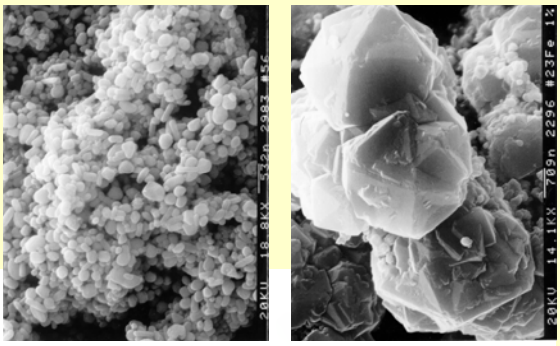
Thermodynamics of Materials

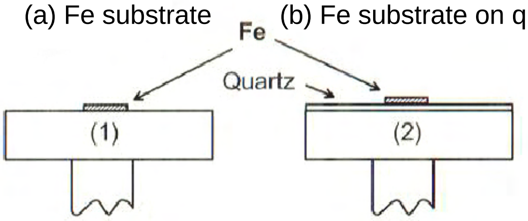
21th Lecture

2008. 6. 2 (Monday)

Deposition Behavior between Conducting and Insulating Blocks beneath Fe Substrate



(a) Fe substrate (b) Fe substrate on quartz



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

$T_{f,1} = 2473$ K, $T_{f,2} = 2323$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.)

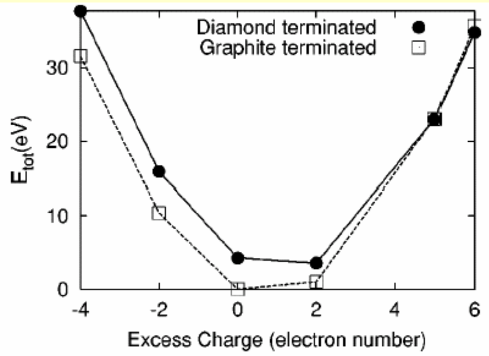
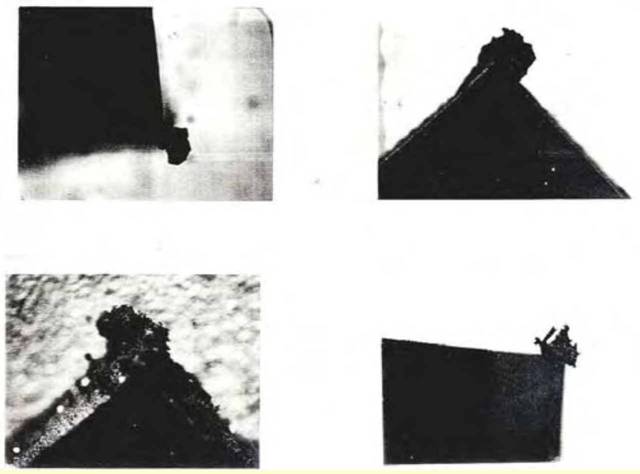


FIG. 3. Total energy of diamond terminated and graphite terminated cases with respect to various charging states. The abscissa is the excess charge in electron numbers and the ordinate is total energy with respect to that of charge-neutral graphite terminated case.

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)

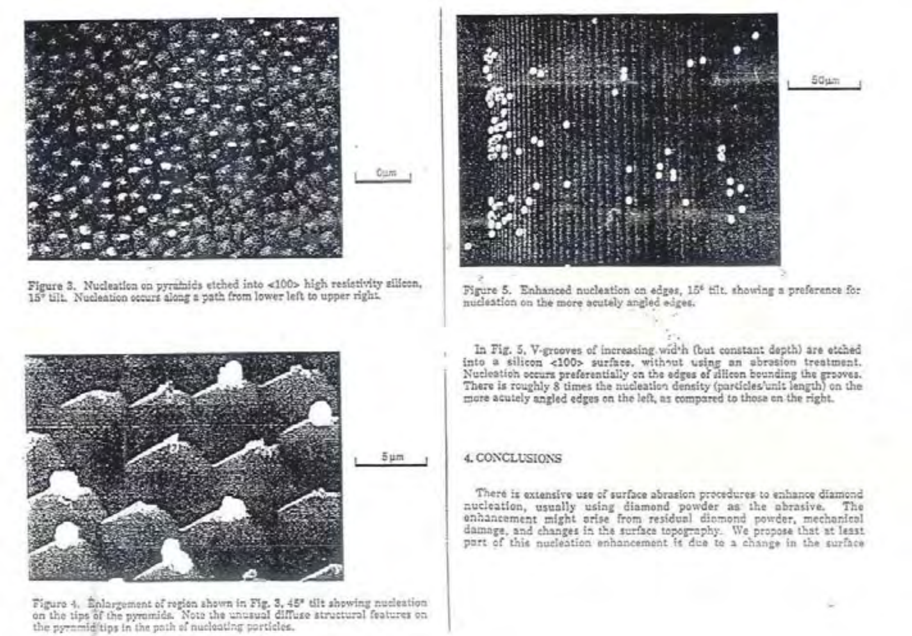


Figure 3. Nucleation on pyramids etched into <100> high resistivity silicon, 15° tilt. Nucleation occurs along a path from lower left to upper right.

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 <100> surface, without using an abrasion treatment. Nucleation occurs preferentially on the edges of silicon bounding the 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

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the pyramids. One may even closely observe the high nucleation rate of diamond particles on all the apexes in Figs. 4(a) and 4(b). The substrate was not damaged with diamond paste prior to the fabrication of pyramids

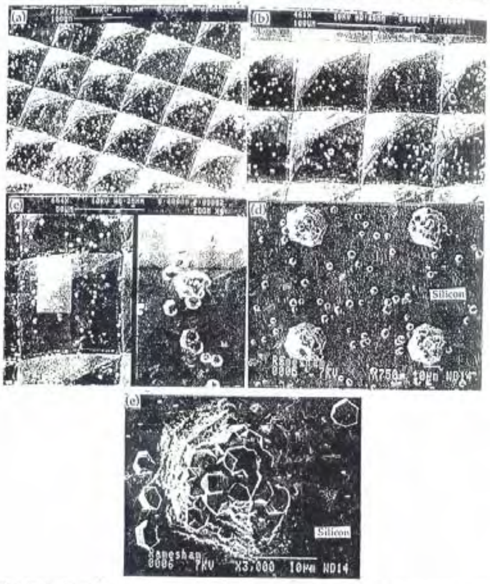
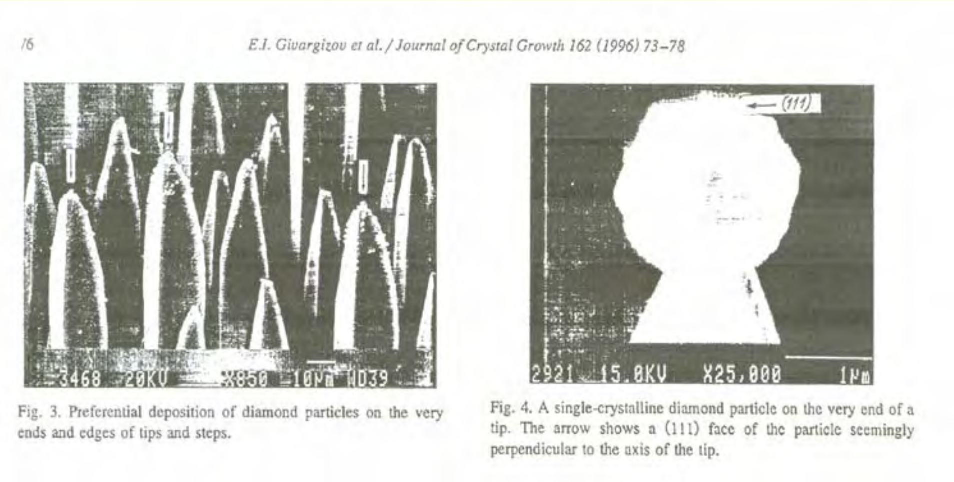


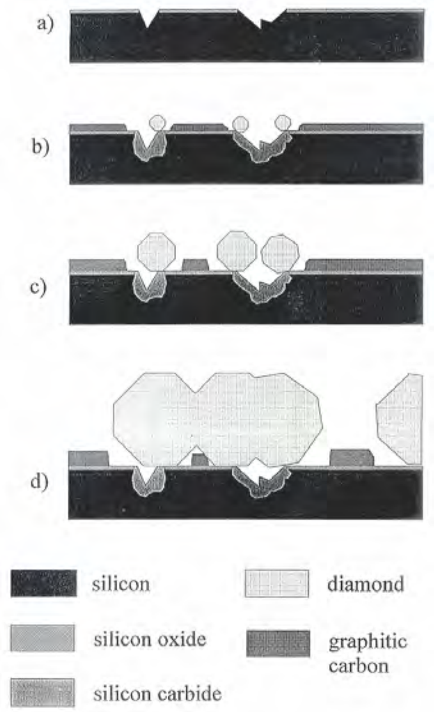
FIG. 4. Scanning electron micrographs of diamond growth on (a) sharp silicon pyramids, (b) magnified view of (a), (c) magnified view of single pyramid in (a) and also zooming of an apex of pyramid in (c), (d) growth of diamond on the apex of silicon pyramids, and (e) a magnified view of single pyramid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



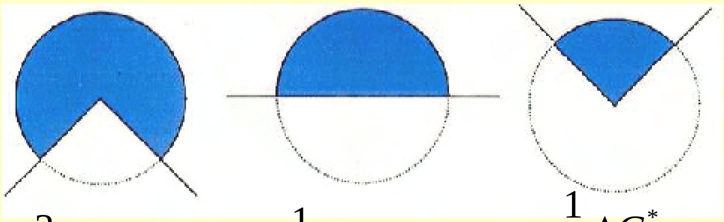
76 E.I. Givargizov et al. / Journal of Crystal Growth 162 (1996) 73–78

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



$$\frac{3}{4}\Delta G^*_{\text{homo}} \qquad \frac{1}{2}\Delta G^*_{\text{homo}} \qquad \frac{1}{4}\Delta G^*_{\text{homo}}$$

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

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

Nucleation Rate (Heterogeneous)

$$\Delta G^* = \frac{16\pi v^2\gamma^3}{3\left(RT\ln\alpha\right)^2}$$

$v = 3.41 \times 10^{-6}$ M^3/mole, $\gamma = 3.7$ J/M^2

$\alpha = 10$, T = 1200 K

$R = Nk = N \times 1.38 \times 10^{-23}$ J/K = 8.31 J/K

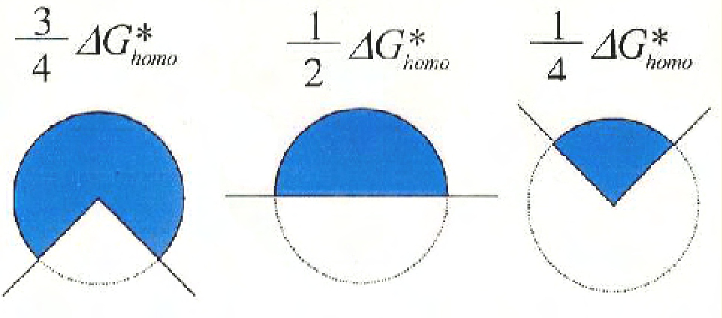
$$\Delta G^* = \frac{2.96\times10^{-8}}{1.58\times10^{9}} = 1.87\times10^{-17}\,J$$

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

10^{123} $\qquad$ 10^{245} $\qquad$ 10^{368}

1 $\qquad$ 10^{122} $\qquad$ 10^{245}

Nucleation Rate (Heterogeneous)



$$\alpha = 10 \qquad \frac{I_{hetero}}{I_{homo}} = \frac{10^{123}}{1} \qquad \frac{10^{245}}{10^{122}} \qquad \frac{10^{368}}{10^{245}}$$

$$\alpha = 100 \qquad \frac{I_{hetero}}{I_{homo}} = \frac{10^{31}}{1} \qquad \frac{10^{62}}{10^{31}} \qquad \frac{10^{93}}{10^{62}}$$

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)

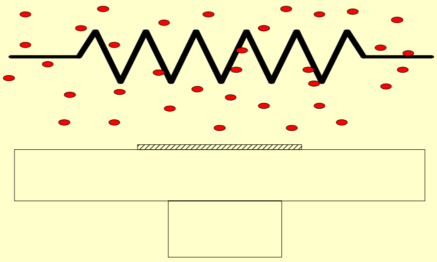
1. ***Bias Effect***
   (Sawabe et al. Thin Solid Film 137 (1986) 89)
2. ***Preferential formation on the convex edge***
   (Dennig et al. Appl. Phys. Lett. 59 (1991) 1562)
3. ***Preferential formation of soot on the Fe edge***
4. ***Halogen elements replace the gas activation***
   (Patterson et al. 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.***

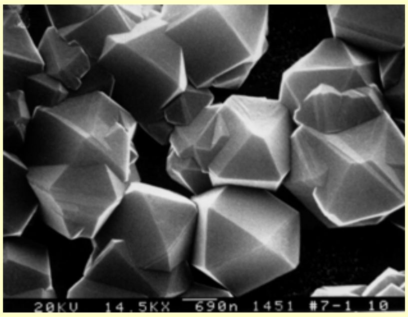
Puzzling Phenomena in Diamond CVD (Implication of Gas Phase Nucleation)

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.

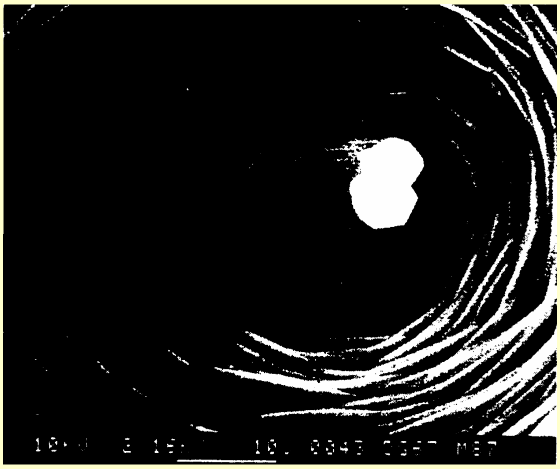
Invisible Charged Clusters of ~ 1 nm





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

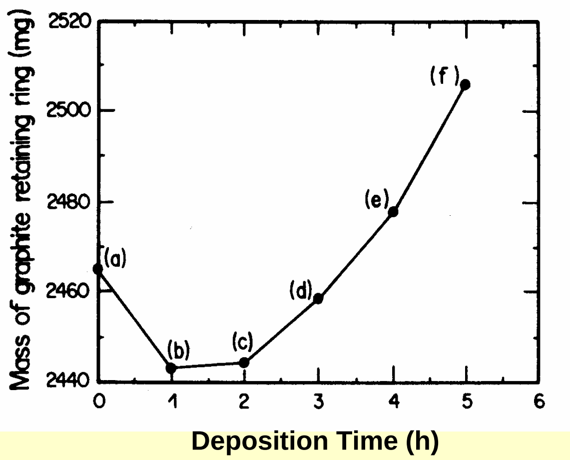
Diamond Deposition on the Etch Pit of Graphite Substrate



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

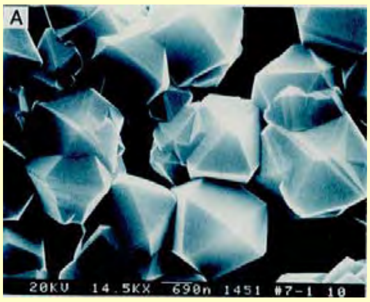
Weight Change of Graphite Ring

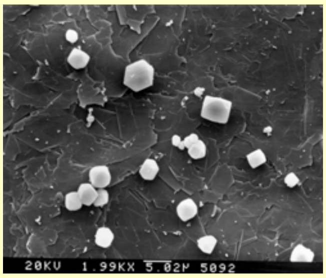
0.5%CH_4-H_2, 80 Torr. T_{sub}= 870 °C

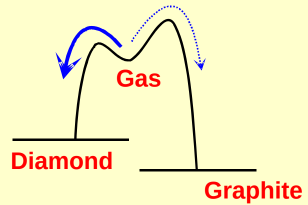


M. C. Salvadori et al, J. Electrochem. Soc., 139 (1992) 558

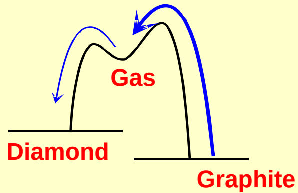
Thermodynamic Paradox in CVD Diamond Growth





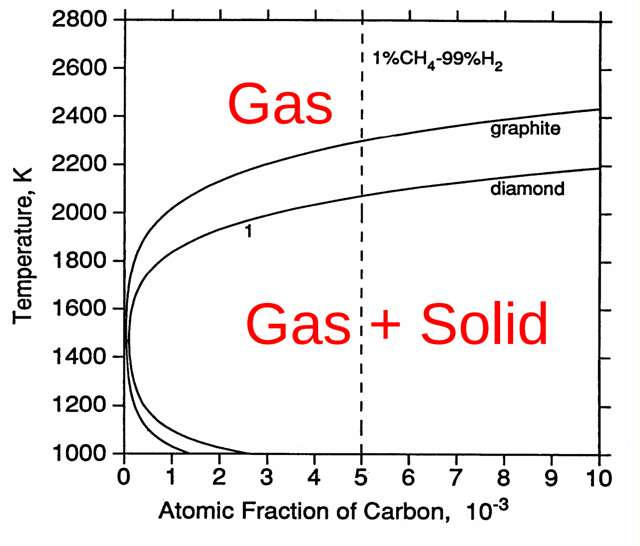


Hwang et al.
Diamond Relat. Mater. 1 (1992) 9
J. Crystal Growth 160 (1996) 87

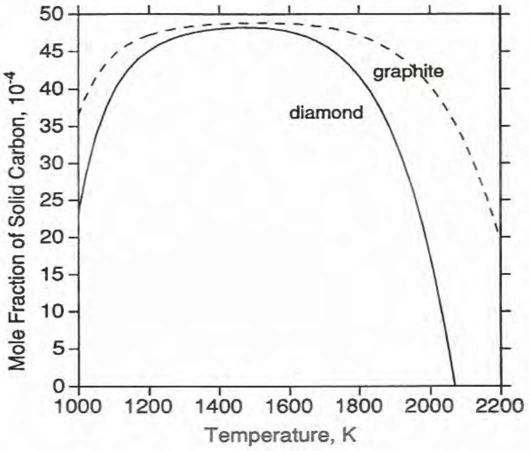


Simultaneous Diamond Deposition and Graphite Etching

CVD phase diagram of C-H system at 2700 Pa



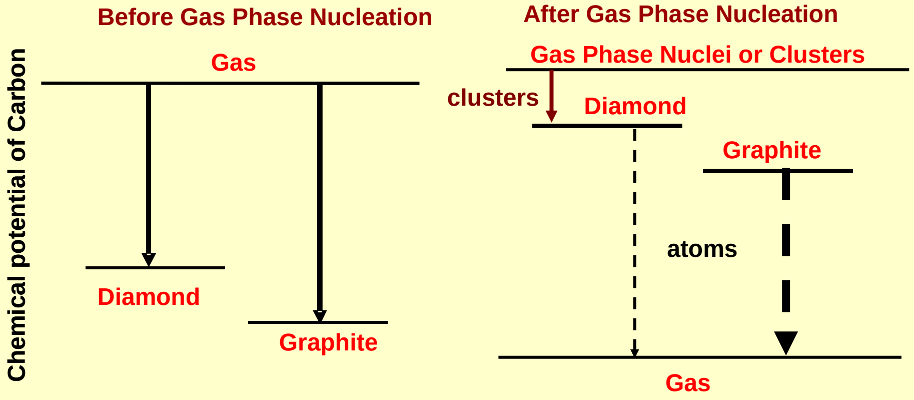
Equilibrium Amount of Precipitated Solid Carbon



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



Chemical potential of Carbon

Before Gas Phase Nucleation

Gas

Diamond

Graphite

After Gas Phase Nucleation

Gas Phase Nuclei or Clusters

clusters

Diamond

Graphite

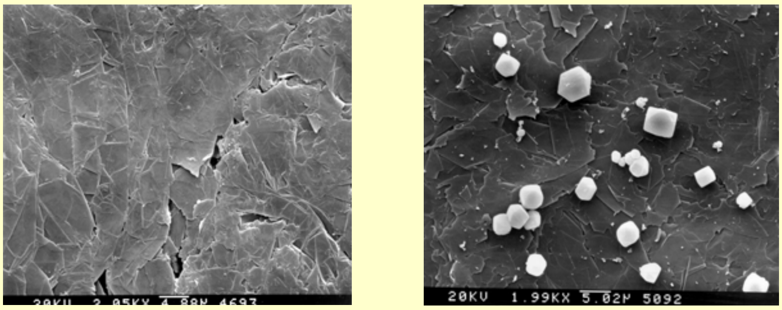
atoms

Gas

Paradox or Diamond Deposition by Clusters ?

Simultaneous Diamond Deposition and Graphite Etching

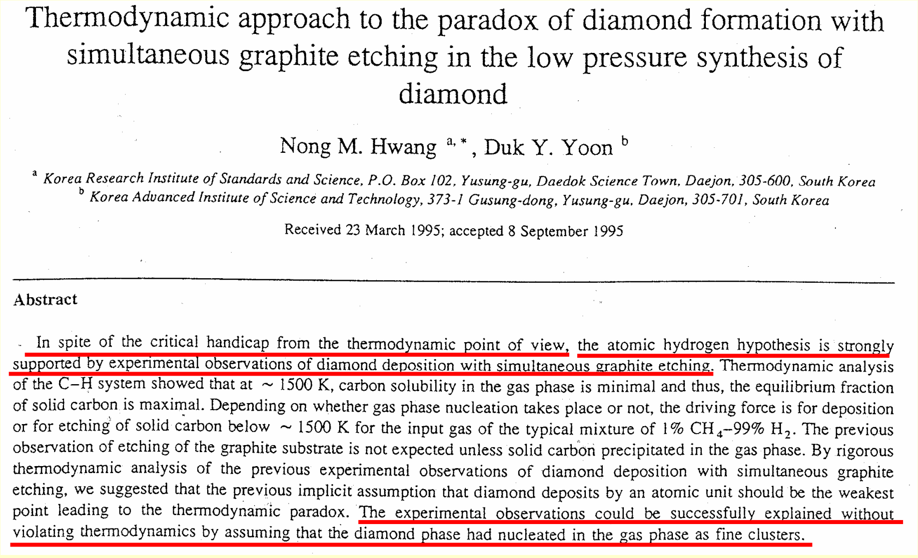
T_F : 2100°C, T_s : 1050°C, 1% CH_4 - H_2, 2h



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

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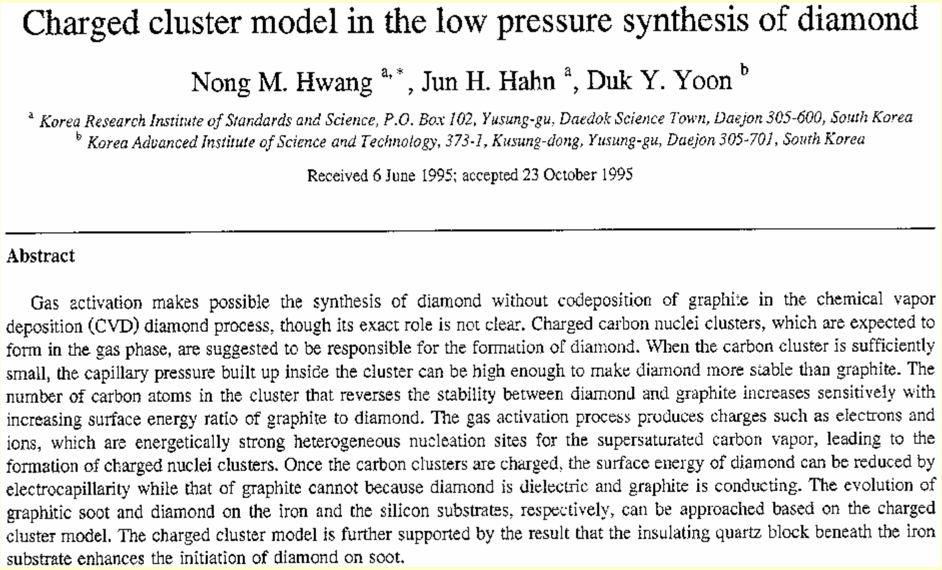
Received 23 March 1995; accepted 8 September 1995

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% CH_4–99% H_2. 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

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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.

Charged Cluster Model

10. ***Small clusters undergo epitaxial recrystallization and deposit as high quality diamond crystals.***
    → tend to be accommodated to the substrate structure.

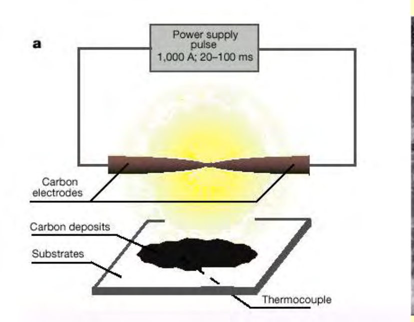
11. ***Medium-size clusters made twins or stacking faults.***

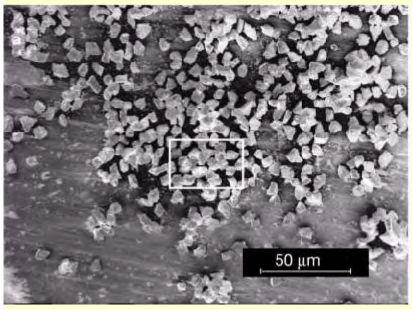
12. ***Large clusters deposit as a cauliflower structure.***

13. ***High substrate temperature enhances epitaxial recrystallization and is favorable for deposition of epitaxial films.***

14. ***Low substrate temperature enhances non-epitaxial recrystallization and is favorable for deposition of nano-structure or cauliflower structure.***

Diamond Synthesis without Hydrogen

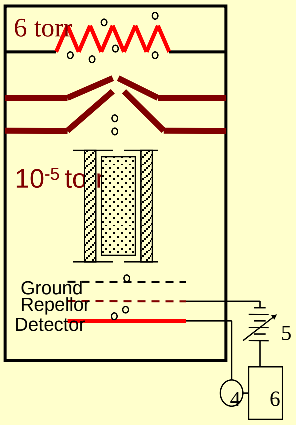


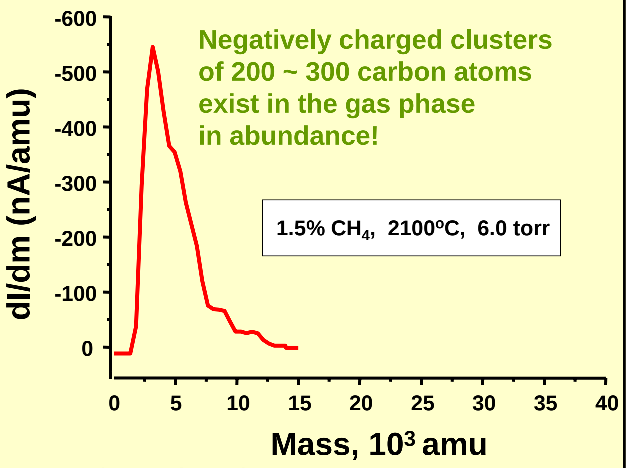


Palnichenko et al., Nature 402 (1999) 162

How can we experimentally confirm the existence of hypothetical negatively-charged nanoparticles in the diamond CVD reactor?

Experimental Confirmation of Negatively-Charged Carbon Clusters in the Diamond CVD Process by Wien Filter combined with Energy Analyzer.



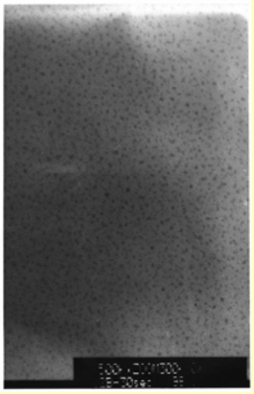


Negatively charged clusters of 200 ~ 300 carbon atoms exist in the gas phase in abundance!

1.5% CH_4, 2100°C, 6.0 torr

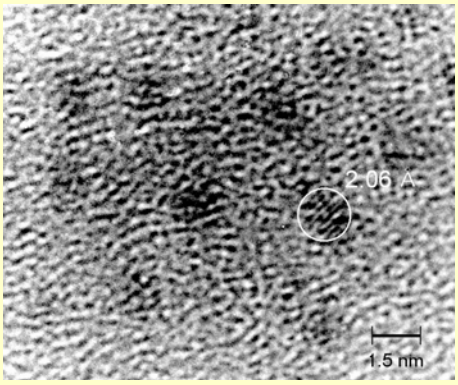
J. Crystal Growth 213 (2000) 79

For TEM observation, individual clusters were captured on a TEM grid with Mo mesh and a silica membrane during oxy-acetylene synthesis of diamond.



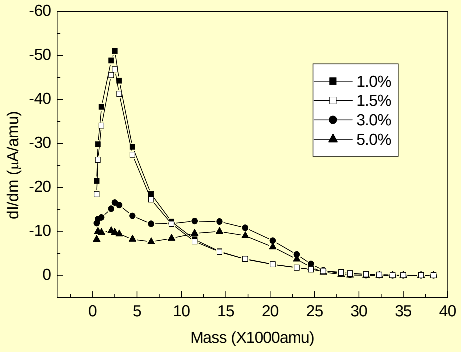
(a) TEM observation of clusters of 1 ~ 1.5 nm

J. Crystal Growth 234 (2002) 399

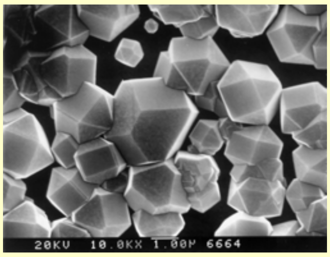


(b) Some clusters show the lattice fringe of diamond with (111) spacing of 2.06 Å.

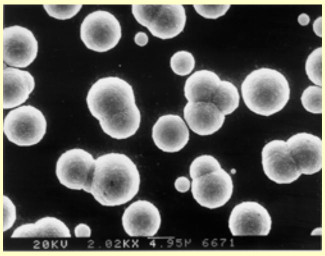
Cluster size Increases with increasing CH_4 concentration.



J. Crystal Growth, 223 (2001) 6

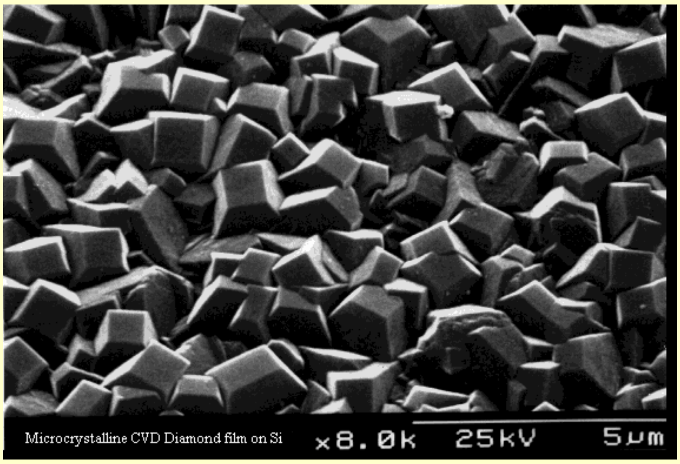


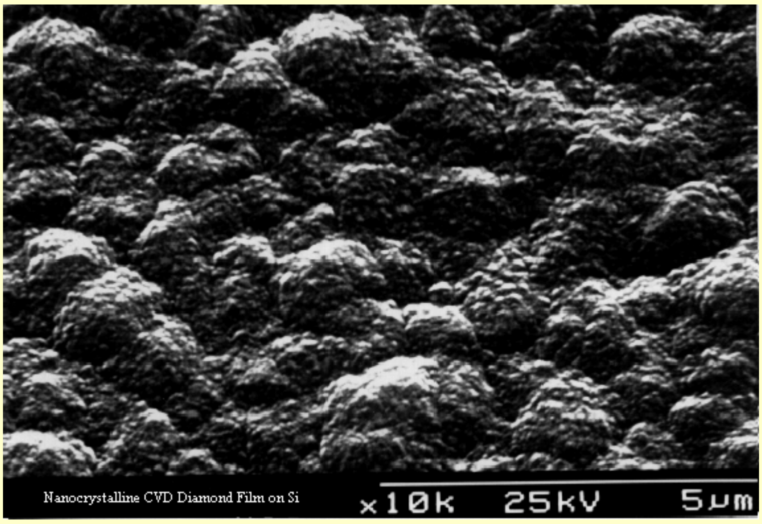
Small Clusters



Large Clusters

How about other CVD films? Do they also grow by charged nanoparticles? How do you know?





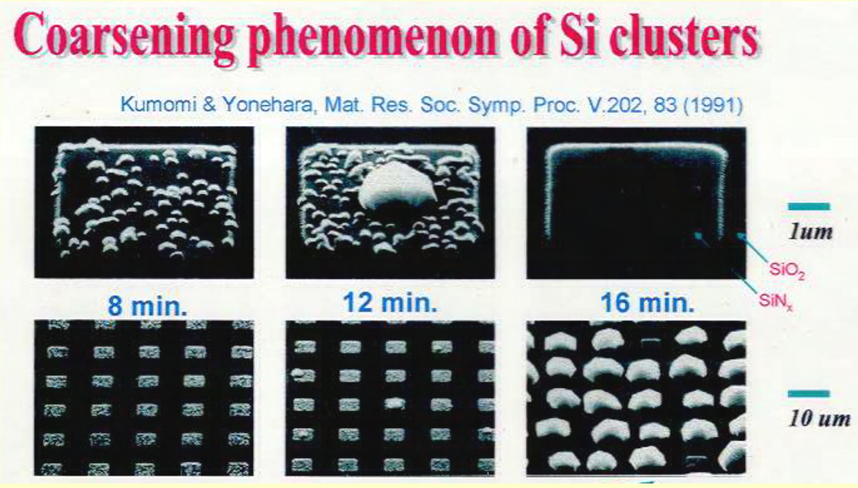
Cauliflower Structure in Diamond and Silicon CVD Processes

(a) Diamond

(b) Silicon

Cauliflower structure is very general in CVD processes.
→ Film growth by CNP might be a general mechanism in CVD.

How do you prove that silicon CVD films grow by charged nanoparticles?



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!

Simultaneous Deposition and Etching of Si

Deposition $\rightarrow \mu_{Si}^{Gas} > \mu_{Si}^{Solid}$

Etching $\rightarrow \mu_{Si}^{Gas} < \mu_{Si}^{Solid}$

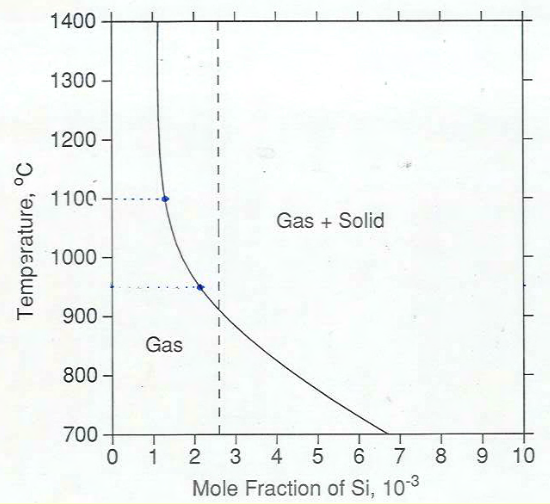
$\rightarrow$ **violate the 2nd Law of Thermodynamics**

Gas Phase Nucleation

$\rightarrow \mu_{Si}^{Gas} < \mu_{Si}^{Solid} \rightarrow$ *etching*

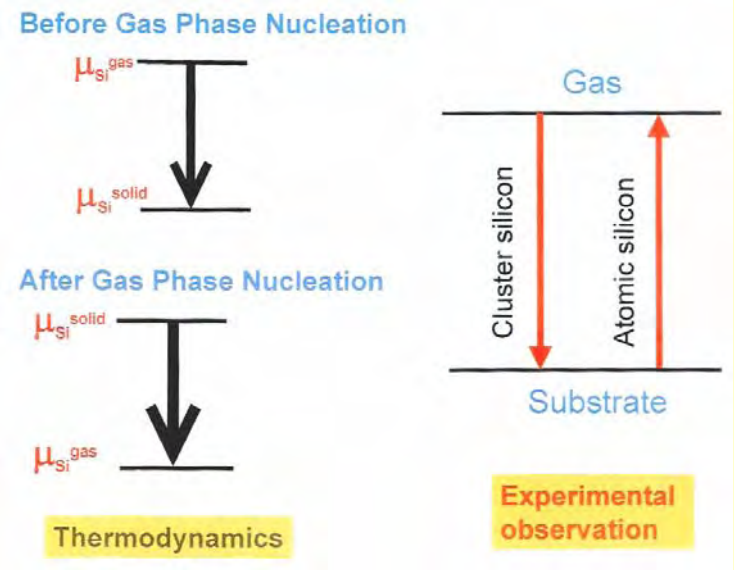
Gas Phase Nuclei **→** ***Deposition***
Atomic unit **→** ***Etching***

CVD phase diagram of Si



SiH_4 : HCl : H_2 =
1:2:97,
100 torr, 950°C

J. Crystal Growth
205 (1999) 59



Before Gas Phase Nucleation

μ_{Si}^{gas}

μ_{Si}^{solid}

After Gas Phase Nucleation

μ_{Si}^{solid}

μ_{Si}^{gas}

Thermodynamics

Gas

Cluster silicon

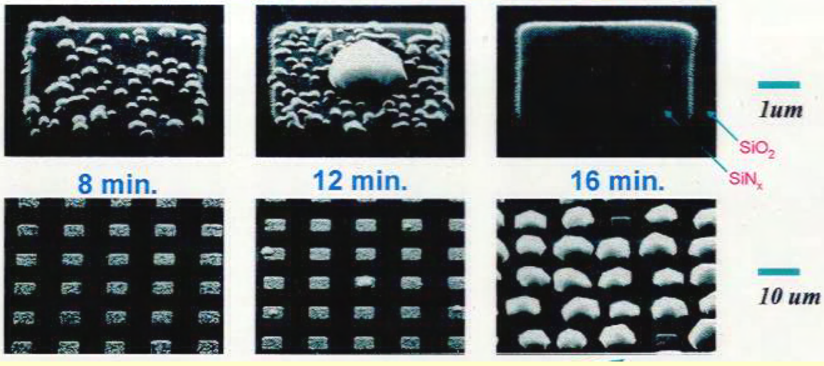
Atomic silicon

Substrate

Experimental observation

Coarsening phenomenon of Si clusters

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

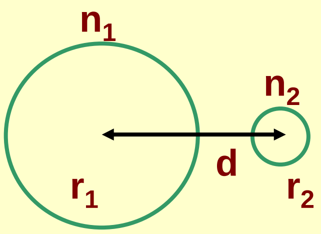


Two irreversible processes of deposition and etching take place simultaneously in opposite directions!

Coulomb Interaction between charged particles

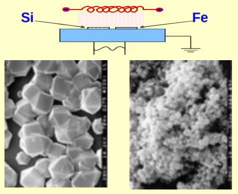
D.B. Dove, J. Appl. Phys. 35 (1964) 2785

$$Force = \frac{n_1 n_2 e^2}{4\pi \ \ \varepsilon_o d^2} - \frac{n_1^2 e^2 r_1 d}{4\pi \ \ \varepsilon_o \left(d^2 - r_2^2\right)} - \frac{n_2^2 e^2 r_2 d}{4\pi \ \ \varepsilon_o \left(d^2 - r_1^2\right)} \cdots$$

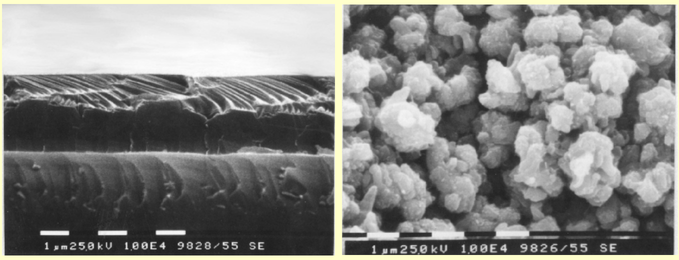


If $r_1 >> r_2$ → Attractive
If $r_1 \sim r_2$ → Repulsive

What would happen in Si CVD?



Si substrate Fe substrate



(a) Si substrate (b) Fe substrate

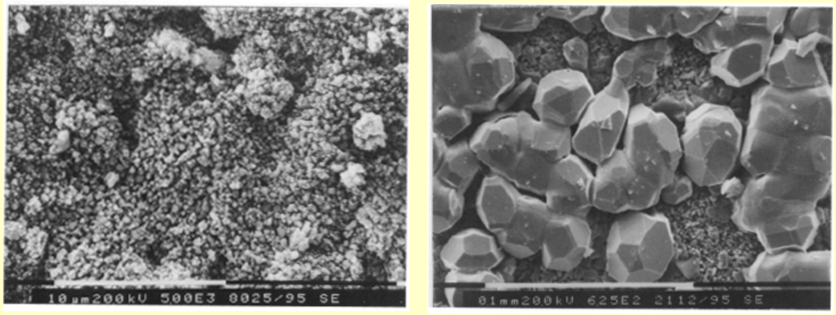
$SiH_4 : HCl : H_2$ = 1:1:98, 1333 Pa, 1123K

J. Crystal Growth, 218 (2000) 27

Neutral NP → porous structure

Self-assembly of CNP comes from electrostatic interaction.

Time Evolution of Microstructure on Ni substrate in Si CVD



(a) 3 min (b) 30 min

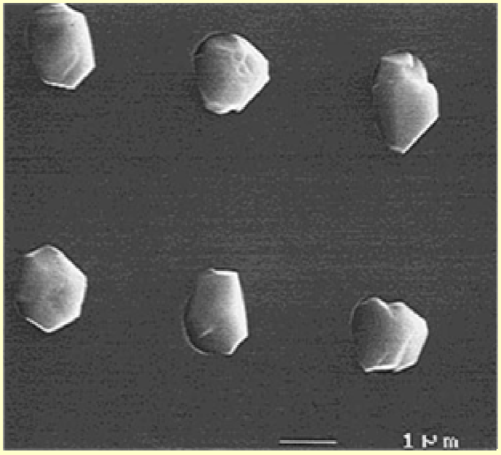
$SiH_4 : HCl : H_2 = 1:1:98$, 1333 Pa, 1123K

J. Crystal Growth, 218 (2000) 27

CNP undergo self-assembly and rotation into epitaxial orientation, which is induced by the electrostatic interaction.

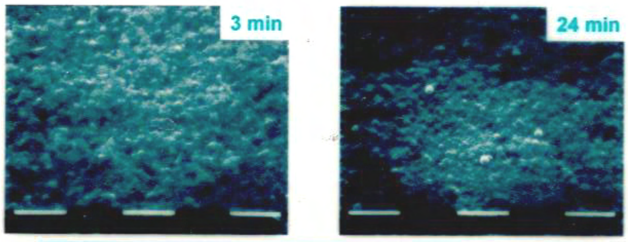
Selective Deposition in CVD

Selective Al growth by MOCVD



Heo Y. et al. Applied Surface Science 142 (1999) 443-446

Silicon Deposition on Mo



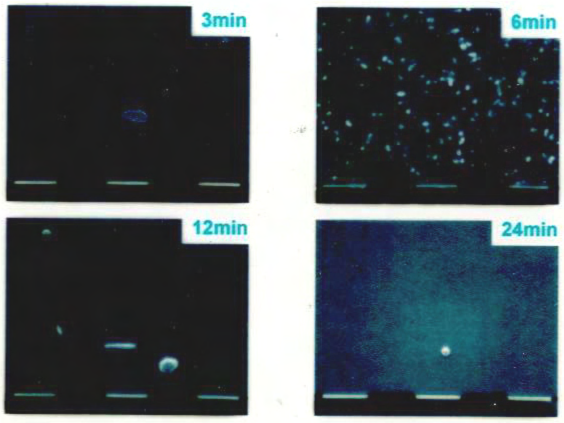
SEG condition[950 °C, SiH_4:HCl:H_2 = 1:2:97, 100 Torr]

Weight measurement of silicon films

mg/cm^2

Time (min)	3	6	12	24
Mo	0.15	0.19	0.19	0.24
Pt	0.19	0.20	0.25	0.34

Silicon Coarsening & Etching on SiO_2



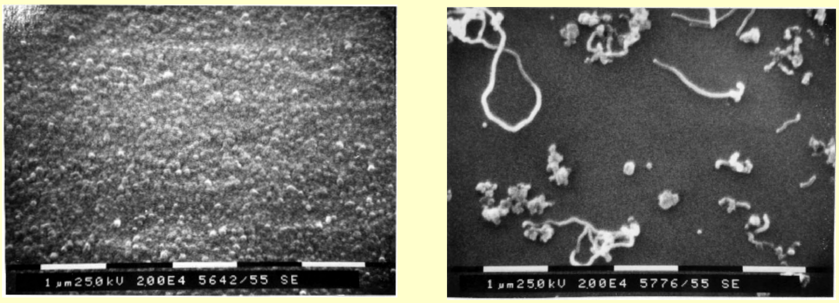
SEG condition[950 °C, SiH_4:HCl:H_2 = 1:2:97, 100 Torr]

Cheong et al.
J. Crystal Growth
206 (1999) 177

We grow nanowires, nanotubes and various nanostructures by CVD. Would they also grow by charged nanoparticles?

Charged Clusters have difficulty in landing on insulators.

→ Selective Deposition in CVD process

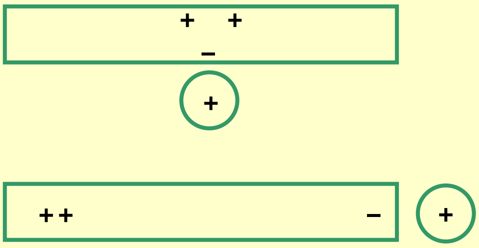


(a) Mo substrate (b) Si substrate

SiH_4 : HCl : H_2 = 3 : 1 : 96, 950°C, 10 Torr, 3 min

Hwang et al. : J. Crystal Growth, 218 (2000) 33

Coulomb interaction between positively-charged rod and cluster



Radial direction

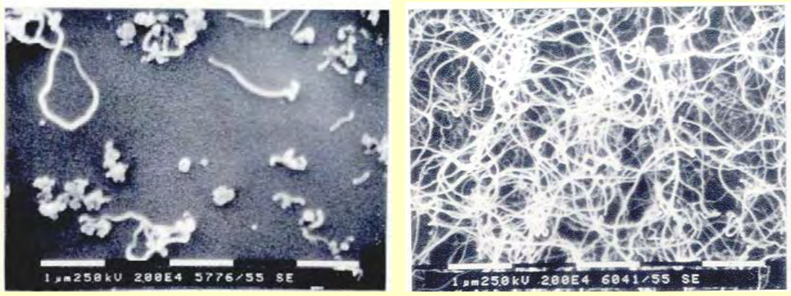
→ Repulsive

Axial direction

→ Attractive

→ One-dimensional nanowire growth

Silicon Nanowires

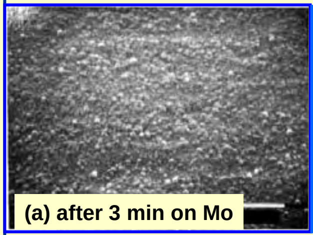


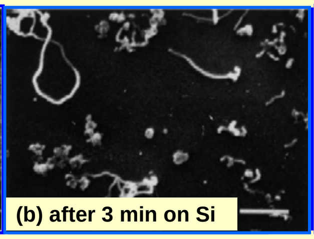
(a) 3 min (b) 6 min

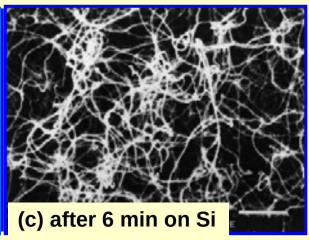
SiH_4 : HCl : H_2 = 3 : 1 : 96, 950^{o}C, 10 Torr, Si substrate

Hwang et al. : J. Crystal Growth, 218 (2000) 33

Selective Deposition and Nanowire Growth by Charged NPs


(a) after 3 min on Mo

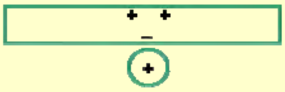

(b) after 3 min on Si


(c) after 6 min on Si

Conductor (Mo)

Insulator (SiO_2)

CNPs have difficulty in landing on insulators.
→ **Selective Deposition**
J. Crystal Growth, 206 (1999) 177



Radial direction
→ Repulsive

Electrostatic Interaction between
CNPs and charged rods
→ **Nanowire Growth**
J. Crystal Growth, 218 (2000) 33

Axial direction
→ Attractive

SiH_4 : HCl : H_2 = 3 : 1 : 96, 950°C, 10 Torr

Rev. Mod. Phys., Vol. 77, No. 2, April 2005

Colloquium: Reactive plasmas as a versatile nanofabrication tool
K. Ostrikov*
School of Physics, The University of Sydney, Sydney NSW 2006, Australia

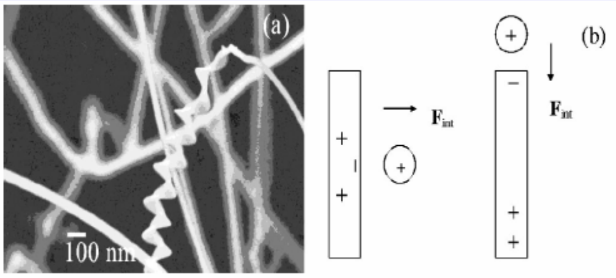
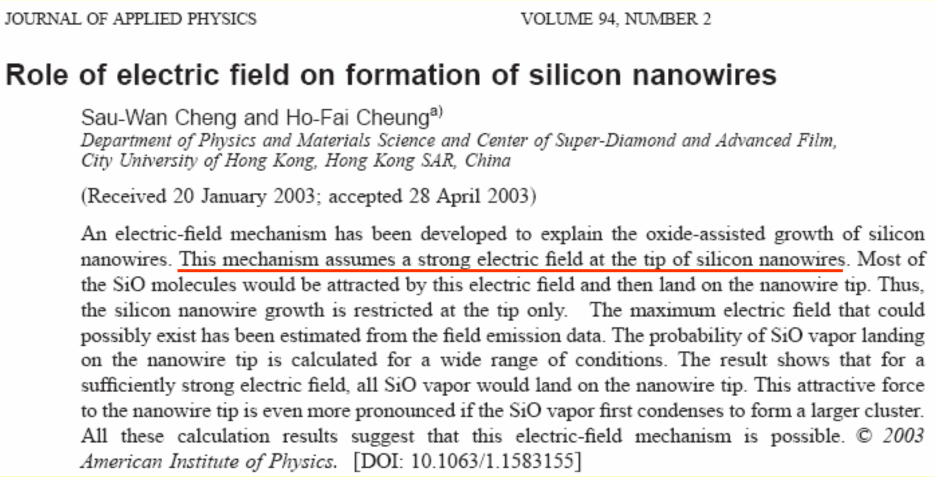


FIG. 9. Silicon nanowire growth and interaction with charged clusters: (a) Scanning electron micrograph of silicon nanowires grown in low-pressure SiH_4+H_2 reactive plasma (Xu, Ostrikov, *et al.*, 2005); (b) schematics of the charged nanocluster-nanowire interaction (Hwang and Kim, 2004). Here, $\mathbf{F}_{\mathrm{int}}$ denotes the force of the electrostatic building-unit–nanowire interaction.



JOURNAL OF APPLIED PHYSICS VOLUME 94, NUMBER 2

Role of electric field on formation of silicon nanowires

Sau-Wan Cheng and Ho-Fai Cheung[a)]
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(Received 20 January 2003; accepted 28 April 2003)

An electric-field mechanism has been developed to explain the oxide-assisted growth of silicon nanowires. This mechanism assumes a strong electric field at the tip of silicon nanowires. Most of the SiO molecules would be attracted by this electric field and then land on the nanowire tip. Thus, the silicon nanowire growth is restricted at the tip only. The maximum electric field that could possibly exist has been estimated from the field emission data. The probability of SiO vapor landing on the nanowire tip is calculated for a wide range of conditions. The result shows that for a sufficiently strong electric field, all SiO vapor would land on the nanowire tip. This attractive force to the nanowire tip is even more pronounced if the SiO vapor first condenses to form a larger cluster. All these calculation results suggest that this electric-field mechanism is possible. *© 2003 American Institute of Physics.* [DOI: 10.1063/1.1583155]

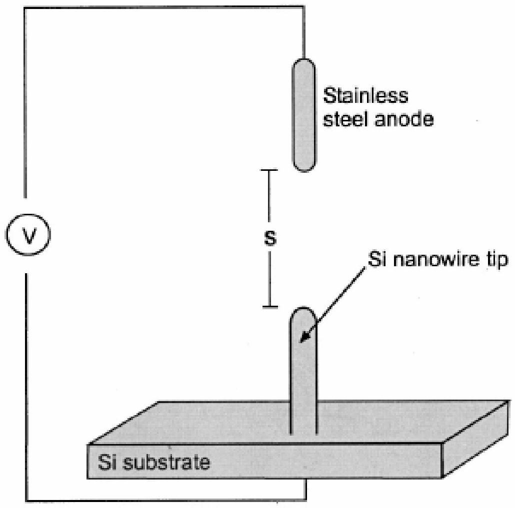


FIG. 1. Schematic diagram showing a Si nanowire tip and the anode for field-emission measurement.

1192 J. Appl. Phys., Vol. 94, No. 2, 15 July 2003 S. Cheng and H. Cheung

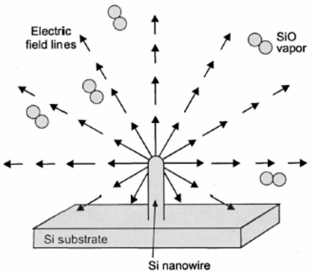


FIG. 3. Electric field originates from the Si nanowire tips.

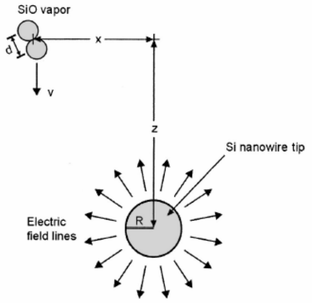


FIG. 4. Geometry of SiO vapor falling on a nanowire tip.

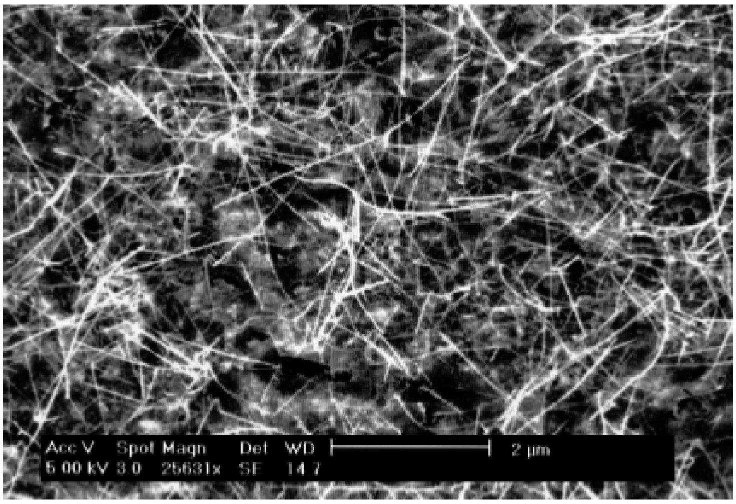
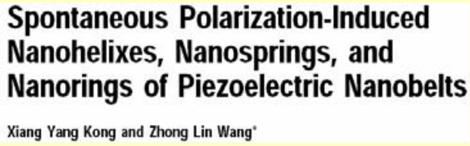


Fig. 2. SEM image of the GaN nanowires on the substrate.

H.Y. Peng et al. / Chemical Physics Letters 327 (2000) 263–270



Spontaneous Polarization-Induced Nanohelixes, Nanosprings, and Nanorings of Piezoelectric Nanobelts

Xiang Yang Kong and Zhong Lin Wang*

NANO
LETTERS

2003
Vol. 3, No. 12
1625−1631

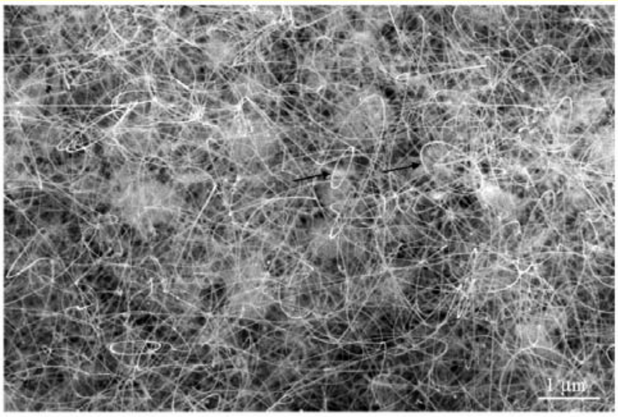
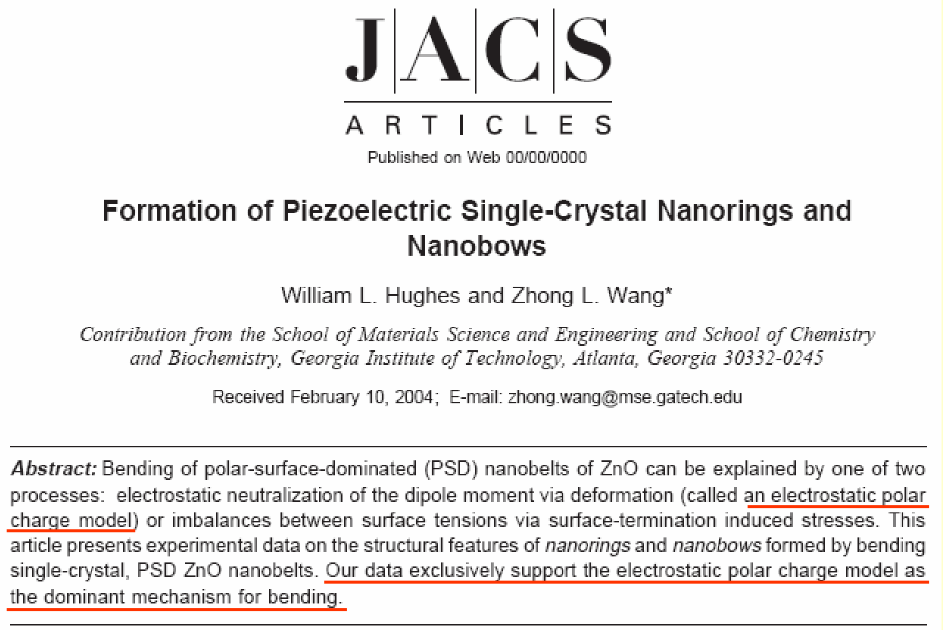


Figure 1. SEM images of the as-synthesized ZnO nanobelts, showing nanobelts of sizes 20−60 nm in widths and a large fraction of nanorings and helical nanostructures.



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Formation of Piezoelectric Single-Crystal Nanorings and Nanobows

William L. Hughes and Zhong L. Wang*

Contribution from the School of Materials Science and Engineering and School of Chemistry and Biochemistry, Georgia Institute of Technology, Atlanta, Georgia 30332-0245

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Abstract: Bending of polar-surface-dominated (PSD) nanobelts of ZnO can be explained by one of two processes: electrostatic neutralization of the dipole moment via deformation (called an electrostatic polar charge model) or imbalances between surface tensions via surface-termination induced stresses. This article presents experimental data on the structural features of *nanorings* and *nanobows* formed by bending single-crystal, PSD ZnO nanobelts. Our data exclusively support the electrostatic polar charge model as the dominant mechanism for bending.