

Correlation of Microstructure and Tribological Properties of Dry Sliding Nanocrystalline Diamond Coatings

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ABSTRACT

Nanocrystalline diamond (NCD) offers great potential for many micro-mechanical systems, particularly where low friction, thermal mismatch and mechanical integrity are of great importance. The reduction of grain size in NCD films to a few nanometers is, however, accompanied by a significant change in morphological, chemical, mechanical and wear properties. The evaluation of these properties is therefore necessary before designing NCD-coated micro-mechanical components for which reliability, wear and long lifetime are critical issues.

Keywords: nanocrystalline diamond, tribology, friction, wear, running-in, reliability

1 INTRODUCTION

Owing to its remarkable properties, synthetic diamond has attracted considerable attention for potential application in optical, electronical and mechanical systems [1-3]. Extreme hardness, high mechanical strength, high thermal conductivity and excellent stability in harsh environments make diamond a unique material. The availability of techniques for structuring diamond down to the nanometer range render it an ideal candidate for micro-electro-mechanical systems (MEMS) [4,5]. MEMS containing free-standing parts or coatings made of NCD may offer performance and reliability advantages over traditional MEMS materials. To date, most MEMS are based on silicon technology, owing to maturity of the latter in fabrication and manipulation. Silicon as a MEMS material, however, has significant disadvantages, since important mechanical properties like hardness, fracture strength and Young's modulus are relatively low. In addition, silicon manifests poor tribological properties, resulting in excessive wear rates induced by high friction [6]. In fact, increasing interest in fabricating active microsystems with lubrication-free moving microparts requires materials with low friction and high wear resistance to ensure high reliability and long lifetimes [7]. Conventional microcrystalline diamond films, in which the grain size exceeds several hundred nanometers, exhibit rough surfaces

and poor tribological properties, consequently limiting their utilization in micro-mechanical systems.

This problem has been addressed by developing nanocrystalline diamond, which combines superior mechanical strength with excellent tribological properties [8-10]. The grain size in NCD typically ranges from less than 100 nm to a few nanometers, leading to a smoother surface topography in the as-deposited state and therefore to a lower friction coefficient. The reduction in crystal size down to a few nanometers is accompanied by a significant increase in the volume fraction of grain boundaries, which, in turn, leads to changes in morphological, chemical, mechanical properties [11]. Simple calculation reveals that the fraction of atoms associated with grain boundaries can easily be as high as 10 %. The evaluation of the mechanical and tribological properties of NCD is therefore necessary before designing MEMS, for which reliability and long lifetime are critical issues. In the present work, NCD films with a thickness of $\sim 6 \mu\text{m}$ and average grain sizes ranging from 60 nm down to 9 nm were deposited on silicon wafers using a hot-filament chemical vapor deposition (HFCVD) process. The HFCVD growth technique offers great advantages over microwave plasma CVD, particularly for upscaling to the coating of large areas or three-dimensional objects. Characterization of our samples was carried out to identify correlations between grain size, chemical composition, mechanical properties and wear.

2 EXPERIMENTAL

Nanocrystalline diamond films were grown in a HFCVD reactor using tungsten filaments. Three sets of diamond films with a thickness of $\sim 6 \mu\text{m}$ were fabricated on 3-inch diameter single-crystalline p-doped silicon (100) wafers. To increase the nucleation density the silicon wafers were seeded with dispersed nanodiamond particles (5-10 nm) [12] in an ultrasonic bath for 10 min, yielding a nucleation density of $\sim 7 \times 10^{10} \text{ cm}^{-2}$. In order to achieve a nanocrystalline microstructure, a process was developed to enhance the secondary nucleation using a mixture of H_2 , CH_4 , N_2 and O_2 . SEM and AFM were used for topographical analysis. Investigation of the microstructure and grain size was performed with HRTEM. For

determination of the sp^2 content of our NCD films, we performed soft x-ray absorption near-edge structure spectroscopy (XANES) experiments. Hydrogen incorporation was investigated by elastic recoil detection analysis (ERDA). Hardness values were obtained by nanoindentation (Nanoindenter XP, MTS). A laser surface acoustic wave technique (LSAW, Fraunhofer IWS Dresden) was used to measure the Young's modulus. Tribology tests were performed using a ball-on-disk tribometer (CSM Instruments). In a dry environment, NCD-coated Si_3N_4 balls (radius 1 mm) were loaded against the NCD films, with the normal load fixed at 250 mN. Considering a Hertzian elastic contact for the Si_3N_4 sphere pressed against a flat silicon wafer, we calculate that the applied loads used in this study produced initial peak pressures under the ball of 0.8 GPa (mean contact pressure 0.5 GPa). Rotating sliding tests were performed in ambient atmosphere (RH of 50–60 %) at room temperature with a total distance of 500 m. The wear coefficients (k) were analyzed by determining the wear volume loss from the coated ball (Archard's law).

3 RESULTS AND DISCUSSION

Three sets of diamond films (samples I-III) were studied and the results of AFM, HRTEM and chemical composition analysis are summarized in Table 1.

Film ID	R_q (nm)	Avg. grain size (nm)	sp^2 carbon (%)	Hydrogen (at.%)
I	41	60	7-6	1.5
II	20	16	5	3.2
III	18	9	4-3	4.3

Table 1: Roughness, grain size and chemical composition

The root-mean-square roughness (R_q) decreases from sample I to sample III by more than 50 %. This decrease in surface roughness can be directly related to the decrease in grain size as determined by TEM. SEM micrographs of the films are displayed in Fig. 1. Sample I shows a highly faceted surface morphology with grains ranging from 25 to 150 nm in diameter. The grains in films II and III are on average much smaller, with sizes around 5-20 nm, and faceting can no longer be resolved. Precise grain-size analysis using HRTEM showed average crystal sizes of 60 nm for sample I, 16 nm for sample II and 9 nm for sample III. Note that we also studied the effect of film thickness (0.1 μm up to 40 μm) and did not observe any increase in grain size or roughness with increasing thickness. In XANES and ERDA studies we observed both hydrogen and sp^2 concentrations. The chemical composition analysis reveals a gradual change in the nature of the grain boundaries, from graphitic in case of 60 nm-grain-size

material to hydrogen-terminated sp^3 carbon in 9 nm-grain size material (more details in [11]). Contrary to previous studies [13], the observed sp^2 carbon values decrease with decreasing grain sizes.

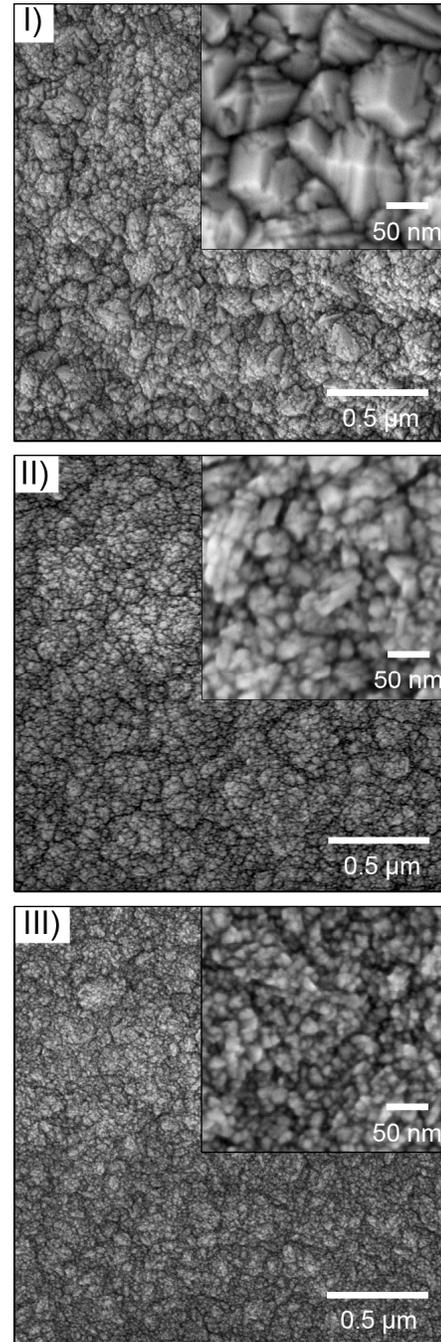


Fig. 1: Top-view SEM micrographs of the three different NCD films

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 III) as the grain size decreases. This

interpretation is consistent with the increase in hydrogen content as the grain size decreases. Investigation of mechanical properties and wear are summarized in Table 2.

Film ID	Hardness (GPa)	Young's modulus (GPa)	Wear coeff. k ($\text{mm}^3 \text{N}^{-1} \text{m}^{-1}$)
I	86 (± 13)	1026 (± 140)	145 x 10^{-8}
II	83 (± 7)	821 (± 48)	10 x 10^{-8}
III	68 (± 5)	703 (± 46)	1 x 10^{-8}

Table 2: Hardness, Young's modulus and wear coefficients

Values for Young's modulus range from 1026 to 703 GPa and hardness from 86 to 68 GPa. These data suggest the general trend that our NCD films become softer and weaker with decreasing grain size. This weakening 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. Results from the sliding experiments are given in Table 2. SEM analysis revealed polished plateaus accompanied by the generation of black deposits during wear (possibly graphitic in nature) on the wear track of the disk. AFM analysis indicated no measurable wear on the flat specimen. On the coated Si_3N_4 ball, an ultra-polished circular scar in the NCD film can be observed. The effect on the running-in i.e. the time in order to achieve a constant coefficient of friction as a function of the surface roughness is presented in Fig. 2. Choosing different thicknesses of the film systems, the surface roughness could be controlled to some extent. The data reveals the influence of large asperities and or protruding grains leading to initial high contact pressures and consequently to a longer running-in sequences.

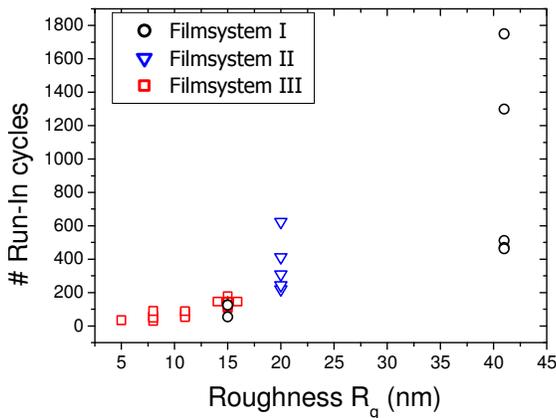


Fig. 2: Running-in behavior

The calculated wear rate coefficients k of the NCD-coated balls were in the range of 10^{-8} - $10^{-10} \text{ mm}^3 \text{N}^{-1} \text{m}^{-1}$ (see Fig. 4). The highest wear resistance of $1 \times 10^{-8} \text{ mm}^3 \text{N}^{-1} \text{m}^{-1}$ was

found in the smoothest film (III) having the smallest grain size, and the lowest k was measured for the coarser-grained film (I). Comparing the running-in cycle and wear values of the three films, we find a distinct correlation between surface roughness, running-in cycles and wear coefficient, indicating that roughness is a significant parameter in order to improve tribological properties.

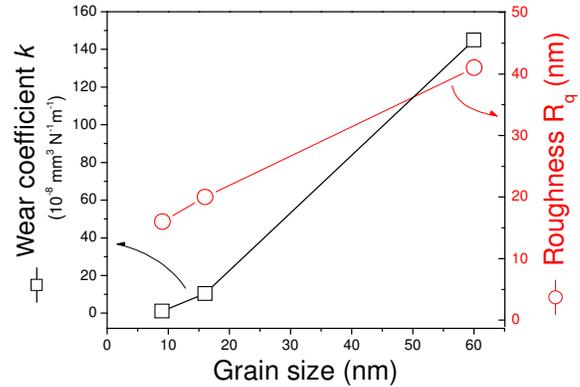


Fig. 3: Correlation of wear-coefficients, grain size and surface roughness

4 APPLICATION

First applications (Fig. 4) of our wear-resistant NCD coatings can be found, for instance, in the watch industry. The most critical component within a mechanical watch movement is the escapement wheel. With a minimum lifetime of ~ 20 years, the surface of these microparts must withstand high contact pressures, shock, dynamic stress and high wear.

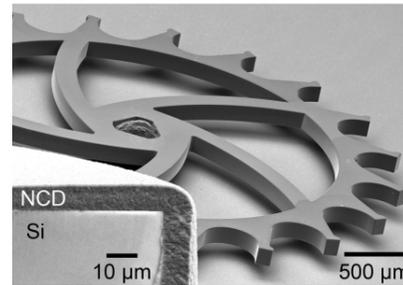


Fig. 4: Diamond-coated silicon escapement wheel

Silicon-based microparts, fabricated by a highly efficient and precise production technology, are promising for application in mechanical wristwatches [14]; however, the poor mechanical properties of Si limit its broader use in lubrication-free movements. In order to overcome this drawback and still take advantage of silicon technology, we propose coating the Si surfaces with a material having high modulus and hardness as well as desirable wear properties. Deep reactive ion etching (DRIE) in conjunction with SOI wafers have been applied for pre-structuring silicon microgears [14]. The combination of a silicon gear with an approximately $5 \mu\text{m}$ thick, 3-dimensionally smooth NCD

coating (Fig. 4) shows extreme stability, low friction and low wear, thereby fulfilling the requirements for lubricant-free watch movements.

5 CONCLUSION

NCD films with different grain sizes were deposited with a HFCVD system, yielding ultra-hard and smooth diamond films manifesting grain-size-dependent chemical, mechanical and wear properties. The simultaneous achievement of low roughness, extreme hardness and high wear resistance makes NCD an ideal material for tribological applications. The use of NCD as a coating material can be considered as an add-on to conventional silicon technology and might be applied in mass-produced devices, like sensors, actuators, medical tools and microgears.

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