High growth rate homoepitaxial diamond deposition on off-axis substrates for detector applications

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Outline

- Motivation
- Growth on on-axis substrates
- Growth on off-axis substrates
- Structural characterisation
  - high resolution x-ray diffraction (HRXRD)
  - μ-Raman
  - photoluminescence
  - chemical purity (N, B)
- Detector properties
- Summary
Motivation

- high quality CVD diamond films on HPHT substrates feasible
  - very high charge carrier mobilities (e.g. \( \mu_{\text{electron}} = 4500 \text{ cm}^2/\text{Vs} \), Isberg et al.)
  - strong excitonic recombination at room temperature (Watanabe et al.)
- high growth rate
  - moderate cost of CVD diamond
  - avoiding of nitrogen (deteriation of electronic properties)
  - stable growth (without forming of non-epitaxial crystallites)
General growth conditions

- substrates:
  - (001)-oriented Ib-HPHT diamond (nominally on-axis or 3-8° off-axis towards [100])
  - containing 10-100 ppm nitrogen

- process parameters:
  - $T_{\text{substrate}} \approx 1200$ °C
  - $p=130-200$ mbar
  - $P_{\text{microwave}} = 1400$ W
  - 5-20% CH$_4$ concentration in H$_2$, for some samples up to 2% CO$_2$
  - nominally no nitrogen

- growth rate: 6-30 µm/h

- film thickness: 100-1300 µm
Growth on on-axis substrates I: pyramidal hillocks/non-epitaxial diamond

- sample:
  - 100 µm thick
  - growth rate: 6 µm/h
- forming of pyramidal hillocks (PH)
  - height \( \approx 20 \) µm, width \( \approx 1000 \) µm
  - inclination \( \approx 3^\circ \) towards [110]
  - non-epitaxial crystallites on top
  - side faces **free** of non-epitaxial crystallites, step bunching
- non-epitaxial crystallites (NC)
  - height \( \approx 30 \) µm
  - growth rate higher than surrounding epitaxial diamond
Growth on on-axis substrates II: formation of pyramidal hillocks

- How do PHs develop?
  1. formation of non-epitaxial crystallites
  2. NCs are nucleation centers for new lattice planes
  3. lateral spread of the lattice planes
  4. macro-steps due to step bunching

- Why are no NCs on side-faces of pyramidal hillocks?
  - growth by lateral step flow mechanism
  - steps of side-faces sources of new lattice planes
    ⇒ suppression of NCs by lateral overgrowth

**Idea:** reproduce conditions on side-faces by using off-axis substrates
Growth on off-axis substrates I

- Idea works

- Complete suppression of NCs and PHs
Growth on off-axis substrates II

- "rough diamond" (after CVD process)
- 0.5 mm thick film on 7° off-axis substrate
- surface almost free of non-epitaxial diamond
- side length increased by about 1 mm mainly by polycrystalline growth
- removing of substrate / polycrystalline rim by mechanical polishing / laser cutting
Growth on off-axis substrates IV: flexible growth conditions

- CH₄ concentration: 5-20 %
- CO₂ concentration: 0-2 %
- samples about 400 µm thick
- no non-epitaxial diamond
- narrow rocking curve line widths
  ⇒ off-axis substrates allow a very broad range of process parameters
- two regions with different morphology
Growth on off-axis substrates V: mechanisms

- Lattice planes of CVD film originate from:
  - Off-axis surface
  - Polycrystalline rim
  - Nucleation on (001) terraces

⇒ Inhomogeneity in structural and electronic properties??
Growth on off-axis substrates VI: varying off-axis angle

- 20h growth @ 10% CH₄
- thicknesses of 0.09 to 0.56 mm
- huge improvement in growth rate
- decreasing off-axis angle during growth causes reappearance of non-epitaxial diamond
- 6° sufficient for desired film thickness of 0.5 mm
Characterisation: HRXRD

- lateral resolved measurement of diamond (004) rocking curves
- beam width: 0.2 mm
- 0.37 mm freestanding CVD film
- line widths homogeneous
- no bending of this CVD film
- line width only slightly higher than substrate (0.0027°)

(a) Ib HPHT substrate
- FWHM$_{avg} = 0.0024^\circ$

(b) free-standing CVD film
- FWHM$_{avg} = 0.0027^\circ$
Characterisation: μ-Raman

- sample: 350 μm thick freestanding CVD film
- λ=514.53 nm
- shown: single point measurement
- average values of 10 measurements:
  - position=1332.25±0.1 cm⁻¹
  - FWHM=1.63 cm⁻¹
- position equals substrate ⇒ no strain (due to N in substrate)
- FWHM very low compared with other diamond samples ⇒ good crystal quality

<table>
<thead>
<tr>
<th>Sample</th>
<th>Linewidth, cm⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Synthetic Ib (Yumi)</td>
<td>1.68</td>
</tr>
<tr>
<td>Natural Ia (Eva)</td>
<td>1.87</td>
</tr>
<tr>
<td>Natural Ia (Liz)</td>
<td>1.92</td>
</tr>
<tr>
<td>Natural Ia (Zsa-Zsa)</td>
<td>2.16</td>
</tr>
<tr>
<td>Polycrystalline (Norton, Run 939)</td>
<td>2.31</td>
</tr>
<tr>
<td>Polycrystalline (Norton, Run 846)</td>
<td>2.40</td>
</tr>
<tr>
<td>Polycrystalline (Crystalume 17z05-2)</td>
<td>2.73</td>
</tr>
<tr>
<td>Polycrystalline (Sumitomo)</td>
<td>7.80</td>
</tr>
</tbody>
</table>

**TABLE I. Phonon linewidths of high quality diamonds.**


1325 1330 1335 1340
RAMAN SHIFT (cm⁻¹)
Photoluminescence

- $\lambda = 488$ nm at room temperature
- Normalization of spectra: identical height of Raman peak
- Measured samples:
  - A: natural detector crystal
  - B: freestanding CVD-film (containing Si)
  - C: freestanding CVD-film (low Si content)
- CVD-film “C” shows only Raman peak (1st and 2nd order) and very weak Si-defect signal
Chemical purity: Nitrogen

- no clear absorption peak
- $N$ concentration of CVD film $\leq 3$ ppm
- ESR measurement in preparation

Chemical purity: Boron

- boron concentration in ppb range
- uncompensated boron would lead to high dark currents

⇒ reducing boron contamination:
  - adding oxygen to process gas
  - removing of boron source
Detector properties I: $^{60}\text{Co}$ gamma

- 0.18 Gy/min, 160 V/mm
- Very good sensitivity: $10^{-6}$ C/Gy (natural detector crystals 0.5-5 $10^{-7}$ C/Gy)
- Fast and reproducible response
- Persistent dark current of several 100 pA (before irradiation < 1 pA)!
Detector properties II: persistent current after irradiation

- before irradiation: boron completely compensated by deep donors (nitrogen?)
- shortly after irradiation: non-equilibrium state with many uncompensated acceptors ⇒ generation of holes in VB ⇒ temporarily high dark current
Detector properties III: persistent current after irradiation

- Are contacts also important?
- P.J. Sellin, A. Galbiati: *Performance of a diamond x-ray sensor fabricated with metal-less graphitic contacts*, APL 87, 093502 (2005), published online 23 August 2005
- Used coplanar electrodes on polycrystalline diamond from E6
- Metal contacts resulted in persistent photocurrent
- **No** persistent photocurrent for graphite electrodes fabricated by boron implantation
Detector properties IV: permanent high conductivity

- high conductivity @ RT
- boron concentration $\approx 10^{15}$ cm$^{-3}$
- activation energy in low temperature range: $\approx E_A(\text{boron})$
- boron not completely compensated
  $\Rightarrow$ very low donor density
- using as Schottky diode type detector?
Detector properties IV: single particle detection

- Results for detection of electrons and alpha particles will be presented at the talk of Christian Grah
  on Thursday @ 9:30 am (Session V)
Summary

- **Growth on on-axis substrates:**
  - non-epitaxial diamond and pyramidal hillocks (at our process conditions)

- **off-axis substrates:**
  - complete suppression of NCs and PHs
  - broad range of process parameters

- **Structural characterisation: CVD-films feature**
  - extremely low FWHM of rocking curve and of Raman peak
  - very low photoluminescence (only very weak Si signal)

- **Detector properties:**
  - very good sensitivity and fast and reproducible response
  - boron causes persistent photo currents and low resistivity
Growth on off-axis substrates III: origin of non-epitaxial diamond

- diamond after mechanical polishing
  - sharp transition between yellow (nitrogen containing) Ib substrate and transparent colorless homoepitaxial diamond film
- dark pyramidal holes
  → NCs broken out during polishing process
  - NCs continuously increase in lateral size during deposition process
  - growth of NCs not necessarily starts directly on Ib surface
  ⇒ nucleation of NCs at local instabilities or impurities of the growing film (not at structural defects of substrate)
Characterisation: HRXRD I

- diamond (004) rocking curves
  - CVD film: 560 µm thick, removed from substrate
  - IIa natural diamond: used as detector crystal
  - FWHM of natural diamond and CVD film extremely low compared with other IIa crystals

Chemical purity: Boron

- measures to decrease B contamination:
  - increasing gas purity
  - adding CO₂ to process gas: Possible etching of the boron source? Removing of B source with CO₂ plasma?
  - replacing parts of the sample holder
  - new CVD chamber

- next steps:
  - thorough cleaning of old CVD setup