Thermodynamics of Materials

17th Lecture
2007. 5. 19 (Monday)

1950s : General Electric
High Pressure and High Temperature
Synthesis of Diamond

1958 : Eversole (Union Carbide)
Diamond Growth on Diamond Seed by Thermal CVD
Very Low Growth Rate (Å/h)
Codeposition of Graphite : Cyclic Process

1950 - 1970s : Angus & Coworkers
Similar to Eversole's results

1975 : Deryaguin's Group (USSR)
Gas Activation by Hot Filament
Dramatic Increase of Growth Rate (μm/h)
No Diamond Seed

1980s : NIRIM (Japan)
Gas Activation by Plasma

Old Diamond CVD Process

Diamond crystals can be grown at sub-atmospheric pressure

Carbonaceous materials → diamond

1050 °C, 0.3 Torr

Diamond has only a growth barrier on a diamond seed.
Graphite has a nucleation barrier on a diamond seed.
→ Metastable diamond can grow dominantly over graphite.

Experimental Method

A. Deposition and Cleaning Procedures

•Deposition and Cleaning Cycles

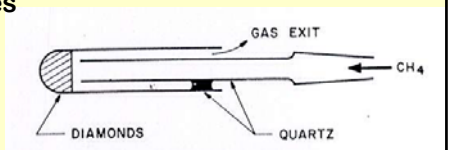

FIG. 2. Details of diamond sample chamber.

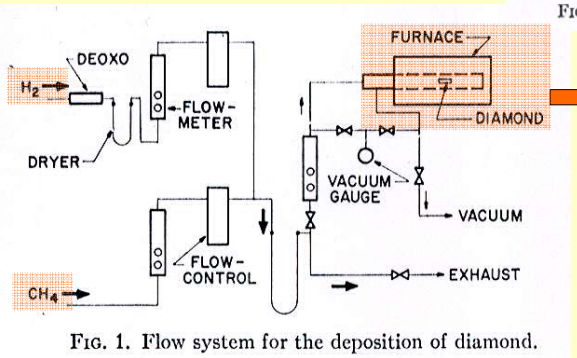

FIG. 1. Flow system for the deposition of diamond.

B. Materials

•aqua regia at 21 °C for 24 h

•HF at 21 °C for 24 h

Analysis of deposit

TABLE VII. Density of diamond samples.

Sample	Description	Measured density gm/cm³
Clean, virgin diamond		3.494 3.504 3.501
Literature value[a]		3.515
14	Diamond seeds +12.19% new diamond	3.520
22	Diamond seeds +15.28% new diamond	3.512
24	Diamond seeds +15.55% new diamond	3.482
17	Diamond seeds +10.4% graphite	3.280
23	Diamond seeds +15.04% graphite	3.039

[a] R. Mykolajewyiz, J. Kalnajs, and A. Smakula, J. Appl. Phys. 35, 1773 (1964).

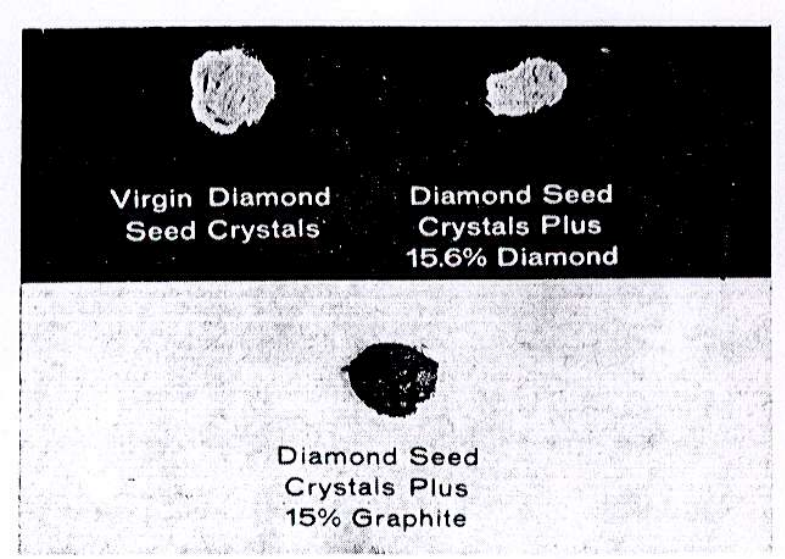

FIG. 3. Diamond powder at different stages of the growth process.

Discussion

A. Identification of Deposits

1. Before and after weighing of the sample chamber
2. Chemical analyses
3. X-ray and electron diffraction

B. Quality of Deposits

1. Not established
2. Slightly difference in conductivity between virgin diamond and deposited diamond
3. 15.6 % new diamond is dark than the virgin diamond
4. Chemical etching
5. Decrease in density

Discussion

C. Mechanism of Growth

1. Surface irregularities; defect, step

D. Operating Conditions

1. High temperature(1050 °C); higher surface mobility => perfection
2. Pressure; reducing the rate of homogeneous and heterogeneous nucleation of graphite

   (At less than 1 Torr CH_4)

Conclusions

1. Diamond growth on diamond seed crystals by vapor deposition from CH_4 at 1050 °C and 0.3 Torr.
2. Quality of new diamond; from polycrystalline to epitaxial (not established)
3. Deposition rate = a few angstroms per hour

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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.