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## Grain size dependent mechanical properties of nanocrystalline diamond films grown by hot-filament CVD

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### Abstract

Nanocrystalline diamond (NCD) films with a thickness of ~6 µm and with average grain sizes ranging from 60 to 9 nm were deposited on silicon wafers using a hot-filament chemical vapor deposition (HFCVD) process. These samples were then characterized with the goal to identify correlations between grain size, chemical composition and mechanical properties. The characterization reveals that our films are phase pure and exhibit a relatively smooth surface morphology. The levels of  $sp^2$ -bonded carbon and hydrogen impurities are low, and showed a systematic variation with the grain size. The hydrogen content increases with decreasing grain size, whereas the  $sp^2$  carbon content decreases with decreasing grain size. The material is weaker than single crystalline diamond, and both stiffness and hardness decrease with decreasing grain size. These trends suggest gradual changes of the nature of the grain boundaries, from graphitic in the case of the 60 nm grain size material to hydrogen terminated  $sp^3$  carbon for the 9 nm grain size material. The films exhibit low levels of internal stress and free-standing structures with a length of several centimeters could be fabricated without noticeable bending.

*Keywords:* Nanocrystalline; Diamond; Hot Filament CVD; Mechanical properties

### 1. Introduction

In the field of wear-resistant coatings for tools or microparts diamond can be the choice of material by virtue of its remarkable properties such as extreme hardness (~96 GPa) and Young's modulus (~1050 GPa), high fracture toughness and very low coefficients of friction. However, conventionally CVD grown microcrystalline (MCD) diamond films (where the grain size exceeds several hundred nm) exhibit a rough surface morphology and therefore show poor friction coefficients, which are especially unfavorable for wear-resistant coatings. This problem has been addressed by developing new nanocrystalline (NCD) and ultra-nanocrystalline (UNCD) CVD diamond materials which combine both superior mechanical strength and excellent tribological properties [1,2].

The grain size in these materials is typically less than 100 nm which leads to a smoother surface topography of the as-deposited material and therefore lowers the value of the friction

coefficient. This dramatic reduction in crystal size down to a few nanometers is accompanied by a significant increase of the grain boundary volume fraction. Simple calculations [3] reveal that the fraction of atoms associated with grain boundaries can be as high as 10%. In general, the development of a nanocrystalline grain structure in CVD diamond requires extremely high secondary nucleation rates. This can be achieved by purposely incorporating defects and impurities. An obvious impurity in CVD diamond growth is hydrogen, which has been shown to preferentially decorate grain boundaries [4], where it can form C-H bonds with  $sp^2$  and  $sp^3$  hybridized carbons [5,6]. Indeed, previous studies revealed that the formation of a nanocrystalline grain structure is accompanied by an increase of the hydrogen content in the NCD films [7]. For example, Xiao et al [8] reported hydrogen concentration of up to 3 - 7 at. % in NCD films with grain sizes of  $\sim 10$  nm.

This dramatic change in the chemical composition and microstructure has not only a significant influence on the morphology but also on the mechanical properties. For example, Catledge *et al.* [9] reported a modulus of 400 to 800 GPa and hardness values ranging from 45 to 90 GPa (measured by nanoindentation) and Phillip *et al.* [10] (using laser pulsed generated acoustic waves) found that the Young's modulus in NCD diamond can vary between 517 to 1120 GPa. In terms of applications, it would be of considerable interest to understand and control the relation between the grain size and mechanical properties. Another critical issue in NCD films is the film stress as it can lead to film fracture or delamination of the film from the substrate. In general, the reduction of crystal size can strongly influence the mechanical stress of the films, and residual stress values in NCD films can range from 0.5 to 5.5 GPa [11]. A systematical investigation of the correlation between grain size, chemical composition and mechanical properties is given in this paper.

## 2. Experimental

Nanocrystalline diamond films were grown in a hot-filament CVD reactor using tungsten filaments. Four sets of diamond films with thickness of  $\sim 6$   $\mu\text{m}$  were fabricated on 3 in. diameter single crystalline p-doped silicon (100) wafers. In order to achieve a nanocrystalline structure, a process has been developed to enhance secondary nucleation using a mixture of  $\text{H}_2$ ,  $\text{CH}_4$ ,  $\text{N}_2$  and  $\text{O}_2$ .

Scanning electron microscopy (SEM) was performed using a Zeiss Leo 1540. The roughness of the diamond surfaces was measured in tapping mode with Atomic Force Microscopy (AFM, Dimension 3100, Digital Instruments) using  $10 \times 10$   $\mu\text{m}$  scans. Investigation of the microstructure was performed with HRTEM (FIE-Titan 300 kV) and Selective Area Electron Diffraction (SAED). To determine the  $sp^2$  content of our NCD films, we performed soft X-ray Absorption Near-Edge Structure spectroscopy (XANES) experiments at the undulator beamline 8.0 at the Advanced Light Source, Lawrence Berkeley National Laboratory. Hydrogen incorporation was investigated

by Elastic Recoil Detection Analysis (ERDA), and stress analysis was performed with a thin-film stress measurement instrument (Flexus, Tencor FLX-2320). The total residual stress (thermal and intrinsic) was calculated from a radius-of-curvature measurement performed with a laser reflection technique using Stoney's equation [12]. Young's modulus and hardness were investigated by nanoindentation (Nanoindenter XP, MTS). Tests were performed with loads ranging from 135 to 500 mN at a fixed penetration depth of 500 nm. The maximum displacement of the Berkovich diamond indenter was regulated at slightly less than one tenth of the film thickness to minimize substrate effects [13]. The Young's modulus and the hardness of the films were determined from the load versus displacement curves in complete load/unload cycles and calculated using the Oliver and Pharr method [14]. Additional to nanoindentation, a Laser Surface Acoustic Wave technique [15] (LSAW, Fraunhofer IWS Dresden) was used for studying Young's modulus. In this method a pulsed laser induces an acoustic wave on the surface of the material. Based on the resulting waveform, several important properties can be measured. The dispersion of the wave is directly related to the thickness, Poisson's ratio, density and the Young's modulus of the film. A data fitting program determines the Young's modulus, and the density, given the film thickness and assuming a Poisson ratio of 0.12 [16].

### **3. Results and discussion**

Four sets of diamonds films (samples I – IV) were studied, and the results of AFM and SEM characterization are summarized in Table 1. The root mean square (rms) roughness decreases from sample I to sample IV by more than 50 %. This decrease in surface roughness can be directly related to a decrease in the grain size as determined by SEM (Fig. 1). Sample I shows a highly faceted surface morphology with grains ranging from 25 to 150 nm in diameter. The grain size of films III and IV is much finer with grains around 10-15 nm, and faceting can no longer be resolved. These values have to be compared to roughness values of MCD films (grain size exceeds several hundred nanometers) which typically have significantly larger roughness values (>100 nm). Note, that we also studied the effect of film thickness (1  $\mu\text{m}$  up to 17  $\mu\text{m}$ ) and did not observe an increase of grain size or roughness with increasing thickness.

The corresponding HRTEM and SAED patterns are shown in Fig. 2. The average crystal size taken from the TEM images are 60 nm for sample I, 16 nm for sample II, 11 nm for sample III and 9 nm for sample IV. SAED was used to examine the phases present in the NCD films. All SAED patterns can be indexed to diamond, and the observation of polycrystalline ring patterns demonstrates the random grain orientation in our materials. No appreciable scattering intensity from graphite crystallites was observed.

The hydrogen content in our NCD films was studied by ERDA, and the results are presented in Table 1. We observe that the hydrogen concentration increases with decreasing crystallite size from 1.5 to 4.3 at. %. This is in good agreement with previous studies [17], and the observation

that hydrogen is preferentially located at grain boundaries [4]. XANES spectroscopy was used to estimate the  $sp^2$  carbon content in our NCD films. This was done by comparing the integrated intensity of the  $sp^2$  related  $s \rightarrow \pi^*$  transition at  $\sim 284.5$  eV of normalized C  $K$ -edge XANES spectra collected from our NCD films with that collected from a highly oriented pyrolytic graphite reference sample (100%  $sp^2$ ) [18]. The results of this analysis are shown in Table 1. Contrary to previous studies [19], the observed  $sp^2$  carbon values decrease with decreasing grain sizes. This unexpected result seems to indicate that the character of the grain boundaries in our NCD samples changes from graphitic  $sp^2$  carbon (sample I) to hydrogen terminated  $sp^3$  carbon (sample IV) as the grain size decreases. This interpretation is consistent with the increase in hydrogen content as the grain size decreases (see ERDA results).

For evaluation of the quality of these films in view of the wear-resistant coating application, it is essential to study mechanical properties such as stress, Young's modulus and hardness. The calculated residual stress for our  $\sim 6$   $\mu\text{m}$  thick films is compressive and varies in the range from 220 – 360 MPa. The films showed no delamination from the substrate, and photographs of a free-standing film (sample IV) in Fig. 3 indicate no visible bending due to mechanical stress.

Nanoindentation was used to investigate the Young's modulus ( $E$ ) and the hardness ( $H$ ) of the grown films. Twenty-five indentations were made on each sample and the final results of  $E$  and  $H$  were averaged. To detect changes of the tip area function caused by the extreme hardness of our material we always performed calibration tests on a fused silica standard before and after indentation. The test confirmed that blunting of the diamond tip was minimal. Fig. 4 shows both Young's modulus and hardness of our NCD films as a function of the grain size. The Young's modulus values range from 597 to 857 GPa, and the hardness values range from 68 to 86 GPa. Although the error bars are large (which is especially true for the coarse-grained sample I due to its higher surface roughness) the data suggest the general trend that our NCD films get softer and weaker with decreasing grain size, and thus points towards grain boundary weakening.

A laser surface acoustic wave technique was used to verify the nanoindentation results concerning Young's modulus, and the results are included in Fig. 4. The LSAW measurement seems to confirm the nanoindentation results. The Young's modulus of sample I (60 nm grains) is close to that natural diamond (1050 GPa) and falls with decreasing grain size to around 700 GPa. The large offset compared to the indentation results can be attributed to the different techniques. Compared to LSAW, the nanoindentation measurement of the elastic modulus of thin films is more strongly affected by the substrate, especially when the film thickness is rather small. Even if we apply the 10% rule, the substrate affects the modulus values, especially in the case of a big mismatch in the modulus between substrate and film.

Thus the grain size clearly influences hardness and elastic properties of our NCD films. The weakening of our films with decreasing grain size can be explained by the increasing number of atoms associated with grain boundaries, and the existence of grain boundary related defects

such as hydrogen impurities ( $sp^3$ -CH groups) and  $sp^2$ -carbon. Also a change of the nature of the grain boundaries, from graphitic in the case of larger grains to hydrogen terminated  $sp^3$  carbon may be important in this context.

#### 4. Conclusion

The correlation between grain size and mechanical properties of NCD films was studied by using four sets NCD films with different grain sizes. The films showed extremely low internal stress levels and smooth surfaces. The surface roughness further decreased with decreasing grain size. The levels of  $sp^2$ -bonded carbon and hydrogen impurities were low, and showed a systematic variation with the grain size. The hydrogen content increases with decreasing grain size, whereas the  $sp^2$  C content decreases with decreasing grain size. This observation seems to indicate a change of the nature of the grain boundaries, from graphitic in the case of larger grains to hydrogen terminated  $sp^3$  carbon. Investigation of mechanical properties showed grain size dependent Young's modulus and hardness which can be associated with change in grain boundary volume fraction and introduction of grain boundary related defects.

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Table 1

Summary of the experimental results of AFM, HRTEM grain size analysis, XANES and ERDA

Sample ID	<i>Avg. roughness RMS (nm)</i>	<i>Avg. grain size (nm)</i>	<i>sp<sup>2</sup> carbon conc. (%)</i>	<i>Hydrogen conc. (at.%)</i>
I	40.96 ( $\pm 7.2$ )	60	7-6	1.5
II	20.18 ( $\pm 2.2$ )	16 ( $\pm 14$ )	5	3.2
III	16.37 ( $\pm 1.3$ )	11 ( $\pm 10$ )	6-5	4.0
IV	18.40 ( $\pm 2.5$ )	9 ( $\pm 8$ )	4-3	4.3

**Figure captions:**

Fig. 1. Top-view SEM micrographs of the four different NCD films.

Fig. 2. HRTEM and selective area electron diffraction pattern of the four NCD films.

Fig. 3. Photographs of a free-standing  $\sim 6 \mu\text{m}$  film of sample IV, showing no noticeable bending due to mechanical stress.

Fig. 4. Young's modulus and hardness as a function of grain size, measured by both nanoindentation and laser acoustic techniques.

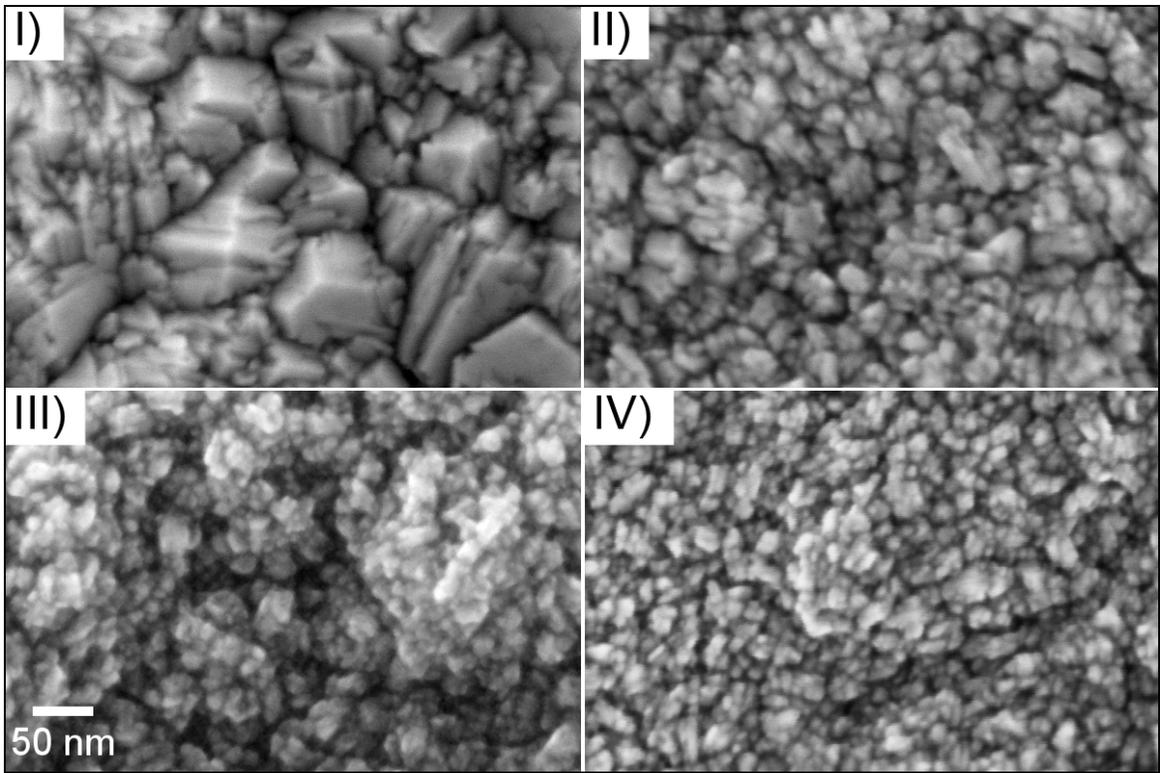


Fig. 1.

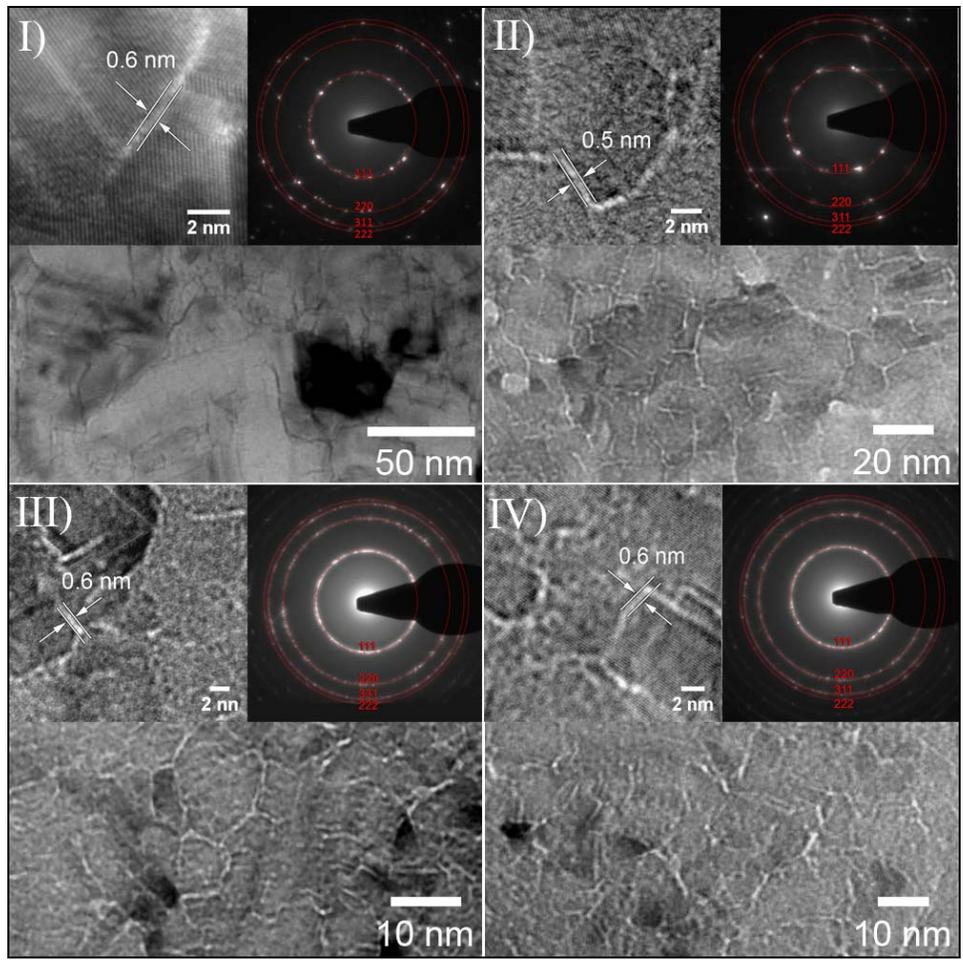


Fig. 2.

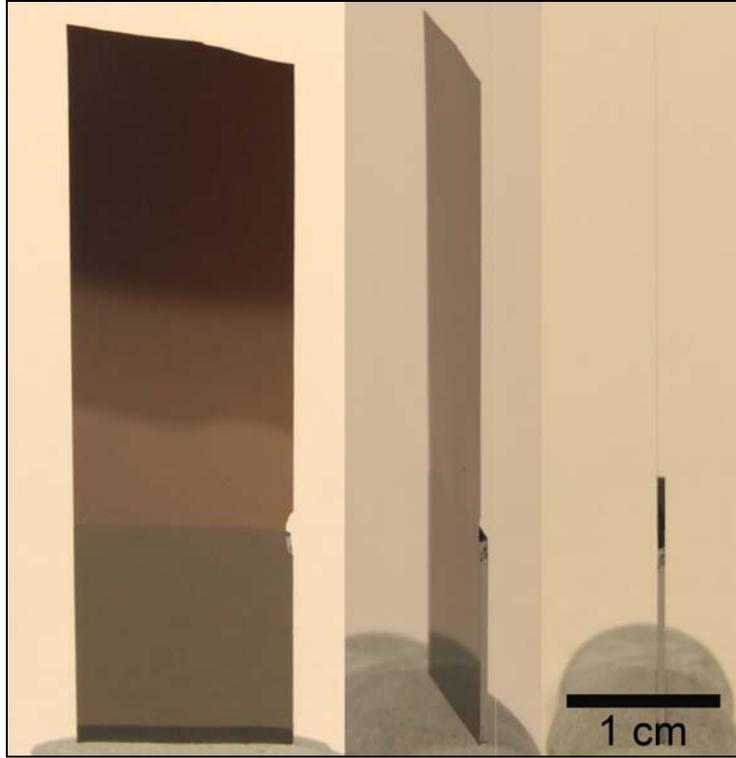


Fig. 3.

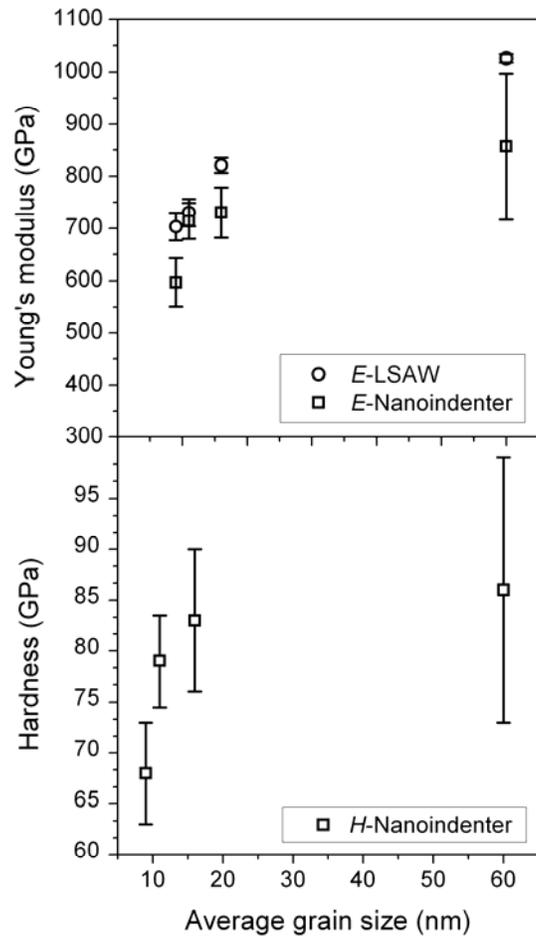


Fig. 4.