New Theory of CVD Diamond by Charged Clusters

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Charged Cluster Model

Hwang et al : J. Crystal Growth 162 (1996) 55
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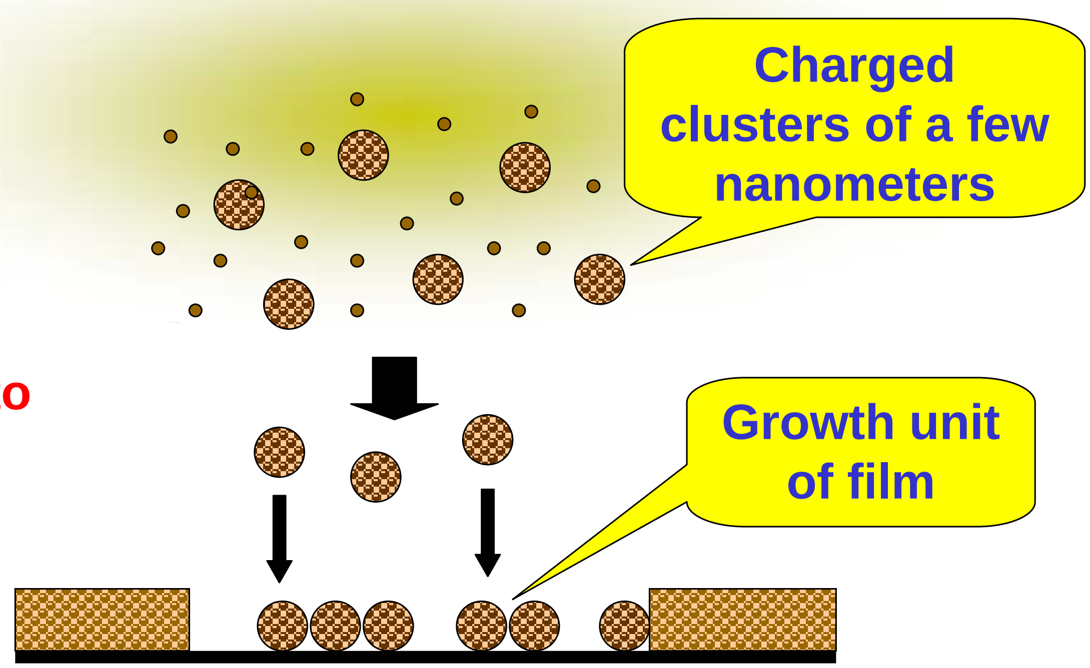
Gas phase nucleation

Transport to Surface

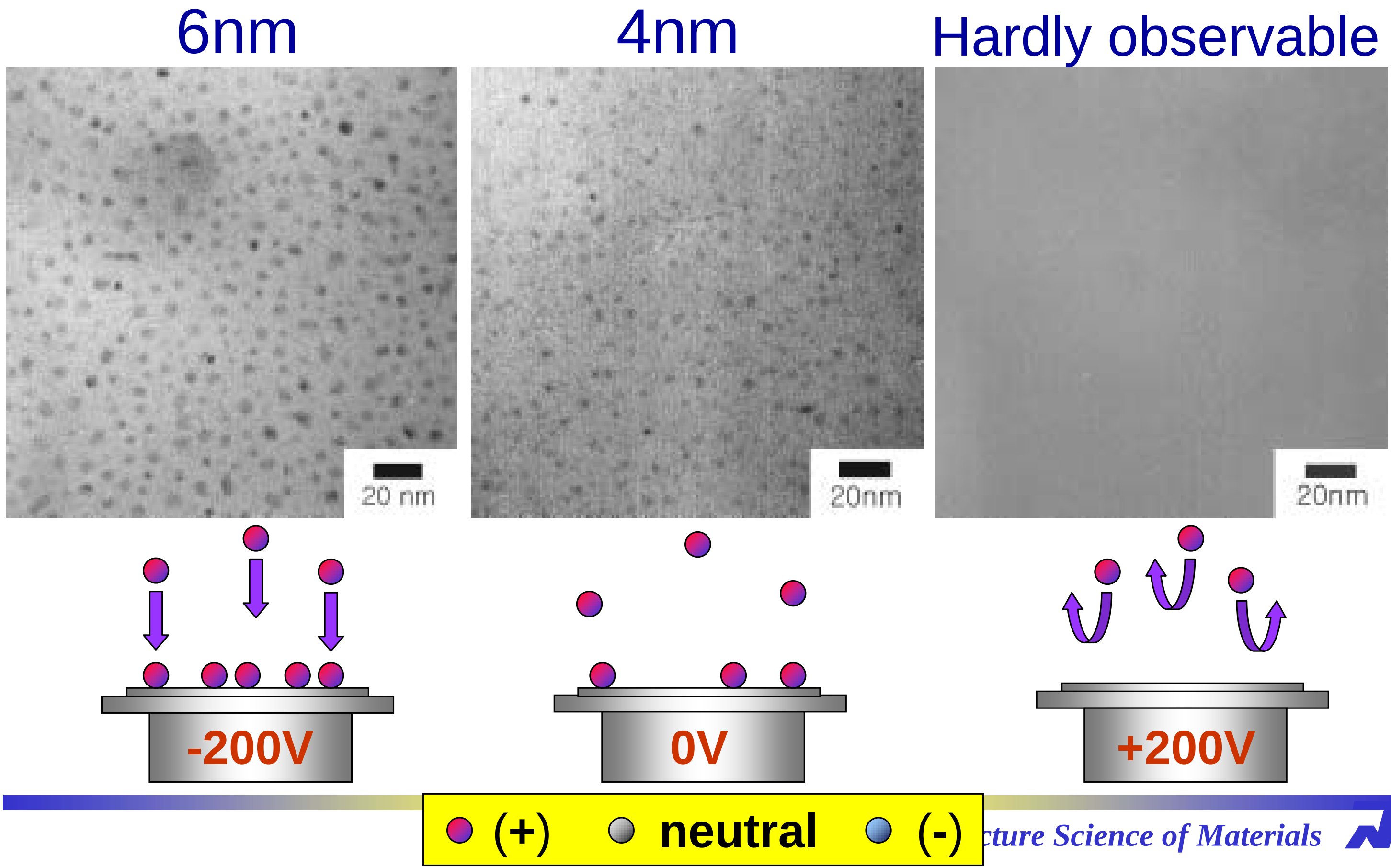
Film formation



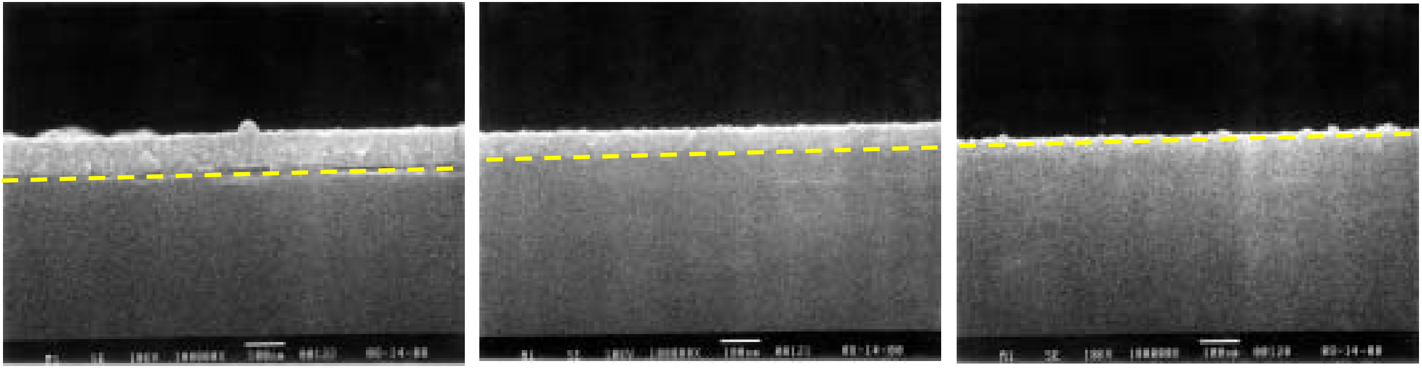
Thin Film Growth by Charged Clusters

1. Diamond CVD
2. Silicon CVD
3. ZrO_2 CVD
4. Thermal Evaporation of Metals
5. Sputtering
6. Laser Ablation

Results Cu Evaporation at 1300^{o}C, 10 sec



Results Cu Evaporation at 1300ºC, 300 sec



Bias voltage : - 400 V	0 V	+ 400 V
Thickness : 100 nm	55 nm	negligible

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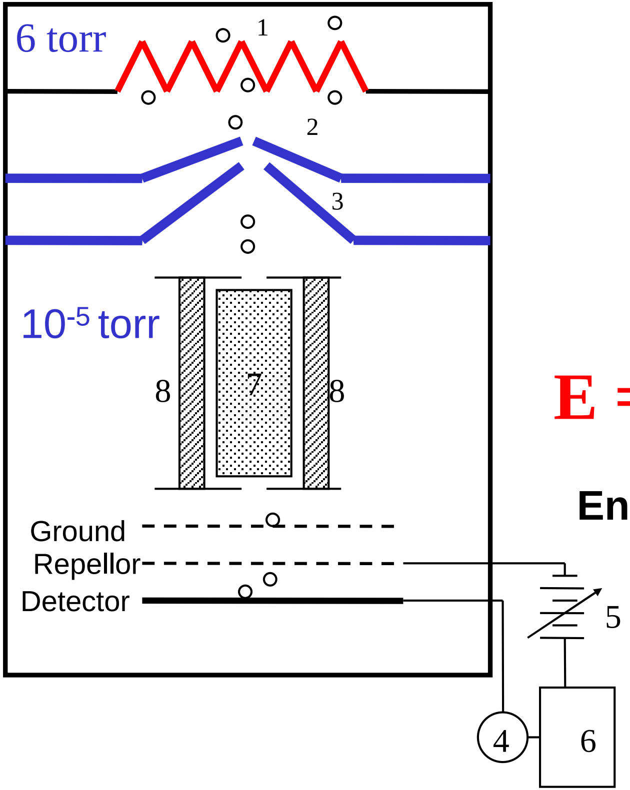
Experimental Confirmation of Charged Clusters in Diamond CVD Process

Bias effect is not so appreciable in the diamond CVD process because of a short mean free path.

Hypothetical charged clusters should be extracted from the reactor into a high vacuum chamber for determination of their mass.

Schematics of Wien Filter and Energy Analyzer for Measurements of Mass Distribution of Clusters



1. Filament (CVD Diamond Reactor)
2. Sampling orifice(1.2 mmØ)
3. Skimmer orifice(2.0 mm Ø)
4.&5. Electrometer(Kethely 617)
6. Computer
7. Electrodes
8. Magnets(7300 G)

$E = \frac{1}{2} mv^2$: energy of cluster

Energy is determined by energy analyzer.

Velocity is determined by Wien filter.

→ **Mass determination !**

Negatively Charged Carbon Clusters containing 200 ~ 300 carbon atoms exist in abundance in the diamond CVD Process!

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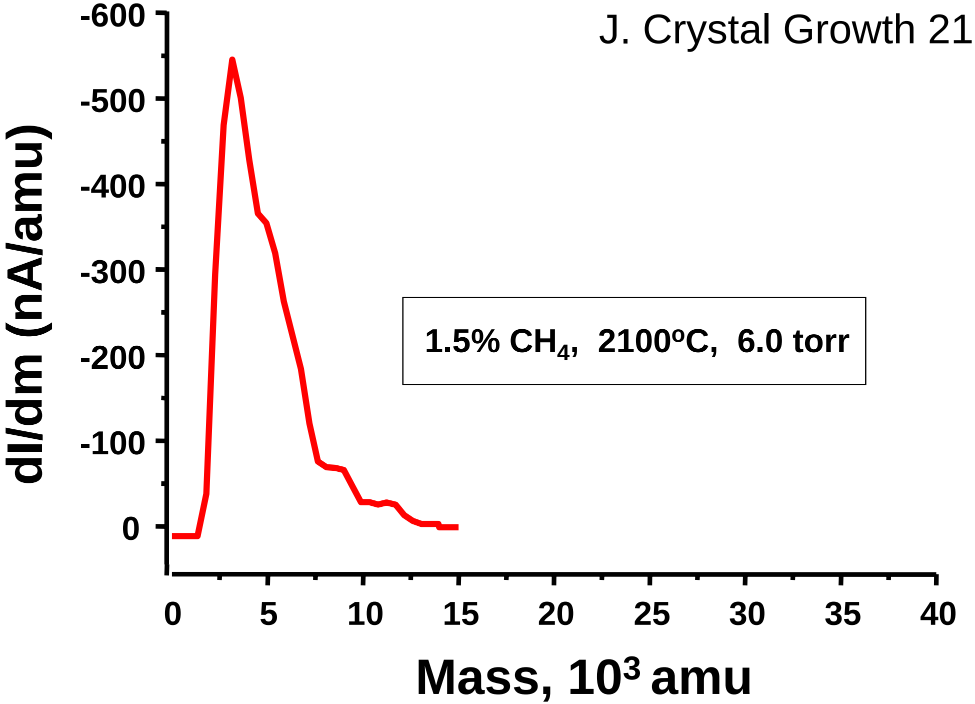
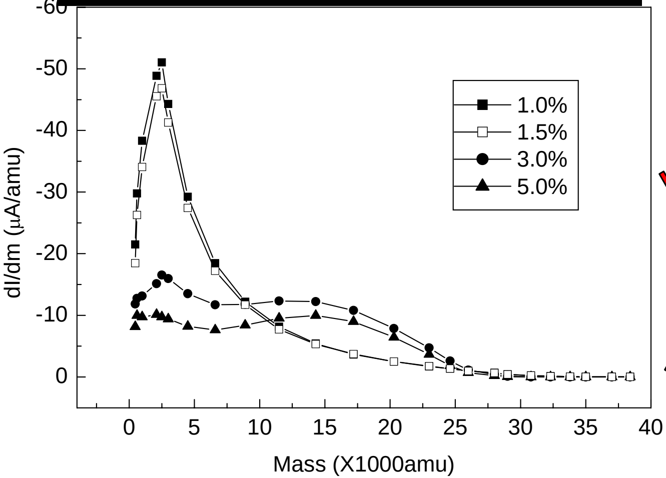
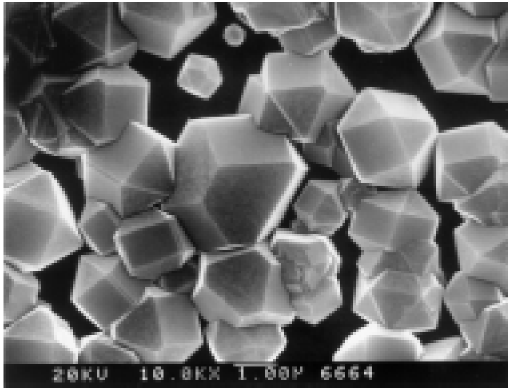
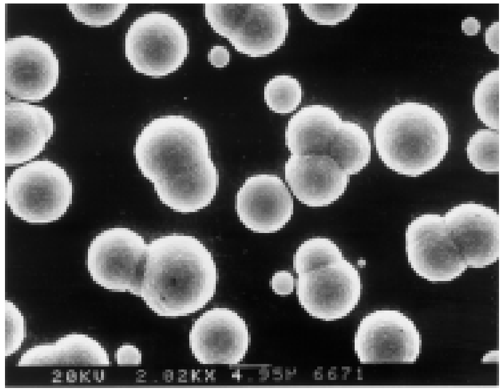


Experimental Confirmation of Charged Clusters





Small Clusters



Large Clusters

Size Distributions of Carbon Clusters with CH_4 Concentration
2100°C, 6 Torr, 1 hr

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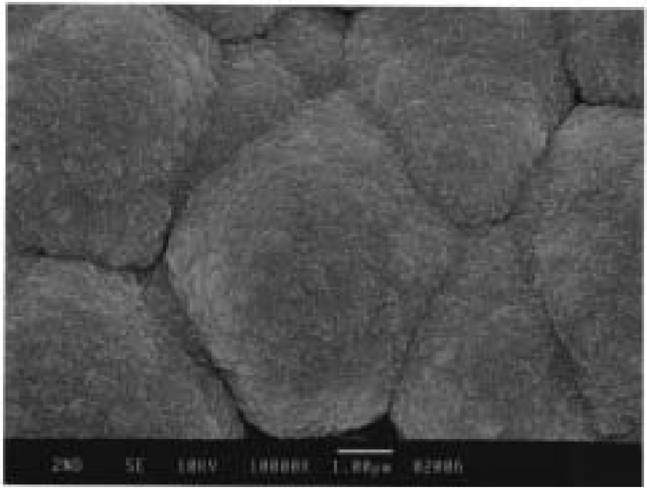
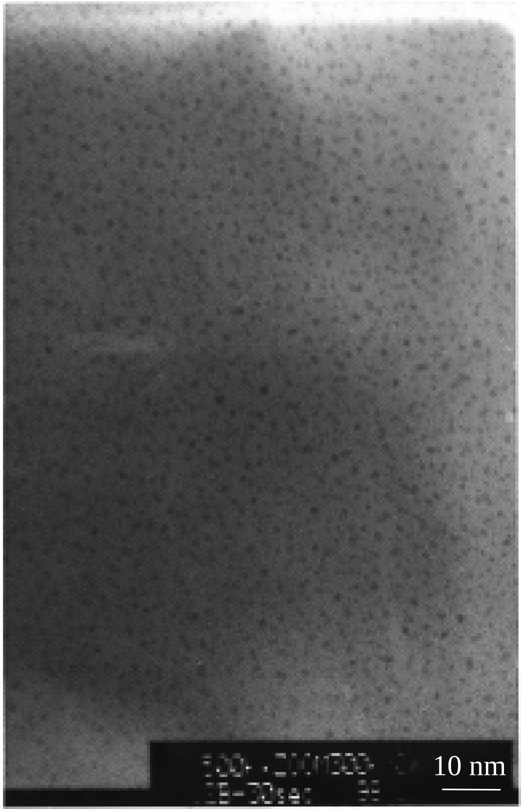
Cauliflower-shaped Nanostructure
deposited by large clusters



(a) Diamond

(b) Silicon

TEM observation



Clusters of ~ 1.5 nm

Flame Synthesis of Diamond
(Mo grid with SiO_2 membrane)
C_2H_2/O_2 = 1.04

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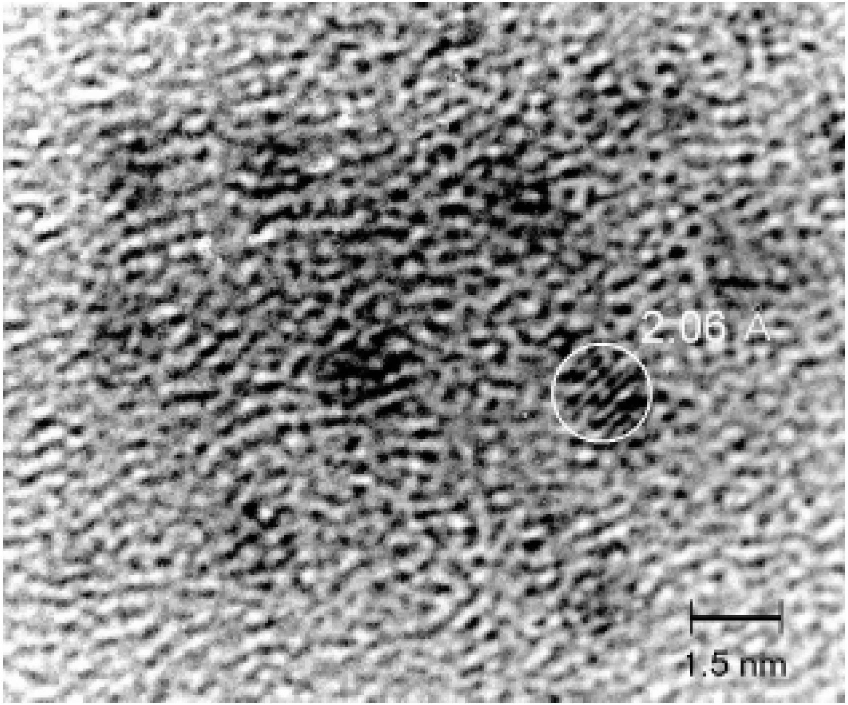
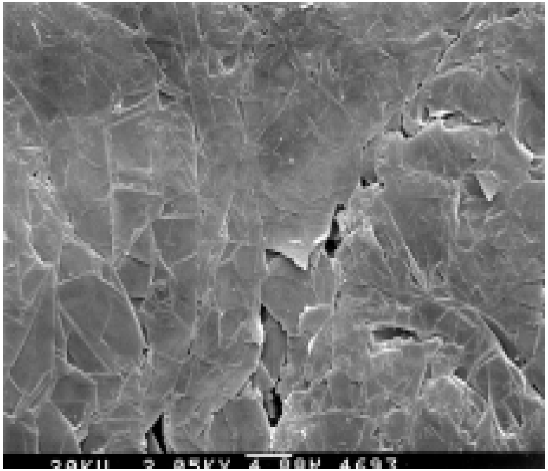
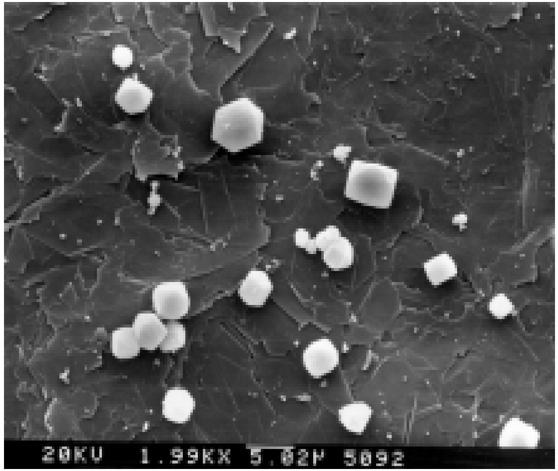


Some clusters show the diamond lattice fringe.

Simultaneous Diamond Deposition and Graphite Etching

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

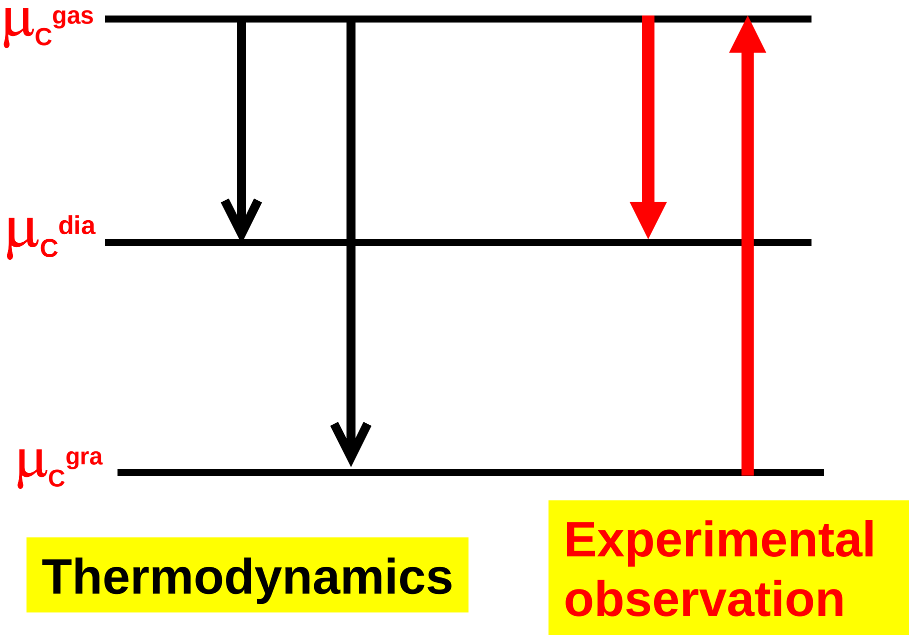




before experiment → after experiment

43.21 mg → 37.06 mg (6.15 mg)

Chemical Potential of Carbon; Thermodynamic Paradox

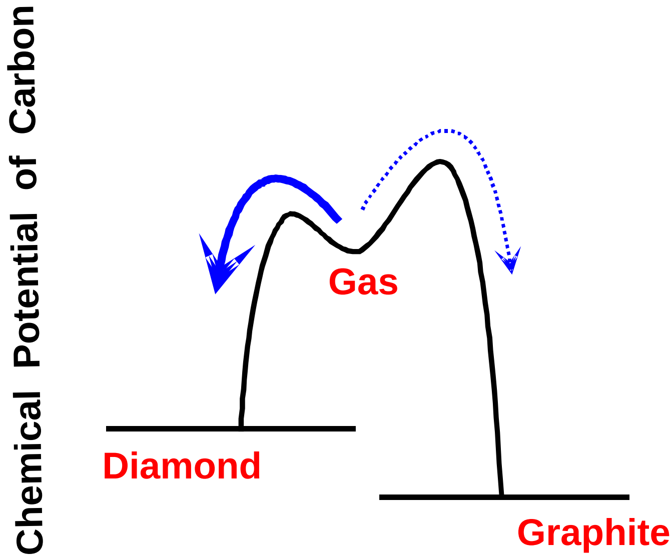


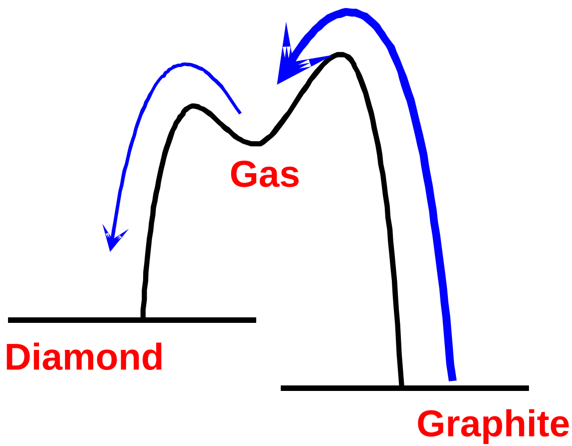
W. A. Yabrough, J. Am. Ceram. Soc., 75, (1992) 3179-3199
N.M. Hwang and D.Y. Yoon, J. Crystal Growth, 160 (1996) 87-97

Dominant Formation of Metastable Diamond over Stable Graphite

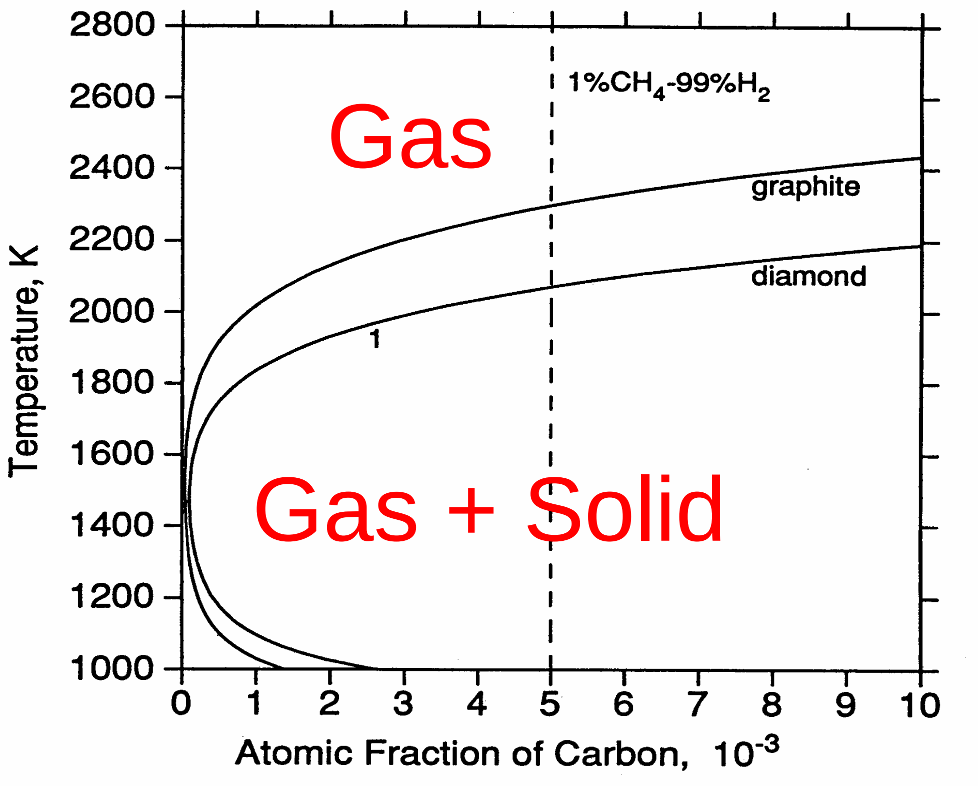
Simultaneous Diamond Deposition and Graphite Etching

- Can be explained by the kinetic barrier possibly in nucleation
- Violate the 2nd Law of Thermodynamics if the growth unit of diamonds is an atom.





CVD phase diagram of C-H system at 2700 Pa



Paradox or indication of diamond growth by clusters?

1. Gas phase nucleation makes both graphite and diamond etched by atomic unit.
2. Diamond crystals grow by gas phase nuclei or clusters.

What we observe macroscopically is deposition of less stable diamond with simultaneous etching of stable graphite.

Hwang & Yoon, J. Crystal Growth 160 (1996) 87

Conclusions

1. **Hypothetical charged clusters predicted in the charged cluster model were experimentally confirmed.**

2. **In order to avoid the violation of 2nd law of thermodynamics, these clusters should deposit as diamond films.**