Phonon Confinement and Size-Effects in the Raman Spectrum of Nanodiamond

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Introduction & Motivation

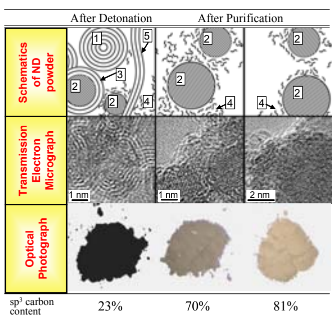
The term "nanodiamond" (ND) is used for different diamond-based materials at the nanoscale (crystal size ~3-100 nm), including pure-phase films, ultra-disperse powders or even diamond additives embedded in a non-diamond matrix. Nanodiamonds were also found in meteorites and are believed to exist in large quantities in interstellar space. ND powders synthesized by detonation are of particular interest because they combine the favorable properties of macroscopic diamond with a high surface reactivity and other size-related characteristics. Currently, ND is mainly used in composite materials or as an additive to cooling fluid and lubricants. Potential future applications include biocompatible composites, drug delivery or the development of transparent coatings for optics, to mention a few.

For most applications it is important to control the size of the diamond crystals and relate it to their properties. Therefore, the ability to accurately measure the crystal size is crucial. Dynamic light scattering and other conventional techniques often do not provide reliable data because of easy agglomeration of ND. Raman spectroscopy is able to measure the size and crystallinity of diamond nanoparticles using the phonon confinement model (PCM).

Nanodiamond

Composition

- **Average crystal size of 4nm**
- **Mixture of sp^2 and sp^3 bonded carbon**
- **Contains iron and impurities such as O, H, N, S and Si**



sp^3 carbon content	23%	70%	81%

Notation in the schematics:
(1) - carbon onion (2) - nanodiamond
(3) - fullerenic shell (4) - amorphous carbon
(5) - graphite ribbon

Synthesis

Detonation of explosives

Other techniques:

- Shockwave compression (powder)
- Chemical vapor deposition (film)
- Arc discharge (film)
- Laser ablation (film)

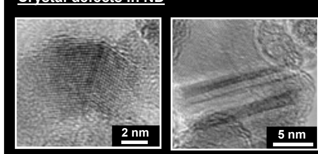
Properties

- High surface reactivity
- Electrical resistivity
- Extreme hardness
- Biocompatibility
- High thermal conductivity

Surface structure and defects

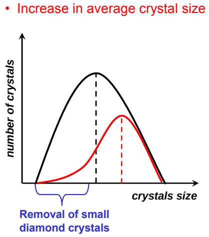
Model of ND surface

Crystal defects in ND



Selective Oxidation

- Removal of non-diamond carbon
- Control of surface chemistry
- Increase in average crystal size



Treatment:

Oxidation of ND powder in air:

T = 430°C

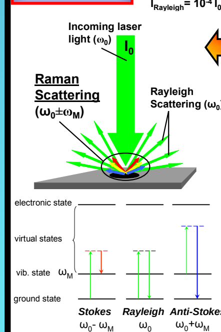
2h, 6h, 17h, 26h and 48h

Raman Spectroscopy

Raman Effect

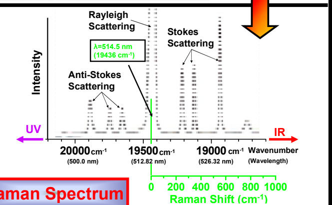
$I_{Raman} = 10^{-10} I_0$

$I_{Rayleigh} = 10^{-4} I_0$



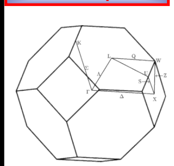
Raman Spectrometer

Raman Spectrum



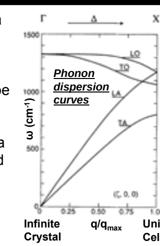
Phonon Confinement

Phonon dispersion



Brillouin Zone of fcc lattice

A phonon is a quantized mode of a vibration occurring in a crystal lattice. There are two types of phonons: "acoustic" phonons and "optical" phonons, which can can be further classified into longitudinal and transverse phonons. The frequencies ω of the phonons are a function of their wavevector's q and vary for different directions in the Brillion zone. The relationship between ω and q is called phonon dispersion curve.



Confined Phonons

In a Raman scattering process, frequency and wavevector are conserved and only phonons with $q/q_{max} \sim 0$ contribute to the Raman signal, where q is the phonon wavevector and q_{max} the size of the Brillouin zone in the reciprocal space.
If the crystal size is reduced to <100 nm the selection rule is relaxed and other phonons are allowed.

Relaxation of selection rule leads to:

- **asymmetric peak-broadening**
- **downshift in peak position**
- **separation of LO and TO modes**

changes can be used to determine the crystal size!!!

Calculated Raman Spectrum

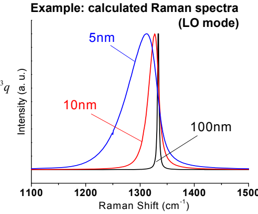
crystal defects

$$I(\omega) = \int_0^1 exp\left(-\frac{C \cdot q_{max}^2 \cdot (q - q_0) L^2}{4}\right) \cdot \frac{4\pi (q/q_0)^2}{[\omega - \omega(q)]^2 + (\Gamma/2)^2} d^3q$$

crystal size linewidth

I(ω): Raman intensity
q_{max}: size of Brillouin Zone
ω: Raman frequency (Raman shift)
ω(q): phonon dispersion curve
q: phonon wave vector
C: constant

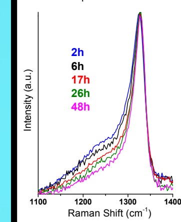
Example: calculated Raman spectra (LO mode)



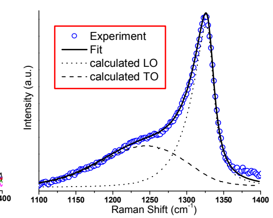
Size Measurement

Raman Spectroscopy

Raman spectra of oxidized ND



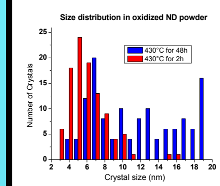
Fitting procedure using calculated data



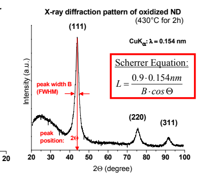
Fitting parameters and corresponding crystal size L:

Oxidation time	TO q_0	TO Γ	LO q_0	LO Γ	L
2h	0.45	35	0.1	20	6.2
6h	0.45	35	0.1	20	6.4
17h	0.44	33	0.1	19	7.0
26h	0.44	30	0.1	19	7.2
48h	0.43	25	0.1	15	7.5

Other techniques

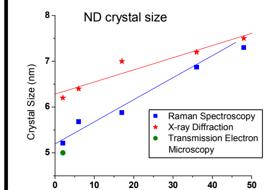


Transmission Electron Microscopy



X-ray Diffraction

Comparison



Summary

- The finite crystal size in ND powders induces changes in the Raman spectrum of diamond and allows characterization of ND with subnanometer accuracy
- The downshift and the asymmetric broadening of the diamond peak can be explained by the phonon confinement model
- The observed changes are used to estimate the average crystal size in ND powders by comparing calculated data with experimental results
- Selective oxidation in air can be used to tune the average crystal size in ND powders
- X-ray diffraction and TEM analysis confirmed the increase in average ND crystal size after oxidation

Acknowledgments

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