

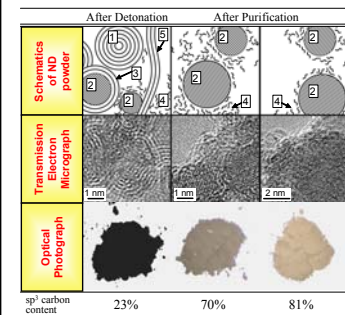
Introduction & Motivation

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).

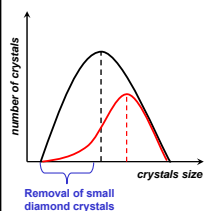
Nanodiamond

- Composition**
- Average crystal size of 4nm
 - Mixture of sp² and sp³ bonded carbon
 - Contains iron and impurities such as O, H, N, S and Si



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

- 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

Synthesis

Detonation of explosives



Other techniques:

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

Properties

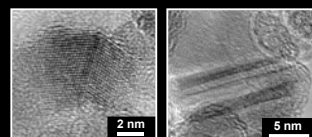
- High surface reactivity
- Electrical resistivity
- Extreme hardness
- Biocompatibility
- High thermal conductivity

Surface structure and defects

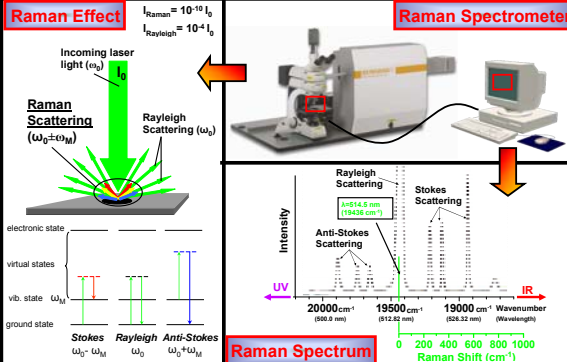
Model of ND surface

- Diamond
- Graphitic
- Hydrocarbon
- Oxygen
- Nitrogen
- Sulfur
- Hydrogen

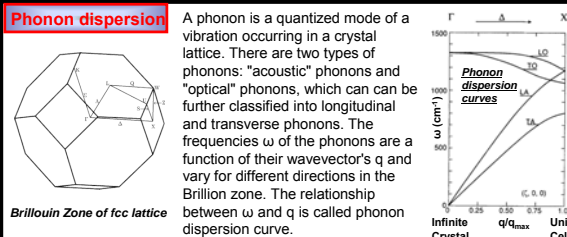
Crystal defects in ND



Raman Spectroscopy



Phonon Confinement



Confined Phonons

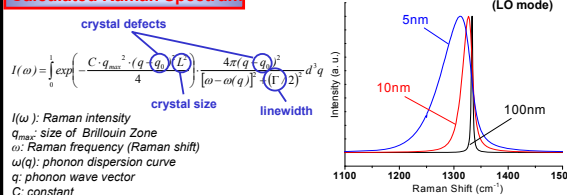
In a Raman scattering process, frequency and wavevector are conserved and only phonons with $q/q_{\text{max}} \sim 0$ contribute to the Raman signal, where q is the phonon wavevector and q_{max} is the size of the Brillouin zone in the reciprocal space. If the crystal size is reduced to <100 nm the selection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

Relaxation of selection rule leads to:

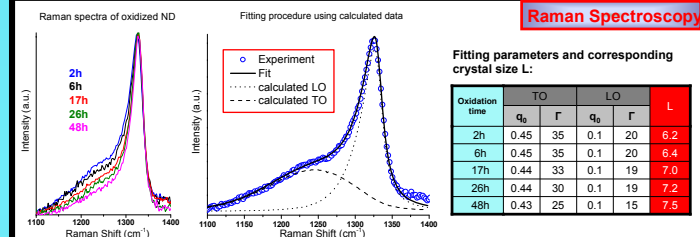
- asymmetric peak-broadening
- downshift in peak position
- separation of LO and TO modes

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

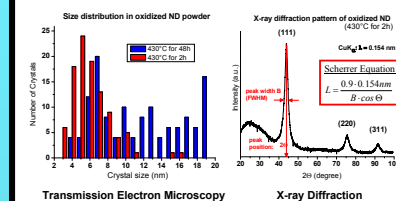
Calculated Raman Spectrum



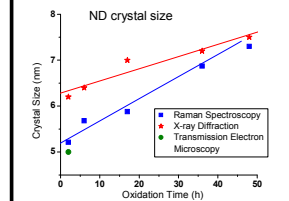
Size Measurement



Other techniques



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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