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FRACTURE SIZE EFFECT IN ULTRANANOCRYSTALLINE DIAMOND – WEIBULL THEORY APPLICABIILITY

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ABSTRACT

Strength characterization and analysis of fracture size effect in ultrananocrystalline diamond (UNCD) thin films are presented. In this work, we report the changes in mechanical properties of UNCD by the addition of nitrogen gas to the Ar/CH4 microwave plasma. Both undoped and doped UNCD films show a decrease in fracture strength with an increase in specimen size. The strength data, obtained by using the membrane deflection experiment (MDE) developed at Northwestern University, is interpreted using Weibull statistics. The capability of the theory is examined in conjunction with detailed fractographic analysis. The Weibull parameters are estimated by maximum likelihood estimation (MLE) based on 480 tests when the specimen volume varies from 500 to 16000 cubic microns. The results show that one can predict the fracture strength of a component possessing any arbitrary volume to within ±3% from the fracture strength identified from the tested specimens. The failure mode of UNCD is suggested to be volume controlled.

INTRODUCTION

Failure of brittle materials is caused by the unstable propagation of cracks initiating at surface or volume defects. These defects have a random distribution in size, orientation and location. At the millimeter or larger size scales, microstructure details are averaged, and material strength is less dependent upon the size and shape of the system. By contrast, at the micron and sub-micron scales, where the number of defects can be greatly reduced by decreasing the size of the interrogated volume or surface, fracture strength is strongly size dependent. This size effect can in principle be explained by the statistical theory first proposed by Weibull [1]. This theory describes strength variability in brittle materials by means of well defined statistical parameters. Knowledge of these material parameters, i.e., Weibull modulus and characteristic strength, is the first step in the prediction of the strength of MEMS components with specific size, shape and boundary conditions, Bagdahan *et al*. [2].

In previous work, we have measured the elastic modulus and strength of Ultrananocrystalline Diamond (UNCD), Espinosa *et al*. [3, 4]. The Young's modulus of UNCD was consistently measured to be between 950 and 970 GPa, while the strength decreased from 4.13 GPa to 1.74 GPa when surface roughness increased from 20 nm to 107 nm (RMS). Due to limited number of tested specimens possessing the same surface finish but different volumes prompted us to further examine the validity of Weibull theory in the prediction of UNCD strength.

In this paper we examine the applicability of the Weibull statistics in the prediction of strength of doped and undoped UNCD thin films. A particular emphasis is placed in assessing the role of volume vs. surface in the prediction of the material strength. The article begins with a description of the investigated materials, and a short description of the testing methodology followed by the reporting of experimental results including fractographic observations. A statistical analysis of the reported data based on the maximum likelihood estimation is used to identify Weibull parameters. Discussion of results and their implication in the design of MEMS based on UNCD completes the article.

EXPERIMETNAL METHODOLOGY

Specimen Preparation

Deposition of UNCD films was performed in a 6" Cyrannus-IPLAS (Innovative Plasma Systems GmbH) at Argonne National Laboratory. This process utilizes argon rich CH_4/Ar plasma chemistries [5], where C_2 dimers are the growth species derived from collision induced fragmentation of CH_4

molecules in an Ar plasma. In this paper 5% doped UNCD means that during film deposition the percentage of the nitrogen gas is 5% in the total gas flow. Likewise, for 10% and 20% doped UNCD.

The surface roughness of undoped and doped UNCD films was identified by atomic force microscopy (AFM). The study shows that roughness decreases gradually from 20.3 nm (RMS) to 13.9 nm (RMS) when the N_2 content in the plasma increases from 0% to 20%. By contrast, the morphology of the grain nucleation layer (bottom surface) is quite different from the surface layer. AFM images reveal a bottom surface RMS roughness in the range of 3.5 – 8.4 nm, independently of the N_2 content, which is much lower than that of the film top surface.

The specimens used in this investigation are attached to the substrate at both ends and span a micromachined window beneath (see Figure 1.a). The geometry of membranes can be described best as a double dog-bone tensile specimen. Undoped and doped (5%, 10% and 20%) UNCD films were deposited on silicon substrates. Thicknesses were accurately controlled during the deposition process and then measured. Raman spectroscopy was used to assess the chemistry of the deposited films. Subsequently, the films were patterned using an aluminum masking layer and the structures were released by KOH etching from the back side (see Figure 1.b). The details of the specimen microfabrication are reported in [4].

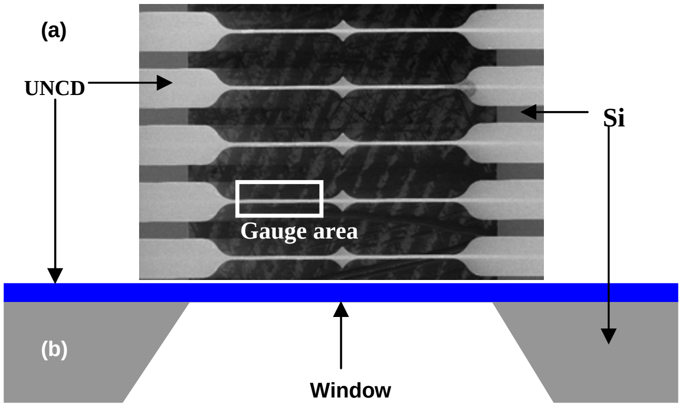

Figure 1. (a) SEM image of the top view of the micro-fabricated UNCD tensile specimens, and (b) a schematic drawing of the side view of the wafer.

Tensile Testing

The Membrane Deflection Experiment (MDE) developed by Espinosa *et al.* [7] was used to deform and stress the specimens until failure. A combined Nanoindenter and Atomic Force Microscope (AFM) apparatus was used in this investigation to apply a line load to the center of the membranes (Figure 2). The procedure involves applying a line-load, with a nanoindenter, at the center of the spanning membrane. Simultaneously, an interferometer focused on the bottom side of the membrane records the deflection. The result is direct tension with load and deflection being measured independently. A calibration plot and more experimental details can be found in [7]. Likewise concerning the formulas used to compute stress and strain.

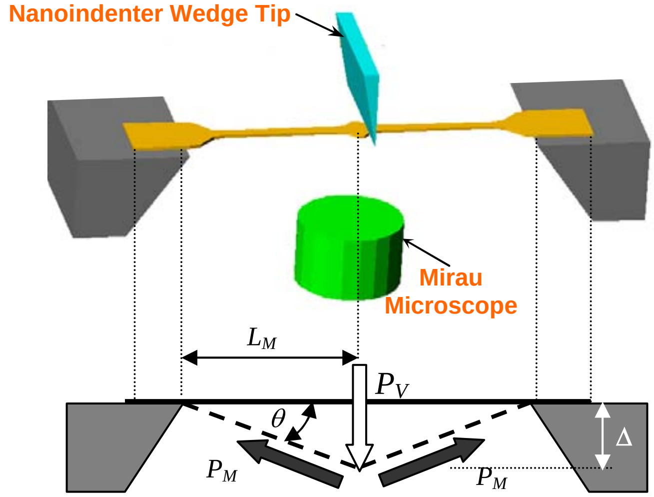

Fig. 4. A schematic drawing of the MDFE setup. Parameters are defined in the text.

A critical aspect in assessing the applicability of the Weibull theory is the examination of specimens with gauges dimensions spanning a range of volumes and surface areas. For both undoped and doped (5%, 10% and 20%) UNCD films, specimens with gauge dimensions A (width=40 μm, length=400 μm, thickness =1.0 μm), B (width =20 μm, length=200 μm, thickness=1.0 μm), C (width=20 μm, length=200 μm, thickness=0.5 μm), and D (width=5 μm, length=100 μm, thickness=1.0 μm) were tested to examine the effect of size on strength. Note that gauge volume was varied from 500 to 16,000 μm^3 while the total surface area was varied from 1200 to 32800 μm^2. Thirty tests were performed for each type of sample exhibiting the same size. Hence, a total of 480 tests were performed.

RESULT AND DISCUSSION

Young's Moduli and Characteristic Strengths

The values of the Young's modulus and the characteristic strengths, σ_0, are reported in Table I. The characteristic strength is defined as the stress with a 63% failure probability.

Table I shows that the Young's modulus decreases gradually from about 960 GPa to about 850 GPa when the percentage of nitrogen increases from 0% to 20% during the UNCD deposition process. This is likely due to the segregation of N_2 to the grain boundaries and to the fact that C-N bonds have less stiffness than that of C-C bonds. Also note that the fracture strength drops abruptly from 4,172 MPa to 2,713 MPa when N_2 increases from 0% to 5%. Then the decline becomes much less pronounced when N_2 increases from 5% to 20%.

Based on Weibull's "weakest link" theory we infer that by adding nitrogen into the plasma either defects are produced and/or that N_2 segregation to the grain boundaries result in a weaker grain boundary. The mere presence of nitrogen in the plasma is enough to produce a major strength drop. The exact mechanism leading to this weakening requires further investigation.

Table I. Comparison of Young's modulus and fracture strengths of undoped and doped UNCD.

Sample	Undoped	Doped		
N_2 %	0%	5%	10%	20%
No. of tests	30	30	30	30
E (GPa)	940-970	878-921	854-880	833-865
σ_0 (MPa)	4172	2713	2446	2350

Size Effect and Weibull Analysis

As it is customary for brittle materials, the strength data is interpreted statistically by assuming that specimen strength obeys a probability density function. In this case, we further assume that the probability function is Weibull's probability function [1]. The experimentally determined probability of failure is defined by ranking the specimen in ascending order of failure stress. Thus the probability of failure of the *i*th specimen out of N total is given by

$$P_f = \frac{i - 1/2}{N} \quad (1)$$

For specimens with the same shape and size the cumulative probability of failure, P_f, for uniaxial tensile specimens subjected to a stress, σ, is:

$$P_f = 1 - \exp\left[-\left(\frac{\sigma_{\max}}{\sigma_0}\right)^m\right] \quad (2)$$

where m is the Weibull modulus and σ_0 is the Weibull characteristic strength. The two Weibull parameters (m and σ_0) are obtained from the slope and intercept of a plot (Figure 3.a) of $\ln(\ln(1/(1-P_f)))$ versus the measured failure stress σ_{max}. To take into account the effect of volumes or areas the probability of failure can be written as:

$$P_f = 1 - \exp\left[-\left(\frac{\sigma_{\max}}{\sigma_{0V}}\right)^m V_e\right]$$

or

$$P_f = 1 - \exp\left[-\left(\frac{\sigma_{\max}}{\sigma_{0A}}\right)^m A_e\right] \quad (3)$$

where σ_{0V} and σ_{0A} are strengths relative to unit size (Weibull scale parameters), and V_e or A_e is the effective volume or area of the samples subjected to uniform stress. If the uniaxial Weibull model described above is valid, then the two adjustable parameters, m and σ_{0V}, are material constants. However, the estimation of the Weibull parameters is not simply an averaging of the results; the size must be included. The maximum likelihood estimation (MLE) was used to estimate the Weibull parameters by transforming discrete data sets into a single data set with respect to their effective volume, total surface area, or the sidewall area [8].

Figure 3.a presents the Weibull plot for undoped specimens. Four sets of data were obtained employing sample sizes A to D. The modulus, m, and the characteristic strength, σ_0, of each data set were obtained from the straight line fitted to the data. The MLE method is used to improve the accuracy of the statistical estimation for the Weibull parameters by transferring the four discrete data sets into a single large data set. Likewise, the data analysis is performed assuming that strength scales with volume, total surface area, or sidewall area [8]. Figure 3.b shows the comparison between experimental results, for undoped samples (size C), with the estimated (or predicted) values using MLE based on volume, total surface area, and sidewall area. By examining these plots, it is clear that the estimation based on volume captures best the trends in the measured data. The estimation based on total surface area or sidewall area is either on the left or the right of the experimental results and bound the data in some fashion. This result implies that the failure of UNCD is controlled by a distribution of volume defects. We will reinforce this finding by examination of features in the fracture surface, see fractography section.

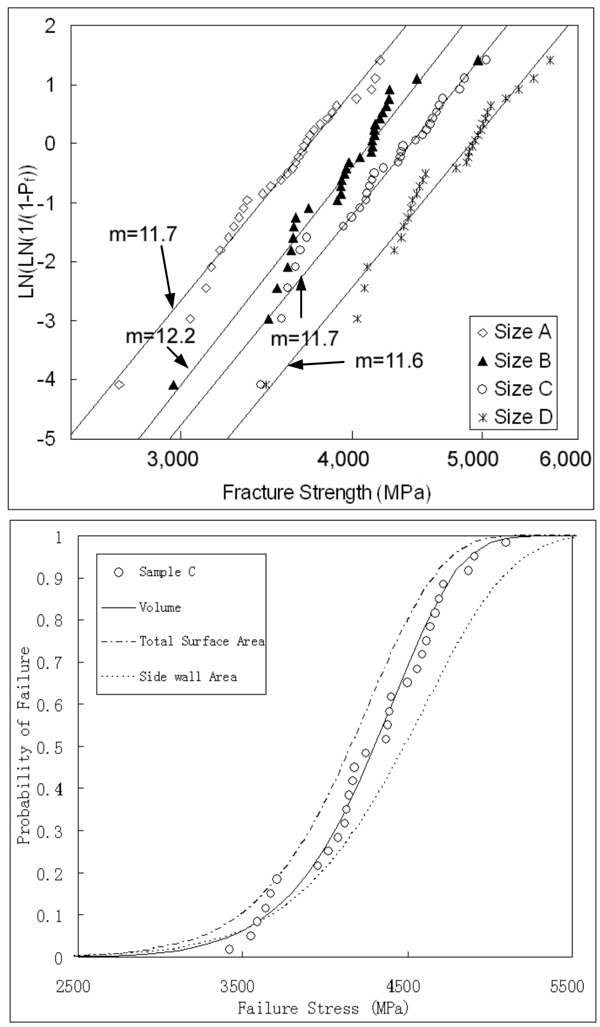

Figure 3. (a) Weibull plot for undoped UNCD with various sizes. The Weibull modulus and the characteristic strength for each set of data are obtained from the straight line fitted to the data. (b) Comparison of experimental results with statistically predicted values based on volume, total surface area, and sidewall area.

Table II. Weibull modulus values, characteristic strengths and the Weibull parameters determined from experimental data.

Sample	Undoped						Doped					
N_2 %	0%						5%					
Size	No.	m	σ_0 (MPa)	σ_{0V} *	$\sigma_{0,MLE}$ (MPa)	Error (%)	No.	m	σ_0 (MPa)	σ_{0V} *	$\sigma_{0,MLE}$ (MPa)	Error (%)
A	30	11.7	3714		3725	-0.3	30	10.6	2411		2401	0.4
B	30	12.2	4172		4198	-0.6	30	9.9	2713		2733	-0.7
C	30	11.7	4430		4456	-0.6	30	10.9	2889		2916	-0.9
D	30	11.6	5003		5022	-0.4	30	10.3	3304		3319	-0.5
MLE Volume	120	11.6		8581			120	10.7	--	5933		

Sample	Doped											
N_2 %	10%						20%					
Size	No.	m	σ_0 (MPa)	σ_{0V} *	$\sigma_{0,MLE}$ (MPa)	Error (%)	No.	m	σ_0 (MPa)	σ_{0V} *	$\sigma_{0,MLE}$ (MPa)	Error (%)
A	30	9.2	2195		2133	2.9	30	8.8	2034		2020	0.7
B	30	9.7	2446		2461	-0.6	30	9.7	2350		2344	0.3
C	30	9.1	2641		2643	-0.1	30	9.5	2539		2526	0.5
D	30	10.2	3019		3049	-1.0	30	8.9	2922		2932	-0.3
MLE Volume	120	9.7		5786			120	9.3	--	5719		

∗ σ_{0V} has the unit of MPa×μm$^{3/m}$

The Weibull parameters of doped and undoped UNCD obtained from the tests are summarized in Table II. The scale parameter were determined using maximum likelihood estimation (MLE) based on volume. The last two columns show the predicted characteristic parameters ($\sigma_{0V,\ MLE}$) and the difference between the predicted values and the measured value. It is shown that the differences are within 2.9% which means the tests are quite consistent. This indicates that Weibull statistics is indeed capable of predicting the strength of UNCD materials as a function of component size.

Fractographic Analysis

In all tests, failure occurred at the gauge area. The fracture surfaces were then examined using high resolution SEM. Figure 5 shows a typical fracture surface, for a 20% doped sample, at various magnifications. In principle, the fracture origin could be on the sidewalls, the top or bottom surfaces, or within the volume. However, there is no evidence of fracture initiation at the surface area or the sidewalls as was found for poly-silicon [2]. Figure 5 shows that fracture most likely initiates from interior defects introduced during the film deposition process. Figure 5.b reveals that the grooves observed in Figure 5.a are actually clusters of grains. It is clear that intercluster failure dominates the failure process in the tested UNCD films. The size of the defects is in the range of 20-30 nm, Fig. 5.b. The fracture surfaces of undoped UNCD are similar to that of doped UNCD except that a larger number of defects appear to be present in the fracture surface.

CONCLUSION

The fracture strength of UNCD thin films was investigated by testing straight tensile specimens. The characteristic strengths of undoped and 5%, 10%, 20% N_2 doped UNCD films were found to be 4172, 2713, 2446, and 2350 MPa, respectively. The decrease in material strength with doping can be clearly attributed to defects introduced in the films by adding N_2 into the plasma. For both undoped and doped UNCD the strength decreases as the specimen volume is increased. Fractographic analysis shows that the source of failure initiation is *volume control*. Hence, this investigation confirms that Weibull statistics, based on volume, is quite successful in predicting the fracture strength of UNCD.

Future work will examine the applicability of the Weibull theory at even smaller sample sizes, i.e., structures representative of NEMS.

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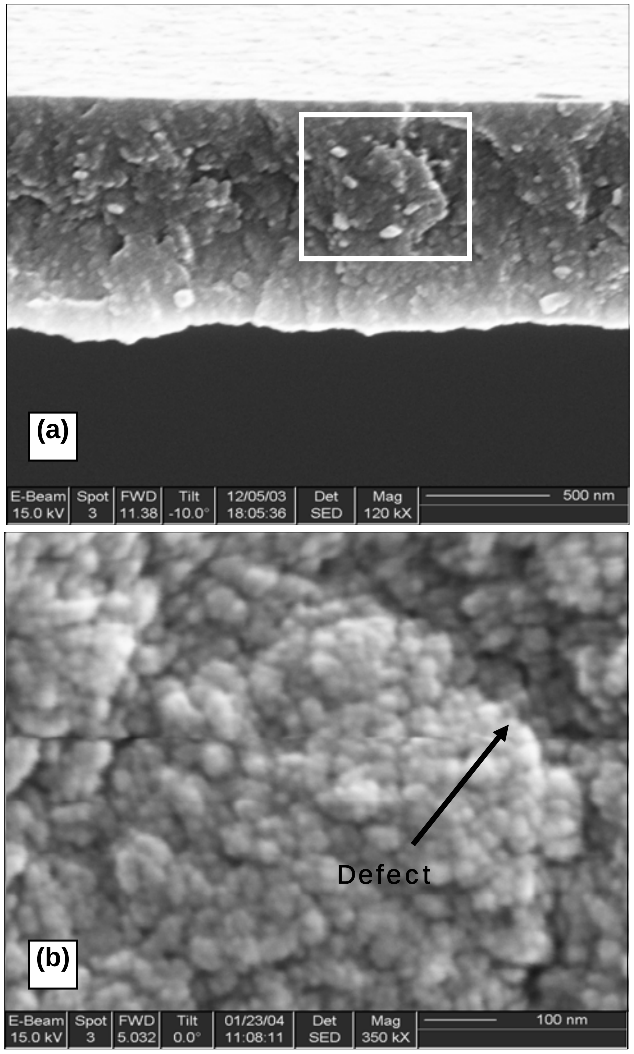

Figure 5. (a) Overview of the fracture surface of a 20% N_2 UNCD specimen and (b) magnified view of the area within the white rectangle. The arrow in (b) points to a defect in the bulk of the specimen.

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