CHAPTER 2

Theory of MOS Sensors

This chapter briefly describes the phenomenon of gas adsorption on the solid surface and then elaborates the operation principle of MOS gas sensor. The theory of MOS capacitor with its gas sensing mechanism has been discussed.

2.1 MOS (Metal-Oxide-Semiconductor) Structure

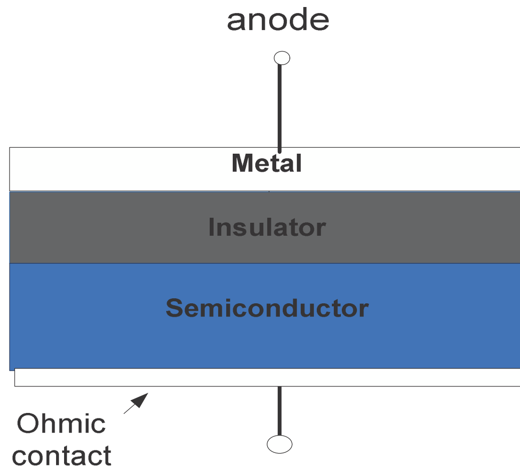
In 1975 Lundstrom *et al*. [Lundstrom *et al*. (1975)] invented first MIS-FET sensor. They observed that MIS-FETs with a catalytic metal as the gate can be used as hydrogen sensor. Another breakthrough was made by inventing a porous metal film which makes the structure sensitive to gases such as NH_3, not detected with MIS-sensors with thick metal film [Spetz *et al.* (1983); Winquist (1983)]. Field effect gas sensor operates by employing the concept that electrical field distributions in such devices get modulated in accordance to the exposure of gas. The structure of the device consists of junctions of metal, insulating and semiconducting materials. Direct measurements of current, capacitance and conductance are made as function of bias voltage, and important parameters including barrier height, interface state density, fixed charge density etc. may be evaluated from them. The degree of dependency of these parameters on the composition of gas actually determines the sensitivity of the device towards a particular species of gas.

The MIS sensor structure has a catalytically active and hydrogen permeable gate contact. These devices are classified into two categories: metal-oxide-semiconductor capacitor (MOSCAP) and metal -oxide-semiconductor field effect transistor (MOSFET) shown in Fig. 2.1. In the present work only MOS capacitors have been used as a gas detector, hence principle of operation and gas sensing mechanism of MOS capacitor has been described exclusively.

2.2 MOS Capacitor

A MOS capacitor consists three layers: the metal gate electrode, the insulating oxide layer and p-type bulk semiconductor (Si), which is called substrate. In the MOS capacitor, the supply of charge carriers is limited and the compensating sheet of

charge may appear at various depths within the semiconductor depending on the applied voltage where as in the conventional capacitor metallic plates are abundant source of charge carriers, and the charge appears in a very thin sheet at the conductor surface.



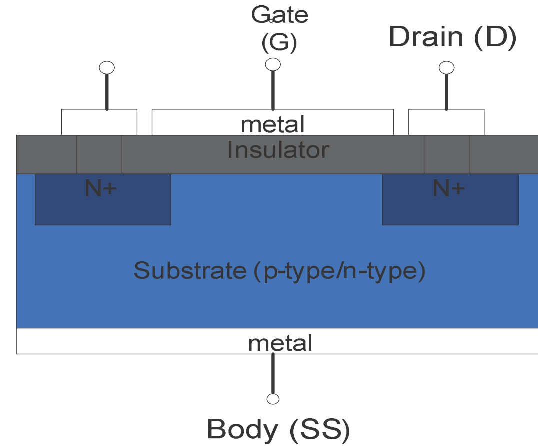


Fig. 2.1(a) MOS Capacitor **Fig. 2.1(b)** MOSFET

Fig. 2.1 Various MOS devices used as gas sensors [Sze (1987)]

2.2.1 An Ideal MOS Structure

An ideal MOS capacitor fabricated on p-type substrate is shown in Fig. 2.2. When a negative voltage (-V) is applied to the metallic gate, the majority carriers (holes) attracted to the semiconductor-oxide interface (Fig. 2.3a). In this condition, the majority carriers concentration near the surface becomes larger than the equilibrium hole concentration in the substrate and hence this condition is known as carrier accumulation. Since the accumulation of the holes takes place at the semiconductor surface, the surface conductivity is increased. In this region, MOS capacitor behaves just like a conventional capacitor with a layer of charge at the interface and capacitance per unit area is given by

$$C_O = \frac{K_O\, \varepsilon_O}{X_O} \tag{2.1}$$

Where, ε_o -free space permittivity, K_o- dielectric constant of the oxide, X_o- thickness of the oxide layer.

Now consider the next case where a small positive voltage is applied to the gate electrode, the majority carriers (holes) are repelled back into the substrate i.e away from the oxide-silicon interface, establishing a space-charge region consisting of static negative acceptor ions (Fig 2.3 b). This region is called depletion region. The space-charge of the depletion layer acts as another capacitor C_d in series with oxide capacitance C_0, giving an overall capacitance.

$$\frac{1}{C} = \frac{1}{C_o} + \frac{1}{C_d} \tag{2.2}$$

Where, C= equivalent capacitance of MOS capacitor, C_o = oxide capacitance,

C_d = depletion capacitance

$$C_d = \frac{K_S \varepsilon_O}{x_d} \tag{2.3}$$

Where, K_s - dielectric const. of the semiconductor, x_d - depth of depletion layer

ε_o - free space permittivity

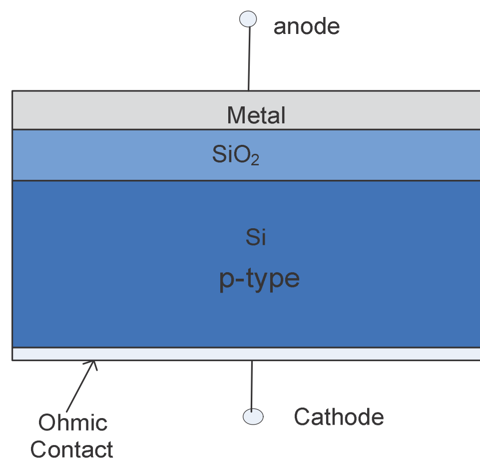


Fig 2.2 Cross sectional view of MOS capacitor [Sze (1987)]

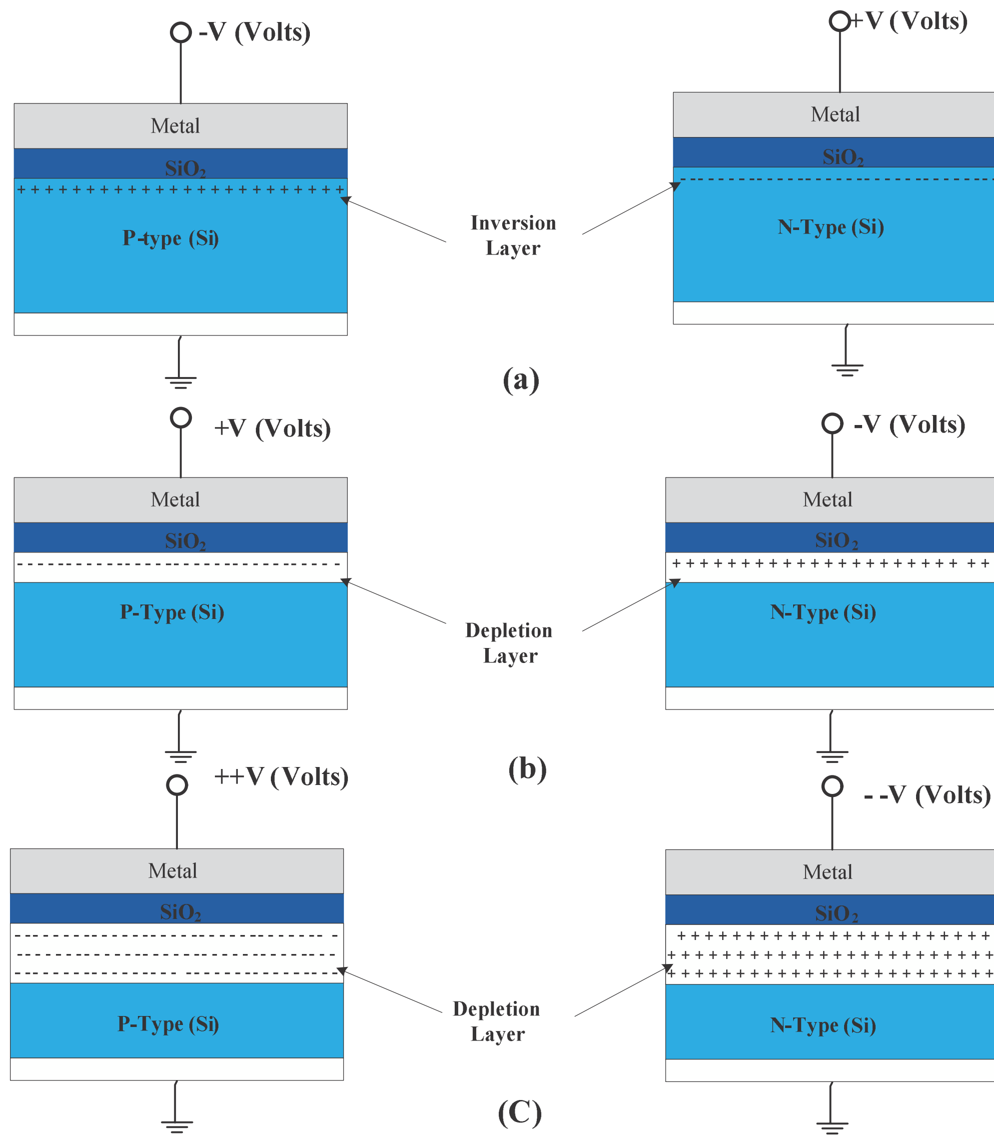


Fig 2.3 The charge distribution in p- type (left) and n-type (right) Si in

(a) accumulation (b) depletion and (c) inversion region [Salomonsson (2005)]

If the gate bias voltage is more positive which increases depletion layer and decreases the overall capacitance. In condition of depletion, though the majority carriers (holes) are repelled but minority carriers (electrons) get attracted. When sufficiently large positive gate voltage is applied this effect predominates and the semiconductor enters into inversion region as shown in Fig. 2.3c. In inversion region number of minority carriers (electrons) at the surface finally becomes larger than the number of majority carriers (holes) and this condition is called surface inversion and the surface effectively becomes n-type. The maximum width of depletion layer $X_{d,max}$ before inversion occurs is given by;

$$x_{d,\max} = \sqrt{\frac{2K_S \varepsilon_O \Psi_S}{qN_A}} \tag{2.4}$$

Where,

ψ_s - surface potential, qN_A - charge density in the depletion region, K_s- dielectric const. of semiconductor

A simple equivalent circuit of such MOS capacitor is shown in Fig. 2.4. At zero bias voltage there is no deletion layer underneath the silicon dioxide layer (silicon surface), and the overall capacitance (C) is equal to accumulation capacitance (C_0).

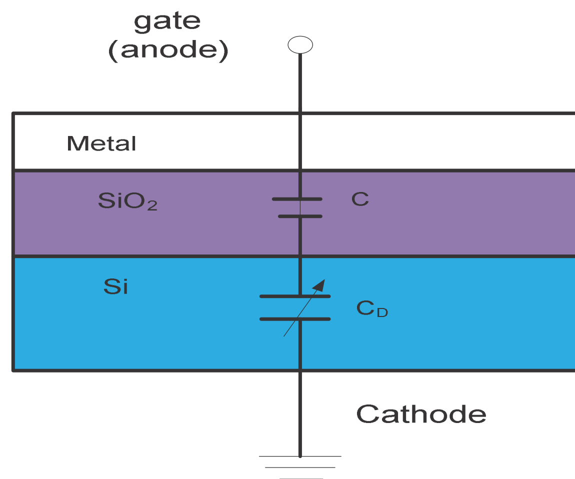


Fig. 2.4 Equivalent circuit of MOS capacitor [Nicollian and Brews (1982)]

Once inversion starts, additional charge on the gate electrode is balanced by negative charge (electrons) in the semiconductor. If capacitance is measured using high frequency signal, the minority carriers (electrons) can not follow the applied alternating voltage and the formed depletion region will not change when the voltage is further changed as rapid change interchange from the bulk is not possible at higher frequencies. Then the capacitance is given by the following formula:

$$C = \left(\frac{1}{c_o} + \frac{1}{K_s \dfrac{\varepsilon_o}{x_{d,\max}}} \right)^{-1} \tag{2.5}$$

If a low frequency (≤ 100 Hz) is used in C-V measurement then these minority carriers can move to semiconductor surface which reduces the depletion layer width and thereby the capacitance increases again [Sze (1987)].

For n- type MOS capacitor accumulation and depletion conditions occur at positive and negative bias voltage respectively and inversion occurs at higher negative voltage. The charge distribution in n- type device is shown in Fig. 2.3. From the view of band theory, the space charge created during the three separate modes (accumulation, depletion and inversion) of MOS capacitor corresponds to band bending in the energy band diagram of MOS structure. The energy band diagram of an ideal MOS structure for V_G=0 is shown in Fig. 2.5. For an ideal MOS structure, with no applied voltage at the gate, the work function difference between metal and semiconductor is supposed to be zero [Sze (1987)].

$$\Phi_{ms} = \Phi_m - \left(\chi + \frac{E_g}{2q} - \Psi_B \right) = 0 \qquad \text{for n-type} \tag{2.6}$$

$$\Phi_{ms} = \Phi_m - \left(\chi + \frac{E_g}{2q} + \Psi_B \right) = 0 \qquad \text{for p-type} \tag{2.7}$$

Where,

Φ_m- metal work function, χ - semiconductor electron affinity, E_g - energy band gap,

Ψ_B - potential difference between the fermi level E_F and the intrinsic fermi level E_i.

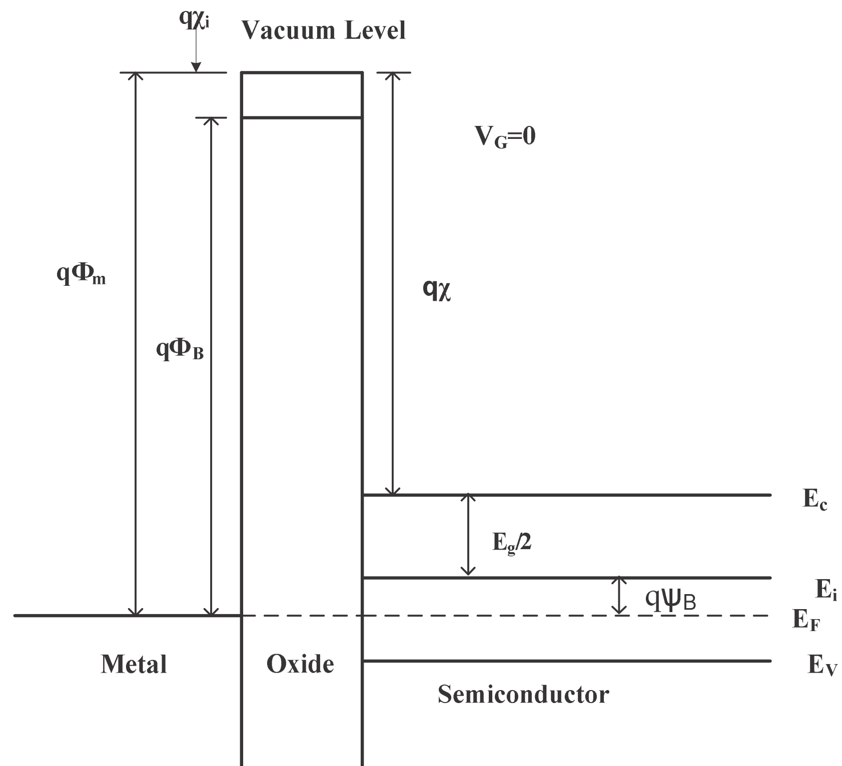


Fig 2.5 Energy band diagram of an ideal MOS structure at V_G = 0 V for p-type semiconductor [Sze (1987)]

For zero Bias Gate Potential (V_G = 0 Volts): The energy bands of ideal MOS structure remains flat (as shown in Fig. 2.5) as the work function remains constant and there is no charge transfer takes place with the assumption that is no charge available inside the oxide or at the interface between oxide and the semiconductor.

Under Bias Condition: An electric field E_0 is established between the plates of an ideal MOS capacitor, which causes the displacement of mobile carriers near the surface of each plate, giving rise to two space charge regions. The density of the induced charge Q_s is given by Gauss's law:

$$-Q_s = K_o \varepsilon_o E_s = K_s \varepsilon_o E_s \quad (2.8)$$

Where, ε_o – free space permittivity

K_o – dielectric constant of free space

E_s – electric field at semiconductor surface

K_s – dielectric constant of semiconductor

Neglecting the voltage drop in the metallic gate, the applied voltage will partly appear across the insulator and partly across the silicon substrate. Thus,

$$V_G = V_i + \psi_s \tag{2.9}$$

Where, V_G is gate voltage (V), V_i is the potential across the insulator and ψ_s is the surface potential.

The electric field that exists in the semiconductor modifies the band diagram and establishes a space charge region beneath the surface. Depending on the polarity of applied voltage three surface conditions (accumulation, depletion and inversion) can arise as they have been already described previously. The energy band diagram of an ideal MOS structure in three regions or surface conditions is shown in Fig 2.6. Under the thermal equilibrium condition, the carrier densities in p-type and n-type semiconductor are given by the following equations.

$$n = n_i e^{\frac{E_f - E_i}{kT}}; \tag{2.10}$$

$$p = n_i e^{\frac{E_i - E_f}{kT}}; \tag{2.11}$$

Where, E_f -fermi energy level, E_i - intrinsic energy level, k- Boltzmann's const.,

T- temperature in Kelvin (K)

These equations are used to determine the carrier concentration at the surface under different biasing voltages on the MOS structure.

Fig. 2.6 shows three surface conditions i.e accumulation, depletion and inversion. These conditions have been discussed below in brief.

(a) Condition of Carrier Accumulation

The condition of carrier accumulation is achieved when the carrier density just below the silicon surface (p-type) is greater than the equilibrium hole density in bulk. This condition occurs on the application of negative voltage at the gate electrode. The accumulation condition results in an upward band bending in the energy band diagram, as it is shown in Fig. 2.6a. Since E_F does not shift, the band bending gives larger value of (E_i-E_F) near the surface which, in turn, increases the hole density at the surface as compared with that of the bulk. As a result, the accumulation of holes takes place at the surface and surface conductivity is increased.

(b) Condition of Carrier Depletion

This condition is achieved when a small positive voltage is applied to the gate electrode. In depletion region, the surface potential is positive and the downward band bending takes place as it is shown in Fig 2.6b. The hole concentration is now smaller as compared to the bulk since the value of (E_i-E_F) is decreased. Thus, the concentrations of holes are depleted in the vicinity of the oxide-Silicon interface, establishing a space-charge region consisting of stationary acceptor ions.

(c) Condition of Carrier Inversion

This condition is achieved when a large positive gate voltage is applied, a significant downward band bending occurs than that in carrier depletion case as shown in Fig. 2.6c, which causes the midgap energy E_i to cross over the Fermi level near the silicon surface. Consequently, an inversion layer is formed in which the electron density is higher than the hole density.

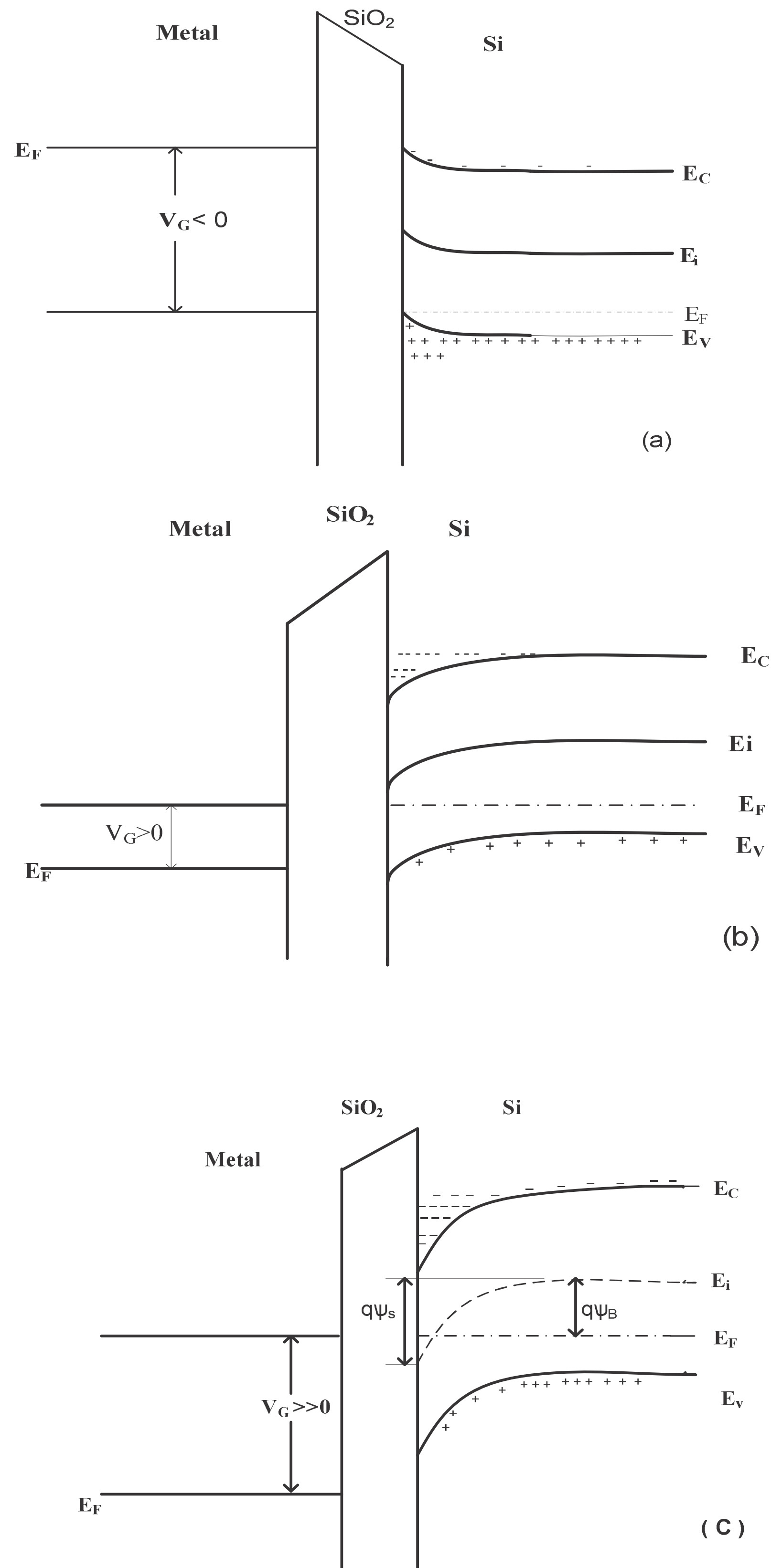


Fig. 2.6 Energy band diagram of Ideal MOS in (a) accumulation; (b) depletion; (c) inversion region [Sze (1987)]

2.2.2 C-V Characteristics of an Ideal MOS Capacitor

The C-V characteristics of an ideal MOS capacitor with P-type Si substrate at high frequency (f > 500 KHz) is shown in Fig. 2.7. The shape of the C–V curves varies with the doping of the semiconductor material, measurement frequency, temperature etc. [Sze (1987); Eriksson (1997)]. The C-V curve is divided in three regions i.e. accumulation, depletion, and inversion. When a MOS capacitor is exposed to hydrogen this will introduce extra charges or dipoles at the metal-insulator interface which causes a shift in the C-V characteristics, as illustrated in Fig. 2.7.The magnitude of the voltage shift ΔV, can be expressed as the amount of hydrogen adsorbed at the interface:

$$\Delta V - \frac{\mu}{\varepsilon} n_i \tag{2.12}$$

Where, ΔV is the voltage shift, ε is the permittivity, n_i is the concentration of dipoles at the interface (in the range $7x10^{17}$-$2x10^{18}m^{-2}$ [Solomonson *et al*. (2005)] for Pt and Pd-MIS devices), μ is the effective dipole.

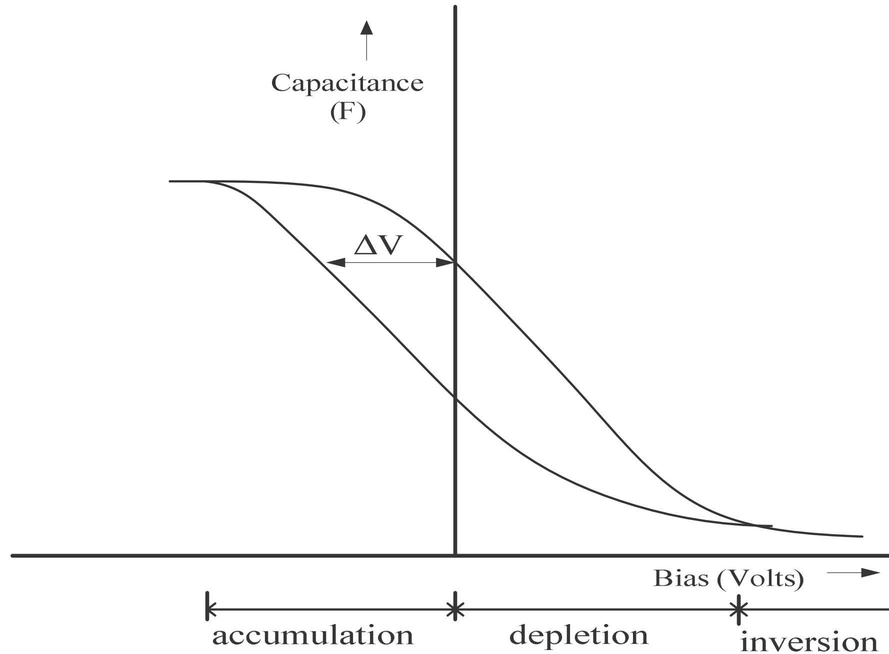


Fig. 2.7 C-V characteristics of p-type MOS capacitor showing various surface conditions (a) accumulation (b) depletion (c) inversion [Sze (1987)]

2.2.3 Influence of Oxide Charges and Work Function Difference on the C–V Characteristics of MOS Capacitor

In an ideal MOS capacitor, it has been assumed that the work function difference between metal and Si, 'Φ_{ms}' is zero and no oxide charges are present. But in the practical MOS capacitors, Φ_{ms} is not zero and oxide charges are also present. In such case, the experimental C-V curves are shifted from the ideal theoretical curves by an amount,

$$V_{FB} = \Phi_{ms} - \frac{Q_o}{C_i} \quad (2.13)$$

Where, V_{FB} - flat band voltage shift (V), Q_o - effective net oxide charge per unit area. Φ_{ms} - metal-semiconductor work function difference (eV).

The gate voltage at which the net effective oxide charges become zero (assuming $\Phi_{ms} = 0$) or the gate voltage which is required to produce zero band bending at the silicon surface is termed as the flat band voltage.

Work function of material is defined as the energy required in bringing an electron from the Fermi level to the vacuum level. If no oxide charges are present but the work function difference between metal and silicon Φ_{ms} is non zero, there will be parallel shift in the C-V curve without distortion along the voltage axis an amount equal to work function difference. If $\Phi_{ms} > 0$, the shift is towards positive gate bias, if $\Phi_{ms} < 0$, the shift is towards negative gate bias.

In addition to non zero work function difference, if oxide charges are present, whose occupation is independent of dc bias, the C-V curve will undergo an additional translation along the voltage axis. This shift is the measure of charges in the oxide. Four types of charges mainly contribute to the net effective oxide charges: interface trapped charges (Q_{it}), mobile ionic charges (Q_m), fixed oxide charges (Q_f), and the oxide trapped charges (Q_{ot}) as illustrated in Fig. 2.8.

(a) Interface trapped charges (Q_{it}) arises from allowed energy states that exists in the forbidden gap of the silicon in the region very close to Si-SiO_2 interface. These interface traps are obtained due to structural Si defects from dangling bonds (bond breaking) at the interface.

(b) Fixed oxide charges (Q_f) (usually positive) is located in the oxide within 3 nm of the Si–SiO_2 interface also called as the strained oxide region [Nicollian and Brews (1982)]. These charges arise due to the incomplete oxide silicon, or in other words due to excess ionic silicon. The magnitude of fixed charges is affected by oxidation temperature, annealing conditions and the substrate orientation.

(c) The mobile ionic charges (Q_m) arise from the presence of highly mobile ions of impurities, mostly sodium (Na^+), potassium (K^+) and lithium having very high diffusivities in the oxide. Their presence leads to flat band instabilities and to the deterioration of oxide reliability.

(d) The oxide trapped charge (Q_{ot}) due to holes or electrons trapped in the bulk of the oxide and hence can be positive or negative. Q_{ot} is associated with defects in SiO_2 which may arise from ionizing radiation, hot carrier injection or high current through the oxide.

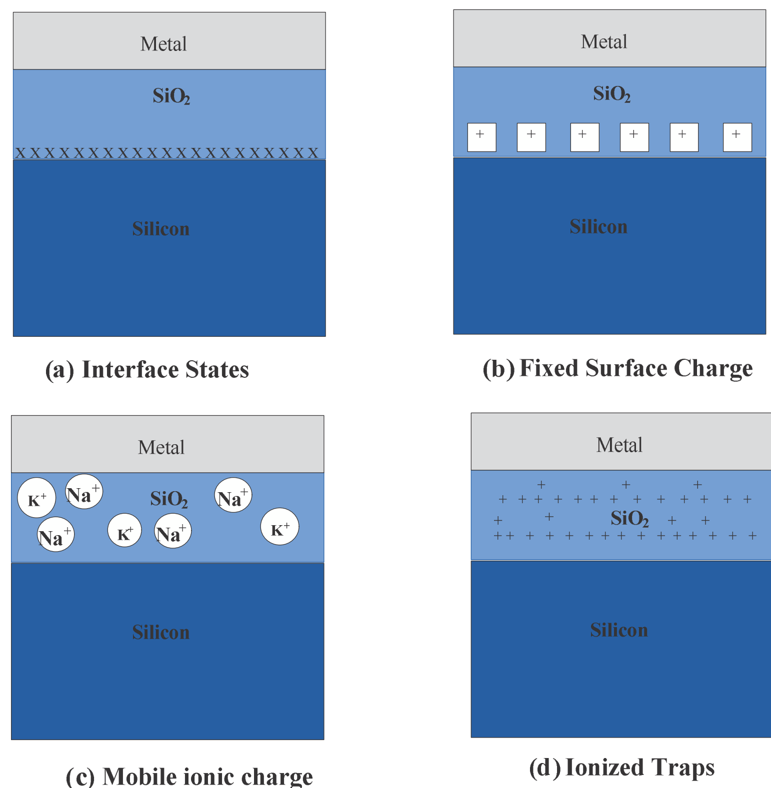


Fig. 2.8 Schematic illustration of oxide charges in non ideal MOS capacitor

The band diagram of MOS capacitors with fixed oxide trapped charges is shown in Fig. 2.9. It is found that for same surface potential $\psi_{s,}$ the applied voltage V is less than in case of ideal MOS capacitor; indicating a voltage shift of the C-V curve towards negative voltage. The shift, due to the fixed oxide trapped charges is given by [Sze (1987)].

$$\Delta V_{ot} = \frac{Q_{ot}}{C_i} = \frac{1}{C_i}\left[\frac{1}{a}\int_0^d x\rho_{ot}(x)dx\right] \tag{2.14}$$

Where, Q_{ot} is the effective net charge in bulk oxide traps per unit area at the Si–SiO_2 interface. $\rho_{ot}(x)$ is the volume oxide trap density. The net voltage shift due to all the oxide charges is given by

$$\Delta V = \Delta V_{it} + \Delta V_f + \Delta V_m + \Delta V_{ot} = \frac{Q_0}{C_i} \tag{2.15}$$

Where, $Q_o = Q_{it} + Q_f + Q_m + Q_{ot}$ is sum of the effective net oxide charge per unit area.

2.3 Interactions between Gas and Solid Surface

Gas sensors operate by binding molecules to the device surface through one or more mechanisms including adsorption, absorption, chemisorptions and co-ordination chemistry. The choice of binding mechanism has important implications for the selectivity and reversibility of the sensing system. For highly selective system, a high binding interaction will be required; however, it results in poor reversibility. Weaker adsorption interactions are preferred for good reversibility but as a consequence the selectivity is poor. The ideal gas sensor would exhibit reliability, robustness, sensitivity, selectivity and reversibility [James *et al*. (2005)]

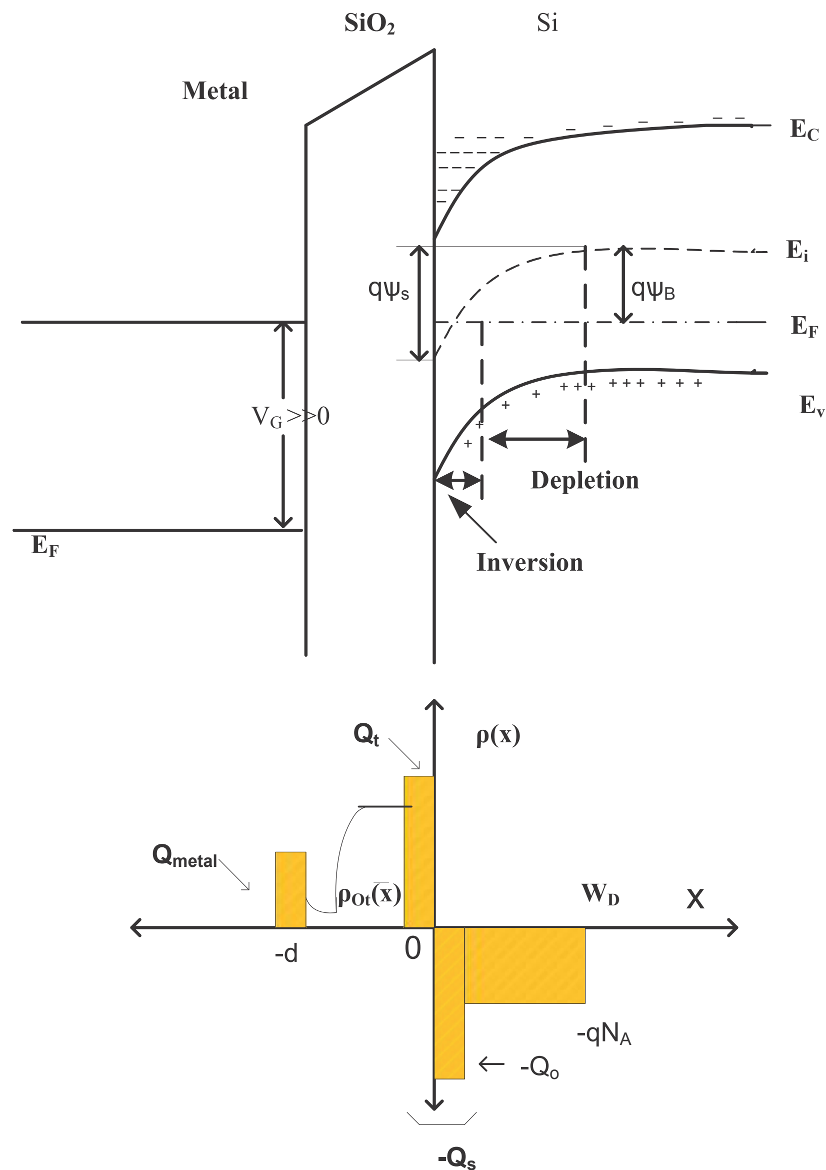


Fig. 2.9 Energy band diagram and the charge distribution for a practical MOS structure [Sze (1987)]

2.3.1 Gas Adsorption Processes

When a gas or vapour comes in contact with a clean solid surface, some of it will adhere to the surface in the form of an adsorption layer. The solid is generally referred to as the adsorption, the adsorbed gas or vapour as adsorbate. Any solid is capable of

adsorbing a certain amount of gas and the quantity at equilibrium depends on the temperature, partial pressure of the gas and the effective surface area of the solid [Puzzovio (2008)].

2.3.1.1 Physisorption and Chemisorptions

Adsorption occurs when an attractive interaction between a gaseous particle and a solid surface is strong enough to overcome the disordering effect of thermal motion. From a thermodynamic point of view, adsorption is a spontaneous process, which means that the change in free energy ΔG of the system is negative. The change in entropy ΔS is negative, because the translational freedom of the adsorption is reduced when it is adsorbed [Atkins (1998)]. Therefore, considering the thermodynamic relationship:

$$\Delta G = \Delta H - T\Delta S < 0; \qquad (2.16)$$

The enthalpy of adsorption ΔH_{ads}, must be negative. Thus, the adsorption of gases on solid is an exothermic process. Two types of adsorption are generally discussed: Physical adsorption or physisorption and chemisorptions. Physisorption is the weakest where no real chemical bonds are created. The binding to the surface involves weak interactions, such as Vander Waals forces. Indeed, physisorptive bonds are characterized by dissociation energies below 50kJ/mol (approximately) [Puzzovio (2008)]. When real bonds are created between the surface and the adsorbates, the adsorption is described as chemisorptions. Stronger forces are responsible for chemisorptions and cause the formation of short chemical bonds with dissociation energies typically exceeding 50kJ/mol. Since an activation barrier needs often to be overcome, chemisorptions is considered an activated process [Show and Middelhoek (1966)]. The equilibrium condition in physisorption is attained rapidly, as there is no activation energy involved and the process is readily reversible. On the other hand chemisorptions may require activation energy, and may therefore, be relatively slow and not readily reversible. Fig. 2.10 illustrates a schematic potential diagram for the adsorption of a die atomic molecule of gas X_2, on a surface M. physisorption is described by a Lennard-Jones potential, whereas chemisorptions by a Morse potential. The physical interaction energy includes a short range negative (attractive) contribution arising from London–Vander Waals dispersion forces and an even shorter-range positive contribution (Born repulsion) due to an overlapping of electron

clouds. In chemisorptions, the adsorbate, X_2, dissociates to 2X. The dissociation energy of X_2 (ΔE_{dis}) is represented at large distances. Both potential curves are characterized by the presence of a minimum, which corresponds to the heat of the process (ΔH_{GGS}).The heat of chemisorptions is at a shorter distance from the solid surface than the heat of physisorption. A gas molecule is first physically adsorbed, which means that it approaches the solid surface along a low-energy path. The intersection point of the two curves represents the transition from physisorption to chemisorption, where the energy is the activation energy of chemisorptions,(ΔE_{ads}). The magnitude of this value depends on the shapes of the physical adsorption and chemisorption curves, thus it is variable according to the system [Shaw and Middelhoek (1966)].

2.3.2 Adsorption Isotherms

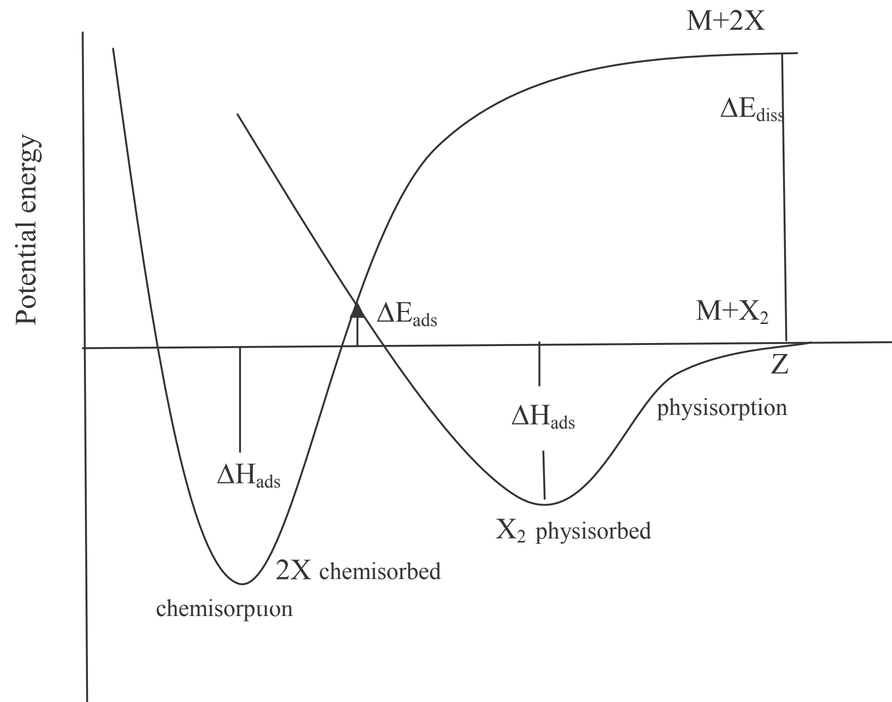
At a given temperature, the equilibrium relationship between the amount of adsorbed gas and the pressure of a gas at the surface is known as adsorption isotherm. Adsorption isotherm generally relates the applied gas pressure to the coverage surface. The extent of surface coverage is expressed as a fractional coverage Θ,

$$\Theta = \frac{Number\ of\ adsorption\ sites\ occupied}{Number\ of\ adsorption\ sites\ available} \qquad (2.17)$$

The change of fractional coverage with time ($\frac{d\theta}{dt}$) determines the rate of surface coverage or rate of adsorption. The fractional coverage Θ is in equilibrium with the free overlying gas. This equilibrium, which is dynamic it is generated by two opposite processes (adsorption and desorption) occurring at the same rate, depends on the pressure of the free gas and on the temperature of the surface/system where adsorption and desorption is taking place simultaneously.

The variation of Θ with pressure at a chosen temperature is represented by a curve, called adsorption isotherm. This function has a particular importance in the determination of information about the active surface of a material, and the same is elaborated in subsequent sections. Several adsorption isotherms [Wanger *et al*. (1938)] have proved to be useful in the understanding of the adsorption process. However, the three most frequently used isotherms are as follows:

1. Langmuir Isotherm
2. Brunauer, Emmet and Teller (BET) Isotherm
3. Freundlich Isotherm



Where,

ΔH_{ads} - Heat of adsorption, ΔE_{dis} - dissociation energy, ΔE_{ads} - activation energy of chemisorptions

Fig. 2.10 Potential energy curves for physisorption and chemisorption of a molecule X_2 that approaches a surface along the trajectory z [pandey *et al.*(2010)]

2.3.2.1 Langmuir Isotherm

Langmur adsorption isotherm is based on the concept that adsorption is a chemical process and the adsorbate layer is unimolecular. The Langmuir isotherm is based on the following characteristic assumptions:

- Adsorption of a single layer (monolayer coverage);
- Equivalence of all adsorption sites and surface uniformity;
- No interactions between adsorbed molecules.

According to Langmur there are different number of active sites (proportional to the surface area) on the adsorbate surface. One site adsorbs one molecule. When the whole surface is completely covered by a unimolecular layer of gas further adsorption is not possible and indicates the saturation of adsorption. If the adsorbate is gas, then adsorption equilibrium can be represented by;

$$X(gas) + M(surface) \leftrightarrow XM\ (surface) \qquad (2.18)$$

The rate of adsorption is proportional to the partial pressure P of the gas X and to the uncovered surface, expressed by (1-Θ):

$$\frac{d\theta}{dt} = k_a P(1-\theta) \qquad (2.19)$$

Where, k_a is the rate constant for adsorption .

The rate of desorption is proportional to the number of adsorbed species, represented by the surface coverage Θ

$$\frac{d\theta}{dt} = -k_d \theta \qquad (2.20)$$

Where, k_d is the rate constant for desorption.

When adsorption equilibrium is established, Θ is independent of time, thus both Eq.

2.19 and 2.20 are equal. Solving this condition for Θ, we obtain the Langmuir isotherm:

$$\theta = \frac{KP}{1+KP} \qquad (2.21)$$

With

$$K = \frac{k_a}{k_d} \qquad (2.22)$$

When considering a dissociative adsorption (X_2(gas) $\rightarrow$ 2X (surface)), the Langmuir isotherm has a different form. In this case, the rate of adsorption is proportional to the pressure and to the probability that both atoms will find sites, that is to say the square of the number of vacant sites:

$$\frac{d\theta}{dt} = k_a P(1-\theta)^2 \qquad (2.23)$$

The rate of desorption is proportional to the frequency of encounters of atmos on the surface, thus proportional of the square of the number of atoms present:

$$\frac{d\theta}{dt} = -k_d \theta^2 \qquad (2.24)$$

The equilibrium condition is expressed in the form of following mathematical equation:

$$\Theta_i = \frac{K(P)^{1/2}}{1/K(P)^{1/2}} \qquad (2.25)$$

In case of dissociative adsorption, the dependence of fractional coverage on the pressure is weaker. At low temperature, $K_P << 1$ and $\Theta_i = K_P$, hence, Θ_i increases

linearly with pressure. At high pressure, KP >> 1 and Θ_i = 1.The surface is nearly fully covered with a monomolecular layer at high pressures, so that change in pressure produces a little change in amount adsorbed.

2.3.2.2 The BET Isotherm

As it has been discussed above that Langmuir isotherm is applicable in the situation of low coverage, but it fails at high adsorbate pressure where the coverage is high. Brunauer, Emmet and Teller (BET) isotherm is based on multilayer adsorption. Brunauer, Emmet and Teller (BET) derived the isotherm for such case, with the assumptions that (a) adsorption is multi molecular, and each separate layer obeys a Langmuir equation; (b) the average heat of adsorption in the second adsorbed layer is same as in the third and higher layer and it is equal to heat of condensation of the vapour and (c) the average heat of adsorption in the first adsorbed layer is different from that of second and the subsequent layer. The BET equation is given by;

$$\frac{P}{V(P_s-P)} = \frac{1}{V_m c} + \frac{(c-1)}{V_m c}\frac{P}{P_s} \tag{2.26}$$

Where, P_s is saturation pressure of vapour, c is constant at constant temperature,

P is partial pressure and V_m is total volume available for adsorption.

The BET isotherm is reasonably valid over restricted pressure ranges but it is not accurate at all values; it under estimates the extent of adsorption at low pressures and overestimates at high pressure [Puzzovio (2008)].

2.3.2.3 The Freundlich's isotherm

The Freundlich isotherm is one of the first equation proposed to relate the amount of material adsorbed to the concentration of material. The change of adsorption with pressure can be given by other equation, when deviations from the assumptions of the Langmuir model occur. The Freundlich isotherm corresponds to a Logarithmic change.

$$\theta = c_1 P^{1/\varepsilon_2} \tag{2. 27}$$

Where, c_1 and c_2 are constant , c_2 usually being greater than unity.

Taking logarithms of equation (2.27),

$$\log V = \log c_1 + 1/c_2 \log P \quad (2.28)$$

Plotting logV versus logP, the result is a straight line. This adsorption equation is a good interpretation of an adsorption model in which the variation of the magnitude of the heat of adsorption with surface coverage is exponential [Puzzovio (2008)].

2.4 Gas Sensing Mechanism of MOS Gas Sensor

The gas sensing mechanism of MOS sensor is explained by the following steps [Lundstrom *et al*. (1985); Lundstrom *et al*. (1991); Ekedahl *et al.* (1998)]].

Step 1: Dissociation of H_2 molecules on the catalytic surface into atomic Hydrogen.

Step 2: Adsorption of atomic H_2 on metal surface.

Step 3: Diffusion of atomic H_2 to the Pt/SiO_2 interface.

Step 4: Formation of dipole layer at Pt/SiO_2 interface.

Step 5: Which results decrease in metal-semiconductor work function causes decrease in flat band voltage of MOS sensor.

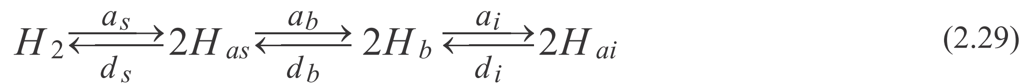
Step 6: Change in V_{FB} causes a shift in C-V.

Step 7: Further, H^+ ions will reach at SiO_2/Si interface through oxide layer where accumulation of H^+ ions occurs at SiO_2/Si interface which modulates the interface states due to the reaction of H^+ ions with interface traps.

Upon exposure to reducing gases, such as H_2 and hydrocarbons, the I-V and C-V characteristic curves will shift towards lower voltages, and towards higher voltages for oxidizing gases such as O_2 and NO_x. The detection of some gaseous species, such as ammonia requires the use of a porous gate material. There are special sites (triple phase boundaries were the gate material, and the insulator are Θ exposed to the gas phase on the gate region where ammonia, NH_3 molecules are dissociated and provide hydrogen atoms (or protons), which form the dipole layer at the interface.

2.4.1 Hydrogen Sensing by MOS Sensor in an Inert Atmosphere

The gas sensing mechanism of the MOS sensor is based on the ability of the catalytic gate material to dissociate adsorb hydrogen molecules**.** The hydrogen sensing mechanism of the Pt-MOS device is schematically presented in Fig. 2.11 in inert ambient atmosphere. When a MOS gas sensor with a thin Pt- gate film is exposed to hydrogen gas, the hydrogen molecules are adsorbed at the platinum (Pt) surface and gets dissociate into atomic hydrogen due to the catalytic behaviour of metal. Some of these H_2 atoms will diffuse through the metal film and reach at the Pt-SiO_2 interface, where they become polarized, while other atoms get desorbed. The resulting dipole layer is in equilibrium with the outer layer of chemisorbed hydrogen and hence in phase with the gas. The dipole layer produces an abrupt rise in the surface potential at the metal-oxide interface which is seen as an effective change in flat- band voltage of the device. By taking the metal surface, bulk and the interface (with oxide) of the metal together into consideration, the interaction of the hydrogen gas with the Pt surface, in an inert atmosphere can be summarized in the following equation:



$$H_2 \underset{d_s}{\overset{a_s}{\rightleftarrows}} 2H_{as} \underset{d_b}{\overset{a_b}{\rightleftarrows}} 2H_b \underset{d_i}{\overset{a_i}{\rightleftarrows}} 2H_{ai} \qquad (2.29)$$

Where, H_{as} is Hydrogen at Pt surface, H_b is Hydrogen in the bulk of Pt, H_{ai} is Hydrogen at Pt-SiO_2 interface. *a* and *d* are rate constants for adsorption and desorption, respectively. The catalytic film is a polycrystalline film, and diffusion via grain boundaries will be more important than through the bulk metal grains [Salomonsson (2005)]. According to Lundstrom theory, the hydrogen adsorption at Pt/SiO_2 interface should follow the Langmuir isotherm (based on three assumptions described in sec. 2.3.2.1) and since the dissociation of the hydrogen gas involves two hydrogen atoms hence second order equation should be applicable. Therefore, the fractional coverage of the sites Θ_i of hydrogen atoms at the interface is discussed earlier in equation (2.25) can be modified and the modified equation is given below as equation (2.30).

$$\theta_i = \frac{K[P(H_2)]^{1/2}}{1+K[P(H_2)]^{1/2}} \quad (2.30)$$

Assuming that the response (shift in ΔV) is proportional to the hydrogen coverage at the interface:

$$\Delta V = \Delta V_{max}\,\Theta_i \quad (2.31)$$

Where, ΔV_{max} is maximum voltage change for fully saturated adsorption sites (Θ_i=1). Combining eq. 2.30 and 2.31, this results

$$\Delta V = \Delta V max \frac{K[p(H_2)]^{1/2}}{1+K[p(H_2)]^{1/2}} \quad (2.32)$$

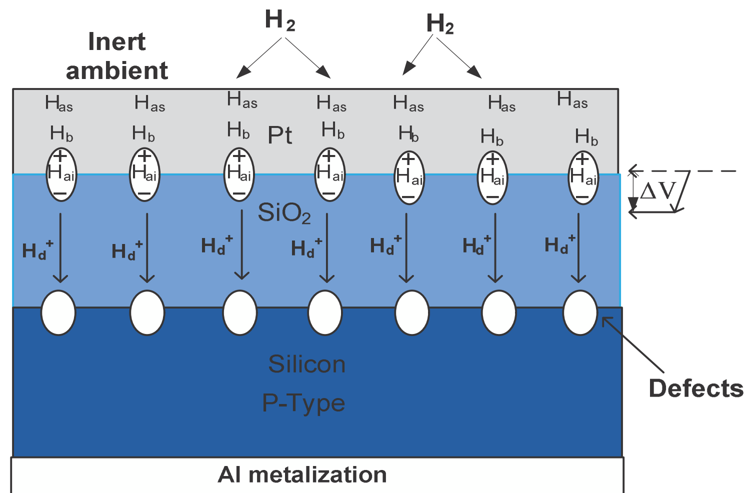


Fig. 2.11 Schematic representation of hydrogen sensing by MOS sensor

where,

H_{as} = adsorbed hydrogen at Pt surface, H_b = Hydrogen in the bulk of Pt

H_{ai} = Hydrogen at Pd-SiO_2 interface, H_d^+ = Hydrogen ions drifting in SiO_2

Lundstrom theory is based on the assumption that heat of adsorption is constant and independent of the number of filled sites, However, Pertersson *et al*. [pertersson *et al*. (1985)] considered that the already adsorbed species may affect nearby adsorption sites and modified the theory. The Temkin isotherm was used and it yielded a theory that predicted that the flat band voltage is dependent on the logarithm of the hydrogen pressure for Pt-MOS capacitor.