Thermodynamics

Thermodynamics of CVD

Byeong-Joo Lee

POSTECH - MSE

calphad@postech.ac.kr

포항공과대학교
Pohang University of Science and Technology

Byeong-Joo Lee
www.postech.ac.kr/~calphad

Scope

CVD

1. Too much changeable results depending on the condition
2. Beyond Scientific Explanation for long time
3. Process development has been mostly empirical

Approach (by Nong Moon Hwang, KRISS/SNU)

1. How to define the driving force of CVD
2. Low pressure synthesis of Diamond
3. Charged Cluster Model in CVD

References

▶ N.M. Hwang et al., Diamond and Related Materials, 1 (1992) 191-194.; 3 (1993) 163-167.

▶ N.M. Hwang et al., J. Crystal Growth 135 (1994) 165-171; 143 (1994) 103-109; 160 (1996) 87-97; 160 (1996) 98-103; 162 (1996) 55-68.

Homogeneous Nucleation

Nucleation of liquid from vapor
assume spherical nucleus

$$dG = -S\, dT + V\, dP + \sum \mu_i\, dn_i + \gamma\, dA$$
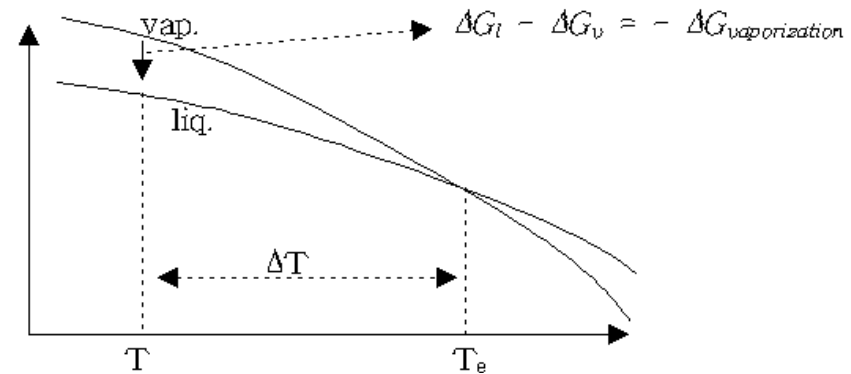
at constant T, P

$$dG = \mu_{vap}\, dn_{vap} + \mu_{liq}\, dn_{liq} + \gamma\, dA$$

$$= -(\mu_{vap} - \mu_{liq})\, dn_{liq} + \gamma\, dA$$

set driving force, $\Delta G_v = -(\mu_{liq} - \mu_{vap}) = \Delta G_{vaporization}$ (per volume of liquid)

$$\Delta G = -\frac{4}{3}\pi r^3\, \Delta G_v + 4\pi r^2\, \gamma$$

or   if set molecular (atomic) volume, v
      number of molecules (atoms) in cluster, n

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

Homogeneous Nucleation

Critical size calculation

@ critical size

$$\left.\frac{\partial \Delta G}{\partial r}\right)_{r=r^*} = 0, \qquad \left.\frac{\partial \Delta G}{\partial n}\right)_{n=n^*} = 0$$

$$\Rightarrow \quad r^* = \frac{2\gamma}{\Delta G_v}, \qquad\qquad \Delta G^* = \frac{16}{3}\pi\frac{\gamma^3}{(\Delta G_v)^2}$$

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

※ $\Delta G_{vaporization} \simeq \Delta H_{vaporization} - T\Delta S_{vaporization}$

when assuming
$$\Delta H_{vap}(T) \simeq \Delta H_{vap}(T_e)$$
$$\Delta S_{vap}(T) \simeq \Delta S_{vap}(T_e)$$

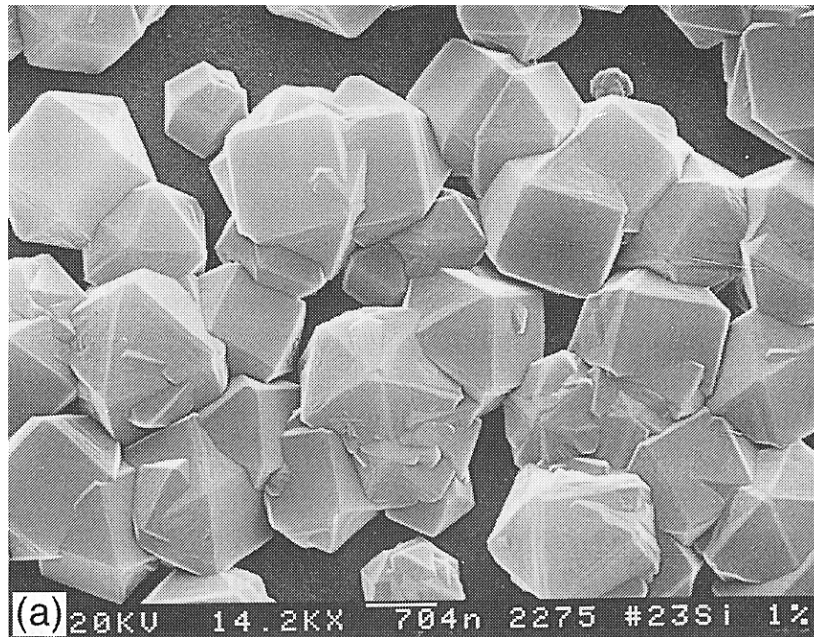$\Delta G_{vaporization} \simeq \Delta H_{vap} \cdot \Delta T/T_e$

※ nucleation rate $I = f_o\, N_o\, \exp(-\Delta G^*/kT) = f_o\, N_o\, \exp\left(-\frac{A}{(\Delta T)^2}\right)$

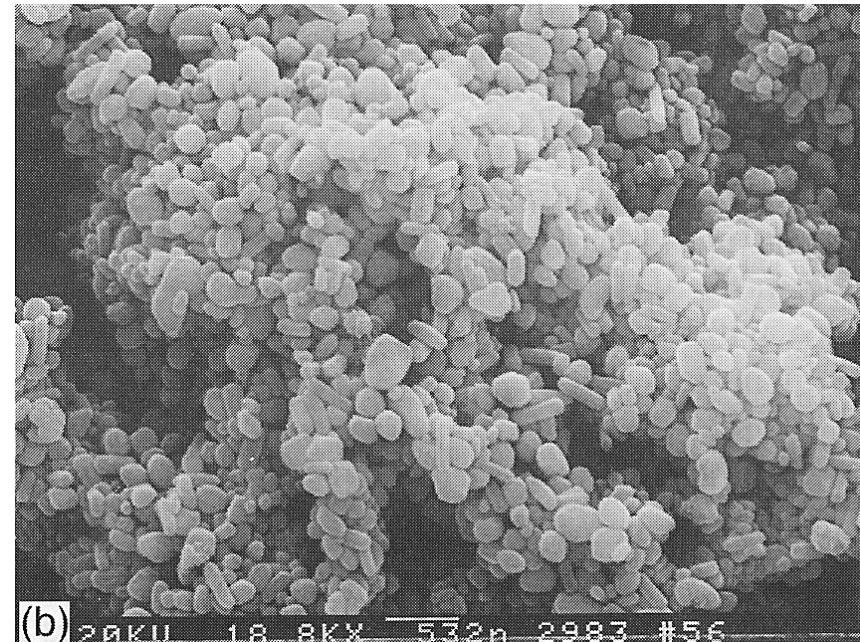$\Rightarrow$ nucleation rate sharply increases over a very narrow Temperature range

CVD Diamond - N.M. Hwang et al., J. Crystal Growth 162, 55 (1996)

Diamond deposited on silicon substrate   Soot deposited on the iron substrate

W.S. Cheong et al. / Journal of Crystal Growth 218 (2000) 27–32   29
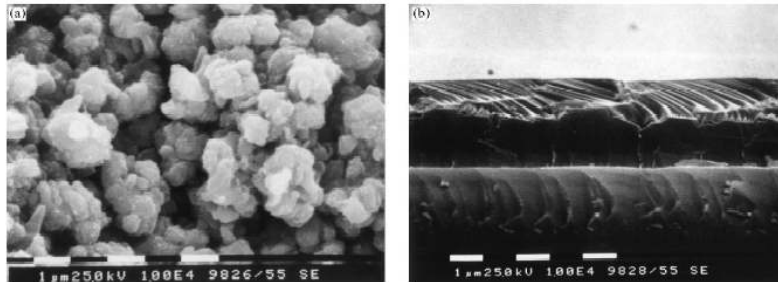

Fig. 1. SEM photographs of silicon deposits on (a) Fe and (b) Si substrates with the SiH$_4$: HCl : H$_2$ gas ratio of 1 : 1 : 98 under a reactor pressure of 1333 Pa at a substrate temperature of 1123 K.
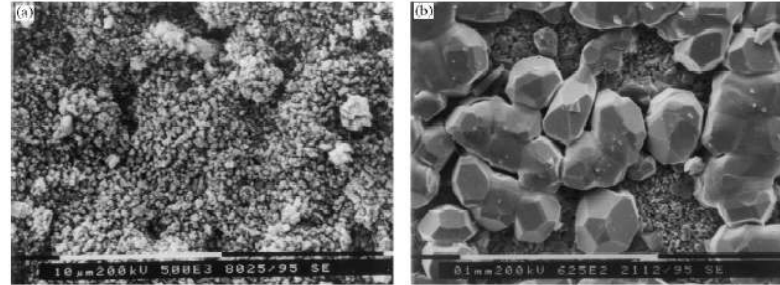

Fig. 4. SEM photographs of silicon deposits after (a) 3 and (b) 30 min on the Ni substrate with other conditions being the same as those for Fig. 1.
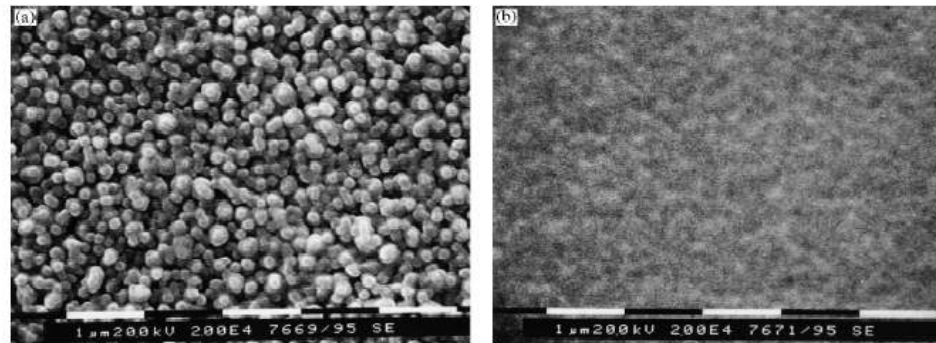

Fig. 3. SEM photographs of sputtered Al$_2$O$_3$ films on (a) Fe and (b) Si substrates with a RF power of 100 W at a substrate temperature of 873 K under a reactor pressure of 2.7 Pa.

CVD Si Nanowire - N.M. Hwang et al., J. Crystal Growth 218, 33 (2000)

Growth of silicon nanowires by chemical vapor deposition: approach by charged cluster model

Nong M. Hwang[a,b,*], Woo S. Cheong[c], Duk Y. Yoon[c], Doh-Y. Kim[a]

[a]Center for Microstructure Science of Materials, School of Materials Science and Engineering, Seoul National University, Seoul 151-742, South Korea
[b]Korea Research Institute of Standards and Science, P.O. Box 102, Daedok Science Town, Daejon 305-600, South Korea
[c]Korea Advanced Institute of Science and Technology, 373-1 Kusung-dong, Yusung-gu, Daejon 305-701, South Korea

By the silicon CVD process using the gas ratio of $SiH_4 : HCl : H_2 = 3 : 1 : 97$, we were able to grow the silicon nanowires on Si, SiO_2 and Si_3N_4 substrates but not on Mo substrates. The growth mechanism of silicon nanowires was approached by the CCM. The highly anisotropic growth of nanowires could be explained by Coulomb interactions between nanowires and charged clusters, which tends to be attractive in the axial direction but repulsive in the radial direction.

Driving force of CVD Deposition

※ **Example: Deposition of Silicon Carbide**

$$SiH_4 + CH_4 = SiC + 4H_2$$
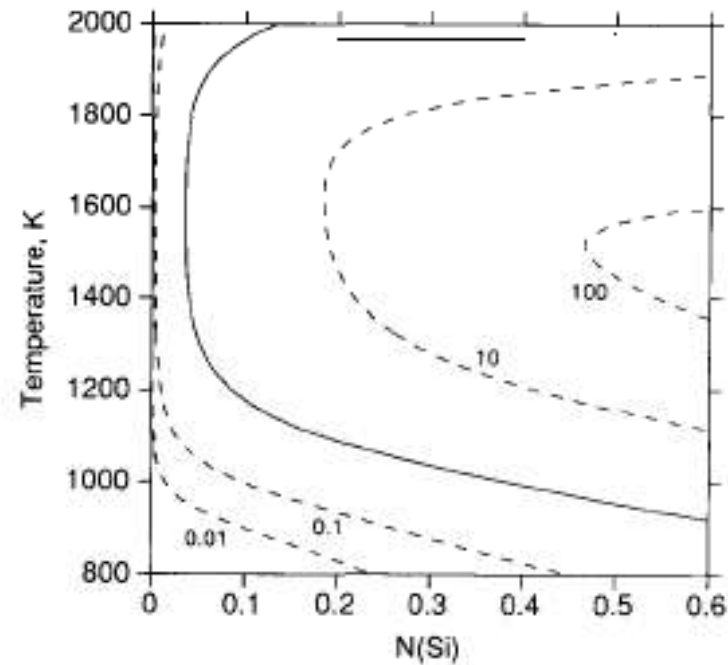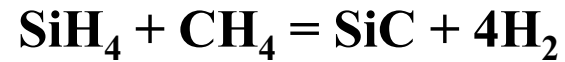

Fig. 1. CVD phase diagram of the Si–Cl–H system at 10666
Pa and composition of $N(H) = 200$ and $N(Cl) = 1$. The dashed

Thermodynamic Paradox

Diamond formation with simultaneous graphite etching
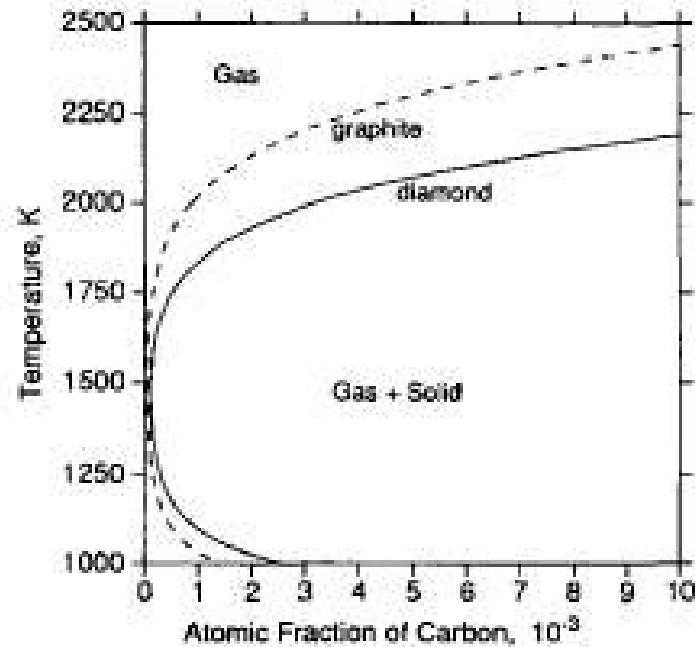## in low pressure synthesis of diamond

Fig. 1. The calculated CVD phase diagram of the C–H system at 2700 Pa. The dashed and the solid lines correspond to the solubility limit of carbon in the gas phase with respect to graphite and diamond, respectively.

$$\Delta G = n\Delta\mu^{gas \to solid} + 4\pi\left(\frac{3\Omega}{4\pi}\right)^{2/3} n^{2/3}\sigma$$

$$I = q_o O_c\left(\frac{\Delta G^*}{kT}\right)\exp\left(-\frac{\Delta G^*}{kT}\right)$$

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

$$\Delta G^*_{gra} - \Delta G^*_{dia} = \frac{16\pi\ \Omega^2_{gra}\sigma^3_{gra}}{3(\Delta\mu^{gas \to gra})^2} - \frac{16\pi\ \Omega^2_{dia}\sigma^3_{dia}}{3(\Delta\mu^{gas \to dia})^2}$$

The nucleation ratio is very sensitive to the variation of the surface energy ranging from 10^{10} to 10^{-6} with $\sigma_{dia} = 3.7$ and 4.1 J/m^2 at 1200K and $\sigma_{gra} = 3.1$ J/m^2

$\to$ There must be some factor that modifies the surface energy of diamond

$\to$ **Creation of the *Charged Cluster Model***