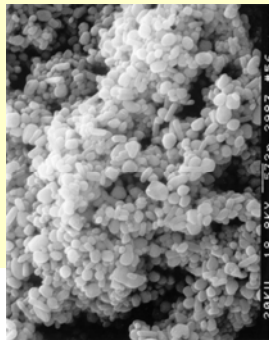


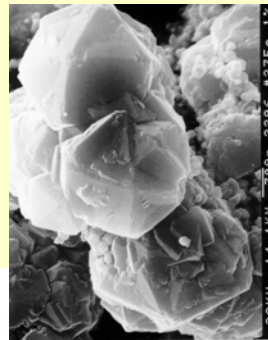
Thermodynamics of Materials

21th Lecture
2008. 6. 2 (Monday)

Deposition Behavior between Conducting and Insulating Blocks beneath Fe Substrate



(a) Fe substrate



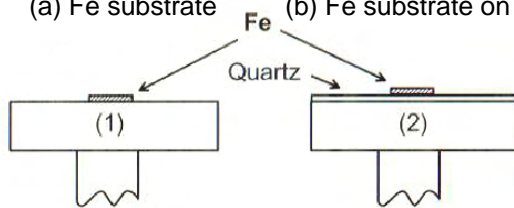
(b) Fe substrate on quartz

$$T_{s,1} = T_{s,2} = 1263 \text{ K}$$

$$T_{f,1} = 2473 \text{ K}, \quad T_{f,2} = 2323 \text{ K}$$

Deposition Time = 2 hr

(* s : substrate f : filament)



Charge stabilizes diamond.

Charge induces self-assembly.

Effect of Negative Charge on Stability of Diamond Nanoparticle (Ab-initio Calc.)

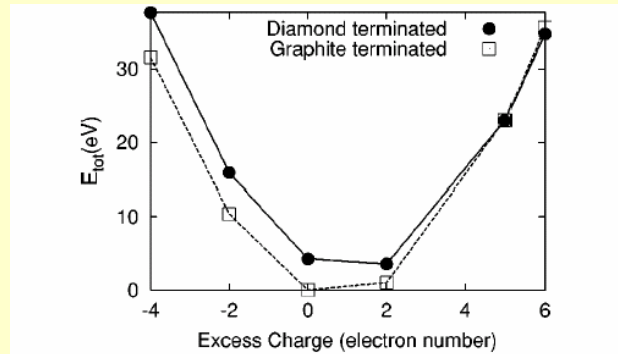
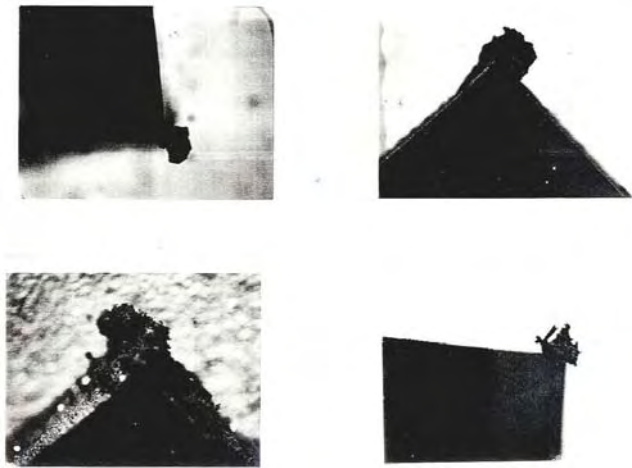


FIG. 3. Total energy of diamond terminated and graphite terminated cases with respect to various charging states. The abscissa is the excess charge in electron numbers and the ordinate is total energy with respect to that of charge-neutral graphite terminated case.

Park, Park, Hwang, Ihm, Tejima, Nakamura,
Phys. Rev. B 69 (2004) 195411

Experimental Facts implying that
the growth flux is electrically
charged.

Preferential formation of Soot at the Edge



These results imply that the growth source might be electrically charged.

Preferential Diamond Formation along scratches on Substrates

What would be the role of scratch?

Scratches are made by diamond paste.

→ Diamond debris

Scratches by SiC also induce preferential formation of diamonds.

→ Geometric effect

On the edge or on the groove?

Dennig et al., Appl. Phys. Lett. (1991)



Figure 3. Nucleation on pyramids etched into $\langle 100 \rangle$ high resistivity silicon, 15° tilt. Nucleation occurs along a path from lower left to upper right.



Figure 4. Enlargement of region shown in Fig. 3, 45° tilt showing nucleation on the tips of the pyramids. Note the unusual diffuse structural features on the pyramid tips in the path of nucleating particles.



Figure 5. Enhanced nucleation on edges, 15° tilt, showing a preference for nucleation on the more acutely angled edges.

In Fig. 5, V-grooves of increasing width (but constant depth) are etched into a silicon $\langle 100 \rangle$ surface, without using an abrasion treatment. Nucleation occurs preferentially on the edges of the V-grooves. There is roughly 8 times the nucleation density (particles/unit length) on the more acutely angled edges on the left, as compared to those on the right.

4. CONCLUSIONS

There is extensive use of surface abrasion procedures to enhance diamond nucleation, usually using diamond powder as the abrasive. The enhancement might arise from residual diamond powder, mechanical damage, and changes in the surface topography. We propose that at least part of this nucleation enhancement is due to a change in the surface

B. Hanuman and C. Chiriac, Surface growth of diamond crystals on the apex of silicon pyramids

the pyramids. One may even closely observe the high nucleation rate of diamond particles on all the apices

in Figs. 4(a) and 4(b). The substrate was not damaged with diamond paste prior to the fabrication of pyramids

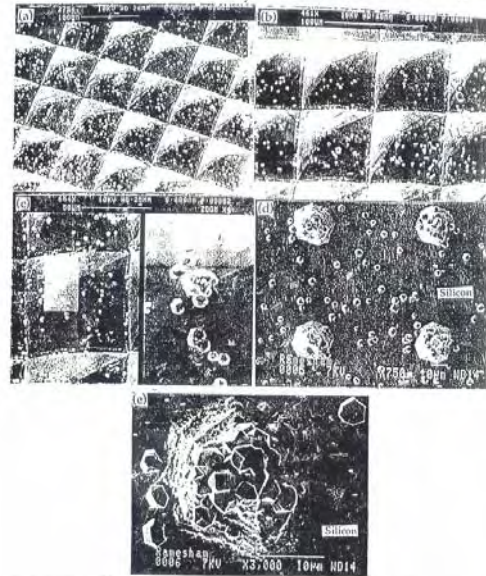


FIG. 4. Scanning electron micrographs of diamond growth on (a) sharp silicon pyramids, (b) magnified view of (a), (c) magnified view of sharp pyramid in (b) and also showing of an apex of pyramid in (c), (d) growth of diamond on flat apex of silicon pyramids, and (e) magnified view of sharp pyramid in (d).

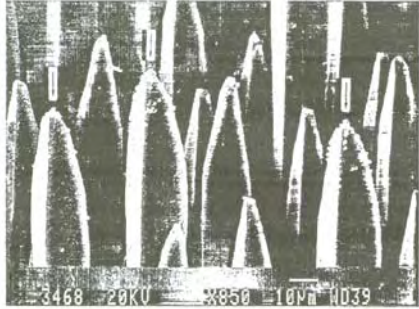
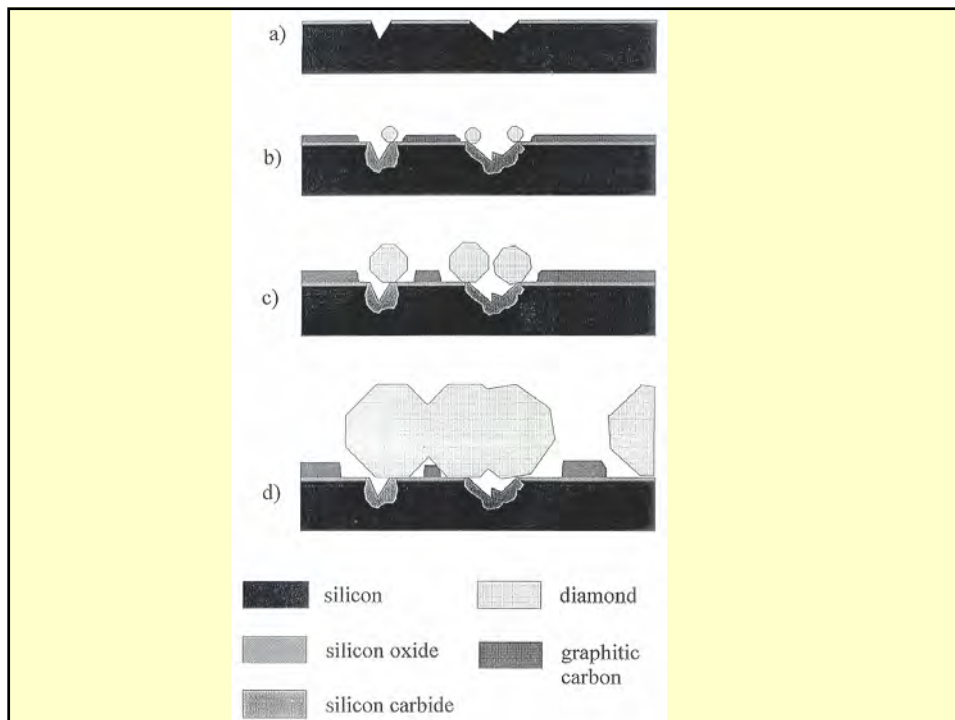


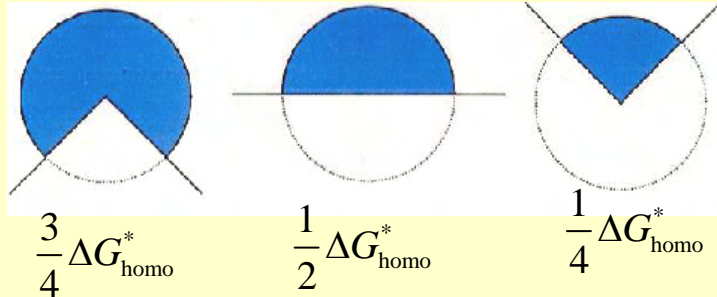
Fig. 3. Preferential deposition of diamond particles on the very ends and edges of tips and steps.



Fig. 4. A single-crystalline diamond particle on the very end of a tip. The arrow shows a (111) face of the particle seemingly perpendicular to the axis of the tip.



Effect of Substrate Geometry



Estimate the ratio of $I_{\text{homo}}/I_{\text{hetero}}$ for the three cases.
 the supersaturation ratio (α) = 10, $T = 1200 \text{ K}$
 $v = 3.41 \times 10^{-6} \text{ M}^3/\text{mole}$, $\gamma = 3.7 \text{ J/M}^2$

$$\frac{I_{\text{hetero}}}{I_{\text{homo}}} = \exp\left\{-\frac{1}{kT}(\Delta G_{\text{hetero}}^* - \Delta G_{\text{homo}}^*)\right\} \quad \Delta G_{\text{homo}}^* = \frac{16\pi v^2 \gamma^3}{3(RT \ln \alpha)^2}$$

Nucleation Rate (Heterogeneous)

$$\Delta G^* = \frac{16\pi v^2 \gamma^3}{3(RT \ln \alpha)^2} \quad v = 3.41 \times 10^{-6} \text{ M}^3/\text{mole}, \gamma = 3.7 \text{ J/M}^2$$

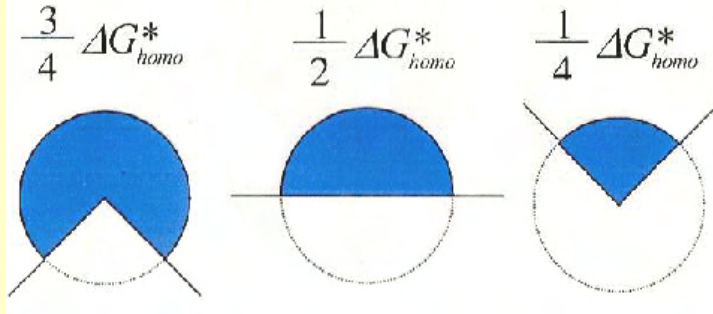
$$\alpha = 10, T = 1200 \text{ K} \quad R = Nk = N \times 1.38 \times 10^{-23} \text{ J/K} = 8.31 \text{ J/K}$$

$$\Delta G^* = \frac{2.96 \times 10^{-8}}{1.58 \times 10^9} = 1.87 \times 10^{-17} \text{ J}$$

$$\frac{I_{\text{hetero}}}{I_{\text{homo}}} = \exp\left\{\frac{\Delta G_{\text{homo}}^*}{4kT}\right\}, \exp\left\{\frac{\Delta G_{\text{homo}}^*}{2kT}\right\}, \exp\left\{\frac{3\Delta G_{\text{homo}}^*}{4kT}\right\}$$

10^{123}	10^{245}	10^{368}
1	10^{122}	10^{245}

Nucleation Rate (Heterogeneous)



$\alpha = 10$	$\frac{I_{\text{hetero}}}{I_{\text{homo}}} = 10^{123}$	10^{245}	10^{368}
	1	10^{122}	10^{245}
$\alpha = 100$	$\frac{I_{\text{hetero}}}{I_{\text{homo}}} = 10^{31}$	10^{62}	10^{93}
	1	10^{31}	10^{62}

All the puzzling phenomena are solved when negatively-charged diamond clusters are formed in the gas phase and they deposit as diamond films.

Puzzling Phenomena in Diamond CVD (Implication of Charge)

1. Bias Effect

(Sawabe et al. Thin Solid Film 137 (1986) 89)

2. Preferential formation on the convex edge

(Dennig et al. Appl. Phys. Lett. 59 (1991) 1562)

3. Preferential formation of soot on the Fe edge

4. Halogen elements replace the gas activation

(Patterson et al. Diamond Relat. Mater. 1 (1992) 768)

5. High growth rate without gas phase nucleation

→ In analogy with electrodeposition

6. Enhanced diamond formation on soot when the iron substrate is electrically insulated.

Puzzling Phenomena in Diamond CVD (Implication of Gas Phase Nucleation)

1. Deposition of graphitic soot on the iron substrate

2. Microcrystalline or nanocrystalline diamond Ball-like diamond, Cauliflower structure

3. All kinds of carbon allotropes are favorable for diamond formation.

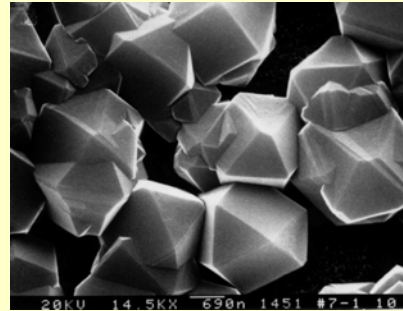
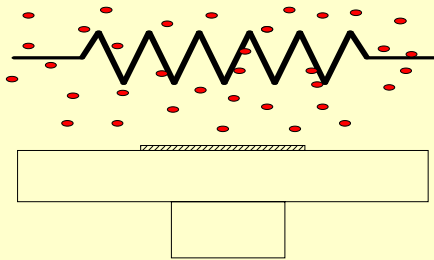
4. Diamond deposition on graphite with simultaneous etching of graphite

5. Confirmation of gas phase nucleation of diamond powder particles

(Mitura, J Crystal Growth, 80 (1987) 417)

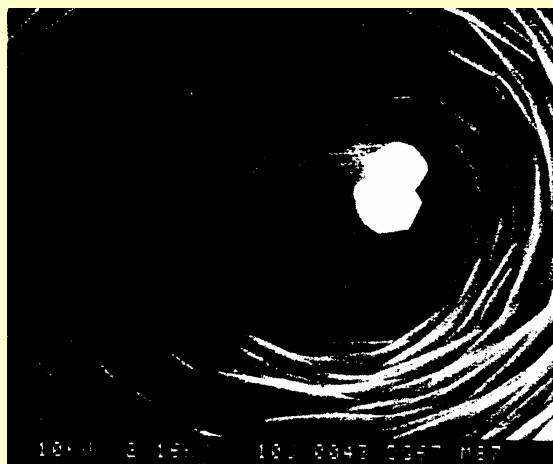
All puzzling phenomena can be explained only when we assume that charged clusters are formed in the gas phase and deposit as diamond films.

Invisible Charged Clusters of ~ 1 nm



Who would believe that diamond crystals grow by charged gas phase nuclei?

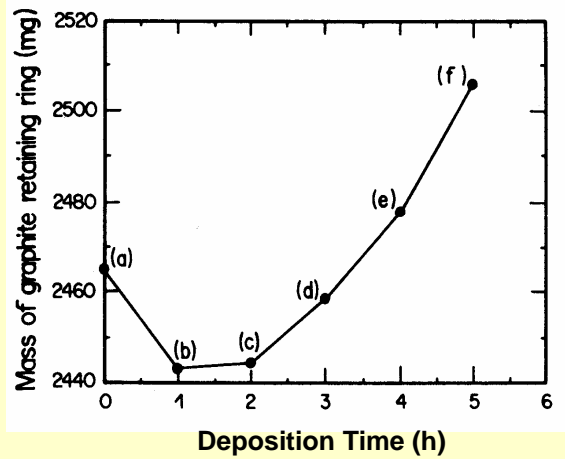
Diamond Deposition on the Etch Pit of Graphite Substrate



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

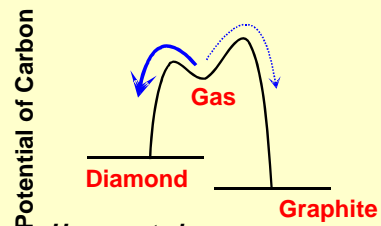
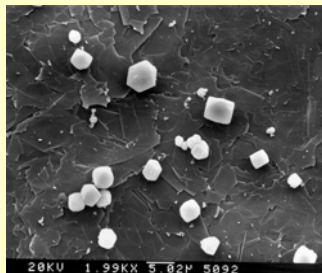
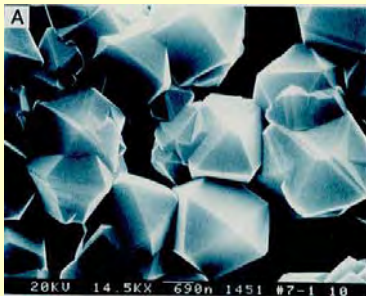
Weight Change of Graphite Ring

0.5%CH₄-H₂, 80 Torr. T_{sub}= 870 °C

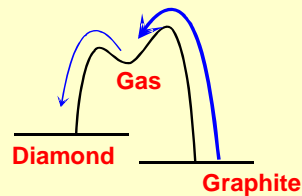


M. C. Salvadori et al, *J. Electrochem. Soc.*, 139 (1992) 558

Thermodynamic Paradox in CVD Diamond Growth

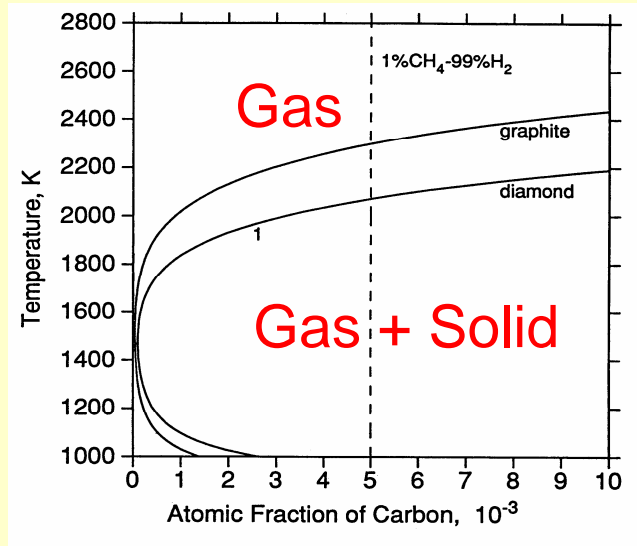


Hwang et al.
Diamond Relat. Mater. 1 (1992) 9
J. Crystal Growth 160 (1996) 87

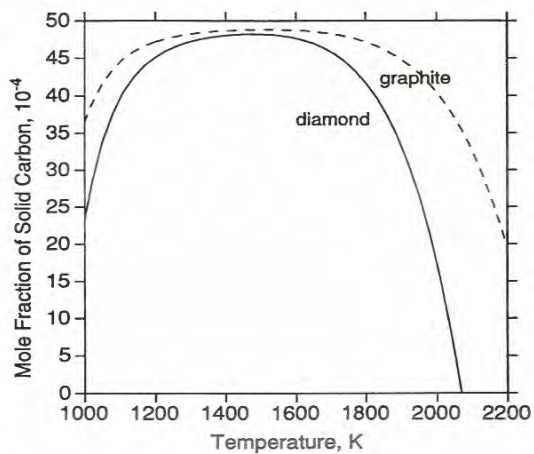


Simultaneous Diamond Deposition
 and Graphite Etching

CVD phase diagram of C-H system at 2700 Pa

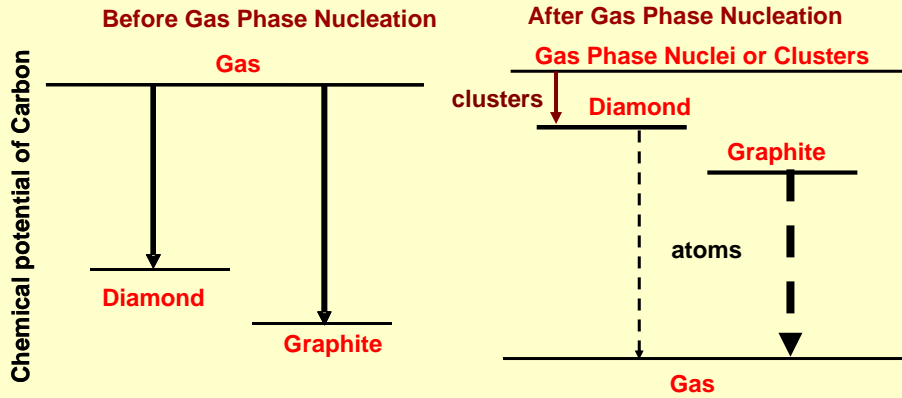


Equilibrium Amount of Precipitated Solid Carbon



The thermodynamic paradox can be avoided if diamond deposits by clusters.
Hwang et al. *J. Crystal Growth*, 160 (1996) 87 : *Diamond growth by clusters*

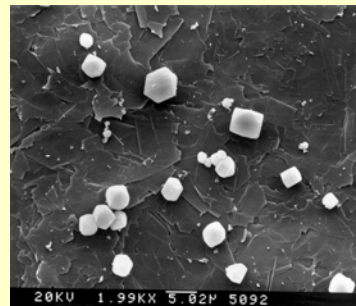
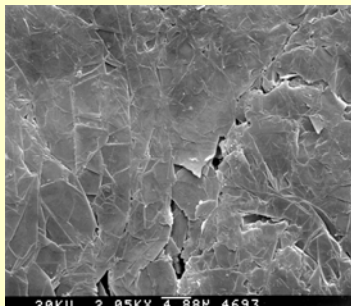
Paradox-free direction of carbon flux



Paradox or Diamond Deposition by Clusters ?

Simultaneous Diamond Deposition and Graphite Etching

T_F : 2100°C, T_s : 1050°C, 1% CH₄ - H₂, 2h



before experiment



after experiment

43.21 mg

37.06 mg (6.15 mg)

Thermodynamic approach to the paradox of diamond formation with simultaneous graphite etching in the low pressure synthesis of diamond

Nong M. Hwang ^{a,*}, Duk Y. Yoon ^b

^a Korea Research Institute of Standards and Science, P.O. Box 102, Yusong-gu, Daedok Science Town, Daejeon, 305-600, South Korea

^b Korea Advanced Institute of Science and Technology, 373-1 Gusung-dong, Yusung-gu, Daejeon, 305-701, South Korea

Received 23 March 1995; accepted 8 September 1995

Abstract

In spite of the critical handicap from the thermodynamic point of view, the atomic hydrogen hypothesis is strongly supported by experimental observations of diamond deposition with simultaneous graphite etching. Thermodynamic analysis of the C-H system showed that at ~ 1500 K, carbon solubility in the gas phase is minimal and thus, the equilibrium fraction of solid carbon is maximal. Depending on whether gas phase nucleation takes place or not, the driving force is for deposition or for etching of solid carbon below ~ 1500 K for the input gas of the typical mixture of 1% CH₄-99% H₂. The previous observation of etching of the graphite substrate is not expected unless solid carbon precipitated in the gas phase. By rigorous thermodynamic analysis of the previous experimental observations of diamond deposition with simultaneous graphite etching, we suggested that the previous implicit assumption that diamond deposits by an atomic unit should be the weakest point leading to the thermodynamic paradox. The experimental observations could be successfully explained without violating thermodynamics by assuming that the diamond phase had nucleated in the gas phase as fine clusters.

Charged cluster model in the low pressure synthesis of diamond

Nong M. Hwang ^{a,*}, Jun H. Hahn ^a, Duk Y. Yoon ^b

^a Korea Research Institute of Standards and Science, P.O. Box 102, Yusung-gu, Daedok Science Town, Daejeon 305-600, South Korea

^b Korea Advanced Institute of Science and Technology, 373-1, Kusung-dong, Yusung-gu, Daejeon 305-701, South Korea

Received 6 June 1995; accepted 23 October 1995

Abstract

Gas activation makes possible the synthesis of diamond without codeposition of graphite in the chemical vapor deposition (CVD) diamond process, though its exact role is not clear. Charged carbon nuclei clusters, which are expected to form in the gas phase, are suggested to be responsible for the formation of diamond. When the carbon cluster is sufficiently small, the capillary pressure built up inside the cluster can be high enough to make diamond more stable than graphite. The number of carbon atoms in the cluster that reverses the stability between diamond and graphite increases sensitively with increasing surface energy ratio of graphite to diamond. The gas activation process produces charges such as electrons and ions, which are energetically strong heterogeneous nucleation sites for the supersaturated carbon vapor, leading to the formation of charged nuclei clusters. Once the carbon clusters are charged, the surface energy of diamond can be reduced by electrocapillarity while that of graphite cannot because diamond is dielectric and graphite is conducting. The evolution of graphitic soot and diamond on the iron and the silicon substrates, respectively, can be approached based on the charged cluster model. The charged cluster model is further supported by the result that the insulating quartz block beneath the iron substrate enhances the initiation of diamond on soot.

Charged Cluster Model

- 1. Negatively charged clusters are formed in the gas phase of hot filament CVD diamond process.***
- 2. Their size are of a few nanometers and invisible, suspended in the gas phase like colloidal particles.***
- 3. These clusters have the diamond structure.
The diamond stability comes from the two factors: capillary pressure and electrical double layer.***
- 4. If they lose charge, they will transform to graphite.***
- 5. When CCs approach the Fe substrate of the high charge transfer rate, they lose charge just before landing.***

Charged Cluster Model

- 6. After losing charge, they lose the diamond stability coming from the electrical double layer and instantly transform into graphite clusters.***
- 7. These neutral graphite clusters undergo random Brownian coagulation, producing soot on Fe.***
- 8. When CCs approach the Si substrate, they retain charge and maintain the diamond structure.***
- 9. They undergo repulsion dominant sedimentation and result in the highly ordered packing and self-assembly combined with epitaxial recrystallization, growing into diamond crystals.***