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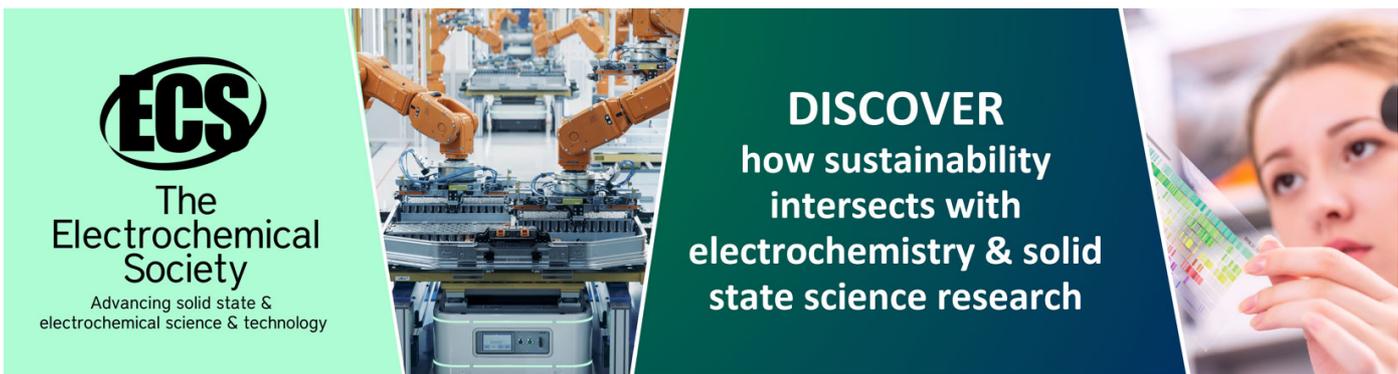
## Sp<sup>2</sup> carbon defects in nanocrystalline diamond detected by Raman spectroscopy

To cite this article: M Veres *et al* 2010 *IOP Conf. Ser.: Mater. Sci. Eng.* **15** 012023

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# Sp<sup>2</sup> carbon defects in nanocrystalline diamond detected by Raman spectroscopy

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**Abstract.** The properties of nanocrystalline diamond (NCD) thin films are significantly affected by the defects found in the interfacial regions between the diamond crystallites (in the so called grain boundaries). Dominant sources of these defects are the sp<sup>2</sup> hybridized carbon atoms that terminate the sp<sup>3</sup> diamond lattice and interconnect the neighboring crystallites. The detailed evaluation of these structural units is of great importance for practical applications of NCD. Since sp<sup>2</sup> hybridized C atoms have high Raman scattering cross-section, Raman spectroscopy could be a valuable method for the determination of bonding configuration of these defects. In this work near-infrared excited Raman spectroscopy and surface-enhanced Raman spectroscopy were used to investigate the sp<sup>2</sup> structural units in grain boundaries of different NCD thin films.

## 1. Introduction

Detailed surface characterization of nanocrystalline diamond (NCD) grains and thin films is of great importance for both fundamental and applied research of these materials. While earlier mechanical properties, adhesion and morphology were the key characteristics during the application of diamond layers [1], new applications [2,3] require not general but grain by grain information on the surface, preferably on the nanoscale.

NCD is a composite material in which the few-nanometer sized diamond grains (or crystallites) surrounded by an amorphous carbon matrix. Usually a third component is also distinguished, namely the interfacial region of these two phases, called grain boundaries. But because of the small volumes of the amorphous carbon regions the latter two constituents are usually considered as one phase. While the mechanical properties of NCD films are determined by the crystallites, optical and electrical characteristics and surface chemistry are controlled by the grain boundaries [4,5]. The diamond grains contain only sp<sup>3</sup> hybridized carbon atoms, while the amorphous carbon phase consists of both sp<sup>3</sup> and sp<sup>2</sup> hybridized C atoms (and hydrogen). Because of the  $\pi$  bonds the latter are distributed not randomly in the matrix, but couple together, forming sp<sup>2</sup> “islands” (or clusters) surrounded by the matrix of sp<sup>3</sup> C atoms. These clusters have  $\pi$  states close to the Fermi level, so these will determine the optical and electronic properties of nanocrystalline diamond films. Therefore, it is extremely important to characterize the grain boundaries and particularly the bonding configuration of sp<sup>2</sup> carbon atoms.

Since both the diamond grains and the grain boundaries are built of the same element and the latter has small volumes and in addition is sandwiched between the crystallites, the realization of this task is rather difficult. Theoretical calculations [6,7] and some experimental studies [5,8-10] were published

in this topic earlier. They revealed that the hydrogen in diamond films is incorporated mainly at the grain boundaries and imperfections of the crystallites and bonded mostly to  $sp^3$  hybridized C atoms. In addition, with lowering of the grain size the amount of the graphitic inclusions in the grain boundaries decreases and the H content increases. While these studies provided extremely important information on the structure of grain boundaries, they cannot be used for a routine characterization of NCD and UNCD films. Earlier we found [11,12] that by optimizing the measurement conditions Raman spectroscopy could be an effective tool for the characterization of the grain boundaries.

In general the Raman spectrum of nanocrystalline diamond contains characteristic peaks of both the diamond crystallites and the grain boundaries. A narrow diamond peak appears at  $1333\text{ cm}^{-1}$ , the broad D and G bands of the  $sp^2$  clusters can be seen at  $1330\text{-}1380\text{ cm}^{-1}$  and  $1550\text{-}1600\text{ cm}^{-1}$ , respectively, while clusters of conjugated  $sp^2$  C chains contribute to the spectrum in the form of broad peaks at  $1050\text{-}1200\text{ cm}^{-1}$  and  $1420\text{-}1470\text{ cm}^{-1}$  (the positions of the peaks vary depending on the excitation energy [13]). The latter are the so called fingerprint bands of nanocrystalline diamond, and were assigned to vibrations of  $sp^2$  carbon chains terminating the  $\sigma$  bonds of the surface atoms in diamond crystallites [11].

Because of the resonant Raman scattering the intensity of the bands related to  $sp^2$  C clusters is a few orders of magnitude higher than that of the  $sp^3$  C matrix and the diamond grains. These clusters have different topologies and therefore different band gaps and characteristic vibrational frequencies. Usually the larger the size of the cluster the lower the band gap it has. As a result, the Raman spectrum measured with particular excitation energy will be dominated by the resonantly enhanced peaks of  $sp^2$  C clusters. By changing the excitation wavelength vibrations of a different set of  $sp^2$  C clusters will be enhanced selectively.

The resonantly excited bands overlap and, as a consequence, the resulting broad peaks provide only generalized information on the bonding configuration of carbon atoms in grain boundaries. However, by suppressing the resonant Raman scattering the characteristic peaks of specific structural units would become detectable. This was achieved by using lower excitation energies [11]. Using near-infrared excitation and lowering the excitation spot size we were able to detect characteristic vibrations of structural units of grain boundaries.

By using this method it is possible to characterize the bonding configuration of atoms on the surface of individual crystallites, while statistical analysis of the spectra measured in different points of the sample surface gives information on dominant structural units [14]. It works well with layers having grain size down to 100 nm. Below that size, because of the much higher number of crystallites falling into the excitation spot and the larger amount of amorphous carbon phase the Raman spectra are again dominated by the broad amorphous carbon bands. In such samples the excitation volume can be lowered further by using surface-enhanced Raman spectroscopy (SERS) [11], where a vast increase of the scattering intensity can be observed from the vicinity of rough metallic surfaces (or nanoparticles). The effective region of the enhancement constitutes a few atomic layers from the metal surface, which is the surface region of nanocrystalline diamond crystallites.

This work focuses on the bonding configuration of  $sp^2$  carbon atoms in grain boundaries of NCD thin films. Nanocrystalline diamond layers having different grain size were investigated using normal and surface-enhanced near-infrared excited Raman spectroscopy and the spectra were analyzed with respect to vibrations of  $sp^2$  C atoms.

## 2. Experimental

NCD and UNCD thin films of different average grain size were purchased from Advanced Diamond Technologies (Romeville, USA). The films were prepared by microwave enhanced chemical vapor deposition onto crystalline silicon substrates. The thickness of the films was 1 or 2 microns. Colloidal gold (10 nm average particle size) was purchased from Sigma-Aldrich.

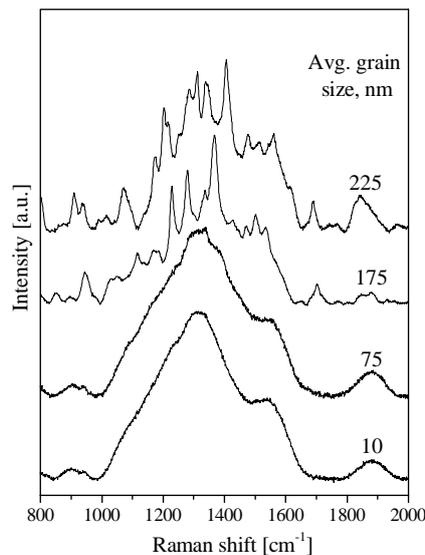
Raman spectra were recorded on a Renishaw 1000 Raman spectrometer attached to a Leica DM/LM microscope. A 785 nm diode laser served as excitation source. The excitation beam was focused into a spot having diameter of 1 micron. The power of the laser beam on the sample surface

was 5 mW. Each spectrum was measured in the 800-2000  $\text{cm}^{-1}$  region with an integration time of 10 seconds. The resolution was 1  $\text{cm}^{-1}$ .

For SERS measurements the gold colloid was dropped onto the diamond film surface. The measurements were performed after the evaporation of the water.

### 3. Results and discussion

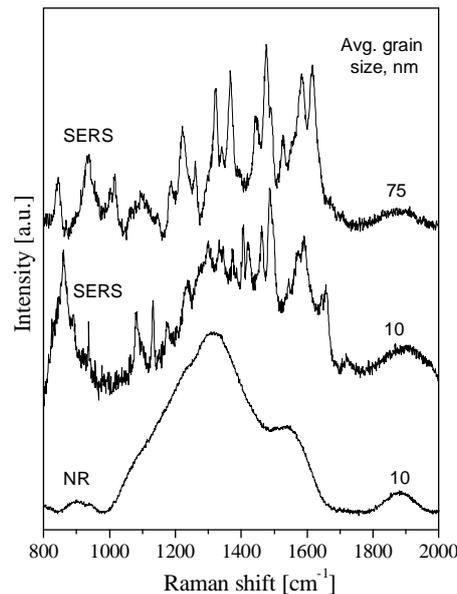
Fig. 1 shows typical near-infrared excited Raman spectra of NCD thin films having different average grain size. The spectra of the layers with average crystallite sizes above 100 nm contain narrow peaks, while broad bands dominate the spectra of the samples having grain sizes below 100 nm.



**Figure 1.** Typical Raman spectra of NCD thin films measured using near-infrared excitation.

Because of the large number of crystallites falling into the excitation volume and the higher amount of the amorphous carbon phase (being proportional to the overall surface of the crystallites) the latter spectra (lower curves in Fig. 1) are dominated by the broad bands of the amorphous carbon phase. However, using SERS the characteristic vibrations of these films can also be enhanced selectively (Fig. 2). The character of the SERS spectra is similar to that observed in the upper curves in Fig. 1: it contains a number of narrow peaks in the 800-1700  $\text{cm}^{-1}$  region. The excitation takes place in different regions of the samples: while normal Raman scattering was excited in a 2-300 nm thick surface region of the films, surface enhancement takes place only on the outer surface, where the gold nanoparticles contact the layer, and so it provides information only on the bonding configuration of the surface region. Normal Raman scattering excited in deeper regions of the film also contributes to the spectra in form of broad bands seen as a background for the narrow peaks.

For both normal Raman and SERS, the position and the intensity of the narrow bands shows lateral dependence when measuring the spectrum in different points on the sample surface, but particular crystallites had definite Raman peaks that were observable in each spectrum recorded with the excitation of that given crystallite [14]. Therefore, these peaks were assigned to characteristic vibrations of diamond grains, arising from the grain boundary region of the crystallites.



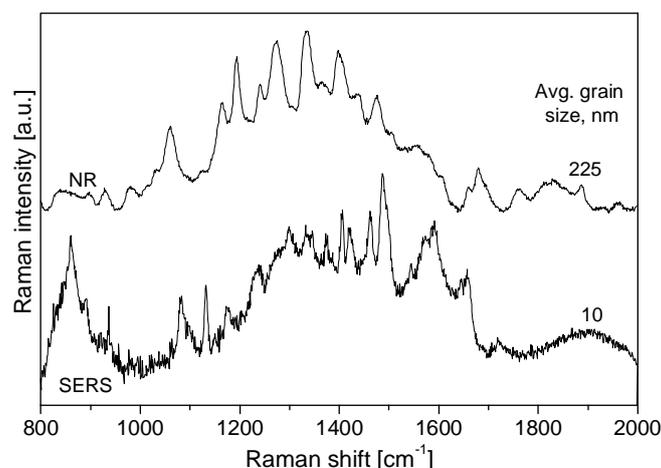
**Figure 2.** Normal (lower curve) and surface-enhanced Raman spectra of UNCD films having average grain size of 10 and 75 nm.

The interpretation of the spectra shown in Figures 1 and 2 is rather difficult. Peak positions and intensities are affected by a number of different factors, including the effect of the surrounding atomic environment (which could change both the frequency and the Raman activity of a particular vibration), the internal stress and the dispersion of the Raman bands due to the resonant scattering. In addition, SERS spectra could contain bands arising from new structural units formed by chemical interaction of gold nanoparticles with the diamond film.

Considering the above factors with respect to bonding configuration of  $sp^2$  C atoms, the analysis of the shown spectra was restricted to regions of "classical" nanocrystalline diamond peaks, assuming that the narrow peaks in these regions are the selectively enhanced components of the broad bands. Several spectra were measured and analyzed using normal (for grain sizes above 100 nm) and surface-enhanced (for samples with crystallites below 100 nm) Raman spectroscopy in different points on each sample. Figure 3 compares the typical Raman spectra of the samples having largest and smallest average crystallite size.

An intense diamond peak can be observed in the spectrum of the sample with large grains at  $1333\text{ cm}^{-1}$ . Here the D and G band regions are of small intensity without intense narrow peaks. The region of the conjugated  $sp^2$  chains is dominated by one band around  $1060\text{ cm}^{-1}$ , the accompanying pair of which appears at  $1400\text{ cm}^{-1}$ . In addition, C=O vibrations also contribute to the spectrum around  $1700\text{ cm}^{-1}$ .

The diamond peak can be seen also in the SERS spectrum of the layer with small crystallites, but it is of much less intensity. Intense peaks appear in the region of D and G bands, while the region of conjugated chains contains several peaks around  $1100\text{ cm}^{-1}$ . C=O peaks are almost undetectable in this spectrum. Spectral features of the other two samples with medium grain size fall in between those shown in Fig. 3: as the grains size decreases, narrow peaks start to appear in the G band region and the peaks of the conjugated chains shift to higher wavenumbers.



**Figure 3.** Typical features of the Raman spectra of NCD films with average grain size of 225 nm and 10 nm.

The low intensity in the G band region of the sample with large crystallites indicates the low amount of  $sp^2$  C rings and graphitic inclusions in the grain boundaries of this film. The narrow peaks appear between  $1100$  and  $1500\text{ cm}^{-1}$ , in the region of C-C and C-H vibrations of both  $sp^2$  and  $sp^3$  structural units. The region of conjugated chains around  $1100\text{ cm}^{-1}$  is dominated by one intense peak. This implies a rather narrow length distribution of the conjugated chains in the sample.

As the grain size decreases (and the sample contains higher amounts of the amorphous phase), the intensity increases in the spectral regions characteristic for aromatic rings. Narrow peaks appear around  $1600\text{ cm}^{-1}$  indicating the increased amount of structural units containing  $sp^2$  C rings. Several peaks appear around  $1100\text{ cm}^{-1}$  and  $1450\text{ cm}^{-1}$ , in the region of conjugated chains. Compared to the normal Raman spectra shown in Fig. 3, peaks of conjugated chains around  $1100\text{ cm}^{-1}$  are shifted to higher wavenumbers, which indicates the lowering of the chain length. This supports that these chains are located on the surface of diamond grains –shorter chains were formed on the surface of smaller crystallites.

#### 4. Conclusions

Bonding configuration of  $sp^2$  carbon atoms in NCD grain boundaries was investigated using normal and surface-enhanced near-infrared excited Raman spectroscopy. A comparative analysis was performed on Raman spectra of diamond thin films having different average grain size. Long conjugated  $sp^2$  C chains were found in layers with large crystallites, while aromatic rings and shorter conjugated chains were identified in ultrananocrystalline diamond films containing a few nanometer sized diamond grains.

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