A Dissertation

entitled

Enhancement of Nanocrystalline Zinc Oxide based Electronic Gas Sensor by Surface Modification

by

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Submitted to the Graduate Faculty as partial fulfillment of the requirements for the

Doctor of Philosophy Degree in Engineering

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An Abstract of

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The increasing concerns of industrial safety, chemical control and environmental pollution are spurring demand for high performance gas sensors. Growing use of gas sensors is making gas sensors on demand. After decades of research and development activities, semiconductor based gas sensors are now used in a variety of applications. However, challenges still remain in the area of sensitivity, selectivity, response and recovery speeds and power consumption. Therefore, improvement of metal oxide gas sensors by the incorporation of different technology is important. In this research, modification of metal oxide semiconductor based gas sensor by impurity doping, laser irradiation, and plasma treatment was investigated.

Zinc oxide (ZnO) is an n-type semiconductor with a wide direct band gap (~3.3 eV) and large binding energy (~60 meV). Due to its superior electrical properties and chemical stability, ZnO has been considered one of the most promising materials for gas sensor applications. ZnO thin films have been fabricated by different techniques, such as rf magnetron sputtering, pulsed laser deposition, molecular beam epitaxy, and sol-gel. Sol-gel is a powerful alternative for vacuum deposition.
The purpose of this research was to enhance properties and gas sensor performance of nanocrystalline so-gel derived ZnO thin films via surface modification techniques. The effects of process conditions, impurity doping, laser irradiation, laser doping and plasma treatment on properties and gas sensor performance were investigated. The gas sensor performance of ZnO thin films was investigated at different operating temperatures for various reducing and oxidizing gases such as H₂, NH₃, CH₄ and NOₓ.

Al-doped ZnO thin films were prepared using the sol-gel process by changing the Al concentration from 0 to 5.0 at% using two different Zn precursors. It was found that 3.0 at% Al-doped ZnO films had optimum properties such as high electrical conductivity, crystallinity, high sensing response and short response time for ZnO films derived with both Zn precursors. Ga-doped ZnO thin films were also presented by changing the concentration of Ga from 0.1 to 1.0 at%. The gas sensing behavior was investigated at an operating temperature of 130°C. It was found that the 0.3 at% Ga-doped ZnO thin film sensor had more than a 40% higher sensing response and a shorter response time than the sensors made with as-deposited films.

Laser irradiation was utilized as a novel heat treatment method in this dissertation. A pulsed laser system with a wavelength of 532 nm was used as the irradiation source. Laser irradiation produced two kinds of Al-doped ZnO films depending on the laser energy level. The impact of laser irradiation was also varied according to the film thickness. The Al-doped ZnO sensors exhibited enhanced sensor performance with optimum laser fluence compared with that of as-deposited sensors. The results suggested that the crystallinity of the Al-doped ZnO thin films was essential to achieve an optimum
gas detection capability. A laser doping process using a pre-deposited Al precursor layer for ZnO thin films was also investigated.

Plasma treatment was utilized in the research with the intention to adjust the number of intrinsic defects in ZnO films. Both O$_2$ and H$_2$ plasmas were carried out with the treatment time varying from 3 to 15 min. The gas sensor performance was investigated for NH$_3$ and NO$_x$ at various concentrations. An improvement of more than 50% in sensing response was observed with the optimum treatment time for NH$_3$ detection. The impact of H$_2$ plasma treatment of ZnO sensors on its gas sensor performance was also studied.

The selectivity was studied for a likelihood mixture of reducing gases. The results indicated that ZnO sensors had a low detection limit towards NH$_3$. It was found that the selectivity of these reducing gases was in the order of NH$_3$ > H$_2$ > CH$_4$. However, unless high concentration of NH$_3$ exposure is a factor, ZnO sensors are selective respond to H$_2$. Furthermore, the ZnO sensors are also capable of discriminating different gases such as NH$_3$, H$_2$, CH$_4$ and NO$_x$.

This research involves different techniques, which have been employed on the ZnO thin film based gas sensors in order to enhance the gas sensing characteristics such as sensing response and response time. As expected, the ZnO sensors exhibited high response, short response time and decent selectivity toward target gases with optimum treatment conditions. The results also suggested that the ZnO sensors were capable of detecting ppm level gases at relatively low operating temperature range (100 ~ 200°C), which is beneficial in many applications. Therefore, these techniques can be utilized to manufacture gas sensors using metal oxide semiconductors.
To my parents for their endless love, support and encouragement
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List of Abbreviations

BAW ...................... Bulk Acoustic Wave
CVD ....................... Chemical Vapor Deposition
DC ......................... Direct Current
EDX ........................ Energy Dispersive X-ray analysis
FWHM ........................ Full width half maximum intensity
JCPDS ........................ Joint Committee on Powder Diffraction Standards
LD ......................... Laser Diode
LPG .......................... Liquefied Petroleum Gas
MFC .......................... Mass Flow Controller
MOS .......................... Metal Oxide Semiconductor
MOSFET ........................ Metal Oxide Semiconductor Field Effect Transistor
PPM .......................... Part Per Million
PVD .......................... Physical Vapor Deposition
RF .......................... Radio Frequency
SAW ........................ Surface Acoustic Wave
SEM ........................ Scanning Electron Microscopy
UV-VIS .................... Ultraviolet Visible
XRD ........................ X-Ray Diffraction
VOCs ........................ Volatile Organic Compounds
List of Symbols

\( \alpha \) ........ Absorption Coefficient
\( \beta \) ........ Line Broadening at FWHM
\( \lambda \) ........ Wavelength
\( E_C \) ....... Energy of Conduction Band
\( E_V \) ....... Energy of Valence Band
\( E_F \) ....... Energy of Fermi Level
\( K \) ....... Shape Factor
\( R \) ....... Resistance
\( R_{\text{air}} \) ...... Resistance in air
\( R_{\text{gas}} \) ...... Resistance in exposure to an analyte gas
\( S \) ........ Sensitivity
\( T \) ....... Temperature
\( L_D \) ...... Debye Length
\( L_S \) ...... Depletion Layer Thickness
\( N_d \) ...... Concentration of the donor impurity
\( N_S \) ...... Concentration of the surface charge states
\( ns \) ...... Nanoseconds
\( k \) ........ Boltzmann constant
\( t \) ....... Time
\( h\nu \) ....... Incident photons energy
\( E_g \) ....... Electronic bandgap
Chapter 1

Introduction

Monitoring environmental gases and controlling industrial emissions are key targets for many industrial applications and domestic activities. The largest barrier to achieving improved process and environmental control is the interface between the system and the environment, i.e. the sensor [1]. Without sensors, significant advances in control and instrumentation will not be possible. Therefore, gas sensors play an important role of interface between environment and electronic system. Gas sensors have been employed in some dangerous working places in order to evaluate the air quality. Inevitably, occasional escapes of gas occur, which create a potential hazard to the industry plant, its employees, and people living nearby. Worldwide incidents involving asphyxiation, explosions, and loss of life are a constant reminder of this problem. For example, a gas detection system for ammonia could have helped preventing tragedy happened in fertilizer plant in west Texas in April 2013. In-situ exhaust gas sensors have been installed in automobiles to optimize the efficiency of internal combustion engines and to monitor their emission levels.
Table 1.1: Examples of gas sensor applications [2].

<table>
<thead>
<tr>
<th>Field of application</th>
<th>Function</th>
<th>Detected gases</th>
</tr>
</thead>
<tbody>
<tr>
<td>Environment</td>
<td>Monitoring toxic gases present in the atmosphere</td>
<td>CO, CH₄, humidity, CO₂, O₃, NOₓ, VOCs, SOₓ, HC₈, NH₃, H₂S</td>
</tr>
<tr>
<td>Safety at work</td>
<td>Control of indoor air quality</td>
<td>Toxic gases, combustible gases, O₂</td>
</tr>
<tr>
<td>Domestic safety/household</td>
<td>Detection of poisonous gases or smoke in households</td>
<td>CO₂, CH₄, humidity, CO₂, VOCs</td>
</tr>
<tr>
<td>Safety in car</td>
<td>Car ventilation control; gasoline vapor detection; alcohol breath tests</td>
<td>CO₂, CH₄, LPG, VOCs</td>
</tr>
<tr>
<td>Medical/clinical</td>
<td>Diagnostics (breath analysis, disease detection); point-of-care patient monitoring; drug monitoring; artificial organs and prostheses; new drug discovery</td>
<td>O₂, NH₃, NOₓ, CO₂, H₂S, H₂, Cl₂, anesthetics gases</td>
</tr>
<tr>
<td>Agriculture</td>
<td>Plant/animal diagnostics; soil and water testing; meat/poultry inspection; waste/sewage monitoring</td>
<td>NH₃, amines, humidity, CO₂</td>
</tr>
<tr>
<td>Food quality control</td>
<td>Detection of particular molecules</td>
<td>Humidity, CO₂</td>
</tr>
<tr>
<td>Industry: petrochemical</td>
<td>Process monitoring and control; quality control, workplace monitoring; wastewater monitoring; leakage alarms</td>
<td>HCs, conventional pollutants</td>
</tr>
<tr>
<td>Aerospace</td>
<td>Monitoring of oxygen and toxic and flammable gases in the environment</td>
<td>H₂, O₂, CO₂, humidity</td>
</tr>
</tbody>
</table>

Due to the international legislations of clean air laws, gas sensors are often used to continuously monitor air quality and the emission rate of specific chemical species. Therefore, gas sensors are critical electronic components in various modern technological processes, where control and analysis of gases are necessary. Table 1.1 gives some examples of gas sensor applications [2].
1.1 History and evolution of the gas sensor

Today, there are a large variety of gas sensors that have been developed [3-10]. These sensors are designed for the detection of a specific gas species or the identification of a gas mixture. The first method for detecting gases was to take a canary into a mine to detect exposure of methane (CH₄). Canaries were used because they are more susceptible than humans to low oxygen (O₂), methane and carbon monoxide (CO). The next type of gas detection was the catalytic combustion sensor. It uses a hot platinum wire working at several hundred degrees. A hot wire catalytic platinum filament oxidizes flammable gases or vapors at lower levels than they would normally oxidize in air. Oxidizing gases or vapors cause increase in temperature of hot wires, which increases electrical resistance of the wire. The “real” modern gas sensor became a reality in 1962. Seiyama et al. [11] first reported on a semiconductor gas sensor. They utilized the semiconductor catalysis mechanism, that is, the measurement of resistance change in a metal oxide (zinc oxide) upon gas absorption. After the invention of the semiconductor gas sensor, the targets of the investigation were closely related to daily life. After that, semiconductor combustible gas sensors, solid electrolyte oxygen sensors and humidity sensor were developed and commercialized for public use in the 70s. Today, extensive efforts are being made to advance these sensors and also to develop various new gas sensors due to the great demand from the market.
1.2 Definition and classification of gas sensors

1.2.1 Definition of gas sensor

A gas sensor is categorized as a chemical sensor. According to the International Union of Pure and Applied Chemistry (IUPAC), a gas sensor is defined as: a device that transforms chemical information, ranging from the concentration of a specific sample component to total composition analysis, into an analytically useful signal. The chemical information mentioned above, may originate from a chemical reaction of the analyte or from a physical property of the system investigated [12].

1.2.2 Classification of gas sensors

Gas sensors are classified in a number of different ways. One can classify gas sensors based on the type of sensing material, fabrication technology, field of application, detection principle and so on. Different classification approaches may be helpful in different sensor development stages. Below, the gas sensors are classified based on their gas detection principles.

1.2.2.1 Semiconductor gas sensor (SGS)

This type of gas sensor is operated based on the variation of electrical resistance/conductance of the sensing layers upon contact with the target gases. The semiconductor gas sensor typically utilizes metal oxides such as SnO₂, TiO₂, In₂O₃, WO₃, NiO and ZnO [13-19]. A semiconductor gas sensor element normally comprises 4 parts: sensing layers, substrate, electrodes and heater. The heater is separated from the sensing layer and the electrodes by an electrical insulating layer. The exact fundamental
mechanisms that cause a gas response are still controversial, but it is thought that the trapping of electrons at adsorbed molecules and band bending induced by these charged molecules are responsible for a change in resistance/conductance. Molecular oxygen adsorbs on the metal oxide surface by trapping an electron from the conduction band of the semiconductor. As a result, it generates a depletion layer and causes a bending of the energy band. For example, the negative surface charge causes an upward band bending and thus a reduced conductivity compared to the flat band situation.

Figure 1-1: Schematic diagram of band bending after chemisorption of charged species [20].

Figure 1-1 shows the schematic diagram of band bending. $E_C$, $E_V$ and $E_F$ denote the energy of the conduction, valence band and Fermi level, respectively. $\Delta_{air}$ denotes the
thickness of the depletion layer, and $eV_{\text{surface}}$ denotes the potential barrier. The conduction electrons are represented by $e^-$ and the donor sites are represented by $+$ [20]. The depletion region is also called the space charge layers, of which the thickness is the length of band bending region. Figure 1-2 illustrates the experimental results of oxygen species absorbed on the SnO$_2$ surfaces [21]. It can be found that at a relatively low temperature range, the molecule-ion species (O$_2^-$ or O$_{2\cdot}$) dominated the surface of metal oxide, whereas at relatively high temperature range, the atomic-ion species (O$^-$ or O$_{2\cdot}$) dominated the metal oxide surface. Yamazoe et al. [22] reported that four kinds of oxygen species formed on the SnO$_2$ surface, which is O$_2$ at 80°C, O$_2$ at 150°C, O$^-$ or O$_{2\cdot}$ at 560°C and a part of lattice oxygen above 600°C. O$^-$ (300-500°C) is found to be the most reactive oxygen species with gases. Therefore, most metal oxide gas sensors are operated within that temperature range.

![Figure 1-2: Experimental results of oxygen species absorbed on SnO$_2$ surface [21].](image)

Operating temperature is an important factor that greatly influences the gas response of semiconductor gas sensors. A higher temperature results in higher sensing response due to the lowering of activation energy for gas adsorption and desorption. One of the major objects in current research of semiconductor gas sensor is to decrease the operating temperature in order to lower the power consumption and also eliminate the safety concern. In the meantime, the stability of gas sensors becomes an issue when they operate at room temperature [23]. Therefore, a little higher temperature (100 ~ 200°C) would be better to improve the stability.

1.2.2.2 **Field effect sensors**

This type of sensor is operated based on the variation of work function induced by target gases. The field effect sensors generally consist of metal/oxide/semiconductor (MOS) layers. The field effect sensor can be divided into 3 major types based on different structures: the Schottky diode type, MOS capacitor type and the MOS field transistor (MOSFET) type.

1.2.2.3 **Piezoelectric sensor**

This type of sensor is operated based on the variation of acoustic wave properties of the piezoelectric materials to the exposure of target gases. The resonance frequency of bulk and surface acoustic wave (BAW, SAW) devices is sensitive to the accumulation of mass on the sensing material surface. Therefore, those devices are always used to measure the mass concentration of loading matter in ambient or in liquid conditions and process ultra-high sensitivity.
1.2.2.4 Fiber optic sensor

This type of sensor is operated based on the variation of optical properties of the sensing material induced by target gases. Generally, optical sensors form by coating thin films on the tips or sidewalls of optical fibers. The fiber optic sensors are also known as optrodes or optodes [24].

1.2.2.5 Electrochemical gas sensors

This type of gas sensor is operated based on the variation of electromotive force or electrical current in solid-state electrochemical cell. Electrochemical gas sensors employ an electrochemical cell consisting of a casing that contains a collection of chemical reactants in contact with the surroundings through two terminals of identical composition. The top of the casing has a membrane, which can be permeated by the gas sample. Oxidization or reduction occurs at one of the terminals. A current is created as the positive ions flow to the cathode and the negative ions flow to the anode [25].

1.3 Important factors in gas sensing properties

Based on the absorption and desorption model of semiconductor sensors, the factors that influence the gas sensor performance of semiconductor gas sensors such as dopant and grain size will be discussed briefly here.

1.3.1 Dopant effect

Doping is widely used in metal oxide materials to improve their physical and electrical properties. Physically, the dopant atoms segregate to grain boundaries and prohibit grain growth in subsequent annealing and also increase the chemical diversity of
metal oxides, which is beneficial for stability and selectivity. Electrically, foreign atoms incorporate into the lattice and generate ionic and electronic defects. These defects impact the position of the Fermi level, which in turn is expected to influence the gas response of the metal oxides [26]. The dopant has many other complex effects. Further investigation is expected to reveal the influence of doping on gas sensing.

1.3.2 Grain size effect

The sensors that consist of small crystalline particles generally show high sensing response due to the high surface-to-volume ratio. Recent reports on nanostructured materials for gas sensing applications further confirm that using fine particles as an active material can significantly enhance sensor performance [27].

The change in electrical resistance can be attributed to the variation of the thickness of the depletion layer. The depletion layer is characterized by thickness \( L_S \), \( L_S \), and surface potential \( V_S \). The Schottky approximation leads to:

\[
V_S = \frac{2\pi Q_s^2}{\epsilon N_d} = \frac{2\pi (qN_s)^2}{\epsilon N_d},
\]

(1)

Where, \( Q_s \) is the space charge density, \( \epsilon \) is the dielectric constant, \( N_d \) is the concentration of donor impurity, \( q \) is the surface state charge, and \( N_S \) is the concentration of surface charged states. The thickness of depletion layer can be expressed by:

\[
L_S = L_D \sqrt{\frac{eV_s^2}{kT}},
\]

(2)

Where, \( k \) is the Boltzmann’s constant and \( T \) is the temperature. \( L_D \) is a Debye length, which is given by:
The thickness of a depletion layer is generally around 1-100 nm [28].

1.3.3 Other factors

Many other factors, like crystallographic plane, catalytic noble metals, porosity of metal oxide can also influence the performance of gas sensors.

1.3.3.1 Crystalline facet effects

The effects of crystalline facet can be summarized as below [29]:

(1) The growth of grains is consistent with the size and the external shape of crystallites. Even a crystal in the initial state of growth has micro-planes and facets.

(2) External planes of nanocrystals determine the gas sensing properties when they participate in the gas-solid interaction.

(3) Every crystal has its own combination of crystallographic planes. This determines the surface state density, energy position, and adsorption/desorption energy.

The crystalline facet can be controlled in the deposition process.

1.3.3.2 Porosity

A porous structure of material helps gas molecules diffuse into or out of the metal oxide easily and also increases the reaction surface area. Therefore, high material porosity not only increases the response speed but also improves the sensitivity [30-32].
1.4 Gas sensor requirements & characteristics

Practically, a gas sensor should fulfill many requirements, which depend on the purpose, location and condition of sensor operation. The characteristics of sensors may help to assess sensor performance in a specific application. Among these requirements, the most important would be sensor performance related including sensitivity, response, selectivity, response time and recovery time.

**Sensitivity** \( (S) \) describes the change in the sensor response due to a specified change in the gas concentration, i.e., the slope of a calibration graph [33].

**Response** \( (R) \) of a sensor can be defined as \( (R_a - R_g) \times 100% / R_a \) for an n-type metal oxide gas sensor or \( (R_g - R_a) \times 100% / R_a \) for a p-type metal oxide gas sensor. Where, \( R_a \) stands for the resistance of the gas sensor in a reference gas (usually air) and \( R_g \) stands for the resistance in a reference gas containing the target gases.

**Selectivity** refers to the ability of gas sensors to identify a specific gas within a gas mixture. Investigation of selectivity for metal oxide based gas sensors is critical because metal oxides are normally sensitive to more than one chemical species in air and usually show cross sensitivities. Therefore, one of the main challenges to the researchers of metal oxide based gas sensors is high selectivity.

**Response time** \( (T) \) is the time required for a sensor to respond to a step concentration change from zero to a certain concentration value. The response time is defined as the time taken to reach a certain percent (50%, 70% or 90%) of the saturation value when the sensor is exposed to a target gas. A small value of response time indicates a fast sensor.

**Recovery time** is the time it takes for the sensor signal to return to its initial value after a step concentration change from a certain value to zero.
Other parameters such as stability, detection limit, dynamic range, linearity, resolution and life cycle are also important based on different demands of applications.

1.5 Metal oxide gas sensor

Semiconductor gas sensors also known as chemiresistive gas sensors, they are typically based on metal oxide materials such as SnO$_2$, TiO$_2$, WO$_3$, NiO, ZnO and so on. The use of metal oxide semiconductors as sensing materials provides several advantages such as low cost and high sensitivity.

1.5.1 Zinc oxide

Zinc oxide crystallizes in two main forms, hexagonal wurtzite and cubic zincblend. The wurtzite structure is most stable at ambient conditions and thus most common. The hexagonal structure has a point group of 6 mm, and the space group is P6$_3$mc or C$_{6v}$. The lattice constants are $a=b=3.25$ Å and $c=5.2$ Å with $c/a = 1.60$, which is close to the ideal value for a hexagonal cell $c/a = 1.633$ [34]. As in most group II-VI materials, the bonding in ZnO is largely ionic (Zn$^{2+}$– O$^{2-}$) with corresponding radii of 0.074 nm for Zn$^{2+}$ and 0.140 nm for O$^{2-}$. This property accounts for the preferential formation of wurtzite rather than zinc blende structure, as well as the strong piezoelectricity of ZnO [35]. The exciton binding energy of ZnO is 60 meV as compared to that of GaN, which is 25 meV [36]. This energy value is an indicator of radiative recombination efficiency of photogenerated carriers, which seems to improve for ZnO and thus indicates that ZnO may be an alternative to GaN in optoelectronic applications in the visible and near infrared wavelength range. Due to its unique properties, ZnO is widely used in various applications such as piezoelectric devices, varistors, surface
acoustic wave devices, transparent conductive oxide electrodes and so on. The point defects in ZnO can be zinc interstitial (Zn\textsubscript{i}) or oxygen vacancies (V\textsubscript{O}) [37], however, there is still debate about whether zinc interstitial or oxygen vacancy is the dominant defect.

### 1.5.2 Other metal oxides

Metal oxides such as SnO\textsubscript{2}, Al\textsubscript{2}O\textsubscript{3}, CuO, In\textsubscript{2}O\textsubscript{3}, Cr\textsubscript{2}O\textsubscript{3}, NiO, WO\textsubscript{3} and TiO\textsubscript{2}, can be utilized to detect combustible, reducing, or oxidizing gases with sensors which are mainly based on the resistance change responses to the target gases [38]. For example, TiO\textsubscript{2} is a common commercial material, which has a lot of valuable properties [39, 40]. TiO\textsubscript{2} is sensitive to a wide variety of gas species, e.g., liquefied petroleum gas (LPG) [41], methane (CH\textsubscript{4}) [42], carbon monoxide (CO) [43], ethanol [44] and hydrogen sulfide (H\textsubscript{2}S) [45]. Another widely used metal oxide semiconductor is tungsten trioxide (WO\textsubscript{3}) [46, 47]. WO\textsubscript{3} is the most widely used materials for the detection of nitrogen oxides, i.e. NO\textsubscript{2} and NO. It provides the highest response to NO\textsubscript{2} compared to other metal oxide semiconductor materials with minimal cross sensitivity and is used in many commercial products.

### 1.6 Synthesis of nanocrystalline metal oxide for gas sensor

Many techniques can be used to fabricate metal oxide semiconductor sensors, including screen printing and chemical or physical vapor deposition (CVD or PVD). When selecting proper fabrication methods, several aspects e.g., expense, purity, porosity, must be considered based on different application demands.
1.6.1 Screen printing

Screen-printing is the most widely used method for producing metal oxide semiconductor gas sensors commercially. The ink used for screen-printing contains the material to be deposited. The ink is pushed through a porous layer or mesh to produce the required layout on the substrates. After a heat treatment, a layer of solid material is deposited on the specific area [48].

1.6.2 Chemical vapor deposition (CVD)

Chemical vapor deposition is the process of one or more volatile compound reacting and/or decomposing on the substrate to produce high purity solid materials [49, 50]. The CVD process has a high deposition rate at relatively low temperature. Generally, CVD deposited films exhibit good conformal coverage, uniformity, adhesion and high purity. CVD produces dense films, which is a disadvantage for gas sensor applications [78].

1.6.3 Physical vapor deposition (PVD)

Physical vapor deposition is a vaporization coating technique, which involves the transfer of material on an atomic level. The process is similar to chemical vapor deposition except the material to be deposited is usually in solid form [51-55].

1.6.4 Sol-gel

Physical/chemical vapor deposition techniques require vacuum or reduced pressure conditions, which are time-consuming to achieve and maintain, as well as expensive evaporation/sputtering/ablation equipment, which increases production costs
The sol-gel process is a powerful alternative to the vacuum deposition methods due to its simple procedure, film quality controllability, cost effectiveness and large-area coating capability [56]. Also, dopants can be easily introduced using a sol-gel process.

1.7 Literature review

Many materials such as metal oxide semiconductors [57, 58], polymers [59-63], carbon nanotubes [64-66] and moisture absorbing materials [67], have been investigated for gas sensing purposes based on their electrical variation. Among them, nanocrystalline semiconducting metal oxide based gas sensors are of increasing interest in gas sensing and constitute a new and exciting subject of fundamental research [25]. Metal oxide semiconductors are the most widely used sensing materials and they have been studied in the last several decades [68-77]. For instance, Adamyan et al. [74] used a sol-gel process, which is a common method for fabricating nanocrystalline oxide thin films to produce SnO$_2$ thin films. The materials demonstrated a high sensitivity to the presence of H$_2$. Choi et al. [75] studied the H$_2$ sensing response of SnO$_2$ thin films with different crystal orientations. They suggested that the (101) orientated SnO$_2$ films exhibited higher gas response than (002) and (101) orientated ones. Gong et al. [76] has investigated the role of Cu doping in ZnO film in enhancing the capability of the films to adsorb CO molecules. They suggested that the Cu site in ZnO films play an important role in adsorbing CO molecules at both low and high temperatures. Navale et al. [77] reported the selective NO$_x$ sensing characteristics of Al-doped ZnO synthesized in the form of porous pellets. They compared its gas sensing performance in presence of different gases such as SO$_x$, HCl, Liquefied petroleum gas (LPG), H$_2$S, H$_2$, NH$_3$, alcohol and acetone, and found it selectively detects NO$_x$ due to Al-doping.
1.8 Significance of surface modification

The semiconducting metal oxide gas sensor is categorized in surface chemistry, because the gas detection through redox reactions with gas molecules is carried out at the surface, and the reactivity and the kinetics are closely related to surface feature [79]. The gas response is a surface-controlled process, and therefore surface modification techniques can strongly affect the gas sensor properties.

1.9 Organization of this dissertation

Chapter 2 of this dissertation is devoted to the undoped ZnO thin film gas sensor derived by sol-gel technique. Undoped ZnO is the basis for doping, which is also very important. The general sol-gel spin coating parameters such as precursor composition, solution concentration, preheating temperature and aging period are critical for deposition of ZnO films. In this chapter, the effect of preheating temperature on the properties of nanocrystalline ZnO thin films was presented.

Chapter 3 discusses the Al doping in ZnO. The Al-doped ZnO films were successfully prepared with two different precursors by a sol–gel process. The effect of starting material on the microstructure, surface morphology, electrical conductivity and gas sensing performance was investigated as a function of Al dopant concentration.

Chapter 4 focuses on the laser irradiation effect on Al-doped ZnO thin films. A pulsed laser system with a wavelength of 532 nm was used to performance the laser irradiation on the AZO surface. The microstructure, optical transmittance, electrical properties, surface morphology and gas sensing characteristics of laser-irradiated AZO films were investigated and compared with that of the as-deposited AZO films. The gas
sensor performance of AZO films was studied as a function of film thickness as well as laser energy level toward H₂.

Chapter 5 discusses Ga doping in ZnO. The properties and gas sensing behaviors were comprehensively characterized as a function of Ga doping concentration. The Ga concentration was varied in a low concentration range from 0.1 to 1.0 at%. The effect of Ga doping on structural, optical, morphological, electrical and gas sensing properties were comprehensively characterized.

Chapter 6 analyzes the effect of laser doping process on ZnO. We focused on developing and improving the nanocrystalline ZnO processing technique using an Nd:YVO₄ laser to produce ZnO sensors with high sensitivity and selectivity for the detection of H₂. We examined the effects of laser doping fluence on ZnO thin films and their gas sensor application.

Chapter 7 is dedicated to the influence of O₂ plasma treatment on nanocrystalline ZnO thin films and its impact on gas sensor performance. The ZnO thin films were O₂ plasma treated for a variety of time durations (3~15 min). The gas sensor performance under different concentrations of NH₃ was investigated.

Chapter 8 summarizes the results of this dissertation.
Chapter 2

Gas Sensor Based on Undoped Nanocrystalline Zinc Oxide

2.1 Introduction

Zinc oxide, as a well-known semiconducting material, has attracted extensive research interests mainly due to its wide direct band gap and large binding energy. With these appealing properties, ZnO has been widely used in microelectronics, optoelectronics and information technology applications including light emitting diodes [80, 81], transparent electrodes in solar cell [82], photodetectors [83] and surface acoustic wave devices [84]. The ability of ZnO to detect chemical species at low concentration levels (ppm level) in the atmosphere enables its applications of gas sensors, which are important for industrial emission control, environmental pollution monitoring, medical diagnosis and so forth. ZnO is a promising material because of its low cost, nontoxicity and simplicity. ZnO thin film based gas sensors can be prepared in a variety of nanostructures such as nanoparticles, nanorods, and nanowires. Nanoparticles possess unique size-related properties such as high surface-to-volume ratio, which is beneficial to gas sensor applications. The sol-gel process is known as a wet chemical deposition
method, which is a powerful alternative to the vacuum deposition methods. The advantages of sol-gel process include easy handle process, large area deposition, economy and easy control of the final quality of the thin films [85, 86]. The chemical and physical parameters of sol-gel process such as precursor composition, solution concentration, preheating temperature and aging period strongly influence the properties of ZnO films. Among these parameters, the preheating temperature plays an important role on the evolution of texture in ZnO films.

2.2 Experimental

The sol-gel process, also known as soft chemistry allows synthesize a solid material from a solution by using a sol or a gel as an intermediate step at a low temperature compared with that of traditional methods.

![Schematic diagram of preparation of ZnO thin films by the sol-gel process.](image)

Figure 2-1: Schematic diagram of preparation of ZnO thin films by the sol-gel process.

The synthesis of solid materials via chemistry often involves wet chemistry reactions and sol-gel chemistry based on the transformation of molecular precursors into an oxide network by hydrolysis and condensation reactions [87]. Figure 2-1 shows the
main steps of preparation of ZnO thin films by the sol-gel process in this study. This preparation procedures can be summarized in three parts: (i) preparation of precursor, (ii) deposition of ZnO thin films by spin coating, (iii) heat treatment of the ZnO thin films.

2.2.1 Preparation of precursor

Many zinc compounds can be used as a precursor such as zinc nitrate, zinc chloride and zinc perchlorate. But the most often used one is the zinc acetate dehydrate. The sol-gel precursor was prepared by dissolving zinc acetate dehydrate (ZnAc, Zn(\(\text{CH}_3\text{COO}\))\(_2\cdot2\text{H}_2\text{O}\), 99%) in isopropyl alcohol. Monoethanolamine (MEA) was added into the solution as a well-know sol-gel stabilizer regent [88, 89]. The solution concentration was maintained at 0.3 M and the molar ratio of zinc acetate to MEA was 1.0. The solution was then ultrasonically dissolved for 15 min to yield a homogenous and transparent solution. Before serving as a coating precursor, the solution was aged at room temperature for 12 h while magnetic stirring.

2.2.2 Sol-gel processing of ZnO thin films

Alkali-free glass was used as substrate. Before spin coating, the glass substrates were rinsed with detergent to remove the organic residuals and then were washed completely with deionized water. After that the glass substrates were immediately dried in the air. Finally, the glass substrates were ultrasonically cleaned in acetone bath for 15 min. The ZnO thin films were coated on the glass substrates at a rotation speed of 3000 rpm for 30 s to ensure the solution uniformly covered the whole substrate surface. Four sets of samples were prepared. After each coating process, the films were preheated at 75,
150, 250 and 350°C for 3 min, respectively. This coat-preheating process was repeated for 5 times for all the samples to form uniform multilayered ZnO thin films.

2.2.3 Calcination

After spin coating, all the ZnO thin films were annealed in ambient air at 550°C for 3 h to enhance crystal growth. We obtained homogenous and transparent thin films without cracks. Figure 2-2 shows the deposition steps of ZnO thin films.

![Deposition steps of ZnO thin films](image)

Figure 2-2: Deposition steps of ZnO thin films.

2.2.4 Characterization

The XRD analysis was carried out by an X-ray diffractometer (PANalytical X’Pert Pro MPD) using Cu Kα radiation source. The scanning range was from 2θ = 25° to 45° with λ=1.5418 Å. Scherrer equation $D = \frac{K\lambda}{\beta\cos\theta}$ was used to estimate the average grain size from XRD data. Where, $K (=0.94)$ is the shape factor, $\beta$ is the full
width at half maximum (FWHM) of the XRD peak corresponding to $2\theta$. Optical transmittance was measured in the wavelength range of 365 – 965 nm using ultraviolet visible spectrometer (SHIMADZU UV-1650PC). The surface morphology was determined by scanning electron microscopy (Hitachi S-4800). The electrical property was investigated in vacuum environment (100 mTorr). The resistances of the samples were collected in the temperature range of 298 K to 473 K. The gas sensor performance was examined in a homemade testing system. The configuration of the system was showed in Figure 2-3.

![Figure 2-3: Schematic diagram of the gas testing setup.](image)

Vacuum thermal evaporation was used to deposit a thin layer of Au on the surface of the ZnO thin film. Two finger-patterned electrodes were developed by optical
lithography. The dimension of the finger pattern was given in Figure 2-4. The sensors were heated to 150°C by a heater made of a Ni-Cr coil while the temperature was monitored by a thermocouple and controlled by a power supply (VIZATEK MPS-3003LK-2). The resistance of sensors were measured by a high mega-ohm multimeter (KEITHLEY 2001) and collected by the computer system. Different concentrations of mixture gases were introduced into the test chamber with a constant airflow of 100 ccm. The sensing response of sensor is defined as,

\[ S = \left( \frac{R_a - R_g}{R_a} \right) \times 100\% \]  

Where, \( R_a \) is the resistance of the sensor measured in the air and \( R_g \) is the resistance in the presence of both air and the target gas.

Figure 2-4: Dimensions of Au finger-patterned electrodes.
2.3 Results and Discussions

2.3.1 Structural properties

Figure 2-5 shows the X-ray diffraction spectra of ZnO thin films preheated at 75, 150, 250 and 350°C, respectively. It was clearly shown that all the ZnO films had a polycrystalline structure. Three peaks corresponding to the (100), (002) and (101) planes were detected in the range of 2θ = 30° - 40°, which confirmed the presence of ZnO.

![X-ray diffraction spectra of ZnO thin films preheated at different temperatures.](image)

Figure 2-5: X-ray diffraction spectra of ZnO thin films preheated at different temperatures.
Figure 2-5(b) shows the XRD pattern of ZnO thin films preheated at 150°C. Three peaks with similar intensity were detected. However, the films became more c-axis oriented as the increase of preheating temperature from 150 to 350°C. This phenomenon may be due to the grains try to grow along with the surface which has the lowest free energy. This result suggests that the crystal orientation of ZnO thin films is preheating temperature dependent.

Figure 2-6(a) shows the relative intensities $i_{(002)}$ of ZnO thin films as a function of preheating temperature.

![Graph](image)

**Figure 2-6:** (a) Relative intensities of ZnO thin films. (b) Grain sizes of ZnO thin films.

It was shown that the relative intensity of (002) peak increased significantly with the increase of the preheating temperature from 75 to 350°C. Figure 2-6(b) illustrates the grain sizes of ZnO thin films with different preheating temperatures. The average grain size decreased from 67 nm to 50 nm with increasing the preheating temperature. This
result suggests that the grain size decreases with the increase of the preheating temperature.

2.3.2 Optical properties

Figure 2-7 shows the optical transmittance spectra of ZnO thin films preheated at different temperatures in the wavelength range of 365 to 965 nm. It was shown that all the films were highly transparent in the visible wavelength range (390 to 750 nm).

![Optical transmittance spectra of ZnO thin films.](image)

The average transparency of the films was around 87%. The high transparency suggested that the thin films had a good structural homogeneity and crystallinity. The transmittance spectra fell down sharply in the ultraviolet region (100 - 400 nm) due to the onset of the light absorption. The inset of Figure 2-7 shows the transmittances of ZnO thin films in the range of 370 ~ 390 nm. It was also observed that the absorption
thresholds shifted to the shorter wavelength (blue shift) as increasing the preheating temperature. This feature was known as the Burstein-Moss (BM) shift.

2.3.3 Morphological properties

Figure 2-8 shows the SEM images of ZnO thin films preheated at 75, 150, 250 and 350°C, respectively. The grains of ZnO films preheated at 75°C did not fully develop.

![SEM images of ZnO thin films](image)

Figure 2-8: SEM images of ZnO thin films preheated at (a) 75°C, (b) 150°C, (c) 250°C and (d) 350°C.

As the preheating temperature increased to 150°C, the grains became larger than that of ZnO films preheated at 75°C. The large and small grains were mixing together in the figure (Figure 2-8). In contrast, the grain size of the ZnO thin films decreased significantly as the preheating temperature increased to 250°C. Some joint grains were
also observed on the surface. On the other hand, the grain size slightly increased with further increase of the preheating temperature to 350° C.

2.3.4 Electrical properties

Figure 2-9 shows the variation of logarithm of conductivity against reciprocal of temperature for ZnO films. The temperature dependence of conductivity can be described by Arrhenius equation, which is given by:

\[ \sigma = \sigma_0 \left( \frac{-E_a}{kT} \right) \]  \hspace{1cm} (5)

Where, \( \sigma, T, \sigma_0, E_a \) and \( k \) are the conductivity, temperature, co-factor, activation energy and Boltzmann constant, respectively.

![Graph showing the variation of logarithm of conductivity against reciprocal of temperature for ZnO thin films.](image)

Figure 2-9: Variation of logarithm of conductivity against reciprocal of temperature for the ZnO thin films.
It was seen that the conductivity of the ZnO thin film increased as the increase of preheating temperature due to the intrinsic characteristics of semiconducting ZnO. The ZnO thin film preheated at 75°C exhibited a low conductivity due to the poor development of grains. The ZnO thin films preheated at higher temperatures showed higher conductivities. The activation energy of conduction was estimated by measuring the slope of the linear zone of Arrhenius plot. The activation energies for all the films were listed in the figure (Figure 2-9). The activation energy of the ZnO thin film increased as the increase of the preheating temperature.

2.3.5 Gas sensor performance

The gas sensor performance towards H₂ was examined in this study. The operating temperature was 150°C.

Figure 2-10: The gas response versus H₂ concentration ranging from 500 to 3000 ppm for ZnO sensors preheated at different temperatures.
Different concentrations of H$_2$ ranging from 500 to 3000 ppm were introduced into the testing chamber. Figure 10 shows the dependence of sensing response versus H$_2$ concentration ranging from 500 to 3000 ppm in the air for ZnO sensors preheated at different temperatures. It was apparently shown that the sensing response increased as the increase of H$_2$ concentration from 500 to 3000 ppm. Upon 3000 ppm H$_2$ exposure, the sensing response increased from 13.13 to 76.17% as the preheating temperature increased from 75 to 250°C. The sensing response enhanced significantly with optimum preheating temperature (~ 250°C). However, with further increase of the preheating temperature to 350°C, the sensing response slightly decreased.

![Sensing Response vs Time](image)

Figure 2-11: Dynamic response and recovery of ZnO sensors for 1000 ppm of H$_2$.

Figure 2-11 shows the dynamic response and recovery of ZnO sensors upon 1000 ppm H$_2$ exposure. The sensors preheated at 150, 250 and 350°C exhibited immediately response to the H$_2$. All the sensors recovered to their baseline after stopping H$_2$. 
2.4 Summary

Nanocrystalline ZnO thin films were successfully synthesized using sol-gel process with different preheating temperatures. The XRD patterns show that all the ZnO thin films have a polycrystalline structure. Three peaks corresponding to the (100), (002) and (101) crystal planes were detected in the range of $2\theta = 30^\circ$ to $40^\circ$. The XRD result indicates that the ZnO thin films become highly c-axis oriented as the preheating temperature increased. The grain size was estimated using Scherrer equation. The result indicates that the grain size decreased as the increase of preheating temperature. The optical transmittance shows that all the thin films are highly transparent in the visible wavelength range. A blue shift of band gap was observed on the thin films preheated at $250^\circ$C. The SEM images show that the grain size becomes smaller at high preheating temperatures, which have good agreement with the XRD result. The gas sensor performance was measured at an operating temperature of $150^\circ$C. The concentration of H$_2$ ranging from 500 to 3000 ppm along with 100 ccm air was introduced into the testing chamber. It was found that the sensing response increased as the increase of H$_2$ concentration. The best sensor performance was obtained at ZnO sensors preheated at $250^\circ$C, which possessed highest gas response and shortest response time.
Chapter 3

Gas Sensor Based on Aluminum Doped Nanocrystalline Zinc Oxide

3.1 Introduction

3.1.1 Background of gas sensing studies in ZnO

It is generally believed that the oxygen adsorbate (O$_2^-$) in metal oxide layer is reactive with reducing gas in the temperature range of 300–500°C [89] and a high operating temperature is usually used to utilize this phenomenon in the metal oxide-based sensors. Many researchers have reported ZnO gas sensors for different gases, such as CO, ethanol, and NH$_3$ [90-92]. For instance, Bott et al. [93] reported that ZnO sensors reached the maximum sensitivity for H$_2$ and CO at an operating temperature of around 400°C. Although a high operating temperature enhances sensitivity, there exist some limitations to gas sensor applications because of the stability of metal electrode/oxide interface and power requirements. Most investigations have been focused on highly sensitive gas sensors, which usually require high power levels to constantly heat the sensing components to several hundred degrees of Celsius in ambient conditions. Although a low
operation temperature is desired, few investigations have been done in a low temperature range (100–200°C). The fabrication of room temperature hydrogen sensors has been reported using single ZnO nanorods [95]. This sensor has been tested only in dry air and it is not clear whether this sensor works in ambient conditions, which have higher concentrations of water vapor. The gas sensing behavior of metal oxide thin film based sensors also depends on the size of the nano-particles and the porosity of the films.

3.1.2 Current status of gas sensing studies in Al-doped ZnO

One way to achieve a low operating temperature is to apply impurity doping in ZnO. Aluminum, as a dopant, plays a very important role in ZnO gas sensors. Nanto et al. [96-98] reported that an Al-doped ZnO film could be applied as a smell sensor. Mukhopadhyay et al. [94] reported on the hydrogen sensing behavior of Al-doped ZnO, however, no detail about the performance of the gas sensor was reported. Undoped ZnO films possess high resistance and therefore measurement of sensor characteristics or other electrical conductivity in low temperature region needs high impedance electronic circuits and systems. Therefore, it is worthwhile to investigate whether the resistance of ZnO films can be reduced without affecting the gas sensing properties. One way to address this issue is impurity doping in ZnO films in nanocrystalline form.

3.2 Experiments

3.2.1 Preparation of sol–gel mixtures

Figure 3-1(a) and (b) shows the flow charts for the preparation procedures of precursor-1 and precursor-2, respectively. Precursor-1 was prepared by dissolving zinc-
acetate dihydrate (ZnAc, Zn(CH$_3$COO)$_2$·2H$_2$O, 99%) in isopropyl alcohol, in which MEA (ethanolamine) was added as a stabilizer.

Figure 3-1: Preparation steps of sol-gel mixtures: (a) preparation procedures of precursor-1 using zinc acetate and (b) preparation procedures of precursor-2 using zinc nitrate.

Precursor-2 was prepared by dissolving zinc nitrate into a mixture of isopropyl alcohol and glycol. Aluminum nitrate (Al(NO$_3$)$_3$·9H$_2$O) was added to both mixtures with [Al]/[Zn] atomic ratio varying from 1.0 to 5.0 at% as a dopant material in ZnO. The solution concentration was kept at 0.5 M by adjusting the amount of isopropyl alcohol in the solutions. Then the resultant solutions were placed in an ultrasonic bath at room temperature for 15 min to yield clear and homogenous solutions. Prior to the coating of sol–gel mixtures on a substrate, these precursor solutions were aged for 12 h at the room temperature under magnetic stirring.
3.2.2 Coating and calcination

Glass substrates were cleaned ultrasonically with acetone for 10 min. The sol-gel mixtures were spin-coated on the glass substrates at a rotation speed of 3000 rpm for 30 seconds to ensure the solution spreads over the whole substrate surface uniformly. In order to remove the extra solvent and organic residuals, the coated films were preheated on a hotplate at 150°C for 10 min. This coating process was repeated for 5 times to form a uniform multi-layered film. Finally, the films were annealed in a furnace at 550°C for 3 h in air.

3.2.3 Characterization

The electrical properties of Al-doped ZnO films were investigated by measuring the resistance of the samples as a function of temperature. An X-ray diffractometer (PANalytical X’Pert Pro MPD) with Cu-K radiation was used to study the crystal structure of the films. The scanning range was from $2\theta = 30^\circ$ to $50^\circ$ with $\lambda = 1.5418$ Å. The average grain size ($D$) of Al-doped ZnO films was estimated as described in 2.2. The surface morphology was observed with scanning electron microscopy (SEM, JEOL 6100). The thicknesses of films were measured with atomic force microscopy (AFM) measurements. Also, the thickness of films was estimated with optical reflectance of films by model fitting based on Fresnel approach [99]. The average thickness of films was estimated to be $\sim 180 \pm 4$ nm.
3.3 Results and Discussions

3.3.1 Electrical properties

Figure 3-2(a) and (b) shows the variation of logarithm of conductivity against reciprocal of temperature for Al-doped ZnO films prepared by precursor-1 and -2, respectively. The temperature dependence of conductivity can be described with the Arrhenius equation as described in previous work. The measurements were carried out under a vacuum (<10 mTorr) in the temperature range of 50-200 °C. The conductivities of the films increased with the increase of temperature due to the intrinsic characteristics of semiconducting ZnO. The conductivities of samples made with both precursors were enhanced by doping of Al compared with their undoped counterparts. The increase in conductivity may be due to the enhancement of the electron concentration by Al donors. In Figure 3-2(a), the 1.0 at% Al-doped sample showed the highest conductivity in a given temperature range. However, a further increase in Al dopant concentration resulted in a systematically decrease of the conductivity. A similar behavior was also observed in Figure 3-2(b). It showed that the conductivity increased to the maximum value at an Al doping level of 2.0 at%, and thereafter, it decreased to the minimum value at Al doping level of 5.0 at%. This phenomenon can be attributed to the buildup of space charge potential barriers across the grain boundaries [100]. High Al doping resulted in a dramatic decrease of grain size and therefore, a sufficient space charge region was generated. Due to the low resistance of the core region of the grain and the high resistance of the space charge region, the resistance increases with decreasing grain size after the grain size exceeding a critical value. It was also observed that the films prepared by precursor-1 had a higher conductivity than the films prepared by precursor-2.
Figure 3-2: Variation of logarithm of conductivity against reciprocal of temperature for Al-doped ZnO films prepared by (a) precursor-1 and (b) precursor-2.

3.3.2 Structural properties

Figure 3-3(a) and (b) shows the XRD patterns of Al-doped ZnO films prepared by precursor-1 and -2 in the range of $2\theta = 30$-$50^\circ$. Three peaks corresponding to the (100), (002) and (101) planes were detected in the range of $2\theta = 30$-$40^\circ$. It indicated that ZnO thin films had a wurtzite structure according to the report in JCPDS file [102]. The XRD patterns of the films prepared by precursor-2 (Figure 3-3(b)) show peaks corresponding to the crystal planes of (002) and (101). There was no evidence to indicate the formation
of other phases, such as $\text{Al}_2\text{O}_3$ or $\text{ZnAl}_2\text{O}_4$. However, due to the low Al solubility in ZnO, the real Al doping concentration in the films can be lower than 5.0 at%. In both cases, we observed a drastic deterioration of film crystallinity at high Al doping concentrations in comparison with their undoped counterparts, which had a well-developed crystalline structure. The degradation of the film crystallinity can be attributed to the deformation of the lattice structure due to the smaller ionic radii of $\text{Al}^{3+}$ (~0.053 nm) than $\text{Zn}^{2+}$ (~0.075 nm) [102].

![X-ray diffraction patterns of Al-doped ZnO films](image)

Figure 3-3: X-ray diffraction patterns of Al-doped ZnO films prepared by (a) precursor-1 and (b) precursor-2.

Figure 3-4(a) shows the relative intensities of $i_{(002)}$ for the films prepared by precursor-1. Relative intensity of (002) peak is defined as,
\[ i_{(002)} = \frac{I_{(002)}}{I_{(100)} + I_{(002)} + I_{(101)}} \]  

(6)

The calculated values of relative intensities \(i_{(002)}\) were between 22\% and 43\%. It increased to 43\% for 3.0 at\% of Al concentration suggesting that the crystallites grown were more c-axis orientated. However, \(i_{(002)}\) decreased to 22\% at 5 at\% of Al dopant concentration suggesting that the c-axis orientation was deteriorated when the Al dopant concentration was higher than 3 at\%.

The average crystallite size as a function of Al dopant concentration was estimated by Scherrer formula. Figure 3-4(b) illustrates the crystallite size of the films prepared by precursor-1. As the dopant concentration varied from 0 to 5 at\%, the average crystallite size decreased from 48 to 11 nm, which is significantly smaller than the crystal size of undoped films. Since the radii of Al\(^{3+}\) ion (~0.053nm) is smaller than Zn\(^{2+}\) ion
(\sim 0.075 \text{ nm}), with more Al$^{3+}$ ions emerging and replacing the Zn$^{2+}$ ion in the lattice, the crystallite size becomes smaller.

3.3.3 Morphological properties

Figure 3-5 shows the surface morphology of undoped and Al-doped ZnO films prepared by two precursors. Two distinct microstructures of Al-doped ZnO were observed. As seen in Figure 3-5(a), (c) and (e), a porous wrinkle network structure was appeared and uniformly distributed over the sample surfaces. The formation of this structure increased the roughness of the films. The width of the ZnO pipe systematically decreased with the increase in Al dopant concentration. Also, the grain size gradually decreased as the Al dopant concentration increased from 0 to 3 at\%. This phenomenon had a good agreement with the XRD results. It has been reported that the formation of wrinkles is due to the existence of MEA in the precursor [103]. Based on our previous work [105], little evidence showed that MEA was the critical factor for the formation of wrinkle structures. Nevertheless, the formation of the wrinkle structure may be related to the release of mechanical stress, which was generated during the preheating process [105-106]. By comparing our results with previous studies [105], the formation of the wrinkle structure can be carefully controlled by adjusting the preheating conditions in the spin coating process. The films prepared with precursor-2 (Figure 3-5 (b), (d) and (f)) exhibited a lower roughness and a higher density than films prepared by precursor-1, which produced wrinkle free ZnO films.
3.3.4 Gas sensor performance

Figure 3-6(a) and (b), respectively, shows the sensing response of ZnO films prepared by precursor-1 and -2 as a function of $\text{H}_2$ concentration. As can be seen, the response increased when the concentration of $\text{H}_2$ increased. It was also observed that the sensors prepared by precursor-1 showed a higher response than the sensors prepared by
precursor-2 under the same concentrations of H\textsubscript{2}. The response and recovery processes of sensors prepared by precursor-1 were faster than sensors prepared by precursor-2. The difference of response between sensors prepared with precursor-1 and precursor-2 became smaller with the decrease of H\textsubscript{2} concentration from 2000 to 50 ppm.

Figure 3-7 shows the sensing response of Al-doped ZnO films for H\textsubscript{2} concentrations ranging from 400, 800, 1200 and 2000 ppm. The doped films exhibited an enhanced response compared with the undoped films. In both cases (precursor-1 and -2), the sensing response increased with increasing the concentration of H\textsubscript{2} from 400 to 2000 ppm.

![Figure 3-6: The sensing response and recovery time versus sensing response of undoped ZnO sensors prepared by (a) precursor-1 and (b) precursor-2 for different H\textsubscript{2} concentrations. The numbers at each curve indicate the concentration of H\textsubscript{2} in ppm.](image)

For the sensors prepared with precursor-1, a large difference was observed in the sensing response at a low concentration of H\textsubscript{2} (e.g. 400 ppm). On the other hand, the responses of sensors prepared with precursor-2 exhibited a convergent behavior. Also,
the effect of the doping level was larger for precursor-1 than precursor-2 for low concentrations of H$_2$. When the concentration of H$_2$ increased, the effect of doping level on the response was not significant for precursor-1. The sensing response reached to the maximum (~70%) when the Al dopant concentration was 3 at%. However, further increase of the doping level resulted in a decrease of the response.

![Graph](image)

Figure 3-7: Variation of sensing response as a function of H$_2$ concentration for sensors prepared by (a) precursor-1 and (b) precursor-2.

These results indicated that the response of Al-doped ZnO was strongly influenced by the doping level. It may be due to the fact that when the optimum amount of Al atoms was incorporated into the ZnO lattice, the electron density in the lattice was enhanced and also the crystallite size was decreased. When the crystallites became smaller, more reaction surface had been created and the crystallite size reached the thickness of the depletion layer [107]. These combined phenomena enhanced the sensing response at moderately high doping level (~3 at%).
Figure 3-8(a) and (b) shows the dynamic response behaviors at an operation temperature of 160°C under 1200 ppm of H₂ for sensors prepared with precursor-1 and -2, respectively.

Figure 3-8: Comparison of sensing response, response and recovery under 1200 ppm H₂ concentration for sensors prepared by (a) precursor-1, (b) precursor-2 and (c) the response time for undoped and 3.0 at% of Al-doped sensor for different H₂ concentrations.

When H₂ was introduced into the chamber, a rapid response was observed in both
cases, especially for the 3 at% Al-doped sensors. Figure 3-8(c) shows the response time for undoped and 3 at% Al-doped sensors when exposed to different H₂ concentrations. It was revealed that the response time was H₂ concentration dependent. When H₂ concentration was increased to 2000 ppm, the response time decreased to 50% of the response time for 400 ppm H₂ for both precursors. Furthermore, when the concentration of Al increased to 3.0 at%, the response time exhibited a distinct decrease for both precursors. However, no significant improvement was observed in the recovery process of the sensors by changing the doping level of Al. The recovery process of the sensor depends on the re-adsorption behavior of oxygen and removal of hydrogen from the surface [108], which mainly depends on the operating temperature. Since the operating temperature in the chamber was unchanged, no significant improvement in the recovery of the sensors could be observed during the tests.

The selective detection capability of a target gas is one of the critical properties of gas sensors. In order to quantify the effect caused by other gases, the sensors were tested in the presence of different compositions of the background gas. Here, the sensor selectivity was investigated for a likelihood mixture of reducing gases, such as H₂, CH₄ and NH₃. Figure 3-9(a) shows the gas sensitivity for H₂ in the presence of CH₄ in the air. The gas sensor made with 3.0 at% Al-doped film was tested at 160°C for different H₂ concentrations while passing 2000 ppm CH₄ in the air. The sensitivity for 2000 ppm of CH₄ was less than 10% whereas a rapid response was observed when 400 ppm of H₂ was introduced to the system in the presence of CH₄.
Figure 3-9: Sensing response of 3.0 at% of Al-doped sensor prepared by precursor-1 for
(a) H₂ in presence of CH₄ and (b) CH₄ in presence of H₂.

The sensitivity reached the maximum (~70%) while introducing 2000 ppm of H₂ indicating that the presence of CH₄ has no significant effect on H₂ detection. The sensitivity for CH₄ in the presence of H₂ in the air is shown in Figure 3-9(b). The concentrations of CH₄ were increased from 1000 to 3000 ppm while 2000 ppm H₂ are in the background gas. It was clearly seen that the sensor had a fast response to the background H₂, however; no significant change was detected after introducing CH₄ into the chamber. Therefore, the Al-doped ZnO gas sensor has a better selectivity for H₂ than CH₄ at 160°C.

Figure 3-10(a) shows the sensitivity for H₂ in the presence of NH₃. The selectivity of H₂ versus NH₃ was tested under the same conditions used for H₂ versus the air. In this case, 15–100 ppm of NH₃ was used because hazardous level of NH₃ was established within this range [109]. The sensor response for 75 ppm NH₃ in the air is around 40%. The sensitivity reached to 70% while passing 2000 ppm H₂ to 75 ppm NH₃ containing air (Figure 3-10(a)). Figure 3-10(b) shows the gas sensitivity for CH₄ in the presence of 75
ppm NH₃ in the air. The results shown in Figure 3-10(b) indicated that the selectivity of NH₃ versus CH₄ was excellent. The results indicated that the selectivity of these reducing gases was in the order of NH₃ > H₂ > CH₄.

![Figure 3-10: Sensing response of 3.0 at% of Al-doped sensor prepared by precursor-1 for (a) H₂ in presence of NH₃ and (b) CH₄ in presence of NH₃.](image)

The gas sensing properties of nanocrystalline ZnO thin films have been reported by early researchers. It is important to reduce the operation temperature of gas sensor without affecting the performance of the sensors. However, the sensor properties are affected by lowering the operating temperature due to several reasons, such as high impedance of sensors, poor response and recovery speeds, and poor selectivity. In this paper, we investigated the dependence of microstructure and sensing properties of ZnO films on the selection of precursors and impurity doping in the synthesis of ZnO films. The results indicated that the material fabrication process could be optimized to achieve high performing sensors within a low temperature region. A skeletal wrinkle network structure was observed in films prepared with zinc acetate. Also, it was found that this
structure was critical to gas sensing properties. Furthermore, the sensitivity of Al-doped films reached a sensitivity of 70% in 87 s at operating temperature around 160°C. For sensors prepared with both precursors, the 3.0 at% Al-doped ZnO gas sensors are found to have optimal sensor performance. Our findings also indicate that the Al-doped samples have low resistance and these sensor devices can be used in a low temperature system.

3.4 Summary

Al-doped ZnO films were fabricated using the sol–gel process with different Al doping concentrations using zinc acetate and zinc nitrate as the starting materials. The microstructure and electrical properties of Al-doped ZnO films were investigated as a function of doping concentrations and the type of the precursor. The crystallinity of films dramatically deteriorated with an increase in Al dopant concentration for both precursors. When zinc acetate was used as the starting material, a skeletal wrinkle network structure formed and it affected the roughness, conductivity and gas response of ZnO films significantly. The films prepared by both precursors with 3.0 at% of Al dopant concentration have an improved conductivity and gas response. Furthermore, the response times of sensors were enhanced by Al doping for films prepared with both precursors. The gas selectivity of 3.0 at% Al-doped ZnO sensor also reported in this study, which suggested that the sensor had an excellent selectivity for H₂ in the air. This investigation suggests that the Al-doped ZnO films have several advantages over undoped ZnO in gas sensor applications, such as (i) low resistive devices, which do not require high impedance peripheral circuits and systems, (ii) tunability of selectivity based on response time constant, and (iii) low operation temperature.
Chapter 4

Laser Irradiation Effect on Aluminum Doped Nanocrystalline Zinc Oxide

4.1 Introduction

4.1.1 Background of laser irradiation on metal oxide materials

In recent years, laser irradiation has emerged as a novel heat treatment method substituting conventional furnace heating due to its local and rapid thermal heating ability [110-112]. Compared with conventional furnace annealing, a laser beam heats a small local area rather than an entire system. Therefore, the process of laser irradiation using continuous wave laser or pulsed laser has been mainly confined to the post annealing of materials. Little information has been reported on surface modification of thin films using laser treatment. As well, the effect exerted by laser irradiation on the properties of thin films is complicated. The kinetic evolution during the laser irradiation process is driven by the fast variations of the thermal field, inducing rapid melting, solidification and dopant redistribution [113-115].
4.1.2 Laser irradiation parameters

The laser irradiation source can be a continuous wave laser or pulsed laser. The pulse width of a solid-state laser used for the post treatment of semiconductors is typically in the range of tens of nanoseconds (ns). The pulse energy of the laser beam is dependent on the laser diode current. The higher the laser diode current is, the larger the energy of the beam is. The size of the irradiated area depends on the size of the laser focus on the sample surface. Under the same laser power, the smaller of the focus area is, the higher the laser energy deposited.

4.2 Experiments

4.2.1 Sample preparation

The AZO films were deposited on the alkali-free glass substrates by a sol-gel spin coating technique. The preparation process of the ZnO precursor was described in 2.2. Depending on the required Al doping concentration, aluminum nitrate (Al(NO$_3$)$_3$·9H$_2$O, 98.0~102.0%) was dissolved in isopropyl alcohol. The doping concentration of Al was 1 at%. Both Zn and Al solutions were ultrasonically dissolved for 15 min to yield clear and transparent solutions, then the two solutions were mixed together under magnet stirring. The concentration of the mixture was kept at 0.3 M by adjusting the solvent. The precursor was finally obtained after 12 h aging of the mixture at room temperature. The cleaning and drying processes of glass substrates was described in our previous work. The precursor was spin-coated on the glass substrate at a rotation speed of 3000 rpm for 30 s to make sure the solution covered the whole substrate surface uniformly. In order to remove the extra solvent and organic impurity, the films were preheated on a heater at
250°C for 3 min. This process was repeated 2 or 5 times, in order to obtain uniform multilayer thin films with a desired thickness. The post annealing condition was the same as the previous samples. The thicknesses of 2-layer and 5-layer AZO films were approximately 68 and 187 nm, respectively.

4.2.2 Laser irradiation on Al-doped ZnO

A diode-pumped, Q-switched Nd: YVO₄ laser system (Osprey-532-5-0) with a wavelength of 532 nm was used to perform the irradiation of the AZO film surfaces. The laser beam diameter was about 80 µm, and the incident laser fluence was varied from 1.06 to 3.58 J/cm² by changing the diode current. We named the as-deposited films, laser-irradiated films with 1.06 J/cm², films with 2.92 J/cm² and films with 3.58 J/cm² as a, b, c and d, respectively. Therefore the AZO films were designated according to both their coated layers and laser fluence, e.g. sample-2a. The names of the samples were listed in Table 4.1.

Table 4.1: The designated names for the samples.

<table>
<thead>
<tr>
<th>Laser Fluence (J/cm²)</th>
<th>2-Layer</th>
<th>5-Layer</th>
</tr>
</thead>
<tbody>
<tr>
<td>As-deposited</td>
<td>2a</td>
<td>5a</td>
</tr>
<tr>
<td>1.06</td>
<td>2b</td>
<td>5b</td>
</tr>
<tr>
<td>2.92</td>
<td>2c</td>
<td>5c</td>
</tr>
<tr>
<td>3.58</td>
<td>2d</td>
<td>5d</td>
</tr>
</tbody>
</table>

4.2.3 Characterization

In our study, the scanning range was from 2θ = 30° to 40°. Optical transmittance was measured in the wavelength range of 370 – 1000 nm using an UV/Vis
spectrophotometer (SHIMADZU UV-1650PC). The surface morphology was examined by scanning electron microscopy (Hitachi S-4800). The electrical properties and gas sensor performance were tested on a homemade device. The configuration of the system was described in our previous work [116]. During testing, the sample was placed in an insulated glass test chamber with a controlled temperature. The operating temperature was constantly monitored by a thermocouple. During testing, 100 ccm of air was used as a carrier gas. Different amounts of test gases were introduced to obtain the required ppm level concentration.

4.3 Results and Discussions

4.3.1 Structural properties

Figure 4-1 shows the X-ray diffraction patterns of as-deposited and laser-irradiated 5-layer AZO films. All the films exhibited only one prominent peak at around $2\theta = 34.4^\circ$, which indicated a (002) preferential growth orientation along the c-axis perpendicular to the substrate surface. The c-axial preferred orientation can be attributed to the nature of the grain that it tends to grow along the lowest surface energy plane. It is believed that the preferential orientation is caused by the minimization of the surface energy and internal stress [117]. By comparing the results with our previous work [105], it was clearly showed that the crystal orientation could be controlled in the preheating process. The preparation of highly oriented films on amorphous substrates by sol-gel technique and the understanding of the role of the different parameters that are involved is an interesting research area that should be further explored [118]. The XRD spectra revealed the effect of laser irradiation on the microstructure of AZO thin films.
Figure 4-1: X-ray diffraction patterns of 5-layer as-deposited and laser-irradiated AZO films.

Table 4.2: The FWHMs, average grain sizes and 2θ for 5-layer as-deposited and laser-irradiated AZO films.

<table>
<thead>
<tr>
<th>Sample #</th>
<th>FWHM. [Deg.]</th>
<th>Height [cts]</th>
<th>2θ [Deg.]</th>
<th>Grain Size [nm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>5a</td>
<td>0.231</td>
<td>1388</td>
<td>34.386</td>
<td>37.65</td>
</tr>
<tr>
<td>5b</td>
<td>0.220</td>
<td>2337</td>
<td>34.394</td>
<td>39.53</td>
</tr>
<tr>
<td>5c</td>
<td>0.250</td>
<td>504</td>
<td>34.379</td>
<td>34.77</td>
</tr>
<tr>
<td>5d</td>
<td>0.251</td>
<td>389</td>
<td>34.372</td>
<td>34.63</td>
</tr>
</tbody>
</table>

According to Figure 4-1 and Table 4.2, the (002) diffraction peak of sample-5b became strong and narrow indicating that grain growth had occurred, and the shift of (002) peak to higher 2θ angles indicated the partial relief of residual stress within the laser irradiated AZO films. However, a continuous shift of (002) peak to lower 2θ was observed on sample-5c and sample-5d, which implied that high residual stress was
introduced by high laser fluence. The average grain sizes of the films are listed in Table 4.2. It can be observed that sample-5b exhibited an increase in both grain size and peak intensity. On the other hand, both grain size and peak intensity decreased significantly with high laser fluence irradiation (sample-5c and sample-5d).

4.3.2 Optical properties

Figure 4-2 shows the optical transmittance spectra of as-deposited and laser-irradiated 5-layer AZO thin films.

![Transmittance spectra of 5-layer as-deposited and laser-irradiated AZO films.](image)

All the films were transparent in the visible range with an average transparency of more than 80%. The transmittance of sample-5b increased, whereas the transmittance of sample-5c and sample-5d continuously decreased. The increase of the optical
transmittance of sample-5b can be attributed to the weakening of scattering and absorption of light due to better crystallinity. A sharp absorption edge was observed in the UV region on all the films due to the onset of fundamental absorption. The absorption edge shifted to a shorter wavelength (blue shift) with the increase of laser fluence indicating the broadening of optical band gap induced by laser irradiation. Both the stress relaxation and the increase of defects density could result in the shift of optical band gap.

4.3.3 Morphological properties

Figure 4-3 shows the surface morphology of as-deposited and laser-irradiated 5-layer AZO thin films. It was noted that the grain size of sample-5b slightly increased compared with that of sample-5a. However, a continuous decrease in grain size was observed on sample-5c and sample-5d. This observation is consistent with the XRD results. Furthermore, it was worthwhile to notice that sample-5d exhibited a surface with extremely high densification and flatness. The histogram of grain size distribution was obtained from SEM images. It was apparent that the distribution of grain size showed strong laser fluence dependence. The distribution peak gradually shifted to the smaller grain size range as the increase of laser fluence. It was also observed that the range of the grain size distribution noticeable narrowed as the increase of laser fluence.

55
Figure 4-3: SEM images of 5-layer Al-doped ZnO films: (a) sample-5a, (b) sample-5b, (c) sample-5c and (d) sample-5d.

4.3.4 Electrical properties

Figure 4-4 shows the variation of $\ln(\sigma)$ against the reciprocal of temperature ($1/T$). It revealed that the resistance decreased with an increase of temperature indicating the semiconducting nature of AZO films. Laser irradiation influenced the electrical properties of AZO films exhibiting a variation of conductivity. The conductivity of sample-5b decreased compared with sample-5a whereas the conductivity of sample-5c and sample-5d enhanced remarkably after laser irradiation. A tendency that the conductivity of AZO thin films is inversely proportional to the intensity of the (002) diffraction peak was observed after comparing Figure 4-4 and Figure 4-1.
Figure 4-4: Variation of logarithm of conductivity against reciprocal of temperature for 5-layer as-deposited and laser-irradiated 5-layer AZO films.

By measuring the slope of a linear zone of Arrhenius plot, the activation energy of conduction was estimated to be 0.345, 0.398, 0.402 and 0.482 eV for sample-5a, 5b, 5c and 5d, respectively. As the laser fluence increased, the activation energy increased.

4.3.5 Discussion of laser irradiation effect on structural, optical and electrical properties

The laser irradiation produces two kinds of AZO films according to its energy level: (1) low laser fluence produces highly crystallized AZO film with large grains and low conductivity, and (2) high laser fluence produces low crystallized AZO films with small grains and high conductivity. It has been reported that the highly crystalline films are likely to contain a lesser number of charge carriers such as electrons, whereas films with lower crystallinity may contain a higher number of charge carriers [119]. In the first
case, low laser fluence promotes the growth of the grains in order to minimized free energy of the film. This process decreases the crystal lattice deficiencies and thus enhances the crystallinity in the films, which results in a decrease in electrical conductivity. In contrast, high laser fluence is likely to generate more donor defects and consequently causes the increase of conductivity.

4.3.6 Gas sensor performance

The effect of laser irradiation on gas sensor performance of 2-layer and 5-layer AZO sensors to detect the presence of H\textsubscript{2} at various concentrations in the air was examined at an operating temperature of 130\textdegree C.

Figure 4-5: Sensing response and recovery versus time of (a) 2-layer and (b) 5-layer as-deposited AZO sensors.

Figure 4-5 shows the response and recovery characteristics of (a) 2-layer and (b) 5-layer as-deposited AZO sensors for various H\textsubscript{2} concentrations. It was seen that the response increased as H\textsubscript{2} concentration increased from 1000 to 2500 ppm. The
dependence of response on concentration can be explained as a high concentration of \( \text{H}_2 \) provides more \( \text{H}_2 \) molecules to be absorbed on the oxide surface per unit time, therefore the response increases as a result of favoring the fast electron transport kinetics [120]. Although the 5-layer AZO sensor exhibited higher response than the 2-layer AZO sensor under the same concentration of \( \text{H}_2 \) exposure, the response and recovery time of the 2-layer AZO sensor were around twice as fast as the 5-layer AZO sensor.

Figure 4-6 shows the sensing response of (a) 2-layer and (b) 5-layer as-deposited and laser-irradiated AZO sensors as a function of \( \text{H}_2 \) concentration. The laser irradiation influenced the AZO sensors by increasing or decreasing the sensing responses. As shown in Figure 4-6(a), the sensing responses of 2-layer AZO sensors increased with increasing laser fluence and reached their maximum at 2.92 J/cm\(^2\) (sample-2c), and then decreased with further increasing the laser fluence to 3.58 J/cm\(^2\) (sample-2d). Thus, the 2-layer AZO sensors yielded the higher sensing response at a moderate laser energy level. It was observed in Figure 4-6(b) that the sensing response of sample-5b was notably higher than the as-deposited AZO sensor (sample-5a). However, it was also seen that laser fluence greater than 1.06 J/cm\(^2\) resulted in deterioration in sensing response (sample-5c and 5d). Therefore, the 1.06 J/cm\(^2\) would be an appropriate energy level for the modification of 5-layer AZO sensors. The results suggest that the sensing response of AZO sensor can be improved by laser irradiation with optimal laser fluence. The sensing response of AZO sensors varied depending on the film thickness as well as pulse laser energy. The thicker AZO sensor demonstrated an optimum sensing response at a low laser energy level and the thinner AZO films showed an optimum sensing response at a moderate laser energy level.
Figure 4-6: The variation of sensing response of (a) 2-layer and (b) 5-layer as-deposited and laser-irradiated AZO sensors as a function of H$_2$ concentration.

Figure 4-7 shows the dynamic response and recovery of (a) 2-layer and (b) 5-layer as-deposited and laser-irradiated AZO sensors under 1666 ppm H$_2$ concentration. When H$_2$ was introduced, the response of all the sensors increased with operation time, especially for sample-2c and sample-5b. The response of all the sensors recovered to their baseline after turning off the H$_2$. Figure 4-7(c) shows the T$_{70}$ response time of 2-layer and 5-layer as-deposited and laser-irradiated AZO sensors. The response time decreased as the increase of H$_2$ concentration indicating H$_2$ concentration dependence of response time. The response time of 2-layer AZO sensors was shorter than that of 5-layer AZO sensors under every given H$_2$ concentration. It was also observed that the optimum laser fluence irradiated AZO sensors exhibited a faster sensing response than that of as-deposited AZO sensors, which indicated that optimum laser fluence remarkably shorten the response time of the AZO sensor.
Figure 4-7: Response and recovery characteristics of (a) 2-layer and (b) 5-layer as-deposited and laser-irradiated AZO sensors upon 1666 ppm H₂ exposure, (c) T₇₀ response time of 2-layer and 5-layer as-deposited and laser irradiated AZO sensors.

The ability of a sensor to respond to a certain gas in the presence of other gases is known as selectivity. In this work, the selectivity of sample-5b was examined for a reducing gas mixture of H₂ and CH₄. Figure 4-8(a) shows the sensing response and recovery characteristic of sample-5b to H₂ in the presence of CH₄. The H₂ concentration was varied from 1000 to 2500 ppm while 2500 ppm CH₄ was presented in the
background gas.

![Graph showing sensing response](image)

Figure 4-8: Sensing response of sample-5b for (a) H\textsubscript{2} in presence of CH\textsubscript{4}, (b) CH\textsubscript{4} in presence of H\textsubscript{2}.

The sensor slowly responded to 2500 ppm CH\textsubscript{4} and saturated to around 3\% within 10 min. When 1000 ppm H\textsubscript{2} was introduced into the system, a rapid response to H\textsubscript{2} was detected. The response of the sensor reached its maximum value under 2500 ppm H\textsubscript{2} concentration. The results indicated that the presence of CH\textsubscript{4} had no significant effect on the detection of H\textsubscript{2}. The response and recovery characteristic of sample-5b to CH\textsubscript{4} in the presence of H\textsubscript{2} was shown in Figure 4-8(b). The CH\textsubscript{4} concentrations increased from 1000 to 3000 ppm with 2500 ppm H\textsubscript{2} presented in the background gas. It was apparent that the sensor had a rapid response to H\textsubscript{2}. However, no significant difference on sensing response was detected after CH\textsubscript{4} exposure. Therefore, the selectivity of H\textsubscript{2} in comparison with CH\textsubscript{4} was excellent, as indicated by the relatively high response to H\textsubscript{2}.

Figure 4-9 shows the comparison of 70\% gas response slope for sample-5b to H\textsubscript{2} and NH\textsubscript{3}. In this case, 15–100 ppm of NH\textsubscript{3} was used because the hazardous level of NH\textsubscript{3}
was established within this range. The response slope increased with increasing H$_2$ or NH$_3$ concentration. The response slope of H$_2$ was much larger than NH$_3$. The results implied that unless a high concentration of NH$_3$ exposure is a factor, sample-5b is more sensitive to H$_2$, and the influence of NH$_3$ on the detection of H$_2$ is negligible.

![Figure 4-9: Comparison of 70% gas response slopes of sample-5b for H$_2$ and NH$_3$.](image)

4.3.7 Discussion of laser irradiation effect on gas sensing performance

Carrier concentration or structural defect in the films would be different by changing the film thickness [122, 123]. Generally, there are larger carrier concentrations or structural defects with increasing the film thickness, which could behave as traps for photons. Therefore, the thicker films have larger laser absorptivity than that of the thinner films and hence require lower laser fluence. The results also strongly suggest that the smaller grain size of the AZO films does not necessarily mean the enhancement of sensor
performance, but the crystallinity of the AZO films is essential to achieve optimum gas detection capabilities. It is known that the surface-to-volume ratio plays an important role in gas sensing. Smaller grained films generally possesses larger surface-to-volume ratio. Therefore higher sensing responses are expected. However, our study showed larger grained films exhibited better sensor performance, which seems counter-intuitive. This is because the enhancement of crystallinity overcomes the adverse effect of grain growth [119]. In the case of the high laser fluence irradiated sensors, although the surface-to-volume ratio enhances significantly, the sensing response decreased as a result of crystallinity degradation. Other researchers have also reported the significance of crystallinity towards gas sensing behavior of metal oxides [119-124]. It is known that the oxygen adsorbates cover AZO surface that induce a depletion layer. The sensing response is associated with the variation of the depletion layer. Since the depletion width is inversely proportional to the square root of carrier concentration, a decrease of carrier concentration results in an increase of the variation of depletion width [125]. Low laser fluence decreases the conductivity of the films, which results in a greater variation of resistance. High laser fluence significantly increased the conductivity of the AZO films, which in turn decreased the number of available adsorption sites. Thus, laser irradiation can be utilized as a surface modification technique for AZO gas sensor.

4.4 Summary

In conclusion, laser irradiation was introduced to modify the gas sensing properties of AZO thin films by adjusting the laser fluence from 1.06 to 3.58 J/cm². The structural, optical, morphological and electrical properties of 5-layer AZO films were investigated and compared with that of as-deposited AZO films. It was found that the
crystalline quality was enhanced by laser irradiation with optimum laser fluence. The optical transmittance increased and then decreased with increasing laser fluence. The SEM images showed that low laser fluence produced slightly larger grains and a more porous surface than that of as-deposited film, whereas high laser fluence resulted in small grains and a dense surface. The sensing response of AZO sensors towards $\text{H}_2$ varied depending on the film thickness as well as the laser energy level. Optimum laser fluence enhanced both the sensing response and the response time. However, excessive laser fluence deteriorated the gas sensing properties of AZO sensors by decreasing sensing response. The thicker AZO sensor demonstrated an optimum sensing response at a low laser energy level and the thinner AZO films showed an optimum sensing response at a moderate laser energy level. Furthermore, the optimum 5-layer AZO sensor exhibited an excellent selectivity towards $\text{H}_2$. Based on these analyses, laser irradiation was found to be an effective method to modify the gas sensing properties of AZO films.
Chapter 5

Gas Sensor Based on Gallium Doped Nanocrystalline Zinc Oxide

5.1 Introduction

5.1.1 Background of Ga doping in ZnO

ZnO is a widely investigated metal oxide semiconductor due to its potential applications in UV light emitters, gas sensors, transparent electronics, piezoelectric devices [126-129]. As a gas sensing material, ZnO is found to be sensitive to many sorts of gases with satisfactory chemical stability. Typically, the resistances of undoped ZnO films are relatively high. One effective way to further improve the electrical properties of ZnO is doping with impurities such as Al, Ga, In. Moreover, it is believed that the dopants can modify the gas sensing characteristics to some extent. For example, the sensing response (or sensitivity) and the temperature where the sensing response maximum is gained ($T_M$) can be significantly changed by the dopant [130, 131]. In order to achieve doping, the impurity atoms have to satisfy several criteria to substitute the host atoms in the lattice, e.g. similar atomic radii with host atom, higher valency than host...
atom. Gallium, as one of the element in the group-III with an ionic radius of 0.062 nm, becomes the best candidate of doping source for ZnO.

5.1.2 Current status of Ga-doped ZnO study

It is found that the Ga-doped ZnO is relatively less studied compared with that of Al-doped ZnO [132]. Most previous studies on Ga-doped ZnO have focused on the investigation of optical and electrical properties of Ga-doped ZnO transparent conducting oxide thin films for display and solar cell applications [133, 135]. There is a lack of information on the effect of Ga doping on gas sensor applications. On the other hand, researchers have reported the low solubility of Ga in ZnO. For instance, Yoon et al. [136] investigated the solubility limits of Al and Ga in ZnO and found that the solubility of Ga is 0.5 at%. Goncalves et al. [137] reported that Zn and Ga compound was observed even in ZnO:Ga at 1 at%. Therefore, it is worthwhile to conduct a systematic experiment to investigate the gas sensing properties of low concentration Ga doped ZnO gas sensors.

5.2 Experiments

5.2.1 Sample preparation

The preparation procedure of ZnO precursor was as described in 2.2. Gallium nitrate (Ga(NO₃)₃·xH₂O) was selected as a doping source. In order to achieve low concentration doping, desired amount of gallium nitrate was dissolved in isopropyl alcohol with Ga dopant concentration [Ga]/[Zn] varying from 0 to 1.0 at%. The two solutions were mixed together and then ultrasonically dissolved for another 10 min. The final precursor was obtained after aging at room temperature for 12 h at room
temperature under magnet stirring. The solution concentration was maintained 0.25 M. Alkali-free glass was used as deposition substrate. Before spin coating, the substrate was cleaned. The cleaning process was described in previous work. The spin coating, pre-heating and post-heating processes of Ga-doped ZnO was described in 2.2. After each coating process, the films were preheated at 250°C for 3 min. As a result, we obtained homogenous and transparent thin films without cracks and with satisfactory adhesion to the substrates.

5.2.2 Characterization

The scanning range of XRD was from 2θ = 25° to 75°. Optical transmittance and reflectance were measured in the wavelength range of 200 – 1200 nm using ultraviolet visible spectrometer (Cary 5 Diode Arrary HP8452A). The surface morphology was determined by scanning electron microscopy (Hitachi S-4800). The average thickness of samples were estimated to be 200 nm from the cross sectional SEM images. The electrical properties and gas sensor performance was measured on a homemade device, which was presented in Figure 2-3. The resistance of the sample was collected in the temperature range of 298 to 473 K as a function of temperature. The sensors were heated to 130°C by a heater made of a Ni-Cr coil while the temperature was monitored by a thermocouple and controlled by the power supply (VIZATEK MPS-3003LK-2). The other working conditions were the same as described in previous chapters.
5.3 Results and discussions

5.3.1 Structural properties

Figure 5-1(a) shows the XRD patterns of undoped and Ga-doped ZnO thin films with Ga concentrations varying from 0.1 to 1.0 at%. One predominant peak and two small peaks were detected in the range of $2\theta = 25^\circ$ to $75^\circ$, which correspond to (002), (101) and (202) planes, respectively. The predominant peak implied that all the films had a preferential growth orientation along (002) plane.

![XRD patterns and grain sizes](image)

Figure 5-1: (a) XRD diffraction patterns of undoped and Ga-doped ZnO films, (b) grain sizes of undoped and Ga-doped ZnO thin films.

The Ga-doped ZnO films exhibited higher peak intensities than undoped ZnO film. The intensity of the (002) peak increased significantly with the increase of Ga concentration ($0 - 0.1$ at%) and then decreased with further increase of Ga concentration ($0.3 - 1.0$ at%). The 0.1 at% Ga-doped ZnO films exhibits the highest peak intensity
suggesting that Ga$^{3+}$ ions replace Zn$^{2+}$ in the lattice substitutionally, due to their small ionic radius compared with that of Zn$^{2+}$. Other researchers also reported the same behavior [138, 139]. For example, Dghoughi et al. [138] reported the same behavior in his study on Al doping in ZnO. The decrease of intensity on higher Ga doping concentrations may be due to the formation of stresses induced by the difference of ionic radius and the segregation of Ga in grain boundaries. Figure 5-1(b) shows the grain sizes estimated along the (002) peaks versus Ga doping concentrations for the undoped and Ga-doped ZnO thin films. It was seen that the grain size decreased rapidly as the Ga doping level increased up to 0.5 at% and then reached a plateau afterwards.

5.3.2 Optical properties

Figure 5-2(a) shows the optical transmittances and reflectances of undoped and Ga-doped ZnO thin films. All the films were highly transparent in the visible region (390-750 nm). The average transparency of the films in the visible range was around 85%, which indicated a good structural homogeneity and crystallinity of the thin films.

Figure 5-2: (a) Optical transmittance spectra of undoped and Ga-doped ZnO thin films, (b) plot of $(a h \nu)^2$ versus $h \nu$ for undoped and Ga-doped ZnO thin films.
The Ga-doped ZnO films exhibited higher transparencies in the comparison with undoped film, which may be due to the weakening of light scattering caused by c-axis orientation enhancement after Ga doping. Moreover, a continuously shift of absorption edge to the shorter wavelength (blue shift) with the increasing Ga doping concentration was observed in Ga-doped ZnO thin films in Figure 5-2(a). This behavior is known as Burstein-Moss shift [140]. In order to estimate the band gap, the $(\alpha h\nu)^2$ versus $h\nu$ plot is required. The absorption coefficient $\alpha$ was calculated by [141],

$$T = \frac{(1-R)^2 \exp (-\alpha d)}{1-R^2 \exp(-2\alpha d)}.$$  \hspace{1cm} (7)

Where, $T$ is the transmittance, $R$ is the reflectance, $\alpha$ is the absorption coefficient and $d$ is the thickness of the thin films. Figure 5-2(b) shows the plot of $(\alpha h\nu)^2$ versus $h\nu$ for undoped and Ga-doped ZnO thin films as a function of Ga doping concentration. It can be seen that the optical band gap values were in the range of 3.278 to 3.285 eV. The band gap of Ga-doped ZnO thin films were slightly increased from 3.278 to 3.285 eV with the increase of Ga concentration from 0.1 to 1.0 at%. Both the stress relaxation and the increase of defects density could result in the shift of optical band gap. However, the variation of optical band gap is not significant, which may be due to the low doping concentration of Ga in ZnO thin films.

5.3.3 Morphological properties

Figure 5-3 shows the surface morphology of undoped and Ga-doped ZnO thin films studied by SEM. The SEM image of undoped ZnO thin film showed a dense surface covered with irregular shaped grains in which had an average grain size of 80.37 nm. A similar surface morphology was observed for 0.1 at% Ga-doped ZnO thin film.
(Figure 5-3(b)). It can be noticed that the grain size significantly decreased as the Ga doping concentration increased, up to 0.5 at%. The 0.3 and 0.5 at% Ga-doped ZnO thin films showed surfaces with small and large grains randomly distributed.

Figure 5-3: SEM images of (a) undoped, (b) 0.1 at%, (c) 0.3 at%, (d) 0.5 at% and (e) 1.0 at% Ga-doped ZnO thin films.
The average grain sizes of 0.3 and 0.5 at% Ga-doped ZnO thin films decreased to 60.98 nm and 48.73 nm, respectively. Beyond 0.5 at%, the surface of the film became porous and the average grain size slightly increased to 65.89 nm. The increase of grain size of 1.0 at% Ga-doped ZnO thin films can be attributed to the improvement of surface diffusion at 1.0 at% Ga doping concentration. It was also observed that the porosity increased after Ga doping. The histogram of the grain size distribution was obtained from the SEM images. The grain size distribution peak gradually shifted to the small grain size range with the increase of Ga doping concentration, which indicated that more small grains were created. It was also observed that the range of the grain size distribution narrowed from 30 – 150 nm to 30 – 90 nm as the Ga doping concentration increased to 0.5 at%. The SEM observation of grain size was in a good agreement with XRD result.

5.3.4 Electrical properties

Figure 5-4(a) shows the variation of logarithm of conductivity against reciprocal of temperature for undoped and Ga-doped ZnO films. The electrical resistances of the films were measured in a vacuum environment in the temperature range of 298 to 473 K. It can be seen that the conductivity of all the films increased with the increase of temperature, which indicated the semiconductor nature of ZnO. The conductivity of ZnO thin film significantly increased after doping with Ga. The highest conductivity was obtained at 1.0 at% Ga doping concentration. The increase of conductivity can be attributed to the increase of free electrons generated by Ga incorporated in ZnO lattice. The linear relationship between logarithm of conductivity and reciprocal of temperature with a negative slope is described by Arrhenius equation. Therefore, the activation energy can be estimated from Figure 5-4(a) using the slope of fitted line. Figure 5-4(b) shows the
calculated activation energies for undoped and Ga-doped ZnO thin films. It can be observed that the activation energy decreased drastically after Ga doping and then the decreasing trend of activation energy gradually slowed down with the further increase of Ga doping concentration.

Figure 5-4: (a) Variation of logarithm of conductivity against reciprocal of temperature for undoped and Ga-doped ZnO thin films, (b) Activation energies of undoped and Ga-doped ZnO thin films.

The inset of Figure 5-4(b) shows the I/V curve of Ga-doped ZnO films. It showed that the conductivity gradually increased with the increase of Ga concentration. No current flow was observed for undoped ZnO film at room temperature.

5.3.5 Gas sensor performance

We studied the sensing response of the Ga-doped ZnO sensors to the presence of different H₂ concentrations in the air at an operating temperature of 130°C. The variation
of response for undoped and Ga-doped ZnO sensors under 500, 1000, 2000 and 3000 ppm H₂ exposure was showed in Figure 5-5. It was clearly shown that the response value of every sensor increased with the increase of H₂ concentration from 500 to 3000 ppm. The increasing trend of response implied that the response of Ga-doped ZnO sensor was H₂ concentration dependent.

![Graph showing variation of response as a function of H₂ concentration for undoped and Ga-doped ZnO sensors.](image)

Figure 5-5: Variation of response as a function of H₂ concentration for undoped and Ga-doped ZnO sensors.

The phenomenon can be explained as a result of the increase of surface coverage of H₂ on the sensors [141]. It was also observed that Ga-doped ZnO sensors exhibited higher H₂ response than that of undoped sensor except for that of 0.1 at% Ga-doped ZnO sensor. The 0.3 at% Ga-doped ZnO sensor reached the highest response to every H₂
concentration. Moreover, the difference of sensor responses at high H\textsubscript{2} concentration was larger compared with sensor response at low H\textsubscript{2} concentrations.

Figure 5-6(a) shows the dynamic variation of response to 3000 ppm of H\textsubscript{2} at an operation temperature of 130\textdegree C for undoped and Ga-doped ZnO sensors. When H\textsubscript{2} was introduced into the chamber, the response increased sharply in the beginning (~200 s) and then gradually slowed down and finally saturated at the maximum value. After stopping the H\textsubscript{2}, the response of the sensors recovered to the baseline.

![Figure 5-6: (a) Dynamic response and recovery characteristics of undoped and Ga-doped ZnO sensors for 3000 ppm H\textsubscript{2} in the air, (b) The response time of undoped and Ga-doped ZnO sensors as a function of H\textsubscript{2} concentration.](image)

Figure 5-6(b) shows the response time T\textsubscript{70} of undoped and Ga-doped ZnO sensors for different concentrations of H\textsubscript{2}. It was seen that the response time decreased with the increase of H\textsubscript{2} concentration from 500 to 3000 ppm, which suggested that the response time was also H\textsubscript{2} concentration dependent. It was also observed that 0.3 at% Ga-doped ZnO sensor showed the shortest response time under every H\textsubscript{2} concentration. A
slight improvement in response time was also observed on 1.0 at% Ga-doped ZnO sensor.

Here we examined the gas selectivity of 0.3 at% Ga-doped ZnO sensor for a mixture of reducing gases such as H₂, CH₄ and NH₃ at an operating temperature of 130°C. Figure 5-7(a) shows the response to H₂ in presence of CH₄ in the air. After 3000 ppm CH₄ exposure, the sensor slowly responded to CH₄ and reached a maximum response of 12% for approximately 10 min. However, a rapid response was observed when 1000 ppm H₂ was introduced into the chamber. The response reached the maximum value while introducing 3000 ppm H₂. The result suggested that the presence of CH₄ has no significant effect on H₂ detection. The response to CH₄ in presence of H₂ in the air showed in Figure 5-7(b).

Figure 5-7: Gas response of 0.3 at% Ga-doped ZnO sensor for (a) H₂ in presence of CH₄ and (b) CH₄ in presence of H₂ in the air.

It was clearly seen from the figure that the sensor responded immediately to the gas after 2000 ppm H₂ exposure, whereas no significant change on response was
observed after introducing various concentrations of CH$_4$ into the chamber. Therefore, we can conclude that the 0.3 at% Ga-doped ZnO sensor had a superior selectivity to H$_2$ in comparison of CH$_4$ at an operating temperature of 130$^\circ$C.

The response of H$_2$ versus NH$_3$ was also tested. Figure 5-8(a) shows the response to H$_2$ in the presence of NH$_3$. In this case, 15-100 ppm of NH$_3$ was used because hazardous level of NH$_3$ was established within this range. The response to 50 ppm NH$_3$ in the air was around 45%. The response reached to 62% while passing 1500 ppm H$_2$ in the presence of 50 ppm background NH$_3$.

Figure 5-8: Gas response of 0.3 at% Ga-doped ZnO sensor for (a) H$_2$ in the presence of NH$_3$ and (b) NH$_3$ in presence of H$_2$ in the air.

Figure 5-8(b) shows the response to NH$_3$ in the presence of 2000 ppm H$_2$ in the air. The sensor showed a rapid response to the background gas. After 30 ppm NH$_3$ exposure, the response of the sensor increased and finally reached the maximum value while passing 50 ppm NH$_3$ into the chamber. The results indicated that unless high
concentrations of NH$_3$ exposure are a factor, the Ga-doped ZnO sensor is more sensitive with H$_2$, and the influence of NH$_3$ on the detection of H$_2$ is negligible.

5.4 Summary

Nanocrystalline low concentration Ga-doped ZnO thin films were synthesized by sol gel process as a function of Ga doping concentration. All the thin films exhibited a preferential growth orientation along the (002) plane. The average grain size decreased as the increase of Ga concentration up to 0.5 at%. The optical transmittance indicated these thin films had a high average transparency over than 85% in the visible region. A slight increase on band gap was also observed on the Ga-doped ZnO thin films. The SEM images showed that the grain size became significantly smaller at 0.5 at% Ga doping concentration compared to that of undoped film. The gas sensing performance was carried out at an operating temperature of 130°C. Different concentrations of H$_2$ were tested. A 30% enhancement on gas response was observed with optimum Ga doping concentration of 0.3 at%. Moreover, the 0.3 at% Ga-doped ZnO sensor showed a shorter response time than that of undoped ZnO sensor. The selectivity results suggested that the 0.3 at% Ga-doped ZnO sensor had a good selectivity to H$_2$ in a mixture of H$_2$, CH$_4$ and NH$_3$ gases at 130°C.
Chapter 6

Laser Doping Effect on Nanocrystalline Zinc Oxide Thin films

6.1 Introduction

Due to the unique properties and chemical stability, semiconducting metal oxides are one of the first considered and also the most widely used gas sensing materials. The dependence of conductivity of semiconducting metal oxides on environmental gases enables their applications as gas sensors. It was generally believed that the gas sensing behaviors of metal oxide materials is surface controlled [143]. Some factors, such as particle size, porosity, crystallographic orientation, doping effect, noble metal compositing are believed critical in the sensing mechanism. For example, one of the main objectives in this field is to decrease the size of the surface nanoparticles, because the nanosized particles generally exhibit high sensitivity of the sensors.

One way to improve the sensing properties of semiconducting metal oxides is the optimization of their electronic properties by impurity doping. Researchers have reported that the impurity doping resulted in a decrease in grain size, an increase in conductivity and an enhancement in sensor performance [144-148]. Conventionally, thermal diffusion
and ion-implantation methods have been employed for impurity doping in metal oxides. These methods can produce heavily doped materials with good doping profiles. However, they usually require high temperature process of semiconductor and the instruments are expensive. Recently, in order to overcome the difficulties of conventional methods, laser doping technique has been recognized as a promising alternative due to its ability to precisely apply energy in a very localized and confined way. Researchers have reported laser doping used for silicon materials to make polycrystalline silicon with different types of precursors and laser systems, which are used in solar cell applications [149].

6.2 Experiments

6.2.1 Preparation of ZnO thin films

The ZnO thin films were deposited on alkali free glass substrates by a sol-gel spin coating process. The procedure was described in previous chapter. A piece of pre-cleaned alkali free glass was used as a substrate. The dimension of the substrate is 38 x 38 x 1 mm$^3$. The precursor was spin coated on the substrate at a high rotation speed of 3000 rpm for 30 seconds to allow the solution to disperse and spread over the substrate. Then, the film was preheated at 300°C for 3 min on a hotplate to evaporate the residual solvent.

6.2.2 Laser doping process

Aluminum containing liquid (Al(NO$_3$)$_3$·9H$_2$O, 98.0% ~ 102.0%) was used as a dopant source. The dopant precursor was spin-coated on the ZnO thin films. The precursor layer was directly in touch with the ZnO thin film without any interlayer in between.
Figure 6-1: Schematic diagram of the Nd: YVO₄ laser system.

After the coating of dopant precursor, the sample was subjected to laser irradiation by an Nd: YVO₄ pulsed laser source (Quantronix Osprey-532-5-0) with a wavelength of 532 nm. The pulsed width was ~ 8 ns and the frequency was 10 kHz. Figure 6-1 shows the illustration of the laser doping set-up. The laser doping effect on the ZnO thin films was investigated as a function of laser energy level. Here, the ZnO thin films were designated according to the laser fluence. The as-deposited ZnO thin film was named as sample-a and the thin films with laser fluence 0, 1.0, 3.8, 11.6, 15.9 and 25.8 J/cm² were named as sample-b, c, d, e, f and g, respectively. After the laser doping process, all the ZnO thin films were rinsed thoroughly with isopropyl alcohol followed by de-ionized water.
6.3 Results and Discussions

6.3.1 Optical properties

Figure 6-2(a) shows the optical transmittance spectra of as-deposited and laser-doped ZnO thin films as a function of laser fluence in the wavelength range of 300 to 1200 nm. The optical transmittance spectra indicated that all the thin films were highly transparent in the visible wavelength range (390 - 750 nm). The average transparency of all the films was over 85%. The laser-doped ZnO thin films showed higher optical transmissions than that of as-deposited ZnO thin film and this property is good for device application.

![Optical transmittance spectra](image)

Also, the high transparency in the visible range suggested good structural homogeneity and crystallinity of the ZnO thin films. Zhou et al. [150] reported that the transmittances of Al-doped ZnO films were higher than that of the undoped films. On the
other hand, the transmittances fell down sharply in the ultraviolet wavelength range (100 - 400 nm) due to the onset of fundamental absorption. The inset of Figure 6-2(a) shows the transmittances in the range of 340 - 420 nm. It was apparently seen that the absorption threshold shifted to the shorter wavelength (blue-shift) for the laser-doped ZnO thin films. This feature is commonly observed in the heavily doped conducting films, which have carrier concentration greater than critical Moss density and is known as the Burstein-Moss (BM) shift [151]. This behavior has been reported in literatures [152-154]. For example, Jun et al. [152] reported a blue shift with the increase of Al contents in Al-doped ZnO thin films derived by sol-gel spin-coating process.

The optical band gaps of ZnO thin films were obtained by applying Eq. 7. Figure 6-2(b) shows the plot of $(\alpha h\nu)^2$ versus photon energy ($h\nu$) for as-deposited and laser-doped ZnO thin films. The extrapolation of the graph gives the optical band gap. The optical band gap was calculated to be 3.280, 3.285, 3.292, 3.295, 3.296, 3.292 and 3.293 eV. The band gap was varied from 3.280 to 3.296 eV after laser doping process. The small variation of the band gap is due to the laser induced crystallization of ZnO changes the defects level in ZnO. Therefore, the laser doping process increased the optical band gap of the ZnO thin film. The enhancement of optical transparency and band gap can be attributed to the increase of carrier concentration due to the doping of Al [154, 155].

6.3.2 Structural properties

Figure 6-3(a) shows the X-ray diffraction patterns of as-deposited and laser-doped ZnO thin films in the range of $2\theta = 25^\circ$ to $45^\circ$. It was clearly showed that all the ZnO thin films consisted of a strong diffraction peak at around $34.4^\circ$ and two small
diffraction peaks at around 31.8° and 36.2°, which correspond to the (002), (100) and (101) diffraction peaks of hexagonal wurzite structure, respectively.

Figure 6-3: (a) X-ray diffraction patterns and (b) the grain sizes of as-deposited and laser-doped ZnO thin films.

It revealed that all the films had a preferred orientation along the c-axis normal to the substrate surface. Laser-doped ZnO thin films with low laser fluence (sample-b and c) exhibited a decrease in crystallinity compared with that of as-deposited ZnO thin film. Sample-b showed the lowest intensity of the (002) peak. However, as the laser fluence successively increased from 1.0 to 25.8 J/cm², a noticeable crystallization was produced to the ZnO phase along the c-axis. Therefore, the laser doping process deteriorated the crystallinity of the ZnO thin films initially with low laser fluence whereas increased the crystallinity with the further increase of laser fluence. Figure 6-3(b) shows the variation of grain sizes estimated along the (002) peak for as-deposited and laser-doped ZnO thin films. The grain size was found to decrease with increasing the laser fluence. The laser doping process produced a noticeable shrink of grain size. When the laser fluence
exceeded 11.6 J/cm\(^2\) (sample-e), a sharp decrease in grain size was observed. The result indicated that the laser doping process efficiently decreased the grain size of ZnO thin film. The possible explanation of this observation is that the laser doping process is dominated by two separate mechanisms: the doping mechanism and laser annealing mechanism. As the increase of laser fluence, the laser annealing mechanism becomes prominent. The intensity of the peak increased with increasing laser fluence [156-158]. On the other hand, the laser fluence enhances the doping mechanism and promotes the incorporation of Al\(^{3+}\) into the ZnO lattice. Therefore, the grain size decreased. It has been reported that the grain size decreased after the doping of Al in ZnO [159, 160].

6.3.3 Morphological properties

Figure 6-4 shows the SEM micrographs of as-deposited and laser-doped ZnO thin films with different laser fluences. The as-deposited ZnO thin film (sample-a) showed a flat surface covered by irregular shaped grains. In contrast, sample-b exhibited a smaller grain size than the as-deposited ZnO sample (sample-a), which implied that the spin-coated thin layer of Al precursor affected the surface morphology of the film. It was also observed that the low laser fluence (sample-c and d) efficiently decreased the grain size. However, high laser fluence (sample-e, f and g) resulted in the melting and aggregation of grains. Sample-e showed a porous structure with larger grains, which was consistent with the XRD results.
Figure 6-4: SEM images of (a) sample-a, (b) sample-b, (c) sample-c, (d) sample-d, (e) sample-e, (f) sample-f and (g) sample-g.
Figure 6-5: The EDS spectra of (a) sample-a, (b) sample-b and (c) sample-d.

The EDS spectra are showed in Figure 6-5. The peaks, O-K\(\alpha\) and Zn-L\(\alpha\) were detected for as-deposited ZnO thin film (sample-a) at 0.518 and 1.109 keV, respectively. In addition to O and Zn peaks, Al- K\(\alpha\) peak was also observed at 1.496 keV for both sample-b and sample-d. The EDS results confirmed the existence of Al in ZnO films.

6.3.4 Electrical properties

The electrical resistance was measured in the temperature range of 60 - 200°C. Figure 6-6(a) shows the Arrhenius plots of electrical conductivities of as-deposited and laser-doped ZnO thin films. It was seen that the conductivities of all the films increased
with the increase of temperature. A notable enhancement in electrical conductivity was observed on laser-doped ZnO thin films (sample-b, c, d, e, f and g). The highest conductivity was obtained on sample-f. $\Delta E$ was estimated from Figure 6-6(a) by using the slope of fitted line.

![Figure 6-6: (a) Variation of logarithm of conductivity against reciprocal of temperature and (b) the activation energies for as-deposited and laser-doped ZnO thin films.](#)

Figure 6-6(b) shows the calculated $\Delta E$ of as-deposited and laser-doped ZnO thin films. For as-deposited ZnO thin films (sample-a), the estimated $\Delta E$ was 0.72 eV, which was closed to the $\Delta E$ of oxygen vacancy in ZnO reported by Soulelie et al [161]. After the laser doping process, the $\Delta E$ decreased to 0.307 eV as the laser fluence increased to 15.9 J/cm² (sample-e). With further increase of the laser fluence to 25.8 J/cm², the thin film showed a remarkable decrease in $\Delta E$ to 0.212 eV and this behavior may be attributed to the increase of defects and imperfections concentrations.
6.3.5 Gas sensor performance

The gas sensing behavior of ZnO films is profoundly influenced by the working conditions such as operating temperature. These experiments were performed at an operating temperature of 160°C with 100 ccm of air to search for the optimum laser energy level. The sensing response was obtained when various concentrations of H$_2$ were introduced into testing chamber. By measuring the change of resistance, the sensing response was estimated. Figure 6-7 shows the dependence of sensing response versus H$_2$ concentration in the air for as-deposited and laser-doped ZnO sensors.

![Graph showing the dependence of sensing response versus H$_2$ concentration](image)

Figure 6-7: Variation of response as a function of H$_2$ concentration for as-deposited and laser-doped ZnO sensors.

It was apparently shown that the sensing response decreased as the decrease of H$_2$ concentration from 3000 to 500 ppm. No significant difference was observed between
sample-a and sample-b. The sensing response of sample-c improved slightly compared with that of as-deposited ZnO sensor (sample-a). Sample-d, e and f exhibited remarkably higher sensing responses than that of as-deposited ZnO sensor (sample-a). However, the sensing response decreased with a further increase of laser fluence to 25.8 J/cm². In the H₂ concentration range of 1000 to 3000 ppm, no obvious difference in sensing response was observed among sample-d, e and f. However, the sensing responses of these sensors exhibited significant differences upon 500 ppm H₂ exposure. The maximum sensing response was obtained on sample-d, which showed a high sensing response even at relatively low H₂ concentration. Our studies indicate that the excessive laser fluence irradiation results in a decrease of sensing response. In order to exclude the possibility of laser irradiation induced enhancement of sensing response, the sensing responses of as-deposited and laser-irradiated ZnO sensors were also presented.

![Figure 6-8: Variation of response for as-deposited and laser-irradiated ZnO sensors.](image)

Figure 6-8: Variation of response for as-deposited and laser-irradiated ZnO sensors.
Figure 6-8 showed the variation of sensing response for the as-deposited and laser-irradiated ZnO sensors under different concentrations of H₂ exposure. The laser fluence used for laser irradiation was 6.4 J/cm². As expected, the laser-irradiated ZnO sensor exhibited a lower sensing response than the as-deposited ZnO sensor. The results indicated that the sensing response improved substantially through laser doping with optimum laser fluence.

Figure 6-9 shows the comparison of sensing response for 1000 ppm H₂ for as-deposited and laser-doped ZnO sensors.

Figure 6-9: Dynamic response and recovery characteristics of as-deposited and laser-doped ZnO sensors for 1000 ppm H₂ (hollow triangle: gas on, solid triangle: gas off).

All the sensors exhibited a fast response when H₂ was introduced into the chamber. The sensor responses reached 50% of their saturation value within tens of
seconds and saturated in minutes. After stopping H₂ flow, the responses gradually recovered to the baseline for all the sensors. The response time T₉₀, T₇₀ and T₅₀ for as-deposited and laser-doped ZnO sensors exposed to H₂ are showed in Figure 6-10.

![Figure 6-10: The response time (a) T₅₀, (b) T₇₀ and (c) T₉₀ for as-deposited and laser-doped ZnO sensors as a function of H₂ concentration.](image)

It can be seen that the response time increases with the decrease of H₂ concentration from 3000 to 500 ppm. For sample-b and c, the response time curves overlapped with each other at certain H₂ concentration. On the other hand, noticeable
improvements of response time were observed on sample-d, e and f. The minimum response time was obtained on sample-f. From the above results, it was concluded that the sensor performance of ZnO sensor could be significantly improved in both sensing response and response time through laser doping process with optimum laser fluence.

Figure 6-11 shows the sensing response and recovery behavior of sample-d recorded successively by introducing different concentrations of H\textsubscript{2} from 150 to 3000 ppm.

![Figure 6-11](image.png)

Figure 6-11: The sensing response and recovery time versus sensing response of sample-d exposed to H\textsubscript{2} in the concentration range of 150 to 3000 ppm (hollow triangle: gas on, solid triangle: gas off).

It was important to note that the sensing response presented an immediate increase after the introduction of H\textsubscript{2}. The maximum sensing response (~94\%) was achieved under 3000 ppm of H\textsubscript{2} exposure whereas the minimum sensing response was
around 50% under 150 ppm of H$_2$ exposure. The sensing response of sample-d for H$_2$ concentration below 100 ppm is valuable for future research.

Selectivity is one of the most important characteristics of gas sensors. The gas selectivity of sample-d was investigated for a gas mixture of H$_2$, CH$_4$ and NH$_3$ at an operating temperature of 160°C in the air. Figure 6-12(a) shows the response and recovery characteristics of sample-d for H$_2$ with 5000 ppm CH$_4$ in the background gas. As shown in Figure 6-12(a), the response increased to around ~35% in 12 min for 3000 ppm CH$_4$ exposure. Rapid response was exhibited when 1000 ppm H$_2$ was introduced into the chamber. The response increased with the sequential increase of H$_2$ concentration. Figure 6-12(b) shows the response for CH$_4$ in presence of H$_2$ in the air.

![Diagram](image)

Figure 6-12: Sensing response of sample-d for (a) H$_2$ in the existence of CH$_4$ and (b) CH$_4$ in existence of H$_2$ in the air.

It was observed that the sensor immediately responds to 1000 ppm H$_2$. Nevertheless, even under high concentrations of CH$_4$ exposure, no significant change of
response was observed. Therefore, it was concluded that the sample-d was more sensitive to H₂ other than CH₄ at 160°C.

Figure 6-13(a) shows the response for H₂ in the existence of 50 ppm NH₃. It can be seen that the sensor responds rapidly to 50 ppm NH₃ indicating that the sensor has a low detection limitation toward NH₃. When H₂ was introduced, a stepwise increase of response was detected with increasing the concentration of H₂ from 1000 to 3000 ppm. Figure 6-13(b) shows the response to NH₃ in the existence of 1000 ppm H₂. The sensor responded to the background H₂ gas immediately. The response slightly increased after introducing 30 ppm of NH₃. No significant change was observed in response after successive injection of NH₃.

Figure 6-13: Sensing response of sample-d for (a) H₂ in the existence of NH₃ and (b) NH₃ in existence of H₂ in the air.

Therefore, unless high concentration exposure of NH₃ is a factor, sample-d is selective responded to H₂.
6.4 Summary

A laser doping process was demonstrated using a pre-deposited aluminum salt layer on the ZnO thin films derived by a sol-gel process. The optical, structural properties, surface morphology, electrical conductivity and gas sensor performance of laser-doped ZnO thin films were investigated as a function of laser energy level. After the laser doping process, an increase in transmittance and a remarkable blue shift of optical bandgap were observed on the laser-doped ZnO films. Deterioration of crystallinity was observed on the ZnO films with low laser fluence whereas an enhancement in crystallinity was observed on ZnO films with high laser fluence. The grain size of ZnO thin film decreased continuously from 46 to 33 nm as the increase of laser fluence. The electrical conductivities of ZnO thin films enhanced after the laser doping process, and the maximum conductivity was found on 15.9 J/cm² laser-doped ZnO thin film. The gas sensor performance indicated that both the sensing response and response time were improved significantly after laser doping with optimum laser energy level. The selectivity of the best sensor was also examined. It was found that the sensor had a good selectivity for H₂ and NH₃ in the presence of CH₄. The existence of large amount of NH₃ may affect the detection of H₂, however, small amount of NH₃ (<100 pm) has a negligible effect in the detection of H₂.
Chapter 7

Plasma Treatment Effect on Nanocrystalline Zinc Oxide Thin Films

7.1 Introduction

7.1.1 Defects in ZnO

ZnO usually contains a large number of defects due to the synthesis conditions. The origin of intrinsic n-type electrical conductivity of ZnO is still under debate. However, oxygen vacancies (Vo) and Zn interstitials (Zni) have often been invoked as most possible sources [162-166]. Therefore, the defects concentration in ZnO nanostructure and the presence of intrinsic or extrinsic defects directly affect the properties of ZnO materials. The existence of such defects exerts profound influence on the performance of electronic devices and as a result methods for their modification are of interest.

7.1.2 Background of plasma treatment on metal oxide materials

Plasma treatment is known as a useful method to adjust charge carrier density and
surface morphology because of the high reactivity of radical elements than gas phase. Moreover, it is found to be more suitable for the treatment of nanoparticles because of their large surface area than that of bulk materials. For example, Jiang et al. [167] treated SnO\textsubscript{x} thin films with oxygen (O\textsubscript{2}) plasma and investigated its effect on structural properties. Cai et al. [168] utilized the H\textsubscript{2} plasma to enhance the conductivity and transmittance of ZnO films. It is known that the gas response is a surface-controlled process. Therefore we propose to apply O\textsubscript{2}/H\textsubscript{2} plasma treatment as a surface modification technique to modify and improve the sensing response of ZnO thin film based gas sensors.

7.2 Experiments

7.2.1 Sample preparation

ZnO thin films were prepared by sol-gel spin coating technique. The preparation procedure was described in previous chapter. The solution concentration was kept at 0.25 M in this study. The films were preheated at 300°С for 3 min to remove the residual solvent.

7.2.2 Plasma treatment

O\textsubscript{2}/H\textsubscript{2} plasma treatment was applied to ZnO samples with the intention to modify the defects concentrations in ZnO thin films. The chamber was first evacuated to 1.0 Torr and then purged with O\textsubscript{2}/H\textsubscript{2}. The applied rf power was 100 W. The ZnO samples were treated with O\textsubscript{2}/H\textsubscript{2} plasma with treatment time varying from 3 to 15 min.
7.2.3 Characterization

The structures of samples were examined by an X-ray diffractometer (PANalytical X’Pert Pro MPD) using Cu Kα radiation source. The scanning range was from 2θ =25° to 65°. Optical transmittance was measured in the wavelength range between 300 – 1000 nm using an UV/Vis spectrophotometer (SHIMADZU UV-1650PC). The surface morphology was determined by a scanning electron microscopy (Hitachi S-4800). The electrical properties and gas sensor performance were studied in a homemade testing system. The configuration of the system was described in 2.2.

7.3 Results and discussions for O₂ plasma treated ZnO thin films

7.3.1 Structural properties

The XRD spectra of as-deposited and O₂ plasma treated ZnO samples are presented in Figure 7-1 as a function of treatment time. All patterns show only a predominant peak at diffraction angle 2θ near 34.4°, which indicate the (002) preferential growth orientation along the c-axis for all the samples. It is seen that the peak intensities of 3 and 5 min plasma treated ZnO samples increase slightly compared with that of as-deposited samples, whereas the peak intensity decreases with further increasing treatment time to 11 min. The increase in crystallinity of short time (3 or 5 min) O₂ plasma treated samples may be attributed to the reduction of oxygen vacancies. For long time (11 min) O₂ plasma treated samples, Zn vacancies are likely generated by oxygen plasma because the Zn vacancies have the lowest formation energy in an oxygen rich atmosphere.
compared with other possible defects [169], which in turn decreases the crystallinity of ZnO films.

Figure 7-1: XRD patterns of as-deposited and O₂ plasma treated ZnO thin films.

The variation of grain size estimated along the (002) peak is presented in Figure 7-2. It is shown that the grain size is related to the O₂ plasma treatment time. The grain size decreases from 44 to 40 nm after O₂ plasma treatment. In Figure 7-2, it is possible to distinguish two discrete regions corresponding to different changing tendency. The grain size decreases initially with O₂ plasma and then researches a plateau within the treatment time ranging from 3 to 8 min. After that, the grain size decreases again as the increases of treatment time from 8 to 15 min. The decrease in grain is attributed to the oxidation of Zn interstitial atoms caused by O₂ plasma. During the treatment, the excess Zn atoms that segregated in the grain boundary region are oxidized to ZnO and thus the sizes of ZnO nanoparticles become smaller after treatment of O₂ plasma. Mukgamedshina et al. [170]
also reported that the treatment of SnO$_x$ films in the O$_2$ plasma led to a reduction of grain size.

7.3.2 Optical properties

Figure 7-3 shows the UV/Vis transmittance spectra of as-deposited and O$_2$ plasma treated ZnO films. All the films exhibit a transmittance higher than 80% in the visible wavelength range and an onset steep absorption edge in the UV region, which indicate the high quality of ZnO thin films [171]. The sharp absorption edge is at about 370 nm, which is close to the intrinsic band gap of ZnO (3.3 eV). It is found that the visible transparencies of ZnO thin films increase after O$_2$ plasma treatment. In particular, the samples treated by 8 min O$_2$ plasma show a significant difference in the visible transparency in comparison with as-deposited ZnO samples. This phenomenon may attribute to the weakening of scattering and absorption of light due to the oxidative effect.
and better crystallinity induced by O$_2$ plasma treatment. However, longer treatment time in O$_2$ plasma (11-15 min) may lead to the formation of V$_{Zn}$ and then results in decreasing in transmittance. Cai et al. [168] treated the ZnO films with O$_2$ plasma and indicated that the average transmittance in the 460-800 nm wavelength range slightly increased after O$_2$ plasma treatment. After O$_2$ plasma treatment, the absorption edge does not vary significantly and the variation of the absorption edge does not show any clear trend.

![Optical transmittance spectra of as-deposited and O$_2$ plasma treated ZnO thin films.](image)

**Figure 7-3:** Optical transmittance spectra of as-deposited and O$_2$ plasma treated ZnO thin films.

### 7.3.3 Morphological properties

Figure 7-4 presents the SEM images of as-deposited ZnO thin film together with 3, 8, 15 min O$_2$ plasma treated ZnO samples. The as-deposited ZnO sample (Figure 7-4(a)) shows a fine-grained and dense surface with clear grain boundaries. The irregular shaped grains have an average grain size smaller than 50 nm. The 5 min O$_2$ plasma
treated ZnO sample Figure 7-4(b)) shows a surface consists of smaller grains with blur boundaries.

Figure 7-4: SEM images of (a) as-deposited ZnO thin film together with (b) 3 min, (c) 8 min and (d) 15 min O₂ plasma treated ZnO thin films.

For the 8 min O₂ plasma treated sample (Figure 7-4(c)), the grain size is similar with 5 min O₂ plasma treated sample but more neck areas are created. As shown in Figure 7-4(d), 15 min O₂ plasma produces much smaller grains than as-deposited ZnO film. The results are in good agreement with the XRD estimation. According to Figure 7-4, the O₂ plasma treated ZnO samples exhibit a different morphology, which is mainly dominated by grains agglomerations and neck features whereas as-deposited sample shows a fine-grained and dense surface. The results indicate that O₂ plasma as well as the
treatment time has a significant influence on the morphology and microstructure of ZnO thin films.

7.3.4 Electrical properties

To investigate the variation of electrical conductivity after O₂ plasma treatment, the resistances of samples over different temperatures were measured. Figure 7-5 shows the temperature dependence of resistance for as-deposited ZnO thin films together with 3, 8 and 15 min O₂ plasma treated ZnO thin films.

![Figure 7-5: Variation of logarithm of conductivity against reciprocal of temperature for as-deposited and O₂ plasma treated ZnO thin films.](image)

The conductivities of all the samples increase with the increase of temperature from 35 to 200°C indicating the semiconducting nature of ZnO. O₂ plasma influences the electrical properties of ZnO thin films exhibiting a decrease of conductivity. For O₂
plasma treatment time as short as 3 min, a notable decrease of conductivity is observed. With increasing O$_2$ treatment time to 8 min, the conductivity decreases substantially to the minimum value indicating decreasing of carrier concentration in ZnO thin films. Other authors also reported the similar results [170, 172, 173]. For example, Lee et al. [172] reported that carrier concentration of ZnO decreases from $4.9 \times 10^{15}$ to $1.2 \times 10^{14}$ cm$^{-3}$ and resistivity increases from $1.22 \times 10^3$ to $9.8 \times 10^3$ Ωcm as the O$_2$ plasma exposure times increased. The decrease of electrical conductivity is due to the reduction of net electron carriers during the O$_2$ plasma treatment. The 15 min O$_2$ plasma treatment results in an increase in conductivity of ZnO films. The phenomenon may attribute to the formation of high mobility intragranular neck region on the surface.

7.3.5 Gas sensor performance

The effect of O$_2$ plasma treatment on gas sensing properties of ZnO sensors to the presence of NH$_3$ at various concentrations in air was studied. It is generally believed that the sensor behavior of semiconductor gas sensor materials is surface controlled. Plasma treatment, as a surface modification technique, is expected to influence their gas sensing properties. In this work, 12-50 ppm NH$_3$ was tested within the hazardous level of NH$_3$. Figure 7-6 illustrates the sensing response versus NH$_3$ concentration for as-deposited and O$_2$ plasma treated ZnO sensors. It is clearly seen that the sensing response increases with the increase of NH$_3$ concentration indicating the response dependence of NH$_3$ concentration. As shown in Figure 7-6, the O$_2$ plasma significantly influences the response of ZnO sensors. The differences of responses between as-deposited, 3 and 5 min plasma treated ZnO are not significant, which suggest that the short time (3~5 min) O$_2$ plasma treatment is insufficient to modify the gas sensor performance. The maximum
sensor response is obtained while increasing the O₂ plasma treatment time to 8 min, which indicates that optimum plasma treatment time would remarkably enhances gas response of ZnO sensors. Further increase of treatment time to 11 or 15 min results in a continuously decrease in sensing response. This result indicates that an excessive O₂ plasma treatment has a deleterious effect on ZnO surface, and as a consequence leads to a loss of sensor response.

![Graph showing variation of sensing response as a function of NH₃ concentration for as-deposited and O₂ plasma treated ZnO sensors.](image)

**Figure 7-6:** Variation of sensing response as a function of NH₃ concentration for as-deposited and O₂ plasma treated ZnO sensors.

Figure 7-7 shows the response and recovery characteristics of as-deposited ZnO together with 8 and 15 min O₂ plasma treated ZnO sensors under 12, 25 and 50 ppm NH₃ exposure. Under 50 ppm NH₃ exposure, all the sensors respond immediately and then gradually saturate to their maximum values. The final saturation takes about 500 s while
in the first 200 s the response increases sharply. The responses of all the sensors recover to their baselines after stopping NH₃. It is worthwhile to notice that the response time differs from different NH₃ concentrations as well as different sensors, whereas the recovery rate is similar to all the NH₃ concentrations and sensors.

Figure 7-7: Sensing response and recovery characteristics of as-deposited and O₂ plasma treated ZnO sensors.

Figure 7-8 shows the response time T₇₀ for as-deposited and O₂ plasma treated ZnO sensors as a function of NH₃ concentration. The response time decreases with increasing NH₃ concentration. In particular, the response time for 50 ppm NH₃ shorten to 60% of the response time for 12 ppm NH₃. In this study, the response time exhibited a strong dependence of gas concentration. On the other hand, the O₂ plasma effect on the
response time is not significant. The parameters change irregularly with the increase of treatment time.

![Graph showing response time (T70) vs. NH3 concentration for as-deposited and O2 plasma treated ZnO sensors.]

Figure 7-8: 70% of the response time (T70) for as-deposited and O2 plasma treated ZnO sensors as a function of NH3 concentration.

Selectivity plays a major role in gas identification. In this work, the gas selectivity of 8 min plasma treated ZnO sensor was examined for three similar reducing gases: H2, CH4, and NH3. Figure 7-9(a) shows the response and recovery characteristics of 8 min plasma treated ZnO sensor to CH4 with 25 ppm NH3 in the background gas. The sensor responds rapidly to the background NH3 and saturated to around 40% within 12 min. After introducing 2000 ppm CH4 into the chamber, the response slowly increases to around 45%. With the sequential increase of CH4 concentration, the response increases continuously and reaches the maximum value upon 6000 ppm CH4 exposure. The response to NH3 in the presence of CH4 illustrates in Figure 7-9(b). It can be observed
that the sensor responds immediately to 12 ppm NH₃ with 2000 ppm CH₄ in the background gas. The response continuously increases with increasing NH₃ concentration from 12 to 50 ppm. These results indicate that the 8 min O₂ plasma treated ZnO sensor is more sensitive to NH₃ other than CH₄ and thus the presence of CH₄ has very limited influence on the detection of NH₃.

Figure 7-9: Sensing response of 8 min O₂ plasma treated ZnO sensor for (a) CH₄ in presence of NH₃ and (b) NH₃ in presence of CH₄.

Figure 7-10 shows the cross sensitivity towards H₂ and NH₃. It is shown that 8 min O₂ plasma treated ZnO sensor is also very sensitive to H₂. As shown in Figure 7-10(a), the sensor responds rapidly to 500 H₂ and saturates to around 85% within 10 min. The response reaches the maximum value while passing 2000 ppm H₂. The sensing response to NH₃ in the presence of H₂ shows in Figure 7-10(b). The sensor responds to the background H₂ quickly. When NH₃ is introduced, a stepwise increase of response can be observed with increasing NH₃ concentration from 12 to 50 ppm. The results suggest
that unless high concentration of H\textsubscript{2} is a factor, the 8 min plasma treated ZnO sensor is applicable to H\textsubscript{2}.

Figure 7-10: Sensing response of 8 min O\textsubscript{2} plasma treated ZnO sensor for (a) H\textsubscript{2} in presence of NH\textsubscript{3} and (b) NH\textsubscript{3} in presence of H\textsubscript{2}.

7.3.6 Discussion of O\textsubscript{2} plasma effect on gas sensor performance of ZnO thin films

By applying O\textsubscript{2} plasma treatment on the surface of ZnO sensor as a post-treatment process leads to a significant improvement in gas sensing response. This enhancement in sensing response can be explained by a reduction of V\textsubscript{O} on the ZnO surface. Figure 7-11 shows the structural and band model of (a) as-deposited and (b) 8 min plasma treated ZnO sensors. When the sensor is exposed to atmosphere, the oxygen species adsorb on the surface grain boundary by trapping electrons from the lattice. The formation of the oxygen adsorbates builds up a space large region on the surface of the oxide grains resulting in the development of a potential barrier. After the oxygen plasma treatment, the number of V\textsubscript{O} on the ZnO surface reduced, which indicates less amount of oxygen.
species adsorb on the surface which in turn results in a decrease of the height of the potential barrier. Yan et al. [174] has reported that the adsorption is fully molecular on stoichiometric ZnO surface with small adsorption energy.

Figure 7-11: Structural and band model of (a) as-deposited and (b) 8 min plasma treated ZnO thin films.

The adsorption energy of O$_2$ molecule on perfect site is much lower than V$_o$ site, which means O$_2$ molecule bind loosely with oxygen-vacancy-free surface. O$_2$ plasma removes oxygen vacancies on ZnO surface and therefore the loosely adsorbed O$_2$
molecules dominant the ZnO surface which ensures the completely desorption of adsorbed O$_2$ molecules from the surface when the sensor is exposed to target gases. Figure 7-12 shows the variation of resistance for as-deposited and 8 min O$_2$ plasma treated ZnO sensors under argon exposure at (a) room temperature and (b) 160°C. Therefore, the incorporation and diffusion of oxygen in the lattice induced by O$_2$ plasma treatment reduces the V$_{o}$ on the surface and therefore enhances the gas response of ZnO sensor. The results indicate that O$_2$ plasma treatment has the potential to be used as a surface modification technique to improve the gas sensor performance of ZnO sensor.

Figure 7-12: Variation of resistance for as-deposited and 8 min plasma treated ZnO sensors under argon exposure at (a) room temperature and (b) 160°C.

7.4 Results and discussions for H$_2$ plasma treated ZnO thin films

7.4.1 Structural properties

In order to investigate the effect of different plasma types on the structural properties of ZnO thin films, XRD measurement was performed on as-deposited, 8 min
O₂ treated and 10 min H₂ plasma treated ZnO thin films and the corresponding results are shown in Figure 7-13. Only one prominent peak is observed at diffraction angle of 2θ = 34.4°, which is corresponding to the (002) crystal plane for all the films. The intensity of (002) peak increases for both O₂ and H₂ plasmas treated ZnO films compared with that of as-deposited ZnO film indicating an enhancement of crystallinity. The peak intensity of H₂ plasma treated ZnO thin film increases more significantly than that of O₂ plasma treated ZnO film. The average grain sizes for as-deposited, O₂ and H₂ plasmas treated ZnO thin films were calculated to be 43.83, 40.08 and 30.46 nm, respectively. Both the O₂ and H₂ plasma treatments lead to a reduction of the grain size. Similar results have been reported by other researchers. For instance, Wang et al. [175] reported a decrease of grain size of Al-doped ZnO thin films after room temperature H₂ plasma treatment. Mukgamedshina et al. [170] reported that the treatment of SnOₓ films in the O₂ plasma leads to a reduction of grain size.

![XRD patterns of as-deposited and plasma treated ZnO thin films.](image)

Figure 7-13: XRD patterns of as-deposited and plasma treated ZnO thin films.
7.4.2 Electrical properties

To investigate the variation of electrical conductivity of O$_2$ and H$_2$ plasmas treated ZnO thin films, the resistances of samples over different temperature were measured. Figure 7-14 shows the temperature dependence of conductivity for as-deposited ZnO thin films together with 8 min O$_2$ plasma treated and 10 min H$_2$ plasma treated ZnO thin films.

![Figure 7-14: Variation of logarithm of conductivity against reciprocal of temperature for as-deposited, O$_2$ and H$_2$ plasmas treated ZnO thin films.](image)

The conductivities of all the samples increase as increasing temperature from 35 to 200°C. Two different phenomena are observed for O$_2$ and H$_2$ plasmas treated ZnO thin films. The O$_2$ plasma affected the electrical properties of ZnO thin films exhibiting a decrease in conductivity. However, the conductivity increases after H$_2$ plasma treatment.
The substantial decrease of conductivity of O\textsubscript{2} plasma treated ZnO thin film implies a decrease of carrier concentration. The significant increase of conductivity of H\textsubscript{2} plasma treated ZnO thin films indicates an increase of carrier concentration. The increase of electrical conductivity resulting from H\textsubscript{2} plasma treatment can be attribute to two reasons: (1) the formation of a shallow donor level as a result of H\textsubscript{2} having been incorporated into the ZnO film, (2) desorption of negatively charged oxygen species, which increase oxygen vacancies or interstitial Zn atoms [175].

7.4.3 Comparative study of O\textsubscript{2} and H\textsubscript{2} plasma treated ZnO sensors for reducing and oxidizing gases

The response of gas sensor is defined according to different types of gases. For reducing gases, such as NH\textsubscript{3} and H\textsubscript{2}, the response is given by:

\[
S = \left( \frac{R_a - R_g}{R_a} \right) \times 100\% , \quad (8)
\]

For oxidizing gases, such as NO\textsubscript{x} and H\textsubscript{2}S, the response is given by:

\[
S = \left( \frac{R_g - R_a}{R_g} \right) \times 100\% . \quad (9)
\]

Where, \( R_a \) is the resistance of the sensor measured in the air, while \( R_g \) is the resistance in the presence of both air and the target gas. The effects of O\textsubscript{2} and H\textsubscript{2} plasma treatments on gas sensing behavior of ZnO sensors to the presence of both oxidizing and reducing gases under various concentrations in air were investigated. According to the toxic threshold limit values of NO\textsubscript{x} and NH\textsubscript{3}, 12-50 ppm NO\textsubscript{x} and NH\textsubscript{3} was tested within the hazardous level [170]. Figure 7-15(a) illustrates the dynamic response and recovery
characteristics of as-deposited, O$_2$ and H$_2$ plasmas treated ZnO sensors for different concentrations of NH$_3$ exposure ranging from 12 to 50 ppm.

Figure 7-15: Dynamic response and recovery of as-deposited and plasma treated ZnO sensors for (a) NO$_X$ and (b) NH$_3$.

Under 50 ppm NH$_3$ exposure, all the sensors respond immediately and then gradually saturate. The final saturation takes about 500 s and in the first 200 s the response increases sharply. The responses recover to the baseline after stopping NH$_3$.

Figure 7-15(b) shows the dynamic response and recovery characteristics of as-deposited, O$_2$ and H$_2$ plasmas treated ZnO sensors for different concentrations of NO$_X$ exposure.
ranging from 12 to 50 ppm. When NO\textsubscript{X} is introduced into the chamber, all the sensors respond immediately, especially for the plasmas treated ZnO sensors. It is worthwhile to notice that the ZnO sensors treated with plasmas do not fully saturated within the given exposure time. The responses of plasmas treated ZnO sensors for NO\textsubscript{X} keep increasing with time. After stopping the gas, all the sensors recover to the baseline within minutes. It is worthwhile to notice that the response time is different according to gas concentrations as well as the sensors, whereas the recovery rate of all sensors is similar under all gas concentrations.

Figure 7-16(a) shows the variation of response towards different concentrations of NO\textsubscript{X} for as-deposited and O\textsubscript{2} plasma treated ZnO sensors. It is clearly seen from the figure that the sensor response increases with the increase of NO\textsubscript{X} concentration indicating the response dependence of NO\textsubscript{X} concentration. The difference of response between as-deposited and 3 min O\textsubscript{2} plasma treated ZnO is not significant, which suggests that for the treatment time as short as 3 min is insufficient to modify the sensing response. With increasing O\textsubscript{2} plasma treatment from 3 to 11 min, a significant enhancement on response is observed. The response decreases drastically with further increasing of the O\textsubscript{2} plasma treatment time. Moreover, it is noticed that the O\textsubscript{2} plasma induced enhancement is more significant under high concentration of NO\textsubscript{X} exposure. The optimum O\textsubscript{2} plasma treatment time is found to be 11 min for the detection of NO\textsubscript{X}. The variation of response to NO\textsubscript{X} for as-deposited and H\textsubscript{2} plasma treated ZnO sensors is demonstrated in Figure 7-16(b). It is seen that the sensing response increases significantly after H\textsubscript{2} plasma treatment. The response increases with the increase of H\textsubscript{2} plasma treatment time. By comparing Figure 7-16 (a) and (b), it is observed that the O\textsubscript{2} plasma treated ZnO sensor
exhibit a higher sensing response toward NO\textsubscript{X} than that of the H\textsubscript{2} plasma treated ZnO sensor.

![Graph showing variation of sensing response as a function of NO\textsubscript{X} concentration for as-deposited and plasma treated ZnO sensors.](image)

Figure 7-16: Variation of sensing response as a function of NO\textsubscript{X} concentration for as-deposited and plasma treated ZnO sensors.

Figure 7-17(a) shows the variation of response towards different concentrations of NH\textsubscript{3} for as-deposited and O\textsubscript{2} plasma treated ZnO sensors. It is clearly seen from the
figure that the response increases with the increase of NH$_3$ concentration, which indicates that the response is also dependent of NH$_3$ concentration.

![Graph showing the variation of sensing response as a function of NH$_3$ concentration for as-deposited and plasma treated ZnO sensors.](image)

Figure 7-17: Variation of sensing response as a function of NH$_3$ concentration for as-deposited and plasma treated ZnO sensors.

As shown in Figure 7-17(a), the O$_2$ plasma significantly influences the response of ZnO sensors. The maximum sensor response is obtained while increasing the O$_2$
plasma treatment time to 8 min, which indicates that optimum plasma treatment time would remarkably enhance gas response of ZnO sensors. Further increase of treatment time to 11 or 15 min results in a continuously decrease in sensing response. Figure 7-17(b) shows the variation of response toward different concentrations of NH₃ for as-deposited and H₂ plasma treated ZnO sensors. The H₂ plasma treatment also has a positive impact on the sensing response of ZnO sensors. The sensing response increases and then decreases with the increase of H₂ plasma treatment time from 5 to 10 min. The optimum H₂ treatment time is found to be 5 min where the ZnO sensor exhibits the highest sensing response to NH₃.

7.5. Summary

In conclusion, the O₂ and H₂ plasma treatments were applied to nanocrystalline ZnO thin films for the purpose of defects and surface modifications. Various O₂ and H₂ plasma treatment times have been examined. The results indicate that the surface grain size decreases after both O₂ and H₂ plasma treatments. The grain size decreases more significantly after H₂ plasma treatment. The O₂ and H₂ plasmas strongly influence the surface morphology and microstructure of ZnO thin films. Gas sensing performance was tested under different concentrations of NH₃ exposure. By optimizing the O₂ plasma treatment time, a 50% improvement on gas response is observed on O₂ plasma treated ZnO sensor compared with as-deposited ZnO sensor. Therefore, the relatively simple O₂ plasma treatment process is an effective way to improve the gas sensor performance of metal oxide based materials. A comparative study of O₂ and H₂ plasma treatments on ZnO thin films for both reducing and oxidizing gases (NH₃ and NOₓ) was also conducted. O₂ and H₂ plasmas treated ZnO sensors were investigated upon different
concentrations of NH$_3$ and NO$_x$ exposure. It is found that the sensing response for NO$_x$
also enhances significantly after O$_2$ or H$_2$ plasma treatment. The enhancement of sensor
performance is more significant upon O$_2$ plasma treatment rather than that of H$_2$ plasma
treatment.
Chapter 8

Conclusions

ZnO is a wide band gap semiconducting materials with a direct band gap of 3.37 eV and large excitation binding energy of 60 meV at room temperature. It has attracted intensive interests for its unique properties and versatile applications in many areas. Since the known of the adsorption/desorption phenomenon and the development of the nanotechnology, many researchers have begun to exploit the gas sensor applications of ZnO. ZnO has many advantages toward gas sensor applications, such as low cost, easy production and various nanostructures. On the other hand, the gas sensor performance of semiconducting metal oxide materials is significantly influenced by the microstructure and morphology of the sensing layer due to the gas response is a surface controlled process. Thus, one effective way to improve the sensor performance is by surface modification. In this dissertation, the influences of surface modification techniques on the properties and gas sensor performance of sol-gel derived nanocrystalline ZnO thin films have been intensively investigated.
1. ZnO thin films were successfully synthesized by a sol-gel technique. The preheating process plays an important role to the microstructure and gas sensing behavior of ZnO thin films. The effect of different preheating temperatures in the sol-gel spin coating process was investigated. The preheating temperature varied from 75 to 350°C. The ZnO thin films became highly c-axis oriented as increasing preheating temperature, which indicated the preferential orientation of ZnO thin films was strongly influenced by preheating temperature. An optimum gas sensor performance was observed on ZnO thin films preheated at a moderate temperature, which showed a higher sensing response and a better stability compared with that preheated at low temperature.

2. The doping effect of ZnO was comprehensively studied. Group III elements, Al and Ga, were selected as n-type doping sources. For Al doping, two different starting materials, zinc acetate (precursor-1) and zinc nitrate (precursor-2), were used in the sol-gel precursors for comparison. The precursor-1 derived ZnO films exhibited a skeletal wrinkle and porous structure, which influenced the properties of ZnO films significantly. This is believed to be due to the releases of the mechanical stress, which is generated during the preheating process. In comparison, the precursor-2 derived ZnO films showed flat and dense surfaces. Different Al doping concentrations ranging from 1 to 5 at% were also compared. The conductivity of ZnO films increased with Al doping. The highest conductivity was obtained at the 1 at% Al-doped ZnO film. Moderate amount of Al doping optimized the gas sensor performance by enhancing the sensing response and response time. Ga, as one of the element in group-III with an ionic radius of 0.062 nm, becomes an excellent...
candidate of n-type dopant in ZnO. The effect of low concentration Ga doping on structural, optical, morphological, electrical and gas sensing properties was systematically studied. The low concentration doping of Al enhanced the crystallinity and transmittance of ZnO films. The conductivity of ZnO films increased as increasing Ga doping concentration. The optimum gas sensor performance was found at the 0.3 at% Ga-doped ZnO film, which showed a high response, a short response time and a good selectivity towards H₂.

3. Laser irradiation was utilized as a novel heat treatment method in this dissertation. A pulsed laser system with a wavelength of 532 nm was used as the irradiation source. Sol-gel derived Al-doped ZnO films with different thicknesses were irradiated by laser fluence varying from 1.06 to 3.58 J/cm². The effect of laser energy on film thickness and properties of Al-doped ZnO films was studied. Laser irradiation produced two kinds of AZO films: (1) highly crystallized AZO films with small grains and high conductivity, and (2) low crystallized AZO films with small grains and high conductivity. The impact of laser irradiation was different according to the film thickness. The thicker AZO films demonstrated an optimum gas sensor performance at a low laser energy level and the thinner AZO films exhibited an optimum sensor behavior at a moderate laser energy level. A laser doping process using pre-deposited Al precursor layer for ZnO thin films was illustrated. The effect of the laser doping process on ZnO properties was investigated as a function of laser fluence. The crystallinity improved with increasing laser fluence. The laser doping process increased the conductivity of ZnO films. The EDX results confirmed the
existence of Al in ZnO films. The results showed that the gas sensor performance was significantly improved via laser doping process.

4. The O$_2$/H$_2$ plasma treatment was used with the intention of adjusting the charge carrier density and surface morphology of ZnO thin films. The effect of plasma treatment time on the sensing behavior of ZnO thin films was examined. The microstructure and surface morphology of ZnO thin films were modified significantly by both O$_2$ and H$_2$ plasma treatments. O$_2$ plasma treatment decreased the conductivity of ZnO films, whereas H$_2$ plasma treatment significantly increased the conductivity of ZnO thin films. O$_2$ plasma treatment improved the gas response to NH$_3$ by 50% compared with as-deposited ZnO thin films. A comparative study of O$_2$ and H$_2$ plasmas treated ZnO thin films for the detection of NH$_3$ and NO$_X$ was also presented. The gas sensing response towards NO$_X$ was found improved significantly after both O$_2$ and H$_2$ plasma treatments.


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