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Friction and wear properties of as-deposited and carbon
ion-implanted diamond films

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Friction and wear properties of as-deposited and carbon ion-implanted diamond films

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Abstract

Recent work on the friction and wear properties of as-deposited and carbon ion-implanted diamond films was reviewed. Diamond films were produced by the microwave plasma chemical vapor deposition (CVD) technique. Diamond films with various grain sizes and surface roughnesses were implanted with carbon ions at 60 keV ion energy, resulting in a dose of 1.2×10^{17} carbon ions per cm^2 . Various analytical techniques, including Raman spectroscopy, proton recoil analysis, Rutherford backscattering, transmission and scanning electron microscopy, X-ray photoelectron spectroscopy, and X-ray diffraction, were utilized to characterize the diamond films. Sliding friction experiments were conducted with a polished natural diamond pin in contact with diamond films in the three environments: humid air (40% relative humidity), dry nitrogen (<1 percent relative humidity), and ultrahigh vacuum (10^{-7} Pa). The CVD diamond films indeed have friction and wear properties similar to those of natural diamond in the three environments. The as-deposited, fine-grain diamond films can be effectively used as self-lubricating, wear-resistant coatings that have low coefficients of friction (0.02 to 0.04) and low wear rates (10^{-7} to 10^{-8} $\text{mm}^3 \text{N}^{-1} \text{m}^{-1}$) in both humid air and dry nitrogen. However, they have high coefficients of friction (1.5 to 1.7) and a high wear rate (10^{-4} $\text{mm}^3 \text{N}^{-1} \text{m}^{-1}$) in ultrahigh vacuum. The carbon ion implantation produced a thin surficial layer (<0.1 μm thick) of amorphous, nondiamond carbon on the diamond films. In humid air and dry nitrogen, the ion-implanted, fine- and coarse-grain diamond films have a low coefficient of friction (around 0.1) and a low wear rate (10^{-7} $\text{mm}^3 \text{N}^{-1} \text{m}^{-1}$). Even in ultrahigh vacuum, the presence of the nondiamond carbon layer reduced the coefficient of friction of fine-grain diamond films to 0.1 or lower and the wear rate to 10^{-6} $\text{mm}^3 \text{N}^{-1} \text{m}^{-1}$. Thus, the carbon ion-implanted, fine-grain diamond films can be effectively used as wear-resistant, self-lubricating coatings not only in air and dry nitrogen, but also in ultrahigh vacuum.

Keywords: Wear; Friction; Diamond films; Ion implantation; Tribology; Superhard coatings

1. Introduction

In aerospace and automotive industries, composites, aluminum alloys, and nonmetallics are becoming the dominant materials. However, the composites, high silicon-content aluminums, and ceramics used in these industries are extremely abrasive and, in many cases, corrosive, making them difficult to machine with existing tools. Chemically vapor-deposited (CVD) diamond provides the answer to many of these hard-to-machine materials because it possesses many of the most desirable properties of a cutting tool: extreme hardness, high abrasion and wear resistance, low coefficient of friction, high seizure and galling resistance, good fatigue strength, high thermal conductivity, chemical and thermal inertness, high corrosion resistance, and environmental compatibility. As such, CVD diamond is also being considered for tribological parts and com-

ponents applications, such as jet nozzles, computer disks, extrusion and drawing dies, medical implants, and bearings and valves for aeropropulsion systems, rocket propulsion systems, and automotive engines [1–3].

However, these physical properties are altered when the clean surface of diamond is brought into contact with a clean counterfacing material and strong bonds form between the two materials. As a result, diamond possesses high friction and poor abrasion and wear resistance [4–10]. This situation applies to some degree in the machining process or in the sliding contacts where fresh surfaces are continuously exposed by the cutting tool or counterfacing material. Under actual conditions of machining or sliding operations, direct contacts of fresh surfaces are unavoidable and the cutting or tribological performance of clean, unlubricated diamond is actually of paramount importance.

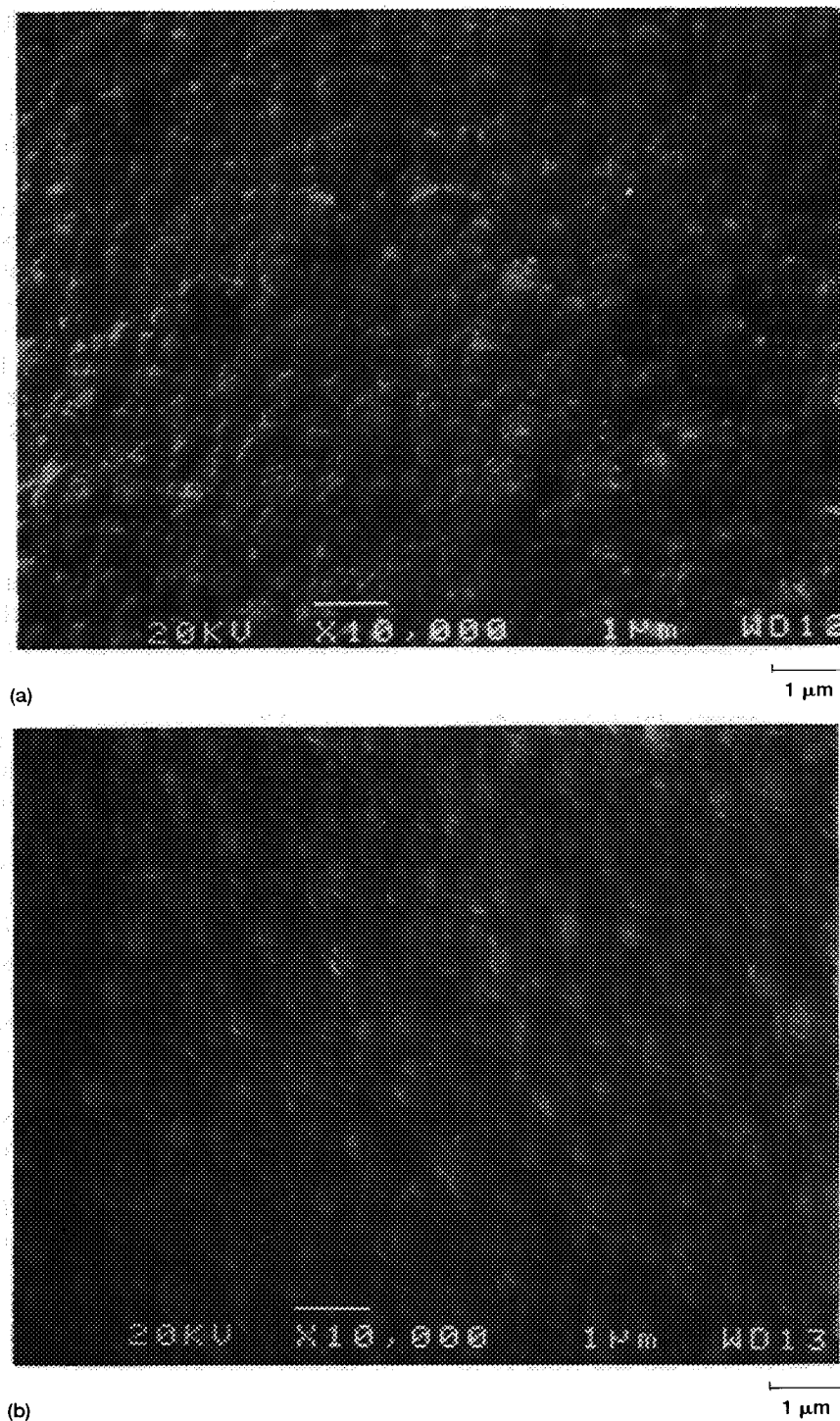


Fig. 1. SEM images of fine-grain diamond films on polycrystalline silicon nitride (Si_3N_4) substrates. (a) As-deposited. (b) Carbon ion-implanted.

To achieve the best performance from CVD diamond as a cutting tool or a self-lubricating, wear resistant barrier for many moving mechanical assemblies, we must have a good understanding of diamond itself, the counterfacing material or material to be machined, and the type of environment and operation. Understanding the behavior of CVD diamond in the applications of diamond-coating technology is challenging.

The objective of this paper is to review the friction and wear behavior of as-deposited and carbon ion-implanted, fine- and coarse-grain CVD diamond films in humid air, dry nitrogen, and ultrahigh vacuum environments. Some earlier data and experimental details on this research are given in Refs. [10–15].

The as-deposited diamond films were produced on the flat surfaces of silicon (Si), polycrystalline α -silicon

carbide (SiC), and polycrystalline silicon nitride (Si_3N_4) substrates using the microwave-plasma-assisted CVD technique. The ion-implanted diamond films were produced by impacting carbon ions into the as-deposited CVD diamond films using an accelerating energy of 60 keV and a current density of $50 \mu\text{A cm}^{-2}$ for approximately 6 min, resulting in a dose of 1.2×10^{17} carbon ions per cm^2 less than $0.1 \mu\text{m}$ thick in a ballistic layer.

A variety of analytical techniques was used to characterize the as-deposited and the carbon ion-implanted, diamond films: scanning and transmission electron microscopy (SEM and TEM) to determine surface morphology and grain size measurements; Rutherford backscattering spectroscopy (RBS) to identify impurities (if any) in the films and to determine carbon and impurity concentrations; Raman spectroscopy and Fourier transform infrared spectroscopy (FTIR) to characterize diamond quality and structure; proton recoil detection (PRD) to measure the hydrogen concentration; X-ray photoelectron spectroscopy (XPS) to characterize surface chemistry; and X-ray diffraction to determine the crystal orientation of the films.

Reciprocating and rotating sliding friction experiments were conducted in humid air at a relative humidity of 40%, in dry nitrogen at a relative humidity of less than 1%, and in ultrahigh vacuum at a pressure of 10^{-7} Pa. The experiments were conducted with the as-deposited and the carbon ion-implanted diamond films in contact with a natural bulk diamond pin (1.3 mm rad.).

2. Microstructural and chemical properties

The morphology, microstructure, and properties of the diamond films deposited onto Si, SiC, and Si_3N_4 substrates vary as a function of substrate temperature, gas ratio, and intensity of the plasma at the deposition surface [10,11].

2.1. Grain size, surface roughness, and morphology

The grain size and surface roughness of the diamond films deposited on the flat surfaces of Si, SiC, and Si_3N_4 substrates ranged from 20 to 3300 nm and from 15 to 160 nm root-mean-square (rms), respectively. The surface roughness increased as the grain size increased [10].

The morphologies of the as-deposited diamond films used in the friction and wear experiments are two types: smooth fine-grain and rough coarse-grain. In the first type, the crystallites have a granulated or spherulitic morphology. The surfaces contained spherical asperities of different sizes as shown in Fig. 1(a). The grain size and surface roughness of the as-deposited, fine-grain diamond films ranged from 20 to 100 nm and from 6 to 37 nm rms, respectively.

In the second type of diamond films, the crystallites

have a triangular faceted morphology typical of diamond. The surfaces contained cubic and octahedral asperities and a rough morphology as shown in Fig. 2(a). The grain size and surface roughness of the as-deposited, coarse-grain diamond films ranged from 1000 to 3300 nm and from 48 to 160 nm rms, respectively.

No significant changes in surface roughness and morphology resulted from the carbon ion implantation (Figs. 1 and 2). The surface features of both carbon ion-implanted, fine- and coarse-grain diamond films were almost the same as those of the as-deposited, fine- and coarse-grain diamond films. The only effect of the carbon ion implantation on the morphology of the diamond films was the rounding of edges (Figs. 1(b) and 2(b)).

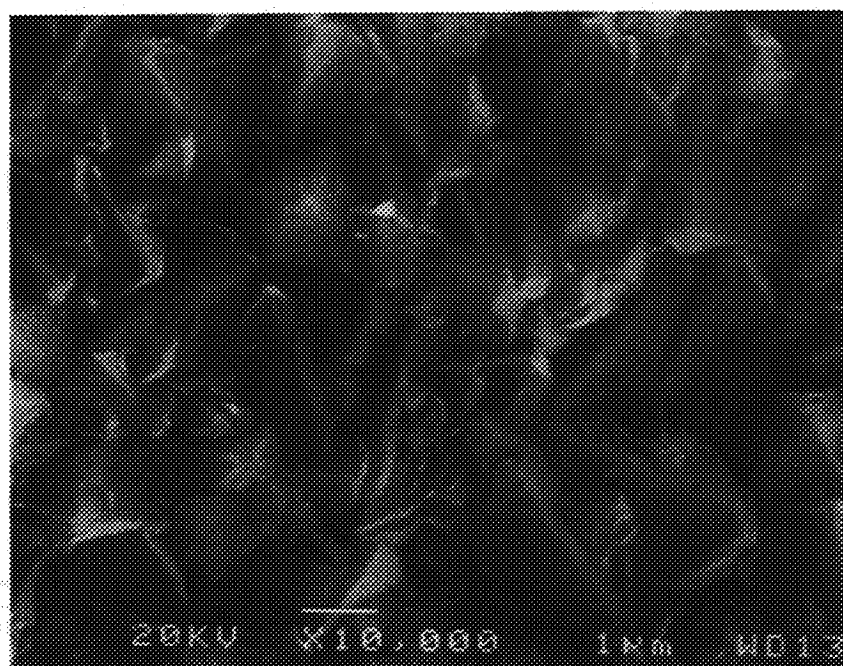
2.2. Bulk and surface chemistry

Rutherford backscattering spectroscopy of the as-deposited diamond films revealed that they consisted of carbon and some elements from the substrate material such as Si [10,11].

Figs. 3(a) and 3(b) present a Raman spectrum of type IIa, single-crystal (111) diamond as a reference and a Raman spectrum of the as-deposited, coarse-grain diamond film, respectively [15]. In Fig. 3(a), the presence of diamond bonding is unambiguous and clear in the Raman spectrum of the single-crystal diamond. Single-crystal diamond is identified by a single sharp Raman peak at 1332 cm^{-1} (wave number).

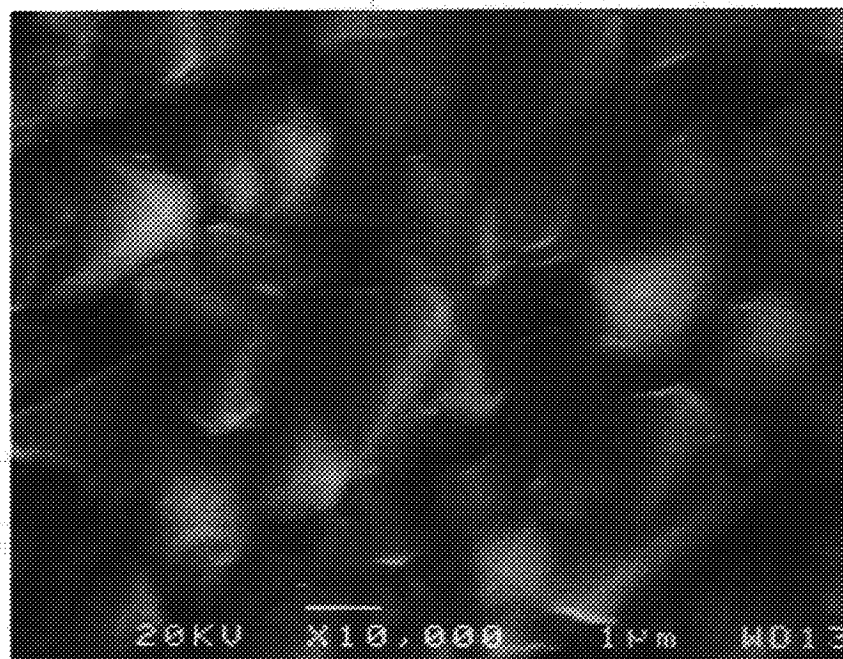
In Fig. 3(b), the Raman spectrum of the as-deposited, fine- and coarse-grain diamond film is deconvolved. When the Raman spectra of both the as-deposited, fine- and coarse-grain diamond films are deconvolved, three bands, which are characteristic of CVD diamond films, are revealed: (1) a sharp band centered near 1332 cm^{-1} , (2) a broad band centered in the $1500\text{--}1530 \text{ cm}^{-1}$ range, and (3) an even broader band centered near 1320 cm^{-1} . The sharp band centered near 1332 cm^{-1} is characteristic of the sp^3 bonding of diamond. The two broad, overlapping bands centered near the range of 1500 to 1530 cm^{-1} and near 1320 cm^{-1} are characteristic of the nondiamond form of carbon and are referred to as the G-band and D-band, respectively. The Raman shifts referred to as the G-band are attributed to the sp^2 bonded carbon, whereas the Raman shifts referred to as the D-band are attributed to the disorder of the nondiamond carbon present in the films.

Figs. 4 and 5 present Raman spectra of the as-deposited and the carbon ion-implanted, fine- and coarse-grain diamond films. The as-deposited, fine-grain diamond films contained considerably more nondiamond carbon than the as-deposited, coarse-grain diamond films as indicated by the relative intensities of the diamond band and the nondiamond carbon bands.



(a)

1 µm



(b)

1 µm

Fig. 2. SEM images of coarse-grain diamond films on polycrystalline silicon nitride (Si_3N_4) substrates. (a) As-deposited. (b) Carbon ion-implanted.

Because the Raman scattering efficiency for sp^2 bonded form of carbon is more than 50 times the efficiency for the sp^3 bonded diamond form of carbon [3], the as-deposited diamond films actually contain much more of the diamond form of carbon than may be inferred from the spectra shown in Figs. 4(a) and 5(a).

Both the frequency and half-width of the diamond band were related to the grain size of the diamond films. The diamond peak is broader and located at a higher phonon frequency for smaller grain-sized films. In addition, micro-Raman spectroscopy shows the presence of Si–O in the fine-grain diamond film on (100) silicon, whereas hexagonal α -SiC is present in the

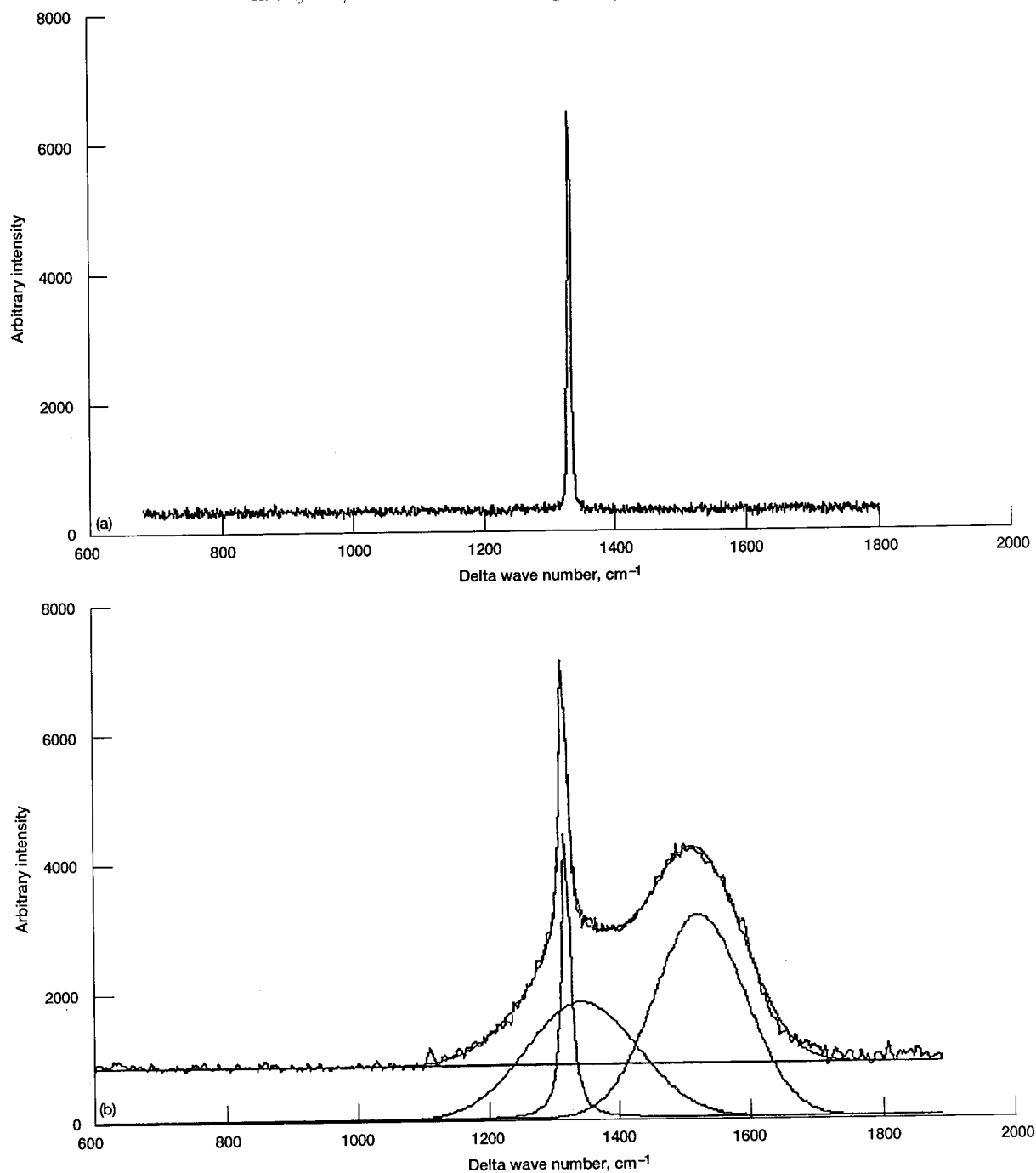


Fig. 3. Raman spectra of a bulk diamond and an as-deposited, coarse-grain diamond film. (a) Bulk diamond. (b) Deconvolution of Raman bands from coarse-grain diamond film on SiC.

coarse-grain diamond film deposited on the silicon nitride substrate.

The characteristic diamond peak is absent from the micro-Raman spectra of the carbon ion-implanted diamond films. In Figs. 4(b) and 5(b), the very broad band with a peak near 1500 to 1530 cm^{-1} and a shoulder near 1320 cm^{-1} , indicative of the amorphous nondiamond form of carbon, is the prominent feature in the Raman spectra. However, no significant change in the surface morphology as a result of carbon ion implantation was observed by scanning electron microscopy and

surface profilometry. Hence, the difference between the Raman spectra of the as-deposited and carbon ion-implanted diamond films can be interpreted as twofold: (1) the intensity of the Raman bands from the nondiamond carbon increased, and (2) the intensity of the diamond peak has decreased to the extent that the diamond peak could not be resolved from the much larger nondiamond carbon bands in the time that the spectra were collected.

Because the depth sensitivity of micro-Raman spectroscopy is 1 μm or less, the significant decrease in the

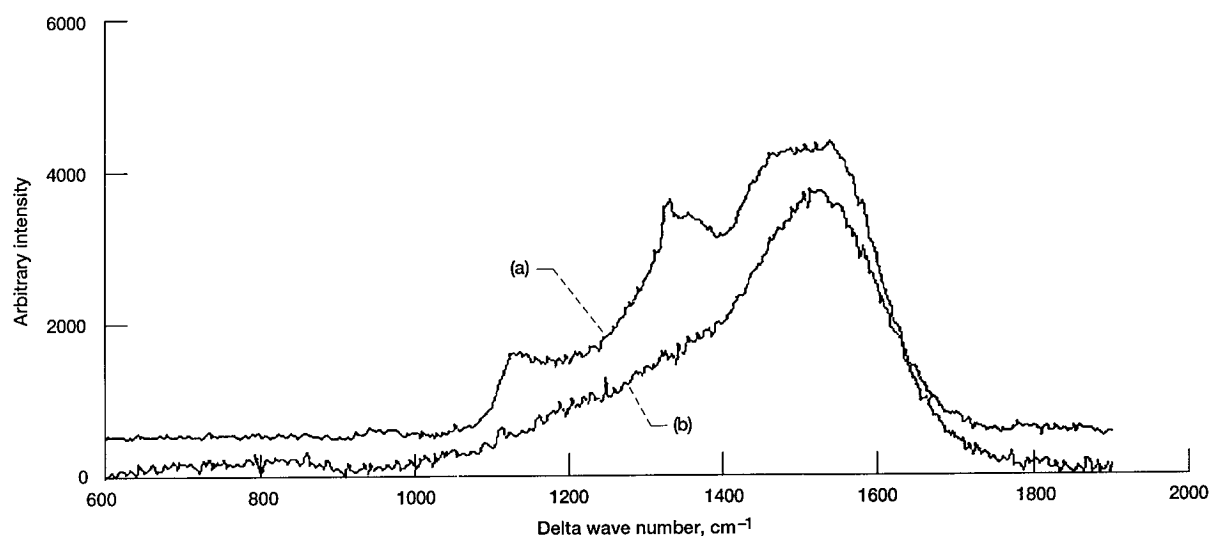


Fig. 4. Raman spectra of fine-grain diamond film of silicon (100) substrate. Spectra are vertically displaced for viewing purposes. (a) As-deposited. (b) Carbon ion-implanted.

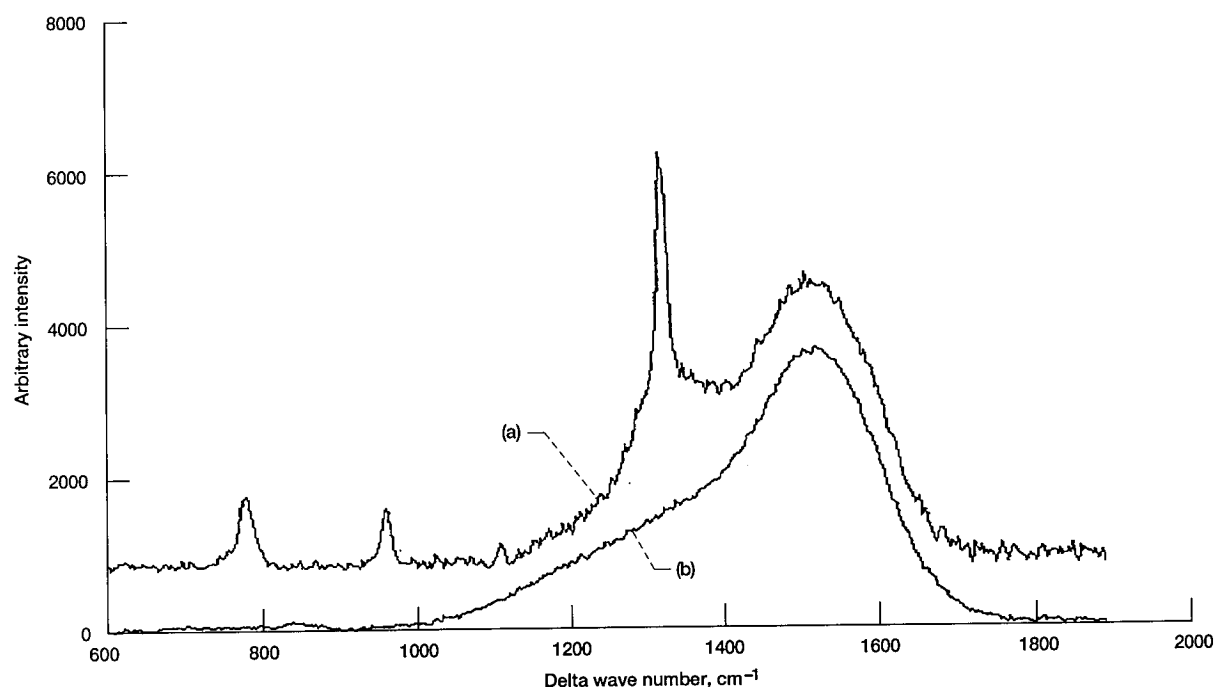


Fig. 5. Raman spectra of coarse-grain diamond film on a Si_3N_4 substrate. Spectra are vertically displaced for viewing purposes. (a) As-deposited. (b) Carbon ion-implanted.

intensity of the diamond peak observed after carbon ion implantation is evidence of both the formation of a nondiamond surface layer on top of the diamond films and of structural damage and distortion from the cubic diamond structure. Furthermore, the increased frequency shift of the G-band and the D-band after carbon ion implantation indicates the nondiamond carbon present in the as-deposited diamond films. These results are consistent with those from the Raman analysis conducted in the previous study [13,14]. The carbon (with an accelerating energy of 160 keV and a dose of

6.7×10^{17} carbon ions per cm^2) and the nitrogen (with an accelerating energy of 35 keV and a dose of 5×10^{16} nitrogen ions per cm^2) ion implantation in diamond films caused structural surface damage to the fine-grain and coarse-grain diamond films, as well as to the polished diamond films. The ion-implantation processes also produced a thin layer of nondiamond carbon [13,14].

Fourier transform infrared (FTIR) spectroscopy of both the as-deposited and carbon ion-implanted diamond films showed absorbance only in the 600–1500 cm^{-1} range [15]. Only very weak absorbance was ob-

served in the carbon–hydrogen (C–H) stretch region for either the as-deposited or the carbon ion-implanted diamond films. This finding is consistent with the low hydrogen concentration determined by proton recoil detection analysis. From the FTIR spectra, the composition of the sampling region appeared quite uniform. However, absorbances from both the films and the substrates were observed in the FTIR spectra. The FTIR spectrum of the carbon ion-implanted diamond

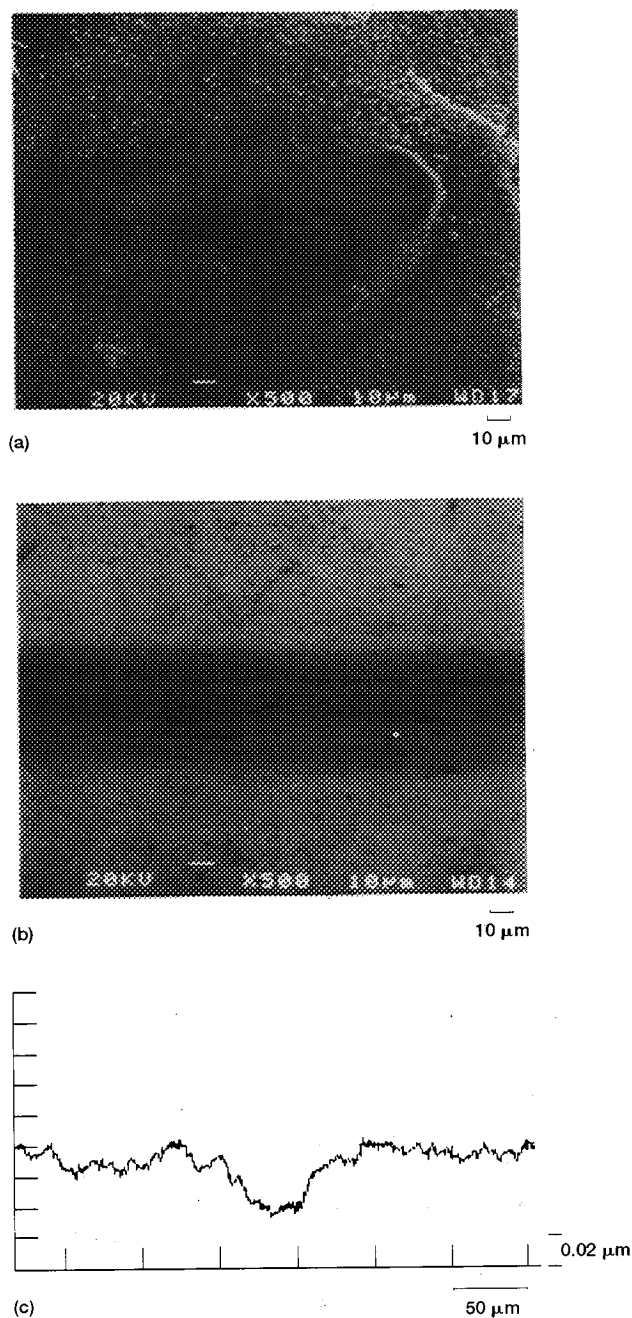


Fig. 6. Wear scar produced on diamond pin and wear track produced on diamond film after sliding contact in vacuum. (a) SEM image of wear scar and its surroundings on diamond pin. (b) SEM image of wear track and its surroundings on diamond film. (c) Profilometer record of wear track.

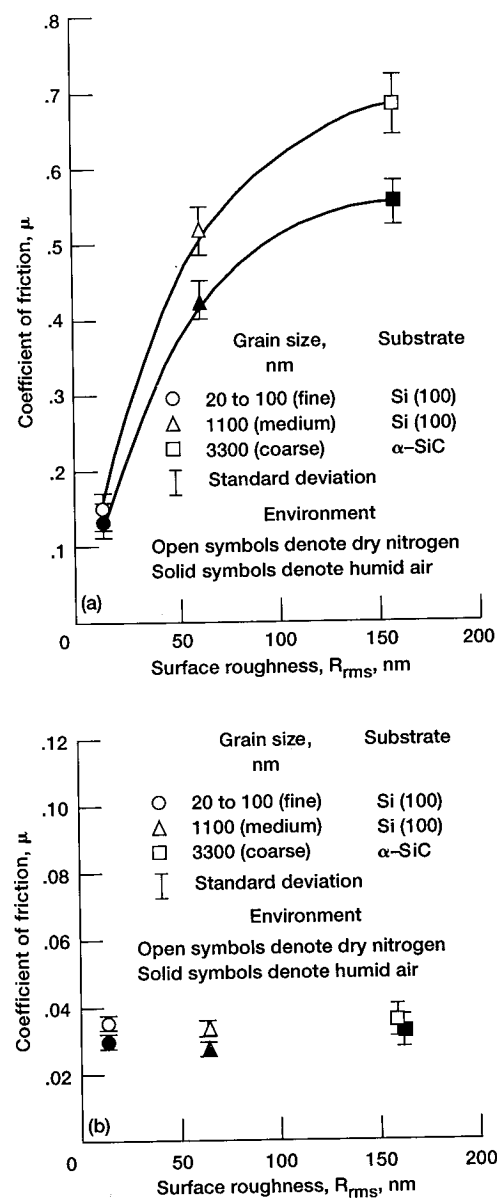


Fig. 7. Coefficients of friction as function of initial surface roughness of as-deposited diamond films in humid air and in dry nitrogen. (a) Initial coefficients of friction. (b) Equilibrium coefficients of friction at 30 000 passes.

film has a much larger peak about 832 cm^{-1} than the as-deposited diamond film has. This absorption band, which seemed to vary in intensity across the ion-implanted film, has been attributed to aromatic ring breathing [16]. This attribution is consistent with the Raman spectra interpretation that carbon ion-implanted diamond films have more sp^2 bonding than the as-deposited diamond films have.

X-ray photoelectron spectra of the surfaces of as-deposited and carbon ion-implanted, fine- and coarse-grain diamond films revealed that all four surfaces contained oxygen (O) [15]. The C/O ratio ranged between 8 and 12. Several atomic percent of nitrogen and silicon were detected in the surfaces of both the as-de-

posited and carbon ion-implanted, coarse-grain diamond films. The plasmon loss structure of the C_{1s} peak of as-deposited and carbon ion-implanted diamond films indicated that carbon ion implantation decreased the sp^3/sp^2 ratio of carbon bonds at the surface [17]. Furthermore, the carbon ion-implanted diamond films were more conductive than the as-deposited diamond films during analysis, indicating that carbon ion implantation alters the normally insulating diamond surface to a conductive carbon surface.

2.3. Crystal structure

X-ray diffraction data revealed that although most of the crystallites in the as-deposited, fine-grain diamond films were oriented along (110) planes, those of the as-deposited, coarse-grain diamond films were oriented along (111) planes [10,11]. The well-formed triangular facets of the coarse-grain diamond films observed in SEM photomicrographs (e.g. Fig. 2) confirm the $\langle 111 \rangle$ orientation.

3. Friction and wear characteristics

In the three environments, humid air, dry nitrogen, and ultrahigh vacuum, the bulk diamond pin tended to produce a wear track (groove) on both as-deposited and carbon ion-implanted diamond films (e.g. Fig. 6). Abrasion or adhesion interaction, or the combination of both, occurred during sliding action.

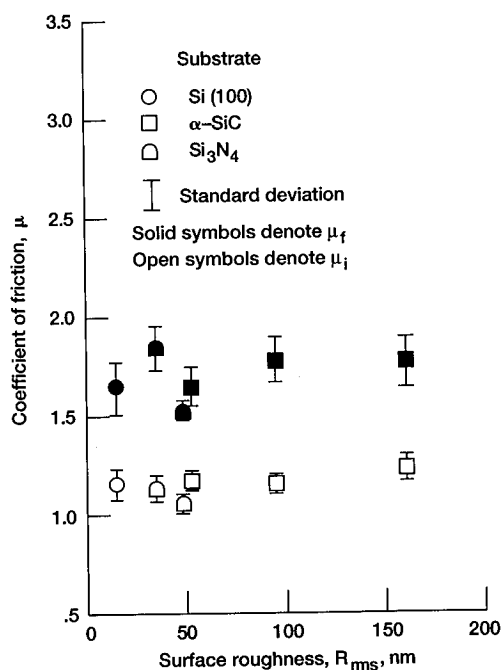


Fig. 8. Initial (μ_f) and equilibrium (μ_i at 100 passes) coefficients of friction as functions of initial surface roughness of as-deposited diamond films in ultrahigh vacuum.

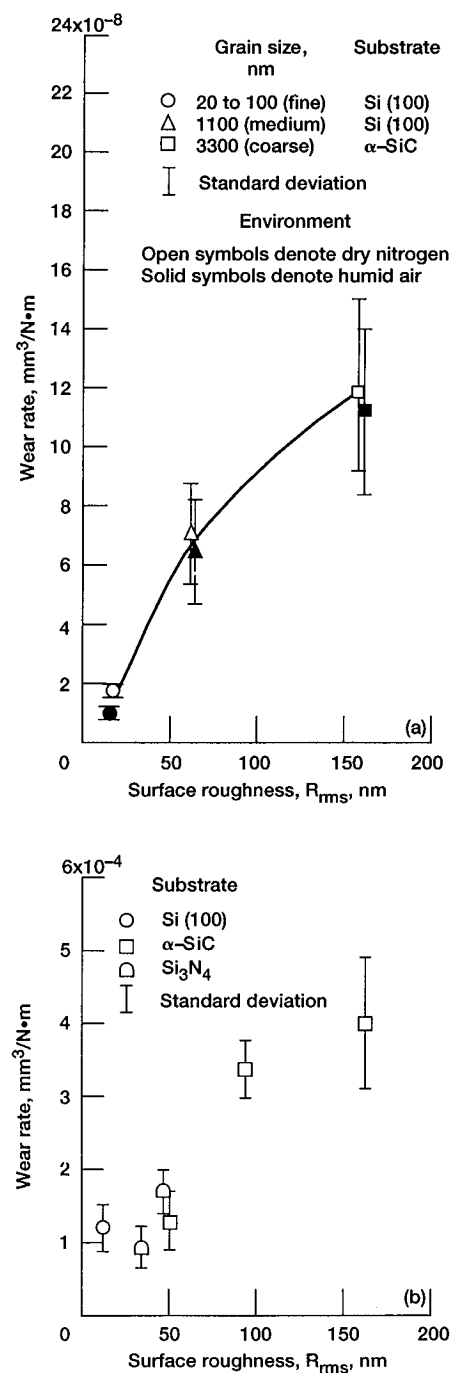


Fig. 9. Wear rates of as-deposited, fine- and coarse-grain diamond films in humid air, dry nitrogen, and ultrahigh vacuum as function of initial surface roughness. (a) Humid air and dry nitrogen. (b) Ultrahigh vacuum.

3.1. As-deposited diamond films

3.1.1. Friction in humid air and in dry nitrogen

In humid air and in dry nitrogen, abrasion occurred and dominated the friction and wear behavior [10,11, 15]. The bulk diamond pin tended to dig into the surface of diamond films during sliding and produce a wear track (groove).

Overall, the friction behavior of as-deposited, fine- and coarse-grain diamond films in contact with a bulk diamond pin in dry nitrogen was similar to their friction behavior in humid air: the coefficient of friction started relatively high (0.13 to 0.52), depending on the initial surface roughness of the diamond films; it rapidly decreased after 60 to 200 passes; and then it gradually decreased with the increasing number of passes, reaching an equilibrium value of between 0.03 and 0.04.

When interactions between the diamond pin surface and the initially sharp tips of asperities on the as-deposited diamond film surfaces were strong, the initial friction was high. The surface roughness of as-deposited diamond films can appreciably influence initial friction: the greater the initial surface roughness, the higher the initial coefficient of friction (Fig. 7(a)). These frictional results are consistent with the work on single-crystal diamond and on diamond coatings [18,19].

As sliding continued and the pin passed repeatedly over the same track, the coefficient of friction was appreciably affected by the wear on the as-deposited diamond films; that is, by the blunted tips of asperities. When repeated sliding produced a smooth groove or a groove with blunted asperities on the surface of the diamond films, the coefficient of friction was low, and the initial surface roughness effect became negligible (Fig. 7(b)); this result showed that the equilibrium

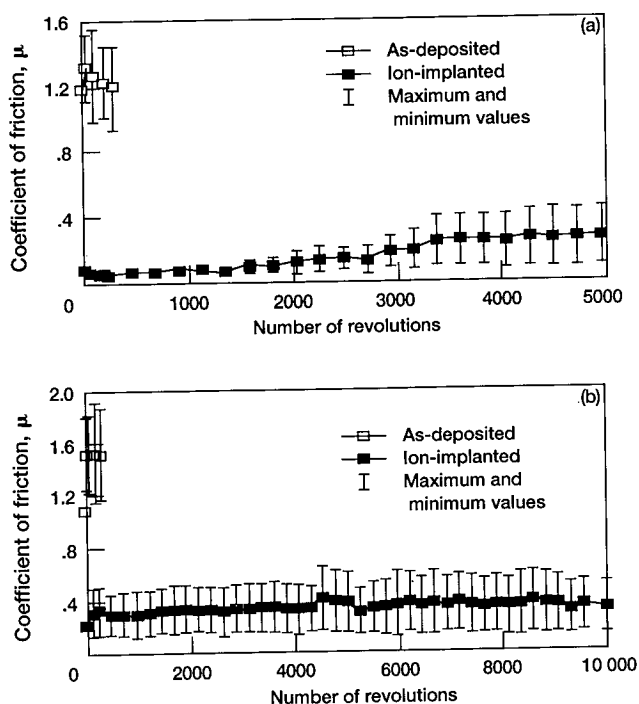


Fig. 10. Coefficient of friction of as-deposited and carbon ion-implanted, fine- and coarse-grain diamond films on Si_3N_4 substrate as functions of number of revolutions in ultrahigh vacuum. (a) Fine-grain. (b) Coarse-grain.

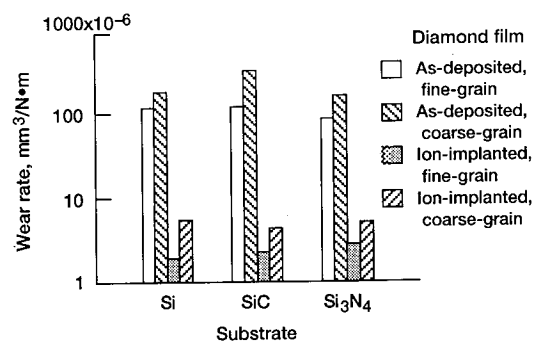


Fig. 11. Wear rates of as-deposited and carbon ion-implanted, fine- and coarse-grain diamond films on Si, SiC, and Si_3N_4 substrates sliding against a diamond pin in ultrahigh vacuum.

coefficient of friction at 30 000 passes was independent of the initial surface roughness of the diamond films.

3.1.2. Friction in ultrahigh vacuum

In ultrahigh vacuum, as in humid air and in dry nitrogen, the bulk diamond pin produced a wear track (e.g. Fig. 6). Both abrasion and adhesion occurred during sliding action, but adhesion dominated the friction and wear behavior.

Generally, the coefficient of friction increased with an increase in the number of passes, reaching an equilibrium value after a certain number of passes in ultrahigh vacuum [10]. This trend in friction behavior is just the opposite of that in humid air and in dry nitrogen.

The initial surface roughness of the as-deposited diamond film had no effect on friction, as presented in Fig. 8. The equilibrium coefficients of friction (1.5 to 1.8) obtained at 100 passes were greater than the initial coefficients of friction (1.1 to 1.3), regardless of the initial surface roughness of the as-deposited diamond films. These results lead us to ask, What factors determine the friction behavior? Which is more important for diamond surfaces in ultrahigh vacuum: abrasion or adhesion?

Our results showed that removing some contaminant surface layer from the contact area of diamond films resulted in a stronger interfacial adhesion between the diamond pin and diamond films and raised the coefficient of friction [10]. A contaminant surface layer was removed by repeatedly sliding the pin over the same track in ultrahigh vacuum.

Our results are in agreement with other researchers' results for single-crystal diamond rubbing against diamond and for CVD diamond sliding against CVD diamond in vacuum [4,9]. At a pressure of 9.3×10^{-8} Pa, Bowden and Hanwell [4] observed an initial coefficient of friction 0.1 for diamond on diamond; within several hundred passes, however, the coefficient of friction rose rapidly to 0.9 and remained constant. Dugger, Peebles and Pope [9] also found that in vacuum

($< 6 \times 10^{-7}$ Pa) the coefficient of friction increased to 0.47 when CVD diamond slid against itself [9]. In both cases, the increase in friction was attributed to cleaning the adsorbed contaminants from the surface by rubbing or sliding in ultrahigh vacuum at room temperature.

An opposite trend in friction behavior was observed in an investigation conducted on CVD diamond films in the relatively modest vacuum (1.3×10^{-3} Pa) of a scanning electron microscope. Gardos and Ravi [7] and Gardos and Soriano [20] found that the coefficient of friction began at 0.5 to 0.8 and dropped within several hundred passes. According to the authors, this resulted from the removal of absorbed oxygen and water vapor. Such an explanation for the decrease in initial friction, however, is not shared by Dugger, Peebles, and Pope, [9] who see the decrease as more likely attributable to a reduction in surface roughness than to the desorption of surface contaminants.

When sliding continues, the wear dulls the tips of the diamond grains and increases the contact area in the wear track, thereby causing an increase in friction. The increase in friction that results from cleaning off the contaminant surface layer by sliding and from increasing the contact area is greater than the corresponding decrease in friction that results from blunting the tips of surface asperities. This relationship is apparent in Fig. 8; here the coefficients of friction (1.5 to 1.8) at 100 passes are greater than the initial coefficients of friction (1.1 to 1.3) regardless of the initial surface roughness of the diamond films. In ultrahigh vacuum, therefore, the friction arises primarily from adhesion between the sliding surfaces of the diamond pin and diamond films.

Gardos, Ravi, and Soriano found that the coefficients of friction for CVD diamond on CVD in vacuum (1.3×10^{-3} Pa) sometimes increased to as high as 0.8 as the temperature increased [7,20]. They attributed this high friction to the presence of dangling bonds on the surfaces of the diamond coatings. Dugger, Peebles, and Pope [9] attributed the high “clean state” value of the coefficient of friction (as high as about 0.5) to the adhesive interaction of CVD diamond surfaces. Under the ultrahigh vacuum condition of our experiments, it was adhesion between the sliding surfaces of the diamond pin and diamond films that played a significant role in the friction process; the surface roughness of the diamond films did not have much influence on the friction of as-deposited diamond films in ultrahigh vacuum [10].

3.1.3. Wear rate

In humid air, dry nitrogen, and ultrahigh vacuum, the diamond pin grooved the surfaces of diamond films. The groove surface was smoother than the original surface of the as-deposited diamond films. Further analysis of the grooves by scanning electron microscopy revealed that the tips of the diamond coating asperities

were worn smooth and the gaps between asperities were filled by wear debris.

Fig. 9 presents the wear rates of the as-deposited diamond films as a function of the initial surface roughness in the three environments. The wear rate was strongly dependent on the initial surface roughness of as-deposited diamond films; it increased markedly with an increase in the initial surface roughness.

The wear rates of the as-deposited diamond films measured in dry nitrogen were similar to those measured in humid air. However, the wear rates of the as-deposited diamond films measured in ultrahigh vacuum were 10 000 times higher than those measured in humid air and in dry nitrogen. Obviously, under these vacuum conditions, adhesion between the sliding surfaces of the diamond pin and diamond film plays an important role in the wear process.

Note that the wear rates of the as-deposited diamond films in humid air and in dry nitrogen were comparable to the wear rates of single-crystal diamonds and other CVD diamond films [8,12,21].

3.2. Ion-implanted diamond films

3.2.1. Friction and wear in humid air and in dry nitrogen

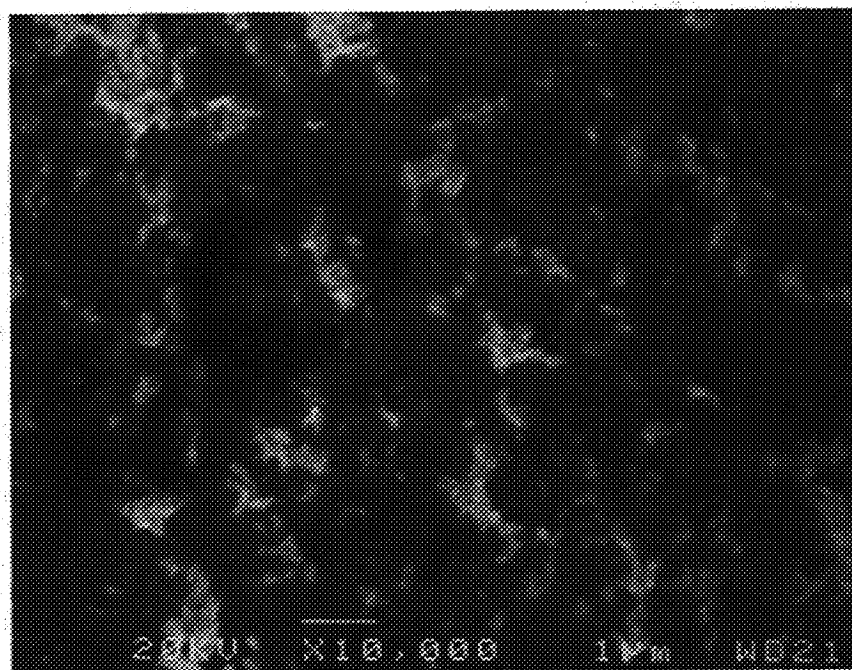
The effect of carbon ion implantation on the coefficients of friction in humid air and in dry nitrogen was small. The coefficients of friction were low, around 0.1.

Although the wear rates of the ion-implanted diamond films were higher than those of the as-deposited diamond films, they were on the order of $10^{-7} \text{ mm}^3 \text{ N}^{-1} \text{ m}^{-1}$, which were at an acceptable level of wear resistance for tribological applications,

3.2.2. Friction and wear in ultrahigh vacuum

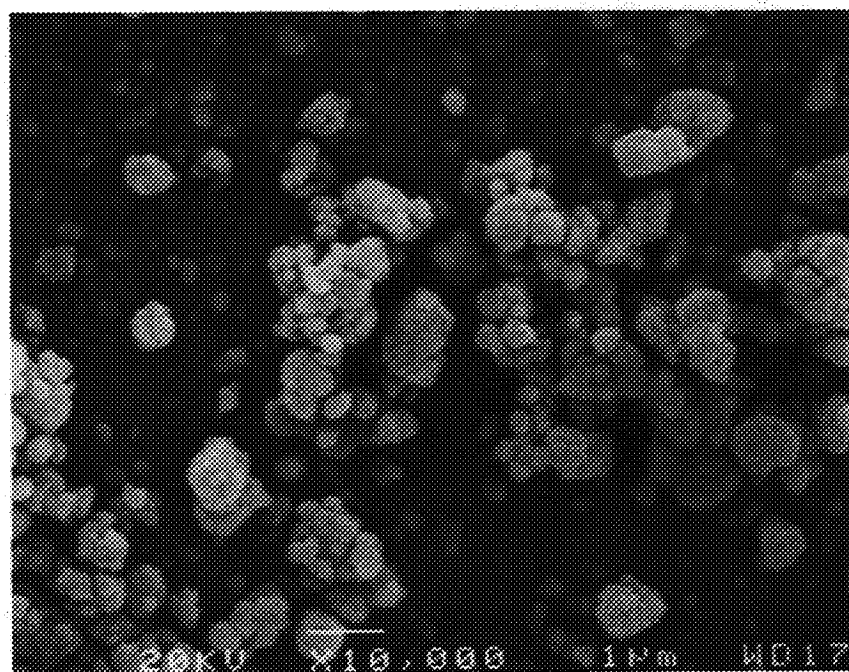
The effects of carbon ion implantation on the friction and wear behavior in ultrahigh vacuum were twofold: (1) a reduction in the coefficient of friction and (2) a decrease in the wear rate. The coefficient of friction obtained for the carbon ion-implanted, fine-grain diamond films were less than 0.1, which were lower than those obtained for the as-deposited, fine-grain diamond films by factors of 20 to 30 (e.g., Fig. 10 (a)). Likewise, the coefficients of friction obtained for the carbon ion-implanted, coarse-grain diamond films were approximately 0.35, which were lower than those obtained for the as-deposited diamond films by a factor of 5 (Fig. 10 (b)).

The average wear rates for the carbon ion-implanted, fine-grain diamond films were on the order of $10^{-6} \text{ mm}^3 \text{ N}^{-1} \text{ m}^{-1}$, which were lower than those obtained for the as-deposited, fine-grain diamond films by factors of 30 to 60 (Fig. 11). Similarly, the average wear rates for the carbon ion-implanted, coarse-grain diamond films were on the order of $10^{-6} \text{ mm}^3 \text{ N}^{-1} \text{ m}^{-1}$, which were



View at center of wear track

1 µm



(a)

View on side of wear track

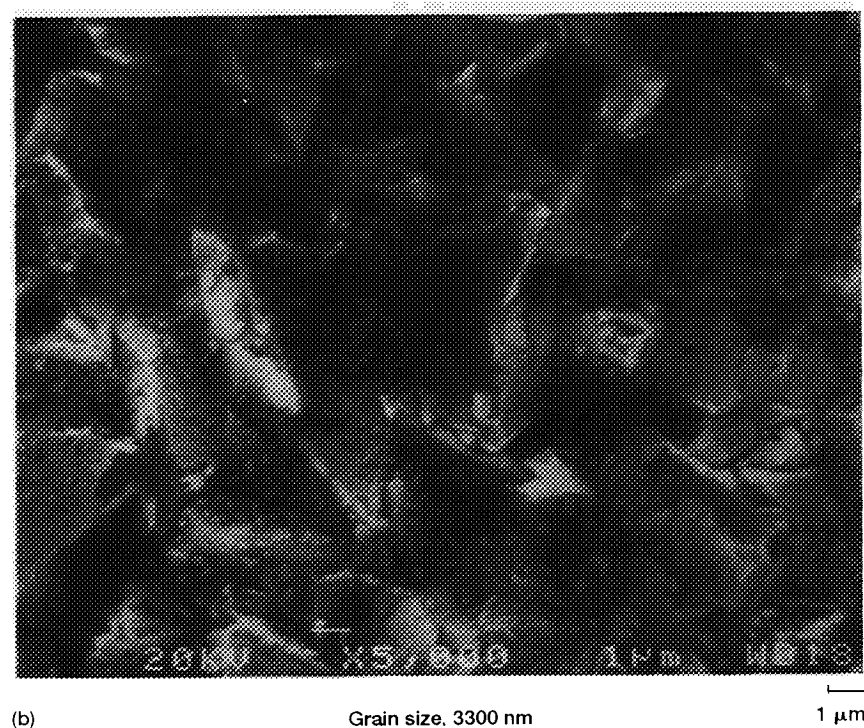
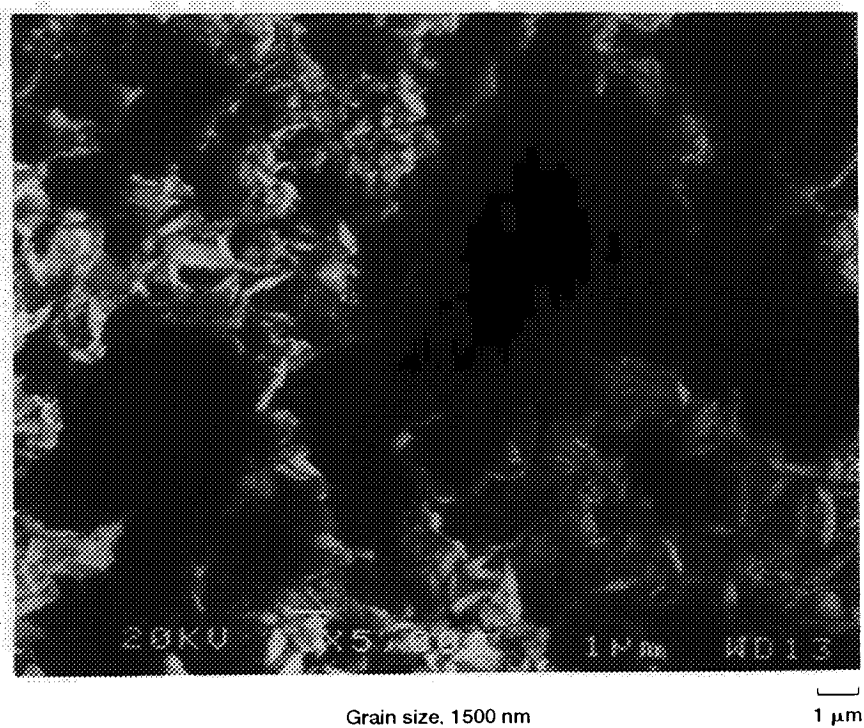
1 µm

Fig. 12. SEM images of a wear track and their surroundings produced on as-deposited, fine-grain diamond film, as-deposited, coarse-grain diamond films, and carbon ion-implanted, fine-grain diamond film after sliding against a diamond pin in ultrahigh vacuum. (a) As-deposited, fine-grain diamond film.

lower than those obtained for the as-deposited, coarse-grain diamond films by factors of 30 to 80.

With the ion-implanted, fine-grain diamond films, both the coefficient of friction and wear rate were at acceptable levels for tribological application in ultra-

high vacuum. With the ion-implanted, coarse-grain diamond films, however, the coefficient of friction (0.35) was too high for use in tribological applications in ultrahigh vacuum, even though the wear rate was acceptable.



(b)

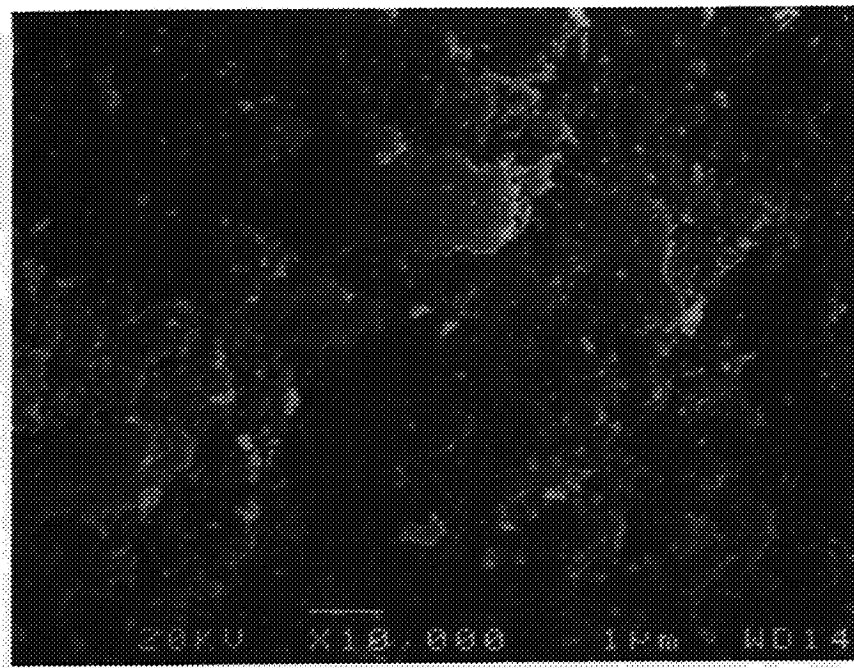
Fig. 12 (b) As-deposited, coarse-grain diamond films.

4. Mechanisms of friction

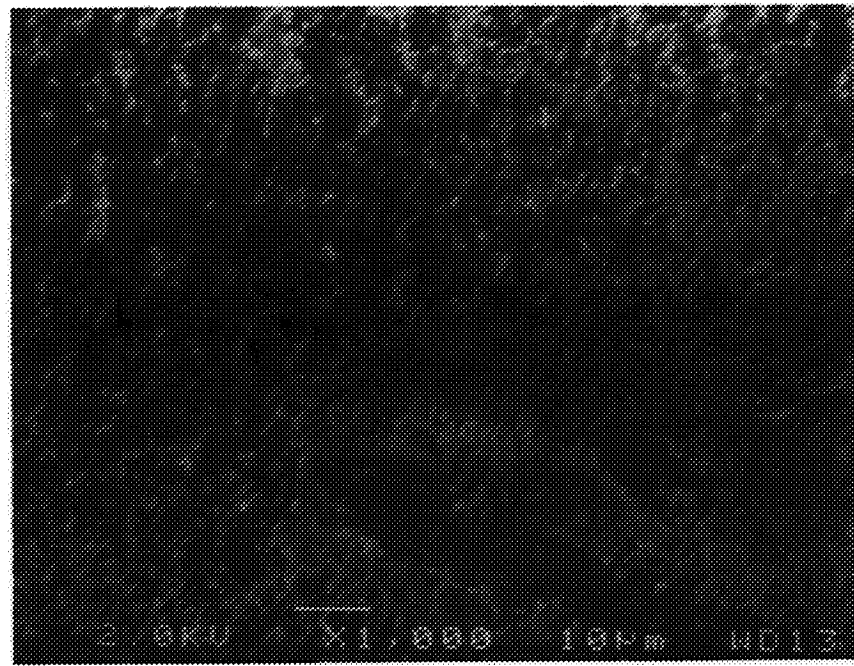
4.1. Fine-grain diamond films

Because the surface of fine-grain diamond films is smooth and the asperities are round, if we neglect the

plowing term, the friction arising between the fine-grain diamond film and the diamond pin is described by the equation $\mu = sA/W$, where μ is the coefficient of friction; s , the shear strength of junctions (contact area); A , the true contact area; and W , the normal contact load [22,23].



View at center of wear track

1 μm 

(c)

View on side of wear track

10 μm

Fig 12 (c) Carbon ion-implanted, fine-grain diamond film.

4.1.1. Humid air and dry nitrogen environment

In humid air and in dry nitrogen, the atmosphere provides a strongly attached contaminant layer which has a low shear strength s [6,15]. However, the load is

largely supported by hard as-deposited diamond films because the contaminant layer is thin (~ 2 nm). Consequently, the true area of contact A is small. For this reason the coefficient of friction for both the as-de-

Table 1
Summary of physical properties of diamond films

(a) As-Deposited		
As-deposited diamond films	Fine-grain	Coarse-grain
Grain size, nm	20 to 100	1000 to 3300
Surface roughness, nm, rms	15 to 50	52 to 160
Shape of asperities	Spherical	Cubic and octahedral
Morphology	Granulated or spherulitic	Triangular faceted
Hydrogen concentration, at.%	2.5	<1
Crystal orientation	<110>	<111>
sp ³ bonded carbon	Less	Greater
sp ² bonded carbon	Greater	Less
(b) Carbon ion-implanted, fine- and coarse-grain		
Presence of a thin layer (<0.1 μm thick) of amorphous, nondiamond carbon in the near surface region of diamond films		
No appreciable change in surface roughness and morphology		

posited, fine-grain diamond films is low (<0.1) in humid air and in dry nitrogen. In the case of the carbon ion-implanted, fine-grain diamond films, because both the contaminant layer and nondiamond carbon surface layer have a low shear strength, the coefficient of friction is low (<0.1) in humid air and in dry nitrogen.

4.1.2. Ultrahigh vacuum environment

In ultrahigh vacuum, the high coefficients of friction

(>1.0) for the as-deposited diamond films arise primarily from the adhesion between the sliding surfaces [10]. In this case, the area of contact A is small, resulting from the high elastic modulus and high hardness of the as-deposited diamond film, but the shear strength of the junctions s is correspondingly high. The presence of dangling bonds on the surfaces of the diamond films may play a significant role in the high shear strength of the junctions in vacuum [5,7]. For this reason, the coefficient of friction of the as-deposited diamond films is high (>1.0) in ultrahigh vacuum.

In the case of the carbon ion-implanted diamond films, because the nondiamond carbon surface layer formed is thin (<0.1 μm), the contact load is largely supported by the hard, underlying diamond films. Consequently, the true area of contact A , resulting from the high elastic modulus of the underlying diamond, is again small. However, the nondiamond carbon has a low shear strength s . The combination of the low shear strength s of the thin nondiamond carbon surface layer and the small true contact area A gives rise to low coefficients of friction (<0.1) for the carbon ion-implanted, fine-grain diamond films, even in ultrahigh vacuum. Thus, the thin nondiamond carbon surface layer produced by carbon ion implantation provides lubrication in ultrahigh vacuum.

Note that when the nondiamond carbon surface layer is removed from the diamond film during repeated sliding action, the coefficient of friction increased to a greater value (0.35) even with the fine-grain diamond films.

Table 2
Summary of tribological properties of diamond films

Environment	Properties	Fine-grain	Coarse-grain
(a) As-deposited			
Air and dry nitrogen	Coefficient of friction in running-in	0.15	>0.4
	Coefficient of friction at 30 000 passes	0.03 to 0.04	0.03 to 0.04
	Wear rate, $\text{mm}^3 \text{N}^{-1} \text{m}^{-1}$	10^{-8}	10^{-8} to 10^{-7}
Ultrahigh vacuum	Coefficient of friction in running-in	1.2	1.2
	Coefficient of friction at 100 passes	1.7	1.7
	Wear rate, $\text{mm}^3 \text{N}^{-1} \text{m}^{-1}$	1×10^{-4}	1 to 4×10^{-4}
(b) Carbon ion-implanted diamond films			
Air	Coefficient of friction in running-in	0.1	0.3
	Wear rate, $\text{mm}^3 \text{N}^{-1} \text{m}^{-1}$	10^{-7}	10^{-7}
	Coefficient of friction at 30 000 passes	0.08	0.1
Dry nitrogen	Coefficient of friction in running-in	0.06	0.12
	Coefficient of friction at 30 000 passes	0.05	0.08
	Wear rate, $\text{mm}^3 \text{N}^{-1} \text{m}^{-1}$	10^{-7}	10^{-7}
Ultrahigh vacuum	Coefficient of friction in running-in	0.1 to 0.15	0.2
	Coefficient of friction at 100 passes	<0.1	0.35
	Wear rate, $\text{mm}^3 \text{N}^{-1} \text{m}^{-1}$	10^{-6}	10^{-6}

4.2. Coarse-grain diamond films

The friction of the coarse-grain diamond films may be attributed to the sum of an adhesion and a plowing (a fracture and deformation) resulting from the interaction of the sharp asperities with the diamond pin.

4.2.1. Humid air and dry nitrogen environment

In humid air and in dry nitrogen, the atmosphere provides a strongly attached contaminant which has a low shear strength. However, plowing (abrasive interaction) is significant. For this reason, the coefficient of friction for both the as-deposited and the ion-implanted coarse-grain diamond films is high and surface roughness can influence friction.

4.2.2. Ultrahigh vacuum environment

With the as-deposited, coarse-grain diamond films, even though the surface asperities have sharp tips, adhesion between the sliding surfaces of the diamond pin and diamond films still plays the most significant role in the friction in ultrahigh vacuum; plowing resulting from the interaction of the sharp asperities with the diamond pin was insignificant. As stated earlier, the surface roughness of the as-deposited diamond films does not have much influence on the coefficient of friction of as-deposited diamond films in ultrahigh vacuum [10].

With the ion-implanted, coarse-grain diamond films, however, surface roughness affects the initial coefficients of friction in ultrahigh vacuum. Although the nondiamond carbon surface layer provides low shear strength at the contact areas, the coefficients of friction of the carbon ion-implanted, coarse-grain diamond films are still 3 to 4 times higher than those of the carbon ion-implanted, fine-grain diamond films in ultrahigh vacuum. The higher coefficient of friction is caused by the interactions of the asperities on the coarse-grain diamond films. This surface roughness effect on friction of the carbon ion-implanted diamond films in ultrahigh vacuum is similar to that on the friction behavior of as-deposited diamond films in humid air and in dry nitrogen. The two most significant factors influencing the coefficients of friction of the carbon ion-implanted, coarse-grain diamond films are (1) plowing between the surface asperities and the diamond pin, and (2) adhesion at the frictional junction, which is relatively low because the nondiamond carbon surface layer produced by carbon ion implantation has a low shear strength.

5. Mechanisms of wear

The generally accepted mechanism of wear for diamond is that of small fragments chipping off the surface

[8,12,21,24], which is in agreement with the SEM observations of the diamond films and their wear debris particles (e.g. Fig. 12). Debris generated by sliding action provide a useful history of the wear process. In addition to the quality and size of the wear debris particles, much useful information is obtainable from microscopic observation of their nature and shape [25,26].

Wear debris particles (submicron to micron in size) were observed on the surfaces of both the diamond pin and the diamond films. Much finer particles were generated on the surfaces of the carbon ion-implanted diamond films than those generated on the surfaces of the as-deposited diamond films, regardless of grain size. The generation of finer wear debris particles from the surfaces of carbon ion-implanted diamond films primarily resulted from the wear and removal of amorphous, nondiamond carbon by sliding action. The size differences of the wear particles contributed to their respective wear rates. The wear rates of the carbon ion-implanted diamond films (on the order of 10^{-6} mm³ N⁻¹ m⁻¹) are considerably lower than those of the as-deposited diamond films (on the order of 10^{-4} mm³ N⁻¹ m⁻¹).

6. Summary of properties of diamond films

The physical properties of the as-deposited and ion-implanted diamond films are summarized in Table 1. The carbon ion-implantation process using an accelerating energy of 60 keV and a dose of 1.2×10^{17} carbon ions per cm² changes the surface chemistry of the microwave-plasma-vapor-deposited, fine- and coarse-grain diamond films and causes structural damage to the diamond lattice. As a result, a thin layer of amorphous, nondiamond carbon is produced in the near surface region of the fine- and coarse-grain diamond films.

For comparison, the coefficients of friction and wear rates of the as-deposited and ion-implanted, fine- and coarse-grain diamond films are summarized in Table 2.

7. Conclusions

From the results of characterization and sliding friction experiments on as-deposited and carbon ion-implanted, fine- and coarse-grain diamond films in ultrahigh vacuum, the following conclusions were drawn.

(1) The as-deposited, fine-grain diamond films can be effectively used as wear-resistant, self-lubricating coatings in humid air and in dry nitrogen, but they have a high coefficient of friction (> 1) and wear rate (10^{-4} mm³ N⁻¹ m⁻¹) in ultrahigh vacuum.

(2) The carbon ion-implanted, fine-grain diamond films can be effectively used as wear-resistant, self-lubricating coatings not only in humid air and in dry nitrogen but also in ultrahigh vacuum.

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References

- [1] Y. Tzeng, M. Yoshikawa and M. Murakawa (eds.), Applications of Diamond Films and Related Materials, *Proc. First Int. Conf. on the Applications of Diamond Films and Related Materials*, Elsevier, New York, 1991.
- [2] R.E. Clausing et al., (eds.) *Diamond and Diamond-like Films and Coatings*, Plenum Press, New York, 1991.
- [3] H.O. Pierson, *Handbook of Carbon, Graphite, Diamond and Fullerenes*, Noyes Publications, Park Ridge, NJ, 1993.
- [4] F.P. Bowden and A.E. Hanwell, The Friction of Clean Crystal Surfaces, *Proc. R. Soc. London ser. A*, 295 (1966) 233–243.
- [5] D. Tabor, in J.E. Field (ed.), *Properties of Diamond*, Academic Press, New York, 1979, pp. 325–350.
- [6] K. Miyoshi and D.H. Buckley, Adhesion and Friction of Single-Crystal Diamond in Contact with Transition Metals, *Appl. Surf. Sci.*, 6 (1980) 161–172.
- [7] M.N. Gardos and K.V. Ravi, Tribological Behavior of CVD Diamond Films, *Electrochem. Soc.*, 89 (12) (1989) 475–493.
- [8] I.P. Hayward, Friction and Wear of Properties of Diamonds and Diamond Coatings, *Surf. Coat. Technol.*, 49 (1991) 544–559.
- [9] M.T. Dugger, D.E. Peebles and L.E. Pope, in Y.-W. Chung, A.M. Homola and G.B. Street, (eds.) *Surface Science Investigations in Tribology: Experimental Approaches*, American Chemical Society, ACS Symp. Series no. 485, Washington DC, 1992, pp. 72.
- [10] K. Miyoshi et al., Friction and Wear of Plasma-Deposited Diamond Films, *J. Appl. Phys.*, 74 (7) (1993) 4446–4454.
- [11] R.L.C. Wu et al., Synthesis and Characterization of Fine Grain Diamond Films, *J. Appl. Phys.*, 72 (1) (1992) 110–116.
- [12] K. Miyoshi, R.L.C. Wu and A. Garscadden, Friction and Wear of Diamond and Diamondlike Carbon Coatings, *Surf. Coat. Technol.*, 54/55 (1–3) (1992) 428–434.
- [13] R.L.C. Wu et al., Ion-Implanted Diamond Films and Their Tribological Properties, *Surf. Coat. Technol.*, 62 (1993) 589–594.
- [14] R.L.C. Wu et al., Tribological and Physical Properties of Ion-Implanted Diamond Films, *Diamond Films Technol.*, 3 (1) (1993) 17–29.
- [15] K. Miyoshi et al., *Physical and Tribological Characteristics of Ion-Implanted Diamond Films*, NASA TM-106682, 1994.
- [16] J.W. Robinson (ed.), *Practical Handbook of Spectroscopy*, CRC Press, Boca Raton, FL, 1991.
- [17] S.J. Schmieg and D.N. Belton, Polycrystalline Diamond Film on Si (100) by XPS, *Surf. Sci. Spectra*, 1 (4) (1993) 331–332.
- [18] M. Casey and J. Wilks, The Friction of Diamond-Sliding on Polished Cube Faces of Diamond, *J. Phys. D.: Appl. Phys.*, 6 (1973) 1772–1781.
- [19] I.P. Hayward, I.L. Singer and L.W. Seitzmann, The Tribological Behaviour of Diamond Coatings, *Proc. Second Int. Conf. on The New Diamond Science and Technology*, Materials Research Society, Pittsburgh, PA, 1991, pp. 785–789.
- [20] M.N. Gardos and B.L. Soriano, The Effect of Environment on the Tribological Properties of Polycrystalline Diamond Films, *J. Mater. Res.*, 5 (11) (1990) 2599–2609.
- [21] D. Crompton, W. Hirst and M.H. Howse, The Wear of Diamond, *Proc. R. Soc. Lond. A.*, 333 (1973) 435–454.
- [22] F.P. Bowden and D. Tabor, *The Friction and Lubrication of Solids*, Clarendon Press, Oxford, England, 1958.
- [23] E.W. Roberts, Ultralow Friction Films of MoS₂ for Space Applications, *Thin Solid Films*, 181 (1989) 461–473.
- [24] M. Seal, The Wear of Diamond, *Ind. Diam. Rev.*, (1965) 111–116.
- [25] F.T. Barwell, Metallic Wear, in E.R. Booser (ed.), *CRC Handbook of Lubrication: Theory and Practice of Tribology*, vol. 2, CRC Press, Boca Raton, FL, 1984, pp. 163–184.
- [26] E. Rabinowicz, Wear Coefficients, in E.R. Booser (ed.), *CRC Handbook of Lubrication: Theory and Practice of Tribology*, vol. 2, CRC Press, Boca Raton, FL, 1984, pp. 201–208.

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