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Small Amplitude Reciprocating Wear Performance of Diamond-like Carbon Films: Dependence of Film Composition and Counterface Material

Abstract

Small amplitude (50 μ m) reciprocating wear of hydrogen-containing diamond-like carbon (DLC) films of different compositions has been examined against silicon nitride and polymethyl-methacrylate (PMMA) counter-surfaces, and compared with the performance of an uncoated steel substrate. Three films were studied: a DLC film of conventional composition, a fluorine-containing DLC film (F-DLC), and siliconcontaining DLC film. The films were deposited on steel substrates from plasmas of organic precursor gases using the Plasma Immersion Ion Implantation and Deposition (PIIID) process, which allows for the non-lineof-sight deposition of films with tailored compositions. The amplitude of the resistive frictional force during the reciprocating wear experiments was monitored *in situ*, and the magnitude of film damage due to wear was evaluated using optical microscopy, optical profilometry, and atomic force microscopy. Wear debris was analyzed using scanning electron microscopy and energy dispersive spectroscopy. In terms of friction, the DLC and silicon-containing DLC films performed exceptionally well, showing friction coefficients less than 0.1 for both PMMA and silicon nitride counter-surfaces. DLC and silicon-containing DLC films also showed significant reductions in transfer of PMMA compared with the uncoated steel. The softer F-DLC film performed similarly well against PMMA, but against silicon nitride, friction displayed nearly periodic variations indicative of cyclic adhesion and release of worn film material during the wear process. The results demonstrate that the PIIID films achieve the well-known advantageous performance of other DLC films, and furthermore that the film performance can be significantly affected by the addition of dopants. In addition to the well-established reduction of friction and wear that DLC films generally provide, we show here that another property, low adhesiveness with PMMA, is another significant benefit in the use of DLC films.

Keywords

small amplitude reciprocating wear, diamond-like carbon films, plasma, friction

Comments

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Small amplitude reciprocating wear performance of diamond-like carbon films: dependence of film composition and counterface material

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Small amplitude (50 µm) reciprocating wear of hydrogen-containing diamond-like carbon (DLC) films of different compositions has been examined against silicon nitride and polymethyl-methacrylate (PMMA) counter-surfaces, and compared with the performance of an uncoated steel substrate. Three films were studied: a DLC film of conventional composition, a fluorinecontaining DLC film (F-DLC), and silicon-containing DLC film. The films were deposited on steel substrates from plasmas of organic precursor gases using the Plasma Immersion Ion Implantation and Deposition (PIIID) process, which allows for the nonline-of-sight deposition of films with tailored compositions. The amplitude of the resistive frictional force during the reciprocating wear experiments was monitored in situ, and the magnitude of film damage due to wear was evaluated using optical microscopy, optical profilometry, and atomic force microscopy. Wear debris was analyzed using scanning electron microscopy and energy dispersive spectroscopy. In terms of friction, the DLC and silicon-containing DLC films performed exceptionally well, showing friction coefficients less than 0.1 for both PMMA and silicon nitride counter-surfaces. DLC and silicon-containing DLC films also showed significant reductions in transfer of PMMA compared with the uncoated steel. The softer F-DLC film performed similarly well against PMMA, but against silicon nitride, friction displayed nearly periodic variations indicative of cyclic adhesion and release of worn film material during the wear process. The results demonstrate that the PIIID films achieve the well-known advantageous performance of other DLC films, and furthermore that the film performance can be significantly affected by the addition of dopants. In addition to the well-established reduction of friction and wear that DLC films generally provide, we show here that another property, low adhesiveness with PMMA, is another significant benefit in the use of DLC films.

KEY WORDS: small amplitude reciprocating wear, diamond-like carbon films, plasma, friction

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34 1. Introduction

35 Diamond-like carbon (DLC) films have attracted considerable attention in research and commercial are-36 37 nas because they possess a unique combination of 38 properties including high hardness, low friction, chemi-39 cal inertness, biocompatibility, hydrophobicity, high 40 electrical resistivity, and high transparency to visible and 41 infrared wavelengths [1-3]. Examples of present and 42 potential applications of DLC films include coatings for 43 manufacturing tools, magnetic storage devices, micro-44 electromechanical systems (MEMS), scratch-resistant 45 glasses and lenses, razor blades, and prosthetic devices 46 [4-8]. DLC films are synthesized by ion- or plasma-47 based processes using hydrocarbon precursor gases and 48 therefore contain substantial amounts of hydrogen 49 (usually 10-50 atomic%). Techniques for DLC film 50 deposition include direct ion beam processes, plasma-51 enhanced chemical vapor deposition, and electron

The tribological characteristics of DLC films have 62 been the subject of a large number of investigations 63 because of the high hardness and low friction that these 64 films generally possess [14-18]. A wide range of results 65 has been reported because of differences in methods of 66 synthesis, film structure, and thickness, and test envi-67 ronment and procedures. Almost all macro-tribological 68 69 studies on DLC films have been performed using pinon-disk or conventional high displacement reciprocating 70 wear testers. Relatively few studies have been performed 71 on DLC films under small amplitude wear conditions 72

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cyclotron resonance CVD processes [1, 9–11]. DLC films are amorphous with no long-range order, and the carbon is present in both the hybridized sp³ (diamond) and sp² (graphite) bonding configurations, although sp¹ (polymeric) configuration has also been observed. The sp³/sp² ratio, which strongly influences film properties, depends on the hydrogen content of the film and the deposition parameters, such as pressure, ion impingement energy, and the surface power density at the substrate [12, 13].

73 (fractions of a micrometer to a few 100 μ m) and/or at 74 relatively high reciprocating frequencies (10–100s of Hz) 75 [19–22]. This type of wear usually occurs as a result of 76 an unintended vibrations and is quite prevalent in many 77 industrial applications such as aircraft, press-fit pros-78 thetic devices, electrical contacts, nuclear reactors, and 79 automobiles. The wear mechanisms in small amplitude 80 reciprocating wear conditions are fundamentally differ-81 ent in many respects from unidirectional and high dis-82 placement reciprocating wear [23-26]. The localized 83 concentration of wear in a small region can lead to the 84 accumulation of wear debris and environmental reaction 85 products in the relatively small region of the wear scar. 86 Moreover, the sliding velocities can be very high and 87 heat transfer is limited due to the small affected region. 88 A strong dependence of friction on sliding velocity even 89 in the regimes, achievable by conventional reciprocating 90 wear testers has been recently demonstrated for DLC 91 films [27–29], and the sliding velocity attained during 92 small amplitude, high frequency reciprocating wear can 93 be significantly higher than the velocities used in that 94 study. This motivates the study of DLC films under 95 small amplitude sliding conditions.

96 DLC films are often modified to improve their tri-97 bological performance by incorporating other elements, 98 thus altering not only the composition but also the 99 structure of the films. For example, compressive stresses 100 adversely affect the tribological performance of DLC 101 [30], and addition of metallic phases (e.g., W, Ta) to the 102 film, as well as the use of a metallic interlayer, mitigates 103 the sensitivity of tribological characteristics to com-104 pressive stresses [31]. This also reduces the sensitivity to 105 humidity [31].

It is desirable to mitigate the effect of humidity, and 106 to lower the adhesiveness and wettability of DLC, par-107 108 ticularly for small-scale applications where capillary 109 condensation and adhesion become critical [32, 33]. The 110 addition of F or Si to the DLC network structure not 111 only lower the surface energy and wettability of DLC 112 [34-38] but also influences the tribological characteris-113 tics [16, 31, 34-36, 39]. The reduction of surface energy by the addition of F is attributed to the presence of – 114 115 CF₂ and -CF₃ groups [34, 38-41]. However, higher fluorine contents lead to a decrease in hardness, 116 117 approaching the properties of poly-tetra-fluoro-ethylene 118 (PTFE) [34, 38-41]. The deposition parameters, in 119 addition to the fluorine content, dictate its wear resis-120 tance. The addition of silicon reduces the surface energy, 121 possibly by decreasing the dispersive component of 122 surface energy [31, 34]. As well, Si addition increases the 123 hardness of the DLC films by promoting sp³ carbon 124 hybridization [42-44].

The objective of this study was to examine the small
amplitude reciprocating wear performance of DLC films
synthesized from acetylene plasma, and fluorine-containing and silicon-containing DLC films synthesized

using plasmas of acetylene mixed with tetra-fluoro-eth-129 ane and hexa-methyl-disiloxane, respectively. The for-130 mer adds F to the DLC film, while the latter adds both 131 Si and O. The fluorine- and silicon- containing carbon 132 films can also be referred to as fluorocarbon films and 133 C-Si-O films, respectively. However, the terms F-DLC 134 and Si-DLC will be used in this paper, consistent with 135 terminology used in studies on similar films [16, 34, 38]. 136 Small amplitude reciprocating wear testing of these 137 DLC films was performed against hard silicon nitride 138 and soft PMMA counter-surfaces to capture a range of 139 wear damage effects from abrasive material removal to 140 141 counterface material adhesion and build-up. The findings of this study are expected to be of general relevance 142 143 to applications such as manufacturing tools and components, MEMS devices, hard disks, and even nano-144 mechanical data storage, for which DLC coatings may 145 play a highly practical role in alleviating tribological-146 related failures. While we do not attempt to match 147 length scales, stresses, and velocities for any of these 148 applications specifically, the smaller length scale and 149 reciprocating nature of our wear tests, in contrast to 150 151 conventional pin-on-disk testing, is a useful step toward the smaller length-scales and confined geometries that 152 are found in the aforementioned applications. 153

2. Experimental methodology

2.1. Plasma-based deposition of DLC films 155

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The three carbon-based films investigated in this 156 157 study, a DLC, a fluorine-containing diamond-like carbon (F-DLC), and a silicon-containing diamond-like 158 carbon (Si-DLC), were deposited using the Plasma 159 Immersion Ion Implantation and Deposition (PIIID) 160 process [45-49]. The PIIID process is inherently non-161 line-of-sight in nature and allows for uniform surface 162 163 treatment of 3-dimensional parts without the necessity of part manipulation in the vacuum chamber during the 164 165 surface treatment. The process does not require active heating of the sample being coated, minimizing thermal 166 mismatch stresses and enabling the coating of thermally-167 sensitive materials. It also allows for in situ substrate 168 cleaning prior to deposition by, for example, Ar ion 169 sputtering, and for the creation of an adhesion-pro-170 moting layer by ion implantation into the substrate 171 prior to film deposition. 172

For this study, AISI 4140 steel samples were polished 173 with a wet grinder by progressively using 240, 320, 400, 174 and 600 grit silicon-carbide abrasive and then subjected 175 to a final polishing step using 1 μ m diamond paste. Prior 176 to being introduced into the plasma chamber, the sam-177 ples were cleaned ultrasonically using acetone and 178 179 alcohol. Once in the PIIID system, the samples were cleaned using an Ar⁺ plasma in a glow discharge mode 180 at a pressure of 12 mTorr using a stage bias of -5 kV181

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182 183 taminants and native oxides. The DLC films were then 184 deposited using a plasma of acetylene precursor gas at a 185 pressure of 10 mTorr and a stage voltage bias of -5 kV. 186 The Si-DLC films were deposited using a plasma of 187 hexa-methyl-disiloxane precursor gas at a pressure or 188 15 mTorr and a stage voltage bias of -3 kV. This oxy-189 gen-containing precursor gas leads to the incorporation 190 of oxygen into the film along with silicon. The F-DLC 191 films were deposited using a plasma of a mixture of 192 acetylene and tetra-fluoro-ethane gases (4:1 ratio) at a 193 pressure of 15 mTorr and a stage voltage bias of -3 kV. 194 The samples were cooled during film deposition by the 195 flow of coolant oil through the sample stage. The 196 thickness of the deposited films (as measured by profil-197 ometry on semi-masked silicon coupons that were also 198 placed in the system) was in the range of 1–1.5 μ m 199 depending on the particular film.

200 2.2. Surface roughness and microhardness measurements

201 Surface roughness measurements of the films and 202 the uncoated steel were performed using an atomic force microscope (AFM) (QScope 250, Quesant 203 204 Instruments, Santa Cruz, CA) in contact mode, and 205 using SPIP software for analysis (Image Metrology A/ 206 S, Lyngby, Denmark). The root mean square rough-207 ness (RMS), R_q, was determined by scanning 208 $20 \times 20 \ \mu m$ areas. The effective hardness of the 209 as-deposited films and the uncoated steel were 210 measured using a microhardness tester with a Knoop 211 indenter at a 10-g load. These tests were performed on 212 fresh (unworn) regions of the samples.

213 2.3. Small amplitude reciprocating wear testing

214 Small amplitude reciprocating wear tests were per-215 formed using a ball-on-flat configuration. Silicon nitride 216 and PMMA ball bearings (3 mm dia) were used as the 217 counterbodies (also referred to as styli). The instrument 218 used for these wear studies employs an electromagnetic 219 actuator to generate oscillatory slip motion between the 220 contacting surfaces. A closed-loop control system 221 maintains constant displacement amplitude of the stylus 222 during the course of the wear test regardless of the fre-223 quency and loading conditions. The feedback loop 224 maintains a desired stylus displacement, which can be in 225 the range of 10–500 μ m. The slip amplitude is moni-226 tored using a linear variable displacement transducer 227 (LVDT). The frequency dependence of the system 228 response results in a high Q mechanical resonance of the 229 actuator at ~ 40 Hz. At resonance, the power needed by 230 the stylus actuator is particularly sensitive to dissipative 231 loading caused by the frictional interaction of the stylus 232 and the sample. Therefore, by monitoring the power

applied to the actuator, a measure of the average power 233 234 per cycle expended by frictional processes is determined. This power is directly proportional to the force required 235 to move the contacting stylus against the flat sample in 236 an oscillatory motion and thus incorporates the effects 237 of friction and any other dissipative forces during the 238 wear process. We conservatively report the measured 239 raw signal and label this as "Measured Resistive Force 240 (arb. units)". The absolute scale of this signal is the same 241 for all data presented here. In addition, the calibration 242 of this measured signal against published friction coef-243 ficients is also measured, and discussed further below. 244 Based on multiple tests performed with this instrument, 245 the calibration provides a reasonable estimate of the 246 actual friction coefficients. Details of the design and 247 construction of this instrument are given elsewhere [19, 248 249 50].

The wear tests were performed under an applied load 250 of 0.196 N and stylus displacement amplitude of 50 μ m. 251 This corresponded to a nominal Hertzian contact pres-252 sure of ~ 620 MPa for the silicon nitride stylus, and 253 \sim 50 MPa for the PMMA stylus, roughly calculated by 254 255 assuming a Young's Modulus of 180 GPa for the DLC films. Tests were performed for 20,000 cycles. Addi-256 tionally, tests for DLC and Si-DLC against PMMA 257 countersurfaces were also performed up to 100,000 258 cycles to examine PMMA build-up at larger total sliding 259 distances. The oscillation frequency was maintained at 260 37 Hz, which is close to the resonant frequency, which 261 allowed for continuous monitoring of the resistive fric-262 tional force at 1 s intervals. All tests were conducted in 263 duplicate under dry sliding conditions in ambient air 264 (relative humidity $\sim 50\%$). 265

2.4. Characterization of wear damage

The wear damage and debris on the three DLC films 267 and the control steel sample were imaged using optical 268 microscopy and optical profilometry using a scanning 269 270 white light interferometer (Zygo Corp., Middlefield, CT). Wear scars on the flat samples were imaged by 271 AFM in contact mode. The SPIP software program was 272 used to analyze AFM data, and a custom MatLab 273 software routine was used to analyze both the optical 274 profilometry and AFM data. These are used to calculate 275 the wear volume for tests against the silicon nitride 276 counter-surface, and the volume of polymer debris 277 build-up for tests against the PMMA counter-surface. 278 Wear scars on the PMMA and silicon nitride styli were 279 not observable by optical microscopy; therefore, no 280 measurement of the stylus wear volume could be made. 281 Chemical analysis of wear debris was carried out by 282 energy dispersive spectroscopy (EDS) in a scanning 283 284 electron microscope (SEM) (JEOL JSM 6400, JEOL 285 Ltd., Waterford, VA).

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Table 1 Summary of the surface roughness, microhardness, and small amplitude reciprocating damage volume for the uncoated steel and the DLC films.

* Wear volume refers to volume of material lost from sample after tests against silicon nitride stylus.** Debris volume refers to volume of polymer build-up on sample after tests against PMMA stylus.

286 3. Results and discussion

287 Table 1 summarizes the results of the wear volume 288 and polymer debris volume measurements as well as surface roughness and microhardness of the materials 290 used in this study. Wear volume in table 1 refers to volume removed for each sample (steel or DLC film) in tests using the silicon nitride countersurface, while debris volume refers to the extent of polymer build-up on each 294 sample in tests using the PMMA countersurface. While the steel surface is initially very smooth (4 nm RMS roughness), all three DLC films are rougher. This is 297 likely the result of substrate roughening due to the Ar 298 ion sputtering performed prior to deposition.

299 Due to the incorporation of substrate effects, the 300 hardness values reported are underestimated as they 301 represent a composite hardness of the film-substrate 302 system. They simply provide a means of gauging the 303 relative film hardness. Most notably, the composite 304 hardness of the DLC and Si-DLC coatings on steel are high (in excess of 1000 HK). These values are compa-305

rable to those obtained in other studies of DLC and Si-306 DLC. Savvides and Bell measured hardness of DLC 307 308 films using an ultralow-load microhardness tester and found values ranging from 12 to 30 GPa while varying 309 film deposition parameters [51]. Achanta, Drees, and 310 Celis reported a hardness of 24.7 GPa for DLC as 311 measured by nanoindentation [52]. Varma, Palshin, and 312 Meletis measured the microhardness of Si-DLC films 313 using a Knoop indenter (0.1 N load) and found hard-314 ness values of 11.2-17.3 GPa for various processing 315 conditions [43]. However, the F-DLC coating on steel is 316 significantly softer, with the composite hardness com-317 parable to that of the base steel. Although, a wide range 318 of hardness values have been reported for F-DLC films 319 of different compositions and preparation methods 320 [53–55], hardness results from this study are comparable 321 to those obtained by Hatada and Baba [54]. 322

323 Optical micrographs of the wear damage on the three films and steel samples after testing with the silicon ni-324 tride counter-surface are shown in figure 1, and the wear 325



Figure 1. Dark field optical micrographs of wear scars on DLC films and uncoated steel produced by small amplitude reciprocating wear against a silicon nitride counter-surface: (a) DLC, (b) Si-DLC, (c) F-DLC, and (d) uncoated steel. The scars on DLC and Si-DLC films have been circled for clarity.

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volumes reported in table 1. The wear scars for DLC 327 and Si-DLC films, shown in figures 1a and b respec-328 tively, reveal an impressively small wear volume and 329 little or no observable wear debris. These two films 330 showed no evidence of fracture or breakthrough at the 331 coating-substrate interface. The F-DLC film, shown in 332 figure 1c, exhibited a much larger wear scar and more 333 wear debris generation. Furthermore, the wear rate was 334 rapid enough for breakthrough to occur at the film-335 substrate interface as evidenced by the reddish region of 336 oxidized steel at the bottom the wear scar. This suggests 337 that the wear debris contain oxidized steel particles in 338 addition to F-DLC particles. An SEM image of the 339 F-DLC wear scar along with corresponding EDS dot 340 map for oxygen are shown in figure 2, confirming that film breakthrough occurred, and the underlying steel 341 342 substrate oxidized. This is consistent with the low 343 microhardness of this film and shows the F-DLC film is 344 not able to provide adequate abrasive wear resistance. 345 EDS analysis of the F-DLC wear track also showed the 346 presence of silicon, from wear of the silicon nitride sty-347 lus, and chromium, from wear of the 4140 steel sub-348 strate. The wear scar formed on the uncoated control 349 steel, shown in figure 1d, is substantially larger than that 350 on any of the carbon films, and exhibits evidence of 351 surface oxidation and wear debris generation. AFM and 352 optical profilometry (not shown) reveal a build-up of 353 material in the wear track, indicating that steel debris 354 particles had oxidized, as expected, and confirmed by 355 EDS (figure 2). Low concentrations of silicon, derived

357 wear track region. 358 AFM images of the wear scars from testing against 359 silicon nitride support the observations in figure 1. Both 360 DLC and Si-DLC (figure 3a) exhibit very little material loss and show negligible wear debris. The approximate 361 wear volume of the DLC wear scar is $2.6 \times 10^{-8} \text{ mm}^3$ 362 while the wear volume of the Si-DLC wear scar was 363 higher at 1.7×10^{-7} mm³ (table 1). This corresponds to 364 wear rates of $6.6 \times 10^{-8} \text{ mm}^3 \text{ N}^{-1} \text{ m}^{-1}$ and $4.4 \times$ 365 10⁻⁷ mm³ N⁻¹ m⁻¹ for DLC and Si-DLC, respectively. 366 For comparison, a wear rate of 2.5×10^{-8} mm³ N⁻¹ m⁻¹ 367 368 was found for pin-on-disk testing of silicon nitride on 369 DLC in dry air by Jia et al. [56]. Kim, Fischer, and 370 Gallois also performed pin-on-disk testing of the same 371 material system and found higher wear rates $(\sim 10^{-7} \text{ mm}^3 \text{ N}^{-1} \text{ m}^{-1})$ for 50% RH air [57]. The F-DLC 372 373 and uncoated steel surfaces show a build-up rather than 374 a loss of material in the most severely worn areas. This 375 build-up is a manifestation of film wear, smearing, 376 delamination, oxidation of the underlying steel in the 377 case of F-DLC, and wear and oxidation for the 378 uncoated steel. For the F-DLC film, a considerable 379 amount of wear debris resides throughout the wear scar, 380 whereas for the uncoated steel the wear debris is pushed 381 towards the sides of the wear scar due to the force of the

from the silicon nitride stylus, were also detected in the

moving stylus. As a result of this stochastic build-up due 382 to wear products, smearing effects, and oxidation, the 383 calculated wear volumes for the F-DLC and steel sam-384 ples are not representative of their actual wear behavior. 385 The calculations of "volume removed" and "debris 386 volume" were also influenced by AFM scanning arti-387 facts resulting from the topography of the debris. Thus, 388 wear rates for these samples were not reported due to 389 inaccuracy. 390

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Figure 4 shows the variation in frictional force 391 392 amplitude (raw signal units) against a silicon nitride counter-surface over the course of a 20,000 cycle recip-393 rocating wear test for all four samples. The uncoated 394 steel consistently exhibited the highest friction force. 395 396 DLC and Si-DLC films demonstrated significantly lower friction forces than the uncoated steel, while the F-DLC 397 398 film exhibited a coarsely periodic variation with the peak friction force approaching the values of steel, and then 399 lowering to a minimum value of approximately half that 400 of steel. This undulating behavior is indicative of third-401 402 body wear processes involving material removal and subsequent smearing of the wear debris, and is consis-403 404 tent with the optical microscopy, optical profilometry, and AFM images of the wear scar discussed earlier. The 405 partially polymeric nature of F-DLC may lead to the 406 407 formation of a transfer film between the stylus and sample which is periodically created and detached from 408 the wear surface, causing substantial variations in 409 410 friction.

Optical micrographs of the wear scars on all three 411 films and uncoated steel after testing against PMMA are 412 shown in figure 5. The DLC film in figure 5a and the 413 Si-DLC film in figure 5b show negligible amounts of 414 PMMA debris, and this debris is observed predomi-415 nantly on the sides of the wear scar while the interior of 416 the wear scar remains free of any polymer build-up. The 417 exclusion of wear debris to the extremities of the wear 418 419 scar indicates that PMMA does not have a propensity to adhere strongly to these films. The F-DLC film shows 420 PMMA build-up in the interior of the wear track, as 421 shown in figure 5c, but much of the debris is pushed 422 423 towards the sides of the wear scar due to the low surface energy of this film. However, the greater amount of wear 424 debris is likely due to the low hardness of this film. In 425 contrast, the uncoated steel sample in figure 5d showed 426 excessive amounts of PMMA at the ends of the wear 427 scar and also its accumulation throughout the interior of 428 429 the scar.

430 AFM images of the wear tracks formed by PMMA counter-surfaces showed varying amounts of polymer 431 and wear debris build-up on each film. Consistent with 432 the optical micrographs shown in figure 5, AFM mea-433 surements showed substantially larger amounts of 434 PMMA build-up and wear for the F-DLC film and 435 uncoated steel compared to DLC and Si-DLC 436 (figure 3b). The debris volume for F-DLC may be 437



(g)

Figure 2. Images of wear scars generated on steel and F-DLC films after wear against Si_3N_4 counterface showing the effects of oxidation (a) optical profilometry image giving the topography of the wear scar on F-DLC film, (b) SEM image of the wear scar on F-DLC film, (c) EDS oxygen dot map of the wear scar on F-DLC film (white represents oxygen), (d) Optical profilometry image giving the topography of the wear scar on steel, (e) SEM image of wear scar on steel, (f) EDS iron dot map of the wear scar on steel (white indicates presence of iron), and (g) EDS oxygen dot map of the wear scar on steel (white represents oxygen).

438 somewhat overestimated due to the wearing of the film
439 itself, which is much softer than the either DLC or
440 Si-DLC. Also, the Si-DLC exhibits greater adhesion and
441 build-up of PMMA than DLC, despite its lower surface

energy [38]. Adhesion is affected by interfacial interactions as well as the surface energy, and interactions 443 between oxygen groups in both the PMMA and the 444 Si-DLC could contribute to this effect [58], or this could 445



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Figure 3. AFM images of wear scars on the Si-DLC films produced by small amplitude reciprocating wear against (a) silicon nitride and (b) PMMA counter-surface.



Figure 4. Plot of measured resistive force versus number of reciprocating cycles for wear tests against silicon nitride counter-surface.

446 simply be a result of the higher initial roughness of the 447 Si-DLC film. The RMS roughness on DLC, F-DLC, 448 and Si-DLC films deposited on semiconductor grade Si 449 wafers were measured to be ~ 0.3 , ~ 0.5 , and ~ 1.0 nm, 450 respectively, over a $1 \times 1 \ \mu m$ area using Atomic Force 451 Microscopy. The amount of polymer debris on the 452 surface of each sample is listed in table 1. For all sam-453 ples except the DLC film, small amounts of debris 454 existed outside the field of view used in debris volume 455 calculations for the coatings; therefore, debris volumes 456 listed in table 1 underestimate the actual amount of 457 debris on the film surfaces. For example, the total 458 amount of polymer debris on the steel surface including 459 all debris outside the wear track could not be measured. The interior of the wear scar alone had a debris volume 460 of 4.8×10^{-7} mm³, so the total debris volume, including 461 debris outside the field of view, is much greater than this 462 463 amount and far greater than that for any of the three 464 films.

Figure 6 shows the trends in frictional force amplitude (raw signal units) as a function of the number of cycles for all four samples when sliding against PMMA. 467 Once again, all films displayed lower friction forces than 468 the uncoated steel. The higher friction force for the steel 469 is consistent with adhesion and build-up of a PMMA 470 471 film on the steel surface, as observed in the optical microscope, optical profilometry, and AFM images. The 472 F-DLC does not exhibit the undulating trend observed 473 with the silicon nitride counterface. This is likely 474 because of the relatively low hardness of PMMA. DLC 475 and Si-DLC exhibited comparably low friction forces 476 477 that remained relatively constant throughout the wear tests. 478

479 For the DLC and Si-DLC films, additional tests were performed for 100,000 cycles with the goal of inducing 480 PMMA adhesion on these surfaces, which in turn would 481 lead to a higher friction force. However, friction force 482 data and imaging of the wear scars verified that 483 increasing the sliding distance had no effect on the 484 friction force or the amount of polymer build-up on the 485 486 film surface.

To correlate the coefficient of friction with the mea-487 sured raw friction force signal, small amplitude recip-488 rocating wear tests were performed with the same 489 490 instrument for several common material pairs whose coefficient of friction values are documented extensively 491 492 in literature. These material pairs were tested under the same conditions as the three films and the steel sample. 493 Figure 7a shows the average measured raw friction force 494 495 signal along with published coefficient of friction values 496 for these material pairs. For certain material pairs, a range of friction coefficients are shown based literature 497 sources that were reviewed [59-64]. The plot does show 498 a roughly linear trend, in that the friction force signal 499 increases with increasing coefficients of friction. The 500 lack of complete correlation suggests that other factors 501 such as wear debris generation, three-body wear, and 502 adhesion are also incorporated in the measurements, 503 and the coefficient of friction alone does not determine 504 the wear process. Nevertheless, this relates the friction 505



Figure 5. Optical micrographs of wear scars on DLC films and uncoated steel produced by small amplitude reciprocating wear against polymer PMMA counter-surface: (a) DLC, (b) Si-DLC, (c) F-DLC, and (d) uncoated steel.



Figure 6. Plot of measured resistive force versus number of reciprocating cycles for wear tests against PMMA counter-surface.

506 force signal measured in the wear tests in this study with 507 documented friction coefficients and allows us to ascribe 508 approximate friction coefficients for the DLC films 509 investigated in this study. The estimates of friction 510 coefficients for the DLC films, as obtained from this plot and shown in figure 7b, indicate that these films have 511 512 friction coefficients substantially lower than several 513 common material pairs, and approach low coefficient of 514 friction materials such as poly-tetra-fluoro-ethylene 515 (PTFE).

The estimated friction coefficients from this study for DLC and Si-DLC against silicon nitride compare favorably with other published values. Jia *et al.* obtained a friction coefficient of ~ 0.05 for pin-on-disk



Figure 7. (a) Plot of average resistive force measured against published values for coefficient of friction for five different material pairs [38–43]; (b) Table of estimated coefficients of friction based on the information in Fig. 7(a).

0.07

FDLC

sliding of DLC against silicon nitride in dry air [56].520Kim, Fischer, and Gallois also investigated pin-on-disk521sliding of Si₃N₄ on DLC in various gaseous environments522

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and reported a friction coefficient of 0.08 in air (50% RH) [57]. Achanta, Drees, and Celis found a decrease in surface roughness of DLC films (quantified by AFM) with increasing number of reciprocating cycles in contact with a spherical silicon nitride counterbody, and reported a steady state friction coefficient of 0.1 in air (0.10 N load, 400 μ m sliding amplitude at 0.2 Hz for 1000-5000 cycles) [52]. Drees, Celis, and Achanta reported friction coefficients of ~0.19-0.25 for reciprocating sliding of silicon nitride against DLC under similar conditions (0.25 N load, 300 μ m sliding amplitude at 0.5 Hz for 1000 cycles) [22].

535 Few studies have been performed with polymeric 536 counterbodies sliding against DLC films. Tsuchiya and 537 Suzuki reported a friction coefficient of ~ 0.18 for 538 PMMA sliding against metal-containing DLC films in a 539 flat-on-flat configuration (2.6 N load, no reciprocation) 540 [65]. He et al. used HDPE, which has properties similar 541 to PMMA, as the pin material for pin-on-disc testing 542 (1.5 N load, 120 cycles/min, 15,800 total cycles) of 543 DLC-coated PMMA and reported a friction coefficient 544 of ~0.25 and wear rate of $4.14 \times 10^{-8} \text{ mm}^3 \text{ N}^{-1} \text{ m}^{-1}$ in 545 air (15% RH) [66].

546 4. Conclusions

547 The small amplitude reciprocating wear behavior of a DLC film and fluorine-containing and silicon-contain-548 549 ing DLC films deposited on steel using the PIIID 550 process were evaluated against silicon nitride and 551 PMMA counter-surfaces, and compared to the perfor-552 mance of uncoated steel. For abrasive wear conditions 553 against silicon nitride, the DLC and Si-DLC films 554 exhibited an extremely low wear volume, wear rate, and 555 amount of debris generation, as well as a much lower 556 frictional force as compared to the control steel sample. 557 The softer F-DLC coating exhibited a higher wear 558 volume, wear rate, and greater debris generation, and 559 undulating trends in friction force indicate a cycling of 560 material wear and smearing at the interface. For wear 561 against the softer PMMA counter-surface, all three films 562 exhibited lower adhesion, transfer, and build-up of 563 PMMA compared to the control steel sample. The DLC 564 and Si-DLC exhibited the least amount of PMMA 565 build-up. A plot of the friction force signal against 566 coefficients of friction for a range of known material 567 pairs showed a linear trend, but a lack of complete 568 correlation indicates that other factors in addition to 569 coefficient of friction also dictate the wear process. 570 Estimates from this calibration indicate that carbon-571 based films investigated in this study have coefficients of 572 friction significantly lower than common material pairs 573 and comparable to other high-performance DLC films.

574 Low friction, high hardness films such as those 575 examined in this study have a wide range of potential 576 applications in industry for manufacturing tools and components. Furthermore, the decreasing size scale of 577 578 technology leads to increased influence of surface effects including friction, adhesion, and wear for small device 579 applications. Thus, these types of films may hold 580 promise for technologies such as MEMS devices, small-581 scale machining applications, and even nanomechanical 582 583 data storage.

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