CHAPTER-2
2.1 Introduction

Modern semiconductor devices rely on the technologist's ability to introduce predetermined amounts of impurity into precisely defined regions of a chip. It follows that any movement of impurities within the semiconductor must be carefully controlled or, at the very least, predictable. Whenever the chip is raised to a high temperature during processing, movement of impurities is likely to occur. Sometimes the diffusion is deliberately initiated by the manufacturer, e.g. when an acceptor is diffused into n-type material in order to make p-n junction. On other occasions the diffusion occurs due to some subsequent processing step which requires a heat treatment. This latter 'accidental' diffusion is becoming of increasing importance as the dimensions of individual devices in integrated circuits are decreased.

The aim of the diffusion studies is to develop improved models from experimental data for predicting diffusion results from theoretical analysis. The ultimate goal of diffusion studies is to calculate the electrical characteristic of a semiconductor device from the processing parameters.
Diffusion theories have been developed from two major approaches, namely, the continuum theory of Fick's diffusion equation and the atomistic theory which involves interactions between point defects, vacancies and interstitial atoms and impurity atoms. The continuum theory describes the diffusion phenomenon from the solution of Fick's diffusion equation with appropriate diffusivities. The diffusivities of dopant element can be determined from experimental measurements, such as surface concentration, junction depth, or the concentration profiles, and the solutions of Fick's diffusion equation. The solution of Fick's diffusion equations gives good results in low concentration regions of impurities. When impurity concentrations are high, the diffusion profiles deviate from the predictions of simple diffusion theory and the impurity diffusion is affected by other factors which are not considered in Fick's simple diffusion laws. In such cases, we apply Fick's diffusion equation with concentration dependent diffusivities.

2.2. Nature of diffusion:

Solid state diffusion is a process by which atoms move in a crystal lattice. This is done to change the electronic properties of the material. The diffusion process depends on a number of factors such as, temperature, concentration gradient, crystal orientation, defect concentration etc. Usually diffusion is done at a very high temperature ranging
from 900°C to 1200°C. The movement of atoms in the lattice takes place in a series of random jumps. These jumps occur in all the three dimensions and a flux of diffusion species result, if there is a concentration gradient. The mechanisms by which these jumps may take place are the following:

2.2.1. Vacancy Diffusion

Diffusion in a solid can be visualized as atomic movement of the diffusant in the crystal lattice by vacancies or self interstitials. At elevated temperatures the lattice atoms vibrate around the equilibrium lattice sites. Occasionally a host atom acquires sufficient energy to leave the lattice site, becoming an interstitial atom and creating a vacancy. When neighbouring atom (either the host or impurity atom) migrates to the vacancy sites, the mechanism is called diffusion by vacancy. If the migrating atom is a host atom, the diffusion is referred to as self diffusion, if it is an impurity atom, the diffusion is referred to as impurity diffusion.

2.2.2 Interstitial Diffusion

If an interstitial atom moves from one place to another without occupying a lattice site, the mechanism is interstitial diffusion. An atom smaller than the host atom often moves interstitially. The activation energies required
for diffusion of interstitial atoms are lower than those for diffusion of lattice atoms by vacancy mechanism.

2.2.3. Extended Interstitial Diffusion

Sometimes the atomic movement of interstitial atom displaces a lattice atom, which in turn becomes an interstitial atom. This is an example of extended interstitial mechanism, sometimes called the "interstitialcy" mechanism.

2.3. Simple One-Dimensional Diffusion Equation

The Fick's one-dimensional diffusion theory is based on the analogy between material transfer in a solution and heat transfer by conduction (2,3). Fick assumed that in a dilute liquid or gaseous solution convection, the transfer of solute atoms per unit area in one dimensional flow can be expressed by the following equation:

\[ J = - D \frac{\partial C(x,t)}{\partial x} \] ...

\[ (2.3-1) \]

Where \( J \) is the diffusion flux, \( C \) is the concentration of solute, \( x \) is the Co-ordinate axis in the direction of flow, \( t \) is the diffusion time, and \( D \) is the diffusivity. The above mentioned equation is called Fick's first law of diffusion.

From the law of conservation of matter, the change of solute concentration with time must be the same as the local decrease of diffusion flux, that is,
Elimination of $J$ from equation (2.2-1) and (2.2-2) yields Fick's second law of diffusion in one dimensional form:

\[
\frac{\partial C(x,t)}{\partial t} = - \frac{\partial}{\partial x} [D \frac{\partial C(x,t)}{\partial x}] \quad \ldots (2.3-3)
\]

When the concentration is low, the diffusion coefficient (diffusivity) can be described as constant and equation (2.2-3) becomes

\[
\frac{\partial C(x,t)}{\partial t} = D \frac{\partial^2 C(x,t)}{\partial x^2} \quad \ldots (2.3-4)
\]

Equation (2.3-4) is often referred to as Fick's simple one-dimensional diffusion equation. Solutions for equation (2.3-4) with various simple initial and boundary conditions have been obtained (4,5).

2.3.1. Ideal Diffusion Theory

Solid state diffusion is one of the most practical ways of achieving desired concentration of dopants in silicon. Usually the diffused layers are formed in a two step process. In the first step, known as the 'deposition' or 'pre-deposition' step, a thin layer of dopant, typically a few tenths of a micron, is formed with the help of diffusion source. The source is then removed and the thin layer is
further diffused to give a required concentration distribution in the silicon. This step is known as the 'drive-in' diffusion step.

Simple-one-dimensional diffusion theory may be used to study the diffusion kinetics of various impurities, both in the case of deposition as well as drive-in. If \( C(x,t) \) is the impurity concentration per unit volume at a distance 'x' and time 't', then the diffusion may be described (3) by the equation,

\[
\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} \quad \ldots \quad (2.3-5)
\]

where \( D \) is a constant known as diffusion coefficient. This equation is known as the diffusion equation.

In the case of pre-deposition, the diffusion is usually done under the conditions of constant surface concentration (1), equal to the solid solubility limit \( C_s \). Accordingly, the impurity distribution may be determined by solving the diffusion equation, subject to the following initial and boundary conditions:

\[
C(0,t) = C_s \quad \ldots \quad (2.3-6)
\]

\[
C(\infty,t) = 0 \quad \ldots \quad (2.3-7)
\]

\[
C(x,0) = 0 \quad \ldots \quad (2.3-8)
\]

The resulting solution (2) is

\[
C(x,t) = C_s \text{ erfc} \left( \frac{x}{2 \sqrt{Dt}} \right) \quad \ldots \quad (2.3-9)
\]

The factor \( 2 \sqrt{Dt} \) is known as the 'diffusion length'.

In the case of drive-in, the total number of impurity atoms per unit area of the diffused layer may be assumed constant (1).

Thus, the initial and boundary conditions are:

\[
\frac{\partial c}{\partial x}(0,t) = 0 \quad \ldots \quad (2.3-10)
\]

\[
c(\infty,t) = 0 \quad \ldots \quad (2.3-11)
\]

\[
c(x,0) = C_s \text{ erfc} \frac{x}{(2 \sqrt{Dt})_{\text{dep}}} \quad \ldots \quad (2.3-12)
\]

Where \( C(x,0) \) represents the impurity distribution just before drive-in which would be the distribution after the pre-deposition step. The solution of the diffusion equation subject to these initial and boundary conditions is difficult to obtain analytically. If the initial distribution \( C(x,0) \) is approximated by a delta function, the solution becomes,

\[
c(x,t) = \frac{Q}{\sqrt{4\pi Dt}} \exp \left( -\frac{x^2}{4Dt} \right) \quad \ldots \quad (2.3.13)
\]

Where \( Q \) is the total number of impurity atoms in silicon after pre-deposition.

This is the well-known 'Gaussian' distribution. The delta function approximation made here is justified provided \( \sqrt{Dt} \) for pre-deposition is much smaller than \( \sqrt{Dt} \) for drive-in, In practice, this condition is usually met. It has been shown (1), by obtaining the exact solution without making the
delta function approximation, that for values of the ratio \((\sqrt{Dt})_{dep}/(\sqrt{Dt})_{drive-in}\), as large as 0.25, the delta function approximation provides an excellent fit. It is only when this ratio approaches unity that the delta function approximation starts giving large errors.

2.3.2. Concentration Dependent Diffusivities

The simple atomic mechanism are not adequate for describing the diffusion when concentrations are high. Dislocation or other impurities are present at high concentrations. In such cases, the measured impurity profiles deviate from equation (2.3-9) to (2.3-13) and the impurity profile can be represented by concentration dependent diffusivities. Equation (2.3-3) is used to determine the concentration dependent diffusivities from experimentally measured concentration profiles in the following cases:

2.3.2.1 Constant Surface Concentration

If diffusivity \(D\) is only a function of concentration \(C\) and the surface concentration is maintained at a constant value, equation (2.3-3) can be transformed into an ordinary differential equation (4) with a new variable \(\eta\), where

\[
\eta = \frac{x}{\sqrt{t}} \quad \cdots (2.3-14)
\]

Thus both \(c\) and \(D\) depend on \(x\) implicitly. Substituting the
value of \( n \) in equation (2.3-3), following equation can be obtained.

\[
D(c) = -1/2 \int_{0}^{c_1} \frac{dc}{d\eta} \quad \ldots \quad (2.3-15)
\]

The process is therefore to plot out an experimentally determined profile and at some concentration \( C_1 \) measure the slope and area under the profile. Equation (2.3-15) is then used to calculate the value of diffusion coefficient corresponding to \( C_1 \).

In this way, the diffusion coefficient can be determined over the whole range of concentration covered by the profile.

2.3.2.2 Constant Total Dopant

In most device fabrications, the diffusion is done after the introduction of impurity into silicon, thus, equation (2.3-15) can not be used to determine the concentration dependent diffusivity from the measured concentration profiles under such circumstances. Equation (2.3-14) is suitable for the determination of diffusivity, at high concentration, only for the pre-deposition step. For the drive-in case this equation is not valid. An alternative expression is used to remove the constant surface concentration and it is replaced by a requirement that the
total concentration of dopant remain invariant with diffusion time (i.e., constant total dopant) (7,8). This requirement is expressed as

\[ Q = \int_{0}^{x} C(x,t) \, dx = \text{constant} \quad \ldots \quad (2.3-16) \]

where \( Q \) is the total dopant per unit area in the diffused layer and is independent of the diffusion time. Equation (2.3-16) has been applied to the redistribution diffusion of Arsenic from an ion implanted layer (9). The expression for determining the diffusion coefficient from the concentration profile is given by (6).

\[
D \left[ \frac{-C(x_0,t)}{C_s} \right] = \frac{-C(x_0,t)_{x_0}}{2t \left[ \frac{dc}{dx} \right]_{x=x_0}} \quad \ldots \quad (2.3-17)
\]

Where \( C_s \) is the surface concentration, \( x_0 \) is the location at which \( D \) is determined and \( \left( \frac{dc}{dx} \right)_{x=x_0} \) is the concentration gradient at \( X=X_0 \).

2.3.3. Temperature Dependence of Diffusivities

The temperature dependence of the diffusivities determined experimentally over a range of diffusion temperature can be represented by the equation

\[
D = D_0 e^{-E_a/kT} \quad \ldots \quad (2.3-17)
\]

Where \( D_0 \) is the frequency factor (in cm²/s), \( E_a \) is the activation energy (in eV), \( T \) is the temperature (in Kelvin),
$K$ is Boltzmann constant (in eV/Kelvin). Thus when $D$ is plotted against $1/T$ on semilogarithmic co-ordinates, $D$ is a straight line with slope $E_a/KT$. From the atomic diffusion theories involving the defect – impurity interactions, $D_0$ is related to the atomic jumping frequency or the lattice vibration frequency. The activation energy $E_a$ is related to the energies of motion and energies of formation of defect – impurity complexes.

Thus measuring the diffusivity as a function of temperature, it can be determined whether the diffusion is dominated by interstitial or vacancy mechanism.

2.4 Atomic Diffusion Mechanism

To understand the diffusion process at high concentration levels and the physical mechanisms for the impurity diffusion at various concentration levels, atomic models of solid state diffusion have been proposed and compared with experimental measurements. The atomic mechanism of solid state diffusion was established from the diffusion study in metals. The vacancy mechanism is most probable in a cubic face centered crystal (9). Diffusion in silicon can be described by mechanisms involving impurity and point defect interactions with the point defects at different charge states.
It can be shown (10) that any "flow" in a semiconductor lattice can usually be represented by a series of energy levels, in the sequence \( E^+, E^-, E^2, E^{3-} \), --- in addition to being neutral. In general all deep levels as well as vacancies, exhibit on or more of these charge states, all in this sequence. Let us assume that vacancies can be represented in this way, corresponding to \( V^+, V^-, V^{2-}, V^{3-} \), in addition to \( V^0 \) for the sake of specificity.

Consider the dilute case, where an extremely small amount of impurity diffuses in the Zincblende lattice. Diffusion under this condition can be characterized by intrinsic diffusion coefficients, \( D^{0}_i \), \( D^{+}_i \), \( D^{-}_i \), \( D^{2-}_i \), and \( D^{3-}_i \), where these terms are associated with \( I-V^0 \), \( I-V^+ \), \( I-V^- \), \( I-V^{2-} \), and \( I-V^{3-} \), pair interaction respectively (I represents the impurity). It follows that overall intrinsic diffusivity is given by

\[
D_i = 0.5 \left[ D^{0}_i + D^{+}_i + D^{-}_i + D^{2-}_i + D^{3-}_i \right] \quad \ldots \quad (2.4-1)
\]

Where 0.5 is a correlation factor for tracer self diffusion in the zincblende lattice.

Diffusion under extrinsic conditions result in a displacement of the Fermi level and a change in the concentration of the various defects species. Consequently, the diffusivity for this condition is given (11) by
\[
D = D_1^0 \frac{[V^0]}{[V^0]} + D_1^+ \frac{[V^+]}{[V^+]} + D_1^- \frac{[V^-]}{[V^-]} + \\
D_1^{2-} \frac{[V^{2-}]}{[V^{2-}]} + D_1^{3-} \frac{[V^{3-}]}{[V^{3-}]} \ldots (2.4-2)
\]

It must be recognized that the neutral vacancy concentration remains the same throughout the semiconductor, since it is unaffected by the electric field due to the impurity concentration gradient. It follows that the extrinsic concentration of neutral vacancies will be equal to the concentration in the intrinsic material, which is only a function of temperature. On the other hand, the concentration of the various ionized states is still determined by the position of the Fermi level, so that the total defect concentration changes with shifts in its position.

The ionized vacancy ratio can be determined using the law of mass action. Thus extrinsic diffusion is characterized by

\[
D = D_1^0 + D_1^+ \frac{n}{n_i} + D_1^- \frac{n}{n_i}^2 + D_1^{2-} \frac{n}{n_i}^3 + D_1^{3-} \frac{n}{n_i}^3 \ldots (2.4-3)
\]

This equation is further modified by a field enhancement factor which takes into consideration the internally generated electric field term (which is often
ignored in diffusion calculations). Thus the effective diffusivity is given by

$$D_{\text{eff}} = n \left[ D_i^0 + D_i^+ \left( \frac{p}{n_i} \right) + D_i^- \left( \frac{n}{n_i} \right) + D_i^{2-} \left( \frac{n}{n_i} \right)^2 + D_i^{3-} \left( \frac{n}{n_i} \right)^3 \right] \ldots (2.4-5)$$

where

$$h = 1 + \left[ 1 + \left( \frac{2n_i}{N} \right) \right]^{-1/2} \ldots (2.4-5)$$

and $N$ is the volume concentration of diffusant.

Not all these terms apply to every situation, so that only relevant terms must be considered.

It is seen that only I-V$^+$ interactions are present during the diffusion of P-type impurities, since the Fermi level is close to the valence band edge. By the same reasoning, the diffusion of n-type impurities is dominated by interactions with the negatively charged species. This equation is simplified when applied to specific diffusion situation.

2.5 Evaluation Techniques for Diffused Layers

A number of measurements are required in the evaluation of diffused layers. Some of the important techniques used in practice are discussed below:
2.5.1. Junction Depth

Routine evaluation of diffused layers is relatively simple if diffused layer forms a p-n junction with the underlying substrate. The depth of the junction \( X_j \) can be delineated by grooving into the semiconductor and etching the surface with a solution which reacts selectively with the two sides of the junction, thus resulting in a colour variation between p and n sides. With the aid of the interference fringe technique of Tolonsky (12), the junction depth can be measured accurately from 0.5 to over 100 \( \mu m \).

2.5.2 Sheet Resistance

It is not possible to specify resistivity of a diffused layer, because it is not homogeneous. For a layer of this type, a sheet resistance is more appropriate. The sheet resistance of a diffused layer can be measured by a four point probe technique. A geometric correction factor is required to convert the measured resistance \( V/I \) into sheet resistance. This factor is a function of sample size, shape and the probe spacings. The sheet resistance \( R_s \) is given by:

\[
R_s = \frac{V}{I} \cdot C.F. \quad \ldots \ (2.5-1)
\]

where \( R_s \) is the sheet resistance of a diffused layer in \( \Omega/\square \), \( V \) is the measured dc voltage across the voltage probes (in volts), \( I \) is the constant dc current passing
through the current probes (in amperes), C.F. is the correction factor.

For a diffused layer, an average sheet resistance $R_s$ is related to the junction depth $x_j$, the carrier mobility $\mu$ and the impurity distribution $C(x)$ by the following expression

$$R_s = \frac{1}{q \int_0^{x_j} \mu C(x) \, dx}$$

...(2.5-2)

The depletion of charge carriers near $x_j$ can be neglected in the above calculation. In general, the mobility is a function of the total impurity concentration. An effective mobility often be defined as:

$$\mu_{\text{eff}} = \frac{\int_0^{x_j} \mu [C(x)] C(x) \, dx}{\int_0^{x_j} C(x) \, dx}$$

...(2.5-4)

Equation (2.4-2) can be expressed as:

$$R_s = \frac{1}{q \mu_{\text{eff}} \int_0^{x_j} C(x) \, dx}$$

...(2.5-4)

Where $q$ is the electronic charge.
For a given profile, the average resistivity \( \rho = R_s X_j \) is uniquely related to the surface concentration of the diffused layer and the substrate dopant concentration for an assumed diffusion profile. Design curves relating to the surface concentration and the average resistivity (or the average conductivity) have been calculated for simple diffusion profiles, such as exponential, Gaussian or erfc distribution. They are often called Irvin curves (13). For high concentrations and shallow diffusions, the diffusion profiles can not be presented by these simple functions. The measured sheet resistance and junction depth can not be used to find the impurity surface concentration or calculate the diffusivities of the diffusion layer with the Irvin curves.

2.6 Deviation from Simple One-Dimensional Diffusion Theory:

The one dimensional diffusion model discussed earlier gives good results only in the low concentration region of impurities. When the impurity concentration is high the diffusion profiles deviates from the prediction of one-dimensional diffusion model. A large no. of deviations have been reported, few of them are reported below:

2.6.1 Effect of Oxidation on Impurity Redistribution

It has been found (14) that impurities in silicon will be redistributed near a growing oxide, that requires that some of the substrate silicon is incorporated into the
silicon dioxide film as the process continues. The impurity atoms which were present in the layer of silicon must therefore be redistributed between the silicon dioxide and the remaining silicon. The redistribution depends upon the relative solubility of the impurity in silicon and silicon dioxide. In the case of boron the impurity is more soluble in oxide than in silicon. As a result, the concentration of boron on silicon side of the silicon-silicon dioxide interface is reduced. This process, known as the gathering, is often employed to reduce the total number of impurities during the drive-in step in order to increase the final sheet resistivity. A danger implicit in boron gathering is the possibility of inversion of the impurity type of a highly boron doped surface to n-type because of the surface depletion of boron. To avoid inversion, the surface concentration of boron profiles must remain relatively high. For this reason, base and resistor of p-type diffusion sheet resistances are limited to approximately 200 ohm per square.

Huang and Welliver (15) have investigated the problem of boron redistribution during the oxide growth, and have found that in extreme cases as much as 80% of the predeposited boron can dissolve in oxide.

The opposite effects are impurity build up in the silicon, occurs when the impurity is less soluble in silicon dioxide than in silicon. This situation which pertains to the
case of phosphorous cause the so called "snowplow" effect and leads to a steadily increasing surface concentration as oxide growth proceeds.

2.6.2 Lateral Diffusion Effects

In practice diffusion in micro-circuits is always carried through windows cut in the mask that is placed on the slice. The one dimensional diffusion equation represents a satisfactory means of describing this process, except at the oxide edge of the mask window. Here the dopant source provides impurities which diffuses at right angles to the semiconductor surface as well as parallel to it (i.e. laterally). It is seen that the lateral penetration is about 75-85% of the penetration in the vertical direction for concentrations that are two or more orders of magnitude below the surface concentration.

2.6.3 Emitter Push Effect

In n-p-n narrow-base transistors using phosphorous diffused emitter and boron diffused based, the base region under the emitter (phosphorous) region is deeper than that outside the emitter region by 0.2 to 0.6 μm. This phenomenon is called emitter push effect.

This effect leads to very serious limitation in the fabrication of high frequency transistors which requires spacing between two diffusions.
2.6.4 The Electric Field Effect

When donor or acceptor impurities enter the silicon crystal, they become ionized, consequently a local electric field is set up between the ionized impurity atoms and the electrons or holes. The concentration gradient of these ionized impurity (donors or acceptors) produces an internal electric field that enhances the diffusivity of the ionized impurity atoms.

Detailed consideration of the problem of the motion of donor or acceptor ions in a semiconductor (16) leads to a modified formula for the flux of the ions.

\[ F = -D \frac{1}{\sqrt{1 + 4(n_i/c)^2}} \frac{\partial c}{\partial x} \] \hspace{1cm} (2.6-1)

Where \( c \) is the concentration of the ions and \( n_i \) denotes the concentration of electrons or holes in a semiconductor containing no donors or acceptors at all the temperature of diffusions.

Equation (2.6-1) can also be written as

\[ F = -D_{\text{eff}} \frac{\partial c}{\partial x} \] \hspace{1cm} (2.6-2)

where

\[ D_{\text{eff}} = D \left[ 1 + \frac{1}{\sqrt{1 + 4(n_i/c)^2}} \right] \]
is the effective diffusivity of the impurities, which incorporates the effect of the built in electric field. At a given temperature, hence at a given value of $n_i$, if the impurity concentration is relatively low, i.e. $C \ll n_i$, $D_{\text{eff}} = D$. Thus the built in field has no effect. In the opposite case, when the impurity concentration is high, i.e. $C \gg n_i$, $D_{\text{eff}} = 2D$. Thus the electric field can bring about an effective doubling of the diffusion coefficient.