## THE NANOSCALE STRENGTH OF ULTRA NANO CRYSTALLINE DIAMOND

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**Abstract.** Aim of this paper is the estimation of the still unknown ultrananocrystalline diamond nanoscale strength. In spite of its measured strength at the microscale, of ~4 GPa, for a hypothetical nanowire with specified geometry  $(10\times10\times100~\text{nm}^3)$  we have deduced a tremendously higher tensile strength, of ~23 GPa, as well as a bending strength of ~30 GPa. A fractal exponent of ~2.5 and a Weibull modulus of ~10 are also derived. Such results are shown to be compatible with a theoretical estimation of the ideal strength, deduced as ~52 GPa by applying Quantized Fracture Mechanics, assuming the fracture quantum coincident with a grain size of ~3 nm. Doped materials are also treated.

### 1. INTRODUCTION

Ultrananocrystalline diamond (UNCD) material [1] has been recently developed at Argonne National Laboratory and possesses unique properties particularly suitable to the design of micro electromechanical systems (MEMS). The UNCD films are grown by microwave plasma enhanced chemical vapor deposition (MPCVD) synthesis method, involving a rich CH<sub>4</sub>/Ar plasma chemistry, where C<sub>2</sub> dimers are the growth species derived from collision induced fragmentation of CH, molecules in Ar plasma. The UNCD film growth proceeds via the reactions 2CH<sub>4</sub> $\rightarrow$ C<sub>2</sub>H<sub>2</sub>+3H<sub>2</sub>& C<sub>2</sub>H<sub>2</sub> $\rightarrow$ C<sub>2</sub>+H<sub>2</sub> in atmosphere containing very small quantities of hydrogen [1]. UNCD films can be doped with nitrogen using a CH<sub>4</sub> (1%Ar) gas mixture and nitrogen gas added, to increase the electrical conductivity of the material, as required in MEMS applications. Strength of undoped [2,3] and doped [4] UNCD has been recently investigated at microscale considering 0, 5, 10, 15, and 20% of nitrogen gas added in the controlled atmosphere. We demonstrate that the observed size-effects [4] can be successfully rationalized on the light of the fractal statistics [5]; it shows that an increasing in the nitrogen content corresponds to a lower dimension of the fractal domain in which the energy dissipation during stretching occurs, resulting at microscale in a more brittle behavior. From the experimental results, the measured strength of UNCD at microscale was found to be ~4 GPa, strongly reduced (by a factor of about 50%) from the presence of the doping, with fracture toughness of ~4 MPam<sup>0.5</sup> and Young's modulus of ~1 TPa [2-4]. Unfortunately, until now no information was deduced regarding the fundamental issue, especially for novel nanoelectromechanical system

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(NEMS) applications [6], of the UNCD nanoscale strength. In contrast to the limits of the experimental analysis, unable until now to investigate the UNCD at such a scale, we obtain here an indirect 'experimental' estimation of the UNCD nanoscale tensile strength by virtue of fractal statistics [5]. It is found to be of ~23 GPa for a hypothetical nanowire of given width W=10 nm, thickness t=10 nm and length L=100 nm; the nanoscale bending strength is estimated as ~30 GPa. A surprising additional result is that, from the statistical data analysis, it seems that the presence of the doping basically would not affect the nanoscale strength. Even if such a result must be taken with caution, it clearly shows that doped UNCD nanowires, can be considered good candidates for NEMS applications. In addition to this general statistical/experimental procedure for the indirect observation of the nanoscale strength, we show that the UNCD nanoscale strength is compatible with its ideal strength, estimated as ~52 GPa by applying Quantized Fracture Mechanics (QFM) [7], assuming the fracture quantum coincident with a grain size d of ~3 nm.

### 2. MICRO-STRENGTH: EXPERIMENTS ON THIN FILMS

In order to investigate the strength of freestanding UNCD thin films at microscale, the membrane deflection experiment was considered [2,3]. The technique involves the stretching of freestanding specimens with micron thickness in a fixed-fixed configuration. The specimen geometry utilized by such a technique resembles the typical dog-bone tensile specimen, but with an area of additional width in the specimen center, designed to prevent failure at the point of application of a line load. The suspended membranes are fixed to the wafer at both ends such that they span a bottom view window. In the areas where the membrane is attached to the wafer and in the central area the width is varied in such a fashion to minimize boundary-bending effects. These effects are also minimized through large specimen gauge lengths. Thus, a line load applied by a nanoindenter in the center of the span results in direct stretching under large displacements of the membrane (as would be for a cable) in the two areas of constant width as in a direct tension test. Simultaneously, an interferometer focused on the bottom side of the membrane records the deflection. The interferometer yields vertical displacement information in the form of monochromatic images taken at periodic intervals. The relationship for the distance between fringes, is related through the wavelength  $\lambda$  of the monochromatic light used. Assuming that the membrane is deforming uniformly along its gauge length, the relative deflection between two points can be calculated, independently from the nanoindenter measurements, by counting the total number of fringes and multiplying by  $\lambda/2$  [2,3]. The result is direct tension of the gauged regions, in the absence of strain gradients, with load and deflection being measured independently. The data directly obtained from the experiment is processed to arrive at a stress-strain signature for the membrane.

An important aspect of the UNCD specimens was that each membrane bowed upward as processed, i.e., out of the wafer plane. This is believed to result from the difference in thermal expansion coefficients between the UNCD film and Si wafer substrate such that cooling down from the deposition temperature, approximately 800 °C, resulted in the Si shrinking more than the UNCD film. The film curvature is indicative of a gradient of residual stresses across the film thickness. The out-of plane profile was obtained through the interferometric measurements [2]. From this profile, the height above the plane of the wafer was determined. Also, the profile was used to measure the actual length of the curved membrane, which is used to determine the downward deflection, corresponding to the beginning of uniform specimen straining, after the snapthrough instability.

Such micro-tests have emphasized significant size-effects on UNCD strength. By a statistical data analysis the nanoscale strength can be estimated, as shown in the next section. This rather general experimental procedure can be applied to different materials [8].

# 3. NANO-STRENGTH: ESTIMATION BY FRACTAL OR WEIBULL STATISTICS

The strengths of UNCD membranes of 1 mm thick with width/length of 5/100, 10/200, 20/200 and 40/400 microns, also with nitrogen gas added of 5, 10, 15, and 20% in the atmosphere, were reported in [4]. Thirty tests were performed for specimens with specified doping and size, for a total of 480 tests, making it possible to apply statistical concepts. In particular, we apply fractal statistics [5] to these results for predicting the still unmeasured strength of UNCD at nanoscale. The coefficient of correlations are found basically identical to 1, showing that fractal statistics can be applied with confidence to these tests.

Failure can be also described by the widely used Weibull's statistics. Weibull statistics allow exami-

158 Nicola M. Pugno

nation of strength (or time to failure or fatigue life) in the sense of failure probability at a certain stress level. The simplest Weibull distribution is defined as  $P_f$ =1-exp((- $R/R_0$ ) $^n$ ( $\sigma_f/\sigma_0$ ) $^m$ ), where  $\sigma_f$  is the failure stress,  $\sigma_0$  is the stress scaling parameter: in other words, it is the nominal stress that would result in 63% (i.e., $(1-e^{-1})\cdot 100\%$ ) of the specimen to fail, having characteristic size R, i.e., volume  $V=R^3$ ; n=3 if we classically assume volume predominant defects. For predominant surface defects  $A=R^2$ , A is the specimen surface area, and thus n=2; m is the Weibull modulus, which can be identified from a loglog plot of the probability of failure;  $R_0$  is the reference size on which the Weibull parameters are identified. It is not clear if volume or surface has to be considered, even if at small scale surface defects should become predominant. Accordingly, the sizeeffect on the strength  $\sigma_{i}$  (at a specified  $P_{i}$ ) is predicted as  $\sigma_{\ell} \propto R^{-n/m}$ .

Based on the fractal statistics [5], that assumes energy dissipation in a fractal domain of dimension  $n-1 \le D \le n$ , e.g., comprised between Euclidean surface (D=2) and volume (D=3) if a three-dimensional object (n=3) is considered (here the size-effect on Young's modulus is neglected), we have:

$$\sigma_{f} \propto R^{\frac{D-n}{2}}, n-1 \leq D \leq n, n=2,3.$$
 (1)

Note that Eq. (1) can be applied also to one-dimensional objects, for which n=1.

Thus, we can demonstrate the equivalence between the size effects predicted by the Weibull and fractal statistics (if the Young's modulus scaling is neglected) in terms of:

$$m = \frac{2n}{n - D}. (2)$$

The advantage of the fractal statistics, Eq. (1), is the clear interpretation of D, whereas the physical meaning of m remains partially unclear. If the fractal approach is correct, the experimental size effect must give good fits with fractal exponents in the ranges (n-1,n). Assuming the investigated microspecimens as two-dimensional objects, i.e., as thin films (energy dissipations invariable along the thickness t, n=2,  $R=\sqrt{WL}$ ), the observed sizeeffects on doped and undoped UNCD microfilms compared with the fractal statistics are depicted in Fig. 1a showing a very good fit. If the specimen is considered as a three-dimensional microbeam (energy dissipations can vary along the thickness t, n=3,  $R=\sqrt[3]{WLt}$ ) the interpretation is different (but here similar as a consequence of the constant thickness of the specimens), as shown by the comparison reported in Fig. 1b; in both the cases the fractal approach seems to be consistent, showing a very good fit – the coefficient of correlation is basically identical to 1 for all the fits—with  $n-1 \le D \le n$ . Clearly the doping decreases the fractal dimension of the energy dissipation. Even if the UNCD electrical conductivity is strongly increased by the presence of nitrogen, its strength at microscale is strongly reduced by the presence of the doping [4]. Something different could happen at nanoscale.

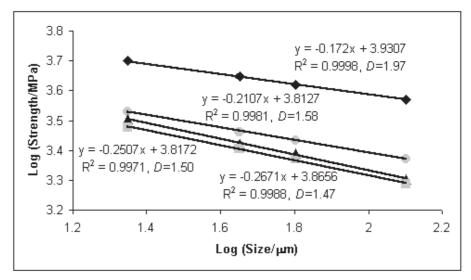
On the basis of the fractal statistics an estimation of the strength of UNCD at nanoscale can be derived. For example, considering a UNCD nanowire  $(n=3, R = \sqrt[3]{WLt})$  with W=t=10 nm, L=100 nm, the fractal statistics predicts a strength for the undoped UNCD of ~23 GPa (against the maximum value observed at microscale of ~5 GPa), with fractal exponent D=2.48 (and Weibull modulus m=11.6, from Eq. (2)); for 5% doping the nanoscale strength is ~22 GPa and D=2.37 (m=9.5); for 10% the strength is of ~28 GPa and D=2.25 (m=8.0); finally for 20% doped UNCD the strength is of ~34 GPa (against the maximum value observed at microscale of ~3 GPa) and D=2.20 (m=7.5). Thus, the fractal exponent is progressively reduced by the presence of the doping.

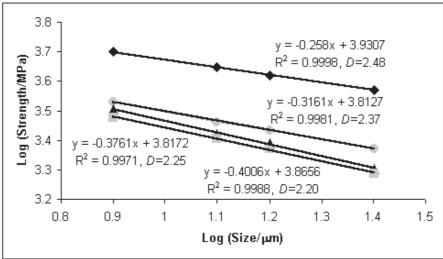
For cantilever nanowires the nanoscale bending strength  $\sigma_{fB}$  is also of interest. It is expected to be larger than the corresponding tensile strength  $\sigma_{f}$  as a consequence of the reduced volume undergoing larger stresses. According to Weibull  $\sigma_{fB} = \sigma_{f} (2m+2)^{1/m}$ . Thus, we expect nanoscale bending strengths of about 30, 30, 40, and 50 GPa respectively for 0, 5, 10, and 20% UNCD doping.

We note that the strength for doped nanowires is predicted larger than for the undoped nanowires. This last consideration has to be taken with caution (see the Conclusions); however, it would be a consequence of the lower fractal dimension imposed by the presence of the nitrogen, resulting in a larger negative slope for the doped curves in Fig. 1 with respect to the undoped ones.

### 4. IDEAL-STRENGTH: QFM ESTIMATION

The computed nanoscale UNCD strength is compatible with a simple estimation of the UNCD ideal strength  $\sigma_c$ , obtained by applying QFM [7]. We expect an even higher value for the UNCD ideal strength, as suggested by the observed size effects (smaller is stronger). Assuming the fracture quantum coincident with the grain size d of the UNCD,





**Fig. 1.** (a) Comparison between fractal statistics (straight lines) and experimental size-effects (data points) on UNCD strength, for undoped (fractal exponent D=1.97) and nitrogen doped (5%, D=1.58; 10%, D=1.50; 20%, D=1.47) specimens at microscale; such specimens are here treated as two-dimensional structures, i.e., as thin films. (b) Comparison between fractal statistics (straight lines) and experimental size-effects (data points) on UNCD strength for undoped (fractal exponent D=2.48) and nitrogen doped (5%, D=2.37; 10%, D=2.25; 20%, D=2.20) specimens at microscale; such specimens are here treated as three-dimensional structures, i.e., as microbeams.

the ideal strength is estimated according to QFM as:

$$\sigma_c \approx \frac{K_{lc}}{\alpha} \sqrt{\frac{2}{\pi d}},$$
(3)

where  $K_{IC}$ =4MPa is the fracture toughness of the UNCD and  $\alpha$  is a parameter equal to 1 for structures without free surfaces, (e.g., an infinite plate) or equal to 1.12 for structures with free surfaces (e.g., finite plate); it takes into account the 'edge-

effects'. Accordingly the surfaces are predicted weaker than the inner parts of a solid by a factor of ~10%. For finite structures, we find a reasonable estimation of the ideal UNCD strength of ~52 GPa, if d~3 nm is assumed. If the structure is assumed infinite the result would be ~58 GPa. The size R in Eq. (1) corresponding to a strength equal to the ideal strength of the solid fixes the limit size that can be treated by the fractal approach. From Eq. (3)  $\sigma_{\rm C}^{\infty} d^{-1/2}$ , in agreement with the well-known Hall-Petch relationship, that suggests nanostructured

160 Nicola M. Pugno

materials (small grain size d) for high strength applications; however, we have to note that the constant of proportionality, not specified by the Hall-Petch relationship, is related to  $K_{\rm IC}$  and could decrease itself by decreasing the grain size (here we assume  $K_{\rm IC}$  as a constant), limiting the fracture toughness and the applicability of nanostructured materials. Thus, the fracture toughness more than the strength could be the real critical point in designing nanostructured materials.

### 5. CONCLUSIONS

From the fractal statistics, Eq. (1), the nanoscale strength of doped and undoped UNCD is estimated; thus, it is demonstrated that the proposed methodology can be applied in general for estimating the nanoscale (tensile and bending) strength of materials, experimentally investigated at the more accessible microscale. Weibull statistics would give the same prediction, on the basis of the correlation of Eq. (2). A simple application of QFM is demonstrated to be able to give estimations for the ideal material strength, Eq. (3). Accordingly, the surfaces are predicted weaker than the inner parts of a solid by a factor of ~10%. Obviously the extrapolation of the nanoscale strength from Eq. (1) is based on the assumption that the dimension of the fractal domain (exponent in Eq. (1) or slope of the straight lines in Fig. 1) can be considered as a constant from micro- to nano-scales. And this could be not fully verified especially for the more complex case of doped UNCD specimens. Similarly, the validity of the simple approach summarized in Eq. (3) (that assumes fracture quantum identical to the grain size

for UNCD, assumed in addition identical to 3nm) is approximated. Thus, the UNCD predictions here reported must be considered simple reasonable estimations. Detailed quantum mechanical calculations are needed for deriving better predictions.

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