The Influence of Substrate Holder Depth on the Surface Morphology and Crystal Shapes of Single Crystal Diamonds Grown via MPACVD

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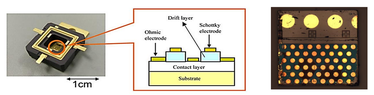
Experimental Objectives

- Investigate microwave plasma assisted chemical vapor deposition (MPACVD) single crystal diamond (SCD) growth in a pocket substrate holder
- Investigate SCD growth versus the pocket holder depth while the reactor is operating at a constant pressure of 240 Torr and at a constant substrate temperature of ~ 1020 ºC
- Develop a SCD growth recipe versus growth time the produces a PCD rimless SCD
- Characterize the grown SCD substrates

Background

Diamond Material

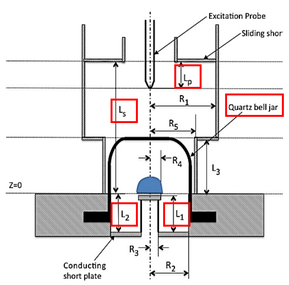
Single crystal diamonds (SCD) exhibit exceptional and unique properties which are promising for several applications, such as, optical, mechanical and high-power electronics.



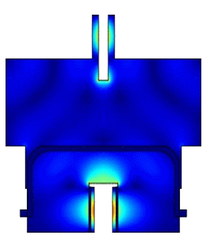
Schottky diodes and transistors

Diamond wafer cutting - Optical windows | Heat spreaders | Cutting tools | Boron-doped diamond electrodes

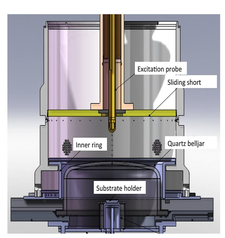
Experimental reactor: microwave cavity plasma reactor (MCPR)



The MCPR Reactor C operates at 2.45 GHz



Electric field variation vs Substrate position



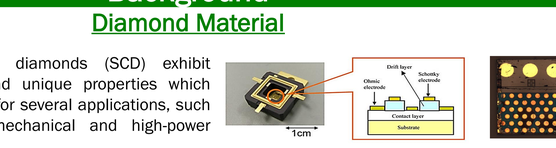
Reactor C – Cross section [1]

The experimental variables:

- Variable input variables
  Incident Power, P_{inc}; $P_{inc} \approx P_{abs}$; the reactor is operated in well matched condition.
- Fixed input variables : Pressure, p=240 Torr; Total flow rate 420 sccm (5% CH4/H2); Residual nitrogen < 10 ppm

Big Challenges Ahead

Large Area

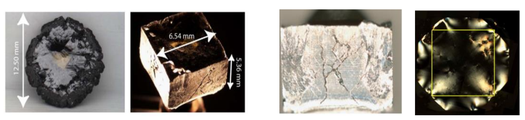


Thick polycrystalline (PCD) rim growth

Solution (new holder design by MSU)

High Quality

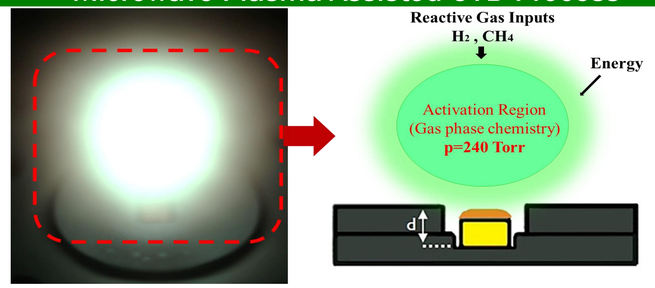
- Electronic device
- Optical applications



Goals: Develop growth strategies to produce thick, rim free, large and high-quality single crystal diamond

Y. Mokuno, et al. *Diam. Relat. Mater.*, vol. 15, no. 4–8, pp. 455–459, 2006
B. Willems, et al. *Diam. Relat. Mater.*, vol. 41, pp. 25–33, 2014

Microwave Plasma Assisted CVD Process



$$pressure = p = 240Torr$$

$$Absorbed.power.density = \frac{P_{abs}}{Plasma.volume} = 1000W/cm^3$$

$$Gas.Temperature \approx 3000K - 4000K$$

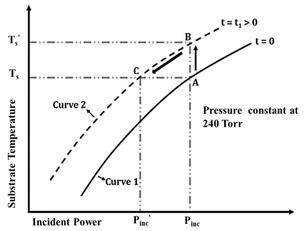
$$Electron.density, N_e \approx 1.5x10^{11} cm^{-3} - 3.3x10^{12} cm^{-3}$$

$$Electron.Temperature, T_e \approx 10{,}000K$$

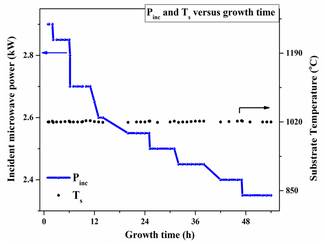
The pocket holder design created an appropriate thermal environment to shield the seed from the intense microwave discharge and the impressed microwave EM fields.

The Diamond Growth Recipe: constant temperature deposition

1. Place the single crystal diamond (SCD) seed in the pocket holder
2. Insert the gases, ignite the discharge and establish the initial operating conditions, i.e. the initial $T_s \approx 1020$ ºC, p = 240 Torr at t=0.
3. If P_{inc} is held constant as the deposition time increases, then T_s increases versus time. This is because as diamond deposition proceeds the CVD SCD volume increases, and grows into the discharge. Also other characteristics change versus time; i.e. a PCD rim form on the substrate holder. These changes versus time result in a varying reactor operating curve versus time. See Curve 2.

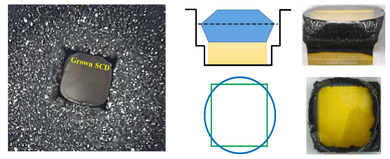


Reactor operating field map



Diamond growth recipe versus time

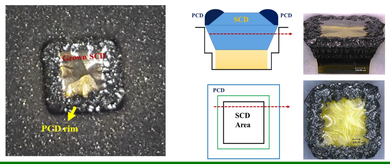
4. As shown in the figure in order to achieve constant temperature during the growth process, P_{inc} must be continuously decreased through out the process cycle. This is shown by the blue curve in the figure below
5. By continuously adjusting P_{inc}, T_s is held ~ 1020ºC ± 5ºC over the entire process cycle. See the array black experimental data points. Temperature measurement every thirty minutes.
6. The growth process cycle is ended when the grown diamond grows out the pocket. This prevents the growth of the PCD rim



An example of the grown SCD when the top surface is still entirely in the pocket

ACH02 – 60 hours deposition
Growth rate: 26.5 µm/h
Thickness: 1.42 mm
Area gain: 0.96 times
Shape: **circle**

7. If the process is not stopped in the right time the SCD protrudes into the plasma and the microwave fields. Then a PCD rim is formed as shown below



An example of the grown SCD when the top surface grown out the pocket. As is shown a PCD rim is formed.

ACH22 – 48 hours deposition
Growth rate: 31.5 µm/h
Thickness: 1.51 mm
Area gain: 2.3 times
Shape: **square**

References

[1] S. Nad, Y. Gu, and J. Asmussen, Diam. Relat. Mater., vol. 60, pp. 26–34, 2015
[2] Y. Gu, J. Lu, T. Grotjohn, T. Schuelke, and J. Asmussen, Diam. Relat. Mater., vol. 24, pp. 210–214, 2012.
[3] A. Charris, S. Nad, J. Asmussen, ICDCM, Le Corum, Montpellier, France

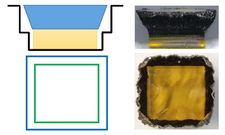
Experimental Results

SCD growth versus pocket holder depth

d_1= 2.0 mm

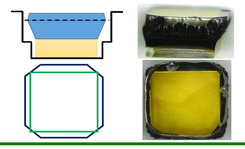
ACH31 – 40 hours
Growth rate: 30 µm/h
Thickness: 1.20 mm
Area gain: 1.94 times
Shape: **square**

d_2= 2.3 mm



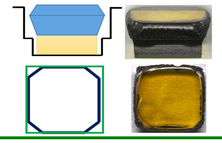
ACH42 – 42 hours
Growth rate: 29.1 µm/h
Thickness: 1.22 mm
Area gain: 1.78 times
Shape: **square**

d_3= 2.6 mm



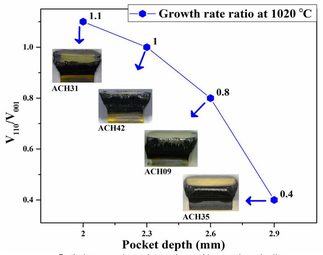
ACH09 – 50 hours
Growth rate: 28 µm/h
Thickness: 1.42 mm
Area gain: 1.4 times
Shape: **regular octagon**

d_4= 2.9 mm

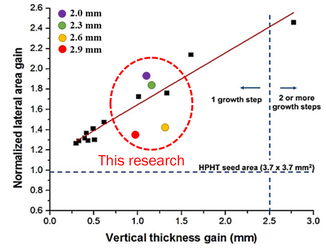


ACH35 – 46 hours
Growth rate: 23.5 µm/h
Thickness: 1.08 mm
Area gain: 1.38 times
Shape: **regular octagon**

Influence of the pocket depth on the lateral surface



Ratio between lateral growth rate V_{110} and vertically growth rate V_{100} versus pocket depth

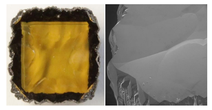


Normalized lateral area gain versus vertical thickness gain

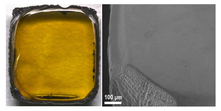
- Black point are form reference: *S. Nad et al. Diam. Relat. Mater., vol. 60, pp. 26–34, 2015*

Optical microscope and SEM analysis

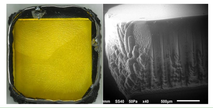
Optical microscopy and SEM images of all substrates exhibit a smooth top surface and no evidence of PCD rim



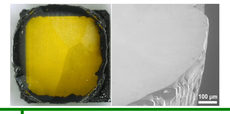
ACH42 – 42 hours
Growth rate: 29.1 µm/h
Area gain: 1.78 times
Pocket holder: 2.3 mm



ACH35 – 45 hours
Growth rate: 23.5 µm/h
Area gain: 1.38 times
Pocket holder: 2.9 mm

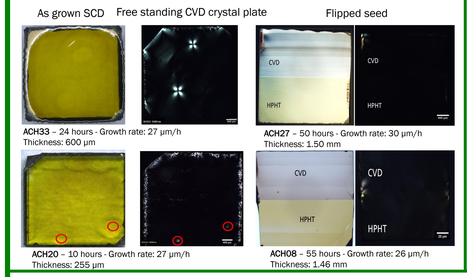


ACH09 – 50 hours
Growth rate: 28 µm/h
Area: 1.4 times
Pocket holder: 2.6 mm



ACH02 – 60 hours
Growth rate: 26.5 µm/h
Area gain: 0.96 times
Pocket holder: 2.6 mm

Birefringence Imaging



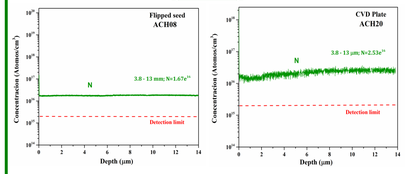
ACH33 – 24 hours - Growth rate: 27 µm/h
Thickness: 600 µm

ACH27 – 50 hours - Growth rate: 30 µm/h
Thickness: 1.50 mm

ACH20 – 10 hours - Growth rate: 27 µm/h
Thickness: 255 µm

ACH08 – 55 hours - Growth rate: 26 µm/h
Thickness: 1.46 mm

Secondary ion mass spectroscopy (SIMS)



The nitrogen depth profiles of an as-grown CVD SCD plates ACH20 and ACH08. Nitrogen concentrations in the diamond are <120 ppb.

Summary

A MPACVD growth recipe was developed to grow PCD rim free SCD. T_s was held approximately constant at 1020 ºC, and the process was stopped when the SCD grew out of the pocket. The PCD rim was eliminated for all pocket depths. Under the constant pressure and T_s growth conditions the normalized lateral area gain decreased as the pocket depth was increased. SIMS analysis shows that Nitrogen concentrations in the diamond are <120 ppb. Birefringence imaging displays low stress in the substrate. A new MPACVD SCD process was developed where thick SCD is grown without an accompanying PCD rim.