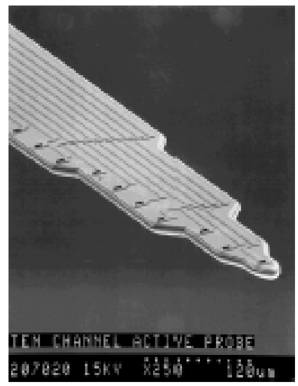
Chemical Reaction Engineering in the Electronics Industry

Microelectronic Sensing Devices



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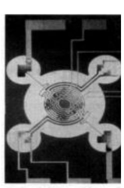
Chemical Reaction Engineering in the Electronics In



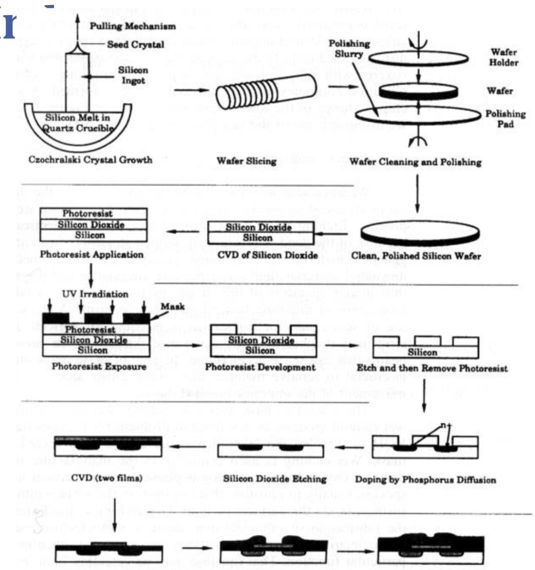


Figure 10-34 Microelectronic fabrication steps.

Chemical Vapor Deposition

- Important process in the formation of microcircuits (electrically interconnected films ICs), microprocessors & solar cells
- Used to deposit thin films of material, such as Si, SiO_2, and germanium (Ge)
- Mechanism of CVD is similar to those of heterogeneous catalysis ***except that site concentration (C_V) is replaced with fraction of surface coverage (f_V)***

Chemical Vapor Deposition

The 5 steps

1. Postulate Mechanism (sometimes first includes a gas phase reaction, then adsorption and surface reaction)
2. Postulate Rate Limiting Step
3. Evaluate Parameters in Terms of Measured Variables
4. **Surface Area Balance**
5. Evaluate Rate Law Parameters

Chemical Vapor Deposition

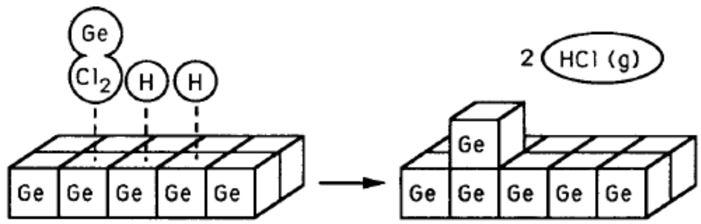


Figure 10-21 CVD surface reaction step for Germanium.

Ge is used in solar cells

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Growth of Germanium Films by CVD

Germanium films have applications in microelectronics & solar cell fabrication

Gas-phase dissociation $GeCl_{4(g)} \underset{k_{-dis}}{\overset{k_{dis}}{\rightleftarrows}} GeCl_{2(g)} + Cl_{2(g)}$

Adsorption (1) $GeCl_{2(g)} + S \underset{k_{-A}}{\overset{k_A}{\rightleftarrows}} GeCl_2.S$

Adsorption (2) $H_{2(g)} + 2S \underset{k_{-H}}{\overset{k_H}{\rightleftarrows}} 2H.S$

Surface reaction $GeCl_2.S + 2H.S \overset{k_S}{\rightarrow} Ge_{(S)} + 2HCl_{(g)} + 2S$

Surface reaction is believed to be the rate-limiting step

Growth of Germanium Films by CVD

What is the rate of Ge deposition if the surface reaction is rate limiting?

a) $r''_{Dep}=k_{dis}P_{GeCl4}-k_{-dis}P_{GeCl2}P_{Cl2}$

b) $r''_{Dep}=k_{A}P_{GeCl2}f_{v}-k_{-A}f_{GeCl2}$

c) $r''_{Dep}=k_{H}P_{H2}f_{v}^{2}-k_{-H}f_{H}^{2}$

d) $r''_{Dep}=k_{S}f_{GeCl2}f_{H}^{2}-k_{-S}C_{Ge}P_{HCl}^{2}f_{v}^{2}$

e) $r''_{Dep}=k_{S}f_{GeCl2}f_{H}^{2}$

$$GeCl_{4(g)} \underset{k_{-dis}}{\overset{k_{dis}}{\rightleftarrows}} GeCl_{2(g)} + Cl_{2(g)}$$

$$GeCl_{2(g)} + S \underset{k_{-A}}{\overset{k_{A}}{\rightleftarrows}} GeCl_2.S$$

$$H_{2(g)} + 2S \underset{k_{-H}}{\overset{k_{H}}{\rightleftarrows}} 2H.S$$

$$GeCl_2.S + 2H.S \overset{k_S}{\rightarrow} Ge_{(S)} + 2HCl_{(g)} + 2S$$

Growth of Germanium Films by CVD

Surface reaction is believed to be the rate-limiting step:

Rate of Ge deposition (nm/s): $r''_{Dep} = k_S f_{GeCl_2} f_H^{\,2}$

k_s: surface specific reaction rate (nm/s)

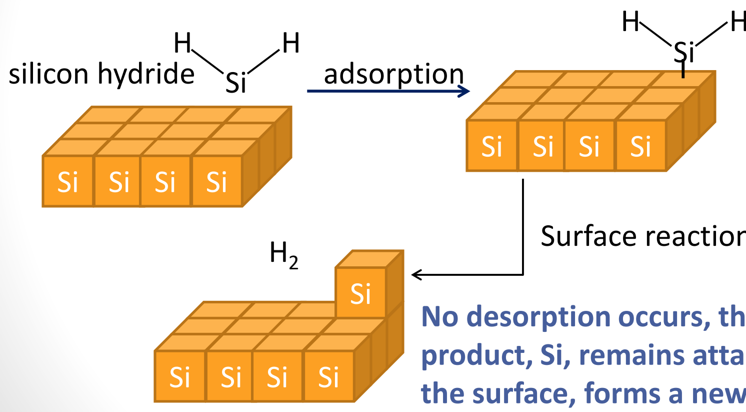
f_{GeCl2}: **fraction** of the surface covered by $GeCl_2$

f_{H2}: **fraction** on the surface occupied by H_2

***Surface coverage is in terms of fraction of surface, not concentration of active sites**

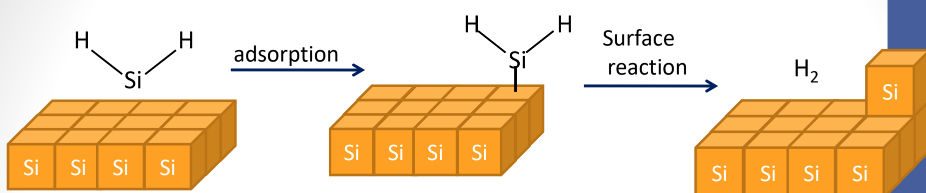
Chemical Vapor Deposition

$$SiH_{4(g)} \leftrightarrow SiH_{2(g)} + H_{2(g)}$$
$$SiH_{2(g)} \rightarrow Si_{(S)} + H_{2(g)}$$



No desorption occurs, the product, Si, remains attached to the surface, forms a new surface

Growth of Silicon Film by CVD



Write out elementary reactions and assume a rate-limiting step

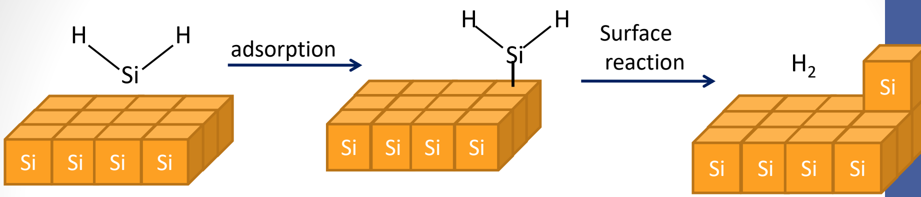
1. Adsorption $SiH_2(g) + S \leftrightarrow SiH_2.S$

Rate of adsorption = rate of attachment – rate of detachment

$$r_{AD} = k_{SiH_2} P_{SiH_2} f_v - k_{-SiH_2} f_{SiH_2} \quad \rightarrow r_{AD} = k_{SiH_2}\left(P_{SiH_2} f_v - \frac{f_{SiH_2}}{K_{SiH_2}}\right)$$

f_v & f_{SiH2}: fraction of the surface covered by vacant sites or SiH_2, respectively

Growth of Silicon Film by CVD

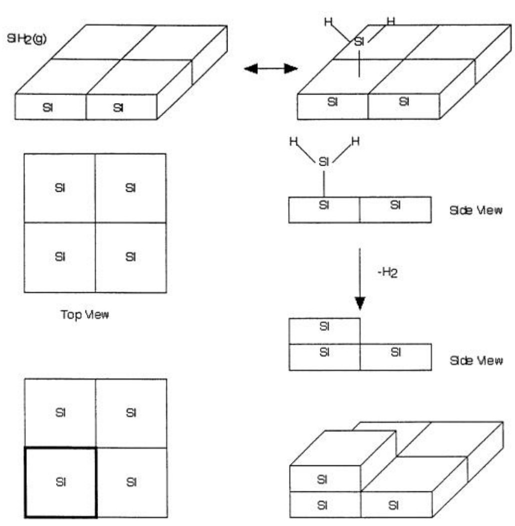


2. Surface reaction $SiH_2.S \rightarrow Si + S + H_2(g)$

$$r_S = k_S f_{SiH_2} - k_{-S} C_{Si} P_{H_2} f_v \quad \rightarrow r_S = k_S \left(f_{SiH_2} - \frac{C_{Si} C_{H_2} f_v}{K_S} \right)$$

Surface coverage is in terms of fraction of surface, not concentration of active sites

Chemical Vapor Deposition



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Chemical Vapor Deposition

1) Mechanism

Gas Phase Dissociation

Homogeneous

$$SiH_4 \rightleftarrows SiH_2 + H_2 \qquad -r_{SiH_4} = k_{SiH_4}\left[P_{SiH_4} - \frac{P_{H_2}P_{SiH_2}}{K_P}\right]$$

Heterogeneous

$$SiH_2 + \tilde{S} \leftrightarrow SiH_2 \bullet \tilde{S} \qquad r_{AD} = k_A\left[P_{SiH_2} f_V - \frac{f_{SiH_2}}{K_{SiH_2}}\right]$$

$$SiH_2 \bullet \tilde{S} \rightarrow Si + \tilde{S} + H_2 \qquad r_{Dep} = r_S = k_S f_{SiH_2}$$

f_V = fraction of surface that is vacant

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Chemical Vapor Deposition

2) Rate Limiting Step

$$r_{Dep} = r_S = k_S f_{SiH_2}$$

3) Express f_i in terms of P_i

$$r_{AD} = k_A\left[P_{SiH_2} f_V - \frac{f_{SiH_2}}{K_{SiH_2}}\right]$$

$$\frac{r_{AD}}{k_A} \approx 0$$

$$\Rightarrow f_{SiH_2} = K_{SiH_2} f_V \ P_{SiH_2}$$

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Chemical Vapor Deposition

4) Surface Area Balance

$$1 = f_V + f_{SiH_2} = f_V + K_{SiH_2} P_{SiH_2} f_V$$

$$f_V = \frac{1}{1 + K_{SiH_2} P_{SiH_2}}$$

5) Combine

$$\left.\begin{aligned} r_{Dep} &= r_S = k_S f_{SiH_2} \\ f_{SiH_2} &= K_{SiH_2} f_V \; P_{SiH_2} \\ f_V &= \frac{1}{1 + K_{SiH_2} P_{SiH_2}} \end{aligned}\right\} \Rightarrow r_{Dep} = \frac{k_S K_{SiH_2} P_{SiH_2}}{1 + K_{SiH_2} P_{SiH_2}}$$

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Homogeneous Reaction

$$SiH_4 \leftrightarrow SiH_2 + H_2 \quad -r_{SiH_4} = k_{SiH_4}\left[P_{SiH_4} - \frac{P_{H_2} P_{SiH_2}}{K_P}\right]$$

$$\frac{-r_{SiH_4}}{k_{SiH_4}} \approx 0 \Rightarrow P_{SiH_2} = \frac{K_P P_{SiH_4}}{P_{H_2}}$$

$$r_{Dep} = \frac{k_S K_{SiH_2} P_{SiH_2}}{1 + K_{SiH_2} P_{SiH_2}} = \frac{k_S K_P K_{SiH_2} P_{SiH_4}}{P_{H_2} + K_{SiH_2} K_P P_{SiH_4}} = \frac{k_1 P_{SiH_4}}{P_{H_2} + K_1 P_{SiH_4}}$$

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Exercise: find the rate law!

Germanium films have applications in microelectronics & solar cell fabrication

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Surface reaction $GeCl_2.S + 2H.S \overset{k_S}{\rightarrow} Ge_{(S)} + 2HCl_{(g)} + 3S$

Surface reaction is believed to be the rate-limiting step

Exercise: find the rate law!

$$GeCl_{4(g)} + H_{2(g)} \rightarrow Ge_{(S)} + 2HCl_{(g)} + Cl_{2(g)}$$

$$r''_{Dep} = \frac{k' P_{GeCl_2} P_{H_2}}{\left(1 + K_A P_{GeCl_2} + \sqrt{K_H P_{H_2}}\right)^3}$$

$$r''_{Dep} = \frac{k' P_{GeCl_4} P_{H_2} P_{Cl_2}^2}{\left(P_{Cl_2} + K_A P_{GeCl_4} + P_{Cl_2}\sqrt{K_H P_{H_2}}\right)^3}$$

If hydrogen is weekly adsorbed $\sqrt{K_H P_{H_2}} < 1$

$$r''_{Dep} = \frac{k' P_{GeCl_4} P_{H_2} P_{Cl_2}^2}{\left(P_{Cl_2} + K_A P_{GeCl_4}\right)^3}$$

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