Thermodynamics of Materials

20th Lecture

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LETTERS TO NATURE

Nanometre-sized diamonds are more stable than graphite

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DIAMONDS just 3–5 nm in diameter have recently been recovered from carbonaceous residues of detonations[1]. They have also been found in meteorites[2], nucleate homogeneously in the gas phase[3], and diamond-like films can be grown in low-pressure hydrogen[4]. Conditions are very different in these four cases, but the nearly equal sizes in both meteorites and detonations, and the necessity of nucleation centres for growth of synthetic diamonds, indicate the existence of a common underlying factor. Ultra-small diamonds, too small to be detected readily, may in fact be far more prevalent than presently realized. We arrive at this conclusion by comparing calculated heats of formation of small tetrahedral (diamond) and hexagonal (graphitic) clusters. In agreement with Nuth's discussions on diamonds in interstellar media[5,6], we conclude that surface energies are an important aspect in the stabilization of microcrystalline diamonds. For surface bonds terminated with hydrogen atoms, we find that diamonds smaller than ~3 nm in diameter are energetically favoured over polycyclic aromatics (the precursors to graphite), without requiring the high pressures or extreme kinetic conditions usually associated with diamonds.

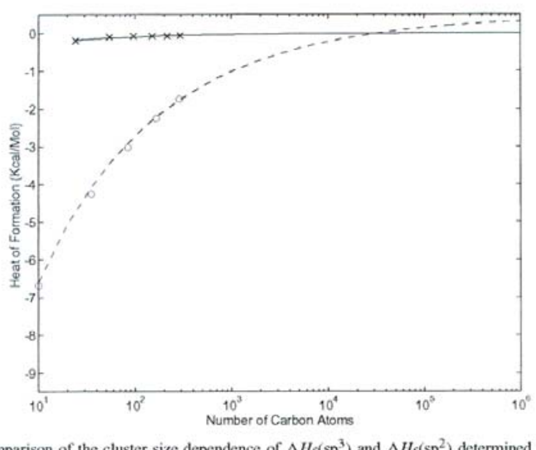

Figure 12. Comparison of the cluster size dependence of $\Delta H_f(sp^3)$ and $\Delta H_f(sp^2)$ determined by the PM3 HF method. The fits to the sp^3 (plotted as o's) and sp^2 (plotted as ×'s) data are given by the dashed and solid lines, respectively.

Winter et al. J. Computer- Aided Mater. Des. 5 (1998) 279

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Size dependent phase stability of carbon nanoparticles: Nanodiamond versus fullerenes

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Over the past 15 years, a number of studies have reported findings comparing the relative stability of diamond and graphite, at the nanoscale. In light of more recent experimental and theoretical results concerning the transformation of nanodiamonds into carbon-onions, it is considered important to extend this body of work to included fullerenes. Presented here is a study of the phase stability of carbon nanoparticles, with particular attention given to the relative stability of nanodiamonds and fullerenes. The structural energies have been calculated using density functional theory within the generalized gradient approximation using the Vienna *ab initio* simulation package, and used to determine the standard heat of formation for respective carbon phases as a function of the number of carbon atoms. Our results show that in contrast to previously reported studies, nanodiamond is not necessarily the stable phase a the nanoscale, but instead occupies a "window" of stability between ~1.9 and ~5.2 nm.
[DOI: 10.1063/1.1545450]

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Size and temperature dependence of nanodiamond–nanographite transition related with surface stress

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Abstract

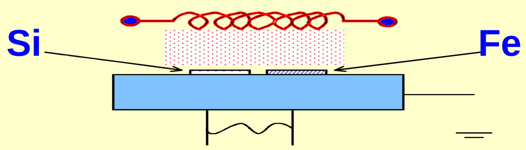
A model for the equilibrium transition size and temperature between nanodiamond and nanographite was established in terms of the effect of surface stress on the internal pressure of nanocrystals. It was found that as size and temperature decreased, the relative stability of diamond in comparison with graphite increased. The obtained result is consistent with other theoretical and experimental results.

Keywords: Diamond; Graphite; Grain Size; Temperatures

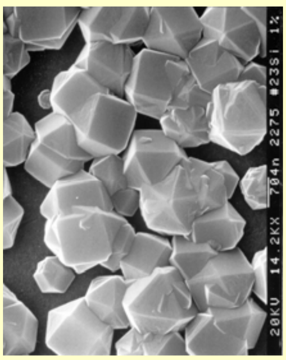
[3] J.A. Nuth, Nature 329 (1987) 589.
[4] P. Badziag, W.S. Verwoerd, W.P. Ellis, N.R. Greiner, Nature 343 (1990) 244.
[5] M.Y. Gamamik, Nanostruc. Mater. 7 (1996) 651.
[6] N.M. Hwang, J.H. Hahn, D.Y. Yoon, J. Crystal Growth 160 (1996) 87.

Experimental Aspects of CVD Diamonds

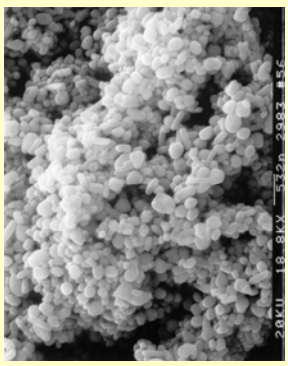
Experimental Facts in Diamond CVD Processes



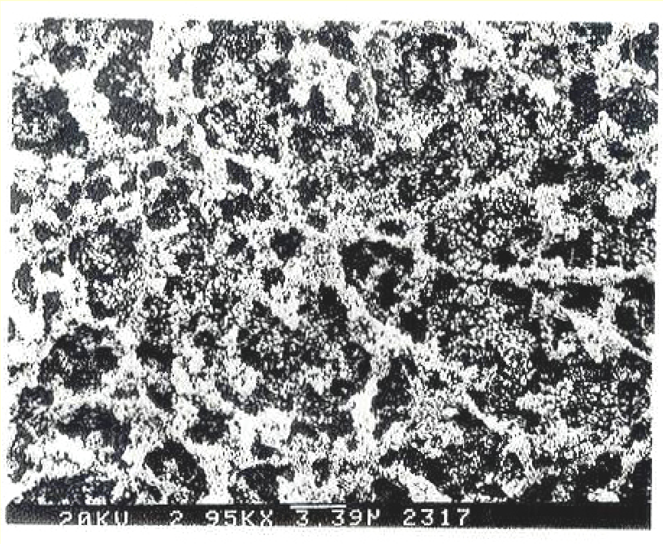
P = 20 Torr
T_f = 2100ºC
T_s = 990ºC
$CH_4 – H_2$: 100 sccm
CH_4 : 1%
2 h deposition



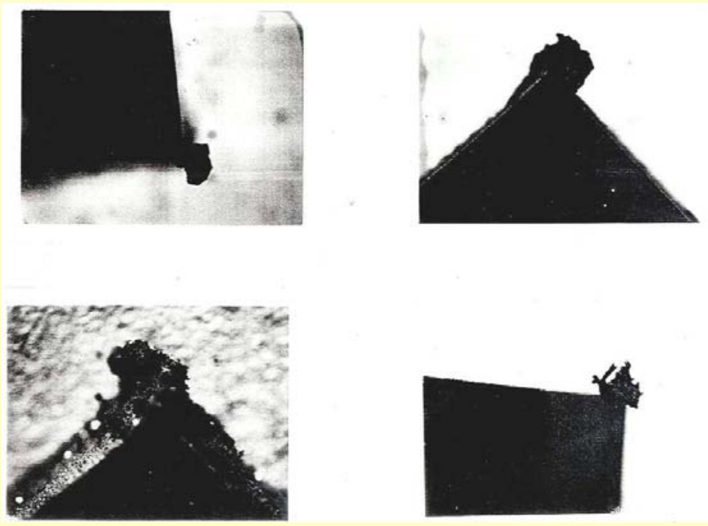
Si substrate



Fe substrate



Preferential formation of Soot at the Edge



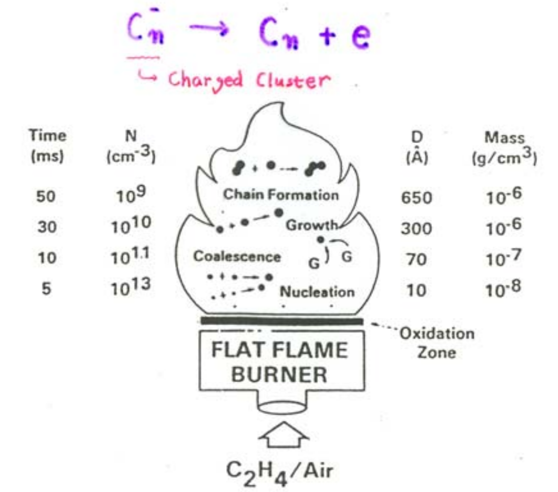


Figure 2 Schematic drawing of soot formation above a flat flame burner.

Formation Mechanism of Soot Particles
→ Neutralization of Charged Nanoparticles

Figure 1 Transmission electron micrograph of soot particles. Courtesy of B. Wicke, GM Research Labs.

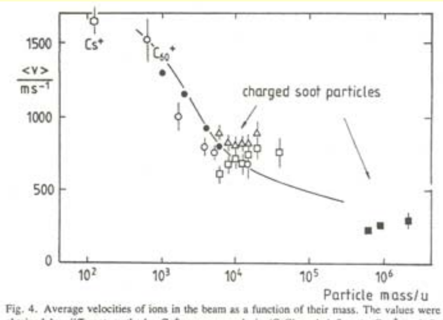
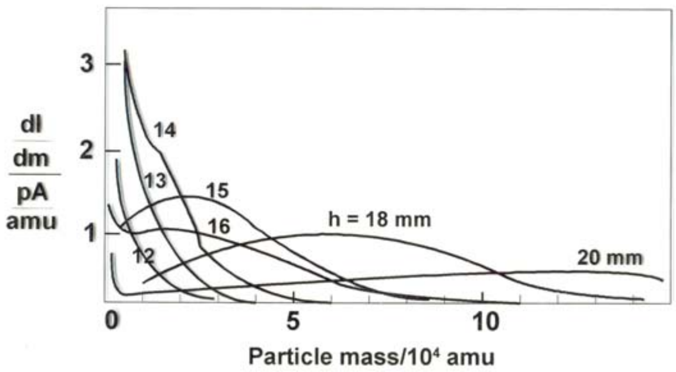


Fig. 4. Average velocities of ions in the beam as a function of their mass. The values were obtained by different methods. Cs^+, energy analysis (CsCl-seeded flame), C_{60}^+ and ○, electric deflection with TOF analysis; ●, Wien-filter experiments [13]; △, ion draw pulse-method, f = 10 kHz; □, ion draw pulse-method, f = 5 kHz; ■, electric deflection with electron micrographic size determination; p = 2.70 kPa.

Gerhardt and Homann
Combst. Flame 81 (1990) 289

Ph. Gerhardt and K.H. Homann, Combst. Flame 81 (1990) 289



Mass distribution of positively charged caron clusters with varying distances from the burner of acetylene/oxygen flame (C/O = 1.12)

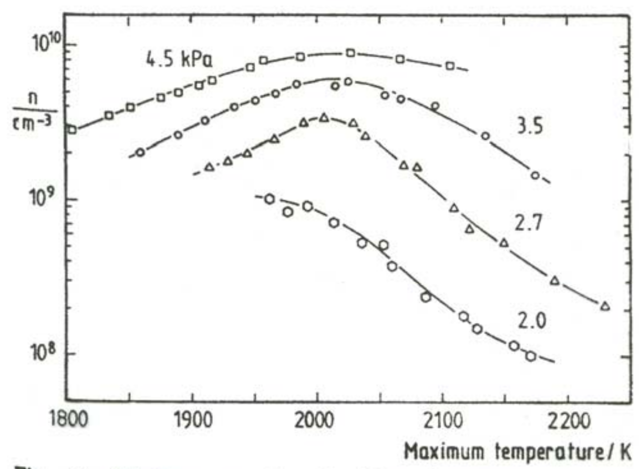
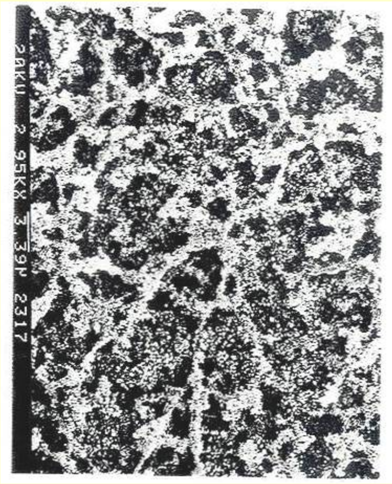


Fig. 11. Maximum number densities of positively charged soot particles as a function of maximum flame temperature; parameter is the burning pressure, C/O = 1.12, sintered plate.

Microstructural Feature of Soot

1. Porous and skeletal
2. Fragile and easily rubbed by a finger

→ Neither atomic nor molecular growth
→ Aggregation among particles



Analysis of Growth Mechanism of Soot

1. Porous and skeletal structure
2. Fragile and easily rubbed by a finger

→ Neither atomic nor molecular growth
→ Aggregation among particles

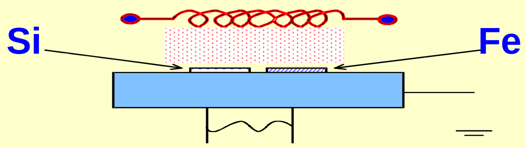
3. Preferential growth at the edge

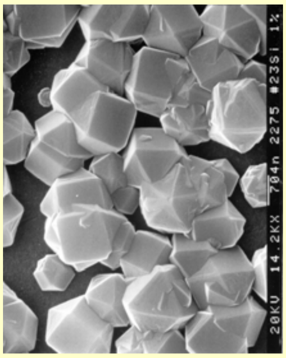
→ Growing sources might be charged.

4. Growth mechanism of soot in combustion

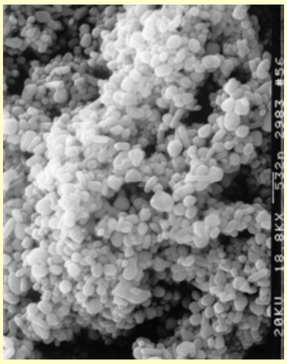
→ Ionic mechanism : Formation of CNPs and their neutralization

Experimental Facts in Diamond CVD Processes





Si substrate

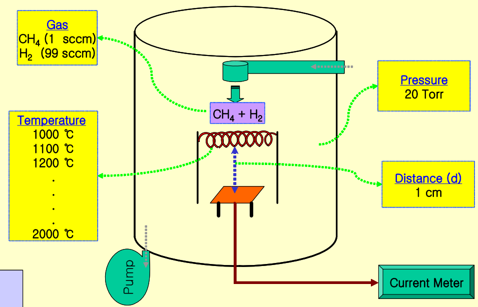


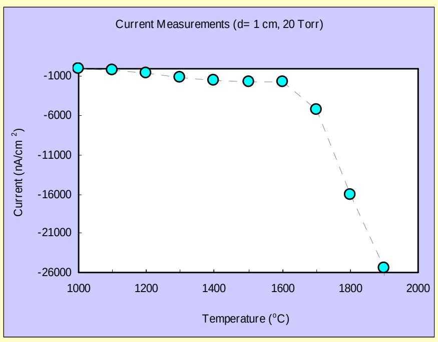
Fe substrate

Soot formation can be explained by charged clusters formed in the gas phase.

Then, why can diamond crystals grow on the silicon substrate in the presence of charged clusters?

Current Measurements in CVD Diamond Process





1 A = ~10^{19} ions /s

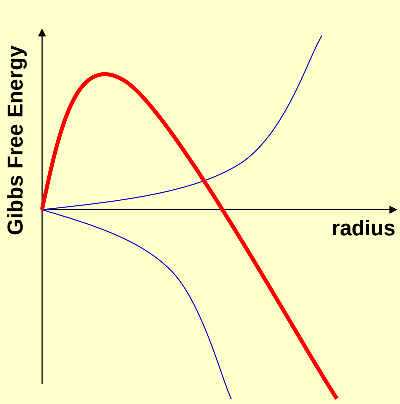
~ 20 μA/cm^2

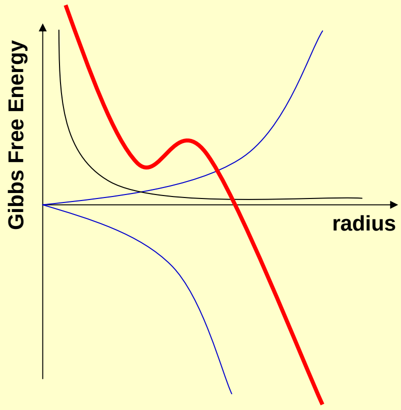
→ 2 x 10^{14} ions /s

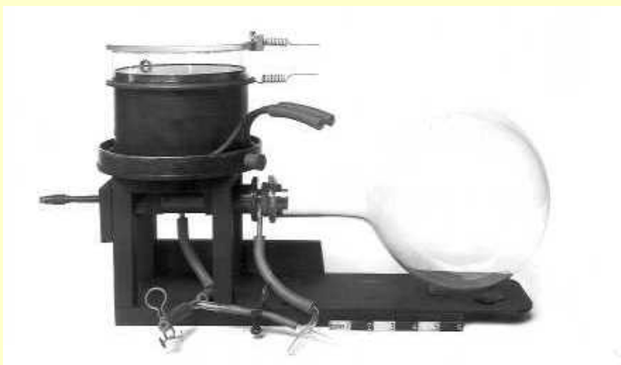
Ion-Induced Nucleation

$$\Delta G = \frac{4\pi r^3}{3}\Delta f + 4\pi r^2 \sigma$$

$$\Delta G = \frac{4\pi r^3}{3}\Delta f + 4\pi r^2 \sigma + \frac{e^2}{r}$$







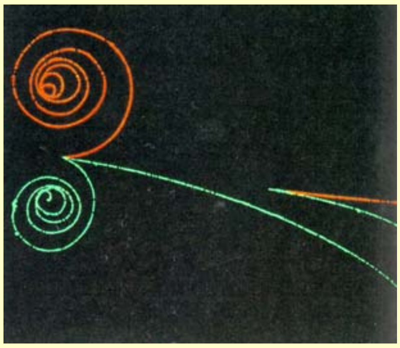
Wilson Cloud Chamber

- Designed to test the nucleation behavior

- Ion induced nucleation could not be avoided!

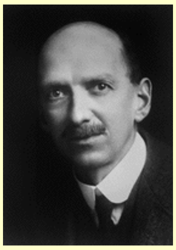
- Utilized to detect the track of the high energy particle (Bubble Chamber Experiment)

Ion-induced nucleation
in cloud and bubble chambers



Discovery of the Positron (the anti-electron)

Nobel Prize Works related to Ion-Induced Nucleation



C.T.R. Wilson
in 1927
For his invention
of Wilson cloud chamber

C.D. Anderson
in 1936

For his discovery
of positron

D.A. Glaser
in 1960

For his invention
of bubble chamber

P.M.S. Blackett
in 1948

For his works on
of Wilson cloud chamber
method and cosmic rays

Why don't we worry about Ion-Induced Nucleation in Thin Film, Nanotube, Nanowire Processes?

Wilson or Bubble Chamber Experiments

- Small amount of ions
- Large amount of a medium to precipitate
  → Charged nuclei grow instantly into visible size.

Thin Film, Nanotube, Nanowire CVD Reactor

- Large amount of ions
- Small amount of a medium to precipitate
  →Charged nuclei maintain invisible nanosize, suspended in the gas phase like nano-colloids.

CNPs are suspended in the gas phase like colloids.. How are they related with the growth?

How do they sediment?

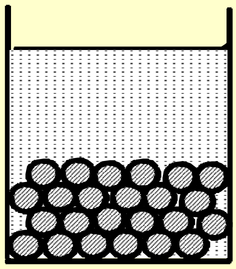
The sedimentation behavior of CNPs has not been studied.

However, the sedimentation behavior of micron-size colloidal particles is well established.

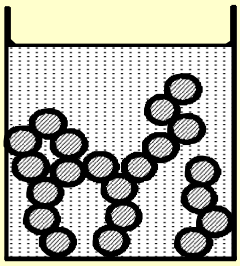
The sedimentation behavior of CNPs can be deduced from that of micron-sized particles.

Sedimentation Behavior of Colloidal Particles

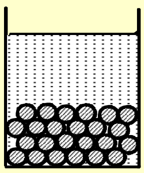
Repulsion Dominant Colloid
↓
Slow Flocculation
↓
Highly Selective Landing



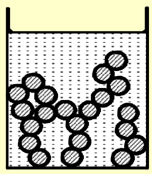
Attraction Dominant Colloid
↓
Fast Flocculation
↓
Random Landing



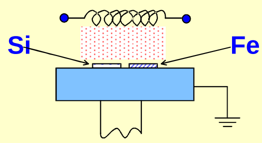
Sedimentation Behavior of Micron-Size Colloids

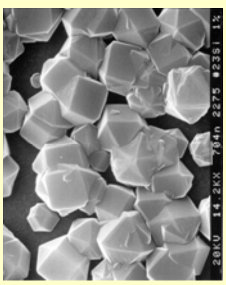


Slow Flocculation
Self-Assembly

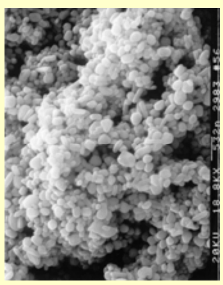


Fast Flocculation
Random Coagulation

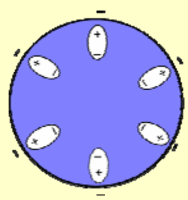




(a) Si substrate



(b) Fe substrate



Electrical double layer stabilizes dielectric diamond cluster.

Charged NPs are suspended in the gas phase.

These CNPs make soot on Fe.

These CNPs seem to make also diamond on Si.

Which property of substrates does determine diamond or soot deposition?

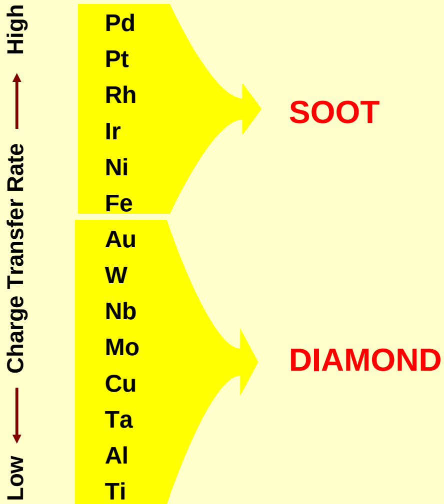
The property seems to be related with the interaction with the charge.

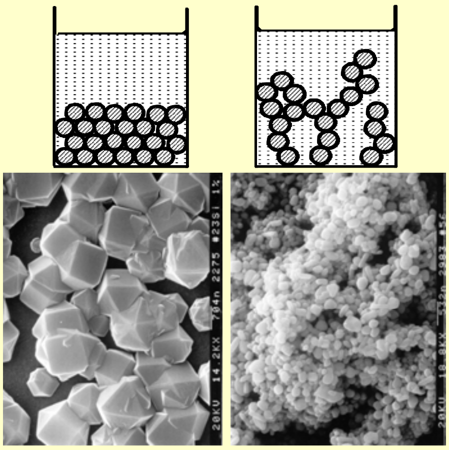
The property is not simply conductivity.

Rate of Hydrogen Evolution Reaction at Equilibrium Potential

Metal	log rate (A/cm)	Metal	log rate (A/cm)
Pd	-3.0	Ag	-6.1
Pt	-3.1	Nb	-6.4
Rh	-3.2	Mo	-6.5
Ir	-3.7	Cu	-6.7
Ni	-5.2	Ta	-7.0
Fe	-5.2	Bi	-8.0
Au	-5.7	Al	-8.1
W	-5.9	Ti	-8.2

SUBSTRATE





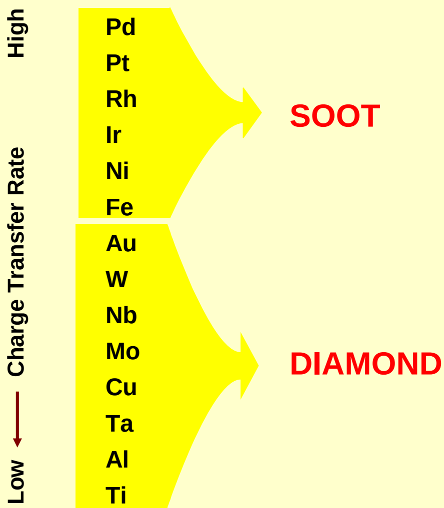
(a) Si substrate (b) Fe substrate

Neutral NP → porous structure

Self-assembly of CNP comes from electrostatic interaction.

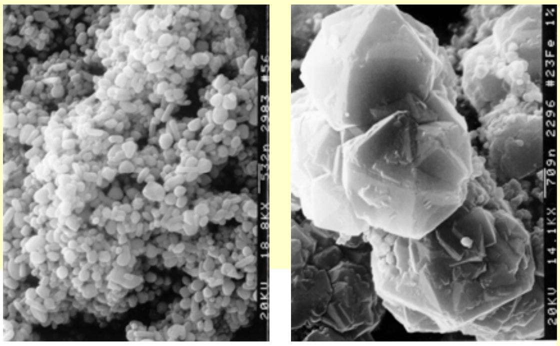
CNP → diamond, NNP → graphite

SUBSTRATE

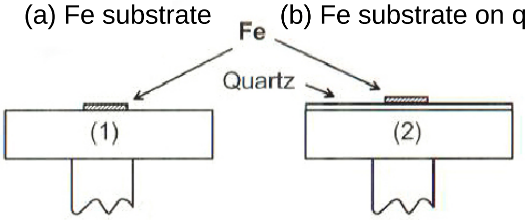


Charge stabilizes diamond.

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.