

National Center of Competence in Research "Nanoscale Science"

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Molecular and carbon-based electronic systems

Diamond films and particles

- Diamond structure
- Optical and thermal properties
- Diamond synthesis
- Defects
- Nanodiamonds
- Detection of NV-centers



Input & slides from Patrick Maletinsky & Stepan Sthelik!



Structure of Diamond

carbon atoms are arranged in a variation of the face-centered cubic crystal structure called "*diamond lattice*"



Similar to coal, HOPG, or graphene





Theoretically predicted phase diagram of carbon



triple point at 10.8 \pm 0.2 MPa and 4600 \pm 300 K

General properties of diamond

The most important properties of CVD diamond are the

- unsurpassed hardness
- extremely high thermal conductivity (>1800 W/mK, five times that of copper)
- broad band optical transparency
- extremely chemically inert:
 Not affected by any acid or other chemicals
- Graphitization only at very high temperatures
 (T > 700°C in an oxygen containing and 1500°C in an inert atmosphere

Properties of diamond

Property	Value
Vickers hardness*	10,000 kg/mm ²
Young's modulus*	1050 GPa
Poisson's ratio	0.1
Density	3.515 g/cm ³
Atom density*	1.77×10 ²³ 1/cm ³
Thermal expansion coefficient	1.0×10 ⁻⁶ /K @300K
Sound velocity*	17,500 m/s
Friction coefficient	0.1
Specific heat @ 20°C	0.502 J/gK
Debye temperature*	1860±10K
Bandgap	5.45 eV
Resistivity	10 ¹³ - 10 ¹⁶ Ωcm

*highest value of all solid materials

Optical Properties

Property	Value
Transmission	225nm to far IR , > 70% @ 10μm
Refractive index	2.38 @ 10µm, 2.41 @ 500nm
Absorption coefficient	≤ 0.10 cm ⁻¹ @ 10μm
Bandgap	5.45 eV
Tensile strength (0.5mm thick)	
Nucleation surface in tension	600 MPa
Growth surface in tension	400 MPa
Loss tangent (tanδ @140 GHz)	< 2.0×10 ⁻⁶
Dielectric constant	5.7





Thermal Properties



Thermal Properties



Phase diagram of carbon



Synthetic Diamonds high pressure and high temperature (HPHT)



Yearly Production~4400Mio ct. = ~1000t

"natural" growth conditions at high temperatures and pressures (~6GPa & ~1500°C)

Synthetic Diamonds high pressure and high temperature (HPHT)



CVD Synthetic Diamonds







low pressure and temperature growth (~0.5GPa & ~700-1000°C)

CVD Synthetic Diamonds



growth rates $1mm/h - 1\mu m/h$



Different growth material?

Rev.Adv.Mater.Sci. 21(2009) 134-138

GROWTH OF DIAMOND FILMS FROM TEQUILA

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Received: February 19, 2009

Abstract. Diamond thin films were growth using T Ised Liquid Injection MMMN. Chemical Vapor Deposition (PLI-CVD) onto both sil ainless steel 304 at 850 °C. The diamond films were characterized by Scanning E croscopy (SEM) and Raman spectroscopy. The spherical crystallites (100 to 400 nm) where the characteristic 1332 cm⁻¹ Raman band of diamond.

CVD diamond applications



Ultrasharp wear resistant diamond knife



Flexible CVD diamond heatspreaders



CVD diamond laser windows



CVD diamond window in UHV flange



Decorative CVD diamond dial



CVD diamond anchor wheel

Color of diamonds, defect centers



Defects in Diamonds Nitrogen-vacancy centers (NV)



- Color centers : Nitrogen, boron...

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- Diamond structure = mechanical, electronic and magnetic shield for the NV centers
- Long-life spin states events even at RT
- Optical properties (single photon source)
- -> quantum computing with NV⁻¹
- -> application in photonics and bio-medical imaging

J.R. Weber et al. *PNAS*, **17**, 85158518, (2010) Alivisatos Paul, *Nature Biotech.*, **22**, 4752, (2004)

NV-centers in diamond



The vacancy can be occupied by an electron with a spin!

NV- fluorescence



Nanodiamonds

HPHT: High Pressure High Temperature

by milling of diamond microcrystals, various sizes and shapes
 better crystallinity, less non-diamond phase than UDD

UDD: Ultradispersed Detonation Diamond

- from oxygen-deficient explosions in a reactor
- typical size 3-8 nm, given by explosion conditions, "spherical" shape
- obtained from the detonation soot (~60%), needs purification and deaglomeration
- various surface functional groups, poor crystallinity (lattice defects)



A. Krueger, J. Mater. Chem., 2008, 18, 1485–1492 K. lakoubovskii et al. Nanotechnology 19 (2008) 155705

Synthesis of nanodiamonds Detonation Technique (RDX+TNT)



Bucky-diamond structure ?

- Coexistence of *diamond structure* (core) and *graphite-like reconstructions* (surface)?

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V. N. Mochalin *et al., Nature Nanotechnol.* , **7**, 11-16 (2012) J.-Y. Raty, G. Galli, Nature Mat., **2**, 792–795 (2003)

Molecular-sized DNDs



S. Stehlik et al., Scientific Reports 6, 38419 ,(2016).

Surface of H-/O-diamond



TNE, $\mathsf{E}_{\mathsf{vac}}$ E Wf conductive **O-terminated diamond** E_{vac} Ĵ₽E_ Wf surface states resistive

H-terminated diamond

M. Tachiki et al. Surface Science 581 (2005) 207–212 B. Rezek et al. APL 82 (2003) 2266

Water Interaction with H- and O-DNDs



S.Stehlik, Th. Glatzel, et al., Diamond and Related Materials 63, 97-102 ,(2016).

Surface influence on NV centers



- detected even in UDD nanoparticles

I. Aharonovich et al. Rep. Prog. Phys. 74 (2011) 076501 V. Petráková et al. Adv. Funct. Mater. 2012, 22, 812-819

Tuning fork based LT-AFM/STM



- **qPlus tuning fork** with separate wire at low temperature 4K
- Preparation of metals, oxides and semi-conductors
- Molecular evaporator, spray deposition technique
- Optical excitation from an ex-situ LED source (4 wavelengths, P = 10 mW/cm²)

Sub-monolayer of nanodiamonds/HOPG Electrophoresis deposition technique



Surface structure of nanodiamonds



It = 20pA, V = -1.8 V

Surface structure of nanodiamonds



It = 20pA, V = -1.8 V

- Facets with C(111) structure
- Graphitic defects.

Light-assisted tunneling spectroscopy



Light-assisted tunneling spectroscopy



Kelvin spectroscopy under illumination



 $\Phi[C(111)] = 4.7 \text{ eV}, \quad \Phi[Cu(111)] = 4.95 \text{ eV}$ => Absolute Contact Potential Difference (CPD) = $\Phi_{tip} - \Phi_{sample} = -250 \text{ meV}$

> C. Barth et al., Phys. Rev. Lett., **98**, 136804 (2007) L. Gross et al., Science, **325**, 1110 (2009)

Kelvin spectroscopy under illumination



 Φ [C(111)] = 4.7 eV, Φ [Cu(111)] = 4.95 eV => **Absolute Contact Potential Difference (CPD)** = $\Phi_{tip} - \Phi_{sample}$ = -250 meV

- Long-range electrostatic force regime = *surface photo-voltage* (band bending)
- Short-range E_{ts} force regime = *sensitive to charges of NV centers*

C. Barth et al., Phys. Rev. Lett., **98**, 136804 (2007) L. Gross et al., Science, **325**, 1110 (2009)

Kelvin spectroscopy under illumination



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C. Barth et al., Phys. Rev. Lett., **98**, 136804 (2007) L. Gross et al., Science, **325**, 1110 (2009)

Presence of the NV⁻¹ electronic states



Presence of the NV⁻¹ electronic states



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Presence of the NV⁻¹ electronic states



Applications

Promising DNPs applications

Biomedical (drug delivery, fluorescence imaging) [1,2] Sensors (MEMS sensing, SAW sensing) [3,4] Color centers (spintronics, single photon sources) [5] Other (thermal [6], neutron physics [7], ...)

Crucial properties and challenges: state of surface (chemical, structural, electronic)

Need of sensitive characterization of individual DNP on surfaces Surface potentials related to surface termination and applications KPFM – proven to be sensitive and effective on bulk diamond

- [1] Nanodiamonds: Applications in Biology and Nanoscale Medicine, edited by Dean Ho, Springer **2009**
- [2] T. Takimoto et al. Chem. Mater. 22, 2010, 3462-3471
- [3] R. K. Ahmad et al. Appl. Phys. Lett. 97, 2010, 093103

[4] E. Chevallier et al. Sensors and Actuators B 154, 2011, 238-244
[5] Y. Chang et al. Nature Nanotechnology 3, 2008, 284-288
[6] M. Abyzov et al. J. Mater. Sci. 46, 2011, 1424-1438
[7] V. Nesvizhevsky et al. Materials 3, 2010, 1768-1781

Drug delivery

