

Mapping crystalline quality in diamond films by micro-Raman spectroscopy

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Abstract

It is known that different growth sectors within diamond films grown by chemical vapor deposition can contain different concentrations of defects. The defects in the diamond can be in the form of inclusions of non-diamond carbon. The quality of the diamond can be observed by the change in the ratios of diamond and non-diamond components in the Raman spectrum and in the widths of the Diamond Raman Line. In (001) textured growth, the (001) sectors are observed to be made up of good quality diamond, whereas the neighboring (111) growth sectors have high concentrations of defects and inclusions. Because of the transparency of diamond, it is possible to map the Raman signal with a confocal microscope to depths of hundreds of microns. In this way, it has been possible to show that the regions of relatively defect-free diamond lie within inverted pyramids. The bases of these pyramids correspond to the observed square (001) facets, whereas the sides of the pyramid correspond to (111) planes. This feature of textured diamond films has been observed by transmission electron microscopy of cross-sections of such films, but this is the first time that it has been shown in-situ. The “Blue-Cross” of defect related luminescence [N.C. Burton, J.E. Butler, A.R. Lang, J.W. Steeds, *Proc. R. Soc. Lond. A* 449 (1995) 555–566] is observed by PL and correlates well with a mapping of the FWHM. The result demonstrates the ability of confocal micro-Raman spectroscopy to map the crystalline quality in diamond films on a micron scale. It is demonstrated for the first time that the pattern of defect densities previously observed by TEM can be observed in particular growth features of diamond films by confocal Raman spectroscopy. © 1998 Published by Elsevier Science S.A.

Keywords: Oriented growth; Defect density; Growth sectors; Confocal Raman Spectroscopy

1. Introduction

The material properties of diamond make thin diamond films grown by chemical vapor deposition a potentially valuable resource for the technologies of the future (D.S. Hoover, Invited speaker, Diamond 1996, Tours, France). The applications of these films at the present time are limited primarily by their cost and quality. Quality may be rated in terms of microscopic quantities such as defect and impurity content within grains, grain size or amount of non-diamond inclusions at grain boundaries. Alternatively, quality may be defined in terms of macroscopic measurements such as thermal conductivity, heat capacity, electrical conductivity or optical clarity. The macroscopic properties are directly relevant and are often easier to measure, but although it is clear that these depend on the microscopic properties, the relationship between the two is not

always straightforward. A better understanding of the microscopic structure of the films is important to improvements in their production. In this paper, Raman spectroscopy and Photoluminescence will be used to investigate the microstructure of particular common growth features of diamond films. This mapping will be compared to the results of previous investigations.

2. Background

Raman spectroscopy is one of the most commonly used investigative techniques for diamond films, because it is cheap, fast and non-destructive [1–3]. The Raman spectrum of diamond films contains a wealth of information, some aspects of which are still not fully understood. In this investigation, we shall show that micro-Raman spectroscopy can be used to map crystalline quality on a micron scale. Raman scattering is the inelastic scattering of light by the vibrational excitations of crystals [4].

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In diamond crystals, incident polarized laser light is scattered by the triply degenerate optical phonon at the Brillouin zone center. In natural diamond, a single sharp peak is observed at 1332 relative wavenumbers corresponding to the first order Raman scattering effect. In CVD diamond, a broader line is observed at approximately the same position and additionally, features can be seen in the Raman spectrum that originate from scattering from graphitic or other non-diamond components [1–3].

In principle, the amount of diamond and non-diamond might be deduced from the ratios of the diamond and non-diamond components in the Raman spectrum. However, there are several factors that make such a determination currently unreliable. Firstly, the non-diamond components are strongly absorbing at the laser frequencies commonly used in Raman spectroscopy. Secondly, the Raman scattering efficiency of non-diamond carbon is between 50 and possibly over 100 times as efficient as diamond, so a small amount of non-diamond carbon in the film can swamp the diamond signal [5]. Thirdly, several features in the non-diamond and possibly some features in the diamond Raman spectrum may be explained by non-zone center or surface-related scattering effects, and therefore, the intensities of these features are not directly proportional to the volume of material present [6]. Fourthly, the Raman spectrum of diamond films has been shown to be dependent on the wavelength of the incident laser [7]. This dependence may be caused by a mixture of absorption and resonance effects and means that Raman spectra from the same position on the same film taken with two different lasers may look completely different. Therefore, a quantitative determination of the quality of the film in terms of the local or global sp^2/sp^3 ratio is not currently possible by Raman spectroscopy. In this investigation, we show that a careful analysis of Raman spectra can reveal the qualitative difference between different areas within a large grained crystal within a diamond film and therefore in principle between different diamond films.

Non-diamond inclusions have signatures in the intensity of the Raman spectrum above the first-order diamond line. These are generally split up in the literature into a G or graphite peak at 1580 cm^{-1} in crystalline graphite or a band around $1450\text{--}1500\text{ cm}^{-1}$ in amorphous sp^2 and another band at around 1350 cm^{-1} referred to as the D or disordered peak. The D peak has been identified with scattering from the edge of the Brillouin zone due to a surface effect in microcrystalline graphite [6]. The intensity of the D band will not be proportional to the volume of material, but only the surface area therefore it will be systematically ignored, and the quality factor will be taken from the ratio between the integrated intensities of the diamond line and G band.

The linewidth of the diamond line in natural diamond is related to the lifetime of the phonons from which the light is scattered [4]. This lifetime is dictated by the anharmonicity of the bonding and in diamond is very long, hence giving very sharp peaks for scattering from natural diamond crystals $\text{FWHM} = \Gamma = 1.9\text{ cm}^{-1}$. In CVD diamond, this line may be much broader. The broadening may arise from a number of factors. There will be an instrumental broadening induced by the laser linewidth and the spectrometer, and this can be systematically subtracted. The interaction of the phonons with defects or grain boundaries in the film will cause a reduction in phonon lifetime and an inversely proportional increase in the diamond linewidth [8]. Assuming a homogeneous distribution of defects, the linewidth will be inversely proportional to the defect density to first approximation. Phonon confinement [9] is a second-order effect that is of considerable importance in describing the Raman scattering from nano-crystals, but this effect can be ignored in this investigation. Broadening may also occur because of non-homogeneous distributions of stress or defects. In all experiments, only homogeneous, Lorentzian, broadening was detected, and it was assumed that non-homogeneous effects were negligible.

3. Results

The film under investigation was grown by J. Butler at the Naval Research Labs in Washington, DC. The film contained a number of large crystallites with a (001) growth orientation that had flattened off during growth to give large square facets. Fig. 1 is an SEM micrograph of a typical crystallite from the film on

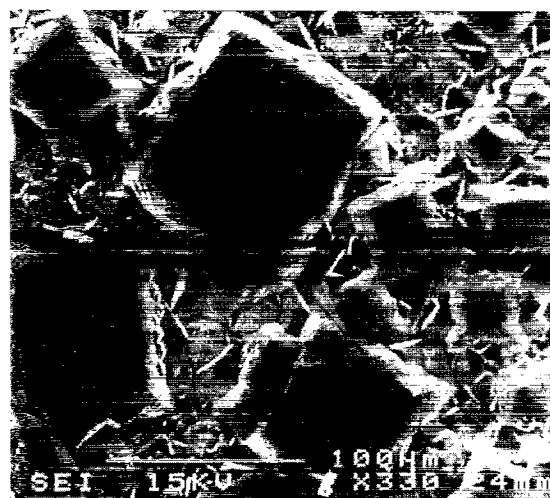


Fig. 1. A scanning electron micrograph of a specific region of sample 5K06, a diamond film grown at the NRL by Jim Butler. Facet A, a large square faceted diamond crystal within the film is identified at the top of the picture.

which the investigation was conducted. TEM can show the microstructure of specially thinned samples [10]. Previous investigations [11] of cross-sections and carefully prepared plan view TEM specimens had shown that similar crystallites were made up of a central (001) growth zone with very few defects and neighboring (111) growth zones containing high defect concentrations. Fig. 2 shows a TEM image which illustrates the central relatively defect-free region. Fig. 3 shows diagrammatically how the growth sectors are related to each other in a cross-section of such a diamond film.

Raman spectroscopy was performed on a Renishaw



Fig. 2. A transmission electron micrograph of a plan view specimen prepared by thinning from the front and back a film of similar morphology to that studied. The picture shows the square defect-free region of the crystal associated with the (001) growth sector surrounded by defective (111) growth zones.

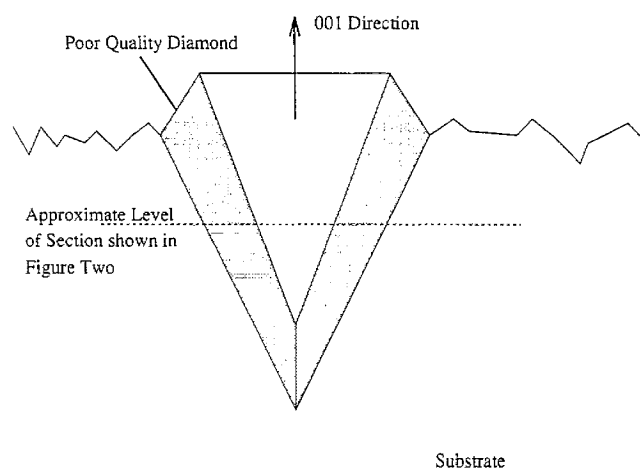


Fig. 3. A diagrammatic representation of the growth sectors within large (001) oriented crystallites, such as facet A. Fig. 2 would correspond to a section at approximately the level indicated.

2000 Raman imaging spectrometer, fitted with HeNe and Ar⁺ lasers and with a confocal spectrometer capable of achieving spot sizes of 1 μm and approximately 2 μm vertically. In the Renishaw system, the confocality is obtained via the slitwidth and the number of pixels used on the CCD in the detection optics. The spectral resolution of the detector was just below 1 cm⁻¹, the statistical effect of linefitting gave an enhanced resolution for the linewidths of approximately 0.1 cm⁻¹. The microscope was equipped with an xyz μm mapping stage. One particularly large facet was identified (see Fig. 1) and maps were taken in an xz plane. The spectra obtained from these maps was curve-fitted, and the maps were generated from the ratio of the G band to diamond intensities and the width of the diamond line. These maps are shown in Fig. 4. The two maps correlate well with each other, and the angle shown for the boundary between good and defective material corresponds well to the boundary between (001) and (111) growth sectors shown in Fig. 3. The maps also show that the 100 growth sectors do contain some defective material and that the distribution of this material within

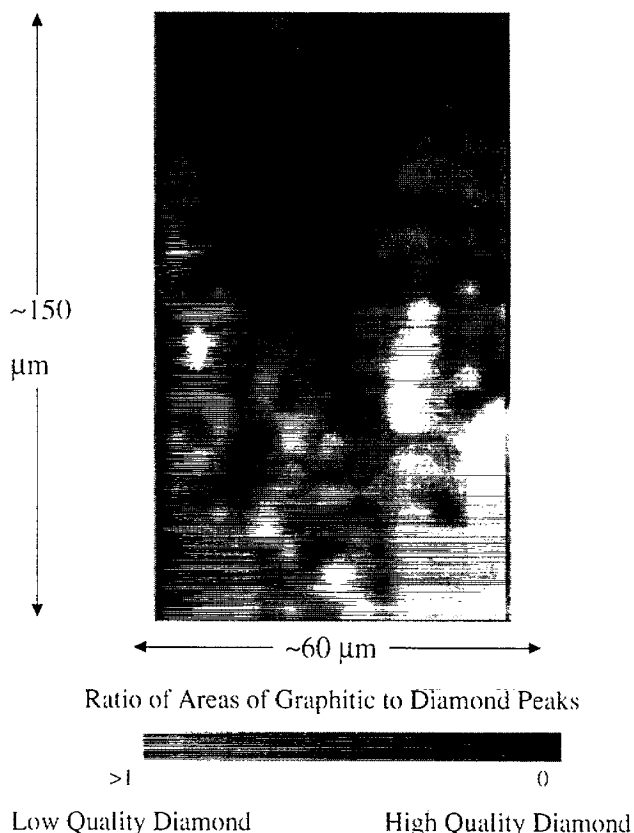


Fig. 4. Mapping of the ratio of 1332 cm⁻¹ diamond and graphitic G band Raman signals along a 110 direction across the center of the square facet and over depth (the z-axis has been stretched to account for the effect of the refractive index of diamond). The angle between the boundary of the defect free and defective areas and the vertical corresponds to the angle expected of a <111> plane boundary between (001) and (111) growth sectors.

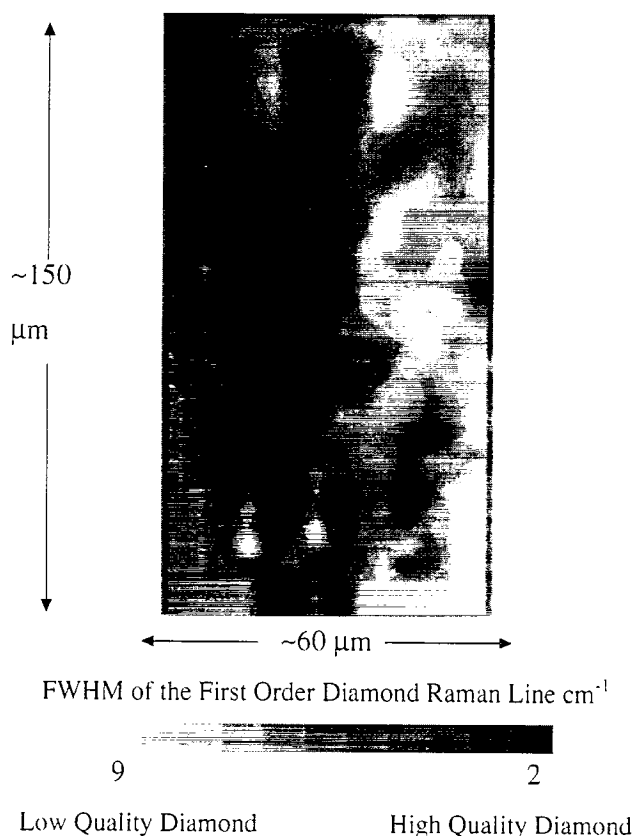


Fig. 5. Mapping of the same area as illustrated in Fig. 4 but with the intensity scale measuring the full width at half maximum of the first order diamond Raman line at approximately 1332 wavenumbers.

the growth sector is non-homogeneous. Most importantly, the best quality crystal, illustrated by the darkest shading, lies towards the apex of the pyramidal sector.

Certain luminescence features are associated with defects in diamond [12,13], principally a broad blue band [14] that is visible in diamonds with certain defect concentrations in both CL and PL. A map of the intensity of the blue band luminescence from facet A with a 325-nm HeCd UV laser focused on to the surface of the facet is shown in Fig. 6. The intensity of the luminescence and therefore the concentration of the defects can be seen to be highest in a characteristic cross shape at the center of the facet. The defects may be concentrated here due to strains in the film causing a tensile stress at the surface of the crystal, or they may be due to incorporation of impurities during growth. A map constructed from the width of the diamond line across the facet can be seen in Fig. 7 and a good correlation to the position of the blue cross can be observed.

4. Conclusions

Comparison of features in the Raman spectrum of diamond films has been shown to give qualitative infor-

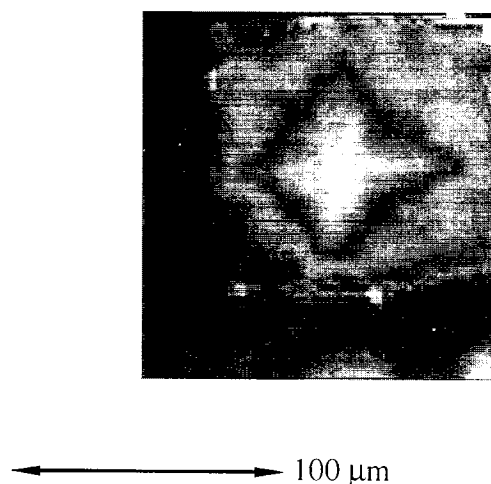


Fig. 6. Intensity of the Broad band blue luminescence mapped with a Raman spectrometer using a 325-nm HeCd laser focused at the surface of the crystallite to excite the luminescence.

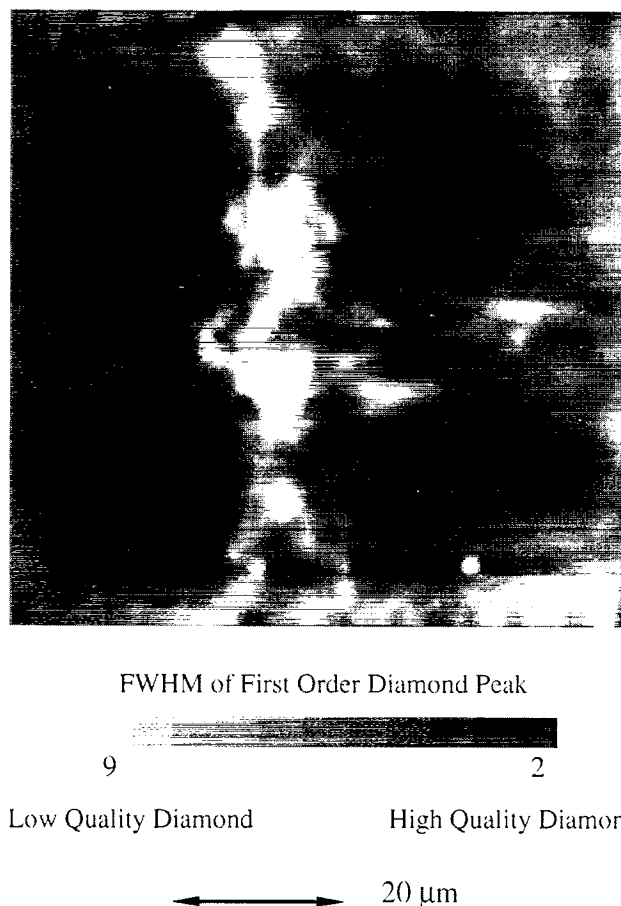


Fig. 7. Mapping of the FWHM of the first order diamond line obtained at the surface of facet A. Increase in intensity at the edges of the map is due to an inclusion in the interaction volume of parts of the (111) growth sectors.

mation about the relative amount of non-diamond inclusions or defect density within the crystallites. It has been shown that confocal micro-Raman when used with

appropriate mapping stages can give information on the quality of the film at a microscopic level. It is further shown that this technique can be sensitive both to large changes in defect concentration such as between (001) and (111) growth sectors as well as to more subtle changes in concentration such as those associated with the blue cross. It is observed that the best quality diamond within the crystallites may not lie at the surface. The techniques illustrated here could give qualitative differences between films in a fast, cheap and non-destructive manner and could be used efficiently as a quality control.

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