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Investigation of the Tribological Properties of Diamond Films

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A chemical vapor deposition (CVD) system has been used to produce polycrystalline and nanocrystalline diamond (NCD) films. For biomedical and electronic engineering applications, it is highly desirable to deposit smooth films with decreased crystal size. In general, diamond coatings with a crystal size of 10-100 nm range are known as NCD. There are several ways in which NCD may be deposited including growth from fullerene precursors with argon dilution. Several workers have proposed various mechanisms for the growth process using inert gas dilution to conventional hot filament (HF) or microwave chemical vapor deposition (MWCVD) systems, or NCD growth through the deployment of CO_2/CO or O_2-rich gas environments. However, the use of inert gas dilution, with carbon containing species is the least complex approach to growing nanocrystalline, and more recently, ultrananocrystaline diamond (UNCD). Mechanical properties of UNCD have been determined by nanoindentation, and their nanotribological properties have been measured by nano-scratch and nano-impact testing. The relative importance of toughness (~E/H ratio) and elastic strain-to-break (~H/E ratio) of these systems on their behavior in nano-scratch and nano-impact tests is considered, and strategies for optimizing the deposition conditions for enhanced durability under different contact conditions are suggested in this short communication.

Keywords coatings, diamond, nanotechnology, thin films, tribology

1. Introduction

Nanocrystalline Diamond (NCD) has in recent years attracted considerable attention for its possible applications in microelectronic devices and biomaterials, owing to its exceptional optical and electronic properties (Ref 1–3). Nanotechnology diamond growth has been reported by a number of workers (Ref 4–7) using techniques such as hot filament (HF) and microwave chemical vapor deposition (MWCVD) systems. Diamond is exhibits a high hardness and Young's modulus and is a very practical material for uses in the mechanical industries (Ref 8–14). Diamond coatings with a grain size in the order of 2-10 nm, known as ultrananocrystalline diamond (UNCD), are well suited to these applications. Several approaches to the deposition of NCD films have been reported (Ref 4, 5), including the use of fullerene precursors (Ref 6–9) and using CH_4 in H_2, or Ar-rich, plasmas at high pressures (Ref 10). In this work, the tribological properties of the diamond films such as wear and friction properties have been evaluated using nanoindentation, nano-stratch, and nano-impact testing and then directly compared against polycrystalline diamond films.

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2. Experimental Results and Discussion

2.1 Chemical Vapor Deposition of UNCD

UNCD was deposited onto Si substrates, using a HFCVD system as described previously (Ref 10). The precursor gas, CH_4 (1 vol.%) was diluted in Ar or He (0-99 vol.%) with additions of H_2 gas (0-99 vol.%). All films were deposited at a substrate temperature of 900 K, using a gas pressure of 2.6×10^{-3} Pa (Nm^{-1}). Prior to deposition, all substrates where ultrasonically abraded using diamond particles (5 -1000 nm) this was followed by cleaning in acetone, in order to remove any residual particles. The diamond films were characterized in terms of crystal size film quality and sp^3 content using Raman spectroscopy (Kaiser Holoprobe) with a 532 nm Nd:-YAG laser as the excitation source. X-ray diffraction analysis (XRD) using a Philips W170 diffractometer was used for further confirmation of the film quality. The morphology and growth rates of the NCD films were investigated by the use of a Jeol scanning electron microscope (Jeol model JSM 5600LV) that was used to measure the depth of diamond film over a known period of time. Atomic force microscopy (AFM) using a silicon tip, was performed in the contact mode with a force constant of 0.12 nm^{-1} (Quesant Instruments, California, U.S.A.) also completed in order to calculate the surface roughness, and also as a further confirmation of the film's morphology. The experimental parameters are shown in Table 1.

Table 1 Experimental conditions used for HFCVD diamond films

Sample material	Si polished wafers	Area = 5 mm^2
Sample number		#4
Pre-treatment method	Manual abrasion diamond powder	1 μm diameter diamond powder
Deposition gases	Precursor	1.5 vol.% CH_4 gas
	Carrier	H2/Ar gas mix
Deposition periods		4, 6, 8, 10 h
Deposition pressure		0.266 Pa (Nm^2)
Temperature	Filament	2200 K
	Substrate	1000 K

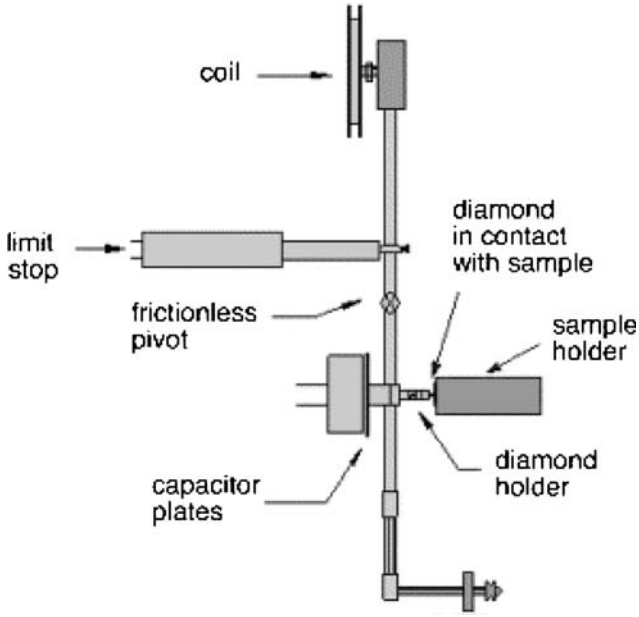

Fig. 1 Schematic configuration of the NanoTest system

2.2 Nano-scratch Testing of UNCD

Nano-scratch testing was performed with a Micro Materials NanoTest instrument. The NanoTest instrument is shown schematically in Fig. 1 (Ref 6). The NanoTest instrument is a pendulum-based depth-sensing system, with the sample mounted vertically and the load applied electromagnetically. Current in the coil causes the pendulum to rotate on its frictionless pivot so that the diamond probe penetrates the film surface. Test probe displacement is measured with a parallel plate capacitor with sub-nanometer resolution. Transverse sample stage motion enables nano-scratch testing, friction, wear and profilometry to be performed as required.

2.3 Nanoindentation Testing of UNCD

Nanoindentation testing was performed in the load-controlled mode using a NanoTest system depicted in Fig. 1. The area function for the Berkovich diamond indenter was determined by indentations into fused silica from 0.5 mN to 200 mN in 5 nm increments. Indentations were 20-cycle load-controlled load-partial unload experiments from 1 mN to 20 mN maximum load on the 5-80 nm thickness diamond films on Si substrates. Other experimental conditions were: preset initial load 0.03 mN; loading rate = unloading rate = 0.5 mN s^{-1}; and a 60 s holding period at 90% unload to account for thermal

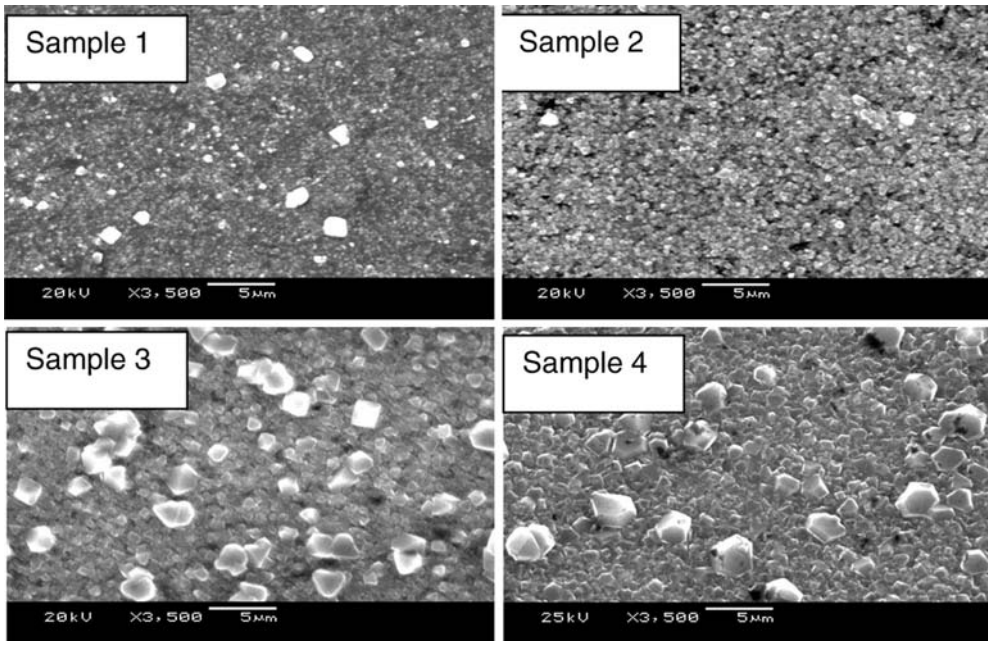

Fig. 2 SEM images of deposited diamond films

drift corrections. The data were analyzed with the Oliver and Pharr method and five repeat load-partial unload experiments were performed on each sample.

2.4 Characterization of UNCD films

An SEM image of a diamond film deposited for 6 h using 1 vol.% CH_4 in 97 vol.% Ar/2 vol.% H_2 is shown in Fig. 2(a). The film is nanocrystalline with crystallites in the range of 50 nm thickness where the film thickness is gauged to be ~250 nm ± 50 nm, the average surface roughness being 25 nm. The reduction of argon from the gas mixture alters the gas phase characteristics and these are reflected in the as-grown films. When argon is reduced there are notable changes in the crystallinity of the films with a significant increase in the average crystallite size and growth rate. Figure 2(b) shows an SEM image of diamond deposited for 6 h using 1 vol.% CH_4 in 90 vol.% Ar/9 vol.% H_2. There is a significant decrease in the crystallinity; the film exhibits nanocrystalline and microcrystalline structures with crystallites approximately 100 nm in size. The films are uniform with a mean surface roughness (Ra) of 54.14 nm ± 20 nm. The films are smooth with no apparent voids or pits across the surface. Figure 2(c) shows an SEM image of a diamond film deposited for 6 h using 1 vol.% CH_4 in 60 vol.% Ar/39 vol.% H_2. The films are microcrystalline, with mixed facets; the average diamond crystal dimensions are approximately 400 nm. Figure 2(d) shows a diamond films deposited for 6 h, using 1 vol.% CH_4 in 99 vol.% H_2, without the presence of Ar. Examination of the films shows that it is uniform, the crystals are well faceted and are predominately in {111} orientations, the average crystallite size is ~3 μm and the surface morphology is fairly rough with average surface roughness value (Ra) of 700 nm ± 200 nm.

2.5 Measurement of Surface Roughness

Figure 3 shows a graph of surface roughness (Ra) for each given sample set. The graph shows that sample set 1 (nanocrystalline diamond) exhibits a low surface roughness below 250 nm, with a standard deviation of 36 nm. Microcrystalline diamond (sample set 2) also exhibits a low value Ra with a mean value of 64 nm and θ = 30 nm, using both a 250 μm and 1 mm scanned distance (where a 3 μm and a 25 μm probe are used, respectively). The greatest surface roughness (Ra) is observed with sample set 3. The calculated surface roughness is 300 nm (θ = 175 nm) over a 250 μm area and 240 nm (θ = 40 nm) observed over a 1 mm scanned area. When examining the micrograph (Fig. 2) of sample set 3, it is observed that the films exhibit a mixed morphology, with evidence of both micro- and NCDs present on the surface of the substrate.

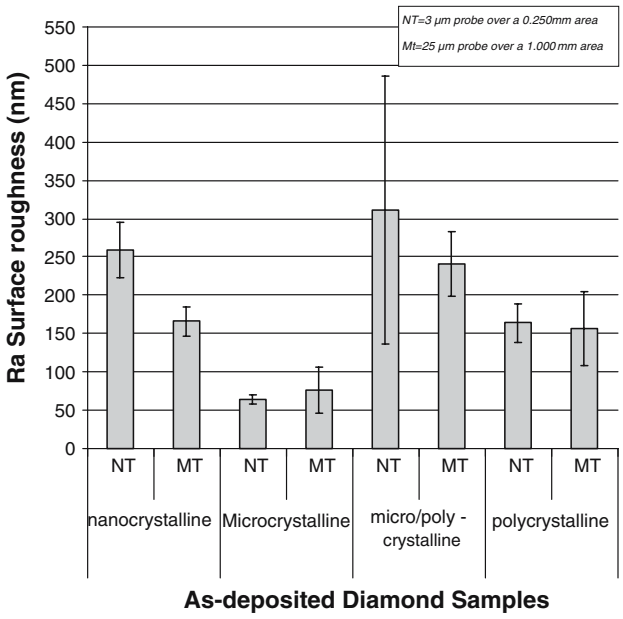

Fig. 3 A graph of surface roughness (Ra) for each given sample set using a 3 μm (NT) and 25 μm (MT) probe, respectively

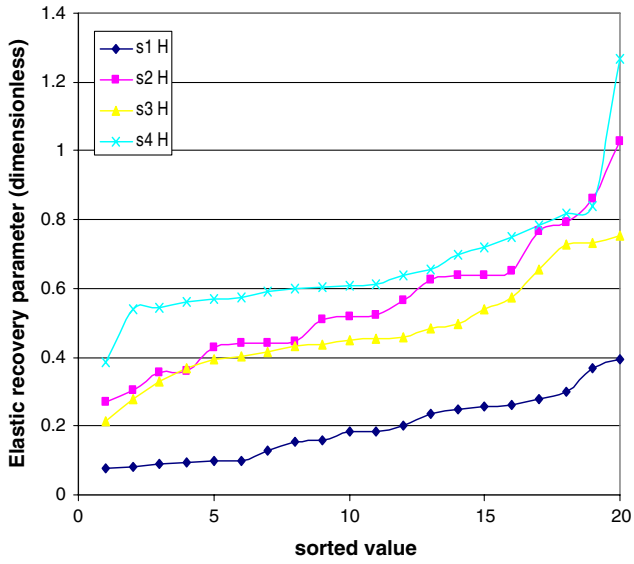

Fig. 4 A graph of elastic recovery against number of indentations

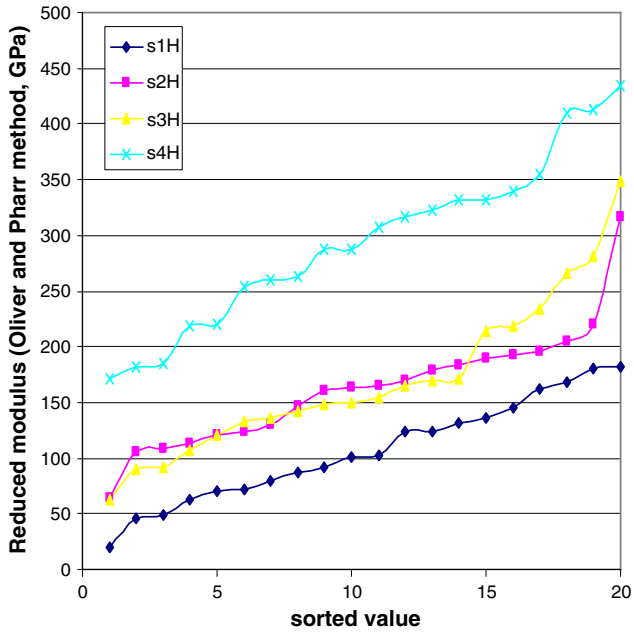

Fig. 5 A graph of reduced modulus (using the Oliver and Pharr method) against number of indentations

2.6 Nano-scratch Testing of UNCD

A graph of elastic recovery versus the number of indentations is shown in Fig. 4. The results show that sample set 1 exhibits the least amount of elastic recovery over repetition, ranging from 0.1 to 0.4 at 20 indentations.

2.7 Nanoindentation of UNCD

Nanoindentation to 10 mN peak force results are shown in Fig. 5. Sample 4 showed fracture-free indentation behavior; all other samples showed some degree of fracturing including sample set 1 that exhibited the highest reduced modulus and an increased amount of plastic deformation. Critical load for failure was beyond the maximum load (500 mN) of the NanoTest stylus when using the 8 μm probe, but below it for the 3 μm probe. However, a general correlation with H/E ratio is apparent with a reasonably consistent scaling-to-tip radius.

3. Conclusions

Surface roughness shows that sample set 3 exhibits the largest deviation in surface roughness (Ra) and is thought to be due to the presence of both nano- and micro-crystals. The results of the nanoindentation and nano-scratch experiments suggest that all samples showed a high resistance to indentation. The plasticity and the critical load for failure limit were beyond the maximum load (500 mN) of the NanoTest apparatus. The high value of reduced modulus for sample set 1 is thought to be due to increased number of grains with NCD samples. This causes increased numbers of dislocations to form on the surface and creates a lack of symmetry at specific locations in the crystal plane.

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