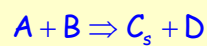


Thermodynamics of Materials

16th Lecture
2007. 5. 14 (Wednesday)



Find the expression for supersaturation and driving force for deposition.

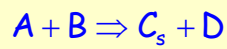
$$\alpha = \frac{p_A^i p_B^i}{p_A^f p_B^f} \quad \Delta\mu = -RT \ln \alpha$$

Usually very high value of α

When 'D' is supplied,

$$\alpha = \frac{p_A^i p_B^i p_D^f}{p_A^f p_B^f p_D^i} \quad \Delta\mu = -RT \ln \alpha$$

Is this thermodynamic scheme correct?



A, B: Reactants, C, D : Products

C_s : deposition species

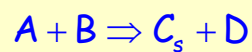
$$\mu_A^i = \mu_A^s + RT \ln P_A^i$$

$$\mu_B^i = \mu_B^s + RT \ln P_B^i$$

Initially, C and D are absent.

$$\mu_C^i = \mu_C^s + RT \ln(0) = -\infty$$

$$\mu_D^i = \mu_D^s + RT \ln(0) = -\infty$$



Driving force for forward reaction = ?

$$\Delta\mu = \sum (\mu_j^{\text{right side}} - \mu_j^{\text{left side}})$$

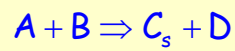
$$= \mu_C^i + \mu_D^i - \mu_A^i - \mu_B^i$$

$$= \mu_C^s + RT \ln P_C^i + \mu_D^s + RT \ln P_D^i$$

$$- \mu_A^s - RT \ln P_A^i - \mu_B^s - RT \ln P_B^i$$

$$= \Delta\mu^s + RT \ln \left(\frac{P_C^i P_D^i}{P_A^i P_B^i} \right)$$

$$\Delta\mu = \Delta\mu^s + RT \ln \left(\frac{0}{P_A^i P_B^i} \right) = -\infty$$



Driving force for overall reactions = ?

- = Total free energy at final state
- Total free energy at initial state

Final state \Rightarrow Equilibrium state of
minimum Gibbs free energy

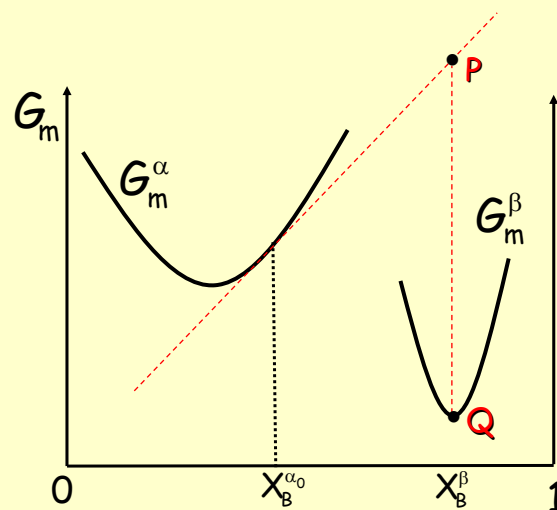
$$\Delta G^{i \rightarrow f} = G^f - G^i$$

$$= \sum \mu_j^f n_j^f - \sum \mu_j^i n_j^i$$

$$= \mu_A^f n_A^f + \mu_B^f n_B^f + \mu_C^f n_C^f + \mu_D^f n_D^f - \mu_A^i n_A^i - \mu_B^i n_B^i$$

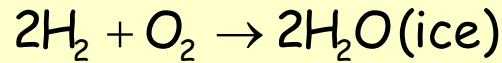
\Rightarrow always negative!

What is the driving force for precipitation of β from α ?



$$\Delta G = \bar{G}_A X_A^\beta + \bar{G}_B X_B^\beta - G_m^\beta(X_B^\beta)$$

Driving Force for Deposition in Chemical Vapor Deposition



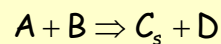
What is the condition for the ice to form or precipitate?

Chemical reactions take place one by one and two molecules of H_2 plus one mole of O_2 will produce two moles of H_2O .

Which phase would these two moles of H_2O belong to, solid, liquid or gas?

What is the thermodynamic condition for H_2O gas to form its solid?

$$P_{\text{H}_2\text{O}} > P_{\text{H}_2\text{O}}^{\text{eq}} \quad \text{or} \quad \mu_{\text{H}_2\text{O}}^{\text{gas}} > \mu_{\text{H}_2\text{O}}^{\text{solid}}$$



Driving force for deposition of C_s

$\Delta\mu_C^{\text{gas} \rightarrow \text{solid}}$ = Chemical potential of C of the film (C_s)
– Chemical potential of C adjacent
to the growing surface

$$= \mu_C^{\text{solid}} - \mu_C^{\text{gas}}$$

$$= \mu_C^{\text{o, gas}} + RT \ln P_C^{\text{eq.}} - \mu_C^{\text{o, gas}} - RT \ln P_C^{\text{gas}}$$

$$= -RT \ln \left(\frac{P_C^{\text{gas}}}{P_C^{\text{eq.}}} \right) = -RT \ln(\alpha)$$

Supersaturation Ratio

$$\alpha = \frac{P_C^{\text{gas}}}{P_C^{\text{eq.}}}$$

The remaining problem is how we determine P_c^{gas} .

Normally, the gas species are adsorbed on the growing surface.

How can we treat thermodynamically the species adsorbed on the surface?

$P_c^{gas, surface}$ depends on kinetics of chemical reactions.

What would be the minimum and maximum values of $P_c^{gas, surface}$?

$$0 \leq P_c^{gas, surface} \leq P_c^{gas \text{ phase equilibrium}} (= P_c^*)$$

How do we determine $P_c^{gas \text{ phase equilibrium}}$ in thermodynamic calculation?

$P_c^{gas \text{ phase equilibrium}} (= P_c^*)$ can be determined by Gibbs free minimization **excluding all the condensed phases.**

$$0 \leq p_c^{\text{gas, surface}} \leq P_c^*$$

$$0 \leq p_c^{\text{gas, surface}} < P_c^{\text{eq}}$$

$$\Rightarrow \alpha = \frac{p_c^{\text{gas, surface}}}{P_c^{\text{eq}}} < 1 \Rightarrow \Delta\mu_c^{\text{gas} \rightarrow \text{solid}} > 0$$

\Rightarrow Driving force is for **etching**.

$$P_c^{\text{eq}} < p_c^{\text{gas, surface}} \leq P_c^*$$

\Rightarrow Driving force is for **deposition**.

When $p_c^{\text{gas, surface}} = P_c^*$, the driving force is maximum.

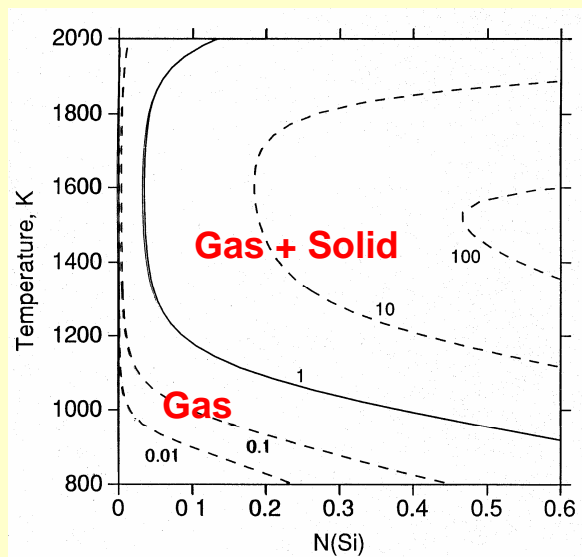
If $P_c^{\text{gas}} \ll P_c^*$, most reactant gases flow in the reactor, being unreacted. \Rightarrow low efficiency!

P_c^{gas} increases monotonically with chemical reactions.

Process parameters are adjusted to maximize the chemical reaction of reactants so that the condition of $P_c^{\text{gas}} \approx P_c^*$ may be achieved.

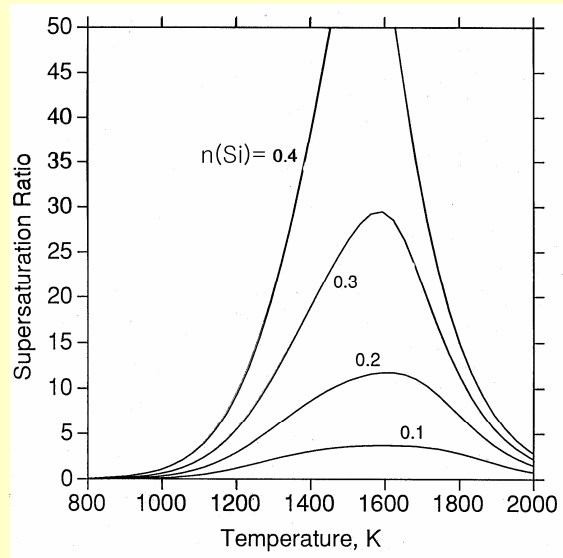
$P_c^{\text{gas}} \approx P_c^*$ may be a good approximation.

Since P_c^* can be determined by thermodynamic calculations, $\alpha = \frac{P_c^*}{P_c^{eq}}$ can be calculated with respect to thermodynamic parameters such as Temperature, Pressure and Composition.

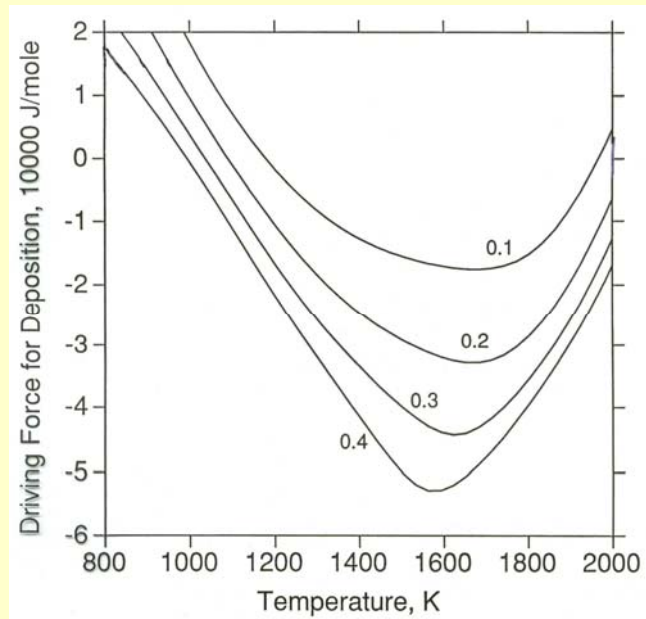


Si-Cl-H
80 Torr
N(H)=200
N(Cl) = 1

Hwang et al.
J. Crystal Growth
143 (1994) 103



Hwang et al. *J. Crystal Growth*, 143 (1994) 103

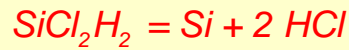


Selective Epitaxial Growth (SEG)

Si-SEG

- Growth of Si on Si
- No growth of Si on SiO₂

Gas mixture of SiCl₂H₂ + HCl



Calculations by Thermo-Calc

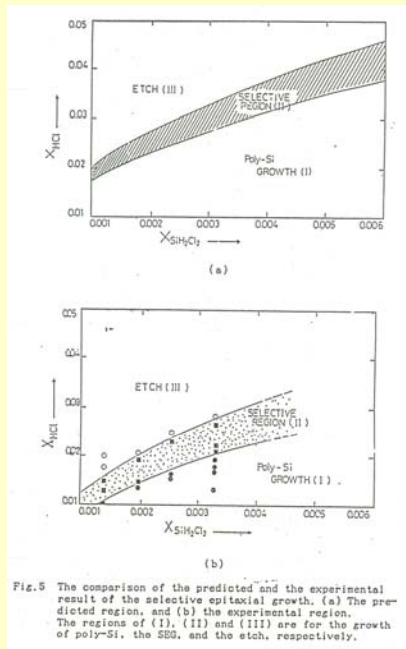
Conditions:

T=1323, P=10666, N(SI)=1.4E-1, N(CL)=9.2E-1, N(H)=199.36

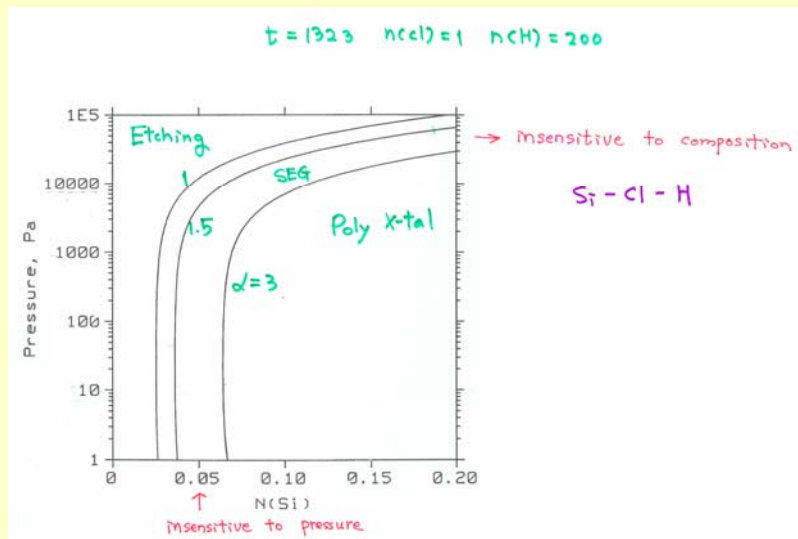
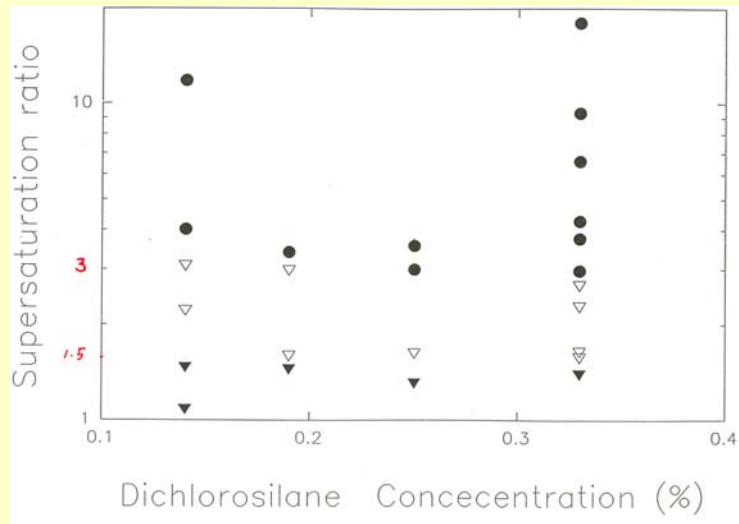
H2	9.91047E-01	CL2H2S11	3.78938E-06	<u>S11</u>	<u>7.97411E-10</u>
CL1H1	8.72066E-03	CL4S11	7.88797E-07	CL2	5.88841E-13
CL2S11	2.12707E-04	H4S11	8.60203E-08	S12	2.60034E-13
CL3S11	5.55192E-06	CL1	3.56902E-08	S13	3.14674E-14
H1	4.83980E-06	CL1S11	9.72339E-09	H6S12	6.50693E-15
CL3H1S11	4.57379E-06	H1S11	2.01285E-09		

SI1_S#1 Status ENTERED Driving force 0.0000E+00
Number of moles 1.1722E-01, Mass 3.2921E+00 Mole fractions:
SI 1.00000E+00 CL 0.00000E+00 H 0.00000E+00

H2	9.92254E-01	H1	4.84275E-06	<u>S11</u>	<u>9.40131E-09</u>
CL1H1	6.34253E-03	CL4S11	2.59578E-06	S13	5.15678E-11
CL2S11	1.32491E-03	H4S11	1.01663E-06	S12	3.61445E-11
CL3S11	2.51360E-05	CL1S11	8.33246E-08	H6S12	9.07768E-13
CL2H2S11	2.36321E-05	CL1	2.59417E-08	CL2	3.11097E-13
CL3H1S11	2.07202E-05	H1S11	2.37455E-08		



SiCl ₂ H ₂ (%)	HCl (%)	P/P _e	Region
0.33	0.80	18.00	Poly-Si
	1.10	9.35	Poly-Si
	1.30	6.61	Poly-Si
	1.60	4.27	Poly-Si
	1.70	3.76	Poly-Si
	1.90	2.97	Poly-Si
	2.00	2.66	Selective
	2.15	2.28	Selective
	2.50	1.64	Selective
	2.55	1.57	Selective
	2.70	1.39	No Deposition



Compound (Solid Solution)

Consider the deposition of compound of A_aB_b

$$\alpha = \frac{P_{A_aB_b}^*}{P_{A_aB_b}^{eq}}, \Delta\mu = -RT \ln \alpha$$

In many cases, gas species of A_aB_b does not exist.

ex) Al_2O_3 , Si_3N_4 , SiC

Express the chemical potential or supersaturation ratio

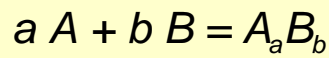
in terms of existing species, which is equivalent to $\frac{P_{A_aB_b}^*}{P_{A_aB_b}^{eq}}$

using the law of mass action for compound formation at final and gas phase equilibria.

Consider the reaction, $a A + b B = A_aB_b$

i) At final equilibrium, $a \mu_A^{eq} + b \mu_B^{eq} = \mu_{A_aB_b}^{eq}$

ii) At gas phase equilibrium, $a \mu_A^* + b \mu_B^* = \mu_{A_aB_b}^*$



i) At final equilibrium

$$a \mu_A^{\text{eq}} + b \mu_B^{\text{eq}} = \mu_{A_a B_b}^{\text{eq}}$$

ii) At gas phase equilibrium

$$a \mu_A^* + b \mu_B^* = \mu_{A_a B_b}^*$$

Driving force for deposition

$$\Rightarrow \Delta \mu_{A_a B_b}^{\text{gas} \rightarrow \text{solid}} = \mu_{A_a B_b}^{\text{eq}} - \mu_{A_a B_b}^* = a \mu_A^{\text{eq}} + b \mu_B^{\text{eq}} - a \mu_A^* - b \mu_B^*$$

$$= a \mu_A^s + a RT \ln P_A^{\text{eq}} + b \mu_B^s + b RT \ln P_B^{\text{eq}}$$

$$- a \mu_A^s - a RT \ln P_A^* - b \mu_B^s - b RT \ln P_B^*$$

$$= -RT \ln \left(\frac{(P_A^*)^a (P_B^*)^b}{(P_A^{\text{eq}})^a (P_B^{\text{eq}})^b} \right)$$

Supersaturation ratio

$$\alpha = \frac{(P_A^*)^a (P_B^*)^b}{(P_A^{\text{eq}})^a (P_B^{\text{eq}})^b} = \frac{P_{A_a B_b}^*}{P_{A_a B_b}^{\text{eq}}}$$

$P_{A_a B_b}^{\text{eq}}, P_{A_a B_b}^*$: hypothetical indeterminable value

$$\Delta \mu = -RT \ln \alpha$$

\Rightarrow Driving force for 1 mole of $A_a B_b$

Solid Solution $\Rightarrow a + b = 1$

Find the expression for the supersaturation for deposition of SiC in the CVD process using the reactant gases of SiH₄ and CH₄.

$$\text{SiH}_4 + \text{CH}_4 = \text{SiC} + 4\text{H}_2 \quad \alpha = \frac{P_{\text{SiC}}^*}{P_{\text{SiC}}^{\text{eq}}} = \frac{P_{\text{SiH}_4}^* P_{\text{CH}_4}^* (P_{\text{H}_2}^{\text{eq}})^4}{P_{\text{SiH}_4}^{\text{eq}} P_{\text{CH}_4}^{\text{eq}} (P_{\text{H}_2}^*)^4}$$

Consider a simpler reaction.

$$\text{Si} + \text{C} = \text{SiC} \quad \alpha = \frac{P_{\text{SiC}}^*}{P_{\text{SiC}}^{\text{eq}}} = \frac{P_{\text{Si}}^* P_{\text{C}}^*}{P_{\text{Si}}^{\text{eq}} P_{\text{C}}^{\text{eq}}}$$

In a real calculation using Thermo-Calc,

$$\alpha_1 = 8128745, \quad \alpha_2 = 8128752$$

H2	8.30213E-01	C1H3	5.15943E-06	C1SI1	5.66556E-11
C1SI2	1.11284E-01	C3H4_1	5.12173E-06	C3	1.70796E-11
C2H2	5.29783E-02	SI2	3.17637E-06	H6SI2	2.97979E-12
C1H4	4.61561E-03	H4SI1	1.59469E-06	C3H8	1.91491E-12
C2H4*	3.45682E-04	C2H3	1.48171E-06	C5	5.42009E-13
C2SI1	3.41494E-04	C3H6_2	6.19877E-08	C1H1	5.17529E-14
SI3	1.17524E-04	C2H6	5.67915E-08	C	4.29435E-15
H	4.43787E-05	C2H1	2.27117E-08	C4	2.46159E-15
SI	1.98744E-05	C2H5	2.54647E-09	C2	1.75758E-15
C3H4_2	1.48358E-05	C1H2	2.03572E-10	C4H12SI1	5.68974E-16
H1SI1	9.54028E-06	C3H6_1	9.86377E-11		

< Gas Phase Equil. >



1 1 0 0

$$P = 1000 \text{ Pa} \quad T = 1400 \text{ K}$$

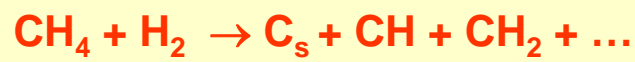
< Final Equil. >

H2	9.99951E-01	C2H4	3.00948E-13	C3H4_1	1.09232E-19
H	4.87045E-05	C1H2	6.00656E-15	C	1.05200E-19
C1H4	1.64031E-07	C2H3	1.17540E-15	C3H6_2	1.59231E-21
SI	9.98049E-08	C2SI1	1.02915E-15	C3H6_1	2.53376E-24
H1SI1	5.25792E-08	H6SI2	1.31302E-16	C2	1.05475E-24
H4SI1	1.16175E-08	C2H6	5.95508E-17	C3	2.51092E-25
C1H3	1.67072E-10	C2H1	1.49582E-17	C3H8	5.92461E-26
SI2	8.01027E-11	C1SI1	6.96977E-18	C4	1.00000E-30
C1SI2	6.87487E-11	C2H5	2.43303E-18	C4H12SI1	1.00000E-30
C2H2	3.82934E-11	C1H1	1.39138E-18	C5	1.00000E-30
SI3	1.48834E-11	C3H4_2	3.16405E-19		

Example: CVD Diamond Process

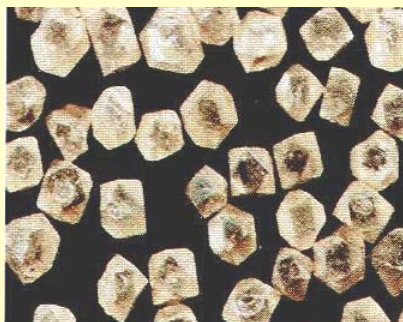
→ *Thermodynamics of Metastable Phase*

reactants : 99% H_2 + 1% CH_4

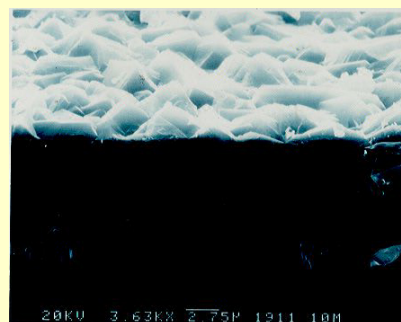


Precipitation of solid from chemical reactions

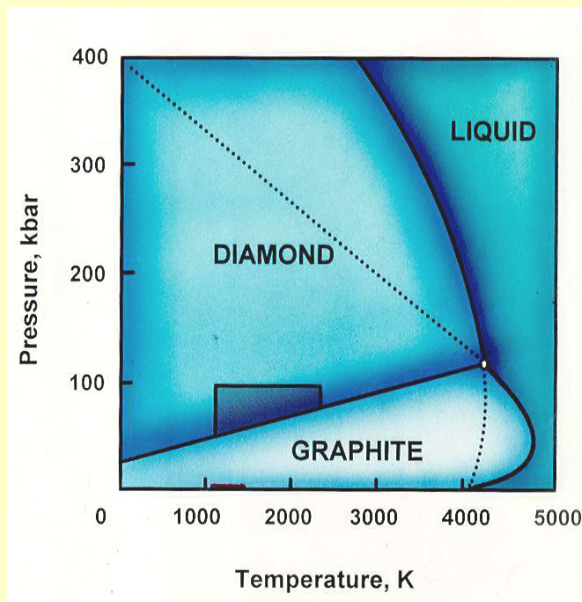
Synthetic Diamond



(a) Bulk (HPHT)



(b) Film (CVD)



1950s : General Electric

High Pressure and High Temperature
Synthesis of Diamond

1958 : Eversole (Union Carbide)

Diamond Growth on Diamond Seed by Thermal CVD
Very Low Growth Rate ($\text{\AA}/\text{h}$)
Codeposition of Graphite : Cyclic Process

1950 - 1970s : Angus & Coworkers

Similar to Eversole's results

1975 : Deryaguin's Group (USSR)

Gas Activation by Hot Filament
Dramatic Increase of Growth Rate ($\mu\text{m}/\text{h}$)
No Diamond Seed

1980s : NIRIM (Japan)

Gas Activation by Plasma