Microwave Plasma Assisted Synthesis of Single Crystal Diamond at High Pressures and High Power Densities

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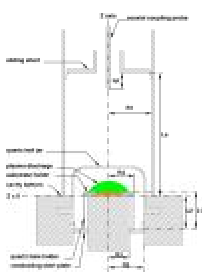
ABSTRACT

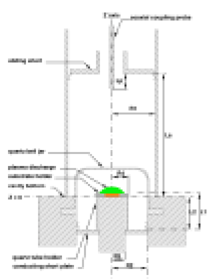
Current microwave plasma assisted chemical vapor deposition (MPACVD) diamond synthesis theory suggests that CVD synthesized diamond quality and growth rates can be improved by using high power density microwave discharges operating at pressures above 160 Torr [1]. Thus we are experimentally exploring single crystal diamond (SCD) synthesis under high pressure and high power density conditions that take advantage of the improved deposition chemistry and physics that may exist in the high pressure (180-300 Torr) regime. Here in this poster paper the experimental results for SCD synthesis are presented using a recently improved 2.45 GHz microwave plasma assisted CVD reactor design [2].

The SCD synthesis was carried out using H_2/CH_4 input gas chemistries over the 180-300 Torr regime. SCD growth rates versus pressure, input gas chemistry (with and without N_2 addition), and substrate temperature are presented, and output SCD quality was evaluated by Micro-Raman, IR-UV transmission spectrometry and SIMS analysis. SCD growth rates increase as pressure, methane concentration and discharge power density increase. Linear growth rates of 70-80 micron/hr are achieved without N_2 addition. SCD growth rates additionally increase with small amounts of N_2 additions (10-200 ppm) to the feed gas. Under similar growth conditions, i.e. temperature, methane concentration, etc., growth rates increase faster vs. N_2 addition at higher pressures than at lower pressures. A SCD growth window was observed between 950 - 1300 °C, the details of which have not been published by other investigators up to now. Micro-Raman spectroscopy, IR-UV transmission spectrometry and SIMS measurements showed that the synthesized SCD was of excellent quality (type IIa, gem quality or better) within the growth window of 1030 – 1250 °C with high growth rates of 40-45 micron/hr.

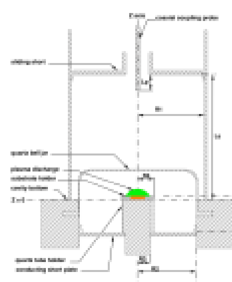
REACTOR DESIGNS



Reactor A

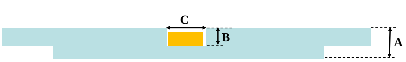


Reactor B



Reactor C [3]

SUBSTRATE HOLDER DESIGN



Pocket substrate holder cross sectional view. The design of the pocket holder is varied by varying dimensions A, B and C.

EXPERIMENTAL VARIABLES

Independent Process Variables

- Pressure: 160 - 300 Torr
- Absorbed power: 1.4 - 2.1 kW
- Gas feed composition: variable CH_4/H_2 = 3-9%
- Total gas flow rate constant ~ 400sccm
- Input gas purity: 6N - H_2; 5.5N – CH_4
- Deposition time: 6 - 24 hours
- Substrate type: 3.5 x 3.5mm² HPHT diamond substrates

Internal Variables

- Substrate temperature (Ts): 900-1400 C
- Plasma volume: 4-10 cm³
- Absorbed power density P_{abs} / plasma volume: 200-650 W/cm³

Reactor Geometry Variables

- Reactor size and Configuration: Reactors A, B, and C
- Substrate holder design: pocket holders
- Substrate position: Δz = L2- L1
- Electromagnetic excitation mode: Hybrid TM013/TEM mode

Reactor Performance and Diamond Quality

- Linear growth rate (μm/hr)
- SIMS and RAMAN measurements

REFERENCES

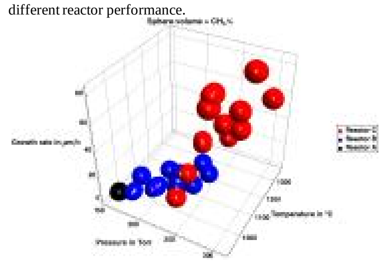
[1] D. G. Goodwin, J. Appl. Phys. 74, 6888 (1993).

[2] K. W. Hemawan, et al., Diamond and Related Materials, 19, 1446-1452 (2010).

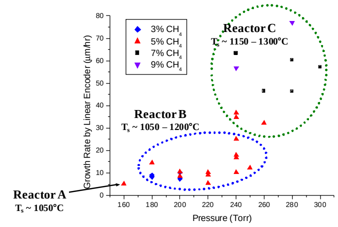
[3] Y. Gu, et al., 2nd MIPSE (2011).

EXPERIMENTAL RESULTS

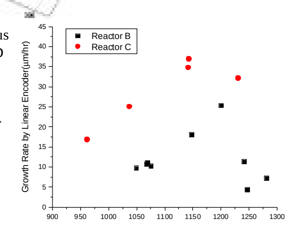
SCD synthesis is a multi-variable optimization problem – when holding substrate size and flow rate (~400 SCCM) constant the major variables are pressure, CH_4/H_2, substrate temperature, and reactor design. A multi-dimensional plot is necessary to evaluate different reactor performance.



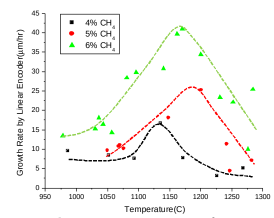
- Growth rates versus pressures for Reactor A, B, and C (N2 = 0).
- Reduction of powered electrode area and the increase in pressure increases the deposition rate.



- For both reactors and various Methane concentration, SCD growth window is observed approximately from 950 to 1300 °C.
- The higher discharge power density in Reactor C yields higher deposition rate.
- The growth rate exhibits a maximum between 1125 – 1225 °C, which shifts as methane concentration varies.

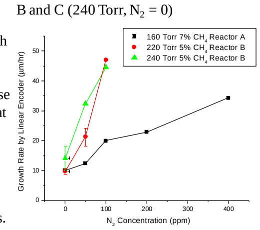


Growth rate versus pressure for Reactors B and C (240 Torr, N_2 = 0)

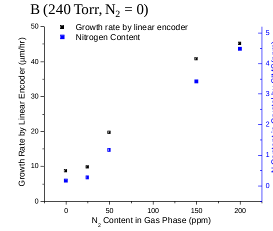


Growth rate versus temperature for Reactor B (240 Torr, N_2 = 0)

- SCD growth rates increase with N_2 addition to the feed gas.
- Under similar growth conditions, growth rates increase faster at higher pressures than at lower pressures respect to N_2 concentration.
- The Raman FWHM and N content by SIMS of the synthesized SCD both increase with N_2 addition to the feed gas.



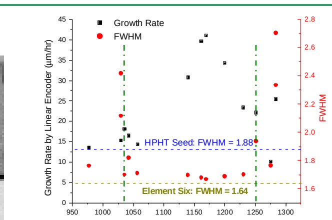
Growth rate versus N_2 concentration



Growth rate & N content versus N_2 concentration

DIAMOND QUALITY

- Thick diamond plates were fabricated by removing the SCD layer from the seed by laser cutting.
- The plates were mechanically polished and the edges were laser trimmed.
- The large size SCD plate on the right is near colorless, type IIa, 1.1 carat.



For Reactor B (240 Torr, 6% CH_4, N_2 = 0)

- Synthesized SCD was characterized by micro-Raman spectroscopy, IR-UV transmission spectrometry and SIMS.
- A good quality SCD growth window was observed between 1030 – 1250 °C.
- The Raman FWHM ranged from 1.65 – 2.0 cm⁻¹. SIMS analysis shows less than 300 ppb N and Si in the synthesized SCD. IR-UV transmission measurement also indicates type IIa diamond.

SUMMARY

At high process pressures of 180-300 Torr ,

- SCD growth rates increase as pressure, methane concentration and discharge power density increase and linear growth rates of 70 - 80 microns/hr are possible without N_2 addition.
- A SCD growth window was observed between 950 – 1300 °C, the details of which have not been published by other investigators up to now.
- Micro-Raman spectroscopy, IR-UV transmission spectrometry and SIMS measurements showed that the synthesized SCD was of excellent quality (type IIa: gem quality or better) within the growth window of 1030 – 1250 °C with high growth rate.
- SCD growth rates increase with N2 addition to the feed gas. Under similar growth conditions, i.e. temperature, methane concentration, etc. , growth rates increase faster at higher pressures than at lower pressures.
- The trends of the results of diamond quality and growth rate are consistent with the predictions from the simple theory of diamond growth and quality from Harris and Goodwin [1].

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