Lecture 18

Chemical Reaction Engineering (CRE) is the field that studies the rates and mechanisms of chemical reactions and the design of the reactors in which they take place.

Web Lecture 18
Class Lecture 23–Tuesday 4/16/2013

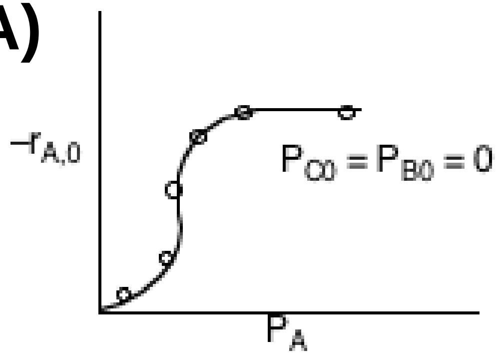
- Catalytic Mechanisms
- Data Analysis
- Chemical Vapor Deposition (CVD)

Catalytic Mechanisms

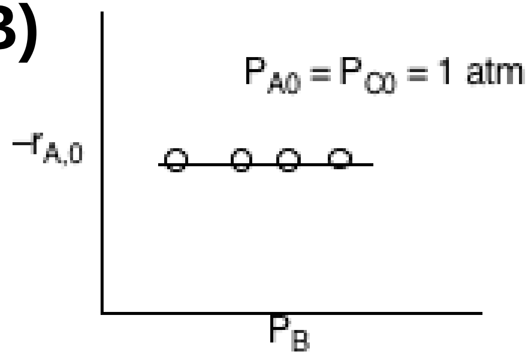
$$2A \underset{\text{cat}}{\rightleftarrows} B + C$$

(a) The initial rate of reaction is shown below

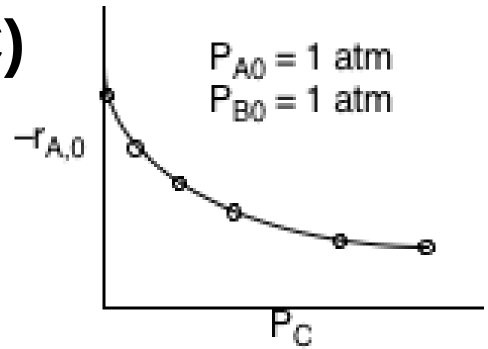
(A)



(B)



(C)



Catalytic Mechanisms

$$A \rightleftharpoons B + C$$

(A)

$$-r_A = \frac{kP_A}{1 + K_A P_A + K_B P_B}$$

(B)

$$-r_A = \frac{kP_A}{(1 + K_A P_A + K_C P_C)}$$

(A)

$$A + S \rightleftharpoons A \bullet S$$

$$A \bullet S \longrightarrow B \bullet S + C$$

$$B \bullet S \rightleftharpoons B + S$$

(B)

$$A + S \rightleftharpoons A \bullet S$$

$$A \bullet S \longrightarrow B + C \bullet S$$

$$C \bullet S \rightleftharpoons C + S$$

Catalytic Mechanisms

$$2A \rightleftarrows B + C$$

(C)

$$-r_A = \frac{kP_A^2}{\left(1 + K_A P_A + K_C P_C\right)^2}$$

(D)

$$-r_A = \frac{kP_A^2}{\left(1 + K_A P_A + K_C P_C\right)^2}$$

(C)

$$A + S \rightleftarrows A \bullet S$$

$$A \bullet S + A(g) \longrightarrow B + C \bullet S$$

$$C \bullet S \rightleftarrows C + S$$

(D)

$$A + S \rightleftarrows A \bullet S$$

$$A \bullet S + A \bullet S \longrightarrow B + S + C \bullet S$$

$$C \bullet S \rightleftarrows C + S$$

Catalytic Mechanisms

$$2A \longrightarrow B + C$$

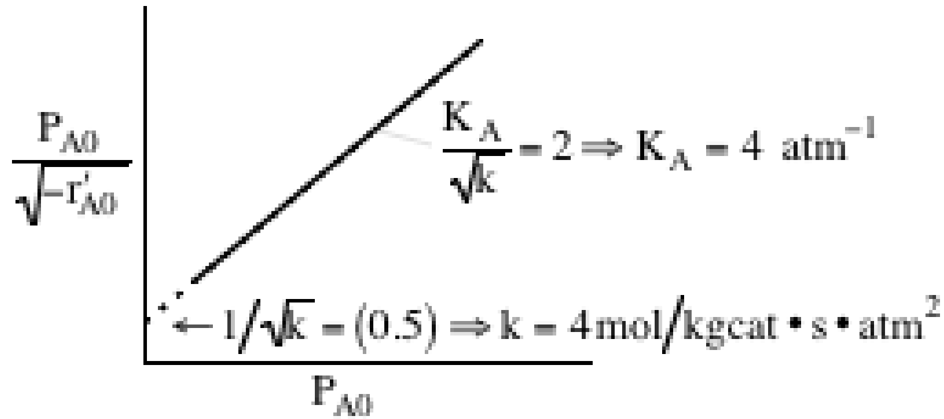
$$A + S \rightleftarrows A \bullet S$$

$$A \bullet S + A \bullet S \longrightarrow B + C \bullet S$$

$$C \bullet S \rightleftarrows C + S$$

$$-r'_A = \frac{kP_A^2}{\left(1 + K_A P_A + K_C P_C\right)^2}$$

Catalytic Mechanisms



$$-r'_{A0} = \frac{4P_A^2}{1 + 4P_{A0} + K_C P_{C0}}$$

For $P_{C0} = 2$ atm and $P_{A0} = 1$ atm, then $-r'_{A0} = 0.0138 \dfrac{\text{mol}}{\text{kgcat} \bullet \text{s}}$

$$-r'_{A0} = \frac{4}{(1 + 4 + 2K_C)^2} = 0.0138$$

One equation and one unknown

$$K_C = 6\ \text{atm}^{-1}$$

$$-r'_{A0} = \frac{4P_A^2}{(1 + 4P_A + 6P_C)^2}$$

Catalytic Mechanisms

$$2A \rightleftarrows B + C$$

$$A + S \rightleftarrows A \bullet S \qquad -r'_A = r_{A0} = k_A\left[P_A C_V - \frac{C_{A\bullet S}}{K_A}\right] \Rightarrow C_{A\bullet S} = K_A P_A C_V$$

$$A \bullet S + A \bullet S \rightleftarrows B + S + C \bullet S \qquad -r'_A = r_S = k_S C^2_{A\bullet S}$$

$$C \bullet S \rightleftarrows C + S \qquad -r_A = r_{DC} = k_{DC}\left[C_{C\bullet S} - P_C C_V K_C\right] \Rightarrow C_{C\bullet S} = K_C P_C C_V$$

Where $K_A = 4\ atm^{-1}$ and $K_C = 6\ atm^{-1}$

1) At what is the ratio of sites with A adsorbed to those sites with C adsorbed when the conversion is 50%?
2) What is the conversion when the sites with A adsorbed are equal to those with C adsorbed?

Catalytic Mechanisms

$$2A \longrightarrow B + C$$

$$A \longrightarrow \frac{B}{2} + \frac{C}{2}$$

$$K_A = 4 \text{ and } K_C = 6$$

Ratio of site concentrations

$$\frac{C_{A\bullet S}}{C_{C\bullet S}} = \frac{K_A\ P_A\ C_V}{K_C\ P_C\ C_V} = \frac{K_A\ P_A}{K_C\ P_C}$$

$$P_A = P_{A0}(1-X)/(1+\varepsilon X)$$

$$P_C = P_{A0}\frac{X}{2(1+\varepsilon X)}$$

$$\frac{C_{A\bullet S}}{C_{C\bullet S}} = \frac{K_A\ P_{A0}\left(\frac{1-X}{1+\varepsilon X}\right)\frac{P}{P_0}}{K_C\ P_{A0}\left(\frac{X/2}{1+\varepsilon X}\right)\frac{P}{P_0}} = 2\frac{K_A(1-X)}{K_C\ X}$$

Catalytic Mechanisms

1) At X = 0.5

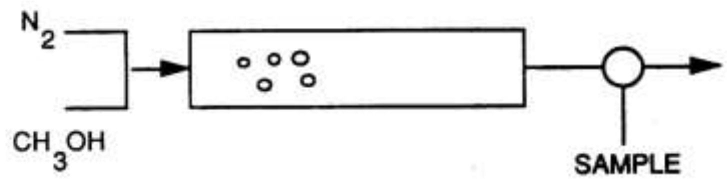
$$\frac{C_{A\bullet S}}{C_{C\bullet S}} =\sim \frac{(2)(4)(1-0.5)}{6(0.5)} = 1.33$$

2) At an equal concentrations of A and C sites, the conversion will be

$$\frac{C_{A\bullet S}}{C_{C\bullet S}} = 1 = \frac{2K_A(1-X)}{K_C\ X}\ ,\ \text{then}\quad X = \frac{2K_A}{K_C + 2K_A} = \frac{(2)(4)}{6+(2)(4)} = \frac{8}{14}$$

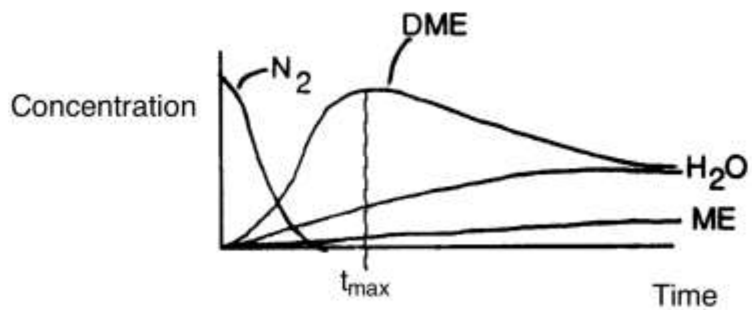
$$X = 0.57$$

Dimethyl Either



$$2CH_3OH \longrightarrow CH_3 - O - CH_3 + H_2O$$

$$2ME \longrightarrow DME + W$$



Initially water does not exit the reactor the same as DME because
Which of the following best describes the data

- **A** There is more DME than water.
- **B** Steady state has been reached.
- **C** Water reacts with ME.
- **D** Water is adsorbed on the surface.

Chemical Reaction Engineering in the Electronics Industry

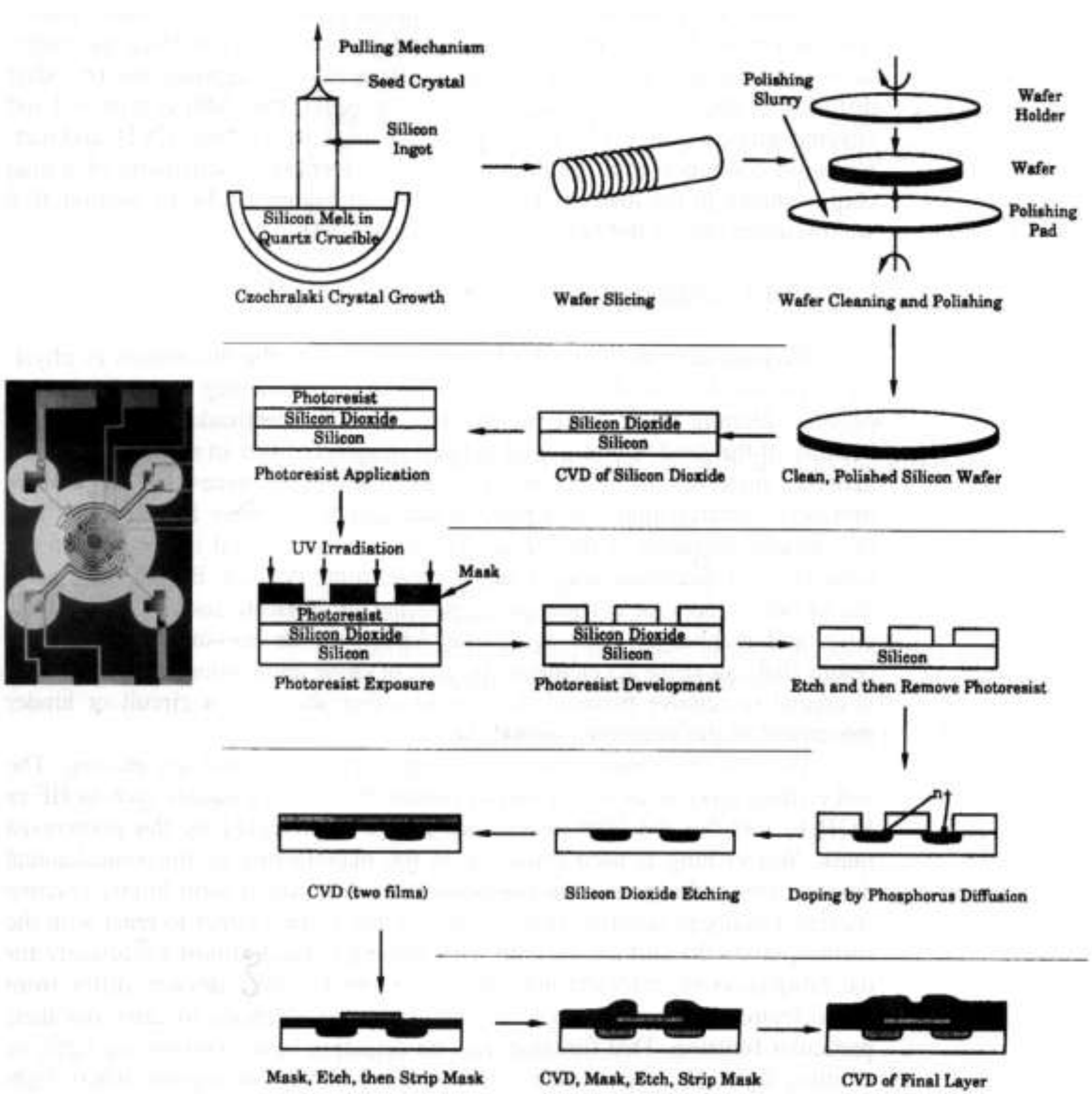


Figure 10-34 Microelectronic fabrication steps.

Chemical Reaction Engineering in the Electronics Industry

<u>ChE 342</u>

Czochralski Crystal Growth – Heat Transfer

Doping of n/p junction – Diffusion

<u>ChE 344</u>

Chemical Vapor Deposition (Catalysis Analogy)

Photo Resist Formation

Photo Resist Dissolution

Etching

<u>The 5 steps</u>

1. Postulate Mechanism

   (sometimes first includes a gas phase reaction (then adsorption, surface reaction and desorption)

2. Postulate Rate Limiting Step
3. Evaluate Parameters in Terms of Measured Variables
4. Surface Area Balance
5. Evaluate Rate Law Parameters

Chemical Reaction Engineering in the Electronics Industry

Chemical Vapor Deposition

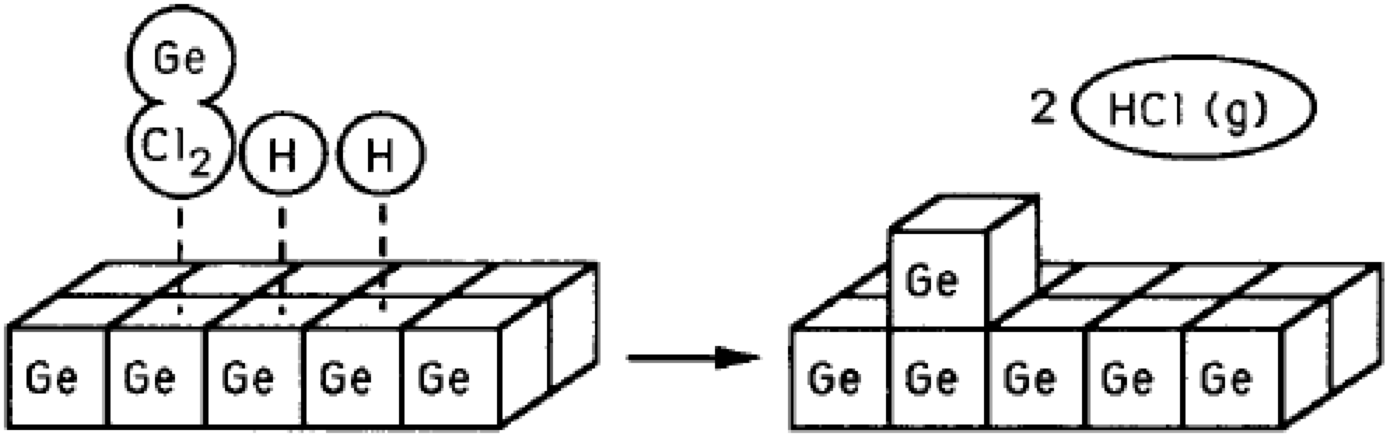
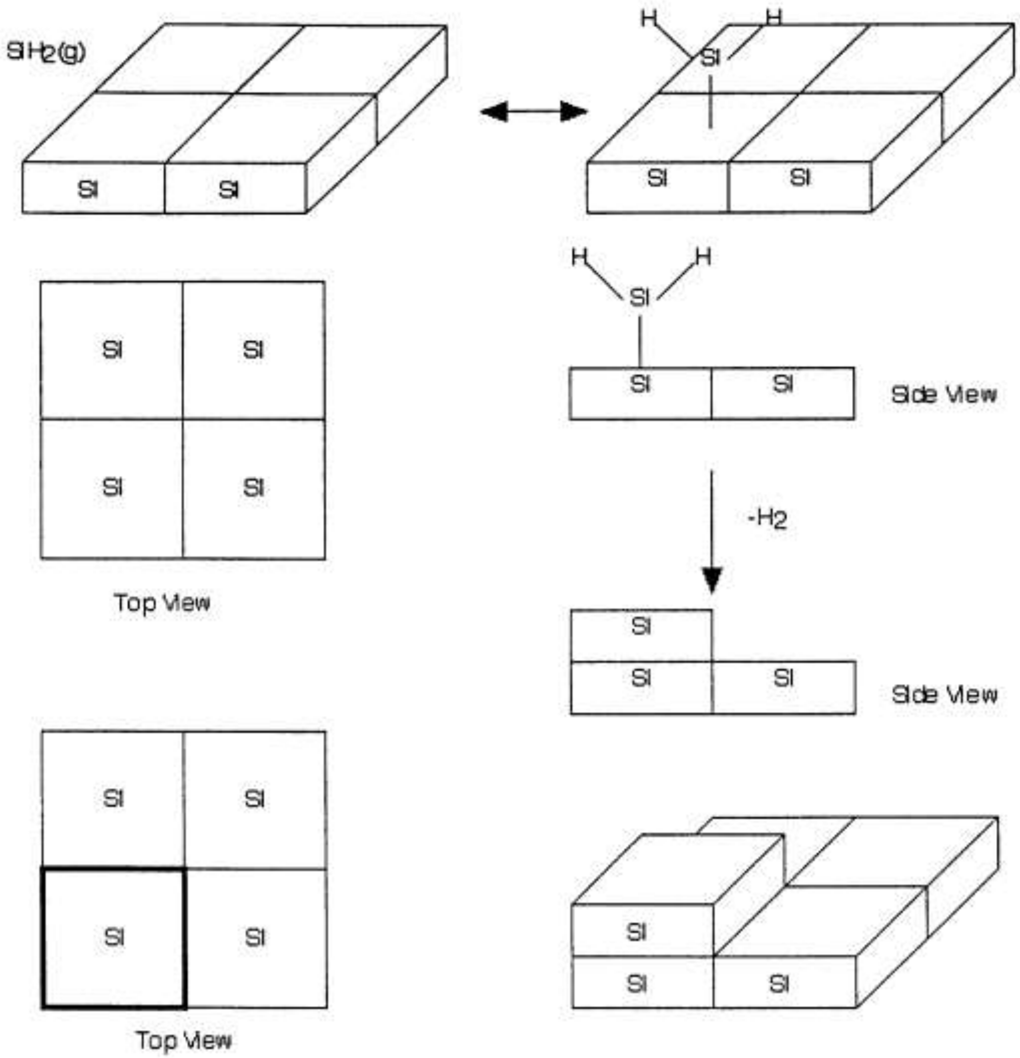


Figure 10-21 CVD surface reaction step for Germanium.

Chemical Vapor Deposition



Chemical Vapor Deposition

1) Mechanism

Gas Phase

<u>Homogeneous</u>

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

<u>Heterogeneous</u>

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

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

f_V = fraction of surface that is vacant

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

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

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

4) Area Balance

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

Chemical Vapor Deposition

4) 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

$$r_{Dep} = \frac{k_S K_{SiH_2} P_{SiH_2}}{1 + K_{SiH_2} P_{SiH_2}}$$

Homogeneous Reaction

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

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

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

End of Web Lecture 18
End of Class Lecture 23