### **CHAPTER 1**

### **INTRODUCTION**

### 1.1 Background

Semiconductor sensors are widely used for gas sensing. One research interest in this field is the search for materials that exhibit high sensitivity and fast response times. Recently, semiconducting nanostructures have earned attention due to their huge surface-to-volume ratios. In general, a gas sensor performance is highly dependent on the sensor material surface area. Gas sensors based on semiconducting metal oxide nanostructures are expected to exhibit better sensing properties than gas sensors based on bulk or thin films [1]. However, the band-gap energy of semiconductor is directly related to its preparation method. Wang and coworkers [2] reported that the size and composition induced the band-gap change in nanostructured compound of group II–VI semiconductors i.e. when the particle size decreased, the band–gap energy increased.

ZnO is an interesting chemically and thermally stable n-type semiconductor of wurtzite structure with large-band gap energy of 3.37 eV at low temperature and 3.3 eV at room temperature [3–6], and with high sensitivity to toxic and combustible gases. Moreover, it has pronounced gas sensitivity to such gases as, C<sub>2</sub>H<sub>2</sub>, H<sub>2</sub>, CO, NO<sub>2</sub>, SO<sub>2</sub>, ethanol and other species [7–23]. ZnO is one of the most widely applied oxide-gas sensor. ZnO gas sensing materials owe to their high chemical stability, low cost, and good flexibility in fabrication. Various types of ZnO–based gas sensors, such as single crystal [24–26], sintered pellet [27–30], heterojunctions, thin film [31–35], and thick films [4–5, 36–38], were demonstrated. The application of

nanomaterials to the design of gas sensor is currently one of the most active research fields, due to their high activity, high surface-to-bulk ratio, good adsorption characteristics and high selectivity. The gas sensing mechanism involves chemisorptions of oxygen on the oxide surface followed by charge transfer during the reaction between chemisorbed oxygen reducing and target gas molecules. However, the physical and sensing properties of semiconductor gas sensors are directly related to their preparation e.g. particle size, sensing film morphology, crack surface [5], and film thickness [4, 39–47] as well as sensing film characteristics. One research interest in this field is the search for materials that exhibit high response and fast response time.

The preference of zinc oxide has gained impetus during the last few years because of the possibility of its relatively simple synthesis into nanoscale structures. Nanostructures like rods and particles have become the most promising research materials due to their wide range of applications. Different techniques namely sol-gel [32], spray pyrolysis [33], hydrothermal method [14, 25, 29], thermal decomposition [3], are prevalent for the synthesis of zinc oxide nanoparticles and nanorods. In the present work, nanorods and nanoparticles have been synthesized by flame spray pyrolysis.

Flame spray pyrolysis (FSP) is a promising technique for the synthesis of high purity nano-sized materials with controlled size and crystallinity in a single step. It was systematically investigated by using an external-mixing gas-assisted atomizer supported by six premixed methane-oxygen flamelets [48]. With decreasing oxidant flow rate, specific surface area increased as the spray flame length was reduced leading to a shorter residence time allowing less time for particle growth. When using oxygen as oxidant, the droplets burn much faster than in air. Thus the product particles experience longer residence times at higher temperature causing lower specific surface area. Therefore, the specific surface area of the nanoparticles can be controlled by adjusting the oxidant flow rates. After evaporation and combustion of precursor droplets, nanoparticles were formed by nucleation, condensation, coagulation, coalescence and Pt formation deposited on the ZnO support. The effect of Pt dopant on the specific surface area of the nanoparticles and crystalline sizes were also investigated [48–49]. The addition of noble metals to semiconducting oxide is known to be an effective mean to enhance the response for detection of specific gases. Pt is found to be the most effective catalyst. There were no previous studies on gas-sensing behaviors of Pt-doped ZnO nanoparticles synthesized by FSP.

### 1.2 Zinc oxide (ZnO) [49–50]

Zinc oxide (ZnO) exhibits a wide range of electrical properties depending on minor constituents and sintering conditions. It is also remarkable for the case with which high-density ceramic can be achieved over a wide range of sintering temperature and for its excellent resistance to thermal shock. ZnO has the wurtzite (ZnS) structure comprising hexagonal close-packed oxygen ions with half the tetrahedral interstices containing  $Zn^{2+}$  ions. On heating to high temperatures in air it loses oxygen thus creating oxygen vacancies, and early models attributed the resulting non-stoichiometry to the information of ZnO atoms on interstitial sites. It is now accepted that the defect is a neutral oxygen vacancy and that thermal energy at room temperature is sufficient to ionize the vacancy, thus promoting electrons into the conduction band. Conductivities exceeding  $10^2$  Sm<sup>-1</sup> can be obtained in ceramics that

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have been cooled sufficiently rapidly after sintering to preserve a high concentration of oxygen vacancies.

### 1.2.1 Basic properties [51–55]

ZnO is a direct band gap semiconductor with  $E_g = 3.37$  eV. The energy gap at room temperature for crystal free donors is 3.2 eV. The band gap of ZnO can be tuned via divalent substitution on the cation site to produce heterostructures. Cd doping can decrease the band gap (to as low as  $\sim 3.0$  eV), whereas Mg doping can increase the band gap (to as high as ~4.0 eV). ZnO normally forms in the hexagonal (wurtzite) crystal structure with a = 3.25 Å and c = 5.12 Å. Electron doping in nominally undoped ZnO has been attributed to Zn interstitials, oxygen vacancies, or hydrogen. The intrinsic defect levels that lead to n-type doping are approximately 0.01–0.05 eV below the conduction band. The optical properties of ZnO, studied using photoluminescence, photoconductivity, and absorption reflect the intrinsic direct band gap, a strongly bound exciton state, and gap states arising from point defects. At room temperature, a near-band-edge UV photoluminescence peak at ~3.2 eV is attributed to an exciton state, as the exciton binding energy is in the order of 60 meV. In addition, visible emission is also observed as a result of defect states. The basic materials parameters of ZnO are shown in Table 1.1 [50]. To realize any type of device technology, it is important to have control over the concentration of intentionally introduced impurities, called dopants, which are responsible for the electrical properties of ZnO. The dopants determine whether the current (and, ultimately, the information processed by the device) is carried by electrons or holes.

Table 1.1	The properties	of zinc oxide	(ZnO)[50]
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Properties	Values
Lattice parameters at 300 K	
$a_0, c_0, a_0/c_0$	0.32495 nm, 0.52069 nm, 1.602 nm (1.633 for ideal hexagonal structure)
u	0.345
Density	$5.606 \text{ g/cm}^3$
Stable phase at 300 K	Wurtzite
Melting point	1975°C
Thermal conductivity	0.6, 1–1.2
Linear expansion coefficient (/°C)	$a_0: 6.5 \times 10^{-6}, c_0: 3.0 \times 10^{-6}$
Static dielectric constant	8.656
Refractive index	2.008, 2.029
Energy gap	3.4 eV (direct)
Intrinsic carrier concentration	$< 10^{6} / \text{cm}^{3}$
Exciton binding energy	60 meV
Electron effective mass	0.24
Electron hall mobility at 300 K for lo n-type conductivity	$200 \text{ cm}^2/\text{V.s}$
Hole effective mass	an <sup>0.59</sup> Aai Universit
Hole hall mobility at 300 K for low p-type conductivity	$5-50 \text{ cm}^2/\text{V.s}$

In semiconducting oxides, it is generally possible to achieve one or other of these types, but not both. The dopants are also called shallow level impurities because they introduce energy levels close to one of the allowed energy bands in the material and are easily ionized as a result. There may also be unintentional impurities introduced during the growth of ZnO that have a deleterious effect on the properties of the material. These are called deep level defects or impurities and may be either elemental impurities arising from contamination of the growth environment or structural defects in the ZnO crystal lattice. These structural defects can be vacancies in the crystal structure or interstitials, i.e. atoms sitting in the open regions around lattice sites. In both cases, they may introduce energy levels deep within the forbidden band gap of ZnO and act as traps for carriers in the material. These uncontrolled defects make it very difficult to obtain reproducible device performance and reliability.

### 1.2.2 Crystal structure [51–52] 1.2.2.1 Wurtzite structure [51]

The wurtzite structure is based on the HCP close-packing of anions, with one half of the tetrahedral sites occupied by the cations. The coordination number of each ion is 4. Let's examine the spatial distribution of tetrahedral sites in HCP to determine how they can be one-half filled, with maximum separation between cations. There are two orientations of tetrahedral sites between closepacked anion layers: those with the apex "up" and those with the apex "down". It can be seen that there are equal numbers of each, and that each forms a hexagonal array with the spacing as the anions. One can therefore fill one-half the total tetrahedral sites with maximum separation by filling only tetrahedral of one orientation. This is shown in the unit cell for the wurtzite structure in Figure 1.1, where all of the filled tetrahedral sites have their apex upward. The coordination of anions around cations and of cations around anions is four, as in the zincblende structure, thus the wurtzite structure also meets the requirements of Pauling's second rule. The unit cell for wurtzite is smaller than that of zincblende (it contains only two MX formula units rather than four), so it is more difficult to visualize the interconnections between tetrahedral; they are also linked by corners. Since each has one–half of the tetrahedral sites filled as well it is reasonable that compounds of one structure often have a polytype of the other. Furthermore, since both atoms are tetrahedrally coordinated in wurtzite, it, likes zincblende, is the preferred structure of a number of covalent compounds, including aluminum nitride (AIN) and the  $\alpha$  phases of silicon carbide (SiC).



Figure 1.1 The wurtzite crystal structure of ZnO [51].

### 1.2.2.2 The hexagonal close–packed crystal structure [52]

Not all metals have unit cells with cubic symmetry; the final common metallic crystal structure to be discussed has a unit cell that is hexagonal. Figure 1.2 (a) shows a reduced-sphere unit cell for this structure, which is termed hexagonal closed-packed (HCP): an assemblage of several HCP unit cells is presented in Figure 1.2 (b). The top and bottom faces of the unit cell consist of six atoms that form regular hexagons and surround a single atom in the center. Another plane that provides three additional atoms to the unit cell is situated between the top and bottom planes. The atoms in this midplane have as nearest neighbors atoms in both of the adjacent two planes. The equivalent of six atoms is contained in each unit cell; one-sixth of each of the 12 top and bottom face corner atoms, one-half of each of the 2 center face atoms, and all 3 midplane interior atoms. If a and c represent, respectively, the short and long unit cell dimensions of Figure 1.2 (a), the c/a ratio should be 1.633; however, for some HCP metals this ratio deviates from the ideal value. The coordination number and the atomic packing factor for the HCP crystal structure are the same as for FCC: 12 and 0.74, respectively. The HCP metals include cadmium, magnesium, titanium, and zinc.

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Figure 1.2 The hexagonal close–packed crystal structure [52].

### 1.2.3 Chemical sensing of ZnO nanostructures [53]

Oxygen vacancies on metal-oxide surfaces are electrically and chemically active. These vacancies function as n-type donors; often significantly increase the conductivity of oxide. Upon adsorption of charge accepting molecules at the vacancy sites, such as NO<sub>2</sub> and O<sub>2</sub>, electrons are effectively depleted from the conduction band, leading to a reduced conductivity of the n-type oxide. On the other hand, molecules, such as CO and H<sub>2</sub>, would react with surface adsorbed oxygen and consequently remove it, leading to an increase of conductivity. Most metal–oxide gas sensors operate based on this principle. As one of the major materials for solid state gas sensor, bulk and thin films of ZnO have been proposed for CO, NH<sub>3</sub>, ethanol, and H<sub>2</sub> sensing under elevated temperature (~400°C). From the aspect of sensing performance, quasi-one-dimensional (Q1D) ZnO, such as nanowires and nanorods, is expected to be superior to its thin film counterpart. Since their diameter is small and comparable to the Debye length, chemisorption induced surface states effectively affect the electronic structure of the entire channel, thus confer Q1D ZnO higher sensitivity than thin film. In addition, ZnO nanowires and nanorods can be configured as either two terminal sensing devices or as filed effect transistor (FET) in which a transverse electric field can be utilized to tune the sensing property. Recently, the fabricated ZnO nanowire chemical sensor using microelectromechanical system technology has been reported. Massive nanowires were placed between Pt interdigitating electrodes. Under an operation temperature of 300°C, the resistance of nanowires significantly decreases upon exposure to ethanol. Electrical transport studies show that O<sub>2</sub> ambient has considerable effect on the ZnO nanowires. In addition, it is observed that the sensitivity is a function of back gate potential, i.e., above gate threshold voltage of FET, sensitivity increases with decreasing gate voltage. This implies that the gate voltage can be used to adjust the sensitivity range. Furthermore, a gate-refresh mechanism was proposed. The gas selectivity for NO<sub>2</sub> and NH<sub>3</sub> using ZnO nanowire FET was also investigated under the gate refresh process, exhibiting a gas distinguishability function. The large surface to volume ratio of nanowires not only results in their enhanced gas sensing performance, but also facilitates potential hydrogen storage property. Furthermore, the hydrogen storage characteristics under room temperature were investigated. The highest storage of 0.83 wt% was achieved at a pressure of 3.03 MPa. It was suggested that hydrogen storage was due to not only surface adsorption but also the incorporation of H<sub>2</sub> into the crystal interstitial sites.

### **1.3** Platinum (Pt) [54]

Platinum is a chemical element with the chemical symbol Pt and an atomic number of 78. Its name is derived from the Spanish term platina del Pinto, which is literally translated into "little silver of the Pinto River." It is in Group 10 of the periodic table of elements. A dense, adaptable, ductile, precious, gray–white transition metal, platinum is resistant to corrosion and occurs in some nickel and copper ores along with some native deposits. Platinum is used in jewelry, laboratory equipment, electrical contacts and electrodes, platinum resistance thermometers, dentistry equipment, and catalytic converters. Platinum's most common oxidation states are +2, and +4. The +1 and +3 oxidation states are less common, and are often stabilized by metal bonding in bimetallic (or polymetallic) species. As is expected, tetracoordinate platinum (II) compounds tend to adopt a square planar geometry. While elemental platinum is generally unreactive, it dissolves in aqua regia to give soluble hexachloroplatinic acid.

The most common use of platinum is as a catalyst in chemical reactions. It has been employed in this application since the early 1800s, when platinum powder was used to catalyze the ignition of hydrogen. The most important application of platinum is in automobiles as a catalytic converter, which allows the complete combustion of low concentrations of unburned hydrocarbon from the exhaust into carbon dioxide and water vapor. Platinum is also used in the petroleum industry as a catalyst in a number of separating processes, but especially in catalytic reforming of straight run naphthas into higher-octane gasoline which becomes rich in aromatic compounds. PtO<sub>2</sub>, also known as Adams' catalyst, is used as a hydrogenation catalyst, specifically for vegetable oils. Platinum metal also strongly catalyzes the decomposition of hydrogen peroxide into water and oxygen gas. The chemical and physical properties of platinum are shown in Table1.2

Properties	Values	
Synonyme	Platinum (Pt)	
Atomic number	78	
Structure	Face-centered cubic	
Molecular weight	$195.084 \mathrm{g \cdot mol}^{-1}$	
Density	21.45 g·cm <sup>-3</sup>	
Melting point	2041.4 K, 1768.3 °C, 3214.9 °F	
Boiling point	4098 K, 3825 °C, 6917 °F	
Atomic radious	0.139 nm	
Ouridation states	6, 5, 4, 3, 2, 1, -1, -2	
Oxidation states	(mildly basic oxide)	
Thermal conductivity	71.6 W·m <sup>-1</sup> ·K <sup>-1</sup> (300K)	

 Table 1.2 Chemical and physical properties of platinum [54]

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### 1.4 Flame spray pyrolysis (FSP) [55–66]

Flame aerosol technology is the key process for large-scale production of nano-structured materials such as carbon blacks, fumed  $SiO_2$  and  $TiO_2$  and to a lesser extent, for specialty chemicals such as  $Al_2O_3$  and ZnO powders. Flame aerosol synthesis is a cost-effective and versatile process for controlled production of

nanoparticles [55-57]. Flame spray pyrolysis (FSP) process was systematically investigated using an external-mixing gas-assisted atomizer supported by premixed methane and oxygen flamelets [58–59]. In flame reactors, the energy of flame is used to drive chemical reactions of precursors resulting in clusters which further grow to nanoparticles by surface growth and/or coagulation and coalescence at high temperature [64]. The advantages of FSP include the ability to dissolve the precursor directly in the fuel, simplicity of introduction of the precursor into the hot reaction zone (e.g. a flame), and flexibility in using the high-velocity spray jet for rapid quenching of aerosol formation. In general, a flame is used to force chemical reactions of precursor compounds, finally resulting in the formation of clusters, which increase their size to a range of some nanometers by coagulation and sintering. Finally, the nanostructured powders are collected on a filter [58–59]. The more fuel is introduced the higher the flame and due to that the residence time of particles in the flame is increased. As a consequence time for particle growth is increased and bigger particles are formed. External electric field reduces the average particle size in a narrow range up to a factor of two. Electric fields can be introduced in some applications as control devices [65–66]. The steps of particle formation and growth by flame spray pyrolysis of Pt-doped ZnO were shown in Figure 1.3.

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**Figure 1.3** The steps of particle formation and growth of Pt-doped ZnO by flame spray pyrolysis [55].

Moreover, at low oxidant flow rates, the specific surface area increased with increasing oxidant flow rate as the spray flame length was reduced, leading to shorter residence time and allowing less time for particle growth. Using oxygen as oxidant the droplets burn much faster than with air, thus, product particles experience longer residence times at higher temperature [57–61]. The effect of solution feed rate on particles specific surface area and crystalline size was also investigated [56]. The solution feed rate increased the flame height, and therefore coalescence was enhanced, resulting in large primary particles [56]. Furthermore, the flame conditions can be used to control the morphology of particles.

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#### **1.4.1** The FSP evaluations of particle formation [62–63]

In the FSP process, the evaluation of the particles formation is multifunctional significance on background of both Chemistry and Physics. Several mechanisms in particles formations are formed, and can be described. The pathway of particle formation in high-temperature processes can often be characterized by nucleation of condensable material and subsequent particle growth by coagulation. Depending on the temperature, particles formed in this way may have different morphological structures. Spherical particles are produced when the colliding particle coalesce. However, when coalescence is quenched agglomerates are formed. The size of the primary particles composing the agglomerates depends on the temperature history of the particle-formation process and on the temperature dependence of the material properties determining particle coalescence. These mechanisms were discussed in the details.

### 1.4.1.1 Evaporation-condensation [62–63]

Evaporation is the reverse of growth by condensation in which more molecules leave the particle surface than arriving. With evaporation, there is no counterpart to the threshold of formation that must be reached for condensation to commence, and droplets of pure liquid will evaporate completely. Evaporation followed by condensation of a species is a convenient method for the formation of nanometer-size particles that is used for the synthesis of metal nanoparticles. The technique is called inert gas condensation in that field. Metals and nanocrystalline ceramics with improved mechanical properties can be produced by these methods. A metal is vaporized into a host gas where the vapor is cooled resulting in particle

formation by nucleation. Cooling of the vapor can be accomplished by contact with a cooler inert gas or by expansion through a nozzle. Expansion of a supercritical fluid through a nozzle can also be used for particle formation. The process of evaporationcondensation is often carried out below atmospheric pressure in inert gases. A typical system involves a vacuum chamber that can be evacuated to pressures of  $10^{-6}$  to  $10^{-10}$ torr in order to reduce contamination levels. Often a boat is used to hold a metal heated to vaporize it into the gas phase. A natural plume is established by free or forced convection from the metal containing boat. This boat can be heated continuously or in pulses. Temperatures are usually lower than those in plasma and flame reactors. In evaporation-condensation/ reaction processes, reactions take place at the newly formed particle surface altering the chemical and/or phase composition of the particles. A precursor compound is vaporized into a carrier gas, which is then cooled resulting in droplet formation by nucleation (Figure 1.3). After the droplet formation a reaction step particle formation takes place resulting in solid. Evaporation-condensation processes are reasonably well understood especially when precursors with known physicochemical properties are employed and well defined flow patterns exist such as in tube flows. Aerosol processes are used industrially to produce a variety of products. Each of the gas to particle conversion processes discussed in each particular application has its own advantages and disadvantages.

### 1.4.1.2 Nucleation [62–63]

Homogeneous nucleation is the formation of particles from a supersaturated vapor without the assistance of condensation nuclei or ions. This process is also called self-nucleation. This type of particle formation seldom occurs naturally but can be produced readily in the laboratory to study in process of formation and growth. It is covered here because it serves as a framework for understanding the more common heterogeneous nucleation processes covered in nucleated condensation.

### 1.4.1.2.1 Nucleated condensation [62–63]

Nucleated condensation or heterogeneous nucleation is a process of particle formation and growth that is promoted by the presence of condensation nuclei or ions. Whereas homogeneous nucleation usually requires saturation ratios of 2–10, nucleated condensation can occur at supersaturations of only a few percent. In the case of soluble nuclei, condensation can occur in insaturated conditions and size-stable droplets can be formed. Nucleated condensation is the primary mechanism for cloud formation in the atmosphere

### 1.4.1.3 Coagulation [63]

Coagulation of aerosols is a process whereby aerosol particles collide with one another due to a relative motion between them and adhere to form larger particles. The net result is a continuous decrease in number concentration and an increase in particle size. When the relative motion between particles is due to Brownian motion, the process is called thermal coagulation. Thermal coagulation is a spontaneous and ever-present phenomenon for aerosols. When the relative motion arises from external forces such as gravity or electrical forces or from aerodynamic effects, the process is called kinematic coagulation. Coagulation is the most important interparticle phenomenon for aerosol. The theory of coagulation was originally devised for liquids and was later extended to aerosols. The original name has continued. In the case of solid particles, this process is sometimes called agglomeration and the resulting particle clusters, agglomerates.

### 1.4.1.4 Coalescence [62–63, 67]

Coalescence is a process in which grains are pulled into contact by a wetting liquid, allowing coalescence at points of contacts. A sketch of a possible coalescence mechanism is given in Figure 1.4 Contacting grains of dissimilar size fuse into a single grain by a continuous process of directional grain growth, grain reshaping, and grain rotation. The reshaping process is by concurrent solutionreprecipitation. The grain size grows by coalescence while the number of grains decreases continuously. Grain coalescence is observed in most systems. Contacts form after the liquid appears and there is a small probability that the contact will have a low-angle grain boundary that allows coalescence. Alternatively, for grains with different sizes, the driving force for coalescence is the boundary migration due to curvature, which suggests that coalescence is favored at the large-small grain contacts. Other causes of coalescence are gradients in chemistry or strain state.



Figure 1.4 Steps loading to grain growth by coalescence [67].

Contact formation is a precursor to neck growth and coalescence. New contacts between grains are induced by gravity, thermal motion, and settling. Many contacts exist prior to liquid formation, especially with high solid contents and high green densities. Since the packing coordination of a grain increase by a high-volume fraction of solid, the probability of coalescence is increased by a high-volume fraction of solid. However, the grain motion in the liquid is inhibited by a high-volume fraction of solid and rigid solid skeleton. Consequently, coalescence is most important shortly after liquid formation. Several mechanisms act to coalescence contacting grains as: grain boundary migration by solid-state diffusion, grain boundary migration by diffusion across an intermediate thin liquid layer, grain rotation to eliminate the grain boundary, or solution-reprecipitation from the small to the large grain.

### **1.5** Sensing performance factors [49, 68–69]

As a new technique is developed, one needs to establish fairly quickly the criteria by which its performance can be measured. These criteria have to be refined continuously as expectations are raised. This is especially true for a device containing biological materials. A number of different factors will be referred to in this part that applies to both biosensors and chemical sensors. Unfortunately, different researchs express these factors in different ways, and worse still, some do not give much data at all about their performance in published papers. Anyone developing a new sensor needs to have some idea of what performance requirements are likely to be needed for a particular application.

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#### 1.5.1 Selectivity [68–69]

The selectivity can be defined as the ability of a sensor to respond primarily to only on a specific species in the presence of other species. This is the most important characteristic of sensors; the ability to discriminate between different substances. Such behavior is principally a function of the selective component, although sometimes the operation of the transducer contributes to the selectivity. This factor is the essence of sensors. It is a race rate to find a sensor which will respond to only one analyte, although some do exist. It is more usual to find a sensor that will respond mainly to one analyte, with a limited response to other similar analyte. Alternately, the response may be to a group of analytes of similar chemical structure, such as carbonyl compounds.

### 1.5.2 Sensitivity [49, 69]

This usually need to be sub-millimolar, but in special cases can go down to the femtomolar ( $10^{-15}$  M) range. With any analytical technique, it is important to know what concentration range is covered and from the calibration point of view, over what section of this range the response in linear. At the lower level is the detection limit. This has a precise definition according to the IUPAC convention. It is the concentration of analytes at which the extrapolated linear portion of the calibration graph intersects the baseline, a horizontal line corresponding to zero change in response for several decades of concentration change. With chemical sensor, the result usually shows the change in resistance lead to the sensing performance. The sensitivity (or sensor signal, sensor response), *S* is defined (Figure 1.5) as the several ratios depending on the types of a semiconductor, and the types of the analyte gases

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i.e.  $R_a/R_g$  [77–88],  $R_a-R_g/R_g$  [89–90],  $R_a-R_g/R_a$  [91–94],  $R_f-R_o/R_o$  [95],  $G/G_o$  [96], where  $R_a$  is the resistance in dry air,  $R_g$  is the resistance in test gas,  $R_f$  is the full–scale conductance when the sensor is in equilibrium with the gas,  $R_o$  is the baseline conductance when the sensor is in equilibrium with air, G is the conductivity in presence of gas, and  $G_o$  is the conductivity in air. The sensitivity is given in the following as the resistance ratio  $R_a/R_g$  for reducing gases e.g.  $C_2H_5OH$ ,  $NH_3$ ,  $SO_2$ , CO, propanol and as  $R_g/R_a$  for oxidizing gases e.g.  $NO_x$  [97] as shown in Equations 1.1 and 1.2 as follows:

$$S = \frac{R_a}{R_g} \quad \text{(for reducing gas)} \tag{1.1}$$

$$S = \frac{R_g}{R} \quad \text{(for oxidizing gas)} \tag{1.2}$$

### 1.5.3 Time factors [49, 69]

### 1.5.3.1 Response times [49, 69]

Many analytical devices require some "settling-down" time, i.e. time to allow the system to come to equilibrium, the response time. This is true to some extent with many chemical methods. For example, recent extensive studies with amperometric sensor showed that the most reproducible results were obtained after stirring the solution in contact with the electrode for ca. 30 s. However, with sensors of a chemical or biochemical nature, this response time is greatly offset by the simplicity of the measurement and the minimal sample preparation time. Normally, the response times can vary from a few seconds to a few minutes. Up to 5 min may be acceptable, but if the time exceeds 10 min this may be too long. Normally, the response time,  $T_{\rm res}$  is defined as the time required until 90 % of the response signal is reached [76, 98–100].



**Figure 1.5** Change in resistance of several gases corresponded to the sensing performance in terms of sensitivity, response, and recovery times [70].

### 1.5.3.2 Recovery times [49, 69]

Very much related to the response time is the recovery time. The recovery time is the time that elapses before a sensor is ready to be used for another sample measurement. The resulting response time may be immediate or it may be that after one measurement the sensor system has to rest the resume its base equilibrium before it can be used with the next sample. In many publications, these times are combined and the result is given as the number of samples that can be analyzed per hour, which obviously is the main practical point at the end. In this research, the response and recovery times are important parameters for designing sensors for the desired application. The response/recovery times are defined as the time required for adsorption and desorption of oxygen on, or from the sensor surface to reach the saturation or to reduce the conductivity back to the baseline conductance. A good sensor is the one that shows a short response and recovery time. Normally, the recovery times,  $T_{\rm rec}$  denotes the time needed until 90 % of the original baseline signal is recovered [4–5, 49, 71]. The response and recovery time can be calculated using Equations 1.3 and 1.4 as follows:

$$T_{res} = \left[ T_{R_o} - \left\{ \left( T_{R_o} - T_{R_g} \right) \right\} \times \frac{90}{100} \right] - T_{R_o}$$
(1.3)

$$T_{rec} = \left[ T_{R_g} - \left\{ \left( T_{R_o} - T_{R_g} \right) \right\} \times \frac{90}{100} \right] - T_{R_g}$$
(1.4)

where  $T_{R_0}$  is defined the as the time (s) at the baseline resistance in dry air ( $R_a$ ) and  $T_{R_g}$  is denoted as the time (s) at the resistance in test gas ( $R_g$ ).

# 1.6 Characterization techniques 1.6.1 X-ray diffraction method [62, 72–74]

X-ray diffraction (XRD) is a standard tool for identification of crystalline phases in powder samples. The crystalline phase in the sample diffracts X-rays according to Bragg's equation [72–74] which relates lattice spacing to the wavelength

of the X-ray. The amount of sample needed in practice is roughly 100 mg or more. Crystalline phases present at levels of about 1 percent or greater can be detected. The unit cell dimension (a,b,c) of the crystal can also be determined and provide more information for complex structure materials. Amorphous materials are not observed. In routine work, XRD relies on availability of standards that allow identification of peaks in the diffraction pattern.

### 1.6.1.1 The advantage of X-ray diffraction method [75–77]

The simplicity and advantages of the powder diffraction method for identification of an unknown substance are as follows:

- The powder diffraction pattern is determined by the exact atomic arrangement in a material, so it is like a "fingerprint" of the material.
- Each substance in a mixture produces its own characteristic diffraction pattern independently of the others.
- The X-ray diffraction pattern discloses the presence of a substance as that substance actually exists in the specimen.
- Only a small amount of the material is required for recording the X-ray diffraction pattern.
- The method is nondestructive.

### **1.6.1.2** Identification of crystal structure by XRD [75–77]

The X-ray diffraction pattern is a fingerprint of any substance, it should be possible to unambiguously identify that material from its X-ray diffraction

pattern. A large collection of X-ray diffraction pattern from a number of substances are available, then the unknown material can be identified by obtaining its diffraction pattern and then determining which pattern from the collection matches exactly recorded by the diffraction pattern. The Powder Diffraction File (PDF) organized by the Joint Committee on Powder Diffraction Standards (JCPDS).

# 1.6.1.3 Diffraction from crystalline materials–Bragg's law [62, 72–74]

Bragg's law, formulated by W.L. Bragg in 1913 [78–80], relates the wavelength of the X-rays to the spacing of the atomic planes. Consider the diffracted wave in Figure 1.6. It is assumed to make the same angle,  $\theta$ , with the atomic planes as does the incident wave. Now the criterion for the existence of the diffracted wave is that the scattered (reflected) X-rays should all be in phase across a wave front. This turns out to be a real convenience, so we set d = d'/n and write the Bragg's law in the form as follows:

#### $\lambda = 2d \sin \theta$

(1.5)

This equation is known as Bragg's law [72–74] and is extremely important in indexing X-ray diffraction patterns and, hence, for determining things like the crystal structure of the material. The scattering of electrons, X-rays and neutrons by crystals can be described as a reflection of the beams at planes of atoms (lattice planes), independent of the actual physical reason causing the diffraction event. If the incident plane wave hits the crystal at an arbitrary angle, the interference of the reflected waves can be either destructive or constructive. To obtain constructive interference, the path difference between the two incident and the scattered waves, which is  $2d\sin\theta$ , has to be a multiple of the wavelength  $\lambda$ . For this case, the Bragg law then gives the relation between interplanar distance d and diffraction angle  $\theta$ .



Figure 1.6 Diffraction of X-ray by a crystal [74].

### 1.6.1.4 Particle size measurement by XRD [75–77]

For good quality crystalline material of dimension 0.1 nm is made up of approximately 1,000,000 crystal planes (assuming that  $d_{hkl} = 1$  nm). When an X-ray collides with these planes close to the Bragg angle, diffraction intensity is not observed because the X-rays reflected from the multitude of parallel planes annihilate one another. With such materials diffraction peaks are produced only within a very narrow window very close to the Bragg's angle. Particle sizes are often in the range of 1–100 nm for heterogeneous catalysts. In such circumstances, the number of stacked planes per particle is in the range of 5–100. This results in the broadening of the XRD peaks because there are insufficient reflecting planes to annihilate phase reflection at angle that are fairly far and removed from the Bragg's angle.

This effect has been quantified as the Scherrer equation:

$$t_{hkl} = K\lambda / B_{hkl} \cos \theta_{hkl}$$

(1.6)

Where:

t<sub>hkl</sub>

 $B_{\rm hkl}$ 

K

is the particle size measured from X-rays diffracted from the (*hkl*) planes

is the peak width measured at half height measured in radian from the (*hkl*) planes

 $\theta_{hkl}$  is the Bragg's angle for the reflection from the (*hkl*) planes

is a constant which depends to some extent on the particles shape. For spherical particles K = 0.9.

### 1.6.1.5 Sample preparation [75–77]

In X-ray diffraction work, we normally distinguish between single crystal and polycrystalline or powder applications. The single crystal sample is a perfect (all unit cells aligned in a perfect extended pattern) crystal with a cross section of about 0.3 mm. The single crystal diffractometer and associated computer package is used mainly to elucidate the molecular structure of novel compounds, either natural products or man made molecules. Powder diffraction is mainly used for "fingerprint identification" of various solid materials, e.g. asbestos, quartz.

In powder or polycrystalline diffraction, it is important to have a sample with a smooth plane surface. If possible, we normally grind the sample which was normally ground down to particles of about 0.002 mm to 0.005 mm in cross section. The ideal sample is homogeneous and the crystallites are randomly distributed. The sample is pressed into a sample holder so that a smooth flat surface is obtained. Ideally, it should be a random distribution of all possible h, k, 1 planes. Only crystallites having reflecting planes (h, k, l) parallel to the specimen surface will contribute to the reflected intensities. In a truly random sample, each possible reflection from a given set of h, k, 1 planes will have an equal number of crystallites contributing to it. The sample needs to be fixed through the glancing angle  $\theta$  in order to produce all possible reflections.

### 1.6.2 Scanning electron microscopy (SEM) [ 63, 81–83]

In a scanning electron microscope, a tiny electron beam is scanned across the sample. Schematic diagram of a scanning electron microscope was shown in Figure 1.7. Simultaneously, the generated signals are being recorded, and an image is formed pixel by pixel. In SEM, the signals are observed on the same specimen site as the incoming electron beam (cf. STEM, using transmitted electrons). In contrast to TEM methods needing very thin samples, compact samples can thus be investigated by SEM. Valuable information about morphology, surface topology and composition can be obtained. SEM microscopes achieving resolutions below 1 nm are available now. The resolution of a typical SEM is about 0.01  $\mu$ m, not as good as a TEM but much better than an optical microscope and adequate for most particle studies. Like the TEM, the SEM is limited to solid, nonvolatile particles. Unlike the TEM, the electron beam does not have to penetrate the sample support, so SEM samples are usually mounted on the end of an aluminum cylinder 1–3 cm in diameter. Precautions must be

taken to prevent the buildup of electric charge on the sample surface, which would deflect the electron beam and cause distortion of the image and particle loss by electrostatic repulsion. This is usually done by applying a very thin (< 0.01  $\mu$ m) coating of gold or carbon to the surface of the particle with a sputter-coating apparatus. Particles can be deposited onto any surface that can be attached to the sample cylinder and made conductive. The smooth surface of a Nuclepore filter provides a suitable surface for viewing particles, and particles larger than its pore size can be sampled directly onto the filter surface. Scanning electron microscopes have a depth of field that is over 300 times greater than that of optical microscopes and wide range of magnifications, 20-100,000X. For particle evaluation, а a magnification range of 100-10,000X is most commonly used. The great depth of field and the accurate rendition of surface features make the SEM well suited to particle sizing and morphology studies. A scanning electron microscope can be used as a microprobe to determine elemental composition of particles. The electron beam is held fixed on a particle and the X-rays emitted are detected by a solid state X-rays is related to the Z number of the elements in the particle and provides an elemental analysis of the particles for Z > 12. Although less common, an Auger electron velocity analyter can be used in the same way to determine elemental composition for Z < 20. The adjustable electron beam voltage of 1–30 kV facilitates these analyses.

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Figure 1.7 Schematic diagram of a scanning electron microscope [84].

1.6.3 Transmission electron microscopy (TEM) [63, 85–86]

The TEM is used heavily in both materials science/metallurgy and the biological sciences. In both cases the specimens must be very thin and able to withstand the high vacuum present inside the instrument.

To examine particles smaller than the resolution limit of optical microscopes,

one must use an electron microscope. In TEM, the resolution is not 100,000 times smaller than that of an optical microscope because of the small value of angular aperture used in electron microscopes to minimize distortion. The limit of resolution for a typical TEM is in a few angstroms (1 Å =  $10^{-4} \mu m$ ). The small value of aperture angle used has the advantage of providing a large depth of field, more than 100 times the resolution. Transmission electron microscopes permit size measurement of the smallest aerosol particles, but they can be used only for solid particles that do not evaporate or degrade under the combined effect of high vacuum and heating by the electron beam. Particles must be deposited on specially prepared 3 mm diameter grids that are mounted in a grid holder and inserted in the microscope. The grids are 200 mesh electrodeposited screen with a thin film of carbon or Parlodion (1-4% nitrocellulose in amyl acetate) covering the screen openings. The film is sufficiently thin, compared to the particles, on the other hand, extensively scatter and absorb the electron beam to form a high-contrast silhouette type of image. Particles can be deposited directly onto the film surface of a grid by electrostatic precipitation using the miniature type of precipitator. In some cases replication or transfer procedures can be used to deposit particles or their replicas from another surface onto a grid.

For biological specimens, the maximum specimen thickness is roughly 1  $\mu$ m. To withstand the instrument vacuum, biological specimens are typically held at liquid nitrogen temperatures after embedding in vitreous ice, or fixated using a negative staining material such as uranyl acetate or by plastic embedding. Typical biological applications include tomographic reconstructions of small cells or thin sections of larger cells and 3-D reconstructions of individual molecules via Single Particle Reconstruction.

### 1.6.3.1 Image modes in TEM-Bright-field images [86]

In the bright-field (BF) mode of the TEM as shown in Figure 1.8, an aperture is placed in the back focal plane of the objective lens which allows only the direct beam to pass. In this case, the image results from a weakening of the direct beam by its interaction with the sample. Therefore, mass-thickness and diffraction contrast contribute to image formation: thick areas, areas in which heavy atoms are enriched, and crystalline areas appear with dark contrast. The interpretation of images is often impeded by the simultaneous occurrence of the contrast-forming phenomena.



### 1.6.3.2 Image modes in TEM-Dark-field images [86]

In dark-field (DF) images as shown in Figure 1.9, the direct beam is blocked by the aperture while one or more diffracted beams are allowed to pass the objective aperture. Since diffracted beams have strongly interacted with the specimen, very useful information is present in DF images, e.g., about planar defects, stacking faults or particle size.



Figure 1.9 The schematic of dark-field imaging of TEM (a) off-axis dark-field imaging and (b) on-axis dark-field imaging [87].

### 1.6.4 Energy dispersive X-ray spectroscopy (EDS) [83, 88–89]

The energy dispersive X-ray spectroscopy (EDS) involves the probing of a sample with electrons resulting in emission of X-rays with energies characteristic of the elements present in the sample. Because an electron beam is used to probe the sample, the composition of particles in the nm range can be examined. Single particles can be examined by this technique. The probing depth is on the order of 1  $\mu$ m. EDS has 0.1% detectability for Z > 11. Thus, elements with atomic weights greater than sodium can be detected in most instruments. Resolution down to 1  $\mu$ m is available with SEM and down to 50 nm is available with TEM instruments. X-rays maps of a particle can be used to examine the chemical homogeneity of a given element. The technique can also be used to examine a larger number of particles and to look for variations in stoichiometry from particle to particle. Quantitative measurements usually require flat surfaces, but semiquantitative information can be obtained for particles.

The electron beam applied in SEM and TEM also can be focused on a certain point of the analyted sample and is used to measure the X-rays spectrum at this location. Each element of the periodic table has its characteristic peak positions where a transition in its electron shell can occur. An incoming high energy electron hits an electron out of a shell which creates an electron hole in the target atom. This is also called ionization. An electron of an outer shell fills the hole in the shell again. This electron emits a characteristic X-rays quantum which is measured by EDS. The development of the energy-dispersive X-rays spectrometer has made "easy" X-rays spectrometry available to virtually all types of electron-beam instruments. However, one must recognize that, because of the nature of the EDS technique, distortions are introduced into the ideal X-rays spectrum ("spectral artifacts") during the measurement process which must be dealt with in practical analytical spectrometry. In the discussion which follows, we will consider these artifacts at each stage of the detection and amplification process.

### 1.6.5 The Brunauer-Emmett-Teller (BET) [62, 90–91]

Surface areas of powders are usually measured using nitrogen or helium adsorption followed by analysis of the data using the Brunauer-Emmett-Teller isotherm. Estimation of surface areas provide information about the porosity of particles and the primary particle size in particles that consist of agglomerates of smaller particles. The primary particle size can be related to surface area assuming that the particles are smooth monodisperse spheres. Specific surface areas can range from a few  $m^2/g$  to hundreds of  $m^2/g$  in the case of highly porous materials or very fine particles.

### **1.6.5.1** Particle Size (*d*<sub>BET</sub>) [4, 5, 62, 90, 91]

The Brunauer-Emmett-Teller (BET) method uses the adsorption of nitrogen on the particle surface and the measurement is operating at low, constant temperature (boiling point of liquid nitrogen at around -200°C). This method was introduced by Brunauer et al. [91]. Increasing the partial pressure over a particle sample the uptake of nitrogen by the sample is measured. Following the IUPAC classification and assuming that the measured particle samples which means that they are mesoporous (pores are in the size range of 2 nm to 50 nm) or even microporous (pores larger than 50 nm) only monolayer of adsorptive nitrogen is built up at the surface by increasing the partial pressure. Knowing the amount of adsorbed nitrogen and assuming that there is only one monolayer a specific surface area ( $SSA_{BET}$ ) of metal oxide and metal-doped metal oxide particles can be calculated. To calculate the mean particle diameter or as well called Sauter mean diameter ( $d_{BET}=d_{SMD}$ ) by assuming that the particles do have spherical shape the following Equation 1.7 is used:

 $d_{BET} = \frac{1}{SSA_{BET}\rho_{sa}}$ 

(1.7)

where  $\rho_{sample}$  is the density of sample.

#### 1.6.6 Atomic force microscopy (AFM) [92]

Scanning probe microscope (SPM) form a new family of microscopes developed from the invention of the scanning tunneling microscope (STM). These microscopes have no lens but simply scan and sharp probing tip over a sample surface, providing high resolution information about the surface characteristics of solid samples. Among them, the atomic force microscope (AFM) has been widely applied to the study of surface structures, especially in the field of materials science. This is because the AFM can create topographic images of the sample surfaces from the micrometer scale to the atomic scale. This microscope has always been expected to become an essential tool for the study of biological structures for the following reasons: - The AFM enables direct observation of non-conductive samples without metal coating or any conductive treatment, in contrast to scanning electron microscopy.

The AFM has the advantage that it creates images not only in vacuum but also in an air or liquid environment, indicating that functional information can be expected concerning living cells.

- The AFM provides quantitative information on the sample height, in contrast with scanning electron microscope images.

### **1.6.6.1** Principles of atomic force microscopy [92]

The AFM is roughly composed of the microscope unit, control unit, and computer (Figure 1.10). In this microscope unit, the probe is attached to the end of a cantilever. When the probe approaches the sample surface, a tiny interaction force occurs between the probe and sample, and this influences the position of the cantilever. The cantilever position is usually measured by the optical lever method. Using an appropriate feedback system in the control unit, the distance between the probe and sample is accurately regulated by changing the height of the sample. A piezoelectronic xyz-scanner is usually used both to control the vertical position of the sample (z) and to raster-scan the sample in the xy-plane. There are two different operating modes in AFM: a contact mode and a dynamic force mode. In contact mode AFM, the tip is simply dragged across the sample surface whilst measuring the deformation of the cantilever. Dynamic force mode AFM, on the other hand, scans the sample surface with a vibrating cantilever. In this mode, the probe-sample interaction force is controlled by alterations in the resonance frequency of the cantilever, since



Figure 1.10 The schematic of the atomic force microscope (AFM) [93].

the resonance frequency shifts to reflect changes in probe-sample distance. The vertical interaction force in dynamic force mode AFM can be smaller  $(10^{-9}-10^{-10} \text{ N})$  than in contact mode AFM (about  $10^{-8}$  N) and is suitable for imaging very soft samples. AFM images are thus created either by measuring the cantilever deflection (in contact mode AFM) or the resonance frequency (in dynamic force AFM). Images produced by the feedback voltage are called constant force images (or height images). These reflect the topographical height of the sample. On the other hand, images constituted by changes in the cantilever deflection (in contact mode AFM) or the constituted by changes in the cantilever deflection (in contact mode AFM) or the change of amplitude (in dynamic force mode AFM) are called variable deflection

images. These are suitable for visualizing the details of sharp contour changes in the sample. There are different graphic modes for computer display. The most popular mode is the gradation mode, which represents the sample height or cantilever deflection by color gradations or a gray scale. In constant force images, the shading mode displayed by an illuminated three-dimensional rendering is also used to represent surface details of specimens.

### 1.7 Sensor experiment [94–95]

### 1.7.1 Semiconducting oxide sensors [94–95]

The principle subject to which these sensors operate can be summarized as follows. There is a finite density of electron donors (e.g., adsorbed hydrogen) and/or electron acceptor (e.g., adsorbed oxygen) bound to the surface of a wide-band gap semiconducting oxide, such as ZnO or SnO<sub>2</sub>. They represent surface states which can exchange electrons with the interior of the semiconductor, thus forming a space charge layer situated close to the surface (Figure 1.11). The position of the surface state relative to the Fermi level of the semiconductor depends on its affinity to electrons. If its affinity is low, it will lie below the Fermi level and donate electrons (reducing agent) to the space-charge region. If it is an acceptor, it will be positioned above the Fermi level and extract electrons (oxidizing agent) from the space-charge region. By changing the surface concentration of the donors/acceptors the conductivity of the space-charge region is modulated.



Figure 1.11 Space charge modulations by adsorption in a n-type semiconducting oxide sensor [94].

In an n-type semiconductor, such as SnO<sub>2</sub> and ZnO, the majority carriers are electrons therefore the change in surface conductivity,  $\Delta \sigma_s$  is given from Equation 1.8 in the form:  $\Delta \sigma_s = e \,\mu_s \Delta n_s \qquad (1.8)$ 

where *e* is the electron charge and  $\mu_s$  is the electron mobility at the surface. The excess density  $\Delta n_s$  of charge carriers in the space-charge region of thickness *d* is obtained by integrating the difference between the electron density in the space charge region and in the bulk  $(n_b)$  over the thickness *d*:

$$\Delta n_s = \int_0^d [n(z) - n_b] dz \tag{1.9}$$

The change in surface conductance  $\Delta G_s$  is then:

$$\Delta G_s = \Delta \sigma_s W / L \tag{1.10}$$

(1.11)

For an n-type semiconductor (such as ZnO) an increase in the surface concentration of the electron donor (e.g. hydrogen) will therefore increase the conductivity. On the other hand, adsorption of hydrogen on a p-type oxide (such as CoO) will decrease its conductivity by the same argument. The bulk conductance which is not modulated by the surface reactions is represented by a parallel conductor (Figure 1.12):

 $G_b = n_b e \,\mu_b W d \,/\, L$ 

The terms in Equation 1.11 have the same meaning as those in Equation 1.9 and 1.10. Subscript b refers to the bulk quantities while d is the total thickness of the oxide layer. Since the overall conductance is measured, it is advantageous to have the films as thin as possible. The relative change in the conductance of the whole device is obtained from Equation 1.9, 1.10, and 1.11 and by assuming that  $\mu_b \sim \mu_s$ . Hence:

$$\Delta G / G = \Delta n_s / n_b d \tag{1.12}$$

For the value of the relative conductance change (high sensitivity) it is necessary to have a low density of bulk carrier and a thin film. The space-charge thickness is typically 100–1000 Å, depending on the doping. As an example let us consider a typical value of the excess surface-state density  $n_s = 10^{12}$  electrons cm<sup>-2</sup> and the bulk density  $n_b = 10^{17}$  electron cm<sup>-3</sup>. This means that for a 100  $\mu$ m thick film the sensitivity  $\Delta G_s/G_b = 10^{-3}$ . However, for d = 100 Å the sensitivity is 10 and for thin films (< 1000 Å) the space-charge region extends throughout the whole film thickness.



**Figure 1.12** Schematic representation of a semiconducting oxide sensor with bulk ( $g_B$ ) and surface ( $g_S$ ) conductivities [94].

It is convenient to present the elemental aspects of the sensing mechanism assuming a regular crystal lattice, i.e., a monocrystal. Indeed the fundamental studies into reactions at oxide surfaces were conducted on well-defined surfaces. On the other hand, practical sensors are prepared by techniques which yield polycrystalline layers. For the dimensions of the film at which the surface conductance begins to dominate the overall conductance, the film morphology becomes the most important parameter. A schematic representation of three types of oxide surface is shown in Figure 1.13. Although an adsorbate capable of being involved in the electron exchange with the surface can act as the surface state which dominates the space charge, oxygen and hydrogen are by far the most important species. The chemical interaction leading to changes in the density of surface states are complex and form part of the surface catalytic processes. In addition to the above-mentioned interaction of adsorbates, the diffusion of lattice defects from the bulk of the crystal also takes place. The defects can act as donors or acceptors. Oxygen vacancies  $V_{O^+}$  are presumed to be intrinsic donors as shown in Equation 1.13 and 1.14:

and  $(Zn^{2+}O^{2-})_{lat} = V_{O}^{+} + e^{-} + \frac{1}{2}O_{2}(gas)$ (1.13)  $(Zn^{2+}O^{2-})_{lat} = V_{O}^{2+} + e^{-} + \frac{1}{2}O_{2}(gas)$ (1.14)



Figure 1.13 The Schottky-barrier model assumes a tunneling mechanism for the electrons. Conductivity of the closed–neck and of the open-neck sample is modulated by the density of surface states  $(O_2^-)$  [94].

while adsorbed  $O_2^-$  and  $O^-$  species act as electron acceptors. Their relative population at the oxide surface to a large extent determines the type of chemical interaction which will take place. This issue of the selectivity of these surfaces has been treated comprehensively and in great detail elsewhere; here only a few examples will be mentioned. Moreover, the conductivities of certain transition-metal oxides are affected by the adsorption of gas species on to their surfaces. The best examples of these are ZnO and SnO<sub>2</sub> (see Figure 1.11 earlier). Sensors based on this principle can be designed to detect carbon monoxide (CO), carbon dioxide (CO<sub>2</sub>), ethanol (C<sub>2</sub>H<sub>5</sub>OH; EtOH), and other organic vapors down to 1–50 ppm [20, 23, 33–34, 45]. This type of sensor is fabricated by using vapor deposition techniques. A 0.3  $\mu$ m layer of palladium-doped SnO<sub>2</sub> is grown on a silicon oxide layer on top of a ferrite substrate [95]. On the other face of the ferrite is a thick layer of ruthenium oxide which acts as a heater to bring the sensor to its semiconducting operating temperature. The electrical resistance is measured between two gold contacts situated on the SnO<sub>2</sub> layer.

In such a system, n-type semiconductors are preferred because they give an electrical resistance change from high to low in the presence of the analyte gas. Some atmospheric oxygen is chemisorbed on the surface by reacting with the excess of electrons from the SnO<sub>2</sub> to give adsorbed oxygen anions ( $O_{ads}^{-}$ ), which results in a low conductivity (high resistance). The adsorbed gas reacts with the chemisorbed oxygen anions, according to the following:

The gas removes the chemisorbed oxygen and is oxidized. Thus, gases which are reducing agents can be detected. The electrons produced cause an increase in the electrical conductivity of the SnO<sub>2</sub>, which is measured as a decrease in resistance, and is proportional to the amount of gas present. ZnO is an n-type semiconductor and can act in a similar way, although such sensors are somewhat lacking in selectivity. An improved selectivity can be obtained by varying the operating temperature and by the addition of other metal elements, such as platinum (Pt) or palladium (Pd), which catalyze the oxidation of certain gases. Sensors of this type are available commercially for the detection of flammable gases in buildings and homes. Another application is in the automotive industry. For example, a TiO<sub>2</sub>-based sensor has been used to measure the organic vapors content [71]. The resistance of the active layer increases with the amount of oxygen.

### 1.7.2 ZnO gas sensing mechanism and reactions [4–5, 49]

The sensing mechanism of material is shown in Figure 1.14. The analyte gases adsorbs on the ZnO sensing layer and causes a change in resistance depending on the gas concentration. This is monitored by a digital multimeter connected to the sensor substrate with Au wires. The corresponding resistance and time showed the sensing characteristics in terms of sensitivity, response, and recovery time. The gas sensing behavior of a semiconducting oxide can be attributed to both surface and bulk interactions, depending on grain size or film thickness. If grain size or film thickness is much larger than the Debye length, L of the material, the bulk interactions will dominate the sensor response. On the other hand, if grain size or film thickness is smaller than or in the same order of magnitude as L: surface interactions will

dominate the sensor behavior. The large surface to volume ratio and small size of the ZnO flake sample suggest that analyte gases-ZnO interactions on the surface may play an important role.



**Figure 1.14** Schematic of the sensing mechanism of semiconducting material with the analyte gas exposure [4–5, 49].

Oxygen from the ambient adsorbs on the exposed surface of ZnO and, extracting an electron from the ZnO conduction band, ionizes to  $O^-$  or  $O^{2^-}$ ;  $O^-$  is believed to be dominating [96]:

 $O_{(gas)} + 2e^- \rightarrow 2O_{des}$ 

When metal oxide surfaces are exposed to oxidizing gas such as NO<sub>2</sub>, this gas react with the adsorbed  $O^-$  ions as well as adsorb directly on the surface of metal oxide surface. The oxidizing reactions between metal oxide and the oxidizing gas follow the reaction paths [97–98]:

$$NO_2 (gas) + 2e^- \to NO_2^{2-} (ads)$$
 (1.17)

$$NO_2^{2-} (ads) + O^- (ads) + 2e^- \rightarrow NO (gas) + 2O^{2-} (ads)$$
 (1.18)

And then the metal oxide surface is exposed to reducing gases, the gas reacts with the chemisorbed oxygen thereby releasing electrons back to the conduction band. The overall reducing reactions between NH<sub>3</sub>, H<sub>2</sub>S, CO, SO<sub>2</sub> CH<sub>4</sub>, H<sub>2</sub> and C<sub>2</sub>H<sub>2</sub> gases, and the chemisorbed oxygen species ( $O^-$  and  $O^{2-}$ ) are given by [99–113]:

$$2NH_{3} + 3O^{-} (ads) \rightarrow N_{2} + 3H_{2}O + 3e^{-}$$
(1.19)  

$$2NH_{3} + 3O^{2-} (ads) \rightarrow N_{2} + 3H_{2}O + 6e^{-}$$
(1.20)  

$$H_{2}S + 3O^{-} (ads) \rightarrow H_{2}O + SO_{2} + 3e^{-}$$
(1.21)  

$$H_{2}S + 3O^{2-} (ads) \rightarrow H_{2}O + SO_{2} + 6e^{-}$$
(1.22)  

$$CO + O^{-} (ads) \rightarrow CO_{2} + e^{-}$$
(1.23)  

$$CO + O^{2-} (ads) \rightarrow CO_{2} + 2e^{-}$$
(1.24)  

$$SO_{2} + O^{-} (ads) \rightarrow SO_{3} + e^{-}$$
(1.25)  

$$SO_{2} + O^{2-} (ads) \rightarrow SO_{3} + 2e^{-}$$
(1.26)  

$$CH_{4} + 4O^{-} (ads) \rightarrow 2H_{2}O + CO_{2} + 4e^{-}$$
(1.27)  

$$CH_{4} + 4O^{2-} (ads) \rightarrow 2H_{2}O + CO_{2} + 8e^{-}$$
(1.28)  

$$H_{2} + O^{-} (ads) \rightarrow H_{2}O + e^{-}$$
(1.29)  

$$H_{2} + O^{2-} (ads) \rightarrow H_{2}O + 2e^{-}$$
(1.31)

$$C_2H_2 + O^{2-} (ads) \rightarrow H_2O + 2C + 2e^{-}$$
 (1.32)

The interaction between the reducing gas ethanol and lattice oxygen,  $\mathcal{O}_0^*$  in a metal oxide such as ZnO can be described in general by the following defect reaction (in Kröger-Vink notation) [96]:

$$6O_0^x + C_2 H_5 O H_{(g)} \to 2CO_{2(g)} + 3H_2 O_{(g)} + 6V_0^{"}$$
(1.33)

Similarly, the interactions between reducing gas ethanol and surface-adsorbed oxygen species [96, 114–115] such as superoxide ion  $Q_2^-$  (Equation 1.34) and peroxide ion  $Q_2^-$  (Equation 1.35) can be described as

$$3O_2^- + C_2H_5OH_{(g)} \to 2CO_{2(g)} + 3H_2O_{(g)} + 3e^-$$
(1.34)

$$3O_2^{2-} + C_2H_5OH_{(g)} \to 2CO_{2(g)} + 3H_2O_{(g)} + 6e^-$$
(1.35)

These reactions produce more electrons and thus increase the conductivity of n-type semiconductor (ZnO) upon exposure to ethanol. When ZnO sensor is maintained at equilibrium at the appropriate operating temperature, oxygen in the form of oxide species like  $O^-$ ,  $O^{2-}$ ,  $O_2^-$  localize mobile electrons the n-type semiconducting oxide in air, creating a depletion layer at the surface of the individual particles. The most widely accepted model is based on the modulation of the depletion layer within ZnO due to the chemisorption as illustrated schematically in Figure 1.14. Thereafter, the reaction of reducing gas ethanol with the charged oxygen species

destroys the electron localization process and is observed as a change in conductivity. These interactions corresponded well with the sensing reaction. For example, Figure 1.15 shows ZnO nanowire is surrounded by air, oxygen molecules will adsorb on the nanowire surface to generate chemisorbed oxygen species  $(O^-, O^{2-}, O_2^-)$  by capturing electrons from the conductance band. Thus, the ZnO nanowire will become highly resistive. When the analyte ethanol gas is introduced, the ZnO nanowire is exposed to the traces of reductive gas. By reacting with the oxygen species on the nanowire surface, the reductive gas will reduce the concentration of oxygen species on the nanowire surface and thus increase the electron concentration, as shown in Figure 1.15 (b) [116]. As a result, the ZnO nanowire should become more conductive. The dependence of conductivity on partial pressure of ethanol can be derived from these reactions using mass-action law and charge neutrality relations. It is noted, however, that these reactions are very general and schematic; ethanol molecules may dissociate to other intermediate species before oxidation at ZnO surfaces. However, identification of the intermediates requires some sensitive surface spectroscopic techniques and tremendous effort. Investigation into the detailed sensing mechanisms is still underway and will be reported subsequently.

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(b) ethanol gas [116].

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### **1.8** Literature reviews

### 1.8.1 Literature review of Pt/ZnO particles for gas sensing application

In 1996, effects of structural defects and alloying on the FTIR spectra of CO adsorbed on Pt/ZnO were investigated by Boccuzzi *et al.* [118] showing the curve fitting analysis of the FTIR spectra of two differently pretreated Pt/ZnO. Carbon monoxide adsorbed on a photodeposited 1 at% Pt/ZnO sample mildly reduced in a 0.5% H<sub>2</sub>/N<sub>2</sub> mixture at 493 K showing a main band at 2100 cm<sup>-1</sup>, shifting to the red and reducing its intensity by decreasing the surface coverage. The spectra were well fitted by the addition of five Lorentzian bands. The spectra of CO adsorbed on the same Pt/ZnO sample reduced in pure H<sub>2</sub> at 523 K exhibited a main band at ~2070 cm<sup>-1</sup> at lower frequency, therefore the alloying of Pt with Zn atoms coming from the support occurred. The opposite frequency shift was observed and the change in the shape of the band could be assumed to the chemical effect of the alloying of platinum with zinc.

In 1999, high performances of Pt/ZnO catalysts in selective hydrogenation of crotonaldehyde were reported by Consonni *et al.* [119] at atmospheric pressure and 353 K over 5 wt% Pt/ZnO catalyst. The (Pt(NH<sub>3</sub>)<sub>4</sub>(NO<sub>3</sub>)<sub>2</sub> and H<sub>2</sub>PtCl<sub>6</sub> precursors were designated to as A and B catalysts respectively. The reducibility of the support and the catalysts was followed by temperature programmed reduction (TPR). Catalysts were also analysed by XPS and XRD. A catalyst had the highest activity when reduced at 473 K; a further increase in the reduction temperature led to a decrease in the activity, but at 673 K both catalysts A and B showed nearly the same activity. On the B catalyst, the crotyl alcohol selectivity reached a value as high as 75–80%, at any reduction temperatures. The B catalyst was better dispersed than a catalyst and

formed a Pt/Zn alloy at low reduction temperature (473 K). In contrast, Pt metal particles were only formed on the A catalyst, reduced at 473 K, and then showed low selectivity in crotyl alcohol. However, when the reduction temperature was increased, activity decreased and crotyl alcohol selectivity increased parallel to Pt/Zn alloy formation. One can speculate that Pt sites, when alloyed to Zn, formed Pt<sup>-</sup>-Zn<sup>+</sup> entities, on which the crotonaldehyde adsorbed by the carbonyl group rather than by the C=C double bond. On the B catalyst, the high selectivity observed, at any reduction temperatures, assuming that besides the alloying effect, chlorine had an important promoter effect by increasing the polarity of Zn<sup>+</sup> in the Pt/Zn catalytic sites and facilitating the carbonyl adsorption.

In 2000, sensing characteristics of double layer film of ZnO was reported by Xu *et al.* [7]. The pure ZnO powders were prepared by chemical precipitation. Precipitation was carried out by mixing the solutions of ZnSO<sub>4</sub> and Na<sub>2</sub>CO<sub>3</sub> under the conditions of pH 8–9. ZnO–based gas sensing materials and Al<sub>2</sub>O<sub>3</sub> based catalysts doped with noble metals (Ru, Rh, Pt, Ag) were impregnated in 0.5 wt% doping level. The nanostructures of ZnO were characterized by XRD and TEM. The particle size of polycrystal ZnO was about 0.4  $\mu$ m. The sensitivity of ZnO to C<sub>2</sub>H<sub>5</sub>OH was higher than that to gasoline, H<sub>2</sub> and C<sub>4</sub>H<sub>10</sub>. The 0.5 wt% Pt/ZnO showed the highest sensitivity at 330°C of 23 for 0.01% C<sub>2</sub>H<sub>5</sub>OH. Whereas, the sensitivity was 7 for both 0.01 and 0.2 % for gasoline and C<sub>4</sub>H<sub>10</sub>. 0.2 % of H<sub>2</sub> showed sensitivity of 2.

In 2004, Pt/ZnO catalyst for selective hydrogenation of crotonaldehyde was studied by Ammari *et al.* [120]. The chemical interaction of modifiers in platinum catalysts. It is possible to modulate the hydrogenation selectivity in  $\alpha,\beta$ -unsaturated aldehydes carbonyl bond with regards to olefinic bond hydrogenation. The challenge

was found an emergent catalytic material able to produce 100% unsaturated ethanol. In this case, 1 and 5 wt% Pt/ZnO catalysts were tested in hydrogenation of crotonaldehyde, in gas phase at an atmospheric pressure. The ZnO catalysts were prepared by the impregnation method using H<sub>2</sub>PtCl<sub>6</sub> and Pt(NH<sub>3</sub>)<sub>4</sub>(NO<sub>3</sub>)<sub>2</sub> precursors, followed by calcination at 673 K. The samples were tested after reduction with different temperatures between 473–773 K. The ex-nitrate and ex-chloride catalysts showed quite different catalytic behaviors. The ex-chloride was much more active and selective; in certain conditions 90% crotyl alcohol selectivity was reached. Different techniques such as TPR, XRD, TEM, XPS, FT-IR were used to characterize both types of catalysts and to correlate the structure with the reactivity. The Lewis acidity of ZnO after the reduction treatment and the formation of Pt/Zn alloy were found to be the key factors leading to high crotyl alcohol yield. The 1 wt% Pt/ZnO catalysts were found to be more efficient than the corresponding 5 wt% Pt/ZnO catalyst due to the lower amount of chlorine.

In 2004, sensitivity of Pt/ZnO Schottky diode was characterized to H<sub>2</sub> by Kim *et al.* [121]. The changes in Pt/ZnO Schottky diodes (20 nm Pt) in forward current of 0.3 mA at a forward bias of 0.5 V or alternatively a change of 50 mV bias at a fixed forward current of 8 mA when 5 ppm of H<sub>2</sub> was introduced into a N<sub>2</sub> ambient at 25°C. The rectifying current-voltage (*I-V*) characteristic showed a nonreversible collapse to Ohmic behavior when as little as 50 ppm of was present in the N<sub>2</sub> ambient. At higher temperatures, the recovery was thermally activated with activation energy of 0.25 eV. This suggested that introduction of hydrogen shallowed donors into the ZnO was a contributor to the change in current of the diodes.

In 2005, the detection of CO using bulk ZnO Schottky rectifiers was reported by Kang *et al.* [122]. The bulk ZnO crystals from Cermet, Inc. showed an electron concentration of  $9 \times 10^{16}$  cm<sup>-3</sup> and an electron mobility of 200 cm<sup>2</sup>/Vs at room temperature from van der Pauw measurements. Bulk Pt/ZnO Schottky (20 nm Pt) rectifiers showed gas sensitivities to CO of 4% and 8% at 150°C for 1 and 10% CO in N<sub>2</sub> respectively. The current or voltage changes were time dependent, with an activation energy of 40.7 kJ.mol<sup>-1</sup>. Over a limited range of partial pressures of CO ( $P_{CO}$ ) in the ambient gas, the on–state resistance R of the sensor at fixed bias voltage decreased according to  $R = (R_0 + A(P_{CO})^{0.5})^{-1}$ , where A was a constant and  $R_0$  was the resistance in N<sub>2</sub>. Since these devices were also sensitive to H<sub>2</sub> and C<sub>2</sub>H<sub>4</sub>, the ZnO rectifiers appeared promising for a range of gas–sensing applications.

In 2005, the detection of hydrogen at room temperature with catalyst-coated multiple ZnO nanorods were studied by Wang *et al.* [10]. The comparison of several metal catalyst such as Pt, Pd, Au, Ag, Ti and Ni deposited on multiple ZnO nanorods for their effectiveness in enhancing sensitivity for detecting hydrogen at room temperature. Pt–coated nanorods showed a relative response of up to 8% in room temperature resistance upon exposure to a hydrogen concentration in N<sub>2</sub> of 500 ppm. This was a factor of two larger than that obtained with Pd and more than an order of magnitude larger than that achieved with the remaining metals. The power levels for these sensors were low approximately 0.4 mW for the responses noted above. Pt-coated ZnO nanorods easily detected hydrogen down to 100 ppm, with a relative response of 4% at this concentration after 10 min exposure. The nanorods showed the conductance upon switching back to a pure-air ambient with time constants of the

was a drawback in some applications, but the sensors offered a low-power operation and ppm detection sensitivity.

In 2005, hydrogen sensing at room temperature with Pt-coated ZnO thin films and nanorods were reported by Tien *et al.* [11]. A comparison of the response for detecting hydrogen with Pt-coated single ZnO nanorods and thin films of various thicknesses (20–350 nm). The Pt-coated single nanorods showed a current response of approximately a factor of 3 larger at room temperature upon exposure to 500 ppm H<sub>2</sub> in N<sub>2</sub> than the thin films of ZnO. The power consumption with both types of sensors could be very small (in the nW range) when using discontinuous coatings of Pt. Once the Pt coating became continuous, the current required to operate the sensors increased to the  $\mu$ W range. The optimum ZnO thin film thickness under these conditions was between 40–170 nm, with the hydrogen sensitivity falling off outside this range. The nanorod sensors showed a slower recovery in air after hydrogen exposure than the thin films, but exhibited a faster response to hydrogen, consistent with the notion that the former adsorbed relatively more hydrogen on their surface. Both ZnO thin films and nanorods could not detect oxygen.

In 2006, ZnO nanoparticles were synthesized by the sol-gel method using zinc acetate as a zinc precursor by Rout *et al.* [8]. The nanopowders were further characterized by XRD, SEM and TEM. The particles and gas sensing properties were dissussed. The morphology of particles was observed having a clear rod-like shape with diameter of 35 nm. The film morphology and sensing characteristics of thick films fabricated using the ZnO nanorods, 3 mol% Co doped ZnO, 1 mol% Pt-impregnated ZnO and 1 mol% Pt-impregnated with 3 mol% Co doped ZnO were investigated. Hydrogen sensing performances in terms of the sensitivity of Pt-impregnated ZnO in thick films were dramastically increased to 912 and 1065 at the operating temperature of 32°C and 125°C respectively. ZnO nanoparticles impregnated with Pt and Co showed a high sensitivity for H<sub>2</sub> at relatively low temperatures. Thus, the sensitivity for 1000 ppm of H<sub>2</sub> reached the values of over 1000 and 1500 for Pt impregnated ZnO and 3 mol% Co doped ZnO respectively at 125°C or lower temperatures.

In 2006, the ZnO nanorods, nanowires and nanotubes were prepared by Rout et al. [9]. ZnO nanorods were prepared (designated as nanorods-1) by adding triethanolamine to a fine powder of Zn(CH<sub>3</sub>COO)<sub>2</sub>·2H<sub>2</sub>O. The second procedure (designated as nanorods-2) were prepared by dissolving Zn(CH<sub>3</sub>COO)<sub>2</sub>·2H<sub>2</sub>O in ZnO nanowires prepared by electrochemical deposition in alumina methanol. membranes as well as ZnO nanotubes were investigated for hydrogen and ethanol gas sensing. The ZnO nanostructures were characterized by XRD, SEM and TEM. The average diameters of the nanorods-1 were in the range of 30-40 nm. The sizes of nanowires and nanotubes were ranging from 20-30 nm and 60-100 nm, respectively. The sensing characteristics were also investigated after impregnation with 1 at% Pt. The response of Pt-impregnated nanorods-1 exhibited a slightly increased to 17 and 56 at the operating temperature of 125°C and 200°C respectively. Whereas, the response nanorods-2 increased to 60 at 150°C and 82 at 200°C for 1000 ppm of H<sub>2</sub>. The response was 43 at 150°C for the as-prepared nanowires and reached a value of 825 after Pt-impregnation while the Pt-impregnated ZnO nanotubes showed a response of 500 at 100°C and 740 at 200°C for 1000 ppm of H<sub>2</sub>. The response were 300 and 480 for the as-prepared and Pt-impregnated nanowires respectively at 150°C for 1000 ppm of ethanol. The response were in the range from 2200-2500 and 1200 at

the operating temperature of 200°C and 100°C of Pt-impregnated nanorods-1 respectively for 1000 ppm of ethanol. The nanowires exhibited excellent hydrogen sensing characteristics at relatively low temperatures ( $\leq 150$ °C) especially when impregnated with Pt. One type of nanorods showed a satisfactory dependence of response on the hydrogen concentration, along with short response and recovery times. The nanorods and nanowires impregnated with Pt also showed high response for 1000 ppm of ethanol at below 150°C with short response and recovery times.

In 2006, the nanostructures of 1.5 wt% Pt/ZnO were synthesized and characterized by Nakatou *et al.* [123]. The impedancemetric sensor based on yttriastabilized zirconia (YSZ) could respond to propene ( $C_3H_6$ ) in term of sensitivity under wet condition. The nanostructures of 1.5 wt% Pt/ZnO were characteristics of SEM (back scattering) image of the cross-section. It was the ZnO-SE [sensing-electrode (SE)] layer was rather porous and the Pt particles were dispersed in the ZnO layer. If the SE material and the operating condition were selected properly. Among the various single-oxide SEs examined, ZnO was found to give rather high sensitivity to  $C_3H_6$  as well as negligible sensitivity to  $CH_4$  at 600°C in the presence of 1 vol.% H<sub>2</sub>O. When 1.5 wt% Pt was loaded on ZnO-SE and the SE was polarized at +50 mV versus Pt counter electrode (CE), the present sensor was found to detect  $C_3H_6$  rather sensitively with little interference of other gases, such as CO, NO, NO<sub>2</sub>, H<sub>2</sub>, CH<sub>4</sub>, CO<sub>2</sub>, H<sub>2</sub>O and O<sub>2</sub> at the operating temperature of 600°C. The C<sub>3</sub>H<sub>6</sub> gas sensitivity was independent of the total flow-rate of the sample gas.

In 2007, zirconia-based amperometric sensor using ZnO sensing-electrode for selective detection of propene were investigated by Ueda *et al.* [124]. The sensing characteristics to propene ( $C_3H_6$ ) were examined at the operating temperature of

600°C under wet condition for the amperometric sensor using a yttria-stabilized zirconia (YSZ) tube and ZnO (+8.5 wt% Pt) sensing-electrode (SE). In order to improve the sensitivity to  $C_3H_6$ , the "pulsed-potential method" was adopted. It was found that the current response varied almost linearly with  $C_3H_6$  concentration in the range of 0–200 ppm when SE was polarized at +1.0 V (vs. Pt/air reference electrode) for a period of 0.3 s. By using the "pulsed-potential method", the sensitivity to 100 ppm  $C_3H_6$  was increased about 1000 times, compared with the normal "constant potential method". The excellent selectivity to  $C_3H_6$  was also obtained for the sensor without the influence of other hydrocarbons, NO<sub>x</sub>, CO, H<sub>2</sub>, etc.

A summary comparing  $H_2$  sensing with metal-doped ZnO prepared by several synthetic methods is shown in Table 1.3.

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Sensing materials	Method	Gas concentration	Response	Reference
0.5 wt% Pt 0.5 wt% Ru	Chemical precipitation	0.2 % in air 0.2 % in air	2 at 330°C 6 at 230°C, 2	[7]
0.5 wt% Rh	20	0.2 % in air	at 400°C 115 at 300°C	
0.5 wt% Ag		0.2 % in air	9 at 400°C	
0 at% Pt	ZnO nanowires and ZnO	1000 ppm in air	43 at 150°C	[9]
1 at% Pt	nanotubes by		825 at 150°C	
0 at% Pt	electrochemical		18 at 150°C	~
1 at% Pt	deposition	\$ 12 ×	740 at 150°C	
Pt-coated	ZnO nanorods	500 ppm in N <sub>2</sub>	Relative	[10]
	deposited by		response of up	
	Molecular Beam		to 8 % $H_2$ at	
	Epitaxy		room	
	(MBE)		temperature	
Pt-coated	ZnO nanorods /	500 ppm in N <sub>2</sub>	Response of	[11]
	thin films	Control Co	Pt-coated	
	deposited by		nanorods was	
	Molecular Beam	INTVE	3 times of thin	
	Epitaxy	UNI	films as	
	(MBE)		prepared ZnO	
C				

Table 1.3 A summary comparing  $H_2$  sensing with metal-doped ZnO

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## **1.8.2** Literature review of pure ZnO for NO<sub>2</sub>, SO<sub>2</sub> and ethanol gas sensing application

In 2005, the NO<sub>2</sub> gas sensors based on single-crystalline ZnO nanobelt sensitive layers were developed by Sadek *et al.* [15]. These layers were deposited using a rf magnetron sputterer. TEM and SEM characterization methods were employed to study the morphology of the nanobelts. These sensors were exposed to NO<sub>2</sub> gases at operating temperatures between 225°C and 420°C. Study showed that sensors responded with highest magnitude at above 300°C. The fastest response and recovery times, with greater repeatability occurred at 350°C for NO<sub>2</sub> gases. The sensitivity showed ~1.81 to 10 ppm NO<sub>2</sub> gases at 350°C. Sensor with ZnO nanobelts has a much lower optimum operational temperature than that of conductometric sensors with other forms of ZnO crystal layers.

In 2006, the ZnO nanorods were prepared via a hydrothermal reaction in a solution containing Zn(NO<sub>3</sub>)<sub>2</sub>.6H<sub>2</sub>O, NaOH, cyclohexylamine, ethanol and water, and their NO<sub>2</sub> sensing behaviors were investigated by Cho *et al.* [14]. The morphology and agglomeration of ZnO nanorods could be manipulated by controlling the amount of water in the solution, which was explained by the variation in the [OH<sup>-</sup>] due to an interaction between the water and cyclohexylamine. Sea-urchin-like and well-dispersed ZnO nanorods were prepared at low and high water content, respectively. A well-dispersed ZnO nanorods showed response of 1.8 and change in resistance at 1 ppm NO<sub>2</sub>.

In 2007, thin films of zinc oxide (ZnO) for gas–sensor applications deposited on platinum coated alumina substrate, using electrostatic spray deposition (ESD) technique were studied by Ghimbeu *et al.* [13]. As precursor solution of zinc acetate in ethanol was used. Scanning electron microscopy (SEM) evaluation showed a porous and homogeneous film morphology and the energy dispersive X-ray analysis (EDX) confirmed the composition of the films with no presence of other impurities. The microstructure studied with X-ray diffraction (XRD) and Raman spectroscopy indicated that the ZnO oxide films are crystallized in a hexagonal wurtzite phase. The films showed good sensitivity was ~1.84 to 1 ppm nitrogen dioxide (NO<sub>2</sub>) at  $300^{\circ}$ C.

In 2008, the sensing responses of zinc oxide nanoparticles and nanorods to ethanol vapors were reported by Singh *et al.* [20]. Zinc oxide powder has been synthesized as nanoparticles and nanorods by following a chemical route. The reaction temperature is found to be playing a critical role in the selective synthesis of morphologically distinct nanostructures. Synthesized zinc oxide powder was characterized by using TEM and XRD techniques. Zinc oxide samples were deposited as thick films to act as gas sensors and their comparative response to ethanol vapours was investigated at different temperatures and concentrations. In this work the effect of sintering temperature on the particle size and sensor response was also studied. The studies revealed that particle size increases with the sintering temperature while response decreases. The investigations also revealed that sensing response of ZnO nanoparticles is exceptionally higher than that of ZnO nanorods. The films showed good response was ~6.5 to 250 ppm ethanol at 400°C. Moreover, the films showed response were ~5.6 and 4 to 250 ppm ethanol at 600 and 800°C, respectively.

In 2008, ZnO nanorods, nanobelts, nanowires, and tetrapod nanowires were synthesized via thermal evaporation of Zn powder at temperatures in the range 550–600°C by Hieu *et al.* [23]. Uniform ZnO nanowires with diameter 15–25 nm and

tetrapod nanowires with diameter 30–50 nm were obtained by strictly controlling the evaporation process. The experimental results revealed that the concentration of  $O_2$  in the carrier gas was a key factor to control the morphology of ZnO nanostructures. The sensor response to 500 ppm ethanol was up to about 5.3 at the operating temperature  $300^{\circ}$ C. Both response and recovery times were less than 20 s. The gas–sensing mechanism of the ZnO nanostructures is also discussed and their potential application is indicated accordingly.

In 2009, transferable ZnO tetrapods were grown by an aqueous solution method were presented by Lupan *et al.* [18]. Anindividual ZnO tetrapod-based sensor was fabricated by in situ lift-out technique and its ultraviolet (UV) and gas sensing properties were investigated. This single tetrapod-based device responds to the UV light rapidly and showed a recovery time of about 23 s. The response of a single ZnO tetrapod sensor to oxygen concentration was also investigated. They found that when UV illumination is switched off, the oxygen chemisorption process would dominate and assists photoconductivity relaxation. Thus relaxation dynamics was strongly affected by the ambient  $O_2$  partial pressure as described. They also studied the response of ZnO tetrapod-based sensor in various gas environments, such as 100 ppm H<sub>2</sub>, CO, *i*-butane, CH<sub>4</sub>, CO<sub>2</sub>, and SO<sub>2</sub>. The response 100 ppm SO<sub>2</sub> at room temperature was less than 0.5.

A summary comparing  $NO_2$ ,  $SO_2$  and ethanol sensing with pure ZnO prepared by several synthetic methods is shown in Table 1.4.

Sensing materials	Method	Gas concentration	Response	Reference
Pure ZnO	Hydrothermal	1 ppm of NO <sub>2</sub> , at 300°C	~ 1.8	[14]
Pure ZnO	Electrostatic spray deposition (ESD) technique.	1 ppm of NO <sub>2</sub> , at 300°C	~ 1.84	[13]
Pure ZnO	Conventional solid–state method	10 ppm of NO <sub>2</sub> , at 350°C	~ 1.81	[15]
Pure ZnO	A simple chemical route	250 ppm of ethanol, at 400, 600 and 800°C	~ 6.5, 5.6 and 4	[20]
Pure ZnO	Thermal evaporation	500 ppm of ethanol, at 300°C	5.3	[23]
Pure ZnO	A solution method	100 ppm of SO <sub>2</sub>	< 0.5	[18]

Table 1.4 A summary comparing  $NO_2$ ,  $SO_2$  and  $C_2H_5OH$  sensing with pure

ZnO

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### **1.9** Objectives of the research

- 1.9.1 To study the synthesis of pure ZnO and Pt-doped ZnO nanoparticles by FSP
- 1.9.2 To characterize the flame-made pure ZnO and Pt-doped ZnO nanoparticles particles
- 1.9.3 To study the gas sensing properties of pure and Pt-doped ZnO nanoparticles
- 1.9.4 To study the effect of dopant (Pt) concentrations on gas sensing properties of pure ZnO and Pt-doped ZnO nanoparticles
  - 1.9.5 To study the morphology of nanoparticles and sensing films on their gas sensing properties

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