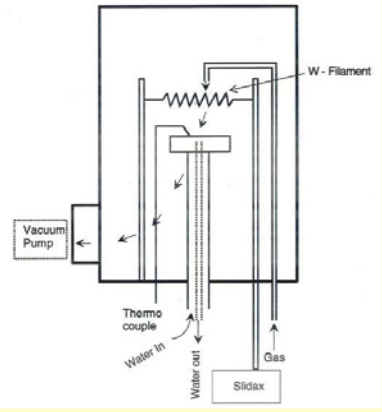
Thermodynamics of Materials

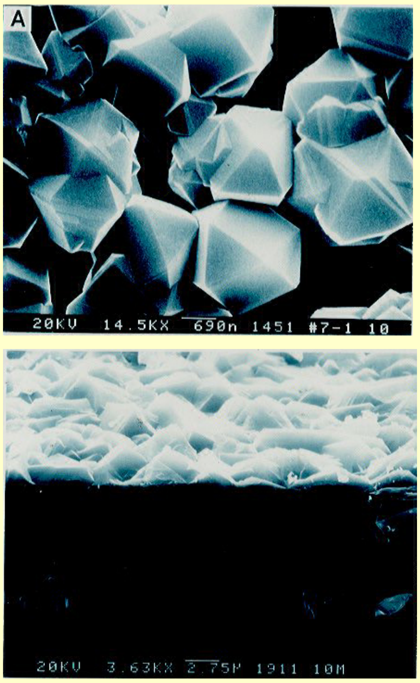
19th Lecture

2007. 5. 27 (Monday)

CVD Diamond



$P = 20 \sim 100$ Torr
$T_f = 1900 \sim 2200^oC$
$T_s = 800 \sim 1100^oC$
$CH_4 - H_2$: 100 sccm
CH_4 : 1 ~ 3%



Atomic Hydrogen Hypothesis

Spitsyn, Bouilov and Derjaguin, J. Cryst. Growth (1981)

- Atomic hydrogen etches graphite much faster than diamond. (Exp. Observation)
- Difference in etching kinetics can lead to dominant formation of diamond or to diamond deposition with simultaneous graphite etching.

Atomic Hydrogen Hypothesis

Apply thermodynamics to etching or deposition.

Graphite Etching	$\mu_C^{gas} < \mu_C^{graphite}$
Diamond Etching	$\mu_C^{gas} < \mu_C^{diamond}$
Graphite Deposition	$\mu_C^{gas} > \mu_C^{graphite}$
Diamond Deposition	$\mu_C^{gas} > \mu_C^{diamond}$
Graphite vs Diamond	$\mu_C^{graphite} < \mu_C^{diamond}$

Atomic Hydrogen Hypothesis

Thermodynamics of simultaneous graphite etching and diamond deposition

Graphite Etching and Diamond Deposition

$$\mu_C^{gas} < \mu_C^{graphite} \quad \text{and} \quad \mu_C^{gas} > \mu_C^{diamond}$$

$$\mu_C^{graphite} > \mu_C^{gas} > \mu_C^{diamond}$$

The inequalities do not satisfy

$$\mu_C^{graphite} < \mu_C^{diamond}$$

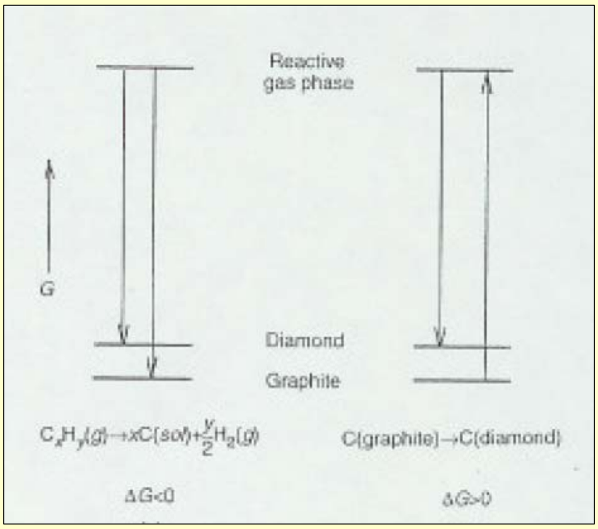


Fig. 4

The simultaneous CVD of diamond and gasification of graphite is recognized as the vapor-phase transport of carbon from graphite to diamond. Summing Eqs. (5) and (6) to obtain an overall process gives

$$(y+m)H^{o}+C_{graphite}\rightarrow\frac{y+m}{2}H_{2}+C_{diamond} \qquad (7)$$

which, if separated into independent reactions, is simply the recombination of atomic hydrogen with the conversion of graphite into diamond, i.e.,

$$(Y+M)H^{\circ}\rightarrow\frac{y+m}{2}H_{2} \qquad (8)$$

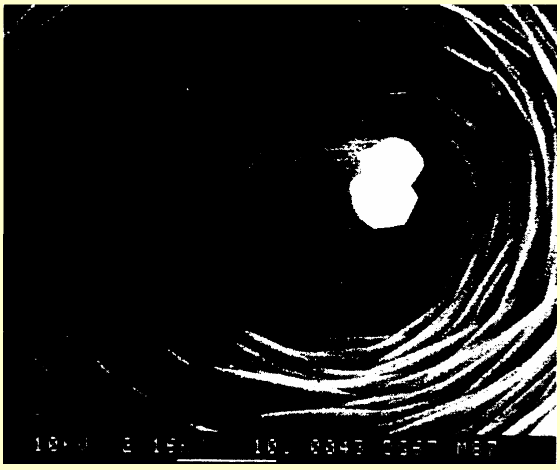
$$C_{graphite}\rightarrow C_{diamond} \qquad (9)$$

Equation (9) conflicts with the accepted phase diagram for carbon, and the paradox that has disturbed the early skeptics becomes apparent.

Thus, there must be an error either in *re* (in fact) or *in voce* (in discourse or logic), and there has been much debate as to the proper synthetic paradigm for the CVD of diamond.

Atomic hydrogen hypothesis is not an hypothesis but an experimental fact!

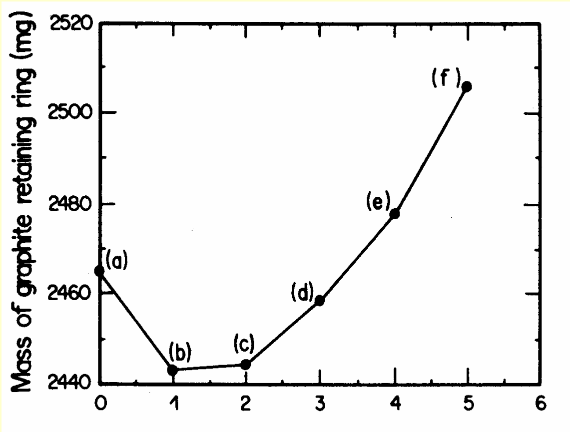
Diamond Deposition on the Etch Pit of Graphite Substrate



A.R. Badzian et al., Mat. Res. Bull., 23 (1988) 531

Weight Change of Graphite Ring

0.5%CH_4-H_2, 80 Torr. T_{sub}= 870 ºC

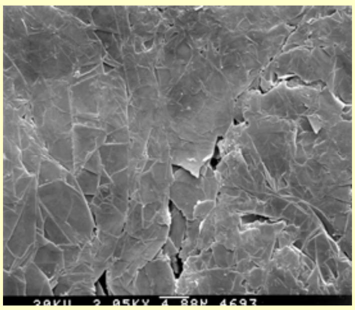


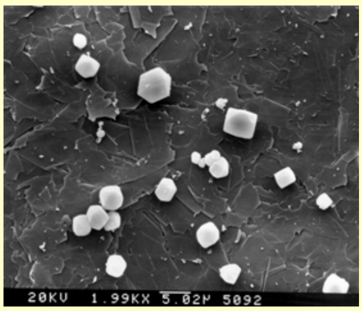
Deposition Time (h)

M. C. Salvadori et al, J. Electrochem. Soc., 139 (1992) 558

Simultaneous Diamond Deposition and Graphite Etching

T_F : 2100ºC, T_s : 1050ºC, 1% CH_4 - H_2, 2h





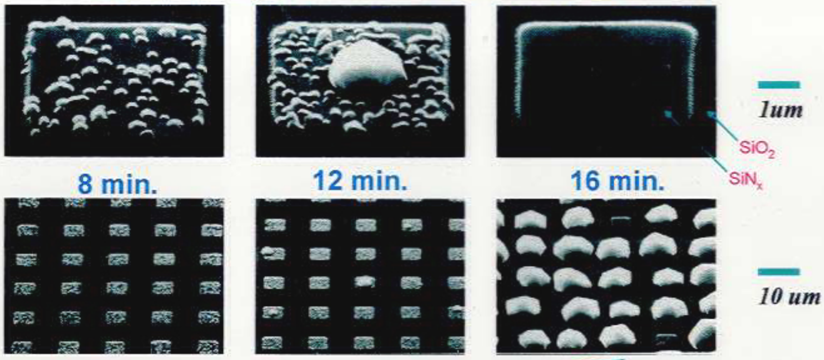
before experiment → after experiment

43.21 mg

37.06 mg (6.15 mg)

Coarsening phenomenon of Si clusters

Kumomi & Yonehara, Mat. Res. Soc. Symp. Proc. V.202, 83 (1991)



Two irreversible processes of deposition and etching take place simultaneously in opposite directions!

Contradiction between Experimental Facts and the 2nd Law of Thermodynamics

Which should we believe, experimental facts or the 2nd law of thermodynamics?

What should we do in this situation?

How about thermodynamics of CVD?

Do we understand it clearly?

Simultaneous Deposition and Etching

→ Simultaneous condensation & evaporation

→ Simultaneous Si deposition by SiH_4 and its etching by HCl in Si CVD.

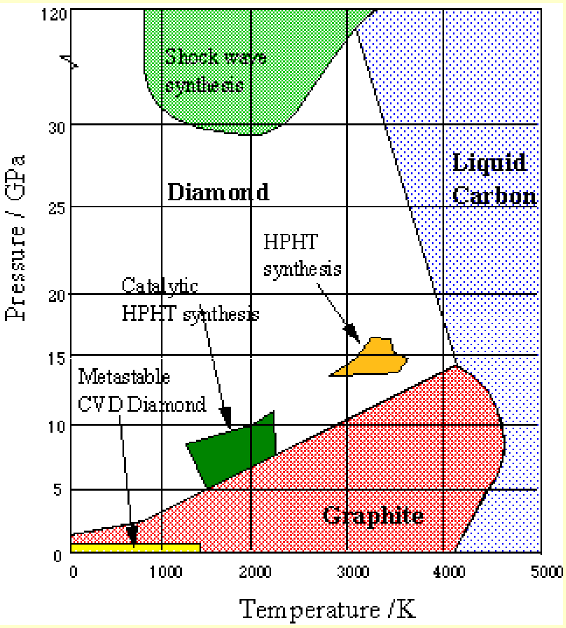
What is the thermodynamic meaning?

Condensation → $\mu_{H_2O}^{vapor} > \mu_{H_2O}^{liquid}$

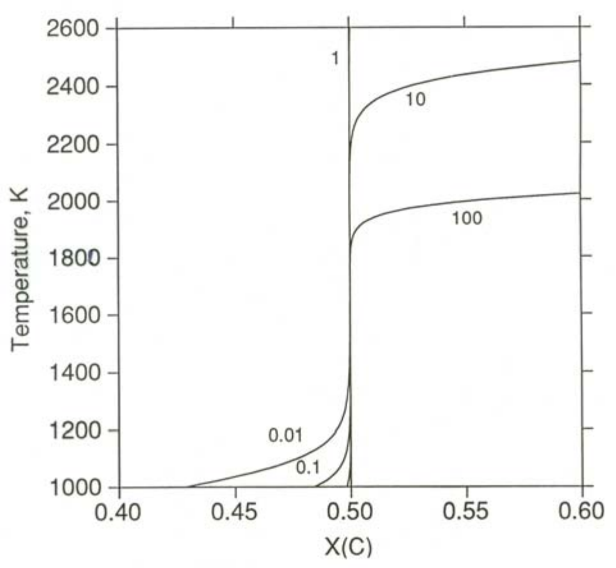
Evaporation → $\mu_{H_2O}^{vapor} < \mu_{H_2O}^{liquid}$

Simultaneous condensation & evaporation

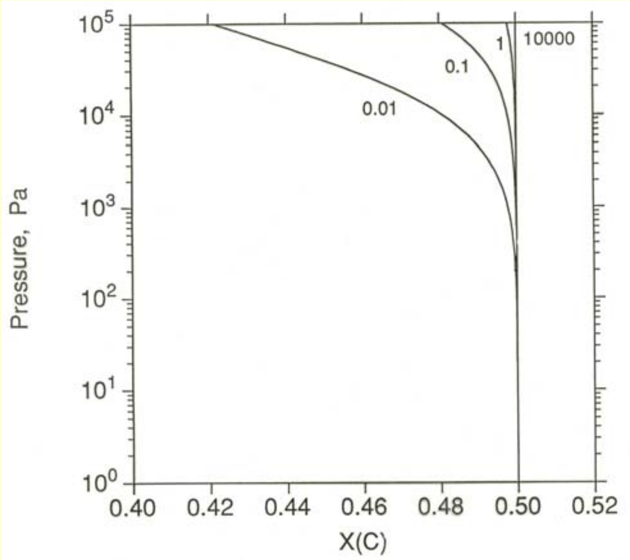
$\mu_{H_2O}^{vapor} > \mu_{H_2O}^{liquid}$ and $\mu_{H_2O}^{vapor} < \mu_{H_2O}^{liquid}$



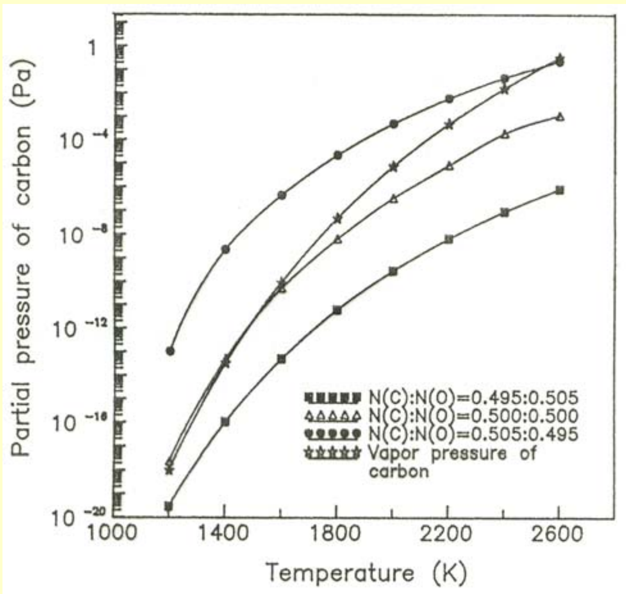
Lower Limit of Deposition Temperature of CVD Diamond in the C-H-O System



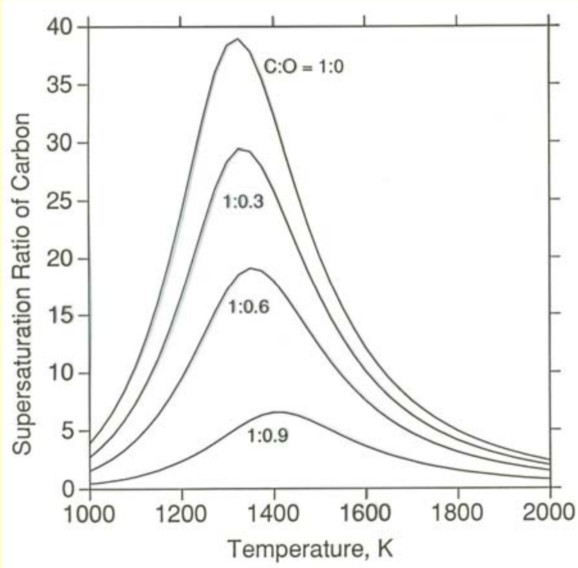
Hwang, *J. Crystal Growth*, 135 (1994) 165

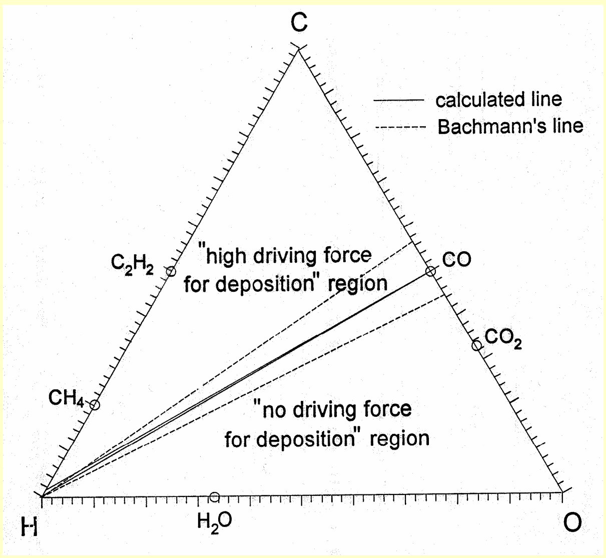


Pressure, Pa
X(C)
0.01
0.1
1
10000

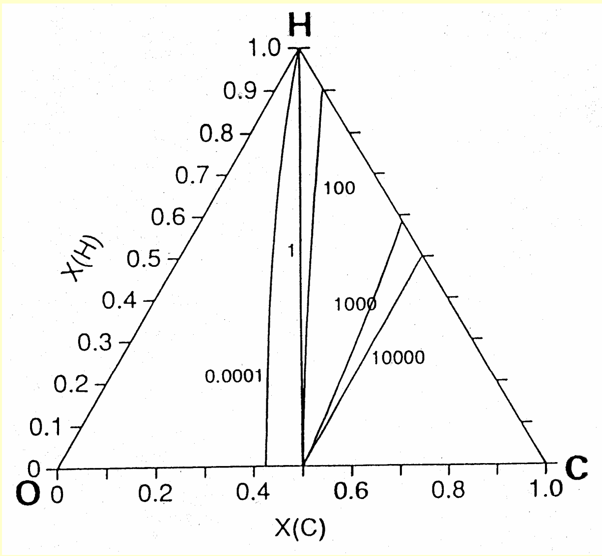


Partial pressure of carbon (Pa)
Temperature (K)
N(C):N(O)=0.495:0.505
N(C):N(O)=0.500:0.500
N(C):N(O)=0.505:0.495
Vapor pressure of carbon

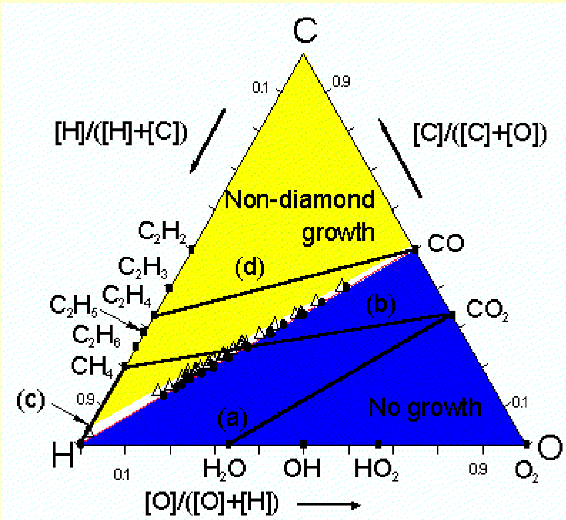




Hwang et al. *Diamond Relat. Mater.*, 3 (1993) 163

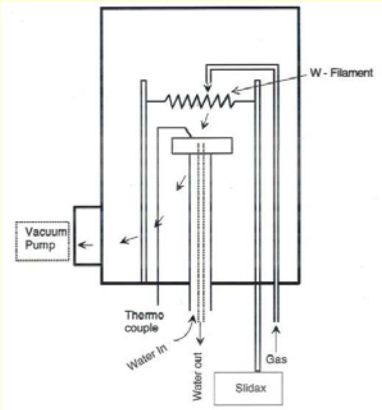


Hwang, *J. Crystal Growth*, 135 (1994) 165



Bachmann*et al*, Diamond Relat. Mater. 1 (1991) 1
Petherbridge et al. *J. Appl. Phys.*, 89 (2001) 5219

CVD Diamond



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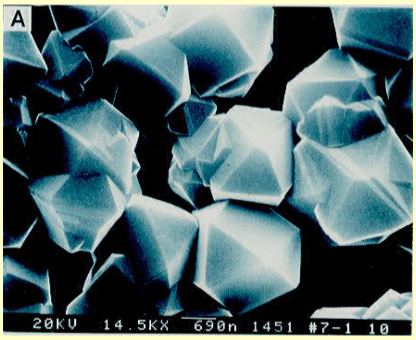
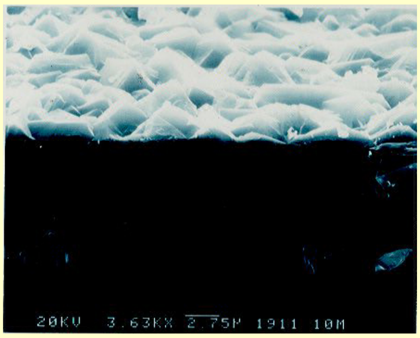


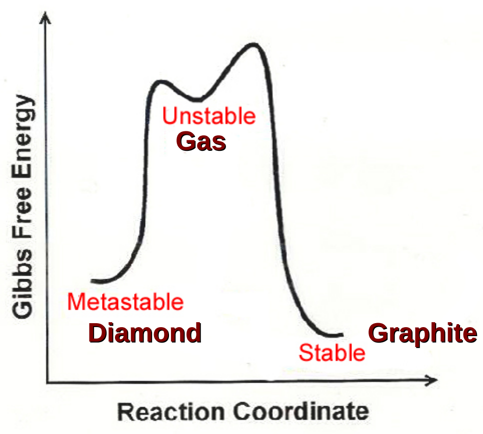


Anybody can make CVD diamond.

Nobody knows why!

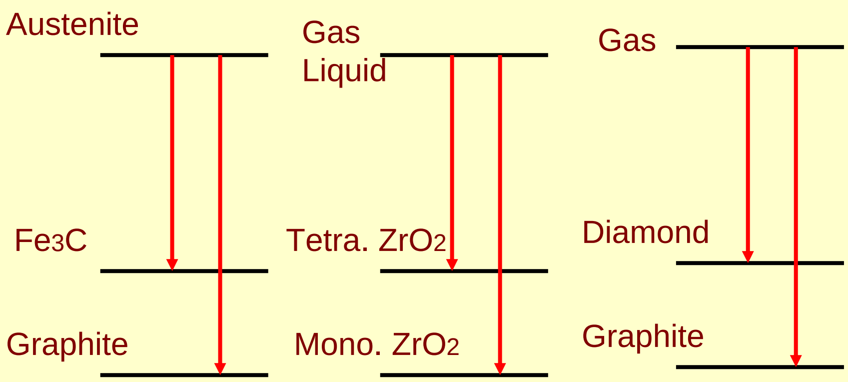
CVD Diamond Film

$$CH_4 + H_2 \Rightarrow C_{solid} + H + CH + C_2H_2 + \ldots$$



Thermodynamic and Kinetic Description of Metastable Phase Formation

Examples of Dominant Formation of Metastable Phase

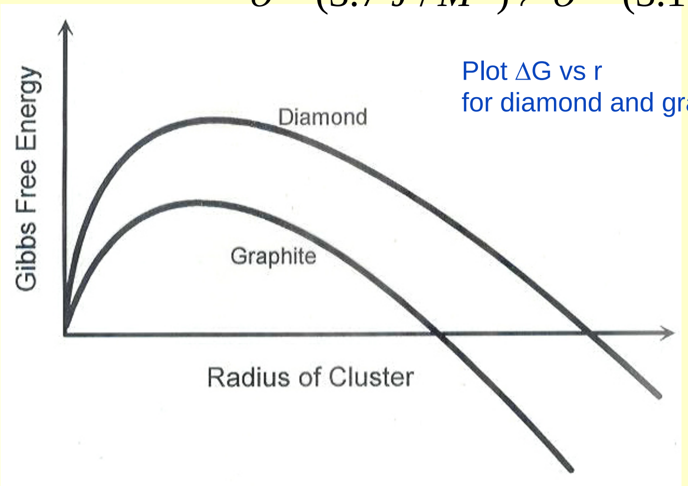


Comparison of stability and nucleation barrier

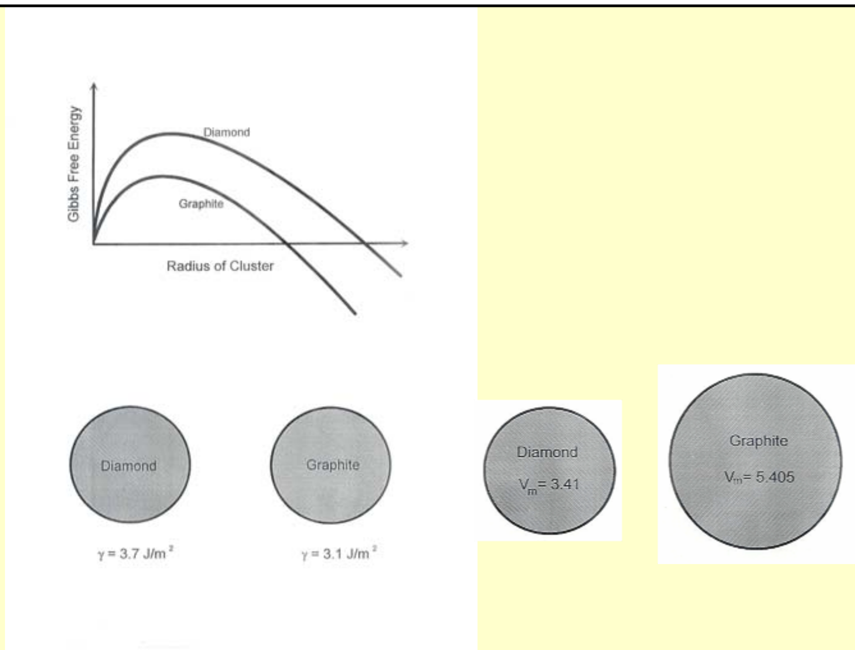
$$\Delta G = \frac{4\pi r^3}{3}\Delta f^{\,gas\rightarrow solid} + 4\pi r^2\sigma$$

$$\Delta f^{\,gas\rightarrow dia} \succ \Delta f^{\,gas\rightarrow gra}$$

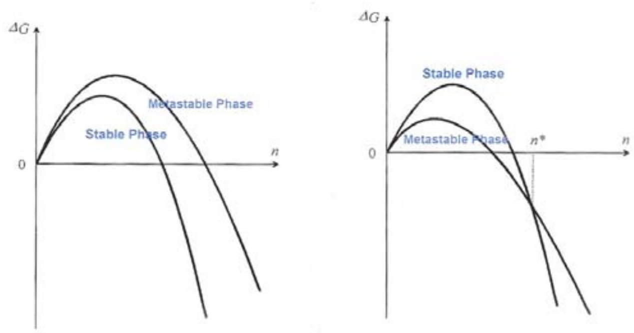
$$\sigma^{dia}(3.7\ J/M^2) \succ \sigma^{gra}(3.1\ J/M^2)$$



Plot ΔG vs r
for diamond and graphite.



Necessary Condition for Dominant Precipitation of Metastable Phase over Stable Phase



$$\Delta G_{dia} = \frac{4}{3}\pi r^3 \Delta f_{vol}^{gas\rightarrow solid} + 4\pi r^2 \sigma$$

$$\Delta G_{dia} = n\Delta\mu^{gas\rightarrow dia} + \eta_{dia}\sigma_{dia}n^{2/3}$$

$$\Delta G_{gra} = n\Delta\mu^{gas\rightarrow gra} + \eta_{gra}\sigma_{gra}n^{2/3}$$

$$\eta = (4\pi)^{1/3}(3\Omega)^{2/3} \; \textit{for sphere}$$

Derive n*.

$$n\Delta\mu^{gas\rightarrow gra} + \eta_{gra}\sigma_{gra}n^{2/3} - \left(n\Delta\mu^{gas\rightarrow dia} + \eta_{dia}\sigma_{dia}n^{2/3}\right) = 0$$

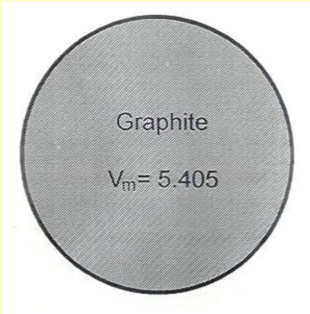
$$= n\left(\Delta\mu^{gas\rightarrow gra} - \Delta\mu^{gas\rightarrow dia}\right) + n^{2/3}\left(\eta_{gra}\sigma_{gra} - \eta_{dia}\sigma_{dia}\right)$$

$$= n\left\{\Delta\mu^{gas\rightarrow gra} - \Delta\mu^{gas\rightarrow dia} + n^{-1/3}\left(\eta_{gra}\sigma_{gra} - \eta_{dia}\sigma_{dia}\right)\right\}$$

$$n^* = \left(\frac{\eta_{gra}\sigma_{gra} - \eta_{dia}\sigma_{dia}}{\Delta u^{gas\rightarrow dia} - \Delta u^{gas\rightarrow gra}}\right)^3 = \left(\frac{\eta_{gra}\sigma_{gra} - \eta_{dia}\sigma_{dia}}{\Delta u^{gra\rightarrow dia}}\right)^3$$

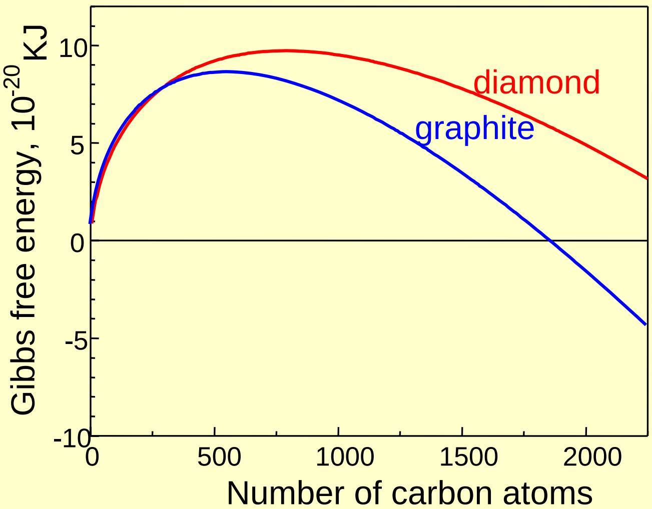
$$= 36\pi\left(\frac{\Omega_{gra}^{2/3}\sigma_{gra} - \Omega_{dia}^{2/3}\sigma_{dia}}{\Delta\mu^{gra\rightarrow dia}}\right)^3$$

$$\boxed{n^* = 36\pi\left(\frac{\Omega_{gra}^{2/3}\sigma_{gra} - \Omega_{dia}^{2/3}\sigma_{dia}}{\Delta\mu^{gra\rightarrow dia}}\right)^3}$$



$$V_{dia}^{2/3}\sigma_{dia}(8.38) \prec V_{gra}^{2/3}\sigma_{gra}(9.55)$$

Size Dependence of Clusters on Stability between Diamond and Graphite



Hwang et al.
Diamond Relat. Mater.
1 (1992) 9

No Gas Activation
→ Graphite

Gas Activation
→ Diamond

n^* > 1,000,000 for other metastable phases such as Fe_3C and t-ZrO_2

→Dominant nucleation of a metastable phase is a rule rather than exception.

In the case of carbon,

Surface Energy *is the only one that can be varied by the processing condition*

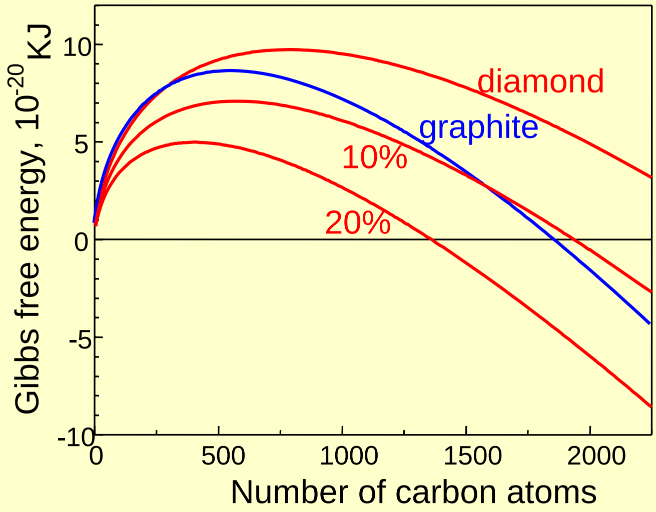
$$n^* = 36\pi\left(\frac{\sigma_{dia}(\Omega_{dia})^{\frac{2}{3}} - \sigma_{gra}(\Omega_{gra})^{\frac{2}{3}}}{f_{gra} - f_{dia}}\right)^3$$

Role of the Gas Activation *is to modify the surface energy in the way favoring the stability of diamond over that of graphite*

↑

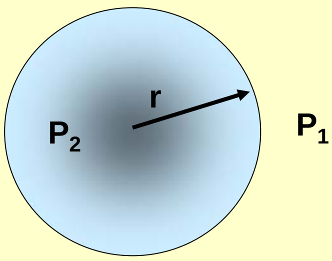
essential to the dominant formation of diamond over graphite

Size Dependence of Clusters on Stability between Diamond and Graphite



Hwang et al.
J. Crystal Growth
172 (1997) 416

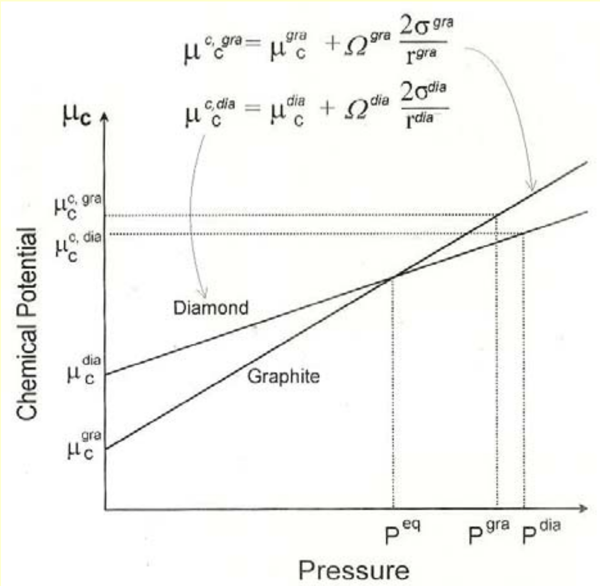
Capillary Pressure in the Nucleation Stage of Diamond or Graphite



$$\Delta P = P_2 - P_1 = \frac{2\sigma}{r}$$

Cluster of 1 nm in radius

$$\frac{2\sigma}{r} = \frac{2 \times 3.7 J / M^2}{10^{-9} M} = \boxed{7400 \quad MPa}$$



$$r = \left(\frac{3\Omega}{4\pi}\right)^{1/3} n^{1/3}$$

Find n, where

$$\mu_C^{c,gra} = \mu_C^{c,dia}$$

$$\mu_C^{c,dia} = \mu_C^{dia} + \Omega^{dia} \frac{2\sigma^{dia}}{r^{dia}}$$

$$\mu_C^{c,gra} = \mu_C^{gra} + \Omega^{gra} \frac{2\sigma^{gra}}{r^{gra}}$$

$$r = \left(\frac{3\Omega}{4\pi}\right)^{\frac{1}{3}} n^{\frac{1}{3}}$$

$$n = \frac{32\pi}{3}\left(\frac{\overbrace{\sigma^{dia}(\Omega^{dia})^{\frac{2}{3}}}^{D} - \overbrace{\sigma^{gra}(\Omega^{gra})^{\frac{2}{3}}}^{G}}{\underbrace{\Delta\mu_C^{dia\to gra}}_{\text{negative}}}\right)^3$$

$$D < G \longrightarrow n > 0$$

$$r = \left(\frac{3\Omega}{4\pi}\right)^{\frac{1}{3}} n^{\frac{1}{3}}$$

$$n = \frac{32\pi}{3}\left(\frac{\overbrace{\sigma^{dia}\left(\Omega^{dia}\right)^{\frac{2}{3}}}^{D} - \overbrace{\sigma^{gra}\left(\Omega^{gra}\right)^{\frac{2}{3}}}^{G}}{\underbrace{\Delta\mu_c^{dia\to gra}}_{\text{negative}}}\right)^3$$

$$n^* = 36\pi\left(\frac{\Omega_{gra}^{2/3}\sigma_{gra} - \Omega_{dia}^{2/3}\sigma_{dia}}{\Delta\mu^{gra\to dia}}\right)^3$$

$$\frac{\partial \Delta G^{gas\to dia}}{\partial n} = -\Delta\mu^{gas\to dia} + \frac{2}{3}(4\pi)^{1/3}(3\Omega_{dia})^{2/3}\sigma_{dia}n^{-1/3}$$

$$\frac{\partial \Delta G^{gas\to gra}}{\partial n} = -\Delta\mu^{gas\to gra} + \frac{2}{3}(4\pi)^{1/3}(3\Omega_{gra})^{2/3}\sigma_{gra}n^{-1/3}$$

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