

1. Nucleation energy can be written as.

$$\Delta G = -\Delta G_v \cdot V + \sum A_i \gamma_i \quad \text{for spherical core} \quad \Delta G = -\Delta G_v \cdot \frac{4}{3} \pi r^3 + 4\pi r^2 \cdot \gamma \quad (r: \text{nuclei radius})$$

Setting atomic volume as  $u$ , the volume of nuclei can be expressed as.

$$\frac{4}{3} \pi r^3 = n u \quad \therefore r = \left( \frac{3}{4\pi} \cdot n \cdot u \right)^{\frac{1}{3}}$$

$$\therefore \Delta G = -\frac{4}{3} \pi r^3 \cdot \Delta G_v + 4\pi r^2 \cdot \gamma = -n \cdot u \cdot \Delta G_v + 4\pi \cdot \left( \frac{3}{4\pi} \cdot n \cdot u \right)^{\frac{2}{3}} \cdot \gamma = -n u \cdot \Delta G_v + (36\pi)^{\frac{1}{3}} n^{\frac{2}{3}} u^{\frac{2}{3}} \gamma$$

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a) Same with Problem 1.  $\Delta G = -n \cdot u \cdot \Delta G_v + (36\pi)^{\frac{1}{3}} \cdot n^{\frac{2}{3}} \cdot u^{\frac{2}{3}} \cdot \gamma$

b) Critical value of  $n$  is obtained at  $\frac{d\Delta G}{dn} \Big|_{n=n^*} = 0$ .

$$\therefore \frac{d\Delta G}{dn} = -u \cdot \Delta G_v + \frac{2}{3} \cdot (36\pi)^{\frac{1}{3}} \cdot u^{\frac{2}{3}} \cdot \gamma \cdot n^{-\frac{1}{3}} = 0 \quad \therefore n^{\frac{1}{3}} = \frac{\frac{2}{3} (36\pi)^{\frac{1}{3}} \cdot u^{\frac{2}{3}} \cdot \gamma}{u \Delta G_v}$$

$$\rightarrow n^* = \frac{32\pi}{3u} \cdot \left( \frac{\gamma}{\Delta G_v} \right)^3$$

Substituting this value at  $\Delta G = -n u \cdot \Delta G_v + (36\pi)^{\frac{1}{3}} \cdot n^{\frac{2}{3}} \cdot u^{\frac{2}{3}} \cdot \gamma$

$$\Delta G^* = \frac{1}{-\Delta G_v^2} \cdot \frac{32\pi \gamma^3}{3} + (36\pi)^{\frac{1}{3}} u^{\frac{2}{3}} \gamma \left( \frac{32\pi}{3u} \right)^{\frac{2}{3}} \cdot \left( \frac{\gamma}{\Delta G_v} \right)^2 = \frac{16\pi}{3} \cdot \frac{\gamma^3}{(\Delta G_v)^2}$$

c) From CVD, C will deposited from the vapor phase, the free energy is written as.

$$\left. \begin{aligned} \Delta G_{\text{dta}} &= -n(G_v - G_{\text{dta}}) + (36\pi)^{\frac{1}{3}} n^{\frac{2}{3}} u_{\text{dta}}^{\frac{2}{3}} \gamma_{\text{dta}} \\ \Delta G_{\text{gra}} &= -n(G_v - G_{\text{gra}}) + (36\pi)^{\frac{1}{3}} n^{\frac{2}{3}} u_{\text{gra}}^{\frac{2}{3}} \gamma_{\text{gra}} \end{aligned} \right\} \begin{array}{l} \text{the given condition } \Delta G_{\text{dta}} = \Delta G_{\text{gra}} \\ \text{re-writing the equation gives} \end{array}$$

$$0 = -n(G_{\text{gra}} - G_{\text{dta}}) + (36\pi)^{\frac{1}{3}} \cdot n^{\frac{2}{3}} \left( \gamma_{\text{dta}} \cdot u_{\text{dta}}^{\frac{2}{3}} - \gamma_{\text{gra}} \cdot u_{\text{gra}}^{\frac{2}{3}} \right)$$

$$\therefore n = 36\pi \frac{(u_{\text{dta}}^{\frac{2}{3}} \cdot \gamma_{\text{dta}} - u_{\text{gra}}^{\frac{2}{3}} \cdot \gamma_{\text{gra}})^3}{(G_{\text{gra}} - G_{\text{dta}})^3}$$

$$\left. \begin{aligned} \gamma_{\text{dta}} = 3.6 \text{ J/m}^2 = 0.2246 \text{ eV/\AA}^2 & \therefore n = 36\pi \left( \frac{0.1934 - 6^{\frac{2}{3}} \cdot 0.2246}{0.02} \right)^3 = 469 \\ \gamma_{\text{dta}} = 3.6 \text{ J/m}^2 = 0.2248 \text{ eV/\AA}^2 & \therefore n = 36\pi \left( \frac{0.1934 - 6^{\frac{2}{3}} \cdot 0.2248}{0.02} \right)^3 = 145 \\ \gamma_{\text{dta}} = 3.75 \text{ J/m}^2 = 0.2309 \text{ eV/\AA}^2 & \therefore n = 36\pi \left( \frac{0.1934 - 6^{\frac{2}{3}} \cdot 0.2309}{0.02} \right)^3 = 21 \end{aligned} \right\}$$

d) Graphite's free energy should be higher than that of diamond for diamond stabilization

$$\Delta G_{gra} > \Delta G_{dia} \quad \therefore \quad \Delta G_{gra} - \Delta G_{dia} > 0 \quad \text{for}$$

$$\therefore 36\pi \left( \frac{V_{dia}^{2/3} \gamma_{dia} - V_{gra}^{2/3} \gamma_{gra}}{G_{gra} - G_{dia}} \right)^3 < n.$$

$\gamma_{dia} = 3.6$	$\rightarrow n < 464$
$\gamma_{dia} = 3.65$	$\rightarrow n < 145$
$\gamma_{dia} = 3.7$	$\rightarrow n < 21$

e) assuming critical number as 100. we can write equation

$$100 = \frac{32\pi}{3V_{gra}} \left( \frac{\gamma_{gra}}{\Delta G} \right)^3 \quad \therefore \quad \Delta G = \left( \frac{32\pi}{3V_{gra} \cdot 100} \right)^{1/3} \cdot \gamma \quad \therefore \quad \Delta G = 1.076 \times 10^{10} \text{ J/m}^3$$

f) Growth rate can be written as  $I = A \cdot \exp(-\Delta G^*/kT)$   
 assuming the constant A is same for graphite and diamond.

$$I_{gra}/I_{dia} = \exp\left(\frac{-\Delta G_{gra} + \Delta G_{dia}}{kT}\right)$$

$$\Delta G_{gra} = \frac{16\pi}{3} \cdot \left( \frac{\gamma_{gra}^3}{\Delta G_{gra}^2} \right) = 4.3 \times 10^{-18} \text{ J}$$

$$\Delta G_{dia} = \frac{16\pi}{3} \cdot \left( \frac{\gamma_{dia}^3}{\Delta G_{dia}^2} \right)$$

$\gamma = 3.6 \rightarrow \Delta G = 4.104 \times 10^{-18}$
$\gamma = 3.65 \rightarrow \Delta G = 4.278 \times 10^{-18}$
$\gamma = 3.7 \rightarrow \Delta G = 4.457 \times 10^{-18}$

Setting the temperature as 800 K (R-T), the nucleation rate is.

$$\therefore I_{gra}/I_{dia} \rightarrow \begin{array}{l} \gamma = 3.6 : I_{gra}/I_{dia} = 3.4 \times 10^{-4} \\ \gamma = 3.65 : I_{gra}/I_{dia} = 5.9 \times 10^{-3} \\ \gamma = 3.7 : I_{gra}/I_{dia} = 2.6 \times 10^{-6} \end{array}$$

g) nucleation rate dramatically change with the surface energy, as readily expected lower surface energy increases the diamond nucleation rate.

h)  $\text{CH}_4$  decomposition to C and  $\text{H}_2$  increases the pressure of C and cluster size.

smaller size particle has large capillary effect,  $\Rightarrow$  that relatively unstable diamond film can be formed. And the driving force of this reaction is  $\text{CH}_4$  partial pressure.