Channeling 2008: Physics of Diamond

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1. Synthesis
2. Properties
3. Applications
"... It seems, indeed, to be a general truth, that there are comparatively few diamonds without cavities and flaws and that this mineral is a fouler stone than any other used in jewelry ...."

Sir David Brewster
1862
Diamond IR Spectra

P1 nitrogen peak at 1130 cm$^{-1}$

HPHT and SC-CVD (many HPHT and SC-CVD)
In nature: nitrogen aggregates
The A-centre
(two neighbouring substitutional N atoms)
In nature: nitrogen aggregates
The B-centre: four $N_S$ near a $V$
Decomposition of the IR Spectrum

The functional forms of the absorption for:
- $N_S$ – single substitutional N
- A centers - pair of adjacent $N_S$
- $N_{S^+}$ - positively charged $N_S$
- B centers – four $N_S$ at a V platelets

Are regarded as completely spanning the space of the nitrogen region absorption curve.

Very rare to find even a small region within a very good natural diamond which approaches the quality (low impurities, low strain) of a very good modern synthetic diamond.

…. see eg … papers by A Lang ….
**Diamond**

**Natural**

**Type I**
- IR visible N: 5-5000 ppm
  - **Type Ib**: P1 centre N is single substitutional
  - **Type Ia**: aggregated N

**Type II**
- N: < 5 ppm
  - **Type IIa**: strained
  - **Type IIb**: substitutional B
    - Partially compensated p-type semi-cond

**Synthetic**

**HPHT**
- P = 50-60 kbar
- T = 1250-1400°C
- Metal solvent

**CVD**
- T = 800-1000°C
- P = 100 mbar
- H₂ and hydrocarbon mix

**PC-CVD**
- Non diamond substrates

**SC-CVD**
- Ib: P1 nitrogen
  - Diamond substrates
- Illa: low impurities
  - Diamond substrates

**Gemological classification – related to defects**
- Nitrogen, boron, aggregates, intrinsic defects (dislocations)
“Moore’s Law” for the brilliance of Synchrotron X-Ray beams

- First generation: X-ray tubes
- Second generation: ESRF (1994)

Increasing need for diamond

$\sigma \sigma' \sim \lambda/4\pi$: diffraction limit

Peak Brilliance [photons/sec/mm$^2$/mrad$^2$/0.1%BW]

10$^{11}$ 10$^{12}$ 10$^{13}$ 10$^{14}$ 10$^{15}$ 10$^{16}$

Energy [eV]

10$^{-1}$ 10$^{-2}$ 10$^{3}$ 10$^{4}$ 10$^{5}$ 10$^{6}$

TTF-FEL spontaneous
TTF-FEL
ESRF Undulator (JPO)
SPS Undulator
TESSLA Undulator
SPS Undulator
PETRA Undulator

σσ' ~ $\lambda/4\pi$: diffraction limit
- Example of FEL Science

- Analyse a single bio-molecule with “one shot” per projection.
- No need for a crystal
- PoP demonstrated.

From LCLS brochure
Why diamond Beam Optical Elements

For Silicon:
liquid $\text{N}_2$ cooling works up to 400 W/mm$^2$

For FEL:
Response to transients important
## Properties of importance for X-ray applications

<table>
<thead>
<tr>
<th>Material</th>
<th>Beryllium</th>
<th><strong>Diamond</strong></th>
<th>Silicon</th>
<th>Germanium</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atomic number Z</td>
<td>4</td>
<td>6</td>
<td>14</td>
<td>32</td>
</tr>
<tr>
<td>Debye Temp $T_d$, K</td>
<td>1188</td>
<td>1860</td>
<td>532</td>
<td>293</td>
</tr>
<tr>
<td>Absorption coefficient, $\mu$ at 8 keV (cm$^{-1}$)</td>
<td>1.7</td>
<td>14</td>
<td>143</td>
<td>350</td>
</tr>
<tr>
<td>Thermal conductivity, $\kappa$, at 297K (W cm$^{-1}$ K$^{-1}$)</td>
<td>2.0</td>
<td>Type I: 5-18 Type IIa: 20-25 Iso-pure: 35 PC: 4-20</td>
<td>1.5</td>
<td>0.64</td>
</tr>
<tr>
<td>Thermal conductivity, $\kappa$, at 80K (W cm$^{-1}$ K$^{-1}$)</td>
<td></td>
<td>Ia: 20-40 IIa: 150 Iso-pure: 2000</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Thermal exp coef, $\alpha$, at 297K (10$^{-6}$K$^{-1}$)</td>
<td>11</td>
<td>1</td>
<td>2.4</td>
<td>5.6</td>
</tr>
<tr>
<td><strong>Figure of merit, 100·$\mu\kappa/\alpha$ at 297K</strong> (MW)</td>
<td>11</td>
<td>36-180</td>
<td>0.44</td>
<td>0.03</td>
</tr>
</tbody>
</table>
**Additional properties for applications at FEL’s**

1. Requires thin crystals (time response) \(\rightarrow\) framed plates
2. Time structure of beam –
   a. Time average heat load OK,
   b. Must dissipate high peak power on
      - 100 fs time scale (pulse)
      - 1ms time scale (bunch train)
3. Fast thermalisation time, damage resistant
4. Large head spreader, (isotopically enriched diamond)

<table>
<thead>
<tr>
<th></th>
<th>Diamond (nat)</th>
<th>Diamond (0.07% $^{13}$C)</th>
<th>Silicon</th>
<th>Copper</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diffusivity (cm$^2$/s)</td>
<td>12.4</td>
<td>18.5</td>
<td>0.86</td>
<td>1.25</td>
</tr>
</tbody>
</table>

PRB42(1990)1104 – T Anthony et al

Laser ablation damage threshold for isotopically enriched diamond (0.1% $^{13}$C) 10 x higher than for natural diamond.

Need also data for the melt limit and photo-ionisation cross section
X-FEL situation

Assume

1. Scaling from experiments with $\lambda=100\text{nm}$
2. Inst abl threshold $\sim 0.01\text{ eV/atom}$
3. Need to be $\sim 1000\text{m}$ from undulator
4. Diamond $>10$ x better than Si
5. Situation still marginal

10-100 GW/pulse
75 W/mm$^2$ continuous (500m from undulator)
Conclusions: “Diamond in Modern Light Sources 1 & 2”

1. Diamond is a very attractive material for Synchrotron applications
2. Symbiosis: optical and electronic (and many others)
3. Synthesis quality improving
4. Type IIa for more demanding applications
5. Require larger plate area and variety of orientations (100), (110), (111)
6. Require lower strain (low + homogenous impurities, no dislocations etc)
7. Coherence preservation not yet established
8. Surface quality must be improved!
9. Diamond mounting technologies
CVD Deposition Methods

- Hot Filament
- Microwave Plasma
- dc arcjet
- Combustion Torch
Diamond Chemical Vapor Deposition

Gaseous Reagents

Gaseous Processes

Surface Processes

Bulk Processes and Properties

Reactants

H₂ + CH₄

Activation

H₂ \xrightarrow{e-, heat} 2H

CH₄ + H \xrightarrow{\text{\textendash}} CH₃ + H₂

Flow and Reaction

Diffusion

Substrate
Electronic grade SC-CVD (100 – 200 $ /mm$^3$)
Optical grade PC-CVD (10 – 20 $ /mm^3$)
Nano diamond
How good can CVD get?

1. Size ☺
2. Purity ☺
3. Strain (not as good as HPHT yet)

$\phi = 6.7\text{mm} \times 12\text{mm}$

5ct cut from 10 ct
HPHT synthesis of diamond

Reconstitution method
- Temperature driven
- Dissolution from diamond seeds
- Temperature gradient $T_2 > T_1$
- Type IIa ~ 300 hours

N,B < 10ppb

p-type due to shallow B level

n-type due to deep N level

Graphite P1

Diamond P1

Graphite P2

$P_2 > P_1 \approx 5-6 \text{ GPa}$

$\Delta C / \Delta T = 35 \text{ ppm/C}$

$\Delta C = k(P_2 - P_1)$
Sectoral variation and striata - (HPHT)
Growth rate related to surface density of atoms

Growth sector dependence of N concentration,
[111]>[100]>[113]>[110]

B concentration,
[111]>[110]>[100]=[113]>[115]

Ni concentration,
[111]

Cube growth sectors have
A high density of perp. dislocations
Images from Growth program of the DTC
Clockwise
Visible
Birefringence
Top-face UV
Schematic
Bot-face UV
White Beam X-ray Topography

Transmission (Laue) geometry

Each Laue spot is a topographic image of diffraction contrast in sample

White Beam X-ray Topography

Laue spot

Beams stop shadow

High resolution film ($\Delta x \sim 1\mu m$)

Can see $\Delta d/d \sim 1 \times 10^{-6}$
HPHT vs CVD
Techniques are complimentary – both are necessary

1. CVD growth conditions cold for diamond – allow better control of impurities however, defects can freeze in. Leads to purer diamond (c<1ppb), but residual strain is compromised (bundles of dislocations emanating from defects in substrate, maybe more still $\Delta \theta > 10^{-6}$).
Niche is Electronic Applications

2. HPHT growth conditions hotter, and in the pressure capsule its more difficult to control impurities, growth is in “annealing” conditions. Leads to low strain diamond $\Delta \theta \sim 10^{-8}$, but more impurities, c<10ppb.
Niche is Optical Applications

White Beam Topographs - In each case illustrative samples (not the best available)
Very strong PL features

Burns (1990)
For very pure diamond

Point defects
1. Boron (acceptor, $E_A = 0.37\text{eV}$)
2. Nitrogen (deep donor, $E_D = 1.7 \text{ eV}$)
3. Hydrogen
4. Vacancy
   a. GR1 (neutral for Type IIa)
   b. ND1 (negative for Type Ib)
5. NV (in CVD)
6. Ni and Co (in HPHT)

Annealing leads to aggregation
B, N are soluble (size)
Defect Characterisation

..... low strain diamond .... considering central cubic region of top plate

Classical Techniques

1. **EPR** (defect concentration in ppb region)
2. **IR-Vis-UV Abs Spectroscopy** (defect concentration in ppm region)
3. **Photo / Cathodo - Luminescence / Phosphorescence** (defect concentration in ppb region)
4. **Birefringence** – for strain sensitivity ... down to ppm
5. **Raman Spectroscopy** – for strain sensitivity ... down to ppm
6. **SIMS** (some defects down to ppb region)

Difficulty
- Beyond MDL of many techniques
- No single technique can quantify all impurities, or all molecular forms or even charge states of the same impurity .....
Birefringence

Contrast

Phase difference

\[ \delta = \frac{2\pi d \Delta n}{\lambda} \]

\[ C = 3.24 \times 10^{-12} \text{ Pa}^{-1} \]

\[ \Delta n \approx 3 \frac{\Delta d}{d} \]

\[ Y = 10.54 \times 10^{11} \text{ Pa} \]

Metripol: MDL, \( \Delta n \sim 10^{-6} \)

Can’t characterise low strain diamond

Differential strain

stress-Optic coefficient

strain

Can’t characterise low strain diamond
Metripol image – strain induced birefringence

Thickness = 0.619 mm

$\Delta n = 1.8 \times 10^{-5}$

$\Delta n = 3.7 \times 10^{-6}$

Ian Friel, Element Six
Rocking curve
Rocking Curves

- Beam divergence – $\Delta \theta \sim 0.2''$
- Beam energy resolution $\Delta \lambda / \lambda \sim 10^{-8} \Rightarrow \Delta \theta' \sim 0.0023''$

<table>
<thead>
<tr>
<th>Sample</th>
<th>Theoretical Width</th>
<th>Exp. Width Full Beam</th>
<th>Broadening Full Beam</th>
<th>Exp. Width 100 $\mu$m Center</th>
<th>Broadening Center</th>
</tr>
</thead>
<tbody>
<tr>
<td>1173 – 001a</td>
<td>1.045”</td>
<td>1.15”</td>
<td>0.48”</td>
<td>1.10”</td>
<td>0.20”</td>
</tr>
<tr>
<td>1173 – 001b</td>
<td>0.986”</td>
<td>1.39”</td>
<td>0.98”</td>
<td>1.03”</td>
<td>0.30”</td>
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<tr>
<td>1173 – 001d</td>
<td>1.056”</td>
<td>1.30”</td>
<td>0.76”</td>
<td>0.97”</td>
<td>0.00”</td>
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<tr>
<td>1173 – 001e</td>
<td>1.018”</td>
<td>2.36”</td>
<td>2.13”</td>
<td>1.03”</td>
<td>0.30”</td>
</tr>
<tr>
<td>1186 – 001a</td>
<td>1.021”</td>
<td>1.09”</td>
<td>0.38”</td>
<td>1.04”</td>
<td>0.20”</td>
</tr>
<tr>
<td>1186 – 001c</td>
<td>1.021”</td>
<td>1.14”</td>
<td>0.52”</td>
<td>1.09”</td>
<td>0.38”</td>
</tr>
<tr>
<td>1186 – 001d</td>
<td>1.012”</td>
<td>2.47”</td>
<td>2.25”</td>
<td>1.73”</td>
<td>1.40”</td>
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<tr>
<td>1149/13R</td>
<td>1.059”</td>
<td>1.33”</td>
<td>0.80”</td>
<td>1.13”</td>
<td>0.39”</td>
</tr>
</tbody>
</table>
High-resolution diffractometry set-up

$E = 14.413$ keV

$\Delta \lambda / \lambda \approx 10^{-8} (\approx 0.0023\text{”})$

$\delta \theta \approx 0.18\text{”}$
WHITE BEAM TOPOGRAPHY

type IIa HPHT with a large inclusion

footprint = 1 x 0.4 mm

fit after convolution “defects broadening”

“defects broadening” function

FWHM 0.07"
FW20%M 0.14"
FW2%M 0.48"
Rocking Curve Imaging: Principle

- Wide, parallel X-ray beam
  ID19 @ ESRF: 15 x 40 mm

- Record monochromatic X-ray topographs digitally
- „Rock“ sample; take one exposure per angular position

- $(\Delta \omega)^2_{\text{obs}} = (\Delta \omega)^2_{\text{def}} + (\Delta \omega)^2_{\text{Darwin}} + (\Delta \omega)^2_{\text{source}}$
  
  - vert. gradient
  - const.
Non-dispersive and dispersive set-ups

(n, -n) set-up

- Range of wavelengths on detector
- What passed 1st crystal passes 2nd
- Full beamwidth reflected larger than source width

(n, -m) set-up

- Small range of wavelengths on detector
- Only small band passes 2nd crystal
- Narrow beam reflected

Also (n, +n) and (n, +m) set-ups
Curved Crystal Topography (CCT)
The consequence of dispersion

110-oriented plate
slightly distorted

100-oriented plate
non-distorted
Dispersive – non-dispersive

Non-dispersive set-up:
whole crystal illuminated for one angular position, higher strain sensitivity
White beam topograph of a HPHT “last” diamond (Laue)

Rocking curve imaging with the Curved Collimator (Bragg)

E = 12keV
Si [444] - C* [-115]
\( \Delta d/d > 3.7 \times 10^{-8} \)
(detection limit)
Also with this very high strain sensitivity a rather homogenous zone is present, there crystal quality close to that of silicon.
\[ \delta \theta(\vec{r}) = \theta - \theta^\text{perf}_B - \tan \theta_B \frac{\Delta d}{d}(\vec{r}) \pm \Delta \varphi(\vec{r}) \]

Quantification

\[ \delta \theta = \left. \frac{d \theta}{d R} \right|_{\theta_{wp}} \cdot \frac{\Delta I}{I_{\text{max}}} \]
Thermo-chemical-mechanical Processing

Feed-throughs for rotation, sensing and power

Insert shows hot metal polishing in operation
The crystal quality seen with the strain sensitivity of white beam topography is very good! No macroscopic defects like dislocations are visible.

Dislocation free
-220 and 220-reflections
sample dimension 4x4 mm²

White beam topographs in transmission
Quantum Communication

1. Photoluminescence
2. Polarised
3. Triggered
4. Photostable
5. Monochromatic (nm)
6. Short Lifetime (ns)

N-V

1. N-V, spin-encoded
2. $\tau \sim 58 \mu s$ atomic $\rightarrow$ 20 hr nuclear
3. Single and two qubit gates
4. So far 5 states coupled
Diamond detectors

Diamond’s unique position

<table>
<thead>
<tr>
<th>Properties</th>
<th>Si</th>
<th>SiC-4H</th>
<th>GaN</th>
<th>Diamond</th>
</tr>
</thead>
<tbody>
<tr>
<td>Band gap (eV)</td>
<td>1.1</td>
<td>3.2</td>
<td>3.44</td>
<td>5.5</td>
</tr>
<tr>
<td>Breakdown field (MV/cm)</td>
<td>0.3</td>
<td>3</td>
<td>5</td>
<td>10**</td>
</tr>
<tr>
<td>Electron mobility (cm²/Vs)</td>
<td>1450</td>
<td>900</td>
<td>440</td>
<td>4500</td>
</tr>
<tr>
<td>Hole mobility (cm²/Vs)</td>
<td>480</td>
<td>120</td>
<td>200</td>
<td>3800</td>
</tr>
<tr>
<td>Dielectric constant</td>
<td>11.7</td>
<td>9.7</td>
<td>8.9</td>
<td>5.68</td>
</tr>
<tr>
<td>Thermal conductivity (W/cmK)</td>
<td>1.5</td>
<td>5</td>
<td>1.3</td>
<td>24</td>
</tr>
<tr>
<td>Johnson’s Figure of merit</td>
<td>1</td>
<td>410</td>
<td>280</td>
<td>8200</td>
</tr>
<tr>
<td>Keyes’ Figure of merit</td>
<td>1</td>
<td>5.1</td>
<td>1.8</td>
<td>32</td>
</tr>
<tr>
<td>Baligas Figures of Merit</td>
<td>1</td>
<td>290</td>
<td>910</td>
<td>17200</td>
</tr>
</tbody>
</table>

Study

- Charge carrier dynamics
- Near surface defects
- Electrically active defects
High Energy Photon physics

Technology –
use aligned particle incidence on diamond to
1. Produce >100 GeV quasi-monochromatic photons
2. Manipulate polarisation
3. Measure polarisation

Physics (QED) -
1. Strong field effects (Lorentz boost)
2. Coherent enhancements

Polarised photons from Coherent Bremsstrahlung by 200 GeV electrons incident on aligned diamond → quasi monochromatic tagged photons

NA43
NA59
NA63
Fig. 2. Spectral distributions of the total radiation emitted in forward direction for $\varepsilon = 500$ MeV positrons channeling in Si along the (1 1 0) crystallographic planes for $a/d = 10$.
CL image

WB Topo

220 reflection

14 keV

With laser trenches
White Beam Topography

Transmission (Laue) geometry

Each Laue spot is a topographic image of diffraction contrast in sample

white X-Ray Beam

sample

High resolution film
($\Delta x \sim 1\mu m$)

Laue spot

Beam stop shadow

220

400
Focussing in vertical plane

Bending across crystal corresponds to:
1 mrad/mm crystal!

$3.6 \text{ mm}$

$\theta = 1.8 \text{ mrad}$

$0.98 \text{ m}$
Diamond Superlattice

Lang Dilatation Formula

Doping with nitrogen $\rightarrow$ expands the lattice

$$\frac{\Delta a}{a_0} = 0.116 \pm 0.02 \times C_N \quad \leftarrow \quad C_N \text{ in ppm}$$

Intrinsic

N substitutional

KEY PHYSICAL PARAMETERS:
- Undulator wavelength = $\lambda_u$ ($\approx 0.1 \text{ mm}$)
- Undulator amplitude = $a$ ($\approx 50 \text{ Å}$)
- Interplanar distance = $d$ ($\approx 1-2 \text{ Å}$)
- Crystal thickness = $t$ ($\approx 1-4 \text{ mm}$)
- Number of undulator oscillations = $N_u = t/\lambda_u$ ($> 10$)
Conclusions

Showed improvements in diamond targets to eff misorientation of few $10^{-8}$

Acknowledgements

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