Diamond Growth at Michigan State University

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Methods of Diamond Growth

High-pressure, High-temperature (HPHT)

GE, Sumitomo, De Beers, Gemesis, not at MSU

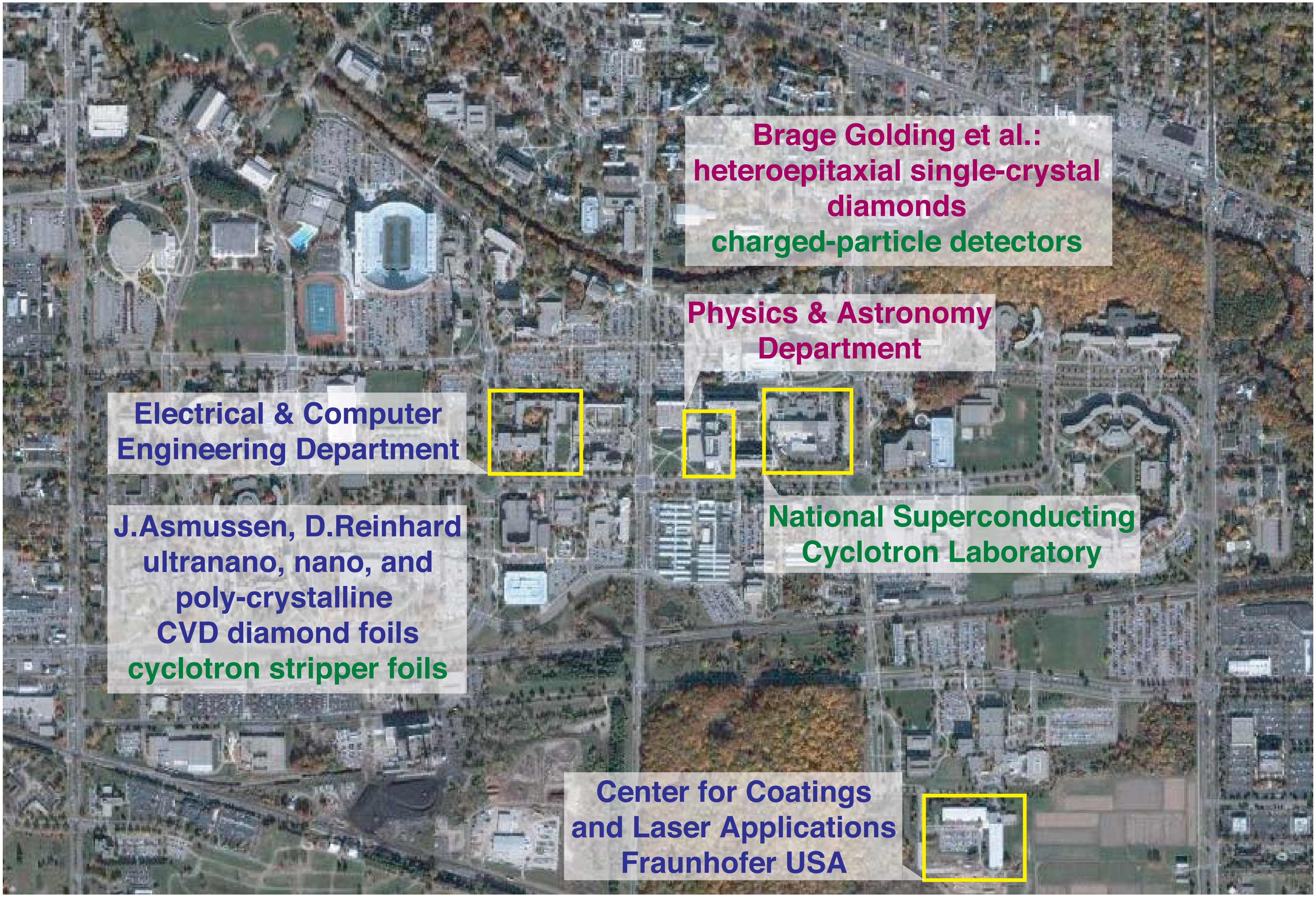
Chemical Vapor Deposition (CVD)

Microwave or hot-filament plasma
Methane and hydrogen, 800 C, 50 Torr

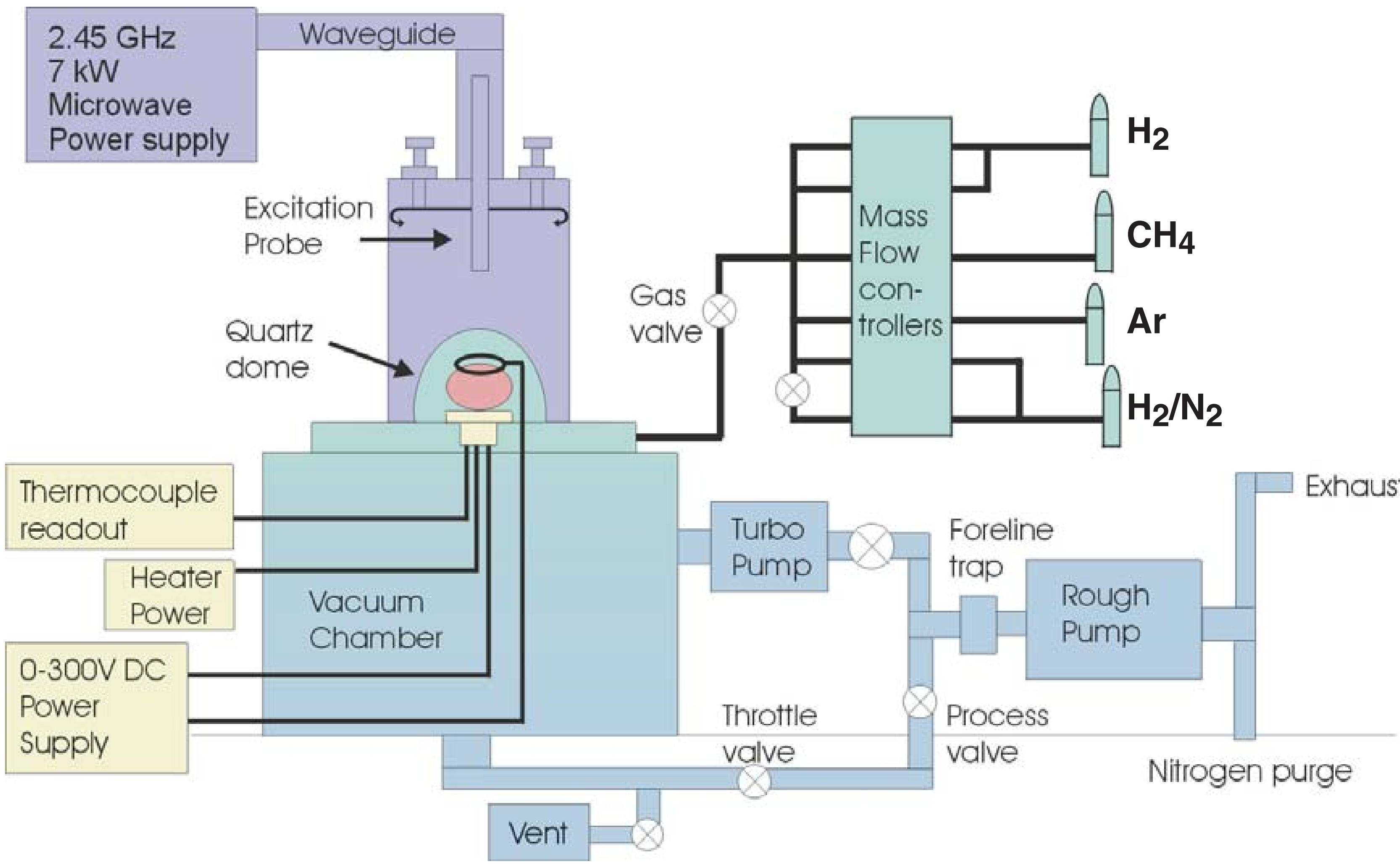
Homoepitaxial (diamond on diamond)

Heteroepitaxial (diamond on non-diamond)

Diamond Growth at Michigan State University



Microwave Plasma Chemical Vapor Deposition System



Growth of diamond on silicon wafers

Fabrication and Properties of Ultranano, Nano, and Polycrystalline Diamond Membranes and Sheets

D. K. Reinhard, J. Asmussen, et al.,
Michigan State University, Electrical & Computer Engineering Department &
Fraunhofer Center for Coating and Laser Applications

- **Polycrystalline:**
  grain sizes measured in micrometers

- **Nanocrystalline:**
  Sub-micron grains; grain sizes measured in hundreds of nanometers

- **Ultrananocrystalline:**
  Grain sizes measured in tens of nm and smaller;
  fabricated with Ar/CH4 chemistry

Growth of diamond on silicon wafers

Nucleation on silicon wafers is facilitated by pre-treatment with diamond powder (< 0.25μm). (scratch-seeding stimulates diamond nucleation)

- **Polycrystalline:**
  Diamond powder is mixed with resist and wafer is spin coated.

- **Nanocrystalline & Ultrananocrystalline:**
  Diamond dry-polished with powder and cleaned.

D. K. Reinhard, et al., "Fabrication and properties of ultra-nano, nano, and polycrystalline Diamond Membranes and Sheets", AVS 50th International Symposium, November 2-7, 2003.

Growth of diamond on silicon wafers

Deposition Parameters:

poly-and nanocrystalline

- Pressure:7 –15 torr (poly); 15 –35 torr(nano)
- Microwave Power: 700 W
- Typical Gas Flow Rates:
  - H_2 200 sccm
  - CO_2 8 sccm
  - CH_4 3 sccm
- Substrate Temperature: 500 - 600°C (poly); 600 - 700°C (nano)

ultrananocrystalline

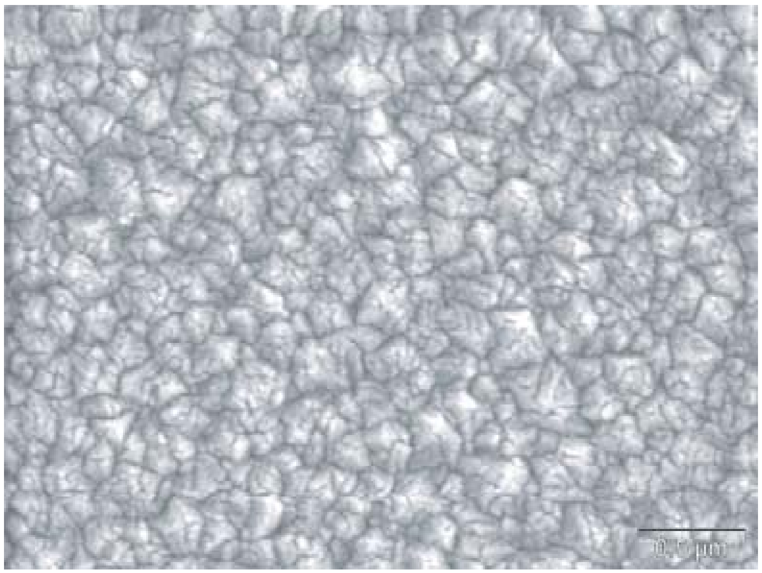
- Pressure:120 torr
- Microwave Power: 1.1 KW,
- Typical Gas Flow Rates:
  - Ar 100 sccm
  - H_2 1 to 4 sccm
  - CH_4 1 sccm
- Substrate Temperature:< 650 C.

3” wafer,
linear growth rate: 1 micron / hour

D. K. Reinhard, et al., “Fabrication and properties of ultra-nano, nano, and polycrystalline Diamond Membranes and Sheets”, AVS 50th International Symposium, November 2-7, 2003.

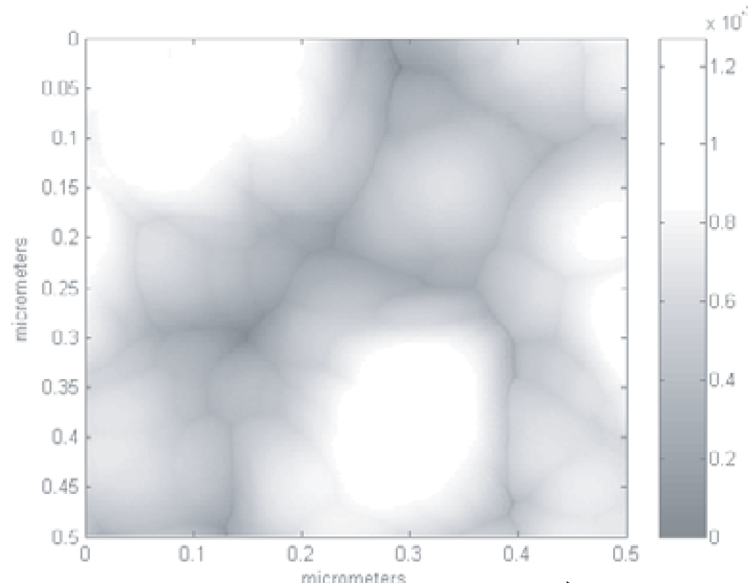
Nanocrystalline Diamond Film

FB16 SEM



1 µm

AFM

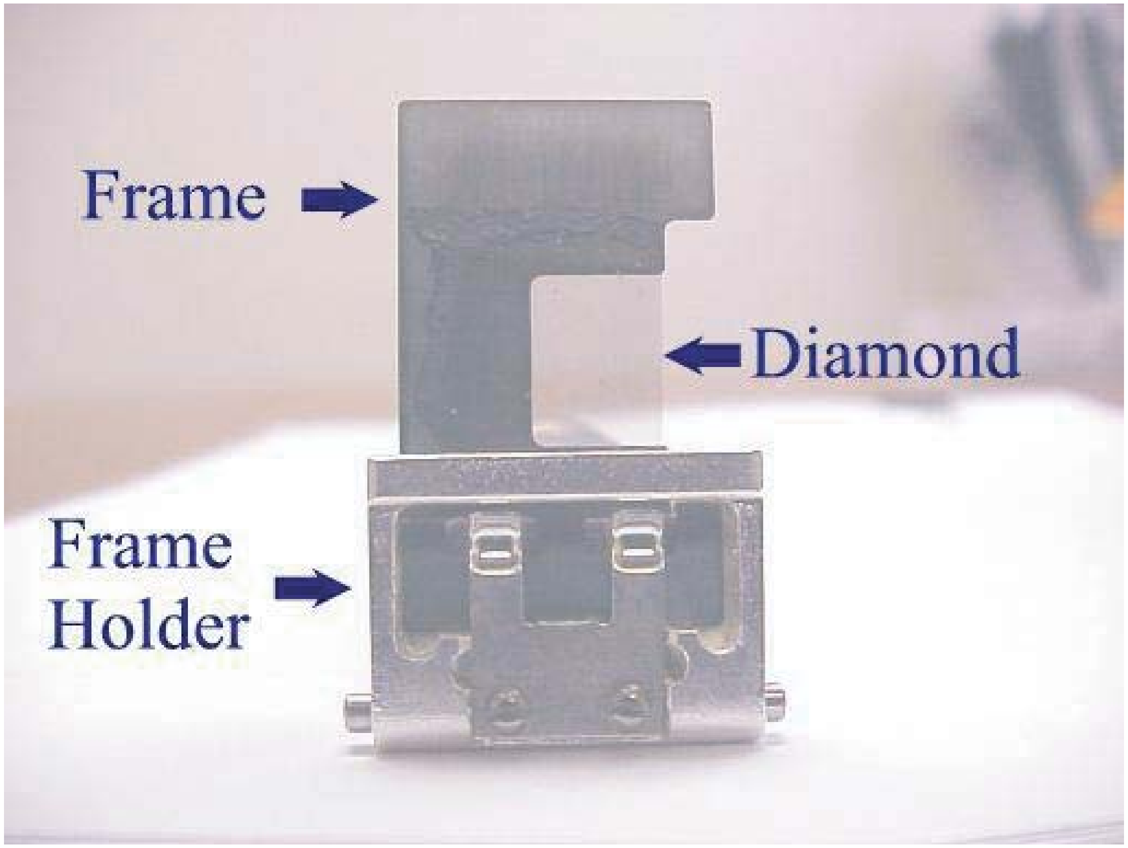


500 nm

$H_2/CO_2/CH_4$ (sccm): 200/8/3. Power = 0.7 kW, P = 33 torr
Polished Seeding

D. K. Reinhard, et al., “Fabrication and properties of ultra-nano, nano, and polycrystalline Diamond Membranes and Sheets”, AVS 50th International Symposium, November 2-7, 2003.

Cyclotron Stripper Foils



Nanocrystalline diamond foils mounted on 3-sided frame

used inside NSCL cylotron as electron stripper foil for heavy ion beam

D. K. Reinhard, et al., “Fabrication and properties of ultra-nano, nano, and polycrystalline Diamond Membranes and Sheets”, AVS 50th International Symposium, November 2-7, 2003.

Heteroepitaxial Single Crystal Diamond

Growth:

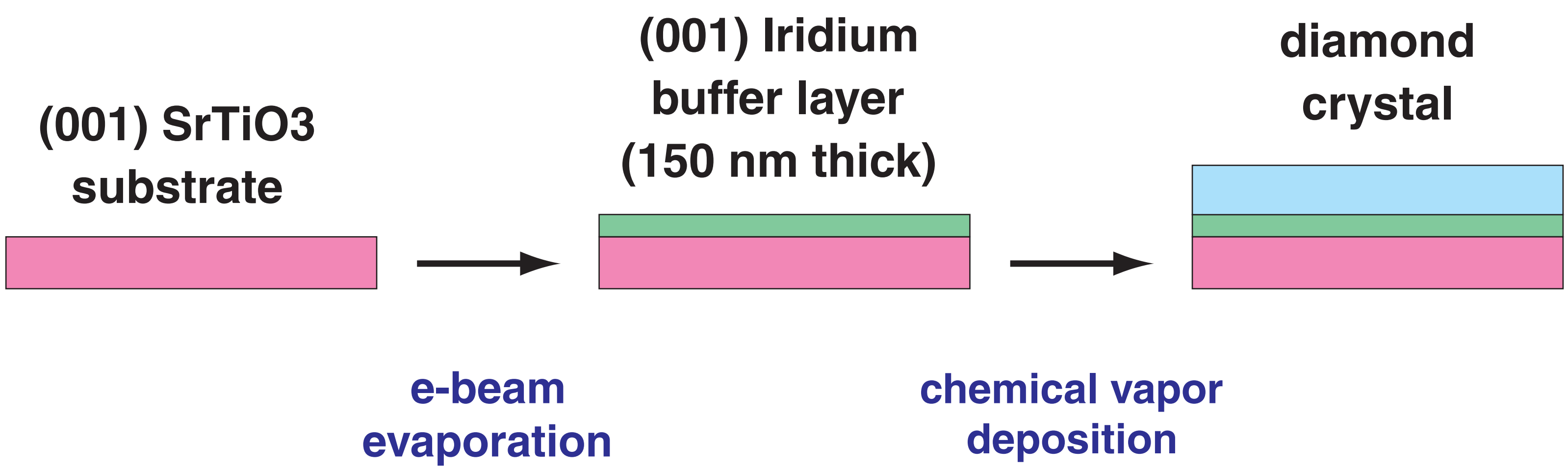
Brage Golding,
C. Bednarski, M. Behravan, Z. Dai, A.-P. Li, M. Regmi

Physics & Astronomy Department, MSU

Application at NSCL:

diamond detectors for medium-energy heavy-ions,
timing and tracking applications

Heteroepitaxial Diamond Growth

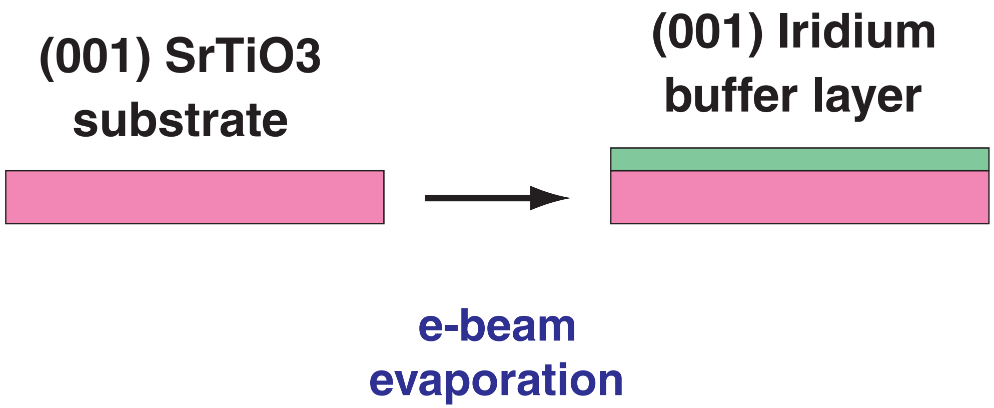


Material Properties of Substrates

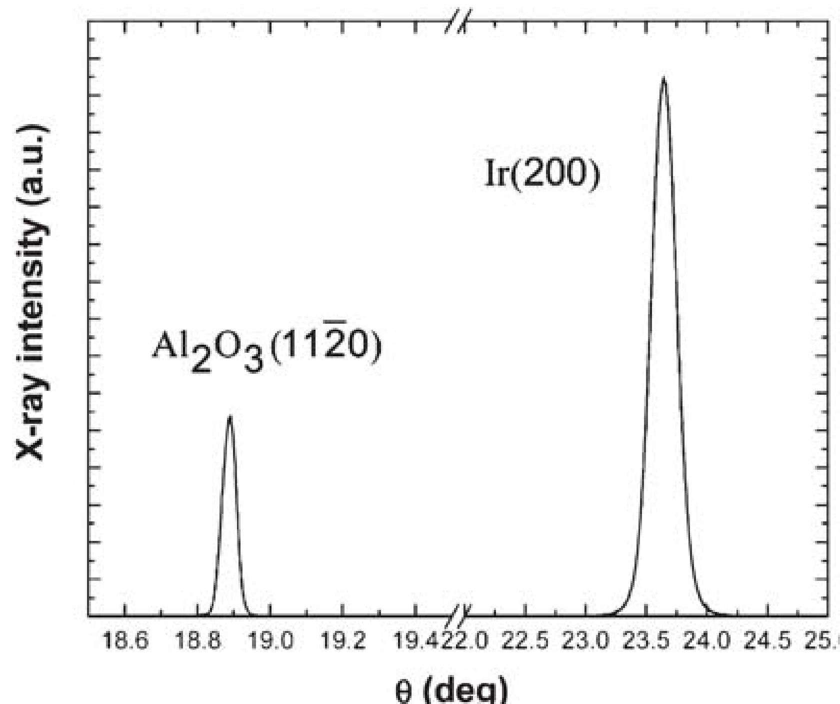
Material	Crystal structure	Lattice constant [nm]	Melting point [C]	Thermal expansivity [10-6 K-1]
Diamond	cubic	0.3567	4027	1.5
Iridium	cubic	0.3839	2484	6.8
Al2O3	hexagonal	a=0.4758 c=1.2991	2040	4.2 5.3
MgO	cubic	0.4216	2800	12.8
SrTiO3	cubic	0.3905	2080	10.3

Z. Dai et al., Diamond and Related Materials 13 (2004) 552

Iridium Growth



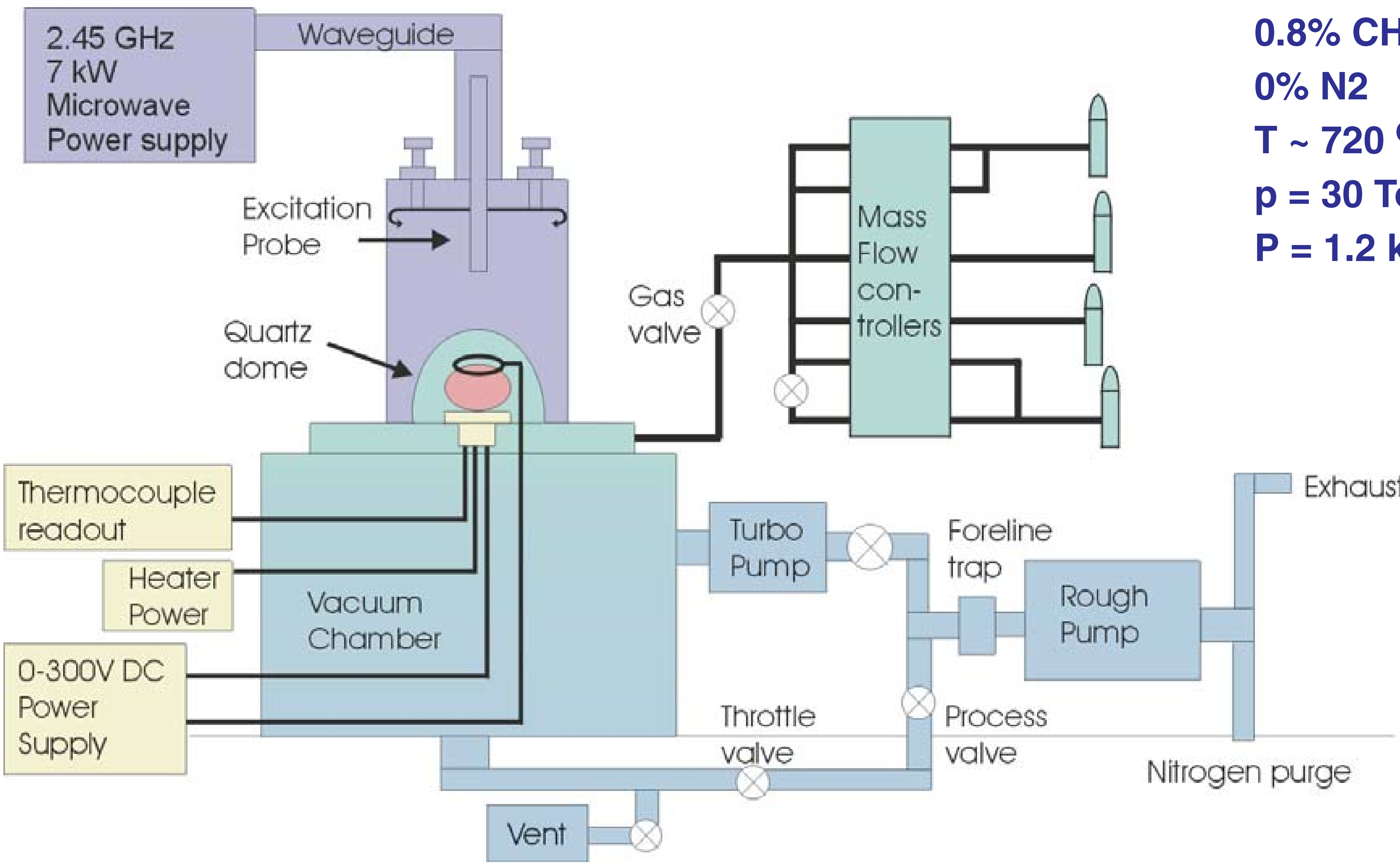
X-ray diffraction for 300 nm Ir grown on sapphire



wet chemical cleaning of substrate
(SrTiO3 or Al2O3)
annealing at 800 C
e-beam evaporation: 2.4 nm / min
no post-deposition annealing

C. Bednarski et al., Diamond and Related Materials 12 (2003) 241

CVD Process Parameters



0.8% CH_4/H_2

0% N_2

T ~ 720 ^oC

p = 30 Torr

P = 1.2 kW

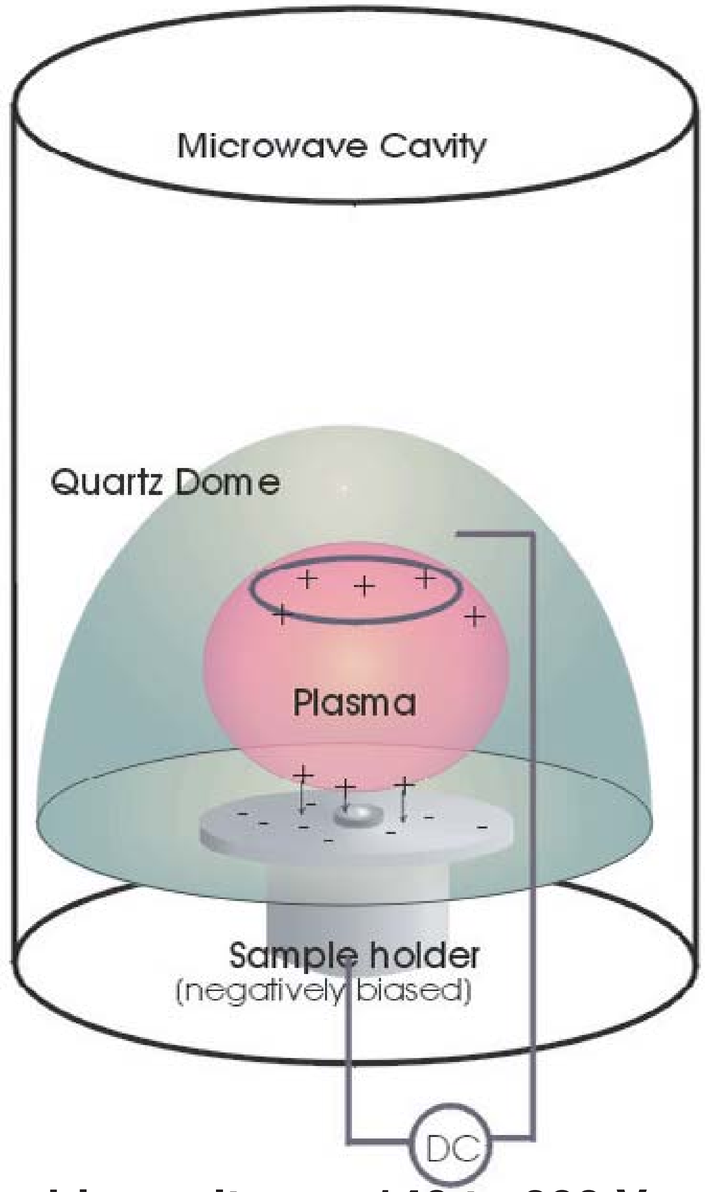
Nucleation Process

How do you induce diamond to start growing on a metal?

Schematic of biasing geometry during nucleation process

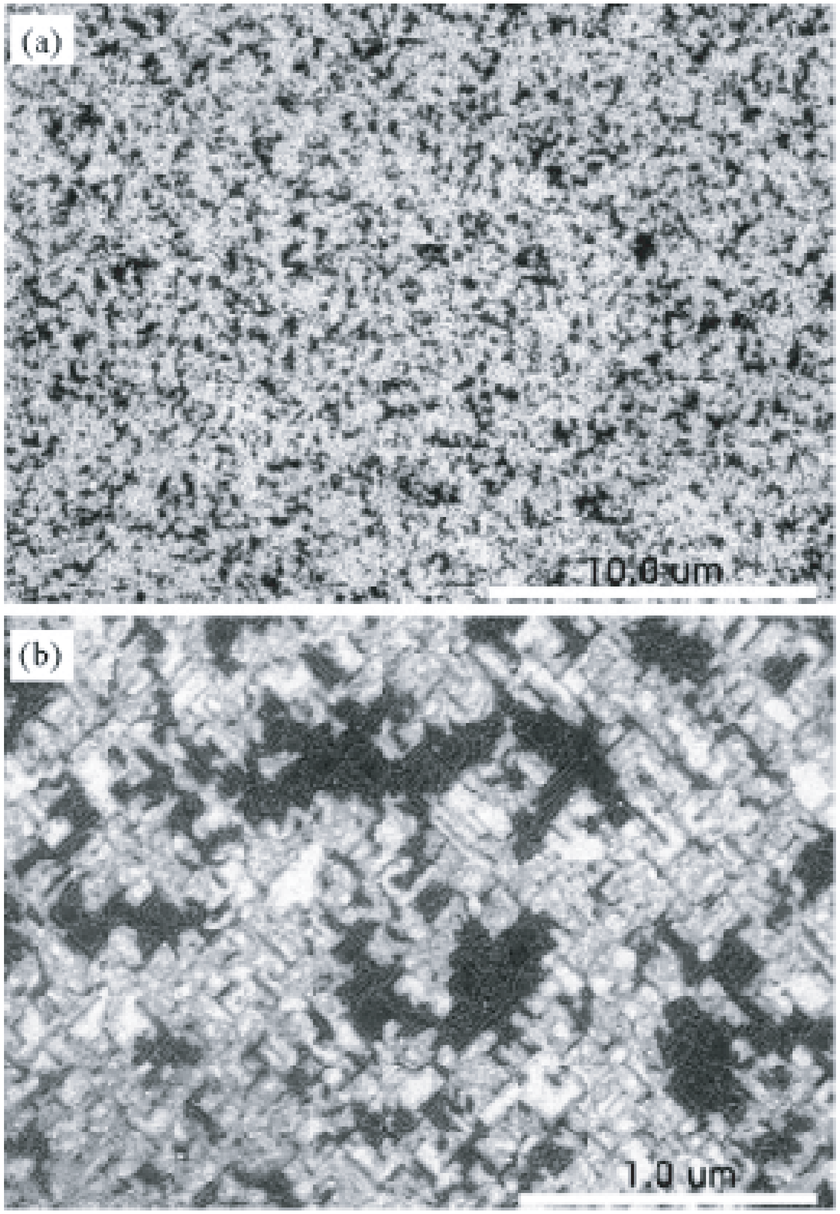
Nucleation occurs with terminating of biasing

With bias: carbon condensate in highly excited non-equilibrium state
Removal of bias: rapid temperature quench initiating nucleation



bias voltage: -140 to 200 V

Deposition of Carbon on Ir (001)



Bias period: 20 min

bright regions are diamond-like carbon condensate

condensate covers 75% of surface

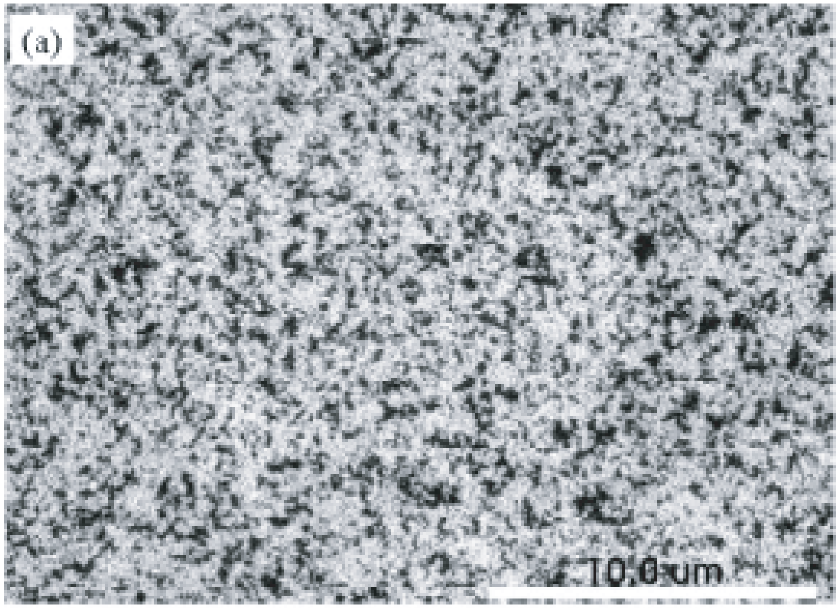
diffuse rectangular blocks of condensate

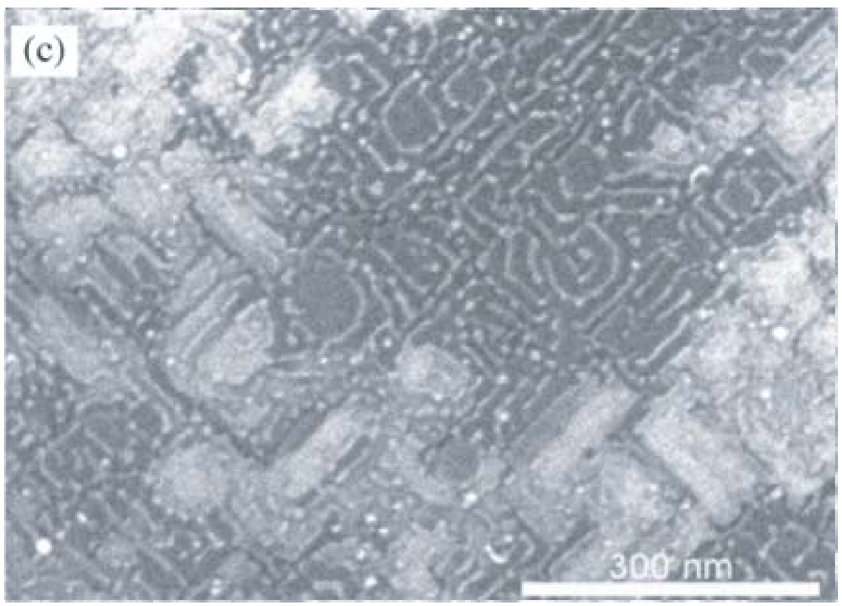
characteristic linear dimensions: 100-200 nm

boundaries parallel to in-plane Ir [110] directions

B. Golding et al., Diamond and Related Materials 13 (2004) 545

Deposition of Carbon on Ir (001)





Bias period: 20 min

bright regions are diamond-like carbon condensate

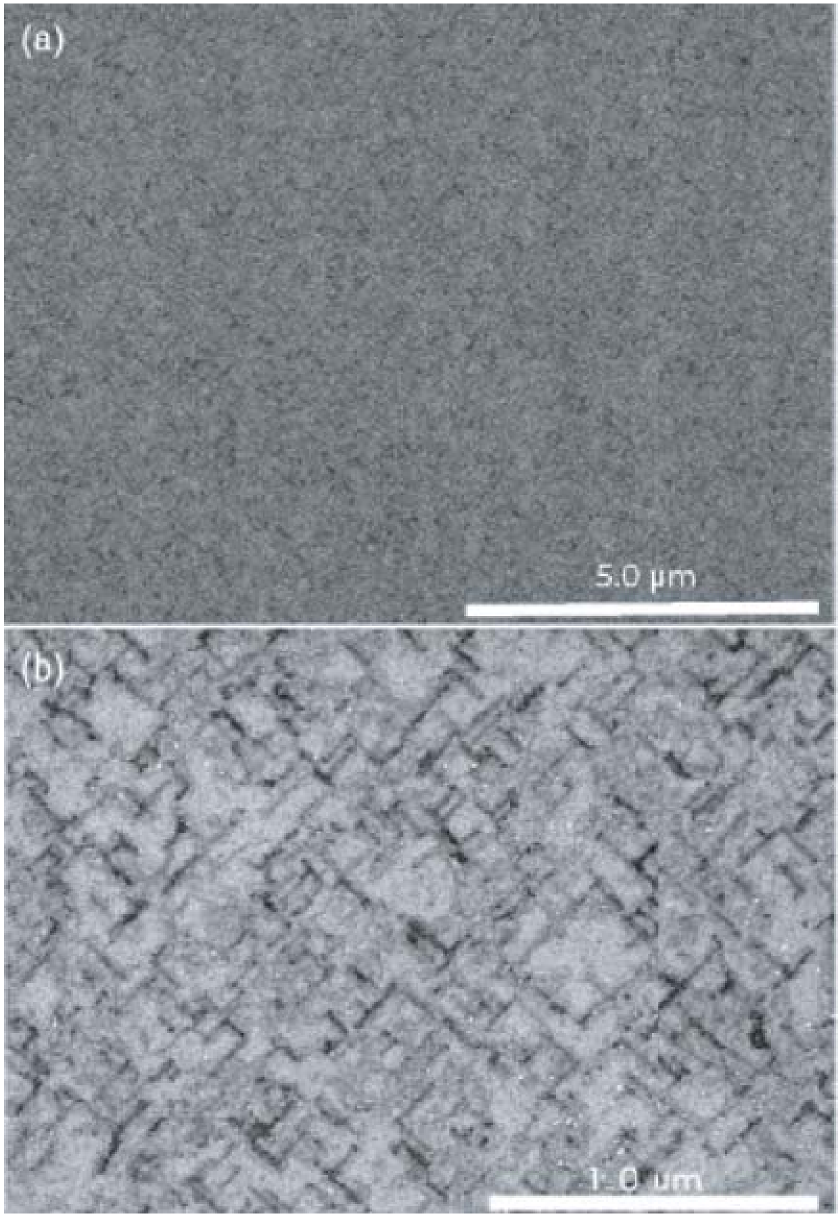
condensate covers 75% of surface

higher magnification of low-density region:

diffuse condensate in the presence of decorated ridges and whorls of Ir surface

B. Golding et al., Diamond and Related Materials 13 (2004) 545

Deposition of Carbon on Ir (001)



Bias period: 60 min

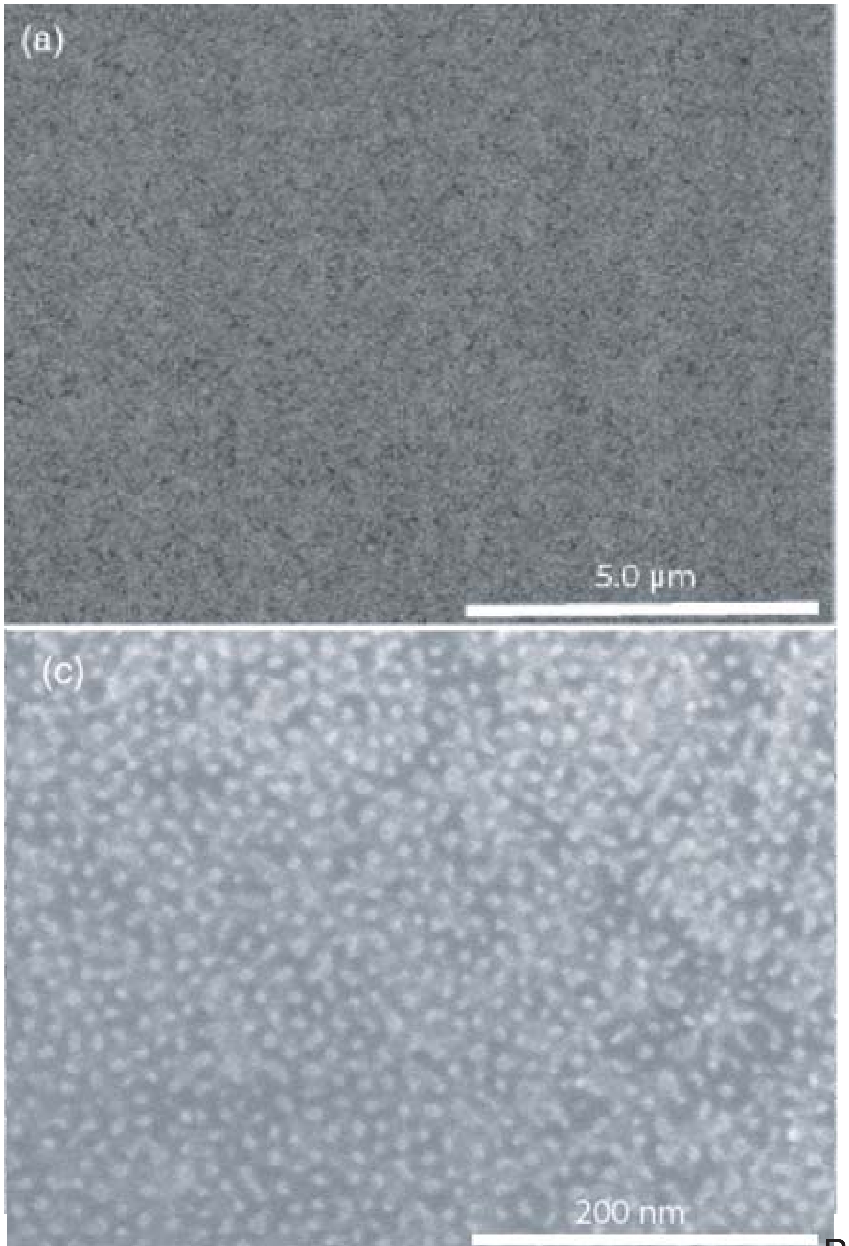
bright regions are diamond-like carbon condensate

condensate covers 82% of surface
increase of thickness of condensate

low -density region with <110> alignment

B. Golding et al., Diamond and Related Materials 13 (2004) 545

Deposition of Carbon on Ir (001)



Bias period: 60 min

bright regions are diamond-like carbon condensate

condensate covers 82% of surface
increase of thickness of condensate

higher magnification reveals diamond nanocrystallites

clusters with diameters near 7 nm
separation ~ twice diameter

B. Golding et al., Diamond and Related Materials 13 (2004) 545

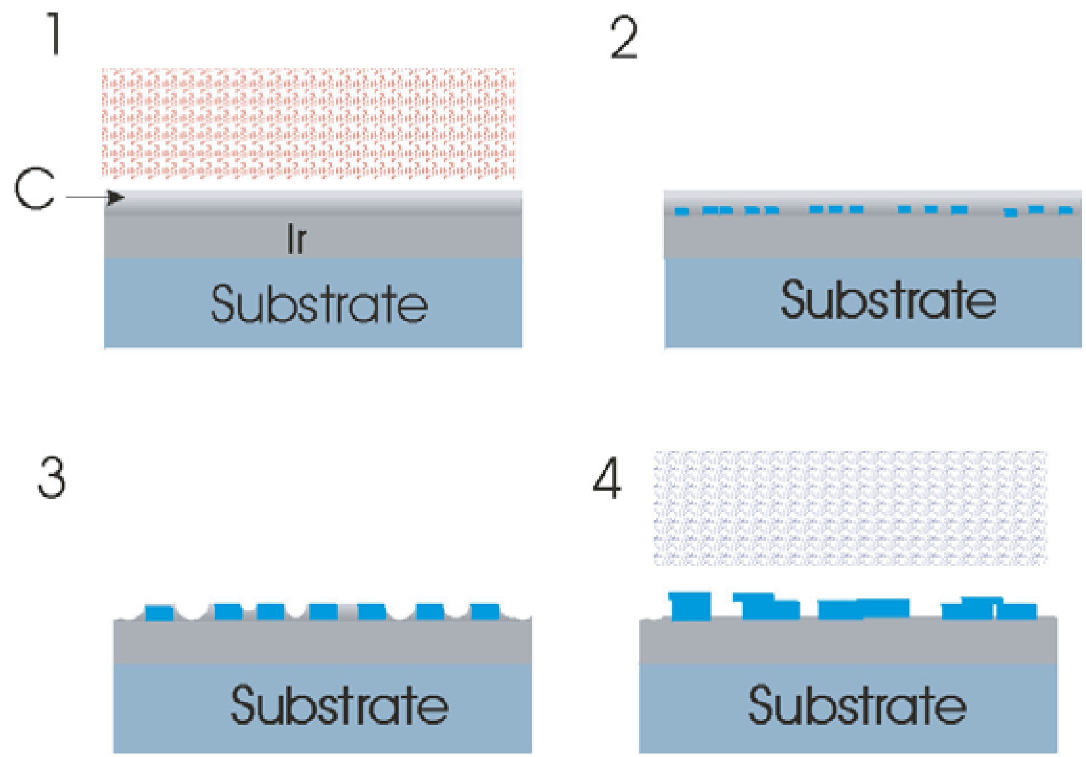
Early Stages of Diamond Evolution

1. Bias
hot plasma discharge
highly excited carbon
condensate
deposition of sp3 carbon

2. Quench
condensate cools rapidly
region of instability
appearance of nanocrystals

3. Growth from matrix
diamond is denser phase
than precursor ->
depletion of condensate

4. Coalescence and growth from vapor



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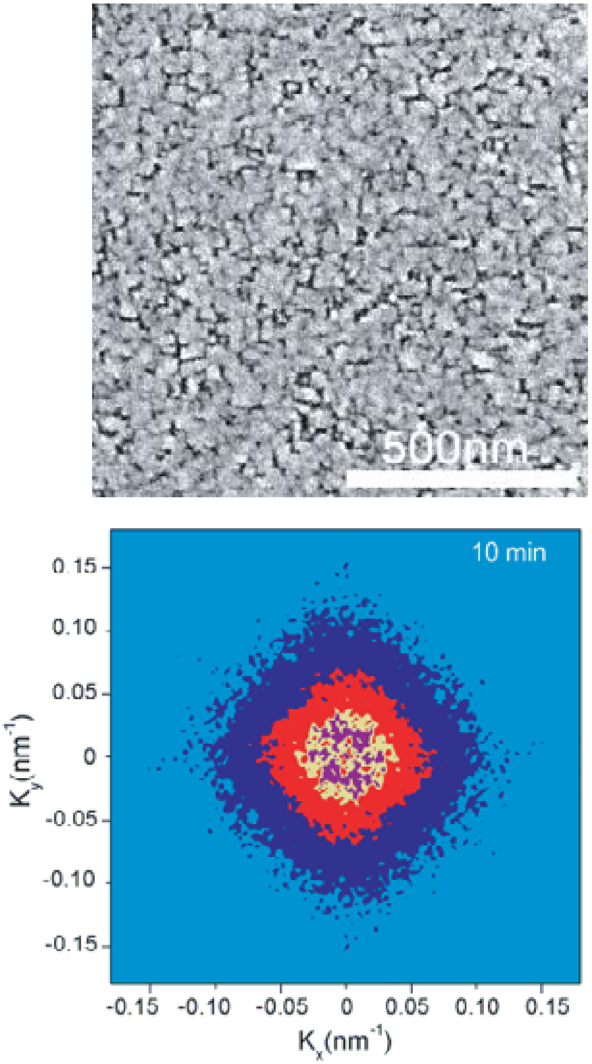
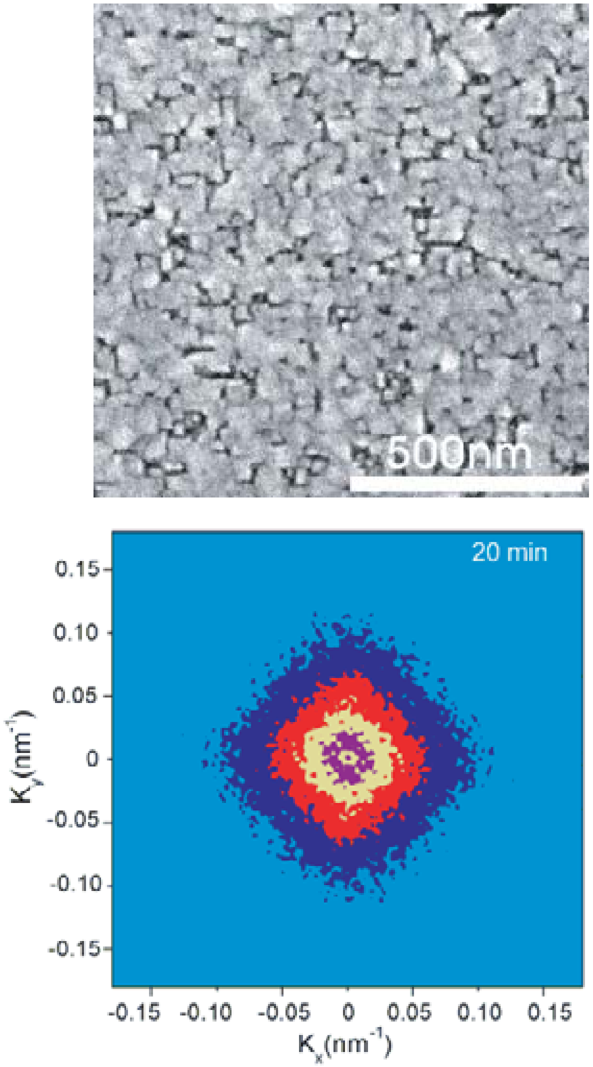
Growth of Diamond on Ir (001)

SEM micrographs and 2D-Fourier transforms



10 min



20 min

The Ir surface is covered with diamond after 10 min growth.
(time after nucleation).

Early coalescence due to high nucleation density

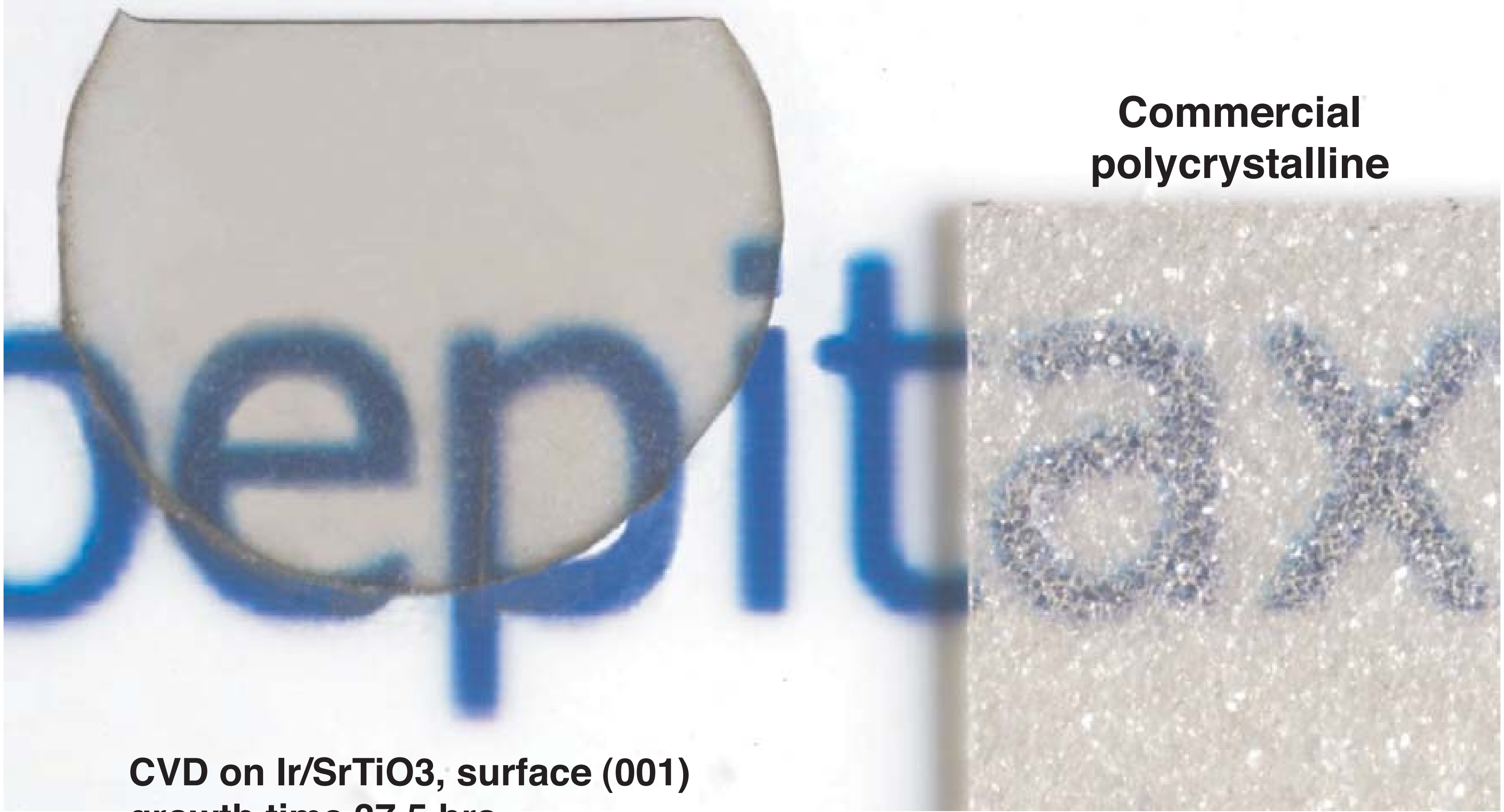
Coalescence occurs after 20 min:
contraction of Fourier transform

C. Bednarski et al., Diamond and Related Materials 12 (2003) 241

Heteroepitaxial Single-Crystal Diamond

3.5 mm diameter, 25 μm thickness
good optical quality

Commercial polycrystalline



CVD on Ir/SrTiO3, surface (001)
growth time 37.5 hrs

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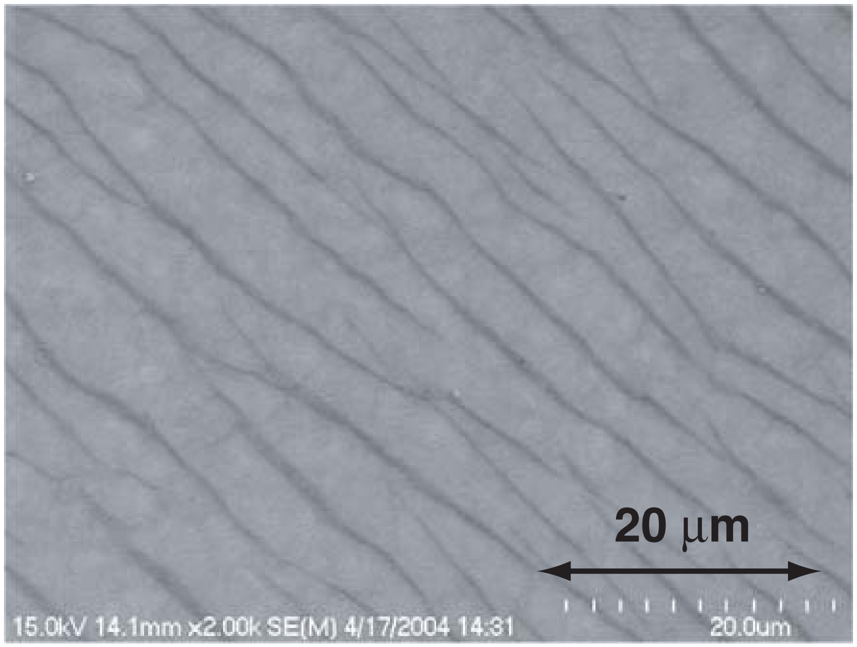
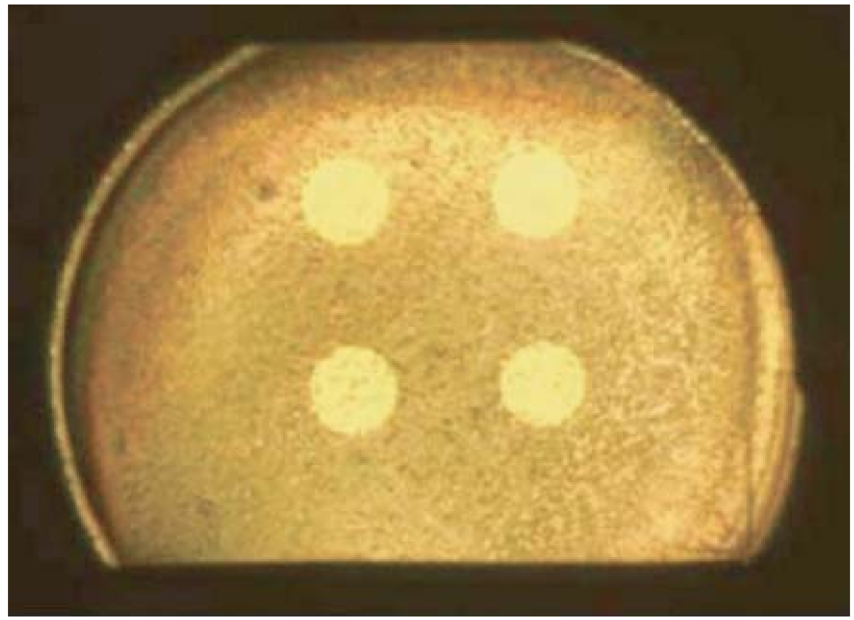
Heteroepitaxial SC diamond

Scanning electron microscope image of the (001) diamond surface



step bunching, parallel to [110]
growth by step-flow mode,
pinning due to imperfections

optical photograph with electrodes



-> investigated use for particle detectors

A. Stolz et al., Diamond and Related Materials 15 (2006) 807