CHAPTER-3
CHAPTER 3
MODELLING OF BORON DIFFUSION IN SILICON

3.1. Anomalous Diffusion of Boron in Silicon

Modelling and simulation of fabrication steps used in IC technologies is an important area of research, principally because of the following important reasons (17).

(i) The number of possible combinations of the processes is too large and hence all of them cannot be pursued experimentally. Therefore, it is essential to screen the possibilities and try only the most promising ones.

(ii) For the high performance devices, it is important to study the process sensitivities, computer models make such a study possible.

(iii) For small geometry devices, it is essential to consider the two dimensional effects, because otherwise the correct prediction of the device performance would be difficult.

Diffusion of Boron into silicon has briefly been discussed on the basis of the simple diffusion theory in chapter 2. Prediction of a diffused layer, in principle, involves the solution of the differential equation
\[
\dfrac{\partial^2 c}{\partial t^2} = D \dfrac{\partial^2 c}{\partial x^2}
\]

under appropriate initial and boundary conditions. However, it has been found that the practical results seldom coincide with the above theory particularly in cases involving concentrations higher than the intrinsic carrier concentration values and thus various 'anomalous' effects are observed. In general, it has been seen that in most of the cases, 'D' is a function of local impurity concentration and hence the differential equation may be modified to (18).

\[
\dfrac{\partial^2 c}{\partial t^2} = \dfrac{\partial}{\partial x} \left[ D(c) \dfrac{\partial c}{\partial x} \right]
\]

Thus an important aspect of modelling the diffusion profile is the determination of D(c). Several techniques for its practical determination exist, viz, p-n junction techniques, radio-chemical techniques, surface concentration techniques and electrical profiling techniques. They have been critically reviewed in ref. (19). One of the most usual techniques is that of extracting diffusion coefficients from the impurity profile using Boltzmann Matano analysis, which has been described in detail by Lee (20). However apart from the local concentration dependence of the diffusion coefficient, several other anomalous effects are found in the diffusion of various impurities. To understand these effects
it is important to understand the fundamental diffusion mechanism of impurities in silicon.

3.2. Diffusion of Boron under Non-oxidising conditions

At low surface concentration (<10^19 atoms cm⁻³), boron diffusion under non-oxidising conditions generally produces diffusion profiles consistent with the simple diffusion theory discussed earlier (21,22). At high surface concentration, the shape of these profiles deviates from the theoretical ones (16,23). It has been shown that the electrically active boron profiles change from complementary error function shape to flat topped shape with the onset of a 'kink' as the surface concentration is increased (24,25). Several models have been studied by a number of workers. Thai (26,27) suggested that the concentration dependence of D is related to plastic deformation and degeneracy. He proposed a quantitative theory to model the diffusion coefficient in terms of two enhancement factors, one arising from plastic deformation and the other from internal field. The validity of this model has been criticised by Hu (19). Several other workers (19, 28) proposed the interaction of B⁻ ions with positively charge defects. A quantitative model based upon this has been proposed by Fair (29). He has collected information on the concentration dependent diffusivity D(c) based upon the studies of several workers and has observed the following relationship:
where $D_i$ is the intrinsic diffusion coefficient and $n_i$ is the intrinsic carrier concentration. This relationship suggests the following mechanism: the interstitialcy mechanism, the vacancy mechanism, and the divacancy mechanism. He argues on the basis of the results presented by Van Vechten (30) that the ratio of the interstitials to vacancies under equilibrium in Si near the melting point would be of the order of $10^{-15}$ or less. With regard to the divacancy mechanism, several workers (19) have argued that in silicon at high temperature, thermal equilibrium should favour the formation of monovacancies and divacancies will dissociate rapidly after their creation. Further on the basis of the arguments of the Van Vechten (30) and others, Fair has postulated that boron generally diffuse by interacting with donor type monovacancies ($V^+$) with an electronic energy level at $E_v + 0.37$ eV ($E_{V^+}$).

Thus this model concluded the following relationship:

$$
\frac{D(c)}{D_i} = \frac{c}{n_i} \sqrt{\frac{\gamma^+}{1 + \exp \left\{ \frac{(E_{F_i} - E_{V^+})}{K T} \right\}}} 
$$

$$
D^* n_i \left[ \frac{\gamma^+}{1 + \exp \left\{ \frac{(E_v + E_{V^+})}{K T} \right\}} \right] \left[ \frac{1 + \exp \left\{ \frac{(E_{F_i} - E_{V^+})}{K T} \right\}}{1 + \exp \left\{ \frac{(E_{F} - E_{V^+})}{K T} \right\}} \right] \quad \ldots (3.2-2)
$$
Fair has claimed that this model predicts boron diffusion profiles under non-oxidising conditions which are found to be in excellent agreement with experimental ones. He has also given approximate relationship between junction depth $X_j$, surface concentration $C_s$ and sheet resistivity $\rho_s$ as follows:

\[ \frac{X_j}{2 \sqrt{D_j t}} = 1.225 \sqrt{C_s/n_i} \quad \ldots (3.2-3) \]

\[ \rho_s = \frac{2.78 \times 10^7}{C_s X_j} \quad \ldots (3.2-4) \]

Fair's model, however is based upon the diffusion of only one species. This is incapable of explaining more advanced phenomena like proton enhanced diffusion and the kink formation (25,31). Thus, multistream diffusion mechanism has been considered to model boron diffusion into silicon. Fair (29) has shown that boron diffuses rapidly in heavily p-type material and very slowly in heavily n-type materials. He relates this to the results of Van Vechten et al. (32) by observing that in p-type material most of the vacancies are in the $V^+$ state, while in n-type material they are in the $V^-$ or $V^+$ state. Since the substitutional boron impurity is negatively charged, it is assumed to interact with $V^+$ state to cause diffusion. J.R. Anderson et al. (33) have made an attempt to incorporate these and other observations into a
model from which the boron impurity profile can be calculated for cases of practical interest. The following diffusion equation will adequately describe the boron diffusion profile:

$$\frac{\partial C_B}{\partial t} = D_i \frac{\partial^2}{\partial x^2} \left( C_B \left( \frac{C_B}{2n_i} + \frac{C_B}{2n_i} \right)^{1/2} \right) \ldots (3.2-5)$$

This equation could be described as a diffusion equation with "concentration dependent" diffusivity.

The models considered so far are based on diffusion through point defects. Morehead and Lever (34,35) have developed a relatively simple model to explain the tail diffusion of boron and phosphorus taking interstitials also into account. They assume that interstitials combine with the impurity at the silicon surface, and the interstitial-impurity pair diffuses into the bulk. When the impurity becomes substitutional, an interstitial is released and may diffuse into the bulk or back toward the silicon surface. They assume that at any point in the crystal, the flux of impurity-interstitial pairs into the bulk is equal to the flux of interstitials towards the surface. In principle, their approach allows both vacancies and interstitials to play the same role. The model gives a supersaturation of interstitials in the bulk, which in turn enhances the impurity diffusivity. In their work, they assume that self-
interstitials dominate and that the local concentration of vacancies is determined by local dynamical equilibrium \( (36) \) from

\[
C_I \ C_V = C_I^{eq} \ C_V^{eq} \quad \ldots \ (3.2-6)
\]

where \( C \)'s represent concentration, \( I \) and \( V \) interstitials and vacancies, and the subscript \( eq \) indicates the thermal equilibrium value.

Mulvaney and Richardson \( (37) \) have generalized the Morehead ad Lever model \( (34) \) to include dynamic effects, and relax their assumption of the equality of the impurity-interstitial pair flux and the interstitial flux. They have derived diffusion equations from consideration of the chemical reactions among the impurity, the defect, and free carriers. For boron these relations are \( (34) \)

\[
\begin{align*}
I + h^+ & \rightleftharpoons I^+; \quad C_I^{+} = K_1 P \ C_I \\
I + B^- & \rightleftharpoons (BI)^-; \quad C_{BI} = K_2 C_I C_B \\
I + B^- + h^+ & \rightleftharpoons (BI); \quad C_{BI} = K_3 P C_I C_B \quad \ldots \ (3.2-7)
\end{align*}
\]

where the \( k \)'s are reaction constants, \( P \) is the whole concentration, \( C_I \) is the interstitial concentration, and \( C_B \) is the boron concentration. This model describe the following relations:

\[
\frac{\partial C_i}{\partial t} = \frac{\partial}{\partial x} \left( f_I D_I \frac{\partial(C_I C_j)}{\partial x} \right) - Z_j \frac{f_I D_I}{C_I^*} \frac{\partial}{\partial x} C_I C_j \frac{\partial}{\partial x} n \ln n \quad \ldots \ (3.2-8)
\]
\[ \frac{\partial C_I}{\partial t} = \frac{\partial}{\partial x} D_I \frac{\partial C_I}{\partial x} + \frac{\partial}{\partial x} \left( f_I \frac{D_j}{C_I^*} \frac{\partial (C_I C_j)}{\partial x} - Z_j \frac{f_I D_j}{C_I^*} C_I C_j \right) \]

where \( Z_j \) is the charge state for the impurity (+1 for donors; -1 for acceptors), \( f_I \) is the fractional contribution of the interstitialcy mechanism to the diffusion, \( C_I^* \) is the equilibrium concentration of Interstitial and \( D_I \) is the interstitial diffusivity.

If \( C_I \) is constant and equal to its equilibrium value, Eqn. (3.2-8) reduces to the standard model for diffusion in silicon (38). Equation (3.2-9) reduces to Morehead and Lever's model (34) if the time derivative is set to zero (steady-state condition). By considering the magnitude of the non-linear coupling term, the following observed diffusion effects can also be explained by the model:

(i) For low peak concentrations of impurity, the coupling is relatively small at all temperatures, so the interstitial concentration will not deviate appreciably from its equilibrium value, and the diffusion of impurity will thus be described by the standard model [Eq. (3.2-8) with \( C_I = C_I^* \)], in agreement with phosphorus experiment (39). Also, since boron has a lower solid solubility limit than phosphorus, the boron kink and tail will be less pronounced.
(ii) As temperature increases, $C_1^*$ increases with an activation energy of about 4.8eV (40,41), thus decreasing the relative strength of the coupling term. Therefore, the tail and kink of the phosphorus and boron profiles disappear at higher temperatures.

The model presented assumes that the impurity diffuses by a defect-impurity pair mechanism, that only one type of defect (interstitial or vacancy) dominates, and that chemical equilibrium is maintained for the defect-impurity pair process.

M. Orlowski (42) have proposed a theoretical framework for impurity diffusion in silicon. The basic mechanism employed is the point defect-impurity pair diffusion as presented by Mulvaney and Richardson (37) in a generalised description of the impurity interstitial model by Morehead and Lever (34). The model consists of coupled equations for the impurities and point defects, in which all species including structural defects are treated on the same footing. The model accounts for long-range point defect mediated enhancement and retardation of the diffusion. In this work, the impurities have been allowed to diffuse partly via interstitials and partly via vacancies. The boundary condition for interstitials and vacancies for high surface concentration effects in the bulk has been relaxed by
assuming that all impurities generate interstitials above the solubility limit (43,44). Thus there is an asymmetry in the equations for vacancies and interstitials.

Recently, Mulvaney et al. (45) have described a hierarchy of physical models for impurity diffusion in silicon in terms of a non-equilibrium kinetic reaction diffusion model. Assuming that solid state diffusion phenomena can be described with a continuum model, they have conducted a system of partial differential equations that governs the behaviour species. The species that are responsible for the transport in silicon are first to be identified. In silicon it has been established (46) that vacancy \( V \) and self interstitials \( I \) in their various charge states play an important role in transporting impurity atoms by the formation of defect-impurity pairs. Taking boron impurity, the following species may be identified

\[
V^0, V^+, V^{++}, I^0, I^+, B^-V^0, B^-V^+, B^-V^{++}, B^-I^0, B^-I^-
\]  

The generalised formulation results in a large system (>10) of partial differential equations for the impurity, point defect, and point defect impurity pair species. Additional simplifying assumptions may be made to reduce this model to a five species model, various three species models and finally the standard one species model.
3.3. Diffusion of Boron under oxidising condition

3.3.1. Redistribution of Impurities During Thermal Oxidation

It has been observed that during thermal oxidation of a boron doped layer, redistribution of predeposited boron in silicon takes place. This is a technological importance in the fabrication of bipolar and MOS devices and circuits. During such a redistribution, boron is preferentially segregated into the growing oxide, in addition to diffusing into the bulk silicon material. A large number of investigations for different cases has been done to understand this effect and to model it. One of the most important parameter which governs the impurity distribution during thermal oxidation is the segregation coefficient, which is defined as the ratio of boron concentration in the oxide to the boron concentration in silicon at the $S_1-S_2O_2$ interface. It also depends on the ratio of the diffusion coefficient in silicon and silicon dioxide and the ratio of the parabolic rate constant of oxidation.

3.3.1.1. The Partial Differential Formulation

A model for the redistribution of a complementary error function boron profile after drive-in in oxidising atmosphere was presented by Kato and Nishi (47). This model which utilizes the method of Green's function can provide an accurate solution of the problem. However, it is computationally difficult to implement and is of restricted
applicability for general use. Subsequently, a few more models, namely Cave's model (48) and Huang and Welliver's model (15) were put forward. A good comparison of these models is given by Allen and Atkinson (49). G. Masetti et al. (50) have modified the Kato and Nishi model making use of the mathematical theory of the conduction of heat in a semi-infinite medium with radiation from the plane boundary. This is a fairly simple model and has overcome the limitations of the original Kato and Nishi model.

Another approach to model the same was used by Guckel and Hall (51) by transforming the diffusion equation to a moving reference frame and subsequently using the laplace transform method. This technique may provide a simple solution to the problem provided that a number of simplifying assumptions are made. However, using this technique it is possible to determine the amount of boron leached out of silicon during the drive-in cycle. It has been shown that the calculations agree with experimental results with a fair degree of accuracy. Thus the total amount of boron left in silicon after the drive-in cycle may easily be used to calculate the final boron distribution, assuming a Gaussian profile. The same technique used in the reverse order may be applied to design the two step boron diffusion process. One important observation confirmed experimentally, is that most of the boron, as much as 80% of the total, is usually leached
out of silicon in the initial few minutes of the oxidising cycle. Therefore oxidation-etchoxide-oxidation cycles may be used to reduce the total amount of boron present in silicon. Another model has been presented by A.V. Ron et al. (52) but it is limited to the redistribution of a uniformly doped sample.

3.3.1.2. The Integro-Differential Formulation

Numerical methods based upon the integro-differential formulation of the conservation law have been used to simplify the problem of redistribution of boron under oxidising conditions (53). The continuity equation in one dimension may be written as

$$\frac{d}{dt} \left[ \int_{\text{left}}^{\text{right}} \right] c \, dx = \text{Flux}_{\text{right}} - \text{Flux}_{\text{left}} + \int_{\text{left}}^{\text{right}} (U-G) \, dx \quad \text{... (3.3-1)}$$

Where $U$ is the recombination rate and $G$ is the generation rate. The advantage of this technique is that effects like generation recombination effects, multi-species interactions, mixed media and concentration dependent diffusivity may be taken into account by modelling appropriately $U, G$ and the flux. Also, it has been suggested that the segregation process may not be in equilibrium during oxidation. This
effect can be considered in the above method by including a first-order kinetic model assuming that the equilibrium of the segregation across the silicon-oxide interface is achieved in a flux limited manner (54). It has been claimed that good agreement between theoretical and experimental results is achieved.

3.3.2 Anomalous effects of oxidation on Boron Diffusion:

Anomalous effects of oxidation on boron diffusion have been observed earlier and have been extensively studied by several workers. It is observed that under oxidising conditions, the diffusion is enhanced and the degree of enhancement varied with the surface orientation of the crystal, increasing in the order <111>, <110> and <100>. Allen et al. (14) suggested that the origin of the enhanced diffusion was defects generated at the interface with the oxide and caused by either a mismatch stress or a vacancy imbalance during oxidation. Allen (54) concluded after certain experiments, that (i) the small difference in oxide growth rate between <111> and <100> orientation can not cause the observed difference in diffusion enhancement; (ii) the presence of oxide is not sufficient to cause enhanced diffusion in <100> silicon, but the oxide must be growing; (iii) the number of boron atoms transported in the oxide by diffusion is negligible in comparison with those transported by the segregation effect and the coefficient is independent
of orientation. Okamura (55) reported that the junction depth in \( \langle 100 \rangle \) silicon increases with the oxide thickness, indicating an influence of the oxidation rate on the boron diffusion coefficient. However, the findings of other workers are opposite to this and no effect of oxidation rate on diffusion coefficient is found (56).

Masetti et al (57,58) concluded that all their experimental data could be very well described in terms of redistribution phenomenon by making used of modified Kato and Nishi model, assuming two different diffusion coefficients. The first diffusion coefficient is to be used for boron diffusion in both \( \langle 100 \rangle \) and \( \langle 111 \rangle \) orientation under inert atmospheres and for \( \langle 111 \rangle \) orientation under oxidising atmospheres. The second, roughly twice that of the first, is to be used for \( \langle 100 \rangle \) silicon under oxidising conditions. They also showed that these diffusion coefficients are independent of oxidation rate and redistribution phenomenon. The anisotropy only depends upon the presence or absence of the oxidising atmosphere during diffusion. Also, they argued on the basis of their experiments that explanations based on the influence of dislocations on the diffusion cannot be accepted. They also confirmed that the segregation coefficient is independent of orientation and oxidation rate. As regards the temperature dependence, Masetti et al. (59)
showed that the above diffusion coefficients under dry oxygen atmosphere could be described by an Arrhenius law of the form

\[ D = D_0 \exp \left( \frac{E}{KT} \right) \]  \( \text{(3.4-1)} \)

and that an average value of 0.4 for segregation coefficient could be in the modified Kato and Nishi model, in a temperature range of 950 to 1200°C.

Sanders et al. (60) and Dobson (61) proposed a quantitative model to explain the effects of oxidation on diffusion, assuming the mass transfer in Si to be responsible for observed behaviour. They showed that for an interstitialcy mechanism, an equation describing the profiles can be readily derived, while for a vacancy mechanism the concepts of irreversible thermodynamics and kinetic theory may be used. He also presented a model based on similar lines, assuming that the thermal oxidation is generally incomplete, producing free silicon atoms which become interstitials and thus super saturate the Lattice. He has derived a theoretical expression for calculating effective diffusivity.

3.4 Diffusion of Boron Through Patterned Silicon
3.4.1. Effects of Masking Oxide

Generally the devices on an Ic chip are fabricated using thin layer of silicon dioxide (SiO₂) as a mask against
the diffusion of common impurities e.g. boron, phosphorous, arsenic etc. These devices are of micron size. However, it has not so far been possible to determine doping profiles in these small regions surrounded by masking oxide. In order to monitor the diffusion steps, large plain unmasked check slices simultaneously doped are, therefore, used for profiling purposes. These profiles thus obtained are used in developing the process models. This is valid only when the doping profiles in the small masked regions of the devices are the same as on the large area plain check slices. In other words, the masking oxide simply acts as the mask and does not interfere with the doping in the windows. This was generally considered to be true.

On the basis of a thorough study on the two dimensional effects on boron diffusion, it has been reported (62,63) that the presence of masking oxide surrounding window seriously affects the diffusion kinetics of boron in the window. The results concerning the effects of masking oxide on boron diffusion are summarized below (62):

1. In the case of boron diffused layers, there is a net discrepancy of 20-30% between the sheet resistance determined from the 4pt, probe measurements on the large area check slice and from the resistance measurements on diffused resistors. In the case of 80 μ resistor, the
sheet resistance is always found to be higher by about 30%.

2. The sheet resistance on diffused resistors increases with an increase in the masking oxide frame width. The increase, in the case of a 40 μm wide resistor, has been found to vary from 115% to 129% with a variation of 4 μm to 100 μm in the masking oxide width.

3. The sheet resistance on fabricated resistors increases with a decrease in the window width. For a reduction from 80 μ to 12 μ in windows width, the increase has been observed to be 129% to 161%.

4. The above mentioned discrepancy is observed only during the pre-deposition of boron. The drive-in either does not have any affect (in the case of pure nitrogen ambient) or tends to reduce it (in the case of oxidising ambient).

5. The removal of Si-B phase does not significantly affect the results.

6. The discrepancy is sensitive to the starting material resistivity and its surface orientation.

7. The results are independent of surrounding oxide thickness.
8. The presence of HCl during the thermal oxidation of Si does not effect the results.

9. A reduction of discrepancy is observed with an increase in the total doping of silicon.

10. The discrepancy disappears when the boron source is spin-on or ion-implanted.

11. In the case of phosphorous, predeposition as well as drive-in do not produce any discrepancy.

12. An attempt at resistivity vs depth profiling and junction depth measurements shows that near the surface, the concentration in the large area check slice and in the resistor surrounded by the oxide is the same and the junction depth in the fabricated resistors is smaller than the other region.

3.5 Discussion

It may be seen that two distinct attempts for modelling of boron diffusion in silicon are required. One for diffusion in silicon bulk to take into account all the effects discussed in section 3.1-3.3. This has been considered in chapter 6. The other attempt is needed to model the diffusion through patterned silicon considering the effects of masking oxide surrounding the diffusion windows discussed in section 3.4. In this case an experimental study is further required.
to develop a theory for the explanation and modelling of the effects. This has been discussed in the following chapters.