

CHAPTER 9 APPENDIX A

Annealing is a process where material is heated to a particular temperature for a particular time, which alters the material's microstructure, thus changing its properties. Since some of the material is sublimated during annealing, it is important to know the relationship between the produced vapour pressure of material and annealing temperature so as to be able to predict the amount of material needed for annealing at a particular temperature. If encapsulation experiments are performed, the state where the amount of atoms sublimated is equal to the amount of atoms condensing is sometimes reached. This state is reached when the vapour pressure has reached a state of equilibrium; the vapour pressure at that state is termed equilibrium vapour pressure. Therefore, for encapsulation experiments the amount of atoms leaving the sample and condensing on the sample can be estimated from the equilibrium vapour pressure at a particular temperature. In this section the relationship between temperature and equilibrium vapour pressure is derived.

In doing so we consider a system A which is in thermal contact with a heat reservoir (system A') at constant temperature T_0 and constant pressure p_0 . The combined system $A^0 = A + A'$ is depicted in figure A 1-1. System A is under vacuum and at room temperature.

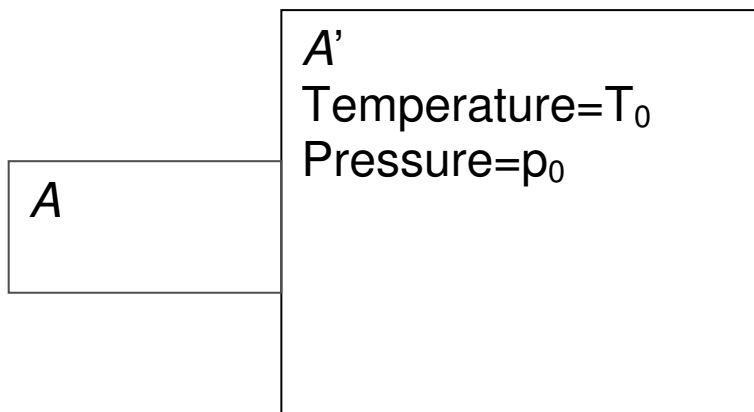


Figure A1-1: System A (in vacuum and at room temperature) in thermal contact with a heat reservoir (system A') at constant temperature T_0 and constant pressure p_0 .

If A^0 is a thermally isolated system, S^0 , which is the entropy of the combined system (A^0), must satisfy the condition of any spontaneous process i.e. $\Delta S \geq 0$: Now consider

a process where heat Q flows from A' to A . The change in entropy of the whole system can be written as:

$$\Delta S^0 = \Delta S + \Delta S' \geq 0 \quad \dots A.1$$

where ΔS is the change in entropy of system A and $\Delta S'$ is the change in entropy of system A' . Since A absorbs heat from A' , the change in entropy of A' can be written as:

$$\Delta S' = \frac{-Q}{T_0} \quad \dots A.2$$

Thus the total change in entropy of the combined system (A^0) is:

$$\Delta S^0 = \Delta S - \frac{Q}{T_0} \quad \dots A.3$$

Applying the 1st law of thermodynamics ($\Delta E = Q - W$) to system A , because the volume of system A alters due to the energy gained, the work done by the system A can be written as: $W = p_0 \Delta V + W^*$, where $p_0 \Delta V$ is the work done by system A against the constant pressure p_0 of system A' while W^* is any work done by A during the process. Therefore, the change in entropy of the whole system becomes:

$$\Delta S^0 = \frac{\Delta S T_0 - \Delta E_{in} - p_0 \Delta V - W^*}{T_0} \quad \dots A.4$$

Rearranging these leads to: $\Delta S^0 = \frac{\Delta(S T_0 - E_{in} - p_0 V) - W^*}{T_0} \quad \dots A.5$

Taking $-G = S T_0 - E_{in} - p_0 V$, thus $G = E_{in} - T_0 S + p_0 V$ and $\Delta G = \Delta E_{in} - T_0 \Delta S + p_0 \Delta V$, where G is the Gibbs free energy. In general [Kub67]:

$$\left(\frac{\partial G}{\partial T} \right)_p = -S \quad \dots A.6$$

$$\left(\frac{\partial G}{\partial p} \right)_T = V \quad \dots A.7$$

Therefore, the total differential equation of G is yielded by:

$$dG = -SdT + Vdp \quad \dots A.8$$

The Gibbs free energy (G) can also be written in term of the enthalpy (H) of system A:

$$H = E + pV \Rightarrow G = H - TS \quad \dots A.9$$

Using the definition of heat capacity at constant pressure:

$$C_p = \left(\frac{\partial Q}{\partial T} \right)_p \quad \dots A.10$$

where $dQ = dE + p_0 dV = dH$

In general the T dependence of H and S at p_0 is given by [Gok96]:

$$\left(\frac{\partial H}{\partial T} \right)_p = C_p \quad \text{And} \quad \left(\frac{\partial S}{\partial T} \right)_p = \frac{C_p}{T} \quad \dots A.11$$

If one integrates equations A.10 and A.11, the change in enthalpy and change in entropy are found respectively as:

$$\Delta H = \int_{T_1}^{T_2} C_p dT \quad \text{and} \quad \Delta S = \int_{T_1}^{T_2} \frac{C_p}{T} dT$$

Since our interest is in the system where the condensed phase and the vapour/gas phase coexist, let us consider the same combined system A^0 with system A that consists of two phases, solid (condensed) and gas (vapour) where system A' remains the same as the previous one in figure A1-1: such a system is schematically shown in figure A1-2 below. In figure A1-2 below, c and g represent the condensed and gas phases respectively.

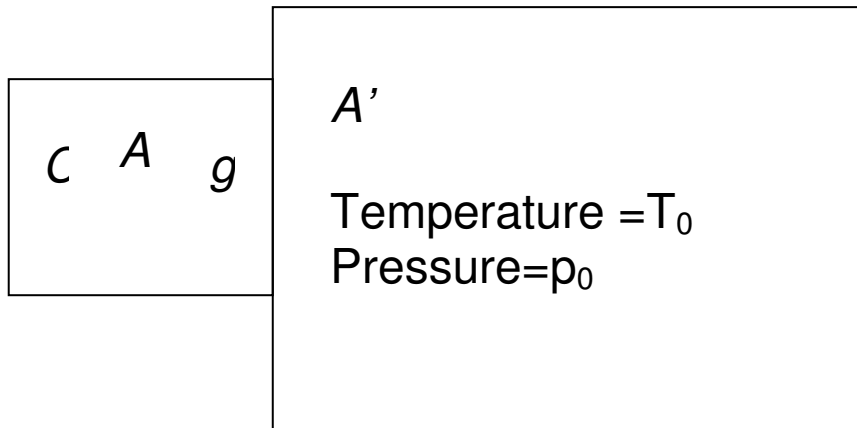


Figure A1-2: System A (where the condensed phase and the gas phase coexist) in thermal contact with a heat reservoir (system A') at constant temperature T_0 and constant pressure p_0 .

The general rule for two or more phases to coexist in equilibrium with each other is that their Gibbs free energy must be minimum, i.e. $\Delta G=0$. To find $\Delta G=0$ for a system consisting of more than one phase, such as system A, the free energy of each phase must be considered separately. This is done by introducing the chemical potential (μ), which for this case is the same as G but refers to 1 g mol. Therefore, for our system, $\Delta G=0$ can be written as:

$$\mu_g - \mu_c = 0 \text{ or } \mu_c = \mu \text{ and } d\mu_c = d\mu_g \quad \dots A.12$$

If equation A.8 is substituted into equation A.12 the relationship between vapour pressure (p^*) and temperature is established:

$$\begin{aligned} -S_g dT + V_g dp &= -S_c dT + V_c dp \\ \Rightarrow V_c dp - V_g dp &= -S_g dT + S_c dT \\ \Rightarrow dp (V_c - V_g) &= dT (-S_g + S_c) \\ \Rightarrow \frac{dp^*}{dT} &= \frac{S_g - S_c}{V_g - V_c} \quad \dots A.13 \end{aligned}$$

In equation A.13 above, p^* now denotes pressure that changes with temperature and is the vapour pressure of the material. Since the Gibbs free energy can be written in terms of enthalpy (H) i.e. $G=H-TS$, the change in entropy in equation A.13 can be written in terms of enthalpy (H), with the aid of the relationship in equation A.12:

$$\begin{aligned}
 H_g - TS_g &= H_c - TS_c \\
 \Rightarrow -TS_g + TS_c &= H_c - H_g \\
 \Rightarrow T(S_g - S_c) &= H_g - H_c \\
 \Rightarrow S_g - S_c &= \frac{H_g - H_c}{T} \quad \dots A.14
 \end{aligned}$$

If equation A.14 is substituted into equation A.13, equation A.15, known as Clausius-Clapeyron's equation, is obtained:

$$\frac{dp^*}{dT} = \frac{H_g - H_c}{T(V_g - V_c)} \quad \dots A.15$$

Solving this equation could lead to determining the relationship between vapour pressure (p^*) and temperature (T). To solve equation A.15 two assumptions are made. The first one is that the molar volume of a condensed phase is neglected since it is very small compared to the molar volume of vapour while the vapour is assumed to be obeying the ideal-gas law ($pV=nRT$), with $n=1$ as specified above.

Based on these assumptions: $V_g - V_c \approx V_g = \frac{RT}{p}$...A.16

The change in enthalpy in equation A.15 refers to the change of one mole of the condensed phase to the vapour phase, which is termed as the heat of sublimation:

$$H_g - H_c = \Delta H_s \quad \dots A.17$$

If equations A.16 and A.17 are substituted back into equation A.15, equation A.18 is obtained:

$$\frac{dp^*}{dT} = \frac{H_g - H_c}{T(V_g)} \Rightarrow \frac{dp^*}{p^*} = \frac{\Delta H_s dT}{RT^2} \quad \dots A.18$$

If equation A.18 is firstly integrated to obtain the relationship between p^* and T by assuming that ΔH_s is independent of temperature:

$$\ln p^* \approx -\frac{\Delta H_s}{RT} + const \quad \dots A.19$$

Now if the same integration is performed from the boiling point (2460K) of silver, where the pressure is assumed to be 1atm (1.0325×10^5 Pa), to the higher temperature (T) with vapour pressure (p^*):

$$\int_{1.0132e5}^{p^*} \frac{dp^*}{p^*} = \int_{2460}^T \frac{\Delta H_s}{RT^2} dT$$

$$\ln p^* = \Delta H_s \left[4.892e-5 \frac{\text{mol}}{\text{J}} - \frac{1}{RT} \right] + 11.5261$$

Fitting the experimental values of vapour pressure as a function of temperature for a particular element, ΔH_s can be obtained.

The second assumption considers the changes that the molar specific heat at constant pressure undergoes with T . From this assumption the accurate p^* function can be derived because the vapour pressure also alters with T . From this assumption:

$$\left(\frac{\partial H}{\partial T} \right)_p = C_p; \Rightarrow \frac{d(\Delta H_s)}{dT} = C_{p,g} - C_{p,c} = \Delta C_p \quad \dots A.20$$

and by considering that near and above room temperature the specific heat may be expressed generally in the form:

$$C_p = a + bT + cT^{-2} \quad \dots A.21$$

where a , b , and c are numerical factors specific to a particular substance, inserting equation A.20 into A.19 leads to:

$$\Delta H_s = \Delta H_s^* + \Delta aT + \frac{\Delta bT^2}{2} - \Delta cT^{-1} \quad \dots A.22$$

And substituting equation A.21 into A.17 and integrating results in:

$$\ln p^* = -\frac{\Delta H_s^*}{RT} + \frac{\Delta a}{R} \ln T + \frac{\Delta b}{2R} T + \frac{\Delta c}{2R} T^{-2} + I \quad \dots A.23$$

In equation A.23, I is the integration constant. Fitting the experimental vapour pressure data to the above equation, the relationship between p^* and T can be found for particular elements. Fitting the experimental data of silver vapour pressure taken

from Kubaschewski et al. [Kub70], as depicted in figure A1-3, equation A.24 was obtained.

$$\ln p^* = -\frac{428075}{T} - 306 \ln T + 0.07T + 8T^{-2} + 2375 \quad \dots A.24$$

The equilibrium vapour pressure at 1000 °C was calculated using equation A.24 and found to be 7.85×10^{-3} Torr. From this equilibrium vapour pressure, the number of atoms condensing and evaporating per unit area per unit time was calculated at 1000 °C using equation A.25 [Kub67]:

$$\frac{dN}{Adt} = 3.513 \times 10^{22} (MT)^{-\frac{1}{2}} p^* \quad \dots A.25$$

where M is the molar mass in grams. The value of $9.47 \times 10^{19} \text{ cm}^{-2} \text{ s}^{-1}$ was found. Taking the annealing time to be 10 h, the number of silver atoms per unit area was found to be $3.41 \times 10^{28} \text{ m}^{-2}$. This value represents the number of silver atoms that are sublimating out and condensing on to the sample during annealing. If these atoms had been condensing on our SiC surface during annealing, they would have been detected by RBS. Therefore, deposited silver is not lost by sublimation but by other mechanisms such as a wetting problem between SiC and silver, which is responsible for the disappearing of deposited layer of silver as discussed in chapter 7.

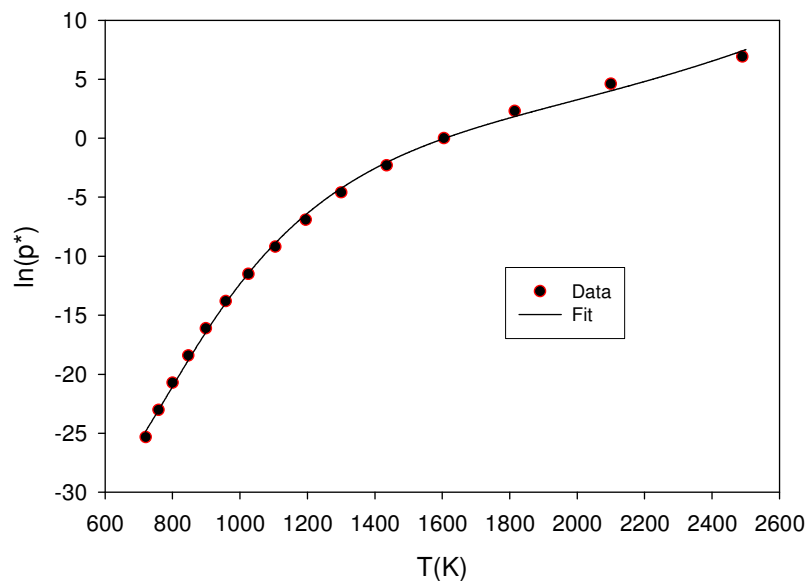


Figure A1-3: The experimental silver vapour data fitted to equation A.23.

9.1 REFERENCES

- [Gok96] N. A. Gokcen, and R. G. Reddy, Thermodynamics, 2nd ed., Plenum Press, New York (1996).
- [Kub67] O. Kubaschewski, E. LL. Evans, and C. B. Alcock, Metallurgical Thermochemistry. 4th ed., Pergamon Press, New York (1967).
- [Mai70] L. I. Maissel and R. Glang, Handbook of Thin Film Technology, McGraw-Hill, New York (1970).
- [Rei65] Federick Reif, Fundamentals of Statistical and Thermal Physics, McGraw-Hill, New York (1965).