상변태 HW#5 20222331 이지수

(a) $\Delta G = \underbrace{-\frac{4}{3}\pi r^3 \Delta G_V}_{①} + \underbrace{4\pi r^2 \gamma}_{②}$

molecular atomic volume x number of molecules in cluster ($v \times n$)
= total volume of cluster ($\frac{4}{3}\pi r^3$)

$v \times n = \frac{4}{3}\pi r^3 \rightarrow r = \left(\frac{3 \cdot v \cdot n}{4\pi}\right)^{\frac{1}{3}}$

① term → $-v \cdot n \cdot \Delta G_V$

② term → $4\pi \times \left(\frac{3 \cdot v \cdot n}{4\pi}\right)^{\frac{2}{3}} \gamma = (4\pi)^{\frac{1}{3}} \cdot (3^2)^{\frac{1}{3}} \cdot v^{\frac{2}{3}} \cdot n^{\frac{2}{3}} \cdot \gamma$
$= (36\pi)^{\frac{1}{3}} \cdot v^{\frac{2}{3}} \cdot n^{\frac{2}{3}} \cdot \gamma$

$\therefore \Delta G = -v \cdot n \cdot \Delta G_v + (36\pi)^{\frac{1}{3}} v^{\frac{2}{3}} \cdot n^{\frac{2}{3}} \cdot \gamma = -n \Delta G_a + (36\pi)^{\frac{1}{3}} v^{\frac{2}{3}} n^{\frac{2}{3}} \gamma$

System에서의 vaporization energy

(b) $\left.\frac{\partial \Delta G}{\partial n}\right)_{n=n^*} = 0 = -v \cdot \Delta G_V + \frac{2}{3}(36\pi)^{\frac{1}{3}} v^{\frac{2}{3}} n^{*-\frac{1}{3}} \gamma$

$v \cdot \Delta G_V = \frac{2}{3}(36\pi)^{\frac{1}{3}} v^{\frac{2}{3}} n^{*-\frac{1}{3}} \cdot \gamma \rightarrow (n^*)^{-\frac{1}{3}} = \frac{v \cdot \Delta G_V}{\frac{2}{3}(36\pi)^{\frac{1}{3}} v^{\frac{2}{3}} \gamma}$

$n^* = \left(\frac{\frac{2}{3}(36\pi)^{\frac{1}{3}} \cdot v^{\frac{2}{3}} \cdot \gamma}{v \cdot \Delta G_V}\right)^3 = \frac{32\pi}{3v}\left(\frac{\gamma}{\Delta G_V}\right)^3$

$\Delta G^* = -v \cdot \frac{32\pi}{3v}\left(\frac{\gamma}{\Delta G_V}\right)^3 \Delta G_V + \frac{2}{3}(36\pi)^{\frac{1}{3}} \times v^{\frac{2}{3}} \cdot n^{*\frac{2}{3}} \cdot \gamma$

$= -\cancel{v} \cdot \frac{32\pi}{3\cancel{v}} \frac{\gamma^3}{\Delta G_V^2} + (36\pi)^{\frac{1}{3}} \times \cancel{v^{\frac{2}{3}}} \times \frac{(32\pi)^{\frac{2}{3}}}{(3\cancel{v})^{\frac{2}{3}}} \cdot \left(\frac{\gamma}{\Delta G_V}\right)^2 \cdot \gamma$

$= \frac{16}{3}\pi \frac{\gamma^3}{\Delta G_V^2}$

(c) $\Delta G_{n,dia} = -n({}^{\circ}G_{gas} - {}^{\circ}G_{dia}) + (36\pi)^{\frac{1}{3}} n^{\frac{2}{3}} V_{dia}^{\frac{2}{3}} \gamma_{dia}$

$\Delta G_{n,gra} = -n({}^{\circ}G_{gas} - {}^{\circ}G_{gra}) + (36\pi)^{\frac{1}{3}} n^{\frac{2}{3}} V_{gra}^{\frac{2}{3}} \gamma_{gra}$

$\Delta G_{n,dia} = \Delta G_{n,gra}$

$n(G^{\circ}_{dia} - G^{\circ}_{gra}) = n^{\frac{2}{3}} \times (36\pi)^{\frac{1}{3}} (V_{gra}^{\frac{2}{3}} \gamma_{gra} - V_{dia}^{\frac{2}{3}} - \gamma_{dia})$

n에 대해 정리하면, $n = 36\pi \left(\frac{V_{gra}^{\frac{2}{3}} \gamma_{gra} - V_{dia}^{\frac{2}{3}} \gamma_{dia}}{G^{\circ}_{dia} - G^{\circ}_{gra}} \right)^3$ → 식 ①

$\gamma_{dia} = 3.6\,J/m^2,\ 3.65\,J/m^2,\ 3.7\,J/m^2$, $G^{\circ}_{dia} - G^{\circ}_{gra} = 0.02\,eV/atom$

$\gamma_{gra} = 3.1\,J/m^2$, $V_{gra} = 8\,\mathring{A}^3/atom$, $V_{dia} = 6\,\mathring{A}^3/atom$

$= 8 \times 10^{-30}\,m^3/atom$ $= 6 \times 10^{-30}\,m^3/atom$

i) $\gamma_{dia} = 3.6\,J/m^2$ 일때 식 ①에 넣어 계산시 $n = 464$

ii) $\gamma_{dia} = 3.65\,J/m^2$ 일때 $n = 145$

iii) $\gamma_{dia} = 3.7\,J/m^2$ 일때 $n = 21$

(d) diamond cluster가 more stable 해지는 조건 $\Delta G_{n,gra} > \Delta G_{n,dia}$

$-n(\Delta G_{gas} - \Delta G_{gra}) + (36\pi)^{\frac{1}{3}} n^{\frac{2}{3}} V_{gra}^{\frac{2}{3}} \gamma_{gra} >$

$-n(\Delta G_{gas} - \Delta G_{dia}) + (36\pi)^{\frac{1}{3}} n^{\frac{2}{3}} V_{dia}^{\frac{2}{3}} \gamma_{dia}$

정리하면 $n(G^{\circ}_{dia} - G^{\circ}_{gra}) < n^{\frac{2}{3}} (36\pi)^{\frac{1}{3}} (V_{gra}^{\frac{2}{3}} \gamma_{gra} - V_{dia}^{\frac{2}{3}} \gamma_{dia})$

$n < 36\pi \times \left(\frac{V_{gra}^{\frac{2}{3}} \gamma_{gra} - V_{dia}^{\frac{2}{3}} \gamma_{dia}}{G^{\circ}_{dia} - G^{\circ}_{gra}} \right)^3$

(e) $n^* = 100 \rightarrow$ driving F for graphite

(b)의 결과3부터 $n^* = \dfrac{32\pi \gamma_{gra}^3}{3 V_{gra} \Delta G_{v,gra}^3} \rightarrow \Delta G_{v,gra} = \gamma_{gra} \times \left(\dfrac{32\pi}{3 n^* V_{gra}} \right)^{\frac{1}{3}}$

$V_{gra} = 8 \mathring{A}^3/\text{atom} = 8 \times 10^{-30} m/\text{atom}$, $\gamma_{gra} = 3.1 J/m^2$

$\therefore \Delta G_{v,gra} = 1.077 \times 10^{10} J/m^3$

(f) (b)의 결과2부터 $\Delta G^* = \dfrac{16}{3}\pi \dfrac{\gamma^3}{\Delta G_v^2}$, $I = A \exp(-\Delta G^*/kT)$, $T = 300K$

$$\frac{I_{gra}}{I_{dia}} = \exp\left(\frac{\Delta G^*_{dia} - \Delta G^*_{gra}}{kT} \right)$$

$G^\circ_{dia} - G^\circ_{gra} = V_{gra} \Delta G_{v,gra} - V_{dia} \Delta G_{v,dia} = 0.02 eV/\text{atom}$

$V_{gra} = 8 \times 10^{-30} m/\text{atom}$, $V_{dia} = 6 \times 10^{-30} m/\text{atom}$

$\Delta G_{v,gra} = 1.077 \times 10^{10} J/m^3$ $\therefore$ $\Delta G_{v,dia} = 1.38 \times 10^{10} J/m^3$

$$\Delta G^*_{gra} = \frac{16}{3}\pi \frac{\gamma_{gra}^3}{(\Delta G_{v,gra})^2} = 4.30 \times 10^{-18} J/m^2$$

i) $\gamma_{dia} = 3.6 J/m^2$ ii) $\gamma_{dia} = 3.65$ iii) $\gamma_{dia} = 3.7$

$\Delta G^*_{dia} = 4.10 \times 10^{-18} J$ $= 4.27 \times 10^{-18} J$ $= 4.45 \times 10^{-18} J$

I_{gra}/I_{dia} at 300K

$\Downarrow$ $\Downarrow$ $\Downarrow$

1.04×10^{-21} 7.12×10^{-4} 5.44×10^{16}

(g) bulk 상태에서는 작은 surface E의 차이가 graphite와 diamond의 안정성 경향에 영향을 미치기 어렵다. 하지만, nano-size에서는 (f)의 결과로부터 알 수 있듯이 nucleation rate ratio가 surface E의 작은 변화에도 매우 민감한 것을 알 수있다. 따라서 nano size에서 diamond의 surface E를 control 할 수있다면 CVD method를 통해 diamond를 얻을 수 있게 될 것이다.