

Young's modulus and Poisson's ratio of CVD diamond

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Abstract

The elastic modulus E of diamond is often set equal to $1/s_{11} = 1050$ GPa, which assumes that it does not vary much with orientation, and many authors use $\nu = 0.2$ as an appropriate average value of Poisson's ratio, which is incorrect. In fact, since the elastic constants of diamond are known with great accuracy, it is a straightforward matter to derive exact numbers for E and ν that take into consideration the stress direction and the intrinsic anisotropy as well as the crystalline configuration. For diamonds synthesized by chemical vapor deposition (CVD) we find that in a first approximation the Hershey–Kröner–Eshelby averaging procedure yields acceptable numbers, $\bar{E} = 1143$ GPa and $\bar{\nu} = 0.0691$, which are quite compatible with available experimental evidence. Our measurements of the biaxial modulus $E' = E/(1 - \nu)$ make use of the bulge test method to characterize the elastic behavior of both microwave-power- and hot-filament-assisted CVD diamond films. High quality deposits yield $E' \approx 1180$ and 1220 GPa for randomly orientated and (110)-textured deposits respectively; these results confirm that state-of-the-art deposits exhibit elastic properties that are in accord with the measured stiffnesses of natural single-crystal diamond. The residual hydrogen content strongly impacts the elastic behavior and appears to be responsible for the degradation of the modulus observed in this and previous work.

1. Introduction

The successful synthesis of diamond by means of chemical vapor deposition (CVD) techniques has stimulated enormous interest in potential applications of diamond for a variety of engineering tasks. Many of these applications involve evaluating thermally or mechanically induced stresses, which requires a proper characterization of the elastic properties, *i.e.* Young's modulus E and Poisson's ratio ν . In this regard it is commonly assumed that the modulus of diamond can be set equal to 1050 GPa, since “ E does not vary greatly with orientation” [1]; furthermore, it has been stated [1] and generally accepted that “ ν varies between 0.1 and 0.29 ($\bar{\nu} \sim 0.2$)”, which is incorrect. In fact, since the elastic constants of diamond are known with great accuracy, it is a straightforward matter to describe the elastic behavior, which includes assessing the directionality of E and ν in single crystals as well as obtaining the elastic coefficients of CVD deposits that may exhibit crystallographic texture. In this paper we will address this problem by first providing numerical results for the orientational dependence of the elastic moduli and the Poisson ratios (Section 2), keeping in mind that there are two ratios to be considered in dealing with anisotropic cubic media. These results will assist us in applying the theory of elasticity to textured CVD diamond films (Section 3) and thus in interpreting

available experimental data. Our own measurements make use of the bulge test method (Section 4) for obtaining the biaxial elastic modulus of both microwave-power- and hot-filament-assisted CVD diamond films. The results are summarized in Section 5 and evaluated in the light of theoretical considerations as well as evidence concerning the impact of residual hydrogen on the modulus of CVD diamond. Finally, the conclusions are stated in Section 6.

2. Single-crystal diamond

In terms of the anisotropy parameter $S = (s_{11} - s_{12}) - s_{44}/2$, the condition for elastic isotropy in cubic crystals is $S = 0$ [2]. Since the compliances of diamond as listed in Table 1 yield $S = 0.1835 \pm 0.0020 \text{ TPa}^{-1}$, it follows that single-crystal diamond is elastically anisotropic, which implies that directionality equations must be used to describe Young's modulus as well as the two Poisson ratios. In this connection we remind the reader that, given a crystallographic plane and a stress within that plane (longitudinal stress), orthogonal strains may vary depending on the direction; the definition of Poisson's ratio must therefore be extended in the sense that ν refers to the longitudinally induced orthogonal elongation whereas ν' refers to the transversely induced

TABLE 1. Elastic stiffnesses (c_{ij}) and elastic compliances (s_{ij}) of single-crystal diamond. The tabulated c_{ij} values reflect the results of the most recent measurements. The compliances are as derived from the stiffnesses by means of standard relations [2]

Measurement technique	c_{11} (GPa)	c_{12} (GPa)	c_{44} (GPa)	s_{11} (TPa ⁻¹)	s_{12} (TPa ⁻¹)	s_{44} (TPa ⁻¹)
Ultrasonic pulse ^a	1079 ± 5	124 ± 5	578 ± 2	0.9493	-0.0978	1.7301
Brillouin scattering ^b	1076.4 ± 0.2	125.2 ± 2.3	577.4 ± 1.4	0.9524	-0.0991	1.7331

^aH. McSkimin and P. Andreatch, *J. Appl. Phys.*, **43** (1972) 3944; ^bM. Grimsditch and A. Ramdas, *Phys. Rev. B*, **11** (1975) 3139.

elongation [3]. A convenient way of visualizing the directionality then consists of focusing attention on a specific crystallographic plane and examining the variations in E , ν and ν' in that plane. By choosing a proper set of "reference" planes, the directionality thus can be assessed for all relevant orientations. In that context, for crystallographic planes identified by Miller indices (hkl), Turley and Sines [4] derive the equations

$$E_{(hkl)} = s_{12} + \frac{s_{44}}{2} + S\Omega_{22}^{-1} \quad (1)$$

$$\nu_{(hkl)} = -(s_{12} + S\Omega_{23})E_{(hkl)} \quad (2)$$

$$\nu'_{(hkl)} = -(s_{12} + S\Omega_{12})E_{(hkl)} \quad (3)$$

where the Ω_{ij} are functions of (a) the two Eulerian angles of the plane under consideration and (b) the angle θ that specifies a direction in the plane. These directionality functions reduce to expressions that are made up of sinusoidal terms involving multiples of the angle of rotation; specifically,

$$\Omega_{12} = a + b \sin(2\theta) + c \cos(2\theta) \quad (4)$$

$$\Omega_{22} = \frac{3(1-a)}{4} - b \sin(2\theta) - c \cos(2\theta) - d \sin(4\theta) - e \cos(4\theta) \quad (5)$$

$$\Omega_{23} = \frac{1-a}{4} + d \sin(4\theta) + e \cos(4\theta) \quad (6)$$

with coefficients a , b , c , d and e that depend on the two Eulerian angles. For our purposes the highest symmetry planes, *i.e.* (100), (110) and (111), are of special interest because of the nature of the texture in CVD diamond films. For such planes the coefficients are as given in Table 2 and the angle θ must be measured from one of the principal axes.

Table 2 immediately tells us that in the {111} orientation the directionality functions are independent of the angle θ , which corroborates the well-known fact [5] that the elastic properties of cubic crystals are always isotropic in the (111) plane. For single-crystal diamond the Turley-Sines equations yield $E_{(111)} = 1164$ GPa, $\nu_{(111)} = 0.0791$ and $\nu'_{(111)} = 0.0435$; note that the Poisson ratios are much smaller than for Ge or Si [6], which Fukumoto [7] attributes to the character of

TABLE 2. Numerical coefficients for the directionality functions Ω_{ij} of highest symmetry cubic crystallographic planes [4]

(hkl)	a	b	c	d	e
(100)	0	0	0	0	$-\frac{1}{4}$
(110)	$\frac{1}{4}$	0	$-\frac{1}{4}$	0	$-\frac{3}{16}$
(111)	$\frac{1}{3}$	0	0	0	0

the carbon atom and in particular to the lack of core p states. In the (100) and (110) planes the elastic response of diamond is much more complex, as illustrated in Fig. 1, which depicts how the elastic properties vary when the stress direction rotates.

Young's modulus exhibits relatively little anisotropy, since the peak value, which always occurs along the [111] direction if the condition $S > 0$ holds [2], does not exceed 1210 GPa. The generally accepted $E = 1050$ GPa value only holds for principal stresses and represents a minimum value. The two ratios ν and ν' differ substantially except for principal stress directions and show much more angular dependence than the moduli. Poisson's ratio has a maximum value of 0.115 in the [011]-[100] geometry and a minimum value of 0.00786 in the [011]-[110] configuration, thus emphasizing the highly anisotropic elastic behavior of diamond in accord with the results of recent, first-principles pseudopotential calculations [7]. The biaxial modulus $E/(1-\nu)$, which relates longitudinal stresses and strains and frequently emerges in situations of practical interest [5], exhibits some angular dependence in the (110) plane but, as expected, turns out to be isotropic in the {100} orientation. In fact, the analytical expression for $[E/(1-\nu)]_{(100)}$ reduces to $1/(s_{11} + s_{12})$, which yields 1173 GPa, *i.e.* less than the 1264 GPa obtained in the fully isotropic (111) plane.

3. Polycrystalline diamond elasticity

Polycrystalline CVD diamonds can be expected to exhibit elastic properties that reflect not only the intrinsic diamond elasticity but also the crystalline orientation of the deposit. In this connection it is important to remember that preferred orientation may

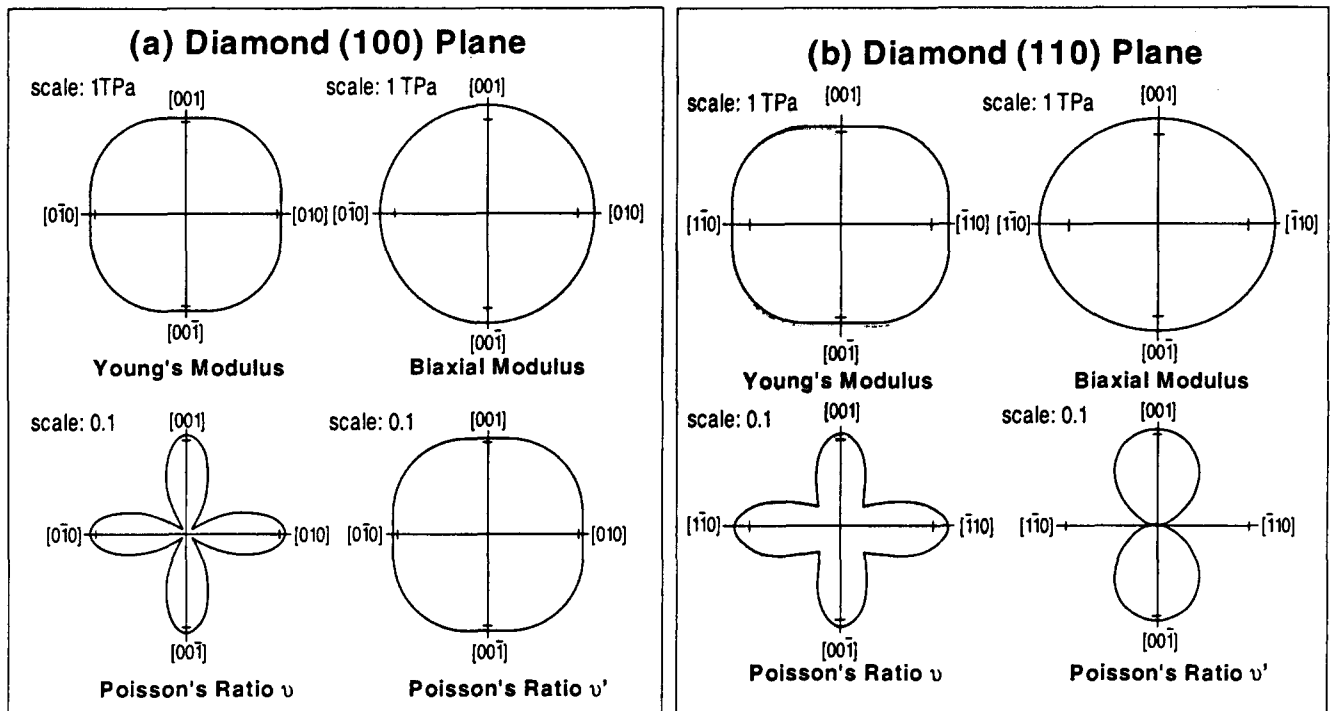


Fig. 1. Rotational dependence of the elastic modulus, the biaxial modulus and the two Poisson ratios of single-crystal diamond: (a) applied stresses within (100) planes; (b) applied stresses within (110) planes. Poisson's ratio ν refers to a longitudinal orthogonal elongation, whereas ν' refers to a transverse orthogonal elongation.

occur as the deposition progresses; in effect, by controlling the deposition conditions, highly oriented structures can be prepared with texture axes that are parallel to the [100], [110] or [111] directions [8]. Within the deposition plane, however, the "distributions" obey rotational symmetry, which means elastic isotropy and therefore average values for the elastic moduli and the Poisson ratios (see Table 3) that can be derived by numerical integration on assuming that the grain boundaries do not impact the elastic behavior of the aggregate. In this context it is also of interest to obtain accurate numbers for Young's modulus and Poisson's ratio of a randomly oriented, densely packed aggregate of diamond grains. This can be done simply by expressing $\bar{E}$ and $\bar{\nu}$ in terms of the bulk modulus B and

the shear modulus G [9] as

$$\bar{E} = \frac{9BG}{G + 3B} \quad (7)$$

$$\bar{\nu} = \frac{3B/2 - G}{G + 3B} \quad (8)$$

since $B = (c_{11} + 2c_{12})/3$ is an invariant and G is a solution of the Hershey-Kröner-Eshelby equation [10]

$$8G^3 + (9B + 4C')G^2 - 3C(B + 4C')G - 6BCC' = 0 \quad (9)$$

where C and C' are the two Zener elastic constants ($C = c_{44}$ and $C' = (c_{11} - c_{12})/2$). On inserting the elastic stiffnesses c_{ij} of Table 1, eqn. (9) yields $G = 535$ GPa; in conjunction with a bulk modulus B of 442 GPa, this leads to the results listed in Table 3, row 4, and the reader may verify that these numbers correlate very well with our evaluation of average elastic properties for the main symmetry planes of diamond.

TABLE 3. Calculated values of Young's modulus ($\bar{E}$), Poisson's ratios ($\bar{\nu}$, $\bar{\nu}'$) and the biaxial modulus for fiber-textured CVD diamond deposits and for random aggregates of diamond crystallites

Texture	$\bar{E}$ (GPa)	$\bar{\nu}$	$\bar{\nu}'$	$\bar{E}/(1 - \bar{\nu})$ (GPa)
(111)	1164	0.0791	0.0435	1264
(110)	1151	0.0730	0.0592	1242
(100)	1106	0.0569	0.1089	1173
Random ^a	1143	0.0691	0.0691	1228

^aBased on the Hershey-Kröner-Eshelby averaging method.

4. Bulge test method

Relevant concepts and instrumentation for obtaining the modulus of diamond films by means of bulge testing are described in a recent paper by Cardinale and Tustison [11]. A circular membrane of radius r_0 and thickness t_0 is subjected to a differential pressure Δp

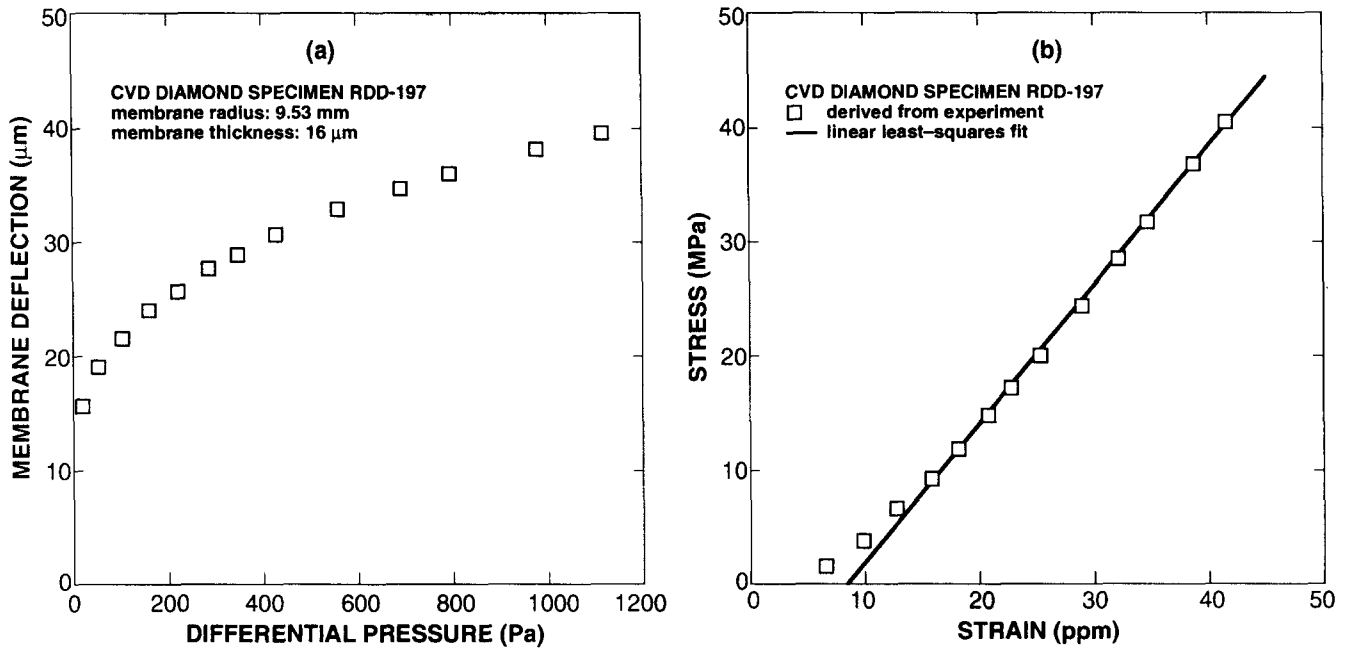


Fig. 2. An illustration of the bulge test method for obtaining the biaxial modulus E' of diamond films: (a) measured peak deflections as a function of the differential pressure; (b) stress-strain plot derived from the deflections upon using eqns. (10) and (11) with β set equal to 2.46; note that the slope yields $E' = 1217 \pm 18$ GPa, in good agreement with the predicted value for randomly orientated diamond aggregates (see Table 3).

which induces a deflection of height h on the center-line. Since the peak tensile stress amounts to [12]

$$\sigma = \frac{\Delta p r_0^2}{4 t_0 h} \quad (10)$$

if the condition $h \ll r_0$ holds, and since the strain obeys the relation [13]

$$\varepsilon = \frac{\beta h^2}{r_0^2} \quad (11)$$

where β represents a numerical factor, it follows that the biaxial modulus can be derived from a stress-strain plot on using the differential pressure as a variable.

For spherical deflections the factor β is known to be equal to $\frac{2}{3}$. In our experiments, however, the shape of the deflected films was found to be non-spherical, which required "calibrating the instrument" in the sense that β had to be determined empirically by performing a sequence of bulge tests on reference materials (silicon and glass) in appropriate geometries. By comparing measured and known values of the biaxial modulus, it was established that $\beta = 2.46$ should be suitable for the range of deflections of interest here.

Figure 2 illustrates the procedure in the light of data collected on a typical diamond film membrane ($r_0 = 9.53$ mm, $t_0 = 16$ μm) obtained by the microwave-power-assisted deposition process. In Fig. 2(a) are the peak deflections recorded for differential pressures ranging up to 1.12 kPa; in Fig. 2(b) the stresses are

plotted as a function of strain, based on the results of evaluating eqns. (10) and (11). A least-squares fit to the linear portion then yields

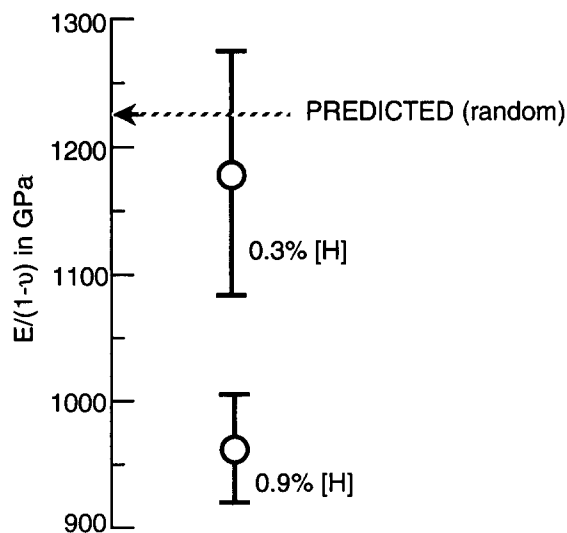
$$\sigma = -10.27 + 1.217\varepsilon \quad (12)$$

where σ is in megapascals and ε is in parts per million, which indicates that this film has a residual compressive stress of 10.3 MPa and a biaxial elastic modulus of approximately 1220 GPa.

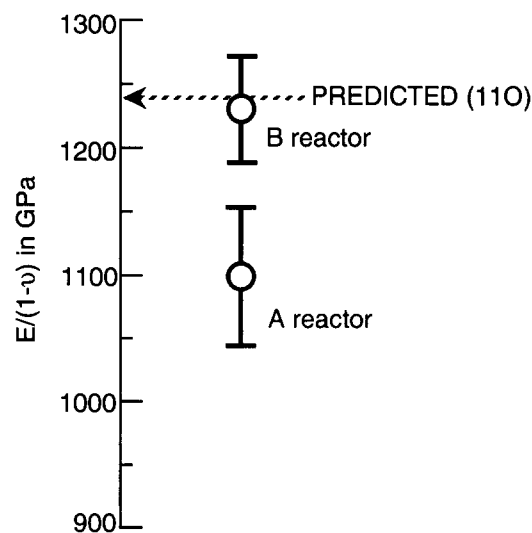
5. Results and discussion

Our results are summarized in Fig. 3. With microwave-power-assisted CVD diamond, which exhibits no or little texture, we find that for high quality deposits with hydrogen contents of less than 0.3% the biaxial modulus $E' = 1177 \pm 98$ GPa is in reasonable agreement with the predicted value for randomly orientated aggregates (see Table 3); specimens of higher hydrogen content have significantly lower moduli, in accord with observations made on hydrogenated hard carbon films [14]. Hot-filament-assisted CVD diamond exhibits a high degree of (110)-preferred orientation, which implies a biaxial modulus of about 1240 GPa, in good agreement with the results of measurements that were carried out on material deposited in our B reactor (see Fig. 3); A-reactor material, which is of lower quality as ascer-

Biaxial Modulus Testing at Raytheon/Research



Microwave-Power Assisted CVD Diamond



Hot-Filament Assisted CVD Diamond

Fig. 3. Summary of biaxial modulus test results. Microwave-power-assisted CVD diamond films have no texture, but the modulus is dependent on the residual hydrogen content. Hot-filament-deposited CVD diamond films exhibit some strong (110) texture; A-reactor deposits are of lower quality than B-reactor material as evidenced in terms of hydrogen and/or silicon carbide content.

tained by Fourier transform IR spectroscopy, again yields moduli that are below the expected value.

Similar but slightly higher numbers have also been reported by Windischman *et al.* [15], who made use of the bulge test technique to measure the biaxial modulus of a broad array of CVD diamond specimens and observed a strong dependence of E' on the methane concentration during deposition. More recently, Gray [16] reported on the results of ultrasound velocity measurements that were performed on "optical grade" CVD diamond and concluded that Young's modulus and Poisson's ratio should be close to 1180 GPa and 0.148 respectively. Since the elastic constants of CVD diamond are known to be similar to those of single-crystal diamond [17], such large Poisson ratios are incompatible with the results of our analysis (see Fig. 1); in this connection we note that Gray's bulk modulus ($B = 558 \pm 12$ GPa *vs.* 442 GPa as derived from the elastic constants) cannot be accurate, since B is an invariant and therefore independent of any preferred orientation (see Section 3).

With regard to *direct* measurements of the elastic modulus of single-crystal diamond, the recent ultralow indentation experiments performed by Cooper and Beetz [18] on (100), (110) and (111) faces of type IIa monoliths probably provide the best available data, but excessive scatter precludes a meaningful assessment of the aniso-

tropy; nevertheless, the data point to an average modulus of about 1150 GPa, in excellent agreement with the predicted value of 1143 GPa, especially since the slope of the unloading curve generated through indentation yields an effective modulus $E^* = E/(1 - \nu^2)$ rather than a true modulus [5]. McHargue's [19] indentation testing of a IIa diamond gave $E^* \approx 1280$ GPa, which is larger than expected though not surprising considering that at higher loads the indenter may cause some densification and thus enhance the effective elastic modulus. Poisson's ratio has not yet been measured on single-crystal diamond, but as early as 1978 it was known that ultrasound propagation experiments yield $\nu = 0.0718$ for sintered polycrystalline diamond compacts [20], which we believe to be a "good number" even though it was not given proper consideration in subsequent work.

6. Conclusions

We have shown that setting E equal to 1050 GPa and ν equal to 0.2 is inappropriate for describing the elastic properties of monocrystalline as well as polycrystalline diamond. Single-crystal diamond exhibits isotropic properties in the (111) plane ($E = 1164$ GPa, $\nu = 0.0791$), but directionality equations must be used

for characterizing Young's modulus and Poisson's ratio when the stresses are not in that plane. Textured CVD diamond films may have significantly different elastic coefficients depending on the nature of the preferred orientation (see Table 3); presently available experimental data are not precise enough to demonstrate unambiguously the elastic anisotropy, but they confirm that the elastic constants of high quality CVD diamonds should be the same as those of natural type IIa diamonds.

Acknowledgments

The authors wish to thank T. Hartnett, R. Miller, P. Morissette and C. Robinson for providing the CVD diamond films that were used in this investigation and for their assistance in the characterization process.

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