THE MECHANICAL PROPERTIES OF CVD DIAMOND FILMS, AND DIAMOND COATED FIBRES AND WIRES

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ABSTRACT

Two areas of thin film property measurement are addressed. The first is that of flat films, either on a substrate or free-standing. The film properties only are of interest. Therefore, when the film remains attached to a substrate during testing, an appropriate analysis is used to subtract the effect of the substrate. The films under test are prospective protective coatings and 'window' materials for infrared applications, namely CVD diamond (Hot filament Assisted, HFACVD and Microwave plasma assisted, MPACVD) and Germanium carbide (Ge:C). The mechanical properties under investigation are the Young's modulus and the internal film stress.

In the second case the substrates are small diameter fibres and wires coated with CVD diamond. The mechanical properties measured were composite, containing contributions from both the substrate and the film. These coated fibres and wires, have possible applications as reinforcement phases in the production of composites. They are silicon carbide (SiC) and Tungsten (W) of diameters varying between 10 and 125 μm. A technique has been developed to measure the Young's modulus of individual coated fibres.

MECHANICAL PROPERTIES OF THIN FILMS

The environments to which infrared (3-5μm and 8-12μm range) transparent 'window' materials used in airborne applications may be subjected include rain and solid particle bombardment and temperatures up to and possibly exceeding 900°C. The use of many bulk infrared materials (e.g. Ge, ZnS) is limited, as they cannot survive such conditions. In order to insure survival one of two routes can be taken; coating existing infrared materials with a resistant film, or replacing the window material with another of superior mechanical properties. Infrared materials tend to lack mechanical strength. There are few exceptions, these include diamond and Ge:C. Young's modulus and internal film stress are two of the properties of most interest.

Young's modulus

For flat films a variety of methods have emerged for measuring the Young's modulus, some of which are reviewed briefly below. A detailed review of techniques is given elsewhere1.

The Young's modulus can be determined from stress-strain properties of the material. An example is the uniaxial tensile test2, which has been used widely for measuring the modulus of metal foils, but not for very thin films produced by vapour deposition. Beam bending methods3

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have also been applied to thin film modulus measurement, the basis of which is the measurement of the deflection, or change in radius of curvature, of a sample by application of a known load. This information, together with the sample dimensions is used to calculate the modulus. The sample can either be deflected centrally whilst being supported at both ends (3-point bend), or loaded at one end with the other rigidly held (2-point bend). The modulus of thin films deposited on substrates can be measured using this technique from the difference in bending behaviour of the composite (film + substrate) and the uncoated substrate.

In the bulge test the stress-strain properties of the film are measured by applying pressure to one side of a free-standing membrane (usually circular but can be square) and measuring the resultant deflection as a function of the applied pressure. This technique is applicable to many film types including diamond. For very thin films on substrates, the substrate can be etched away over a circular region producing a hole through which the film can be bulged. Alternatively, thicker free-standing films can be pressurised through a die of known radius. Pressure can be applied in various ways depending on the modulus, thickness, size of membrane and the degree of deformation required. Techniques include use of a syringe, compressed air, or applying a vacuum to one side of the membrane. Methods of measuring the applied pressure include a calibrated water manometer and a silicon pressure transducer. The height of the pressurised membrane can be measured using techniques such as interferometry, microscopy, displacement probe and surface profilometry. The bulge test has the advantage of simultaneously measuring the internal stress and, if the film is bulged to failure, the fracture strength.

In recent years indentation methods have been extended to the measurement of both hardness and Young's modulus of thin films, through the development of low load indenters known as nano-indenters. The indents produced are nano-sized, thus their depth is only a small proportion of the film thickness (typically < 10%). This should allow the properties of the thin film to be sampled without influence from the substrate material. Nano-indentation has been used to characterise natural diamond and diamond films.

Resonance methods of measuring modulus are a popular choice. Their basis lies in the measurement of the natural or resonant frequency of a sample which together with knowledge of the sample density and dimensions, yields the Young’s modulus. Such methods have been widely used for bulk materials, and have more recently been applied to thin films including diamond.

The most accurate resonance methods impose the minimum constraint on the sample. The simplest method of excitation is by dropping the sample onto a surface. This principle was used by Hunt, who placed rectangular samples in a horizontally mounted drum which was then rotated. When airborne, after hitting the side of the drum, the sample vibrates freely emanating a tone. The vibrational modes of the sample can be detected using a microphone. Knowing the frequencies of these modes the Young's modulus can then be determined using the appropriate analysis.

Another resonance method involves supporting the sample at the nodes for a particular mode of vibration. This can be achieved by suspending the sample (rectangular of cylindrical) by a material that will not restrict its vibration (cotton thread or silica fibre). Resonance can then be produced in a variety of ways e.g. electrostatically or by acoustic waves. Alternatively, the sample can rest on supports positioned at the nodes. These supports may be knife edges, or foam blocks for larger samples. Resonance can be determined, for example, using a record styli or by piezoelectric, capacitive or optical detection. This technique has been used to measure the modulus of diamond coated films as a function of temperature. Samples can also be clamped at one or both ends and excited into vibration, as in the vibrating reed test. Excitation and detection of resonance can be achieved in various ways, as described above. The modulus of very thin films that cannot survive without a supporting substrate, can be measured by any one of the above methods. This is achieved by first measuring the resonant frequency of the composite, then
repeating the experiment for the substrate alone. The shift in resonance frequency that results can be used to calculate the Young's modulus\textsuperscript{13}. The measurement of the resonant frequency and hence the Young's modulus of circular membranes is also possible, using a similar technique\textsuperscript{14}. The bulge test, the vibrating reed test and nano-indentation were chosen for further investigation.

**The bulge test**

Membranes were produced by a cold anisotropic etching technique, at room temperature. The etchant was a 1:1 mixture of HF (40\%\%) and HNO\textsubscript{3}. Five membranes were produced from MPACVD diamond (with thickness varying between 1-9\(\mu\)m); and one from HFACVD diamond of thickness 5.8\(\mu\)m. The samples were 16mm x 16mm squares of silicon with the film deposited on one side. Each had a central membrane of \(\sim\)6mm in diameter. The samples were clamped within a chamber (figure 1), and pressurised (up to 80 mbar) using a syringe. The pressure was measured using a water manometer. Interferometry was used to monitor the membrane deflection.

The appropriate mathematical interpretation relating the central bulge height to the modulus of the film, will depend on the shape of the bulged membrane. In this investigation it was approximately spherical and therefore the spherical membrane model, originated by Beams,\textsuperscript{15} was used. The film stress, \(\sigma\), and strain, \(\varepsilon\), are expressed by the following equations

\[
\sigma = \frac{P a^2}{4 t Y_{\text{max}}} , \tag{1}
\]

\[
\varepsilon = \frac{2 Y_{\text{max}}}{3 a^2} , \tag{2}
\]

where \(P\) is pressure, \(a\) is membrane radius, \(t\) is film thickness and \(Y_{\text{max}}\) is the central membrane deflection. Stress over strain yields the biaxial modulus \(E/(1-\nu)\), from which the Young's modulus \(E\) can be calculated, if the Poisson's ratio \(\nu\) is known. A further refinement by Cabrera (referred to by Beams) takes into account internal tensile stress in the film

\[
P = \frac{8 t Y_{\text{max}}^3 E}{3 a^3 (1-\nu)} + \frac{4 t Y_{\text{max}} \sigma_0}{a^2} , \tag{3}
\]

where \(\sigma_0\) is the internal film stress. Plotting pressure versus deflection, and fitting the curve to a polynomial with first and third- order terms, yields Young's modulus and the internal stress.

During this investigation it was discovered that four of the six films tested were compressively stressed. This technique is not applicable to such films. The results for the remaining two samples are shown in table I. Unfortunately the pressure capabilities did not allow the thicker film to be bulged sufficiently for the modulus to be measured\textsuperscript{1}, however it was possible to measure the internal stress. The errors in measurement of pressure, deflection and variation in membrane thickness, amounted to a total uncertainty of \(\pm\) 8\%. 
Table I. Sample details and moduli measured by the bulge test

<table>
<thead>
<tr>
<th>Sample type</th>
<th>Film thickness (µm)</th>
<th>Young's Modulus (GPa)</th>
<th>Internal stress (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HFACVD diamond</td>
<td>5.8</td>
<td>1040</td>
<td>100</td>
</tr>
<tr>
<td>MPACVD diamond</td>
<td>9</td>
<td></td>
<td>365</td>
</tr>
</tbody>
</table>

Figure 1. Schematic of the bulge test.

The vibrating reed test

The samples tested were CVD diamond films on substrates, free-standing diamond, single crystal silicon and Ge:C. The samples were rectangular, of lengths varying between 15-50mm, width 3-5mm, and were clamped at one end to form a capacitor with a reference electrode. Vibration was produced electrostatically and detected by means of a Michelson interferometer (figure 2). Resonance was detected by placing a photodiode behind a pinhole in a screen on to which the interference pattern falls; the pinhole is positioned at the edge of a bright fringe. When the frequency of the excited signal equals that of the resonant frequency of the beam, the amplitude of vibration passes through a maximum. This is observed as a blurring out of the interference pattern and corresponds to a maximum in the amplitude of the signal and a phase shift, both of which can be seen on an oscilloscope. The actual resonant frequency is, due to the nature of the test, twice that of the applied electrical frequency as the beam is electrostatically attracted to the reference electrode with either voltage polarity. This frequency is then used to calculate the modulus. To achieve an accurate determination of modulus the samples were successively shortened, and the resonant frequency measured as a function of length, l. A plot of frequency versus \( l^2 \) was drawn. The slope of this plot is related to the Young's modulus by equations, the precise form of which depend upon whether the film is free-standing or composite\(^{16}\). The equation for a monolithic beam is

\[
E = f_0^2 l^4 \frac{48 \pi^2 \rho}{l^2 (1.84)^3}
\]  

\( (4) \)
where \( f_{\text{res}} \) is the resonant frequency and \( \rho, l \) and \( t \) are, respectively the density, length and thickness of the beam.

The modulus of single crystal silicon of two thicknesses was measured, as a standard. The results (table II) agree well with literature values. Details of other samples under test and their moduli are also given in table II. The major source of error, for all the samples tested, was due to uncertainty in the clamped length and poor film quality. Perfect sample clamping is difficult and, as the length appears as the fourth power in the equation for modulus, small errors in the measured length result in much larger errors in the modulus. Variation in sample thickness along their length also produced errors. The worst case was for the free-standing diamond films, which is reflected in the total predicted error (15-20\%). The maximum error in the measured modulus for the single crystal materials was \(-5\%\), with the error for the coated substrates slightly higher at 7-10\%.

Table II. Sample details and Young's modulus measured by the vibrating reed test.

<table>
<thead>
<tr>
<th>Sample type</th>
<th>Film thickness (( \mu \text{m} ))</th>
<th>Dimensions (mm)</th>
<th>Young's Modulus (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Free-standing polycrystalline MPACVD diamond D1 (3 samples)</td>
<td>150-180</td>
<td>30 x 3</td>
<td>802 ± 20</td>
</tr>
<tr>
<td>D2 (3 samples)</td>
<td>230-270</td>
<td>30 x 3</td>
<td>795 ± 15</td>
</tr>
<tr>
<td>D3 (4 samples)</td>
<td>230</td>
<td>12 x 4</td>
<td>760 ± 20</td>
</tr>
<tr>
<td>D4 (2 samples)</td>
<td>770-775</td>
<td>30 x 4</td>
<td>860 ± 50</td>
</tr>
<tr>
<td>Composite beams, polycrystalline MPACVD diamond on silicon (3 samples)</td>
<td>1-8</td>
<td>50 x 5</td>
<td>785 ± 15</td>
</tr>
<tr>
<td>Single crystal silicon (100) &lt;100&gt;, 385( \mu \text{m} ) (3 samples)</td>
<td>50 x 5</td>
<td></td>
<td>129.35 ± 4</td>
</tr>
<tr>
<td>(100) &lt;100&gt;, 532( \mu \text{m} ) (3 samples)</td>
<td>50 x 5</td>
<td></td>
<td>129.65 ± 5</td>
</tr>
<tr>
<td>RF-Plasma sputtered Ge:C on Si (6 samples)</td>
<td>13.8 - 15</td>
<td>50 x 4</td>
<td>290 ± 30</td>
</tr>
</tbody>
</table>

*errors are in the mean*

Figure 2. Schematic of the vibrating reed test.
Nano-indentation

The measurement of modulus of thin films by nano-indentation involves continuously recording the depth of the indentation as a function of load, during both loading and unloading\(^1\). The Young's modulus is extracted from the elastic region of the curve produced, whilst the plastic region yields the indentation hardness (H). Tests were carried out using a Nano-Test instrument (Micromaterials Ltd.). The indenter has a 90° trihedral diamond tipped stylus. 15 indents were carried out on each sample, from which a continuous plot of the load versus depth during loading and unloading was produced. These appear as a hysteresis curve, from which the hardness, plastic depth and the elastic recovery parameter can be determined. These values together with knowledge of the indenter shape, can be used to calculate the Young's modulus using the following equation\(^1\).

\[
E = \frac{H(1 - \nu^2)}{2R} \sqrt{\frac{\pi}{K}}, \tag{5}
\]

where R is the elastic recovery parameter and K is the indenter shape parameter which, for a 90° indenter, is 2.6 x (depth)\(^2\). Analysis of polycrystalline diamond films by indentation proved unsuccessful, due to indenter blunting and fracturing. Only the first few indents yielded values. Several samples showed two distinct values of modulus or hardness, suggesting separate regions of differing properties. Samples details, the Young's modulus and hardness are given in table III.

Table III. Sample details, Young's modulus and Hardness measured by indentation.

<table>
<thead>
<tr>
<th>Sample Type</th>
<th>Film thickness (µm)</th>
<th>Young's Modulus (GPa)</th>
<th>Hardness (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MPACVD diamond on Si</td>
<td>11.0</td>
<td>1240</td>
<td>83.1</td>
</tr>
<tr>
<td>HFACVD diamond on Si</td>
<td>5.8</td>
<td>1070, 830</td>
<td>80.3, 52.5</td>
</tr>
<tr>
<td>RF-sputtered Ge:C on Si</td>
<td>14.6</td>
<td>205 ± 4, 300 ± 6</td>
<td>16.4 ± 0.2</td>
</tr>
<tr>
<td>RF-sputtered Ge:C on Ge</td>
<td>9.4</td>
<td>325 ± 13</td>
<td>19.8 ± 0.4</td>
</tr>
</tbody>
</table>

Internal stress

Curvature methods have proved popular for determining the internal stress of thin films on substrates. If the initial curvature of the substrate before the film is deposited is known, the film stress can be determined from the distortion of the substrate due to the presence of the film on its surface. Analyses for relating both the curvature of the samples in the form of long thin beams and a disc have been described. Methods of measuring curvature include interferometry and surface profilometry. Curvature methods are applicable to both compressively stressed and tensile films.

In the calculation of stress, an improved theory was used to determine the internal stress of beam shaped samples. The theory behind this analysis is presented elsewhere\(^1\). In brief, the analysis assumes that the internal stress is defined by the directions and magnitudes of the principle components of stress in the plane of the specimen, and that the principle stress axes coincide with the principle axes of curvature. Thus by measuring the principle curvatures of the
film the principle stresses and their directions can be determined. The equation for stress in the $x$ direction, where $x$ is a direction of principle curvature of the beam, is given by,

$$\sigma_x = \frac{E_s}{6(1-v_s^2)} \frac{\phi_x v_s \phi_y}{t_f} \left[ 6(t_f + t_s) - t_s^2 \right],$$

(6)

where $\phi_x$ and $\phi_y$ are the measured curvatures of the substrate in the $x$ and $y$ directions respectively and $t_s$ and $t_f$ are the thicknesses of the substrate and film respectively. The stress in the $y$ direction can be obtained by interchanging the subscripts $x$ and $y$.

The curvature of coated and uncoated substrates was measured by both profilometry and interferometry. Sample details and measured stress are shown in table IV. Where stress in the $x$ and $y$ directions are approximately equal, the film stress was considered isotropic. A Sloan Dektak II profilometer was used to traverse the central regions of the samples. The length of the traversed segment was between 3 and 20mm depending on the sample size.

A phase-stepping interferometer was also used to determine curvature. In brief it is an automated method of analysing interference patterns, which is more accurate and which dramatically reduces the time required to analyse data\textsuperscript{18}. Using this method the curvature, and hence the stress, in any direction across the surface can be determined. The phase stepped apparatus can be seen in figure 3. A beam splitter divides the light from a He-Ne laser. One half travels directly along the optical fibre to the beam collimator and the other half is phase-stepped. The light then continues down the optical fibre to the beam collimator. Half this light travels to and is reflected from the sample to the beam splitter, where it is reflected in the direction of the camera. The unshifted beam and the sample beam combine producing an interference pattern which is focused on to a video camera plane. Only Ge:C films were tested by this method. Stress was found to be isotropic, and of similar magnitude as measured by profilometry (table IV).

Figure 3. Schematic of the phase-stepped interferometry apparatus
Table IV. Sample details and stress values measured by profilometry and interferometry.

<table>
<thead>
<tr>
<th>Sample Type</th>
<th>Substrate Dimensions (mm²)</th>
<th>Film Thickness (µm)</th>
<th>Internal Stress by profilometry (GPa)</th>
<th>Internal Stress by Interferometry (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MPACVD diamond on (100) silicon sample S5</td>
<td>50x50x 0.385</td>
<td>2.4</td>
<td>0.353 ± 0.003 (x)</td>
<td>0.049 - 0.056 (x,y)</td>
</tr>
<tr>
<td>S4</td>
<td>7</td>
<td></td>
<td>-0.082 ± 0.001 (y)</td>
<td></td>
</tr>
<tr>
<td>RF-sputtered Ge:C on (100) silicon</td>
<td>50 x 4 x 0.532</td>
<td>14.1-15</td>
<td>0.375 ± 0.015 (x)</td>
<td>0.049 - 0.056 (x,y)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>0.078 ± 0.001 (y)</td>
<td></td>
</tr>
</tbody>
</table>

MECHANICAL PROPERTIES OF DIAMOND COATED FIBRES AND WIRES

The continuous effort to develop new materials with improved properties has sparked an interest in diamond coated fibres and wires¹⁹-²¹, which is ever increasing due to many prospective applications. One such application is in the production of composites, for aerospace applications. In the aerospace industry, rigidity and weight savings are of concern, consequently lighter, stronger, stiffer materials are always in demand. A substantial increase in fibre Young’s modulus can be expected by diamond coating existing reinforcement fibres.²¹ These coated fibres, once incorporated into a composite, should transfer their stiffness to the composite. This suggests that fewer fibres would be required in the composite in order to produce significant increases in stiffness compared with uncoated fibre reinforcements. This, together with diamond’s fairly low density, may lead to significant weight savings. In addition, its extremely high thermal conductivity and chemical inertness widen the scope of applications for such a product.

Reinforcement phases can be particles, whiskers, chopped fibres or continuous fibres, while the matrix can be polymeric, metallic, intermetallic or ceramic. In this investigation, metal matrix composites, reinforced with unidirectional, continuous fibres are of interest. Such composites offer outstanding unidirectional mechanical properties, and are particularly attractive for components that exploit these anisotropic properties. Candidate reinforcement fibres include tungsten (W) wire and silicon carbide (SiC) fibre, of diameters ranging from 10µm to 125µm. Tungsten fibres have been used to reinforce superalloys for heat engines and offer the potential for significantly raising hot component operating temperatures and therefore improving heat engine performance²². SiC fibres incorporated in Ti alloy, or Ti aluminate matrices, already in use in the aerospace industry, can lead to significant improvements in specific strength and stiffness of components at ambient and elevated temperatures, with predicted weight savings up to 75%²³.

Matrix materials of interest include metals such as aluminium, magnesium, copper and titanium. Al and Mg are favoured due to their high strength to density ratio, while a Cu matrix composite may be suitable for production of high strength thermal conductors.

The mechanical properties of most interest in this article are the Young’s modulus and strength, both of individual reinforcement fibres and of the resulting composite material. Due to the small size of the coated fibres (10-270 µm diameter) mechanical property measurement is difficult. This investigation concentrated on the measurement of Young’s modulus of individual fibres.
Production of diamond coated fibres and wires: The fibres and wires were coated by HFACVD (Thomas Swan reactor). The sample wires were positioned parallel to and surrounding a vertically held tantalum filament, approximately 5-6mm distant from the filament. The filament was made up of 5 individual filaments, of total length 12-13 cm. Samples were heated by the filament only, the temperature of which was measured using an optical pyrometer. A maximum of 14 substrate fibres/wires may be coated in any one run. The workable sample length is 10-11cm. The samples were tensioned during coating. Deposition was carried out under the following conditions: 20 Torr pressure, 0.75 CH$_4$ in H$_2$, Filament temperature 2150-2180$^\circ$C. Deposition times to date have been $\leq$72 hours, producing coatings of up to 70$\mu$m in thickness.

**Young's Modulus**

Many of the tests mentioned above for flat films are also applicable to long, small diameter fibres. The Young's modulus of high modulus single fibres and wires (including diamond coated fibres), has most often been measured using the tensile test$^{24}$, were $E$ is calculated from the load-elongation of a sample of known cross-sectional area. By stressing the fibres/wires to failure the tensile strength can also be measured. However, difficulties have been experienced in gripping the sample successfully and measuring the very small strains experienced by very stiff fibres.

Bend testing to measure modulus of rod shaped samples, such as coated fibres and wire should also be feasible. Two-point and three-point bend tests have been used to measure stiffness of nickel-titanium alloy wire, of both rectangular and circular cross section$^{25,26}$.

From the resonance tests previously mentioned, we have chosen the technique of supporting the sample at nodes for a particular mode of vibration. As constraints on the sample are less, it was thought more accurate than the vibrating reed test. This test has previously been applied to much larger samples, therefore its applicability to smaller samples is under test here. One advantage of using rod shaped samples is that the mathematical relationship between resonant frequency and Young's modulus is more exact. The Young's modulus can be determined from either the flexural or the longitudinal vibrations. Generally it is easier to excite the flexural vibration than the longitudinal vibration and so this was employed. Knife edges were positioned at the nodes (0.224 of the length from each end) to excite the fundamental flexural vibration. For cylindrical rods, the Young's modulus and the fundamental frequency of the flexural vibration are related by:

$$E = 1.261886 \frac{p d^4}{d^2 f_{res}^2}$$  \hspace{1cm} (7)

Where $d$ is the diameter.

The resonance apparatus is shown in figure 4. The sample mount consists of micrometer calipers attached to an X-Y translation stage. The translation stage is mounted on a ridged platform bolted to a vibration isolated table. Metal shim formed in to knife edges is mounted on the inside edges of the micrometer calipers. Each shim has a central V of material removed, in to which the sample sits. This was thought necessary to prevent lateral movement of the sample during excitation. The distance between the knife edges (15-75mm) is set to that required for fundamental flexural resonance. Sample excitation is achieved using an audio range speaker, located directly beneath the centre of the sample. It is acoustically isolated from the table to prevent coupling to other parts of the apparatus. The frequency of excitation is tuned using a variable frequency function.
generator which is connected to the loud speaker via an audio amplifier. Resonance can be detected in two different ways depending on the nature of the sample surface. For specimens with a fairly smooth reflecting surface, resonance is detected by interferometry, using a similar method to that used for the vibrating reed test. In brief, the sample beam is reflected from the sample surface and interferes with the reference beam. The resultant beam passes through a pinhole and then is incident on the face of a photodiode. When the excitation frequency approaches the resonant frequency of the sample, the sample will start to vibrate. The changes in intensity at the photodiode are measured by an oscilloscope and can be seen as a maximum in the amplitude of the measured signal. Alternatively, for specimens with a rough surface, such as the diamond coated wires and fibres produced in this investigation, resonance was detected using position detection. This works using the same apparatus as above but omits the need for the reference arm of the interferometer. In this case, the intensity of the light detected at the photodiode is attenuated as the fibre moves. At resonance, the attenuation is greatest and again was seen as a maximum in the amplitude of the signal on the oscilloscope. A lens in front of the sample was required to focus the light to a spot on the sample surface, and to collimate the reflected light.

The resonant frequency was measured as a function of length (l=8-12cm). The slope of frequency versus $l^2$, together with the sample density, diameter etc., is used with equation 7 to determine the Young's modulus. The frequency range for the fibre samples tested was 100-500 Hz. Density was determined both by mass and dimension measurements and, theoretically, using the rule of mixtures. Calibration of the equipment was carried out using Pyrex (borosilicate glass) rods of known properties, and of different lengths (8-12 cm). The value of modulus measured, 61.4 GPa, compares well with the data book value of 61 GPa.

Three samples of each CVD diamond coated SiC fibre and of CVD diamond coated W wire were tested. Sample details and measured moduli are given in Table V. SEM photographs of these samples can be seen in Figure 5 and 6.

<table>
<thead>
<tr>
<th>Sample type</th>
<th>Average Diameter (μm)</th>
<th>Film Thickness (μm)</th>
<th>Length (cm)</th>
<th>Young's Modulus (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>W/Diamond 1</td>
<td>202.5</td>
<td>38-40</td>
<td>8.3-12.2</td>
<td>970±195</td>
</tr>
<tr>
<td>2</td>
<td>197.8</td>
<td>38-40</td>
<td>8.4-11.7</td>
<td>1015± 100</td>
</tr>
<tr>
<td>3</td>
<td>197.0</td>
<td>38-40</td>
<td>9.9-12.1</td>
<td>980± 100</td>
</tr>
<tr>
<td>SiC/Diamond 1</td>
<td>195.0</td>
<td>48-52</td>
<td>8.5-11.1</td>
<td>560±78</td>
</tr>
<tr>
<td>2</td>
<td>197.4</td>
<td>48-52</td>
<td>8.8-10.1</td>
<td>690± 95</td>
</tr>
<tr>
<td>3</td>
<td>193.2</td>
<td>48-52</td>
<td>8.5-10.0</td>
<td>522± 73</td>
</tr>
</tbody>
</table>

As the coated fibres under test are not isotropic (which is assumed by equation 7), equation 7 is not exact, and was merely used here as a guide to modulus until a more exact solution is developed. Use of equation 7 gives an overestimation of modulus. Theoretical calculations using the rule of mixtures predicts a modulus of 800 GPa and 897 GPa for the W/diamond and the SiC/diamond samples respectively. The low modulus value for the SiC/diamond fibres was thought to be due to longitudinal cracks in the film. The measured modulus of W/diamond samples may also have been increased by inaccuracies in the density measurements. The measured density of these samples was greater than the theoretical value. The measured density would be expected to be lower as the theoretical value was calculated using the density of single crystal diamond. The diamond film density should be lower than its single crystal form. A 10\% uncertainty is also present, due to errors in length measurement and variation of the fibre diameter. These results are preliminary; future experiments are required for verification.
Figure 4. Schematic of the simply supported fibre resonance test.

Figure 5. Diamond coated silicon carbide fibre, (a) cross section (b) surface.

Figure 6. Diamond coated Tungsten wire, (a) cross section (b) surface.
Diamond Composite Work To Date: Diamond coated fibres produced during this investigation have been incorporated into a Ti-6Al-4V alloy matrix. They were individually coated with the titanium alloy matrix material, using physical vapour deposition, after which they were consolidated by hot vacuum pressing, either unidirectionally or isostatically at 900°C, producing a diamond coated fibre reinforced composite, in which the fibre spacing was controlled primarily by the metal matrix coating thickness and the diamond volume fraction by the diamond deposit thickness. A Ti-alloy composite microstructure containing fibres, with various diamond deposit thickness on SiC fibre cores, is shown in figure 7. The thin and thick diamond deposits were undamaged during consolidation, and Raman spectroscopy confirmed that they were still diamond. A fibre with 85% volume fraction of diamond is shown in figure 8. Such fibres, when coated with 10μm of Ti-alloy and consolidated into a composite will produce a composite with 75% volume fraction diamond, and an elastic modulus of ~720 GPa (based on the rule of mixtures). This value is ~3.5 times greater than the modulus of current Ti-alloy/SiC fibre composites (~206 GPa) with about 30% fibre volume fraction.

![Figure 7: Diamond/SiC fibre-Ti alloy Composite.](image7.png)

![Figure 8: A SiC fibre with 85% volume fraction of diamond.](image8.png)

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