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Fracture Toughness of Chemically Vapor-Deposited Diamond

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The fracture toughness of chemically vapor-deposited diamond is estimated by a Vickers indentation method. Free-standing diamond films of 400-μm thickness are produced with plasma-enhanced chemical vapor deposition and highly polished for indentation testing. Indentation testing was performed with a microhardness tester using a load range of 5 to 8 N. The average fracture toughness is estimated as 5.3 ± 1.3 MPA·m$^{1/2}$. [Key words: fracture toughness, diamonds, chemical vapor deposition (CVD), films, indentation.]

I. Introduction

There is now considerable interest in commercialized diamond film technology produced by chemical vapor deposition (CVD). Numerous applications have been identified, such as detector windows, heat sinks, and tooling, which exploit the superior material properties of diamond. Despite the enormous potential of CVD diamond, the mechanical properties are largely unknown. Measurement of these properties is difficult because of the extreme hardness of diamond, and proper interpretation of test results is complicated by issues of film quality (diamond vs diamond-like carbon) and morphology. A recent review on the physical properties of CVD diamond reveals that fracture properties have been explored by strength measurements from burst testing of films.[1] However, measurements of fundamental fracture properties, such as fracture toughness, K_c, were unavailable. The fracture toughness of CVD diamond is reported here from indentation measurements.

II. Experimental Procedure

A diamond film was grown using plasma-enhanced chemical vapor deposition at 2.45 GHz. The necessary conditions for diamond deposition were achieved at 1.5 to 2.0 kW and a total gas pressure of 80 to 90 torr (~107 × 10^2 to ~120 × 10^2 Pa). Reactant gases H_2, CH_4, and CO were premixed and metered with flow controllers at flow rates of 250 to 200 sccm. The substrate was a 2-in. (~5.1-cm) diameter, 1/4 in. (~0.6 cm) thick [100] silicon wafer. To enhance nucleation, the wafer was polished with 0.1-μm diamond powder, then rinsed in isopropyl alcohol and deionized water to remove all diamond powder from the surface. After deposition, a free-standing diamond film was obtained by backetching the silicon using HF:HNO_3:HAc in a 2:2:1 ratio.

The diamond film used in this investigation had a maximum thickness of 400 μm unpolished, with an approximate 20-μm grain size. The grains are {100} form with (111) perpendicular to the plane of the film. In addition, twinning is observed on {111} (Fig. 1). The film was characterized by Raman spectroscopy (Jobin Yvon, Edison, NJ) scanning from 1200 to 1700 cm^{-1} to determine the presence of diamond, non-diamond carbon, and graphite. The Raman spectrum taken from the top surface of the diamond film shows the characteristic diamond peak at 1331 cm^{-1} (Fig. 2). The lack of broad peaks at 1355 and 1560 cm^{-1} indicates a low concentration of sp^2 bonded non-diamond carbon and graphite.

After characterization, the free-standing film was polished using a cast iron scaife and 4- to 12-μm diamond grit. Surface roughness of the polished film was obtained by contact profilometry using a 5-μm-radius stylus scanning 3 mm. The peak-to-valley surface roughness was found not to exceed 400 Å.

The hardness and fracture toughness of the polished film were measured with a microhardness tester (Zwick of America, Windsor, CT) using a Vickers diamond indenter under 5- to 8-N load performed in air under ambient conditions of temperature and humidity. As described in the next section, the hardness is determined from the impression size, while fracture toughness is related to the radial crack length.[2,3] Measurements of the impression size crack lengths were made with an optical microscope under 1000× (dry lens) magnification. The sample was sputter coated with a thin gold-palladium layer to enhance light reflection. The load range was selected to allow measurable indentation features with optical microscopy while reducing the tendency for indenter failure. Indentations at loads of 8 N or higher caused failure with fewer than five tests for a given Vickers indenter.

III. Results and Discussion

Eleven Vickers indentations of the polished diamond surface were made (Fig. 3), producing a hardness impression and radial crack lengths measurable in the optical microscope (Fig. 4). The hardness, H, is related to the impression size, $2a$, by

$$H = P/2a^2 \quad (1)$$

where P is the applied load. A plot of impression size vs load reveals a power law dependence of $a \sim P^{0.30}$. The hardness follows from Eq. (1) in the range of 57.5 to 108 GPa, with the average H = 80.6 GPa and standard deviation of 17.6 GPa. The size of impressions, $2a$, was 10 to 16 μm, which is smaller than the average grain size. The wide variation in hardness was due to the difficulty in measuring the impression size under low loads and the incidence of damage at the edge of impressions. Despite the large variation in hardness, the mean value is within about 10% of the 90 GPa value measured in other studies.[1,4] A narrower range of values of hardness values is likely to occur with Vickers indentations at higher loads (>10 N); however, indenter damage occurs with these loads after a single test.

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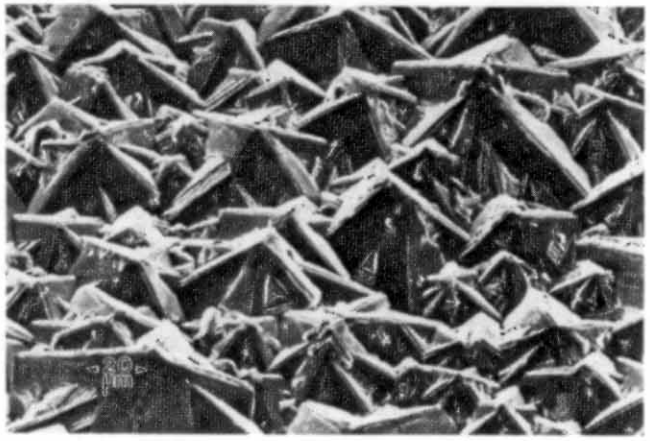

Fig. 1. Scanning electron micrograph of the diamond film surface prior to polishing.

The fracture toughness, K_c, is estimated from the Vickers indentation by measuring the radial crack lengths emanating from corners of the hardness impression. The crack length (c) hardness, and Young's modulus (E) are related to fracture toughness by

$$K_c = \xi(E/H)^{1/2}(P/c^{3/2}) \quad (2)$$

where ξ (=0.016 ± 0.004) is a calibration constant determined in a previous study of indentation fracture.[3] Fracture toughness values were estimated using Eq. (2) with E = 1000 GPa reported in the literature,[4] from values of radial crack length and hardness impression size vs load (Fig. 3). Observations were performed within several hours of the indentation experiments, in which no increase in crack length was observed over time for the samples tested. A plot of radial crack length vs load gives the best-fit slope for a power law function as 0.93. This deviates from the expected dependence of crack length on load given in Eq. (2) and may be the result of uncertainties in crack length measurements as elaborated below. K_c varied from 3.5 to 7.4 MPa·m$^{1/2}$ with an average value of 5.3 MPa·m$^{1/2}$ and a standard deviation of 1.3 MPa·m$^{1/2}$. This compares with K_c = 3.4 MPa·m$^{1/2}$ for natural diamond.[5]

The average K_c = 5.3 MPa·m$^{1/2}$ is an *upper bound* value of the fracture toughness, since the resolution of crack length in this study is limited by 1000× magnification. Higher resolution microscopy may reveal longer crack lengths, thereby reducing K_c for a given load. In addition to optical microscopy, crack length measurements were attempted with scanning electron microscopy (SEM) using a relatively low accelerating voltage of 5 kV to maximize the secondary electron yield. However, the crack lengths measured by SEM were shorter

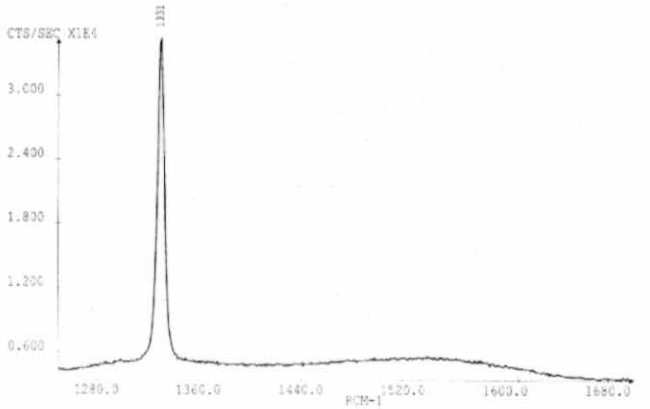

Fig. 2. Raman spectrum of diamond film revealing strong 1331-Å cm^{-1} peak.

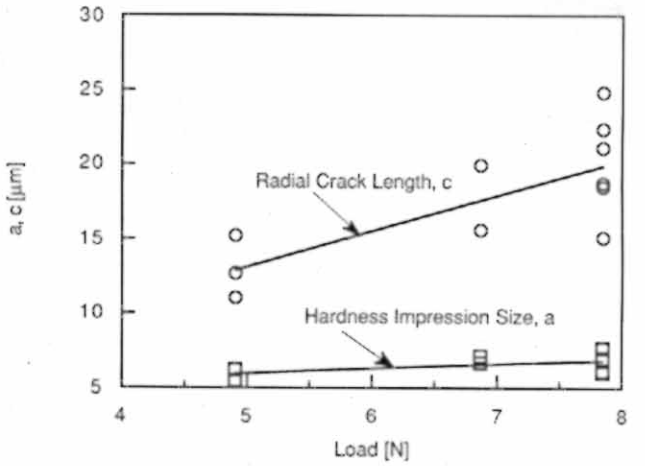

Fig. 3. Plot of radial crack length vs load and hardness impression size vs load.

than those measured by optical microscopy. Additional work is needed to further resolve crack length measurements. This is particularly important for indentation experiments with low loads, which is necessary for reasonable penetrator life.

Crack lengths in this study were a maximum 25 μm, which gives the total crack length, $2c$, on the order of the average grain size. Fracture toughness in this case may represent a mixture of intergranular and intragranular failure which requires microstructure analysis to quantify the fracture path. Ideally, the method for measuring K_c that was used here should use sufficient load to create radial cracks much longer than the grain size. However, the load necessary to create long indentation cracks in polycrystalline diamond far exceeds the fracture strength of the Vickers indenter. Further determination of fracture toughness may use other methods such as testing with double cantilever beam specimens. Additional work for indentation testing of CVD diamond includes verifying the existence of half-penny cracks.

IV. Summary

The fracture toughness of CVD diamond was estimated by the indentation method as 5.3 ± 1.3 MPa·m$^{1/2}$. This represents the first report of fracture toughness for plasma-enhanced CVD diamond and should be considered an upper-bound value for K_c where indentation crack lengths are on the order of the grain size. Additional work is needed to

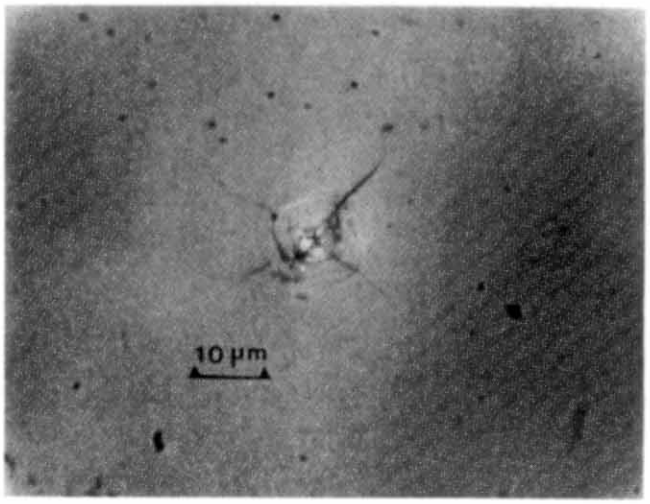

Fig. 4. Optical micrograph of Vickers indentation under 7-N load.

further resolve crack lengths, particularly under low indentation loads.

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