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MECHANICAL PROPERTY MEASUREMENT OF POLYCRYSTALLINE DIAMOND FILMS

by

G. F. Cardinale and R. W. Tustison

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July 8, 1990

Raytheon Company
Research Division
Lexington, Massachusetts 02173

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Mechanical property measurement of polycrystalline diamond films

G. F. Cardinale, R. W. Tustison

Raytheon Company, Lexington, Ma. 02173

ABSTRACT

The biaxial modulus and residual (post deposition) stress of polycrystalline diamond (PCD) films deposited by microwave plasma CVD is determined using the bulge test technique. This method involves measuring the deflection of a circular membrane under an applied differential pressure. A calibration parameter for the bulge test is determined by evaluating the biaxial modulus of a silicon specimen standard. The film is characterized using X-Ray diffraction. Preliminary results yield a biaxial modulus value of 960 GPa for the PCD film.

1. INTRODUCTION

Diamond inherently exhibits several unique physical and optical properties, enabling its use in various applications. Its large bandgap (5.45 ev[1]) and covalently bonded aliphatic sp^3 hybridized carbon atoms arranged tetrahedrally result in an optical transparency in wavelength from 220 to 2500 nm and wavelengths above 6000 nm (beyond mid-infrared). Diamond is extremely hard, highly thermally conductive, and has both low coefficient of thermal expansion as well as high elastic modulus. This combination of properties results in diamond being extremely resistant to thermal shock as is characterized by the thermal shock resistance figure of merit R:

$$R = \frac{(1-\nu)\,\sigma\,\kappa}{E\,\alpha}$$

where ν equals the Poisson ratio, σ is the fracture strength, κ is the thermal conductivity, E the elastic (Young's) modulus, and α is the coefficient of thermal expansion[2]. Similarly, the damage velocity threshold, v_t for brittle materials impacted by water drops has been has been related to the fracture toughness, K_c, and the elastic wave velocity, c_t, which is equal to $(E/\rho)^{1/2}$ where ρ is the density of the material:

$$v_t = a\,K_c^{2/3}\,c_t^{1/3}$$

where a is a constant of proportionality[3]. Thus diamond is an ideal candidate for long wavelength infrared domes or dome coatings which require broadband transmittance, resistance to thermal shock caused by aerodynamic heating, and high impact damage resistance.

It is apparent from the above equations that in order to fully evaluate both the resistance to thermal shock and the damage threshold velocity for a particular material, the elastic modulus must be known. Thus an accurate measurement of Young's modulus is necessary to compare these figures of merit for various materials and coatings. The elastic modulus data for both hard or diamond like carbon (DLC) and diamond thin films in the literature is both scarce and scattered. A summary of this data is provided in table 1.

Several methods have been used to measure the elastic modulus of thin films including cantilevered beam[9], vibrating reed[4], nanoindentation[10,11], and the biaxial modulus (bulge) test[12,13]. Details of these techniques can be found in the literature. The biaxial test is chosen because the necessary apparatus is readily available and the sample preparation is straightforward. A somewhat detailed description of the bulge test method shall be presented in the experimental section of this paper.

Film	Processing Method	Modulus	Measurement Technique	Reference
Carbon	Arc Discharge	20	Vibrating Reed	(4)
DLC	CVD	810, 820	Ultramicroindentation	(5)
DLC	RF Discharge	94	Ultramicroindentation	(10)
PCD	Sintering	749 - 953	Speed of Sound	(6)
PCD	Filament Assisted	536, 874	Nanoindentation	(23)
PCD	MPCVD	960	Bulge Test	Present Study
SCD	(natural)	1050	Speed of Sound	(7)
SCD	(natural)	1054	Brillouin Scattering	(8)

Key: DLC = Diamond Like Carbon, PCD = Polycrystalline Diamond, SCD = Single Crytal Diamond, CVD = Chemical Vapor Deposition, MPCVD = Microwave Plasma CVD.

Table 1.0 Summary of modulus measurements for diamond like carbon and diamond films.

2. THEORY

The hoop stress σ of a thin circular shell is given by[14]

$$\sigma = \frac{PR}{2t}$$

where P is the internal pressure on the membrane, R equals the radius of curvature of the deflected film, and t represents the film thickness (refer to figure 1).

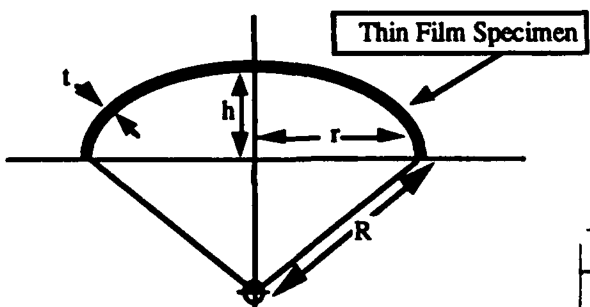

Figure 1. Bulge geometry.

From trigonometric relations, the stress is therefore equal to:

$$\sigma = \frac{Pr^2}{4th} \quad \text{for } h \ll r$$

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Typically, h = 70 to 100 μm and r = 5 to 10 mm, thus the above criterion is satisfied. Since the parameters r and t are known, the biaxial stress in the thin film can be determined by measuring the bulge height at any time. If the residual stress σ_0 as developed by Beams[15] is included, the following pressure height relation is obtained:

$$P = \frac{4\,t\,\sigma_0}{r^2}\,h + \frac{8t}{3r^4}\,\frac{E}{(1-\nu)}\,h^3$$

Therefore if a plot of pressure versus deflection is constructed and the curve is fit to a third order polynomial, the residual stress and the biaxial modulus can be determined from the first and third order terms, respectively, of the polynomial equation. While this technique has been used[12] it is the experience of the authors that the third order term is extremely sensitive to fluctuations in the data at the noise level and therefore an alternate method of evaluating the modulus is chosen. For a circular membrane which is thin compared to the radius of the aperture, the strain at the center of the film, ε, is[13,15]

$$\varepsilon = \beta \frac{h^2}{r^2}$$

Where β is a constant equal to 2/3 for a hemispherical bulge[16]. However, deviations from ideal hemispherical shape are expected and have been studied by Tsakalakos[17]. Therefore, in practice measurements are made on materials of known biaxial moduli to quantify such deviations. A calibration parameter β' can therefore be considered when evaluating the strain in the center of a film bulged to a near-hemispherical geometry. This calibration parameter is considered to be a function of deflection of the membrane since the aspect ratio h/r represents the degree of deviation from hemisphericity of the deflected membrane. Determination of β' involves bulging an elastic material sample of which the mechanical properties are known over a given deflection range and aperture size and comparing the measured biaxial modulus, E_{meas} (using β = 2/3) with the known value, E. An assumption that the calibration parameter β' is not a function of modulus for stiff, elastic materials is made here.

Since the stress and strain of the film is calculated knowing the pressure and deflection of the film, a stress-strain curve is generated using the measured pressure-height data, and the slope of a linear curve fit of the data is the biaxial modulus. An extrapolation of the curve to a state of zero strain is used to obtain the residual stress σ_0.

3. EXPERIMENTAL

3.1 TEST SPECIMENS:

Silicon:

For the calibration parameter determination, a one inch diameter <100> single crystal silicon substrate is lapped and polished to approximately 124 μm thickness measured by micrometer at several locations and taking an average value. The silicon is then placed in a fixture which firmly holds the sample in place so that there is no bowing of the outer edge and thus there is no slippage inward toward the center. The radius of the aperture over which the vacuum is applied is 9.53 mm. A schematic representation of a specimen under test is shown in figure 1. A differential pressure of approximately 0.1 to 0.2 MPa is applied to the circular aperture defined by the specimen holding fixture, and a corresponding deflection of 70 to 80 μm is measured.

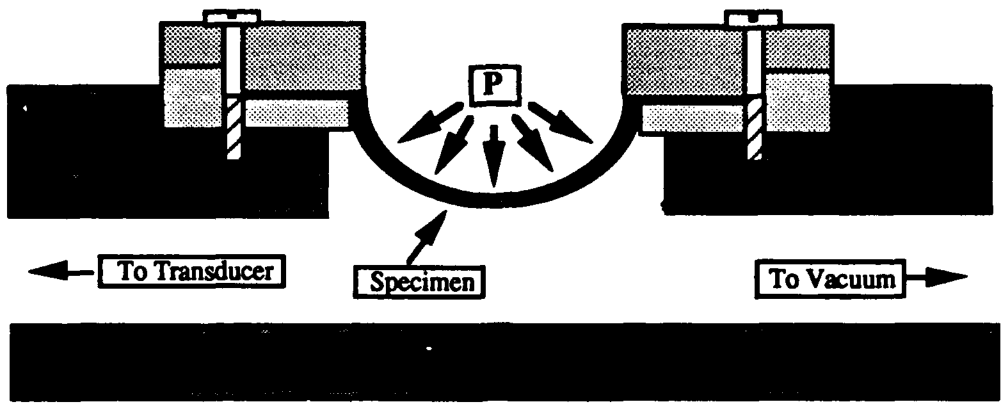

Figure 2. Thin film specimen under test.

Diamond:

The diamond films are deposited on 1 inch diameter, 375 μm thick <100> silicon substrates by microwave plasma CVD. The substrate is ground with 1 μm diamond paste and cutting oil, then ultrasonically cleaned with acetone. A deposition rate of approximately 0.5 μm per hour is obtained using the deposition conditions listed below in table 2.0. Optical interference fringes derived from spectroscopic measurements result in a thickness determination of 9.31 μm assuming an index of refraction value of 2.36. The accuracy of this method depends on the validity of the bulk diamond index value assumption. A cross section SEM micrograph (see figure 3) of the diamond film indicates an approximate thickness of 11 μm however the micron marker has a 10% accuracy compared to 1% for the weighing method, and the nonuniformity in thickness of the film contributes to this discrepancy. SEM analysis shows a dense film with a smooth surface. A 9.61 μm thickness of the diamond film is measured by weighing the substrate before and after deposition and assuming a bulk density value[18] of 3.515 g/cm^3. The thickness calculated by comparative weight analysis therefore represents an average thickness and is the preferred method of measurement.

Parameter	Value	Units
Substrate Temperature	675.0	C
Total Pressure	30.0	Torr
Gas Flow Rate:		
H2	483.0	sccm
CH4	15.0	sccm
O2	2.5	sccm
Microwave Power	1200.0	Watts

Table 2. Deposition parameters for PCD films.

X-ray diffraction analysis (refer to figure 4, note the single crystal diamond peaks along the abscissa) indicates that the film is primarily polycrystalline diamond with some (220) texture. In consideration of the effects of orientation on the measured modulus, the condition for anisotropy is given by the following relation:

$$\frac{2C_{44}}{C_{11}-C_{12}} = 1$$

Substitution of the stiffness coefficients[8] yields 1.21 and thus there is not a high dependence of Young's modulus on orientation. Fourier transform infrared (FTIR) spectroscopy is used to calculate the amount of hydrogen in the film by analysis of absorption by C-H bond stretching[19] and is found to be approximately 0.95 %.

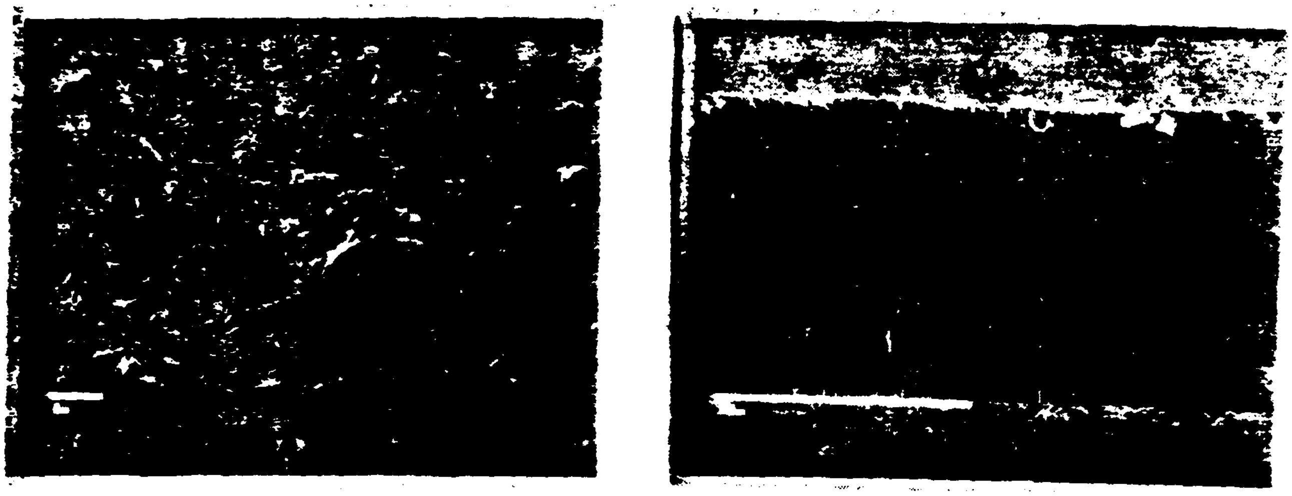

Figure 3. SEM micrographs of Diamond film, surface (l) and cross section (r).

A membrane of polycrystalline diamond in the center of the silicon substrate is formed as follows: A teflon cylinder with a 19.06 mm. inner diameter is used to define the aperture in the diamond film. Apiezon grease is coated on the flat surface of the cylinder and the specimen is brought into contact with the grease layer, silicon side facing the grease. A one-to-one mixture of concentrated nitric and hydroflouric acids is used to anisotropically etch through the silicon with the grease providing an etch stop around the periphery of the silicon substrate. Although this technique does not produce as sharply a defined circular aperture as lithographic processes, visual inspection by optical microscopy indicates an acceptable, near-circular aperture.

3.2 Biaxial Modulus Test System

Figure 5 represents a schematic diagram of the measurement test system. A vacuum is applied to the membrane over a defined area which causes the membrane to deflect in the direction of lower pressure. An MTI-1000 fotonic sensor photo-probe measures the amount of deflection with an accuracy of 0.10 μm. The amount of applied vacuum is measured using an OMEGA vacuum transducer. The outputs of both the transducer and the photo-probe are analog D.C. voltages which are digitized using two separate digital volt meters (DVMs). Both DVMs are equipped with IEE-488 bus capability for the purpose of interfacing with a personal computer. This facilitates both the logging and analysis of the data. The pressure range used is approximately 0 to 200 kPa resulting in a deflection of up to 70 to 100 μm depending on the material tested.

4. RESULTS

4.1 Calibration Parameter

Sample pressure-height and corresponding stress-strain curves for <100> single crystal silicon are provided in figure 6. A total of ten tests results in an average (uncalibrated, $\beta=2/3$) biaxial modulus value of 73.68 ± 4.94 GPa for a 73 to 77 μm deflection range, and 9.53 mm radius aperture. The calculated biaxial modulus for silicon is 180.20 GPa using biaxial modulus equations for an anisotropic elastic solid reported by Nix[20] and the following stiffness coefficients for silicon[21] (in dyne/cm^2): $C_{11} = 1.66 \times 10^{12}$, $C_{12} = 6.39 \times 10^{11}$, $C_{44} = 7.95 \times 10^{11}$. The calibration parameter β' is found to be 2.46 for this deflection range and 9.53 mm radius aperture.

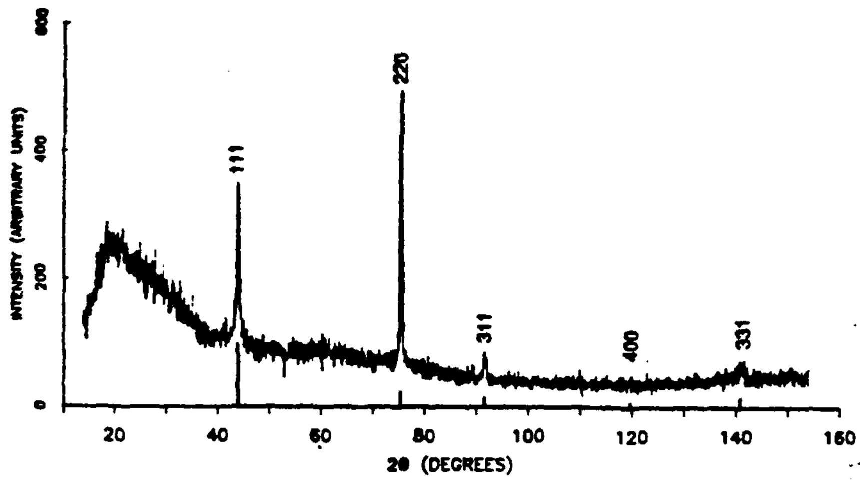

Figure 4. X-Ray diffraction scan of PCD film.

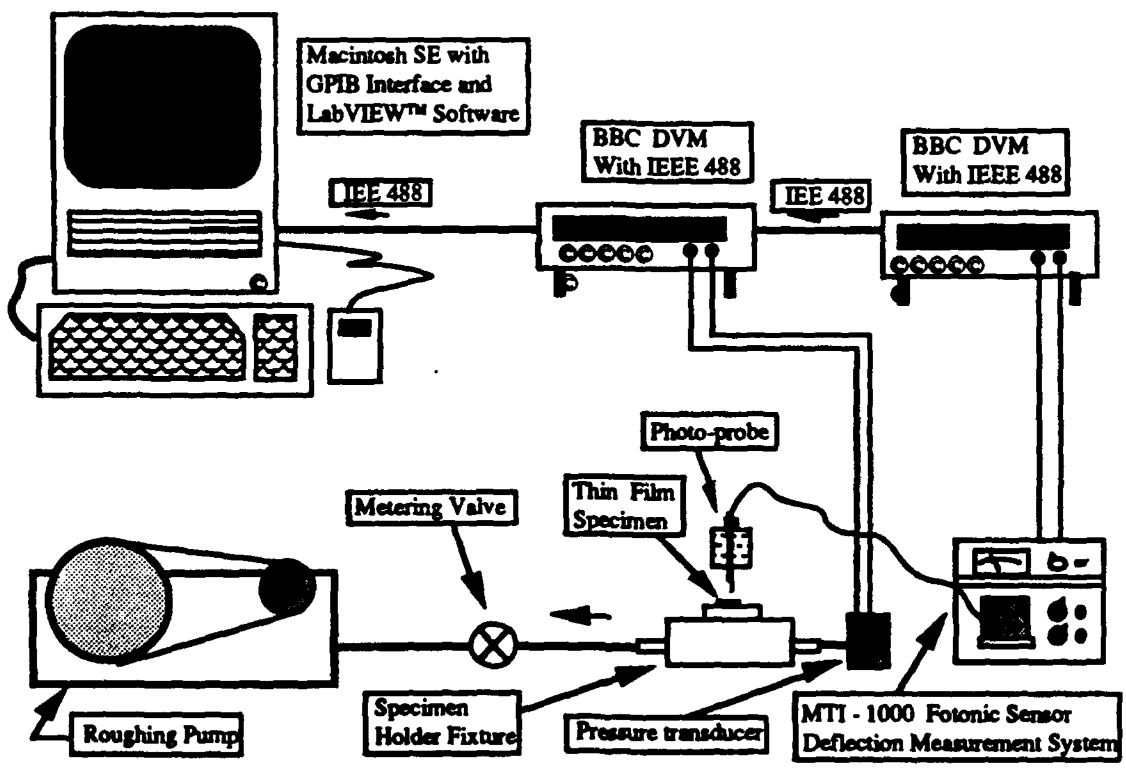

Figure 5. Schematic of Biaxial Modulus Test System.

4.2 Diamond Film

A summary of results of biaxial modulus determination for the 9.61 μm thick polycrystalline diamond film is provided in table 3. Sample pressure-height and stress-strain curves for the diamond film are shown in figure 7. The calculated average biaxial modulus value is 960.14 ± 38.41 (4.01%) GPa. Since the biaxial modulus is related to the elastic (Young's) modulus by a factor of $(1-\nu)^{-1}$, to calculate Young's modulus it is necessary to know Poisson's ratio for polycrystalline diamond films. A calculated value of 0.10 for the Poisson ratio of bulk diamond using the stiffness constants reported by Grimsditch and Ramdas[8], and a value of 0.07 for polycrystalline diamond films measured by ultrasonic means[22] are considered. Substitution of these values into the biaxial modulus-Young's modulus relation yields 864.13 GPa ($\nu = 0.10$) and 892.93 GPa ($\nu = 0.07$) for the elastic modulus. Both values are comparable to the single crystal bulk diamond and polycrystalline diamond films.

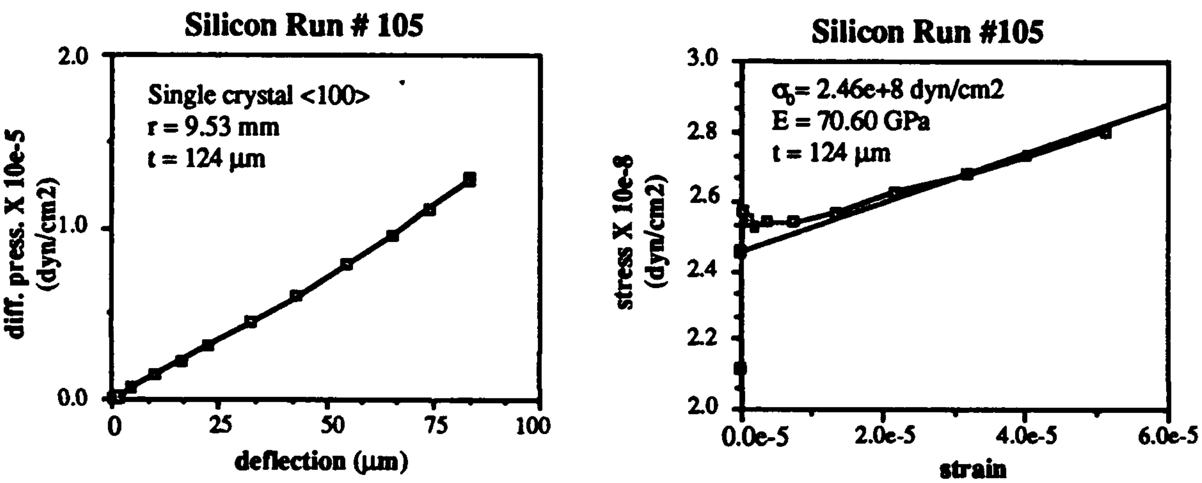

Figure 6. Sample pressure-deflection and stress-strain curves for silicon standard

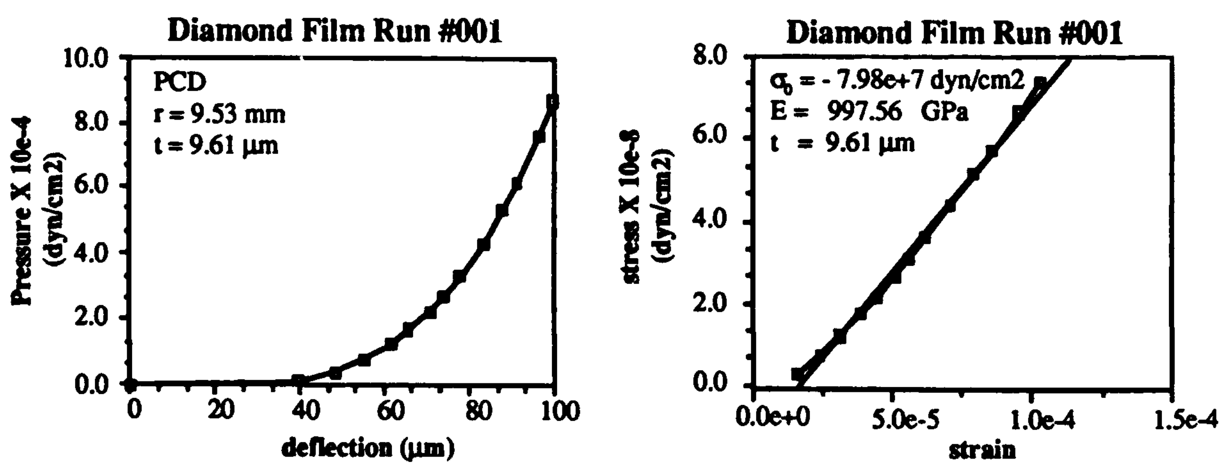

Figure 7. Sample pressure-height and Stress strain curves for PCD film.

Run #	Residual Stress (dyn/cm2)	Biaxial Modulus (GPa)
101	-7.98 X 10 e7	997.56
102	-1.57 X 10 e8	960.02
103	-8.26 X 10 e7	980.18
104	-1.08 X 10 e8	923.81
105	-9.15 X 10 e7	897.75
106	-9.66 X 10 e7	1001.53
Average	-9.57 X 10 e7	960.14
St. dev.	1.41 X 10 e7	41.78

Table 3. Summary of Diamond Film Measurements.

5. DISCUSSION

The biaxial modulus for microwave plasma CVD polycrystalline diamond films is measured and found to be 960 GPa with a standard eviation of 4.3%. This value is within approximately 15% of the value for bulk single crystal diamond. Differences between these values may be attributed to microstructural effects such as grain sixe[6] or crystallographic orientation.

Regarding the bulge test, improvements in the biaxial modulus measurement method might include an AC application of vacuum to the membrane since the photoprobe is capable of measuring dynamic deflections. The benefit of this modification is the reduction in the $1/f$ noise level associated with several types of measurement techniques. Also, lithographically defining the aperture of the free standing membrane would reduce the uncertainty in the measurement of this parameter.

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