Tribological properties of polished diamond films

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Despite the rapid progress being made in the synthesis of diamond films and recent interest in polishing of diamond films, no systematic measurements of friction and wear on polished diamond films have been reported. In the present study, chemomechanical and laser polishing techniques are used, and friction and wear data on the chemomechanically polished diamond films are presented. With the chemomechanical polishing technique used in this study, the rms roughness of hot filament chemical vapor deposited diamond films can be reduced from about 657 to about 170 nm with rounding off of sharp asperities with no change in the diamond structure. The polished films exhibit coefficient of friction (∼0.1) and wear rates much lower than that of unpolished films. Friction and wear properties of the polished films are comparable to that of single-crystal natural diamond. Based on this study, it is concluded that polished films are potential candidates for tribological applications.

I. INTRODUCTION

A natural diamond is well known for its low friction and wear properties. Natural diamonds are very expensive and cannot be formed as thin films. The physical and chemical properties of chemical vapor deposition (CVD) diamond films have been found to be comparable to those of bulk diamond. Sawabe and Inuzuka reported that electron-assisted CVD films had electrical resistivities greater than $10^{13} \, \Omega \, \text{cm}$, microhardness of about 10 000 HV, and a thermal conductivity of about 1100 W m$^{-1}$ K$^{-1}$ close to that of bulk natural diamond ($10^2$ to $10^{20} \, \Omega \, \text{cm}$, 8000 to 40 000 HV, and 900 to 2100 W m$^{-1}$ K$^{-1}$). Kuo et al. reported that microwave-assisted CVD diamond films had a thermal diffusivity of about 200 to 300 mm$^2$/s, a value close to that of bulk diamond (490 to 1150 mm$^2$/s). Based on thermal gravimetric analysis, oxidation rates of PECVD diamond films in the range of 500 to 750 °C have been found to be lower than those of natural diamond. Zhu et al. have reported that the starting temperature of oxidation for microwave-assisted CVD diamond film is about 800 °C, as evidenced by weight loss, while the surface morphology shows visible oxidation etching pits at temperatures as low as 600 °C.

A major roadblock to the wide spread use of diamond films in tribological, optical, and thermal management applications, is the surface roughness. Growth of the diamond phase on a nondiamond substrate is initiated by nucleation either at randomly seeded sites or at thermally favored sites due to statistical thermal fluctuation at the substrate surface. Based 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 size (> 1 μm), and terminating in very rough surfaces with roughnesses ranging from about few tenth of a micron to tens of microns. These films have been reported to have high friction and wear and are not suitable for tribological applications. A crucial need exists to either develop methods to deposit smooth diamond films or to post-process these films to reduce their roughness. Fine-grained diamond films have been deposited with low-surface roughness by several investigators which exhibit low friction. However, these films are believed not to have true diamond structure. Therefore polishing of the true diamond film is required. Thermochemical, chemomechanical, and plasma/ion beam/laser techniques have been explored to polish diamond films. However, no friction and wear data exist on polished diamond films. In this paper, we describe chemomechanical and laser polishing techniques used in the present study and present friction and wear data on chemomechanically polished CVD diamond films in sliding contact with smooth alumina balls.

II. POLISHING TECHNIQUES FOR DIAMOND FILMS

During polishing, material removal takes place initially on the top of asperities resulting in a smoother surface. Since 1988, various physical and chemical means have been explored to polish diamond films. Traditional mechanical polishing methods using diamond or other hard abrasive particles are unsuitable because of extremely low polishing rates (and hence long polishing times) and preferential polishing along specific crystal orientations leaving protruding crystallites on the surface. The existing and potential methods can be broadly classified into three categories: (1) thermochemical, (2) chemomechanical, and (3) plasma/ion beam/laser polishing. A summary of aforementioned polishing techniques is given in Table I. Thermochemical and chemomechanical techniques are contact techniques so these can be used for surfaces that are planar. Between these two techniques, chemomechanical is preferred as it does not require high sample temperatures. Plasma, ion beam, and laser techniques do not require bulk sample heating and are noncontact techniques which can be used on nonplanar surfaces, though these are line-of-sight processes. The material removal rates using these techniques have thus far been small. Consequently,
### TABLE I. Summary of various polishing techniques.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Contact techniques</th>
<th>Non-contact techniques</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Thermochemical</td>
<td>Chemomechanical</td>
</tr>
<tr>
<td>Processing temperature</td>
<td>750–950 °C</td>
<td>350 °C</td>
</tr>
<tr>
<td>Mechanism of material removal</td>
<td>graphitization and diffusion into metal plate</td>
<td>oxidation</td>
</tr>
<tr>
<td>Shape limitation</td>
<td>only planar surfaces</td>
<td>only planar surfaces</td>
</tr>
<tr>
<td>Size limitation</td>
<td>none</td>
<td>none</td>
</tr>
<tr>
<td>Special requirements</td>
<td>need controlled environment</td>
<td>none</td>
</tr>
<tr>
<td>Equipment cost</td>
<td>low</td>
<td>low</td>
</tr>
<tr>
<td>Processing time</td>
<td>several hours</td>
<td>few hours</td>
</tr>
<tr>
<td>Reported roughness achieved</td>
<td>100 nm</td>
<td>165 nm (present study)</td>
</tr>
<tr>
<td>Potential for commercialization</td>
<td>poor</td>
<td>medium</td>
</tr>
</tbody>
</table>

these techniques have primarily been used for final polishing (in order to achieve low surface roughness of about 5 to 10 nm rms) after coarse polishing using other techniques such as thermochemical or chemomechanical. High-energy ion beams and laser sources can be developed for polishing. High-energy ion beams have the potential for high material rates. However, heat generated during sputtering results in graphitization of the diamond film, so that the laser technique emerges as the most desirable among the noncontact techniques. Ideally, development of in situ polishing techniques are needed for commercialization of polished diamond films. Reactive ion etching (RIE) can be readily used for in situ polishing in most existing plasma deposition methods, but laser technique would exhibit fast polishing times both in situ and ex situ, however at greater capital cost. Achievement of surface smoothness without large material removal using noncontact techniques requires surface planarizing before polishing. Planarizing can be achieved by coating the film surface with a photoresist or gold as in the case of RIE and ion bombardment in order to match material removal rates.

In this paper, we have used the chemomechanical and laser techniques to polish HFCVD diamond films, and friction and wear data for the films polished using chemomechanical technique are reported.

### III. PREPARATION OF POLISHED DIAMOND FILMS AND EXPERIMENTAL PROCEDURE

Diamond films were deposited on (100) single-crystal silicon wafers using a previously described HFCVD technique. Before growth, the silicon wafer was abraded with 4–8 μm-sized diamond grit and then cleaned in an ultrasonic bath using acetone. The deposition conditions used were: initial substrate to filament distance = 10 mm, substrate temperature = 800 °C, hydrogen flow rate = 99 sccm, methane flow rate = 1 sccm, chamber pressure = 20 Torr, deposition time = 24 h, average film thickness = 20 μm, and deposition area = 1 cm².

In the chemomechanical polishing technique used in this study, a fused oxidizer, potassium nitrate (KNO₃) was utilized. The choice of the oxidizer was made due to its well-known strong reactive etching affinity towards diamond. The etching rate in the presence of a shearing force field is expected to be higher and more uniform. Therefore, diamond films were polished by mechanical lapping against polycrystalline alumina for coarse polishing and then against another coarsely polished diamond film with the fused oxidizer in the gap. The polishing apparatus shown in Fig. 1 consisted basically of a hot plate and a rotating stage. The hot plate was used to mount either the mating alumina or one of the diamond films. The rotating stage was used to mount another diamond film and operated at 7 rpm. During polishing, the hot plate was maintained at 325 °C in order to maintain the potassium nitrate in the fused form. During the polishing process, the diamond films were coarsely polished against the alumina surface for 3 h followed by fine polishing against another coarsely polished diamond film for 2 h.

In the laser polishing technique, diamond films were polished using an 193 nm wavelength ArF excimer laser pulsed at 100 mJ at a repetition rate of 20 Hz, focused at normal incidence on the diamond surface and in the presence of an oxygen ambient. We were able to achieve polishing down to 97 nm rms over an area of approximately

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50 mm² in 5 min. We clearly note that laser polishing has significant potential for polishing diamond films in a matter of a few minutes.

Unpolished and polished HFCVD diamond films were characterized using Raman spectroscopy, scanning electron microscopy (SEM), atomic force microscopy (AFM), and a stylus profilometer. Statistical roughness parameters are dependent on the lateral resolution of measuring instruments, therefore, roughness values obtained using the AFM and the stylus profilometer were different. For convenience, the data obtained by stylus profilometer are only reported in the text. Polished single-crystal natural diamond (IIa) (from Double Dee Harris Co.) was also used for reference. In Raman measurements, 514.5 nm radiation at a power of 150 mW with a spot size of about 1 mm was used.

Accelerated friction and wear tests were conducted on polished diamond films. Tests were carried out in reciprocating mode on test coupons using a ball-on-flat tribometer. Alumina balls of 5 mm diameter and with a surface finish of about 3 nm rms were fixed in a stationary holder and the diamond-coated silicon coupons were mounted on a reciprocating table. The friction force was measured using a strain gage ring. Wear of the diamond film and the mating balls was estimated using microscopy and surface profiling before and after the wear tests. Additionally, Raman spectroscopy and SEM imaging were performed before and after the wear test. The tests were carried out at different loads, various speeds, in air at ambient temperatures (22 °C) and under dry conditions. Limited tests were conducted under lubricated conditions. Multiple tests were run at different conditions and the reproducibility was more than 95%. The typical test conditions were as follows: reciprocating amplitude 0.8 mm, normal load 0.1 to 10 N, frequency 0.1 to 10 Hz, average linear speed 0.08 to 8 mm/s, test temperature 20 °C, ambient humidity (35% RH) and the ambient air. For lubricated tests, about 10 cc of lubricant was placed in a reservoir surrounding the ball-film interface. The interface was flooded with a petroleum-based oil (68% paraffinics, 28% naphthenes, 4% aromatics) lubricant without any additive.

IV. EXPERIMENTAL RESULTS AND DISCUSSION

A. Surface characterization

Figure 2 shows the Raman spectra of unpolished film, polished film before the wear test, and polished film after the wear test. The sharp line at or near 1332 cm⁻¹ is attributed to 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 sp²-bonded amorphous carbon (broad-band centered at 1550 cm⁻¹) also known as diamond-like carbon. The Raman spectrum of polished diamond film after wear test shows that there is no phase change, however, the reduction in intensity of the diamond Raman peak may have been from the presence of alumina wear debris. The Raman data show that there is no significant increase in graphitization or amorphization as a result of polishing. Figures 3-5 show SEM micrographs, AFM images, and stylus profilometer scans of unpolished and polished surfaces. We note that the film surface has been planarized with asperity peaks having been knocked off or rounded. We also note that the rms roughness for polished surfaces has decreased from about 657 nm to about 170 and 97 nm for chemomechanically and laser-polished samples, respectively. Although the rms roughness of the chemomechanically polished film is slightly higher than that of the laser-polished film, the peak-to-valley (P-V) distance is lower and as a result of run in during mechanical lapping, the asperities appear to be more rounded which may be desirable for low friction and wear.

B. Friction and wear data

The friction data of typical as-deposited diamond films, chemomechanically polished diamond films, and single-crystal natural diamond (IIa) are shown in Fig.
FIG. 3. SEM micrographs of (a) unpolished, (b) chemomechanically polished, (c) laser polished diamond films. Note (111) orientation of the diamond films.

6(a). The polished diamond films exhibit low coefficients of friction (about 0.11) when slid against the alumina ball, much lower than that for unpolished films and very close to the values exhibited by natural diamond. We note that the coefficient of friction of polished film and natural diamond remained constant throughout the sliding test. However, friction decreased during sliding in the case of unpolished film. This observation suggests that the chemomechanically polished films do not exhibit any run-in effect. Figure 7 shows SEM micrographs for polished and unpolished films and mating ball surfaces after wear. The wear of the mating alumina ball slid against an unpolished film indicated by the scratches on the ball surface and wear debris generated during the test and deposited on the unpolished diamond film, is significant. The rough as-deposited diamond film cuts through the alumina ball easily like "cheese" and a large concentration of alumina shavings on the film surface can be clearly seen. The wear of the alumina ball was negligible in the case of the chemomechanically polished diamond film, comparable to wear for the natural diamond sample. AFM imaging of the polished diamond film and of natural diamond after wear showed negligible change as a result of the sliding process.

Coefficient of friction was found to be strongly dependent on the direction of the polishing tracks. We found that the coefficient of friction was high (0.25) when the alumina ball slid perpendicular to the polishing tracks (i.e., radial direction of the sample during polishing) and low (0.12) when slid parallel to or along the polishing tracks. This difference in friction is attributed to the difference in the surface roughness along (~125 nm rms roughness) the polished track versus across (~200 nm rms roughness) the polished tracks.

The role of roughness of polished diamond film on friction is illustrated in Fig. 6(b). The coefficient of friction decreased from 0.4 to 0.09 as the rms roughness of the polished films was reduced from 500 to 30 nm. There are three mechanisms of friction—adhesion, ploughing, and ratchet that may be operative either individually or in combination for diamond films sliding against a softer material. If two rough surfaces are placed in contact, in addition to adhesion at the asperity contacts, asperities of the mating surfaces may interlock. The interlocked asperities either ride over each other (ratchet mechanism) or push past each other or fracture (ploughing) during relative motion. The adhesion mechanism does not appear to account for the observed reduction in friction as the real area of contact or friction is expected to increase with a decrease in roughness. With rough diamond films sliding against a softer material, ploughing and ratchet may be operative. Since the slope of the mating ball asperities are lower than that of polished diamond films, ball asperities can not ride over asperities of the diamond film. Therefore, ratchet mechanism is not relevant here and ploughing is expected to be the major contributor to the effect of roughness on the friction. The rounding off of asperities from polishing facilitate an easy slip which minimize interface damage.

Blau et al.11 reported that the coefficient of friction of as-deposited 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 Soriano12 and Kohzaki et al.13 also reported rather high values of coefficient of friction and wear rates of PACVD diamond films slid against SiC pins. Jahanmir et al.16 and Hayward et al.17 reported lower values of coefficient of friction (~0.1) of various diamond films sliding against a diamond or sapphire slider. The surface roughnesses of their films were as low as 7 nm rms which suggests that these films were fine grained and probably with significant nondiamond components. (For friction and wear properties of as-deposited diamond films, also see Refs. 14 and 15.) Plano et al.18 and Wu et al.19 have reported the deposition of "fine-grained" (20-100 nm) diamond films having a relatively smooth surface (15 nm rms). They produced fine-grained films using a low-pressure and low-power microwave-assisted CVD technique on (100) Si surface having scratched with diamond paste prior to growth.
Wu et al. reported coefficient of friction of 0.03 for their “fine-grained” diamond film sliding against natural diamond in air. Although no data were presented in this work regarding friction of CVD diamond sliding against aluminum, it is likely that the coefficient of friction for such a case would be larger than 0.03. Further, the significant amorphous carbon peak evident from the Raman spectra of these fine-grained diamond films shows that these may not be true diamond, but composite films of diamond and nondiamond carbon. Therefore if the coarse-grained (true) diamond films are required for tribological applications with low friction and wear, they need to be polished.

Coefficient of friction of polished diamond films at different loads and speeds is shown in Fig. 8. Friction data for natural diamond at different loads and speeds are also shown for comparison. The coefficient of friction of the polished diamond film did not increase significantly as the normal load increased from 0.1 to 10 N and the speed increased from 0.08 to 8 mm/s. However, the lower coefficient of friction (0.05) at higher load (10 N) was observed when alumina ball slid over the natural diamond.

Some roughness on the surface of the diamond film may actually be useful in lubricated sliding because the valleys could act as reservoirs for a liquid lubricant. Friction and wear tests on polished films were also carried out under lubricated conditions. The coefficient of friction values and optical micrographs of worn ball surfaces (alumina and 52100 steel balls) slid against polished diamond film under dry and lubricated conditions are shown in Fig. 9. As expected, the coefficient of friction and wear scar diameters are significantly lower for the case of lubricated sliding. It appears that lower friction and wear of soft mating surfaces can be achieved in lubricated sliding.
V. CONCLUSIONS

We have shown that HFCVD “true” diamond films can be polished without any graphitization or significant amorphization during polishing. The polished diamond films and natural single-crystal diamond (IIa) slid against alumina balls (of about 3 nm rms roughness) have comparable coefficients of friction and observed wear of the mating alumina balls. The coefficient of friction of polished diamond films (with average roughness on the order of 170 nm) exhibit reproducible decrease in the coefficient of friction from about 0.4 down to about 0.09 when compared with their unpolished counterparts. The wear debris generated from the alumina ball during the test with the unpolished films was significant but was negligible with polished diamond films. The friction and wear data of the polished films are almost identical to those obtained for single-crystal natural diamond samples with average roughness of 1.7 nm.

The operative mechanism for the role of roughness on friction appears to be ploughing. In sliding with polished diamond films, the dominant effect on the coefficient of friction and wear of the mating ball surface is the rounding off of sharp asperities along with the reduction in the surface roughness (reduction in the asperity slope) while sliding against a smoother mating surface. We find that, it is
not necessary to achieve roughnesses on the order of a few nm for low friction and wear as long as the mating surface has a lower surface roughness compared to that of diamond film. Some roughness on the surface of the diamond film may actually be useful in lubricated sliding because the valleys could act as reservoirs for a liquid lubricant. From this study, it is concluded that polished diamond films can be used for tribological applications.

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