Growth and properties of (ultra) nano crystalline diamond

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nanoTUM

- Nano-related research at the Technische Universität München: more than 50 research groups from several faculties and central institutes are working on nanoscience and nanotechnology
- Broad range of research topics (theoretical work, fundamental research, applied science, technology)
- Many topics/research fields are interdisciplinary

2004: start of nanoTUM – TUM Institute for Nanoscience and Nanotechnology

- Coordination of all activities in the field of nanoscience/nanotechnology in one virtual institute
- Cross-links to other nano clusters/networks in and around Munich by concomitant members in Clusters of Excellence etc.
- Intensive collaboration with partner universities DTU and TU/e
Chemical vapour deposition (CVD) of diamond

- Gas mixture of carbon containing gas and hydrogen e.g. 1-5% CH$_4$ in H$_2$
- Formation of radicals and atomic hydrogen by plasma or hot filament
- High enough substrate temperature: diamond deposition
- Role of atomic hydrogen:
  - stabilisation of sp$^3$ carbon phase
  - etching of sp$^2$ carbon phase
- Deposition on non-diamond substrates: pretreatment required to enhance nucleation density
- Morphology: from monocrystalline to (ultra)nanocrystalline
Monocrystalline CVD diamond films

- **Homoepitaxy:** diamond substrates limited by size of substrates

- **Heteroepitaxy:** bias enhanced nucleation
  - Ir/SrTiO$_3$/Si(001) (Schreck et al. 2004)
  - Ir/YSZ/Si(001), Ir/YSZ/Si(111) (Schreck et al. 2004, 2008) up to 4 inch.

Diamond on Ir/YSZ/Si(001)

Diamond on Ir/YSZ/Si(111)
Polycrystalline CVD diamond films

- Substrates: Si, SiC, glass, metals (e.g. Ti, Mo, WC) etc
- Columnar growth
- Roughness increases with film thickness

Sternschulte et al. Diamond 2006
Polycrystalline diamond (PCD) films: Van der Drift growth model

- Van der Drift growth model: overgrowth of crystallites

  ⇒ Development of surface texture depending on fastest growth direction

  ⇒ Fastest growth direction influenced by growth parameters e.g. by CH₄ concentration, substrate temperature
PCD with short deposition times: “pseudo” nanocrystalline diamond films

Very high diamond nucleation density on substrate and short deposition times:
⇒ thin fully closed films with small diamond crystallites
   grain size (lateral) up to 100nm

But: Anisotropic properties
(Ultra) Nanocrystalline CVD diamond films

- Fine grained material with structureless cross section
- “Homogeneous” material compared to PCD
- Roughness $\approx 10$-15nm
  independent from film thickness up to several $\mu$m
- Different growth mode

Sternschulte et al. Diamond 2006
Growth of ultra nano crystalline diamond (UNCD) films

- CVD with oversaturated carbon precursor concentration
e.g. by replacement of hydrogen gas by Ar or N₂
  or drastically increased carbon concentration in H₂ gas mixture

- Other possibility: applied bias voltage during growth process

⇒ Generation of high concentrations of defects at the surface

- Defect sites cause formation of twins, nucleation of new crystallites

⇒ Extremely high secondary nucleation rate during diamond deposition

⇒ small diamond grains

- Ultrananocrystalline diamond (UNCD): diamond grains ≤10nm
  Nanocrystalline diamond (NCD): diamond grains ≈10-100nm
Structural properties of UNCD films

- Small crystalline diamond grains embedded in amorphous sp²/sp³ C:H matrix

- No preferred orientation: powder like

⇒ Model system for amorphous materials

TEM: R. Brescia (Uni Augsburg)
Morphology of UNCD on Si: low nucleation density with $10^8$/cm$^2$

- Rough surface with circular shaped diamond islands
- Each sphere consists of nanocrystalline diamond

Sternschulte et al., Diamond 2007
• Diamond island size distribution independent from deposition time

⇒ no diffusion controlled growth

Sternschulte et al., in preparation
Growth mechanism

• Growth mechanism: growth perpendicular to surface (Huygens principle)

⇒ Smoothening via growth and coalescence of diamond islands

• From PSD analysis of surface roughness: Indication for smoothening effect by surface diffusion

Sternschulte et al, in preparation
Properties of UNCD and NCD: how large is the influence of the grain boundaries?

- UNCD/NCD consists of diamond nano particles embedded in a matrix

  ⇒ High fraction of atoms located at grain boundaries:

  cubic diamond grain with a = 3.6nm: 38% C at surface
  a = 36nm: 3.8% C at surface

  ⇒ Small volume fraction of diamond:

  grain boundary width 4nm and \( \varnothing_{\text{dia}} = 10\text{nm} \): 36% of volume is diamond
  \( \varnothing_{\text{dia}} = 20\text{nm} \): 58%
  \( \varnothing_{\text{dia}} = 5\text{nm} \): 17%

- “Number“ of grain boundaries:

  UNCD: grain boundaries in 3D: 10nm grain size \( \Rightarrow 10^{18}/\text{cm}^3 \)
  100nm grain size \( \Rightarrow 10^{15}/\text{cm}^3 \)

  “pseudo“ NCD with perfect columns: grain boundaries only lateral (2D)
  10nm diameter \( \Rightarrow 10^{12}/\text{cm}^3 \)

Kulisch et al. (2006)
Properties of UNCD films: sp$^2$ carbon

- NEXAFS to determine fraction of sp$^2$ carbon:
  C1s absorption with clearly separated signal of sp$^2$ and sp$^3$ C

- In this example: less than 5% sp$^2$ bonded carbon

- Most probably at the grain boundaries/boundary between grains and matrix

⇒ Influence of grain size on sp$^2$ concentration
Determination of sp² carbon: EELS

- Another possibility: Energy electron loss spectroscopy (EELS)
- XPS or TEM
- Advantage of TEM: mapping

Liu et al. Diamond Relat. Mater. 2007
EELS at TEM:
sp² carbon at grain boundaries

Okada et al.
J. Appl. Phys. 2003
H concentration: IR absorption

- IR absorption shows clear signal of C-H modes
- Measurement of bulk material

Sternschulte et al. Diamond 2006
H concentration in NCD films

- H concentration scales with grain size
  \[\Rightarrow H \text{ is incorporated in the grain boundaries}\]
H incorporation in UNCD films

- High resolution electron loss spectroscopy (HREELS): inelastic scattering of electrons near the surface
  ⇒ Excitation of C-C and C-H vibration modes
  ⇒ Identification of H bonding: H-sp\(^2\) C and H-sp\(^3\) C
- H concentration calibrated with SIMS

Williams et al. Diamond Relat. Mater. 2008
Optical properties: Raman

- With decreasing grain size: diamond Raman line at $1333\text{cm}^{-1}$ weaker and broadened

- Strong signal of D and G band i.e. sp$^2$ C

- Diamond peak more pronounced with UV excitation

- New lines at $1140\text{cm}^{-1}$ and $1480\text{cm}^{-1}$: trans-polyacetylene at grain boundaries

Raman: influence of growth parameters

- Signal of trans-polyacetylene influenced by growth conditions
- Annealing at 1200°C: trans-polyacetylene lines vanish
Optical absorption UV-VIS

• UNCD/NCD: strong absorption in the visible spectral range

Sternschulte et al. Diamond 2007
UNCD: Optical absorption by matrix

- Absorption depends strongly from grain size
  ⇒ Absorption caused by grain boundary material
Optical properties of UNCD/NCD and “pseudo” NCD

• “Pseudo” NCD: order of magnitudes lower number of grain boundaries
⇒ Weaker absorption signal

Williams et al. phys. stat. sol. (a) 2006
Electronic properties: doping of UNCD/NCD

• Undoped UNCD/NCD: high electrical resistivity
  ⇒ Doping required to enhance electrical conductivity

• Doping of diamond
  p-type doping: Boron  $E_{AB} = 370\text{meV}$
  n-type doping: Phosphorus  $E_{DP} = 600\text{meV}$
  Nitrogen  $E_{DN} = 1700\text{meV}$

  ⇒ Doping of UNCD/NCD with similar approach
UNCD/NCD: p-type doping with boron

- Most literature about boron-doped NCD: “pseudo” NCD i.e. growth parameters as PCD
- Influence of boron addition during CVD deposition of UCND?
UNCD deposition without boron addition

- Deposition of UNCD with hot filament reactor and CH$_4$/H$_2$/Ar gas mixture with 0.5sccm CH$_4$/50sccm H$_2$/200sccm Ar

UNCD deposition with boron addition

- Addition of $B_2H_6$ (300ppm with respect to $CH_4$)
  $\Rightarrow$ Change of morphology and growth mode!

Influence of boron addition on UNCD growth

- Reduced secondary nucleation rate
  ⇒ Change to columnar growth behaviour

M. Dipalo, Dissertation Uni Ulm 2008
Boron doped "pseudo" NCD

- Doping behaviour comparable to polycrystalline diamond
- Metallic doped "pseudo" NCD: superconductive behaviour observable with $T_C = 1.7K$
Electrical properties of boron doped NCD: influence of grain size

- Conductivity is strongly dependent from grain size

M. Dipalo, PhD thesis, Universität Ulm 2008
Influence of grain size on mobility

- Hole mobility drops down with decreasing grain size

M. Dipalo, PhD thesis, Universität Ulm 2008

Mobility of B-doped monocrystalline diamond

Barjon et al. phys. stat. sol. RRL2009
n-type doping of UNCD with Nitrogen

- n-type conductivity is observable
- Low activation energies of 10meV
Nitrogen doped UNCD

• By Nitrogen addition: larger diamond grains
  increased grain boundary width
  slightly increased sp\(^2\) C concentration

• “Grain boundary” doping: modification of the matrix by nitrogen
  similar to DLC but with much higher mobility
Thermal properties

- Thermal conductivity decreases with smaller grain size
  \[ \Rightarrow \text{Thermal properties of UNCD rather poor} \]

But: very smooth surface can be advantageous

\[ \Rightarrow \text{Thermal transport of “pseudo” NCD much better} \]

Angadi et al. J. Appl. Phys. 2006
Mechanical properties

- Young modulus depends on grain size
- UNCD with 10nm grains: reduction of Young modulus by 30%
- For comparison:
  - Si: 130GPa
  - SiC: 450GPa
  ⇒ UNCD ideal for MEMS

Summary

- Ultra nanocrystalline diamond films:
  very smooth diamond films
  “homogeneous” isotropic material

- Optical properties dominated by matrix:
  strong absorption in the visible spectral range

- Electronic properties:
  n-type doping of UNCD by modification of matrix ⇒ n-type possible!
  p-type doping of NCD: comparable to diamond but low mobility

- Mechanical properties:
  influence of grain size on Young modulus
  but much higher Young modulus compared to other material

⇒ It depends on the application if UNCD is the material of choice!