor sensing layer can be activated by photons, a phenomenon which is called “photo-activation”. UV irradiation also enhances the desorption process of adsorbed unwanted materials from the surface (de-contamination) and elongates the useful lifetime of the sensor.

In spite of this, the idea was not taken enough attention initially because the applications of conventional UV lamps were severely limited. The wide range of emitted wavelengths which could possibly destroy exposed materials as well as long warm up time and the harmful environmental effects
of UV lamps were the main drawbacks of these sources. Additionally, high energy requirements to provide a high voltage for UV lamps imposes great loss in energy and shortens useful lifetime of the lamp.

The idea of functionalizing chemical gas sensors at room temperature as well as making them smaller, greener and more efficient has initiated important progresses and demonstrations in the last few years among scientists worldwide. UV-LED technology has shown its capability to fulfill the gap between laboratorial and industrial production of room temperature gas sensors. UV-LEDs are promising replacements for mercury lamps since they are small, have instant on/off operation, are environmentally friendly and able to produce exact wavelengths at specific intensity. They pull significantly lower energy and have long lifetime. To become familiar with the importance and applicability of UV-LEDs, a review on gas sensors activated by photons emitted from UV-LEDs is presented in the next chapter.

Although several metal oxide semiconductors have been recently investigated for UV based gas sensors, the performance characteristics and operating conditions of the materials are not properly compared. In this study, the recent advances in UV-activated metal oxide gas sensors in general, and the operating principles and sensing performances of UV-LED based sensors in particular are reviewed for the first time. Also, no comprehensive study has been performed in the literature, comparing the photo-activated gas sensing performances of ZnO and In$_2$O$_3$ sensors. Thus, we synthesized and used these semiconductors to analyze and compare the gas sensing responses in similar conditions.

In addition, to author’s knowledge, no report in the open literature has investigated the photo-activated ZnO/In$_2$O$_3$ composite semiconductors for gas sensing application. Therefore, the current study focused on the development of the sensitive and efficient gas sensors by mixing ZnO and In$_2$O$_3$ as two promising metal oxide semiconductors in various compositional formations to detect traces of NO$_2$ gas which is one of the most hazardous gases in the environment.
1.7 Thesis Objectives

Based on the concepts reviewed in the previous sections, considering the inspiring works on photo-activated gas sensors, and to meet the increasingly need for high performance gas sensors operating at ambient temperature, the main objective of this research was set to develop room temperature gas sensors with good responses by utilizing promising nano materials activated by new UV-LEDs.

To meet the overall goal, the following specific objectives are considered:

1. To design, build and operate a setup required for testing and analyzing UV-LED based gas sensor responses.

2. To explore the performance of ZnO and In$_2$O$_3$ sensors towards NO$_2$

3. To study the extent to which more sensitive gas sensors can be developed using ZnO/In$_2$O$_3$ composition, based on the privileged performances of composite materials in gas sensing applications, reported in the literature.

4. To study the effects of target gas concentrations, and to investigate the effects of UV source parameters on the sensitivity and response time of the developed sensors by utilizing photonics science and technology.

1.8 Thesis Outline

In this introduction chapter, metal oxide gas sensors in general, and the sensing mechanism and effective parameters on the performance of a typical gas sensor device towards NO$_2$ in particular have been investigated.

Chapter 2 reviews the researches in literature on UV-LED activated chemical gas sensors, accompanies by the evaluation and comparison of different sensor types, as well as their advantages and shortcomings.
Chapter 3 is dedicated to a comparative study on UV based gas response of two semiconductor metal oxides, ZnO and In$_2$O$_3$, and reports preparation routes, specifically the nano-particles synthesis recipe including the deposition techniques and demonstrates the experimental setup built for experiments as well as gas responses to low concentrations of NO$_2$. (Objective 2 and part of objective 1 and 4)

Chapter 4 introduces a sensitive gas sensor developed by addition of a secondary semiconductor to the structural lattice of a semiconductor, utilizing ZnO and In$_2$O$_3$. Different characterization methods are used to imply the inherent properties of composite materials and suitable conditions to have the optimal set of responses towards NO$_2$ are presented (Objective 3 and part of objective 1 and 4).

At the end of each chapter, qualitative and quantitative results are summarized and important discussions on the performance of developed gas sensors are conducted.

Chapter 5 represents the final conclusion and suggestions for future work.
2.1 Introduction

One of the main problems that the world facing is the environmental pollution, increasing with every passing year and causing irreparable damages to the earth. The development of civilization and industrial expansion have caused the enormous injurious smoke emissions by cars, trucks, trains, and factories. Produced gaseous pollutants namely sulphur dioxide, carbon monoxide and nitrogen oxides contribute to a great extent in composition variations of the atmosphere and are mainly generated in combustion of fossil fuels [19]. Evidence of increasing air pollution is seen in lung cancer, asthma, allergies, and various breathing problems [20]. Thus, the need for devices that could detect and monitor environmental emissions has been increasing significantly, motivating researchers to manufacture gas sensors with high performance and reliable stability.

Depending on the sensing mechanism, gas sensors are divided into several types, optical sensors, piezoelectric sensors, electrochemical sensors and solid state resistive gas sensors are four of the commonly utilized classes [4,21]. Figure 1 shows various classes of available gas sensors. Every sensor has its own advantages and disadvantages, so depending on the sort of the facility, one of the gas detection systems must be selected. Solid-state chemical gas sensors are typically made of semiconductor metal oxides as the sensing material to detect pollutant gases. There are wide variety of advantages for these gas sensors including simplicity, fast response and being very inexpensive. However they have some issues in selectivity and stability [22,23].
The beginning of metal oxide semiconductor (MOS) gas sensors production backs to 1957, following by an important work triggered by Bielanski et al. [1] that showed a relation between the electrical conductivity and catalyst activity of semiconductors. Seiyama et al [24] succeeded in developing a gas detector based on resistance variations incurred by gaseous adsorption/desorption processes. In this invention, they noticed that at high operating temperatures the adsorption and successive desorption processes on the surface of thin film semiconductors cause a marked change in electrical conductivity. This suggested the idea of having a thin film gas chromatographic detector instead of the ordinary thermal conductivity cells.

The first commercial MOS gas sensor was manufactured by Taguchi, in 1962 (Figure 2-2). He filed the patent of the first generation of MOS gas sensor devices which could detect low concentrations of combustible and reducing gases based on thick films of SnO$_2$ and employed them in warning devices with a simple electrical circuit [2].
Since then, the manufacturing of low-cost gas sensitive devices received great attention from researchers worldwide. Although several detecting mechanisms were proposed at first to change the electrical conductivity of metal oxides including the growth of semiconductor film and etching of the semiconductor layer, the effort was mainly focused on reversible oxidation/reduction reactions in which excited electrons induced by thermal treatments played the key role in the sensing process. The fundamental mechanism of chemi-resistive gas sensing is based on the reaction of the generated electrons with the ambient oxygen or surrounding gas. Adsorption of oxygen molecules on the surface of metal oxides is accompanied by an electron extraction from the conduction band, leading to the formation of an electron-depleted region and band bending. Removing oxygen ions by their reaction with the surrounding gases or replacement of the adsorbed oxygens by other molecules can reverse the band bending, resulting in an increased conductivity that could possibly indicate the amount and type of the gas to be detected [9].

Figure 2-2: A schematic illustration of the first manufactured MOS gas sensor
Since Taguchi innovation, many investigations have been conducted to study the performance and functionality of developed chemi-resistive sensors by employing wide variety of metal oxides in various compositions with different dopants, catalysts, adhesives and binders to enhance the sensing activity of sensor materials that directly affect the performance of gas sensors. However the major issues associated with the operating condition, stability and selectivity were still existed. The problem originated from the fact that electrochemical reactions involved in the detection mechanism of these gas sensors required high working temperatures to proceed at sufficient rates and the layer should have been able to provide the adequate amounts of negative/positive charge density on the surface to activate adsorbed oxygen and to enhance the reactivity with analyte gas [23,25].

Conventional thermally activated metal oxide semiconductor gas sensors showed sensing responses around the temperature range of 175–425 °C [26,27]. The necessity of heating the device to reach to the suitable temperature makes some technical limitations in applicability of these gas sensors such as utilization in the environments containing explosive species since high temperature could trigger an explosion. Heating also requires high energy and frequent maintenance and will affect the stability and economic aspects. Although miniaturization helped to develop efficient types of sensors recently, the preparation time is still an important concern. Besides, another critical concern of sensor setups is the potential for unwanted, unpredicted contamination, which introduces spurious measurements and shortens the useful lifetime of the sensor [28].

The aforementioned problems of high temperature MOS gas sensors and the complex circuitry required to maintain accurate temperature control, motivated investigators toward developing sensors that are able to work at lower temperatures by capacitively coupling the nanostructure to a nearby gate electrode and by applying high electric field across the sensor terminals [29]. They also tried to utilize
conducting polymer gas sensors that could be used as room temperature sensors, but their reluctance for organic vapours limited their applications [30].

A great breakthrough occurred on this way in 1994 by Saura [31] who described the gas sensing properties of UV radiated SnO$_2$ pyrolytic films towards trichloroethylene and acetone. The main idea of having photo-activated gas sensors was initiated from the fact that irradiating UV to the surface of the sensor film could change the resistance, indicating the generation of electron hole pairs required for gas sensing. The UV irradiance reported in this study was 20 mW/cm$^2$ and it was proposed that the selectivity can be altered by using appropriate UV wavelength.

Indeed, photo-excitation can increase the density of charge carriers throughout the material and can decrease the intergrain barrier height by changing the intergrain state’s charges, leading to increase the probability of tunneling by decreasing the depletion layer widths in the adjacent grains [26,32].

In 1996, P. Camagni et al. [33] employed Xenon UV sources to perform photoconductivity measurements of Rheotaxial Growth and Thermal Oxidation (RGTO) SnO$_2$ thin films in lower operating temperatures using volt-amperometric technique in which the MOS was biased with a constant voltage and the current was measured continuously. The illuminated SnO$_2$ sensor showed remarkable resistant changes for low concentrations of CO at room temperature compared to dark condition. In further study of this group, Comini et al. [32] observed that the 40 min response time of a SnO$_2$ gas sensor can be decreased to 10 s under UV illumination and the sensor can return to 80% of its initial value. They then proposed that the sensitivity of photo-activated RGTO tin dioxide thin films responses towards NO$_2$ can be increased by using a lamp with higher irradiance (3500 mW/cm$^2$) attached with optical fibres aligned to the surface [34]. They also observed that by increasing working temperature to 200 °C the sensitivity, response and recovery times will increase. However by further increasing of temperature over 300 °C the parameters will decrease eventually.
In a parallel work performed by K. Anothainart et al. [35] on sputtered SnO$_2$ samples, they observed that the NO$_2$ is desorbed upon exposure to the UV. They concluded that the desorption depends on the radiation intensity, in which increasing the intensity causes decreasing time constants for desorption and thus helps to reduce poisoning by an enhancement in desorption process. Beside the empirical researches initiated for developing high performance photo-activated gas sensors, Mishra et al. [27] theoretically concluded that the sensitivity is inversely proportional to the grain size. During the last decade, room temperature UV-based gas sensing technology has been significantly developed due to its increasing role in human’s daily life. Several studies have been performed to develop room temperature gas sensors afterwards, utilizing UV illumination to excite electrons and to improve the performance [27,35–42].

Until recent years, the main sources for industrial production of UV devices relied on the principle that when a small amount of mercury was energized with a high-voltage electric current, electrons in the mercury atoms are excited to a higher energy state and emitted energy on the way back to the ground level, the energy which is in the form of UV, visible light and heat. However, as we will discuss in the following, using conventional UV lamps for the activation of gas sensors was not the best option.

The first drawback of conventional mercury UV lamps was the broad range of emitted wavelength which could possibly destroy exposed materials. Additionally, high energy requirements to provide the high voltage for UV lamps could deteriorate electrode material and as a result, cause a small amount of electrode material to evaporate leading to darkening or blacking of the lamp near the terminals which imposes loss of energy and shortens useful lifetime of the lamp. Another drawback of UV lamps was the long warm up time required to reach to the operational condition as well as the time required for internal pressure to return to initial value. As a conclusion, because of the aforementioned drawbacks, as well as the harmful environmental effects and severe respiratory problems that may occur by using UV lamps, the need for smaller, greener and more efficient replacements became progressively more important.
The great advances that have been made in UV-LED technology in recent years providing them with higher power and more efficiency has made them suitable candidates to fulfill the gap between laboratorial and industrial production of room temperature gas sensors. UV-LEDs can be designed in small sites and have instant on/off operation. Besides, their environmentally friendliness and ability to produce exact wavelengths at specific intensity has improved their capability. They pull significantly lower energy (in the order of tens of milliWatts for optimum working condition) and have long lifetime. The idea of functionalizing chemical gas sensors at room temperature as well as making them smaller, greener and more efficient has initiated significant progresses in the last few years among scientists worldwide. Therefore, room temperature gas sensors activated by photons emitted from UV-LEDs have been introduced recently.

In an introductory work by Han et al. [43] on UV-LED based catalytic combustion hydrogen sensors using drop coated TiO₂ doped with palladium and platinum metals on alumina substrate, it was reported that the use of UV-LED can facilitate the oxidation of hydrogen on the surface and improve low temperature gas sensing characteristics and self-cleaning effects of the developed sensors.

There have been several research reports in the literature in the last few years concerning photo-activation of sensors by UV-LED. However, to author’s knowledge, there is no review article published in the literature on the recent advances in UV-LED based sensors. Such information is essential for developing new generations of low cost, small size sensors. In this article, the recent developments on UV based gas sensors in general, and photo-activated MOS gas sensors working under UV-LED irradiation in particular, have been reviewed and the advantages and disadvantages of each sensor system have been presented and compared, along with their performance levels, and their capabilities and limitations.
2.2 Gas Sensing Mechanism of UV Illuminated Metal Oxide Semiconductors

The principles of chemical gas sensing in photo-activated gas sensors is independent of the light source, as long as the energy of photons emitting from the UV source is equal or greater than the metal oxide band gap. However the pattern and intensity of the emitted light will apparently affect the flow of the photons, the performance and sensing characteristics accordingly, due to the change in carriers density incurred by photons interactions.

Regardless of the type of the photon source, it is well-known that the work function of the photo-activated gas sensors is governed by various electrochemical sensing reactions that involve electrons/holes created by the interactions of photons and metal oxide surface at room temperature. However a consistent general explanation of the underlying mechanism has not reported yet. Although the overall logic of photo-activated gas sensing principle is generally identical, some differences will be induced in different types of oxidizing/reducing reactions and metal oxide semiconductor layer structures as well as inherent toxicity of the gases. Therefore, we require to divide discussion into several subsections in order to span all important aspects.

Target gases are classified into two major groups based on the electron transfer direction in respective reactions and their oxidizing/reducing effects. Oxidizing gases include any gases containing oxygen at higher than atmospheric concentrations such as Ozone, Nitrogen Oxides, CO₂, chlorine and fluorine, while reducing gases are referred to many of VOCs, CO, H₂S, SO₂ and NH₃ which donate electrons in reactions.

In a gas sensing experiment, when air is introduced to the metal oxide semiconductor at room temperature, oxygen is adsorbed either molecularly or in the atomic form on the surface. At lower temperatures, oxygen is adsorbed molecularly but as the temperature increases, it tends to be adsorbed in the form of O²⁻ and O⁻ [10]. Adsorption of oxygen is accompanied by an electron extraction from the
conduction band, forming negative sites on the surface and positive holes in the conduction band. The separation of charge carriers makes an electric field and leads to formation of a stable electron-depleted region. The formed potential barrier is usually between 0.5 to 1 eV that acts as a barrier for remaining electrons to excite [8,9,44–46]. The negatively charged oxygen ions produce an upward band bending resulting in reducing conductivity [9].

Illumination, changes the occupancy of the defects and thus changes the capacity of adsorption concentration on the surface by enhancing charge carriers [34]. Two mechanisms are proposed for the direct desorption of adsorbates upon the exposure to UV radiation, direct excitation of a binding electron to the conduction band or recombination with a photon generated hole in the valence band [47]. In other words, as the photons irradiate to the surface, the photo-induced holes/electrons interact with the adsorbed oxygen causing to desorb oxygen ion species (photo-desorption) simultaneously along with the photo-induced electrons interaction with oxygen in the gas phase. This phenomenon continues to reach a new equilibrium state in which the rate of arrival of holes and electrons to the surface becomes equal [48,49]. Interaction and recombination of a hole with a binding electron of the layer could also break the bond and provide oxygen atom that is able to diffuse to the crystal surface, react with oxygen ions and form into $O_2(g)$ and leave an oxygen vacancy behind [47]. The reactions occur on the surface are as follow:

$$O_2^{\text{gas}} \leftrightarrow O_2^{\text{ad}}$$

$$O_2^{\text{ad}} + e^- \leftrightarrow O_2^{-}(\text{ad})$$

$$O_2^{-}(\text{ad}) + h^+_{(hv)} \leftrightarrow O_2^{\text{gas}}$$

$$O_2^{\text{gas}} + e^-_{(hv)} \leftrightarrow O_2^{-}(\text{ad})$$

$$O_2^{-}(\text{ads}) + e^- \leftrightarrow 2O_2^{-}(\text{ad})$$

$$O_2^{-}(\text{ad}) + e^- \leftrightarrow O_2^{2-}(\text{ad})$$
Oxidizing gases have extremely high catalytic activity. Upon exposure of the layer to an oxidizing gas, the gas reacts with the adsorbed oxygen ions as well as directly adsorbs on the surface. A dynamic equilibrium could exist between the adsorption and photo-excited desorption of gas molecules on the surface. In other words, target gas and O₂ molecules compete for the available adsorption sites. The high number of occupied sites by oxygen ions in equilibrium with molecules in air, remains only a small fraction of sites available for target gas which could result in a weak and non-reversible response in dark conditions [50]. Under continuous irradiation, photons help to partially desorb oxygen species from the surface, provides available vacant sites for target gas molecules. Thus a new steady equilibrium state based on the dynamic balance between adsorption and desorption of oxygen and gas is formed [50–52]. When the physisorbed gas molecules accepts an electron from oxygen ions (particularly O₂⁻ which is the dominant form at room temperature) a stable chemisorbed state of the gas created which can only be desorbed by UV radiation [35]. The reaction and desorption take place simultaneously to reach to an equilibrium state under constant flow of photons. In other words, UV irradiation accelerate the rate of reactions and shifts the equilibrium positions towards consuming more electrons, having a stable amount of adsorbed species on the surface. The most stable state determines the visualized resistance of sensing material during the exposure. Figure 2-3 shows a schematic of surface reaction occurs in a photo-activated chemi-resistive gas sensor.
Several reactions that oxidizing gases such as NO$_2$, CO$_2$ and O$_3$ follow by their interaction with the adsorbed oxygen ions are presented here [38,47,53–55].

$$\text{NO}_2(\text{gas}) + e^-_{(hv)} \rightarrow \text{NO}^2-(\text{ad})$$

$$\text{NO}^2-(\text{ad}) + O_2^{--}(\text{ad}) + 2e^-_{(hv)} \rightarrow \text{NO}(\text{gas}) + 2O^{2--}(\text{ad})$$

$$\text{CO}_2(\text{gas}) + e^-_{(hv)} \rightarrow \cdot \text{CO}_2^{2--}(\text{ads})$$

$$\cdot \text{CO}_2^{2--}(\text{ads}) + 2h^+_{(hv)} + e^- \rightarrow \cdot \text{CO}_{(ad)} + H_2O$$

$$2 \cdot \text{CO} + O_2^{--}(\text{ad}) \rightarrow 2\text{CO}_2 + e^-$$

$$O_3 + e^-_{(hv)} \rightarrow O^- + O_2^{--}(\text{gas})$$

$$2O^- + h^+_{(hv)} \rightarrow O_2(\text{gas}) + 2e^-$$
As the gas molecules adsorb on the surface and follow the previously described reactions, due to the electron consumption, the resistance of n-type metal oxide layer increases. In p-type semiconductors the resistance decreases upon exposure to the gas because extracted electrons result in an increase in the number of holes in the valence band.

In case of exposure of the layer to reducing gases, the gas participates in a reaction with the adsorbed oxygen releasing and accumulating electrons back to the conduction band and resulting in a decrease of resistance in n-type semiconductors. This change in resistance is due to charge density enhancement and increase in p-type semiconductors because of the reduction in hole concentration. Examples of reaction of some reducing gases such as NH₃, HCHO and ethanol are presented as follows [45,56–59]:

\[
\begin{align*}
2\text{NH}_3 + 3\text{O}^{-}_{(ad)} & \rightarrow \text{N}_2 + 3\text{H}_2\text{O} + 3\text{e}^- \\
2\text{NH}_3 + 3\text{O}^{2-}_{(ad)} & \rightarrow \text{N}_2 + 3\text{H}_2\text{O} + 6\text{e}^- \\
\text{H}_2 + \text{O}^{-}_{(ad)} & \rightarrow \text{H}_2\text{O} + \text{e}^- \\
\text{H}_2 + \text{O}^{2-}_{(ad)} & \rightarrow \text{H}_2\text{O} + 2\text{e}^- \\
\text{CO} + \text{O}^{-}_{(ad)} & \rightarrow \text{CO}_2 + \text{e}^- \\
\text{CO} + \text{O}^{2-}_{(ad)} & \rightarrow \text{CO}_2 + 2\text{e}^- \\
\text{HCHO} + \text{O}^{-}_{2(ad)} & \rightarrow \text{CO}_2 + \text{H}_2\text{O} + \text{e}^- \\
\text{CH}_3\text{CH}_2\text{OH} + \text{O}^{-}_{2(ad)} & \rightarrow \text{CO}_2 + \text{H}_2\text{O} + \text{e}^- \\
\text{CH}_2\text{O} + \text{O}^{-}_{2(ad)} & \rightarrow \text{CO}_2 + \text{H}_2\text{O} + \text{e}^- 
\end{align*}
\]
Due to the strong influence of the structural formation and surface states of sensing layer materials, the governing mechanism and sensing reactions could be subjected to alter as a result of a change in film properties such as in the presence of moisture or by addition of any dopant to the structure. For instance, it has been suggested that the possible mechanism in metal doped semiconductor layers is totally different from that of pristine samples. For metal doped semiconductors, the mechanism could be explained based on the charge transfer transition of metal ion by UV illumination which leads to create additional holes that react with chemisorbed oxygen ions and desorb oxygen [60]. The gas sensor sensitivity for n-type and p-type semiconductors is defined as follows:

\[ S = \frac{|R_g - R_a|}{R_a} \quad \text{or} \quad S\% = \frac{|R_g - R_a|}{R_a} \times 100 \]

Where \( R_a \), \( R_g \) are the electrical resistances of the sensor measured at the presence of pure dry air and target gas respectively. Sensitivity is sometimes expressed as the percentage change of initial resistant value.

Figure 2–4, shows a typical response of a metal oxide layer when the sensor is exposed to the target gas. The sensitivity or sensor response is one of the main factors which can be used to compare performance results reported in literature. The response and recovery time are also important in making a fast and flexible gas sensor, however due to the configuration differences in flow conditions, they might not be precise factors for the comparison.
2.3 Photo-activated Semiconductor Metal Oxides as Room Temperature Gas Sensors

The gas sensing characteristics of different metal oxide gas sensors towards several hazardous gases under UV irradiation are presented in this section. The sensors are organized with respect to the sensing materials including ZnO, TiO$_2$, SnO$_2$, In$_2$O$_3$, and metal oxide composites. UV-activated sensors that employ conventional UV lamps in their structures are presented in tables, while UV-LED based sensors are discussed individually in details in the following sub-sections. It is well known that the performances of metal oxide sensors considerably depend on the layer configurations and preparation methods. Therefore, preparation routes, techniques and manipulations that have been made in the structures of MOS sensors to enhance their sensing capabilities and performances are reported.

2.3.1 ZnO Photo-activated Sensors

ZnO is one of the most favorite materials for room temperature photo-activated sensors because of its unique optical, catalytic, and electrical features. ZnO has a large surface to volume ratio, large band
gap (3.37 eV at room temperature) and a high exciton binding energy (60 meV). Furthermore, it is highly transparent and completely bio-safe [61]. ZnO can be modified for multiple applications by incorporation of doping ions which act as donors or by creating oxygen vacancies [62]. In terms of applicability in gas sensor devices, the properties which make ZnO more attractive are essentially chemical sensitivity to different adsorbed gases, possibility for doping, chemical stability as well as versatility and low cost. Table 2-1 shows a summary of the preparation techniques and the sensing performances of developed ZnO gas sensors for different target gases working under conventional UV lamps illumination.

In terms of UV-LED application in gas sensor setups, the first UV-LED based MOS chemi-resistive gas sensor was manufactured by Costello et al. [63] in 2008. The authors reported the sensing properties of ZnO nano-particulates under UV-LEDs with a 400nm wavelength peak. The investigation of the effects of the incident irradiance in the range of 0.36–22 mW/cm² on the sensitivity and selectivity of the developed sensors for methane, propane, butane and hexane showed that there is a maximum response in an optimum irradiance for each gas. In addition, the optimal light irradiance for any given analyte is grain size dependent indicating that the intensity can be used to tune the selectivity towards specific target volatiles. The maximum responses of developed sensors in their optimal conditions (1.5 mW/cm² for ethanol, 3 mW/cm² for propane, 3 mW/cm² for hexane, 2.2 mW/cm² for methane) were 0.85, 0.7, 2 and 0.25 to 10 ppm ethanol, 100 ppm propane, 10 ppm hexane and 100 ppm methane, respectively. Detection limit analysis (the lowest concentration of the analyte that can be detected) was performed to investigate the applicability of developed sensors in flammable gases detection. For both acetaldehyde and acetone 1 ppb was reported whereas the detection limit for pentane was 0.01 ppm and toluene 0.05 ppm. The results showed that at 35% relative humidity the sensitivity of the sensors can be 50% reduced compared to dry conditions.
Thick film ZnO layers synthesized by precipitation route for ozone detection under UV-LED illumination were studied by Carotta et al. [64]. The material were screen printed over miniaturized alumina substrates and were irradiated by a UV-light emitting diode with 397 nm wavelength. The operating radiation flux density ($\phi$) over the sensor was reported to be around $5.1 \times 10^{17}$ photons/cm$^2$ (approximately 0.25 W/cm$^2$ in the measured time scale), where the maximum total power of the used UV-LEDs is reported to be 10 mW by the manufacturer. In terms of the gas sensing performances of the developed sensors, the highest response was reported approximately 1.35 towards 70 ppb of ozone while the sensors didn't show any response to ozone in dark condition. When the UV intensity decreased from 30% to 2% of the typical radiation flux density, the ozone response continuously increased, and the recovery time also increased significantly. The effect of humidity in their experiments were quite significant; the response time and the recovery time at relative humidity of 50% at 25 °C were much lower than that of the dry condition (Figure 2-5). However in heated mode sensor, the ozone response in dry air was only slightly lower than those in wet air, while the recovery time was significantly longer.

Figure 2-5: Dynamical responses to ozone in dry or wet air for RT-UV-assisted ZnO sensor [64]
Geng et al. [65] performed a study on ZnO thick films sensing performances towards ethylene and acetone under white LED illumination behind different bandpass filters with 420–520 nm as wavelength range. The activation in longer wavelengths could possibly be explained by multi photon excitation phenomenon in which collision with two or three incident photons with lower energy leads to excite electrons from valence band into conduction band. Sensor responses towards 700 and 900 ppm acetone were 0.15 and 0.2 respectively at wavelengths shorter than 420 nm. However the response values decreased by increasing exposed wavelength.

Fabbri et al. [66] compared the gas sensing characteristics of thick and thin films ZnO layers prepared by screen printing and spin coating methods, respectively, under wide range of UV-LED wavelengths (365–525 nm) in environments containing various gases including NO$_2$, alcohols and hydrocarbons. The appropriate wavelength was determined to be 365 nm which resulted in higher response/recovery time constants and higher sensitivity. The authors observed that the responses of thick films have negligible values in comparison with those of thin films. For instance, the responses to 5 ppm NO$_2$ for thin and thick films of ZnO layers were reported to be 0.08 and 0.03, respectively.

Fan et al. [49] suggested a mechanism for UV activated polycrystalline ZnO sensors by employing a 400 nm UV-LED to detect H$_2$. ZnO nanolines were able to detect ppm levels of H$_2$ (100 ppm) at room temperature, however, the sensitivity was not significant (0.015) and the performance degraded over time because of the strong adsorption bonds between the gas molecules and surface sites. Applying continuous UV illumination during the gas sensing process solved the degradation problem and enhanced sensor responses to 0.1 for thin film ZnO and 0.2 for ZnO nanoline sensors (towards 100 ppm H$_2$).

In a separate study on ZnO nano lines, Fan et al. [67] prepared nano-patterned polycrystalline ZnO layers by a sol–gel route followed by spin coating and soft e-beam lithography, making 100 and 400 nm wide ZnO lines as well as ZnO thin films. The prepared sensors were tested against H$_2$ and NO$_2$ gases,
where the actual power density of 365nm UV-LEDs on the surface of sensors (at the distance of 6 mm from the UV source) was measured to be 25 mW/cm². Thin film and 400nm wide line ZnO showed almost no response to H₂ and NO₂, however, the 100nm wide ZnO line sensitivity towards 20 ppm NO₂ and 100 ppm H₂ were 0.83 and 1.6 respectively. They also analysed the Joule self-heating effect and subsequent increase in temperature of sensing layer area under illumination and realized that self-heating enhances the sensor performance up to around 110 °C, which is not dangerous for the risk of explosion of combustible gases.

Another research on photo-activated detection systems based on ZnO nano-rods was conducted by Youn et al. [68] working on two different structures of ZnO nanowire arrays by applying spatial confinement on photoresist-structured substrate and by preferential chemisorption on Au electrodes deposited on Si substrates (Figure 2-6). The sensor results towards different concentrations of carbon monoxide under 354 nm UV-LED illumination was promising. The sensor prepared by selective chemisorption method exhibited a better response with higher sensitivity of about 900 towards 40 ppm of CO compared to the other sensor which was 50. However, using nitrogen as the carrier gas in this study doesn’t allow to be compared with other sensors.

Ahn et al. [60] applied doping Ni agents on ZnO nanorods under UV radiation to enhance gas sensitivity. They fabricated Ni-doped ZnO nanorods by RF magnetron sputtering in varied concentrations of Ni from 0 % to 10 % and tested for acetone sensing. An array of five 2.2 mW of Bulb type 365 nm UV LEDs located at a distance of 0.5 mm from ZnO nanorods was used in the sensors. It was observed that excessive Ni doping (i.e. 8 % and 10 % ) could lead to the formation of a secondary NiO phase which deteriorates the sensing results compared to sensors with lower Ni contents. In terms of gas sensing performance, 6% Ni-doped ZnO nanorods responded roughly 1.61 while the sensitivity for pure ZnO nanorods was reported 1.34 for 100 ppm acetone under UV illumination.
In a recent study by Catto et al. [69], one-dimensional ZnO nanorods grown via hydrothermal method activated by 351 nm UV-LED irradiation were used for ozone detection. The 1-D ZnO nanorods showed promising gas sensing responses towards different ozone levels under continuous UV irradiation. The response range was from 0.6 to 0.95 in concentrations ranging from 0.1 to 1.2 ppm. The response time was between 40 and 44 s, and the recovery time varying between 9 and 11 mins, depending on O₃ concentration.
Table 2-1: A summary of the development techniques and performances of ZnO gas sensors activated by conventional UV lamp sources to various gases at room temperature

<table>
<thead>
<tr>
<th>Material</th>
<th>Target gas</th>
<th>Method</th>
<th>Gas Conc. (ppm)</th>
<th>Sensing Performance</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnO</td>
<td>Ethanol</td>
<td>Spin Coating</td>
<td>200</td>
<td>1.45 annealed at 800 °C</td>
<td>[70]</td>
</tr>
<tr>
<td>ZnO</td>
<td>Ethanol</td>
<td>Electrospinning</td>
<td>60</td>
<td>0.8</td>
<td>[71]</td>
</tr>
<tr>
<td>C-doped ZnO</td>
<td>Ethanol</td>
<td>Hydrothermal</td>
<td>100-400</td>
<td>5 @ 400 ppm</td>
<td>[72]</td>
</tr>
<tr>
<td>Sn-ZnO</td>
<td>Ethanol</td>
<td>Co-Precipitation</td>
<td>1000</td>
<td>~390 (static)</td>
<td>[58]</td>
</tr>
<tr>
<td>La-ZnO</td>
<td>Benzene</td>
<td>Sol–Gel</td>
<td>100</td>
<td>16 at 420 °C</td>
<td>[41]</td>
</tr>
<tr>
<td>Cu-ZnO</td>
<td>Ethanol, Acetone</td>
<td>Sol–Gel</td>
<td>1000 – 25000</td>
<td>~63 @ 1120 ppm</td>
<td>[73]</td>
</tr>
<tr>
<td>ZnO</td>
<td>Ethylene</td>
<td>Drop-Coating</td>
<td>3600 ppm</td>
<td>1.13</td>
<td>[65]</td>
</tr>
<tr>
<td>ZnO</td>
<td>Acetone</td>
<td></td>
<td>700 ppm</td>
<td>1.02</td>
<td></td>
</tr>
<tr>
<td>ZnO nanorods</td>
<td>TEA</td>
<td>Hydrothermal</td>
<td>300</td>
<td>0.08</td>
<td>[74]</td>
</tr>
<tr>
<td>ZnO nanorods</td>
<td>Formaldehyde</td>
<td>Hydrothermal</td>
<td>5-50</td>
<td>~7 @ 50 ppm</td>
<td>[75]</td>
</tr>
<tr>
<td>Ag–ZnO</td>
<td>Formaldehyde</td>
<td>Precipitation</td>
<td>5-40</td>
<td>1.2 @ 40 ppm</td>
<td>[76]</td>
</tr>
<tr>
<td>Au-ZnO</td>
<td>NO₂</td>
<td>Therm. Evap.</td>
<td>1-5</td>
<td>4.5 @ 5 ppm</td>
<td>[77]</td>
</tr>
<tr>
<td>ZnO tetrapods</td>
<td>H₂, i-butane</td>
<td>Lift-out</td>
<td>100</td>
<td>0.06 to H₂</td>
<td>[78]</td>
</tr>
</tbody>
</table>

2.3.2 TiO₂ Photo-activated Sensors

TiO₂ is a widely used organic gas sensor material which can be activated under light. However TiO₂ based sensors have been relatively less studied compared to ZnO sensors. A summary of the performance of TiO₂ gas sensors operating under conventional UV lamps is provided in Table 2-2 while the study on UV-LED based sensors are described below.
In terms of applied LED based UV sources, Zhang et al. [79] used a platform of UV activated TiO$_2$ for formaldehyde sensing under different humidities at different working temperatures. They used laser scribing to groove a tortuous path on the deposited Pt layer to create the electrodes required for resistance monitoring and installed an array consisting of 6×6 365nm UV-LEDs with 3.6 mW/cm$^2$ irradiance to activate screen printed TiO$_2$ layer. Gas sensor responses for 100 ppm formaldehyde at room temperature and zero humidity was significantly high, roughly 10000, while it dropped down to 4.5 when the humidity changed to 18.24 mg/L. The results ascertained that super hydrophilic TiO$_2$ layers are not suitable for formaldehyde sensing at ambient environments, since the active sites can be occupied by water. The authors suggested to solve the problem by increasing the working temperature to 40 °C, 60 °C, and 80 °C and concluded that 60°C could be the best working temperature for achieving responses (roughly 10000) and short recovery time constants under UV radiation.

The influence of Au and Pt electrodes on the photo-activated TiO$_2$ sensor structural stability as well as gas sensing stability towards 100 ppm formaldehyde in different moisture circumstances, under 365 nm UV light-emitting diodes with 36 W/m$^2$ irradiance was studied by Lei et al. [80]. The color of TiO$_2$ thick films upon exposure to 100 ppm formaldehyde in 11 mg/L humidity was different for Au and Pt electrodes. The production of Ti$^{3+}$ defects on Au electrodes changes the layer color, however, the TiO$_2$ layer on Pt electrodes was stable without any change in color. Figure 2-7 shows a schematic illustration of the reactions in TiO$_2$ thick films in the presence of Au and Pt electrodes.
Liu et al. [81] presented a highly ordered TiO$_2$ nanotube array grown by electrochemical anodization method for using in formaldehyde photo-activated gas sensors. The sensor performances for various concentrations of formaldehyde from 10 ppm to 50 ppm in the relative ambient humidity of 33% at room temperature under 4 mW UV-LED illumination with 360–365 nm wavelength range were promising (i.e. 90 to 50 ppm formaldehyde). The synthesized TiO$_2$ showed almost linear response as a function of the concentration of formaldehyde and also a good stability and reproducibility.

Xiaogan Li et al. [82] used a 2.5 mW UV-LED with 365 nm photon’s energy to activate mesoporous hollow TiO$_2$ microspheres sensors synthesized by hydrothermal method to detect sub-ppm levels of formaldehyde (1-5 ppm). The sensor sensitivity towards 5 ppm formaldehyde was reported to be 40.

Finally, Chen et al. [26] compared the sensing performance of prepared TiO$_2$ and ZnO films prepared by screen printing method to detect ethanol and formaldehyde gases by performing simultaneous measurements. A UV-LED array with 365 nm wavelength and 36 W/m$^2$ power was utilized for this
purpose. The response values of TiO$_2$ to 100 ppm ethanol and 100 ppm formaldehyde gases were 1700 and 220, that are much larger than those for ZnO which were reported 224 and 1.4, respectively. It was proposed that the different behavior of ZnO and TiO$_2$ sensing layers is as the result of different quantity of O$_2^-$ ions absorbed on the surfaces of the sensors under UV light irradiation.

Table 2-2: A summary of the development techniques and performances of TiO$_2$ gas sensors activated by conventional UV lamp sources to various gases at room temperature

<table>
<thead>
<tr>
<th>Material</th>
<th>Target gas</th>
<th>Method</th>
<th>Gas Conc. (ppm)</th>
<th>Sensing performance</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Macroporous TiO$_2$</td>
<td>Formaldehyde</td>
<td>Anodization</td>
<td>10-50</td>
<td>0.8 @ 50 ppm</td>
<td>[25]</td>
</tr>
<tr>
<td>Nanoporous TiO$_2$</td>
<td>Formaldehyde</td>
<td>Anodization</td>
<td>10-50</td>
<td>9.7 @ 50 ppm</td>
<td>[81]</td>
</tr>
<tr>
<td>TiO$_2$ nanotube</td>
<td>Formaldehyde</td>
<td>Anodization</td>
<td>10-50</td>
<td>3.7 @ 50 ppm</td>
<td>[83]</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>VOCs</td>
<td>Screen Printing</td>
<td>-</td>
<td>-</td>
<td>[42]</td>
</tr>
<tr>
<td>Nano-TiO$_2$</td>
<td>CO</td>
<td>Thermal Evaporation</td>
<td>80-300</td>
<td>87 @ 300 ppm</td>
<td>[38]</td>
</tr>
<tr>
<td>Nanoporous TiO$_2$</td>
<td>Dodecane, IPA,</td>
<td>Anodization</td>
<td>-</td>
<td>-</td>
<td>[84]</td>
</tr>
<tr>
<td></td>
<td>Pentane</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nano-Structured TiO$_2$</td>
<td>Ethylene</td>
<td>Drop-Coating</td>
<td>400-1600</td>
<td>-</td>
<td>[85]</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>H$_2$</td>
<td>Hydrothermal</td>
<td>-</td>
<td>0.9 @ 250</td>
<td>[86]</td>
</tr>
</tbody>
</table>

2.3.3 SnO$_2$ Photo-activated Sensors

SnO$_2$ was one of the first candidates for gas sensing measurements due to its exclusive chemical features. Table 2-3 represents the preparation techniques and sensing performances of SnO$_2$ based sensors towards different gases under conventional UV sources.

For UV-LED activated sensors, monocrystalline SnO$_2$ nanowires were studied by Prades et al. [50] through a comparative study on thermally activated and photo-activated sensor responses to detect NO$_2$. 

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SnO₂ nanowires were grown by chemical vapor deposition method and two kinds of UV-LEDs with wavelengths from 309 nm to infrared region were employed to illuminate the surface. As expected, nanowires exhibited extremely low responses under dark conditions without any noticeable recovery while reversible responses acquired with response and recovery time constants of only a few minutes under UV illumination. Best reversible responses for 100 ppb to 10 ppm NO₂ pulses were reported to be in the range of 0.1 to 0.8. The investigation of the effect of photon’s energy (i.e. different wavelengths) on sensing responses confirmed that the sensitivity increases significantly by using photons with higher energy (i.e. 3.67 eV energy). The results confirmed that comparable responses can be achieved for photo-activated sensors under appropriate illumination conditions, since the performance of sensors were strongly dependent on the flux and energy of impinging photons. A quantitative model of the role of impinging photons on the responses towards oxidizing gases at room temperature based on the competition between oxygen molecules in air and oxidizing target gases was developed to explain possible mechanism of sensing behaviors.

J. Chien-Chung et al. [87] studied sensing characteristics of RF sputtered samples towards O₃ under UV-LED irradiation. Sensors were irradiated by a single 370 nm UV-LED at the distance of 1 cm from the sensor surface at different irradiances (the output power range measured by a power meter was 1710 µW) under varying O₃ concentrations. The response time constants were reported to be several seconds and the sensitivities for 5, 10 and 14 ppm were approximately between 1.3 and 1.4, where the small values were attributed to the low power irradiation provided by the LEDs. The experiments in higher humidity condition (i.e. RH levels 38% and 70%) at room temperature showed no effect on the sensor responses.

Guo et al. [88] presented an investigation on the effects of adding dopants to the coral-like SnO₂ layers and applied the synthesized materials for ethanol sensing. They utilized a 365 nm UV-LED at 0, 10, 30,
60, and 90% of its total power intensities corresponding to 0, 80, 240, 480, and 720 mW/cm² output irradiance, respectively, and monitored the photocurrent behaviors as well as gas sensing performance of developed sensors. The observation of ethanol sensing performance under 480 mW/cm² at room temperature indicated that the sensitivity of Pd-doped and undoped SnO₂ layers to 100 ppm ethanol was 9.2 and 4.1, respectively, which clearly show an increase of response for the doped layer.

Table 2-3: A summary of the development techniques and performances of SnO₂ gas sensors activated by conventional UV lamp sources to various gases at room temperature

<table>
<thead>
<tr>
<th>Material</th>
<th>Target gas</th>
<th>Method</th>
<th>Gas Concentration</th>
<th>Sensing performance</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>SnO₂</td>
<td>NO₂</td>
<td>Sputtering</td>
<td>100 ppm</td>
<td>1.9</td>
<td>[35]</td>
</tr>
<tr>
<td>SnO₂</td>
<td>NO₂</td>
<td>RGTO</td>
<td>1.3 ppm</td>
<td>0.28 @ 3 ppm</td>
<td>[34]</td>
</tr>
<tr>
<td>SnO₂</td>
<td>H₂</td>
<td>Photochemical</td>
<td>5% H₂</td>
<td>-</td>
<td>[89]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Deposition</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SnO₂</td>
<td>CO</td>
<td>RGTO</td>
<td>100 ppm</td>
<td>0.8 @ 300 C</td>
<td>[48]</td>
</tr>
<tr>
<td>SnO₂</td>
<td>CO</td>
<td>RGTO</td>
<td>250 ppm</td>
<td>0.12</td>
<td>[33]</td>
</tr>
<tr>
<td>SnO₂-Pt</td>
<td>LPG</td>
<td>RF Sputtering</td>
<td>50-200 ppm</td>
<td>4.4 × 10^3 @ 200 ppm</td>
<td>[90]</td>
</tr>
</tbody>
</table>

2.3.4 In₂O₃ Photo-activated Sensors

In₂O₃ is an n-type semiconductor with interesting characteristics and important features such as wider band-gap and transparency. Thus, wide variety of routes have been tried to obtain In₂O₃ powders and nano-structures, and to apply these semiconductors in gas sensors. However there have been only few reports on UV-based In₂O₃ sensors. Table 2-4 shows the studies on conventional UV-lamp based In₂O₃ sensors reported in the literature. Photo-activated gas sensors operating under UV-LED illumination are presented in the following.
Wagner et al. [47] analyzed the photo-reduction influence of 350 nm UV lamp on the electronic resistance of In$_2$O$_3$ and measured the sensitivity of as-prepared mesoporous In$_2$O$_3$ in 5 ppm NO$_2$ (to be approximately 45 at 100 °C). However, in a separate work [91], they reported a comparative study on NO$_2$ sensing behavior of non-structured In$_2$O$_3$ and ordered mesoporous In$_2$O$_3$ under 400 nm UV-LED irradiation at different temperatures and proposed a new sensing model for the observed data. The response of the illuminated sensors to 5 ppm NO$_2$ for non-structured In$_2$O$_3$ and ordered mesoporous In$_2$O$_3$ at 25 °C were 1.5 and 1.9 respectively, while at 45 °C the responses increased to 1.9 and 4.4. At higher temperatures (100 °C < T < 200 °C), the responses were lower in the illuminated case, meaning that thermal activation that leads to an increase of free charge carriers in the conduction band, superimposes the effect of the photo-activation. The study suggested that 100 °C is the best operating temperature in accordance with the measured sensitivities of the mesoporous In$_2$O$_3$ (37.8 @ 100°C) and non-structured In$_2$O$_3$ (2.3@100°C).

Table 2-4: A summary of the development techniques and performances of In$_2$O$_3$ gas sensors activated by conventional UV lamp sources to various gases at room temperature

<table>
<thead>
<tr>
<th>Material</th>
<th>Target gas</th>
<th>Method</th>
<th>Gas Concentration</th>
<th>Sensing performance</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>In$_2$O$_3$</td>
<td>CO, NO$_2$</td>
<td>Sputtering</td>
<td>CO 100-200 ppm</td>
<td>0.63 for 100 ppm</td>
<td>[32]</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>NO$_2$ 1-3 ppm</td>
<td>16 for 1 ppm</td>
<td></td>
</tr>
<tr>
<td>In$_2$O$_3$/</td>
<td>NO$_2$</td>
<td>Structure replication</td>
<td>5 ppm NO$_2$</td>
<td>2.5 @ 100 °C</td>
<td>[47][92]</td>
</tr>
<tr>
<td>Mesoporous In$_2$O$_3$</td>
<td></td>
<td>procedure</td>
<td></td>
<td>(non-structured)</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>45 @ 100 °C</td>
<td>(mesoporous)</td>
</tr>
</tbody>
</table>
2.3.5 Composite Semiconductor Photo-activated Sensors

The multi-compositional semiconductors by addition of a secondary component oxide (semiconductor composites) are applicable to develop active gas sensors. The influence of nano-composite material is mainly through increasing adsorption capability by injecting more electrons into the active surface as well as reducing the rate of recombination. The logic of this approach mainly relies on the fact that synergetic effects of combining various gas sensing materials is a promising way to achieve selective and sensitive gas detection. It actually can prevent grains to grow in calcination processes [93] and thus can enhance the sensor performance when the grain sizes are comparable with or smaller than twice of the thickness of the depletion layer [94]. Figure 2-8 represents the electrical structure and electron/hole displacements in a composite material consisting of two semiconductors with different band-gaps.

Figure 2-8: Electrical structure of composite materials

Since coupling a wide band-gap semiconductor with a narrow one makes more negative conduction band level at the hetero-interfaces, it can control the charge transfer and enhance the sensitivity [95]. The numerous benefits of nanocomposites have motivated researches to put efforts on the development of
new composite materials. Several composites that have been introduced in the literature for gas sensing applications (thermo-activated) include: SnO$_2$/ZnO [96], SnO$_2$/In$_2$O$_3$ [95,97], SnO$_2$/Zn$_2$SnO$_4$ [98], SnO$_2$/NiO [99], SnO$_2$/Co$_3$O$_4$ [100], Fe$_2$O$_3$/In$_2$O$_3$ [101], Fe$_2$O$_3$/SnO$_2$ [102], and In$_2$O$_3$/ZnO [103–105]. However, there are a few reports on photo-activated composite semiconductor sensors operating at room temperature. Table 2-5 shows the studies in the literature on photo-activated metal oxide semiconductor composites using conventional UV lamps. are described below.

In terms of the studies on UV-LED activated composite semiconductor gas sensors, Sun et al.[106] used a commercial UV-LED with the power of 0.7 Cd/m$^2$ to examine the photo-activated sensing behavior of SnO$_2$–TiO$_2$ hollow spheres to 100 ppm ethanol. A 400 nm Aluminum layer was coated at the backside of the quartz substrate as reflector to enhance the sensing performance. The results with and without reflector in different thicknesses of sensing layer at room temperature and 10% relative humidity confirmed the positive effect of the reflector in sensing responses. For the sensor attached with reflector, the maximum response was 160 while it was more selective to ethanol compared to other test gases (CO, H$_2$S, NH$_3$). The reflector enhanced the photon utilization ratio and provided faster response and recovery rates. The critical sensing layer thickness to have the maximum response was reported 26.5 µm, because of optimum numbers of active sites, while low responses of thinner and thicker thicknesses contribute to the limited active sites and penetrating prevention for ethanol molecules, respectively.

Lu et al. [107] presented a work based on sensing layers of ZnO/SnO$_2$ composite materials synthesized by hydrolyzing Tin (II) chloride on ZnO nanorods for NO$_2$ gas detection at room temperature. UV-LEDs with 380 nm peak wavelength and 0.7 Cd/m$^2$ power (measured at the operated distance of 2 mm) were employed in this research. The authors conducted the experiments in a static test system and measured the responses of sensor at various relative humidities. The results of varied molar ratio of ZnO to SnO$_2$, indicated that the molar ratio of 1:1 gives the maximum response which is considerably higher than those
of pristine samples of ZnO and SnO$_2$. The response of the sensor with molar ratio 1:1 to 500 ppb NO$_2$ reported to be 1000, while the response of the sample with 1:2 ZnO to SnO$_2$ molar ratio was approximately 4.5 under UV illumination. ZnO nanorods were suggested to act as active light absorption centers whereas SnO$_2$ nanoparticles increase surface area and chemisorption ability, favoring electrons to flow from ZnO nanorods to SnO$_2$ nanoparticles.

Single-walled carbon nanotubes (SWCNT) are expected to be compatible with integrated circuits and have extremely high sensitivity and fast response at relatively lower temperatures in chemical gas detection systems [108]. Ueda et al. [109] studied on (SWCNTs)/TiO$_2$ hybrid gas sensors operated at room temperature to detect various concentrations (50–100 ppb) of NO gas. They aimed to use SWCNTs attached with photocatalytic TiO$_2$ particles to extract or decompose the target gas molecules under UV-LED irradiation. Therefore, a 377 nm UV-LED (at 5mm distance) was employed to compare the photocatalytic behavior of SWCNT/TiO$_2$ and pure SWCNTs. The prepared SWCNT/TiO$_2$ gas sensors showed high sensitivity of almost 0.09 to 50 ppb NO gas and 0.15 to 100 ppb, which could rapidly recover to its initial value while the SWCNT sensitivity in the latter condition (100 ppb) was only 0.065. The observations showed that the gas sensitivities of the illuminated sensors were lower than that of without illumination, originating from the fact that UV irradiation enhances the desorption process of gas molecules.

Herran et al. [110] presented a CO$_2$ room temperature photo-activated sensor working with BaTiO$_3$–CuO thin films deposited by DC-sputtering technique, utilizing a 465nm UV-LED with 3.8 Cd luminous intensity. They measured the 125 nm thick BaTiO$_3$–CuO layer resistance under different carbon dioxide concentrations (500, 1000, 2000 and 5000ppm) at 40 %RH and found a linear relationship between sensor response and log \{CO$_2$ concentration\}. The highest response of the layer in 5000 ppm CO$_2$ concentration was $2.5 \times 10^{-3}$ where the sensing mechanism was proposed to be based on gas reaction
with the formed surface hydroxyl groups. Karaduman et al. [55] synthesized TiO$_2$/Al$_2$O$_3$ heterojunction samples (Al/TiO$_2$/Al$_2$O$_3$/p-Si) by atomic layer deposition method to use in CO$_2$ sensors. A 361 nm UV-LED was utilized to detect different CO$_2$ gas concentrations from 5 to 25 ppm at room temperature. The sensor sensitivity to 5 ppm CO$_2$ and 20 ppm NO$_2$ gas was reported to be 0.3 and 0.11, respectively [54].

Further, to explore new sensing materials, Giberti et al. [111] fabricated a photo-activated sensor of 25 µm layer of nanostructured WO$_3$ by screen printing method and tested the performance in dark and under 397 nm UV-LED illumination. The responses and preparation techniques of different photo-activated composite gas sensors operating under conventional UV-lamp irradiation are listed in Table 2-5.

<table>
<thead>
<tr>
<th>Material</th>
<th>Target gas</th>
<th>Method</th>
<th>Gas Concentration</th>
<th>Sensing performance</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>SnO$_2$/ZnO</td>
<td>NO$_2$</td>
<td>Thermal</td>
<td>1-5 ppm</td>
<td>6.2 @ 5 ppm</td>
<td>[112]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Evaporation/ALD</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bi$_2$O$_3$/ZnO</td>
<td>NO$_2$</td>
<td>Thermal</td>
<td>1-5 ppm</td>
<td>6.1 @ 5 ppm</td>
<td>[113]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Evaporation/ALD</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BaTiO$_3$/CuO</td>
<td>CO$_2$</td>
<td>RF Sputtering</td>
<td>500-5000 ppm</td>
<td>$2 \times 10^{-3}$</td>
<td>[23]</td>
</tr>
<tr>
<td>ZnO/WO$_3$</td>
<td>H$_2$</td>
<td>Thermal</td>
<td>200-1000 ppm</td>
<td>6.45 @ 1000 ppm</td>
<td>[114]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Evaporation/Sputtering</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>ZnO/TiO$_2$</td>
<td>Ethanol</td>
<td>Thermal</td>
<td>50.100.200 ppm</td>
<td>1.8 @ 200 ppm</td>
<td>[115]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Evaporation/Solution</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SnO$_2$/GaN</td>
<td>Alcohol</td>
<td>Epitaxy/Sputtering</td>
<td>500 ppm</td>
<td>1.65% to methanol</td>
<td>[116]</td>
</tr>
<tr>
<td>NiO/ZnO</td>
<td>VOC</td>
<td>Sputtering/Vacuum</td>
<td></td>
<td></td>
<td>[117]</td>
</tr>
</tbody>
</table>
In summary, depending on the sort of the facility and the operating conditions, one of the MOS gas sensors must be selected. In order to be able to select the appropriate sensor for a particular gas, we have listed the previously described UV-LED based sensors in Table 2-6 and Table 2-7, organized by the type of the gas to be detected, and reported the preparation routes, as well as the specifications of the UV sources. This information can be utilized to select an appropriate option for a specific gas, depending on the conditions.
Table 2-6: A summary of gas sensing properties of different metal oxide semiconductors towards reducing gases under UV-LED radiation

<table>
<thead>
<tr>
<th>Gas</th>
<th>Material</th>
<th>Method</th>
<th>Conc.</th>
<th>UV Source</th>
<th>Wavelength (nm)</th>
<th>Irradiance</th>
<th>Sensitivity</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>H₂</td>
<td>Thin Film ZnO</td>
<td>Sol-Gel</td>
<td>100 ppm</td>
<td>UV-LED</td>
<td>400</td>
<td>0.1</td>
<td>[49]</td>
<td></td>
</tr>
<tr>
<td></td>
<td>ZnO Nanolines</td>
<td>Sol-Gel</td>
<td>100 ppm</td>
<td>UV-LED</td>
<td>400</td>
<td>0.2</td>
<td>[49]</td>
<td></td>
</tr>
<tr>
<td></td>
<td>100 nm Wide Line ZnO</td>
<td>Sol-Gel</td>
<td>100 ppm</td>
<td>UV-LED</td>
<td>400</td>
<td>1.2</td>
<td>[67]</td>
<td></td>
</tr>
<tr>
<td>Alcohol</td>
<td>Ethanol</td>
<td>ZnO Nano-Particulates</td>
<td>Drop Casting</td>
<td>10 ppm</td>
<td>400</td>
<td>1.5 mW/cm²</td>
<td>0.85</td>
<td>[63]</td>
</tr>
<tr>
<td></td>
<td>Thin Film ZnO</td>
<td>Spin-Coating</td>
<td>5 ppm</td>
<td>UV-LED</td>
<td>365</td>
<td>0.47</td>
<td>[66]</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Thick Film TiO₂</td>
<td>Screen Printing</td>
<td>100 ppm</td>
<td>UV-LED</td>
<td>365</td>
<td>3.6 mW/cm²</td>
<td>1700</td>
<td>[118]</td>
</tr>
<tr>
<td></td>
<td>Thick Film ZnO</td>
<td>Screen Printing</td>
<td>100 ppm</td>
<td>UV-LED</td>
<td>365</td>
<td>3.6 mW/cm²</td>
<td>224</td>
<td>[118]</td>
</tr>
<tr>
<td></td>
<td>Pd-SnO₂</td>
<td>Hydrolysis</td>
<td>100 ppm</td>
<td>UV-LED</td>
<td>365</td>
<td>480 mw/cm²</td>
<td>9.2</td>
<td>[88]</td>
</tr>
<tr>
<td></td>
<td>SnO₂-TiO₂ (Reflector)</td>
<td>---</td>
<td>100 ppm</td>
<td>UV-LED</td>
<td>400</td>
<td>0.7 cd/m²</td>
<td>160</td>
<td>[106]</td>
</tr>
<tr>
<td>Mehanol</td>
<td>Thin Film ZnO</td>
<td>Spin-Coating</td>
<td>5 ppm</td>
<td>UV-LED</td>
<td>365</td>
<td>1.1</td>
<td>[66]</td>
<td></td>
</tr>
<tr>
<td>Butanol</td>
<td>Thin Film ZnO</td>
<td>Spin-Coating</td>
<td>5 ppm</td>
<td>UV-LED</td>
<td>365</td>
<td>0.44</td>
<td>[66]</td>
<td></td>
</tr>
<tr>
<td>Methane</td>
<td>ZnO Nano-Particulates</td>
<td>Drop Casting</td>
<td>100 ppm</td>
<td>UV-LED</td>
<td>400</td>
<td>2.2 mW/cm²</td>
<td>0.25</td>
<td>[63]</td>
</tr>
</tbody>
</table>
Table 2-6: A summary of gas sensing properties of different metal oxide semiconductors towards reducing gases under UV-LED radiation – Continued

<table>
<thead>
<tr>
<th>Gas</th>
<th>Material</th>
<th>Method</th>
<th>Conc.</th>
<th>UV Source</th>
<th>Wavelength (nm)</th>
<th>Irradiance</th>
<th>Sensitivity</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Propane</td>
<td>ZnO Nano-Particulates</td>
<td>Drop Casting</td>
<td>100 ppm</td>
<td></td>
<td>400</td>
<td>2.9 mW/cm²</td>
<td>0.7</td>
<td>[63]</td>
</tr>
<tr>
<td>Hexane</td>
<td>ZnO Nano-Particulates</td>
<td>Drop Casting</td>
<td>10 ppm</td>
<td></td>
<td>400</td>
<td>3 mW/cm²</td>
<td>2</td>
<td>[63]</td>
</tr>
<tr>
<td>Formaldehyde</td>
<td>TiO$_2$</td>
<td>Screen Printing</td>
<td>100 ppm</td>
<td>UV-LED</td>
<td>365</td>
<td>3.6 mW/cm²</td>
<td>10000 dry</td>
<td>4.5@18.24</td>
</tr>
<tr>
<td></td>
<td>TiO$_2$ Nanotube</td>
<td>Anodization</td>
<td>50 ppm</td>
<td>UV-LED</td>
<td>365</td>
<td>4 mW</td>
<td>90</td>
<td>[81]</td>
</tr>
<tr>
<td></td>
<td>Mesoporous Hollow TiO$_2$</td>
<td>Hydrothermal</td>
<td>5 ppm</td>
<td>UV-LED</td>
<td>365</td>
<td>2.5 mW</td>
<td>40</td>
<td>[82]</td>
</tr>
<tr>
<td></td>
<td>Thick Film TiO$_2$</td>
<td>Screen Printing</td>
<td>100 ppm</td>
<td>UV-LED</td>
<td>365</td>
<td>3.6 mW/cm²</td>
<td>220</td>
<td>[118]</td>
</tr>
<tr>
<td></td>
<td>Thick Film ZnO</td>
<td>Screen Printing</td>
<td>100 ppm</td>
<td></td>
<td>365</td>
<td>3.6 mW/m²</td>
<td>1.4</td>
<td>[118]</td>
</tr>
<tr>
<td>Acetone</td>
<td>ZnO Nanorods</td>
<td>RF Sputtering</td>
<td>100 ppm</td>
<td>UV-LED</td>
<td>365</td>
<td>2.2 mW</td>
<td>1.34</td>
<td>[60]</td>
</tr>
<tr>
<td></td>
<td>ZnO Thick Films</td>
<td>Drop Coating</td>
<td>700 ppm</td>
<td>UV-LED</td>
<td>400</td>
<td></td>
<td>0.15</td>
<td>[65]</td>
</tr>
<tr>
<td></td>
<td>Ni-ZnO Nanorods</td>
<td>RF Sputtering</td>
<td>100 ppm</td>
<td>UV-LED</td>
<td>365</td>
<td>2.2 mW</td>
<td>1.61</td>
<td>[60]</td>
</tr>
</tbody>
</table>
Table 2-7: A summary of gas sensing properties of different metal oxide semiconductors towards oxidizing gases under UV-LED radiation

<table>
<thead>
<tr>
<th>Gas</th>
<th>Material</th>
<th>Method</th>
<th>Conc.</th>
<th>UV Source</th>
<th>Wavelength (nm)</th>
<th>Irradiance</th>
<th>Sensitivity</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO₂</td>
<td>100 nm Wide Line ZnO</td>
<td>Sol-Gel</td>
<td>20 ppm</td>
<td>UV-LED</td>
<td>400</td>
<td>0.83</td>
<td>[67]</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Thin Film ZnO</td>
<td>Spin-Coating</td>
<td>5 ppm</td>
<td>UV-LED</td>
<td>365</td>
<td>0.08</td>
<td>[66]</td>
<td></td>
</tr>
<tr>
<td></td>
<td>SnO₂ Nanowires</td>
<td>CVD</td>
<td>10 ppm</td>
<td>UV-LED</td>
<td>338</td>
<td>0.8</td>
<td>[50]</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Mesoporous In₂O₃</td>
<td>Structure-Replication</td>
<td>5 ppm</td>
<td>UV-LED</td>
<td>400</td>
<td>1.9</td>
<td>[91]</td>
<td></td>
</tr>
<tr>
<td></td>
<td>ZnO/SnO₂</td>
<td>Hydrolyze</td>
<td>500 ppb</td>
<td>UV-LED</td>
<td>380</td>
<td>0.7 Cd/m²</td>
<td>1000 (Static)</td>
<td>[107]</td>
</tr>
<tr>
<td></td>
<td>Al/TiO₂/Al₂O₃/P-Si</td>
<td>ALD</td>
<td>20 ppm</td>
<td>UV-LED</td>
<td>361</td>
<td>0.11</td>
<td>[119]</td>
<td></td>
</tr>
<tr>
<td>NO</td>
<td>SWCNT/TiO₂</td>
<td>PLA</td>
<td>50 ppb</td>
<td>UV-LED</td>
<td>377</td>
<td>0.09</td>
<td>[109]</td>
<td></td>
</tr>
<tr>
<td>O₃</td>
<td>ZnO</td>
<td>Precipitation</td>
<td>70 ppb</td>
<td>UV-LED</td>
<td>397</td>
<td>0.25 W/cm²</td>
<td>1.35</td>
<td>[64]</td>
</tr>
<tr>
<td></td>
<td>One-Dimensional ZnO Nanorods</td>
<td>Hydrothermal</td>
<td>100 ppb</td>
<td>UV-LED</td>
<td>351</td>
<td>0.6</td>
<td>[69]</td>
<td></td>
</tr>
<tr>
<td></td>
<td>SnO₂</td>
<td>RF Sputtering</td>
<td>10 ppm</td>
<td>UV-LED</td>
<td>370</td>
<td>1710 µw</td>
<td>1.3</td>
<td>[120]</td>
</tr>
<tr>
<td></td>
<td>Output</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SO₂</td>
<td>Thin Film ZnO</td>
<td>Spin-Coating</td>
<td>10 ppm</td>
<td>UV-LED</td>
<td>365</td>
<td>0.38</td>
<td>[66]</td>
<td></td>
</tr>
</tbody>
</table>
Table 2-7: A summary of gas sensing properties of different metal oxide semiconductors towards oxidizing gases under UV-LED radiation – Continued

<table>
<thead>
<tr>
<th>Gas</th>
<th>Material</th>
<th>Method</th>
<th>Conc.</th>
<th>UV Source</th>
<th>Wavelength (nm)</th>
<th>Irradiance</th>
<th>Sensitivity</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO</td>
<td>ZnO Nanowires</td>
<td>Selective Chemisorption Method</td>
<td>40 ppm</td>
<td>UV-LED</td>
<td>354</td>
<td>900 (N₂ Carrier)</td>
<td>[68]</td>
<td></td>
</tr>
<tr>
<td>CO₂</td>
<td>BaTiO₃–CuO</td>
<td>DC-Sputtering</td>
<td>5000 ppm</td>
<td>UV-LED</td>
<td>465</td>
<td>3800 mCd</td>
<td>2.5 × 10⁻³</td>
<td>[23]</td>
</tr>
<tr>
<td></td>
<td>Al/TiO₂/Al₂O₃/P-Si</td>
<td>ALD</td>
<td>5 ppm</td>
<td>UV-LED</td>
<td>361</td>
<td>0.3</td>
<td>[55]</td>
<td></td>
</tr>
<tr>
<td>SnO₂–TiO₂(Reflector)</td>
<td>---</td>
<td>100 ppm</td>
<td>UV-LED</td>
<td>400</td>
<td>0.7 Cd/m²</td>
<td>2</td>
<td>[106]</td>
<td></td>
</tr>
</tbody>
</table>
2.4 Conclusion

Metal oxide semiconductors, activated by UV-LEDs have shown to be promising alternatives for conventional high temperature gas sensors. UV-LEDs can be integrated into chemi-resistive gas sensors to produce low cost, small size, sensitive sensors that are able to operate at room temperature and to be integrated into micro-electronic technology. In this study, to realize the fundamentals of sensing process, possible mechanisms and a number of practical issues of photo-activated gas sensors were discussed in details. Subsequently, the performances, preparation techniques, and most influential factors of several metal oxide semiconductor photo-activated gas sensors under UV-LEDs were presented. The effects of temperature, irradiance, humidity and sensor configurational design on the sensing performance were reported. It was shown that for the UV-LED based gas sensors, the selectivity can be tuned by adjusting appropriate irradiance, and the performance can be improved by manipulating the sensor platform design and the sensitivity can be enhanced by increasing operating temperature to an optimal value or modifying semiconductor layer structure. Given their advantages, UV-LED activated semiconductors are expected to play a significant role in the future of gas sensing devices.
Chapter 3: A Comparative Study on Thin Film ZnO and In$_2$O$_3$ Properties in Photo-activated Gas Sensing Application

3.1 Introduction

ZnO and In$_2$O$_3$ semiconductors are very well recognized for their promising sensing performances in various oxidizing and reducing gas detection systems due to their prominent features such as chemical stability, versatility, possibility for doping and low cost. They have been extensively studied in thermo-activated chemi-resistive sensors operating usually between 200 °C to 500 °C [56]. However, the high operating temperature adversely affects the stability, economic aspects and useful lifetime of the sensors as well as limits technical applicability in environments containing explosive gases [26,28]. A few reports have been introduced to the literature recently indicating the possibility of employing UV illumination to increase the sensing performance and lower the operating temperature [32,92,107]. It has been proposed that the selectivity can be tuned by selecting an appropriate UV intensity and wavelength [31]. The preliminary results of SnO$_2$ thick and thin films gas sensing performances studied under UV lamp irradiation were promising towards several oxidizing gases such as NO$_2$ [31,32,34]. Since then, several UV-based gas sensors were developed to evaluate the performance of different sensing semiconductor layers at room temperature [27,35–42]. These sensors wholly relied on conventional UV-lamps. However, the newly emerged UV-LEDs, available in wide ranges of emitting power intensities and wavelengths are potentially capable of being applied to produce selective, sensitive, room temperature, environmental friendly and small gas sensors. The progresses that have been made in UV-LED based sensors were discussed in the previous chapter through a review in this area. There have been a few reports in the literature on photo-activated gas sensors employing UV-LEDs as the photon source.
Costello et al. [63] used the newly developed UV-LEDs with shorter wavelengths to study sensing characteristics of thin ZnO nano-particulate layers and to detect hydrocarbon gases at different temperatures, humidities and incident irradiances in the range of 0.36–22 mW/cm² and found that the optimal irradiance to have the maximum sensitivity for any given analyte is grain size dependent. Prades et al. [50] studied wavelength dependency of SnO₂ nanowires for 100 ppb to 10 ppm NO₂ gas using two kinds of UV-LEDs with different photon energies and confirmed that the sensitivity could be changed significantly by using different photon energies/wavelengths. Wagner et al. [91] studied the gas sensing characteristics of two In₂O₃ structures and confirmed that mesoporous In₂O₃ can be employed for NO₂ sensing with high performance at room temperature.

Although several metal oxide semiconductors have been studied to be used in UV-LED based gas sensors, the performance characteristics have not been properly compared. Comparative studies help to select the appropriate sensor material with suitable irradiance for any specific target gas. For instance a comparison of photoactivated ZnO and TiO₂ gas sensing films prepared by screen printing method to detect ethanol and formaldehyde gases in similar conditions under UV-LED irradiation and revealed that TiO₂ responses were much higher than ZnO response values, probably because of differences in the amount of absorbed O²⁻ ions on the surface [118].

In this study, we performed a comparative study on ZnO and In₂O₃ semiconductors, which are commonly used as gas sensing materials, for the detection of low concentrations of NO₂ gas, which greatly contributes to the environmental and human health problems. The intensity of the UV-LED radiation played an important role on the sensitivity and stability of developed sensors and the optimal light irradiance for providing the maximum sensitivity with complete recovery was achieved for the manufactured sensors. Although In₂O₃ showed higher sensitivity to NO₂, faster and more stable behavior was observed for ZnO in all the irradiances.
3.2 Experimental

3.2.1 Sensing Layer Preparation

3.2.1.1 Material Synthesis

All chemicals used were of analytical grade and purchased from Sigma-Aldrich Canada Corporation. Zinc nitrate hexahydrate (Zn(NO$_3$)$_2\cdot 6$H$_2$O), indium nitrate hydrate (In(NO$_3$)$_3\cdot x$H$_2$O) and 2.0 M ammonia (NH$_3$) solution in ethanol (CH$_3$CH$_2$OH) were used as source materials. To gain the pastes suitable for spin coating on the Al$_2$O$_3$ substrate, 0.89 gr of zinc nitrate powders and 0.9 gr of indium nitrate hydrates were dissolved in 100 ml of two separate solutions containing 85% ethanol and 15% methanol. The obtained solutions were vigorously stirred for 30 min at 50 °C in water bath under fume hood. The ammonia solution then added dropwise to zinc and indium containing solutions at the speed of 1 drop/s at the same temperature, while measuring the pH value continuously to reach PH>9. The resulting solutions were then stirred for 4 hours and cooled slowly to room temperature. The obtained solutions containing precipitates of Zn and In nano-particles were used to deposit Zn and In hydroxyl layers over Al$_2$O$_3$ substrate. Deposited materials were calcined at 550 °C afterwards to perform further oxidation. Figure 3-1 represents a schematic illustration of the synthesis process and Figure 3-2 shows the as-prepared materials.
Figure 3-1: Synthesis route of ZnO and In$_2$O$_3$ metal oxide semiconductor materials using precipitation method

Figure 3-2: Synthesized Material powders, A) In$_2$O$_3$, B) ZnO
3.2.1.2 **Electrode Deposition**

Prior to sensing layer deposition, for the electrical measurements, a thin layer of gold was deposited over a ceramic sheet through an interdigitated comb shape shadow mask. The shadow mask was initially designed in AutoCAD and built using laser ablation method. Prior to any deposition, the substrates were cleaned by oxygen ion bombardment using Plasma-Enhanced Chemical Vapor Deposition (PECVD) setup to improve the adhesion of the film to the substrate by removing moisture and any organic contaminants on the surface.

For the deposition, E-Beam Physical Vapour Deposition (EBPVD) method was selected. The 2000 e-beam evaporator system used, was an automated vacuum process control system for Physical Vapour Deposition (PVD) of metals, and non-metals, consisting of a control cabinet, chamber, electron-beam power supply, cryo pump compressor and mechanical vacuum pump. The control cabinet houses a microprocessor, operation control panel, thermocouples gauges controller, Inficon Film thickness monitor, CTI cryo pump temperature monitor and Airco CV8 electron beam control module.

In physical vapor e-beam deposition method, target anode is bombarded with huge numbers of high energy electrons given off by a charged tungsten filament under high vacuum. The electron beam causes atoms to transfer from the target into the gaseous phase. These atoms then precipitate into solid form, coating everything inside the vacuum chamber with a thin layer of the anode material. Multiple types of materials can be used simultaneously in a single EBPVD system in designated source areas. Figure 3-3 shows how the e-beam process works to deposit thin layers of target materials.

To further explain the deposition sequence, the chamber was evacuated to a pressure better than $5 \times 10^{-5}$ Torr. Then the e-beam gun bombarded the targets to evaporate materials to reach to the desired thickness measured by quartz crystal thickness measurer continuously in real time. Details of the setup are shown in the pictures in Appendix A.
In this study, a thin layer of titanium with the thickness of 25 nm was firstly deposited to enhance the stability and adhesion strength of the gold materials. Then 385 nm of gold thin layers were deposited over titanium using a pure gold target as the source. All thickness measurements were certified by ex-situ characterization using ALPHA STEP 200 Profilometer. The width, spacing, and length of deposited interdigitated electrodes are shown in Figure 3-4.
3.2.1.3 Material Deposition

Several deposition techniques including solution impregnation deposition, drop casting and spin coating were used to deposit the prepared materials on the substrate. However, stable, consistent and reproducible results were only observed from the sensing layer prepared by spin coating method. Further to explain the deposition process, a known amount of solution (5 ml) was taken by a pipet and poured dropwise over the substrate while rotating at 500 rpm. Then, the rotating speed was set to 3000 rpm to dry the layer in each stage of development. This process was repeated 10 times followed by a 3 min heating at 80 °C at the middle of coating to let the trapped water evaporate. Then obtained thin film was calcined at 550 °C for 2 hours. Figure 3-5 shows the deposition steps of prepared semiconductor layers.
3.2.1.4 Characterization

To investigate the morphology, particle size and nano-structure of compounds on the surface, two level scanning electron microscopy has been performed. The Hitachi S3000N VP-SEM which is a conventional tungsten hairpin filament source SEM machine, was initially used to check the material deposition patterns and nano-prototype imaging after each synthesis process. The FEI Helios NanoLab 650 dual beam SEM machine was then employed to perform high resolution imaging and nano-structure analysis.

In order to investigate the surface topography, composition of the prepared sensor layers and surface elements, X-ray photoelectron spectroscopy (XPS) was performed. Energy-dispersive X-ray (EDX) spectroscopy was utilized to characterize the chemical composition as well as measure elemental containments. Crystal structure of prepared samples and the atomic structure diffraction patterns were
obtained in X-ray Diffraction (XRD) analysis. The structural properties were investigated by 20 method of XRD with a Cu Kα1 (λ = 0.15406 - λ = 0.154439nm) source at 40 kV and 40 mA.

At the end, to certify the UV wavelengths used in the experiments as well as the photo-reduction behaviour of sample layers, UV-Visible Spectroscopy analysis were carried out over the samples, which gives the relevant absorbance/reflectance spectrum depending on the semiconductor band-gap.

3.2.2 Gas Sensing Measurements

To evaluate the performance of the developed materials as gas sensor, they were placed in the setup specifically designed for this purpose. The setup provides the opportunity to expose the sensor to the exact amount of target gas concentration as well as adjusting other parameters involved in the sensing process such as photons irradiance. The experimental setup was made of three parts, each is in charge of a specific task. Channeling part, chamber and electric part for the resistance measurements including LabView controller are three major parts of the system. Each sensing experiment was repeated at least two times to make sure that the data are reproducible. The schematic illustration of the setup, implemented for this purpose is shown in Figure 3-6.
3.2.2.1 **Channeling**

This section is consisted of several mass flow controllers to precisely measure and control the flow rates of gases going through the chamber (Figure 3-7). Channeling board adjusts the flow rates of different gases and mixing them at specific ratios to obtain the desired concentration for the process. To fully mix gases, a pressurized cylinder is accommodated just before the chamber and a needle valve located by the exterior of the cylinder controls the pressure inside. To make setup more flexible for future works such as testing the humidity effects and selectivity of the sensors, three mass flow controllers are placed in line with three stream control valves. Three safety pressure gauges are positioned just before the mass flow controllers to make sure of the flow and that the pressure is not exceeding the maximum allowable operating pressure of MFCs. The third pressure gauge mounted at the top of pressurized cylinder determines and controls the pressure inside the cylinder.
3.2.2.2 **Reaction Chamber**

The reactor chamber which expose the materials, gases and photons to each other is presented in Figure 3-8. The stainless steel gas-testing chamber is the house of the electrical connectors and wires and needs to be sealed. Chamber design is also very important to ensure that the whole surface, receives adequate irradiation from the UV source and is fully exposed to the transient gas. Before each test, the sensors were heated and blown with dry air for 2 hours to remove moisture or any adsorbed molecules from last experiments from the surface. Purified air was used at a constant flow rate of 0.200 liters per minute to stabilize the sensors before the measurements. The sensors were then exposed to a known concentration of the target gas (for ~500 s) to reach to a stable point in resistance for each gas sensing experiment. The sensors were recovered then by exposing to purified air till the resistance returns to its initial value. The gas concentrations 5, 10, 20, 40 and 100 ppm were measured in these experiments.
3.2.2.3 **Data Acquisition**

For the sensing measurements, the resistances of various sensor layers were continuously monitored. The electrical characterization was carried out by volt-amperometric technique in which the sensors were biased by 5 V and film resistance was measured over time. The electrical measurements were carried out using Keithley digital 6487 Voltage source picoameter. The designated built-in power source in the instrument makes more accurate and more stable current. A LabView code was written to control the whole process remotely. The developed code was able to measure the resistance by the rate of 1000 readings/s. Due to the small current flow in the circuit, standard insulate cables were used to connect sensor electrodes to the multimeter. Figure 3-9 shows a schematic illustration of the implemented electrical circuit.
For a proper sensing performance in UV based gas sensors, exposure to the right wavelength at the right intensity for a sufficient amount of time is required. The newly emerged UV-LEDs provide the opportunity to fully control the important parameters as well as reduce the energy consumption in photo-activated gas sensors. It has been reported that using photons with higher energies would result in having higher responses and shorter recovery time constants due to an improvement in semiconductor activity because of faster kinetics [66].

Two types of high power 365 nm LEDs were used for the experiments, one with 2750 mW total power and the other with 690 mW power. The power of UV-LEDs was adjusted by controlling the operating current. The actual incident irradiances which used for sensing measurements were measured by optical spectroscopy.

**3.2.2.4 UV-LED**

![Figure 3-9: Electrical Measurements in Gas Sensor Setup](image)

Figure 3-9: Electrical Measurements in Gas Sensor Setup
Air cooling is necessary for long period usage of LEDs since high temperature could destroy UV-LEDs or reduce their efficiency and output power. Thermo Electric Cooler (TEC) attached to a circular heatsink with a fan was used to control the UV-LED temperature in the experiments. A separate adjustable voltage/current power supply was in charge of UV-LED system power demand. The 4 digit adjustable power supply made the experiments more accurate. The output UV intensity was adjusted by changing the current going through the LED from 0.1 to 1.2A.

An important concern of UV-LEDs employed in the system was the actions that needed to be taken to prevent water vapor condensation on UV source due to over-cooling of TEC, which reduces the useful and effective photons irradiance that reaches to the surface. In other words, TEC which is required for lowering the LED temperature is sometimes causing to form water droplets on PCB. The produced droplets could possibly play as a barrier for passing photons. To prevent forming water droplets in conducted experiments, a Step-Down board was used to regulate the TEC voltage in such a way that the PCB temperature be anywhere between 10-30 °C. Table 3-1 shows a summary of specifications of the UV-LEDs used in the setup.

Table 3-1: A summary of specifications of the UV-LEDs used in the research

<table>
<thead>
<tr>
<th>Specification Model</th>
<th>Manufacturer</th>
<th>Wavelength (nm)</th>
<th>Lens</th>
<th>Total Radiant Power (mW)</th>
<th>View Angle $2 \theta _{1}/2$ (°)</th>
<th>Appearance</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1) CUN6AF1B</td>
<td>Seoul Semiconductor</td>
<td>365</td>
<td>Flat</td>
<td>690</td>
<td>110</td>
<td></td>
</tr>
<tr>
<td>(2) CUN6AF4A</td>
<td>Seoul Semiconductor</td>
<td>365</td>
<td>Flat</td>
<td>2750</td>
<td>116</td>
<td></td>
</tr>
</tbody>
</table>
3.3 Results and Discussion

3.3.1.1 Morphology and Crystal Structure

Figure 3-10 shows the variable length ZnO particles randomly oriented in the form of a porous mat. It seems that the morphology, and the films have crystalline structure with average grain size less than 100 nm.

The FEI SEM images are presented in Figure 3-11, showing more or less agglomerated ZnO particles (top-view and side-view) with distinguishable boundaries, connected to each other. According to the images, the morphology of the nano-sized ZnO particles are mainly in pseudo-spherical shapes and the average grain size of ZnO is about 40 nm.
The representative SEM photographs of In$_2$O$_3$ nano-particulates (In$_2$O$_3$ clusters) that appear as the product of ammonia and indium nitrate reaction are presented in Figure 3-12. Comparing to the ZnO film (Fig. 3-11), surface of the In$_2$O$_3$ film was much smoother with possibly smaller crystallites and mostly without distinguishable grain boundaries (Figure 3-13). The particles are stacked on each other, forming a unified structure. The average grain size of In$_2$O$_3$ particles is estimated to be 10-15 nm.
Figure 3-12: SEM images of as-prepared In$_2$O$_3$ sensing layers

Figure 3-13: FE-SEM images of prepared In$_2$O$_3$ nano-particulates
To analyze the material structure, crystallinity and the components that are present in the samples, XRD analysis was performed. Figure 3-14 shows the XRD patterns of nano-sized ZnO particles obtained from the calcination of precipitates at 400 °C and 550 °C for 2h. The peaks located at 31.76, 34.42 and 36.25 are representing preferable 100, 002 and 101 crystalline shapes ZnO, respectively, and addressing wurtzite phases [121,122]. Regardless of the upward shift in the background due to the carbon structure formations in the samples originated from the ethanol solution used in the synthesis process, no diffraction peaks related to the possible impurities were observed in the XRD pattern, confirming the high purity of the ZnO samples. Furthermore, the intense and narrow peaks are representing a good crystalline nature as well as the existence of pure phases of the ZnO materials.

Additionally, as the crystallite size gets smaller, the peak gets broader. Therefore the natural configuration of diffraction peaks in ZnO sample was calcined at 400 °C with their high intensities and wider bottoms denotes that the crystalline sizes were relatively small. This observation is in good agreement with the nano-sized particles characteristics reported in the literature [123]. As the calcination temperature increases to 550 °C the peaks intensity rises and the peaks bottom tends to be narrower, representing better crystallinity of the material and bigger crystalline size. According to the Scherrer equation, the peak width is inversely proportional to the crystallite size:

\[ B(2\theta) = \frac{K\lambda}{L\cos\theta} \quad \text{Equation 3-1} \]

where L is the crystalline size (in nm), \(\lambda\) is the wavelength in the diffraction angle, B is the full width at half maximum (FWHM in radian) and \(\theta\) is the Bragg diffraction angle. The constant of proportionality, K (the Scherrer constant), depends on the width determination method, the shape of the crystal, and the size distribution. The most common value of K for spherical crystals and cubic symmetry is 0.89 [121].
Thus the average crystallite size in prepared samples was calculated as approximately 29 nm and 34 nm for ZnO samples calcined at 400 °C and 550 °C respectively for all phases.

![XRD plot of prepared ZnO samples at different synthesis temperatures with corresponding crystalline planes for each diffraction peak](image)

Figure 3-14: XRD plot of prepared ZnO samples at different synthesis temperatures with corresponding crystalline planes for each diffraction peak

For the In₂O₃ nano-particles XRD plot, shown in Figure 3-15, the phase purity was evident and all peaks could be indexed to pure particles of calcined In₂O₃ samples. XRD analysis suggests that the crystallinity was enhanced for In₂O₃ calcined at 550 °C. Using the Scherrer equation, the average crystalline size was approximately 12 nm for all crystalline orientations for In₂O₃ calcined at 550 °C and 10 nm for In₂O₃ calcined at 400 °C.
Therefore, the crystallinity of the surface can be changed by controlling the calcination temperature and synthesis temperature condition (i.e. bath temperature). Indeed, the calcination temperature is proportional to the crystallinity and average particle size of the prepared samples.

Figure 3-15: XRD image of prepared In$_2$O$_3$ samples

The overall results indicated that precipitation method is an effective strategy for nano-sized ZnO and In$_2$O$_3$ synthesis and is very well repeatable and controllable technique. The films fabricated by spin coating are also suitable for gas sensing applications because of the porous structures. Since the preliminary results of the samples calcined at 550 °C were better than those of 400 °C, the gas sensing measurements performed on the well-crystalline samples that were calcined at 550 °C.
3.3.1.2 **Optical Properties of Sensing Materials**

Optical analysis of thin films is a useful method to understand the quality, thickness, optical properties such as band-gap, and dielectric constants of deposited materials. In this analysis, the reflectance/absorbance spectra are investigated in 200-900 nm spectral range. These data are confirmed by repeating the measurements several times. Kubelka—Munk theory is used to theoretically estimate the absorbance of thin films from reflectance measurements [124]. A Band gap analysis is performed for the as-prepared materials using Tauc plot. Tauc plot is a convenient way of displaying the optical absorption spectrum and is used to determine the optical band gap in semiconductors.

The absorbance spectra of materials can explain the contribution of optical properties in the sensing activity. Figure 3-16 shows the Tauc plot of spin coated materials. Using the plotted results, the calculation procedure for determining band gap is explained as follows:

1) The following expression which is proposed by Tauc, Davis, and Mott is used to calculate the band-gap

\[(hν.α)^{\frac{1}{n}} = A(hν − Eg)\]  
Equation 3-2

Where, \(h\) is Planck's constant, \(ν\) is frequency of vibration, \(α\) is absorption coefficient, \(E_g\) is band gap and \(A\) is a proportional constant. The value of the exponent \(n\) denotes the nature of the sample transition, for direct allowed transition \(n=1/2\) is used.

2) The acquired diffuse reflectance spectrum is converted to relative absorbance spectrum using Kubelka-Munk function. The vertical axis containing the absorption coefficient is somehow related to reflectance data.

\[A = kα(λ) = k \frac{(1−R)}{2R}\]  
Equation 3-3
Where A and R are the absorbance and reflectance spectral data respectively, k is proportional constant and α is absorbance coefficient.

3) The wavelength λ (nm) is converted to hν by the following equation. Using Kubelka-Munk function, \((hν\alpha)^2\) is plotted against the hν.

\[ hν = \frac{1239.7}{λ} \quad \text{Equation 3-4} \]

4) A line is drawn tangent to the point of inflection on the curve and the hν value at the point of intersection of the tangent line and the horizontal axis is the band gap \((E_g)\) value. Note that the point of inflection is found by taking the first derivative of the curve.

By using the aforementioned equations, the ZnO band-gap was estimated to be 3.2 eV while \(\text{In}_2\text{O}_3\) band gap was 3.42 eV which are in good agreement with those reported in the literature [125,126].

![Figure 3-16: UV-Vis spectra of ZnO and In2O3 samples prepared by spin coating method](image)

Figure 3-16: UV-Vis spectra of ZnO and In\(_2\)O\(_3\) samples prepared by spin coating method
3.3.2 UV Activated Gas Sensing Performance

The ability of a sensor to detect chemicals in air is what ultimately determines its application. In this section the performance of different fabricated sensors are evaluated towards NO\textsubscript{2}. Sensitivity, response time and stability are three major factors that shows how well a gas sensor device is working. The sensitivity addresses the maximum change in relative resistance of thin films at different conditions. It’s defined as the difference between the thin film resistance when it’s exposed to the target gas and when it’s in pure air normalized by the initial resistance in air. It can also be expressed as percentage sensitivity by multiplying the equation to 100. Equation 3-5 shows the equation which is commonly used for N-type semiconductors in the presence of oxidizing gases:

\[
\Delta R = \frac{R_g - R_a}{R_a}
\]

where \( R_a \) stands for the resistance in pure air and \( R_g \) indicates the resistance of the thin film when it’s exposed to the target gas. Higher sensitivity has always been a factor for a good sensor as it is needed to have more accurate and more sensitive measurements.

Figure 3-17 shows a typical response of a chemi-resistive gas sensor. Initially, the sensor is exposed to the pure air to reach to a stable and constant value in resistance. Then the target gas is introduced to the chamber, resulting in an increase in the resistance due to electrons consumption and physical/chemical adsorption. As the chamber is evacuated from the target gas, the resistance start decreasing to reach to its initial resistance in the presence of pure air. The relevant parameters are shown in the Figure 3-17.
When the sample is irradiated with UV, the conductance rises due to the created electron/hole pairs in the material. As the light is turned on, the current flowing through the thin film increases by about an order of magnitude. The time it takes to reach a stable value after the irradiation is about several seconds and as the irradiation is stopped the recovering time is a few minutes. As it can be noticed, the first time the sample is irradiated, it doesn’t recover to its initial value due to some structural defects in the lattice. In other words, it takes time for the sample to gradually forget the irradiation and return to its first stable value [32]. However the sensor response is subsequently consistent by turning the UV source on and off.

Thus the behaviour has consisted of four characteristic regions:

- A constant layer resistance region in air before UV irradiation
- A rapid resistance decrease upon exposure to UV irradiation,
- A quasi-linear increase under target gas exposure
- A quasi-linear decrease by turning off the target gas exposure

Figure 3-17: Typical sensor response for a MOS gas sensor
In this research, the effect of irradiance and gas concentration on ZnO and In$_2$O$_3$ sensor responses towards low concentrations of NO$_2$ were investigated. The material synthesis and sensing layer depositions performed simultaneously to avoid any possible changes in conditions that may affect fabricated sensors. After successfully fabricating the metal oxide sensors, they were mounted in the chamber and the picoameter wires were connected to designed terminals in order to measure the resistance. The resistance measurements were performed continuously while the sensors were biased by 5V in the room temperature.

3.3.2.1 **Effect of Irradiance**

In addition to the wavelength which indicates the photons energy, the exposure rate or flux of the photons also determines the energy that is received by the surface. Irradiance mostly affects the adsorption/desorption processes in sensing applications resulting in greater/lower reaction rates.
In this study, different irradiances of photons have been presented and the respective results have been evaluated. The irradiances of photons altered by changing the current going through the LEDs in the range of 138 to 1740 mW (total power). Table 3-2 shows an estimation of the actual incident irradiance at 10 cm distance from UV source measured by optical spectrometer. It can be inferred from the results that desorption is depending on the light irradiance in such a way that increasing irradiance will decrease the time constants for desorption, leading to form a saturated surface of generated electrons. The equilibrium reactions are shifted to desorb more ions, leading to have less numbers of active sites for sensing process on the surface.

Table 3-2: Incident irradiance of UV-LEDs at 10 cm distance attributed to different currents

<table>
<thead>
<tr>
<th>UV type</th>
<th>Current (A)</th>
<th>Measured Irradiance (mW/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>UV-LED 1</td>
<td>0.1</td>
<td>1.2</td>
</tr>
<tr>
<td></td>
<td>0.3</td>
<td>1.7</td>
</tr>
<tr>
<td></td>
<td>0.6</td>
<td>2.8</td>
</tr>
<tr>
<td>UV-LED 2</td>
<td>0.65</td>
<td>3.6</td>
</tr>
<tr>
<td></td>
<td>0.9</td>
<td>4.2</td>
</tr>
<tr>
<td></td>
<td>1.2</td>
<td>5</td>
</tr>
</tbody>
</table>

Increasing irradiance, shifts the equilibrium reactions to produce more oxygen gas and desorb more target gas molecules. Therefore, high irradiances facilitate the progressive desorption of all species and results in lowering the number of active sites on the surface and involving less number of electrons, leading to lower resistance variation and lower sensitivity. However, the reaction kinetics becomes faster.
with increasing power, leading to faster responses and lower recovery time. Figure 3-19 shows the effect of irradiance on the sensitivity of the ZnO and In$_2$O$_3$ samples.

![Figure 3-19: Sensitivity analysis of prepared ZnO and In$_2$O$_3$ samples at different irradiances](image)

The results confirm the resistance variations of each sensor type under different incident irradiances. The optimum irradiance is the one for which the sensor provides a good sensitivity, complete recovery, and a reasonable response time. Selectivity can also be taken into consideration to determine the best operating irradiance.

Considering three aforementioned major factors in our gas sensing experiments, the best irradiance for ZnO to have the highest sensitivity and shortest response time while having a complete recovery is 1.2 mW/cm$^2$. However, In$_2$O$_3$ responses failed to recover completely at irradiances lower than 2.8 mW/cm$^2$. Therefore we calculate the optimal light irradiance to be 2.8 mW/cm$^2$ which gives the reasonable response time while having a stable sensor response. At higher irradiances, the sensitivity would decrease due to prevailing desorption process of gas molecules.
To compare the sensing results of In$_2$O$_3$ and ZnO, a representative of sensing performance of prepared ZnO and In$_2$O$_3$ samples towards 5 ppm NO$_2$ at their optimum irradiance has been shown in Figure 3-20.

![Figure 3-20: Typical response of prepared ZnO and In$_2$O$_3$ sensors towards 5 ppm NO$_2$ (at optimum irradiance)](image)

The response time ($\tau_{res}$) is defined as the time that it takes for the sensor to reach from 10% to 90% of its total value. The response time values for each sensor material varies with working irradiance. For ZnO samples, the range of response time variations was observed to be from 166 s at 5 mW/cm$^2$ to 197 s at 1.2 mW/cm$^2$ while complete recovery was observed for all irradiances and relative sensitivities were reported as 0.129 (at 5 mW/cm$^2$) and 0.412 (at 1.2 mW/cm$^2$). Since the differences in response time values were not significant compared to great changes in sensitivities, 1.2 mW/cm$^2$ is suggested to be used as operating irradiance for ZnO towards NO$_2$. This indicates that the equilibrium state of
diffusion/adsorption of NO\textsubscript{2} molecules as well as subsequent reaction/desorption processes in sensing layer are fast enough and with adequate surface coverage percentage. However the optimal irradiance is subjected to change for any other target gases. For In\textsubscript{2}O\textsubscript{3} sensing material, the response time varied at different irradiances from 254s at 5 mW/cm\textsuperscript{2} with 0.247 sensitivity to 300s at 2.8 mW/cm\textsuperscript{2} with 0.674 sensitivity which the latter is suggested as the optimal irradiance because of complete recovery and stable response with relatively high sensitivity. At lower irradiances the sensor didn’t reach to a stable value until 2000s and the complete recovery was not observed after almost 2000s of turning off the gas flow.

Recovery time constant ($\tau_{\text{rec}}$) is the time that the sensor resistance varies from 90\% to 10\% of its maximum value. Contrary to response time values which were short and close, the recovery values were significantly different. Much longer recovery time values were observed for In\textsubscript{2}O\textsubscript{3} compared to ZnO. All ZnO recovery time values were around 300s approximately, however for In\textsubscript{2}O\textsubscript{3} sensors, the shortest $\tau_{\text{rec}}$ was observed to be 480s at 5 mW/cm\textsuperscript{2}. By decreasing the irradiance to 2.8 mW/cm\textsuperscript{2}, $\tau_{\text{rec}}$ increased slightly to 500s and then the slop of changes increased significantly. For instance, for irradiances lower than 2.8 mW/cm\textsuperscript{2}, $\tau_{\text{rec}}$ is expected to even reach 3000s or longer. The long-time recovery of In\textsubscript{2}O\textsubscript{3} can be attributed to the sluggish surface adsorption, and strong physical/chemical bonds of adsorbed molecules with the surface. Oxygen dissociation and ionization is also reported to be another reason [127].

An example of unstable results has been showed in Figure 3-21. The response didn’t reach to a stable value after almost 2000 seconds and continued rising linearly. This was mainly because of permanent adsorption and subsequent poisoning by NO\textsubscript{2} on the surface. The response also didn’t have full recovery by turning off the gas flow. At irradiances much lower than 1.7 mW/cm\textsuperscript{2}, after closing the NO\textsubscript{2} flow, the response didn’t decrease at all.
Figure 3-21: In$_2$O$_3$ sensor failure in NO$_2$ detection due to stable adsorption of NO$_2$ molecules on the surface at lower irradiances (1.7 mW/cm$^2$)

The results indicated that the performance of In$_2$O$_3$ is almost two times greater than that of ZnO samples mainly due to the ability of the In$_2$O$_3$ layers to adsorb more gas molecules. The results are consistent with those in the literature confirming that the photo-activated gas sensitivity of ZnO is low [26,49]. Figure 3-22 shows the ratio of $S_{In}/S_{Zn}$ for different irradiances. In the first two points which belong to lower irradiances, stable results were not observed for In$_2$O$_3$.

The main reason of differences in gas sensitivity cannot be entirely dependent to the differences in grain sizes. In order to be able to explain sensor behaviours, we have to consider resistance values in operating conditions (see next sections).
3.3.2.2 Effect of Concentration

The prepared sensors were tested for different concentrations of NO$_2$ gas, Figure 3-23 shows ZnO and In$_2$O$_3$ responses to 5 ppm – 100 ppm of the target gas under UV-LED irradiation in the optimum irradiance for each sensor material. The responses increased with increasing gas concentration, reaching to 2.95 and 7.5 at 100 ppm NO$_2$ for ZnO and In$_2$O$_3$, respectively. The trend is likely as the result of more electrons being involved in relative reactions at higher concentrations, since high reactant concentration cause to have higher reaction rates.
Figure 3-23: ZnO sensor response at different concentrations of NO₂ gas under UV-LED illumination

Figure 3-24: In₂O₃ sensor response at different concentrations of NO₂ gas under UV-LED illumination
Another important point in the figures is the $\tau_{\text{rec}}$ of the sensors at higher concentrations. For ZnO sensors, the $\tau_{\text{rec}}$ is not changed considerably, however the recovery time constants of In$_2$O$_3$ sensors increased with increasing concentration. At 100 ppm the sensor resistance didn’t return to its initial value because of stable adsorptions at high concentrations.

Figure 3-25 shows the overall trend in response changes in various concentrations, the response of In$_2$O$_3$ increased more rapidly than ZnO, which might be due to the inherent capability of In$_2$O$_3$ to adsorb more target gas molecules and to proceed photocatalytic reactions with higher rate by providing greater number of electrons on the surface. The results are in good agreement with those available in the literature for ZnO, indicating that the photo-activated sensitivity of pure ZnO is low [22]. Saturation limit which is the maximum detectable amount of target gas is another important factor for any gas sensor setup. It seems that the saturation limit of In$_2$O$_3$ sensors is extremely high, compared to ZnO sensors, however as discussed previously, the responses were not recoverable in higher concentrations and post thermal treatments are required to bring the sensor back into standard working condition.

Figure 3-25: Gas sensor sensitivities towards various concentrations of NO$_2$
3.3.2.3 Photo-induced Sensing Mechanism

The NO\textsubscript{2} sensing mechanism can be described as follows. When the sensors are exposed to 200 ml/min of air, the generated electrons recombine with oxygen and form adsorbed oxygen ions, resulting in a decrease of conductivity. [128].

\[ O_2 (\text{gas}) \leftrightarrow O_2 (\text{ad}) \]
\[ O_2 (\text{ad}) + e^- \leftrightarrow O_2^- (\text{ad}) \]

Upon the exposure to NO\textsubscript{2}, a possible explanation for observations could be based on the dynamic equilibrium that exists between the adsorption and photo-excited desorption of molecules on the surface. Under continuous irradiation, when the physisorbed NO\textsubscript{2} accepts an electron from O\textsubscript{2}\textsuperscript{-} which is the dominant form at room temperature, a stable chemisorbed NO\textsubscript{2}\textsuperscript{-} state created which can only be desorbed by light [35]. Then, the reaction and desorption take place simultaneously to reach to an equilibrium state under constant flow of photons. In other words, illumination, changes the occupancy of the defects and thus changes the capacity of adsorption concentration on the surface [34].

\[ \text{NO}_2 (\text{gas}) + e^- \rightarrow \text{NO}_2^- \text{ads} \]
\[ \text{NO}_2^- \text{ads} + O_2^- (\text{ad}) + 2e^- \rightarrow \text{NO} (\text{gas}) + 2O_2^- (\text{ad}) \]

The differences in ZnO and In\textsubscript{2}O\textsubscript{3} sensor responses can be explained based on the number of the active sites available on the surface. Upon exposure to UV, photo-generated charges activate the sensing layer for any subsequent reaction/adsorption process. Excited electrons are required to interact with oxygen
and target gas molecules on the surface. If the grain size is comparable to the depletion region (i.e. smaller than twice of depletion region), a great part of the grain will be depleted upon excitation. Thus, when the conduction path is narrower, a large rapid variation in sensor response will occur [13]. The homo-interfaces between ZnO or \(\text{In}_2\text{O}_3\) particles (i.e. ZnO-ZnO or \(\text{In}_2\text{O}_3\)-\(\text{In}_2\text{O}_3\) interfaces) and the grain boundary potentials (double Schottky barrier) can play a determining role in the amount of successful electrons/holes that are able to reach the surface, resulting in a direct effect on the gas sensing behaviour. For instance, the formation of p-n junctions are reported to be an effective strategy to enhance gas responses in photo-activated gas sensors [117]. In other words, the size of particles and the thickness of depletion layer which are related to the metal oxide semiconductor interfaces, influence the electron/hole path to the surface.

To study the effect of homo-interfaces on the conduction of prepared sensors, resistance variations were measured before and after UV illumination in pure air (Figure 3-26). The observed resistance for ZnO is significant in comparison with that of \(\text{In}_2\text{O}_3\) sensor, indicating that the \(\text{In}_2\text{O}_3\) homo-nanostructure interfaces are not highly resistive. Upon UV exposure, the resistance \((R_a)\) change for \(\text{In}_2\text{O}_3\) is much smaller than that of ZnO values. The slight variation in \(R_a\) for \(\text{In}_2\text{O}_3\) before and after UV illumination can be explained based on the radiation-dependent change in the adsorption of oxygen ions. In other words, the lower resistance (change) can be attributed to the higher mobility of valance electrons throughout the material particles, as the result of more oxygen ion vacant sites [129]. Thus, large amount of oxygen ions are placed on the surface of \(\text{In}_2\text{O}_3\) layer and have trapped a great portion of electrons. On the other hand, only a small amount of \(O_2^-\) is adsorbed on the surface of ZnO sensor before radiation, resulting in higher resistance change when UV activate the layer for subsequent photo-adsorption.
Indeed, the number of adsorbed oxygen ions could be proportional to the final active sites that will be available for target gas, since $\text{O}_2^-$ ions are removed upon exposure to $\text{NO}_2$ either by reaction or desorption. Thus the variation of sensitivity for both prepared sensing materials can be roughly estimated as a result of $\text{NO}_2$ introduction to the sensing layer. If only oxygen ions are removed from the surface, a decrease in depletion layer will happen and film resistance will be reduced, but the simultaneous reaction and photo-desorption that take place before reaching to an equilibrium state under constant flow of photons cause molecules to engage certain amount of excited electrons in a period of time. The most stable state determines the visualized resistance of sensing material during exposure.

3.4 Conclusion

In this study, we showed that UV-LEDs can provide the required energy to activate metal oxide surfaces at room temperature to detect low concentrations of $\text{NO}_2$ gas in the environment. We compared...
two favorable metal oxide semiconductors to be used in photo-activated gas sensors. ZnO and In$_2$O$_3$ sensors were fabricated using precipitation methods and were used in similar conditions to detect low concentrations of NO$_2$. The respective response values were compared and a conclusion in directing the choice of appropriate semiconductor layer was presented. The optimum irradiance for each sensor material to detect NO$_2$ was found to be different. The important factors that have been considered were sensitivity, stability, response and recovery time constants and the ability of the sensor to have complete recovery. The results showed that the sensitivity of In$_2$O$_3$ to different concentrations of NO$_2$ was much greater than that of ZnO layers and the response difference increased significantly for higher concentrations. However the intensity of the UV-source to be used with In$_2$O$_3$ sensors was higher than those for ZnO to prevent permanent adsorption of target gas molecules on the surface. A hypothesis was presented based on the possibility of having different oxygen vacant sites on tested sensors to explain the differences in gas sensing responses.
Chapter 4: Development of Highly Sensitive ZnO/In$_2$O$_3$ Composite Gas Sensor

Activated by UV-LEDs

4.1 Introduction

Recent developments in producing sensitive chemical gas sensors motivated researchers to engineer the composition and morphology of the sensing materials to overcome the issues related to operating conditions and response parameters such as sensing temperature [130], selectivity and stability [131]. Improvements can be achieved through morphology optimizations such as doping [100,132], surface modifications [133,134], micro and nano-structure changes [135], and the design of multi-compositional sensing materials [136]. The multi-compositional semiconductors by addition of a secondary component oxide (semiconductor composites) seem to add significant improvements to gas sensing characteristics of chemi-resitive sensors. Up to recent years, most of the efforts were focused on the synthesis and structural modifications of single nanostructures. A new approach could be to conduct the directions of nanoscience and nanotechnology towards designing various composite nano-structures to utilize the synergetic effects of combining structure of various gas sensing materials to achieve selective and sensitive gas detectors. The influence of nano-composite structure is mainly through the increasing adsorption capability by injecting more electrons into the active surface as well as reducing the rate of recombination by separating active charge carriers and making more negative conduction band levels at the hetero-interfaces as illustrated in Figure 4-1 [95]. In the past several years, a few works were reported on the synthesis and high temperature sensing applications of hetero-nanostructures such as SnO$_2$/ZnO [96,137], SnO$_2$/In$_2$O$_3$ [95,97], SnO$_2$/Zn$_2$SnO$_4$ [98], SnO$_2$/NiO [99], SnO$_2$/Co$_3$O$_4$ [100], Fe$_2$O$_3$/In$_2$O$_3$ [101], Fe$_2$O$_3$/SnO$_2$ [102]. Also, there have been several studies on ZnO/In$_2$O$_3$ composite synthesis
and its high temperature gas sensing capability [105,138]. However several drawbacks of conventional metal oxide gas sensors have still remained such as high power consumption and undesirable long-term drift problems caused by the sintering effects in the metal oxide grain boundaries because of high operating temperature (200-500 °C), resulting in poor selectivity and stability [107]. UV-activated chemical gas sensors have shown excellent capability in room temperature gases detection with adjustable selectivity and self-cleaning specification [31,43]. So far, a few reports have introduced to the literature on photo-activated ZnO/TiO$_2$ [115], In$_2$O$_3$/SnO$_2$ [139], and ZnO/SnO$_2$ [140] nano-composites to be used in room temperature with enhanced gas sensing properties. Reports on band gap engineering effects and compositional properties of ZnO-In$_2$O$_3$ materials confirm that it has the potential to improve sensor responses [103,127,138,141]. However, to the author’s knowledge, there is no report in the literature assessing room temperature sensing behavior of ZnO-In$_2$O$_3$ nano-composites under continuous UV-LED irradiation.

![Figure 4-1: Schematic illustration of band structure of ZnO/In$_2$O$_3$ composite](image)

Figure 4-1: Schematic illustration of band structure of ZnO/In$_2$O$_3$ composite
In the previous chapter, the sensing material properties as well as gas sensing characteristics of pristine ZnO and In$_2$O$_3$ which are two favorable semiconductors for detection of wide variety of gases were evaluated. We observed that the incident irradiance could markedly change the NO$_2$ sensing parameters such as sensitivity and response time constant. We concluded that the maximum stable sensitivity of 0.674 at 2.8 mW/cm$^2$ can be achieved for In$_2$O$_3$ with complete recovery. We also showed that the sensitivity of In$_2$O$_3$ was almost two times greater than that of ZnO in similar conditions of target gas concentration for all irradiances while the response time constant of ZnO sensors were shorter in all performed experiments. The maximum sensitivity of ZnO was 0.412 at 1.2 mW/cm$^2$.

In this study, to further increase the sensitivity and lower the response time, we have coupled n-type semiconductor oxides of ZnO and In$_2$O$_3$ using co-precipitation method to obtain nano-crystalline composites sensing material for low concentration NO$_2$ detection. Further, we have determined the favorable set of synthesis conditions for the formation of composite in the solution to have nano-composite particles with high sensing performance. The sensing experiments showed high sensitivity towards NO$_2$ with a remarking decrease in response time compared to pristine samples previously reported.

4.2 Experimental

4.2.1 Material Synthesis and Deposition

In this study different compositions of ZnO/In$_2$O$_3$ mixture were synthesized through co-precipitation method. The chemical bath precipitation was carried out in 100 ml of Ethanol-Methanol (85%-15%) solution at 55 °C where known quantities of Zn(NO$_3$)$_2$.5H$_2$O and In(NO$_3$)$_3$.xH$_2$O with different molar ratios were mixed and stirred for 30 min. Thereafter, the ZnO/In$_2$O$_3$ precipitates were produced by adding 2M Ammonia solution in Ethanol drop by drop to the target solution to reach PH>9. The details of
synthesis process are presented in Table 4-1. The resulting solution was deposited on the substrate using several methods such as spin coating, solution impregnation deposition and drop casting method. The deposited films were dried at room temperature and annealed at 550 °C for 2 hours to oxidize deposited materials. The gas sensing measurements were not consistent for samples prepared by solution impregnation and drop coating methods probably due to inconsistency in the amount of material deposited over substrate. For the spin coating method, a known amount of solution (5 ml) was taken by a pipet and poured dropwise over the substrate while rotating at 500 rpm. Then for each stage, the rotating speed was set to 3000 rpm to dry the layer. This process repeated 10 times followed by a 3 min heating at 80 °C at the middle of coating to let the trapped water evaporate. The obtained thin films were then calcined at 550 °C for 2 hours.

<table>
<thead>
<tr>
<th>Sample Composition</th>
<th>Zn(NO₃)₂.5H₂O</th>
<th>In(NO₃)₃.xH₂O</th>
<th>Ammonia Solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Zn]:[In] = 33:67</td>
<td>0.595 gr</td>
<td>1.2 gr</td>
<td>~15 ml</td>
</tr>
<tr>
<td>[Zn]:[In] = 50:50</td>
<td>0.89 gr</td>
<td>0.9 gr</td>
<td>~19 ml</td>
</tr>
<tr>
<td>[Zn]:[In] = 67:33</td>
<td>1.189 gr</td>
<td>0.6 gr</td>
<td>~13 ml</td>
</tr>
</tbody>
</table>

4.2.2 Characterization

To realize the properties of the synthesized materials and sensing layers, several analysis have been performed. Elemental analysis and the surface morphology of the samples were studied by energy-dispersive x-ray (EDX) spectroscopy, Field Emission Scanning Electron Microscopy (FE-SEM) and X-ray Photo-electron Spectroscopy (XPS). Powder diffraction analysis were carried out in XRD characterizations, using a Bruker APEX DUO instrument equipped with Mo and Cu sources. To do the
analysis, the composite samples were put in a Bruker APEX DUO instrument equipped with Mo and Cu sources and the Cu Kα1 values were set to $\lambda = 0.15406$ and $\lambda = 0.154439$ nm and voltage and current generators were adjusted at 40 kV and 40 mA, respectively. The imaging started from 5° to 95° angle in 0.04° angle with 109.2 s time step. To investigate the optical properties of the samples such as respective band-gaps, UV-Vis spectroscopy was performed.

4.2.3 Gas Sensing Measurements

To develop the sensors that are able to detect low concentrations of NO$_2$ gas, solutions containing different ratios of ZnO-In$_2$O$_3$ nanostructured composite precipitates were spin coated over interdigitated gold electrodes on Al$_2$O$_3$ substrate. The sensors were then placed inside a stainless steel chamber to be exposed to different flows of target gases and photons. Two types of high power 365 nm UV-LEDs were used, one with 2750 mW total power and the other with 690 mW power. The out irradiance of UV-LEDs were adjusted by changing the operating current. The actual incident irradiances for sensing measurements were within 1.2 to 5 mW/cm$^2$. The total flow rate of gas exposure was set to 200 ml/min. The sensors were connected to electrical circuit using special copper wires/connectors. The DC electrical measurement was carried out by using a Keithley source-meter and by applying 5.0 V onto the sensor. The electrical resistance of the sensors was monitored continuously in real time in a wide range of incident irradiances (1.2–5 mW/cm$^2$) and concentrations (5 to 100 ppm). The gas response was denoted by $S$, as the ratio of $(R_a - R_g)/R_g$, where $R_a$ is the electrical resistance of sensors in air and $R_g$ is the attributed resistance when the sensor is exposed to target gas. $S\%$ denoted the sensitivity percentage by multiplying $S$ to 100.
4.3 Results and Discussion

4.3.1 Morphology and Crystalline Structure

SEM images of ZnO/In$_2$O$_3$ composites are quite different from the ZnO and In$_2$O$_3$ pristine samples. Composite layer consists of empty compartments, long hollow pores of substrate and propagated particles of composite materials with diameters ranging 30-100 nm (Figure 4-2). Although the deposition method played a significant role in the arrangements of composite materials, the ZnO/In$_2$O$_3$ clusters were mainly spread over the substrate in agglomerated porous sites. The observed formation of deposited materials in the form of agglomerated clusters stacked on the substrate could be the result of coating-calcination sequence (rather than drying-calcination-coating).

Additionally, looking closely at different ratios of ZnO/In$_2$O$_3$ composite layers, several cavities are inside each nano-particle, making nano porous structures. For instance, FE-SEM images of Zn1-In2 ([Zn]:[In] 1:2) (Figure 4-3) show distinct distribution particles scattered unevenly in different grain sizes with connecting bridges. Zinc or Indium compartments are not distinguishable in the clusters since they have formed a close heterostructural compound, suggesting that the zinc and indium atoms may have been incorporated to form a single solid component with shared lattice structures; this has been confirmed by XPS analysis. Figure 4-4 and Figure 4-5 feature the FE-SEM images of prepared composites with the ratio of 2:1 and 1:1 of [Zn]:[In], respectively. For Zn2-In1 sample, each cluster contains micro-sized and nano-sized cavities which can enhance the surface area required for gas sensing. However, Zn1-In1 showed a different morphology compared to the other compositions. Prevailing Zn or In content could lead to the formation of more pores and thus, higher surface area. But when zinc and indium are mixed at the same ratio, the structural cavities and holes disappear due to the strong and compact material bonding. The density of cavities in Zn2-In1 is higher than Zn1-In2 sample, suggesting that the porosity decreases with increasing In content. The average particle size of composites cannot be estimated with
respect to the images but it’s expected to be smaller than pristine samples reported earlier, which is in good agreement with our inspection, since two phases in the composite act as the sintering inhibitor to each other [98].

Figure 4-2: Scanning Electron Microscopy showing the depositional formation of ZnO/In$_2$O$_3$ materials
Figure 4.3: Field Emission SEM images of ZnO/In$_2$O$_3$ nano-composites with ratio of [Zn]:[In] 1:2.
Figure 4-4: Field Emission SEM images of ZnO/In$_2$O$_3$ nano-composites with ratio of [Zn]:[In] 2:1.
The SEM images and specifications of our prepared composites, specially Zn1-In1 distinction, are consistent with those reported in literature [103,127].

In addition to the adjustments performed for the Zn$^{2+}$/In$^{3+}$ ratio during the synthesis, the actual contents of Zn and In elements in ZnO/In$_2$O$_3$ composite samples were determined using EDS analysis to identify in what proportion they have been combined (Figure 4-6). The chemical compositional analysis of the composite nanoparticles was performed and the results of the relative total intensity of indium and zinc confirmed the expected values. The Au peaks in EDS plots are related to the coated layer of gold for SEM imaging.
Figure 4-6: EDX analysis of ZnO/In$_2$O$_3$ particles deposited on Al$_2$O$_3$ substrate with respective ratios of A) 1:2, B) 1:1, C) 2:1.
To investigate the composite material structures as well as the components crystallinity, XRD analysis of the ZnO/In$_2$O$_3$ samples annealed at 550 °C was performed (Figure 4-7). Using d-spacing provided by Bragg's Law, the peak positions can be theoretically related to the cell parameters. The results suggest that the sample undergoes a complex morphological evolution when metal oxides are combined. The primary particles sizes and the morphology of the surface were dependent on the composition. The peaks at angles around 30–35 almost show the whole differences in composite samples compared to ZnO and In$_2$O$_3$ pristine samples. ZnO and In$_2$O$_3$ showed hexagonal wurtzite phase (ZnO, JCPDS# 36-1451, hexagonal) and cubic phase (In$_2$O$_3$, JCPDS# 06-0416) in our samples, respectively. Thus, the prepared nano-composites are mixtures of hexagonal ZnO and cubic In$_2$O$_3$ crystallites.

It should be noted that the XRD technique may not be sufficiently sensitive to follow the fine details of changes occurred in the sample in terms of lattice structures. The absence of peaks related to impurities confirm the high purity of the samples. The initial background is related to the carbon structures from ethanol based solution. The peak width $\beta$ in radians (often measured as full width at half maximum, FWHM) is inversely proportional to the crystallite size. Moving from ZnO to In$_2$O$_3$, the intensity of the peaks reduces which could be related to the reduction in crystallinity. The FWHM of samples containing more In$_2$O$_3$ is much greater than samples containing more ZnO, meaning that by increasing In$_2$O$_3$ content, the crystallite size is reduced. This is evident in the crystalline sizes calculated by the Scherrer equation. The crystalline size of pristine ZnO is 35 nm and the crystalline size of pristine cubic In$_2$O$_3$ is 13 nm. However, composite samples crystalline sizes range from 10 to 45 nm.

The shift in the Bragg peaks to higher values as the amount of zinc is increased means that the lattice parameter is changing due to possible elimination of defects or structural relaxation simultaneously by the change in crystalline phases and/or crystal structure. However, the intense peaks remain between the In$_2$O$_3$ (222) and ZnO (002) peak positions and the d-spacing correspond to the distance between two
close packed layers in each of the two oxides. The structure of the composite thin films evolves from cubic In$_2$O$_3$ to hexagonal ZnO. The evolution of the structure in the films has been confirmed in high-resolution SEM images previously explained.

To describe the structure of the composite samples with different element ratios compounds, XPS analysis was performed (Figure 4-8). The primary analysis of the results on the ratio of the semiconductors leads to a consistent conclusion with the previously observed data. The surface ratios of the components obtained by XPS analysis are presented in Table 4-2. The small discrepancy emanates from the inherent feature of this analysis, which is a surface analytical method. The background is probably caused by electrons that are elastically scattered before leaving the sample surface. Such scattering reduces the kinetic energy of the electrons and reduces intensity of the peaks. The surface
The measured binding energies of In 3d, Zn 2p3/2 and O 1s in pure ZnO and In2O3 are 443.9, 1021.4 and 529 eV, respectively, while their observed binding energies in composite samples with ratio Zn2-In1 were 444.25, 1021.55, and 531.45 eV, respectively. Depending on the component ratio of the composite, the binding energies are altered accordingly. For instance, for Zn1-In2 the binding energies of In3d, Zn2p3/2 and O 1s were observed at 444, 1021.7 and 531.12, respectively. This significant positive shifts in In 3d, Zn 2p3/2 and O 1s binding energies are attributed to the electronic interactions existed between components in the composites. Thus synergistic effects of the components can possibly affect the electronic specifications and sensing response.
Table 4-2: Atomic % of different components in prepared composite samples obtained by XPS analysis

<table>
<thead>
<tr>
<th>Sample</th>
<th>C%</th>
<th>O%</th>
<th>Zn%</th>
<th>In%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn1-In2</td>
<td>27.74</td>
<td>50.76</td>
<td>7.60</td>
<td>13.90</td>
</tr>
<tr>
<td>Zn1-In1</td>
<td>24.91</td>
<td>63.01</td>
<td>7.80</td>
<td>4.28</td>
</tr>
<tr>
<td>Zn2-In1</td>
<td>22.55</td>
<td>47.49</td>
<td>19.53</td>
<td>10.43</td>
</tr>
</tbody>
</table>

4.3.2 Optical Analysis

To investigate the optical properties and to determine the band-gap of the three composite samples, UV-Vis analysis was performed (Figure 4-9). The plot shows that at higher wavelengths, the reflectance of Zn1-In1 is higher than those of two other composites, and at wavelengths lower than 480 nm, Zn2-In1 absorbs more photons compare to Zn1-In1 and Zn1-In2 samples.

Figure 4-9: UV-Vis analysis gives reflectance spectrum vs wavelength, the figure shows respective spectra of the three prepared composite samples at different ratios
Tauc plot helps to find the relevant band gap and to study its possible changes in various compositions and layer morphologies and to illustrate the differences in sensors behaviours. To calculate the band-gap from reflectance measurements, the wavelength has to be converted into respective energy eV by applying the Kubelka-Munk equation. The calculation procedure was demonstrated in the previous chapter. Figure 4-10 shows the Tauc plot of spin coated composite materials with different atomic ratios.

![Tauc plot](image)

Figure 4-10: UV-Vis spectra of ZnO-In$_2$O$_3$ composite with different component ratios samples

With respect to the graph and tangent lines, the band-gaps of the composite materials vary slightly, ranging from 3.00 for Zn2-In1 to 3.2 eV for Zn1-In2. The main conclusion to be drawn is that, as the ratio of Zn to In increases in the composite the band-gap tends to smaller values. The lower band gap of Zn rich composite possibly leads to more excited electrons for Zn2-In1 sample, compared to other compositions, making this composition more suitable for gas sensing material.
4.3.3 Gas Sensing Performance

Electron/holes are in charge of resistance changes in the sensing layer. The composition of the sensing material significantly influences the rate of electron production/recombination. The catalytic activity, grain size, thickness, robustness and surface area of the material are among the determining factors for a good and efficient sensor. Three different compositions of ZnO/In$_2$O$_3$ composite were used for NO$_2$ sensing. The compositions of the prepared composites are changed according to the atomic percent of Zn to In in the materials. For simplicity, the samples with [Zn]:[In] ratios of 1:2, 1:1, and 2:1 are denoted as Zn1-In2, Zn1-In1 and Zn2-In1, respectively.

Since the irradiance of the photons that reach the surface considerably influence the subsequent reaction rates and adsorption/desorption equilibrium constants, a study on the incident irradiance was performed. Incident irradiance accounts for the total energy that reaches to sensor surface per unit area and time. For the excitation of the electrons in valence band, a minimum energy equal to the energy of the band-gap of the semiconductor is required. Any photons with energies equal or greater than this value can activate the semiconductor layer. There is also a possibility of activation by incorporating electrons with lesser energies through several mechanisms. Indirect band gap, disturbed crystal structures or defect states on the surface and multi-photon excitation in which several photons collide to a single point at a moment can also excite electrons of a large band gap semiconductor [65,142]. Thus, the semiconductor layers can be activated when they are exposed to visible light irradiation or even by using photons with energies in infra-red region [50,65]. However, in this case, the number of excited electrons would be far less than that of using high energy photons. On the other side, using extremely high energy photons with energies greater than the minimum required values, don’t necessarily give better responses, since limited electrons are accessible for excitation.
For the gas sensing measurements, it has been reported that using photons with higher energies would result in having higher responses and shorter recovery time due to an improvement in semiconductor activity because of faster kinetics [66]. In this research we have used 365 nm UV-LEDs which have enough energy to activate composite semiconductor layers in different irradiances (see optical analysis).

In addition to the photons energy, the exposure rate or flux of the photons determines the energy that is receiving by the surface. Intensity mostly affect the adsorption/desorption processes and reaction rates in sensing applications. Increasing the irradiance improves the desorption process, shifting the equilibrium reactions to produce more oxygen gas. It also facilitate the desorption of adsorbed target gas molecules. In this study, we have analyzed the effect of irradiance on different sensor responses. Working at high irradiances would result in less sensitivity, since surface reactions that are required for the sensing process cannot proceed at sufficient rates and the molecules will desorb before participating in their respective sensing reactions. On the other hand, more stable results with fast response and recovery time constants are achieved at higher irradiances that have enough energy to generate electron/hole pairs as well as removing reacted/unreacted materials from the surface. Thus, an optimum value should be drawn for each sensing material, depending on the equilibrium reactions position, adsorption energy, charge transfer, and electronic band structures of the layers.

In this study, two types of UV-LEDs have been used to evaluate the effect of irradiance of the photons on each sensing material. Figure 4-11 represents the effect of irradiance on all prepared composite samples. According to the experimental results, the optimal irradiance within the experimented range for composite structures to have the highest sensitivity, shortest response time and a complete recovery is set to 1.7 mW/cm².

The NO₂ sensing results at room temperature under appropriate UV irradiance indicated that the sensing performances of composite materials are much better than that of pristine samples considering
both sensitivity and response time. Among the composites, at a constant irradiance, the sensitivity of Zn2-In1 was better than that of Zn1-In1 and Zn1-In2.

Increasing irradiance will reduce the sensitivity due to an increase in induced photo-desorption rates compared to photo-adsorption/reaction processes. Removing oxygen ions and adsorbed target gas molecules from the surface will lead equilibrium reactions to proceed in backward direction towards desorbing more molecules, thus a decrease in sensitivity is observed at higher irradiances. Table 4-3 summarizes maximum responses of different sensing materials to 5 ppm NO\textsubscript{2} in their corresponding optimum irradiance, showing a considerable increase in composite sensors, compared to pristine sensing materials.

![Figure 4-11: Sensitivity increase by using Composite Semiconductor compared to pristine samples](image)

There have been a few reports in literature working on NO\textsubscript{2} detection using ZnO, In\textsubscript{2}O\textsubscript{3} and metal oxide composites in photo-activation mode. The response of sensors in the present study is compared
with those in literature in table 4-3. The ZnO–In$_2$O$_3$ composite in the present study showed higher responses compared to other composites reported elsewhere.

<table>
<thead>
<tr>
<th>Sensing Material</th>
<th>Optimum Irradiance (mW/cm$^2$)</th>
<th>Sensor Response (present study)</th>
<th>Sensor Response (in literature)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ZnO</td>
<td>1.2</td>
<td>0.412</td>
<td>0.08 [66]</td>
</tr>
<tr>
<td>In$_2$O$_3$</td>
<td>2.8</td>
<td>0.674</td>
<td>0.63 for 100 ppm [32]</td>
</tr>
<tr>
<td>ZnO/In$_2$O$_3$ 1:2</td>
<td>1.7</td>
<td>1.81</td>
<td>-</td>
</tr>
<tr>
<td>ZnO/In$_2$O$_3$ 1:1</td>
<td>1.7</td>
<td>1.24</td>
<td>-</td>
</tr>
<tr>
<td>ZnO/In$_2$O$_3$ 2:1</td>
<td>1.7</td>
<td>2.21</td>
<td>-</td>
</tr>
</tbody>
</table>

To investigate the detailed mechanism in a gas sensing process, typical behaviors of different composite sensor materials to 5 ppm NO$_2$ at 1.7 mW/cm$^2$ are shown in Figure 4-12.

Based on the high adsorption capability of pristine In$_2$O$_3$ sensors, observed in the comparative study and with respect to the high porosity of ZnO rich composite samples, we suggest that, ZnO favors the flow of charge carriers and is in charge of surface area in which increasing ZnO content would lead to higher surface area, while In$_2$O$_3$ acts as active light absorption centers and enhances chemisorption ability in the composite.
One of the important parameters in any sensor setup, is the ability to detect and measure wide range of concentrations of target gas in an accurate way. To study the effect of concentration on the sensor response, we changed target gas concentration in the range of 5–100 ppm and have measured sensitivity, response and recovery time constants.

Figure 4-13 shows the sensitivity of developed composite sensors towards different concentrations of NO₂. By increasing the target gas concentration, the sensitivity increases due to the increase in the number of electrons involved in the adsorbed molecules, resulting in higher band bending and more resistance variation. But the slope of increased sensitivity is larger in lower concentrations and it decreases as the concentration approaches to the upper level and reaches to a constant value. In the saturation state, no change is expected to be observed by changing the concentration.
The response time ($\tau_{res}$) varies with working irradiance for each sensor material. The range of the variations of response time for all the three compositions was observed to be from 58s at 5 mW/cm$^2$ to nearly 100s at 1.7 mW/cm$^2$. While complete recovery was not observed for lower irradiances (i.e. 1.2 mW/cm$^2$), the responses were stable throughout the range. Since the differences in response time values were too small compared to sensitivities, using 1.7 mW/cm$^2$ is suggested as optimum irradiance for ZnO/In$_2$O$_3$ composite towards NO$_2$. This observation indicates that the equilibrium state of diffusion/adsorption of NO$_2$ molecules as well as subsequent reaction/desorption processes in sensing layer are fast with adequate surface coverage at 1.7 mW/cm$^2$, compared to other irradiances. However the optimal irradiance is subjected to change for other target gases. To compare the response time of the prepared sensors in their optimal irradiance, Zn1-In2 and Zn1-In1 both reached to their maximum response within 78 seconds, however it took nearly 100 s for Zn2-In1 to reach to a stable value in

![Figure 4-13: Semiconductor composite sensitivity for various concentrations of NO$_2$](image-url)
response. Recovery time constant ($\tau_{\text{rec}}$) values also were slightly different in experimented conditions for different composite materials and the variations were in the range of 610 s -695s.

4.3.4 Photo-induced Sensing Mechanism

To understand the inherent sensing mechanism of the developed sensors, the resistances of the sensors were measured at room temperature before and after UV-LED irradiation in the presence of pure air. The resistance changes before and after illumination for pristine ZnO and In$_2$O$_3$ samples were higher than those of composite materials (Figure 4-14). Among the composite materials, Zn1-In1 has the highest change in value while the decrease in resistance for Zn1-In2 and Zn2-In1 is much lower. Z2-In1 has the lowest resistance values, which is about 2 and 3 order of magnitudes less than those of pristine In$_2$O$_3$ and ZnO samples, respectively. Differences in initial resistances are attributed to the metal oxide semiconductor interfacial resistances which greatly influence the oxygen ion vacancies and the electrons concentration on the surface. The addition of a secondary material and its interaction with a binding electron can make a defect on the host lattice structure, influence the charges mobility, particle sizes, and the thickness of depletion layer. Further, the presence of the secondary material provides oxygen atoms that are able to diffuse to the crystal surface, react with oxygen ions and form into O$_2$(g) and leave an oxygen vacancy behind [47,129].
Figure 4-14: Resistance of sensors in air before and after UV illumination as a function of composition.

To further investigate the effect of addition of a secondary semiconductor to the structure of a primary semiconductors, several factors have to be taken into consideration simultaneously such as surface area, crystalline size, structural deficiencies like oxygen vacancies, and change in chemical reaction mechanism or catalytic activity.

The actual surface area, is the solid interface that is accessible to the gas to proceed chemical reactions on the surface. As the surface area of a typical sensing layer increases, the number of active sites on the surface rises accordingly, leading to higher adsorption and subsequent reactions which could possibly result in higher sensitivity. Theoretically, the addition of a secondary semiconductor to the structure cause to increase the actual surface area since two phases in the composite act as the sintering inhibitor to each other [98].

Second factor is the particle size which has always been a critical parameter in chemi-resistive sensors. For example, 6 nm is the turning point in SnO\textsubscript{2} based sensors in which the sensitivity of SnO\textsubscript{2} grains with
smaller diameters increases significantly because the depletion region constitutes the entire grain [143]. Generally, the critical particle size is approximated to be 2 times greater than the depletion region. The addition of a secondary semiconductor, decreases the grain size and thus increases the sensitivity. The layer capability in adsorbing oxygen molecules is another factor that positively affects the sensitivity due to promoting the number of oxygen vacancies. In$_2$O$_3$ replace the structural metals in ZnO structure (and vice versa) and lead to produce an oxygen vacant site [47,129]. Producing oxygen vacant sites would increase the capability of oxygen ion/target gas adsorption, which can possibly influence the sensitivity in a positive manner.

Another major influence induced by addition of a secondary containment is the change in reactions on the surface. Surface acidity or basicity can change the catalytic behaviour of the surface and influence the reaction directions in response. In catalytic reactions, the aim is to increase the conversion to eliminate more reactants; however, in sensing devices, the goal is to increase the sensitivity which is not achieved by having high conversion in most cases. In other words, the increase in the catalytic activity of the sensor can adversely affect the sensitivity since high reactivity prevents target gas molecules to diffuse into the sensing layer, resulting in lower exchange of electrons. Therefore, there should be a balance between the gas reactivity and diffusion. On the other hand, if the catalytic activity is too low, the interactions of gas molecules with surface would not be enough, resulting in poor sensitivity. Thus, the idea of manipulating the composition arises from the fact that the catalytic activity can be reduced by controlled the addition of a secondary semiconductor and the ideal condition can be met by adjusting the amount of the secondary component. In general, by controlling the parameters in a semiconductor layer such as catalytic activities, gas adsorption behaviors, and acid–base properties we can tune the sensitivity and selectivity of the sensor towards a particular gas.
4.4 Conclusion

UV-activated chemical gas sensors have shown excellent capability for room temperature gas detection with adjustable selectivity and self-cleaning specification. In this study, by incorporating some structural additives to a single metal oxide semiconductor, we succeeded to produce superbly sensitive detectors for NO$_2$ gas. We showed that an optimum value of irradiance should be considered for each sensing material, depending on the equilibrium reactions position, adsorption energy, charge transfer, and electronic band structures of the layers. The results for different compositions of ZnO/In$_2$O$_3$ composites suggested that the sample with [Zn]:[In] ratio of 2:1 could respond to ppm levels of NO$_2$ more effectively than the other compositions studied here. In terms of the contribution of each semiconductor material in overall sensing response, we suggested that, ZnO favors the flow of charge carriers and is in charge of surface area in which increasing ZnO content would lead to higher surface area, while In$_2$O$_3$ acts as active radiation absorption centers and enhances chemisorption ability in the composite.
Chapter 5: Conclusions and Recommendations

5.1 Conclusions

After a brief introduction of the importance of gas sensing technology, specially MOS gas sensors and evaluating its applications to control outdoor harmful gases and monitor indoor air contents, the principles and fundamental mechanisms of chemi-resistive gas sensors were presented and several determining criteria for an efficient, sensitive gas sensor were listed.

In Chapter 2, the researches in the literature on photo-activated chemical gas sensors were reviewed, and the properties of different sensors and their advantages and shortcomings were evaluated. The following highlights were concluded from the studies performed in Chapter 2:

- UV-LEDs were able to activate metal oxide semiconductors, and could be integrated into chemi-resistive gas sensors to produce low cost, small size, sensitive sensors, operating at room temperature.

- The investigation of the effect of incident irradiance on the sensitivity and selectivity of the developed sensors showed that there is a maximum response in an optimum irradiance for each gas, the optimal irradiance for any given analyte was grain size dependent, indicating that the intensity can be used to tune the selectivity towards a specific target gas.

- The investigation of the effect of photon’s energy (i.e. wavelength) on sensing responses confirmed that the sensitivity increases significantly by applying photons with higher energy. The results also confirmed that equivalent responses can be achieved for photo-activated sensors under appropriate illumination conditions compared to thermo-activated high temperature sensors, and the performance of sensors were strongly dependent on the flux and energy of impinging photons.
• Operating at environments with high humidity values usually deteriorated the sensor sensitivity, and the response time and the recovery time constants in a humid environment were much lower than those of the dry condition.

• The sensing layer structure, such as nano-particulates, nano-wires, crystallinity, and thickness, greatly influenced the responses for any specific sensing layer material.

• Generally, thin film sensing layers could respond better to various target gases, compared to thick film layers, since having the large thickness prevent target gas molecules to penetrate into the layer and utilize interior active sites. On the other hand, extremely thin layers result in low sensing responses because of limited active sites.

• Using reflector in sensor devices could enhance the photon utilization ratio and provide faster response and recovery rates.

• Composite semiconductor materials showed promising responses towards various oxidizing and reducing gases, and the results indicated that there is a specific molar ratio of semiconductors in the composites, which the best sensing performance can be observed.

• Selecting the appropriate sensing material depended on several parameters including the sort of the facility, required operating condition and target gas.

In Chapter 3, due to the importance of comparative studies on selecting the appropriate sensor material with suitable irradiance for detection toxic gases such as NO₂, the sensing performances of two semiconductor metal oxides, ZnO and In₂O₃ UV-based sensors were compared, and preparation routes and layer specifications were reported. The following highlights were concluded from studies performed in Chapter 3:
• The precipitation method was an effective strategy for nano-sized ZnO and In$_2$O$_3$ synthesis and was very well repeatable and controllable technique. The films fabricated by spin coating were also suitable for gas sensing applications because of the porous structures.

• High irradiances facilitated the progressive desorption of all species and lowered the resistance variations and made faster responses with lower recovery time constants.

• The optimal irradiances of ZnO and In$_2$O$_3$ layers to have the highest sensitivity and shortest response time while having a complete recovery for NO$_2$ detection were determined to be approximately 1.2 mW/cm$^2$ and 2.8 mW/cm$^2$, respectively, within the experimental range.

• Although In$_2$O$_3$ showed higher sensitivity to NO$_2$, faster and more stable behavior was observed for ZnO within the experimented range of irradiances.

• The performance of In$_2$O$_3$ was almost two times greater than that of ZnO samples, mainly due to the ability of the In$_2$O$_3$ layers to adsorb more gas molecules. However, the response time constant of ZnO sensors was shorter in all the experiments.

• The responses increased with increasing the gas concentration, as the result of more electrons being involved in relative reactions at higher concentrations.

• The saturation limit of In$_2$O$_3$ sensors was extremely high, compared to ZnO sensors, however, the responses were not recoverable in higher concentrations and post thermal treatments were required to bring the sensor back into standard working condition.

• The differences in ZnO and In$_2$O$_3$ sensor responses were explained based on the number of the active sites available on the surface. Compared to ZnO, the In$_2$O$_3$ homo-nano-interfaces were not highly resistive.

In Chapter 4, a sensitive gas sensor material developed by addition of a secondary semiconductor to the structural lattice of the primary semiconductor, forming ZnO/In$_2$O$_3$ composites. Different
characterization techniques were applied to investigate the inherent properties of the prepared composite materials. The following highlights were concluded from studies performed in Chapter 4:

- Zinc and Indium compartments were not distinguishable in the clusters, suggesting that they have formed a close heterostructural compound with shared lattice structures.
- XPS analysis showed positive shifts in binding energies that were attributed to the electronic interactions existed between the components in the composites.
- The addition of a secondary material and its interaction with a binding electron can make a defect on the host lattice structure and provide oxygen atom that is able to diffuse to the crystal surface, react with oxygen ions and form into O$_2$(g) and leave an oxygen vacancy behind itself.
- The synergistic effects of the components significantly affected the electronic specifications and sensing responses. Thus, the response values of all prepared composite sensors at their corresponding optimum irradiance confirmed a great increase in sensing performances, compared to pristine samples.
- A study on the incident irradiance showed that more stable results with fast response and recovery time constants were achieved at higher irradiances that have enough energy to generate electron/hole pairs as well as removing reacted/unreacted materials.
- By increasing the target gas concentration, the slope of sensitivity changes was larger in lower concentrations and decreased as the concentration increased.
- Compared to pristine samples, the range of the variations of response and recovery time constants for all three compositions was shorter, and the responses were stable throughout the operating irradiance range.
• The results for different compositions of ZnO/In$_2$O$_3$ composites suggested that the sample with [Zn]:[In] ratio of 2:1 could respond to ppm levels of NO$_2$ more effectively than the other combinations studied in this work.

It is believed that ZnO sites favored the flow of charge carriers and were in charge of surface area in which increasing ZnO content would lead to higher surface area, while In$_2$O$_3$ sites acted as active UV absorption centers and enhanced chemisorption ability in the composite.

5.2 Recommendations

The idea of using photo-activated chemical gas sensors as an alternative to conventional high temperature sensors has been recently flourished, with the advances in novel high power UV-LEDs. Thus, a broad area is provided for the scientific world to improve the specifications of UV-LED activated sensors. The followings are important areas with great potentials for more investigations, in order to improve gas-sensing performances of photo-activated sensors:

• A very important feature of any gas sensing material is the long life-time and capability of operating at wide ranges of conditions, thus it is necessary to further study the long-term performance of the developed gas sensors to make sure that the efficiency is not degraded over time. This will reduce the maintenance cost required for end-chain products.

• It is essential to do measurements under different humidity conditions, aiming to lower the humidity effects on the operation of sensors at room temperature.

• It is recommended to perform a detailed and precise detection of the principles of surface chemical reactions through analyzing the species leaving the UV-LED gas sensor chamber by a gas chromatographer to fully understand the governing reactions on the surface for future developments.
Performing a selectivity analysis is recommended in the presence of possible interfering compounds for the developed sensing materials, in order to be able to illustrate the sensing results when sensors are exposed to mixtures of gases in the environment.
References


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