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Fracture strength of optical quality and black polycrystalline CVD diamonds ☆

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ABSTRACT

Three-point method has been used to measure bending strength σ_f of optical quality and opaque polycrystalline diamond films with thickness in the broad range of $h = 0.06–1.0$ mm grown by microwave plasma CVD. The free-standing films were characterized with microRaman spectroscopy, SEM, and optical profilography. For transparent samples the value of σ_f is found to approach 2200 MPa for thinnest sample when the substrate side is under tensile stress, reducing with film thickness to 600 MPa at $h \approx 1000$ μm, while for substrate side under the tension exhibits the strength a factor of two lower. The material tested shows transcrystallite fracture and the strength increase with grain size reduction. Also evaluated are Young modulus $E = 1072 \pm 153$ GPa, and the Weibull moduli $m = 6.4$ and $m = 4.5$ for the growth and substrate sides under tension, respectively. In contrast, the (100) textured black diamond films with pronounced columnar structure demonstrate intergranular fracture mode due to relatively weak (with non-diamond carbon component) grain boundaries, lower fracture surface roughness, and the two times lower strength compared to the "white" diamond.

1. Introduction

Polycrystalline chemical vapour deposited (CVD) diamond, owing to its unique combination of extreme physical and chemical properties, finds more and more applications in mechanics, optics, electronics and acoustics. Particularly, high Young's modulus and fracture strengths coupled with high transparency of diamond allow fabrication of advanced MEMS devices [1,2], high power laser [3], X-ray [4] and millimeter wave [5] optics superior to those made of conventional materials.

Previous studies of free-standing diamond films with thickness of a few hundreds microns produced mostly by microwave plasma CVD and DC arc jet CVD [6–15] revealed that the bending strength σ_f is not well-defined value for polycrystalline CVD diamond being dependent on grain size, film thickness, texture, growth conditions, synthesis method, post-growth treatment, geometry of load application. Typical σ_f values of polycrystalline diamond 0.4–2.4 mm in thickness, as measured by the three-point method, vary over the range 300–1200 MPa [6]. Significantly higher bending strength σ_f as large as 2.4 GPa has been reported [6] for IIa single crystal diamond 0.18 mm in thickness, and even higher values, up to 5.1 GPa, were reported for CVD single crystals [16]. A common finding is that (i) the strength is higher for the case of fine-grained nucleation side under tension compared to coarse grain growth side, and (ii) the strength increase with the grain size decrease. This was ascribed to suggestion that the fracture is caused by bulk defects with size comparable to crystallite size [6].

The film texture (grain orientation) and grain boundaries (GBs) structure influence the strength (the fracture takes place easily for more pronounced columnar crystallites) as was observed experimentally for DC arc jet CVD films [9] and studied by molecular-dynamics simulations for <100> and <110> tilt GBs [17]. Practical polycrystalline diamonds may contain disordered GBs, and extended defects (dislocations, pores, amorphous regions) specific for particular technology, therefore it's not clear to what extent the literary data on strength of diamond films grown under certain (or unknown) conditions can be used to predict the strength of the material synthesized by different method and/or under different growth recipe.

In the present paper we measured by a 3-point method the bending strength of two grades of polycrystalline diamond films grown by a microwave plasma CVD: transparent ("white") optical quality samples with thickness ranged from 60 to 1000 μm, and <100> fiber texture opaque ("black") film with rather high quality bulk crystallites but with defected GBs. We found the strength of the white diamond to be at the level of the best transparent polycrystalline films reported by other authors [6,13], while for the black material the columnar grain structure coupled to disordered GBs result in dramatically reduced strength.

2. Experimental

Transparent (white) polycrystalline diamond films with thickness from 60 μm to 1 mm were grown in $CH_4/H_2/O_2$ microwave plasma on

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Si substrates 57 mm in diameter using CVD systems UPSA-100 [18] and ASTeX-PDS19, both operated at 5 kW microwave power and 2.45 GHz frequency. Typical growth conditions were as follows: 1.2–2.5% methane concentration in the mixture, total gas flow rate 1000 sccm, pressure 95–100 Torr, substrate temperature 820–850 °C. The test samples in the form of 2×8 mm^2 or 2×10 mm^2 bars were laser cut from free-standing mother diamond wafers. From 8 to 16 bars were prepared from each wafer to get some statistics, the thickness of the bars being measured with a micrometer and optical microscope. The thickness homogeneity of the as-grown wafers was typically better than 15% (center-to-edge variation). Because of small size of the bars (length of 8 or 10 mm) the thickness variation over a particular bar was less than 4%.

The black diamond wafer of 0.5 mm thickness has been produced in $CH_4(10\%)/O_2(1\%)/H_2$ mixture at elevated substrate temperature 940 °C and laser cut to 2×10 mm^2 bars. For comparison eight samples of 0.5 mm thick white diamond bars with the same size were also prepared. The samples subjected to the bending test were not polished since the extensive previous studies [3,6,10] revealed no significant influence of surface processing (polishing) of CVD diamond on the measured strength values.

The phase purity of the samples was analyzed with micro-Raman spectroscopy using LABRAM HR (Horiba Jobin Yvon) instrument at 488 nm excitation wavelength by focusing Ar^+ laser beam in a spot ca. 1 μm in diameter at the growth side of the film.

Measurements of the fracture strength σ_f and Young's modulus E of 2×8 mm^2 bars were carried out at Fraunhofer Institute for Applied Solid State Physics (IAF, Freiburg) by quasistatic three-point method. The method advantage is the possibility to handle with small samples. The diamond bars to be tested were supported on two cylinders of 3 mm in diameter, the distance between contact points being $L=7.45$ mm. The measuring unit contained a vertical copper tube 100 mm long that was heated electrically. The load cell measured the sample reaction force appeared when moving (expanding) copper tube is in contact with the sample center. The displacement of sample center position (±1000 μm maximum) was measured by inductive transducer with resolution better than 1 μm. The tube was heated with a constant rate in order to provide increasing load F and sample bending D. The F/D ratio kept constant during measurements till to the moment of fracture of the sample.

The fracture strength of black and white 10×2 mm^2 diamond samples was measured at USTB by three point bending method using a DF-500 diamond testing rig [8] with distance between two supporting points of 8 mm and the loading rate of 0.5 N/s.

The strength σ_f was determined from critical load value F_c under which the bar fracture took place [19]:

$$\sigma = \left(3L/2h^2b\right)F_c \quad (1)$$

where b and h are the specimen width and thickness, respectively. Several samples from the batch with the same thickness were loaded in position when the substrate side was under tension (the substrate side is oriented towards supporting cylinders), while the rest part of the samples was tested in a reversed position (growth side in tension).

The topography of fractured surfaces was characterized with SEM and optical profilometry (ZYGO, NewView 5000 model).

3. Results and discussion

SEM examination of surface texture on the growth side revealed that the white diamond specimens usually show predominant (110) texture (Fig. 1a), while the black film exhibits the strong (100) orientation (Fig. 1c) as was confirmed quantitatively by electron backscattering diffraction analysis (EBSD) [20]. No stress was observed with the EBSD for the black diamond, while for white samples the stress often occurred both on GB and in the bulk of crystallites.

Raman spectra of transparent films revealed only sharp 1332 cm^{-1} peak of cubic diamond with width $\Delta\nu$ (FWHM) typically less than 3 cm^{-1}, when probed on growth side (Fig. 2). No signature of sp^2 carbon components was observed independent on sampling location, on grain boundary (Fig. 2a) or on the grain center (Fig. 2b). In contrast, for the black film the Raman spectrum taken from the grain center showed again the 1332 cm^{-1} peak only with $\Delta\nu\sim2.7$ cm^{-1} (Fig. 2d), but also a noticeable contribution of sp^2 carbon (a broad band around 1500 cm^{-1}) when the laser probe beam was focused on the GB (Fig. 2c). The disordered GB with graphite-like phases can be the weak point upon mechanical load. Such defective GB in the films with similar texture were shown to be preferentially etched upon heating in air at $T=700$ °C [21].

The crystallite size as seen on the growth side increased, but non-linearly, with the film thickness h as shown in Fig. 3 for a broader set of white diamond samples produced in similar conditions. We determined the grain size as the mean value of crystallite diameter in the microscope field of view (not less than 50 grains in the picture). Particularly, the grain size d was 12 μm at $h=60$ μm changing to $d\approx200$ μm at $h=1000$ μm, the d/h ratio being ~0.2 at the thicknesses in the range of $h=60$–500 μm. The crystallites on nucleation side show dimensions of the order of 1 μm or less.

The results of the strength tests for white diamonds are presented in Fig. 4. The strength decreases with film thickness both for growth and nucleation side in tension, similar to the observations of other authors [6–8,12,13]. When the tensile stress is applied to fine-grained nucleation side, σ_f is as high as 2194 ± 146 MPa for the thinnest samples ($h=60$ μm) reducing with thickness to 604 ± 95 MPa at $h\approx1000$ μm. Significantly lower strength was measured for the growth side under tension, it spans from $\sigma_f=1200$ MPa at $h=60$ μm to 200 MPa at $h=1000$ μm. The dependence of fracture strength both on the film thickness and on the side being under tension matches qualitatively and quantitatively with results by Pickles [6] and Sporl [13] for optical quality material grown from microwave plasma. We note that the samples of both grades in this study mostly were broken close to their center for approximately two equal parts, so the fracture did occur at location of maximum stress as assumed by Eq. (1).

The comparison of bending strength for white and black grades was performed for the films of comparable thickness (ca 0.5 mm, each batch was cut from a single wafer). Their thermal conductivity was 22.8 W/cmK and 8.8 W/cmK, respectively, as measured at room temperature by laser flash technique [22]. The grain size for black and white samples in this particular test was ca. 10 μm and 75 μm, respectively.

The black diamond possesses a lower strength both for growth and nucleation side in tension (Fig. 5). The mean strength σ_f for black grade is 316 MPa for nucleation side and only 141 MPa for growth side (Table 1), while white diamond shows a factor of two higher values. The fracture surfaces show quite different reliefs as evidenced by SEM pictures (Fig. 6). The area close to substrate side of the white diamond (Fig. 6a) reveals numerous cleavage steps of various height and spacing, of a few microns to tens nanometers, which form very rough surface. Such fracture pattern, typical for entire surface from nucleation to growth side, is a result of transcrystallite crack propagation (see also Fig. 1a), that indicates high enough strength of grain boundaries. In contrast, the fracture surface of black diamond demonstrates predominantly intercrystallite splitting with smooth surface planes in the relief along boundaries of detached columnar grains (Fig. 6b) which extend over the entire film thickness. Relatively weak bonding of the columns reduces the bending strength.

The typical fracture surface topography patterns, as quantified by optical profilometry for the two specimens compared, are shown in Fig. 7. The relief height is coded in color grades. The surface roughness