# CHG 4305 Advanced Materials in Chemical Engineering
University of Ottawa
Solution Assignment #1
Prof. A.Y. Tremblay 2015

1. Using the following data that relate to the formation of Schottky defects in some oxide ceramic (having the chemical formula MO), determine the following:
    - (a) The energy for defect formation (in eV)
    - (b) The equilibrium number of Schottky defects per cubic meter at 1000°C
    - (c) The identity of the oxide (i.e., what is the metal M?)

| T (°C) | ρ (g/cm3) | Ns (m–3) |
|---|---|---|
| 750 | 5.50 | $9.21 \times 10^{19}$ |
| 1000 | 5.44 | ? |
| 1250 | 5.37 | $5.00 \times 10^{22}$ |

## 1 Solution

This problem provides for some oxide ceramic, at temperatures of 750°C and 1250°C, values for density and the number of Schottky defects per cubic meter. The (a) portion of the problem asks that we compute the energy for defect formation. To begin, let us combine a modified form of Equation 5.2 and Equation 5.4 as

$$N_s = N \exp\left(-\frac{Q_s}{2kT}\right)$$

$$= \left(\frac{N_A \rho}{A_M + A_O}\right) \exp\left(-\frac{Q_s}{2kT}\right)$$

Inasmuch as this is a hypothetical oxide material, we don't know the atomic weight of metal M, nor the value of $Q_s$ in the above equation. Therefore, let us write equations of the above form for two temperatures, $T_1$ and $T_2$. These are as follows:

$$N_{s1} = \left(\frac{N_A \rho_1}{A_M + A_O}\right) \exp\left(-\frac{Q_s}{2kT_1}\right) \tag{5.S1a}$$

$$N_{s2} = \left(\frac{N_A \rho_2}{A_M + A_O}\right) \exp\left(-\frac{Q_s}{2kT_2}\right) \tag{5.S1b}$$

Dividing the first of these equations by the second leads to

$$\frac{N_{s1}}{N_{s2}} = \frac{\left(\dfrac{N_A \rho_1}{A_M + A_O}\right) \exp\left(-\dfrac{Q_s}{2kT_1}\right)}{\left(\dfrac{N_A \rho_2}{A_M + A_O}\right) \exp\left(-\dfrac{Q_s}{2kT_2}\right)}$$

which, after some algebraic manipulation, reduces to the form

$$\frac{N_{s1}}{N_{s2}} = \frac{\rho_1}{\rho_2} \exp\left[-\frac{Q_s}{2k}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)\right] \qquad (5.S2)$$

Now, taking natural logarithms of both sides of this equation gives

$$\ln\left(\frac{N_{s1}}{N_{s2}}\right) = \ln\left(\frac{\rho_1}{\rho_2}\right) - \frac{Q_s}{2k}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

and solving for $Q_s$ leads to the expression

$$Q_s = \frac{-2k\left[\ln\left(\dfrac{N_{s1}}{N_{s2}}\right) - \ln\left(\dfrac{\rho_1}{\rho_2}\right)\right]}{\dfrac{1}{T_1} - \dfrac{1}{T_2}}$$

Let us take $T_1$ = 750°C and $T_2$ = 1250°C, and we may compute the value of $Q_s$ as

$$Q_s = \frac{-(2)(8.62 \times 10^{-5} \text{ eV/K})\left[\ln\left(\dfrac{9.2 \times 10^{19} \text{ m}^{-3}}{5.0 \times 10^{22} \text{ m}^{-3}}\right) - \ln\left(\dfrac{5.50 \text{ g/cm}^3}{5.37 \text{ g/cm}^3}\right)\right]}{\dfrac{1}{750 + 273 \text{ K}} - \dfrac{1}{1250 + 273 \text{ K}}}$$

$$= 3.40 \text{ eV}$$

(b) It is now possible to solve for $N_s$ at 1000°C using Equation 5.S2 above. This time let's take $T_1$ = 1000°C and $T_2$ = 750°C. Thus, solving for $N_{s1}$, substituting values provided in the problem statement and $Q_s$ determined above yields

$$N_{s1} = \frac{N_{s2}\,\rho_1}{\rho_2}\exp\left[-\frac{Q_s}{2k}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)\right]$$

$$= \frac{(9.2 \times 10^{19}\ \text{m}^{-3})(5.44\ \text{g/cm}^3)}{5.50\ \text{g/cm}^3}\exp\left[-\frac{3.40\ \text{eV}}{(2)(8.62 \times 10^{-5}\ \text{eV/K})}\left(\frac{1}{1000 + 273\ \text{K}} - \frac{1}{750 + 273\ \text{K}}\right)\right]$$

$$= 4.0 \text{ x } 10^{21}\ \text{m}^{-3}$$

(c) And, finally, we want to determine the identity of metal M. This is possible by computing the atomic weight of M ($A_\text{M}$) from Equation 5.S1a. Rearrangement of this expression leads to

$$\left(\frac{N_\text{A}\rho_1}{A_\text{M} + A_\text{O}}\right) = N_{s1}\exp\left(\frac{Q_s}{2kT_1}\right)$$

And, after further algebraic manipulation

$$\left[\frac{N_\text{A}\rho_1}{N_{s1}\exp\left(\dfrac{Q_s}{2kT_1}\right)}\right] = A_\text{M} + A_\text{O}$$

And, solving this expression for $A_\text{M}$ gives

$$A_\text{M} = \left[\frac{N_\text{A}\rho_1}{N_{s1}\exp\left(\dfrac{Q_s}{2kT_1}\right)}\right] - A_\text{O}$$

Now, assuming that $T_1$ = 750°C, the value of $A_\text{M}$ is

$$A_\text{M} = \left\{\frac{(6.022 \times 10^{23}\ \text{ions/mol})(5.50\ \text{g/cm}^3)(10^6\ \text{cm}^3/\text{m}^3)}{(9.2 \times 10^{19}\ \text{ions/m}^3)\exp\left[\dfrac{3.40\ \text{eV}}{(2)(8.62 \times 10^{-5}\ \text{eV/K})(750 + 273\ \text{K})}\right]}\right\} - 16.00\ \text{g/mol}$$

$$= 136.7\ \text{g/mol}$$

Upon consultation of the periodic table in Figure 2.6, the divalent metal (i.e., that forms $M^{2+}$ ions) that has an atomic weight closest to 136.7 g/mol is barium. Thus, this metal oxide is BaO.

2. A sheet of steel 2 mm thick separates two nitrogen atmospheres. The temperature on both sides is 1200° C. The system is permitted to achieve a steady-state diffusion condition. The diffusion coefficient for nitrogen in steel at this temperature is $6\text{x}10^{-11}$ m²/sec, and the diffusion flux is found to be $1.1\text{x}10^{-7}$ kg/(m² s). Also it is known that the concentration of nitrogen in the steel at the high-pressure surface is 4.1 kg/m³. How far into the sheet from this high-pressure side will the concentration be 2 kg/m³? Assume a linear concentration profile.

2. Solution

This problem is solved by using Equation 6.3 in the form

$$J = -D\frac{C_A - C_B}{x_A - x_B}$$

If we take $C_A$ to be the point at which the concentration of nitrogen is 4.1 kg/m³, then it becomes necessary to solve for $x_B$, as

$$x_B = x_A + D\left[\frac{C_A - C_B}{J}\right]$$

Assume $x_A$ is zero at the surface, in which case

$$x_B = 0 + (6\times10^{-11}\ \text{m}^2/\text{s})\left[\frac{4.1\,kg/m^3 - 2\,kg/m^3}{1.1\times10^{-7}\,kg/m^2\text{-}s}\right]$$

$$= 1.15 \times 10^{-3}\ \text{m} = 1.15\ \text{mm}$$

3. The outer surface of a manufactured steel part is to be hardened by increasing its carbon content. The carbon is to be supplied from an external carbon rich atmosphere that is maintained at an elevated temperature. The diffusion heat treatment at 950°C (1223 K) for 10 min. Increases the carbon concentration to 0.8 wt % at a position 1.2 mm

below the surface. Estimate the diffusion time required at 550°C (820 K) to achieve the same concentration also at a 1.2 mm position. Assume that the surface carbon content is the same for both heat treatments, which is maintained constant. Determine the iron phases from the plot entitled “Classification of Metal Alloys”, on the second slide of the file “CHG4305-1-CR-ch13.ppt” on the course website. Use the diffusion data in table 6.2 CR to solve the problem.

3. Solution

In order to compute the diffusion time at 550°C to produce a carbon concentration of 0.80 wt% at a position 1.2 mm below the surface we must employ Equation 6.6b with position ($x$) constant; that is

$$Dt = \text{constant}$$

Or

$$D_{950}t_{950} = D_{550}t_{550}$$

In addition, it is necessary to compute values for both $D_{950}$ and $D_{550}$ using Equation 6.8. From Table 6.2, for the diffusion of C in α-Fe, $Q_d$ = 80,000 J/mol and $D_0 = 6.2 \times 10^{-7}$ m$^2$/s, for the diffusion of C in γ-Fe, $Q_d$ = 148,000 J/mol and $D_0 = 2.3 \times 10^{-5}$ m$^2$/s. Therefore,

$$D_{950} = (2.3 \times 10^{-5}\ \text{m}^2/\text{s})\exp\left[-\frac{148{,}000\ \text{J/mol}}{(8.31\ \text{J/mol-K})(950+273\ \text{K})}\right]$$

$$= 1.09\times 10^{-11}\ \text{m}^2/\text{s}$$

$$D_{550} = (6.2 \times 10^{-7}\ \text{m}^2/\text{s})\exp\left[-\frac{80{,}000\ \text{J/mol}}{(8.31\ \text{J/mol-K})(550+273\ \text{K})}\right]$$

$$= 5.16 \times 10^{-12}\ \text{m}^2/\text{s}$$

Now, solving the original equation for $t_{550}$ gives

$$t_{550} = \frac{D_{950} t_{950}}{D_{550}}$$

$$= \frac{(1.09 \times 10^{-11} \text{ m}^2/\text{s})(10 \text{ min})}{5.16 \times 10^{-12} m^2 / s}$$

$$= 21.12 \text{ min}$$

4. Phosphorus atoms are to be diffused into a silicon wafer using both pre-deposition and drive-in heat treatments; the background concentration of P in this silicon material is known to be 6x$10^{19}$ atoms/$m^3$. The pre-deposition treatment is to be conducted at 950°C for 50 min; the surface concentration of P is to be maintained at a constant level of 1.6x$10^{26}$ atoms/$m^3$. Drive in diffusion will be carried out at 1250° C for a period of 2.7 hours. For the diffusion of P in Si, values of $Q_d$ and $D_0$ are 3.40 eV/atom and 1.1x$10^{-4}$ $m^2$/s, respectively.

a) Calculate the value of $Q_0$.
b) Determine the value of $x_j$ for the drive-in diffusion treatment.
c) Also for the drive-in treatment, compute the position x at which the concentration of P atoms is $10^{24}$/$m^3$.

4. Solution

(a) For this portion of the problem we are asked to determine the value of $Q_0$. This is possible using Equation 6.12. However, it is first necessary to determine the value of $D$ for the predeposition treatment [$D_p$ at $T_p$ = 950°C (1223 K)] using Equation 6.8. Thus

$$D_p = D_0 \exp\left(-\frac{Q_d}{kT_p}\right)$$

$$= (1.1 \times 10^{-4} \text{ m}^2/\text{s}) \exp\left[-\frac{3.40 \text{ eV}}{(8.62 \times 10^{-5} \text{ eV/atom} - \text{K})(1223 \text{ K})}\right]$$

$$= 1.08 \times 10^{-18} \text{ m}^2/\text{s}$$

The value of $Q_0$ may be determined as follows:

$$Q_0 = 2C_s \sqrt{\frac{D_p t_p}{\pi}}$$

$$= (2)(1.6 \times 10^{26}\ atoms/m^3)\sqrt{\frac{(1.08 \times 10^{-18}\ m^2/s)(50\ \min)(60\ s/\min)}{\pi}}$$

$$= 1.03 \times 10^{19}\ atoms/m^2$$

(b) Computation of the junction depth requires that we use Equation 6.13. However, before this is possible it is necessary to calculate $D$ at the temperature of the drive-in treatment [$D_d$ at 1250°C (1523 K)]. Thus,

$$D_d = (1.1 \times 10^{-4}\ m^2/s)\exp\left[-\frac{3.40\ eV}{(8.62 \times 10^{-5}\ eV/atom-K)(1523\ K)}\right]$$

$$= 6.22 \times 10^{-16}\ m^2/s$$

Now from Equation 6.13

$$x_j = \left[(4D_d t_d)\ln\left(\frac{Q_0}{C_B\sqrt{\pi D_d t_d}}\right)\right]^{1/2}$$

$$= \left\{(4)(6.22 \times 10^{-16}\ m^2/s)(9720s)\ln\left[\frac{1.03 \times 10^{19}\ atoms/m^2}{(6 \times 10^{19}\ atoms/m^2\sqrt{(\pi)(6.22 \times 10^{-16}\ m^2/s)(9720s)}}\right]\right\}^{1/2}$$

$$= 1.60 \times 10^{-5}\ m = 16.0\ \mu m$$

(c) For a concentration of $10^{24}$ P atoms/m$^3$ for the drive-in treatment, we compute the value of $x$ using Equation 6.11. However, it is first necessary to manipulate Equation 6.11 so that $x$ is the dependent variable. Taking natural logarithms of both sides leads to

$$\ln C(x,t) = \ln\left(\frac{Q_0}{\sqrt{\pi D_d t_d}}\right) - \frac{x^2}{4D_d t_d}$$

Now, rearranging and solving for $x$ leads to

$$x = \left\{ (4 D_d t_d) \ln \left[ \frac{Q_0}{C(x,t)\sqrt{\pi D_d t_d}} \right] \right\}^{1/2}$$

Now, incorporating values for $Q_0$ and $D_d$ determined above and taking $C(x,t)$ = $10^{24}$ P atoms/m$^3$ yields

$$x = \left\{ (4)(6.22 \times 10^{-16})(9720) \ln \left[ \frac{1.03 \times 10^{19}}{(10^{24})\sqrt{(\pi)(6.22 \times 10^{-16})(9720)}} \right] \right\}^{1/2}$$

$$= 4.56 \times 10^{-6}\ m = 4.56\ \mu m$$