REPORT

제목 :	Homework #5
수강과목 :	상변태론
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상변태론 HW #5

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a) For a spherical nucleus, derive the following expression, the energy change during nucleation as a function of number of atoms n in cluster (v is atomic volume).

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

sol) $V_{total} = n$ (number of atom) $\times\ v$ (atomic volume)

$= \frac{4}{3}\pi r^3 = nv$ — ①

$A_{total} = 4\pi r^2$ — ②

② 에 ①을 적용하면, $4\pi r^2 = (36\pi)^{\frac{1}{3}} n^{\frac{2}{3}} v^{\frac{2}{3}}$

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

b) Using the result of (a), derive the expression for the critical number of atoms and energy barrier.

$$\frac{\partial \Delta G}{\partial n} = -v\Delta G_v + (36\pi)^{\frac{1}{3}} v^{\frac{2}{3}} \gamma \times \frac{2}{3} n^{-\frac{1}{3}}, \quad \left.\frac{\partial \Delta G}{\partial n}\right|_{n=n^*} = 0$$

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

$$n^{*\frac{1}{3}} = \frac{2(36\pi)^{\frac{1}{3}}}{3v\Delta G_v} v^{\frac{2}{3}} \gamma = \frac{2}{3\Delta G_v} (36\pi)^{\frac{1}{3}} \times \frac{1}{v^{\frac{1}{3}}} \gamma$$

$$\therefore n^* = \frac{8 \times \overset{4}{\cancel{36}}\pi}{\underset{3}{\cancel{27}}\ \Delta G_v^3 \times v} \gamma^3 = \frac{32\pi}{3v\Delta G_v^3} \gamma^3$$

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

c) Assuming isotropic and constant surface energy for both of graphite and diamond, and using the data : $\gamma_{gr} = 3.1\ Jm^{-2}$, $\gamma_{dia} = 3.6, 3.65$ and $3.7\ Jm^{-2}$, respectively
$v_{gr} = 8\ Å^3/atom$, $v_{dia} = 6\ Å^3/atom$, $°G_{dia} - °G_{gr} = 0.02\ eV/atom$

a) 결과를 참고하면, $\Delta G_s = -n(°G_{dia} - °G_{gr})v + (36\pi)^{\frac{1}{3}} n^{\frac{2}{3}} (\gamma_{dia} \cdot v_{dia} - \gamma_{gr} \cdot v_{gr})$ 이고

isotropic & constant 한 상황에서는 $\Delta G_s = 0$, $n = 36\pi \left(\frac{v_{dia}^{\frac{2}{3}} \cdot \gamma_{dia} - v_{gr}^{\frac{2}{3}} \cdot \gamma_{gr}}{°G_{gr} - °G_{dia}} \right)^3$

1) $\gamma_{dia} = 3.6J$

$$n = 36\pi\left(\frac{(6\times10^{-30}m^3/atom)^{2/3}(3.6 \times \frac{1}{1.6\times10^{-19}} eV/m^2)^3 - (8\times10^{-30}m^3/atom)^{2/3}(3.1 \times \frac{1}{1.6\times10^{-19}} eV/m^2)^3}{-0.02eV/atom}\right)$$

$\simeq 465$

2) $\gamma_{dia} = 3.65J$

$$n = 36\pi\left(\frac{(6\times10^{-30}m^3/atom)^{2/3}(3.65\times\frac{1}{1.6\times10^{-19}}eV/m^2)^3-(8\times10^{-30}m^3/atom)^{2/3}(3.1\times\frac{1}{1.6\times10^{-19}}eV/m^2)^3}{-0.02eV/atom}\right)$$

$\simeq 146$

3) $\gamma_{dia} = 3.7J$

$$n = 36\pi\left(\frac{(6\times10^{-30}m^3/atom)^{2/3}(3.7\times\frac{1}{1.6\times10^{-19}}eV/m^2)^3-(8\times10^{-30}m^3/atom)^{2/3}(3.1\times\frac{1}{1.6\times10^{-19}}eV/m^2)^3}{-0.02eV/atom}\right)$$

$\simeq 21$

d) What is the necessary condition for a diamond cluster of any size to be more stable than graphite ?

$$\Delta G_{dia} < \Delta G_{gr}, \quad \Delta G_s = \Delta G_{dia} - \Delta G_{gr} < 0$$

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

e) Assuming that the critical number of atoms for graphite nucleation is 100, estimate the driving force for graphite nucleation.

$$n^* = 100, \quad \frac{32\pi \times \gamma_{gr}^3}{3V_{gr}\Delta G_v^3} = 100(atom)$$

$$\Delta G_{v,gr}^3 = \frac{32\pi\times\gamma_{gr}^3}{300\ V_{gr}}$$

$$\Delta G_{v,gr} = \left(\frac{32\pi\times(3.1\ J/m^2)^3}{3\times(8\times10^{-30}\ m^3/atom)\times(100\ atom)}\right)^{\frac{1}{3}} \simeq 1.08\times10^{10}\ J/m^3$$

f) For the three values of surface energy of diamond, compute the ratio of nucleation rate between graphite and diamond, I_{gra}/I_{dia}.
For the nucleation rate, use the expression: $I = A\cdot\exp(-\Delta G^*/kT)$, and assume that A is the same constant for both of graphite and diamond and T = 300 K.

$\frac{I_{gr}}{I_{dia}}$는 주어진 nucleation rate 식에 따라서 $\exp\left(\frac{\Delta G^*_{dia} - \Delta G^*_{gr}}{kT}\right)$

$$\Delta G_{gr}^* = \frac{16\pi\gamma_{gr}^3}{3\Delta G_{v,gr}^2},$$ $n^* = 100$ 이라고 하고 (e) 결과를 활용하면

$$= \frac{16\pi(3.1\ J/m^2)^3}{3(1.08\times10^{10}\ J/m^3)^2} \simeq 4.28\times10^{-10}\ J$$

$$\Delta G_{dia}^* = \frac{16\pi \gamma_{dia}^3}{3\,\Delta G_{v.dia}^2}$$ 를 구해야 함

$$\Delta G_{v.dia} \times V_{dia} = {}^\circ G_v - {}^\circ G_{dia}$$

$$= \Delta G_{v.gr} V_{gr} + {}^\circ G_{gr} - {}^\circ G_{dia} \quad (\Delta G_{v.gr} \cdot V_{gr} = {}^\circ G_v - {}^\circ G_{gr})$$

$$= \Delta G_{v.gr} V_{gr} - 0.02\,eV$$

$n^* = 100$ 이라고 하면,

$$\Delta G_{v.dia} = \frac{(1.08\times10^{10}\,J/m^3)\times(8\times10^{-30}\,m^3/atom) - 0.02\times1.6\times10^{-19}\,J/atom}{6\times10^{-30}\,m^3/atom}$$

$$\simeq 1.39\times10^{10}\,J/m^3$$

1) $\gamma_{dia} = 3.6\,J/m^2$ 일 때,

$$\Delta G_{dia}^* = \frac{16\pi(3.6)^3}{3\times(1.39\times10^{10})^2}\,J = 4.04\times10^{-18}\,J$$

$$ratio = \exp\left(\frac{\Delta G^*_{dia} - \Delta G^*_{gr}}{KT}\right) = \exp\left(\frac{(4.04-4.28)\,10^{-18}}{1.38\times10^{-23}\times300}\right)$$

$$= 6.66\times10^{-26}$$

2) $\gamma_{dia} = 3.65\,J/m^2$ 일 때,

$$\Delta G_{dia}^* = \frac{16\pi(3.65)^3}{3\times(1.39\times10^{10})^2}\,J = 4.22\times10^{-18}\,J$$

$$ratio = \exp\left(\frac{\Delta G^*_{dia} - \Delta G^*_{gr}}{KT}\right) = \exp\left(\frac{(4.22-4.28)\,10^{-18}}{1.38\times10^{-23}\times300}\right)$$

$$= 5.08\times10^{-7}$$

3) $\gamma_{dia} = 3.7\,J/m^2$ 일 때,

$$\Delta G_{dia}^* = \frac{16\pi(3.7)^3}{3\times(1.39\times10^{10})^2}\,J = 4.39\times10^{-18}\,J$$

$$ratio = \exp\left(\frac{\Delta G^*_{dia} - \Delta G^*_{gr}}{KT}\right) = \exp\left(\frac{(4.39-4.28)\,10^{-18}}{1.38\times10^{-23}\times300}\right)$$

$$= 3.46\times10^{11}$$

(g) (C) 결과를 통해서 작은 표면에너지 차이가 입자의 크기를 4~8배 변화시키는 것을 확인할 수 있었고, (f) 결과를 통해서 입자크기가 동일 할 때는 0.05 J/m^2 정도의 surface energy가 nucleation rate를 약 $10^{17} \sim 10^{18}$ 배의 변화를 이끌어냈다. 두 문제의 결과를 종합하자면, 합성되기 위해 고온, 고압의 공정이 필요한 diamond도 입자크기가 충분히 작다면 진공 상태의 CVD chamber 에서도 합성이 될 수 있다는 예상을 할 수 있다.