

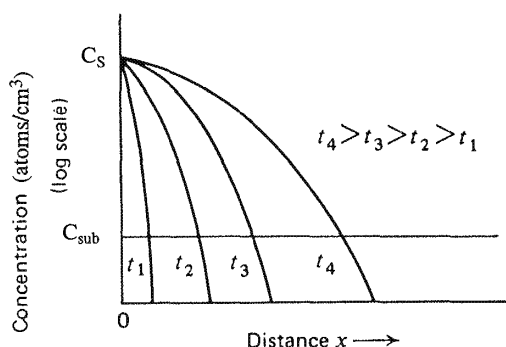


Fig. 9-2 Schematic representation of the diffusion profile for constant source diffusion (pre-deposition). Note the surface concentration remains constant with increasing diffusion time.⁷² From S.K. Ghandi, *VLSI Fabrication Principles*. Reprinted with permission of John Wiley & Sons.

The junction depth, x_j , can be calculated by determining the depth (value of x) at which the diffusing dopant concentration just equals the background concentration in the silicon, C_{sub} . This is accomplished by solving Eq. 9-10 for x when $C = C_{sub}$:

$$x_j = (2\sqrt{Dt}) \operatorname{erfc}^{-1}\left(\frac{C_{sub}}{C_s}\right) \quad (9.12)$$

where erfc^{-1} is the inverse of the complementary error function. Both Eqs. 9-11 and 9-12 contain the "root Dt" term.

9.1.3.2 Drive-In Diffusion: Next consider what happens to the dopant atoms that have been introduced during the predeposition if the silicon is subjected to additional thermal treatment. We would expect that the total dose, Q_0 , in the silicon should remain constant and the diffusant would move deeper into the silicon. This process is termed the *redistribution* or *drive-in* diffusion. The drive-in is used to move the impurities to the desired junction depth following the predeposition. In order to obtain a closed-form solution of Fick's Second Law, it is necessary to assume that the initial dopant is confined to a thin layer at the surface. As a matter of fact, the solution assumes that the dopant Q_0 , exists as a δ -function in a thin rectangular region at the surface. The total quantity of impurity present is fixed at Q_0 (atoms/cm³). For the drive-in case, the initial condition is given by Eq. 9-13:

$$C(x, 0) = 0 \quad \text{for } x > \delta \quad (9.13)$$

and the two boundary conditions are given by Eqs. 9-14 and 9-15:

$$\int_0^{+\infty} C(x, t) dx = Q_0 \quad (9.14)$$

and

$$C(\infty, t) = 0 \quad (9.15)$$

The boundary condition in Eq. 9-14, states that the total amount of dopant is fixed at Q_0 . The solution to Fick's Second Law, under these conditions is:

$$C(x, t) = \frac{Q_0}{\sqrt{\pi Dt}} \exp\left(\frac{-x^2}{4Dt}\right) \quad (9.16)$$

This solution has the form of a *Gaussian distribution*. The surface concentration, C_s (which in this case decreases as a function of time) is determined from Eq. 9-17 when $x = 0$:

$$C_s = C(0, t) = \frac{Q_0}{\sqrt{\pi Dt}} \quad (9.17)$$

From Eq. 9-17 one can see that the surface concentration decreases as the diffusion time increases. The junction depth for the drive-in diffusion case is calculated in a manner similar to that used to obtain Eq. 9-12 and is given by:

$$x_j = 2\sqrt{Dt} \left(\ln \frac{Q_0}{C_{\text{sub}} \sqrt{\pi Dt}} \right)^{1/2} \quad (9.18)$$

Figure 9-3 shows a plot of the concentration profile $C(x)$ for the Gaussian case for several drive-in diffusion times at a constant temperature. The key points to note are that the value of C_s decreases and the junction depth moves deeper into the silicon as the diffusion time increases.

An example of how to use these two diffusion models is now provided. In the first example the diffusion profile, the junction depth, and total dopant concentration after a pre-deposition step are each calculated. In the second example the information from the previous example is used to establish the diffusion profile and junction depth after a drive-in diffusion step.

EXAMPLE 9-1: Calculate: a) diffusion profile; b) junction depth; & c) total amount of dopant introduced after boron predeposition performed at 950°C for 30 min, in a neutral ambient. Assume the substrate is *n*-type with a background doping level of 1.5×10^{16} atoms/cm³ and the B surface concentration reaches solid solubility ($C_s = 1.8 \times 10^{20}$ atoms/cm³).

SOLUTION: a) Under the conditions of the predeposition, the diffusion profile is controlled by the erfc of Eq. 9-10. The profile can be found by using the erfc curve of Fig. 9-4. In order to use this curve, values of $x/(2\sqrt{Dt})$ must be calculated for values of x . Corresponding values of $C(x)/C(0)$ [where $C(0)$ is the B surface concentration C_s], are found from Fig. 9-4, and finally values of $C(x)$ are calculated. First, the value of the B diffusion coefficient at 950°C (1223 K) is found from (i.e., calculated using Eq. 9-38):

$$D_B(1223 \text{ K}) = 0.76 \exp(-3.46 \text{ eV}/k \cdot 1223 \text{ K}) [\text{cm}^2/\text{sec}] = 4.19 \times 10^{-15} \text{ cm}^2/\text{sec}.$$

Next calculate the diffusion length, $z = 2\sqrt{Dt}$, for this process:

$$z = 2\sqrt{Dt} = 2 (4.19 \times 10^{-15} \text{ cm}^2/\text{sec} \cdot 1.8 \times 10^3 \text{ sec})^{1/2} = 5.49 \times 10^{-6} \text{ cm}.$$

Now set up the following table to assist in the calculation of the diffusion profile:

x (cm $\times 10^{-4}$)	$x/(2\sqrt{Dt})$	$C(x)/C(0)$	$C(x)$ (atoms/cm ³)
0	0	1	1.8×10^{20}
0.05	0.91	0.198	3.5×10^{19}
0.075	1.36	0.054	9.7×10^{18}
0.10	1.82	0.010	1.8×10^{18}
0.15	2.73	0.00011	2.0×10^{16}

b) The junction depth, x_j , is defined as the value of x where the concentration of the diffusion profile equals the substrate doping (1.8×10^{16} atoms/cm³). When $C(x) = 1.8 \times 10^{16}$ atoms/cm³, then $C(x)/C(0) = 1.0 \times 10^{-4}$. Next obtain $x_j/(2\sqrt{Dt})$ from Fig. 9-4 (i.e., $x/\sqrt{Dt} = 2.76$)

$$\text{Thus: } x_j/2\sqrt{Dt} = 2.76; \text{ and } x_j = 2.76 \cdot 5.49 \times 10^{-6} \text{ cm} = 1.51 \times 10^{-5} \text{ cm} = 0.151 \text{ } \mu\text{m}$$

c) The total amount of dopant is calculated from Eq. 9-11:

$$Q_0 = C_s(2\sqrt{Dt})/\sqrt{\pi} = (1.8 \times 10^{20} \cdot 5.49 \times 10^{-6})/1.77 = 5.58 \times 10^{14} \text{ atoms/cm}^2.$$

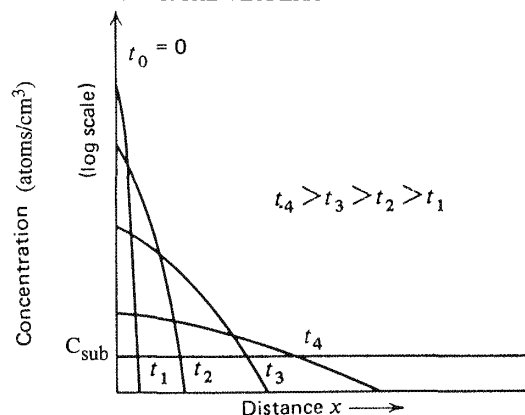


Fig. 9-3 Schematic representation of the diffusion profile for a limited source diffusion (drive-in). Note the surface concentration decreases with increasing diffusion time and the total dopant concentration remains constant.⁷² From *VLSI Fabrication Principles*. Reprinted with permission of John Wiley & Sons.

EXAMPLE 9-2: Calculate the diffusion profile and junction depth after the predeposition of Example 9-1 is subjected to a neutral-ambient drive-in at 1050°C (1323 K) for 60 min.

SOLUTION: For the drive-in diffusion conditions of this example the Gaussian distribution of Eq. 9-16 (the curve labeled *Gaussian* in Fig. 9-4) controls the profile. First calculate the diffusion coefficient, D_B , and the diffusion length ($z = 2\sqrt{Dt}$) for the new diffusion conditions:

D_B (1323 K) = $0.76 \exp(-3.46 \text{ eV}/k \cdot 1323 \text{ K}) = 5.0 \times 10^{-14} \text{ cm}^2/\text{sec}$; and $z = 2\sqrt{Dt} = 2.68 \times 10^{-5} \text{ cm}$
Next calculate the value of the surface concentration C_s from Eq. 9-17:

$$C_s = Q_0 / \sqrt{\pi Dt} = 5.58 \times 10^{14} \text{ atoms/cm}^2 / (\pi \cdot 5.0 \times 10^{-14} \text{ cm}^2/\text{sec} \cdot 3600 \text{ sec})^{1/2} \\ = 2.34 \times 10^{19} \text{ atoms/cm}^3$$

Set up the following table to assist in the calculation, using Eq. 9-16, and $4Dt = 7.2 \times 10^{-10}$:

$x \text{ (cm} \times 10^{-4}\text{)}$	$x^2/4Dt$	$\exp[-x^2/4Dt]$	$C(x) \text{ (atoms/cm}^3\text{)}$
0	0	1	2.34×10^{19}
0.1	0.139	0.87	2.03×10^{19}
0.2	0.55	0.57	1.33×10^{19}
0.3	1.25	0.286	6.69×10^{18}
0.4	2.22	0.109	2.55×10^{18}
0.5	3.47	0.031	7.25×10^{17}
0.6	5.00	0.0067	1.69×10^{18}
0.7	6.81	0.0011	2.57×10^{16}
0.8	8.88	0.00014	3.27×10^{15}

Now calculate x_j directly from Eq. 9-18. First, we estimate x_j from the table above. Since C_{sub} is $1.8 \times 10^{16} \text{ atoms/cm}^3$, x_j must lie between $0.7 \mu\text{m}$ and $0.8 \mu\text{m}$.

$$x_j = 2\sqrt{Dt} [\ln(C_s/C_{\text{sub}})]^{1/2} = 2.68 \times 10^{-5} [\ln(2.34 \times 10^{19}/1.8 \times 10^{16})]^{1/2} = (2.68 \times 10^{-5} \times 2.67) \text{ cm}$$

or:

$$x_j = 0.715 \mu\text{m}.$$

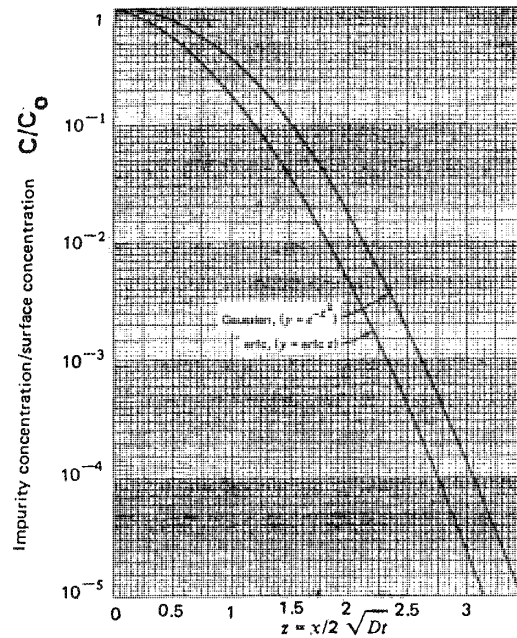


Fig. 9-4 Normalized concentrations $[C/C(0)]$ as a function of normalized distance $(x/2\sqrt{Dt})$ for the erfc and Gaussian curves.

9.1.3.3 Drive-In From An Ion Implantation Predeposition: If the predeposition is from an ion implanted source (which produces a doping concentration with a near-Gaussian distribution close to the surface), the Gaussian profile will move when subjected to a high temperature anneal (see Chap. 10 on Ion Implantation). The solution to Eq. 9-6 (concentration-independent diffusion) with an initially implanted Gaussian profile has been reported for the cases of drive-ins performed in a neutral ambient,⁴ and an oxidizing ambient.⁵ For drive-ins in an oxidizing ambient, the solution to Eq. 9-6 is difficult to obtain in closed form, since it involves a moving boundary problem. Consequently, numerical methods must be employed to obtain the solutions (see Chap. 2, Vol. 3 of this series).

9.1.4 Concentration Dependence of the Diffusion Coefficient

The diffusion profiles that were calculated in the previous section are valid for the case when the diffusion constant is not a function of the doping concentration. That is why solutions of Eq. 9-6 were used, rather than those for Eq. 9-5. Constant-value D prevails when the doping concentration is lower than the intrinsic-carrier concentration n_i at the diffusion temperature, and conversely, concentration dependent diffusion occurs when the doping level is greater than the intrinsic carrier concentration. The first case is termed *intrinsic diffusion* while the latter is called *extrinsic diffusion*. To determine where extrinsic diffusion starts one needs to know the intrinsic carrier concentration at the diffusion temperature. Equation 9-19 is the expression used to calculate the intrinsic carrier concentration in silicon:

$$n_i = p_i = \sqrt{N_v N_c} \exp\left(-\frac{E_g(T)}{2kT}\right) \quad (\text{cm}^{-3}) \quad (9.19)$$

Here, N_v and N_c are the density of states at the valence and the conduction band edges, respect-

ively, E_g is the energy gap of Si, k is Boltzmann's constant, and T is the temperature in kelvins (K). The value of E_g depends somewhat upon temperature and the doping concentration and these factors must be taken into account when determining the intrinsic carrier concentration. The bandgap dependence on temperature in the range of 800–1100°C, and is given by:

$$E_g(T) = E_g(0) - bT \quad (9.20)$$

where $E_g(0) = 1.46$ eV and $b = 2.97 \times 10^{-4}$ eV/K.

There is a "bandgap narrowing" effect, δE_g , that occurs for heavily doped silicon. A "lumped" model has been developed to provide a value for the narrowing effect.⁶ This model is not based upon first principles, since no simple physical model has been found to explain the effect. One proposal is that the lattice strain caused by the presence of heavy doping induces the band gap to change. When bandgap narrowing, $\delta E_g/2kT$ is included, the *effective intrinsic carrier concentration* n_i^{eff} is given by:

$$n_i^{\text{eff}} = n_i (\delta E_g/2kT) \quad (9.21)$$

Under extrinsic conditions, D depends on the doping concentration, and since the concentration changes with distance (i.e., a concentration gradient exists), D also changes with distance. To obtain a solution to Fick's Law one can expand Eq. 9-5 to read:

$$\frac{\partial C(x,t)}{\partial t} = \frac{\partial}{\partial x} \left(D \frac{\partial C}{\partial x} \right) = \frac{\partial D}{\partial x} \frac{\partial C}{\partial x} + D \frac{\partial^2 C}{\partial x^2} \quad (9.22)$$

The $\partial D/\partial x$ term makes Eq. 9-22 an inhomogeneous differential equation making it difficult to solve. Fortunately, a graphical procedure termed the *Boltzmann-Matano analysis* has been developed, which renders a solution for the diffusion coefficient, D , as a function of concentration.⁷ It does not, however, explicitly provide the diffusion profile $C(x,t)$, as was obtained for the intrinsic diffusion case. The Boltzmann-Matano method allows $D(C)$ to be calculated from the experimentally determined concentration profile (C vs. x plot). There are several methods that are commonly used to obtain the concentration profile and they are discussed later in this chapter.

9.2 DEFECTS AND DOPANT DIFFUSION

It has been realized for some time that the diffusion of dopant atoms in Si is strongly coupled to the presence of point defects. This early realization came about when it was found that the diffusion coefficient of the dopant atoms did not follow the behavior predicted by Fick's Laws, but rather exhibited certain anomalous effects. These effects will be described in detail in later sections but are briefly mentioned here. The first anomaly was that the diffusivity of boron was greatly enhanced when phosphorous was subsequently diffused into the Si (the so-called *emitter push effect*). The second was that some dopants exhibited a higher diffusivity when the drive-in diffusion was performed in an oxidizing ambient (*oxidation-enhanced diffusion* or *OED*). Since these effects were initially observed, other anomalous effects have been found, and as a group their behavior can be explained by the presence of point defects in the silicon. Consequently, the types and interaction of point defects and dopants in silicon are now discussed.

9.2.1 Point Defects in Silicon

Chapter 2 described some of the point defects that can exist in silicon, particularly at the temperatures normally associated with diffusion. Some of these defects are now briefly reviewed and how they relate to the diffusion of dopant atoms in silicon is discussed. The nomenclature used in the excellent treatise on diffusion by Fahey, Griffin, and Plummer is employed.⁸

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The first type of point defect to consider is the defect which arises from the introduction of impurity atoms into silicon. An impurity atom, such as a *dopant* atom that sits on a lattice site, is termed a *substitutional defect*. Even though the atom resides on a lattice site it is either larger or smaller than the silicon atom, and thereby causes a local perturbation in the periodicity of the lattice. Any perturbation to the lattice periodicity is termed a *defect*. It turns out that most of the common dopant atoms (P, As, Sb, B, In, Ga) dissolve into silicon as substitutional atoms. That is, they reside on silicon lattice sites in place of silicon atoms. These dopant atoms are also remarkable for their high solubility in silicon when compared to other elements that also dissolve in silicon. The solubilities of these dopants are discussed in Chap. 1.

A dopant atom on a substitutional site is given the designation A and can be either a donor or an acceptor. When a dopant atom occupies a substitutional site it contributes either an electron to the conduction band, or a hole to the valence band. In either case, the dopant atom then becomes an ion. It is the ion (a charged atom) that must diffuse in the silicon. It is not surprising that since the dopant atom (or ion) is charged it would interact with other charged species (e.g., crystalline point defects and free carriers).

As discussed in Chap. 2, there are other point defects that may be present at the diffusion temperature, namely: a) *vacancies*; b) *interstitials*; and c) *interstitialcies*. Such *lattice defects* are designated as X, where X can be either a vacancy or interstitial-type defect. The vacancy defect is defined as a missing Si atom or an empty lattice site and is designated as V. The presence of a vacancy requires the covalent bonds around that site to reconfigure to accommodate the defect. The V defect itself can become charged by capturing one or two electrons (or a hole), or can remain neutral. As discussed in Chap. 2, four vacancy defects have been identified:

1. The neutral vacancy, V^0
2. The singly-charged negative vacancy (in which one electron is captured), V^{-1}
3. The doubly-charged negative vacancy (in which two electrons are captured), V^{-2}
4. The singly-charged positive vacancy (in which one hole is captured), V^{+}

Figures 9-5a1, 9-5a2, and 9-5a3 show how the unsatisfied bonds reconfigure to accommodate the various defects in the silicon lattice.

The next type of defect discussed is the *self-interstitial*, which can be described as a Si atom on an *interstitial* site. Self-interstitials are given the designation I. The term self-interstitial is used to distinguish these defects from those involving extrinsic or foreign atoms (which can also exist in the lattice as interstitials). Figures 9-5b1 and 9-5b2 show the bonding around a tetrahedral and a hexagonal interstitial site, respectively. The last type of defect (not often recognized), is called the *interstitialcy*. The interstitialcy is also designated by I. The interstitialcy defect differs from the interstitial defect in that it has two "associated" atoms in non-substitutional sites, around a substitutional site. The two atoms constituting the interstitialcy can consist of: a) both Si atoms (an I-defect); or b) a Si atom and a dopant atom (an AI-defect). The interstitialcy defects can remain neutral or become charged, and have the following configurations:

1. A neutral interstitialcy with two silicon atoms, I^0 .
2. A singly-charged positive interstitialcy comprised of two silicon atoms, I^{+1} .
3. An associated dopant and silicon interstitial that is neutral, $(AI)^0$. This type of defect behaves as an acceptor site.
4. An associated dopant and silicon interstitial that is singly-negatively charged, $(AI)^{-1}$. This type of defect also behaves as an acceptor site.
5. An associated dopant and silicon interstitials that is singly-positively charged, $(AI)^{+1}$.

This type of defect behaves as a donor site.

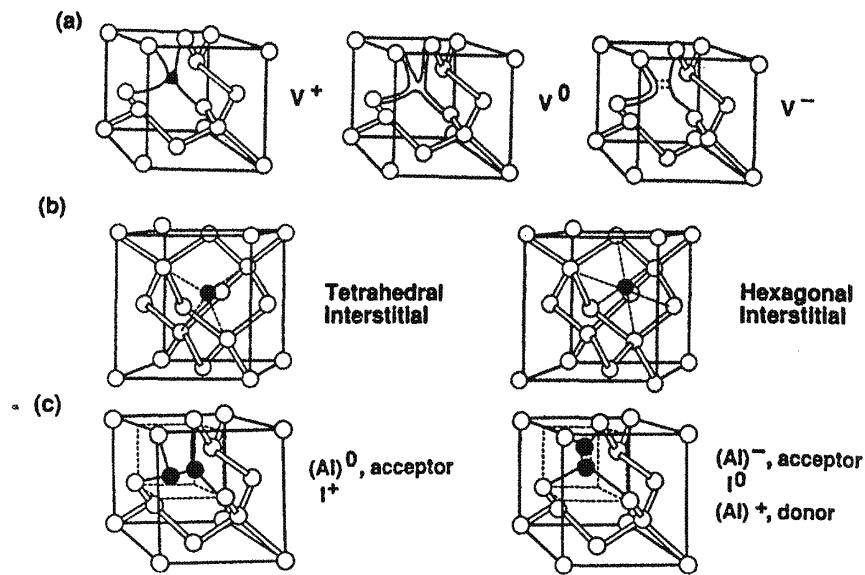


Fig. 9-5 Schematic of how the bonds may reconfigure to accommodate various defects in the silicon lattice: (a) vacancy defects; (b) interstitial defects; and (c) interstitialcy defects. If both dark spheres in (c) are silicon, the defect is the (I) defect. But if one is silicon and one is a dopant atom, the defect is (AI).⁸ Reprinted with permission of the American Physical Society.

Figures 9-5c1 and 9-5c2 show the atomic arrangement of interstitialcy defects. The distinction between the interstitial and the interstitialcy is often not emphasized since it is difficult to discern between the two defect types by experimentation. As a result, both of these defects are referred to as *interstitial-type* defects.

Now that the three defects (i.e., the vacancy V , the interstitial-type I , and the dopant impurity A) have been described, it is appropriate to investigate the interaction among these defects, as this will help in understanding how such interactions may affect diffusion.

The following associated dopant-atom/defect configurations may exist in the lattice: a) a dopant atom is on a lattice site (A); b) a doping atom is adjacent to a vacancy (AV); and c) a dopant atom is one of the atoms of the interstitialcy (AI). If the dopant atom actually occupies the interstitial site, it is designated A_i . It is the dopant-atom/defect pair that migrates during diffusion in one or more of the following configurations: AV , AI , or A_i . The coordinated dopant-atom/defects can be formed by the following reversible equilibrium reactions. The "Law of Mass Action" applies to these reactions.



or:



There is a further equilibrium reaction that should also be mentioned, and that is the creation and annihilation of vacancies and interstitials via the Frenkel defect:



The $\leftrightarrow$ symbolizes that the reaction is reversible, and since the concentrations of I and V can be affected by external forces (i.e., point defects arising from other sources), these reactions may be favored in one or the other direction. For example, if a large concentration of interstitials is created by oxidation, then the forward direction of Eq. 9-23 is favored, and the concentration of AI increases. The increase in AI concentration results in increased dopant diffusion.

A brief description of Eqs. 9-23 to 9-27 is given next. The reaction in Eq. 9-23 represents an exchange between a substitutional atom A and the interstitial(cy) I. It is termed the *kick-out* reaction, since the Si-I kicks out a dopant atom from a substitutional site and forms an AI pair. The reaction in Eq. 9-24 describes the dopant-vacancy reaction and governs vacancy-controlled diffusion. The reactions given in Eqs. 9-25 to 9-27, describe recombination reactions between I and V defects. The reaction in Eq. 9-26 describes a dissociative reaction termed the *Frank-Turnbull* mechanism. This mechanism is not considered to be important for Si diffusion since it is believed to have a low probability of occurrence. Finally, the forward reaction of Eq. 9-27, describes the formation of a Frenkel defect (vacancy and interstitial) as is described in Chap. 2.

In the past it was considered that dopant diffusion in silicon was controlled solely by the vacancy mechanism, but now it is well established through numerous investigations that both I- and V-type mechanisms contribute to dopant diffusion. As it turns out, most of the common dopants have a dominant I-diffusion-controlled mechanism. The evidence for this conclusion is discussed in detail in a later section.

The reactions dealt with above do not give the origin of the defects. There are two possibilities of defect formation that were described in Chap. 2, namely: a) an atom leaving a lattice site and creating a V and I, and b) a silicon atom diffusing from the surface of the silicon into the bulk to create an interstitial or a silicon atom that was on a lattice site moving to the surface (and vanishing by becoming part of the disorder at the surface) and creating a vacancy in the bulk. Another important source of defect production is lattice damage resulting from ion implantation. As a result, the diffusion of dopants from an ion implanted source can substantially differ from that of a chemical source.

9.2.2 Temperature Dependence of the Diffusion Coefficient Under Intrinsic Conditions

The temperature dependence of the diffusion coefficient, D, for intrinsic diffusion for the common dopant atoms will now be examined. However, before we proceed, it is instructive to first inspect the temperature dependence of the self-diffusion of silicon. Most self-diffusion studies used radio-active isotopes of silicon to determine the diffusion profile. Even to this day, however, the basic mechanism of Si self-diffusion is not well understood.

Some results from a study that examined the effect of hydrostatic pressure on Si self-diffusion show the dominant mechanism is interstitial-type-dominated diffusion.⁹ The most interesting aspect about silicon self-diffusion is that the activation energy for the process is about 1 eV greater than that of dopant diffusion. For some reason the movement of silicon-defect pairs takes more energy than that of dopant-defect pairs. The diffusion coefficient for Si self-diffusion D_{self} is given by:¹⁰

$$D_{\text{self}} = 1400 \exp(-5.01 \text{ eV}/kT) \text{ cm}^2/\text{sec} \quad (9.28)$$

**Table 9-2 COMPILED VALUES OF APPARENT ACTIVATION ENERGIES
FOR DIFFUSION OF COMMON DOPANTS⁸**

Donors	$Q_A(\text{eV})$	Acceptors	$Q_A(\text{eV})$
P	3.51–3.67	B	3.25–3.87
As	4.05–4.34	Al	3.36
Sb	3.8–4.05	Ga	3.75
		In	3.60

9.2.3 Intrinsic Diffusion Coefficients

Numerous experimental measurements have been made on the effect of temperature on the diffusion coefficients (D_A) of the common dopants during intrinsic diffusion. In general the resulting data can be represented by an Arrhenius equation.

$$D_A = D_{A0} \exp(-Q_A/kT) \quad (9.29)$$

Here D_A is the diffusion coefficient of the dopant atom, D_{A0} is the pre-exponential term or *frequency factor*, which is related to the *frequency* of the lattice vibrations (i.e., the frequency at which atoms strike the potential barrier that they must overcome to move in the lattice), and Q_A is the *apparent activation energy* of the diffusion process (which is related to the *height* of the energy barrier that the impurity must overcome in order to move within the lattice).

The value of Q_A for the common dopants has been compiled by Wohlbier.¹¹ This data is reproduced in Table 9-2, which was extracted from the summary of Wohlbier's work, given by Fahey, Griffin, and Plummer.⁸ Readers interested in additional details are referred to that article, which lists the original references, or to the Wohlbier monograph. Although the values of apparent activation energy vary somewhat, depending on the particular study and dopant, all of the values range between 3.3 to 4.3 eV.

9.2.4 Fast Diffusers in Silicon

There is another class of impurities that diffuse in silicon much more rapidly than the electrically active dopant atoms. These impurities are called the *fast diffusers* and their diffusion coefficients at 900°C are listed in Table 9-3. The fast diffusers, as evidenced by their name, diffuse much faster in silicon than do the dopants atoms. The fast diffusers (e.g., Fe, Cu, Pt) move great distances in silicon during high temperature processing, thereby increasing their probability of being trapped at an extended defect and causing increased leakage current in a device. The effect of the fast diffusers on device properties is discussed in Chap. 2. The apparent activation energies (0.2–2 eV) for the fast diffusers are much lower than for the substitutional impurities. At one time it was believed that the low values of activation energy implied interstitial diffusion, while the high activation energy values of the dopant atoms were due to vacancy diffusion. This analysis is not correct, and it is now well established that both vacancies and interstitials play a role in the movement of fast diffusers in silicon.

9.3 ATOMISTIC MODELS OF DIFFUSION

Some of the possible ways a dopant atom may move in the crystalline lattice are next explored from an atomistic perspective. The most favorable configuration for a dopant atom to diffuse in silicon is when it is associated with a nearest-neighbor defect. Only a fraction of the dopant atoms are associated with defects in this manner, but it is this fraction that contributes to the

Table 9-3 DIFFUSION COEFFICIENTS of FAST DIFFUSANTS in SILICON @ 900°C

Element	D (cm ² /sec)	Element	D (cm ² /sec)
Na	1.6×10^{-3}	Ag	2.0×10^{-3}
K	1.1×10^{-3}	Pt	1.6×10^{-2}
Cu	4.7×10^{-2}	Fe	6.2×10^{-3}
Au	1.1×10^{-3}	Ni	1.0×10^{-1}
Au _i	2.4×10^{-4}	O ₂	7.0×10^{-2}
Au _s	2.8×10^{-3}	H ₂	9.4×10^{-3}

diffusion. This fraction has been calculated as:¹²

$$C_{AX} = \theta_{AX} \frac{C_A C_X}{C_S} \exp\left(\frac{E_{AX}^b}{kT}\right) \quad (9.29)$$

where C_A is the dopant concentration; C_X is the unassociated defect concentration; C_S is the concentration of lattice sites ($5 \times 10^{22}/\text{cm}^3$), E_{AX}^b is the binding energy of the AX defect. The θ_{AX} factor accounts for the number of equivalent ways of forming the defect AX at a particular site (e.g., $\theta_{AV} = 4$). There have been numerous investigations to determine the value of E_{AX}^b and the reader is referred to the Fahey treatise for further detail.⁸

There are several potential ways dopant atoms may diffuse in the lattice, namely: a) direct dopant exchange (no point-defect interaction); b) vacancy-dopant interaction; c) interstitialcy-dopant interaction; and d) interstitial-dopant interaction. The interstitial and interstitialcy mechanisms are very similar and it is difficult to discern which is actually operative during diffusion.

First consider the possibility that mechanism (a) is responsible for controlling diffusion in Si. That is, what is the likelihood that diffusion proceeds by substitutional dopant atoms exchanging positions with adjacent silicon atoms (the *direct exchange* mechanism, shown schematically in Fig. 9-6a)? For diffusion to continue after the first interchange, the dopant atom must exchange positions again with the next Si atom. If the dopant atom instead exchanges positions with the original Si atom it will not make progress diffusing within the lattice. The continuation of the direct interchange process is unlikely because the activation energy associated with the breaking of Si bonds is high, and at least six Si bonds must be broken for each exchange to occur.

On the other hand, it is much more energetically favorable if the substitutional impurity is adjacent to a silicon vacancy and the exchange happens between the vacancy and the dopant atom. When this exchange occurs, it is termed the *vacancy mechanism* ($A + V \leftrightarrow AV$), as schematically shown in Fig. 9-6b. The uncomplicated motion involved in the vacancy mechanism led early investigators to believe that the vacancy interchange should dominate dopant diffusion in silicon. This belief was supported by the fact that vacancies dominate diffusion in metals. Consequently, detailed models were developed to explain diffusion in silicon according to the vacancy mechanism.^{12,13}

Diffusion via the vacancy mechanism, however, does not occur by a single interchange of a vacancy with a dopant atom. If that was indeed the case, there would be no net diffusion. That is, in order for the dopant to diffuse over a long range, the vacancy must diffuse away from the dopant atom at least to the third nearest neighbor. Only in this way can it return to the dopant atom via a different path, thus allowing diffusion to continue further along. It can be shown that

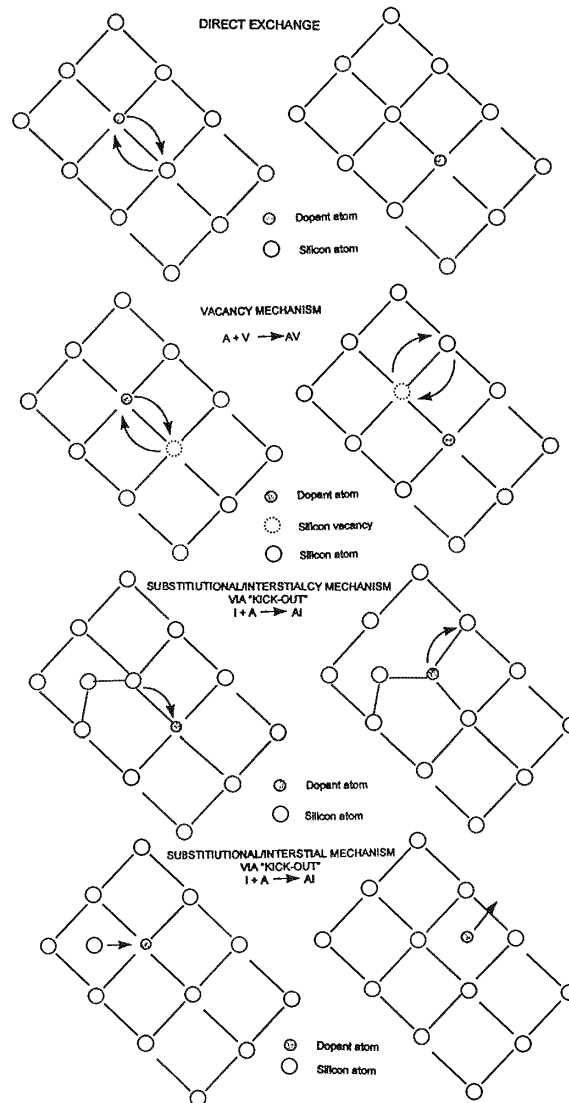


Fig. 9-6 Dopant movement at the atomic level: a) direct exchange; b) vacancy mechanism; c) substitutional-interstitial mechanism via "kick-out"; d) substitutional-interstitial mechanism via "kick-out".⁸ Reprinted with permission of the American Physical Society.

the activation energy for the diffusion of the AV associated pair is less than that of A diffusing by itself, and as a result the vacancy mechanism is more energetically favorable than the dopant atom diffusing by direct interchange.

The *interstitialcy mechanism* ($I + A \leftrightarrow AI$) can be represented on an atomic level as a dopant atom in a substitutional site that is approached by a silicon interstitialcy (Fig. 9-6c).¹⁴ Recall that the interstitialcy defect has two associated atoms in non-substitutional sites around a substitutional site. In the case of the silicon interstitialcy both atoms are silicon. One of the silicon interstitial atoms knocks a dopant atom out of a substitutional site and forms a dopant interstitialcy. The dopant atom then moves toward a silicon atom on a lattice site and *kicks out* the silicon atom and forms a reconfigured dopant-interstitialcy. Unlike the vacancy mechanism, which requires that the AV pair partially dissociate, the interstitialcy mechanism does not have the same restrictions. The energy for this type of motion has been determined to be less than for self-diffusion by about ΔQ_{AI} (the attractive potential between A and I), where ΔQ_{AI} is ~ 1 eV.

The final atomistic mechanism used to explain dopant diffusion is the "pure" *interstitial mechanism* ($I + A_s \leftrightarrow A$). In this mechanism (see Fig. 9-6d), a silicon interstitial replaces a dopant atom on a substitutional site to form a dopant interstitial. The dopant interstitial moves through the interstices of the silicon lattice until it finds a substitutional site to occupy. When the dopant atom occupies the substitutional site it forms another silicon interstitial. This mechanism is very similar to the interstitialcy mechanism discussed above and as a result it is difficult to separate it from the interstitialcy mechanism.

The general consensus among investigators in the field regarding the atomistic mechanism controlling the movement of the common dopants in silicon is as follows: Phosphorus and boron have the largest amount of interstitial-type diffusion, while arsenic exhibits both vacancy and interstitial diffusion, and antimony seems to be dominated by vacancy-controlled diffusion. How these conclusions were reached is discussed in a subsequent section.

9.4 DIFFUSION MODELLING

It is important to be able to predict the movement of dopant atoms in Si during thermal processing with mathematical simulations. Simulation of the diffusion and redistribution of the dopant allows process development and integration engineers to substantially reduce the number of process experiments required during technology development. There are several simulation programs that are commonly used, with the most common being SUPREM (Stanford University Process Engineering Model). The modeling of diffusion in one-dimension is covered by SUPREM III, while the extension to two-dimensions is covered by SUPREM IV. SUPREM IV, of course, is also capable of treating the one-dimensional case. Some of the models that are used in SUPREM III and their extension to SUPREM IV will now be discussed.

9.4.1 SUPREM III

The models in SUPREM III are empirically determined and are derived from the observed dopant-diffusion interactions in silicon. The basis of the diffusion model in SUPREM III is that diffusion is governed by the one-dimensional continuity equation, which accounts for the atom flux from the concentration gradient plus the enhanced flux that results from the built-in electric field formed from ionized impurities in a concentration gradient, and is given by Eq. 9-31:

$$\frac{\partial C}{\partial t} = \frac{\partial}{\partial x} \left(D \frac{\partial C}{\partial x} \right) \pm \frac{q}{kT} \left[\frac{\partial}{\partial x} \left(DC_i \frac{\partial \phi}{\partial x} \right) \right] \quad (9.31)$$

mechanism; c)
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Where D is the dopant diffusion constant, and C and C_i are the total and electrically charged dopant concentrations, respectively. The potential ϕ that results from the concentration gradient is given by:

$$\phi = kT/q [\ln(n/n_i)] \quad (9.32)$$

where n is the carrier concentration resulting from dopant ionization and n_i is the intrinsic carrier concentration at the diffusion temperature. In many real problems the local charge neutrality is maintained and the second term on the right hand side of Eq. 9-31 can be dropped, resulting in Fick's Second Law. More simply, if D does not depend on the concentration of the dopant then the simplified Fick's Second Law holds as expressed in Eq. 9-33, below, which is the same as Eq. 9-6.

$$\frac{\partial C(x,t)}{\partial t} = D \left[\frac{\partial^2 C(x,t)}{\partial x^2} \right] \quad (9.33)$$

- a. If the values of D are known, the solutions to Eqs. 9-31 and 9-33 will provide accurate simulations of the dopant concentrations for many applications.

There are two approaches used to obtain the values of D . In the first approach the value of D is determined from measured diffusion profiles and then plotted for various temperatures and doping concentrations. Solutions to Eq. 9-31 and 9-33 are then fitted to the experimental plots by finding values of D that give solutions that match the D values extracted from the observed data. This type of model is known as a *phenomenological diffusion model*, because it is based on observation.

The second type of model assumes that the correct values of D can be obtained directly from the physics of the dopant-defect interaction. This type of model is referred to as a *point-defect-based diffusion model*. One such advanced model uses a kinetic Monte Carlo simulation to obtain the formation and diffusion energies associated with the defects, dopants, and impurities. The simulations, however, are number-crunching intensive and require a high-end workstation or a supercomputer to be able to get results in a reasonable time. The attraction of these models, however, is that they do not require diffusion profiles and empirical curve-fitting to predict the outcome. The description of such models is beyond the scope of this text and the interested reader is referred to the literature.^{15,16}

Phenomenological models have been implemented into SUPREM III and other 1-dimensional process simulators, such as PREDICT and RECIPE. These models furnish an adequate fit to 1-dimensional diffusions, but are not successful at predicting the two-dimensional diffusion so critical for advanced devices with small feature sizes. The two-dimensional case requires the use of SUPREM IV. Also the phenomenological models are not adequate at predicting diffusion behavior of such defect-dominated phenomena as oxidation-enhanced diffusion (OED).

9.4.2 SUPREM III Models for Boron, Arsenic, Phosphorus, and Antimony Diffusion

The models used in SUPREM III are based on the *vacancy model under non-oxidizing conditions*, proposed by Fair and Tsai.¹⁷ These models, however, do not accurately reflect what is occurring on an atomic scale (since diffusion is related to both dopant/interstitialcy and dopant/vacancy interactions). However, the Fair-Tsai models are nonetheless very useful, since they provide an accurate representation of the diffusion profile for the common dopants.

The Fair-Tsai Model assumes that the diffusivity of an ionized dopant atom is based on the sum of the diffusivities of neutral vacancies and ionized vacancies, weighted by the probability

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of their existence. According to the model there are four possible states of a vacancy: 1) the neutral vacancy V^0 ; 2) the single-negatively-charged vacancy V^{-1} ; 3) the double-negatively-charged vacancy V^{-2} ; and 4) the single-positively-charged vacancy V^{+1} . During *extrinsic diffusion* each contribution must be modified by the ratio of the doping level to the intrinsic carrier concentration raised to the power (including the correct sign) of the charge state. For example the contribution of the *double-negatively-charged* vacancy is modified by $(n/n_i)^2$, while that of the *single-positively-charged* vacancy by (n_i/n) . Thus, the effective diffusion coefficient under non-oxidizing conditions can be calculated from the sum of all the individual vacancy components. The effective D is given by:

$$D = D^0 + D^- \left(\frac{n}{n_i} \right) + D^{-2} \left(\frac{n}{n_i} \right)^2 + D^+ \left(\frac{n_i}{n} \right) \quad (9.34)$$

where the individual diffusivities on the right hand side of the equation correspond to the interaction between dopant atoms and neutral or charged vacancies.

9.4.3 Modeling Intrinsic Diffusion

Intrinsic diffusion is dominant when $n \leq n_i$ at the diffusion temperature. In such cases the effective D is independent of dopant concentration and depends only on the diffusivities of the individual defects. Thus, when intrinsic diffusion is being modeled, Eq. 9-34 is re-written as:

$$D^i = D^0 + D^{-1} + D^{-2} + D^{+1} \quad (9.35)$$

and D^i is referred to as the *intrinsic effective diffusion coefficient*. The models used to determine D^i for boron, arsenic, phosphorus, and antimony are examined next.

9.4.3.1 Boron: Since boron diffuses as a negatively charged "atom" the model assumes that diffusion occurs primarily by the interaction of the boron with the *neutral* and *positively* charged vacancies. In that case the intrinsic diffusion coefficient of boron D_B^i can be represented by:

$$D_B^i = D_{BV}^0 + D_{BV}^{+1} \quad (9.36)$$

where:

$$D_{BV}^0 = 0.037 \exp(-3.46 \text{ eV}/kT) \text{ cm}^2/\text{sec} \quad (9.37a)$$

and:

$$D_{BV}^{+1} = 0.72 \exp(-3.46 \text{ eV}/kT) \text{ cm}^2/\text{sec} \quad (9.37b)$$

resulting in Eq. 9-38 for the total intrinsic diffusivity for boron D_B^i :

$$D_B^i = 0.76 \exp(-3.46 \text{ eV}/kT) \text{ cm}^2/\text{sec} \quad (9.38)$$

9.4.3.2 Arsenic: The intrinsic diffusion of arsenic is assumed to be controlled by neutral and negative vacancies and the intrinsic diffusion coefficient for As (D_{As}^i) is given by:

$$D_{As}^i = D_{As}^0 + D_{As}^{-1} = 0.066 \exp(-3.44 \text{ eV}/kT) + 12.0 \exp(-4.05 \text{ eV}/kT) \text{ cm}^2/\text{sec} \quad (9.39)$$

9.4.3.3 Phosphorus: The intrinsic diffusion of phosphorus is assumed to be controlled by the interaction of the impurity ions with neutral vacancies only. Thus, D_P^i is given as:

$$D_P^i = D_P^0 = 3.85 \exp(-3.66 \text{ eV}/kT) \text{ cm}^2/\text{sec} \quad (9.40)$$

9.4.3.4 Antimony: The intrinsic diffusion of antimony is assumed to be dominated by interaction between neutral and single negatively charged vacancies. Thus, D_{Sb}^i is given by:

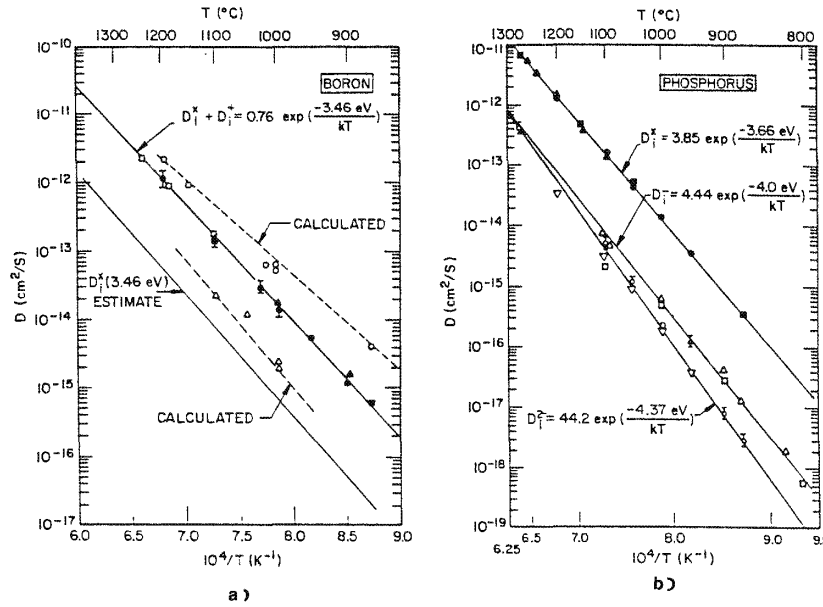


Fig. 9-7 Intrinsic diffusion coefficients vs. temperature for: a) boron; b) phosphorus.¹³ Reprinted with permission of North Holland Publishing Co.

$$D_{\text{Si}}^{\text{i}} = D_{\text{Si}}^{\text{o}} + D_{\text{Si}}^{\text{i}-1} = 0.214 \exp(-3.65 \text{ eV}/kT) + 13 \exp(-4.08 \text{ eV}/kT) \text{ cm}^2/\text{sec} \quad (9.41)$$

Figures 9-7 (a-d) show the Arrhenius plots of the intrinsic diffusion coefficients of B, P, As, and Sb. As can be seen from the plots, the agreement between the measured data and the calculated curves are quite good.

9.4.4 Extrinsic Diffusion Coefficients for the Common Dopants (As, P, and B)

An extensive amount of work has been done relating to the modeling of extrinsic diffusion of the common dopants As, P, and B. The earliest models developed by Fair were phenomenological expressions based on the result of careful determination of diffusion profiles.²⁰ However, these models did not account for the effects of both I and V on dopant diffusion. Uematsu developed an integrated diffusion model based on measurable parameters that can predict the diffusion profiles of these dopants. The model considers contributions from the vacancy mechanism (V), the kick-out mechanism (I), and the Frank-Turnbull mechanism (F-T).⁶⁸ The details of the Uematsu model are beyond the scope of this text and the reader is referred to the original paper. Here only the contributing defects for each of the common dopants are noted.

9.4.4.1 Arsenic: Figure 9-8 shows a typical diffusion profile for arsenic. There are several features that are common to As diffusion profiles. First, arsenic is a relatively slow diffuser and shows a relatively abrupt profile. Such features are desirable when fabricating shallow junctions for advanced CMOS and bipolar devices. Consequently arsenic is the most widely used *n*-type dopant in ULSI processing and is the mainstay for the *n*-channel shallow source/drain diffusion

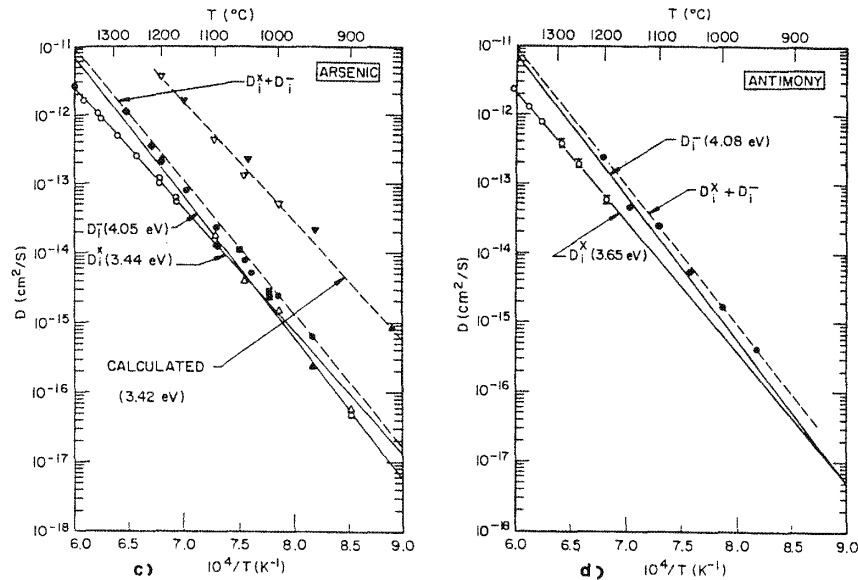


Fig. 9-7 Intrinsic diffusion coefficients vs. temperature for: c) arsenic; d) antimony.¹³ Reprinted with permission of North Holland Publishing Co.

in advanced CMOS devices and the emitter diffusion in bipolar and BiCMOS devices. The second observation is that the total As concentration (C_{As}) is frequently greater than the electrically active (C_T) concentration, particularly at high doping levels. It has been found that the amount of inactive As increases with the fourth power of the active concentration (i.e., $C_{As} - C_T \propto C_s^4$).⁶⁹ Various models have been proposed to explain this phenomenon, including As-vacancy complex, small As clusters, and As-precipitate formation and dissolution. The arsenic-

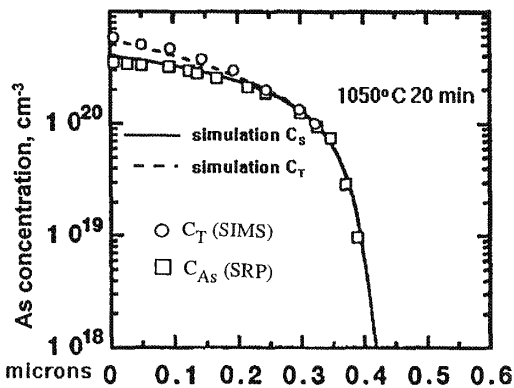


Fig. 9-8 Arsenic diffusion profile. Note the steep diffusion front and the difference between the total As concentration C_T and the active As concentration, C_{As} , for high As concentrations. Excellent agreement exists between simulated and measured profiles.⁶⁸ Courtesy of American Physical Society.

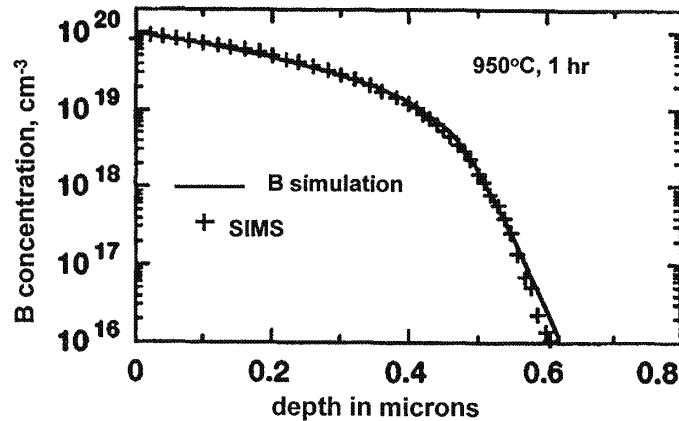


Fig. 9-9 Boron diffusion profile showing agreement between simulated and measured (SIMS) profiles.⁶⁸ Courtesy of American Physical Society.

vacancy cluster model appears to have the most support. Regardless of the mechanism, the fact that the amount of electrically-active As may change during processing must be taken into account. To obtain meaningful As profiles both SIMS (for C_T) and SRP (for C_{As}) should be used.

As discussed previously As diffusion has nearly equal contributions from both I and V. Unlike boron diffusion, which is controlled by the presence of silicon self-interstitials, the I-component in As is controlled by neutral As-interstitials (As_i^0). The vacancy contribution is dominated by the presence of V^{-2} and V^{-1} . The complex formation (As complexes) is dominated by the neutral vacancy complex, $(As_2V)^0$. Excellent agreement is observed between this model and experimental results as shown in Fig. 9-8.

9.4.4.2 Boron Diffusion: Figure 9-9 shows a typical profile for B diffusion. B is a relatively fast diffusant, and consequently great care must be exercised when attempting to fabricate shallow *p*-channel source/drain regions. The diffusion of boron from an implanted source is further increased by transient enhanced diffusion (discussed below). The formation of shallow boron diffusions is a fertile area of research and several techniques are candidates to achieve such shallow junctions. The most prominent approach is the use of *ultra-low-energy (ULE)* ion implantation (<1 keV), followed by high-ramp-rate rapid thermal annealing (see Chap. 10). Other approaches such as P-GILD, solid-source diffusion, plasma doping, and RTP gas doping are also under consideration.

Boron diffusion is known to be dominated by the "kick-out" mechanism. The diffusion profile can be modeled when three parameters are used, namely, neutral B interstitial (B_i^0), a neutral self-interstitial (I^0), and a positive self-interstitial (I^+). As shown in Fig. 9-9, excellent agreement between the model and experimental results have been obtained.

9.4.4.3 Phosphorus Diffusion: Although phosphorus is less commonly used in advanced devices, it still finds some application for the source/drain contacts in CMOS and for emitter diffusion in bipolar devices. Phosphorus diffuses quite normally in the intrinsic regime and is a relatively fast substitutional diffuser. When the dopant concentration exceeds the intrinsic carrier concentration, however, the in-diffusion behaves anomalously. By examining the P-diffusion profile in Fig. 9-10 one observes that at high concentrations the diffusion profile becomes quite complex and has a shape with three distinct regions: a) the *high concentration* or plateau region;

b) the *transition* or *kink* region; and c) the low concentration, or *tail* region. Figure 9-10 provides a schematic representation of these regions. No simple equation has been found to fit the profile and numerous models have been expounded to explain this strange behavior.

The most well known model was proposed by Fair and Tsai.⁷⁰ A key element of that model is that a singly-charged *phosphorus ion-vacancy pair*, $(PV)^{-1}$ controls phosphorus diffusion. This defect is believed to have a negative charge, and is present in the high concentration region. The defect pair becomes important when it dissociates as it diffuses into the kink and tail regions. The dissociation is believed to create excess vacancies, which in turn enhances the phosphorus diffusion in those regions of the profile. The problem with this model is that I-defects are known to dominate P diffusion. Hu *et al.*, described a model for the kink and tail regions that results from a two-stream (interstitial and vacancy) diffusion process.⁷¹

More recently, Uematsu applied the unified model to explain anomalous P diffusion.⁶⁸ In his model the diffusion is described in terms of an interstitial and a vacancy mechanism. For high surface concentration the vacancy mechanism (by way of a V^{-2}) governs the diffusion in the plateau region, while the kick-out mechanism through I and P_i^0 dominates in the kink and tail regions. The changeover from the vacancy to the kick-out mechanism is what is believed to be responsible for the kink and tail profiles observed in P diffusion. For low phosphorus surface concentrations only the kick-out mechanism is operative and no kink and tail are observed.

9.4.5 Modeling Diffusion with SUPREM IV

The most advanced diffusion model in SUPREM IV is a physics-based model that depends on the interaction of point defects (silicon self-interstitials and vacancies) and the diffusant dopants. This model is capable of predicting diffusion in an oxidizing ambient. SUPREM IV is currently supported by the commercial suppliers Avant!/TMA (under the name TSUPREM4) and Silvaco, Inc.¹⁸ The advanced model in SUPREM IV was first developed to solve the coupled oxidation and diffusion problem while using the same grid. Readers interested in the equations used in this model are referred to the suppliers of these programs or the literature.

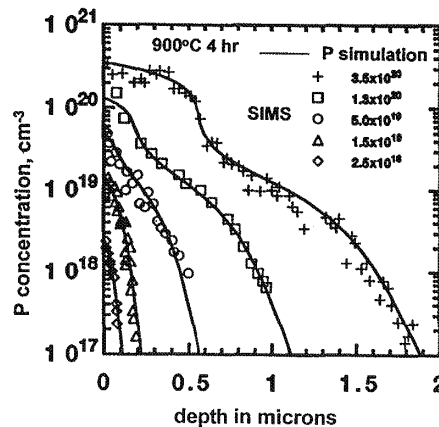


Fig. 9-10 Phosphorus diffusion profile for several surface concentrations. Note the presence of the "kink" and "tail" regions only for the high concentration diffusions. Excellent agreement exists between simulated and measured (SIMS) profiles.⁶⁸ Courtesy of American Physical Society.

Two-dimensional modeling of diffusion is simulated by calculating the local diffusion constants based on the point defect and impurity concentrations at the location of interest.²¹ The more accurately the local defect concentration is known, the more accurately the local value of diffusion can be determined. Since the concentration of the point defects may depend on the geometry at a local region, it may be necessary to simulate the movement of the oxide interface and redistribution of the impurities if diffusion takes place in an oxygen-bearing environment.

To accurately model diffusion in two dimensions the following information is usually required:

1. The nature of the point defects,
2. How far the point defects move into the bulk,
3. How the point defects interact and recombine at the surface of the silicon and in the bulk regions,
4. The predominant mechanism that drives the diffusion (i.e, is it interstitial[cy] or vacancy).

The diffusion equations used in SUPREM IV are non-linear, since the value of D and built-in electric field depend upon the point defects and the carrier concentration (ionized dopants). Hence, a full solution requires the simultaneous solution of a set of non-linear coupled differential equations for the dopants and the defects.²² SUPREM IV solves these equations using numerical methods. The solutions produce several models that are useful for obtaining diffusion profiles in one- and two-dimensions. Models from SUPREM IV are briefly discussed below.

The simplest fastest model to simulate is the *FERMI Model*. It assumes that the point-defect concentrations depend only on the position of the Fermi level in the silicon. The actual point-defect concentrations are not calculated in this model. The FERMI model is most useful when the speed of the simulation is more important than its accuracy. The model does not work for oxygen-enhanced diffusion (OED), high-concentration diffusion, or implant-damage effects.

The *TRANS Model* accounts for the two-dimensional simulation of point defects. This model includes such events as the generation of point defects at interfaces, the diffusion of point defects into the bulk, and the recombination of defects at interfaces and in the bulk. The model is capable of simulating OED, but not high-concentration effects (such as the phosphorus kink and tail). It is also capable of simulating implant damage but not as well as the so-called FULL model. The TRANS model is typically used for routine simulations.

The *FULL Model* is the most accurate and requires significant computer CPU time to perform simulations. The FULL model does everything the TRANS model does, plus it simulates the effects of dopant diffusion on point-defect concentrations. It includes such refinements as pair saturation and dopant-assisted recombination effects. This model simulates high-concentration effects, OED, and implant-damage effects. Since it requires significant computer time, use of the FULL model is only recommended when maximum accuracy is necessary, or when high-concentration effects or implant-damage effects are pertinent.

9.5 DIFFUSION IN POLYCRYSTALLINE SILICON

Polycrystalline silicon is used as the gate electrode (conductor) in CMOS devices, as the emitter in bipolar devices, and as high-value load resistor in SRAMs (see Chap. 6 for more information on polysilicon). CMOS devices require that the polysilicon be heavily doped (degenerate) for maximum conductivity and to minimize the so-called "poly depletion" effect. The doping level

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of the polysilicon at the polysilicon/oxide interface has a strong effect on the device threshold voltage. In deep-submicron CMOS devices it is necessary to dope some of the polysilicon with boron and some with arsenic on the same circuit. In advanced bipolar applications the polysilicon serves as the emitter contact diffusion source. Most often the emitter is doped with arsenic, although phosphorus may be used in less advanced applications. High-value resistors require controlled and repeatable resistivity of the polycrystalline-Si films.

Impurity diffusion in polycrystalline thin films, in general (and in polysilicon in particular), is quantitatively different from diffusion in single crystal material. The difference arises as a result of the grain boundaries present in polycrystalline films. That is, bulk diffusion is the controlling mechanism in single crystal material, while grain-boundary diffusion predominates in polycrystalline films. The diffusivity along grain boundaries can be up to 100 times faster than the diffusivity in bulk material.

Polycrystalline-silicon films are made up of grains with sizes ranging from 50 to 300 nm. The diffusion of the dopants *within* the grains is comparable to that of single-crystal silicon. But, the dopant atoms also diffuse much more rapidly along the grain boundaries, and then diffuse into the grains. Since the grains are small, only a short time is required for the dopant (which is entering from all sides of the grain) to fully diffuse within the grain. As a result, the overall diffusion is controlled by the grain boundaries, the grain structure, and the preferred orientation of the film. These quantities, in turn, depend upon such deposition conditions of the film as temperature, deposition rate, thickness, and post-deposition annealing treatments.

Each measurement of the diffusion constant D in polysilicon depends very much on the film's history, and published results cannot be taken universally. Data has been obtained for the diffusivity of phosphorus, boron, and arsenic in polysilicon, and these diffusivity values are listed in Table 9-4.^{23,24,25,26,27} It has been found that phosphorus and arsenic can precipitate at grain boundaries, resulting in reversible changes of resistivity upon annealing. That is, the precipitates can dissolve at elevated processing temperatures and go into solution in the grains, thereby lowering the resistivity of the film. The final resistivity of the film thus depends not only on the doping level in the grains, but upon the grain size, any precipitates at the grain boundaries, and the presence of other defects that can reduce the mobility of the carriers.

9.6 DIFFUSION IN SILICON DIOXIDE

Silicon dioxide serves as a diffusion mask for both chemical and ion-implanted predeposition. Its sole purpose, in these cases, is to keep the diffusant atoms away from regions where they are not wanted. Silicon nitride (Si_3N_4) can be used for similar purposes. The diffusivities of the

Table 9-4 SOME REPORTED DIFFUSION COEFFICIENTS in POLYSI FILMS³³⁻²⁷

Dopant	$D_0(\text{cm}^2/\text{sec})$	$E(\text{eV})$	$D(\text{cm}^2/\text{sec})$	$T(^{\circ}\text{C})$
As	8.6×10^4	3.9	2.4×10^{-14}	800
As	0.63	3.2	3.2×10^{-14}	950
B	$1.5\text{--}6.0 \times 10^{-3}$	2.4-2.5	9.0×10^{-14}	900
B			4.0×10^{-14}	925
P			6.9×10^{-13}	1000
P			7.0×10^{-13}	1000

common dopants in SiO_2 can be calculated from measured profiles assuming solutions to Fick's second law, with the appropriate boundary conditions.

The Group III and V elements are known to form glassy networks with SiO_2 and accordingly their diffusivity strongly depends on their concentration. The diffusivities of these elements are very low for concentrations less than 1%, and generally do not need to be considered in detail.

A recent paper reports on the diffusion of phosphorus from a phosphorus vapor source into thermal oxides.²⁸ The diffusivity of phosphorus is given by:

$$D_p = 3.79 \times 10^{-9} \exp\left(-\frac{2.3}{kT}\right) \quad (\text{cm}^2/\text{sec}) \quad (9.42)$$

and it was found to be independent of the phosphorus concentration. The solubility of phosphorus in the glass, in the temperature range of 1000°C , was found to vary between 3×10^{20} and $2 \times 10^{22} \text{ cm}^{-3}$. The diffusion mechanism is described as phosphorus dissolving in the interstitial sites as P_2 , where it is incorporated into the network of SiO_2 . The P_2 exchanges sites with silicon atoms and continues diffusing through the silicon sites.

9.6.1 Boron Penetration of Thin Gate Oxides

In the case of thin gate oxides, the diffusion of boron through the gate oxide must be considered. This effect is termed *boron penetration*. During boron penetration, dopant atoms from the heavily-boron-doped polysilicon can diffuse through the thin gate oxide layer and into the device channel, where its presence can then change the device threshold. Also, boron incorporated in the gate oxide during the diffusion can degrade the oxide breakdown characteristics and charge trapping rate.²⁹ It is further noted that the diffusion of boron through oxide is enhanced by the presence of hydrogen and fluorine in the oxide. Fluorine can be incorporated into the gate oxide if the boron is introduced into the polysilicon using BF_2 as the implantation source.

There are two main ways to reduce boron penetration or diffusion through a thin oxide. The most common approach is to incorporate nitrogen into the gate oxide. This technique is known to reduce boron diffusion by the nitrogen bonding in the glassy network, which in turn impedes the boron flux through the glass. A model has been developed to explain why the presence of nitrogen in the oxide hinders the boron diffusion.³⁰ The model explains that the value of D_0 decreases and that of Q_A increases as the nitrogen concentration increases.

The diffusivities (at 900°C) of the common dopants in SiO_2 are listed in Chap. 8, Table 8-5. There is a class of materials that are fast diffusants in SiO_2 , including H_2 , He, OH^{-1} , Na, O_2 , and Ga. Values of D greater than $10^{-13} \text{ cm}^2/\text{sec}$ have been determined for these elements.

9.7 ANOMALOUS DIFFUSION EFFECTS

Any deviation from in the diffusion behavior predicted by Fick's Law may be considered as *anomalous behavior*. The most common anomalous diffusion effects include: a) the effect of high dopant concentration on diffusion behavior (extrinsic diffusion), as discussed earlier; b) the enhancement of diffusion as a result of the built-in electric field; c) the effect of sequential diffusions including the "emitter push effect"; d) lateral diffusion under a window; e) oxidation-enhanced (and retarded) diffusion; and f) transient enhanced diffusion. To a large extent these phenomena are dependent upon the interaction of the dopant atoms with silicon point defects. Their study helps better understand the interactions between dopants and defects.

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(9.42)

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Chap. 8, Table 8-5. e, OH⁻¹, Na, O₂, and elements.

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9.7.1 Electric Field Enhancement

During diffusion at elevated temperatures, the diffusing species are usually ionized. As a result, a gradient of charge (or more formally, a gradient in the Fermi level) will develop in the crystal. The gradient of the Fermi level will result in a *built-in electric field*. The electric field always operates in the direction to enhance the diffusion of the ionized impurities.

For the case of diffusion of a dopant-defect (AX) pair in the presence of an electric field, the total diffusion flux, J , will have both a classical diffusion component and an electric-field drift component. The flux of a dopant-defect pair (AX) in the presence of an electric field is then given by:

$$J_{AX} = -D_{AX} \frac{\partial C}{\partial x} + Z_{AX} \mu_{AX} C_{AX} E \quad (9.43)$$

where Z_{AX} defines the charge state of AX dopant/defect pair and μ_{AX} is the mobility of AX. Assuming Boltzmann statistics pertain and that the Einstein relation between the mobility and the diffusivity also applies, the calculation of the enhancement of the diffusivity due to an electric field is rather straightforward, but lengthy. The reader is referred to the original reference for the complete solution.³¹

The enhanced diffusivity in an electric field is given by:

$$D_A = h \left[D_{A+X^0} + D_{A+X^-} \left(\frac{n}{n_i} \right) + D_{A+X^{2-}} 2 \left(\frac{n}{n_i} \right)^2 \right] \quad (9.44)$$

where h is defined as:

$$h = 1 + \frac{C_A}{2n_i} \left[\left(\frac{C_A}{2n_i} \right)^2 + 1 \right]^{-1/2} \quad (9.45)$$

The value of h varies from 1 for the case of $n \ll n_i$, and reaches 2 for the case of $n \gg n_i$. The field enhancement may not only result from the presence of the diffusing dopant but also from the presence of another dopant in the crystal from a previous diffusion step.

9.7.2 Emitter Push Effect

Since the performance of an *npn* bipolar transistor depends precisely upon the width of the base region, the diffusion of the emitter must be accurately controlled. In the early days of bipolar device fabrication it was found that the measured base width, after the emitter drive, was larger than predicted from the diffusion coefficients of both the phosphorous and the boron. During the emitter drive, the boron (under the phosphorus) diffused deeper into the silicon than expected. This effect became known as the *emitter push* (or *emitter dip* effect). The emitter push effect is depicted schematically in Fig. 9-11.

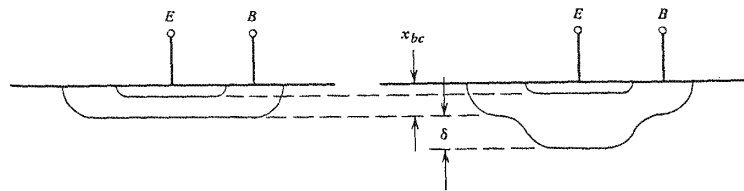


Fig. 9-11 Enhanced base diffusion under the emitter resulting from a heavy phosphorus diffusion. (Emitter push [or dip] effect).

Fair proposed that the enhanced boron diffusion under the emitter results from a combination of effects, related to the creation and dissociation of PV pairs.³² The dissociation of the pairs near the boron increases the vacancy concentration and thereby the boron diffusion. It is now known that interstitials play a key role in both boron and phosphorus diffusion. Other experiments have shown that there is indeed a net interstitial supersaturation below the phosphorus diffused layer and these excess interstitials enhance the boron diffusion.^{33,34,35,36}

Fortunately the importance of the phosphorus emitter push effect has diminished, since arsenic has replaced phosphorus as the emitter dopant. This change was made because arsenic allows shallower and better-controlled junctions to be formed. The use of arsenic, however, is not without its problems, since arsenic tends to form clusters and also tends to interact with the boron. In some cases arsenic was found to retard the diffusion of the boron (emitter pull).

9.7.3 Lateral Diffusion Under Oxide Windows

Since the majority of diffusion processes are carried out in masked areas one must be concerned not only with vertical diffusion, but also with lateral diffusion under the mask. This is not truly an anomalous effect since a concentration gradient exists in the lateral direction, as well as in the vertical direction. Thus, diffusion should proceed in both directions (two-dimensions).

One of the key processing issues related to lateral diffusion occurs when boron is diffused into the source-drain regions of a CMOS device, and the boron diffusion proceeds laterally under the edge of the gate electrode. There are two harmful effects that arise from lateral diffusion under the gate edge. First, the gate/drain overlap capacitance increases, and this can cause a decrease in the circuit performance. Second, the length of the active channel region (the distance between the source and drain) will decrease. If this decrease is excessive, it is possible to reach what is termed a "punchthrough" condition. When punchthrough occurs either the leakage current of the device substantially increases or the device will cease to function. Figure 9-12 shows the effect of boron lateral diffusion in the source/drain region of an MOS device.

For intrinsic diffusion under both constant-source (i.e., pre-deposition) conditions and limited-source (i.e., drive-in) conditions, the lateral penetration is found to be about 75–85% of the vertical diffusion depth (Figs. 9-13a and 9-13b).³⁷ At high-concentration (i.e., extrinsic) diffusion, as well as for shallow diffusions, lateral penetration is found to extend only 65–70% of the vertical diffusion distance.³⁸ There is an additional anomalous effect caused by the stress generated at the edge of an oxide or nitride window. Both enhanced and retarded diffusions

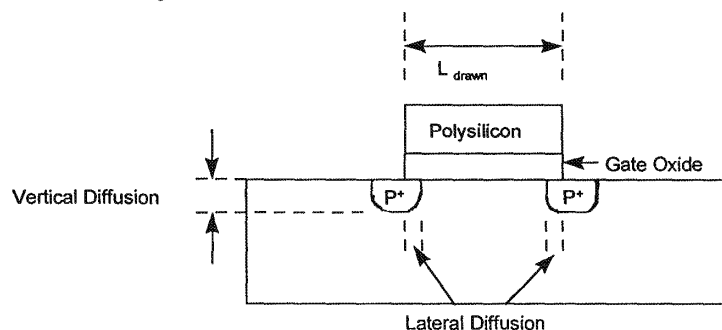


Fig. 9-12 The effect of lateral diffusion in an MOS device. The channel length is reduced to less than the polysilicon line size by the amount of lateral diffusion.

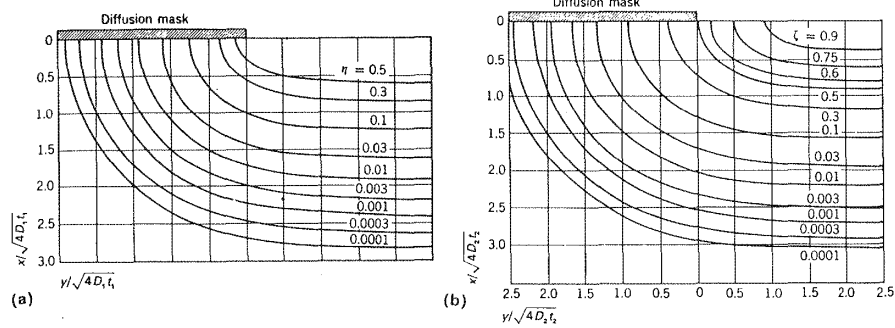


Fig. 9-13 Diffusion contours at the edge of an oxide window: a) constant source diffusion; b) limited source diffusion.³⁷

sions have been observed as a result of elastic strain near the window edge.³⁹ It is known that strain can induce defects which affect the diffusivity of the dopants in silicon.

It is extremely difficult to directly measure the lateral diffusion in shallow junctions and the electrical performance of a MOS device may be used as an indication of lateral diffusion. TEM has been employed for this task, but it is difficult to discern the precise junction location. Some new techniques are beginning to be used for such measurements and they will be discussed in a later section.

9.7.4 Oxidation-Enhanced Diffusion (OED)

It has been known for some time that when diffusion takes place under *oxidizing* conditions the motion of certain dopants is greatly enhanced, as compared to the same diffusion in a neutral ambient. To be more precise, the diffusion of both boron and phosphorus are enhanced during oxidation. While arsenic diffusion is only slightly enhanced under oxidizing conditions, the diffusion of antimony (Sb) is retarded under the same oxidation conditions. The general name for this phenomenon is *oxidation-enhanced diffusion* (OED). There also exists a subsidiary effect called *nitridation retarded diffusion* (NRD), which will be discussed subsequently.

It is important to examine OED from two different perspectives. First of all, the amount of OED that occurs during a drive-in step must be known to accurately model diffusion. From a practical point of view one needs to take OED into account when defining a diffusion schedule. Failure to do so could lead to a much deeper junction than anticipated. It is also important to consider the possibility that different regions on the device may exhibit differing amounts of OED, since the amount of OED depends on the oxidation rate and different parts of the device may have different oxidation rates.

The second perspective is that the study of OED provides a window on how silicon vacancies and interstitials interact with the common dopants during diffusion. There have been a myriad of investigations of OED in silicon, and the treatise by Fahey, Griffin, and Plummer provides an excellent critical review of the OED literature through 1989.⁹ Some of their conclusions are briefly described here, but readers interested in the details of the analysis should refer to the Fahey, *et al.*, paper.

As far back as 1974, S.M. Hu recognized that the growth of oxidation-induced stacking faults, OISF's (see Chap. 2) and OED had a common origin.⁴⁰ Direct observation of stacking faults in the TEM revealed that they consisted of silicon interstitial type defects, bounded by Frank dislocations. It was also known that the stacking faults grew during oxidation and the

growth was controlled by silicon atoms attaching themselves to the ends of the dislocation. The silicon atoms were injected into the bulk of the silicon from the surface during the oxidation process. Armed with the fact that interstitials enter the silicon during oxidation it was postulated that these same interstitials also affect OED.

Based on various OED experiments over the past 20 years a convincing and repeatable correlation between defects and dopants emerged. The conclusions are:

1. Since the diffusion of boron and phosphorus are enhanced by oxidation, the dominant (>50%) mechanism controlling their diffusion is the presence of self-interstitials,
2. Since the diffusion of antimony is retarded during oxidation the dominant mechanism controlling its diffusion is the presence of vacancies,
3. Since the diffusion of arsenic is not greatly enhanced or retarded during oxidation, there is no dominant mechanism, and both vacancies and interstitials play an important role.

The literature is replete with studies on how OED is affected by temperature and time. To perform these studies it is necessary to measure and quantify OED. The measurement technique used is shown in Fig. 9-14. Here the measurement is performed by comparing the diffusion of a dopant during oxidation with the same dopant when the surface is not being oxidized (at the same time and in the same sample). This is accomplished by masking part of the wafer with silicon nitride. It is well known that oxide will not grow under the nitride. The OED is then determined from the difference in the junction depth between the masked and unmasked regions.

The results of these studies are briefly summarized here. The major conclusion is that OED depends on the oxidation rate and the dependence follows the power law:

$$\text{OED} \propto (dx_{\text{ox}}/dt)^n \quad (9.46)$$

where (dx_{ox}/dt) is the oxidation rate and n is an experimentally determined fitting parameter, with a value less than 1, and typically in the range of 0.2–0.3.

When the oxidation rate is increased (for instance, during wet oxidation or during high temperature growth), it is expected that the relative amount of OED should decrease. The

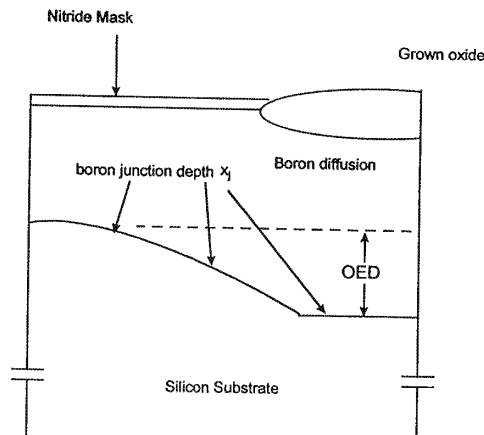


Fig. 9-14 A schematic showing how to measure oxygen enhanced diffusion (OED).

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relative reduction of the OED with higher temperatures has been confirmed. There were also studies performed on the effect of silicon crystal orientation dependence on OED.^{41,42} In these studies it was found that the relative amount of OED decreased in the order (111), (110), and (100) during dry oxidation, in line with the expected oxidation rates. It was also found that for oxidation temperatures in excess of 1150°C, the diffusion of boron was actually retarded, rather than enhanced, implying the injection of vacancies at this high temperature. At the same time antimony exhibited enhanced diffusion, confirming the presence of excess vacancies.

There have also been a series of experiments that studied OISF shrinkage and diffusion during the direct nitridation of silicon by ammonia (NH₃). It was found that during nitridation, OISF actually shrink in size. This shrinkage could result from a vacancy reaching the OISF and changing places with a silicon atom, thus making the stacking fault smaller. It is believed the vacancies are injected from the surface of the silicon during the nitridation. The mechanism for the creation of the vacancies is not yet well understood. One idea is that the stress-relief mechanism prevalent during the high-temperature nitridation is the formation of Frenkel pairs. The silicon interstitials from the Frenkel pairs are consumed by the nitride, while the vacancies enter the silicon where they react with the interstitials from the OISF.

If one considers the results of diffusion studies on the common dopants during *nitridation* one discovers that the diffusion of boron and phosphorus are retarded, while that of antimony is enhanced. This effect is parallel, but opposite, to that observed during oxidation. Since the diffusion of boron and phosphorus is dominated by interstitial defects, their undersaturation in the bulk will result in a reduced diffusivity. On the other hand, since the diffusion of antimony is dominated by vacancies it is not surprising to find enhanced diffusivity along with supersaturation of vacancies. The study of both OED and NRD provide a set of self consistent results which show a clear linkage between the diffusion of the dopants and the presence of defects in the silicon.

9.7.5 Transient Enhanced Diffusion (TED)

After an ion implantation step it is necessary to thermally treat (anneal) the silicon to activate the implanted ions (i.e., to move the dopant atoms to substitutional sites), and to remove residual implantation damage. During this anneal a new type of anomalous diffusion is observed, called *transient enhanced diffusion* or *TED*. The study of TED has become an area of fertile research, and by understanding TED the knowledge of the interaction between dopant atoms and defects has also been increased.

Before the discussion of the models that have been posited to explain TED is undertaken, some of the features that are common to this phenomenon will be described. First, TED is associated with the ion implantation damage and does not occur if the dopant is introduced by chemical means. Second, the diffusion enhancement is transient. That is, it exists for a finite amount of time after which "normal" diffusion returns. Finally, TED takes place in the temperature range where little or no atomic movement is expected (670–900°C). As a matter of fact, as much as 100 nm of boron dopant movement has been measured in this low temperature range.

These observations will now be discussed in terms of the proposed mechanism for TED. Briefly, TED is explained by assuming that silicon interstitials are injected from the implant damaged region into the bulk of the material. Furthermore, this interstitial injection occurs at relatively low temperatures for some finite time. The interstitials, once in the bulk, enhance the diffusion of boron and phosphorus. The sources of these interstitials are {311} defects, which

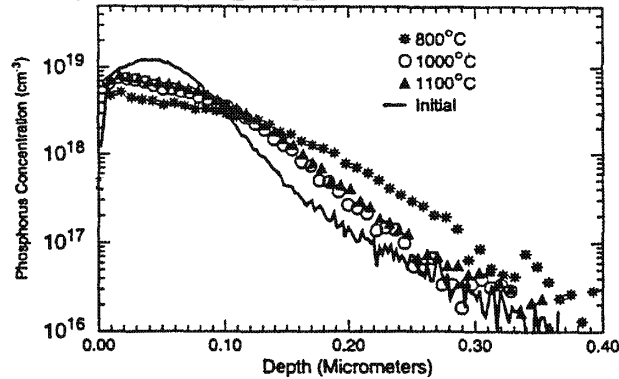


Fig. 9-15 A comparison of P-diffusion SIMS profiles "as-implanted" (initial) vs. after a furnace anneal at 800, 1000, and 1100°C. There is more diffusion occurring at 800°C than at 1100°C as a result of TED.⁷³

coalesce after ion implantation damage. During the anneal cycle, these {311} defects begin to dissolve, and during their dissolution they emit interstitials into the silicon. Figure 9-15 shows a SIMS plot of the phosphorus concentration as a function of distance in both the "as-damage-implanted" case and after anneal at several temperatures. The astonishing result is that diffusion proceeds farther at 800°C than at 1100°C. The fact that so much atomic movement can occur at such low temperatures implies that TED can take place during the loading and unloading of the wafers in a conventional furnace. Before a furnace annealing process even starts, the atoms may have moved too far to make useful junctions. This is one of the reasons why RTA has rapidly replaced furnaces for annealing the implanted atoms for shallow junctions. Fig. 9-16 displays a plot of the enhanced diffusion of phosphorus as a function of time at temperature for two different levels of implant damage. The conclusions that can be drawn from this curve are: a) the enhancement decreases rapidly with time, and b) for short times the enhancement is independent of the amount of damage. A phenomenological equation can be written for the time dependence of the enhanced diffusivity as:^{43,44}

$$D_E = D_i + D_{0TED} \exp(-t/\tau)$$

(9.47)

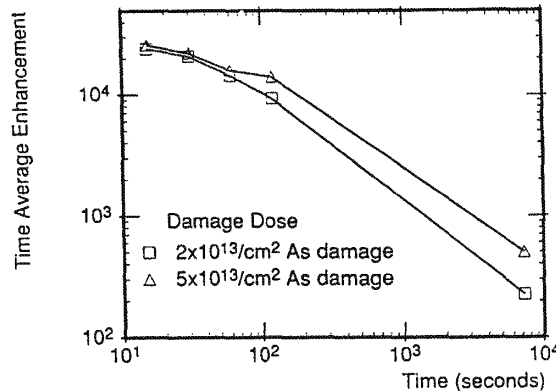


Fig. 9-16 Amount of enhanced diffusion as a function of time at temperature for two different levels of implantation damage.⁷⁴ Reprinted with permission of the American Physical Society.

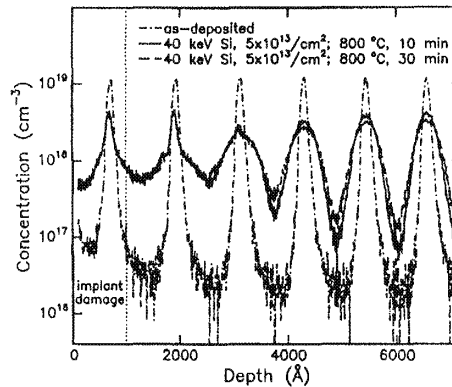


Fig. 9-17 Diffusion of boron (δ -doped using MBE) at 815°C for 10 and 30 min, showing enhanced broadening due to TED arising from a Si-damage implant.⁴⁵

where D_E is the enhanced diffusivity; D_i is the intrinsic diffusivity; D_{0TED} is the enhancement factor at the onset of TED; t is the time into the TED event; and τ is the time constant for the enhanced diffusion. For short times and low temperatures, the total diffusion is dominated by the D_{0TED} term.

It is difficult to measure TED directly from the SIMS profile in the implanted silicon since the measurement is confounded by too many variables, including: a) the TED itself; b) the damage profile; c) the stationary component of the profile; and d) the variation of the interstitial profile in the implant region. A novel technique has been developed to directly measure TED. The technique uses CVD or MBE epitaxially-doped "superlattice" regions on float zone (FZ) silicon. These samples consist of regularly spaced spikes of dopant which are used as "marker" layers to monitor the atom movement during the TED event. A damage implant (either silicon or germanium) is then made into the sample silicon to create the required defects. The distance of the damage layer has been well characterized.

Figure 9-17 shows a SIMS profile of the as-deposited and diffused profiles of these spikes (boron doped in this case), as a function of depth after the introduction of ion implantation damage and anneal. The damage was introduced by a silicon implantation and the furnace anneal was performed at 815°C for 10 and 30 min.⁴⁵ Also shown on that curve is the depth (about 100 nm) of the implant damage. The boron profile before diffusion shows uniform sharp peaks as a result of the doping spikes that were grown-in during the low-temperature MBE. The results after the damage implant and anneal show that some of the boron spikes significantly broaden as a result of the thermal treatment. The amount of broadening is a direct measure of the diffusivity of the boron. From Fig. 9-17 one sees that the boron markers located within and adjacent to the implant damage remain immobile during annealing, while those farther away show broadening (indicating diffusion). The amount of broadening increases, and then decreases, as it moves farther away from the implant damage region. The broadening that is observed at the 350-nm marker corresponds to a 1000 times increase over the normal diffusivity of boron. The fact that no additional broadening takes place after 10 min testifies to the fact that the TED is a transient phenomenon. The duration of the transient, on the other hand, does strongly depend on the annealing temperature and is found to decrease from over 5 hours at 670°C to less than 10 minutes at 815°C. These times are related to the constant τ in Eq. 9-47.

The observation that the concentration peaks of the boron in or near the implanted region remain stationary, suggests that near the implant damage the boron atoms form immobile clusters (BI_n where $n = 1, 2$, or 3) with the excess silicon interstitials. The results of the marker experiments (no broadening) along with the fact that the electrical concentration of B is generally much less than the chemical concentration in that region, provides additional evidence of B-I cluster formation.

The source of the interstitials and their time dependence is now discussed. Eaglesham *et al.*, performed high resolution TEM studies of silicon in the implanted region after very short time anneals in order to observe the defect structure.⁴⁵ The appearance of an extended defect is quite obvious, and the defect has been identified as the *rodlike* or $\{311\}$ defect. These defects are known to be present during oxidation and ion implantation of silicon. It is generally agreed that the $\{311\}$ defect consists of a condensation of interstitials which form five- and seven-member rings. Another way of looking at these defects is that they consist of an extra monolayer of hexagonal silicon in the lattice that has no dangling bonds. As a result, these defects are relatively stable, except at high temperatures ($> 950^\circ\text{C}$).

Using TEM, Eaglesham *et al.*, were able to measure the time dependence of the density and size of the $\{311\}$ defects during short-time anneals and then to calculate the density of silicon interstitials.¹⁹ Figure 9-18 shows the time dependence of the silicon interstitial density (the so-called *evaporation rate*) for several anneal temperatures. The evaporation rate was found to have an exponential dependence on time, with time constants that correspond very well to the duration of the TED as described in Eq. 9-47. Recall that the duration of TED decreased as the temperature increased. This correspondence strongly suggests that TED results from the growth and dissolution of $\{311\}$ defects that are formed as a result of ion implantation. During the dissolution there are a large number of silicon interstitials formed. They greatly enhance the diffusion rate of boron, (and phosphorus) through the "kick-out" or interstitialcy mechanism.

It has been found that the presence of substitutional carbon in silicon in the range of $5 \times 10^{18}/\text{cm}^3$ effectively suppresses TED without affecting the electrical activity of the boron.⁴⁶ It is believed that the carbon atoms absorb the injected interstitials and therefore the interstitials are not available to contribute to TED.

Although TED has been studied most extensively with boron diffusion, both phosphorus⁴⁷ and antimony⁴⁸ also demonstrate the effect. In order to get TED to occur in antimony it is

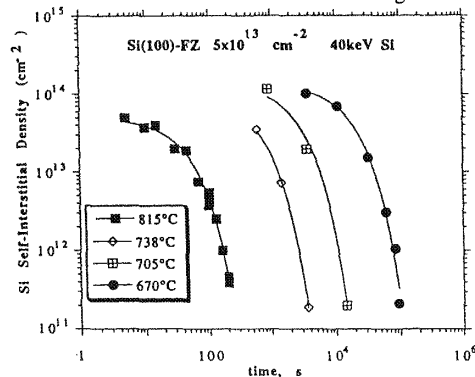


Fig. 9-18 Evaporation of interstitials from $\{311\}$ defects as a function of time at several temperatures.¹⁹