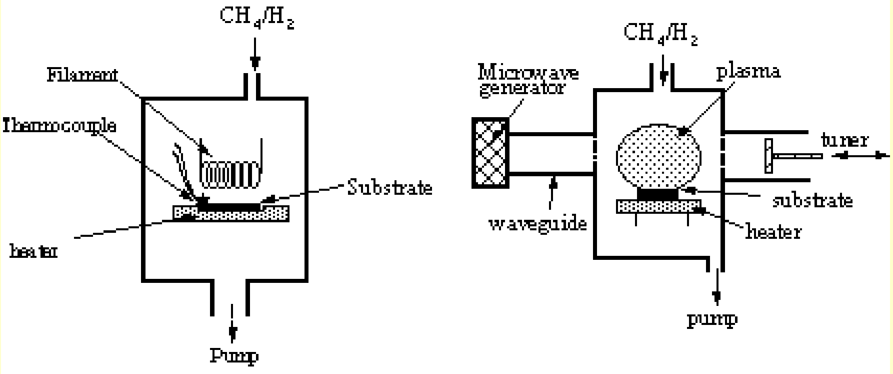
Thermodynamics of Materials

18th Lecture

2007. 5. 21 (Wednesday)

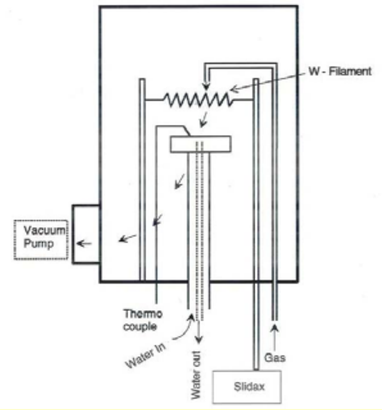
Low Pressure Synthesis of Diamond by Gas Activation



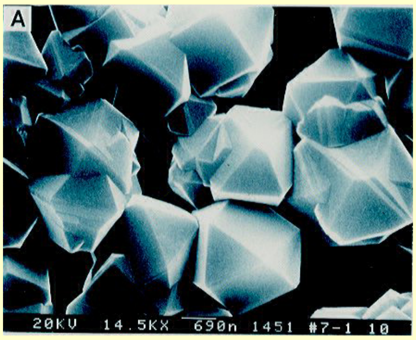
a) Hot Filament

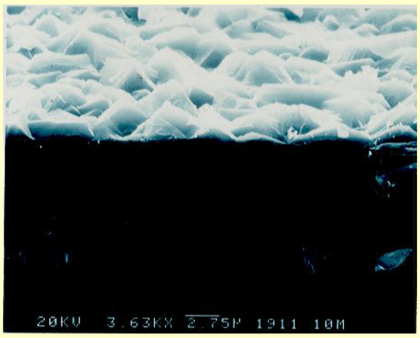
b) Microwave Plasma

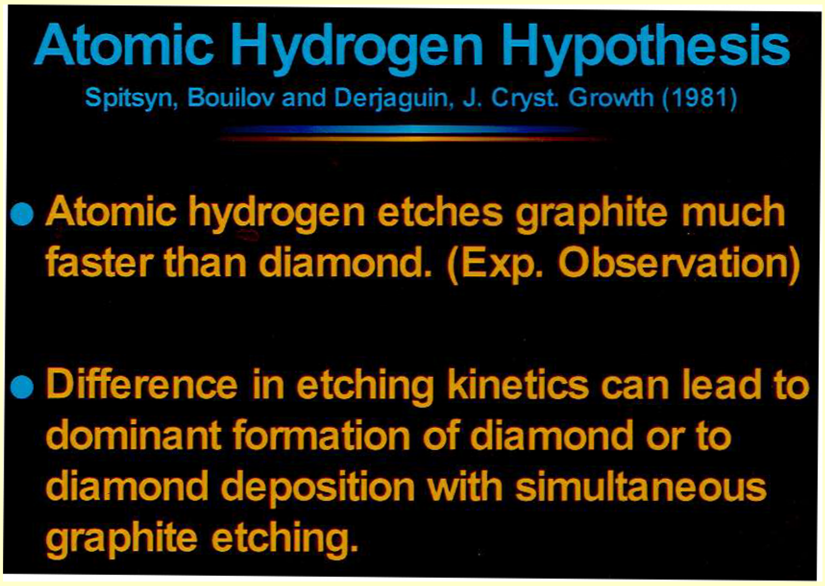
CVD Diamond



P = 20 ~ 100 Torr
T_f = 1900~2200°C
T_s = 800~1100°C
$CH_4 - H_2$: 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.

Review Papers on CVD Diamond (I)

1. J. C. Angus and C.C. Hayman
   "Low-Pressure, Metastable Growth of Diamond and "Diamondlike" Phases,"
   Science, 241 (1988) 913-921.

2. K.E. Spear
   "Diamond-Ceramic Coating of the Future,"
   J. Am. Ceram. Soc. 72[2] (1989) 171-191.

3. W.A. Yarbrough and R. Messier
   "Current Issues and Problems in the Chemical Vapor Deposition of Diamond,"
   Science, 247 (1990) 688-696.

Review Papers on CVD Diamond (II)

4. J.C. Angus, Y. Wang, M. Sunkara
   "Metastable Growth of Diamond and Diamond-Like Phases,"
   Annu. Rev. Mater. Sci. 21 (1991) 221-248.

5. R. J. Nemanich
   "Growth and Characterization of Diamond Thin Films,"
   Annu. Rev. Mater. Sci. 21 (1991) 535-558.

6. W.A. Yarbrough
   "Vapor-Phase-Deposited Diamond – Problems and Potential,"
   J. Am. Ceram. Soc. 75[12] (1992) 3179-3200.

Yarbrough, J. Am. Ceram. Soc. 75 (1992) 3179.

A popular suggestion, originally made by pioneering Soviet Union researchers [64,65], is that atomic hydrogen acts as a means of gasifying or etching graphite or graphitic carbon.

→ In the presence of atomic hydrogen, diamond is kinetically stable relative to graphite [66].

Despite its popularity, this particular approach is not without its problems. Diamond is deposited with the simultaneous gasification of graphite, and diamond can be synthesized with graphite as the only source of carbon. This has been demonstrated most clearly in Vakil's work [67].

CVD of pure carbon from a hydrocarbon can generally be written as a reaction of the form

$$C_xH_y \rightarrow \frac{y}{2}H_2 + xC_{solid} \qquad (3)$$

If an external supply of atomic hydrogen exists and it is presumed a major reactant driving the process, then Eq. (3) can be modified to be of the form

$$mH^o + C_xH_y \rightarrow \frac{y+m}{2}H_2 + xC_{solid} \qquad (4)$$

→ Fig. 4(a)

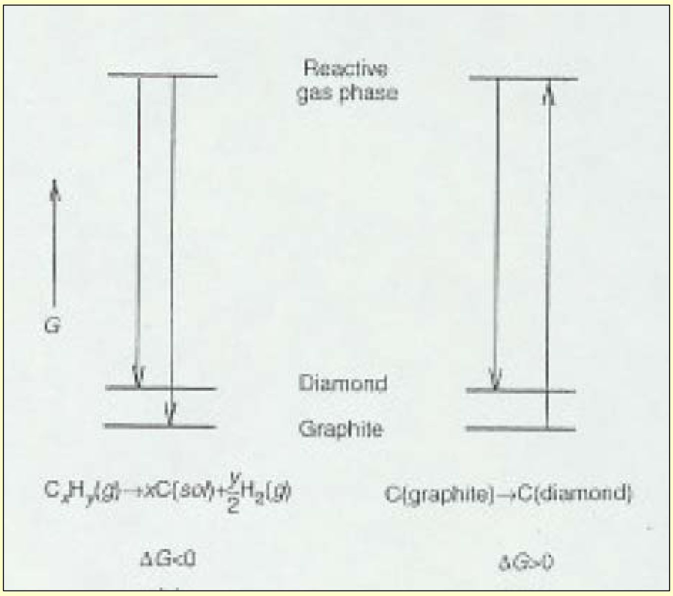


Fig. 4

The simultaneous deposition of diamond with the gasification of graphite using atomic hydrogen suggests that a more accurate schematic is that of Fig. 4(b), rather than that of Fig. 4(a), and that the vapor-phase deposition of diamond from graphite can be described as a sequence of two steps:

$$yH^{o} + xC_{graphite} \rightarrow C_xH_y \qquad (5)$$

(gasification of graphite)

$$mH^{o} + C_xH_y \rightarrow \frac{y+m}{2}H_2 + xC_{diamond} \qquad (6)$$

(diamond deposition)

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.

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

In case of graphite etching

Graphite Etching $\mu_C^{gas} < \mu_C^{graphite}$

Graphite vs Diamond $\mu_C^{graphite} < \mu_C^{diamond}$

$\mu_C^{gas} < \mu_C^{graphite} < \mu_C^{diamond}$ →**Diamond Etching**

If graphite etches by atomic hydrogen, less stable diamond should etch also by atomic hydrogen.

In case of diamond deposition

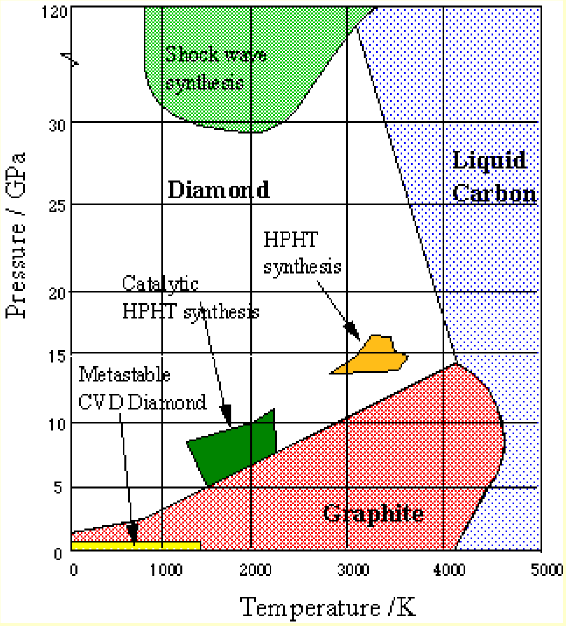
Diamond Deposition $\mu_C^{gas} > \mu_C^{diamond}$

Graphite vs Diamond $\mu_C^{graphite} < \mu_C^{diamond}$

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

→ **Graphite Deposition**

If less stable diamond deposits, stable graphite should deposit also.



CVD Diamond Process

→ *Thermodynamics of Metastable Phase*

reactants : $99\%H_2 + 1\%CH_4$

$$\mathbf{CH_4 + H_2 \rightarrow C_s + CH + CH_2 + \ldots}$$

Precipitation of solid from chemical reactions

$$\mathbf{CH_4 + H_2 \rightarrow C_s + CH + CH_2 + \ldots}$$

1. **Free Energy Change between Initial and Final States**

$$\Delta G^{\text{initial}\rightarrow\text{final}} = G^{\text{final}} - G^{\text{initial}}$$

2. **Driving Force for Forward Chemical Reactions**

$$\Delta\mu^{\text{reactants}\rightarrow\text{products}} = \sum \mu_i^{\text{products}} - \sum \mu_i^{\text{reactants}}$$

3. **Chemical Potential Difference of C between gas and solid**

$$\Delta\mu_C^{gas\rightarrow solid} = \mu_C^{gas} - \mu_C^{solid} = -RT\ln\left(\frac{P_C^{gas}}{P_C^{solid}}\right)$$

Driving force for deposition of diamond?

Gas phase equilbrium

$\Rightarrow$ $C^* + C_2H_2^* + C_2H^* + CH_4^* + CH_3^* + C_2H_4^* + \ldots$

Final equilbrium

$\Rightarrow$ $C^{eq} + C_2H_2^{eq} + C_2H^{eq} + CH_4^{eq} + CH_3^{eq} + C_2H_4^{eq} + \ldots +$ *graphite*

Metastable equilbrium

$\Rightarrow$ $C^{eq,d} + C_2H_2^{eq,d} + C_2H^{eq,d} + CH_4^{eq,d} + CH_3^{eq,d} + C_2H_4^{eq,d} + \ldots +$ *diamond*

$\Delta\mu_C^{gas\rightarrow gra} = -RT\ln\left(\frac{P_{C^*}}{P_{C^{eq}}}\right)$: *driving force for deposition of graphite*

$\Delta\mu_C^{gas\rightarrow dia} = -RT\ln\left(\frac{P_{C^*}}{P_{C^{eq,d}}}\right)$: *driving force for deposition of diamond*

$1\% CH_4 - 99\% H_2$

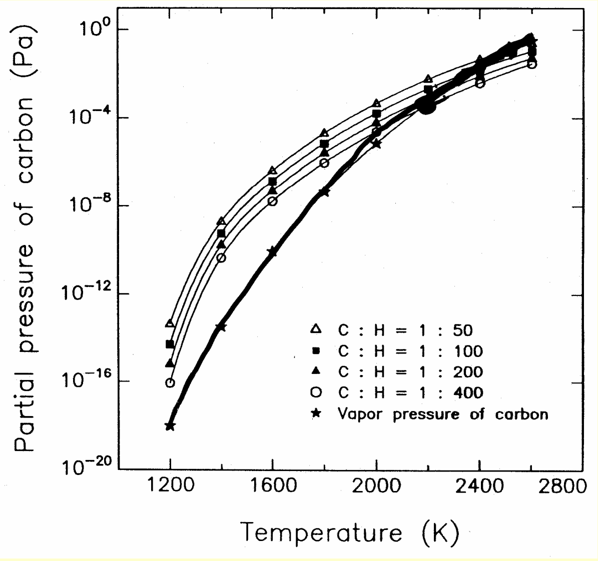
$1200\ K, \quad 2700\ Pa$

$$\alpha = \frac{P^{*}_{gas}}{P^{eq}_{dia}} = 11.9$$

$$\Delta\mu^{gas \to dia} = -4.02 \times 10^{-20}\ J/atom$$

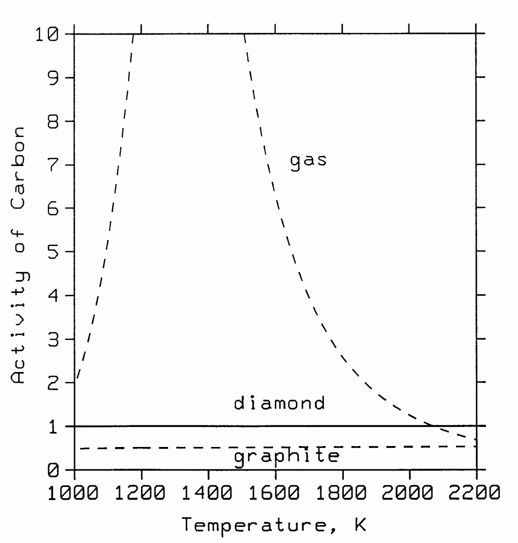
$$\Delta\mu^{gas \to gra} = -5.14 \times 10^{-20}\ J/atom$$

$$\Delta\mu^{dia \to gra} = -1.12 \times 10^{-20}\ J/atom$$

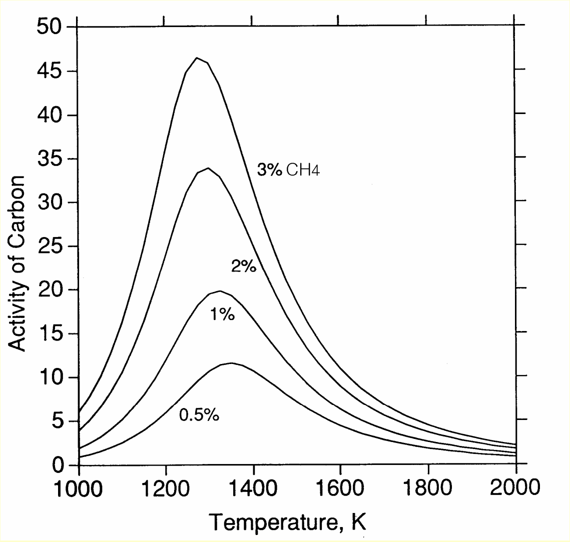


Hwang et al. *Diamond Relat. Mater.*, vol. 3 (1993) 163

Activity of Carbon at $1\%CH_4$-$99\%H_2$, 2700 Pa

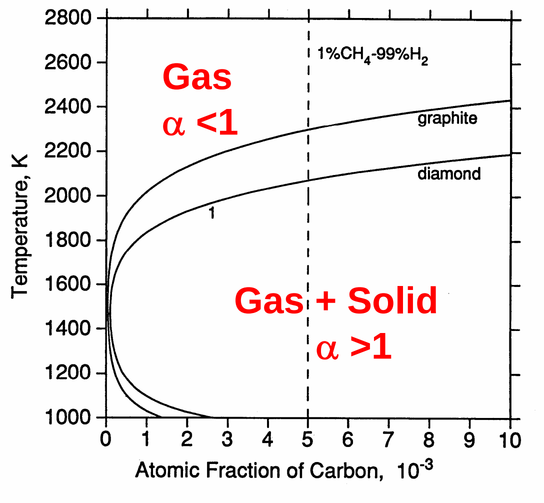


Hwang et al.
J. Crystal Growth
160 (1996) 87



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

CVD phase diagram of C-H system at 2700 Pa



Hwang et al.
J. Crystal Growth
160 (1996) 98

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1. N.M. Hwang, J.H. Hahn and G.W. Bahng,
"Thermodynamic Approach to the C-H-O Deposition Diagram in the Diamond Chemical Vapor Deposition Process"
Diamond Relat. Mater., vol. 3 (1993) 163-167.

2. N.M. Hwang and D.Y. Yoon
"Driving Force for Deposition in the Chemical Vapor Deposition Process,"
J. Mater. Sci. Lett. vol. 13 (1994) 1437-1439.

3. N.M. Hwang
"Thermodynamic Analysis of the Chemical Vapor Deposition of Diamond in the C-H, C-O and C-H-O Systems,"
J. Crystal Growth, vol. 135 (1994) 165-171.

4. N.M. Hwang and D.Y. Yoon
"Thermodynamic Approach to the Chemical Vapor Deposition Process,"
J. Crystal Growth, vol. 143 (1994) 103-109.

Calculating Iso-activity Lines with Diamond as a Reference State

```
$TC
go ges → Go to Gibbs Energy System Module (g)
read chd →Read the data file saved with a file name of chd in the GES module

go poly-3 → Go to Poly-3 modules (p-3)
set-condition (s-c) t= 1200 p=2700  x(c)=0.0049261  n = 1
→ Set the thermodynamic condition so that the degree of freedom may be zero.

set-automatic-starting value (s-a-s)
Yes (Y)
compute-equilibrium (c-e)
set-reference-state (s-r-s) c diamond ,,
change-status (c-st) phase (p) c_s=suspend
change-status (c-st) phase (p) graphite=suspend
change-status (c-st) phase (p) diamond=suspend
set- axis-value 2 t 1000 2800 → Designate y axis and its range

list-equilibrium (l-e)
TERMINAL
VWCs

compute-equilibrium (c-e)
add
set-condition X(c)=none, acr(c)=1
compute-equilibrium
add
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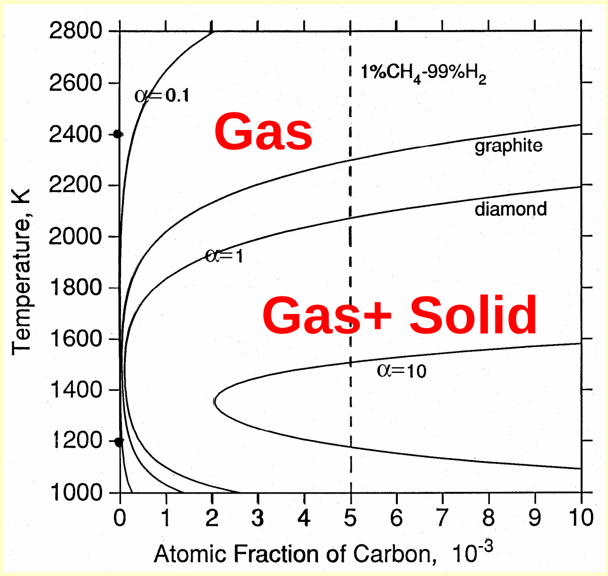
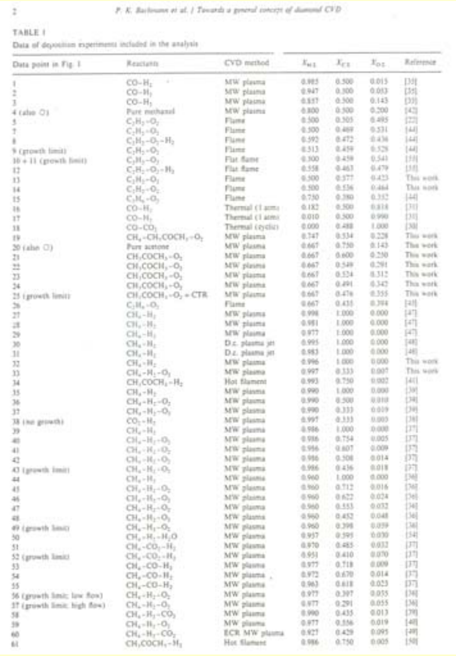


Hwang et al.
J. Crystal Growth
160 (1996) 87

Diamond Deposition Diagram (Bachman Diagram)

Experimental Observations and Thermodynamic Approach



2 P. K. Bachmann et al. / Towards a general concept of diamond CVD

TABLE I

Data of deposition experiments included in the analysis

Data point in Fig. 1	Reactants	CVD method	X_{H}	X_{C}	X_{O}	Reference
1	CO–H_2	MW plasma	0.985	0.500	0.015	[35]
2	CO–H_2	MW plasma	0.947	0.500	0.053	[35]
3	CO–H_2	MW plasma	0.857	0.500	0.143	[33]
4 (also ○)	Pure methanol	MW plasma	0.800	0.500	0.200	[42]
5	C_2H_2–O_2	Flame	0.500	0.505	0.495	[22]
7	C_2H_2–O_2	Flame	0.500	0.469	0.531	[44]
8	C_2H_2–O_2–H_2	Flame	0.592	0.472	0.436	[44]
9 (growth limit)	C_2H_2–O_2	Flame	0.513	0.459	0.528	[44]
10 + 11 (growth limit)	C_2H_2–O_2	Flat flame	0.500	0.459	0.541	[33]
12	C_2H_2–O_2–H_2	Flat flame	0.558	0.463	0.479	[33]
13	C_2H_2–O_2	Flame	0.500	0.577	0.423	This work
14	C_2H_2–O_2	Flame	0.500	0.536	0.464	This work
15	C_2H_4–O_2	Flame	0.750	0.380	0.352	[44]
16	CO–H_2	Thermal (1 atm)	0.182	0.500	0.818	[31]
17	CO–H_2	Thermal (1 atm)	0.010	0.500	0.990	[31]
18	CO–CO_2	Thermal (cyclic)	0.000	0.488	1.000	[30]
19	CH_4–CH_3COCH_3–O_2	MW plasma	0.747	0.534	0.228	This work
20 (also □)	Pure acetone	MW plasma	0.667	0.750	0.143	This work
21	CH_3COCH_3–O_2	MW plasma	0.667	0.600	0.250	This work
22	CH_3COCH_3–O_2	MW plasma	0.667	0.549	0.291	This work
23	CH_3COCH_3–O_2	MW plasma	0.667	0.524	0.312	This work
24	CH_3COCH_3–O_2	MW plasma	0.667	0.491	0.342	This work
25 (growth limit)	CH_3COCH_3–O_2 + CTR	MW plasma	0.667	0.476	0.355	This work
26	C_2H_4–O_2	Flame	0.667	0.435	0.394	[45]
27	CH_4–H_2	MW plasma	0.998	1.000	0.000	[47]
28	CH_4–H_2	MW plasma	0.981	1.000	0.000	[47]
29	CH_4–H_2	MW plasma	0.977	1.000	0.000	[47]
30	CH_4–H_2	D.c. plasma jet	0.995	1.000	0.000	[48]
31	CH_4–H_2	D.c. plasma jet	0.983	1.000	0.000	[48]
32	CH_4–H_2	MW plasma	0.996	1.000	0.000	This work
33	CH_4–H_2–O_2	MW plasma	0.997	0.333	0.007	This work
34	CH_3COCH_3–H_2	Hot filament	0.993	0.750	0.002	[41]
35	CH_4–H_2	MW plasma	0.990	1.000	0.000	[39]
36	CH_4–H_2–O_2	MW plasma	0.990	0.500	0.010	[39]
37	CH_4–H_2–O_2	MW plasma	0.990	0.333	0.019	[39]
38 (no growth)	CO_2–H_2	MW plasma	0.997	0.333	0.003	[38]
39	CH_4–H_2	MW plasma	0.986	1.000	0.000	[37]
40	CH_4–H_2–O_2	MW plasma	0.986	0.754	0.005	[37]
41	CH_4–H_2–O_2	MW plasma	0.986	0.607	0.009	[37]
42	CH_4–H_2–O_2	MW plasma	0.986	0.508	0.014	[37]
43 (growth limit)	CH_4–H_2–O_2	MW plasma	0.986	0.436	0.018	[37]
44	CH_4–H_2	MW plasma	0.960	1.000	0.000	[36]
45	CH_4–H_2–O_2	MW plasma	0.960	0.712	0.016	[36]
46	CH_4–H_2–O_2	MW plasma	0.960	0.622	0.024	[36]
47	CH_4–H_2–O_2	MW plasma	0.960	0.553	0.032	[36]
48	CH_4–H_2–O_2	MW plasma	0.960	0.452	0.048	[36]
49 (growth limit)	CH_4–H_2–O_2	MW plasma	0.960	0.398	0.059	[36]
50	CH_4–H_2–H_2O	MW plasma	0.957	0.595	0.030	[34]
51	CH_4–CO_2–H_2	MW plasma	0.970	0.485	0.032	[37]
52 (growth limit)	CH_4–CO_2–H_2	MW plasma	0.951	0.410	0.070	[37]
53	CH_4–CO–H_2	MW plasma	0.977	0.718	0.009	[37]
54	CH_4–CO–H_2	MW plasma	0.972	0.670	0.014	[37]
55	CH_4–CO–H_2	MW plasma	0.963	0.618	0.023	[37]
56 (growth limit; low flow)	CH_4–H_2–O_2	MW plasma	0.977	0.397	0.035	[36]
57 (growth limit; high flow)	CH_4–H_2–O_2	MW plasma	0.977	0.291	0.055	[36]
58	CH_4–H_2–CO_2	MW plasma	0.990	0.435	0.013	[39]
59	CH_4–H_2–O_2	MW plasma	0.977	0.556	0.019	[40]
60	CH_4–H_2–CO_2	ECR MW plasma	0.927	0.429	0.095	[49]
61	CH_3COCH_3–H_2	Hot filament	0.986	0.750	0.005	[50]

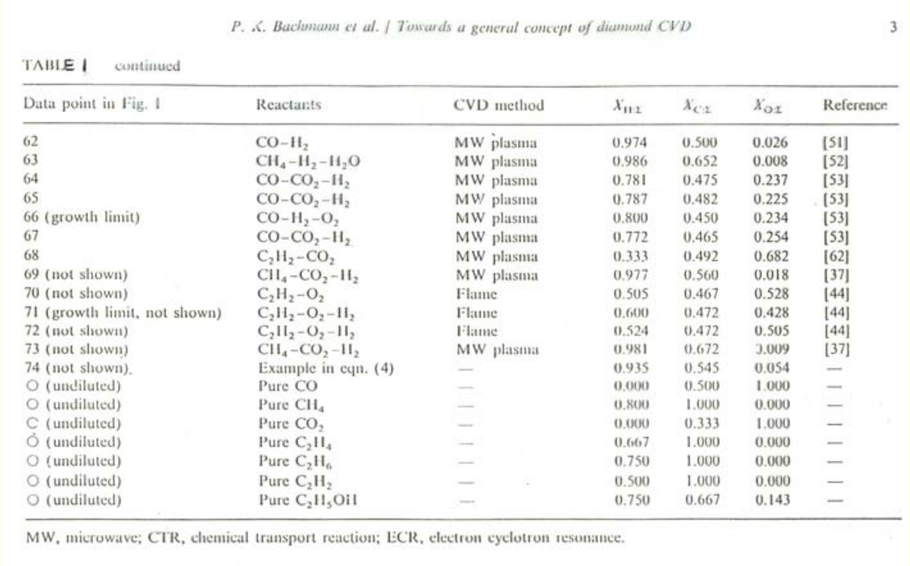
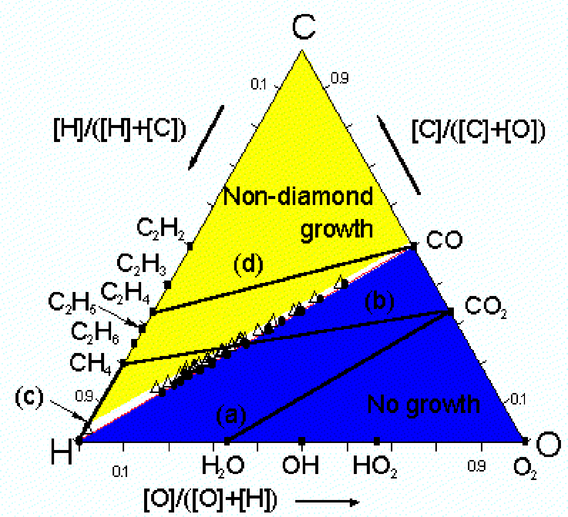


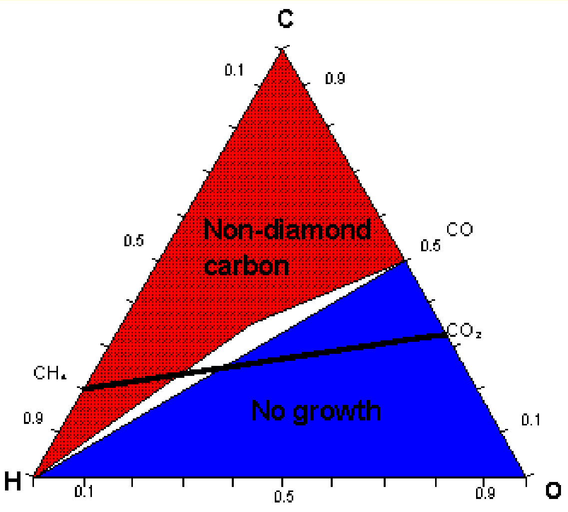
TABLE I continued

Data point in Fig. 1	Reactants	CVD method	$X_{H\Sigma}$	$X_{C\Sigma}$	$X_{O\Sigma}$	Reference
62	$CO-H_2$	MW plasma	0.974	0.500	0.026	[51]
63	$CH_4-H_2-H_2O$	MW plasma	0.986	0.652	0.008	[52]
64	$CO-CO_2-H_2$	MW plasma	0.781	0.475	0.237	[53]
65	$CO-CO_2-H_2$	MW plasma	0.787	0.482	0.225	[53]
66 (growth limit)	$CO-H_2-O_2$	MW plasma	0.800	0.450	0.234	[53]
67	$CO-CO_2-H_2$	MW plasma	0.772	0.465	0.254	[53]
68	$C_2H_2-CO_2$	MW plasma	0.333	0.492	0.682	[62]
69 (not shown)	$CH_4-CO_2-H_2$	MW plasma	0.977	0.560	0.018	[37]
70 (not shown)	$C_2H_2-O_2$	Flame	0.505	0.467	0.528	[44]
71 (growth limit, not shown)	$C_2H_2-O_2-H_2$	Flame	0.600	0.472	0.428	[44]
72 (not shown)	$C_2H_2-O_2-H_2$	Flame	0.524	0.472	0.505	[44]
73 (not shown)	$CH_4-CO_2-H_2$	MW plasma	0.981	0.672	0.009	[37]
74 (not shown).	Example in eqn. (4)	—	0.935	0.545	0.054	—
○ (undiluted)	Pure CO	—	0.000	0.500	1.000	—
○ (undiluted)	Pure CH_4	—	0.800	1.000	0.000	—
○ (undiluted)	Pure CO_2	—	0.000	0.333	1.000	—
○ (undiluted)	Pure C_2H_4	—	0.667	1.000	0.000	—
○ (undiluted)	Pure C_2H_6	—	0.750	1.000	0.000	—
○ (undiluted)	Pure C_2H_2	—	0.500	1.000	0.000	—
○ (undiluted)	Pure C_2H_5OH	—	0.750	0.667	0.143	—

MW, microwave; CTR, chemical transport reaction; ECR, electron cyclotron resonance.



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

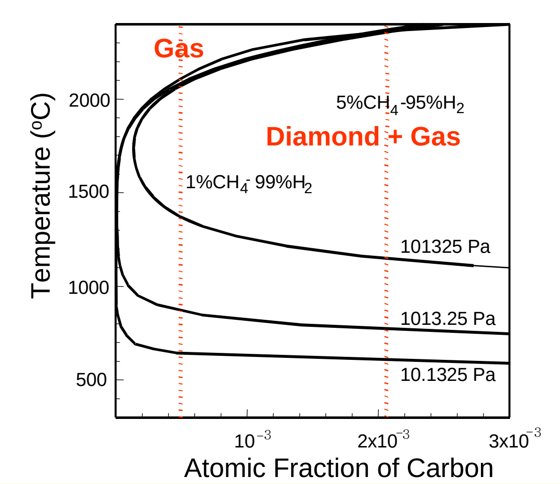


Bachmann C-H-O diamond deposition phase diagram.

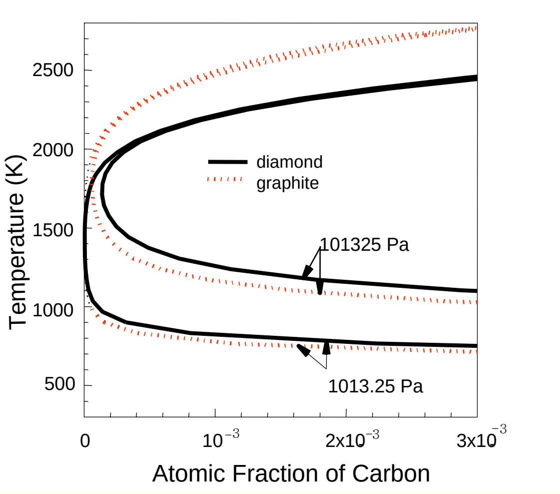
Bachmann *et al*, Diamond Relat. Mater. 1 (1991) 1
Petherbridge et al. *J. Appl. Phys.*, 89 (2001) 5219

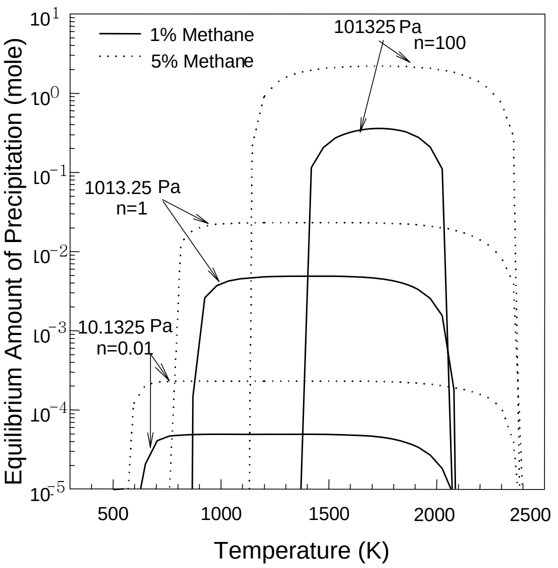
Lower Limit of Deposition Temperature of CVD Diamond in the C-H System

Effect of Pressure on the Lower Limit of Deposition Temperature



Gueroudji and Hwang, Diamond Relat. Mater. 9 (2000) 205





1% Methane
5% Methane
101325 Pa
n=100
1013.25 Pa
n=1
10.1325 Pa
n=0.01
Equilibrium Amount of Precipitation (mole)
Temperature (K)
10^1
10^0
10^{-1}
10^{-2}
10^{-3}
10^{-4}
10^{-5}
500
1000
1500
2000
2500