Fracture strength of freestanding chemically vapordeposited diamond films

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Fracture strength of free-standing chemically vapor-deposited diamond films

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The fracture strength of free-standing chemically vapor-deposited diamond films was assessed by four-point bending. A two-parameter Weibull analysis was performed on 130 μm thick films resulting in a Weibull modulus of 4.3 and a statistical scaling stress of 626 MPa. The residual stress in films was measured from the free-standing film curvature to be 384 ± 10 MPa. The fracture surface chemistry was examined using scanning Auger spectroscopy. The fracture did not occur preferentially along grain boundaries. © *1995 American Institute of Physics.*

Thin to thick polycrystalline diamond films can be produced by chemical vapor deposition (CVD) to be used for a variety of applications. The properties of diamond that make it an extremely viable engineering material are its extreme values of hardness, Young's modulus and (room temperature) thermal conductivity.[1,2] Another property of interest, fracture strength, has received less attention in the literature due to the difficulties involved in testing films. Therefore, fracture related information is available for conformal films on deposition substrate materials (e.g., silicon) or, in limited quantities, for free-standing films. Mecholsky *et al.*[3] report fracture strength measurements for 6–12 μm thick diamond on 2.7 mm thick silicon substrates. They found relatively low fracture strength values due to the influence of the underlying substrate but with an increase in strength over that of the weaker silicon substrate due to a compressive residual stress. Cardinale and Robinson[4] report pressure–rupture strengths for free-standing films of markedly different thicknesses from which fracture statistics have been reported for limited populations of films.[5]

Indentation studies[6] of free-standing diamond films have shown the fracture toughness to be 5.3 ± 1.3 MPa $m^{1/2}$. While fracture toughness data provide a measure of a material's resistance to crack propagation, reliability assessment is essential for material designers by a fracture statistics approach as elaborated below. One means of determining reliability is by examining the inherent strength of a material from naturally occurring flaws. This work employs brittle materials testing methods to study the strength of free-standing diamond films. Bend testing is performed with the planar substrate interface as the tensile surface since strength values are thickness (grain size) dependent[4] and strongly coupled to the stress state upon substrate removal. From individual strength tests, the statistical nature of failure/reliability is assessed using Weibull statistics to provide important design parameters, namely the characteristic strength and the Weibull modulus, a measure of strength variability.[7]

Continuous diamond films were grown on silicon substrates by low-pressure synthesis methods using plasma-enhanced CVD with microwave excitation at 2.45 GHz. Two inch diameter silicon substrates of ⟨100⟩ orientation and approximate thickness of 3.2 mm were abraded with a fine diamond powder for enhanced nucleation. Process conditions were selected to achieve diamond growth in a predominantly hydrogen plasma with carbon-rich precursor gases with a total gas pressure of 80–90 Torr and 200–250 cm^3 min^{-1} total flow rate. Deposition was performed at temperatures between 800 and 950 °C with the reactor operating at less than 2 kW of power. Chemical etching in a solution of hydrofluoric, nitric, and acetic acids provided free-standing diamond films for use in this study. Samples of 130 μm×5 mm×25 mm were laser cut from the free-standing wafers to facilitate testing.

The free-standing films had grain sizes ranging from 2 to 20 μm with smaller, more equiaxed grains forming near the substrate/film interface. The diamond quality was determined using Raman spectroscopy (Fig. 1). The strong characteristic peak at 1333 cm^{-1} indicates a relatively high diamond quality, especially given the absence of broad sp^2 bonded (non-diamond) carbon peaks at 1355 and 1560 cm^{-1}.

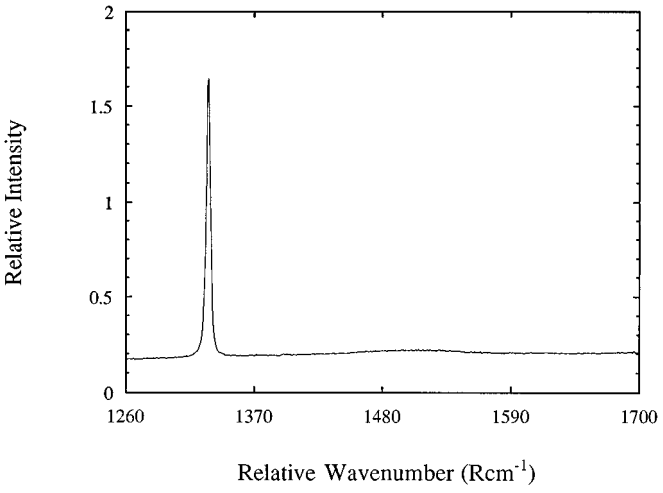

FIG. 1. Raman spectrum of diamond film.

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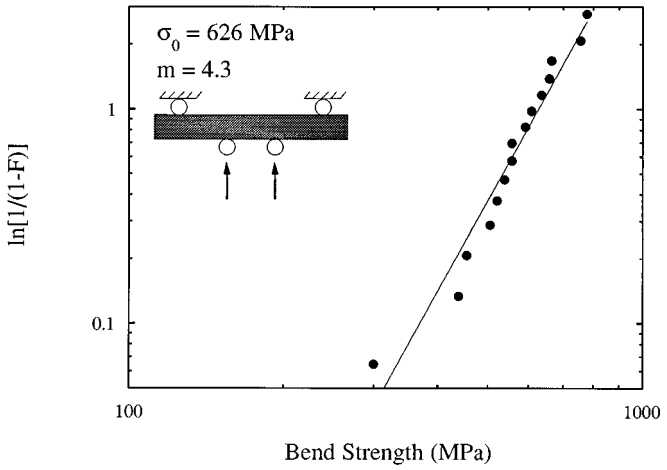

FIG. 2. Weibull plot for free-standing diamond films tested in the four-point bending geometry (shown schematically in inset).

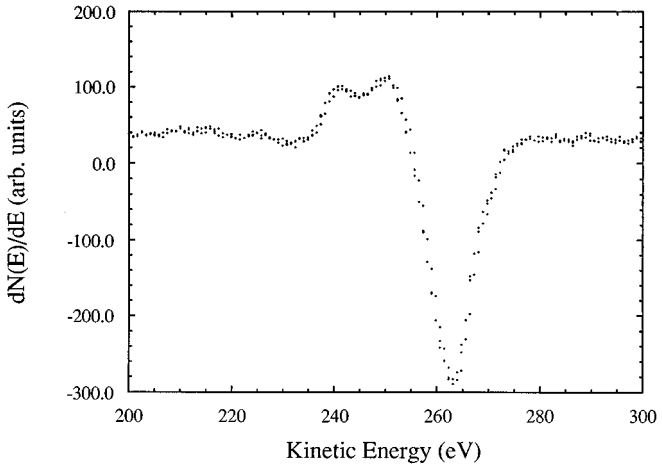

FIG. 3. Auger spectrum of a diamond film fracture surface.

Residual stresses in the free-standing diamond films originate from two primary sources: The stress due to thermal expansion difference between the film and substrate which develops on cooling from the deposition temperature, and the ''intrinsic'' or ''growth'' stresses in the CVD film. When the system is chemically etched to produce a free-standing film, the residual stress is modified by film/substrate bending to produce a film with a convex conformal substrate surface. It remains for future work to decouple the contributions of the thermal mismatch and the intrinsic stresses. For the case where the substrate thickness is much greater than the film thickness, the residual stress σ_R, can be determined from the beam curvature ρ measuring the deflection h_0 over a span length s such that:[8]

$$\rho = \frac{h_0}{2} + \frac{s^2}{8h_0}, \tag{1a}$$

$$\sigma_R = \frac{Ec}{\rho}, \tag{1b}$$

where E is the elastic modulus and $2c$, is the beam thickness. From Eq. (1), the residual stress is readily measured as 384 ± 10 MPa.

Fracture testing was performed by four-point bending as shown schematically in Fig. 2 (inset), and is commonly used to evaluate the strength of brittle materials.[9] A lubricant of lightweight machine oil was applied to the rollers and sample for minimizing tangential loads due to friction at the contact points. Although the outer span was fully constrained, the inner span was positioned on a lubricated spherical washer assembly to accommodate alignment of the bend fixture under low applied loads. Samples were oriented with the conformal substrate side as the tensile surface and tested at a strain rate of 7×10^{-8} s^{-1}. Samples were tested following the initial curvature rather than bending the beam back to horizontal and inducing an opposite curvature (accompanied by buckling). As a result, the maximum tensile stress was located in the diamond coating surface where the surface flaws are expected to be strength-limiting. Films with an average thickness of 130 μm tested in four-point bending demonstrated linear-elastic loading to failure. The strengths of 15 bend specimens were determined and a cumulative probability distribution to failure was calculated to provide the basis for a two-parameter Weibull analysis where the cumulative probability of failure F is given as:[10]

$$F = 1 - \exp\left[-V \left(\frac{\sigma}{\sigma_0} \right)^m \right] \tag{2}$$

for the effective volume V, scaling stress σ_0, and Weibull modulus m. A least squares fit to the data in Fig. 2 yields a Weibull modulus of 4.3 and a scaling stress of 626 MPa which result in an average strength ($F=0.5$) of 533 MPa. The confidence interval for the Weibull parameters is a function of the number of observations[11] with a sample size of 15 being an acceptable lower limit for preliminary testing.

Scanning Auger spectroscopy was performed to examine the chemistry of the fracture surface. Samples were affixed as cantilevers to copper rods with a low vapor pressure resin and fractured *in vacuo* at pressures less than 9×10^{-9} Torr. Auger analysis was performed at 3 kV with 4 V peak-to-peak resolution. Figure 3 shows a characteristic Auger fine structure about the carbon (*KLL*) peak at the fracture surface. Comparing the fine structure information from Fig. 3 to the fine structure of diamond, graphitic, and amorphous carbon[12,13] and Auger spectra of similar films,[14] there is no evidence of a predominantly nondiamond fracture path. Since sp^2 carbon represents a relatively weak plane of bonding in graphite,[15,16] it remains for future work to establish its effect in mixed bonding-type materials such as CVD diamond. A critical consideration is the location of planes of weakness in the microstructure.

In summary, the residual stress resulting from thermal expansion mismatch of a diamond film and a silicon substrate was measured from beam curvature once the silicon was removed. A residual stress of 384 ± 10 MPa was measured from the film curvature. The fracture behavior of free-standing diamond films was examined in four-point bending with the maximum tensile stress on the diamond film surface. From a two-parameter Weibull analysis, the Weibull modulus m was determined as 4.3 with a scaling stress σ_0 of

626 MPa. Auger spectroscopy performed on *in vacuo* fractured specimens showed no evidence of a nondiamond carbon fracture path at the microscopic level. Although the films are of adequate strength, the relatively low Weibull modulus suggests a wide strength distribution which, due to Auger results, does not appear to be the result of a predominantly nondiamond intergranular phase. Further work is needed to identify the sources of the broad distribution of flaw sizes to allow for mechanical design with narrower definition of the failure stress. For example, a Weibull modulus of 10 is deemed acceptable for many designs with structural ceramics.[17,18]

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