

Friction and Wear Properties of Chemomechanically Polished Diamond Films

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The role of surface roughness on the coefficient of friction and wear of polished CVD diamond films has been investigated. Diamond films grown on single crystal silicon (001) substrates by Hot Filament Chemical Vapor Deposition (HFCVD) process were polished by a chemomechanical process in which a diamond film was polished against another diamond film in the presence of a fused alkaline oxidizer at 320°C. Friction and wear properties of these polished films were measured at elevated temperatures and in the presence of various gaseous environments. The coefficient of friction of the polished diamond films was found to be about 0.09, which is very close to that of natural diamond (0.07). The wear rate of the mating alumina ball slid against a polished diamond film was also found to be comparable, when slid against natural diamond.

1 Introduction

Diamond is a unique material that exhibits both low friction and low wear. The strong directional sp^3 bonding of diamond is responsible for a unique combination of properties such as the highest elastic modulus, hardness, and ambient thermal conductivity of any known solid together with a low thermal expansion coefficient, a large optical band gap, chemical inertness to most corrosive environments, and poor adhesion with other solids (Field, 1979). The physical and chemical properties of Chemical Vapor Deposition (CVD) diamond films have been found to be comparable to that of bulk diamond (Bhushan and Gupta, 1991). Sawabe and Inuzuka (1986) reported that electron-assisted CVD films had electrical resistivities greater than 10^{13} ohm.cm, microhardness of about 10,000 HV, and a thermal conductivity of about $1100 \text{ Wm}^{-1}\text{K}^{-1}$, which are all values close to those of bulk natural diamond (10^3 - 10^{18} ohm.cm, 8000-10,400 HV, and 900 - $2100 \text{ Wm}^{-1}\text{K}^{-1}$). In this paper, we focus on the friction and wear of polished CVD diamond films.

Blau et al. (1990) reported that the coefficient of friction of as-deposited Hot Filament Chemical Vapor Deposition (HFCVD) diamond films were up to ten times the value for smooth bulk diamond surfaces sliding against various solids in air. They also reported very high wear of a mating sapphire ball surface. Gardos and Soriano (1990) also reported high values of coefficient of friction and wear rates of Plasma Assisted Chemical Vapor Deposition (PACVD) diamond films slid against SiC pins. Kohzaki et al. (1992) reported high coef-

ficients of friction (0.8) for HFCVD diamond films deposited on a sintered SiC disk, slid against a SiC ball at 600°C in a dry nitrogen atmosphere. Jahanmir et al. (1989), Hayward et al. (1992), and Miyoshi et al. (1992) reported lower values of coefficient of friction (0.1 to 0.3) of fine-grained (20 nm to $2 \mu\text{m}$) diamond films sliding against a diamond or sapphire slider with a spherical tip or a silicon carbide pin/ball. Based on the reported Raman spectra (Miyoshi, 1992), it appears that these fine-grained films contain nondiamond components.

HFCVD technique is presently one of the most attractive techniques for the deposition of diamond film due to its relative ease and low capital cost (Angus et al., 1993). Depending on growth temperature and pressure conditions, favored crystal orientations dominate the competitive growth process. As a result, the grown films are polycrystalline in nature with relatively large grain sizes ($>1 \mu\text{m}$) terminating in very rough surfaces with average roughnesses ranging from about $0.1 \mu\text{m}$ to $10 \mu\text{m}$. In order to apply HFCVD diamond coatings for tribological applications, these films obviously need to be polished after deposition (Bhushan et al., 1993). Thermochemical, chemomechanical, and plasma/ion beam/laser techniques have been explored to polish diamond films (Thorpe et al., 1990; Yoshikawa, 1990; Hickey et al., 1991; Bhushan et al., 1993). Based on previous work, we have found chemomechanical technique to be a low-capital cost and effective method of polishing diamond films (Bhushan et al., 1993).

In this paper, the friction and wear properties of as-deposited and polished diamond films deposited by HFCVD are measured and compared with those of natural diamond. The effects of surface roughness, test temperature, test environments, grain size, and mating materials on friction and wear properties are investigated. This is an important step before these CVD diamond films can be exploited for tribological applications. This paper is organized as follows: all of the steps consisting of

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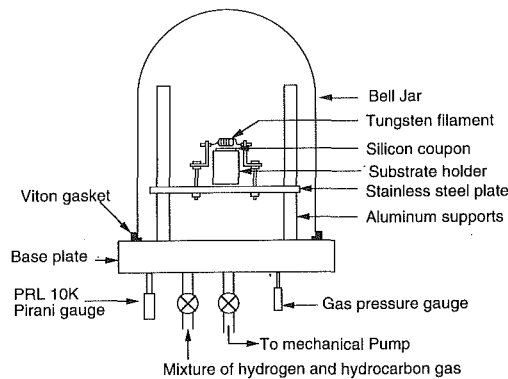


Fig. 1 Schematic of Hot Filament Chemical Vapor Deposition (HFCVD) setup. The substrate chamber was evacuated by a mechanical pump.

deposition, polishing, characterization, and friction and wear measurements are discussed next, followed by a detailed discussion of our results. Unlike previous work in the area, we investigated any changes occurring in the diamond film after each step via thorough characterization by SEM and Raman spectroscopy.

2 Experimental Techniques

2.1 Film Deposition. Diamond films were deposited using HFCVD technique on (001) single-crystal silicon substrates (Rebello et al., 1991). A mixture of methane (typically 1 percent) diluted in hydrogen was passed over a hot tungsten filament suspended above the silicon substrate. The filament simultaneously activates chemical reactions in the gas mixture and heats the substrate. A schematic of the HFCVD set-up used to deposit the diamond films is shown in Fig. 1. The substrate chamber, i.e., the Pyrex bell jar mounted on the top of the 300-mm diameter base plate was evacuated by a mechanical pump down to 2.5×10^{-3} Torr. The evacuated chamber was first flushed with pure hydrogen and a partial pressure of 20 Torr was maintained. The filament was resistively heated and methane was then allowed to pass through the substrate chamber. Filament temperatures were maintained at about 2200 to 2300°C. The temperature of the silicon wafer was monitored by an independently calibrated thermocouple and was usually at about 800°C. The deposition parameters used in this work were: substrate to filament distance = 10 mm, substrate temperature = 800°C, hydrogen flow rate = 99 sccm, methane flow rate = 1 sccm, pressure = 20 Torr, run duration = 24 hrs, average film thickness = 20 μm , and deposition area = 1 cm^2 .

Prior to deposition, the silicon substrates were abraded with 4 to 8 μm or submicron (0.5 μm and less) diamond powder in order to obtain coarse-grain and fine-grain films, respectively. After the abrasion pretreatment, the samples were cleaned in an ultrasonic bath with acetone solvent. The size of the abrading diamond particles plays an important role in the grain growth and ultimately affects their size. Larger diamond particles used for abrading the silicon substrate resulted in diamond films with an average grain size of 10 to 15 μm hereafter referred to in this paper as *coarse-grain films*. Abrading the silicon substrate by submicron diamond particles resulted in diamond films with an average grain size of 3 to 5 μm hereafter referred to as *fine-grain films*.

The linear growth rate, coverage (i.e., fraction of the substrate surface completely covered by diamond), and average surface roughness of HFCVD films are influenced by the size of the abrading diamond particles used in the pre-treatment of these substrates. For instance, 4 to 8 μm size diamond particles used for pretreatment typically yield faster growth rates (about four times), greater coverage, and rougher films

compared to using submicron sized diamond particles. Tribological properties were measured on thick films of equivalent thickness ($\sim 20 \mu\text{m}$) to ensure that competition between the different growth faces is terminated and columnar morphology is well established. We gave more emphasis to the coarse-grain diamond films in this paper because of their higher deposition rate and better coverage as compared to fine-grain films.

2.2 Polishing of Diamond Films. In the chemomechanical polishing technique used in this study, a fused oxidizer, potassium nitrate (KNO_3) was employed. The choice of the oxidizer is based on its strong reactive etching affinity toward diamond (Wilks and Wilks, 1979). The etching rate in the presence of a shearing force field is expected to be higher and more uniform. Therefore, the diamond films were first coarsely polished by lapping against a polycrystalline alumina plate followed next by fine polishing by lapping against another similarly polished diamond film in the fused oxidizer ambient. The diamond film to be polished was mounted on a rotating stage (7 revolutions per minute) and the mating alumina plate or diamond film were mounted on a stationary hot plate. During polishing, the hot plate was maintained at about 320°C in order to maintain the potassium nitrate in fused form. The diamond films were coarsely polished for three hours followed by fine polishing for two hours, in this manner.

2.3 Film Characterization. The surface morphology and grain size of the diamond films deposited on silicon were imaged using Scanning Electron Microscopy (SEM). The samples were imaged in the backscattered mode in bright field. The accelerating voltage of the electron beam was kept low at 3 kV to avoid electrostatic charging of the diamond film. Cross-sections of the film were prepared by breaking them, for grain growth studies. The thickness of the diamond coatings was estimated from their cross-sectional SEM images to be in the range of 15 to 20 μm . Raman measurements were made using an Argon ion laser at 514.5 nm wavelength with an output of about 100 mW and a spot size of 0.1 mm-diameter. This instrument is also equipped with a microprobe with a focal spot size of about 20 microns.

The residual (internal) stresses that develop during the diamond film growth were estimated by measuring the radius of curvature of the sample before and after deposition. The radius of curvature was calculated from the surface profile measured using a stylus profiler, on the center of the coupon with a scan length of 2 mm. Stoney's well known equation was used to calculate the residual stress σ (Bhushan, 1990),

$$\sigma = [(E_s / (1 - \nu_s))](t_s^2 / 6Rt_f) \quad (1)$$

where R is the curvature of the diamond film coated silicon substrate, E_s and ν_s are the elastic modulus (130 GPa) and Poisson's ratio (0.33) of the silicon substrate, respectively, and t_s and t_f are the thicknesses of the substrate (300 μm) and the diamond film (20 μm), respectively.

2.4 Surface Characterization. The roughness of the as-deposited and polished diamond films was measured by a mechanical surface profiler, noncontact optical profiler (NOP), and atomic force microscope (AFM) to obtain roughness data with lateral resolutions differing by three orders of magnitude (Bhushan, 1990). The stylus profiler gives a two-dimensional plot of roughness with a lateral resolution of about 5 μm and a vertical resolution of 0.5 nm. The NOP is a three-dimensional profiler which measures surface features with a lateral resolution of about 1 μm and a vertical resolution of 0.1 to 0.2 nm. The AFM gives a three-dimensional plot with vertical resolution of less than 0.1 nm and a lateral resolution as low as 0.2 nm, depending upon the scan length. For the scan length of 10 μm used in this paper, the lateral resolution was 40 nm. The AFM reveals surface features on a nanometer scale which are not discernible either by the NOP or the stylus profiler.

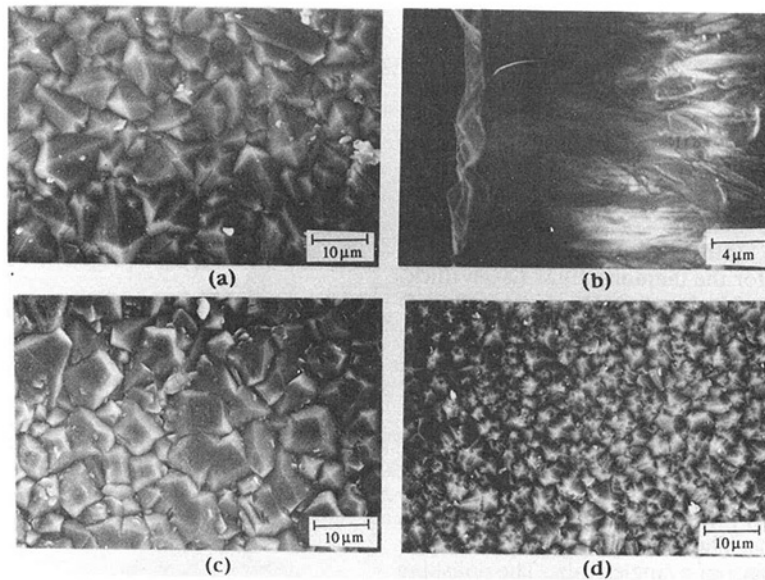


Fig. 2 SEM micrographs of (a) surface of as-deposited coarse-grain diamond film, (b) cross-section of as-deposited coarse-grain diamond film, (c) surface of polished coarse-grain diamond film, and (d) surface of as-deposited fine grain diamond films, deposited by HFCVD technique.

NOP could not be used for rough diamond films, as a result the stylus profiler was used for these films.

The roughness parameters such as rms surface height, surface slope and curvature in the x , y , and radial directions, heights, slopes, and curvatures of all summits, summits density, and autocorrelation distance are calculated by the methods described previously by Bhushan (1990). A summit is defined as a point higher than its four adjacent points in a two-dimensional plot and higher than two adjacent points in a one-dimensional plot. The threshold value is defined as the vertical distance between the higher point and lower adjacent points. To eliminate the effects of noise and ensure that every peak identified is truly substantial, we kept the threshold at 1 nm for the stylus profiler measurements and at 0.25 nm for the AFM measurements, for the diamond films studied here. The threshold for natural diamond and alumina ball was kept at 0.1 nm both for NOP and AFM measurements.

2.5 Friction and Wear Measurements. The friction and wear tests were performed on a ball-on-flat tribometer under reciprocating motion. The alumina ball or 52100 ball-bearing steel ball with a diameter of 5 mm and surface finish of 2–3 nm rms was fixed in a stationary holder and the diamond coated silicon coupons were mounted on a reciprocating stage. The friction force was measured with strain gages and data collected on a personal computer. These tests were carried out under a variety of operating conditions and the reproducibility was better than 95 percent. Typical test conditions were as follows: reciprocating amplitude—0.4 mm, frequency—1 Hz, normal load 1 N, average linear speed 0.8 mm/s, temperature—20 to 500°C, and atmospheric conditions—humidity 1 to 80 percent RH, argon, and nitrogen.

3 Results and Discussion

3.1 Characterization of As-deposited and Polished Diamond Films. SEM micrographs of plan and cross-section images of as-deposited coarse-grain film, plan of polished coarse-grain film, and plan of as-deposited fine-grain film are shown in Fig. 2. We note that the grain size of coarse- and fine-grain films are about 10 to 15 μm and 3 to 5 μm , respectively (Figs. 2(a) and (d)). The columnar growth of the grains of the as-deposited coarse-grain is clearly visible through the

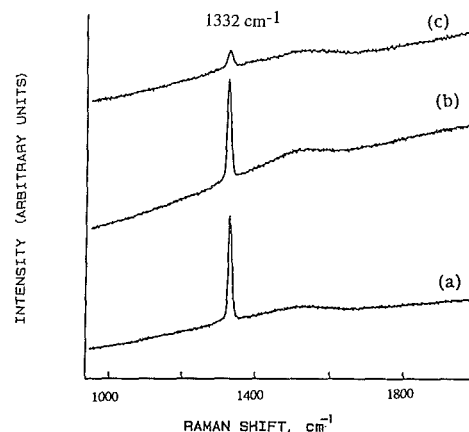


Fig. 3 Raman spectra of (a) as-deposited coarse-grain, (b) polished coarse-grain, and (c) on the wear track of polished coarse-grain diamond films

distinct columns of diamond crystallites, as seen in the cross-section SEM micrograph (Fig. 2(b)). SEM micrographs of the surface of the film show (111) texture. The rounding off of the sharp grains is clearly visible in the micrograph of the polished coarse-grain diamond film (Fig. 2(c)).

Figure 3 shows the Raman spectra of the as-deposited coarse-grain film, polished coarse-grain film, and polished coarse-grain film after the wear test. The Raman spectrum obtained after the wear test was done without removing the wear debris. The sharp line at or near 1332 cm^{-1} is the characteristic feature for diamond and can easily be distinguished from other allotropes such as graphite (“D”—peak at 1343 cm^{-1} and “G”—peak at 1600 cm^{-1}) and amorphous carbon (broad band centered at 1550 cm^{-1}) also known as diamond-like carbon.

The residual stresses are dependent upon the radius of curvature of the coated silicon coupon. A radius of curvature of $\sim 0.8\text{ m}$ was calculated from the surface profile. The substitution of these values in Eq. (1) yields stresses on the order of 1 GPa. In the coatings produced under a typical set of deposition parameters in the present study, we have observed the coated silicon coupons to be of convex shape, which indicates the compressive nature of the residual stresses. However, the

type and magnitude of residual stresses may vary significantly with the deposition conditions such as substrate temperature, deposition rate, and the cooling rates. Mostly compressive stresses are generated during deposition by the competitive growth of the columns. Windischmann et al. (1991) reported that the stresses in diamond films deposited by Microwave Plasma Chemical Vapor Deposition (MPCVD) is sensitive to the deposition conditions and tensile or compressive stress can be achieved depending on methane fraction and deposition temperature. Berry et al. (1990) reported tensile growth stresses of about 0.5 GPa for the diamond films (2 μm thick, 300–700 nm grain size) deposited at 850°C using a MPCVD process. In general, compressive stresses are most advantageous since these can act to close through-thickness cracks and densify the coating as well as retard the crack propagation during the wear particle formation process.

AFM images of as-deposited coarse-grain, as-deposited fine-grain, polished coarse-grain diamond films, and natural diamond are shown in Fig. 4. Rounding off of asperities is observed in the AFM image (Fig. 4(b)) obtained with a scan length of 50 μm over several grains. The AFM images shown in Figs. 4(c) and 4(d) show the surface of a single grain. The polishing process knocks off all high points and leads to a more uniform surface (Fig. 4(d)). The surface of the as-deposited fine-grain film appears rough on an atomic scale (Fig. 4(e)). However, these films exhibit a lower average roughness (rms \sim 180 nm) when measured with a stylus profiler. The surface roughness parameters of as-deposited coarse-grain, polished coarse-grain, as-deposited fine-grain diamond films, natural diamond, and alumina ball, obtained by stylus, NOP, and AFM surface profilers, are summarized in Table 1. We make following observations:

1 Polished coarse-grain diamond films exhibit lower values of rms surface height; profile and surface slopes and curvatures; summit heights, slopes, and curvatures; and summit to

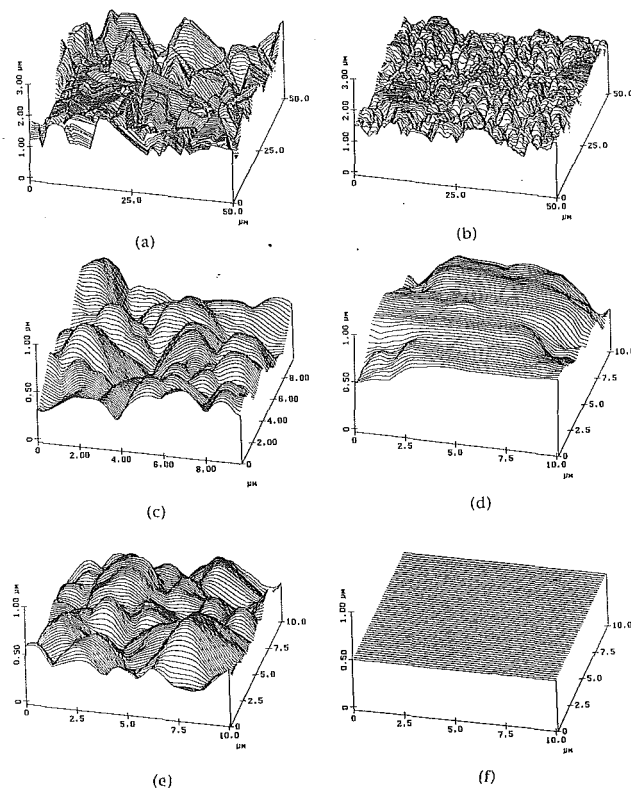


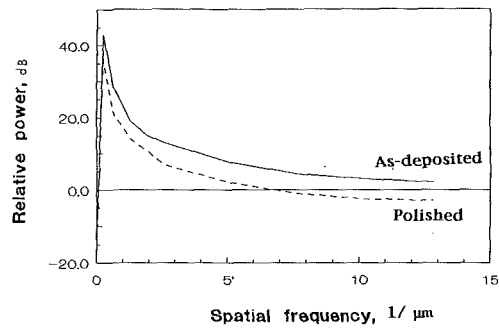
Fig. 4 AFM images (a) as-deposited coarse-grain diamond film (scan length 50 μm), (b) polished coarse-grain diamond film (scan length 50 μm), (c) as-deposited coarse-grain diamond film (scan length 10 μm), (d) polished coarse-grain diamond film (scan length 10 μm), (e) as-deposited fine-grain diamond films, deposited by HFCVD technique and (f) natural diamond.

Table 1 Roughness parameters of as-deposited and polished coarse-grain and as-deposited fine-grain diamond films, natural diamond, and alumina ball

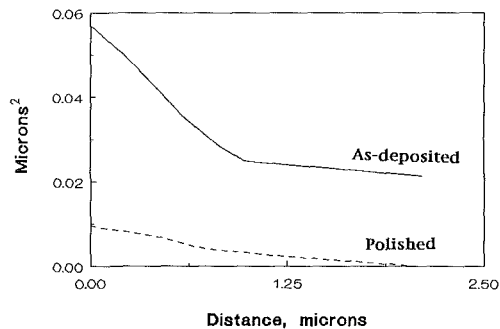
Parameter	As-deposited coarse-grain		Polished coarse-grain		As-deposited fine-grain		Natural diamond		Alumina ball	
	Stylus 2000 $\mu\text{m}/$ 5 μm^*	AFM 10 $\mu\text{m}/$ 40 nm*	Stylus	AFM	Stylus	AFM	NOP 250 $\mu\text{m}/$ 1 μm^*	AFM	NOP	AFM
Rms surface height (nm)	657	304	170	150	183	205	1.72	2.41	2.75	7.0
Rms profile slope x (mrad)	117	492	39.6	274	32.5	378	0.55	14.5	1.55	59.6
Rms profile slope y (mrad)		388		268		294	0.58	10.5	1.45	59.7
Rms profile slope (mrad)		627		383		479	0.80	17.9	1.98	84.4
Rms profile curvature x (1/mm)	43	2940	13	1920	12	2130	0.55	189	1.5	1210
Rms profile curvature y (1/mm)		2730		2470		2200	0.51	194	1.4	1360
Rms profile curvature (1/mm)		2210		1720		1700	0.39	142	1.0	968
Summits height (nm)										
Mean	390	67	125	85	131	136	0.66	2.3	1.4	5.5
Standard deviation	721	377	225	147	172	151	1.66	2.9	2.3	6.1
Summits slope (mrad)										
Mean	73	218	27.3	135	24.1	181	0.20	7.7	0.75	41.5
Standard deviation	47	81	12.4	50	11.1	90	0.25	4.6	0.56	22.2
Summits curvature (1/mm)										
Mean	44	1374	17.4	840	16.8	1219	0.20	158	0.88	893
Standard deviation	24	1773	8.2	611	8.9	1761	0.20	71.6	0.75	570
Summit to valley distance (nm)	4161	1610	1374	995	1154	1280	23	28	23	62
Summit density (mm ⁻²)*	2601	$2.2 \times 10^5 /$ 4.5×10^4	1600	$5.5 \times 10^5 /$ 2.3×10^5	2304	$2.1 \times 10^5 /$ 3.3×10^4	$2.0 \times 10^4 /$ 10^4	$2.4 \times 10^6 /$ 10^4	$1.6 \times 10^4 /$ 217	$1.3 \times 10^7 /$ 1.5×10^5
Autocorrelation distance (μm)		>2		1.84		1.09	16.0	0.51		0.66

*Scan length/lateral resolution.

**All summits/summits with top 25 percent summit height.



(a)



(b)

Fig. 5 (a) Average power spectral density functions (PSDF) and (b) autocovariance functions (ACVF) of as-deposited and polished coarse-grain films. These functions are calculated from the surface profiles shown in Figs. 4(c) and (d).

valley distance, as compared to as-deposited coarse-grain films.

2 As-deposited fine-grain films exhibit almost comparable values of various roughness parameters to that of polished coarse-grain films when measured by stylus profiler and higher values when measured by AFM. This difference in the stylus and AFM data is attributed to the lower lateral resolution ($5 \mu\text{m}$) of stylus profiler and the smaller grain size ($3\text{--}5 \mu\text{m}$) of the film. The fine-grain films exhibit higher summits slopes and curvatures than polished films and lower summits slopes and curvatures than as-deposited coarse-grain films on a microscopic level.

3 The autocorrelation distance of as-deposited coarse-grain films remain almost unchanged after polishing. This is expected as during polishing the asperities are rounded off and the distribution of the asperities does not change.

4 The natural diamond and the alumina ball used in this study were considerably smoother surfaces as compared to diamond films.

So-called texture descriptors, such as power spectral density function (PSDF) and autocovariance function (ACVF), offer a means of representing all wavelengths or spatial sizes of the surface features. The PSDF is interpreted as a measure of frequency distribution of the mean square of the function, that is, the rate of change of the mean square with frequency. The ACVF is most directly interpreted as a measure of how well future values of the function can be predicted based on past observations. PSDF is generally obtained by taking a Fast Fourier Transform of the surface profile and the ACVF can be obtained by the inverse Fourier Transform of the PSDF. These parameters, calculated from the AFM data of as-deposited coarse-grain and polished coarse-grain films, are shown in Fig. 5. The amplitudes of the PSDF and ACVF of as-deposited films are reduced after polishing in agreement with the previous results of Bogli et al. (1992).

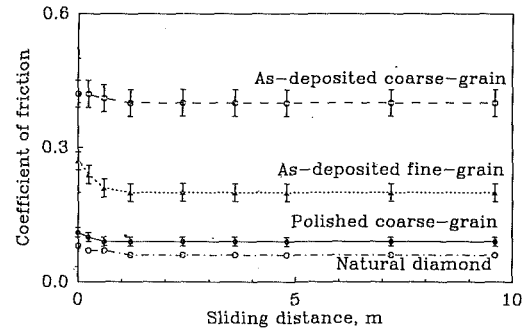


Fig. 6 Coefficient of friction of as-deposited coarse-grain, fine-grain and polished diamond films, and natural diamond versus sliding distance at 1N normal load, 0.8 mm/s sliding speed, and ambient air.

3.2 Friction and Wear Data

3.2.1 Effect of Polishing. The friction profiles of as-deposited coarse-grain (rms $\sim 650 \text{ nm}$) film, as-deposited fine-grain (rms $\sim 180 \text{ nm}$) film, polished (rms $\sim 170 \text{ nm}$) coarse-grain film, and natural diamond (rms $\sim 1.72 \text{ nm}$), slid against an alumina ball (rms $\sim 2.75 \text{ nm}$) are compared in Fig. 6. The polishing of diamond films resulted in a significant reduction of the coefficient of friction from about 0.4 to 0.09. No significant change in the friction was subsequently observed with further reciprocating passes or by increasing the sliding distance. The Raman spectrum of the polished diamond film (Fig. 3, plot c) after the wear test shows that the film retains its diamond phase, although the intensity of the diamond peak is reduced. The decrease in the intensity could have resulted from the presence of alumina wear debris on the sample surface which was not removed. There is no significant increase in graphitic or amorphous carbon as a result of polishing. The coefficient of friction of the polished films is very close to that of natural diamond. This reduction in the friction of the polished film is believed to be as a result of reduction in the ploughing component of friction (see discussion in a later paragraph on the friction mechanisms). Jahanmir et al. (1989) reported low coefficient of friction (~ 0.1) for fine-grained diamond films ($0.5\text{--}2.5 \mu\text{m}$) deposited on SiC disk, sliding against a SiC ball. Hayward et al. (1992) reported a coefficient of friction less than 0.1 for some of their films. Miyoshi et al. (1992) also reported low coefficient of friction (~ 0.2) for films with very fine-grains ($20\text{--}100 \text{ nm}$). Based on the Raman spectra (Miyoshi, 1992), however, it appears that their fine-grained diamond films contained significant amount of nondiamond material.

Wear of the mating alumina ball sliding against diamond surfaces was considerably reduced after polishing. The wear tracks on the mating alumina ball surface and diamond films were examined by optical microscopy and the degree of wear was estimated in terms of the diameter of the round wear scar on the ball and the amount of the wear debris collected on the film. Figure 7 shows the optical micrographs of as-deposited and polished coarse-grain diamond films, as-deposited fine-grain diamond films, and of natural diamond after a wear test. The development of wear scars on the ball surface demonstrates that even natural diamond and polished diamond films can wear ball surfaces. Slight abrasion of the ball surface indicates an abrasive wear type mechanism (Seal, 1965). Abrasion is associated with the formation of patches of wear debris. We note that the wear scar on the alumina ball slid against the polished diamond film is comparable to that against natural diamond after a wear test. Further, the amount of alumina transferred on to the polished diamond film during sliding is considerably lower than that for the as-deposited coarse-grain diamond film (Fig. 7). The debris transferred from the alumina ball to the polished diamond surface fills in the valleys and

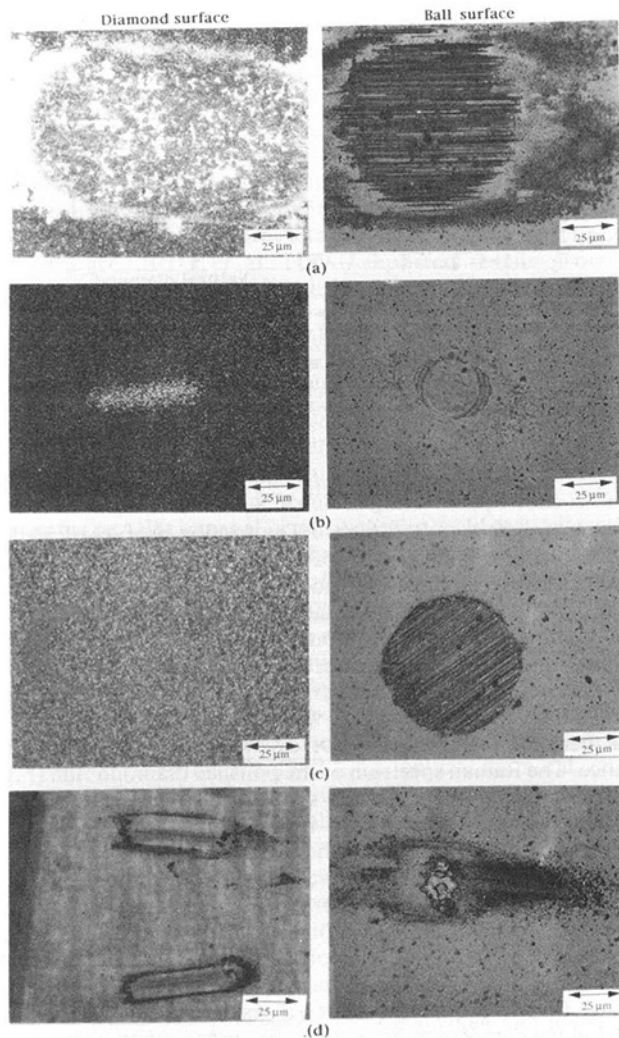


Fig. 7 Optical micrographs of the diamond surface and the alumina balls after the sliding tests on (a) coarse-grain as-deposited diamond film, (b) coarse-grain polished diamond films, (c) fine-grain as-deposited diamond film, and (d) natural diamond.

may therefore help in maintaining low friction even if the alumina ball gets rougher by further sliding. The debris seen on the natural diamond surface comes from the fracture of the asperities on the alumina ball surface. It was observed that most of the debris in natural diamond is generated during the early stage of sliding.

To further demonstrate the influence of roughness on friction, studies were conducted with diamond films of varying roughnesses, Fig. 8. The coefficient of friction decreased from 0.4 to 0.09 as the rms roughnesses of polished films were reduced from 500 to 170 nm, suggesting the important role of surface roughness. There are potentially three mechanisms of friction and one or more of these may be operative in our study. These are adhesive, ploughing, and ratchet mechanisms (Bowden and Tabor, 1950; Tabor, 1979; Seal, 1981; Samuels and Wilks, 1988; and Brookes and Brookes, 1991) which are illustrated in Fig. 9. If two rough surfaces are placed in contact, in addition to adhesion at the asperity contacts, two sets of asperities will interlock. Any attempt to slide one of the surfaces over the other must be impeded by collisions between these asperities which thus gives rise to a friction force. Moreover, continuous relative motion can only occur if the interlocking asperities either ride over each other (ratchet mechanism) or push past each other or fracture (ploughing). Friction force as a result of interfacial adhesion between the asperities of the two mating surfaces is proportional to the real

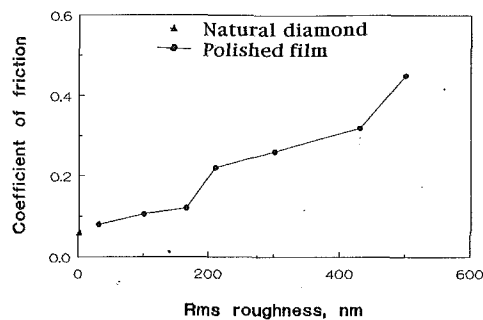


Fig. 8 Effect of surface roughness on the coefficient of friction of diamond films slid against alumina ball at 1N normal load, 0.8 mm/s sliding speed, ambient air, and temperature. The roughnesses of diamond films shown on horizontal axis were obtained by stylus profiler.

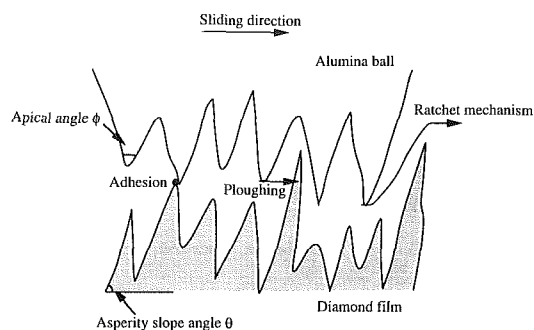


Fig. 9 Magnified view of the asperities contacts of two rough mating surfaces.

area of contact and the shear strength of the contact. The real area of contact increases with a decrease of surface roughness (Greenwood and Williamson, 1966). Since the friction decreased as the roughness decreased in our case, the adhesion mechanism does not appear to account for the observed reduction in friction. With rough diamond films rubbing against softer materials, ploughing and ratchet mechanisms are distinct possibilities.

Based on a model presented by Tabor (1979) for ratchet mechanism, its contribution to the coefficient of friction between two rough surfaces is dependent on the slope of the asperities of a surface having a lower slope. In our studies, the asperities of the ball surface have a lower slope than that of the diamond films (Table 1), therefore, asperity slope of the ball is of importance. As the same topography of the ball surface was used in the experiments conducted in order to study the role of the roughness of the diamond film, ratchet mechanism can not explain the changes in the friction as a function of roughness. However, the ball surface gets rougher during sliding, and ratchet mechanism may contribute to overall friction at a later stage in sliding.

As a hard diamond film slides against a softer ball, plastic flow and grooving of the ball material will occur. For a ball material softer than the diamond film, the ploughing contribution to friction may be significant. The ploughing component of friction also depends on the steepness or slope of the asperities. According to Bowden and Tabor (1950), for a surface with rigid conical asperities sliding over a plane, the ploughing component of friction is approximately equal to $\tan\theta$, where θ is the slope of the asperity with respect to the horizontal. In the present study, polishing reduces the asperity slope angle on both macroscopic and microscopic levels from 73 to 27 mrad and 218 to 135 mrad, respectively. This change may explain to a large extent the decrease in friction from 0.4 to 0.09. The rounded asperities prevent mechanical interlock-

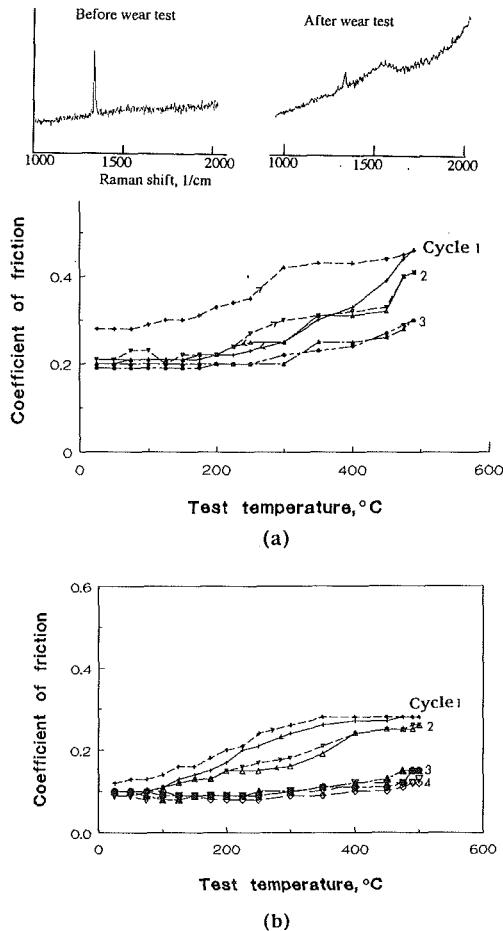


Fig. 10 Coefficient of friction of (a) as-deposited and (b) polished diamond films at 1N normal load, 0.8 mm/s sliding speed, ambient air, and at different temperatures ranging from 20 to 500°C. The Raman spectra of as-deposited film before and after the three cycles of temperatures during the wear test are also shown as insets. Higher background in the Raman spectrum of worn film is due to more fluorescence because of its damage.

ing and ploughing up to some extent and provide an easy slip to the mating surface. Any reaction products generated during the sliding of the alumina ball over the diamond film may also contribute to reducing the coefficient of friction.

It should be noted that for the case of a diamond tip sliding against a diamond film, other mechanisms of friction (such as ratchet and elastic loss mechanisms) may be operative (Samuels and Wilks, 1988).

3.2.2 Effect of Test Temperature. The effect of test temperature on the coefficient of friction of as-deposited and polished diamond films slid against alumina in ambient air is shown in Fig. 10. The coefficient of friction of the as-deposited and polished diamond films increases from 0.29 to 0.45 and 0.11 to 0.28, respectively, as the temperature is increased from 25 to 500°C. This *reproducible* increase in the coefficient of friction at high temperature may be attributed to the combined effects of hydrogen desorption from the diamond surface upon heating (Pepper, 1982; Kohzaki et al., 1992), formation of different tribochemical surface layers on the alumina ball during sliding (e.g., hydrated layer in humid air) (Fischer, 1988), and to increased fracture of the alumina in the contact region as a result of increased plasticity. It was observed that deposition of alumina debris on the surface of the diamond film was thicker when slid at higher temperatures versus at ambient temperature. A significant decrease in the coefficient of friction, from 0.29 to 0.2 and from 0.11 to 0.09 was observed after completion of the first heating cycle for the as-deposited

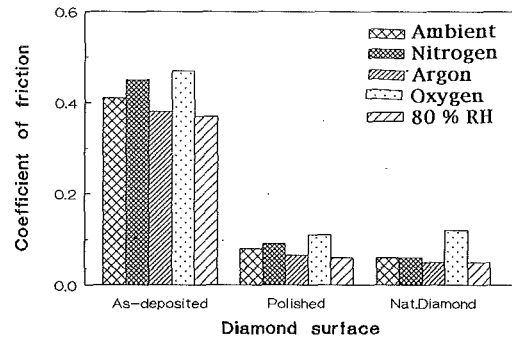


Fig. 11 Coefficient of friction of as-deposited, polished diamond films, and natural diamond at 1 N normal load, 0.8 mm/s sliding speed, and at different environments: ambient air, moist air, dry nitrogen, argon, and oxygen

and polished films, respectively. This reduction in friction is attributed to the combined effects of deposition of alumina debris on the wear track, in-situ graphitization at the micro-contacts (see Raman data in Fig. 10(a) before and after the wear test) and polishing of the film (rms value decreased from 650 nm to 550 nm for the as-deposited film during the sliding process itself).

The friction tests were carried out for four cycles of heating (up to 500°C) and cooling (to ambient). No significant reduction in the coefficient of friction at ambient temperatures upon the completion of the third and fourth (data not shown) heating cycles was found. This insignificant reduction in friction after the third and fourth heating cycle may be because no further graphitization occurred and an increase in the amount of alumina debris deposited on the wear track was negligible. Thus it appears that diamond films can tolerate short high temperature excursions in ambient air without adverse tribological performance during subsequent sliding.

3.2.3 Effect of Test Environments. Friction data for as-deposited coarse-grain and polished coarse-grain diamond films, and natural diamond slid against an alumina ball in various gaseous environments and at different humidities are shown in Fig. 11. The coefficient of friction in nitrogen is slightly higher for as-deposited and polished films, but no significant difference was noticed in the case of natural diamond. The moisture content in air does not seem to have a marked influence on the friction of the diamond films. Miyoshi et al. (1992) have also not observed any effect of moisture on the coefficient of friction and wear of a diamond film sliding against a diamond pin. Minor reductions (5 to 10 percent) in the coefficient of friction of as-deposited diamond films, polished diamond films, and natural diamond were noticed in argon environments. Oxygen environments show an increase of about 20 percent in the coefficient of friction. The exposure of diamond films to an oxygen environment may modify the surface chemistry due to formation of an adsorbed layer which may be instrumental in increasing the adhesion of diamond to the alumina and thus account for an increase in friction. The adsorption of hydrogen on diamond surfaces seems to be unaffected in the presence of nitrogen, argon, and moist air. Tabor (1979) and Chandrasekar and Bhushan (1992) have reported a significant increase in the friction of bulk diamond versus bulk diamond in vacuum. We suspect that diamond films may also exhibit high friction in vacuum. Nevertheless, it is encouraging that the behavior of friction properties of CVD diamond films mimic those of natural diamond in various environments.

3.2.4 Effect of Grain Size. Diamond films with different grain sizes have also been deposited by the HFCVD process by varying the pre-growth substrate preparation. It was ensured

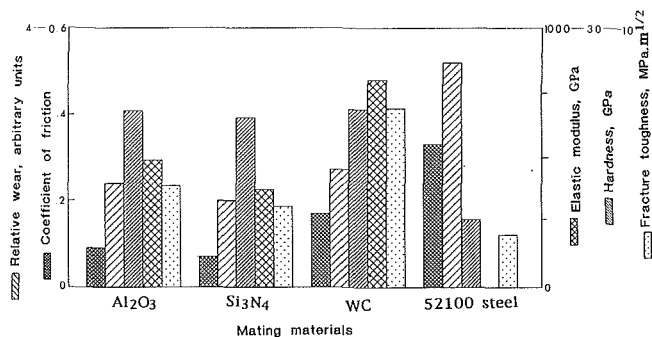


Fig. 12 Effects of mating ball materials (alumina, silicon nitride, tungsten carbide, and 52100 steel balls) on the coefficient of friction and wear of mating materials slid against polished HFCVD diamond films. Wear of the mating balls was determined by measuring the diameter of the round wear scar after a sliding test for 4000 cycles (3.2 m) at ambient conditions.

that both the coarse-grain and fine-grain diamond films had comparable thicknesses of about 20 μm , in order to allow the columnar morphology to be established. Diamond films with fine-grains ($\sim 3\text{--}5$ microns) exhibit considerably lower coefficients of friction (0.20) as compared to the films having larger grains ($\sim 10\text{--}15$ microns). Figures 6 and 7 show a comparison of the coefficient of friction and observed wear of the alumina ball for the coarse-grain and fine-grain diamond films. We see no difference in the Raman spectra of these films (not presented in the paper for the fine-grain film), which implies that our fine-grained diamond films consist of a true diamond phase and have negligible (if any) inclusions of non-diamond phases. The lower coefficient of friction of the as-deposited fine-grain film is attributed to its lower surface roughness (rms ~ 180 nm).

3.2.5 Effect of Mating Ball Materials. Coefficients of friction and relative wear data of polished HFCVD diamond films slid against different mating materials are presented in Fig. 12. The coefficient of friction is minimum (~ 0.06) when slid against silicon nitride and maximum (0.35) when slid against a 52100 steel ball. The wear of the mating materials was obtained by measuring the diameter of the wear scar on the ball surface after 4000 cycles (3.2 m). Wear was maximum for the 52100 steel ball and least in the case of a silicon nitride ball. The higher values of coefficient of friction and relative wear between the diamond film and the 52100 steel ball is likely due to the higher contribution of the ploughing component since the steel has a lower hardness (900 HV) compared with other ceramic ball materials. The debris generated by the 52100 steel ball during the sliding test may also be more adherent on the wear track. The trapped debris on the wear track can cause additional ploughing and can increase the area of contact thereby resulting in higher coefficients of friction and wear.

4 Conclusions

The coefficients of friction of as-deposited 20- μm thick diamond films (rms ~ 650 nm) deposited on silicon by HFCVD, has been reduced (from 0.4 to 0.09) by polishing (rms ~ 170 nm) by a chemomechanical process. Ploughing appears to be the major contributor to high friction of rough diamond films. Rounding off and reduced slope of sharp asperities of the diamond film during the polishing process reduce the contribution of ploughing of the mating materials such as alumina, resulting in lower friction.

Friction of the as-deposited and polished diamond films when slid against alumina, has been observed to increase with increasing temperature likely due to the combined effects of hydrogen desorption, formation of different tribochemical surface layers, and increased fracture of alumina in the contact

region. A considerable reduction in friction at ambient temperature has been observed upon completion of the first heating cycle (up to 500°C) and is attributed to the graphitization of the diamond film due to combined effects of high test temperature and additional temperature rise during sliding.

The moisture content in ambient air and the presence of nitrogen and argon were not observed to affect the friction of diamond coatings. However, the presence of oxygen in the ambient was found to increase the coefficient of friction by about 20 percent.

The nearly identical tribological performance of polished diamond films (in terms of friction ~ 0.09 measured against an alumina ball and of wear of the ball) when compared to natural diamond, demonstrates the feasibility of using HFCVD diamond films for tribological applications.

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