### 3.155J/6.152J

## Microelectronic Processing

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1. a) Mean free path $\quad \lambda=\frac{k_{B} T}{\sqrt{2} \pi d^{2} p}$
where $k_{\mathrm{B}}=1.38 \times 10^{-23}, T=293^{\circ} \mathrm{K}, p=5 \mathrm{~m}$ Torr $=0.66 \mathrm{~Pa}, d \approx 2 \AA=2 \times 10^{-10} \mathrm{~m}$ (http://www.webelements.com/)

$$
\lambda=\frac{\left(1.38 \times 10^{-23}\right)\left(293^{\circ} \mathrm{K}\right)}{\sqrt{2} \pi\left(2 \times 10^{-10} \mathrm{~m}\right)^{2}(0.66 \mathrm{~Pa})}=3.45 \mathrm{~cm}
$$

b) Use the ideal gas law $p V=N k_{\mathrm{B}} T$

$$
\frac{N}{V}=\frac{p}{k_{B} T}=\frac{0.66 \mathrm{~Pa}}{\left(1.38 \times 10^{-23}\right)\left(293^{\circ} \mathrm{K}\right)}=1.6 \times 10^{20} \mathrm{~m}^{-3}=1.6 \times 10^{14} \mathrm{~cm}^{-3}
$$

c) Flux on a surface: $\quad J_{x}=\frac{p}{\sqrt{2 \pi m k_{B} T}}$
where $m=$ mass of particle $=(32 \mathrm{amu})\left(1.67 \times 10^{-27} \mathrm{~kg} / \mathrm{amu}\right)=5.34 \times 10^{-26} \mathrm{~kg}$

$$
J_{x}=1.8 \times 10^{22} \frac{\text { molecules }}{\mathrm{m}^{2} \mathrm{~s}}=1.8 \times 10^{18} \mathrm{~cm}^{-2} \mathrm{~s}^{-1}
$$

d) We are trying to find the average molecular speed of Ar atoms impinging a surface in the chamber. Two ways to do this:

$$
\bar{v}_{x}=\frac{2 J}{n}=200 \frac{\mathrm{~m}}{\mathrm{~s}}=2 \times 10^{4} \frac{\mathrm{~cm}}{\mathrm{~s}}
$$

or

$$
\bar{v}_{x}=\sqrt{\frac{2 k_{B} T}{\pi m}}=220 \frac{\mathrm{~m}}{\mathrm{~s}} .
$$

Some people calculated the average molecular speed in any direction, which is

$$
\bar{v}=\sqrt{\frac{8 k T}{\pi m}}=439 \frac{\mathrm{~m}}{\mathrm{~s}}
$$

This is also accepted. (Note that the molecular speed is independent of pressure because both $J$ and $n$ are proportional to $p$.)
2. The 1" pipe works fine for the cryo-pump, which operates close to atmospheric pressure (small $\Delta p$ across pipe length), because the mean free path of the molecules is much less than the pipe diameter. This is the viscous flow regime, $K<1$. But a 1 " pipe will not work in the range ion pumps are effective, $p<10^{-5}$ Torr because the molecular collisions with the pipe walls dominate the resistance and reduce the pumping speed at low pressure (ballistic flow, $K>1$ ). More quantitatively, the effective pump speed never exceeds the conductance of the worst component: $S_{\text {eff }}=\frac{C S_{\mathrm{p}}}{C+S_{\mathrm{p}}}$ where conductance $C=$ $Q / \Delta p$ and pump speed $S_{\mathrm{p}}=Q / p_{\mathrm{p}} ; \Delta p$ is large and $p_{\mathrm{p}}$ is small.

## CVD

3. Assume chemical equilibrium is established in a CVD reactor according to the equation:

$$
\mathrm{SiH}_{4}(\mathrm{~g}) \leftrightarrow \mathrm{SiH}_{2}(\mathrm{~g})+\mathrm{H}_{2}(\mathrm{~g})
$$

The temperature is maintained at 500 C and the pressure at 10 mT . If the equilibrium constant for the reaction is $K(T)=2 \times 10^{9}$ (Torr) $\exp \left[-1.8 \mathrm{eV} /\left(k_{\mathrm{B}} T\right)\right]$, find the partial pressure of each gas assuming $p\left(\mathrm{H}_{2}\right) \approx p\left(\mathrm{SiH}_{2}\right)$.

$$
\begin{aligned}
K(T=773 \mathrm{~K}) & =2 \times 10^{9} \exp \left[-2.9 \times 10^{-19} \mathrm{~J} /\left(k_{B} \times 773 \mathrm{~K}\right)\right] \\
& =3 \mathrm{mTorr}
\end{aligned}
$$

Also, $K=\frac{p_{\mathrm{SiH}_{2}} \times p_{\mathrm{H}_{2}}}{p_{\mathrm{SiH}_{4}}}=\frac{p_{\mathrm{SiH}_{2}}^{2}}{p_{\mathrm{SiH}_{4}}}=0.003$ Torr (*) (assumption: $p_{\mathrm{H}_{2}}=p_{\mathrm{SiH}_{2}}$ )
In addition, $\left\{\begin{array}{l}p_{\mathrm{SiH}_{4}}+p_{\mathrm{SiH}_{2}}+p_{\mathrm{H}_{2}}=0.01 \text { Torr } \\ \text { or } p_{\mathrm{SiH}_{4}}+2 p_{\mathrm{SiH}_{2}}=0.01 \text { Torr }(* *)\end{array}\right.$
Substituting (**) into (*):

$$
\begin{aligned}
& p_{\mathrm{SiH}_{2}}^{2}=0.003 p_{\text {SiH }_{4}}=0.003\left(0.01-2 p_{\mathrm{SiH}_{2}}\right) \\
& \Rightarrow p_{\mathrm{SiH}_{2}}^{2}+0.006 p_{\mathrm{SiH}_{2}}=3 \times 10^{-5} \\
& p_{\mathrm{SiH}_{2}}=3.33 \mathrm{mTorr} \\
& p_{H_{2}}=3.33 \mathrm{mTorr} \\
& p_{\mathrm{SiH}_{4}}=3.34 \mathrm{mTorr}
\end{aligned}
$$

Check that the sum of the partial pressures, $p_{\mathrm{i}}=0.01$ Torr .
4. Assume a CVD process based on the reaction: $2 \mathrm{AB}(\mathrm{g}) \leftrightarrow 2 \mathrm{~A}(\mathrm{~s})+\mathrm{B}_{2}(\mathrm{~g})$.
a) Sketch and briefly describe the individual steps that control the reaction.


Cg


1) Bulk transport governed by gas velocity outside boundary layer, $u_{\infty}$.
2) Diffusion across boundary layer
$J \propto \frac{D}{\delta(x)}\left(C_{g}-C_{s}\right), \quad \delta(x)$ is the thickness of the boundary layer, a function of $x$.
3) Adsorption involves AB molecule sticking by weak interactions, not chemical bonding.
4) Dissociation of AB due to temperature and possibly catalyzed by interaction of A with surface. B may remain adsorbed or desorb upon dissociation.
5) A (solid) actually bonds with a site on substrate surface (film growth).
6) $\mathrm{B}_{2}(\mathrm{~g})$ must diffuse across boundary layer. $J_{B_{2}}=\frac{D_{B_{2}}}{\delta(x)}\left(C_{g}^{B_{2}}-C_{s}^{B_{2}}\right)$
7) Bulk transport of $B_{2}(\mathrm{~g})$ under carrier gas velocity $u_{\infty}$.
b) How would you distinguish between i) the reaction-limited and ii) a transportlimited cases?

In the reaction-limited regime, the temperature dependence of the film growth rate exhibits Arrhenius behavior:

$$
\begin{aligned}
& v=\frac{k C_{g}}{N}, \quad k=k_{o} \exp \left(\frac{-\Delta G}{k_{B} T}\right) \\
& v \propto \exp \left(\frac{-\Delta G}{k_{B} T}\right)
\end{aligned}
$$

In the transport-limited regime, the deposition rate is given by:

$$
v=\frac{3 \lambda \bar{v}_{x} C_{g}}{4 N_{f} x} \sqrt{\frac{\rho u_{\infty} x}{\eta}},
$$

where

$$
\bar{v}_{x}=\sqrt{\frac{2 k_{B} T}{\pi m}}, \quad \frac{C_{g}}{P_{g}}=\frac{1}{k_{B} T}, \quad \text { and } \quad \lambda=\frac{k_{B} T}{\sqrt{2} \pi d^{2} P_{\text {total }}}
$$

so that

$$
v \propto P_{g} \sqrt{T} \sqrt{u_{\infty}}
$$

Thus, temperature dependence is the biggest differentiator between the two regimes.
c) Sketch the variation of the log of the CVD growth rate as functions of the square root of the gas flow velocity and as a function of $1 / T$.

d) If you wanted to increase the growth rate of a transport-limited CVD process, what processing variables would be most effective? (List them in decreasing order of efficacy, e.g. $v \propto \exp (x)$ first, etc.)

For the fixed length, in the transport-limited regime, in decreasing order of efficacy, we have $\sqrt{u_{\infty}}$, and $\sqrt{T}$. ( $P_{\mathrm{g}}$ could play a role through the viscosity.)

