Optical Spectroscopy Techniques for the NDT of Hard Materials

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Abstract
Raman and photoluminescence (PL) spectroscopy techniques are both optical means of determining residual stresses, crystallinity and defect characteristics in a wide range of materials. Here these techniques are applied to single crystals of diamond and cubic boron nitride (cBN), as well as polycrystalline diamond (PCD) tools. In single crystal diamond, plastic deformation associated with the rosette pattern of an impression created at high temperature was studied. Raman spectroscopy was used to map the residual stresses and degree of plastic deformation in a 3D volume associated with the impression, while PL spectroscopy was used to map the distribution of the nitrogen-vacancy defect centres that were generated during the impression process. The “arms” of the pattern are in compression (~1.5 GPa) while the centre of the impression is in tension (~1 GPa). Similar surface Raman mapping of an indentation in a cBN crystal yielded the stress and deformation profiles for that material. Raman spectroscopy was also applied to the PCD layer of a PCD/Co-WC drilling toolbit. Results are presented showing that thermal annealing at 800 °C for 30 minutes negatively affects the toolbit properties, and that the stress distribution between the top of the PCD table and the PCD-WC interface can be readily determined.

Keywords: Raman spectroscopy, photoluminescence spectroscopy, hard materials, diamond, cubic boron nitride, polycrystalline diamond toolbits

1. Introduction

Optical spectroscopy techniques are attractive as methods for non-destructive testing of materials for various reasons. One of the leading motivations is that these techniques are contact-less probes, i.e. it is relatively easy to make measurements at non-ambient conditions such as high temperature and high pressure. Light beams can also readily be focused to micron-sized spots for analysis of specific morphological features in a sample. Several of these techniques are also capable of rapid data acquisition and analysis. In this paper the techniques of Raman spectroscopy and photoluminescence (PL) spectroscopy are highlighted.

Raman and PL spectroscopy have had wide application in the non-destructive testing of a broad range of materials, including semiconductor materials such as Si [1-3] and GaAs [4], as well as a range of films and composites [5-10]. The paper by Colomban [5] is a very useful review of the use of Raman spectroscopy to analyse strain and stress in fibre-reinforced ceramics and metal-matrix composites. In terms of hard materials, Raman spectroscopy has been used to map residual stresses in β-Si3N4 [11] and both Raman and PL spectroscopy have been used to characterize micro-stresses and defects in various polymorphs of SiC [12,13].

Of particular relevance to this paper is the application of Raman and PL spectroscopy to ultra-hard materials, where research conducted in our group on the NDT of single crystal diamond [14], single crystal cubic boron nitride (cBN) [15] and polycrystalline diamond (PCD) toolbits [16] as well as other results are used to illustrate the capabilities and advantages of these techniques.
2. Theoretical background

In this section, a brief theoretical background for Raman and PL spectroscopy is given in order to highlight the information relevant to NDT that can be gleaned from these techniques.

2.1 Raman spectroscopy

In Raman scattering, the sample under study is illuminated with a laser beam with photons at a specific frequency. A small proportion of these photons interact with the optic modes of lattice phonons in the sample material and are scattered inelastically. These scattered photons have a frequency shifted from the incident photons by the frequency of the mode which is characteristic of the sample material. Diamond has a single, triply degenerate Raman peak at 1332.5 cm\(^{-1}\) [17] (units are in wavenumbers relative to the incident laser beam wavenumber), while cBN has a transverse optical (TO) Raman line at 1054\(\pm0.6\) cm\(^{-1}\) and a longitudinal optical (LO) Raman line at 1305\(\pm1\) cm\(^{-1}\). The frequency and linewidth of the Raman peak thus convey information on the nature and structure of the material under study.

In an ideal crystal, the sample would be stress free and the Raman peak would be measured at its theoretical position. As soon as the crystal is subjected to stresses, be it externally imposed or due to internal imperfections, the frequency of the lattice phonons is subtly affected and thus also the frequency of the Raman peak. In this way, careful measurements of the shift of the Raman peak relative to its unstressed frequency can yield information on the stresses present in the sample. Compressive stress results in a shift of the peak to higher frequencies, and tensile stress to lower frequencies. In order to convert a degree of shift to a stress quantity, use is made of the coefficient of stress-induced shift as follows:

\[
\nu_r - \nu_s = \alpha \sigma
\]

where \(\nu_r\) is the position of the stress-free Raman line, \(\nu_s\) is the measured frequency of the Raman line, \(\sigma\) is the stress at the point in question (in GPa) and \(\alpha\) is the coefficient of stress-induced frequency shift. For diamond the value of \(\alpha\) used was 1.9 cm\(^{-1}\)/GPa [18,19] and for cBN the value of \(\alpha\) used was \(\alpha_{TO} = 3.39\) cm\(^{-1}\)/GPa and \(\alpha_{LO} = 3.45\) cm\(^{-1}\)/GPa. As the exact frequency of the diamond Raman peak is important in determining the nature and magnitude of stresses measured, the spectrograph was very carefully calibrated before each set of acquisitions. For this work, the 546.074 nm line of a Hg discharge lamp was used as the calibration standard. As a reference for the frequency of the diamond Raman peak in an unstressed sample, measurements were conducted on a type IIa diamond used as a standard.

The Raman linewidth broadening for the materials under consideration here is mainly attributable to homogeneous (lifetime) broadening. In this case the Full Width at Half Maximum (FWHM) of the diamond Raman peak is inversely proportional to the phonon lifetime. Since the phonon lifetime is shortened by scatter at grain boundaries and defect sites, the FWHM can be used as a convenient ranking indicator of the degree of “crystal disorder” and hence as an indicator of the degree of plastic deformation.

2.2 Photoluminescence spectroscopy

In the case of diamond specifically, the PL emission that is of interest is not associated with electronic transitions related to the bandgap, but is rather associated with transitions between
the ground and excited states of specific defects in the diamond lattice. Of particular interest is the so-called zero phonon line (ZPL), which is the transition of an electron from an excited state to the ground state of the defect without the participation of any lattice phonons [20]. The energy of this transition is very sensitive to local strain and is thus a complimentary source of information regarding stress and deformation in the crystal lattice. In addition the intensity of this transition is related to the concentration of the defect present.

The specific defect of interest in the diamond lattice is the so-called [N-V]- defect, or 1.945 eV defect. This defect is the negative charge state of a pair that is formed by a vacancy and a substitutional nitrogen atom on adjacent lattice sites. A review of the properties of this defect centre is given by Manson et al. [21]. Measurement of the intensity, position and width of the ZPL gives information on defect concentration, stress and local strain.

3. Experimental details

Sample information and details of the experimental methods and conditions for the different examples of ultra-hard materials are given separately in the sections below.

3.1 Single crystal diamond

For the purposes of the present paper, an impression is defined as a plastic deformation made in diamond at high temperature where no brittle fracture has occurred, while an indentation is considered to be a deformation where brittle fracture has taken place. Impressions were made using a Si₃N₄ impresser on a {001} face of a synthetic High Pressure High Temperature (HPHT) type Ib diamond with a mean contact pressure of 3.1 GPa within a vacuum furnace held at a temperature of 1400 °C. Nitrogen is present in the diamond as a substitutional impurity at the 500ppm level. The diamond slip system is: {111}<110>; applied stress is thus resolved onto {111} planes in <110> directions [22].

Raman spectra were acquired at ambient pressure and temperature using the micro-Raman attachment of a Jobin-Yvon T64000 Raman spectrometer operated in single spectrograph mode. The excitation source was the 514.5nm line of an argon ion laser, and the backscattered light was dispersed onto the liquid nitrogen-cooled CCD detector by an 1800 grooves/mm grating. The confocal pinhole was selected to give a specific Z-depth sampling thickness (exact details are given in the results section). A computer-controlled motorized X-Y stage in conjunction with manual Z-movement was used to map the spectral features within the three-dimensional volume of the impression. The position and width of the diamond Raman peak was extracted by fitting a Lorenztian function to the data using ORIGIN software.

The PL spectra were acquired at 77 K using an Oxford Instrument MicrostatHe microscope cryostat mounted on the microscope stage of the Jobin-Yvon T6400 spectrometer. The 514.5nm line of an argon ion laser was used for the PL studies reported here, with a 600 lines/mm grating to disperse the light. The ZPL peak was fitted to a Voigt lineshape and the intensity of the ZPL at each point was normalized by the area under the Raman peak acquired under the same measurement conditions [23].

3.2 Single crystal cubic boron nitride

The cubic boron nitride samples studied were in the form of small, faceted single crystals. The single crystals varied in size from ~360 µm diameter to ~1 mm diameter and in colour from dark yellow to black. Raman spectra were acquired with a Jobin-Yvon T64000 Raman spectrometer, operated in single spectrograph mode with an 1800 grooves/mm grating and a
The 488.0 nm line of an argon ion laser was used as the excitation frequency. Spectra were acquired with a confocal micro-Raman attachment, where the laser beam was focused down to a 10 \( \mu \text{m} \) diameter spot. A motorised X-Y microscope stage was used to obtain high resolution maps at specific frequencies of the samples under study. Indents were made with polycrystalline diamond conical indentors, of which the tip was ground to a fine point and then very lightly sanded down to a flat of the order of a hundred microns diameter. The indentations were made by lowering the tip at a fixed rate into the sample and then releasing the load when a predetermined value was reached. As the exact position of the TO Raman peak is of importance in determining the nature and magnitude of stressed measured, the spectrograph was carefully calibrated before each set of acquisitions on the 1056.94 cm\(^{-1}\) laser plasma line. During acquisition, this plasma line was removed by means of an interference filter in order to prevent it distorting the position and shape of the cBN TO Raman peak.

### 3.3 Polycrystalline diamond (PCD) tools

The samples used in this work were commercial cylindrical drill-bits manufactured by Element Six (Pty) Ltd, of dimensions approximately 17 mm in length and 19 mm in diameter, consisting of a Co-WC substrate with a PCD layer sintered onto the circular face of the substrate. The diamond used was HPHT-synthesized synthetic grit (type Ib) with nitrogen as substitutional impurity present in excess of 500ppm. Synthesis conditions for PCD generally involve applied pressures of 5 to 10 GPa, sintering temperatures of 1300 \( ^\circ \text{C} \) to 1800 \( ^\circ \text{C} \) and sintering times of 5 to 60 minutes. The average grain size was 10 \( \mu \text{m} \). During the synthesis process, liquid phase sintering facilitated by molten Co takes place, resulting in an extended diamond structure with considerable direct diamond to diamond bonding and cobalt at the grain boundaries (see e.g. [23] and [24]). The PCD layer was 0.6 to 1 mm thick, depending on the processing. Room temperature Raman spectra were acquired with a Jobin-Yvon T64000 Raman spectrometer operated in single spectrograph mode with an 1800 grooves/mm grating and a CCD detector. The 514.5 nm line of an argon ion laser was used as the excitation wavelength. For the data reported here, samples were measured in the macro chamber of the spectrometer, where the diameter of the spot size was ~ 300 \( \mu \text{m} \). The PCD layer was nearly opaque, thus limiting the penetration depth of the laser to several tens of microns.

High temperature measurements were made in situ with a custom-built furnace, fitted into the macro chamber of the spectrometer. The furnace was mounted on an X-Y-Z adjustable stage with micrometer adjustments. Prior to heating the furnace was evacuated to a high vacuum, and backfilled with low pressure argon gas to promote a uniform temperature of the sample. High temperature measurements were only performed on the samples with roughly lapped surfaces, as their spectra had the best signal-to-noise ratios. A single line of measurement points spaced at 2000 \( \mu \text{m} \) intervals was used and the data averaged to give an average surface stress value for the PCD layer. The diamond Raman peak position was determined by fitting a Voigt function to the corresponding data.

### 4. Results

The results of the optical spectroscopy characterization of the different samples are given in the sub-sections below.
4.1 Single crystal diamond

The results are presented in two parts: the first covers Raman results for sections through the impression and the second contains PL results for surface mapping of the impression.

4.1.1 3D Raman mapping

Figure 1. Optical micrograph of an impression on a single crystal synthetic diamond.

Figure 1 is a typical optical micrograph of an impression on single crystal synthetic diamond. The circular dark centre corresponds to the area of contact of the impressor, and the cross-shaped pattern visible around its extremities is the so-called rosette [22]. The fine horizontal and vertical lines are dislocations which have run out on the surface during the impression process, and have been etched to make them visible. It can be seen by referring to the indicators of crystallographic orientation at the top of figure 1 that the rosette shape is determined by the crystallographic plane used for the indentation and the slip system of diamond.

3D sections were obtained by selecting (100) and (110) crystallographic planes within the diamond and focussing the laser beam at appropriately chosen depths from the diamond surface along these planes to create effectively vertical “slices” within the bulk sample. Changes in the Raman peak position and peak width were mapped along these sections. The centre of the impression is at the origin of the arrow “a” in figures 2 and 3. This arrow represents the radius of the circular impression on the surface of the diamond. Each map is thus of dimension 2a on a side. The mapping grid size is 23×23 points, with 10 µm intervals. A 50× ultra-long working distance objective was used with a 0.1 mm pinhole, resulting in the laser beam focal barrel being 10 µm and corresponding to the thickness of the diamond being sampled in the Z-direction for a particular focal position of the microscope.

Compressive stress is indicated by negative stress values and its color range (green) (minimum) to blue (maximum)), while tensile stress is indicated by positive stress values and its color range (yellow minimum) to red (maximum)). The degree of deformation is depicted by a range for colors: the blue color corresponds to a “background” value for the FWHM of 2.00 to 2.88 cm⁻¹ and the maximum peak width (red) corresponds to a peak width of 8.13 to 9.00 cm⁻¹.

The stress and degree of deformation maps for the (100) slice are shown in figures 2(a) and (b) respectively and are located between two arms of the rosette pattern associated with the impression. For the (100) slice, the largest compressive stress values and the greatest degree of plastic deformation are associated with the volume of diamond immediately below
the contact area of the impressor. The greatest magnitude of tensile stress is also located immediately below the contact area of the impressor, but at a depth of approximately 50 µm.

The maps for the (110) slice shown in figures 3(a) and (b) clearly illustrate the presence of the arm of the rosette in the [110] direction by the presence of an extended region of compressive stress. As shown in figure 3 (a) the maximum compressive stress in the arm (-1490 MPa) is associated with a volume located approximately 50 µm below the surface of the diamond. The volume associated with the greatest magnitude of tensile stress is located immediately below the contact area of the impressor, also at a depth of approximately 50 µm. The degree of deformation mapped in figure 3(b) from the data on the FWHM of the Raman peak clearly shows that the maximum deformation is associated with the volume immediately below the contact area of the impressor.

Figure 2 (a). Stress contour map of slice mapped into the diamond along the [100] direction. The centre of the impression is at top left and the radius of the impression is “a = 110 µm”. The values in MPa of the respective stresses are given in the accompanying table. Negative values indicate compressive stress and positive values indicate tensile stress.

Figure 2 (b). Contour map of the FWHM of the diamond Raman peak within the slice mapped into the diamond along the [100] direction. The values in cm⁻¹ of the FWHM in each region are presented in the accompanying table.

Figure 3 (a). Stress contour map of slice mapped into the diamond along the [110] direction. The centre of the impression is at top left and the radius of the impression is “a = 110 µm”. The values in MPa of the respective stresses are given in the accompanying table. Negative values indicate compressive stress and positive values indicate tensile stress.

Figure 3 (b). Contour map of the FWHM of the diamond Raman peak within the slice mapped into the diamond along the [110] direction. The values in cm⁻¹ of the FWHM in each region are presented in the accompanying table.
The respective magnitudes of the tensile stress measured for the (100) slice (maximum of 990 MPa) and the (110) slice (maximum of 830 MPa) slices agree well, and the respective degrees of deformation are also in good agreement (maximum widths of 8.2 cm$^{-1}$ and 9.0 cm$^{-1}$ for (100) and (110) slices).

It is also noted that whereas the degree of plastic deformation as indicated by the linewidth extends approximately 75 µm from the surface of the diamond, the tensile stress field extends to approximately 150 µm from the surface. It follows that the extent of the plastic deformation is less than that of the tensile stress field.

4.1.2 2D PL maps

![Figure 4. Normalized intensity map of ZPL of the 1.945eV defect [N-V]$^-$.](image)

![Figure 5. Map of the position of the ZPL of the 1.945 eV defect.](image)

The intensity of the ZPL associated with the [N-V]$^-$ centre at 1.945eV normalized relative to the area of the diamond Raman peak as described in the Experimental details section is given in figure 4. Note that the intensity is plotted on a logarithmic scale to emphasize the very strong growth of the intensity of the defect over the background level. The black area represents a surface area where the ZPL was not detected. This figure illustrates the very clear association of the negative charge state of the [N-V] defect with the impression in the diamond. The impression under discussion was made at 1400 °C, which is substantially above the temperature (~600 °C) where the vacancy in diamond becomes mobile. Non-conservative slip of dislocations during the impression process generates vacancies, which are then free to diffuse and bind with substitutional nitrogen, which is the dominant form of nitrogen in synthetic type Ib diamond. This gives rise to the [N-V]$^-$ defects observed here. The intensity gradient highlights the fact that most of the vacancy generation takes place in the immediate vicinity of the impression.

Figure 5 maps the position of the ZPL of the 1.945eV defect across the impression. There are clearly two lobes (left and right of the impression in the figure) as well as a much weaker two-lobe pattern at right angles to the strong pair. In relation to figure 5, the electric field of the incoming laser beam is linearly polarized in the [110] direction (i.e. parallel to the x-axis), this being the stress axis associated with the two left-right lobes. These ZPL intensity lobes will thus be greater intensity than the pair at right angles, the difference being the direct result of the polarization of the exciting light.

Davies and Hamer [25] investigated the effect of strain on the optical properties of the 1.945eV defect. Shifting and splitting of the ZPL was reported for various uniaxial stress configurations, chiefly for absorption rather than luminescence of the defect. Comparison
with the calculations for splitting under uniaxial stress in the case of PL [26] shows that although the intensity ratios of the components differ between absorption and luminescence, the rate of shift of the ZPL components for the case of [110] stress and electric field parallel to this stress (as in figure 5) is the same for absorption and luminescence. It is thus possible to use the data of Davies and Hamer to calculate the stress in the two left-right lobes in figure 5. For the two left-right lobes mentioned, the ZPL peak position is shifted downwards by \( \sim 20 \text{ cm}^{-1} \), which converts to an energy difference of \( \sim 2 \text{ meV} \). According to Davies and Hamer this shift is due to a stress of just greater than 200 MPa. This value is in good agreement with that measured via Raman spectroscopy.

### 4.2 Single crystal cBN

The indentations on the single crystals were technically difficult, since the samples were very small and the indentation could not always be centred on the sample as desired. Raman spectra were acquired as described in the previous section and the TO peak was fitted to a Lorentz line shape, which yielded the position and FWHM of the peak. The Lorentz line shape was a good fit to the experimental data, with no asymmetry visible in the peak. This indicates that the dominant broadening mechanism at work is that of phonon lifetime broadening. The TO peak was used in preference to the LO peak, since the latter was frequently less intense and for some samples there was a broad feature present to the lower frequency side of the peak, which complicated background subtraction and introduced uncertainty in the width measurement of the peak. Figure 6 is a micrograph of an indent made in a black cBN crystal at a maximum load of 30N. The circular indent is clearly visible with cracking around its circumference and 2 cracks radiating away from the indent. The leftmost crack runs to the edge of the crystal.

![Figure 6. Micrograph of an indent in a cBN crystal, made at 30N maximum load.](image)

The Raman spectrum of 49 points across the indent was obtained in the shape of a \( 7 \times 7 \) matrix, with a 25 \( \mu \text{m} \) step size between the points and the grid centred on the indent. A 10 \( \mu \text{m} \) diameter laser spot size was used. The position of the TO Raman peak and the FWHM of the same peak across the indent are plotted as contour maps in figures 7 and 8, respectively. It can be seen from figure 7 that there are clear contour lines indicating the presence of the indent. The peak position is shifted to higher frequencies in the vicinity of the centre of the indent, as well as in the region of the crack feature at the top of figure 6. At these positions the stresses are compressive and approximately 0.3 GPa in magnitude. Away from the centre of the indent, the peak has been shifted less, but still to higher frequencies, indicating compressive stresses are present. The lowest value stress is 0.07 GPa. This contour map very clearly illustrates the effect of the indent on the cBN crystal surface. In figure 8, the crack feature at
the top of figure 6 is again clearly visible as the region with the biggest FWHM (8.3 cm\(^{-1}\) to 8.7 cm\(^{-1}\)). The FWHM decreases towards the centre of the contour map, where a clear suggestion of the presence of the indent is visible. The FWHM at the centre varies around 5.5 cm\(^{-1}\). This is somewhat unexpected, as deformation of the cBN would likely lead to an increase in FWHM. This result is not yet understood.

Figure 7. Contour plot of the stress derived from the TO Raman peak position across the indent in figure 6. The greatest degree of shift of the peak to higher frequencies is indicated by red (~0.25 GPa compressive), with smaller shifts progressing through orange, yellow and green to blue, which indicates the smallest shift (~0.02 GPa compressive). The biggest shift in peak position is visible in the centre of the plot and towards the top. The units in the table at top right are GPa.

Figure 8. Contour map of FWHM of the TO Raman line across the indent in figure 6. Red indicates the largest FWHM values (8.3 to 8.7 cm\(^{-1}\)) and blue the smallest (~5.5 cm\(^{-1}\)), with orange, yellow and green indicating intermediate values in order of decreasing magnitude. The units in the table at top right are cm\(^{-1}\).

4.3 PCD tools

4.3.1 Effect of annealing on PCD properties

In order to investigate the effect that repeated cycling to a specific temperature would have on the tool-bit properties, several points (n = 10 to 11) were measured across the surface of the PCD layer or table (figure 11), using the X-Y-Z micrometer-driven mounting stage of the furnace to move the sample. The surface stress state was measured at room temperature (21 \(^{\circ}\)C) prior to annealing and after each annealing cycle for 5 cycles. During each heating cycle, the sample was heated at 15 \(^{\circ}\)C/min to the set temperature, held at the set temperature for 30 minutes, and then cooled at 15 \(^{\circ}\)C/min back to room temperature. In practice the furnace cooled at the set rate to ~200 \(^{\circ}\)C, below which the cooling rate decreased substantially. This did not affect the results, as the temperatures where changes were expected to happen, were substantially above this temperature.

Results for 5 annealing cycles to 600 \(^{\circ}\)C in an argon atmosphere are plotted in figure 9. It is clear that the surface compressive stress as measured at room temperature remains unchanged at approximately 0.9 GPa under these temperature and annealing conditions, indicating that the tool retains its properties. The data for the FWHM of the diamond Raman peak follows a similar trend, i.e. the FWHM remains unchanged at around 12.5 cm\(^{-1}\) with cycling to 600 \(^{\circ}\)C (figure 10).

Results for 5 annealing cycles to 800 \(^{\circ}\)C in vacuum of a different tool-bit from the same manufacturing batch are also plotted in figure 9. Here it is clear that the annealing temperature and cycling is affecting the surface compressive stress, with the magnitude of the stress decreasing from 0.9 GPa to considerably lower values with increasing cycling. The tool-bit properties are thus being modified permanently. The FWHM in this case remains unchanged at around 12.2 cm\(^{-1}\) with cycling (figure 10). Although substantially larger than
the FWHM for single crystal diamond, these values are consistent with those reported by other authors [18] for polycrystalline diamond. The large width is ascribed to both the micro-defects that form due to fracture during the pressure ramp of the synthesis cycle, as well as the plastic deformation that takes place during sintering.

![Figure 9. Surface stress state for the PCD layer of a tool-bit as measured at room temperature after each of 5 cycles to 600 °C and 5 cycles to 800 °C. The solid lines are linear fits to the data to illustrate the trends. The data in the figure represent the average stress value across the surface, and the error bars represent one standard deviation in the data.](image)

![Figure 10. FWHM of the PCD layer of a tool-bit as measured at room temperature after each of 5 cycles to 600 °C and 5 cycles to 800 °C. The data in the figure represent the average width value across the surface, and the error bars represent one standard deviation in the data.](image)

As mentioned earlier, a surface compressive stress state in the PCD layer is desirable, as it would act to prevent the formation and slow the propagation of cracks in application, thus effectively acting as a toughening mechanism. It is clear from our results that the higher annealing temperature thus has a negative effect on the tool-bit properties.

4.3.2 Stress gradients in the PCD layer
In order to investigate the possible stress gradients that are present in the PCD table, Raman spectroscopy was used to measure a series of points between the edge of the PCD table and the PCD – Co/WC interface.

![Figure 11. Diagram of the PCD toolbits, showing the measurements on the PCD with X1 near the edge and X6 as the point near the interface region.](image)
The toolbits were measured in the macro chamber of the spectrograph in a backscattering configuration with a laser beam diameter of ~100 µm. Data points were measured from a point 300 µm from the top edge of the PCD table (point X1) at 500 µm intervals to the PCD/WC interface (point X6), as illustrated in figure 11. The surface stress state was measured at room temperature (23 °C) in all cases. Subsequent annealing of the toolbits took place at 800 °C for 30 minutes in a Carbolite tube furnace under UHP argon. Peak positions were extracted from the data by fitting a linear combination of Lorentzian and Gaussian line shapes. The data in the figures below have been averaged around the circumference of the toolbit to show the variation of stress between the edge of the PCD table and PCD/WC interface.

![Figure 12. Effect of temperature on the PCD stress for sample A before and after annealing to 800 °C for 30 minutes.](image)

The stress distribution between the edge of the PCD table and PCD/WC interface shows a trend, with a smaller compressive stress at the edge and a larger compressive stress near the interface. Measurements carried out after the high temperature anneal (800 °C for 30 minutes) show a significant reduction of stresses in the toolbit. The residual stresses are now largely tensile in the top section of the PCD layer (i.e. nearest the operating face) and are still compressive near the PCD/WC interface. The stress distribution observed prior to annealing has been amplified by the annealing process.

5. Discussion

5.1 Single crystal diamond

The most suitable model at present for indentation hardness is that suggested by Roberts [27] who modelled the whole of the slip pattern over an area of $2a \times 2a$, where $a$ is the contact area radius. This includes the areas directly beneath and adjacent to the contact point. Roberts used extended stress fields produced by a circular contact in an elastically isotropic material to predict the likely slip patterns and their associated stresses. This allowed complete 3D patterns of the relevant slip planes to be visualized together with the resolved shear stresses on them.
To model the magnitude of the resolved shear stresses which control plastic deformation in the bulk of a crystal, the crystallographic plane of the indented surface and the active slip systems must be identified. For this discussion, a (001) surface and \{111\}<110> slip systems are considered, the nomenclature indicating that the applied stress resulting in slip is resolved onto \{111\} planes in the <110> directions. Figures 13(a) and (b) [22, 28] are maps showing the highest resolved shear stresses and the slip systems which are associated with those stresses on a (100) plane and a (110) plane, respectively, where both of these planes represent sections which pass through the centre of a circular contact area and are normal to the indented surface. For each of the (100) and (110) sections, the 12 possible slip systems in diamond cubic crystals are identified and numbered on the respective slip plane pyramids shown in figures 13(a) and (b). In each of these pyramids, the respective apices “C” are assumed to be below the indented (001) plane. A further convention used here is that a bar over the slip system number indicates that material under that slip plane is sheared downwards while a number without the bar corresponds to material above the slip plane being sheared downwards; in other words, negative and positive slip, respectively. The actual slip systems subjected to the highest resolved shear stress in various regions beneath the contact area are shown in rectangular boxes between the solid lines, e.g. the numbers 9, 12 in a box indicate that slip systems 9 and 12 are operative. The dashed lines indicate contours of constant resolved shear stress (RSS), and the number next to each contour indicates the percentage of \( P_m \) that is experienced along the contour, where \( P_m \) is the stress applied by the impressor over a circular contact area of radius \( a \).

For figure 13(a), i.e. on the (100) section or “slice”, the RSS values immediately below the surface are relatively low. The maximum shear stress is about 0.316 \( P_m \) where this lies in a region where slip systems 9 and 12 are those most likely to be activated. This region is \(~0.58a\) beneath the centre and \(~0.54a\) from the centre line of the impression. For figure 13(b), i.e. on the (110) section or “slice”, the maximum shear stress is 0.30 \( P_m \) and this region is \(~0.52a\)
beneath the centre of the impression and \( -0.5a \) from the centre line of the impression. Thus the zone of maximum resolved shear stress is roughly toroidal in shape (doughnut-shaped).

In figures 13 (a) and (b), the volume of maximum tensile stress corresponds fairly closely with the volume of diamond that would experience the maximum resolved shear stress during the impression process (broken line contours of 30\% of the mean applied pressure \( P_m \)). The volume of maximum tensile stress for the (100) slice also appears to be slightly larger than that for the (110) slice, which corresponds to the 30\% contour being larger for the (100) slice. The maps in figures 2(a) and 3(a) thus show a close correspondence with the resolved shear stress contours in figures 13(a) and (b), respectively.

From the description given above the process resulting in the measured contours can be visualized. The first dislocation nucleation takes place in the volume of maximum resolved shear stress (30\% broken line contour). As the impression process continues, dislocations multiply and move to fill the volume under impressor contact area. Material is thus “moving away” from the volume where the dislocations movement originates. At the end of the deformation process, this volume is thus “deficient” in material with the result that it is in tension. Although it would be expected that some relaxation of shear stress were to take place due to plastic deformation, the results show that most of the shear stress is “locked in” on cooling. A 0.316 fraction (maximum shear stress is 0.316\( P_m \), figure 13(a)) of 3.07 GPa = 970 MPa, close to the measured maximum stress of 990 MPa for the (100) “slice” in the vicinity of the 30\% contour. A 0.3 fraction (30\% contour toroid in figure 13) of 3.07 GPa = 920 MPa, comparable with the measured maximum for the (110) “slice” in an equivalent position of 830 MPa. The calculated resolved shear stress contours for the (100) “slice” encompass a larger volume than those for the (110) “slice” and this is reflected to a certain degree in the measured contours as well. A more detailed discussion can be found in [14].

### 5.2 Single crystal cBN

The Raman mapping of the indentation in cBN is less clear than the results obtained for diamond, largely due to the fact that the diamond impression was done at high temperature where only plastic deformation occurred. Nevertheless there is clear evidence of the association of several observed surface features of the cBN indentation with contours in the Raman maps, thus indicating that Raman stress and deformation mapping is equally applicable to cBN.

### 5.3 PCD results

Several possible mechanisms exist that can account for the observed trends in surface stress state with annealing temperature. The temperatures for cyclic annealing were chosen to assist in discriminating between mechanisms. Cobalt undergoes a phase transition from hcp to fcc around 420 °C. It is thus anticipated that annealing at 600 °C would indicate any effect that this process has on the surface stress state. The data shows that the surface stress state remains essentially unchanged during annealing to 600 °C, showing that the cobalt phase transition does not affect the surface stress state. Cobalt-catalysed graphitization of diamond has an onset temperature of around 750 °C at ambient pressure, and thus annealing to 800 °C would show if this mechanism affects the surface stress state. Our data suggests strongly that this mechanism is mainly responsible for the change in surface stress state. It is noted that PCD heated to 1000 °C shows clear evidence of graphitic carbon in the Raman spectra measured on the surface of the PCD.

The results for the FWHM data indicate that no annealing of the diamond material in the PCD layer is taking place, as the FWHM is unchanged with repeated cycling for both
temperatures. This suggests that the stress relieving mechanism is not due to a change in the diamond grains, e.g. possible dislocation movement, but due to changes in the diamond-matrix boundaries. This supports the role of a mechanism such as the cobalt-catalyzed graphitization mentioned in the previous paragraph.

The constituent diamond for the PCD layer in the above tool-bits is Type Ib. It has been shown that the Brittle-Ductile Transition Temperature (BDTT) for single crystal Type Ib diamond is 750 °C [28] suggesting that this might influence the peak width data in figure 10. Due to limited thermal stability of diamond-cobalt materials around 800 °C flow stress data for these materials are inconclusive, but flow stress studies on diamond/β-SiC aggregates have shown that in the range of 800 °C to 1250 °C time dependent plastic deformation does not occur [29]. This indicates that for polycrystalline diamond materials the BDTT is at a higher value than for single crystal diamond. The absence of a change in the Raman peak width data with repeated cycling thus suggests that the BDTT has not been reached yet for the tool-bits considered in this study. Processes in the cobalt matrix and/or graphitization of the diamond are thus the most likely mechanisms to account for the observed reduction in compressive stress.

At room temperature, the overall stress is compressive around the circumference of the toolbit (figures 11 and 12) and is largest at the PCD/WC interface region and lower at the edge confirming the predictions of Finite Element modelling. Compressive stress in the PCD layer is desirable as it opposes the formation and propagation of cracks.

There was a significant change in the PCD stress magnitude after annealing. This implies a negative effect of annealing at 800 °C on the toolbit properties, as crack initiation and propagation is more likely in the presence of reduced compressive stress or any tensile stress. This is a significant observation in determining maximum temperature conditions under which the toolbit may be operated. 2-D Raman mapping of the top of the PCD table after annealing revealed no sign of graphitisation of the PCD. Only after a further anneal at 900 °C was any evidence of graphite noted in the region of the interface.

6. Conclusions

The results presented here in conjunction with the discussions illustrate clearly of what benefit the optical spectroscopy techniques of Raman spectroscopy and PL spectroscopy is to the NDT of hard materials. Raman spectroscopy has the ability to clearly map stress and deformation distributions in materials, as illustrated for single crystal diamond and cBN, as well as PCD. PL spectroscopy plays a supportive role with particular benefit in visualizing the movement and distribution of defects associated with deformation.

Acknowledgements

Financial support from the National Research Foundation of South Africa under Grant No 2053306, the DST/NRF Centre of Excellence in Strong Materials hosted by the University of the Witwatersrand and the University of the Witwatersrand, Johannesburg, is gratefully acknowledged.

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