

## Chapter II

# Basic Theories of Solid/Gas Interfaces

In this chapter, the fundamental processes at the solid/gas interface will be discussed. The effects that lead to gas sensing mechanism are emphasized on the gas/semiconductor interface. Most of the processes described in this chapter are very important to understand the mechanism of semiconductor gas sensors.

### 2.1 Physical and Chemical Adsorption

Adsorption is referred to the situation in which *adsorbate* species is distributed between a solid phase (*adsorbent*) and a gaseous one[61]. In general, the distribution is temperature and pressure dependence, so completely empirical description is in terms of an adsorption function  $n$  or  $\theta = f(P, T)$ , where  $n$  is the number of adsorbate molecules and  $\theta$  is the surface coverage. There are two categories of adsorption: *physical adsorption (physisorption)* and *chemical adsorption (or more commonly chemisorption)*. Physisorption is weak adsorption (weak bonding, heat of adsorption is less than about  $6 \text{ kcal mol}^{-1}$ ), usually associated with van der waals interactions between the adsorbate and adsorbent. In this type of adsorption, there are many interest sites which depend on the size and nature of adsorbent-adsorbate interactions and on those between adsorbate molecules. Therefore, the adsorbate molecules possess some degree of freedom in movement (non-localized). For the stronger adsorption of chemisorption (strong bonding, heat of adsorption is comparable to chemical bond energies, greater than  $15 \text{ kcal mol}^{-1}$ ), normally a gas molecule must be dissociated into atoms and then have interactions with the surface atoms. The adsorbate tends to be localized at a particular sites (although some surface diffusion or mobility may still be present).

Chemisorption may be slow and the rate behavior indicates the presence of an activation energy,  $E_A$ . It may be possible for a gas to be physically adsorbed at first, and then have a chemical reaction with the surface of the solid. At low temperatures, chemisorption may be so slow that for practical purposes only physical adsorption can be observed, whereas, at high temperatures, physical adsorption is small, and only chemisorption occurs. A schematic adsorption isobar is shown in Fig. 2.1. Curve 1 shows the normal decrease in physical adsorption with temperature, and curve 2 is for chemisorption. In the transition region, curve 3, the rate of chemisorption is slow, but not negligible. The extension (dashed lines) of curve 2 represents the chemisorption at low temperature, however, because the rate of adsorption is negligible so in practice, equilibrium is not reached. The characteristics of physical and chemical adsorption are summarized In Table 2.1.

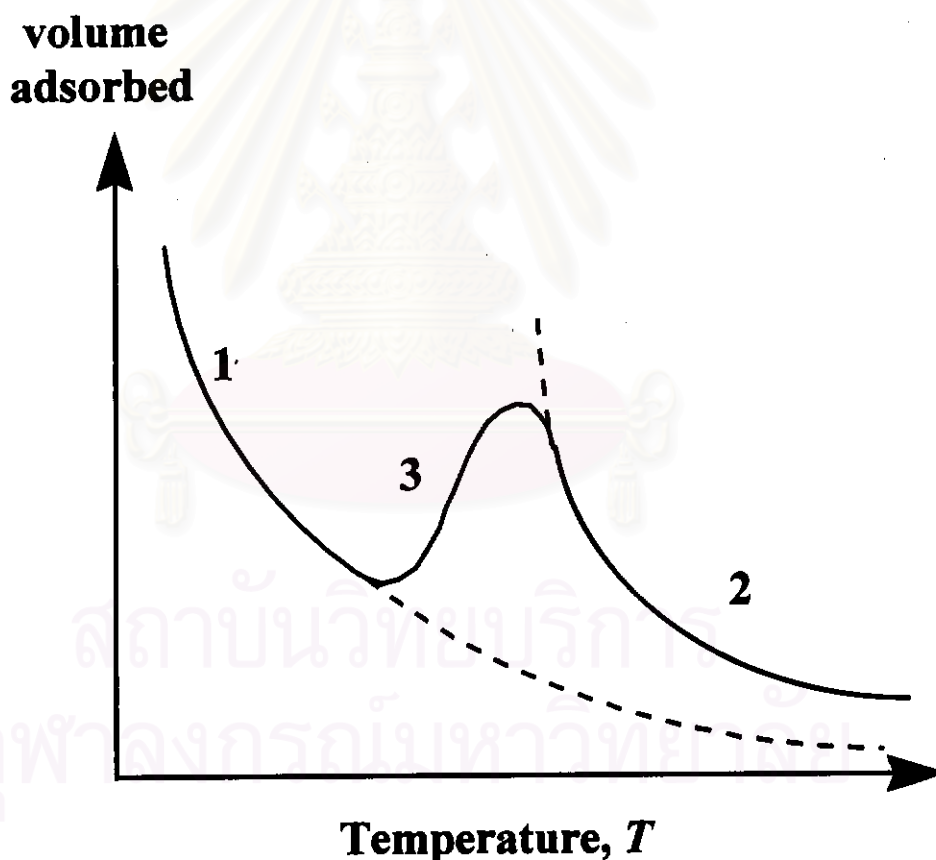


Fig. 2.1 Typical adsorption isobar.

Table 2.1 Characteristics of physisorption and chemisorption [62,4].

Physisorption	Chemisorption
Enthalpy of adsorption less than 6 kcal/mol <sup>-1</sup>	Enthalpy of adsorption greater than 15 kcal/mol <sup>-1</sup>
Adsorption appreciable only at temperature below the boiling point of adsorbate	Adsorption can occur at high temperatures
No peak in the isobar	Peak in the isobar
Multilayer adsorption occurs	Adsorption lead to a monolayer, at most
The amount of adsorption is more a function of the adsorbate than the adsorbent	The amount of adsorption is characteristic of both the adsorbate and the adsorbent
$d\theta/dp$ increases with increase in $p_{\text{adsorbate}}$ for multilayer	$d\theta/dp$ decreases with increase in $p_{\text{adsorbate}}$

Physical adsorption, with low binding energies and without any exchange of electrons between the adsorbate and the solid surface, is not relevant for gas sensors. However, charge transfer, variations of surface conductivity and surface potential can be induced by chemisorption involving chemical binding energies. *Ionosorption* is the case which there is no local adsorbate-to-surface atom bonding. However, the adsorbate acts as a surface state, capturing an electron or hole, and is held to the surface by electrostatic attraction. Ionosorption is very important in gas sensors, particularly the ionosorption of oxygen. There are also other ways that the gaseous species can effect the resistance of a semiconductor. These will be discussed in the section 2.4.

## 2.2 Semiconductor Surface

The surface is an imperfection in a sense even when it is *clean*. It is a region when the normal periodicity of the crystal is interrupted, and quantum analysis leads

to localized energy levels (*surface state*), often in the forbidden gap region. Such energy levels can capture or give electrons. In other words, they can be acceptors or donors or both. When the semiconductor is highly ionic as in the case of most metal oxides, where the metal can be considered to be a cation and the oxygen is the anion, then the surface metal ions have a tendency to capture extra electrons (act as acceptors), and the surface oxygen ions have a tendency to give electrons (act as donors).

There are also some practical conditions which surface states appear due to external factors[1], such as

- adsorption of gases from the atmosphere
- effects caused by a liquid brought into contact with the semiconductor surface
- adsorption of foreign atoms
- modification of the crystalline structure due to deviations from stoichiometry

Fig. 2.2 shows the energy band diagram including a surface, indicating that there are bands of surface state at the *n*-type semiconductor.  $E_c$  is conduction-band edge,  $E_v$  is valence-band edge, and  $E_F$  is Fermi energy level. The surface states are drawn as a band of energy levels of density  $N(E)$ . Here, two bands of energy levels are shown. There are unoccupied acceptor states, here termed A, while, D represents occupied donor states. In Fig. 2.2(a), there is no charge exchange between the semiconductor and the surface states. This is so-called *flat band* case. In this case, we note that the Fermi energy in semiconductor does not have necessarily any relation to the Fermi energy of surface states,  $E_{F_{ss}}$ . Whereas in Fig. 2.2(b), the equilibrium is shown. Electrons have moved from the region of high  $E_F$ , the near surface region of the semiconductor, to the region of low  $E_{F_{ss}}$ , the surface states. The separation of charges leads to the formation of a *double layer*, with the positively charged donor ions in the semiconductor as *space-charge layer* or *depletion layer* on one side, and the negatively charged surface states as a sheet of charges on the other side. According to this space-charge layer, an electric field develops between these two charge layers.

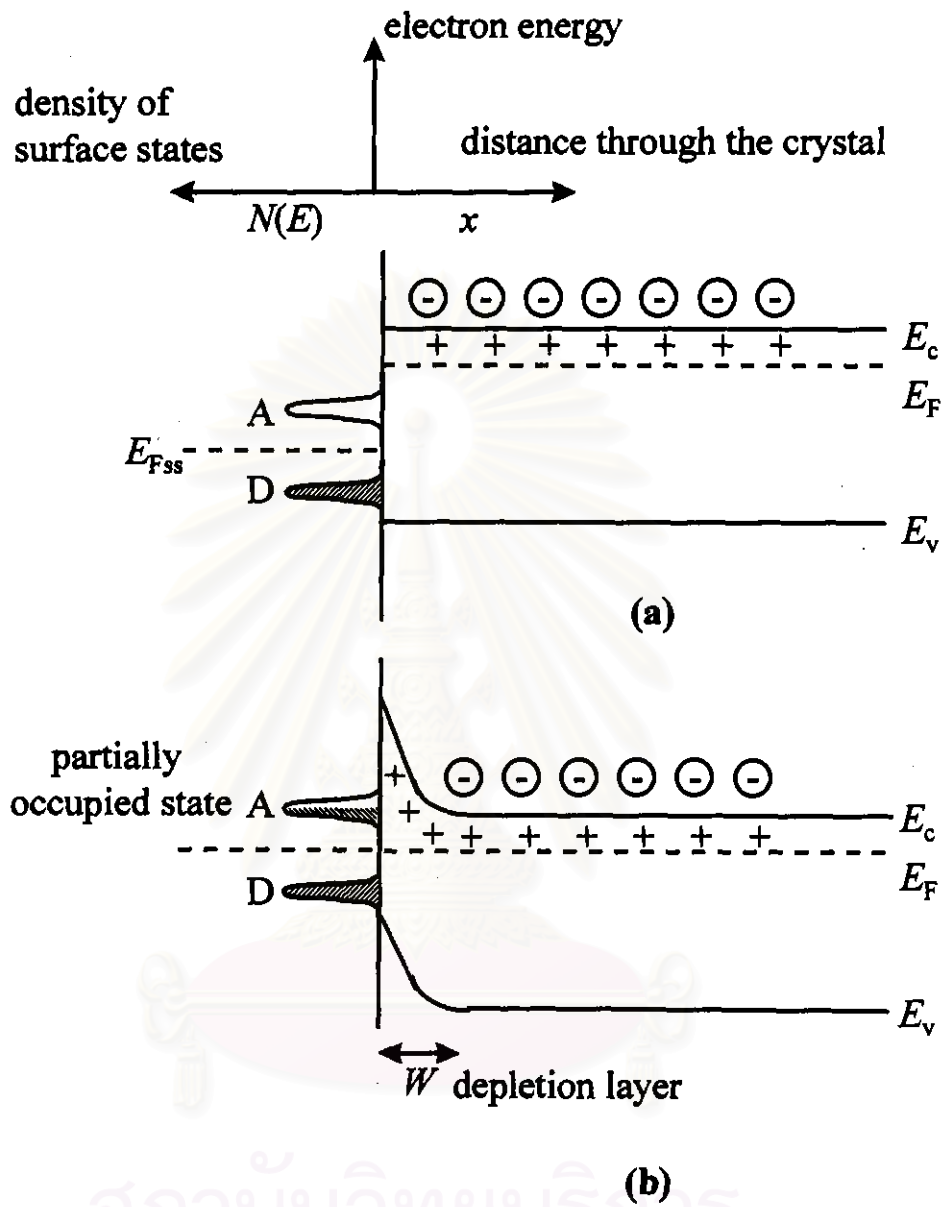


Fig. 2.2 Surface state bands at the  $n$ -type semiconductor surface (a) no charge exchange between the semiconductor and the surface states (flat band condition), (b) the band bending when electrons from the surface region of the semiconductor have moved to the surface states to reach equilibrium.

By consider the one-dimensional Poisson equation[63] we obtain

$$\frac{\partial^2 V}{\partial x^2} = -\frac{q}{\epsilon\epsilon_0} [p(x) - n(x) + N_D(x) - N_A(x)], \quad (2.1)$$

where  $q$  is the electronic charge,  $x$  is the distance from the semiconductor surface,  $V$  is the potential,  $p$ ,  $n$ ,  $N_D$  and  $N_A$  are the concentration of hole, electron, donor ion and acceptor ion in the space charge region, respectively. Here  $\epsilon$  is the dielectric constant of the semiconductor, and  $\epsilon_0$  is the permittivity of the free space. By using the abrupt junction approximation and we assume that the  $n$ -type semiconductor contains no acceptors, and the distribution of the concentration of the fully ionized donors is uniform ( $N_D(x) = \text{constant}$ ). Eq. (2.1) can be expressed as follows.

$$\frac{\partial^2 V}{\partial x^2} \approx -\frac{q}{\epsilon\epsilon_0} N_D \quad (2.2)$$

The solution of this equation is

$$V(x) = V_0 - \frac{qN_D x^2}{2\epsilon\epsilon_0}, \quad (2.3)$$

where  $V_0$  is the potential difference between the surface and the bulk. We can find  $W$  which satisfies the condition:  $V(W) = 0$ , where  $W$  is the thickness of the space-charge region. The thickness of the space-charge is determined by the distance necessary to compensate all the surface charge. At  $x \geq W$  the semiconductor is uncharged. Thus the condition of electrical equilibrium (charge compensation) in eq. (2.4) must be fulfilled.

$$N_D W = N_s, \quad (2.4)$$

Where  $N_s$  is the amount of charge per unit area at the surface. We can use this condition to find  $V_0$  as in eq. (2.5).

$$V_0 = \frac{qN_s^2}{2\epsilon\epsilon_0 N_D} \quad (2.5)$$

This is an important relation describing the potential difference between the surface and the bulk as a function of the amount of charge on the surface. The energy  $qV_0$  is the energy that electrons must attain before they can move to surface energy levels, and is so-called *potential barrier*. In the above, we have assume that the charge to be on *clean* surface, this charge is equivalent to the charge associated with the adsorbed oxygen (e.g.,  $O_2$ ), which is very interest for semiconductor gas sensors operating in air. The density of electrons at the surface on an  $n$ -type semiconductor,  $n_s$  is given by  $N_D$  multiplied by the Boltzmann factor involving  $qV_0$ .

$$n_s = N_D \exp \left[ - \left( \frac{q^2 N_s^2}{2\epsilon\epsilon_0 kTN_D} \right) \right] \quad (2.6)$$

It is clear that the separation of charge in the space-charge layer accompanies with a capacitance. The capacitance per unit area,  $C$  is analogous to that of a parallel plate capacitor which is given by

$$C = \frac{\epsilon\epsilon_0}{d}, \quad (2.7)$$

here  $d$  is the separation of the parallel plate, for our case,  $d = W$ , as given in eq. (2.5). From eqs. (2.5) and (2.7), we can derive the expression of  $C$  as follows.

$$C = \sqrt{\frac{qN_D\epsilon\epsilon_0V_s}{2}} \quad (2.8)$$

In the above, we have discussed the depletion layer, where the majority carrier (electrons in  $n$ -type, holes in  $p$ -type) is captured at the surface, thus giving rise to a double layer between the captured surface charge and the donor (or acceptor) ions remaining behind near the semiconductor surface. This is the usual situation for semiconductor gas sensors.

## 2.3 Effect of Gas Adsorption on Electrical Parameters

In the previous section, the effect of surface charge on the band structure of a semiconductor was discussed. It was shown that the capture of electrons or holes at the surface has a major effect on the surface potential barrier,  $qV_0$ . Here, we will focus on the effect of adsorbed gases, mostly the effect of adsorbed oxygen, on the semiconductor surface properties. In this section, we will describe the electrical properties or quantities that are affected by gas adsorption processes.

(a) electrical resistance: The presence of surface states (or adsorbed gases), which induces a depletion layer at the semiconductor surface, leads to the important changes in the resistance of the semiconductor. For the simplest way, let consider a thin film with no intergranular resistance, or a single crystal. In Fig. 2.3 shows how bulk and surface conductance are connected in parallel.

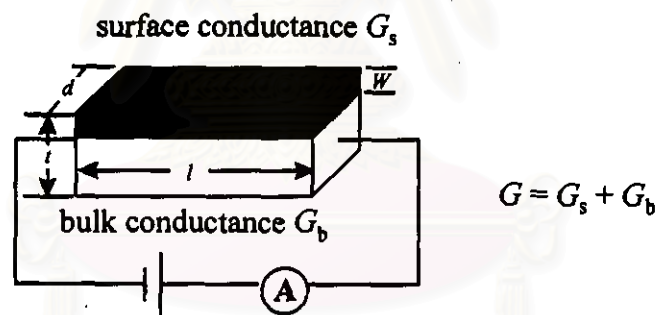


Fig. 2.3 Schematic drawings demonstrating the parallel connection of the surface conductance with the bulk conductance.

The total conductance of the thin film is given by

$$G = G_s + G_b, \quad (2.9)$$

where  $G_b$  is the bulk conductance and  $G_s$  is the surface conductance. If we assume that  $G_b \geq G_s$ , or  $G \approx G_b$  then the conductance of the thin film with bulk conductivity,  $\sigma$  and  $t$ ,  $l$  and  $d$  are thickness, length and width of the thin film gas sensor respectively, can be written as follows.



$$G \approx G_b = \sigma \left( \frac{d \cdot t}{l} \right) \left( 1 - \frac{W}{t} \right) \quad (2.10)$$

It is noted that  $W$  is the thickness of the depletion layer, and assuming only one side of the thin film is exposed to the atmosphere. It is clear from eq. (2.10), the conductance of the thin film is determined by  $W$ , which varies with  $N_s$ .

(b) capacitance: It is clear from eq. (2.7) that a variation of  $W$  due to the gas adsorption causes the change in the sensor capacitance. However, this parameter can be only measured by AC measurement.

(c) work function: The work function has a direct relation with the potential barrier  $V_o$ . The work function,  $\phi$  is defined as the energy required to move an electron at the Fermi level to the vacuum outside a material. Thus, the monitoring of  $\phi$  of the surface under investigation can give important information concerning about the nature of the gas adsorption on the surface as well as the adsorption-desorption process[2]. The work function changes,  $\Delta\phi$  upon the adsorption of gas can be express as follows[64].

$$\Delta\phi = -q\Delta V_o + \Delta\chi + \Delta(E_c - E_f)_b \quad (2.11)$$

Where  $\chi$  is the electron affinity of semiconductor. Many techniques can be used for measuring work function changes, such as retarding potential[84] and Kelvin probe or vibrating capacitor[64]. The shift of work function can also be measured by employing the GasFETs structure.

In summary, we have discussed three measurable quantities which relate to the amount of adsorbed gas on the semiconductor surface. The change of electrical resistance or conductance by gas adsorption is the case of interest because of its simplicity in sensor structure and circuit interface.

## 2.4 Interaction of Gas Species with Semiconductor Surface

There are many ways that the gaseous ambient can change the conductivity of a semiconductor. Some of these are unacceptable for the application of gas sensors, for example, the growth of an oxide film, or any other irreversible surface reaction or bulk reaction, thus such reactions must be avoided as much as possible. However, there are various reactions which are acceptable and have been used in semiconductor gas sensors. Some of these will be discussed in details.

### 2.4.1 Adsorption and reaction with surface state

The gas species can be directly adsorbed on the semiconductor surface. If it is a reducing agent, it gives one or more electrons into the semiconductor. If it is an oxidizing agent, it extracts one or more electrons from the semiconductor. In either case, if the semiconductor has a high surface area and its bulk carrier density is low, the excited carriers can change the effective number of carriers in the solid many folds.

Here we will consider the adsorption of oxygen on semiconductor. Oxygen can be ionsorbed in several formed:  $O_2^-$ ,  $O^-$  and  $O^{2-}$ . However, the study of electron spin resonance indicated that the form of  $O^-$  is more reactive than the others[4]. Adsorbed oxygen is a dominant contributor to the negatively charged surface state referred to eq. (2.5), providing the surface charge  $qN_s$ . When gas sensors are operated in air, oxygen is strongly adsorbed and the negatively charged oxygen dominates the surface charge. The adsorption of oxygen increases the values of  $V_0$  which leads to a high resistance in  $n$ -type semiconductors. Figure 2.4 shows a band model for the surface of an  $n$ -type semiconductor with adsorbed  $O^-$ . When this system comes to the equilibrium, a double layer has formed. The charge transfer process shifts the Fermi energy at the surface to a position of the adsorbed  $O^-$  energy level. The chemical reaction at this state may be described as follows.



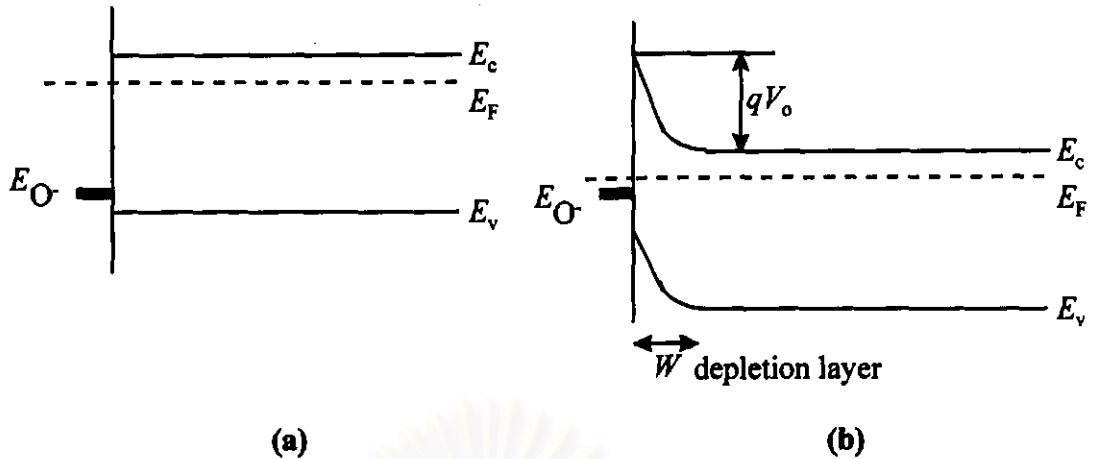


Fig. 2.4 Sketch showing the variation of  $E_F - E_{O^-}$  with  $qV_0$ ; (a)  $qV_0 = 0$ , flat band case,  $[O^-] = 0$ ; (b) equilibrium adsorption.

The reason why, various gases other than oxygen are sensed by  $n$ -type materials, can not be explained by the simple adsorption mechanism. This is because when the measurement is performed in air, oxygen is already adsorbed on the surface of the semiconductor. The adsorption of other gases is normally not a simple adsorption, but the adsorption occurs through a reaction with the surface state associated with pre-adsorbed oxygen. It is found that reducing agents, R such as  $H_2$ ,  $CH_4$ ,  $C_2H_6$ , and  $CO$  interact with the adsorbed oxygen atoms as can be shown in eq. (2.13).



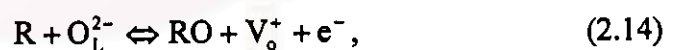
Thus, if a reducing agent is present in the atmosphere, the dynamic equilibrium will be established between the reaction of eqs. (2.12) and (2.13). In other words, oxygen is being adsorbed at a particular rate, but is being removed by reaction with a reducing agent. Since the values of  $V_0$  or the height of potential barrier is determined by the amount of adsorbed oxygen and this amount determines the sensor conductance.

### **2.4.2 Ion exchange[9]**

Another mechanism of the surface interaction between a gas and a semiconductor that will have a strong influence on the conductivity of the semiconductor is ion exchange. There is an observation that when  $\text{WO}_3$  is exposed to  $\text{H}_2\text{S}$  at 340 to 400 °C, a surface layer of  $\text{WS}_2$  is formed[9]. It also has been suggested that ion exchange is the reaction that dominates  $\text{H}_2\text{S}$  sensors based on  $\text{WO}_3$  and  $\text{SnO}_2$ , when thin films are used and the conductance of the film increases with the partial pressure of  $\text{H}_2\text{S}$  in air.

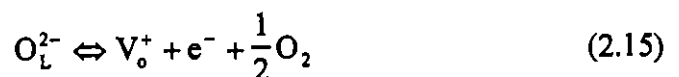
### **2.4.3 Reduction/oxidation of the semiconductor**

The processes described in the two previous subsection are the surface processes. In addition, at adequately high temperatures, the changes in the bulk stoichiometry of an oxide can occur due to the high diffusion of defect[18,65,66]. As the time elapses, an equilibrium between the bulk defect concentration and the ambient gas will be finally established. There are two major ways in which change the bulk stoichiometry of an oxide. One is the extraction of lattice oxygen (reduction) by reducing agents in the ambient atmosphere. This leaves oxygen vacancies and one or more conduction electrons. A reaction as in eq. (2.14) may occur



where  $\text{O}_L^{2-}$  is the oxygen ion in crystal lattice and  $\text{V}_o^+$  is the oxygen ion vacancy.

The other is the extraction of oxygen by the simple dissociation of the oxide as shown in eq. (2.15).



In this reaction, there are two points of interests for gas sensing. One is the possibility of using this reaction as an oxygen pressure sensor. This mode of operation is at sufficiently high temperatures, which the diffusion constant of oxygen defect is highly enough to diffuse rapidly into the bulk of semiconductor materials.

ZrO<sub>2</sub> and TiO<sub>2</sub> are the excellent examples where oxygen dissociation is utilized in the oxygen sensing. The other is a reaction that will occur on the semiconductor at the moderate operating temperature, usually leading to slow and irreversible changes in the resistance of the sensors. Because the diffusion rate of the oxygen vacancy is small but not negligible. This is a highly undesirable results. For the stable sensitivity of an oxide semiconductor gas sensor, normally one prefers an oxide that is not reduced or oxidized as shown in eqs. (2.14) and (2.15). This situation refers to the condition at low enough temperatures, at which the diffusion constant is near zero, the vacancies remain at the surface and the reduction/oxidation with other gases can occur rapidly so that the sensor resistance can come quickly to steady state. In a real sensor, a mixed situation between surface and bulk reaction may occur simultaneously.

In summary, semiconductor gas sensors can be employed for two distinct types of application in gas sensing.

(1) for monitoring atmospheres, in which the primary variable parameter of interest is the partial pressure of oxygen (*Bulk conductance effects*). This is a bulk conductance change which occurs at a high temperature region.

(2) for monitoring the concentration of minor constituents of an atmosphere, normally in air, in which the oxygen partial pressure remains effectively constant. (*Surface conductance effects*) This is a surface conductance change which occurs at a low to intermediate temperature region.

## 2.5 Catalysts

For gas sensors, the catalysts are normally supported on a semiconductor. The *support* is the gas-sensitive oxide whose conductivity can be changed by ambient gases as discussed in the previous section. The catalysts are usually dispersed as small crystallites on the surface of relative large grains of sensor material (SnO<sub>2</sub>, TiO<sub>2</sub> etc.). The catalysts is deposited to speed up the change in the resistance or to improve the selectivity of the system toward certain gases. There are many metallic and nonmetallic catalysts that could be supported on the semiconductor surface. Some of the metallic catalysts are the noble metals such as Pd, Pt and Ag[49,53.85]. On the

other hand, many oxides such as  $V_2O_5$ ,  $Co_2O_3$ ,  $Cu_2O$  and  $NiO$ [42,67] show catalytic activity. There are two possible ways in which supporting semiconductor and catalyst can interact to each other. That are spill over and Fermi energy control.

*Spill over* is a well known effect in heterogeneous catalysis, which probably occurs most often when metallic catalysts, such as Pd and Pt, are used. Spill over is a mechanism where by the oxidation of the reducing agents can be accelerated on the semiconductor by the presence of dispersed metallic catalysts. Hydrogen spill over has been extensively studied. Fig. 2.5 illustrates the phenomenon that catalyst particles are being adsorbed by  $H_2$  and  $O_2$ . The catalyst dissociate  $H_2$  and  $O_2$  into H and O atoms and allow them to spill over onto the support. In the case of gas sensor, the support is the semiconductor whose electrical properties are changes by active oxidation reactions going on its surface.

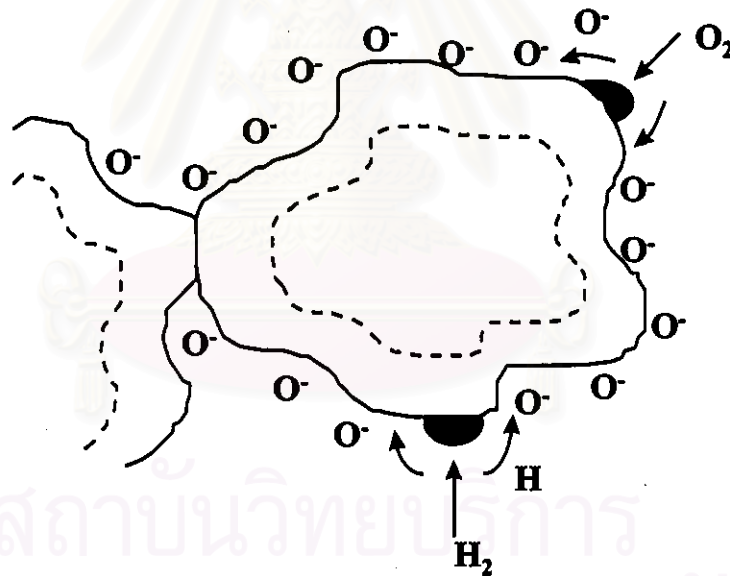


Fig. 2.5 Spill over of hydrogen and oxygen by the deposited catalyst onto the semiconductor support.

By *Fermi energy control*, we are referring to the case where the catalyst pins the Fermi energy of the semiconductor at the Fermi energy of the catalyst. In section 2.2, we have shown that the Fermi energy will be pinned at the surface if surface

states are present. In this case, when a catalyst is deposited on the surface of the semiconductor, surface states will be formed and the catalyst will control the potential barriers. Fig. 2.6 illustrates how a dispersed catalyst will affect the extension of the depletion layer. The oxygen ions, which are adsorbed directly on the semiconductor surface, are neglected. In order to obtain that situation, the catalyst should be dispersed over the semiconductor surface as widely as possible so that the potential barrier extends throughout the whole grain. In summary, if the catalyst dominates as a surface state, it controls the band bending in the semiconductor and therefore, controls the conductance of the semiconductor in the same way as the adsorbed oxygen or other adsorbate. This is the normal model of the semiconductor. The Fermi energy of the catalyst will change if the concentration of oxygen, which is adsorbed onto or adsorbed into the clusters of the catalyst, is changed. This leads to a change in donor density or The processes on the catalyst surface affect the conductivity of the semiconductor support. This will occur due to oxygen adsorption and an oxidation reaction on the catalyst without any appreciable chemical reaction necessary on the surface of the semiconductor.

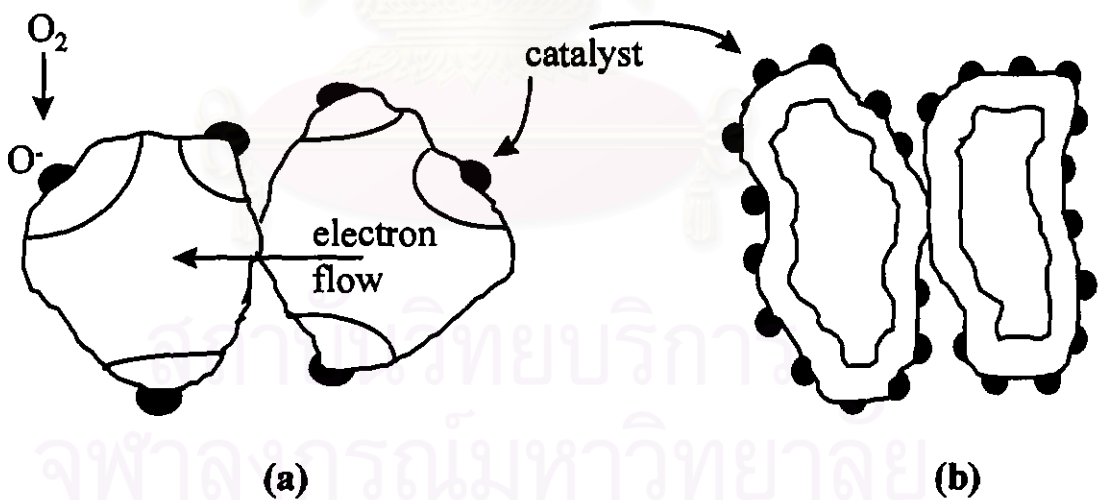


Fig. 2.6 Catalyst dispersion over the grain surface: (a) insufficient dispersion of the catalyst, (b) the whole grain surface covered with the catalyst.

## 2.6 Conduction Mechanism of Semiconductor Gas Sensors

Most of semiconductor gas sensors are in the polycrystalline form with different grain size, the different models for the conduction mechanism are shown schematically in Fig. 2.7. Here the surface processes, which remove or increase the surface conducting electrons as described above, dominate the sensor resistance. If the grains touch each other without sintering to form a neck, the electrons (for  $n$ -type materials) must flow over a surface barrier from one grain to the next. In the other case, the sample can be sintered and the *necks* will be formed between adjacent grains. Then these necks are the resistance-controlling feature of the sensors. The adsorption of a gas modulates the width of the channel through which current flows. In practical, we will have a mixed effect of grain and neck controlled resistance.

By considering the thickness of depletion region,  $W$  compares to the diameter of the grain,  $D$ , the conduction mechanism can be classified into three models[67].

(1)  $D \gg 2W$ : grain-boundary-controlled conduction (sometimes called Schottky-barrier-limited-electronic conduction), the depletion layer affects the local electron concentration of the conduction path at the grain boundary contact.

(2)  $D \geq 2W$ : neck-controlled conduction, the adsorption of a gas changes the width of the conduction channel so narrow that the necks become the most resistance.

(3)  $D < 2W$ : grain-controlled conduction, the whole grain is governed homogeneously by the depletion layer. Here, the conduction mechanism is controlled by the bulk resistivity itself. In this case, the band bending ( $qV_0$ ) is a function of the grain diameter since the space charge neutrality in eq. (2.4) must be satisfied. This means that for the small grain, by solving the Poisson equation in the spherical coordinate, the chemically induced change of the band bending is smaller than for the larger grain[86] as shown in eq. (2.16).

$$V_0 = \frac{qN_D D^2}{24\epsilon\epsilon_0} \quad (2.16)$$



## 2.7 Summary

In this chapter, the mechanisms involving gas adsorption were summarized. This basis is necessary to understand the operating of semiconductor gas sensors. Most of materials were devoted to the interaction between semiconductor and gas. Semiconductor and the development of surface state were described in details. The possible semiconductor/gas interactions, by which the electrical conductance of a semiconductor can be affected, were considered. Finally, catalysts was considered as the method to increase selectivity of gas sensor and conduction mechanism of fine grain of an oxide material was demonstrated.

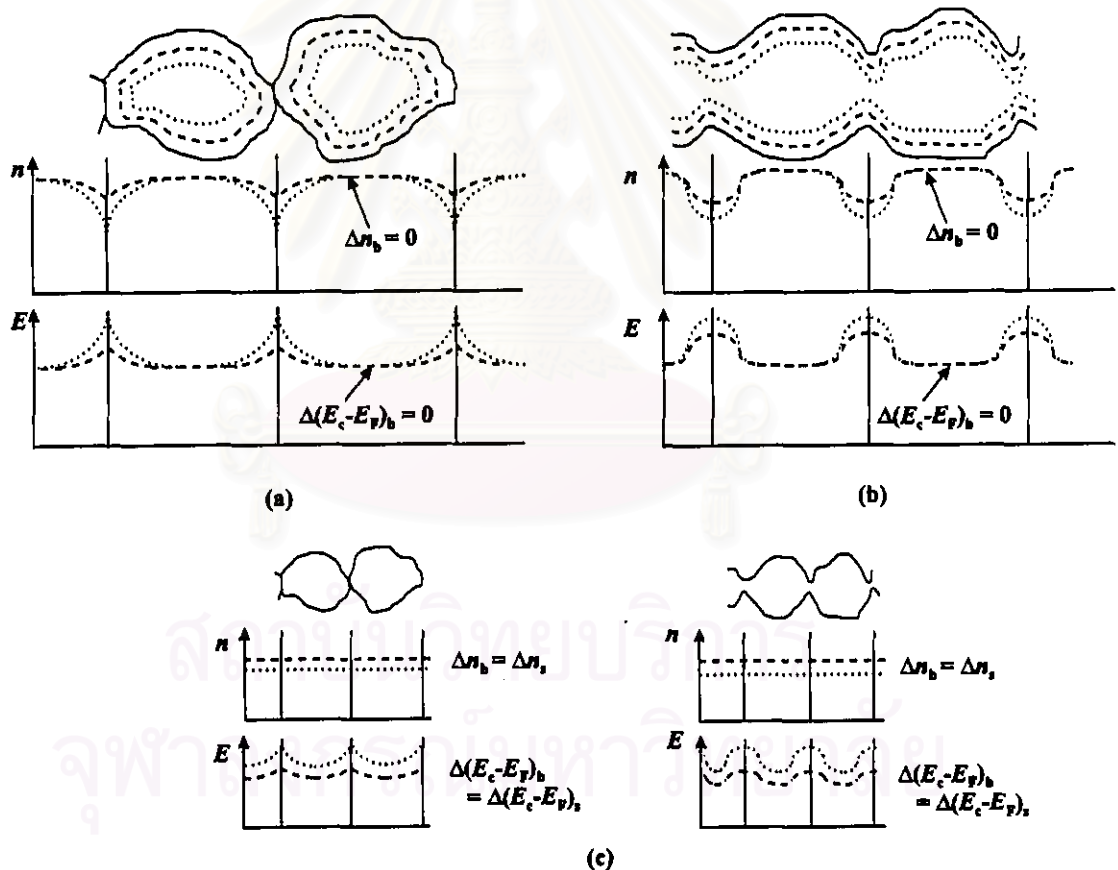


Fig. 2.7 Schematic diagram of conduction mechanism, the dot lines and the dash lines represent the situation in air and gas respectively: (a) grain boundary-controlled conduction; (b) neck-controlled conduction and (c) grain controlled conduction.