Assignment #4

1.15 Thermal expansion

a. If $\lambda$ is the thermal expansion coefficient, show that the thermal expansion coefficient for an area is $2\lambda$. Consider an aluminum square sheet of area 1 cm$^2$. If the thermal expansion coefficient of Al at room temperature (25 °C) is about $24 \times 10^{-6}$ K$^{-1}$, at what temperature is the percentage change in the area +1%?

Solution

a. Consider a rectangular area with sides $x_0$ and $y_0$. Then at temperature $T_0$,

$$A_0 = x_0 y_0$$

and at temperature $T$,

$$A = [x_0 (1 + \lambda \Delta T)] [y_0 (1 + \lambda \Delta T)] = x_0 y_0 (1 + \lambda \Delta T)^2$$

that is

$$A = x_0 y_0 \left[1 + 2\lambda \Delta T + (\lambda \Delta T)^2\right].$$

We can now use that $A_0 = x_0 y_0$ and neglect the term $(\lambda \Delta T)^2$ because it is very small in comparison with the linear term $\lambda \Delta T$ ($\lambda << 1$) to obtain

$$A = A_0 (1 + 2\lambda \Delta T) = A_0 (1 + \alpha_A \Delta T)$$

So, the thermal expansion coefficient for an area is

$$\alpha_A = 2\lambda$$

The area of the aluminum sheet at any temperature is given by

$$A = A_0 \left[1 + 2\lambda (T - T_0)\right]$$

where $A_o$ is the area at the reference temperature $T_0$. Solving for $T$ we obtain,

$$T = T_0 + \frac{1}{2} \frac{A / A_0 - 1}{\lambda} = 25 \degree C + \frac{1}{2} \frac{(1.01) - 1}{24 \times 10^{-6} \degree C^{-1}} = 233.3 \degree C.$$
1.16 Thermal expansion of Si  The expansion coefficient of silicon over the temperature range 120-1500 K is given by Okada and Tokumaru (1984) as

\[ \lambda = 3.725 \times 10^{-6}[1 - e^{-5.88 \times 10^{-3}(T-124)}] + 5.548 \times 10^{-10} T \]

where \( \lambda \) is in K\(^{-1}\) (or \(^\circ\)C\(^{-1}\)) and \( T \) is in Kelvins.

b. The change \( \delta \rho \) in the density due to a change \( \delta T \) in the temperature, from Example 1.8, is given by

\[ \delta \rho = -\rho_o \alpha_v \delta T = -3\rho_o \lambda \delta T \]

Given density of Si as 2.329 g cm\(^{-3}\) at 20 \(^\circ\)C, calculate the density at 1000 \(^\circ\)C by using the full expression, and by using the polynomials expansion of \( \lambda \). What is your conclusion?

NOTE: The exponential term is \(-5.88 \times 10^{-3}\) NOT \(-3.725 \times 10^{-3}\)
NOTE: The example referred to is Example 1.8 NOT Example 1.5

Solution

b. The expansion coefficient at 1000 \(^\circ\)C (1273 K) will be

\[ \lambda(1273 \text{ K}) = 3.725 \times 10^{-6}[1 - e^{-5.88 \times 10^{-3}(1273-124)}] + 5.548 \times 10^{-10} (1273) \]

\[ \lambda(1273 \text{ K}) = 4.4269 \times 10^{-6} \text{ K}^{-1}. \]

The density of Si at 293 K is 2.329 g cm\(^{-3}\), the density at 1000 \(^\circ\)C (1273 K) is thus

\[ \rho = \rho_o + \delta \rho = \rho_o + (-\rho_o \alpha_v \delta T) = \rho_o - 3\rho_o \lambda \delta T \]

\[ = 2.329 \text{ g cm}^{-3} - 3 (2.329 \text{ g cm}^{-3})(4.4269 \times 10^{-6} \text{ K}^{-1})(1273 \text{ K} - 293 \text{ K}) = 2.2987 \text{ g cm}^{-3}. \]

The density changes from 2.329 K to 2.2987 K which is very small change, therefore the density can be roughly assumed as constant.
1.19 Thermal activation  A certain chemical oxidation process (e.g., SiO₂) has an activation energy of 2 eV atom⁻¹.

b. If the temperature is 900 °C, estimate the number of oxygen molecules with energies more than 2 eV. What happens to this concentration if the pressure is doubled?

Solution 1: Method of Estimation

The activation energy \( E_A \) is 2 eV per atom or

\[
E_A = (2 \text{ eV/atom})(1.602 \times 10^{-19} \text{ J/eV}) = 3.204 \times 10^{-19} \text{ J/atom}
\]

b. We are given pressure \( P = 1 \text{ atm} = 1.013 \times 10^5 \text{ Pa} \) and temperature \( T = 1173 \text{ K} \). If we consider a portion of oxygen gas of volume \( V = 1 \text{ m}^3 \) (the unit volume), the number of molecules present in the gas \( (N) \) will be equal to the concentration of molecules in the gas \( (n) \), i.e.: \( N = n \). And since we know \( \eta = N/N_A \), where \( \eta \) is the total number of moles and \( N_A \) is Avogadro’s number, we can make the following substitution into the equation \( PV = \eta RT \):

\[
RT \frac{N_A PV}{N} = \eta RT
\]

isolating \( n \),

\[
n = \frac{N_A PV}{RT} = \left( \frac{6.022 \times 10^{23} \text{ mol}^{-1} \times 1.013 \times 10^5 \text{ Pa} \times 1 \text{ m}^3}{8.315 \text{ m}^3 \text{ Pa K}^{-1} \text{ mol}^{-1} \times 1173 \text{ K}} \right) \left( \frac{1}{1 \text{ m}^3} \right)
\]

\[
\therefore \quad n = 6.255 \times 10^{24} \text{ m}^{-3}
\]

Therefore there are \( 6.255 \times 10^{24} \) oxygen molecules per unit volume.

For an estimation of the concentration of molecules with energy above 2 eV, we can use the following approximation (remember to convert \( E_A \) into Joules). If \( n_A \) is the concentration of molecules with \( E > E_A \), then:

\[
\frac{n_A}{n} = \exp \left( - \frac{E_A}{kT} \right)
\]

\[
\therefore \quad n_A = n \exp \left( - \frac{E_A}{kT} \right) = \left( 6.255 \times 10^{24} \text{ m}^{-3} \right) \exp \left[ -\frac{\left( 3.204 \times 10^{-19} \text{ J} \right)}{\left( 1.381 \times 10^{-23} \text{ J K}^{-1} \right) \times 1173 \text{ K}} \right]
\]

\[
\therefore \quad n_A = 1.61 \times 10^{16} \text{ m}^{-3}
\]

However, this answer is only in the right order of magnitude. For a better calculation we need to use a numerical integration of \( n(E) \) from \( E_A \) to \( \infty \).

Solution 2: Method of Numerical Integration

To find the number of molecules with energies greater than \( E_A = 2 \text{ eV} \) more accurately, numerical integration must be used. The distribution of particles can be expressed by the Maxwell-Boltzmann distribution,
Therefore, number of molecules that have their energy of more than the activation energy, $E_A$, is

$$\int_{E_A}^{\infty} n_A(E) dE = \int_{E_A}^{\infty} \frac{2}{\pi^{1/2}} N \left( \frac{1}{k} \right)^{3/2} E^{1/2} \exp \left( - \frac{E}{kT} \right) dE$$

To integrate we need the upper limit to be $\infty$, but practically we will take it to be a multiple of:

Upper limit = $2 \times E_A = 39.57$

At $T = 300 \text{ K}$, $P = 1 \text{ atm} = 1.013 \times 10^5 \text{ Pa}$, and $V = 1 \text{ m}^3$, the number of molecules per unit volume is $n$:

$$PV = \frac{n}{N_A} RT$$

$$\therefore \quad n = \frac{N_A PV}{RT} = 6.255 \times 10^{24} \text{ m}^{-3}$$

Thus, the integration of the Maxwell-Boltzmann distribution gives:

$$\int_{E_A}^{2E_A} n_A(E) dE$$

$$= \int_{E_A}^{2E_A} \frac{2}{\pi^{1/2}} 6.255 \times 10^{24} \left( \frac{1}{k} \right)^{3/2} E^{1/2} \exp \left( - \frac{E}{1173k} \right) dE$$

$$= 8.27 \times 10^{16} \text{ molecules}$$

where the numerical integration was applied with 2000 steps.

If we compare this value to the one obtained previously through estimation ($1.61 \times 10^{16} \text{ m}^{-3}$), we see that the estimate is out by a factor of about 5. As stated previously, doubling the pressure doubles $n$ and hence doubles $n_A$. In the oxidation of Si wafers, high pressures lead to more rapid oxidation rates and a shorter time for the oxidation process.
Problem 2, e-booklet “Diffusion and Oxidation”

Semiconductor Fabrication Consider a wafer of Si crystal which has uniform boron (B) doping of $1 \times 10^{17}$ cm$^{-3}$ in the bulk. Suppose that the Si wafer is exposed to a phosphorus (P) gas at 1250 °C for 10 minutes. During the diffusion process, the surface P concentration remains saturates at about $1 \times 10^{21}$ cm$^{-3}$. Where is the junction from the surface? How long does it take to have the same junction depth from the surface if the diffusion temperature is 1100 °C? State the assumptions used in your calculations. The diffusion coefficient of P in Si has $D_o = 3.85$ cm$^2$s$^{-1}$, and $E_d = 3.66$ eV/atom.

Solution

Since we know, from the question, that during the diffusion process the surface P concentration remains constant, this diffusion is from unlimited supply. As well as assuming that we have steady state condition, we can now use Fick’s second law:

$$D \frac{\partial^2 C(x,t)}{\partial x^2} = \frac{\partial C(x,t)}{\partial t}$$

Solving this differential equation with boundary conditions:

$$\begin{cases} C(0,t) = C_s & \text{at the surface at any time} \\ C(x,t) = C_o & \text{at } t = 0 \text{ anywhere in the bulk} \\ C(\infty,t) = C_o & \text{anytime at far end} \end{cases}$$

we have the following equation:

$$\frac{C(x,t) - C_o}{C_s - C_o} = 1 - \text{erf} \left( \frac{x}{2\sqrt{Dt}} \right)$$

where erf($z$) is error function of $z$, and $D$ is the diffusion coefficient.

Method using Table 1

Since we need to know the value of $x$ when $C(x, 600s)$ is the same concentration as boron, $1 \times 10$ cm$^{-3}$,

$$\frac{1 \times 10^{17} - 0}{1 \times 10^{21} - 0} = 1 - \text{erf} \left( \frac{x}{2\sqrt{Dt}} \right)$$

$$\text{erf} \left( \frac{x}{2\sqrt{Dt}} \right) = 1 - \frac{1 \times 10^{17}}{1 \times 10^{21}} = 0.9999$$

From Table 1, we know that when erf($z$) = 0.9999, $z \approx 2.75$. Thus, $x = 2.75 \sqrt{Dt}$

At the diffusion temperature 1250 °C, the diffusion coefficient of P atoms is:
\[ D = D_o \exp\left(-\frac{Q_{\text{diff}}}{RT}\right) \]

\[ = 3.85 \times \exp\left(-\frac{353119}{8.3145 \cdot (1250 + 273)}\right) \]

\[ = 2.984 \times 10^{-12} \text{ cm}^2 \text{s}^{-1} \]

where \(Q_{\text{diff}}\) is an activation energy in joule per mole,

\[ Q_{\text{diff}} = 3.66 \text{ [eV/atom]} / q \text{ [C]} \times N_A = 353119 \text{ [J mol}^{-1}]\].

Therefore,

\[ \frac{x}{2\sqrt{D_t}} = 2.75 \]

\[ x = 2.75 \times 2\sqrt{D_t} \]

\[ = 2.75 \times 2\sqrt{2.984 \times 10^{-12} \times 600} \]

\[ = 2.32 \times 10^{-4} \text{ cm} \]

The junction is at 2.32 \text{ \mu m} from the surface.
**Numerical Method**

The concentration profile of P atoms at \( x \) at 10 min (600 sec) can be expressed as:

\[
\frac{C(x,t) - C_o}{C_s - C_o} = 1 - \text{erf} \left( \frac{x}{2\sqrt{Dt}} \right)
\]

\[
C(x,t) = \left[ 1 - \text{erf} \left( \frac{x}{2\sqrt{Dt}} \right) \right] (C_s - C_o) - C_o
\]

\[
= C_s \left[ 1 - \text{erf} \left( \frac{x}{2\sqrt{Dt}} \right) \right] \quad (\because C_o = 0)
\]

\[
C(x,600) = 1 \times 10^{21} \times \left[ 1 - \text{erf} \left( \frac{x}{2\sqrt{2.984 \times 10^{-12} \times 600}} \right) \right]
\]

From this equation, the concentration profile of P atoms at 10 min is graphically shown in Figure 1.

![Figure 1 Concentration profiles of Phosphorus and Boron at 10 min.](image)

From this graph, we can see that the concentrations of phosphorus and boron atoms are equal at \( x = 2.33 \text{ \( \mu \)m}, pn \) junction from the surface.

We are now interested in how long it takes to have the same P concentration at \( x = 2.33 \text{ \( \mu \)m} \) at the diffusion temperature of \( 1100 \^\circ C \). The P concentration at \( 1250 \^\circ C \) at 10 min at \( 2.33 \text{ \( \mu \)m}, C_{1250^\circ C}(2.33 \text{ \( \mu \)m}, 10 \text{ min}) \), must be the same as the one \( 1100 \^\circ C \) at \( t' \) at \( 2.33 \text{ \( \mu \)m}, C_{1100^\circ C}(2.33 \text{ \( \mu \)m}, t') \). Thus,
\[ C_{1250\degree C}(2.33\mu m, 10\ min) = C_{1100\degree C}(2.33\mu m, t') \]

\[ C_s \left[ 1 - \text{erf} \left( \frac{x}{2\sqrt{Dt}} \right) \right] = C_s \left[ 1 - \text{erf} \left( \frac{x}{2\sqrt{D't'}} \right) \right] \]

\[ Dt = D't' \]

\[ t' = \frac{D}{D'} \cdot t \]

where \( D' \) is the diffusion coefficient at 1100 °C:

\[ D' = D_o \exp \left( -\frac{Q_{\text{diff}}}{RT} \right) \]

\[ = 3.85 \times \exp \left( -\frac{353119}{8.3145 \cdot (1100 + 273)} \right) \]

\[ = 1.483 \times 10^{-13} \text{ cm}^2\text{s}^{-1} \]

Therefore,

\[ t' = \frac{Dt}{D'} \]

\[ = \frac{2.984 \times 10^{-12} \times 600}{1.483 \times 10^{-13}} \]

\[ = 12072.8 \text{ sec} \]

\[ = 3.35 \text{ h} \]