Nature of Nanodiamond State and Applications of Diamond Nanotechnology

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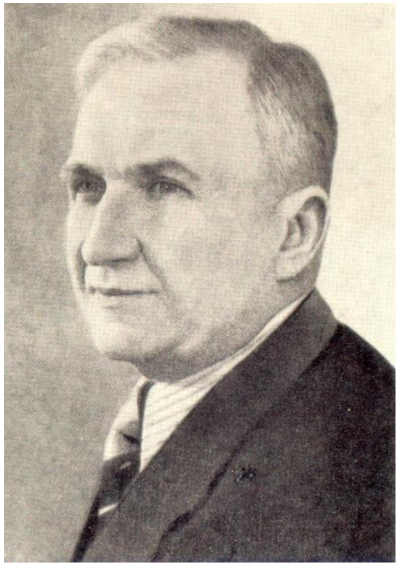
Presentation Outline

- Introduction: Nanodiamond State (NDS)
- Zoo of Nanodiamond (ND) Where? Why? What?
- Well proved data on ND & NDS
- Established Applications
- Physics, Chemistry and Biology – current
- Fundamental and Applied Prospects
- Conclusions

Nanodiamond State (NDS)

Electronic-vibrational Tamm surface state

- 1925 – Quantum theory of paramagnetism – contribution of the orbital moment
- 1929 – The concept of vibrational quanta in solid (later called phonons by Frenkel) ⇒ *Idea of quantum of sound at ND*
- 1933 – «Tamm levels» - certain electron states were due to the existence of the surface ⇒ *1D & 2D ë states at ND*
- 1934 – Any system with virtual separated charges should have magnetic moment ⇒ *Nature of free spin at ND*



Igor Evgen'evich **Tamm**
(8/07/1895 – 12/04/1971)
1958 – Nobel Prize for the Vavilov-Cherenkov effect

Tamm bound states of electrons & surface vibration of atoms (1955)

Size effects in nanocrystals

- Surface 2D (facet) & 1D (edge) bands – surface metal-like conductance
- Metal – $\sigma_S << \sigma_V$
- Dielectric – $\sigma_S \geq \sigma_V$
- $E_{3D} < E_{2D} < E_{1D}$ (bulk solid)
- $E_{3D} > E_{2D} < E_{1D}$ (micro solid)
- $E_{3D} > E_{2D} > E_{1D}$ (nano solid)

Zero Hall effect & $\rho_H = \rho$

- If $E_{2D} > E_{1D}$ ($\sigma_L \geq \sigma_S$), than
- in such semiconductor there should generally be absent both a Hall effect and dependence of an electrical conductivity on a magnetic field
- in case of a linear conduction band the magnetic field does not decline conduction electrons

I M Lifshitz & S P Pekar. Tamm bound states of electrons on a crystal surface and surface vibration of lattice atoms *Sov. Phys. Uspekhi*, **56**, 531-568 (1955).

Zoo of Nanodiamond (ND)

Was discovered in:

- Meteorites
- Detonation soot
- Nozzles of rocket engines
- CVD films
- Onion-like carbon
- HOPG (Ar^{+8} & ë, Kr)
- Ion implanting C in Si
- And in many others

What kind diamond is this?

- Ultra-fine, Ultradispersed
- Nanocrystalline, Cluster
- Modified nanocrystals
- Colloid particles
- Huge diamondoid
- Molecule of bulk diamond
- Carbon diamond-like phase
- Supermolecules

$\Rightarrow$ It requires sure clarification

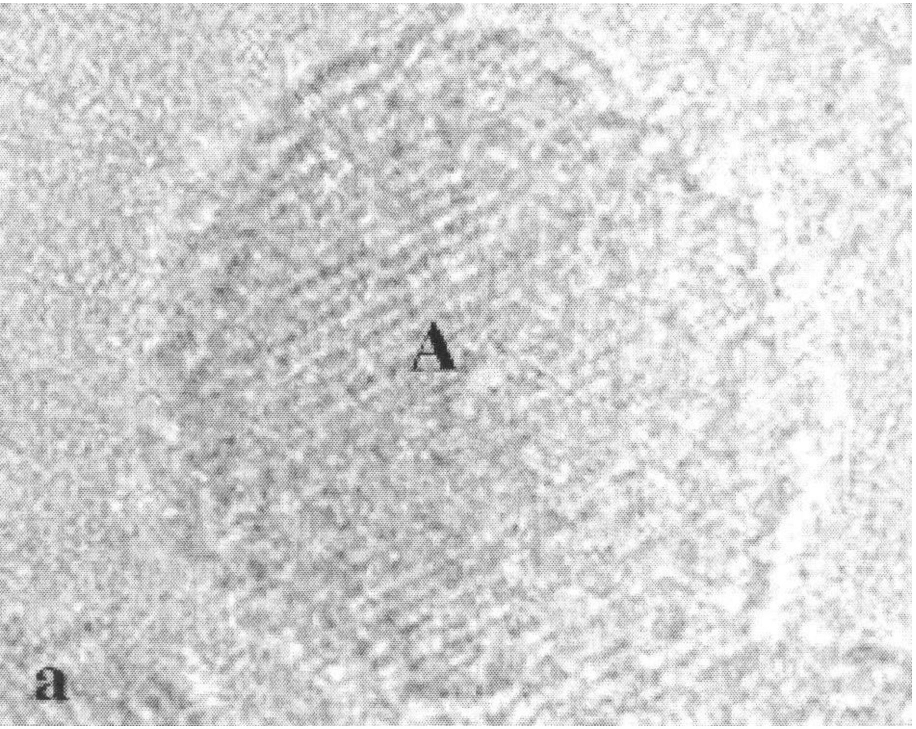
Preparation

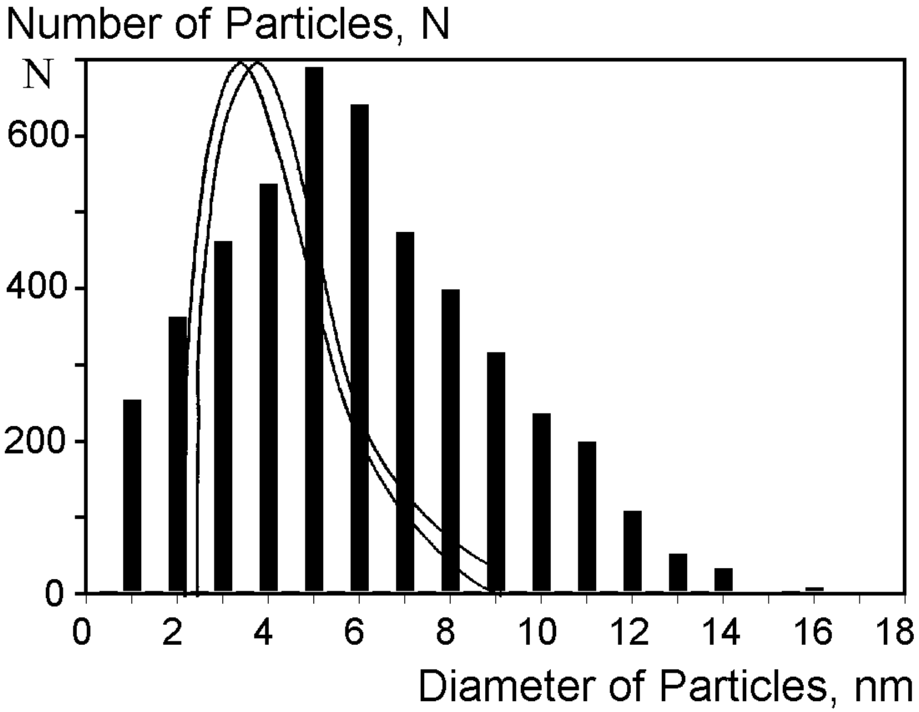
- Available quantities of nanodiamond powder is manufactured from explosive materials
- Main steps:
  - Preparation "by explosive way"
  - Recovering from detonation soot
  - Purification from impurities
  - Post-shock chemical modification
  - Separation of nanocrystals (size, ζ-potential, speed of sedimentation etc.)
  - Passivation and preservation
- *Main mist:* There is no uniform technological protocol yet

Properties of NDS are demonstrated in: (the well proved data is included only)

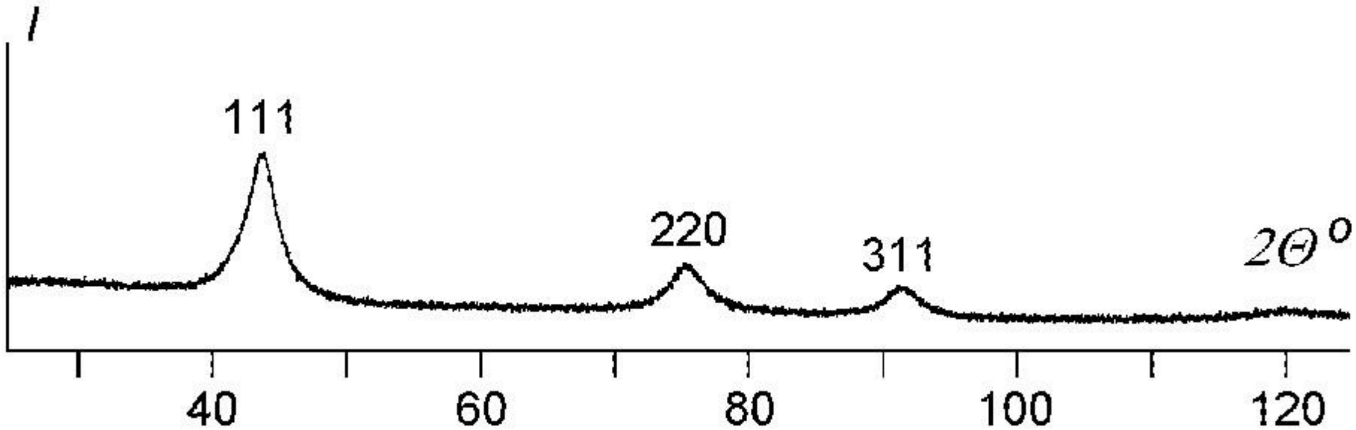
- HRTEM, X-ray and electronic diffraction
- CKVV Auger, EPR & NMR spectra
- Magnetic properties
- Pre peak at X-ray and electronic absorption
- FTIR, HREELS, PEELS
- Thermodynamic stability
- A-band of luminescence, Raman, IR

Molecular-mass (size) distribution

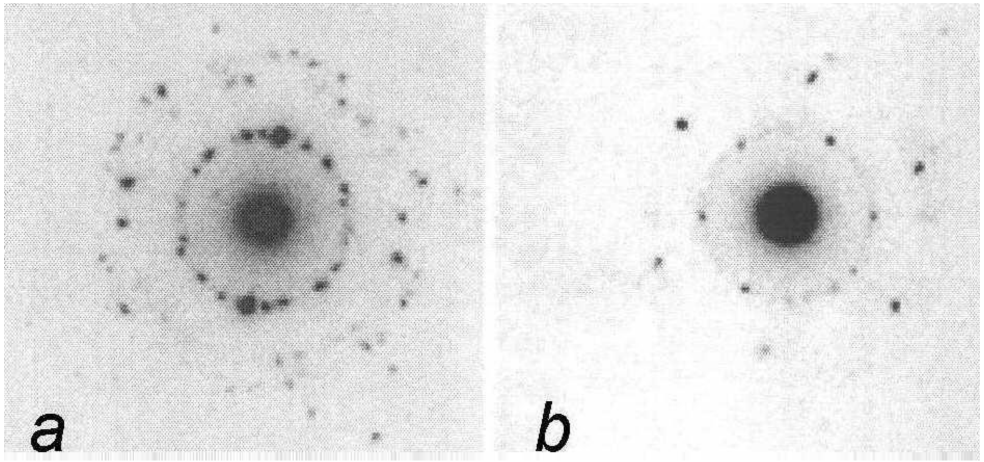




X-ray and electronic diffraction



- Nano-diffraction from
- a) several particles
- b) structure of ND ?
  - two ND particles
  - twinning
  - quasicrystal



L A Bursill at al. *Int.J.Mod.Phys.* **15**, 4071 (2001)

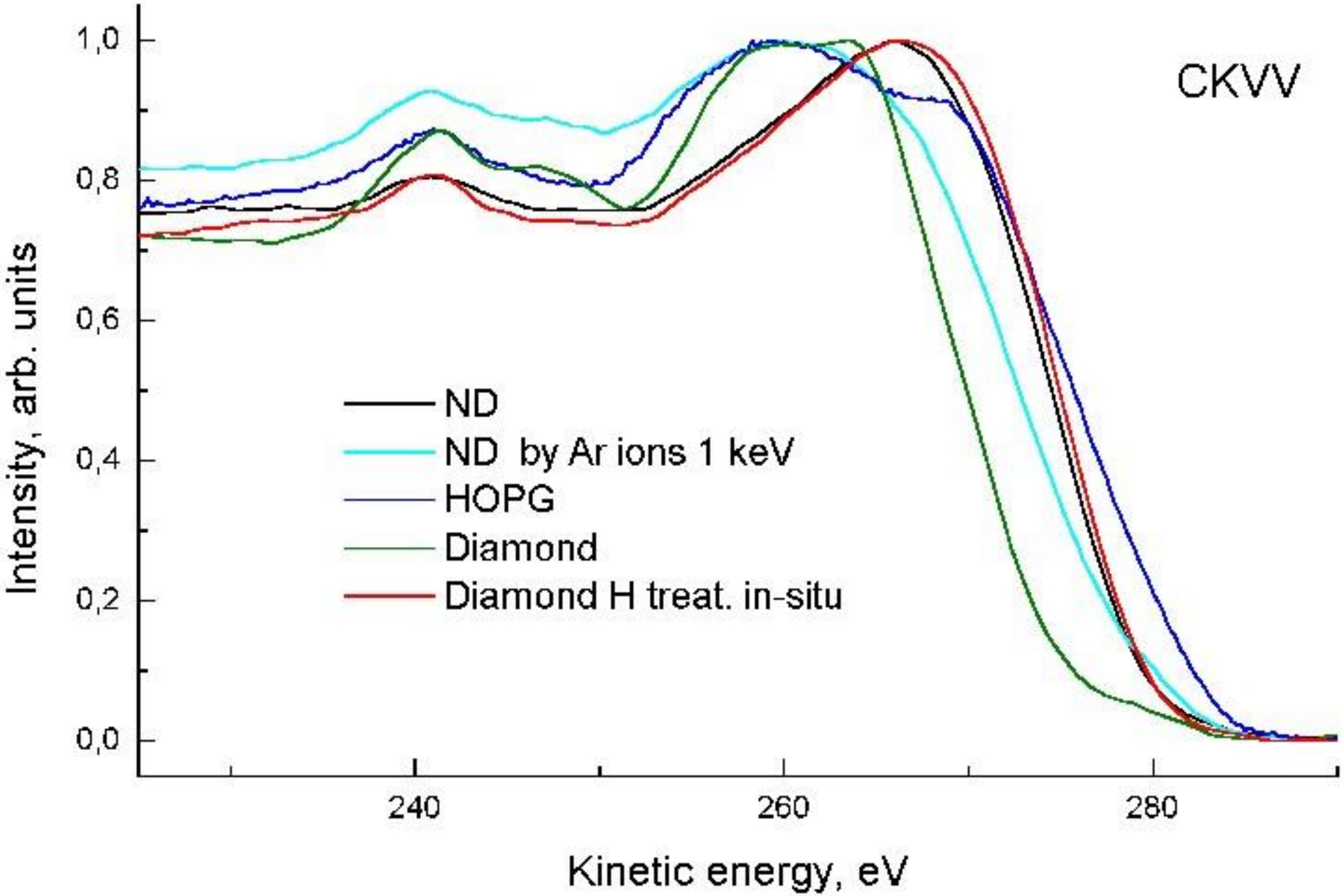
Diamond surface after H treatment ⇒ NDS

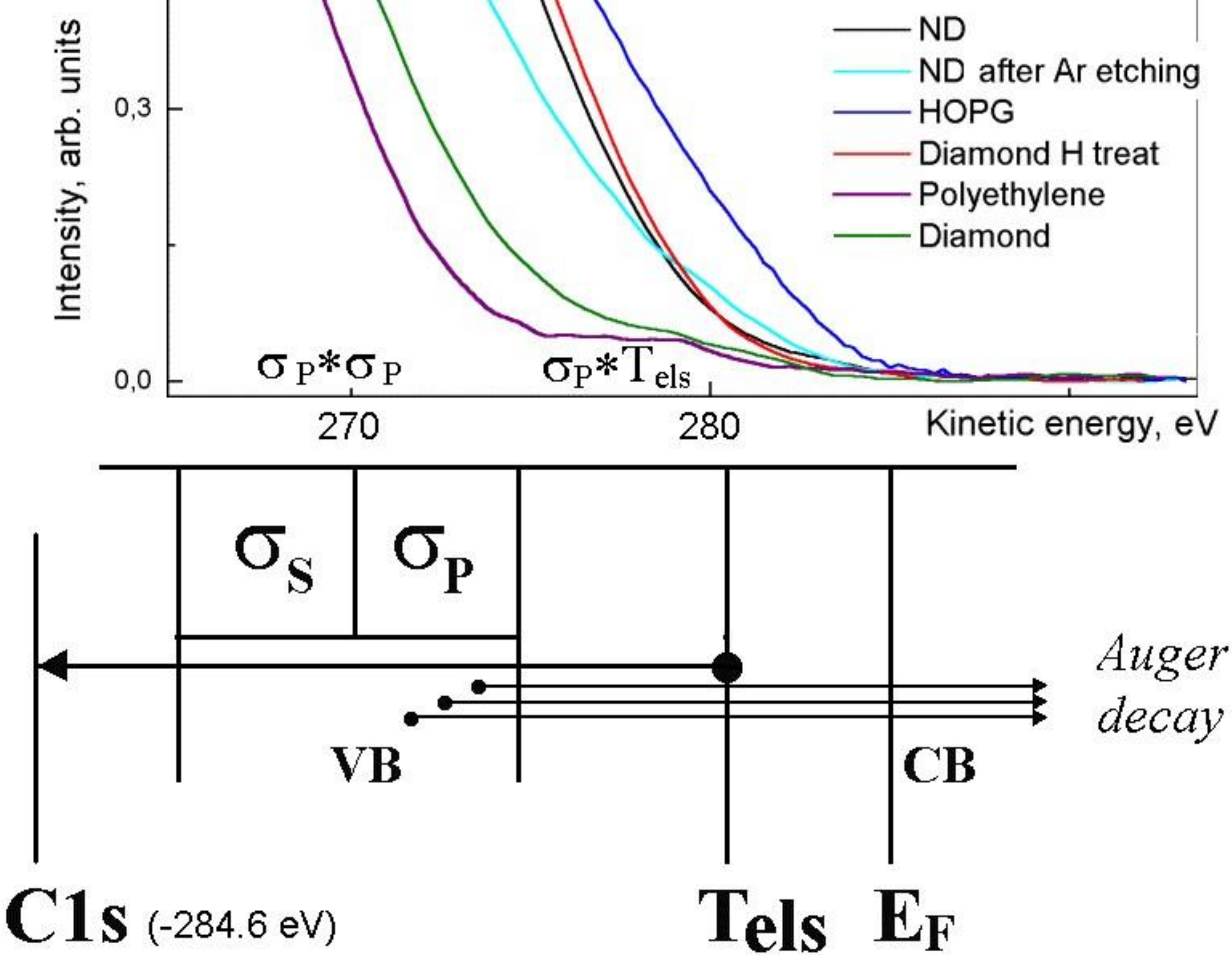
- hydrogen treatment
  - W hot-filament 2300 K
  - substrate up 1000 K
  - H_2 10^{-6} mbar
- 110 single crystal diamond (SCD)
- $ND_{after\ H\text{-}t} = ND_{before\ H\text{-}t}$
- $SCD_{after\ H\text{-}t} = ND$
- Method - CKVV Auger

Dementjev et al. 2001 – 2004

- Important observation
- The reaction of H-treatment with natural diamond produces dramatic changes to the states of the carbon atoms in the upper 2-3 monolayers only and
- i.e. transforms it to NDS
- NDS is chemically inert

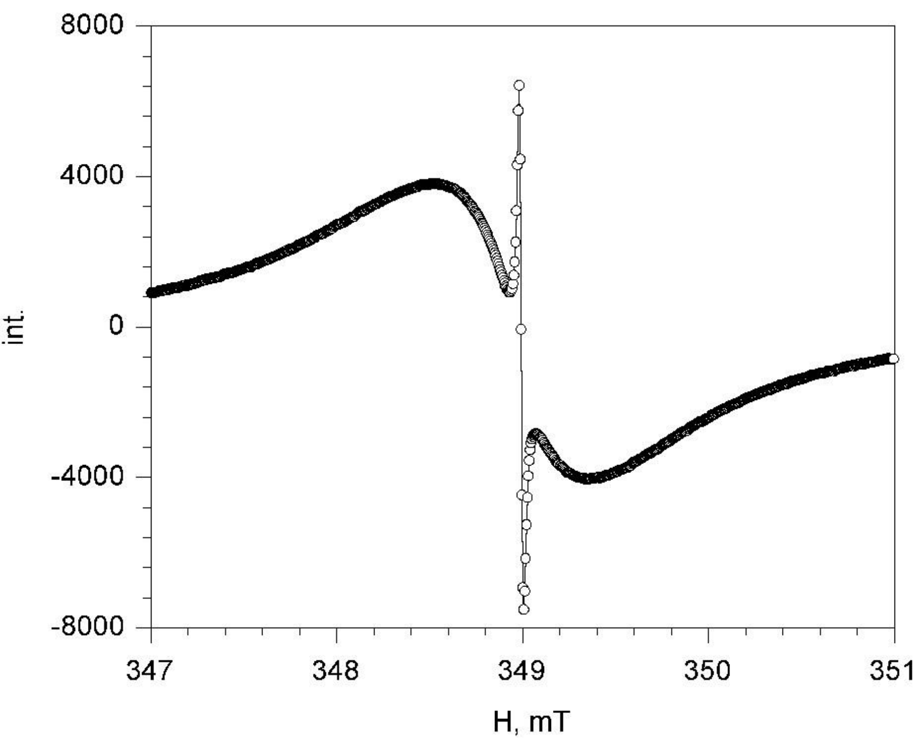
New chemical state is created on the surface ≡ NDS





Intensity, arb. units
0,3
0,0
ND
ND after Ar etching
HOPG
Diamond H treat
Polyethylene
Diamond
σ P*σ P
σP*Tels
270
280
Kinetic energy, eV
σS
σP
Auger
decay
VB
CB
C1s (-284.6 eV)
Tels
EF

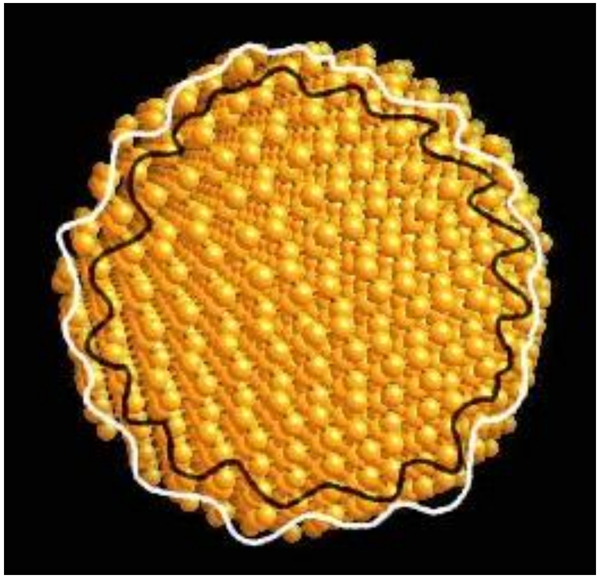
Electron Paramagnetic Resonance

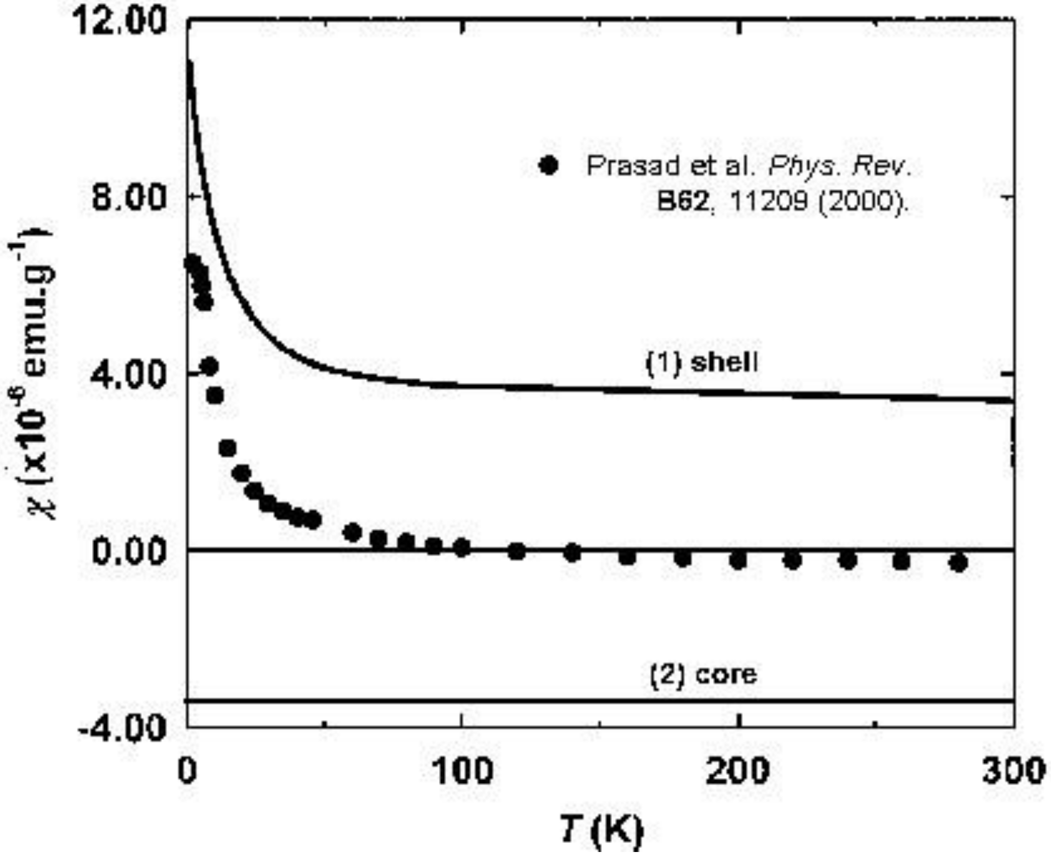


EPR spectrum of ND (NDC 10) with Li standard (g = 2.0023). Scan - 50 mT, modulation 0.01 mT.

- N ≈ $4*10^{19}$ spin / g
- N ~ 1spin per ND particle
- g-value, $g = 2.0027 \pm 10^{-4}$
- line width, $\Delta H = 0.86 \pm 0.02$ mT
- are independent of the
  - temperature (77 - 1000 K)
  - composition
  - structure
  - and state of ND surface
- The absence of saturation

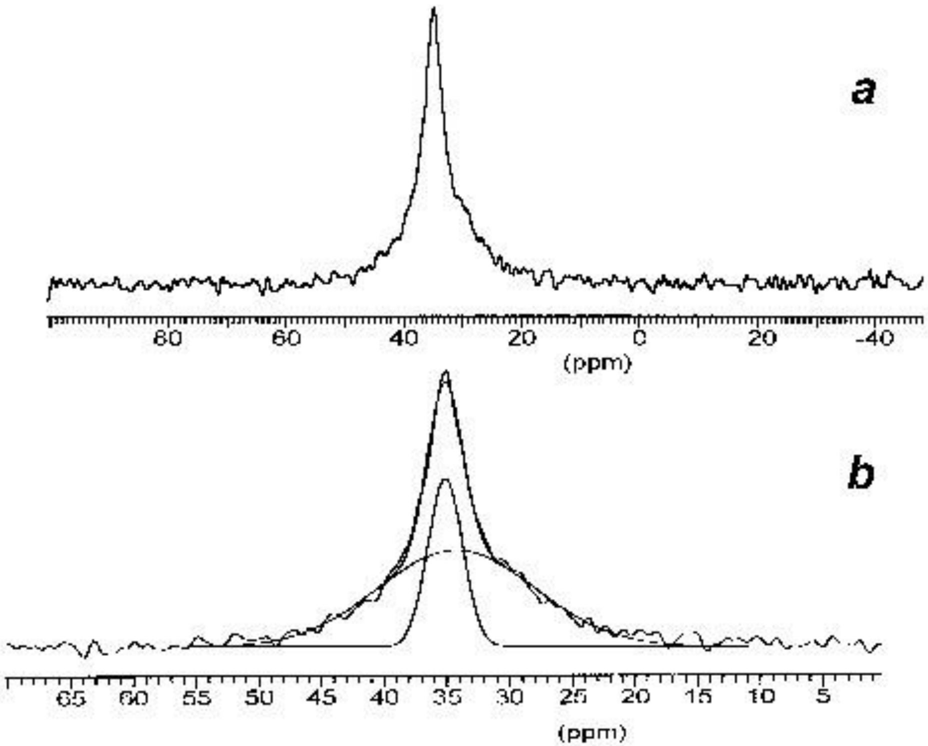
Magnetic properties





- ND consists of
- diamagnetic core and
- paramagnetic shell
- are determined by electronic density at Tamm's surface levels

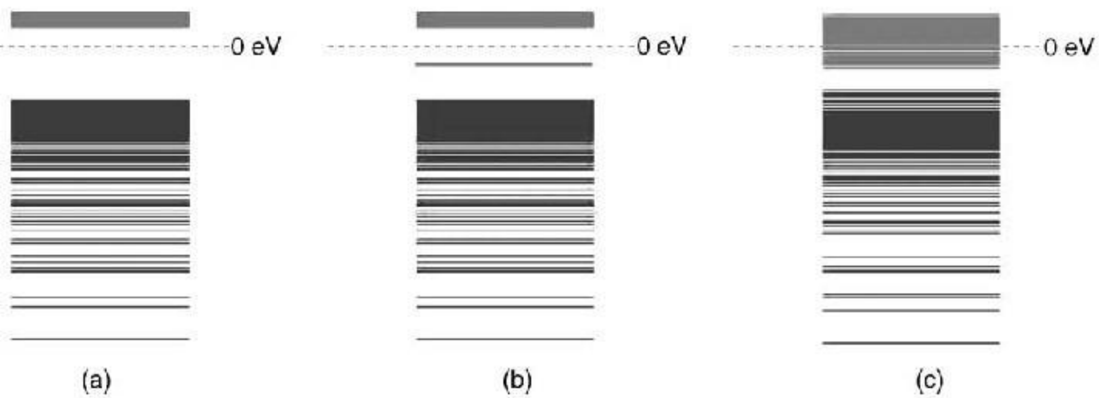
The ^{13}C NMR spectra of ND



Nos.	Position		Width		Amplitude, arb. units	Relative integral intensity
	Hz	ppm	Hz	ppm		
1	3532	35,104	278	2,763	4,18	27,83
2	3445	34,236	1261	12,532	2,39	72,17

- CXP-400 Bruker spectrometer with H_0 = 9.4 T at ω = 100.6 MHz
- The interaction with protons was suppressed
- The rotation under the magic angle at a frequency > 1 kHz was used
- Accumulation - 500 spectra
- Decomposition into two Gaussian components:
  - 1 - 30% normal sp^3
  - 2 - 70% distorted sp^3

Electronic properties



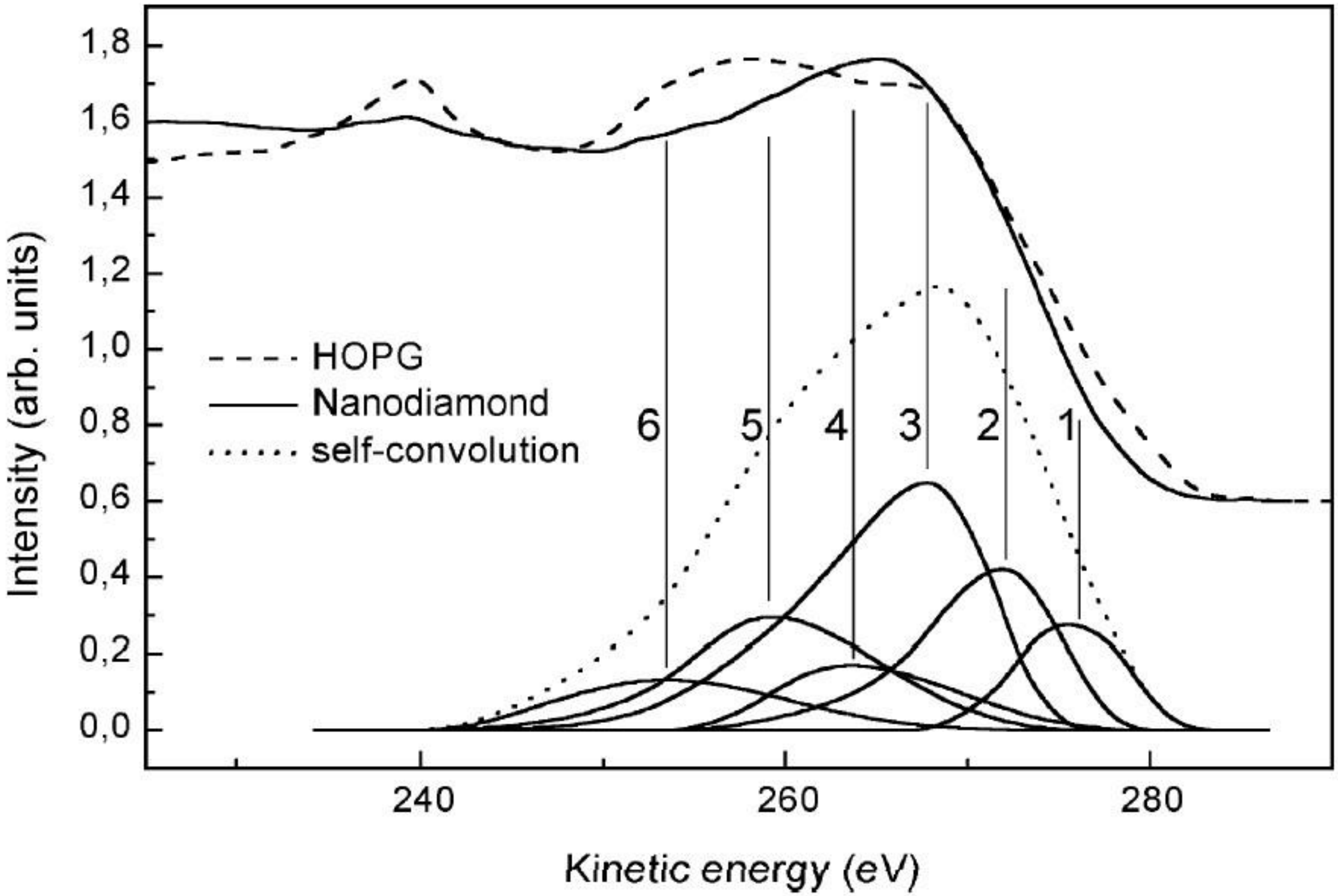
Band diagrams (HOMO and LUMO) of:
(a) $C_{60}H_{60}$ E_g=12.5 eV;
(b) (b) radical state $C_{60}H_{60} \rightarrow C_{60}H_{59}$•;
(c) complete dehydrated state
$C_{60}H_{60} \rightarrow C_{60}$ (relaxed) E_g=5.3 eV.

The NDS electronic structure forms $\sigma_s^1\sigma_p^2\pi^1$ surface states without overlapping of π - levels

- Electronic state is $\sigma_s^1\sigma_p^2\pi^1$ no π-band

- Appl Surf Sci **215**, 169, 2003

CKVV Auger spectroscopy



CKVV Auger spectra from HOPG and nanodiamond with the self-convolution.
1 – $\pi \times \pi$; 2 – $\sigma_p \times \pi$; 3 – $\sigma_p \times \sigma_p$; 4 – $\pi \times \sigma_s$; 5 – $\sigma_p \times \sigma_s$; 6 – $\sigma_s \times \sigma_s$.

DOS and ε" plots for different size carbon clusters: *(i) 528*, *(ii)1050*, *(iii) 4048*, *(iv) 8120*, *and (v) 13464* carbon atoms.

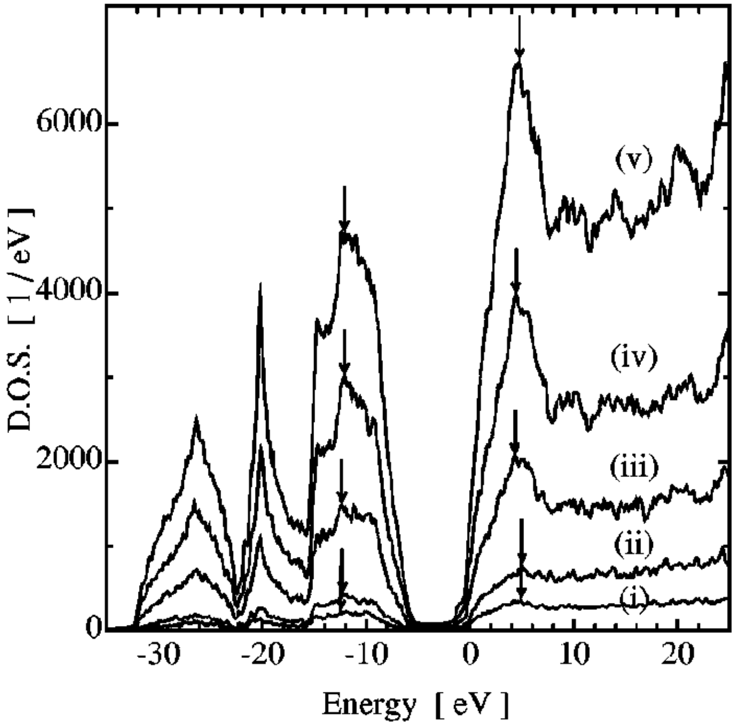
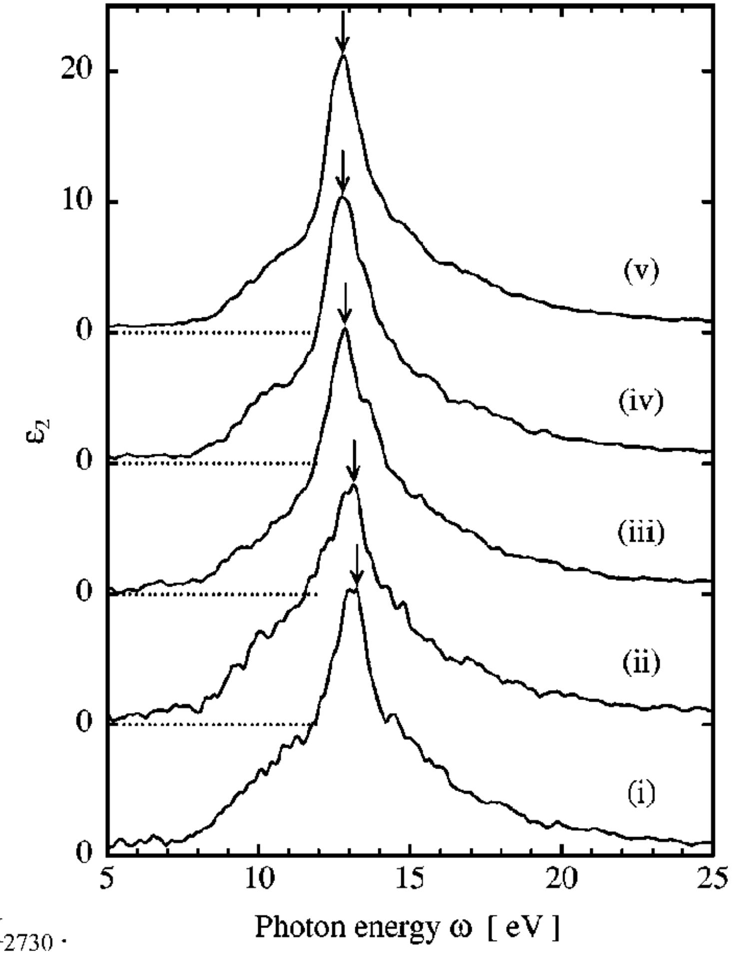


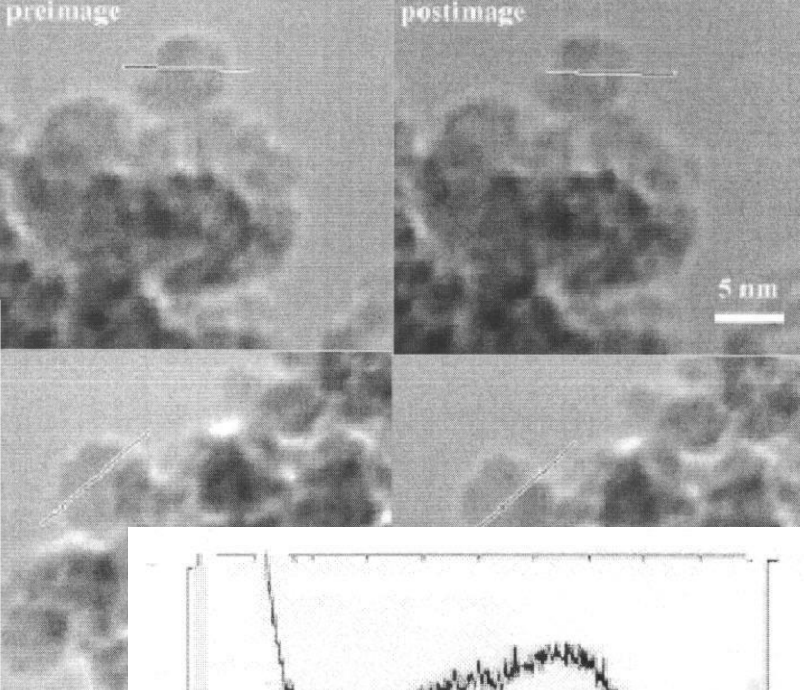
FIG. 2. Density of states of hydrogenated carbon nanocrystallites:

FIG. 3. The imaginary part of the dielectric function of hydrogenated carbon nanocrystals:

(i) $C_{528}H_{294}$, (ii) $C_{1050}H_{498}$, (iii) $C_{4048}H_{1182}$, (iv) $C_{8120}H_{1950}$, and (v) $C_{13464}H_{2730}$.

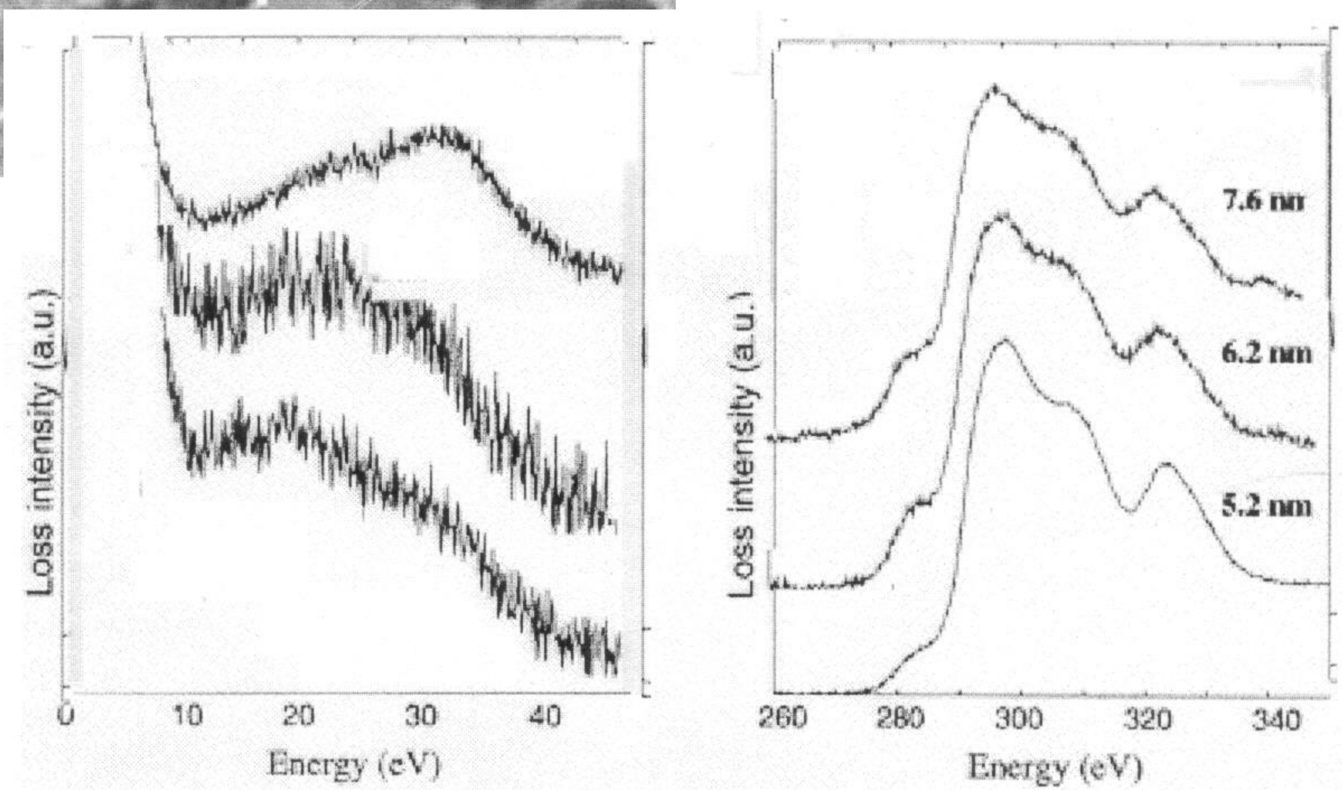


Y. Kurokawa at al. Phys. Rev. B 61, 12616-9 (2000).



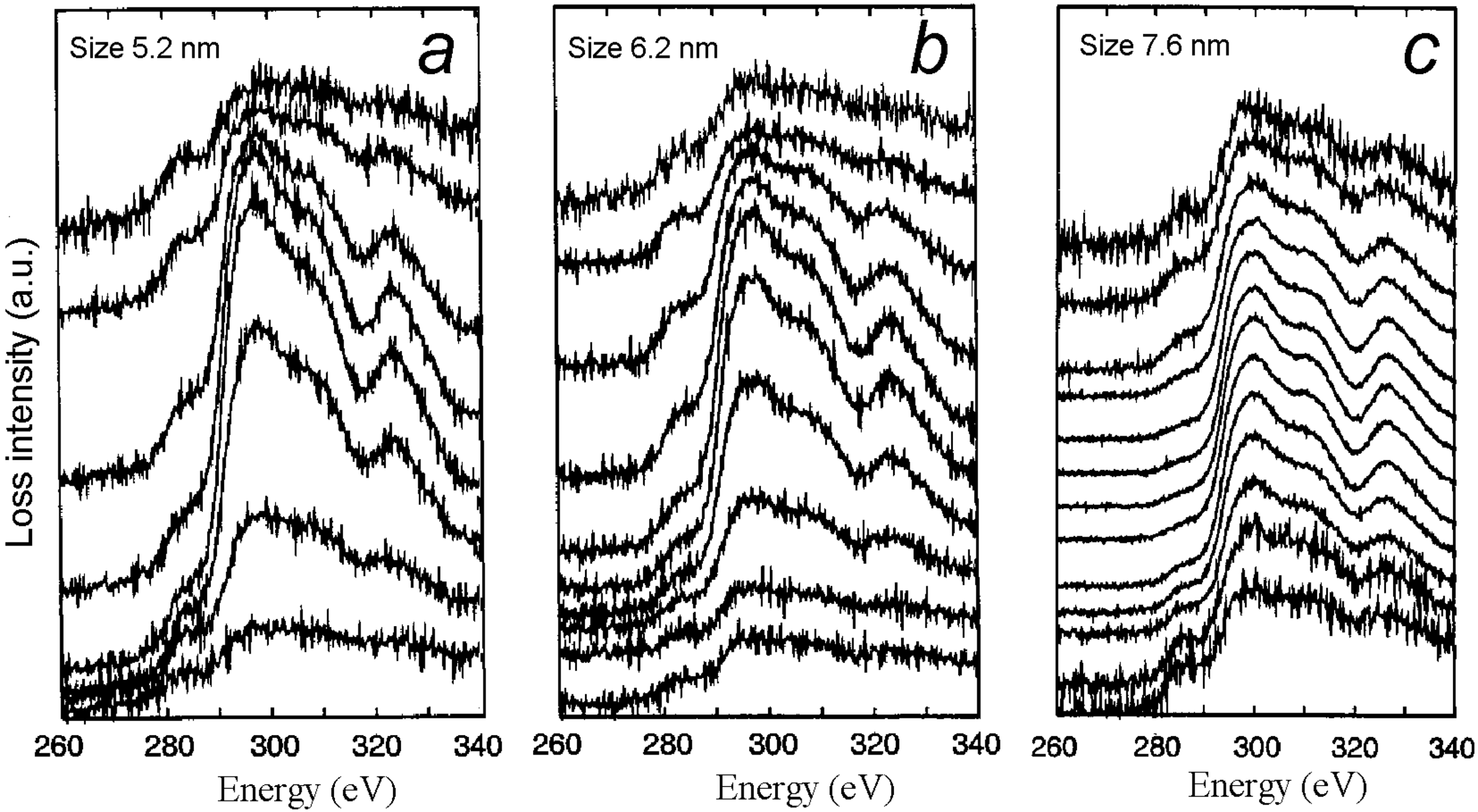
Line scan PEELS for
low-loss and core loss energy ranges

Pre- and post-PEELS images, using to control quality of specimen drift, contamination and beam damage during data collection



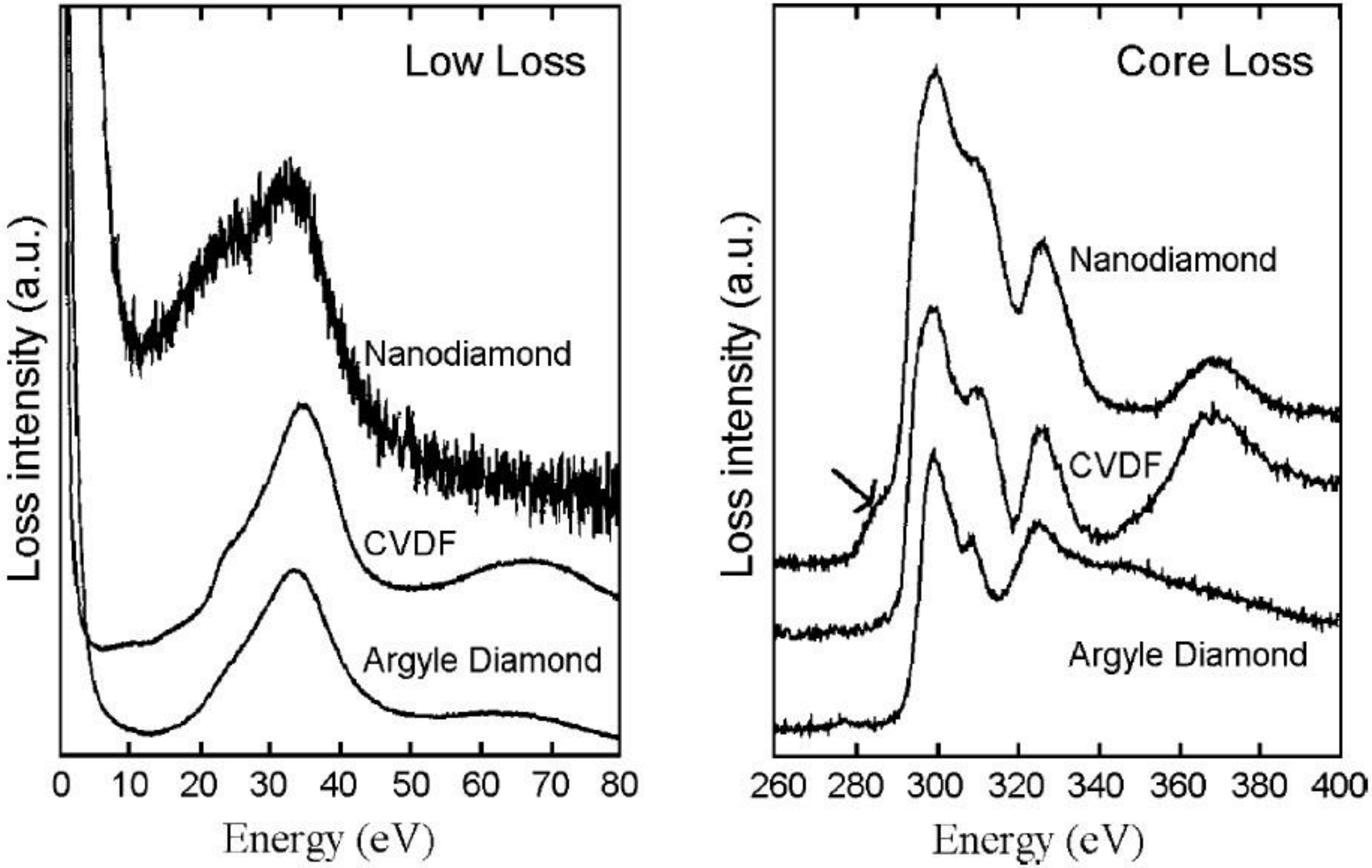
At the low-loss range surface (12–24 eV) and bulk (30–33 eV) plasmons depend on a size of ND.

Pre K-edge signal – main property of ND



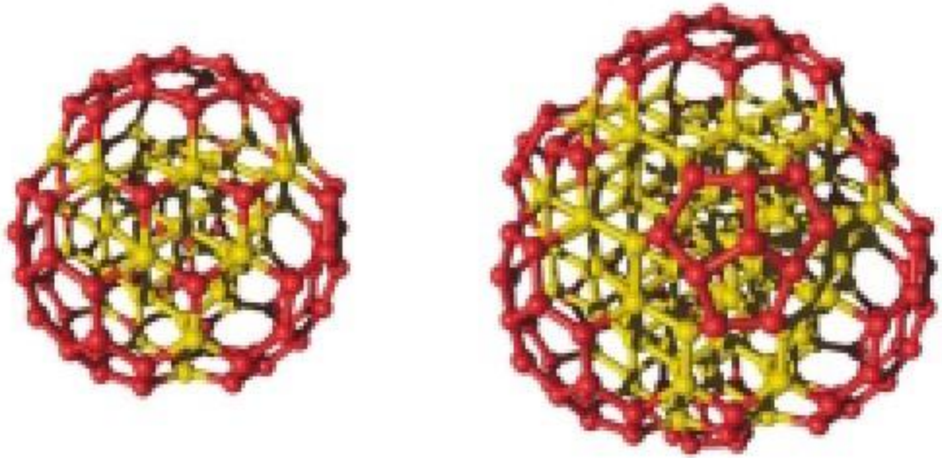
Line scan parallel electron energy loss spectrum for core-loss energy ranges for three ND particles of diameter (a) 5.2, (b) 6.2 and (c) 7.6 nm. Pre-peak (280–295 eV) characterises ND at the core-loss range

PEELS of ND

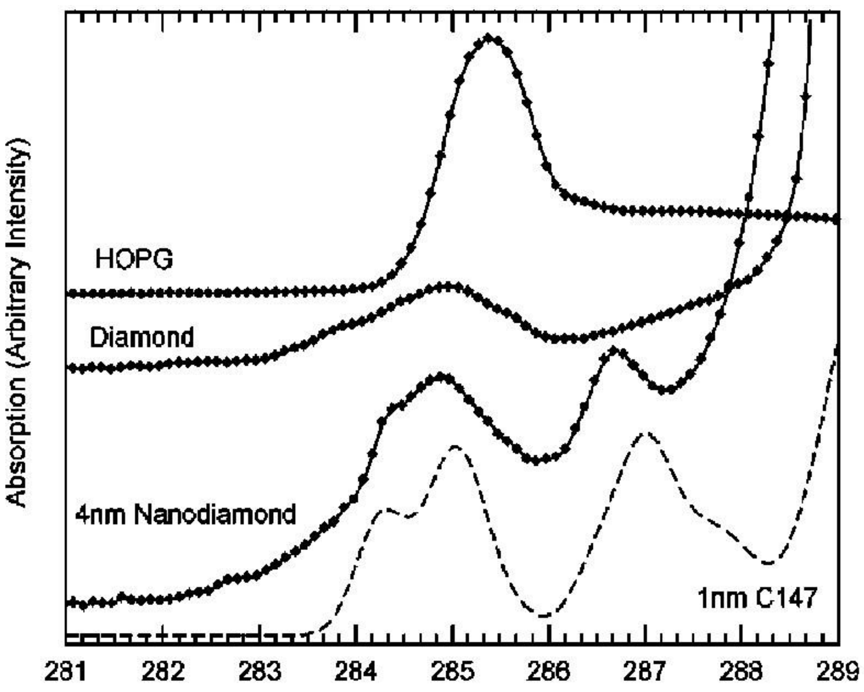


- Integral intensity of electron energy loss spectrum (left) low-loss and (right) core-loss ND diameter 7.6 nm, CVDF micron size diamond, and natural Argyle diamond using 100 keV electrons. Arrow labels pre-peak

«Bucky Diamond»



C_{147} and $C_{275} \simeq$ 1.2 and 1.4 nm in diameter



X-ray absorption and emission experiments and *ab initio* calculations showing

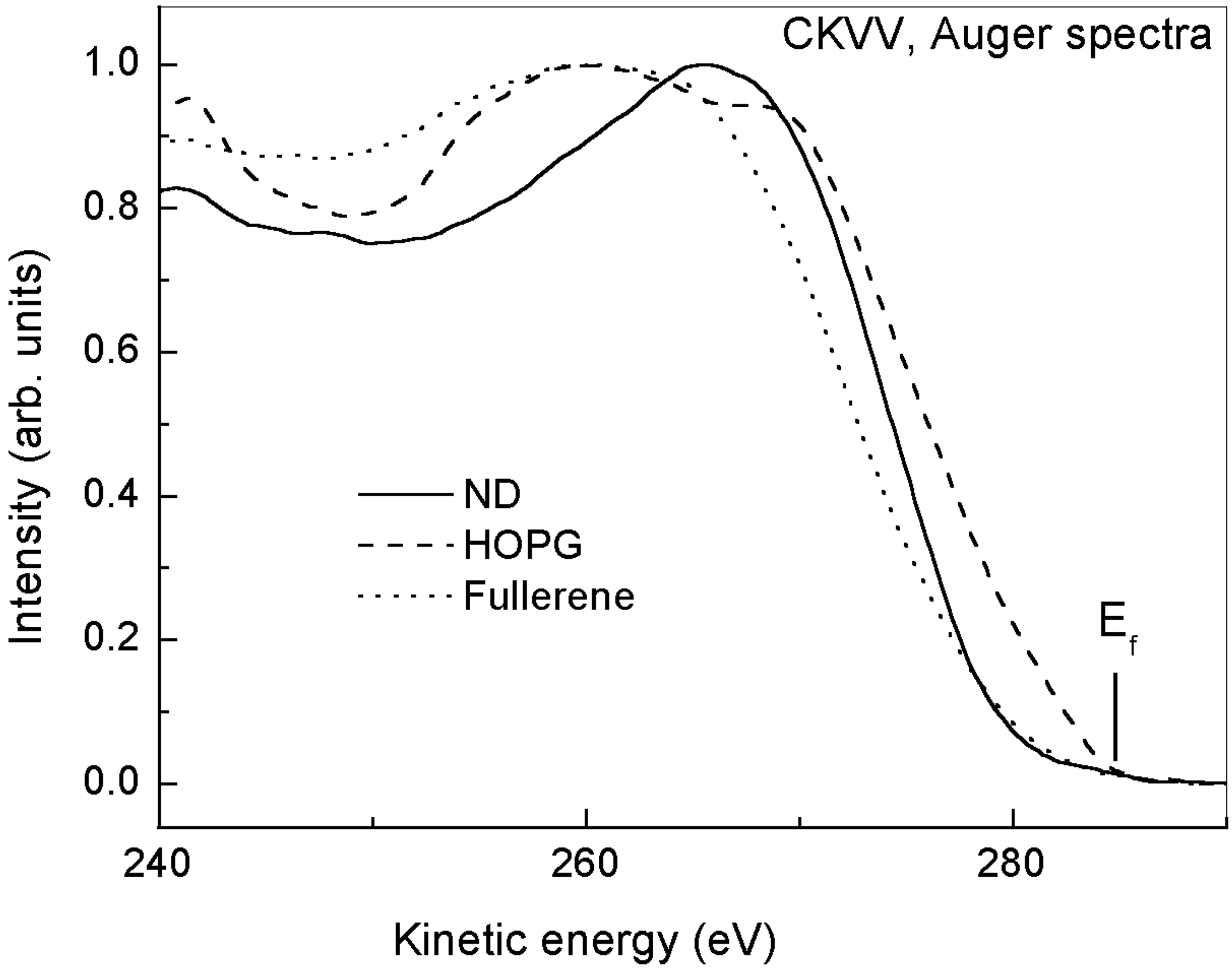
- ND size must be reduced to 2 nm, in order to observe an increase of its optical gap, at variance with Si and Ge where quantum confinement effects persist up to 6-7 nm
- Bucky Diamonds. Signatures: pre-edge features in X-ray spectra

J Y Raty et al. *Phys Rev Lett* **90**, 37401(2003)

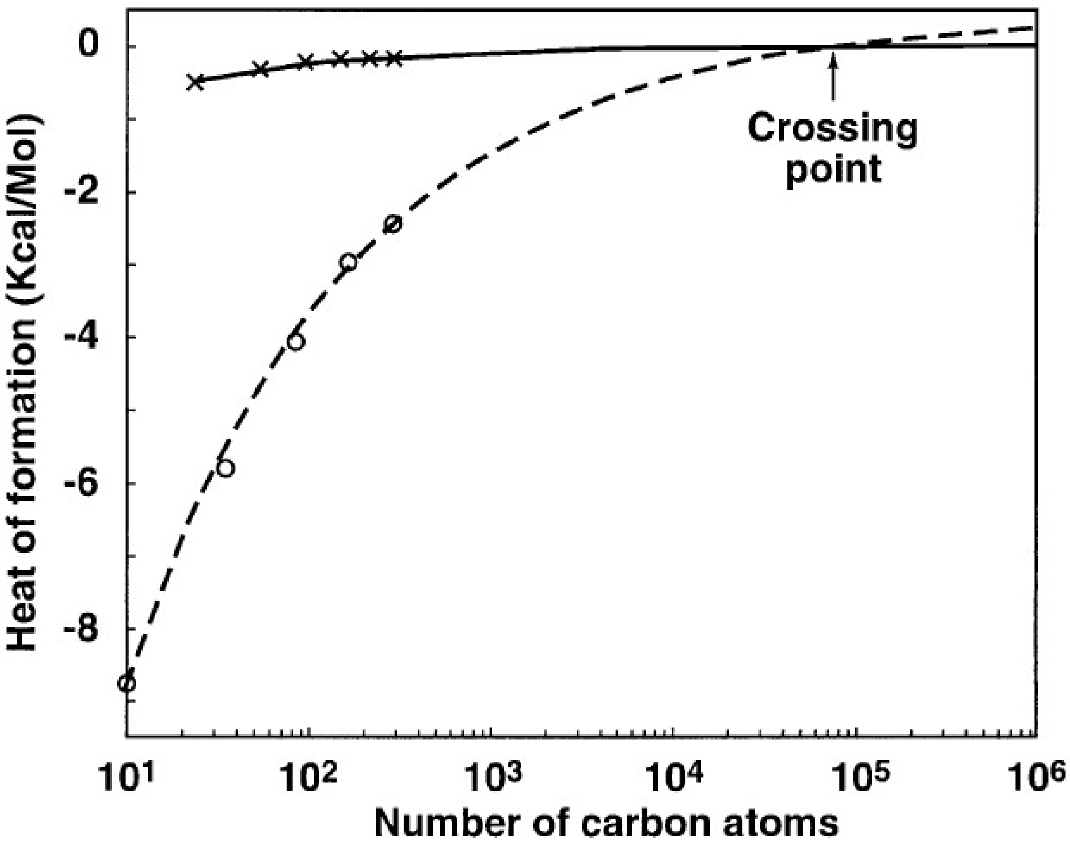
NDS is not «Bucky Diamond»

NDS is not «bucky diamond»

as Fullerene spectrum does not coincide with ND spectrum



Thermodynamic stability



Comparison of the cluster size dependence of the heat of formation, $H_f(sp^3)$ and $H_f(sp^2)$ by using the AM1 HF method. The fits to the sp^3 (plotted as O's) and sp^2 (plotted as X's) data are given by the dashed and solid lines, respectively.

F H Ree et al. Kinetics and thermodynamic behaviour of carbon clusters under high pressure and high temperature // *Physica B: Condensed Matter*, **265** (1-4), 223-229 (1999).

The properties of NDS are uniform

- Paramagnetic invariance
- Auger decay invariance
- Surface plasmon = de Broglie resonance
- Electronic state is $\sigma_s^1\sigma_p^2\pi^1$ no π-band
- NDS of diamond surface = NDS of ND

  i.e. DQD is «dot» of diamond surface

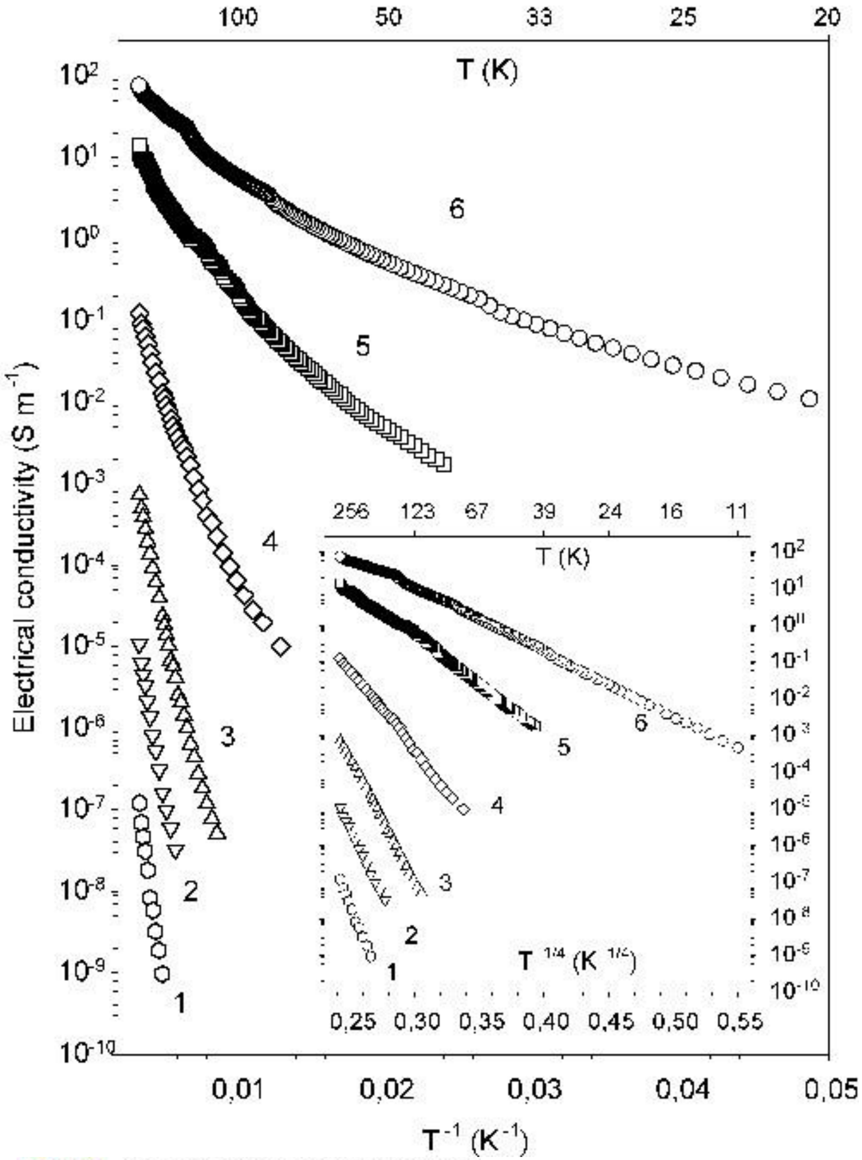
Established Applications

- Precursor of NCD & UNCD films (CVD etc.)
- New Material Development
  - Solid Semiconductor from Nanodiamond (NDC)
  - Nanocrystalline diamond (NCD) films for NEMS
  - Ultrananocrystalline diamond (UNCD) films
- Covering magnetic and optical disks
- Ultra fine polishing of wafers & glasses

Diamond Nanotechnology

- ND discovery – 1963 & 1982 RU, 1988 USA
- Diamond Nanotechnology RU & USA (1991)
- New applications for diamond nanotechnology
- Physics, Chemistry, Biology
- Nanodiamond – Pyrocarbon Composite NDC
- The reconstruction of ND surface

Solid Semiconductor from ND



- Solid (bulk) material
- ND & pyrocarbon (NDC)
- Low-dimensional porous semiconductor of p-type
- Size ND ~ 4 – 5 nm
- Size of pores ~ 8 – 10 nm
- Zero Hall effect & $\rho_H = \rho$
- #1-#6: γ = 0.5, 5, 10, 20, 30, 40 (% mass of pyrocarbon)

Solid Semiconductor from ND

Parameter set of the temperature dependence of NDC conductivity.

Value of parameters is found from the formulas.

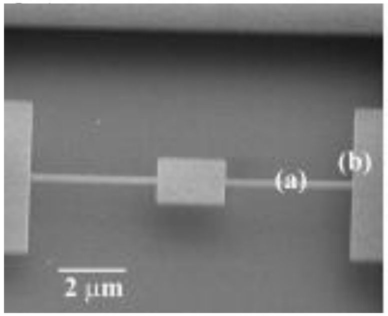
E_a: $\sigma = \sigma_0 \exp(-Ea/kT)$ at σ_0 = const;

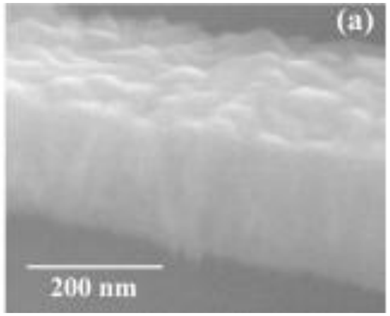
E_σ: $\sigma = (\sigma_m/T) \exp(-E_\sigma/kT)$ and $\sigma_m = 8.6 \cdot 10^5$ S/m for all samples at E_σ =0 и T=290;

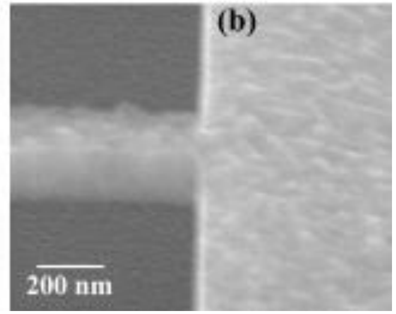
B: $\sigma \sim A \cdot \exp(-B/T^{1/4})$.

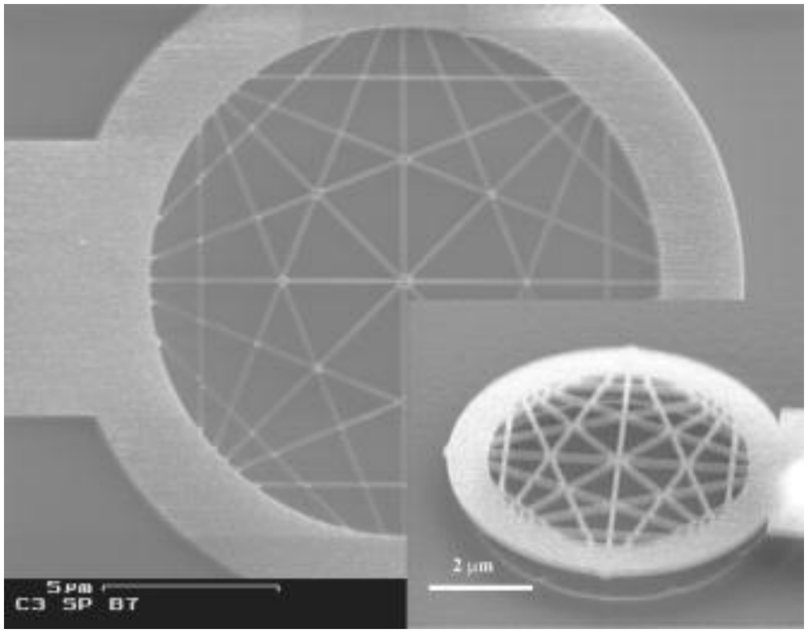
Sample	γ, %	sp2, %	ρ_{290}, ohm*m	E_a, eV	E_σ, eV	B
NDC 0	0	0	$1.2 \cdot 10^9$			
#1 NDC 0,5	0,5	0,5	$8.2 \cdot 10^6$	0,287	**0,311**	
#2 NDC 5	5	5	$9.2 \cdot 10^4$	0,227	**0,248**	
#3 NDC 10	10	9	574	0,155	**0,173**	62
#4 NDC 20	20	17	1,55	0,082	**0,101**	40
#5 NDC 30	30	23	0,096	0,051	**0,069**	24
#6 NDC 40	40	29	0,015	0,033	**0,052**	17

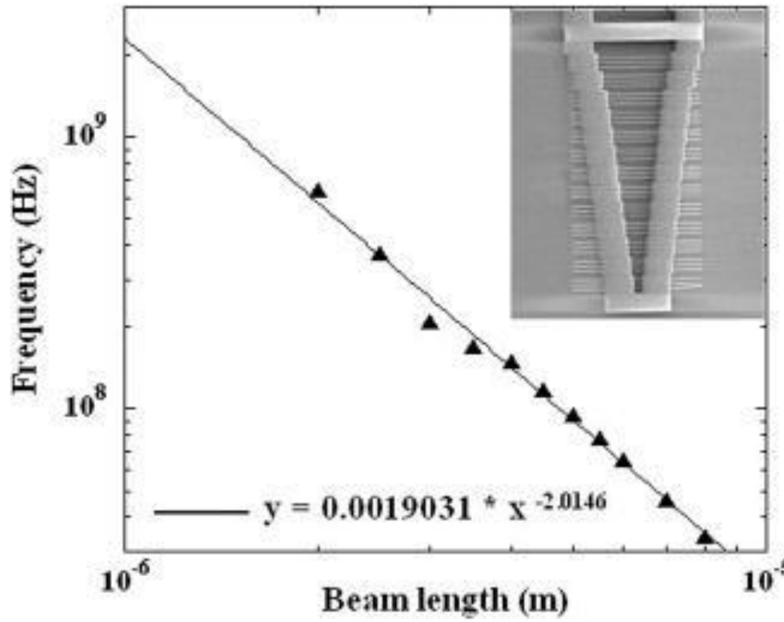
NEMS
J E Butler





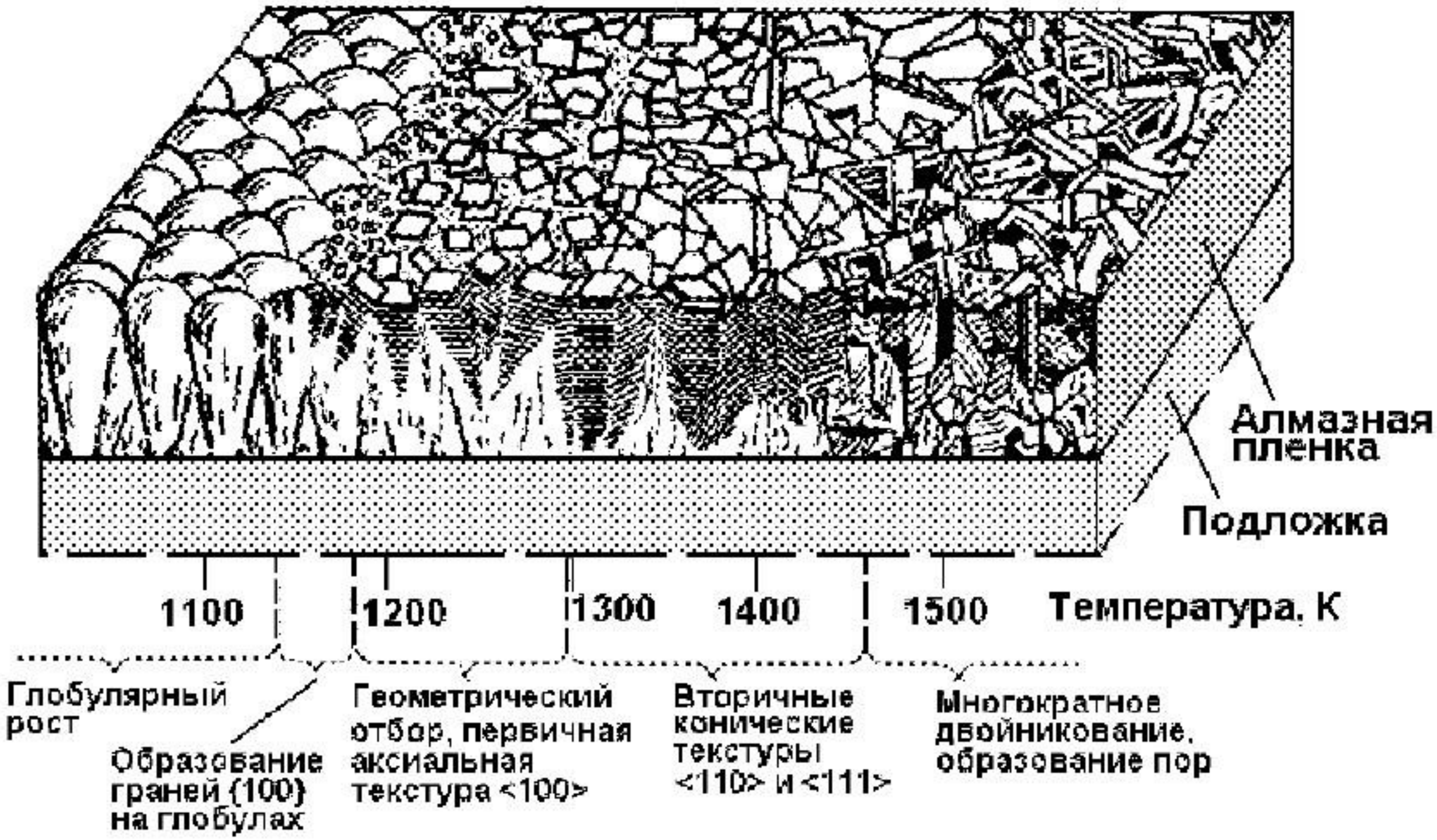






- A B Hutchinson et al. Dissipation in nanocrystalline-diamond nanomechanical resonators *Appl Phys Lett*, **84**, 972-974 (2004).
- L. Sekaric et al. Nanomechanical resonant structures in nanocrystalline diamond *Appl Phys Lett*, **81**, 4455-4457 (2002).

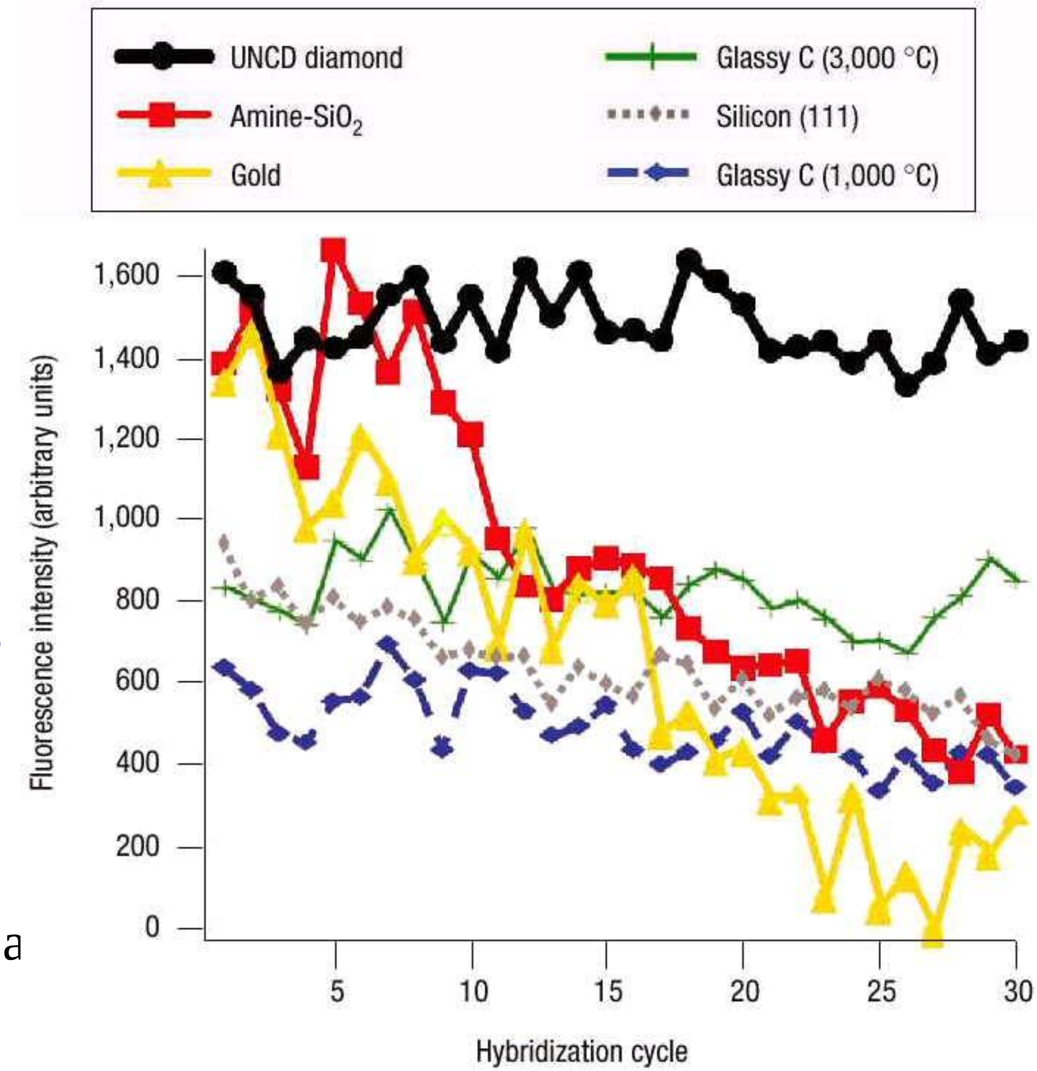
Structure of CVD films



The morphology of CVD films strongly depends on growth temperature

NCD и UNCD films modified by DNA

- Comparison of DNA-modified UNCD films with such as gold, silicon, glass and glassy carbon, showed that
- diamond is unique in its ability to achieve very high stability and sensitivity
- compatible with microelectronics processing technologies
- diamond thin-films - ideal substrate for integration of microelectronics with biological modification and sensing
- W. Yang et al., DNA-modified nanocrystalline diamond thin-films a stable, biologically active substrate *Nature Materials*, **1**, 253-257, 2002



Selective absorption of molecules based on diamond nanotecnology

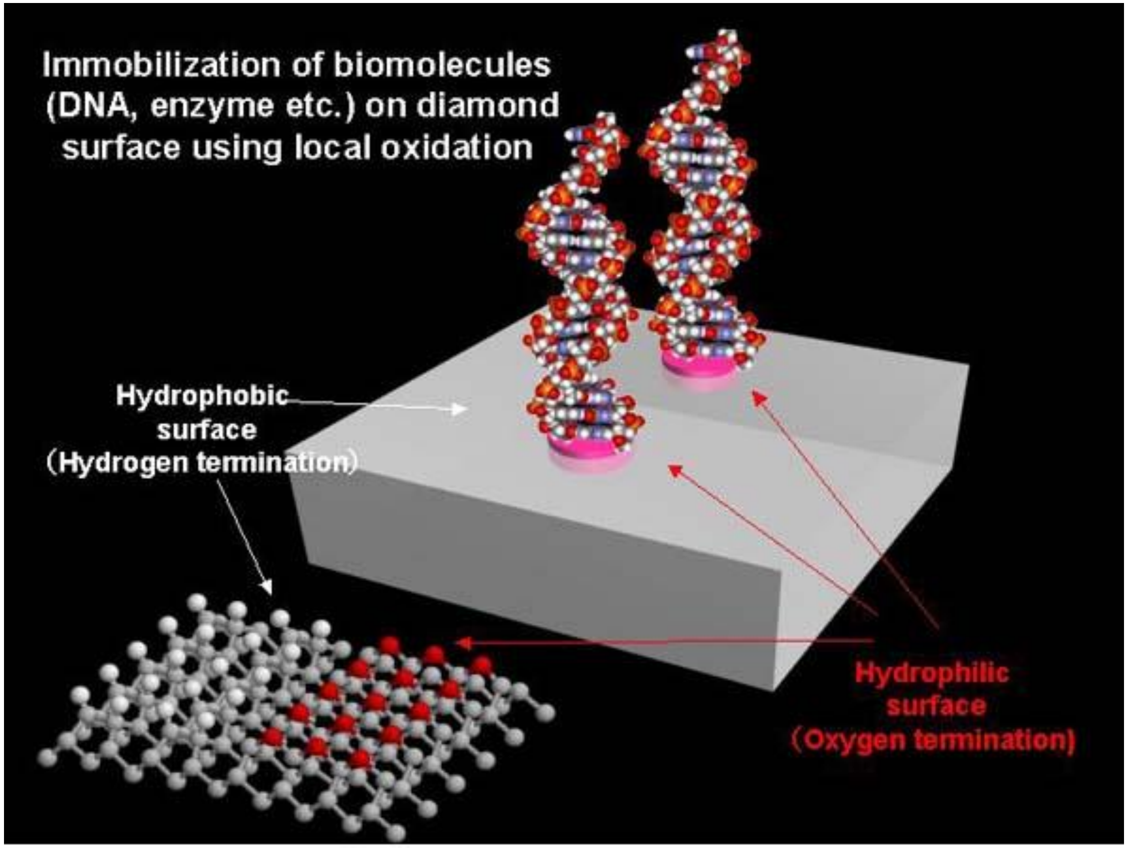


Fig. 1 Immobilization of biomolecules (DNA, enzyme etc.) on diamond surface using local oxidation

- Kawarada Lab

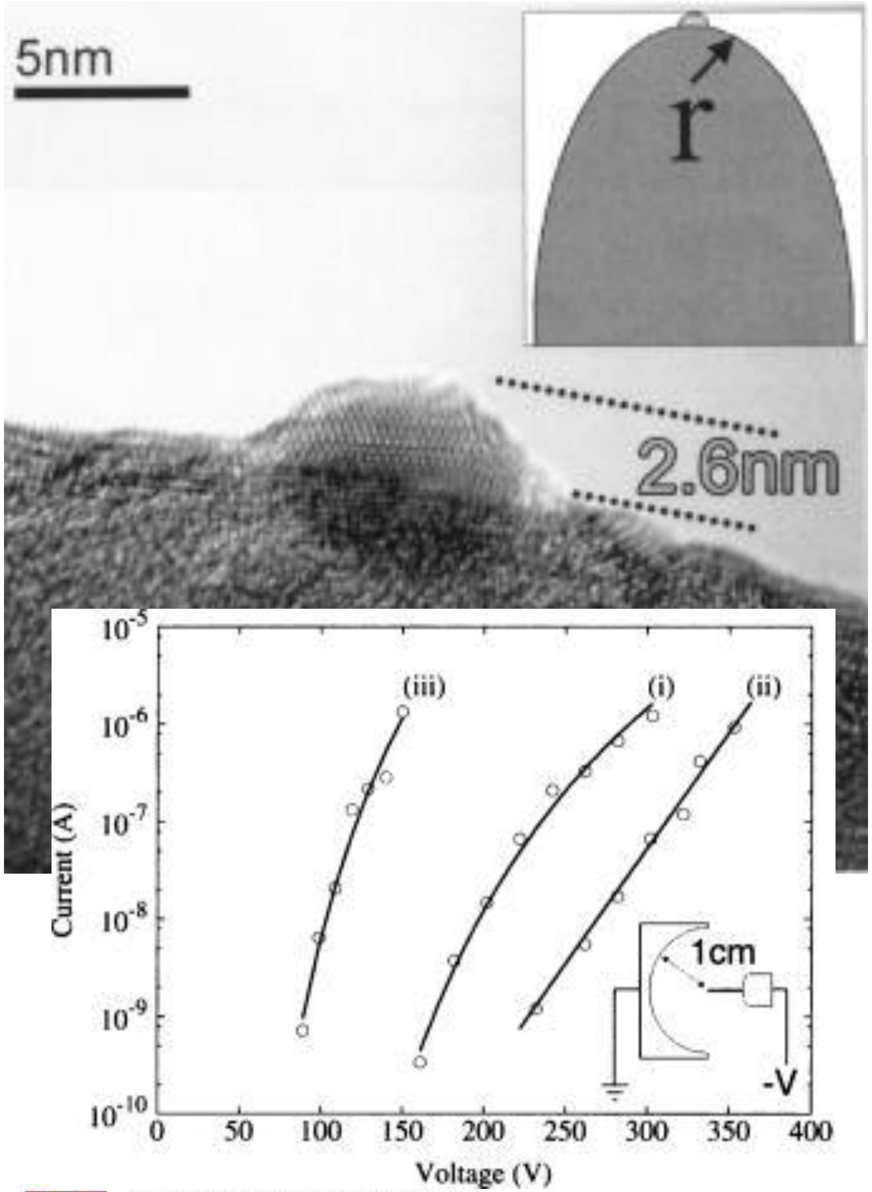
http://www.coe.waseda.ac.jp/kawarada/enzyme/chem.htm

Nanodiamond for Electronics

New technological developments using ND in

- solid-state electronics
- vacuum microelectronics
- the opportunity for making MEMS & NEMS
- new devices in nanoelectronics

FE from a single isolated ND



- High-resolution transmission electron microscope image of isolated ND particle on the surface of Mo tip of 60 nm radius of curvature.

FE from a bare metal tip (i),

the tip with a single ND (ii), and

the same tip with a ND film (iii).

Inset: schematic of tip-to-anode geometry.

T. Tyler et al. *Appl Phys Lett*, **82**, 2904 (2003)

Fundamental & Applied Prospects

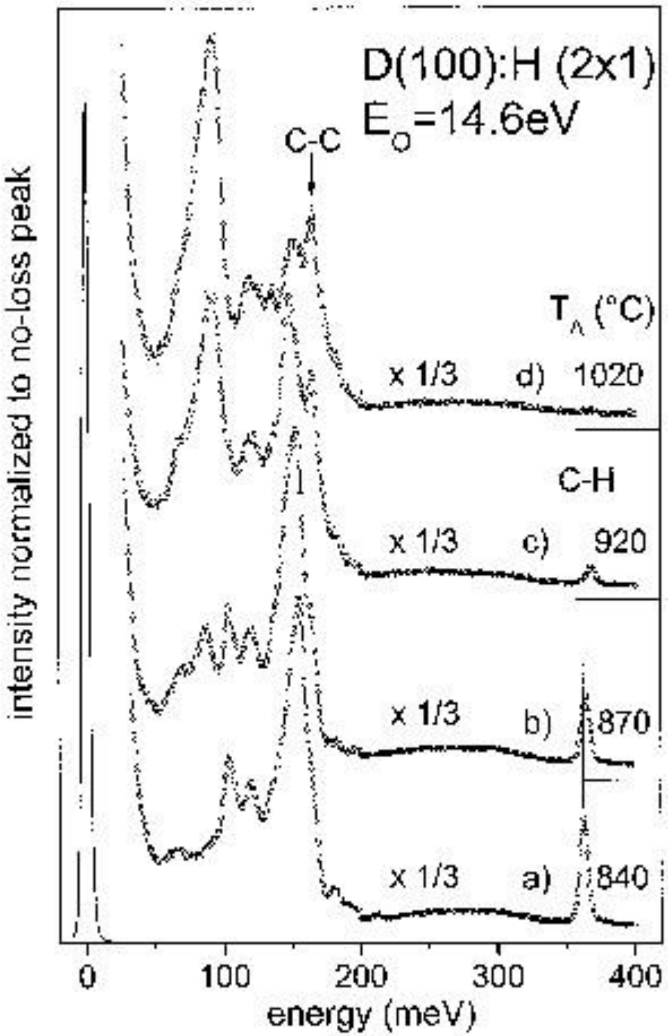
- Hall effect in zero-dimensional dots
- Coulomb and electromagnetic blockade
- EPR – NDS exists at diamond surface
- ND in carbon based electronics
- Potential of ND for spintronics
- UHF and terahertz properties of ND and NDC
- New application of ND – protein interaction

Nanodiamond R&D might be relevant for this as CAPE is involved in Fraunhofer-type research activities

Diamond Quantum Dot (DQD)

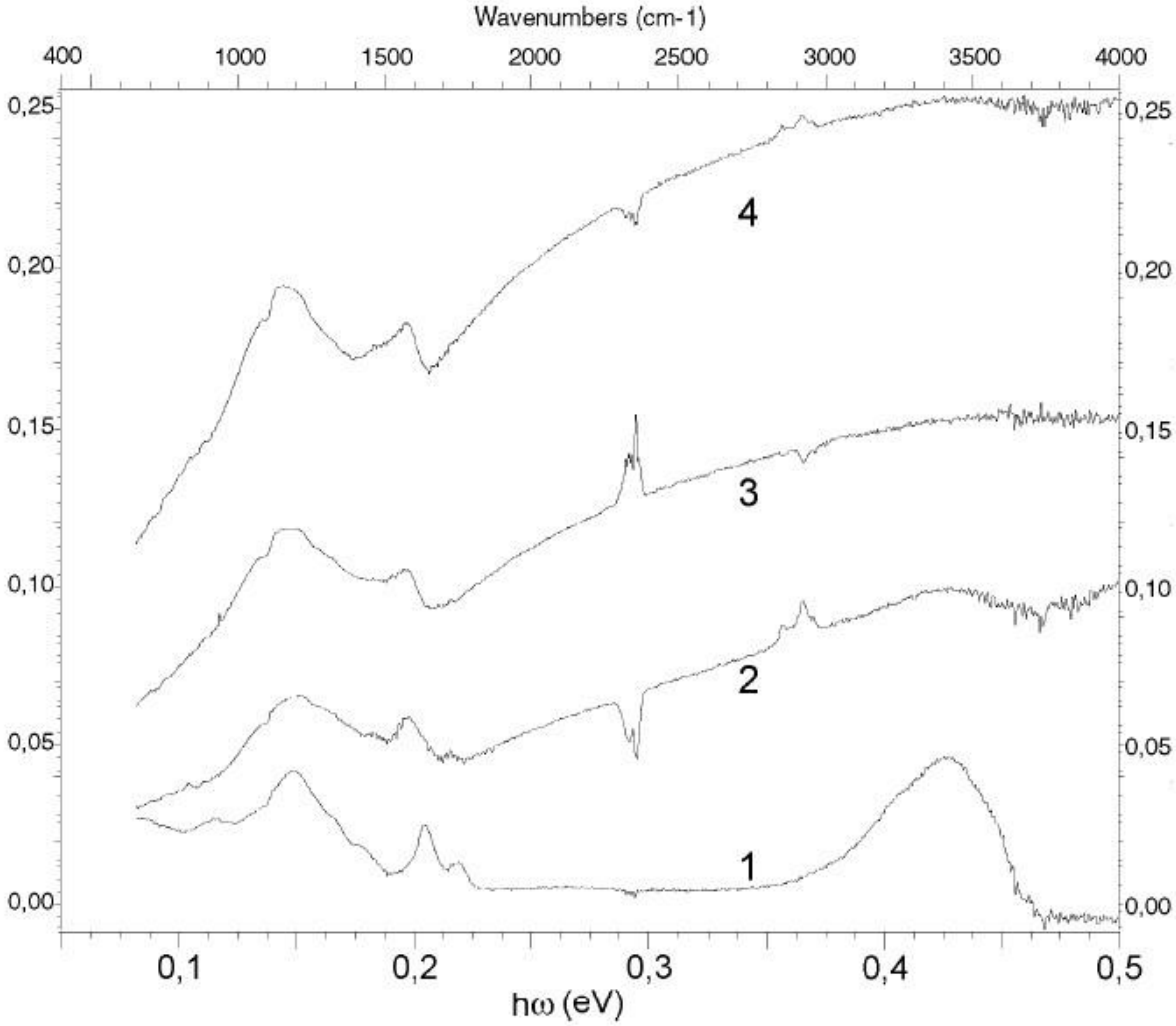
- A model of a diamond quantum dot (DQD) is based on the representation of collective electronic-vibrational states at Tamm levels in clusters with a self-consistent boundary.

HREELS of Diamond Surface



- High-resolution electron energy loss spectroscopy (HREELS) is intrinsically surface sensitive.
- Energy of the vibrational modes diamond surfaces essentially changes in a range 50-400 meV depending on a surface state.
- J. Kinsky et al., Surface vibrations on clean, deuterated, and hydrogenated single crystal diamond (100) surfaces studied by high-resolution electron energy loss spectroscopy // *Diam. Rel. Mater.* **11**, 365-370 (2002).

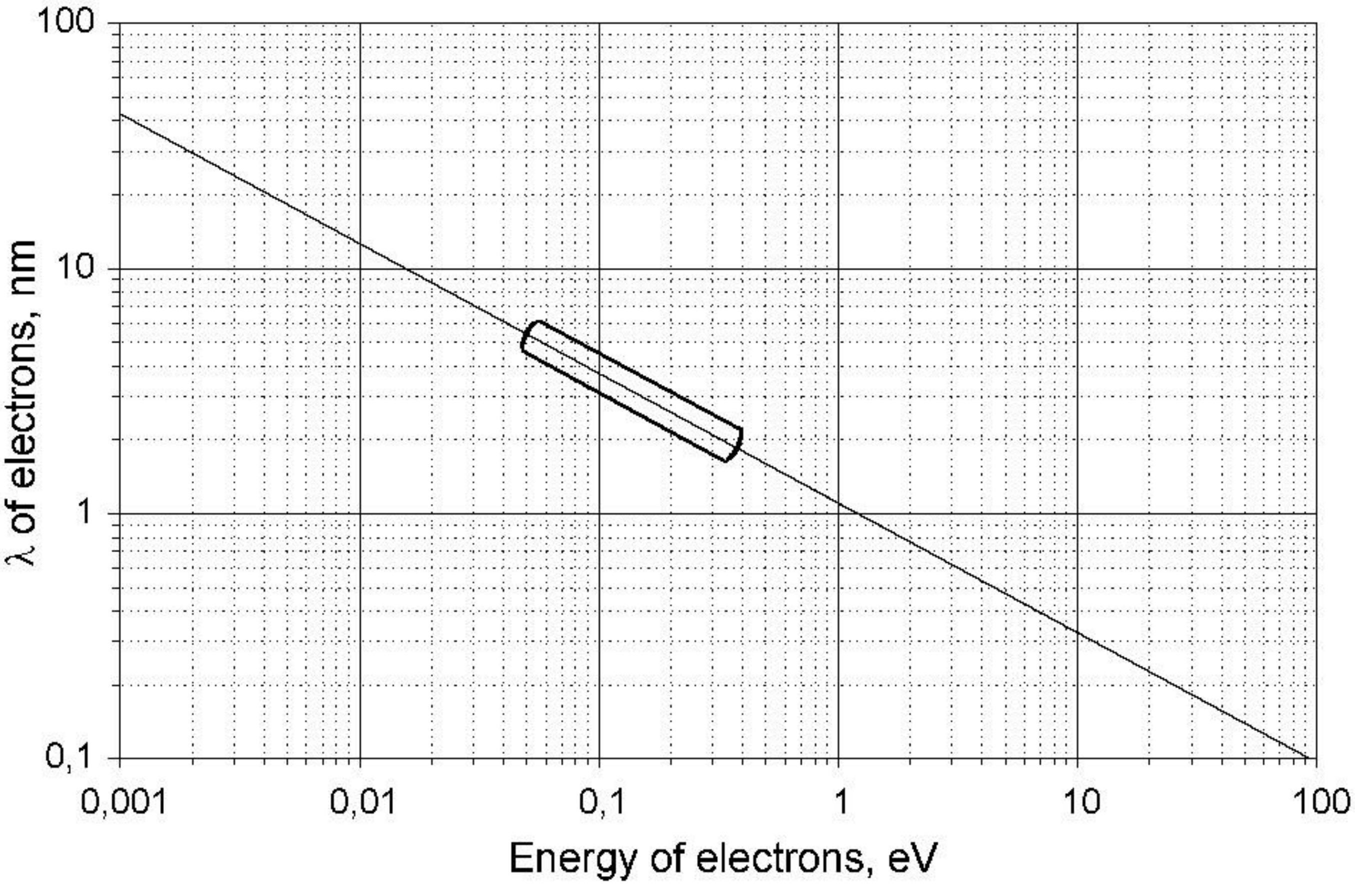
FTIR reflection spectra of NDC



obtained from a few γ. (1) γ = 0; (2) γ = 10; (3) γ = 20; (4) γ = 30.

DQD is good defined by associated (de Broglie) waves of electron

The region of the thermodynamical stability is shown



C atoms ~

1,100-25,000

- 1.9-5.2 nm
- λ ~ 4 nm
- E ~ 0.1 eV
- $E, p;\ \nu = E/h;$ $\lambda = h/p;$ $p = m_e c;$ $h = 6{,}6748 \cdot 10^{-27}.$

Toward wave ψ-function of NDS

- Diamond quantum dot has own electronic states $\sigma_s^1\sigma_p^2\pi^1$ (no π-band)
- "Plasmon" in low-loss spectrum and pre-peak in core-loss (EELS, X-ray absorption)
- This ë state $\sigma_s^1\sigma_p^2\pi^1$ is not sp^2 or linear combination of sp^1, sp^2, sp^3
- Self-consistent quantum of sound exists in DQD
- Free spin (unpaired electron) at NDS

A Model of NDS – Hopf Soliton

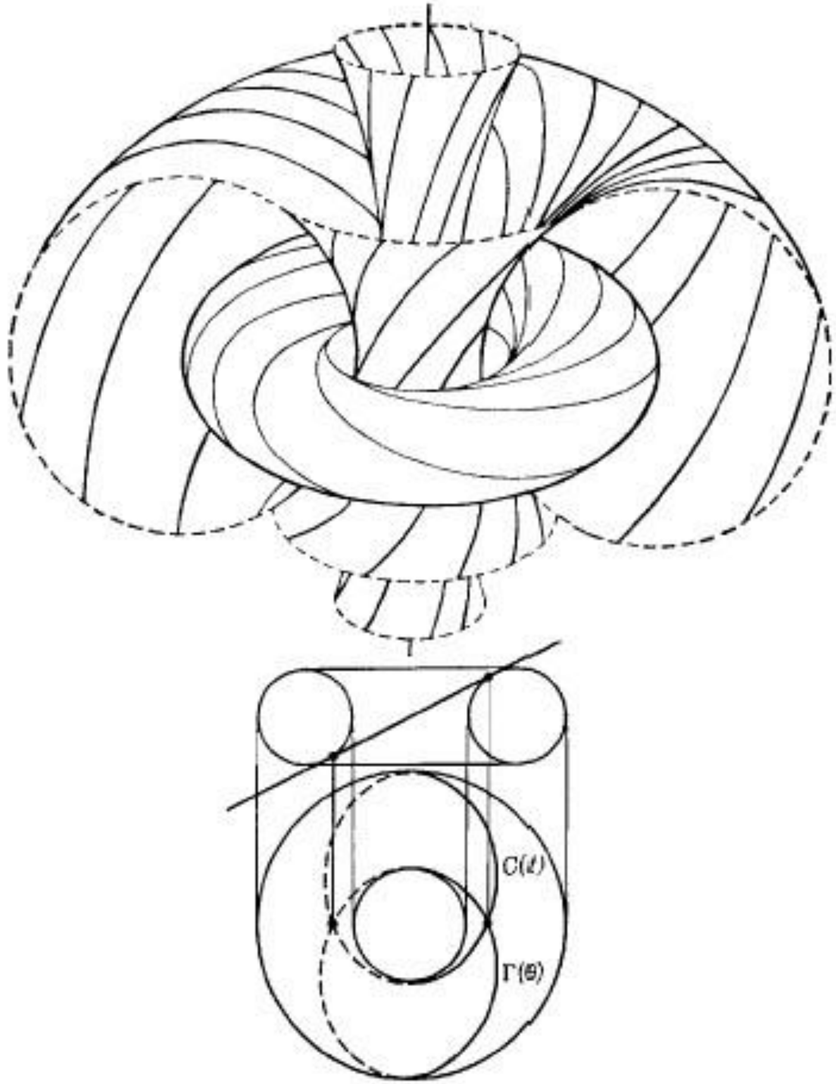
$$\boldsymbol{m}(x,y,z)$$

$$m_1(x,y,z)=\left(\frac{2}{1+r^2}\right)^2[-y-2xz+yr^2],$$

$$m_2(x,y,z)=\left(\frac{2}{1+r^2}\right)^2[x-2yz-xr^2],$$

$$m_3(x,y,z)=-1+\left(\frac{2}{1+r^2}\right)^2[2x^2+2y^2]\cdot$$

$$\mu=\frac{2}{1+r^2}$$



Kitchen Nanotechnology

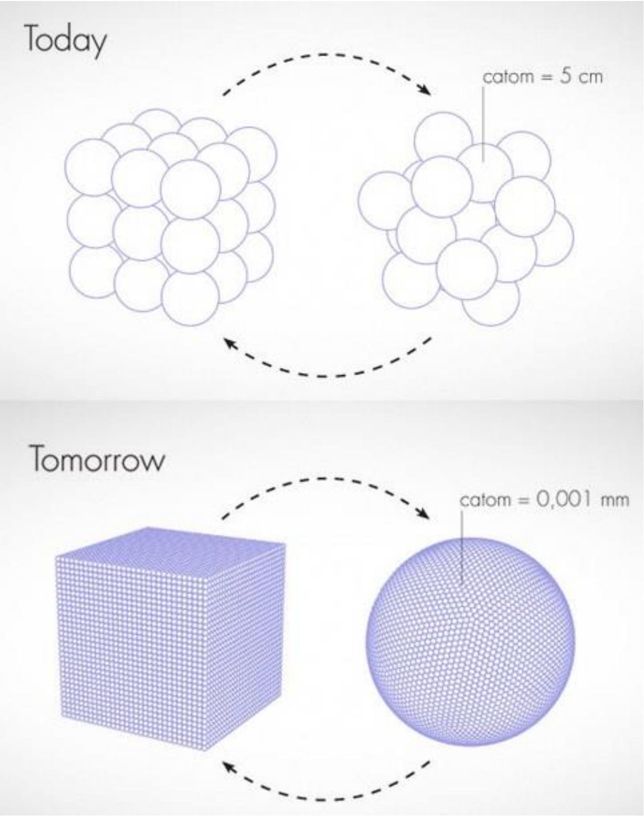
Old before
12 March 2004

https://www.youtube.com/watch?v=QDb83Y_OMts

https://www.youtube.com/watch?v=QDb83Y_OMts

Living Kitchen (2010)
The Future of NanoTech

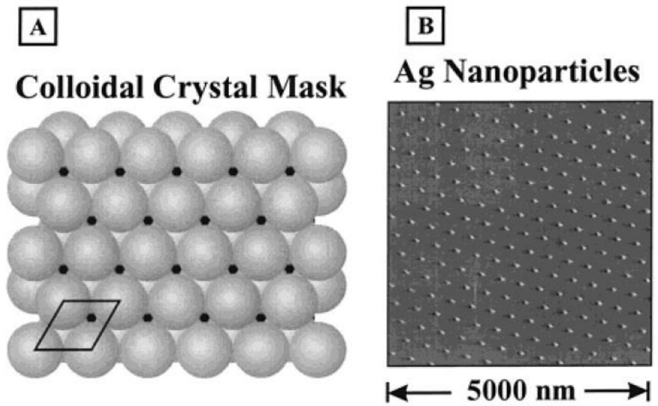
http://michaelharboun.com/livingkitchen.html

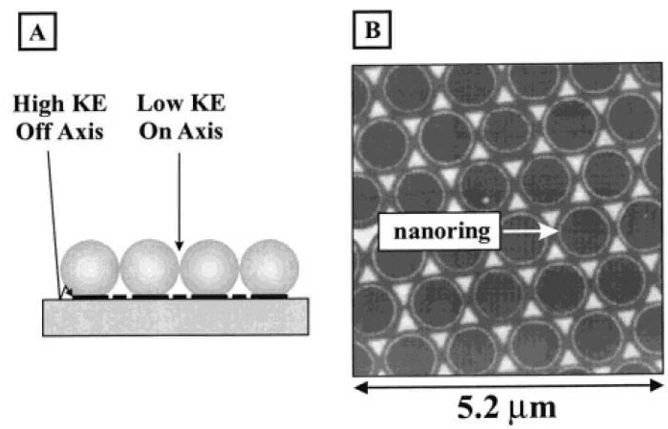


Nanosphere Lithography (NSL)

C L Haynes *et al.*, 2001,
J Phys Chem B, ***105*** (24), 5599
doi: 10.1021/jp010657m

A Drezet *et al.*, 2015
Micron **70**, 55-63.
doi:10.1016/j.micron.2014.12.004





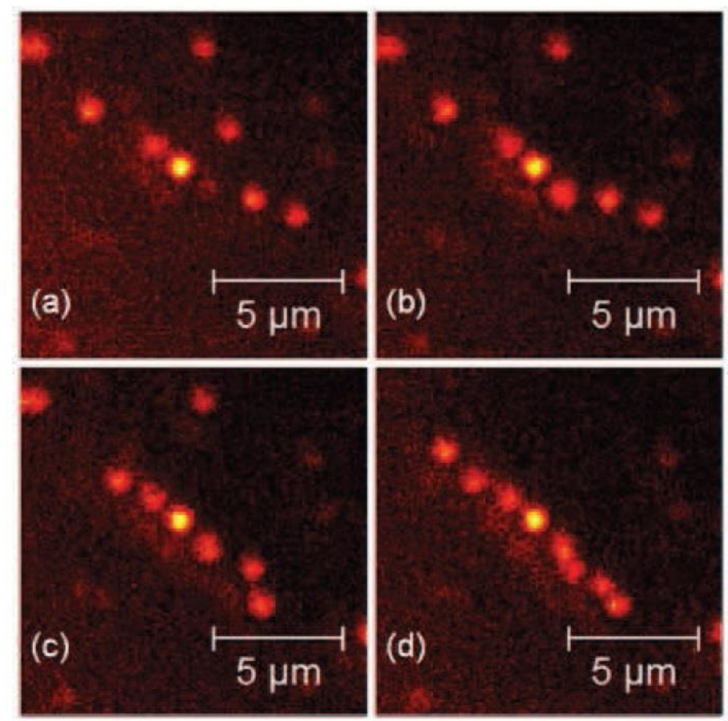
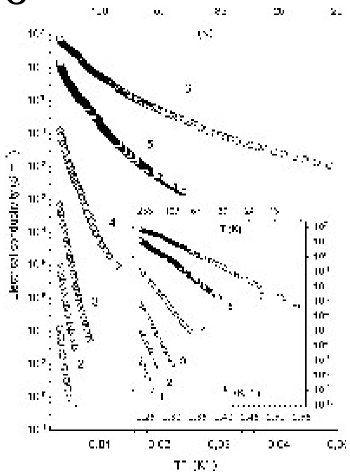
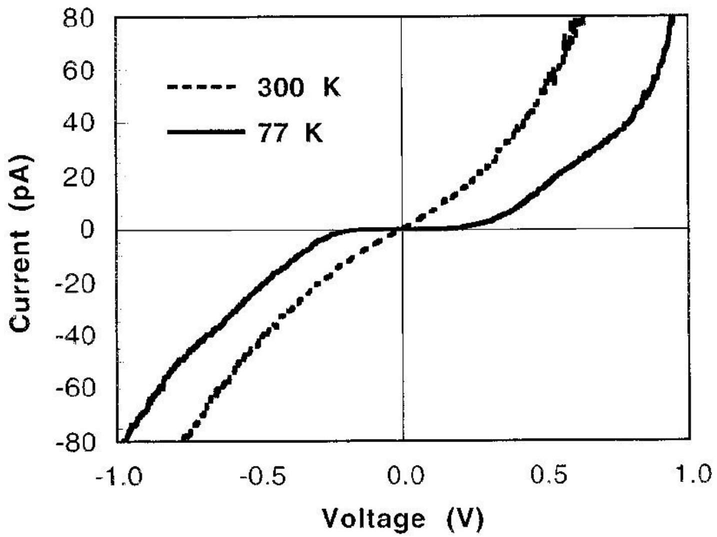


FIG. 8: **(a-d)** An illustration demonstrating how a NSOM tip can be used to align 8 fluorescent diamonds (80 nm diameter) on a glass substrate.



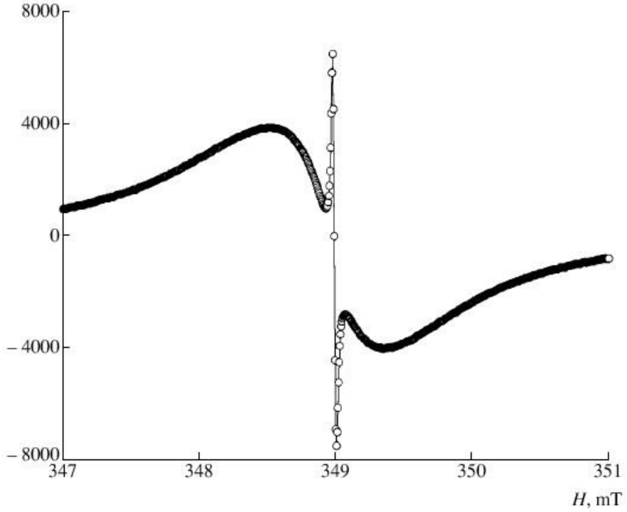
Experiment 1 – new quantum effects

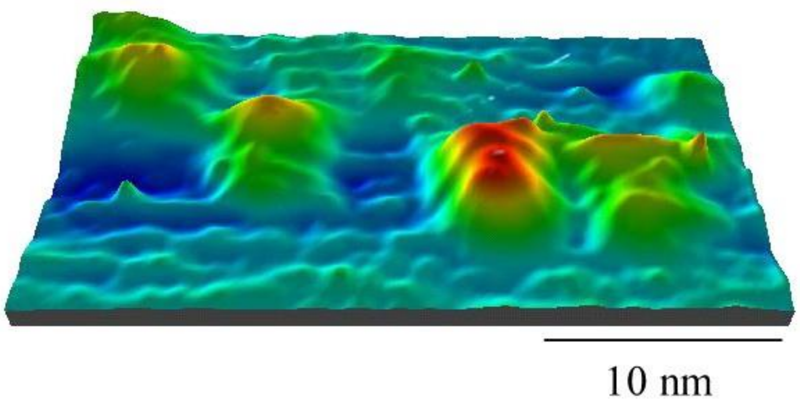
Waiting result



- Hall effect in zero-dimensional dots
- OD Hall effect
- Coulomb and electromagnetic blockade into NDC
- NDS at diamond surface

Experiment 2 – EPR

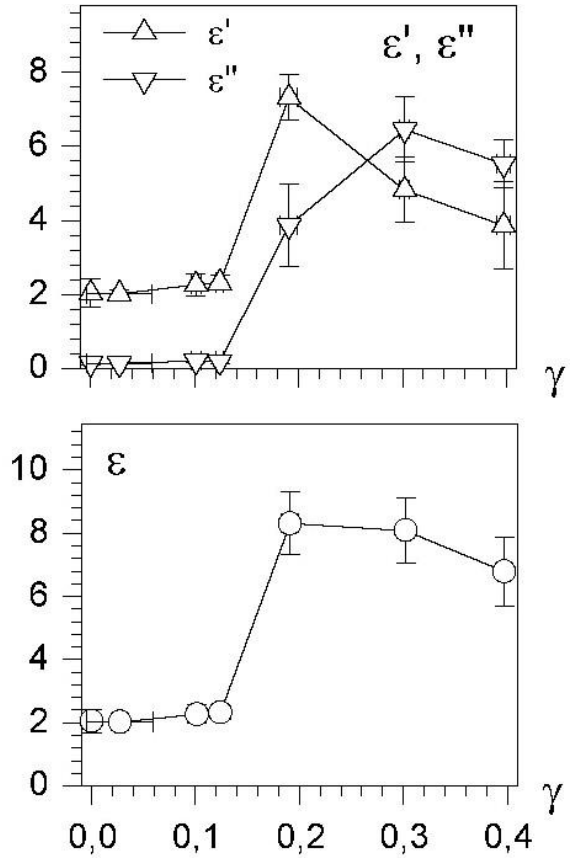




- EPR with optical detection
- Proof of paramagnetic invariant
- Potential of ND for spintronics – nature of free electron

C. Durkan and M. E. Wellan *Appl. Phys. Lett.* ***80****, 458-460 (2002).*

Experiment 3 – terahertz



- UHF and terahertz properties of ND and NDC (perhaps using serial terahertz spectrometer)
- To find NDC regimes at high UHF field
- Gunn had discovered diode oscillators when he studied a noise in semiconductors

Future info to exp.1

- TBA

Future info to exp.2

- TBA

Future info to exp.3

- TBA

Binary Superlattices of Nanoparticles

AL Rogach *et al.*, 2003, Self-Assembly Leads to “Metamaterials”, Ang Chemie, **43** (2), 148
doi: 10.1002/anie.200301704

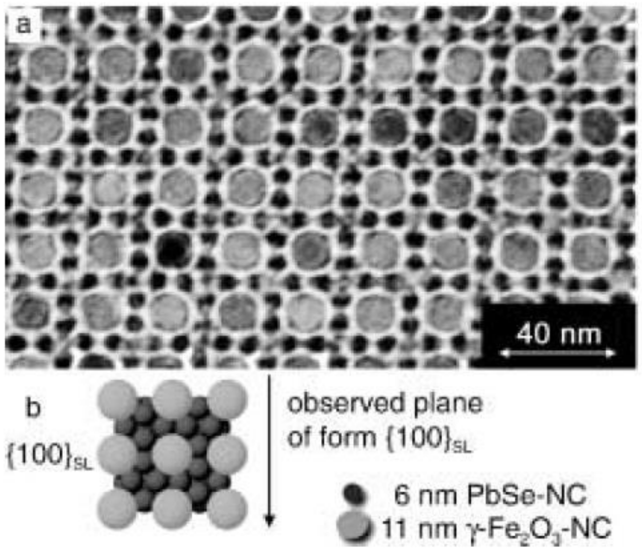


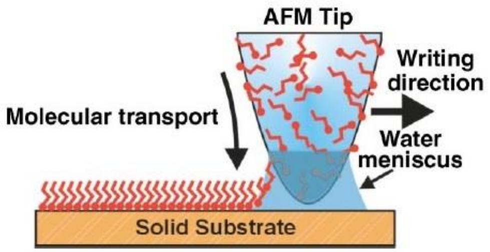
Figure 2. a) TEM image of a 3D superstructure of γ-Fe_2O_3 (11 nm) and PbSe nanoparticles (6 nm). b) Schematic representation of the AB_{13} superlattice (isostructural with intermetallic phase $NaZn_{13}$). Reprinted with permission from reference [6].

(DPG Spring Meeting),
Heidelberg, 23-27 March 2015

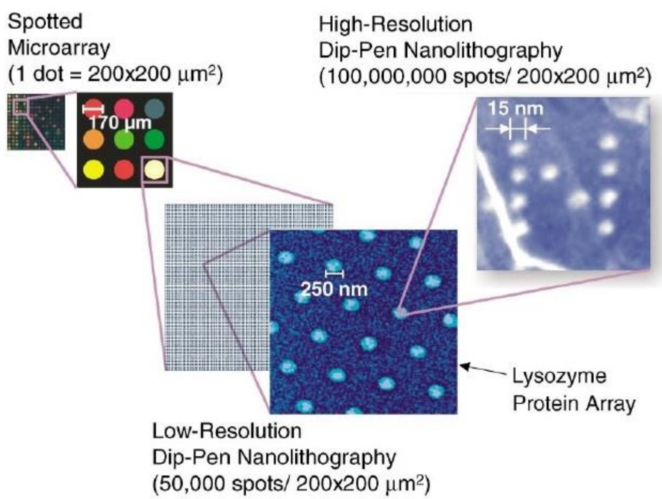
- Quantum Optics and Photonics
- Q 25.4 C Schäfermeier *et al.*, Silicon vacancy (SiV) centers and their electronic-spin coherence in nanodiamonds
  - By investigating SiV centres present in nanodiamonds less than **100 nm** in size, we were not only able to confirm the understanding of the underlying decoherence processes
- Q 41.4 U Jantzen *et al.*, Bulk-like spectral lines from SiV centres nanodiamonds (**~50 nm**)
- etc.

“Dip-Pen” Nanolithography (DPN)

Chad Mirkin *et al.*, 1999, Science **283** (5402), 661-663 doi:10.1126/science.283.5402.661



Schematic representation of the DPN process.

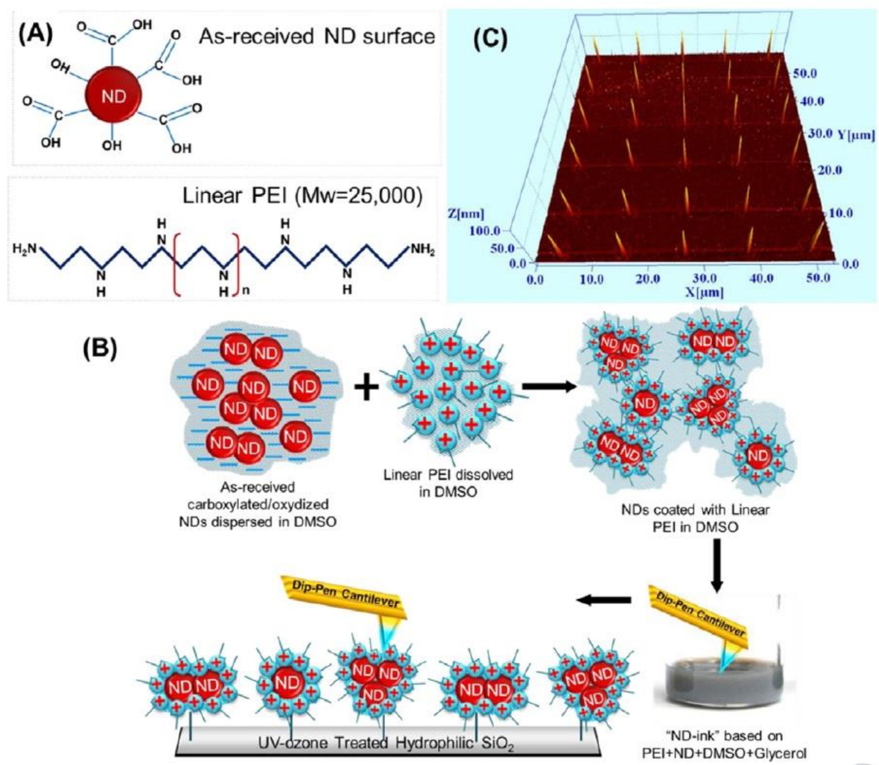


Schematic illustration of the power of DPN resolution in the context of biomolecular nanoarray fabrication.

S Singh *et al.*, 2014, ND array + SiV centers by DPN, Nanotechnology **25**, 045302. <u>ND dot diameter and height</u>

735 nm ± 27 nm and 61 nm ± 3 nm

820 nm ± 20 nm and, 245 nm ± 23 nm



Conclusions

- The properties of NDS are uniform
- Existing of ND is natural phenomena
- There are very useful applications
- NDS is star for nanoelectronics
- ND project is adequate for CAPE set