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Significance of grain and grain boundary characteristics of ultrananocrystalline diamond films and tribological properties

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ABSTRACT

Tribological properties of plasma chemistry dependent ultrananocrystalline diamond (UNCD) films deposited by microwave plasma enhanced chemical vapor deposition system are studied using 100Cr6 steel ball as a sliding counter element. UNCD films synthesized with 1.5% H_2 in Ar/CH_4 plasma consist of large number of clustered diamond grains with small volume fraction of grain boundaries. Decrease in grain boundary volume fraction resulted in simultaneous decline in *trans*-polyacetylene (*t*-PA) chain and sp^2 bonded amorphous carbon (*a-C*) phase fraction. However, UNCD films grown in Ar/CH_4 plasma shows formation of UNCD grains with high volume fraction of grain boundaries, large amount of sp^2 bonding, *a-C* and network of *t*-PA chains. The *t*-PA passivates the dangling bonds and sp^2/*a-C* phase that externally reduces sliding shear resistance, thereby, resulting in ultra-low friction behavior of UNCD films deposited from Ar/CH_4 plasma medium. Load dependent frictional behavior of these films was investigated in present study. These films tested under both low and high normal loadings showed high friction coefficient. Capillary dominated surface interaction and plastic deformation based models were found to be appropriate for describing friction behavior under low and high loads, respectively. However, at specific and intermediate normal loads, both low and ultra-low friction coefficients could be explained through elastic contact model that is accounted by the presence of lubricious phase of sp^2 and *a-C*. In addition, low friction coefficient is also governed by surface passivation mechanism. This mechanism is explained when friction test is carried out in controlled atmospheric condition. Investigating the tribological behavior of these films against steel ball is useful for implementing reliable micro-sliding based device applications.

1. Introduction

Materials with grain size refined to nanometer scale have great potential for several mechanical applications that range from micro-electromechanical systems (MEMS) to macroscopic abrasive coatings for cutting tools used in industrial applications [1–10]. For these applications, diamond coatings are useful due to their unique mechanical properties. Furthermore, UNCD films with such unique characteristic are superior to microcrystalline diamond film in several ways. Such unique characteristics usually occur from surface smoothness, fracture toughness, high electrical conductivity, low thermal expansion coefficient and high chemical inertness. All these basic characteristics of UNCD films cause improved tribological properties such as low friction and high wear resistance [5,7]. Hence, such films are technically reliable for MEMS and other micro/macroscopic device applications [11–20]. Generally, the UNCD films contain diamond grains with 5–10 nm diameters. These grains abruptly terminate at wide angle grain boundaries [21]. These grain boundaries contain sp^2 bonded fraction which result in several unique physical properties. These UNCD films were generally deposited using Ar/CH_4 plasma at substrate temperatures in the range of 400–800 °C [10,22,23]. The grain growth mechanism in UNCD films is explained by considering C_2 dimers present in the plasma medium [24]. On the other hand, several other studies have found that growth of diamond is mediated through H atoms, CH_3 radicals and other C_1 bearing species. This reaction is sustained with renucleated carbon species consisting of dangling bonds at surface [25]. Complexities associated with gas phase kinetics and nucleation/renucleation mechanism are not completely understood. Microstructure of UNCD films is vulnerable to film growth parameters such as reactant gas mass flow ratio, plasma content and substrate temperature. More importantly, hydrogen is always considered as an essential plasma

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constituent for the growth of UNCD films in chemical vapor deposition process. It acts as a key reactant which is likely to etch and restrict the growth of sp^2 bonded nuclei. This process leads to chemically stabilize the growth of diamond nuclei. This also removes the native oxide layer thereby facilitating generation of nascent sites for methyl radical absorption [26]. An efficient nucleation mechanism based on role of hydrogen on subsequent microstructure has been reported [27–29]. Generally, introduction of hydrogen into Ar/CH_4 plasma results in formation of dendritic microstructure. Grain size constituting microstructures further increases with an increase in hydrogen content in the plasma medium. This limits the number density of intrinsic sp^2 sites [30–32]. The chemistry dependent synthesis parameters influence nanomechanical and tribological properties of UNCD films [33–35]. Moreover, friction characteristics of UNCD films deposited in different plasma chemistries widely differ due to the change in transgranular and grain boundary characteristics. In addition, friction and wear resistance of crystalline diamond films also get altered due to extrinsic tribological test conditions such as loading, sliding speed and test atmosphere [9–13]. However, significance of grain and grain boundary effect on tribological properties are subject matter of studies.

In view of the above mentioned facts, the present work focus on UNCD film synthesis in two different gas mixtures such as 1.5% $H_2/Ar/CH_4$ and Ar/CH_4 plasma media at constant substrate temperature of 550 °C. Plasma chemistry dependent grain/grain boundary microstructure, chemical composition and associated tribological characteristics of these films were investigated with change in normal loads. In addition, tribological test was carried out in controlled humid condition to explain dependence of the friction and wear mechanism on surface passivation.

2. Experimental methods

Microwave plasma enhanced chemical vapor deposition (MPECVD) system (IPLAS-Cyrannus, 2.45 GHz) was employed for the deposition of UNCD films. These films were grown under two different plasma chemistry conditions on silicon substrates over duration of 3 h at a substrate temperature of 550 °C. In the first condition, 1.5% of H_2 was introduced to the Ar/CH_4 plasma ($Ar/H_2/CH_4 = 97.5/1.5/1$) at a microwave power and pressure of 1200 W and 147 mbar, respectively. In case of second condition, the plasma gas ratio was maintained as $Ar/CH_4 = 99/1$ and the input microwave power and pressure were kept at 1200 W and 160 mbar, respectively. For simplicity, films grown with 1.5% $H_2/Ar/CH_4$ plasma and Ar/CH_4 plasma (no H_2 addition) are designated as $UNCD_{1.5H}$ and $UNCD_{Ar}$, respectively. Prior to the deposition of UNCD films, the substrates were subjected to ultrasonic abrasion for 45 min in methanol solution containing nanodiamond powders (30 nm) and titanium powders (325 mesh). These suspensions were used to generate nucleation sites necessary for growing UNCD films [36].

Morphological, structural and crystallographic characterizations of UNCD films were carried out with field emission scanning electron microscopy (FESEM; JEOL, JSM-6500F), and transmission electron microscopy (TEM; JEOL, JEM-2100). The preparation of cross-sectional TEM specimens is usually carried out by fabricating a sandwich structure and subsequently thinning until it becomes transparent for electron. Conventional ion-milled samples were prepared by mechanical grinding, followed by dimpling and Ar-ion milling [37]. Chemical structure of UNCD films were characterized by UV-Raman spectroscopy (Renishaw; 325 nm wavelength). Spot size and laser power was 10 μm and 50 mW, respectively. Gaussian fits were used to study these parameters. In the fitting the Gaussian line was justified because this shape is expected for a random distribution of phonon lifetimes in disorder materials [38]. Chemical bonding state of the films was determined by X-ray photoelectron spectroscopy (XPS; PHI, 1600) equipped with monochromatic Al Kα radiation at 1486.74 eV. Spectrometer is attached with a monochromatic X-ray source having an energy resolution of 0.6 eV. Couple of XPS spectra on each sample on different locations was obtained. Therefore, the spectra were found to be reproducible. Before the measurements, the XPS instrument was calibrated to the prevailing ISO standard. The data are fitted with Lorentian peaks and background was subtracted using Shirley's method [39]. Elemental depth profile analysis of the UNCD films was carried out using dynamic secondary ion mass spectroscopy in positive ion counting mode using Cs^+ as a primary ion beam source. The primary ion beam (Cs^+) of 5 keV impact energy and 25 nA current was rastered over an area of 100 μm × 100 μm in order to get a uniform bombardment of the specimen surface. The emitted secondary ion species such as CsC^+, CsH^+, $CsCH^+$, C_2H^+ and $CsSi^+$ were collected with respect to time from a circular area 50 μm in diameter. Pressure inside the chamber during SIMS measurements was around 10^{-9} mbar. The process was repeated at three different locations on the specimen surface and the acquired data was considered to be representative of the whole surface. Elastic Recoil Detection Analysis (ERDA) measurements on the UNCD films were carried out with 2.8 MeV He^{++} ions. The sample was tilted by an angle of 75° from the surface normal and a surface barrier detector with a resolution of 12 keV was kept at a recoil angle of 30°. A mylar foil of 10 μm thickness was placed before the detector to stop the forward scattered He ions and allow only the recoiling H atoms from the sample. In ERDA spectra, the peak around channel number 546 comes from H at the surface and signal at lower channel numbers come from the surface and bulk of the UNCD film.

Nanoindentation measurements were carried out with Berkovich diamond indenter at a constant loading/unloading rate of 5 mN/min. The tests were conducted at a peak load of 10 mN. The formalism of Oliver and Phar was used to calculate the elastic modulus and hardness of all the specimens [40]. Six indentations in each sample were carried out and data were found to be reproducible. Indentation depth was less than 10% of the film thickness to avoid the substrate effect. Linear reciprocating mode of a ball on disk nanotribometer, NTR^2 (CSM Instruments, Switzerland) was used to carry out tribological tests. A contacting 100Cr6 steel ball with 1.5 mm in diameter was used to slide against the statically fastened UNCD specimens. Sliding speed of the specimen against the ball was kept constant at 0.5 cm/s. In addition, sliding speed dependent tribological tests were also carried out for specific measurements. Total sliding distance for each measurement was maintained constant at 5 m. Tribological experiments were conducted in ambient atmospheric condition with residual relative humidity of 72%. Moreover, systematic tribology tests were conducted in controlled humidities of 10%, 40% and 70% at various loading conditions of 5 mN, 100 mN and 500 mN. The controlled humidity atmosphere was obtained by controlling the flow rate of Ar gas in the tribological test chamber. Humidity fluctuations generally varied between 2 and 4% in all these cases. Wear depth was measured by a linear variable differential transformer (LVDT) coupled with the tribometer. The depth resolution of LVDT sensor is 50 nm. Contact angle of the films were measured by sessile drop method with a Kruss EasyDrop contact angle instrument. For these tests, the volume of the water droplet was kept at 0.8 ± 0.15 μL. These measurements were carried out at room temperature and atmospheric pressure with a relative humidity content of ~56%. Standard deviations in contact angle measurements were typically of the value ±3°. Macroscopic film roughness was measured by a Dektak 6 M-stylus profiler using 5 mg normal load with a scanning speed of 30 μm/s. For this measurement, the tip of diamond stylus with a radius of curvature of 12.5 μm was rastered over the film surface in contact mode. The measurements were repeated 5 times on each sample and found to be reproducible. Further, microscopic roughness was measured by a scanning tunneling microscope (UHV-STM, 150 Aarhus, SPECS GmbH, Germany) working at a base pressure of 10^{-10} mbar. The imaging was performed to measure the roughness with a set current of 0.59 nA with a sample bias between 2.5 and 3.5 V.