

CHAPTER 1

INTRODUCTION

1.1 Research overviews

Recently, solid-state gas sensors have played an important role in environment monitoring and chemical process controlling. Among the various solid-state sensors, semiconducting metal oxide sensors have been widely investigated due to their small dimensions and low cost. Many researchers have developed ethanol vapor sensors based on semiconductor metal oxides. In particular, various semiconductor metal oxides commonly used as ethanol gas sensors including pure and metal-doped e.g. SnO_2 [1-12], In_2O_3 [13, 14], TiO_2 [8, 15-20], ZrO_2 [8], WO_3 [7, 19], MoO_3 [19], Cu_2O [21], and ZnO [22-49], especially ZnO is known to be one of the earliest discovered and the most widely applied oxide gas sensing material. Many materials using nanoparticles require non-agglomerated spherical particles. In gas sensors, small-sized particles decrease the response time and increase the gas sensitivity while a low degree of agglomeration facilitates the production of thin or thick film [50].

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 3.30 eV at room temperature [51-54], and with high sensitivity to toxic and combustible gases. It is sensitive to many gases at moderate temperature, especially for ethanol vapor [22-49]. 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 [22, 25,

37], sinter pellet [28, 42-44], heterojunctions [49], thin film [24, 30, 34, 41, 47, 48], and thick films [23, 29, 43, 52, 53], have been demonstrated. In stead of bulk ZnO and ZnO thin films, it was also possible to use one-dimensional (1D) ZnO nanowires for gas sensing. Among them, ZnO nanomaterials with 1D structure, such as nanowires or nanorods, were especially attractive due to their tunable electronic and optoelectronic properties. In the case pf polycrystalline (ceramic or film) devices, only a small amount of the species adsorbed near the grain boundaries was active in modifying the electrical transport properties, which lead to the low maximum sensitivity because of their limited surface-to-volume ratio [33]. The application of nanomaterials to the design of ethanol gas sensor was nowadays 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 [53], and film thickness [52, 55-63] as well as sensing film characteristics.

Flame aerosol synthesis is one of the most promising routes to a range of single and multi-component functional nanoparticles at low cost and high production rate referring to the formation of fine particles from gases in flame [64]. Today, flame technology is employed routinely in large scale manufacture of carbon blacks and metal oxide commodities such as fumed silica and pigmentary titania and, to a lesser extent, for specially chemicals such as zinc oxide and alumina powders. Zinc oxide (ZnO) is the third largest flame-aerosol-made material followed carbon black and

pigmentary titania with global consumption of 600,000 t/y [65]. According to current understanding of flame technology, vapors of the precursor compounds react at high temperature resulting in the product powder, typically in the form of aggregates (clusters of cemented primary particles). The size of the particles ranges from few to several hundred nanometers in diameter depending on material and process conditions [64]. The nanoparticles with high purity and relatively narrow size distribution can be synthesized efficiently in flame aerosol reactor [66]. These reactors are routinely used in industry to make a variety of commodities by combusting halide and hydrocarbon vapors. On the other hand, combustion of sprays is quite attractive as it can utilize a broader spectrum of liquid precursors than conventional vapor flame reactors. Combustion of liquid precursor droplets has been used also in synthesis of mixed oxide powders by the so-called flame spray pyrolysis (FSP) process. The FSP process was systematically investigated using an external-mixing gas-assisted atomizer supported by premixed methane and oxygen flamelets [66-68]. The FSP is capable of producing mixed metal oxide powder in the 1-200 nm size range from low-cost precursors with the production rates up to 250 g/h. In conventional spray pyrolysis, the solution atomized into a hot wall reactor where the aerosol droplets undergo evaporation, drying, thermolysis of the precipitate particles at higher temperature to form a microporous particles, and, eventually the dense particles by sintering. 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 [50]. Using flames as a heat source, one has to further distinguish between FSP processes where the spray forms a self-sustaining flame, made of evaporating and burning droplets from other spray

pyrolysis processes where the supporting fuel is supplied separately from the precursor solution droplets. In the latter the droplets rapidly evaporate so the released precursor can directly react with the oxidant gas provided by the oxy-hydrogen flame. 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 [66].

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 [66, 69]. 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 in air, thus, product particles experience longer residence times at higher temperature [66, 70]. The effect of solution feed rate on particles specific surface area and crystalline size was also investigated [65]. The solution feed rate increased the flame height, and therefore coalescence was enhanced, resulting in large primary particles [65]. Furthermore, the flame conditions can be used to control the morphology of particles. ZnO nanorods formation were produced by FSP, which was described by XRD lattice aspect ratio [71, 72].

Many researchers mentioned a variety of techniques used to prepare the sensing films, i.e. plasma enhanced chemical vapor deposition (PECVD) [34], spray pyrolysis [24, 34], dip-coating [15, 48], and doctor-blade [52, 53, 73, 74].

Particularly, doctor-blade technique has several advantages in producing the sensing thick films suitable for the gas sensor including relatively homogeneous composition, regularities in the film thickness, and easy control of film thickness [52, 53].

Cracking formation phenomenon [52, 53, 63, 75-82], the effect of film thickness [30, 55-63, 75], and the effect of catalysts Pd doping [43, 83-86], as well as the sensing temperature, on the sensor characteristics of sensing films were reported. The sensor characteristics of sensing films were shown to be affected by the film structure, morphology, film thickness, and doping processes. In addition, the sensing temperature, and all cases as in the above are important parameters that affect the gas sensing properties in terms of sensitivity, response, and recovery time. Therefore, it is very significant to investigate the most suitable thickness (5 μm), sensing morphology (crack free), and also Pd doping level for the ethanol sensor based on flame-made ZnO nanoparticles [65, 70, 71].

1.2 Zinc oxide (ZnO)

1.2.1 Background [87, 88]

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^{-1} can be obtained in ceramics that have been cooled sufficiently rapidly after sintering to preserve a high concentration of oxygen vacancies.

1.2.2 Basic properties [89-93]

ZnO is a direct band gap semiconductor with $E_g = 3.37 \text{ eV}$. 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 $\sim 3.0 \text{ eV}$), whereas Mg doping can increase the band gap (to as high as $\sim 4.0 \text{ eV}$). ZnO normally forms in the hexagonal (wurtzite) crystal structure with $a = 3.25 \text{ \AA}$ and $c = 5.12 \text{ \AA}$. 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 lie approximately $0.01\text{-}0.05 \text{ eV}$ 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. A strong room temperature, near-band-edge UV photoluminescence peak at $\sim 3.2 \text{ eV}$ 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 [89]. 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 Properties of wurtzite ZnO [89]

PROPERTIES	VALUES
Lattice parameters at 300 K	
a_0	0.32495 nm
c_0	0.52069 nm
a_0/c_0	1.602 (1.633 for ideal hexagonal structure)
u	0.345
Density	5.606 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 : 6.5×10^{-6} , c_0 : 3.0×10^{-6}
Static dielectric constant	8.656
Refractive index	2.008, 2.029
Energy gap	3.4 eV (direct)
Intrinsic carrier concentration	$< 10^6$ /cm ³
Exciton binding energy	60 meV
Electron effective mass	0.24
Electron hall mobility at 300 K for low n-type conductivity	200 cm ² /V.s
Hole effective mass	0.59
Hole hall mobility at 300 K for low p-type conductivity	5-50 cm ² /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.

1.2.3 Physical properties of ZnO nanostructures [90, 92, 93]

Table 1.1 lists the basic physical properties of bulk ZnO. It is worth noting that as the dimension of the semiconductor materials continuously shrinks down to nanometer or even smaller scale, some of their physical properties undergo changes known as the “quantum size effects”. For example, quantum confinement increases the band gap energy of quasi-one-dimensional (Q1D) ZnO, which has been confirmed by photoluminescence. Bandgap of ZnO nanoparticles also demonstrates such size dependence. X-ray absorption spectroscopy and scanning photoelectron microscopy reveal the enhancement of surface states with the downsizing of ZnO nanorods. In addition, the carrier concentration in Q1D systems can be significantly affected by the surface states, as suggested from nanowire chemical sensing studies. Understanding the fundamental physical properties is crucial to the rational design of functional devices. Investigation of the properties of individual ZnO nanostructures is essential for developing their potential as the building blocks for future nanoscale devices. This section will review the up-to-date research progress on the physical properties of ZnO

nanostructures, including mechanical, piezoelectric, electrical, optical, magnetic and chemical sensing properties.

1.2.3.1 Mechanical properties [93]

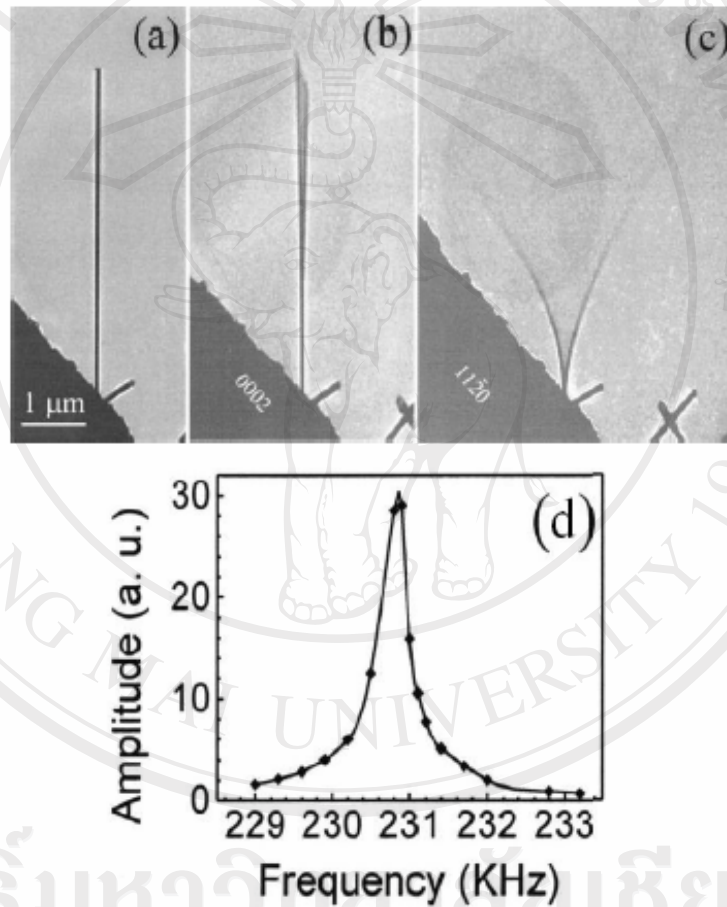


Figure 1.1 TEM images of a ZnO nanobelt at (a) stationary (b) the first harmonic resonance in x (thickness) direction, $x = 622$ KHz, (c) the first harmonic resonance in y (width) direction, $y = 691$ KHz. (d) Resonance peak of a ZnO nanobelt [93].

Direct measurement of the mechanical behavior of individual nanostructures is rather challenging since the traditional measurement method for bulk material does not apply. Based on an electric-field-induced resonant excitation, the bending modulus of ZnO nanobelts was characterized using TEM. In this method, a special TEM sample holder was made to apply an oscillating electric field between a ZnO nanobelt and a fixed electrode. This electric field drove the vibration of the nanobelt, and resonant oscillation was achieved by tuning the driving frequency, as depicted in Figure 1.1. Following the classical elasticity theory, bending modulus was calculated. ZnO nanobelt demonstrates to be a promising material as nanoresonator and nanocantilever. Its small size renders improved sensitivity compared with conventional cantilever fabricated by microtechnology.

1.2.3.2 Piezoelectric effect and polar surfaces [93]

As one of the important properties of ZnO, its piezoelectricity has been extensively studied for various applications in force sensing, acoustic wave resonator, acousto-optic modulator. The origin of the piezoelectricity lies in its crystal structure, in which the oxygen atoms and zinc atoms are tetrahedrally bonded. In such a non-centrosymmetric structure, the center of positive charge and negative charge can be displaced due to external pressure induced lattice distortion. This displacement results in local dipole moments, thus a macroscopic dipole moments appears over the whole crystal. In fact, among the tetrahedrally bonded semiconductors, ZnO has the highest piezoelectric tensile which provides a large electro-mechanical coupling. The piezoelectric property of ZnO nanostructures was also investigated for their potential applications in nano-electromechanical systems.

1.2.3.3 Electrical properties [93]

The fundamental study of the electrical properties of ZnO nanostructures is crucial for developing their future applications in nanoelectronics. Electrical transport measurements have been performed on individual ZnO nanowires and nanorods. Single ZnO nanowire was configured as field effect transistor (FET) following several procedures. They were first dispersed in isopropanol alcohol to form nanowire suspension, and then deposited onto a SiO₂/Si substrate. Photolithography was utilized to define contact electrode array and degenerately doped Si substrate functioned as a back gate electrode. Furthermore, the electrical properties of ZnO nanowire FETs were studied using conductive AFM, the local electrical potential were mapped and the uniformity of nanowire electrical property was demonstrated.

The CVD grown ZnO nanostructures are single crystalline, rendering them superior electrical property than polycrystalline thin film. For example, an electron field effect mobility of 7 cm²/V·s is regarded quite high for ZnO thin film transistors. However, single crystalline ZnO nanowires show mobility as high as 80 cm²/V·s. These results indicate that the ZnO nanostructure based device can achieve a faster operation speed than their thin film counterpart. Furthermore, using a uniquely designed synthesis setup, one can tune the carrier concentration and mobility of the nanowires (Figure 1.4 (c)), providing a way to modify the electrical property.

The major impediment of ZnO for wide-ranging applications in electronics and photonics rests with the difficulty of *p*-type doping. Several *p*-type doping efforts have been reported, with a Ga and N codoping method, low resistivity (0.5 Ω·cm) *p*-type ZnO thin film was obtained.

1.2.3.4 Optical properties [93]

Intrinsic optical properties of ZnO nanostructures are being intensively studied for implementing photonic devices. Photoluminescence (PL) spectra of ZnO nanostructures have been extensively reported. Excitonic emissions have been observed from the photoluminescence spectra of ZnO nanorods. It is shown that quantum size confinement can significantly enhance the exciton binding energy. Strong emission peak at 380 nm due to band-to-band transition and green-yellow emission band related to oxygen vacancy are observed. These results are consistent with those of bulk ZnO. Interestingly, the green emission intensity increases with decreasing nanowires diameter. This observation is attributed to the larger surface-to-volume ratio of thinner nanowires favoring a higher level of defects and surface recombination. Recently, red luminescence band was reported, which was attributed to doubly ionized oxygen vacancies. The well-faceted nanowires also form promising optical resonance cavities which greatly facilitate highly directional lasing at room temperature in well aligned ZnO nanowires. Moreover, a room temperature UV lasing from ordered ZnO nanowires array was reported. Lasing power threshold of $40 \text{ kW/cm}^2 \sim 100 \text{ kW/cm}^2$ was reported and it was suggested that higher crystal quality confers lower threshold. The additional advantages of ZnO nanowire lasers are that the excitonic recombination lowers the threshold of lasing, and quantum confinement yields a substantial density of states at the band edges and enhances radiative efficiency. Optical waveguiding using dielectric nanowire also achieved considerable progress. Recently, ZnO nanowires were reported as sub-wavelength optical waveguide.

1.2.3.5 Magnetic doping [93]

Dilute magnetic semiconductors (DMS) are attracting increasing research interests because spin-polarized DMS can accomplish efficient spin injection as well as overcome the conductance mismatch associated with semiconductor devices. It has been found that ZnO is a promising host material for ferromagnetic doping. Room temperature hole mediated ferromagnetic ordering in ZnO by introducing manganese (Mn) as dopant has been predicted theoretically and reported experimentally in ZnO thin film. Ferromagnetism in ZnO was also observed when Co and Fe were used as dopants. The nanowires were synthesized via a vapor phase evaporation method. Because of its wide band gap, ferromagnetic ZnO is regarded as an excellent material for short wavelength magneto-optical devices. These studies enable the use of magnetic ZnO nanowires as nanoscale spin-based devices.

1.2.3.6 Chemical sensing [93]

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 NO₂ and O₂, 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 H₂, 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, NH₃, alcohol, and H₂ sensing under elevated temperature (~400°C). From the aspect of sensing

performance, 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 FETs 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 O₂ 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 NO₂ and NH₃ 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 H₂ into the crystal interstitial sites.

1.2.4 Crystal structure [87, 90, 94]

1.2.4.1 The hexagonal close-packed crystal structure [94]

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.

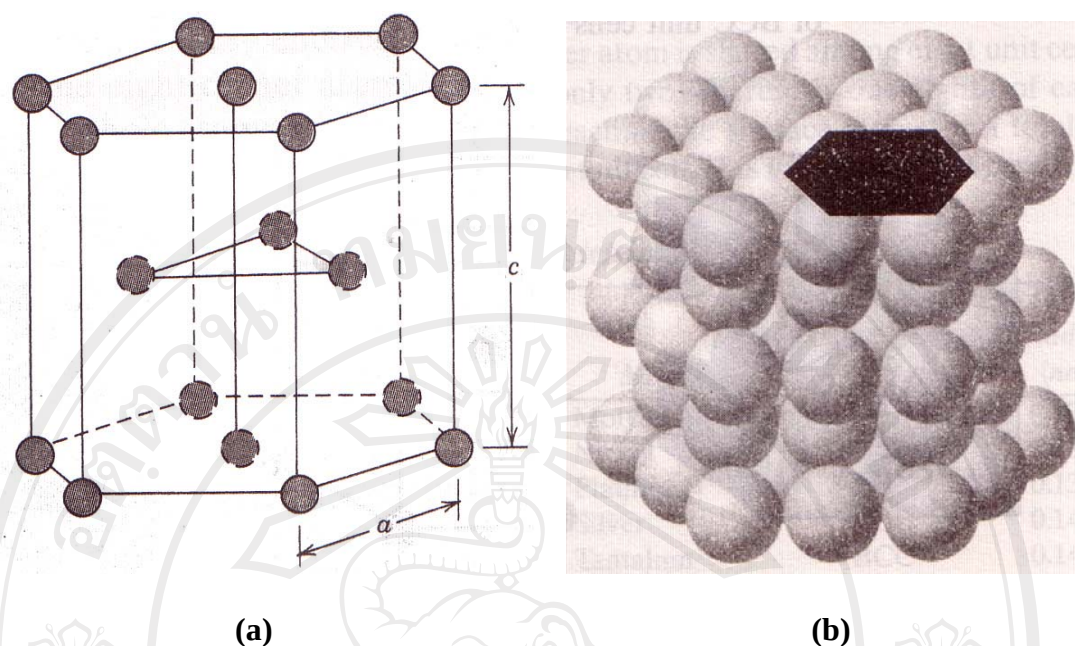


Figure 1.2 For the hexagonal close-packed crystal structure, (a) a reduced-sphere unit cell (a and c represent the short and long edge lengths, respectively), and (b) an aggregate of many atoms [94]

1.2.4.2 Wurtzite structure [87]

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. We earlier showed that there are two orientations of tetrahedral sites between close-packed 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 1.3, 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 we can be satisfied that 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, like zincblende, is the preferred structure of a number of covalent compounds, including AlN and the α phases of SiC.

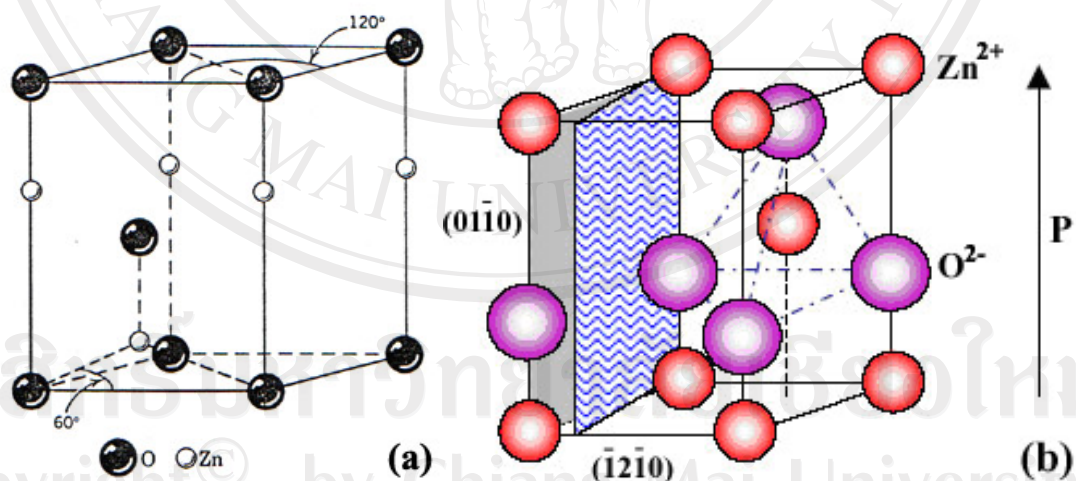


Figure 1.3 (a) Unit cell of the wurtzite structure [87], and (b) the ZnO

wurtzite structure model. The tetrahedral coordination of Zn-O is shown [90].

Wurtzite ZnO has a hexagonal structure (space group $C6mc$) with lattice parameters $a = 0.3296$ and $c = 0.52065$ nm. The structure of ZnO can be simply described as a number of alternating planes composed of tetrahedrally coordinated O^{2-} and Zn^{2+} ions, attacked alternately along the c -axis (Figure 1.3 (b)). The tetrahedral coordination in ZnO results in noncentral symmetric structure and consequently piezoelectricity and pyroelectricity. Another important characteristic of ZnO is polar surfaces. The most common polar surface is the basal plane. The oppositely charged ions produce positively charged Zn-(0001) and negatively charged O-(000 $\bar{1}$) surfaces, resulting in a normal dipole moment and spontaneous polarization along the c -axis as well as a divergence in surface energy. To maintain a stable structure, the polar surfaces generally have facets or exhibit massive surface reconstructions, but ZnO $\pm(0001)$ are exceptions: they are atomically flat, stable and without reconstruction [90]. Efforts to understand the superior stability of the ZnO $\pm(0001)$ polar surfaces are at the forefront of research in today's surface physics [90]. The other two most commonly observed facets for ZnO are $\{2\bar{1}\bar{1}0\}$ and $\{01\bar{1}0\}$, which are non-polar surfaces and have lower energy than the $\{0001\}$ facets.

1.2.5 Typical growth structures of ZnO [90]

Structurally, ZnO has three types of fast growth directions: $\langle 2\bar{1}\bar{1}0 \rangle$ ($\pm[2\bar{1}\bar{1}0]$, $\pm[\bar{1}2\bar{1}0]$, $\pm[\bar{1}\bar{1}20]$); $\langle 01\bar{1}0 \rangle$ ($\pm[01\bar{1}0]$, $\pm[10\bar{1}0]$, $\pm[1\bar{1}00]$); and $\pm[0001]$. Together with the polar surfaces due to atomic terminations, ZnO exhibits a wide range of novel structures that can be grown by turning the growth rates along these directions. One of the most profound factors determining the morphology involves the relative surface activities of various growth facets under given conditions. Macroscopically, a crystal

has different kinetic parameters for different crystal planes, which are emphasized under controlled growth conditions. Thus, after an initial period of nucleation and incubation, a crystalline will commonly develop into a three-dimensional object with well-defined, low index crystallographic faces. Figure 1.4 (b), (c) show a few typical growth morphologies of 1D nanostructures for ZnO. These structures tend to maximize the areas of the $\{2\bar{1}10\}$ and $\{01\bar{1}0\}$ facets because of the lower energy. The morphology shown in Figure 1.4 (d) is dominated by the polar surfaces, which can be grown by introducing planar defects parallel to the polar surface. Planar defects and twins are observed occasionally parallel to the (0001) plane, but dislocations are rarely seen.

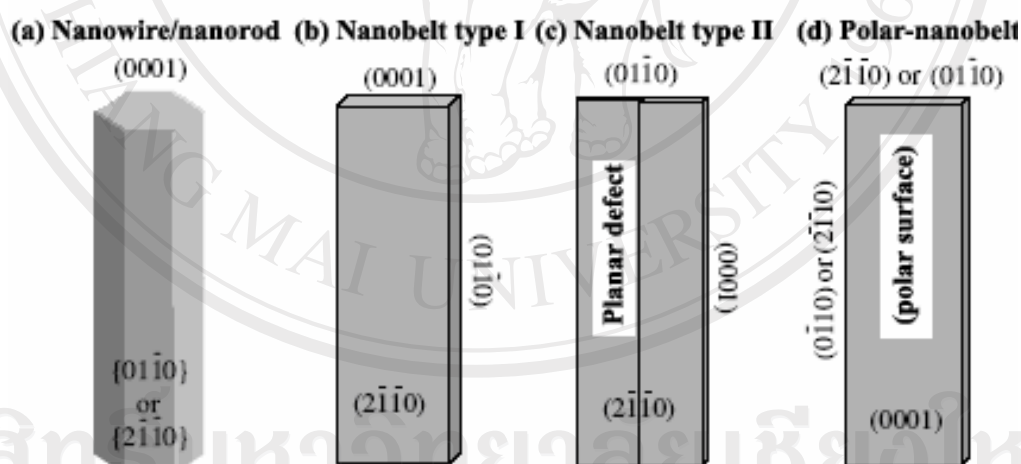


Figure 1.4 Typical growth morphologies of one-dimensional ZnO nanostructures and the corresponding facets [90]

1.3 Palladium (Pd) [95, 96]

Palladium-named after the asteroid Pallas, discovered in 1803; Gr. Pallas, goddess of wisdom), Pd has the molecular weight of 106.42, atomic number of 46, melting point of 1554.9°C, boiling point of 2963°C, specific density of 12.02 g/cm³ (at 20°C), the valence of 2, 3, or 4. Palladium is found along with platinum and other metals of the platinum group in deposits of Russia, South Africa, Canada (Ontario), and elsewhere. Natural palladium contains six stable isotopes. Twenty-nine other isotopes are recognized, all of which are radioactive. Its separation from the platinum metals depends upon the type of ore in which it is found. It is steel-white metal, does not tarnish in air, and is the least dense and lowest melting of the platinum group of metals. When annealed, it is soft and ductile; cold working greatly increases its strength and hardness. Palladium is attacked by nitric and sulfuric acid. At room temperatures the metal has the unusual properties of absorbing up to 900 times its own volume of hydrogen, possibly forming Pd₂H. It is not yet clear if this true compound. Hydrogen readily diffuses through heated palladium and this provides a means of purifying the gas. Finely divided palladium is a good catalyst and is used for hydrogenation and dehydrogenation reactions [95].

1.3.1 Physical and chemical properties [96]

Palladium is gray-white, lustrous metals which are sufficiently ductile and malleable to be drawn in to wire, rolled into sheet or formed by spinning and stamping. It has high melting-point and considerable resistance to corrosion. Their main physical properties are summarized in Table 1.2 which gives the currently acceptable values, some of which are critically dependent on purity.

Table 1.2 The physical properties of palladium [96]

PROPERTIES	VALUES
Atomic number	46
Atomic weight (relative to ^{12}C = 12)	106.4
Density (g/cc at 20°C)	12.02
Crystal lattice	Face-centered cubic
Lattice cell (Å)	3.8825
Atomic radius (Å)	1.375
Allotropic forms	None known
Melting point (°C)	1554
Boiling point (°C, estimated)	3980
Thermal conductivity (cal/cm/cm ² /sec/°C)	0.17
Linear thermal coefficient of expansion at 0°C (per°C)	11.67×10^{-6}
Specific heat at 0°C (cal/g/°C)	0.0584
Electrical resistivity at 20°C (micro ohm-cm)	10.8
Hardness (annealed-Brinell Hardness number)	446
Tensile strength (annealed-ton/in ²)	13.8
Young's modulus (annealed-ton/in ²)	$(8-8.8) \times 10^3$

Palladium is noble metals owing to a combination of high sublimation energy and high ionization potential. In powder form palladium is slowly dissolved by hydrochloric acid in the presence of oxygen. Palladium is oxidized to palladium (II) oxide in air at 700°C. Above 875°C the oxide dissociates to the free metal and oxygen. Palladium is attacked by moist chlorine and bromine at room temperature.

1.4 Flame Spray Pyrolysis (FSP) [64-70, 97-101]

Flame aerosol technology is the key process for large-scale production of nano-structured materials such as carbon blacks, fumed SiO₂ and TiO₂ and to a lesser extent, for specialty chemicals such as Al₂O₃ and ZnO powders. Flame aerosol synthesis is a cost-effective and versatile process for controlled production of

nanoparticles [64-66]. Flame spray pyrolysis (FSP) process was systematically investigated using an external-mixing gas-assisted atomizer supported by premixed methane and oxygen flamelets [67, 68]. 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 [99]. The advantage 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 [67, 68]. The more fuel introduced the higher the flame is and due to that the residence time of particles in the flame is increased. As a consequence time for particle growth is enlarged 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 used in application as control devices [100, 101]. The basic steps of particle formation and growth by gas-to-particle conversion in flame spray pyrolysis were shown in Figure 1.5.

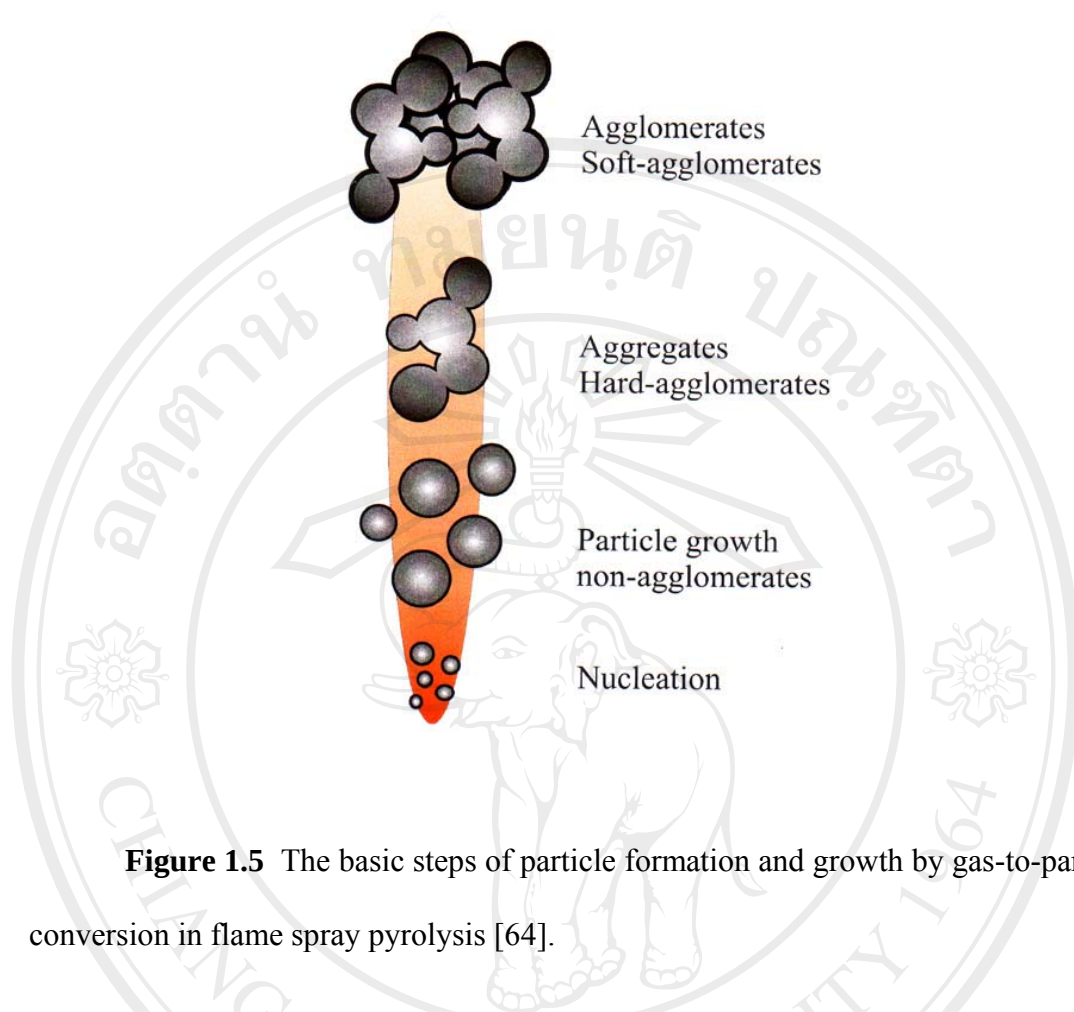


Figure 1.5 The basic steps of particle formation and growth by gas-to-particle conversion in flame spray pyrolysis [64].

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 [66-70]. The effect of solution feed rate on particles specific surface area and crystalline size was also investigated [65]. The solution feed rate increased the flame height, and therefore coalescence was enhanced, resulting in large primary particles [65]. Furthermore, the flame conditions can be used to control the morphology of particles. The more details will be discussed in the literature reviews part.

1.4.1 Effects of flame factors [64, 69, 102]

In flame reactors the energy of a flame is used to drive chemical reactions of precursor compounds that result in the formation of product molecules, which then nucleate to form particles following the mechanism described earlier [69]. High flame temperatures of 1200 to 3000K constitute a self-purifying environment for particle synthesis resulting in high-purity powders as for manufacture of optical fiber preforms [69]. Even though non-oxide ceramic powders like silicon nitride [64] and tungsten carbide [64] have been synthesized in flame reactors, the production of carbon and metal oxide nanoparticles dominates the field. One distinguishes two types of flame reactor: diffusion and premixed. While premixed flames have the advantage of more uniform radial temperature profiles, diffusion flames are safer to operate (no flashback) and offer flexibility in product quality by controlling the reactant gas composition over broad ranges. Turbulent co-flow diffusion flame reactors are used in industry for large-scale manufacture of ceramic powders. Counterflow diffusion flame reactors, on the other hand, are often used in laboratory studies. The flow along the axial stagnation streamline of a counterflow diffusion flame can be approximated as one-dimensional, facilitating the use of optically-based diagnostics for non-intrusive study of nanoparticle formation [102].

A typical laboratory set-up of a diffusion flame aerosol reactor is depicted in Figure 1.6. The co-flow reactor is made of three concentric stainless steel tubes of about 120 mm length. The inner diameter of the center tube is 5 mm, while the o.d. of the outer tube is 18 mm and the width of the two annular ports is about 1.5 mm. Oxygen is delivered through the outer tube while methane flows through the center port. High purity argon loaded with the precursor vapor is added to the fuel and

oxidant streams to prevent deposition of particles on the burner mouth. An evaporator or a bubbler can be used to load the inert gas stream with the precursor. When a bubbler is used, controlled amounts of precursor can be delivered into the reactor by adjusting the temperature of the liquid compound with the help of a thermostated bath. Evaporators offer the advantage of precise precursor dosing, easier handling of moisture-sensitive chemicals and the evaporation of mixtures.

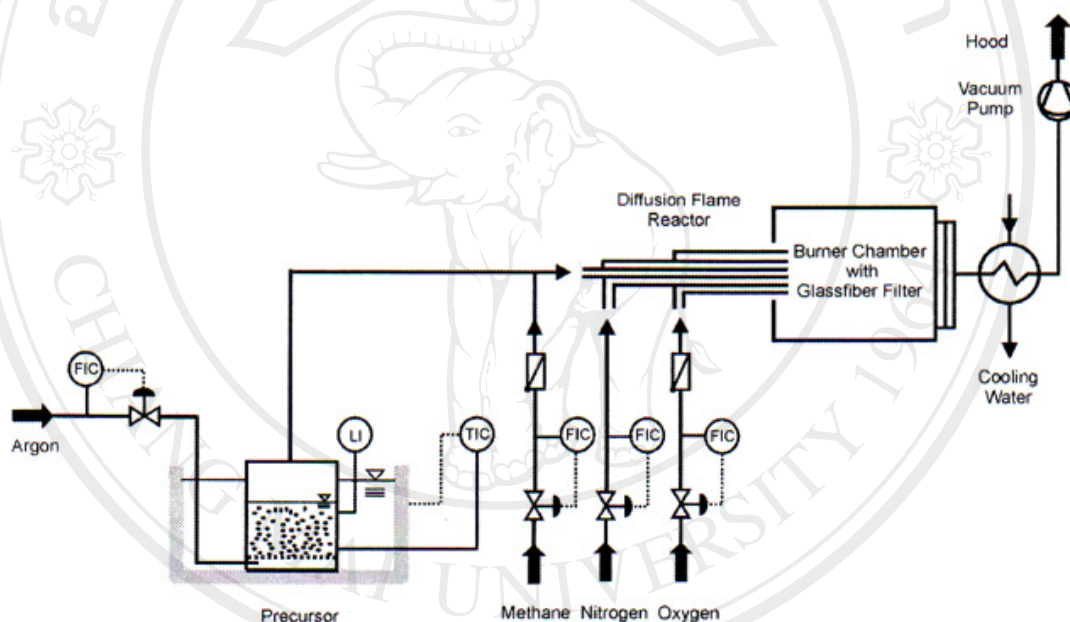


Figure 1.6 Diffusion flame reactor set-up for nanoparticle synthesis [102]

Industrial processes usually operate with halide precursor. In laboratory units organometallic compounds are preferred to circumvent HCl and chlorine removal from the off-gas and to avoid post-cleaning of the powders. In order to prevent condensation of precursor vapor, the precursor delivery tubes and the reactor are heated above the temperature of the evaporator or bubbler. Product particles are

collected on a filter with the aid of a vacuum pump. The flame is surrounded by a quartz glass cylinder in order to achieve stable burning. The outer tube of the reactor can be surrounded by a sheath of nitrogen for flame stabilization.

In diffusion flames, the maximum flame temperature usually occurs at the tip of the cone-shaped flame front, where agglomerates fuse [69]. Upon leaving the flame, the temperature drops quickly and particles continue to coagulate while sintering takes place at much lower rates. In many systems the characteristic time for coalescence is longer or in the same order as the characteristic time for coagulation resulting in agglomerates consisting of a few up to many thousands of primary particles [69, 102]. The characteristics of the product particle such as morphology, crystallinity, and size strongly depend on the precursor concentration, temperature profile and residence time distribution in the flame.

1.4.1.1 Nanoparticles by combustion of gases [69]

Nanoparticles are made from gases by the so-called gas-to-particle conversion in flame reactors, hot-wall or furnace reactors, vapor-phase evaporation-condensation processes, plasma furnace reactors, laser and sputtering reactors, to name a few. The advantages of the gas phase processes are the production of particles of high purity composed of nonporous primary particles with small sizes, and relatively narrow size distribution. Disadvantages include difficulties in producing unagglomerated particles and multicomponent materials. For examples, flame reactors are used in the industrial production of pigments (TiO_2) and reinforcing agents (carbon black and SiO_2). For example, the white pigment market has a world wide annual volume of about 3 Mio.t. Half of it is made by flame technology, the so-called “chloride” process. In the USA

and other developed countries most of the TiO_2 is used for paints (almost 50 %), in paper (25 %) and in the fabrication of plastics (20 %). The last 5 % is used as a pigment (inks, floor coverings, elastomers, roof granules, fibers, fabrics, sealants, foods, to name a few applications) and also has non-pigmentary uses (ceramics, welding rods, catalyst support, etc.) and other applications in specialty products. Rutile TiO_2 particles are preferred in coatings and paints as they contribute a unique light scattering performance. For this, particles with a narrow size distribution around 200 nm and coated with a layer of SiO_2 are desirable.

Silica is used to control thickening, thixotropy, and reinforcement, as well as a stabilizer for suspensions, free flowing, or as a chemical mechanical polishing (CMP) agent. Carbon blacks, however, are the most important fillers in rubber industries. Special properties like UV protection, electrical conductance, and range of darkness, opacity and reinforcement can be achieved by adding carbon black particles to elastomers, plastic and paint.

1.4.1.1.1 Control of flame aerosol reactors [69]

A typical flame aerosol reactor set-up consists of a precursor unit (bubbler or evaporator), a burner accompanied by a gas delivery system and filter unit to collect the product particles. Various flame configurations are used for the manufacture of nanoparticles, such as premixed and diffusion flames run in co-flow, or counterflow. In the diffusion flame configuration the fuel and the oxidizer diffuse into each other determining flame reaction and particle formation, while in premixed flames the precursor and the combustible gases are mixed before they enter the reaction zone (flame). A typical oxide particle producing premixed flame is shown in Figure 1.7.

In this oxygen-rich hexamethyldisiloxane (HMDSO)/ methane/oxygen flame, the luminescence of the flame, Figure 1.7 (a), is quite different to the trail of particle formation and growth as visualized with a laser sheet, Figure 1.7 (b).

Depending on the gas flow rates and burner geometry, flames are either laminar or turbulent. In industry turbulent co-flow reactors are usually used, since large quantities of particles are desired. In academia, laminar flames are preferred as experiments are easier to describe with models in the laminar flow regime than in the turbulent one. Nevertheless, understanding of particle formation in turbulent flames is essential for optimal industrial aerosol reactor design.

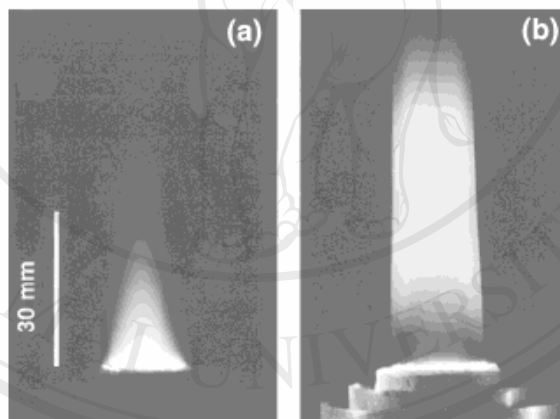


Figure 1.7 Premixed hexamethyldisiloxane (HMDSO)/methane/oxygen flat flame: (a) in the absence and (b) in the presence of a laser sheet [69].

1.4.1.1.2 Effect of reactant mixing [69]

Flame temperature and particle residence time have been shown to be the most important parameters determining the characteristics of the product powder. In flame aerosol reactors the flame temperature field is influenced mostly by the initial

reactants and their mixing, and also by the burner geometry. Typical fuels are hydrogen, methane, or ethylene while oxidants are usually air or oxygen. Sometimes these gases are diluted with inert gases such as argon, helium, or nitrogen.

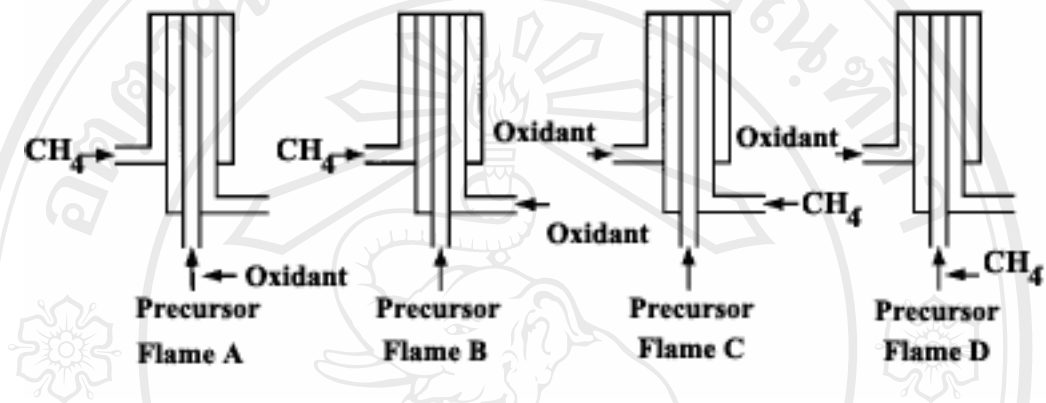


Figure 1.8 Reactant mixing configurations for a double or inverted (Flame A and B) and single or classic (Flame C and D) diffusion flame reactor [69]

Reactant mixing, Figure 1.8, can affect the product particle size by one order of magnitude. Titania particles produced in a double (inverted) diffusion flame (primary particle diameter ~ 10 nm) (Flame A) were up to 10 times smaller than particles produced in a single (classic) diffusion flame (Flame D), where even non-agglomerated particles of a diameter of about 100 nm were made as proven by small angle X-ray scattering. The inverted diffusion flame always produced finer particles (SiO_2 , SnO_2 , TiO_2 , Al_2O_3) than the classic diffusion flame due to lower temperatures in the former flames.

Operating a diffusion flame reactor with oxygen instead of air, an increased the size of silica product particles by about 5 times in a single SiCl_4 /methane diffusion

flame (Flame C). In inverted diffusion flames (Flame B) this difference was less pronounced, as only 50% larger particles were formed with oxygen when compared to air as the oxidant. Using oxygen leads to faster fuel consumption, and therefore to higher flame temperatures and to shorter flames, thus, the precursor oxidation as well as growth and sintering is enhanced. In a similar set-up, it was found a similar increase of the primary product particle size investigating different silica precursors (SiCl_4 , hexamethyldisiloxane (HMDSO), and octamethylcyclotetrasiloxane (OMCTS)), when they replaced air by oxygen.

For SnO_2 particles from SnCl_4 the choice of oxidant (air or oxygen) did not affect the average primary particle size, even though the primary particle size could be closely controlled by the oxidant flow rate as for SiO_2 . For the same flow rates, however, only the flame configuration and therefore reactant mixing affected the SnO_2 product particles. It could be seen that particles produced in an inverted diffusion flame (Flame B) were 1.8-2.4 times smaller than the ones made in a single diffusion flame (Flame C). For Al_2O_3 particles made from aluminium-tri-sec-butoxide, it was observed as particles with 1.2-1.4 times larger specific surface areas in the inverted diffusion flame (Flame B) set-up compared to particles made in a single diffusion flame (Flame C).

For titania the oxidant did not affect the size of the average primary particle in inverted diffusion flames (Flame A, B), while significantly larger TiO_2 particles (2-3 times) were formed in single diffusion flames (Flame C) substituting air by oxygen. In a classic diffusion flame (Flame C) the rutile content was progressively retarded from 13.2 to < 0.1 wt% by increasing the oxygen concentration of the oxidant from 21 % (air) to 100 % (pure oxygen). However, in an inverted diffusion flame (Flame B) the

rutile content remained constant (about 8 wt%) for all the oxidant compositions investigated. At these conditions an increasing number of perfectly spherical unagglomerated particles (200-300 nm) were made by increasing the oxygen concentration of the classic diffusion flame (Flame C).

It was showed that reactor geometry could also significantly change product powder characteristics. Using the same gas and precursor flow rates, they produced primary silica particles which were 4 times smaller using HMDSO in a reactor with a diameter about a quarter of the one. The enhanced mixing of the gases in the smaller reactor leads to a steeper temperature gradient as confirmed by CFD calculations. Furthermore, the burner outlet velocities are significantly higher, which reduces the residence times of the particles in the hot flame zone and consequently there is less time for growth and sintering.

1.4.1.1.3 Effect of precursor [69]

The choice of precursor becomes important when a considerable amount of heat is provided by the combustion of the precursor itself. This becomes more pronounced for higher precursor concentrations. For example, silica particles made from organosilicon compounds had significantly lower specific surface area than those produced from SiCl_4 for all investigated oxidant flow rates in diffusion and premixed aerosol flame reactors. In premixed flames, it was correlated the specific surface area of the product with the adiabatic flame temperature, which is determined by the choice of precursor.

Besides altering the flame structure, the amount of precursor introduced into the flame determines the collision frequency of the particles during the growth

process. It was found that the specific surface area of the titania particles was halved by increasing the inlet TiCl_4 concentration by a factor of 10 for inverted diffusion flames (Flame B). Similarly, the specific surface area was decreased by 1.4-1.6 times in single diffusion flames (Flame C). However, it was observed that the flame temperature is more important than SiO_2 concentration for the particle specific surface area. For silica production in pure HMDSO/oxygen double diffusion flames, it was found that the specific surface area of silica product powders decreased from 175 to 22 m^2/g quadrupling the HMDSO concentration. As HMDSO was the only fuel in these experiments, increasing the HMDSO concentration increased the energy content of the flame, thus, the flame temperature and SiO_2 concentration were increased. At higher flame temperatures the growth and sintering rates are enhanced and increasing the SiO_2 concentration increased the collision frequency of the particles. Additionally, the flame height increased as more fuel was introduced, increasing the residence time of the particles in the flame, and therefore prolonging the time for growth and sintering, resulting in the observed low product specific surface areas.

1.4.1.1.4 Effect of additives [69]

Additives can be used to control the primary particle size or crystallinity and the extent of agglomeration when the purity of the product powder is not a primary concern. For example, small amounts of AlCl_3 are injected to promote the formation of rutile titania and to moderate aggregation in its manufacture from the chloride process. In this study, the effect of additives on phase composition, morphology and size of titania product particles in laminar diffusion flames doping the TiCl_4 stream with various amounts of SiCl_4 , SnCl_4 , and AlCl_3 , respectively. They found that doping

the titania with silica inhibits the titania phase transformation from anatase to rutile, and decreases the primary particle size, thus, increases the specific surface area. In the flame reactor significantly larger amounts of silica had to be added to completely inhibit the phase transformation from anatase to rutile compared to particles made in electrically heated hot-wall reactors as the temperature and residence times of the particles are less homogeneous in flame aerosol reactors. Furthermore, the addition of SnCl_4 , and AlCl_3 promoted the anatase to rutile phase transformation and increased the average primary particle diameter. For example, the addition of 20 mol% AlCl_3 reduced the specific surface area of the product powder from 54 to 35 m^2/g . However, more dopant had to be added to the flame reactor in order to achieve identical product powder crystallinity compared with powders made in the hot wall reactor. In silica synthesis, it can be observed that adding ferrocene to SiCl_4 in methane/air diffusion flames led to an increase in the specific surface area of the silica product powder of up to 150 %. Additives are widely used in the carbon black industry to control the morphology of the product even though their exact mechanism is not well understood.

1.4.1.1.5 Effect of external electric fields [69]

For precise control of the product powder characteristics, external electric fields have been shown to be quite effective and are intriguing as they can be readily implemented into the reactor set-up. The newly formed particles are charged in the electric field either by ion or electron attachment, so the coagulation rate of the particles is reduced, as unipolarly charged particles repel each other. Charged particles are also attracted towards electrodes, thus lowering the local particle concentration and therefore the collision rate. The flame structure, height, and

temperature are also altered by the electric field, which can significantly influence the particle residence time at high temperatures and therefore affect particle growth and sintering. It was shown, that external electric fields can reduce the average particle size by up to a factor of two as determined by nitrogen adsorption.

1.4.1.1.6 Monitoring particle growth in atmospheric flames [69]

The growth of particles is mostly determined by the flame temperature and particle residence time. Therefore, it is of great importance to have accurate temperature profiles in flame aerosol reactors. In principle, conventional laser diagnostic methods are limited for application in particle laden flames, as interferences of the response signal with particulate matter may weaken signal intensity and increase the complexity of signal evaluation. Recently, however, laser-induced fluorescence (LIF), that has been used in gas phase combustion, was successfully used in dilute particle laden low pressure flames to measure flame temperature and to detect local concentrations of SiO, FeO, AlO and TiO.

1.4.1.2 Nanoparticles by combustion of liquid droplets [69]

In flame spray pyrolysis (FSP), sometimes called liquid flame spray (LFS), the heat is provided by the combustion of a gaseous or liquid fuel and the precursor itself. Multicomponent oxide powders and superconductors have been both made by pyrolysis of solutions containing inorganic precursors in oxy-hydrogen flames. Fully dense primary particles in the size range of 100-500 nm were produced which may have resulted from the rapid disintegration of solution droplets when they enter the

high-energy flame [69]. Using organic solvents as liquid fuel, leads to a self-sustaining spray flame. This process has the potential to produce composite mixed-metal oxide powders in the size range of 1 to 200 nm from low cost precursors with production rates up to 250 g/h, as was summarized recently by Pratsinis [64]. Typical products synthesized are titania and MgAl_2O_4 , $\gamma\text{-Fe}_2\text{O}_3$, alumina, manganese oxide, zirconia, and zirconia-ceria particles, or very specific functional particles such as β -alumina for high temperature solid electrolytes, to name a few. These processes clearly differ from the conventional spray pyrolysis [64] as the precursor is released from the droplet environment undergoing gas phase reaction and subsequent particle growth by coagulation, surface growth and sintering. Here, direct parallels can be drawn with vapor flame synthesis.

1.4.1.2.1 Flame spray reactors [64, 69]

A typical set-up for nanoparticle synthesis by flame spray pyrolysis consists of a unit for the generation and dispersion of droplets, a heat source for initial droplet evaporation and ignition (pilot flame or the spray flame itself for combustible liquids), and an oxidant to facilitate combustion. These parameters control the temperature profile and gas phase reaction of the precursor followed by subsequent particle growth and sintering, taking place within and after the spray flame. The product powder is collected by filtration or thermophoresis. The production of micron-sized liquid droplets can be achieved using various atomizers [64, 69], whereas ultrasonic and gas assist pressurized atomizers are most common in spray combustion. Ultrasonic atomizers show good performance with regard to droplet size and homogeneity [69] and the droplets can be embedded in any gaseous flow for transportation into the

reaction zone, where the droplet velocity can be controlled independently. Gas assist pressurized atomizers, however, are easy to incorporate into the spray flame apparatus and their operation is simple and reliable. High shear rates are needed to disintegrate the liquid jet, thus, high gas velocities are inevitable leading to the high quenching ability of such reactors resulting in small product particles [69].

1.4.1.2.2 Effect of spray composition [68-70]

1.4.1.2.2.1 Precursor liquid composition [68-70]

The precursor composition is a key parameter in flame spray pyrolysis (FSP) in order to achieve the preferred product properties. The choice of precursor depends on cost, reactivity, selectivity (e.g. suppression of carbide formation during the production of BaTiO_3), stability before processing, and low toxicity. In wet chemical processing of metal oxides and mixed metal oxides, nitrate precursors are often used. Spraying these precursors as aqueous solutions into hot wall reactors resulted in micrograined amorphous powders. However, it was found that when a solution of nitrate precursors and organic solvents (e.g. ethanol, iso-propanol) was sprayed into a pilot flame crystalline and dense alumina nanoparticles were made.

The flame was self-sustaining, even though a nitrate precursor was used. It was reported that organometallic precursors form particles of improved homogeneity and with smaller grain size distributions when compared to aqueous solutions. This was attributed to the presence of water droplets or vapor in the reaction zone producing larger particles and was also observed for higher gas flow rates during production of metal oxide. Even though organometallic precursors are typically more expensive than their halide or nitrate counterparts, the higher product powder quality

(better homogeneity and smaller grain size distribution) may compensate for this. Organometallic precursors are often used in combination with an organic solvent (e.g. alkoxides, acetates, acetylacetonates, etc.), resulting in a self-sustaining spray flame.

An elegant way for manufacture of mixed metal precursors was performed by the implementation of the stoichiometric preset of the desired metals into an organic complex [64]. This concept was successfully applied in production of mullite nanoparticles from alkoxide complexes. In another example, BaTiO_3 was synthesized from organometallic precursors, where the precursor preparation from ethanol, TTIP and barium-II-ethyl-hexanoate first formed a Ba-Ti alkoxide, which was then introduced into our self-sustaining spray flame reactor. BaTiO_3 nanoparticles with an average particle size less than 50 nm were produced. The precursor release from the droplet, its decomposition and gas phase reaction are important steps in formation of the final product. The precursor composition plays an important role, but this is still not well understood. Although both salts yielded particles consisting of nanocrystallites, it was proposed that the oxidation of the carbonaceous residue from the acetate resulted in non-agglomerated nanocrystallites. In order to improve phase homogeneity, gelation of the precursor within the fuel droplet could be advantageous.

1.4.1.2.2.2 Liquid fuel composition [68-70]

Besides the precursor composition, Mädler et al. [68, 70] found that the total energy content of the spray flame and the evaporation rate of the liquid fuel are important parameters controlling the product powder properties.

At low oxidant flow rates the specific surface area increases with increasing oxidant flow rate as the height of the spray flame is reduced, leading to shorter

residence times, thus, reducing the time for particle growth. At high oxidant flow rate, the fuel is consumed faster leading to shorter flame and higher maximum temperature. The fuel and precursor reaction is more intense for high oxygen flow rates, and takes place in a smaller unit volume initiating fast precursor release at higher temperatures, thus, leading to enhanced sintering rates and, therefore, to smaller specific surface areas. With iso-octane as fuel, only the declining branch of the specific surface area is found, has a 1.5 times higher enthalpy content and a 1.5 times higher evaporation rate during the combustion compared to ethanol [68, 69]. The liquid fuel composition is an important temperature profile defining parameter and therefore influences particle growth and sintering. This example clearly shows the importance of controlling the droplet evaporation and combustion in production of oxide particles by flame spray pyrolysis. Information on burning rates and droplet lifetime and thus precursor decomposition (reaction) can be gained from spray combustion models and incorporated in existing models of particle synthesis in vapor flames.

1.4.2 The FSP evaluations of particle formation [97, 98]

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 partway 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.

1.4.2.1 Evaporation-condensation [97, 98]

Evaporation is the reverse of growth by condensation in which more molecules leave the particle surface than arrive. 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 evaporation-condensation 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 1.5). After the droplet formation a reaction step particle formation takes place resulting in solid.

Table 1.3 Comparison of aerosol processes for powder production [97].

	FLAME	EVAP.- COND. REACTION	LASER	PLASMA	HOT WALL	SPRAY PYROLYSIS
Maximum size	1 μm	0.1-10 μm	1 μm	1 μm	1 μm	0.1-100 μm
Spread	Broad	Narrow	Narrow	Broad	Narrow	Broad
Morphology	Agglomerates solid	Solid	Solid	Agglomerates solid	Spherical solid	Spherical solid, porous hollow
Maximum temp. (K)	2,500	< 2,000	1,000	25,000	1,000	1,600
Material	Oxides	Metals and oxides	Nonoxides oxides	Nonoxides oxides	Nonoxides oxides semiconductors	Nonoxides oxides
Complexity	Low	Low	Medium	High	Low	Low

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 the part has its own

advantages and disadvantages. Table 1.3 presents a comparison of these different processes.

1.4.2.2 Nucleation [97, 98]

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.

1.4.2.2.1 Nucleated condensation [97, 98]

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 unsaturated conditions and size-stable droplets can be formed. Nucleated condensation is the primary mechanism for cloud formation in the atmosphere.

1.4.2.3 Coagulation [98]

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.

1.4.2.4 Coalescence [97, 98, 103]

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 1.9. 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 solution-precipitation. 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 differing sizes, the driving force for coalescence is 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.

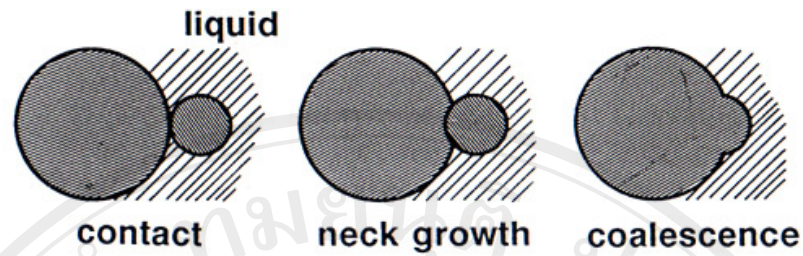


Figure 1.9 Steps leading to grain growth by coalescence of small and large grains with a curved grain boundary [103]

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 increases 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 coalesce contacting grains: 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-precipitation from the small to the large grain. Figure 1.10 compares these mechanisms. There is evidence for coalescence by all of these in both soluble and insoluble systems, so solution-precipitation is not a requirement. Coalescence is easiest when the grain boundary between contacting grains has a low misorientation. A low misorientation angle corresponds to low grain boundary energy and a high

dihedral angle. Grain rotation is brought about by the grain boundary torque, where the grains assume perfect crystallographic alignment and eliminate the grain boundary. Simultaneously, solid-state and liquid diffusion processes give grain growth, with the larger grain consuming the smaller grain.

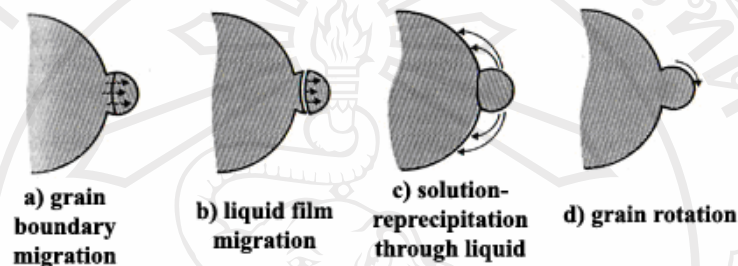


Figure 1.10 Four possible mechanisms of coalescence between contacting grains: (a) solid-state grain boundary motion; (b) liquid-film migration; (c) solution-reprecipitation through the liquid; (d) grain rotation to a zero misorientation configuration [103].

When two contacting grains differ in size, the grain boundary is curved and unstable. Diffusion across the boundary is highest with sharply curved grain boundaries, meaning large grain size differences. At high dihedral angles and large grain size differences, there is no energy barrier to boundary motion. Thus, low misorientation angles between the grains, high dihedral angles, and large grain size differences contribute to easy coalescence. For low dihedral angles, the motion of the boundary through the small grain increases the system energy barrier impeding coalescence. However, the simultaneous action of solution-reprecipitation from the small to large grain can act to eliminate the energy barrier.

1.5 Ethanol vapor sensor [1-12, 22-49, 51-54, 104-112]

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 3.30 eV at room temperature [51-54], and with high sensitivity to toxic and combustible gases. It is sensitive to many gases at moderate temperature, especially for ethanol vapor [22-49]. However, the physical and sensing properties of semiconductor gas sensors are directly related to their preparation e.g. particle size and morphology as well as sensing film characteristics. Several oxides were tested for the ethanol gas sensing and relative high sensitivity was reported with evaporated SnO₂ [1-12, 104], sintered α -Al₂O₃-SnO₂ [104], and sintered CaO-SnO₂ [104]. However, the sensing performances do not seem to be sufficient in sensitivity and response rate. In application, ethanol is one of the most used and widespread alcohols, which imposes the necessity of developing sensors for its detection. Ethanol sensors find application in various areas, such as control of drunken driving and the monitoring of fermentation and other processes in chemical industries, especially the drunken driving is the most serious problem in the society. The crash risk increases steeply with increasing blood alcohol concentration, which has been effected consequently from the alcohol exceeds by far any other single factor as a cause of traffic accidents. In the sensor materials field, most of the early developments in breath-alcohol analysis involved the use of wet chemical reactions for the determination of alcohol, because the concentration of ethanol in blood and breaths after alcohol consumption vastly exceeded the concentration of interfering substances, it occurred to us that this same electrochemical cell might be suitable for breath-ethanol concentrations [105-107].

In particular, the selective and sensitive detection limit of ethanol on the breath of vehicle driver who has drunk alcoholic beverages is essential for the assessment of a drunken driving. In most case, assessing a person's blood ethanol concentration is based on a method of measuring ethanol in the person's breaths. The permissible legal detection limit of blood ethanol for driving in most countries is 0.05-0.08%, which corresponds to 130-208 ppm in human breaths [108]. Generally, reliable sensors which can detect breath ethanol in the concentration ranging from 20-800 ppm are required for the rapid assessment of drunken driving. The detection of breath ethanol has been mostly performed by gas sensors based on chemically sensitive semiconductor. Moreover, previous works have been reported that the ethanol sensors and also detection limit based on semiconductor materials. An ethanol sensor plays an important material on controlling and detection the alcohol concentration level in drunken driving [109, 110], which directly related to the breath analyzer must detect at least 200 ppm corresponds approximately to 0.6 g of alcohol per litre of blood [110-112].

1.5.1 Sensing performance factors [105, 106, 113]

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 workers 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.

1.5.1.1 Selectivity [105, 106]

The selectivity can be defined as the ability of a sensor to respond primarily to only one 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 the 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 analytes. Alternately, the response may be to a group of analytes of similar chemical structure, such as carbonyl compounds.

1.5.1.2 Sensitivity [106, 113]

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 is linear. At the lower level is the *detection limit*. This has a precise definition according to the IUPAC convention. It is the concentration of analyte 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 1.11) as the several ratios depending on the types of a semiconductor, and the types of the analyte gas i.e. R_a/R_g [23, 25, 26, 30, 32, 33, 36, 39, 40, 45-47], R_a-R_g/R_g [15, 42], R_a-R_g/R_a [22, 24, 43, 49], R_f-R_o/R_o [22], G/G_o [41], 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_g/R_a 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 [1] as shown in Equation 1.1 and 1.2 as follow:

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

$$S = \frac{R_g}{R_a}, S = \frac{R_g - R_a}{R_a} \text{ (for oxidizing gas)} \quad (1.2)$$

In this research, the sensitivity is defined as the ratio R_a/R_g which widely used to calculated and compared with the literature reviews [25, 26, 45, 52, 53, 113].

1.5.1.3 Time factors [106, 113]

1.5.1.3.1 Response times [106, 113]

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 nitrate electrodes 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_{res} is defined as the time required until 90 % of the response signal is reached [15, 52, 53, 113].

Example of Layer Response to gases

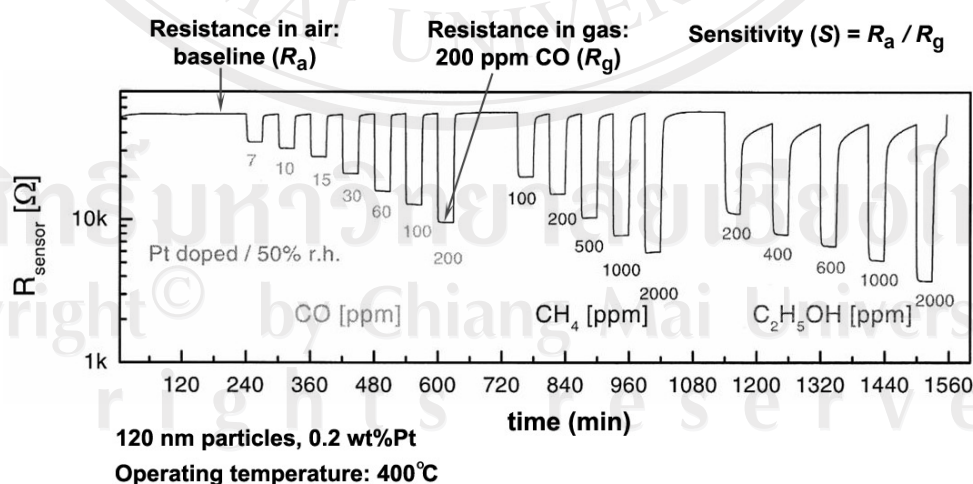


Figure 1.11 Change in resistance of several gases corresponded to the sensing performance in terms of sensitivity, response, and recovery times [12]

1.5.1.3.2 Recovery times [106, 113]

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_{rec} denotes the time needed until 90 % of the original baseline signal is recovered [15, 52, 53, 113].

The response and recovery time can be calculated (Equation 1.3 and 1.4) as follow:

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

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

where T_{R_o} is defined 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) [15, 52, 53, 113].

1.6 Characterizations theories

1.6.1 X-ray Diffraction (XRD) [97, 114-116]

X-ray diffraction (XRD) is a standard tool for identification of crystalline phases in powder samples. The crystalline phase in the sample diffracts X-ray according to Bragg's equation (Equation 1.5) as follow $\lambda = 2d \sin \theta$ [114-116] 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 Diffraction from crystalline materials-Bragg's law [97, 114, 115, 116]

Bragg law, formulated by W.L. Bragg in 1913 [144-146], relates the wavelength of the X-rays to the spacing of the atomic planes. Consider the diffracted wave in Figure 1.12 and 1.13. It is assumed to make the same angle, θ , 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-ray should all be in phase across a

wavefront. This turns out to be a real convenience, so we set $d = d'/n$ and write the Bragg law in the form

$$\lambda = 2d \sin \theta \quad (1.5)$$

This equation is known as Bragg's law [114-116] and is extremely important in indexing X-ray diffraction patterns and, hence, for determining things like the crystal structure of the material.

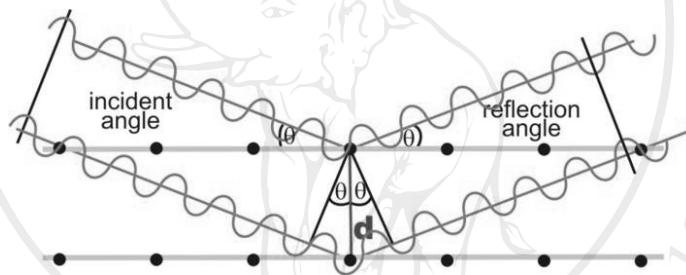


Figure 1.12 Diffraction of x-rays by a crystal. Destructive interference of reflected waves (in the reflected waves, maximum and minimum of the wave amplitude are superimposed) [116]

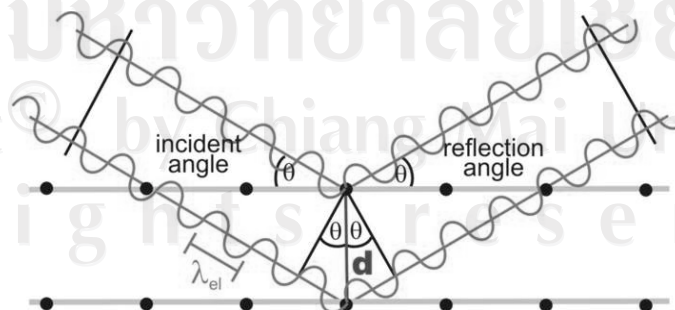


Figure 1.13 Constructive Interference of reflected waves (reflected waves in phase, i.e., maxima are superimposed) [116]

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 λ . For this case, the Bragg law then gives the relation between interplanar distance d and diffraction angle θ

1.6.1.2 XRD analysis-particles sizes [114]

When the size of the individual crystals is less than about $0.1\ \mu\text{m}$ ($1000\ \text{\AA}$), the term “particle size” is usually used. Crystals in this size range cause broadening of the Debye rings, the extent of the broadening being given by Equation 1.6 as follow:

$$B = \frac{0.9\lambda}{t \cdot \cos \theta} \quad (1.6)$$

where B = broadening of diffraction line measured at half its maximum intensity (radians) and t = diameter of crystal particles. All diffraction lines have a measurable breadth, even when the crystal size exceed $1000\ \text{\AA}$, due to such causes as dicergence of the incident beam and size of the sample (in Debye cameras) and width of the X-ray source (in diffractometers). The breadth B refers, however, to the extra breadth, or broadening, due to the particle size effect alone. In other word, B is essentially zero when the particles size exceeds about $1000\ \text{\AA}$.

The main problem in determining particles size from line breadths is to determine B from the measured breadth B_M of the diffraction line. Of the many methods proposed, Warren's is the simplest. The unknown is mixed with a standard which has a particles size greater than 1000 Å, and which produces a diffraction line near that line from the unknown which is to be used in the determination. A diffraction pattern is then made of the mixture in either a Debye camera or, preferably, a diffractometer. This pattern will contain sharp lines from the standard and broad lines from the unknown, assumed to consist of very fine particles. Let B_S be the measured breadth, at half-maximum intensity, of the line from the standard. Then B is given, not simply by the difference between B_M and B_S , but by the Equation 1.7:

$$B^2 = B_M^2 - B_S^2 \quad (1.7)$$

In this project, with the Rietveld method described by Cheary et al. [117] and the knowledge of the possible crystal phases of Pd an approximate crystal sizes of these compounds are calculated using the computer program TOPAS. The reliability of the measured crystal sizes depends on the resolution of the data and the material characteristic peaks.

1.6.2 Brunauer-Emmett-Teller (BET) analysis [97, 118, 119]

Surface areas of powders are usually measured using nitrogen or helium adsorption followed by analysis of the data using the Brunauer-Emmett-Teller isotherm. Estimates 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.

1.6.2.1 Adsorption isotherms [118]

The appropriate IUPAC classification is shown in Figure 1.14. The reversible type I isotherm is concave to the P/P_0 axis and the adsorbed amount approaches a limiting value as $P/P_0 \rightarrow 1$. Type I isotherms are obtained when adsorption is limited to, at most, only a few molecular layers. This condition is encountered in chemisorption, where the asymptotic approach to a limiting quantity indicates that all of the surface sites are occupied. In the case of physical adsorption, sorption isotherms obtained on microporous materials are often of type I. Micropore filling and therefore high uptakes are observed at relatively low pressures, because of the narrow pore width and the high adsorption potential. The limiting uptake is being governed by the accessible micropore volume rather than by the internal surface area.

Type II sorption isotherms are typically obtained in case of nonporous or macroporous absorbent, where unrestricted monolayer-multilayer adsorption can occur. The inflection point or knee of the isotherm is called point B. This point indicates the stage at which monolayer coverage is complete and multilayer adsorption begins to occur.

The reversible type III isotherm is convex to the P/P_0 axis over its entire range and therefore does not exhibit a point B. This indicates that the attractive adsorbate-adsorbent interactions are relatively weak and that the adsorbate-adsorbate

interactions play an important role. Isotherms of this type are not common, but an example is nitrogen adsorption on polyethylene or the adsorption of water vapor on the clean basal plane of graphite.

Type IV isotherms are typical for mesoporous materials. The most characteristic feature of the type IV isotherm is the hysteresis loop, which is associated with the occurrence of pore condensation. The limiting uptake over a range of high P/P_0 results in a plateau of the isotherm, which indicates complete pore filling. The initial part of the type IV can be attributed to monolayer-multilayer adsorption as in case of the type II isotherm.

Type V isotherms show pore condensation and hysteresis. However, in contrast to type IV the initial part of this sorption isotherm is related to adsorption isotherms of type III, indicating relatively weak attractive interactions between the adsorbent and the adsorbate.

Type VI isotherm is a special case, which represents stepwise multilayer adsorption on a uniform, non-porous surface, particularly by spherically symmetrical, non-polar adsorptives. The sharpness of the steps depends on the homogeneity of the adsorbent surface, the adsorptive and the temperature. Type VI isotherms were for example obtained with argon (Ar) and krypton (Kr) on graphitized carbons at liquid nitrogen temperature.

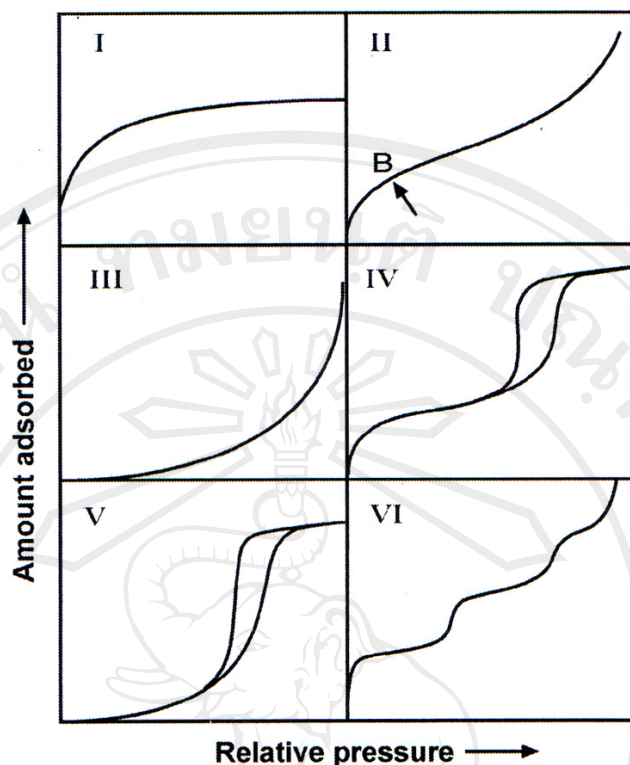


Figure 1.14 IUPAC classifications of sorption isotherms [118]

1.6.2.2 Particle size (d_{BET}) [52, 53, 65, 97, 113, 118, 119]

In an experiment, 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. [119]. 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 have the type II or IV 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 1.6 is used:

$$d_{BET} = \frac{6}{SSA_{BET} \rho_{sample}} \quad (1.8)$$

1.6.3 CO-pulse chemisorption [118, 120-122]

1.6.3.1 Chemical adsorption [118, 120-122]

When the interaction between a surface and an adsorbate is relatively weak, only physisorption takes place via dispersion and coulombic forces. However, surface atoms often process electrons or electron pairs that are available for chemical bond formation. Resulting *chemical absorption* or *chemisorption* has been defined by ICPAC as “*adsorption in which the forces involved are valence forces of the same kind as those operating in the formation of chemical compounds*” and as “*adsorption which results from chemical bond formation (strong interaction) between the absorbent and the absorbate in a monolayer on the surface*”.

It is often found to occur at temperatures far above the critical temperature of the adsorbate. This often-irreversible adsorption, at least under mild conditions, is characterized by large interaction potential that lead to high heats of adsorption. However, to distinguish between physical and chemical adsorption based on heat of adsorption alone is not entirely satisfactory.

1.6.3.2 Active metal area [118, 120-122]

To calculate the equivalent area of exposed active metal area (A_m) one must first know the following: the number of adsorbed gas molecules in the monolayer, N_m , the adsorption stoichiometry, s , and the cross-sectional area occupied by each active surface atom, A_x . N_m is calculated from the experimental determination of V_m thus:

$$N_m = \left(\frac{V_m}{22414} \right) L_{Av} \quad (1.9)$$

where V_m is expressed in mL at standard temperature and pressure (STP), 22414 being the volume, in mL, occupied by one mole of gas at STP and L_{Av} is Avogadro's number or 6.022×10^{23} . The number of metal atoms, N_a , is given by multiplying N_m the number of gas molecules, by S , the stoichiometry:

$$N_a = N_m \cdot S \quad (1.10)$$

The total sample active metal area is simply the product of the number of exposed metal atoms, N_a , and the cross-sectional area of each atom, A_x . It is normal to express the result in terms of specific metal area that is the active metal area per unit mass, W :

$$A_m = \frac{N_a A_x}{W} \quad (1.11)$$

1.6.3.3 Stoichiometry [118]

A simple association of one gas molecule with one exposed metal atom yields the most straightforward determination of the quantity of active sites. However, it is important to recognize that many polyatomic gas molecules do not adsorb in a ratio of unity with each active site. Consider the example of the reaction between a hydrogen molecule (H_2) and a surface constructed of metal atom i.e. platinum (Pt), palladium (Pd). It is generally recognized that the hydrogen is dissociatively adsorbed, that is, the hydrogen splits into two atoms each of which reacts with a single metal atom. Thus, one gas molecule has bound two metal atoms. Therefore, the stoichiometry is said to be two for this surface reaction. Alternatively, one adsorbate molecule might be associated with more than one metal atom without being dissociated (Figure 1.15).

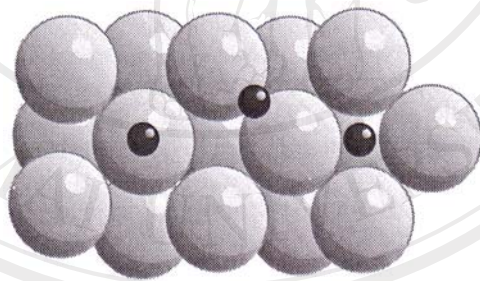


Figure 1.15 There may exist a number of different adsorption sites that involve different numbers of metal atoms per adsorbate molecules [118].

For example, carbon monoxide (CO), which is normally expected to bond in a ratio of one to one, might “bridge” between two metal atoms. This situation would also result in a stoichiometry of two. Excess adsorption beyond a ratio of unity might even lead to compound formation: hydride in the case of hydrogen and carbonyl for

carbon monoxide. Such behavior yields stoichiometries below unity, and should be avoided. The gas-sorption stoichiometry is defined as the average number of metal atoms with which each gas molecule reacts.

Since, in the gas adsorption experiment to determine the quantity of active sites in a catalyst sample, it is the quantity of adsorbed gas that is actually measured, the knowledge of (or at least a reasonably sound assumption of) the stoichiometry involved is essential in meaningful active site determinations. This information is most easily obtained from the catalyst literature, or possibly by using one of the calculation methods described below, the Langmuir method, depending on the exact nature of the sorption process.

1.6.3.4 Dispersion [118]

In the case of supported metal catalysts, it is important to know what fraction of the active metal atoms is exposed and available to catalyze a surface reaction. Those atoms that are located inside metal particles do not participate in surface reactions, and are therefore wasted. Dispersion is defined as the percentage of all metal atoms in the sample that are exposed. The total amount of metal in the sample is term the *loading*, χ , as a percentage of the sample mass, and is known from chemical analysis of the sample. The dispersion is calculated from:

$$Dispersion = M \frac{N_a}{L_{Av}} \times \frac{100}{W_S \chi} \times 100\% \quad (1.12)$$

where M is the molecular weight of the metal and W_S is the mass of the sample.

Similar to the BET measurement CO-pulse chemisorption is a method which uses the adsorptive gas uptake by the particle sample to calculate the specific surface area. But in contrast to the BET method which uses nitrogen as adsorptive gas this method uses carbon monoxide. It is possible to get selectively the surface area of the metal because of its strong chemisorption of carbon monoxide and the fact that the semiconductor material such as ZnO, Al₂O₃, and SnO₂ adsorbs no supplied gas. With this knowledge the dispersion of metal particles are determined. The measurement is carried out with AutoChem II made by Micromeritics.

For example, the absorbed CO can be calculated by the difference of the concentration on front of and behind the sample. Every 0.1 seconds the concentration is measured and the adsorbed carbon monoxide volume is calculated. After the pulse has passed the sample the additional loop is switched off the main circuit and pure helium floods the tube again. The concentration of CO in the gas flow decreases to zero. Repeating the procedure and plotting the measured concentrations behind the probe against time a figure like the one shown in Figure 1.16 appears.

The peaks starting with a small height are getting taller and taller regarding time. A CO-pulse causes a peak and the difference in the height is because of the different amounts of adsorbed carbon monoxide. During the first pulse a lot of CO is adsorbed and there is no big increase in concentration detected behind the sample (for example, see first peak in the measured concentration in Figure 1.16). But later on less and less of the additional gas is adsorbed due to the already occupied amount of CO on the palladium surface. The peaks finally reaching a maximum and integrating the TCD signal over the highest peak and knowing that the sample was provided with 0.35 ml of CO a reference value is defined. Integrating now a smaller peak and

comparing the value with the one calculated above, the remaining amount of CO behind the sample can be calculated. Knowing this value the adsorbed volume is given too. Integrating each smaller peak and calculating the respective adsorbed amount of CO a cumulative adsorbed volume can be determined.

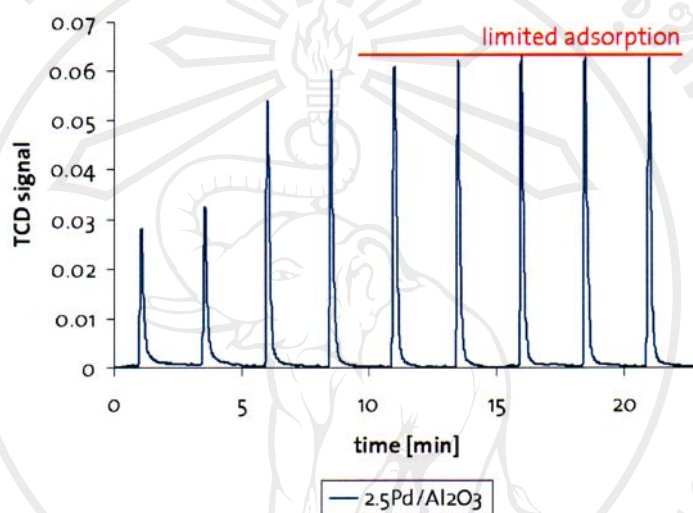


Figure 1.16 Carbon monoxide concentration measured with AutoChem II plotted against the time. The measured data is from the 2.5 wt%Pd/Al₂O₃ nanopowder [118].

Assuming a stoichiometry factor between metal-doped and CO of one causing that each metal atom react with only one CO forming one chemical bond, and active metal specific surface area (SSA_{metal}) can be calculated using the following equations. First of all the volume of one mol carbon monoxide at room temperature has to be calculated using the ideal gas Equation 1.13 and assuming that the temperature T is 273.15 K, the pressure is one atmosphere and R is the gas constant as follow:

$$V_{1\text{mol}} = \frac{n.R.T}{\rho_{\text{atm}}} = 22.4 \text{ liter} \quad (1.13)$$

Knowing the density of metal and the active specific surface area the metal mean diameter can be calculated by Equation 1.14:

$$D_{\text{metal}} = \frac{6}{SSA_{\text{metal}} \rho_{\text{metal}}} \quad (1.14)$$

The dispersion of the metal-doped can also be calculated. Knowing the total amount of metal in the sample that amount of metal atoms can be determined. Out of calculations done earlier we know the amount of atoms on the surface. Now the dispersion is defined by the following Equation 1.15:

$$X = \frac{n_{\text{metal, surface}}}{n_{\text{metal, total}}} \quad (1.15)$$

In Equation 1.15, X signifies the dispersion, $n_{\text{metal, surface}}$ the amount of metal on the surface and $n_{\text{metal, total}}$ the total amount of metal in the sample.

1.6.4 Atomic Force Microscopy (AFM) [123]

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 material 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.

1.6.4.1 Principles of atomic force microscopy [123]

The AFM is roughly composed of the microscope unit, control unit, and computer (Figure 1.17). 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 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} 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 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.

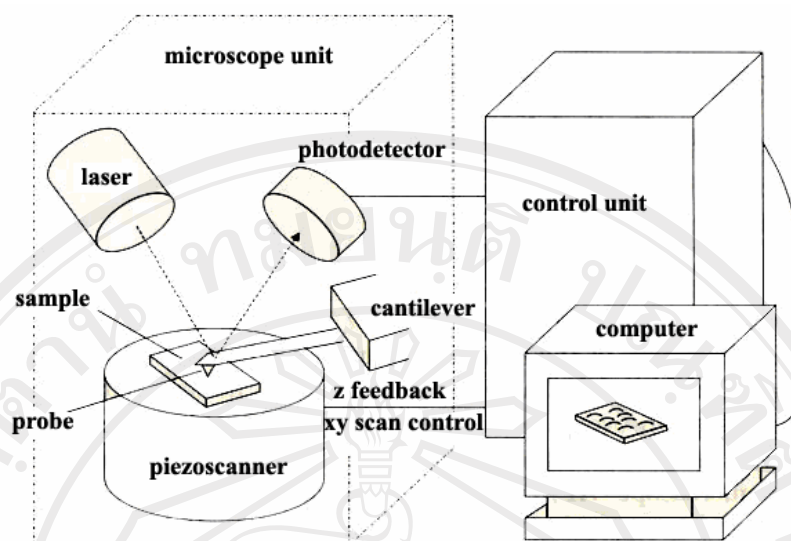


Figure 1.17 The schematic illustration of the atomic force microscope [123]

1.6.5 Optical microscopy [98]

Because the optical microscope is a common instrument used in many areas of science, only those characteristics of microscopes that are important to particle sizing are covered here. It is most suitable for counting and sizing solid particles having diameters of 0.3-20 μm . While any professional-grade compound microscope can be used for particle sizing, those with multiple objectives mounted in a nosepiece and a mechanical stage are the most convenient. Figure 1.18 shows the major components of such a microscope. Other desirable features not shown are a built-in substage illuminator and binocular eyepieces.

A magnified image of the particles is formed by the objective lens positioned just above the slide. This image is located at the eyepieces, where it is further magnified by the eyepiece to create a virtual image at a distance comfortable for viewing. In this situation the eyepiece functions like a simple magnifying glass. The

total magnifications, the ratio of image size to particle size, are approximately equal to the product of the magnifications of the objective and eyepiece lenses. Objective lens magnifications range from 10 to 100. Eyepiece magnifications range from 5 to 25 with 10, 15, and 20 being the most useful. Eyepieces slide into the microscope tube and are easily interchanged. Focusing is accomplished by moving the tube and lens system up or down relative to the sample with a rack-and-pinion mechanism.

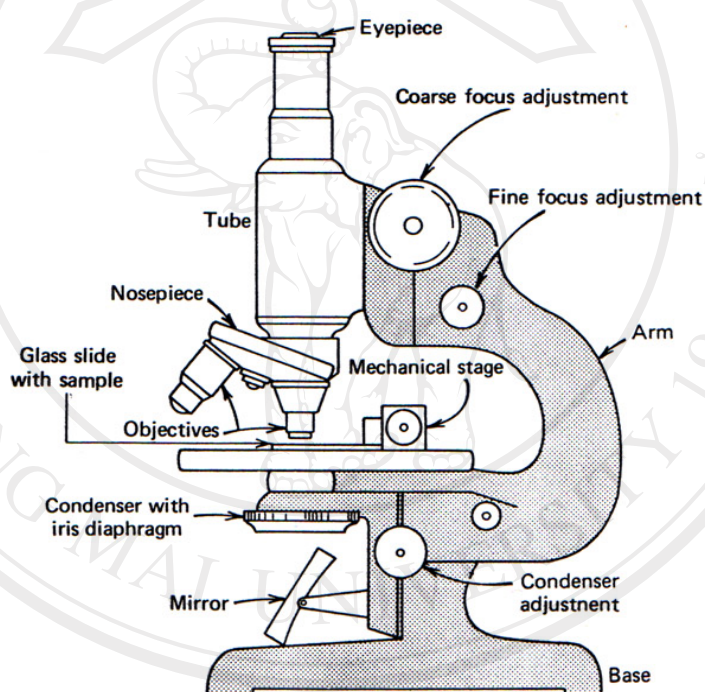


Figure 1.18 Diagram of an optical microscope [98]

1.6.6 Scanning Electron Microscopy (SEM) [94, 98, 124, 125]

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 1.19. 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 $0.01\ \mu\text{m}$, 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 ($< 0.01\ \mu\text{m}$) 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 a wide range of magnifications, 20-100,000X. For particle evaluation, 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 analyzer 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.

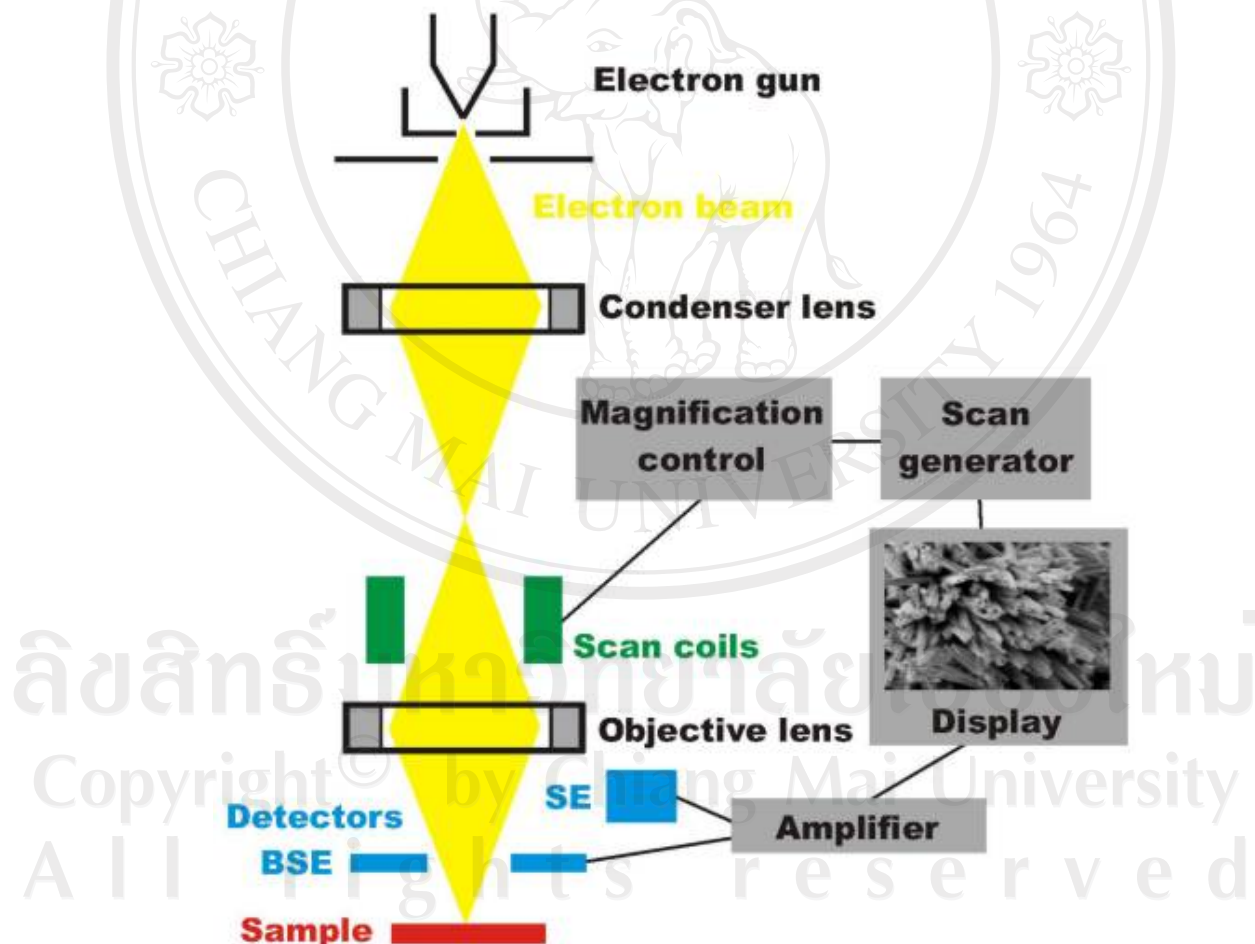


Figure 1.19 Schematic diagram of a scanning electron microscope [124]

1.6.7 Transmission Electron Microscopy (TEM) [94, 98, 126]

To examine particles smaller than the limit of resolution of optical microscopes one must use an electron microscope. Of the two common types, scanning (SEM) and transmission electron microscopes (TEM), the latter is most analogous to the light microscope and is covered first.

The principles of resolution and depth of field discussed in Section 6.5 hold for electron microscopes, but the wavelength of the radiation used in electron microscopes is much less than the wavelength of light. The wavelength of an electron is given by:

$$\lambda_e = \frac{0.0012}{\sqrt{V}} \quad (1.16)$$

where λ_e is in μm and the acceleration voltage V is in V. For typical acceleration voltage of 70,000 V, the wavelength of the electron beam is $5.5 \times 10^{-6} \mu\text{m}$ or 100,000 times smaller than the wavelength of light. 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 a few angstroms ($1 \text{ \AA} = 10^{-4} \mu\text{m}$). The small value of aperture angle used has the advantage of providing a large depth of field, more than 100 times the resolution. Table 1.4 compares the magnification, resolution, and depth of field of different types of microscopes.

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 described in Section 6.5. In some cases replication or transfer procedures can be used to deposit particles or their replicas from another surface onto a grid.

Table 1.4 Magnification, resolution, depth of field, and sample environment for different types of microscope [98]

TYPE OF INSTRUMENT	MAGNIFICATION	LIMIT OF RESOLUTION (μM)	RATIO OF DEPTH OF FIELD TO RESOLUTION	SAMPLE ENVIRONMENT
Eye	1	~ 200		Air
Magnifying glass	2-10	25-100		Air
Compound optical microscope 43 × objective (dry)	200-850	0.3	3	Air
Compound optical microscope 95 × objective (oil immersion)	500-1,300	0.2	2	Oil
SEM	20-100,000	0.01	> 1,000	Vacuum
TEM	100-200,000	0.0002	> 100	Vacuum

Sizing of particles is usually done from photographs made by enlarging a negative exposed to the electron image in the microscope. Special fine-grain, blue-sensitive photographic film is used for this purpose. The sizing procedures are the same as those described in Section 6.5 for optical microscopy except that a transparent overlay of the Porton graticule or other standard circles is used. The exact magnification of the photographs and the calibration of the overlay is determined by photographing a carbon film replica of a diffraction grating under the same conditions of magnification as for the particles. The spacing between the grating lines, usually less than $1\text{ }\mu\text{m}$, is accurately known from independent measurements.

Although the scanning electron microscope (SEM) also uses electron beams, magnetic lenses, and high vacuum, it operates on a different principle than the TEM and creates images having a three-dimensional appearance.

Much progress has been made in improving instruments and methods for exploring the micro and the nano world. Today, electron microscopy comprises a wide range of different methods that use the various signals arising from the interaction of the electron beam with the sample to obtain information about structure, morphology and composition. The focus of these section is to introduce the basics of most methods, without giving too much of the theory and mathematics behind it.

1.6.7.1 Electron Diffraction (ED) [126]

Electron diffraction is a collective elastic scattering phenomenon with electrons being scattering by atoms in a regular array (crystal). The incoming plane electron wave interact with the atoms, and secondary waves are generated which interfere with each other (analogous to the Huygens principle for diffraction of light).

This occurs either constructively (reinforcement at certain scattering angles generating diffracted beams) or destructively (extinguishing of beams). As in X-ray diffraction (XRD), the scattering event can be described as a reflection of the beams at planes of atoms (lattice planes). The Bragg's law (Equation 1.5) gives the relation between interplanar distance d and diffraction angle θ .

Since the wavelength λ of the electrons is known, interplanar distances can be calculated from ED patterns. Furthermore, information about crystal symmetry can be obtained. Consequently, electron diffraction represents a valuable tool in crystallography.

1.6.7.2 Image modes in TEM – Bright-field images [126]

In the bright-field (BF) mode of the TEM as shown in Figure 1.20, 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. It should be mentioned that the interpretation of images is often impeded by the simultaneous occurrence of the contrast-forming phenomena.

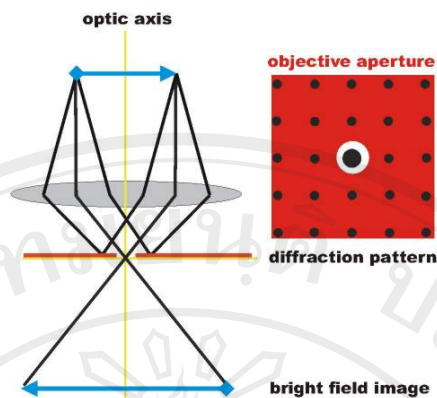


Figure 1.20 The bright-field mode of TEM [126]

1.6.7.3 Image modes in TEM – Dark-field images [126]

In dark-field (DF) images as shown in Figure 1.21, 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.

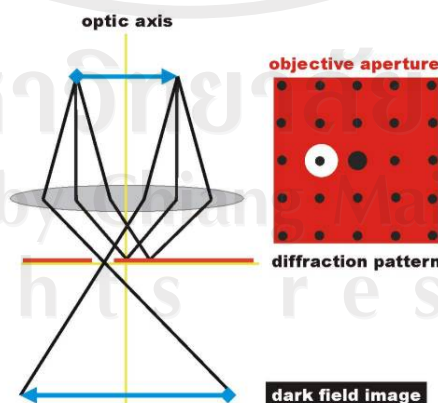


Figure 1.21 The dark-field mode of TEM [126]

1.6.8 Scanning Transmission Electron Microscopy (STEM) [126]

In STEM, a tiny, convergent electron beam is scanned over a defined area of the sample. At each spot, the generated signal is simultaneously recorded by selected detectors, building up an image. Furthermore, such a convergent beam is used to gain a highly localized signal from the specimen in analytical TEM (e.g., EDXS, EELS), and thus the combination of STEM with analytical methods is a main application in practical work.

Scanning transmission electron microscopy is used to detect crystalline area, phase analysis and particle size. An electron beam is scanned over the sample. The electrons of the beam are scattered by the electron cloud of the sample material. Highly sensitive detectors record the scattering image. With this data a visualization of the structure of the examined sample can be found.

1.6.8.1 Point analysis in STEM [126]

In STEM, an electron beam is scanned over a defined area of the sample. The beam can be localized on a certain point in the image and used to measure an EDX and/or EEL spectrum at there. Moreover, line scans and mappings can be obtained by this powerful technique.

In the high-angle annular dark field (Z contrast) image, the metal particles, which have high atomic numbers Z compared to the matrix, are imaged as bright dots. Thus, this method is a valuable tool to investigate catalysts and to determine the sizes of metal particles and the corresponding size distribution.

1.6.9 Energy Dispersive X-ray Spectroscopy (EDS) [125, 127, 128]

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 μm . 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 μm is available with SEM and down to 50 nm is available with TEM instruments. X-ray maps of a particle can be used to examine the chemical homogeneity of multicomponent particles. These maps show regions of high or low concentration 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 STEM, SEM, and TEM also can be focused on a certain point of the analyzed sample and is used to measure the X-ray 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 and ejects 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-ray quantum which is measured by EDS.

The development of the energy-dispersive x-ray spectrometer has made “easy” x-ray 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-ray 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.

1.6.10 Mass Spectrometry (MS) [129, 130]

Mass spectrometry (also known as *mass spectroscopy* or informally, “*mass-spec*” and *MS*) is an analytical technique used to measure the mass-to-charge ratio of ions. It is most generally used to find the composition of a physical sample by generating a mass spectrum representing the masses of sample components. The mass spectrum is measured by a mass spectrometer.

Mass spectrometers are extremely sensitive instruments for detection of elements from H to U can detect ppm levels. The various mass spectrometric methods differ by the method used to introduce the sample into the MS as shown in Figure 1.22. Particles on surfaces can be vaporized using pulsed lasers or can be introduced directly from the gas phase into ionization regions. These methods are usually not used on a routine basis because of their complexity.

A typical mass spectrometer comprises three parts: an ion source, a mass analyzer, and a detector system. The stages within the mass spectrometer are:

1. Production ions from the sample
2. Separating ions of differing masses
3. Detecting the number of ions of each mass produced
4. Collating the data and generating the mass spectrum

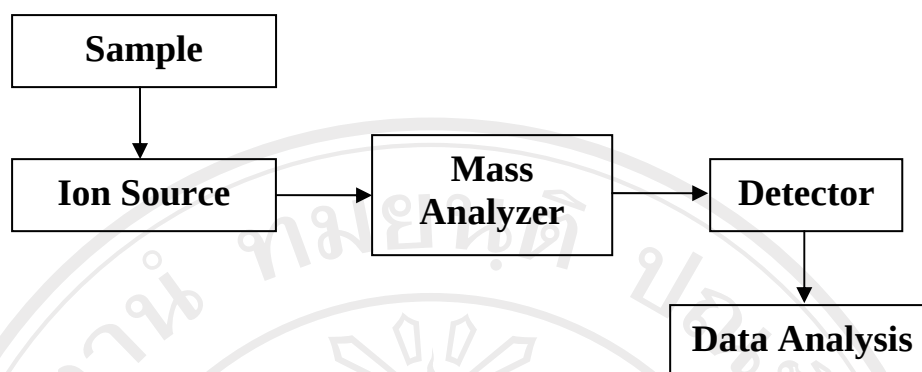


Figure 1.22 Simplified Mass Spectrometer diagram [129]

1.6.10.1 Mass spectrum [129, 130]

A mass spectrum is the intensity vs. m/z (mass-to-charge ratio) plot representing a chemical analysis. Hence, the mass spectrum of a sample is a pattern representing the distribution of components (atoms or molecules) by mass (more correctly: mass-to-charge ratio) in a sample. It is usually acquired using an instrument called a mass spectrometer. Not all mass spectra are the same. For example some mass spectrometers break the analyte molecules into fragments; others observe the intact molecular masses with little fragmentation. A mass spectrum can represent many different types of information based on the type of mass spectrometer and the specific experiment applied; however, all plots of intensity vs. mass-to-charge are referred to as mass spectra.

1.6.11 Sensor experiment [105, 106]

1.6.11.1 Semiconducting oxide sensors [105, 106]

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-bandgap semiconducting oxide, such as SnO_2 or ZnO . 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 1.23). 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. In an n -type semiconductor, such as SnO_2 and ZnO , the majority carriers are electrons therefore the change in surface conductivity $\Delta\sigma_s$ is given from Equation 1.17 in the form:

$$\Delta\sigma_s = e\mu_s\Delta n_s \quad (1.17)$$

where e is the electron charge and μ_s is the electron mobility at the surface.

The excess density Δn_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 :

$$\Delta n_s = \int_0^d [n(z) - n_b] dz \quad (1.18)$$

The change in surface conductance ΔG_s is then:

$$\Delta G_s = \Delta \sigma_s W / L \quad (1.19)$$

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 1.24):

$$G_b = n_b e \mu_b W d / L \quad (1.20)$$

The terms in Equation 1.20 have the same meaning as those in Equation 1.18 and 1.19. 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 1.18, 1.19, and 1.20 and by assuming that $\mu_b \sim \mu_s$. Hence:

$$\Delta G / G = \Delta n_s / n_b d \quad (1.21)$$

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^{-2} and the bulk density $n_b = 10^{17}$ electron cm^{-3} . This means that for a 100 μm 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.

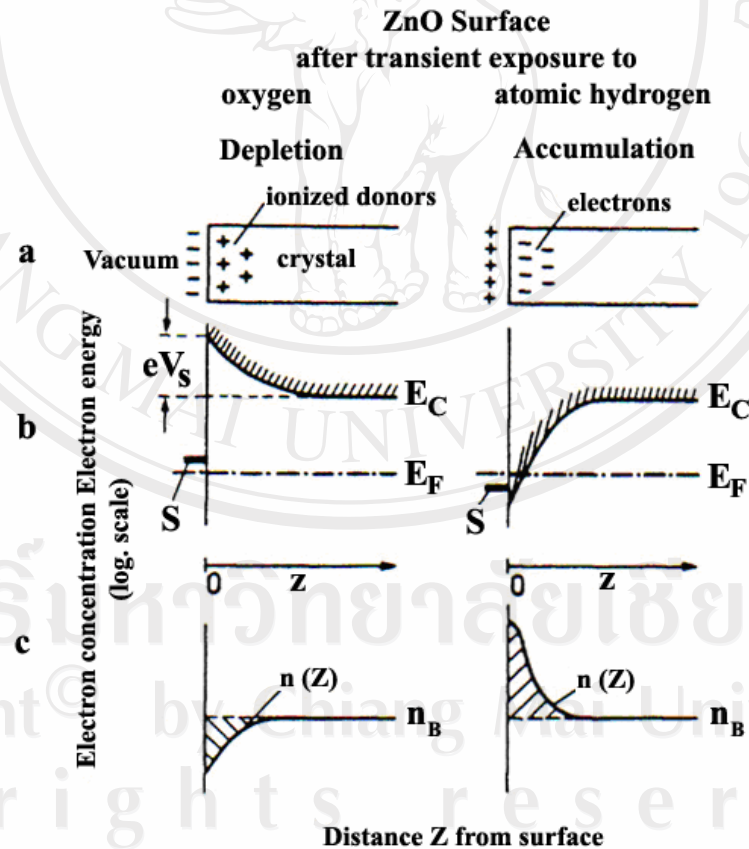


Figure 1.23 Space-charge modulations by adsorption in a semiconducting n -type semiconductor oxide sensor [105]

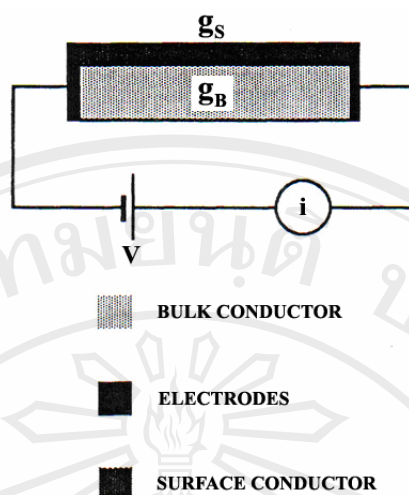
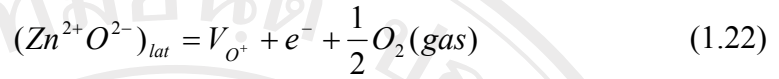


Figure 1.24 Schematic representation of a semiconducting oxide sensor with bulk (g_B) and surface (g_s) conductivities shown [105].

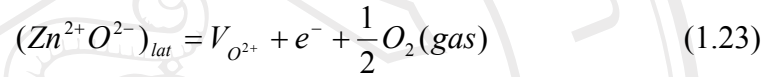
It is convenient to present the elemental aspects of the sensing mechanism assuming a regular crystal lattice, i.e., a monocrystal. Indeed the fundamental studies into reactions at oxide surfaces were conducted on well-defined surfaces. On the other hand, practical sensors are prepared by techniques 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 1.25.

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:



and



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_2 (see Figure 1.23 earlier). Sensors based on this principle can be designed to detect carbon monoxide (CO), carbon dioxide (CO_2), ethanol (C_2H_5OH ; EtOH), and other organic vapors down to 1-50 ppm. This type of sensor is fabricated by using vapor deposition techniques. A $0.3 \mu m$ layer of palladium-doped SnO_2 is grown on a silicon oxide layer on top of a ferrite substrate. 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_2 layer.

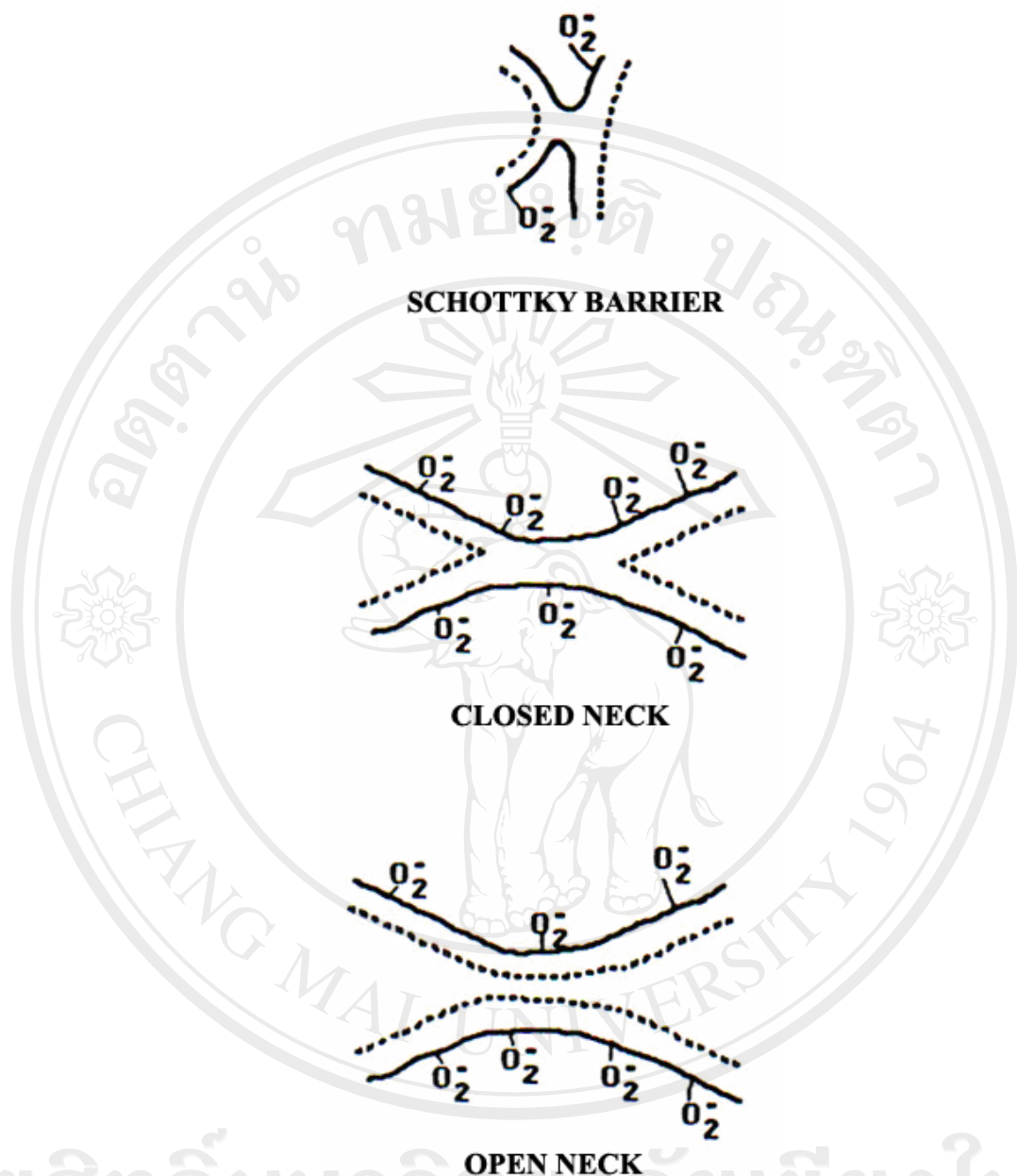
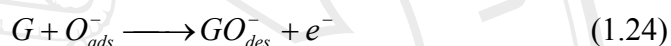


Figure 1.25 Effect of the morphology of a semiconducting oxide on conductivity. The depth of the space-charge region is indicated by the dashed line.

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^-) [105].

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 SnO₂ 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 SnO₂, 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 TiO₂-based sensor has been used to measure the oxygen content of exhaust gases. The resistance of the active layer increases with the amount of oxygen.

1.6.11.2 ZnO/Ethanol gas sensing mechanism and reactions [52, 53, 113]

The sensing mechanism of material was shown in Figure 1.26. The analyte ethanol gas 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 ethanol–ZnO interactions on the surface may play an important role.

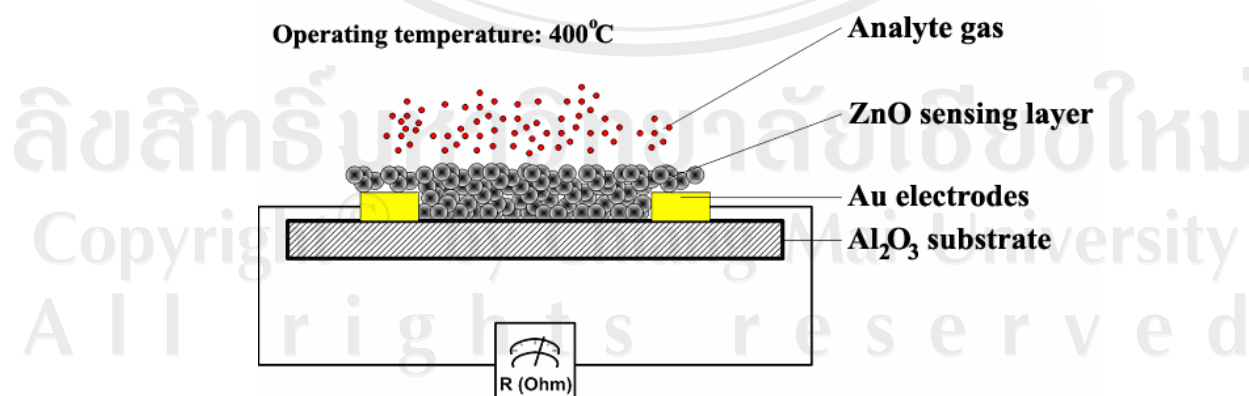
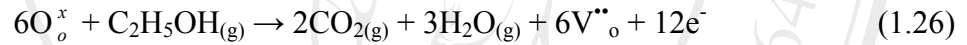


Figure 1.26 Schematic of the sensing mechanism of semiconducting material with the analyte ethanol gas exposure [52, 53, 113]

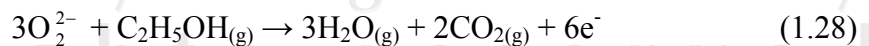
Oxygen from the ambient adsorbs on the exposed surface of ZnO and, extracting an electron from the ZnO conduction band, ionizes to O^- or O^{2-} ; O^- is believed to be dominant [22]:



The interaction between the reducing gas ethanol and lattice oxygen O_o^x in a metal oxide such as ZnO can be described in general by the following defect reaction (in Kröger-Vink notation) [22]:



Similarly, the interactions between reducing gas ethanol and surface-adsorbed oxygen species [22, 43, 131] such as superoxide ion O_2^- (Equation 1.27) and peroxide ion O_2^{2-} (Equation 1.28) can be described as



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 1.27. 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 1.28 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 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 1.28 (b) [49]. 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.

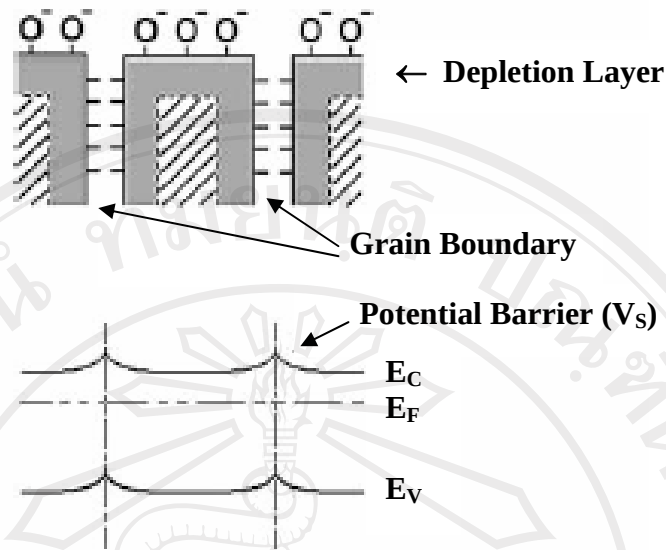


Figure 1.27 Formation of depletion layers in the surface and grain-boundary regions of ZnO due to oxygen chemisorption. The potential barriers at the grain boundaries reduce the carrier mobility [35].

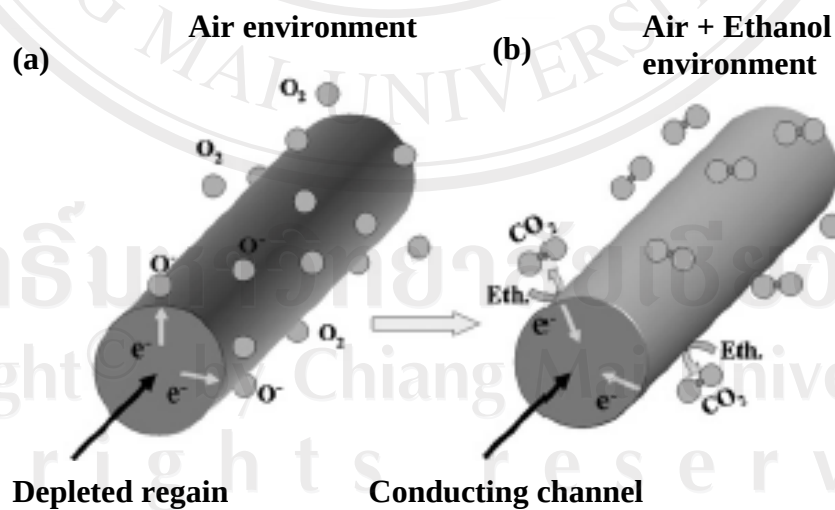


Figure 1.28 Schematic diagram of ZnO nanowire surrounded by (a) air and (b) ethanol gas [49]

1.7 Literature reviews

1.7.1 Flame spray pyrolysis [50, 66-68, 132-135]

Many researchers reported that the nanomaterials were synthesized by flame spray pyrolysis technique for decades. The principals and the background concepts of flame spray pyrolysis have been well established and discussed in the chemistry, physics, and engineering fields. The FSP process can be used to produce the several materials which widely used in both scientific and commercial communities. Applications are rapidly developed in the medical field, consumer goods, and many areas.

Firstly, Wegner et al. [50] reported the flame-nozzle synthesis of nanoparticles with closely controlled size, morphology, and crystallinity. Precise control of the average primary particle size, reduced agglomeration and phase composition was achieved by positioning of the quenching nozzle above the burner and controlling gas and precursor flow rates. Furthermore, the phase composition of the product powders could be controlled also by the burner-nozzle distance. The process had high potential for successful application to other flame configurations and cost-effective synthesis of carbon, silica, alumina and other oxide and non-oxide ceramics with controlled size and limited degree of agglomeration.

Mädler et al. [66] additionally reported about the controlled synthesis of nanostructured particles by flame spray pyrolysis. The flame spray pyrolysis process was systematically investigated using an external-mixing gas-assisted atomizer supported by six premixed methane/oxygen flamelets. As oxidant air and pure oxygen were used, that served also as droplet dispersion gases. The liquid solvent (fuel), especially its enthalpy content, was an important parameter in FSP as it affected the

total net heating value of the spray flame. At low oxidant flow rates, the specific surface area increases with increasing oxidant flow rate as the spray flame length was reduced leading to shorter residence time 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 and, as a result, they had lower specific surface area compared to those made using air as confirmed by in situ flame spray temperature measurements. The product specific surface area exhibited a maximum and decreased for higher oxidant flow rates. At high flow rates the flame height was reduced substantially as fuel and precursor were oxidized faster in a smaller unit volume accelerating, thus, precursor release at higher temperatures leading to high sintering rates and therefore smaller specific surface area of the product.

Müller et al. [67] reported about the high production rate of nanoparticles produced by flame spray pyrolysis using the silica powder as the representative material. The effect of powder production rate, dispersion gas flow rate and precursor concentration on product particle size, morphology and carbon content was investigated. The product primary particle size was precisely controlled from 10 to 75 nm and compared to a well-established vapor-fed flame aerosol reactor. The spray flame height increased when increasing the liquid feed rate that corresponded to the production rates using air as dispersion gas. This prolongs the time for fuel combustion resulting in longer flames. The increased feed (or silica production) rate resulted in higher enthalpy content of the flame that leads to longer particle residence times at high temperatures increasing the particle sintering rate resulting in the formation of larger particles. Furthermore, the precursor concentration increased and

therefore the silica particle concentration leading to more particle collisions and therefore enhanced growth, which increased the particle diameter especially when complete coalescence takes place.

Mädler et al. [68] reported the concept of one-step synthesis of nanoparticles using the liquid-fed aerosol reactor. The utilization of liquid-fed reactors for the aerosol-based production of nano-sized powders was reviewed. Aerosol technology was the key process for large-scale production of nano-structured materials. The understanding of gas-phase synthesis was transferred successfully from classic vapor-fed flames to liquid-fed aerosol reactors, enabling now also the one-step production of demanding and highly functional products. The four main spray methods, namely spray pyrolysis in a tubular reactor (SP), spray pyrolysis using a vapor flame reactor (VFSP), the emulsion combustion method (ECM) and flame spray pyrolysis (FSP), were discussed and main concepts were compared such as the energy source driving the solvent/fuel evaporation and precursor reaction. These methods were discussed and key concepts were compared such as the energy source driving the solvent/fuel evaporation and precursor reaction, final particle formation.

Briesen et al. [132] reported the effect of precursor and oxidant composition in flame synthesis of SiO_2 nanoparticles. The effect of precursor source concentration and oxidant composition on the specific surface area of flame made nanostructured silica particles were investigated in a diffusion flame reactor. This is attributed primarily to the increase of the flame temperature by the additional fuel coming from the organometallic compound. This effect was further pronounced with increasing precursor concentration as it was shown with experiments in a premixed flame

reactor. The choice of precursor affected the particle characteristics of silica made in diffusion and premixed flame reactors.

Kammler et al. [133] described the effect of electrically-assisted flame aerosol synthesis of fumed silica at high production rates. The control of particle size by external electric fields was investigated during flame synthesis of particles at high production rates. The role of external electric fields on flame synthesis of silica was investigated at high powder production rates. The monotonic increase of specific surface area with field intensity showed that electric fields can be used to precisely control the specific surface area of the product particles. Increasing the precursor concentration leads to larger particles. Consequently the particle size distribution widens as particles experience unequal residence times and sintering temperatures. As a result, electric fields could not only facilitate the synthesis of ceramic powders with precisely controlled specific surface area, but could also control powder composition.

Stark et al. [134] gave the role in concepts of aerosol flame reactors for manufacture of TiO_2 nanoparticles as the representative material for studying. Modern flame aerosol synthesis of nanoparticles was a rapidly changing terrain. Advances in process simulation and diagnostics of early particle formation and growth contributed to this development. Classical flame aerosol synthesis was somewhat limited to volatile precursors since the reaction was carried out in a homogeneous gas phase. The concept of flame synthesis could be extended into a heterogeneous system, where the precursor compound was sprayed in the flame. Droplets quickly evaporated and released the compounds into the gas phase. Rapid precursor and solvent evaporation gave products similar to that by classic vapor flame synthesis. For slow evaporation or solvent complexation, even hollow particles could be formed. The reaction and

particle formation then proceeded similar than in the flame aerosol synthesis. The extension of classical flame aerosol synthesis to new processes allowed the manufacture of new, high-value products.

Wegner et al. [135] reported the gas-phase synthesis of nanoparticle based on the scale up and design of flame reactor. The scale-up and design of flame aerosol reactors were investigated for synthesis of silica and titania nanoparticles. At high fuel-oxidant velocity difference at the burner outlet, the operation of diffusion flame reactors converged to that of premixed ones. Operation of a flame reactor with different fuel composition but with the same combustion enthalpy content still results in same size nanoparticles.

1.7.2 Flame-made ZnO nanoparticles and their composites [65, 70-72, 136-138]

Many researchers reported that ZnO nanoparticles were synthesized by flame spray pyrolysis technique since in 2002. The effect of solution feed rate, flame condition, oxidant flow rate, and flame height on particles specific surface area and crystalline size were also discussed.

For example, Tani et al. [65] reported the homogeneous ZnO nanoparticles were made by flame spray pyrolysis of zinc acrylate–methanol–acetic acid solution. The average primary particle diameter was controlled from 10 to 20 nm by the solution feed rate. Increasing the solution feed rate increased the flame height, and therefore coalescence and/or surface growth was enhanced, resulting in larger primary particles. Compared with ZnO nanoparticles made by other processes, the FSP-made powder exhibited some of the smallest and most homogeneous primary particles.

Mädler et al. [70] reported ZnO nanocrystallites down to 1.5 nm in diameter were made by spray combustion of Zn/Si precursors. ZnO nanoparticles smaller than 7 nm in diameter exhibited a so-called quantum size effect. These crystallites exhibited a quantum size effect: blueshift of light absorption with decreasing crystallite size. Stable ZnO quantum dots were made in flames with specifications close to those of wet preparation techniques but at much shorter processing times and without any post-treatment. Table 1.5 summarized prior studies of gas phase synthesis of ZnO, showing precursors and product particle characteristics (BET equivalent average primary particle diameter, d_{BET} , observed particle diameter by TEM or SEM, d_{EM} , and crystalline size calculated from XRD).

Height et al. [71] reported the ZnO nanorods were made by FSP method. Inorganic nanorods with closely controlled aspect ratio were made by flame spray pyrolysis by a single-step, continuous, and scaleable process. Indium and tin dopants selectively affect a specific ZnO crystal plane and are incorporated into its lattice. Dopant concentrations ranged between 1 and 10 at% with respect to the Zn metal. Nanorod formation was attributed to the higher valency and coordination of indium and tin dopants relative to zinc and the associated disruption of crystal growth within the Zn plane. In contrast, lithium, with an equivalent ionic radius to these dopants but lower valency than zinc, had no effect on the ZnO texture. The formation of the nanorods within the flame occurred by annealing crystallization during flame cooling. The formation of the nanorods within the flame occurs by annealing crystallization during flame cooling, with the final nanorod aspect ratio determined by dopant concentration.

Table 1.5 Prior studies of gas-phase synthesis of ZnO [70].

Authors	Process	Precursor	d_{BET} (nm)	d_{EM} (nm)	d_{XRD} (nm)
Marshall et al., 1997	Flame spray pyrolysis	Zinc acetate (ZA)	-	-	-
Teague & Raabe, 1980	Spray pyrolysis	ZA	-	800 (mass median aerodynamic diameter)	-
Carroz et al., 1980	Flame spray pyrolysis	Zinc nitrate (ZN)	-	200 (volume median diameter)	-
McCarthy et al., 1982	Evaporation & Oxidation	Zinc metal (Zn)	-	<30 (TEM)	-
Gandner et al., 1984	Spray pyrolysis	ZN ZA	139 59	$\sim \mu\text{m}$ (SEM)	33 29
Matsoukas & Friedlander, 1991	Flame aerosol synthesis	Spray-dried ZN	-	10 (TEM)	-
Suzuki et al., 1992	Spray-ICP technique	ZN	-	50+ (TEM)	-
El Shall et al., 1995	Laser vaporization/condensation	Zn	-	10-15 (SEM)	-
Kang & Park., 1997	Spray pyrolysis using filter expansion aerosol generator	ZA	11.3 (at 400°C) 21.4 (at 800°C)	5 (TEM: at 400°C) 12 (TEM: at 800°C)	7 (TEM: at 400°C) 12 (TEM: at 800°C)
Li et al., 1999	Hydrothermal gas discharging	ZA	-	$\sim \mu\text{m}$ (TEM)	-
Baklanov et al., 1999	Thermocondensation	Zn	-	$\sim \mu\text{m}$ (TEM)	-
Jensen et al., 2000	Flame aerosol synthesis	Zinc acetylacetonate	25-40	Qualitatively consistent with d_{BET} 20 (TEM)	25 (at d_{BET} = 40 nm)
Lin et al., 2000	Plasma pyrolysis	Zinc carbonate hydrate	13.9	20 (TEM)	-
De Sousa et al., 2000	Combustion of precursor	ZN	389	-	-

Height et al. [72] reported the high surface area Ag-ZnO catalysts were made by flame spray pyrolysis. Zinc naphthanate and silver nitrate were used as zinc and silver precursors, respectively. The flame configurations the ZnO primary particles exhibited a size were increased with increasing the liquid precursor feed rates (3/8, 5/5 and 8/3 flames). In each case silver dopant concentration had no influence on the crystalsize of the ZnO. The photocatalytic performance was improved for flame-made materials made at longer high-temperature residence times in the flame.

Tani et al. [136] reported the synthesis of α -willemite nanoparticles by post-calcination of flame-made ZnO/SiO₂ composites. Composite ZnO/SiO₂ nanoparticles were made by FSP. Powder synthesis was carried out using a spray flame reactor. A short residence time in the flame could result in the co-existence of the ZnO and SiO₂ clusters without substitution or reaction hindering each other's grain growth. The nano-composite structure of the FSP-made particles could suppress crystalline growth of ZnO during calcination to maintain a high reactivity of ZnO with SiO₂, obtaining pure α -willemite with high specific surface area at low calcinations temperatures.

Tani et al. [137] reported ZnO/SiO₂ composite nanoparticles were made by FSP technique. The effects of the Zn/Si ratio on particle properties were examined and compared with those of the pure ZnO and SiO₂ particles made at the same conditions. Polyhedral aggregated of nano-sized primary particles were obtained in all experiments. Powder synthesis was carried out using a spray flame reactor with an oxygen-assisted nozzle. The composite particles exhibited an excellent thermal stability and little crystalline growth of ZnO. The focus was on the size control and stabilization of ZnO nanoparticles and the effect of precursor Zn/Si ratio on the product particle properties.

Seo et al. [138] reported the nanoparticles of ZnO, MgO and NiO were produced from droplets of aqueous salt solution in the FSP reactor. Conventional spray pyrolysis, in which electrical furnace reactor was used, was reported to produce nanoparticles only from acetate precursor. The conversion from droplets to particles took place in the diffusion flame which was generated from the combustion of propane and oxygen gases as fuel and oxidizer. Flame spray pyrolysis of aqueous droplets was applied to the synthesis of nanoparticles in order to investigate if the high flame temperature is favorable for the formation of nanoparticles and to find out how the particle morphology changes at the high temperature flame condition.

1.7.3 Ethanol sensor based on pure ZnO and metal-doped ZnO [22-49]

More than a decade ago, many researchers reported the pure ZnO [22-37, 49] were widely used to detect ethanol vapor. For examples, Liu et al. [22] reported a new two-dimensional structure, ZnO single crystal flakes, synthesized using a simple combustion CVD process. The flakes grew upward from the Si substrate. The as-grown ZnO flakes were less than 200 nm thick and 10–20 mm wide. The sensor was tested at 400°C in ethanol vapor. The sensor responded quickly as the gas was switched from air to different concentration of ethanol vapor and recovered fully when the gas was switched back to air. The sensitivity was defined as the ratio of $(R_t - R_0)/R_0$ was 7.8 and 14.3 when the atmosphere was switched from air to 300 and 500 ppm ethanol vapor, respectively. A gas sensor based on a 200 nm thick ZnO flake exhibited fast response–recovery and high sensitivity to ethanol vapor.

Xiangfeng et al. [23] reported the ethanol sensor based on the ZnO nanotetrapods thick film. ZnO sensors were fabricated from ZnO tetrapod structures

prepared in four different atmospheres (evaporation of pure Zn in gas flow humidified Ar, dry Ar, humidified N₂, and dry N₂) and their gas-sensing properties were investigated. The sensitivity decreased with decreasing ethanol gas concentration. The response times and the recovery times were very short and decreased with increasing operating temperature, the response and recovery times of three sensors were all shorter than 20 s. It was found that the sensors based on tetrapods prepared in humidified Ar flow exhibited the best performance, characterized by high response, good selectivity and very short response time to dilute ethanol.

Sahay et al. [24] reported on the details of preparing of ZnO thin films by spray pyrolysis and the sensing behaviors of the films to ethanol. The sprayed ZnO thin films showed considerable changes in their resistances when exposed to ethanol with different temperature. It was found that the film layers of 20 μm in thickness showed sensitivity in terms of rather high ethanol concentration (1000-5000 ppm) at 150-350°C. It was observed the sensitivity increased with increasing operating temperature. At higher ethanol concentration, the sensitivity increased rapidly with increasing operating temperature. Response and recovery times were found to be sensitively dependent upon the operating temperature.

Xu et al. [25] reported the ZnO nanorods prepared by hydrothermal method used to detect the ethanol vapor. ZnO nanorods were prepared with cetyltrimethylammonium bromide (CTAB) and zinc powder at 182°C. ZnO sensors showed considerable response to alcohol even it concentration as low as 10 ppm. These sensors made from ZnO nanorods have higher sensitivity at 330°C (to 100 ppm ethanol, $S = 13.0$). The response and recovery properties of these sensors were quite good. The response time and recovery time of these sensors were less than 10 s and

30 s, respectively. Also, it was detected the response of these sensors to other gases such as H_2S (2 ppm), HCHO (50 ppm), LPG (500 ppm), and 90[#] gasoline (50 ppm), CO (500 ppm), ammonia (50 ppm) under the heating voltage of 5 V. ZnO sensors showed relative high sensitivity to inflammable gases such as LPG, 90[#] gasoline.

Wan et al. [26] reported the fabrication and ethanol sensing characteristics of ZnO nanowire gas sensors. ZnO nanowires gas sensors were fabricated with microelectromechanical system technology and ethanol-sensing characteristics were investigated. The sensor exhibited high sensitivity and fast response to ethanol gas at concentration up to 200 ppm with operating temperature of 300°C. The much higher sensitivity of our sensor was mainly due to the bigger surface-to volume ratio of ZnO nanowires. The results demonstrated the potential application of ZnO nanowires for fabricating highly sensitive gas sensors.

Xu et al. [27] reported the ethanol sensor based on nano-sized ZnO. Nanometer ZnO gas sensing material with different particle size were made by chemical precipitation, emulsion and microemulsion. Gas sensitivity of ZnO to H_2 , SF_6 , C_4H_{10} , gasoline, and $\text{C}_2\text{H}_5\text{OH}$ was measured. It was shown from experimental results that grain size of ZnO gas-sensitive materials could be controlled by means of different processes or surfactants. The gas sensitivity of ZnO sensor depended upon its grain size. In addition, the decrease in grain size of ZnO decreased its operating temperature due to the increase of surface activity of ZnO. In general, operating temperature of ZnO was 400-500°C, but that of nanometer ZnO made by emulsion was only 300°C [27].

Xu et al. [28] reported the sensor fabricated using a novel ZnO porous nanosolid prepared by hydrothermal hot-press method, and the measurements

indicated that it had very uniform pore size. For the sensor S-1 preparation, The ZnO nanoparticles paste was coated on the outer surface of an Al_2O_3 tube with a pair of Au electrodes attached with Pt lead wires. For the sensor S-2 preparation, The ZnO porous nanosolid was prepared using a hydrothermal hot-press (HHP) method. The organic compound vapors examined were ethanol, acetone, benzene, toluene and xylene, whose concentrations were fixed at 300 ppm in air. Compared with the sensor fabricated from conventional ZnO nanoparticles (denoted as S-1), the sensor from ZnO porous nanosolid (denoted as S-2) showed much better sensing performance towards several organic vapors; the intrinsic resistance of S-2 in air dramatically decreased and its selectivity was improved. The response of sensors S-1 and S-2 was examined to a series of organic compound vapors at different temperatures.

Arshak et al. [29] reported the development of novel sensor based on zinc and iron oxide thick film gas sensors, which fabricated by screen-printing technology on glass substrates that had silver interdigitated electrodes. The sensor was used to detect methanol, ethanol and propanol with a concentration range of 0–8000 ppm. The sensor showed the highest sensitivity to propanol followed by ethanol and methanol when the operating temperature was 25°C

Cheng et al. [30] reported the preparation, the characterization, and the gas sensing property of ZnO nanoparticulate thin film. ZnO thin films were prepared by sol–gel dip coating method. The thin films exhibited high sensitivity and rapid response–recovery characteristics to methanol, ethanol and propyl alcohol vapor as low concentration. The response time of the film to the methanol, ethanol and propyl alcohol were 18, 28, and 25 s, while the recovery time of the film is 51, 49, and 62 s, respectively. The results revealed that ZnO thin film sensor had quick response–

recovery characteristics to alcohols at room temperature and it could be used as the alcohol-sensitive material at room temperature.

Tang et al. [31] reported the ethanol sensor based on cataluminescence (CL) emission from catalytic oxidation of ethanol on the surface of ZnO nanoparticles. The grain sizes were in the range of 20–50 nm. Nanosized ZnO was coated as a layer on a ceramic heating tube which was put into a quartz tube. The air from the pump was mixed with ethanol and flowed through the quartz tube, in which ethanol was oxidized on the surface of the catalyst by the oxygen in the air. The response time and the recovery time were less than 3 and 60 s. The sensor had a significantly high selectivity to ethanol vapor. The CL emission was also detected for benzene, toluene, xylene and methanol, however, compared with ethanol. Compared with the traditional electrical conductivity-based ZnO gas sensor for the determination of ethanol, the proposed ethanol sensor showed the advantages of high sensitivity, high selectivity and low operating temperature.

Choopun et al. [32] reported the ethanol sensor based on ZnO nanobelts were made by RF sputtering. ZnO nanobelts were RF sputtered onto a copper tube. The response and recovery times of the sensor with the ethanol concentration level of 150 ppm, at the operating temperatures of 200–290°C. It was clearly seen that the characteristics of the sensor resistance depended on the operating temperature. The sensitivity of the sensor when exposed to ethanol with the concentration levels of 50–2000 ppm at different operating temperatures. It was observed that the sensor sensitivity increased when exposed to ethanol with higher concentration levels. For example, at 220°C, when the ethanol concentration level was raised from 50 to 1000 ppm, the sensitivity increased from 7.3 to 23.2. The relationship between the sensor's

sensitivity and ethanol concentration level suggested that the adsorbed oxygen species at the sensor's surface is O^{2-} .

Lv et al. [33] reported the gas sensing properties of well-crystalline ZnO nanorods were synthesized by a simple solution route employing dodecyl benzene sulfonic acid sodium salt (DBS) as a modifying agent. ZnO gas sensors were fabricated from ZnO nanorods with an average diameter of around 95 nm and their gas-sensing properties were investigated. The operating temperatures were controlled in the range of 80–500°C. It was important to note that the sensor could detect very low-concentration benzene and ethanol gas and the sensing responses to 0.01 ppm benzene and 1 ppm ethanol were up to 6.8 and 3.2, respectively. Furthermore, the ZnO sensor also had higher sensitivity (to 100 ppm ethanol gas, $R_a/R_g = 45.8$). The response and recovery times for 500 ppm ethanol gas were no more than 10 s when operating at 450°C. In fact, the sensitivity was effected by the specific area and the active site on the surface of materials, the active site can adsorb oxygen and gases to be detected. Normally, the higher its specific surface area and oxygen adsorption quantity was, the higher its gas sensitivity.

Zhou et al. [34] reported an application of quartz tuning forks (QTFs) coated with nanocrystalline ZnO films used as relative humidity sensors. In application, the quartz tuning forks were obtained by removing the metal lids and the both tuning fork beams were exposed. They indicated that the proper thickness of the ZnO film coated on the QTFs can enhance the sensitivity of the sensors. The results showed that the sensors had high humidity sensitivity, good stability, fast response time and well reproducibility, and the QTFs coated with sol–gel-derived nanocrystalline ZnO thin film provided sensitive and rapid detection of water vapor.

Gao et al. [35] reported the synthesis and properties of multipod-shaped ZnO nanorods were used as the ethanol gas sensing applications. The multipod-shaped ZnO (M-ZnO) nanorods, having tens of needle-like nanorods united at a common junction, exhibited different structural and optical characters from those of the tetrapod-shaped ZnO (T-ZnO) nanorods. The M-ZnO nanorod sensors had a fast response time of about 10 s, while the response time of the T-ZnO nanorod devices is about 16 s. At the present operating conditions, for all the ZnO nanorod sensors, it was noticed that the gas sensitivity increased with increasing concentration of ethanol in air. In conclude, it was found that the M-ZnO devices had an improved sensing performance in comparison with that of the T-ZnO sensors.

Feng et al. [36] reported the preparation and gas sensing properties of ultra-fine ZnO nanopowders from roasted zinc-blended. Ultra-fine ZnO powders with particle size of 20–30 nm was prepared from industrial roasted zinc-blended via liquid phase synthesis of basic zinc carbonate by chemical direct precipitation method followed by thermal decomposition. The gas sensing properties of ZnO sensor to ethanol, gasoline, cyclo-hexane, and *n*-hexane were measured using distribution in static state. The sensor was exhibited a higher degree of gas sensitivity at low temperature, and was a stable continuous operation and had quick response and recovery characteristics to ethanol gas. When the operating temperature is 335°C, the sensitivity increased to the maximum, which for ethanol were 37.45. The excellent gas sensitivity and selectivity was achievable at relatively low temperatures, and quick response and recovery properties were exhibited in the ethanol, circumstances that benefit from the ultra-fine particle size.

Feng et al. [37] reported the ethanol gas sensor based on the flowerlike ZnO nanostructures. Contact-controlled sensing was realized from flowerlike ZnO structures composed of rods. The rods were around 150 nm in diameter and upto a few micrometers in length. When they were exposed to air, a depletion region formed below the surface of the rods arising from the adsorption of oxygen. Surface depletion did not greatly reduce either the carrier density or the mobility in the rods but significantly modify the potential barrier of the contacts between the rods. The sensitivity was 1.6 for 0.5 ppm ethanol, and rose up to 11.4 for 50 ppm ethanol and 14.6 for 100 ppm ethanol. The sensitivity rapidly increased with increasing ethanol concentration below 200 ppm. The high-performance sensing was explained in terms of contact-controlled sensing. The present results indicated that contact-controlled sensing was promising in fabricating high-performance.

Stambolova et al. [39] reported the ZnO films doped with 3 at% La showed enhancement of ethanol sensitivity of 350, shorter response and recovery time of about 60 s at an operating temperature of 300°C.

Also, Rout et al. [40] reported the ZnO nanorods and nanowires doped with Pt also showed high sensitivity for 1000 ppm of ethanol at an operating temperature below 150°C, with short response and recovery time.

In addition, Zhu et al. [46] reported the pure ZnO nanorods and nano-needles produced by hybrid induction and laser heating (HILH) technique also showed capability to produce sensors with good sensitivity at a maximum temperature around 400°C for a concentration of 100 ppm of volatile organic compounds (VOCs) including acetone, toluene, and ethanol. 4.58 at% In/ZnO showed highest sensitivity compared to pure ZnO.

Furthermore, Chou et al. [47] reported Al/ZnO thin films were prepared by RF magnetron sputtering on Si substrate using Pt as interdigitated electrodes. The gas sensing results showed the sensor signal for detection 400 ppm ethanol vapor was about 20 at an operating temperature of 250°C.

Hsueh et al. [49] reported the growth of ZnO nanowires on ZnO:Ga/glass templates and the fabrication of laterally grown ZnO nanowire ethanol sensors. The average length and diameter of these ZnO nanowires were around 1 μm and 80 nm and the average length and diameter of these laterally grown ZnO nanowires were 6 μm and 30 nm. The ZnO nanowire ethanol gas sensor was measured to 1500 ppm at various temperatures. It was found that the highest sensitivity were 61% operated at 300°C when the concentration of injected ethanol gas was 1500 ppm. Therefore it was interesting to apply FSP for production of ZnO nanoparticles [65, 70] as used in gas sensor of ethanol vapor.

1.7.4 Ethanol sensor based on Pd-doped ZnO [43-46, 75, 76, 113]

Many researchers reported that the Pd-doped ZnO were widely used to detect several vapors i.e. hydrogen [139-142], ammonia [84, 143], LPG [144], CO [145] gases. In the other hands, a few researchers reported that the Pd-doped ZnO [43, 44, 146] were used to detect an ethanol vapors. In this case, several catalysts such as Pd, Pt, Rh, Ru or Ag are often added to improve selectivity and sensitivity [43-46, 75, 76, 113]. Pd is one of the most versatile and most widely applied catalytic materials and absolutely known to have a catalytic effect [43, 76, 113] due to its excellent oxidation capability to convert hydrocarbons at lower temperature. The details were described as follow;

Baruwati et al. [43] reported the highly crystalline ZnO nanoparticles were synthesized by hydrothermal route at 120°C over a range of different time periods. 0.1 wt% Pd was incorporated into the as-synthesized sample by dissolving PdCl₂ in water along with the sample and then calcining to decompose the PdCl₂. The gas sensing properties were studied towards reducing gases like liquefied petroleum gas (LPG), ammonia, hydrogen, ethanol, etc., and it was observed that the nanoparticles showed high sensitivity to LPG and ethanol at relatively low operating temperatures. 0.1 mol% Pd additive could be drastically decreased the operating temperature for maximum response by more than 100°C. It was found that the operating temperature at 170°C showed the high sensitivity, and shorter response and recovery time within seconds at the concentration of 200 ppm. The response and recovery times for LPG were found to be 100 s and 80 s, while for ethanol they were 60 s and 10 s, respectively. In addition, palladium is known to have a catalytic effect due to its excellent oxidation capability to convert hydrocarbons at lower temperatures making the sensor selective to hydrocarbons [43].

Rao et al. [44] reported the fabrication and the sensing performance of the ethanol sensor based on ZnO ceramic semiconductor doped with lanthanum oxide (La₂O₃) and palladium (Pd) loading. The ZnO powders were prepared by the hydrolysis method, and impregnated with an aqueous solution of lanthanum and palladium chlorides. The gas sensitivity was usually dependent on the sensor operating temperature and additive. It was evident from these results that the sensitivity of the undoped ZnO element was very poor compared to that of La₂O₃ doped in different concentrations. With 4 wt% loading of La₂O₃, the element showed a maximum sensitivity to ethanol vapors at an operating temperature of 200°C. For

increasing catalytic activity of the sensor, these elements were added with 1 wt% of Pd. Further, the operating temperature of the sensor was lowered to 175°C with improved response to ethanol vapor. Pd additive played an important role in improving the sensitivity. The best performance was obtained at 175°C with La₂O₃ and Pd additives. The sensor detected 1000 ppm ethanol in air with a maximum sensitivity of 85%, which was suitable for commercial use. Therefore it was interesting to apply FSP for production of Pd/ZnO nanoparticles [65, 70, 71] as used in gas sensor of ethanol vapor.

1.7.5 Ethanol sensor based on other metal-doped ZnO [41]

In 2000, Paraguay et al. [41] reported that the influence of several metal-doped ZnO thin film such as Al, In, Cu, Fe, and Sn on the response of ethanol gas sensor. In the experiment, a spray pyrolysis technique was used to obtain the metal/ZnO films. All nanopowders were characterized by scanning electron microscopy which used to study the microstructure and surface morphology of the films. The sensitivity of the films was studied in two steps: firstly as a function of their temperature (435-675 K) for a fixed ethanol concentration (40 ppm) and secondly as a function of ethanol concentration (4-100 ppm) for a fixed temperature (675 K). These sensitivities correspond to the saturation sensitivity obtained from the different measurements of sensitivity as a function of time for several temperatures at 40 ppm of ethanol concentration. It was found that presented the typical sensitivity performance as a function of time of tin-doped ZnO film 0.4 at%, for several ethanol vapour concentration and for a fixed temperature (675 K). It showed the maximum sensitivity of different doped ZnO thin films, for 80 ppm of ethanol vapour and for a fixed

temperature (675 K). It was found that the Sn-and Al-doped films with 0.4 at% and 1.8 at%, respectively, gave the highest sensitivity (more than 160).

1.8 Objectives of this research

This research concentrates on the synthesis of flame-made pure and Pd-doped ZnO nanoparticles and their characterization used as an ethanol vapor sensor. The main purposes of this study are:

- 1.8.1 To study the processing of pure and Pd-doped ZnO nanoparticles by FSP for use as an ethanol vapor sensor
- 1.8.2 To characterize the flame-made particles and gas sensing properties of pure and Pd-doped ZnO nanoparticles
- 1.8.3 To study the effect of dopant (Pd) concentrations on gas sensing properties of pure ZnO nanoparticles
- 1.8.4 To study the morphology of nanoparticles and sensing films on their gas sensing properties
- 1.8.5 To study the effect of film thickness on sensing properties
- 1.8.6 To improve the ethanol sensing properties