

UM-P-94/45

**POLARIZED RAMAN SPECTROSCOPY OF CHEMICALLY
VAPOUR DEPOSITED DIAMOND FILMS**

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ABSTRACT

Polarized micro-Raman spectra of Chemically Vapour Deposited Diamond Films are presented. It is shown that important parameters often extracted from the Raman spectra such as the ratio of the diamond to non-diamond component of the films and the estimation of the level of residual stress depend on the orientation of the diamond crystallites with respect to the polarization of the incident laser beam. The dependence originates from the fact that the Raman scattering from the non-diamond components in the films is almost completely depolarized whilst the scattering from the diamond components is strongly polarized. The results demonstrate the importance of taking polarization into account when attempting to use Raman spectroscopy in even a semi-quantitative fashion for the assessment of the purity, perfection and stress in CVD diamond films.

Raman spectroscopy is widely used as a diagnostic tool for the evaluation of the phase purity and perfection of diamond films grown by chemical vapour deposition (CVD) and other techniques [1]. Natural diamond displays a first order Raman line at 1332 cm^{-1} , with a symmetric line-shape. Many non-diamond components are often observed in the Raman spectrum of CVD films, one of the most common being a broad peak at $1500\text{-}1550\text{ cm}^{-1}$ which corresponds to a form of amorphous carbon. The ratio of the intensity of first order diamond line to this broad amorphous background is often used as a semiquantitative measure of the purity of a diamond film [2]. The observation of a 1332 cm^{-1} diamond line on a flat background is taken to be strong evidence for the production of "pure" diamond with virtually no non-diamond components present. In addition, the position of the diamond line is sensitive to stress and large wavenumber shifts have been recorded [3]. Defects in the diamond crystal can result in broadening and skewing of the Raman line shape, and in the case of large single crystals grown on sharp wire tips these defects coupled with the large strains can result in clear splittings of the diamond line into two or even three components [4,5].

Despite this widespread use of Raman spectroscopy for the evaluation of CVD diamond, no work has yet appeared in the literature describing the effects of polarization on the Raman spectrum. In this letter we show that the Raman peak position and lineshape, as well as the ratio of diamond to non-diamond components depends on the polarization of the incident and scattered light, and the orientation of the crystallites with respect to the incident polarization. The results are especially relevant in today's environment in which micro-Raman spectrometers, capable of selecting for study individual diamond crystallites from within polycrystalline films are commonly employed. The results will also be of importance to the interpretation of macro-Raman studies on large grain or oriented polycrystalline CVD diamond films for which a uniform random distribution of orientations within the sampling volume cannot be assumed.

The CVD films used in this study were produced by microwave plasma enhanced chemical vapour deposition onto pre-scratched silicon substrates. The relevant deposition parameters were: Pressure - 20 Torr; Total flow - 100sccm, with 1% CH₄ in 99% H₂; and a deposition time of 4 hours. Under these conditions a continuous film is formed displaying both square ((001)) and triangular ((111)) facets. Square (001) facets of approximate dimensions 10 x 10 μm² were selected for investigation. The Raman measurements were taken using the 514.5 nm line from an argon ion laser and a DILOR XY Confocal Micro-Raman spectrometer with optical multichannel collection using a CCD array detector. The polarization measurements were performed using a fixed analyser in the entrance to the spectrometer and rotating either the incident polarization using a λ/2 plate or the sample, thus avoiding the need for a polarization scrambler. By using a ×100 Olympus objective, and an appropriate confocal pin-hole the sampling volume was restricted to a cylinder of approximate dimensions 1 μm diameter and 2 μm depth.

For single crystal diamond, oriented in the [001] direction, the intensity of the Raman line in backscattering geometry is a strong function of the azimuthal angle the **E** vector of the incident laser beam (**E_i**) makes with [100] direction in the plane of the crystal [6]. When an analyzer is placed in the exit beam, two intensities can be recorded, viz. I_{||} and I_⊥, corresponding to the polarization of the scattered beam (**E_s**) being parallel and perpendicular respectively to the incident polarization. For backscattering geometry, with the light incident onto the (001) face of a diamond crystal, the Raman selection rules yield

$$I_{||} = d^2 \sin^2 2\theta$$

and

$$I_{\perp} = d^2 \cos^2 2\theta \quad (1)$$

where θ is the angle between **E_i** and the [100] direction in the crystal, and d is a parameter proportional to the intensity of the incident light and the Raman scattering cross-section.

When using high numerical aperture objectives, deviations from the ideal intensities predicted by equation (1) can occur due to a number of instrument dependent effects [7]. In order to estimate the magnitude of these effects, a type IIa (001) diamond slab obtained from Drukkers Corp. (3 x 3 x 0.25 mm) was used as a reference sample. For $\theta = 0$, (i.e. $\mathbf{E}_i \parallel [100]$) I_{\parallel}/I_{\perp} was measured to be 0.074 and for $\theta = 45^\circ$, $I_{\perp}/I_{\parallel} = 0.077$. In each case these values are to be compared to value of zero as expected from equation 1. Hence the polarization leakage associated with our instrument using the $\times 100$ objective is estimated to be less than 8%.

Polarized Raman spectra taken from a (001) facet are shown in Figure 1, for $\mathbf{E}_i \parallel [010]$, $\mathbf{E}_s \parallel [100]$, (Fig. 1(a)); $\mathbf{E}_i \parallel [100]$, $\mathbf{E}_s \parallel [100]$, (Fig. 1(b)); and $\mathbf{E}_i \parallel [110]$, $\mathbf{E}_s \parallel [\bar{1}10]$, (Fig. 1(c)); where the directions quoted are with respect to the sample co-ordinates. According to equation (1), the diamond line should only be observed in Figure 1(a). Experimentally, the analyser is kept in a fixed position with respect to the spectrometer gratings and thus the comparison between Fig 1(a) and (b) shows the effect of rotating the polarization of \mathbf{E}_i using the $\lambda/2$ plate with respect to a fixed sample. By contrast, the comparison between Figs 1(a) and 1(c) shows the effect of rotating the sample through 45° about the [001] axis while keeping the polarizations of \mathbf{E}_i and \mathbf{E}_s fixed in the laboratory frame of reference.

The spectra are typical of moderate quality CVD diamond displaying a diamond peak at about 1332 cm^{-1} together with a broad background. (It is worth noting that it is the diagonal of the square face that is parallel to the [100] direction as the edges of the facet are shared with the (111) face of the cubo-octahedron. Thus for the data presented, \mathbf{E}_i is parallel to the diagonal of the square facet, which is the [100] direction.) The details of the diamond Raman line shapes for the spectra displayed in Figure 1 are shown at greater magnification in Figure 2.

The data were fitted with a total of six Lorentzians: Two relatively sharp lines were

required to fit the the diamond line and four broad lines were required for the non-diamond components. Peak positions, and associated integrated intensities are provided in Table 1.

Clearly according to equation 1 the diamond line should not be observed at all for the orientations shown in Figures 1(b) and 1(c) and 2(b) and (c). In fact, Figure 2 shows that the diamond line consists of at least two components and it is, surprisingly, the component at about 1327 cm^{-1} that is almost completely polarized as expected (to within the degree of leakage compatible with the measurements on natural diamond). However, the component at about 1333 cm^{-1} does not show the same degree of polarization dependence, a fact which may be connected with the presence of residual strain within the films.

By contrast, the non-diamond components are only very weakly polarization dependent. The fact that the diamond line is highly polarized whilst the non-diamond components are almost completely depolarized has the effect of changing the apparent diamond/non-diamond ratio by a factor of about 2.5 upon rotating the crystal with respect to a fixed polariser and analyser. For CVD diamond films deposited on Tungsten substrates, this factor was observed to be typically much greater; up to 7.5 in some cases. In addition because one component of the Raman diamond line shape is more strongly polarized than the other component, the apparent position of the diamond peak changes by up to 3 cm^{-1} upon such a rotation (compare figures 2(a) and 2(c)).

It is important to stress that the above results are relevant even when a polariser and analyser are not specifically used in in a Raman spectrometer. This is because the Ar ion lasers commonly employed in Raman spectrometers are linearly polarized and the diffraction gratings used in the spectrometer usually have a strong polarization dependence. Hence the results of Figs 1(a) and 1(c) and Figs 2(a) and 2(c) show that just by rotating the sample, a different estimation of diamond quality and of the level of strain (based on peak position of the diamond line) may be obtained. Thus, differences in the micro-

Raman spectra of adjacent crystals in diamond films may in some cases not be due to intrinsic inhomogeneity, but rather may be attributable to the orientational dependence of the Raman spectra.

Finally, we note that the depolarization ratio has been recently been measured for amorphous carbon and glassy carbon irradiated to a high ion dose [8]. In that work, $D_p = I_{\perp}/I_{\parallel}$ was found to be in the range 0.45 to 0.55, for both the D and G peaks. The authors of ref. [8] concluded that the measured depolarization ratios support the proposition that these disordered graphites are comprised of sp^2 bonded clusters of carbon atoms. In the present work the depolarization ratio for the non-diamond components was found to be about 0.85 (see table I). However, in comparing our result with that of ref [8] it is necessary to apply a correction which takes into account the dependence of the laser power incident on the sample as a function of incident polarization. When this is done, D_p for the non-diamond component in our CVD films works out to be 0.55 ± 0.02 , which is very similar to the result obtained in ref [8] for glassy carbon irradiated with 5×10^{15} B/cm². This suggests that the non-diamond components in our films are predominantly comprised of sp^2 bonded clusters of carbon atoms.

In summary, we have demonstrated the importance of crystallite orientation in the analysis of CVD diamond films using micro-Raman spectroscopy. Diamond peak positions and line shapes, as well as an estimation of the diamond to non-diamond components have been shown to be dependent on the orientation of the crystallite with respect to the **E** vector of the incoming laser irradiation. These results demonstrate the importance of taking polarization into account when attempting to use Raman spectroscopy in even a semi-quantitative fashion for the assessment of the quality, perfection, and residual stress of diamond films.

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FIGURE AND TABLE CAPTIONS

Figure 1. Raman spectra of the (100) face of a CVD diamond crystal taken in backscattering mode, for different incident polarizations and crystal orientations. The key shows the polariser and analyser orientations with respect to the sample co-ordinates. Figure 1(a) is the orientation in which the diamond line is allowed. Figure 1(b) shows the effect of rotating the plane of polarization of the incident laser with respect to the sample, and in (c) the effect of rotating the sample with respect to a polariser and analyzer fixed in the laboratory frame of reference is shown. Note that the apparent "purity" of the film as judged by the ratio of the diamond to non-diamond components changes as a function of the measurement geometry.

Figure 2. The data of Figure 1 shown in more detail to demonstrate that the apparent peak position and linewidth of the diamond line is also a function of the measurement geometry. The peak position for natural single crystal (100) diamond measured under the same conditions was 1331.47 cm^{-1} .

Table I. Raman line positions and integrated peak intensities corresponding to the Raman spectra taken for the different orientations shown in Figures 1 and 2. The peak position for natural single crystal (100) diamond was 1331.47 cm^{-1} .

Table I

Orientation	Raman line	Position (cm ⁻¹)	Integrated peak Intensity
(a)			
E _i \parallel [010], E _s \parallel [100]	Diamond	1328.4	20.3
		1333.7	28.4
Amorphous carbon			
		1510.7, 1590.5	423.9 (total)
		1330.9, 1174.1	419.0 (total)
(b)			
E _i \parallel [100], E _s \parallel [100]	Diamond	1327.7	2.4
		1332.4	9.4
Amorphous carbon			
		1510.7, 1590.5	463.8 (total)
		1330.9, 1174.1	472.8 (total)
(c)			
E _i \parallel [110], E _s \parallel [$\bar{1}$ 10]	Diamond	1327.8	2.3
		1333.0	14.6
Amorphous carbon			
		1510.7, 1590.5	356.9 (total)
		1330.9, 1174.1	361.9 (total)

Intensity (relative units)

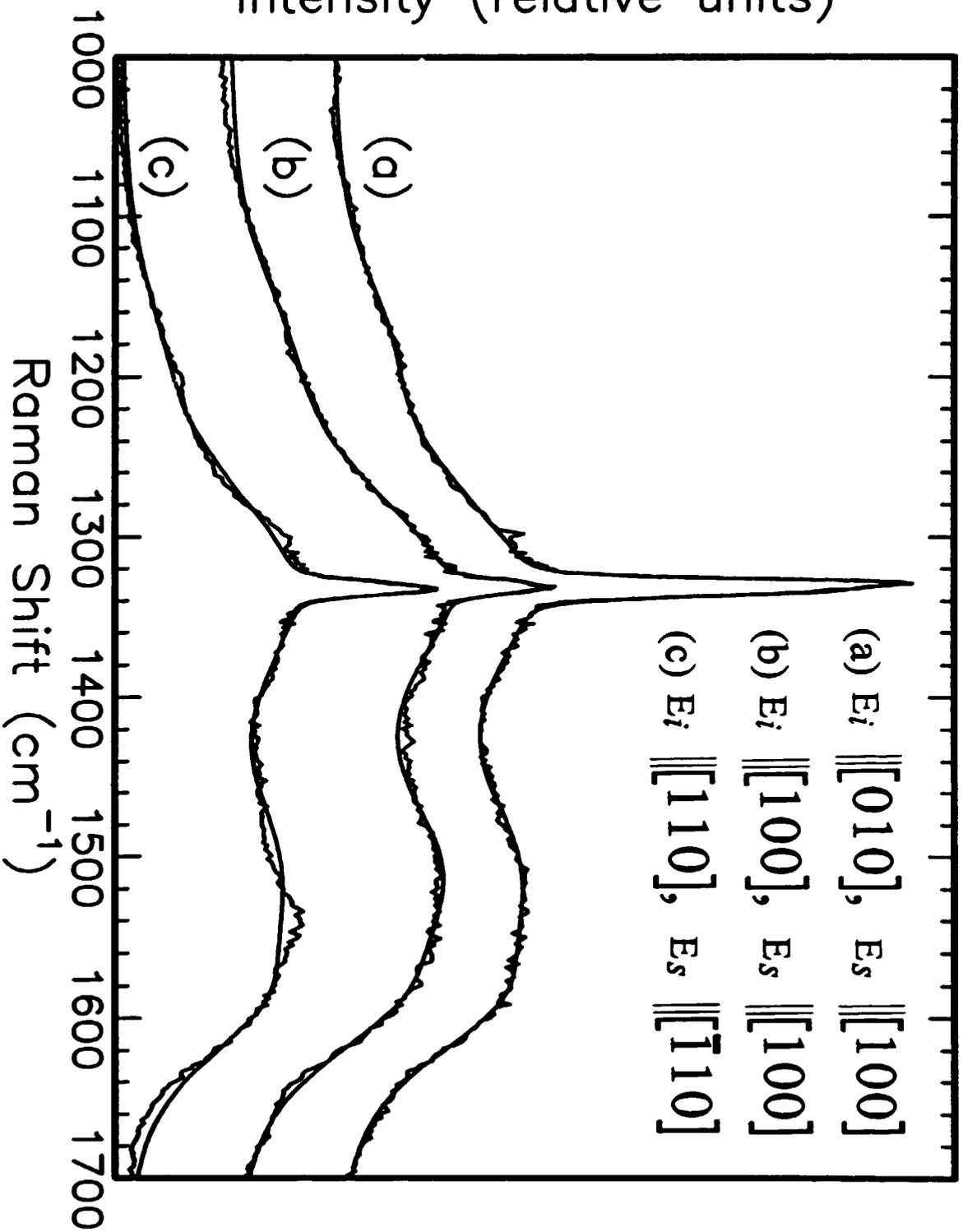


Fig 1

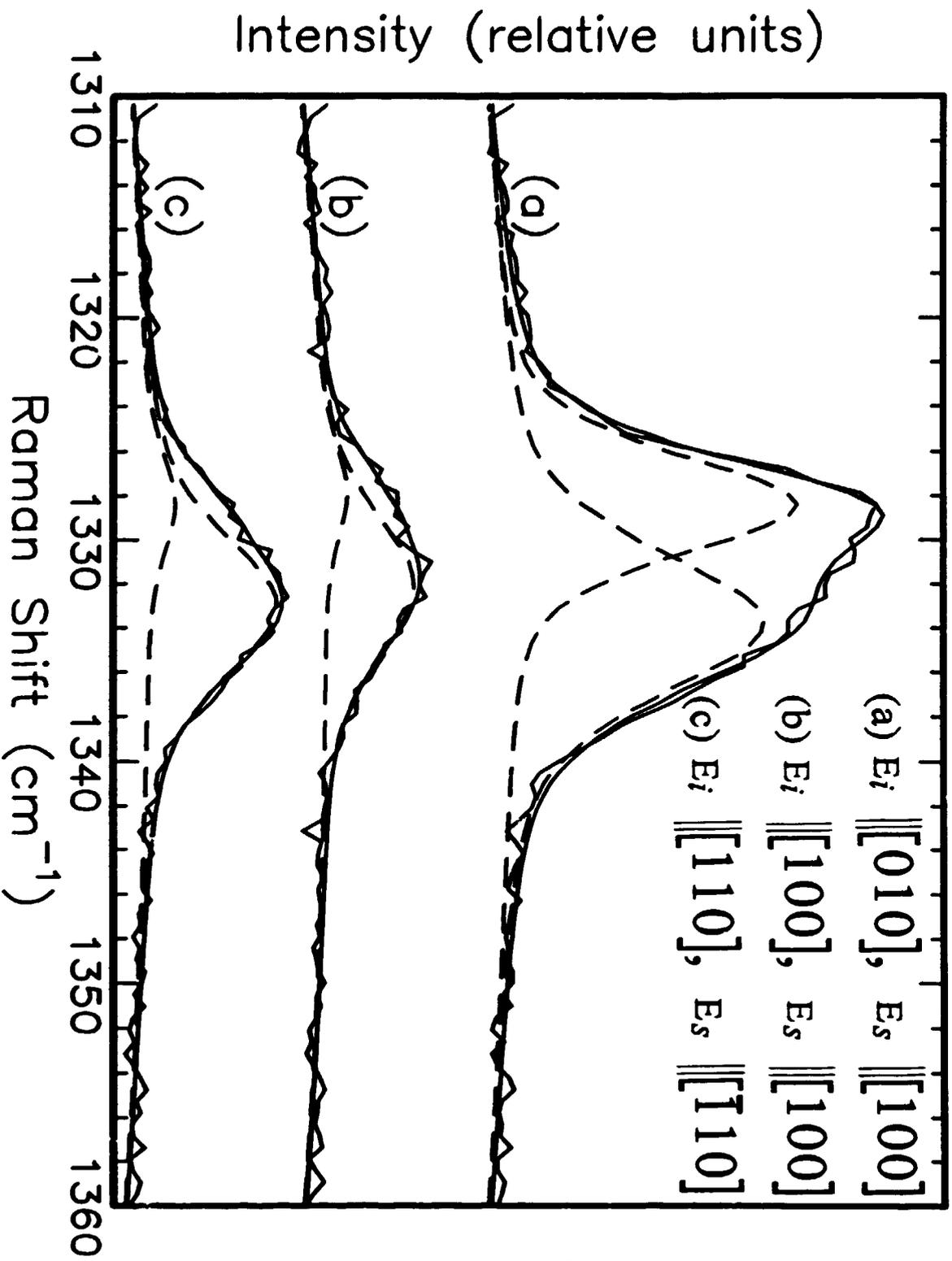


Fig 2