Diffusion coefficient of Impurities in Silicon :—

Revisit:

From Fick's First Law we say

$$j = \text{Flux density} = -D\frac{dN}{dx}$$

But when dopant concentration exceeds n_{ie} (Intrinsic) conc at the Diffusion temperature, Ionised impurities create an Electrical Field., since electron/holes have higher mobilities than ions.

This ε. field $\mathcal{E}$ enhances Diffusion of Impurities

Then $j = -D\frac{\partial N}{\partial x} + \mu n . \mathcal{E}$

However we know this field $\mathcal{E} = -\frac{kT}{q}\frac{1}{n}\frac{dn}{dx}$ & $D = \frac{kT}{q}\mu$

$$\therefore \quad j = -D\left[1+\frac{dn}{dN}\right]\frac{dN}{dx} = -D\,[h]\,\frac{dN}{dx}$$

We then Define $D_{eff} = D\left[1+\frac{dn}{dx}\right]$

Using charge neutrality, & Law of Mass Action for electrons & impurities, we can write

$$\frac{n}{n_i} = \frac{N}{2n_i} + \left[\left(\frac{N}{2n_i}\right)^2+1\right]^{1/2}$$

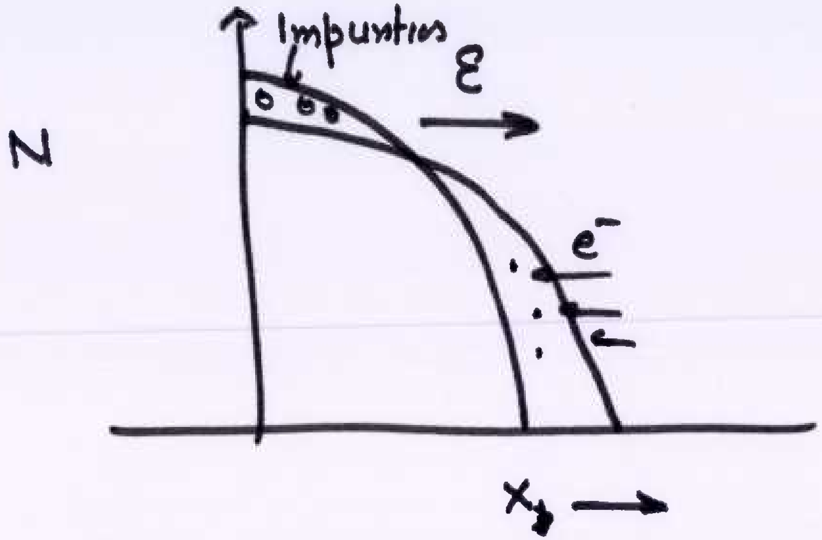
$$\text{or} \quad \frac{dn}{dN} = \frac{1}{2}\left\{1+\left[1+\left(\frac{2n_i}{N}\right)^2\right]^{-1/2}\right\}$$

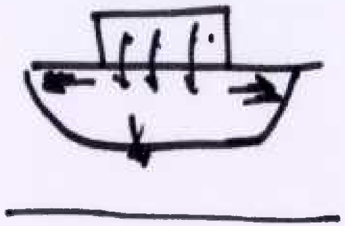
$$\text{or} \quad h = 1+\frac{1}{2}\left\{1+\left[1+\left(\frac{2n_i}{N}\right)^2\right]^{-1/2}\right\} \simeq 1+\frac{N}{\sqrt{N^2+4n_i^2}}$$

$\therefore$ Fick's Law modifies to

$$j = -h\,D\,\frac{dN}{dx} = -D_{eff}\,\frac{dN}{dx}$$

The net effect is enhanced Diffusion.





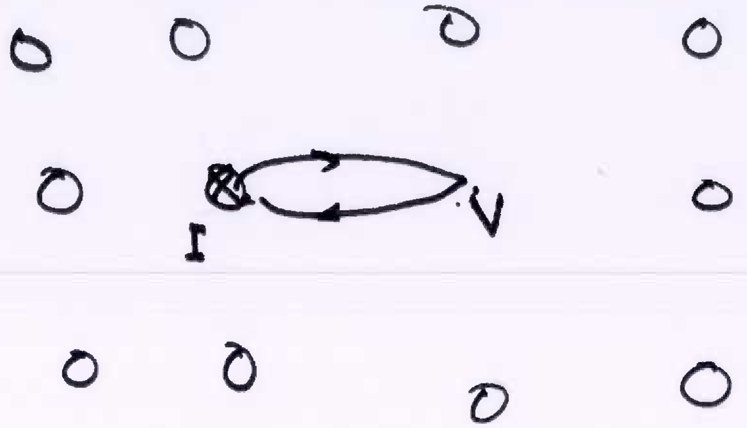
We also know that D is also function of Impurity conc.

It can be shown that Vacancies in presence of electrons & holes can be charged as

$$V^+ = V^0 + h^+$$ where V^0 is Neutral Vacancy

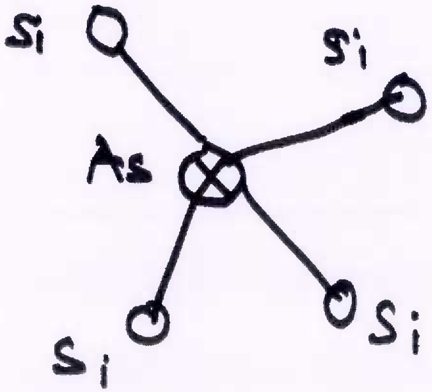
& $$V^{-r} = V^0 + re^-$$

For most Impurities in Silicon we have V^0, V^+, V^- and V^{--} states

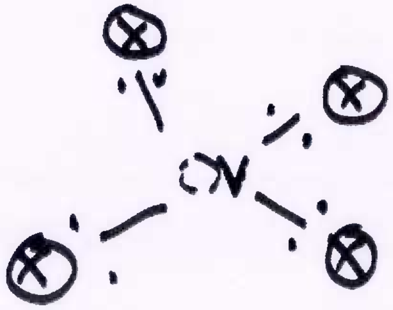


Vacancy - Impurity Pair

Example of Arsnic (Plummer)

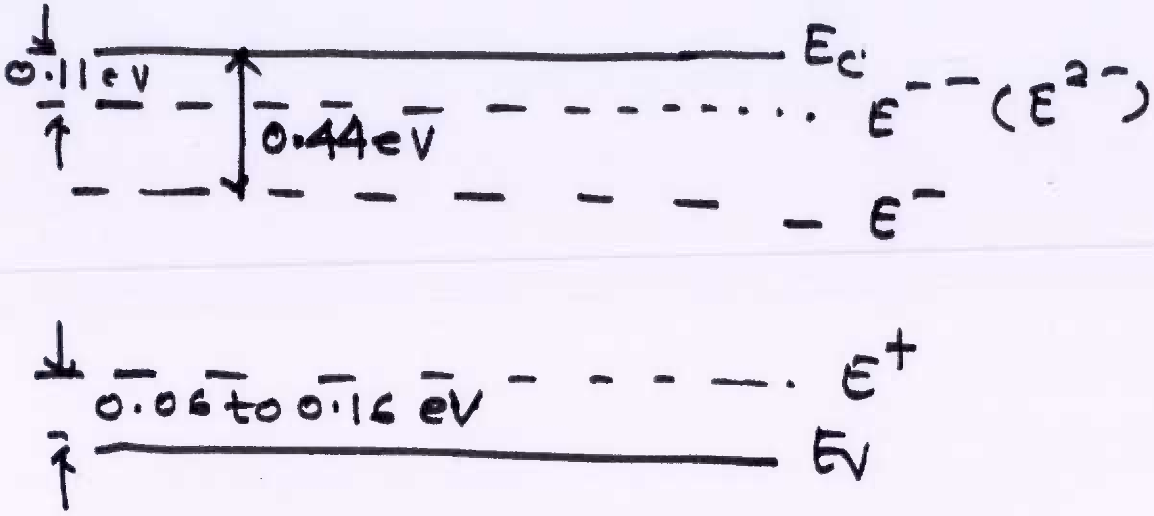


Substitutional site



A Vacancy Surrounded by 4 Arsenic Atom

Energy State Diagram (Imp. in Si)



These Impurities get attached with charged vacancy State and forms Pair, which then diffuse as Pair

Boron :— $I\text{-}V^{+}$, $I\text{-}V^{0}$ Pairs

Phosphorous :— $I\text{-}V^{0}$, $I\text{-}V^{-}$ and $I\text{-}V^{--}$ Pairs

Arsenic :— $I\text{-}V^{0}$, $I\text{-}V^{-}$ and $I\text{-}V^{--}$ Pairs.

These effects can be taken through Diffusion Coefficients.

$$D_{eff} = h\left[D_i^0 + D_i^+ \left(\frac{p}{n_i}\right) + D_i^- \left(\frac{n}{n_i}\right) + D_i^{--} \left(\frac{n}{n_i}\right)^2 \right]$$

For N-type Dopants

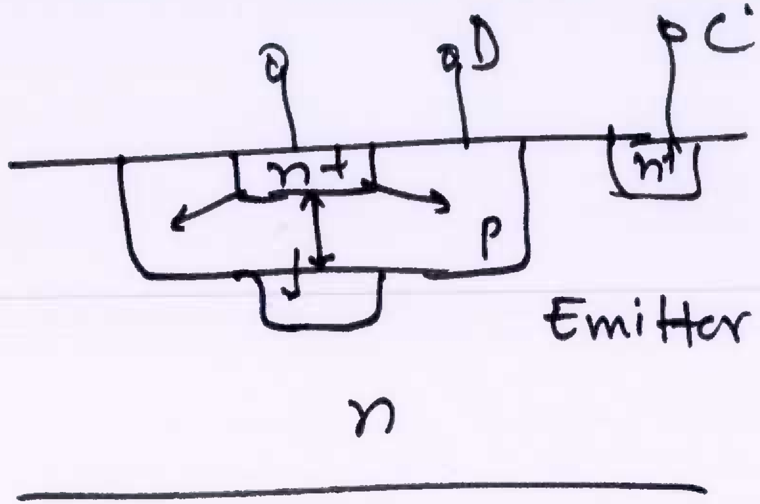
$$D_{eff} = D^0 + D^- \left(\frac{n}{n_i}\right) + D^{--} \left(\frac{n}{n_i}\right)^2$$

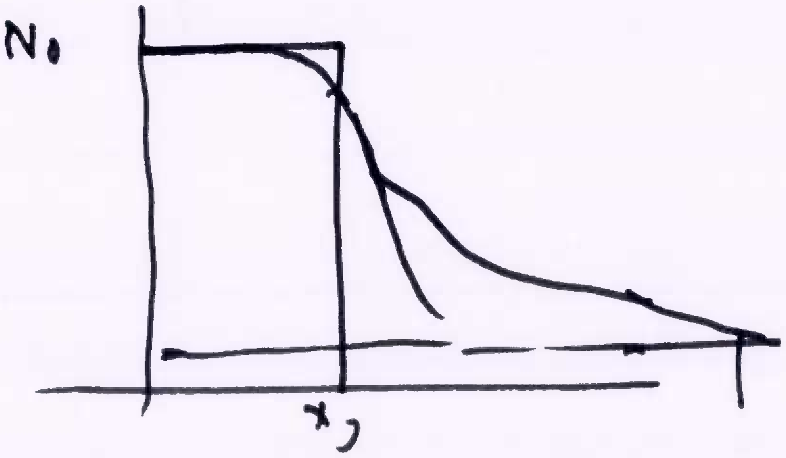
For P-type Dopants

$$D_{eff} = D_i^0 + D^+ \left(\frac{p}{n_i}\right)$$

These effects are required to explain Anomulus Impurity Diffusion Profiles.

Emitter Dip Effect





$$B \qquad I\cdot V^{-} = I + V^{-} = I^{-} + V^{0}$$

DIFFUSION TECHNIQUES

A typical requirement/requirements for Diffusion System :

i Diffusing Impurity should be brought in contact with pre-cleaned Silicon wafer.

ii It should also remain in contact with wafer for given time and specified Temperature.

iii A Diffusing System should be such that it should be possible to vary Surface Conc. N_s upto it's Solid Salubility limits.

iv The Diffusion Process be such that it does not damage the surface of the wafer

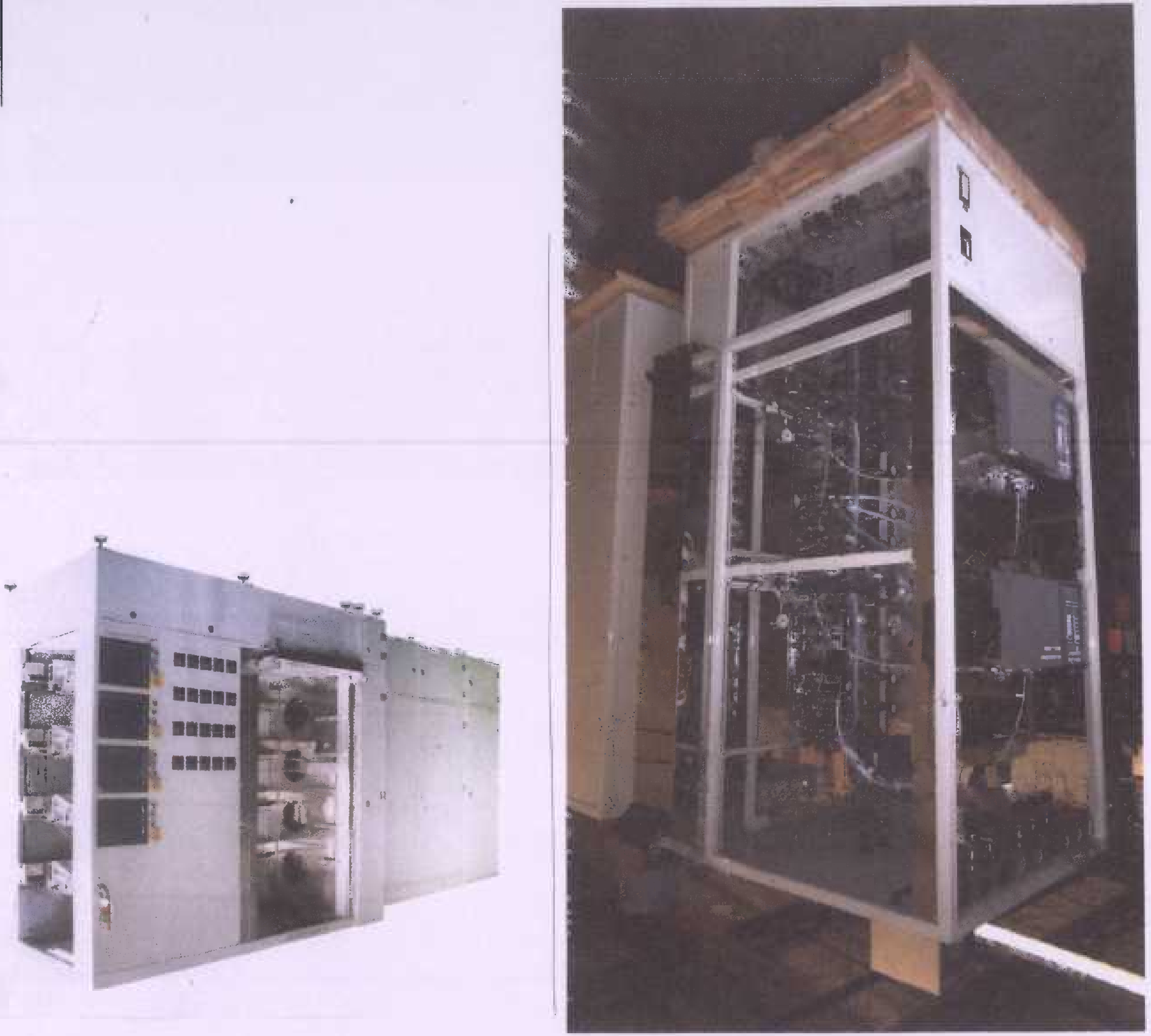
V. Ater diffusion process, the impurities and other materials on wafer Surface, should be easily removable.

Vi The Diffusion System should be able to give Reproducible Results in many runs.

Vii The Diffusion system be such that 'Batch - Processing' is possible as this is the need of Manufacturing.

Typically OPEN-TUBE SYSTEMS are used for Solid State Diffusion.

In very specific case, 'SEALED-TUBE' Diffusion can be done



Types of Sources

i Solid Source - Normally Primary Source

ii Liquid Source - Secondary source

iii Gasious Source - Secondary source

iv Spin-On Sources.

Typical Impurities used in Silicon Processing are

N-Type : As, P and Antimony

P-Type :- Boron, Indium and Aluminium, Gallium

Recombination Centre : Gold

1 Phosphorous Impurity sources

(a) Solid Sources

Red Phosphorous and $(NH_4)_2HPO_4$

Dibasic Ammonium Phosphate

Reactions :

$$4P + 5O_2 \rightarrow 2P_2O_5$$

$$2P_2O_5 + 5Si \rightarrow 4P + 5SiO_2$$ — Diffusion

$(P_2O_5 + SiO_2)$ is called Phosphosilicate Glass.

(b) Liquid Source : $POCl_3$ is Liquid Source for Phosphorous.

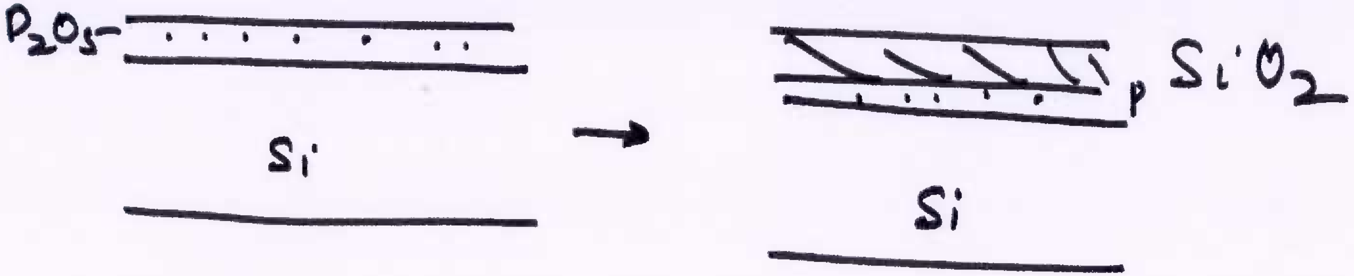
$$4POCl_3 + 3O_2 \rightarrow 2P_2O_5 + 6Cl_2$$

(c) Gasious Source : PH_3 (Phosphene)

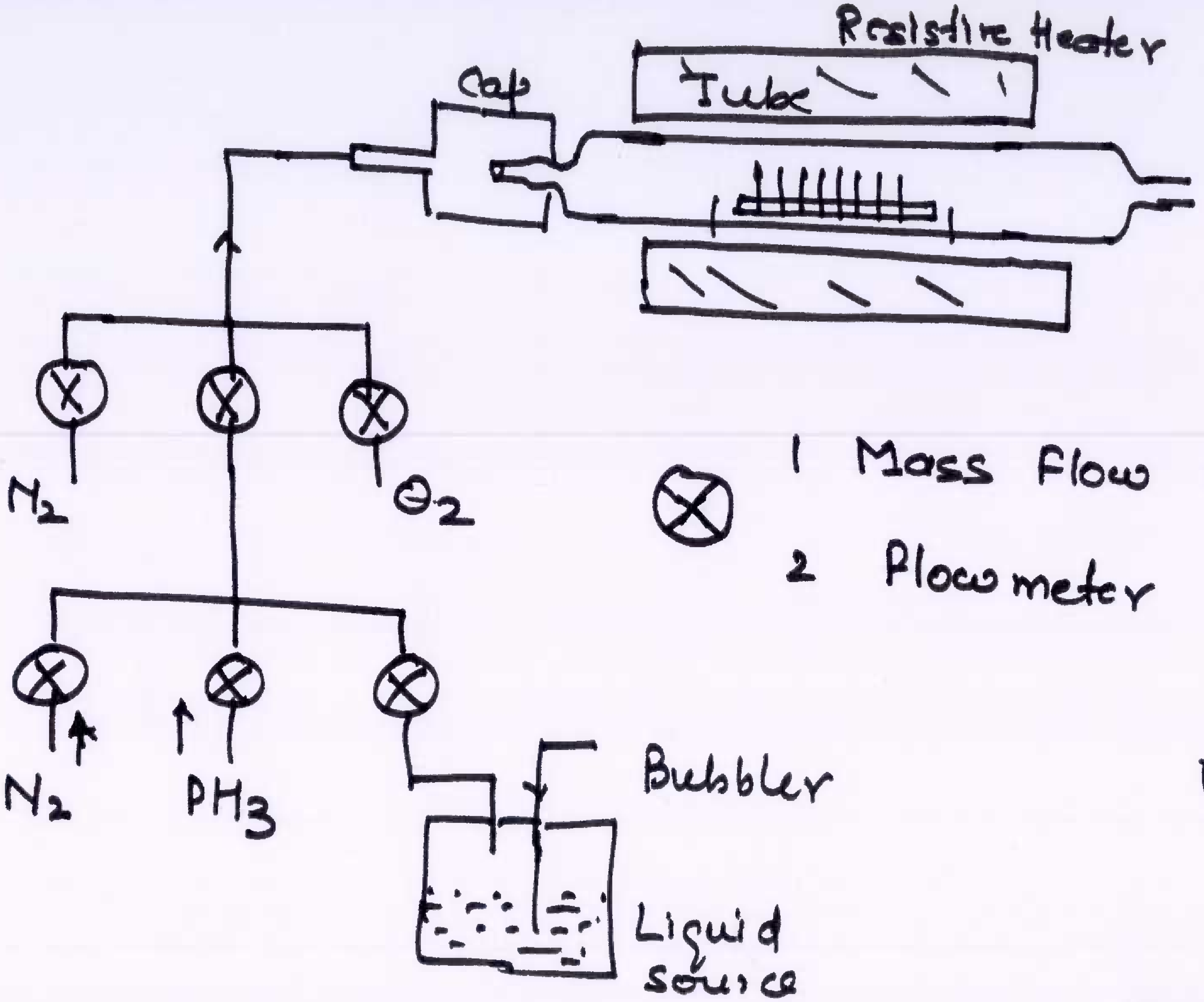
$$2\,PH_3 \xrightarrow{440^\circ C} 3H_2 + 2P$$

$$4P + 5O_2 \rightarrow 2P_2O_5$$

$$2P_2O_5 + 5Si \rightarrow 5SiO_2 + 4P$$

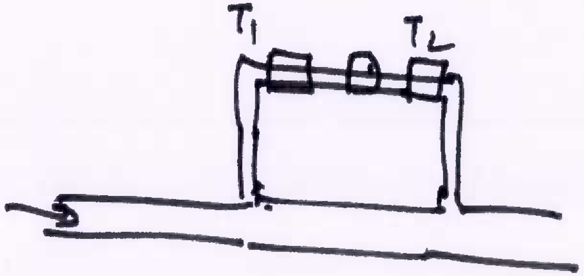


PH_3 is higly Toxic Gas. Normally the diffusing species like PH_3 are diluted with Nitrogen N_2/Argon. Dilution is 99.9%.



⊗ 1 Mass Flow Controller
2 Flowmeter with Valves

Mass Flow Meters



2. Boron Impurity Source

Boron has misfit factor of 0.254. Compare to other P-Impurities, we see Indium has (0.22), Aluminum (0.068) and Gallium (0.068), it has higher misfit factor. But even then Boron is the only P-type Impurity used in Si IC processing. Max. Doping conc. achieved is 4×10^{19}/cc

ⓐ Solid Source :

B_2O_3, BN and H_3BO_3 (Boric Acid) are the sources for Boron.

Reactions:

→ $2B_2O_3 + 3Si \rightarrow 4B + 3SiO_2$

Borosilicate Glass is mixture of ($B_2O_3 + SiO_2$)

→ $2H_3BO_3 \xrightarrow[185^\circ C]{} B_2O_3 + 3H_2O$

∴ For this case Two zone Furnace are needed.

→ $4BN + 3Si \rightarrow 4B + Si_3N_4$

ⓑ Liquid source : BBr_3 is liquid source.

$4BBr_3 + 3O_2 \rightarrow 2B_2O_3 + 6Br_2$ (Bromine is a Toxic Gas)

Halogen pitting of Si Surface is likely.

N_2 = 1.5 lit/min ; $O_2 \cong$ 50-100 cc/min ; N_2 in Bubbler 5-20 cc/min

Temp. : Room temperature

Another Liquid source is TMB – TriMethyle Borate

$$2\,(CH_3O)_3B + 9O_2 \xrightarrow{900^\circ c} B_2O_3 + 6CO_2 + 9H_2O$$

At room temp, TMB has high Vapour Pressure. Hence TMB is used under ~~referigenerah~~ referigeration.

(c) Gasious Source:

BCl_3 or B_2H_6 (Diborane) are Boron Gasious Sources.

$$4BCl_3 + 3O_2 \longrightarrow 2B_2O_3 + 6Cl_2$$

→ Chlorin is Toxic & gives Pitting.

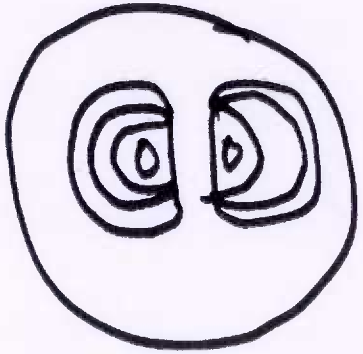
$$2BCl_3 + 3H_2 \rightarrow 2B + 6HCl$$

$$4HCl + Si \rightarrow SiCl_4 + 2H_2$$

Diborane is highly Toxic Gas, but used as Boron Source.

$$B_2H_6 + 3O_2 \xrightarrow{300^{\circ}C} B_2O_3 + 3H_2O$$

Gas-Flow is one parameter for Growth.



Heart - Lobes

Raynold No. and

Raighley No.

3. Arsenic as N-type Impurity Source

Solid :- As_2O_3

($As_2O_3 + SiO_2$) is Arsenosilicate Glass.

Gasious Source :- AsH_3 : Arsene

$$AsH_3 \longrightarrow As + H_2$$

$$As + O_2 \longrightarrow As_2O_3$$

$$As_2O_3 + Si \longrightarrow SiO_2 + As$$