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Abstract

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 fluorine-containing 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 non-line-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.

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 fluorine-containing 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 non-line-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

1. Introduction

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

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 sp^3 (diamond) and sp^2 (graphite) bonding configurations, although sp^1 (polymeric) configuration has also been observed. The sp^3/sp^2 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].

The tribological characteristics of DLC films have been the subject of a large number of investigations because of the high hardness and low friction that these films generally possess [14–18]. A wide range of results has been reported because of differences in methods of synthesis, film structure, and thickness, and test environment and procedures. Almost all macro-tribological studies on DLC films have been performed using pin-on-disk or conventional high displacement reciprocating wear testers. Relatively few studies have been performed on DLC films under small amplitude wear conditions

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(fractions of a micrometer to a few 100 μm) and/or at relatively high reciprocating frequencies (10–100s of Hz) [19–22]. This type of wear usually occurs as a result of an unintended vibrations and is quite prevalent in many industrial applications such as aircraft, press-fit prosthetic devices, electrical contacts, nuclear reactors, and automobiles. The wear mechanisms in small amplitude reciprocating wear conditions are fundamentally different in many respects from unidirectional and high displacement reciprocating wear [23–26]. The localized concentration of wear in a small region can lead to the accumulation of wear debris and environmental reaction products in the relatively small region of the wear scar. Moreover, the sliding velocities can be very high and heat transfer is limited due to the small affected region. A strong dependence of friction on sliding velocity even in the regimes, achievable by conventional reciprocating wear testers has been recently demonstrated for DLC films [27–29], and the sliding velocity attained during small amplitude, high frequency reciprocating wear can be significantly higher than the velocities used in that study. This motivates the study of DLC films under small amplitude sliding conditions.

DLC films are often modified to improve their tribological performance by incorporating other elements, thus altering not only the composition but also the structure of the films. For example, compressive stresses adversely affect the tribological performance of DLC [30], and addition of metallic phases (e.g., W, Ta) to the film, as well as the use of a metallic interlayer, mitigates the sensitivity of tribological characteristics to compressive stresses [31]. This also reduces the sensitivity to humidity [31].

It is desirable to mitigate the effect of humidity, and to lower the adhesiveness and wettability of DLC, particularly for small-scale applications where capillary condensation and adhesion become critical [32, 33]. The addition of F or Si to the DLC network structure not only lower the surface energy and wettability of DLC [34–38] but also influences the tribological characteristics [16, 31, 34–36, 39]. The reduction of surface energy by the addition of F is attributed to the presence of $-\text{CF}_2$ and $-\text{CF}_3$ groups [34, 38–41]. However, higher fluorine contents lead to a decrease in hardness, approaching the properties of poly-tetra-fluoro-ethylene (PTFE) [34, 38–41]. The deposition parameters, in addition to the fluorine content, dictate its wear resistance. The addition of silicon reduces the surface energy, possibly by decreasing the dispersive component of surface energy [31, 34]. As well, Si addition increases the hardness of the DLC films by promoting sp^3 carbon 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-ethane and hexa-methyl-disiloxane, respectively. The former adds F to the DLC film, while the latter adds both Si and O. The fluorine- and silicon- containing carbon films can also be referred to as fluorocarbon films and C–Si–O films, respectively. However, the terms F-DLC and Si-DLC will be used in this paper, consistent with terminology used in studies on similar films [16, 34, 38]. Small amplitude reciprocating wear testing of these DLC films was performed against hard silicon nitride and soft PMMA counter-surfaces to capture a range of wear damage effects from abrasive material removal to counterface material adhesion and build-up. The findings of this study are expected to be of general relevance to applications such as manufacturing tools and components, MEMS devices, hard disks, and even nanomechanical data storage, for which DLC coatings may play a highly practical role in alleviating tribological-related failures. While we do not attempt to match length scales, stresses, and velocities for any of these applications specifically, the smaller length scale and reciprocating nature of our wear tests, in contrast to conventional pin-on-disk testing, is a useful step toward the smaller length-scales and confined geometries that are found in the aforementioned applications.

2. Experimental methodology

2.1. Plasma-based deposition of DLC films

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

For this study, AISI 4140 steel samples were polished with a wet grinder by progressively using 240, 320, 400, and 600 grit silicon-carbide abrasive and then subjected to a final polishing step using 1 μm diamond paste. Prior to being introduced into the plasma chamber, the samples were cleaned ultrasonically using acetone and alcohol. Once in the PIID system, the samples were cleaned using an Ar^+ plasma in a glow discharge mode at a pressure of 12 mTorr using a stage bias of -5 kV

182 for approximately 5 min to remove any traces of con-
 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 $1-1.5 \mu\text{m}$
 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
 203 force microscope (AFM) (QScope 250, Quesant
 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 $20 \times 20 \mu\text{m}$ 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 $10-500 \mu\text{m}$. 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

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

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

266 2.4. Characterization of wear damage

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

Table 1

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

Material	R_q (nm)	Hardness (HK, kg/mm ²)	Wear volume* (mm ³)	Wear rate* (mm ³ N ⁻¹ m ⁻¹)	Debris volume** (mm ³)
Steel	4	300 ± 50	N/A	3.1×10^{-8}	$> 4.8 \times 10^{-7}$
DLC	6	1300 ± 100	2.6×10^{-8}	6.6×10^{-8}	9.5×10^{-9}
Si-DLC	11	1400 ± 200	1.7×10^{-7}	1.7×10^{-8}	$> 4.4 \times 10^{-7}$
F-DLC	6		N/A	2.1×10^{-7}	$> 1.0 \times 10^{-6}$

* 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.

3. Results and discussion

Table 1 summarizes the results of the wear volume and polymer debris volume measurements as well as surface roughness and microhardness of the materials 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 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 likely the result of substrate roughening due to the Ar ion sputtering performed prior to deposition.

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

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

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

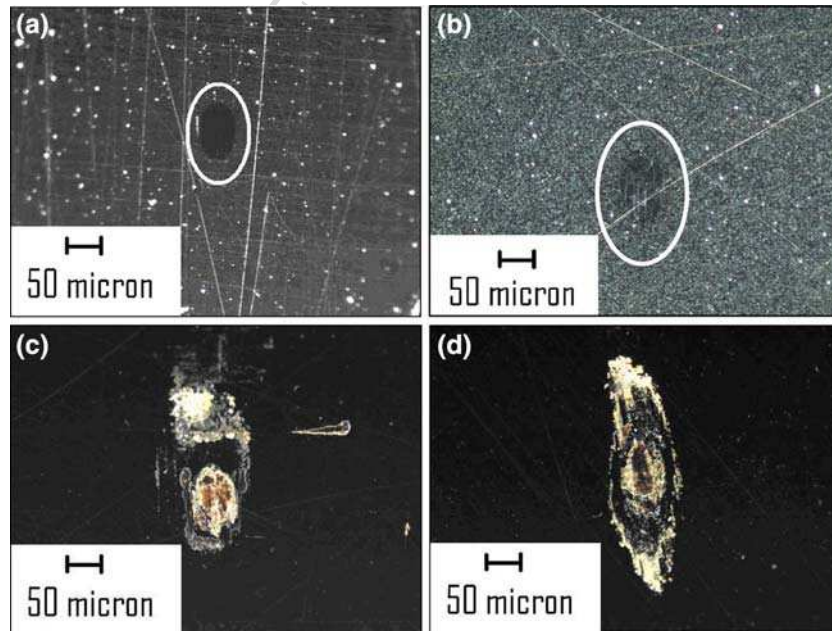


Figure 1. Dark field optical micrographs of wear scars on DLC films and uncoated steel produced by small amplitude reciprocating wear against a silicon nitride counter-surface: (a) DLC, (b) Si-DLC, (c) F-DLC, and (d) uncoated steel. The scars on DLC and Si-DLC films have been circled for clarity.

326 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
 341 film breakthrough occurred, and the underlying steel
 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
 356 from the silicon nitride stylus, were also detected in the
 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
 361 loss and show negligible wear debris. The approximate
 362 wear volume of the DLC wear scar is $2.6 \times 10^{-8} \text{ mm}^3$
 363 while the wear volume of the Si-DLC wear scar was
 364 higher at $1.7 \times 10^{-7} \text{ mm}^3$ (table 1). This corresponds to
 365 wear rates of $6.6 \times 10^{-8} \text{ mm}^3 \text{ N}^{-1} \text{ m}^{-1}$ and $4.4 \times$
 366 $10^{-7} \text{ mm}^3 \text{ N}^{-1} \text{ m}^{-1}$ for DLC and Si-DLC, respectively.
 367 For comparison, a wear rate of $2.5 \times 10^{-8} \text{ mm}^3 \text{ N}^{-1} \text{ m}^{-1}$
 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
 372 ($\sim 10^{-7} \text{ mm}^3 \text{ N}^{-1} \text{ m}^{-1}$) for 50% RH air [57]. The F-DLC
 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

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

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

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

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

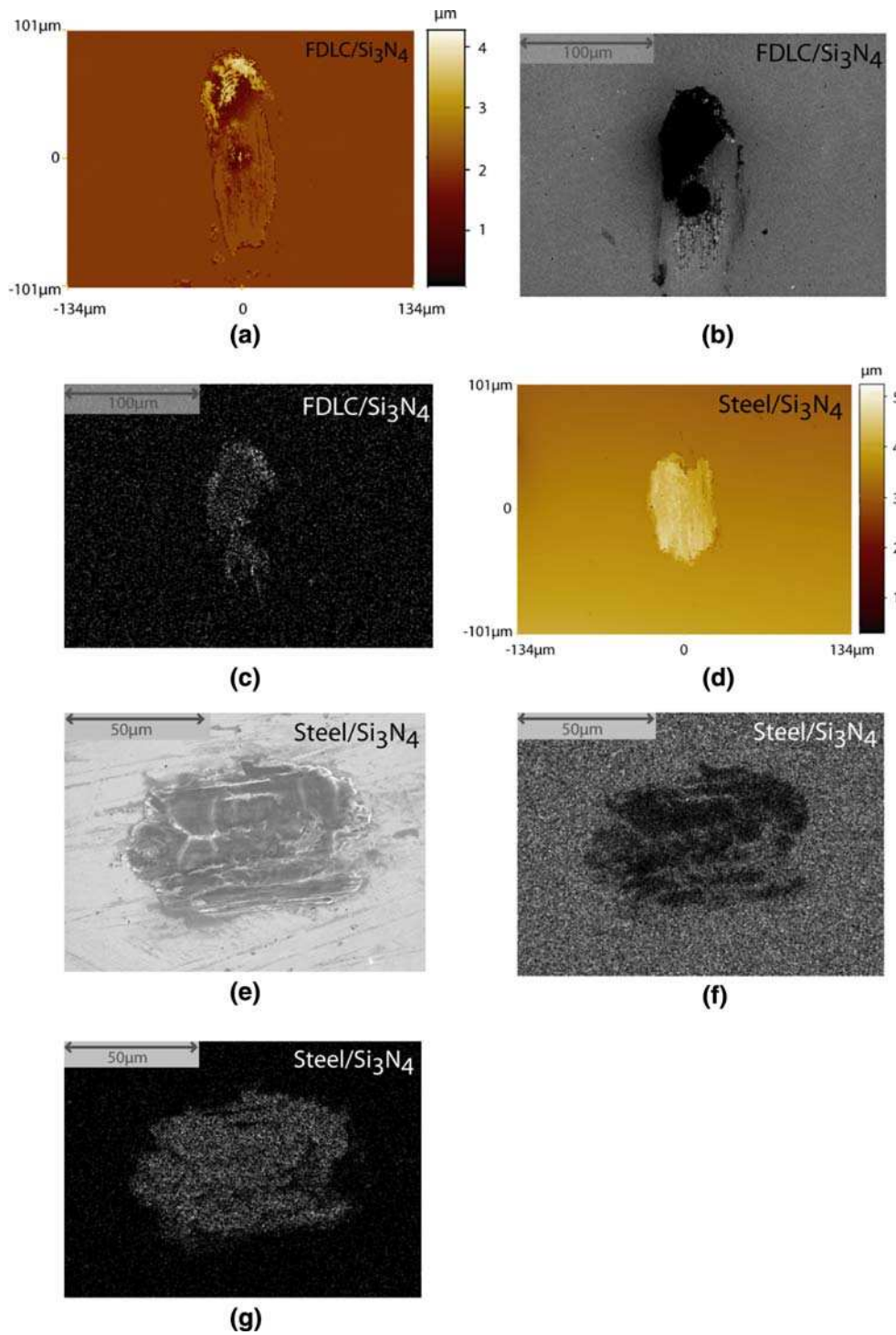


Figure 2. Images of wear scars generated on steel and F-DLC films after wear against Si_3N_4 counterface showing the effects of oxidation (a) optical profilometry image giving the topography of the wear scar on F-DLC film, (b) SEM image of the wear scar on F-DLC film, (c) EDS oxygen dot map of the wear 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 interac-
 tions as well as the surface energy, and interactions
 between oxygen groups in both the PMMA and the
 Si-DLC could contribute to this effect [58], or this could

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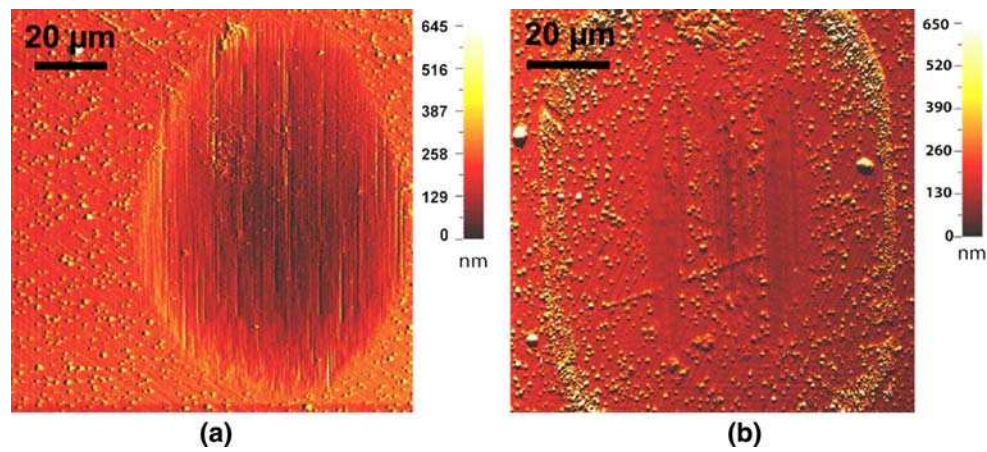


Figure 3. AFM images of wear scars on the Si-DLC films produced by small amplitude reciprocating wear against (a) silicon nitride and (b) PMMA counter-surface.

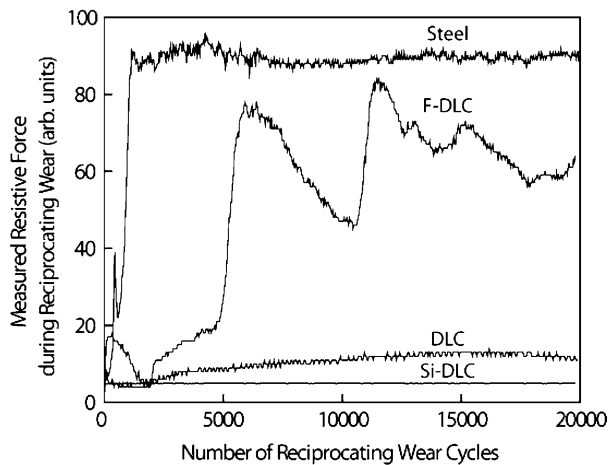


Figure 4. Plot of measured resistive force versus number of reciprocating cycles for wear tests against silicon nitride counter-surface.

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 $1 \times 1 \mu\text{m}$ 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.
 460 The interior of the wear scar alone had a debris volume
 461 of $4.8 \times 10^{-7} \text{ mm}^3$, so the total debris volume, including
 462 debris outside the field of view, is much greater than this
 463 amount and far greater than that for any of the three
 464 films.

465 Figure 6 shows the trends in frictional force ampli-
 466 tude (raw signal units) as a function of the number of

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

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

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

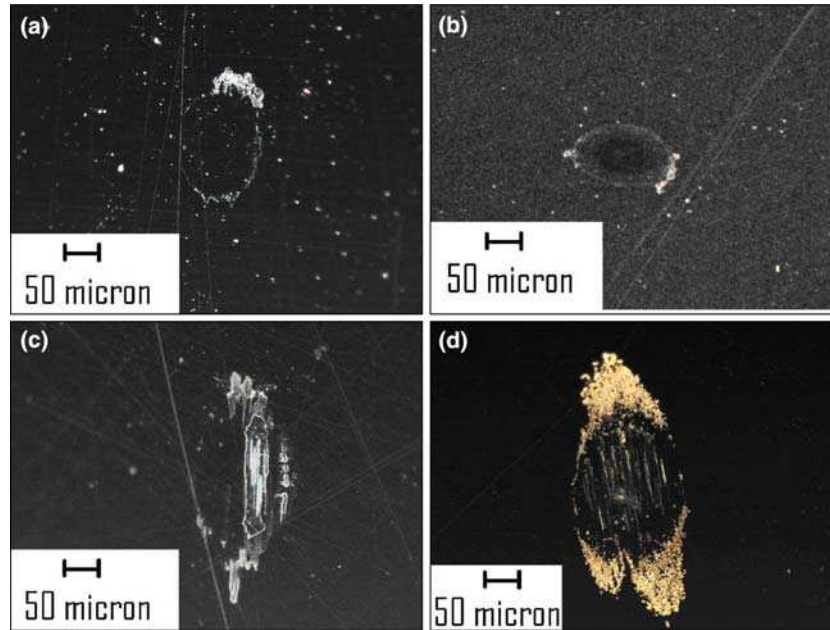


Figure 5. Optical micrographs of wear scars on DLC films and uncoated steel produced by small amplitude reciprocating wear against polymer PMMA counter-surface: (a) DLC, (b) Si-DLC, (c) F-DLC, and (d) uncoated steel.

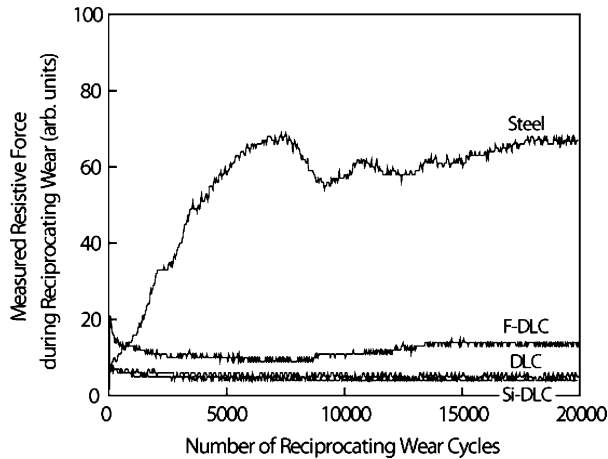
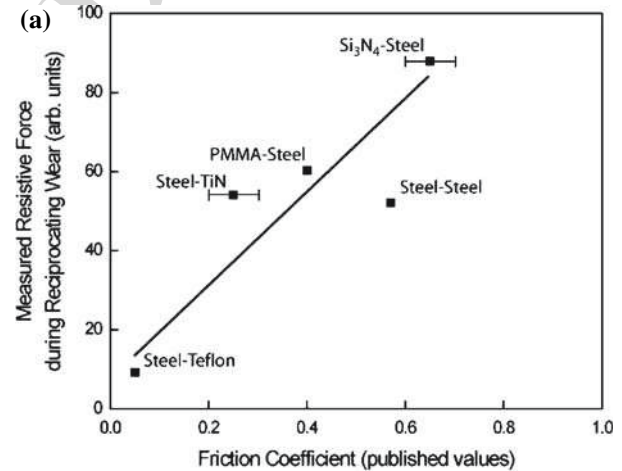


Figure 6. Plot of measured resistive force versus number of reciprocating cycles for wear tests against PMMA counter-surface.



(b)

Slider	Film	Estimated
Si ₃ N ₄	DLC	0.08
	Si-DLC	0.04
	FDLC	0.65
PMMA	DLC	0.04
	Si-DLC	0.04
	FDLC	0.07

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).

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
 511 and shown in figure 7b, indicate that these films have
 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).

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

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

520
 521
 522

523 and reported a friction coefficient of 0.08 in air (50%
524 RH) [57]. Achanta, Drees, and Celis found a decrease in
525 surface roughness of DLC films (quantified by AFM)
526 with increasing number of reciprocating cycles in con-
527 tact with a spherical silicon nitride counterbody, and
528 reported a steady state friction coefficient of 0.1 in air
529 (0.10 N load, 400 μm sliding amplitude at 0.2 Hz for
530 1000–5000 cycles) [52]. Drees, Celis, and Achanta
531 reported friction coefficients of ~ 0.19 – 0.25 for recipro-
532 cating sliding of silicon nitride against DLC under
533 similar conditions (0.25 N load, 300 μm sliding ampli-
534 tude 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
548 DLC film and fluorine-containing and silicon-contain-
549 ing DLC films deposited on steel using the PIID
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

577 components. Furthermore, the decreasing size scale of
578 technology leads to increased influence of surface effects
579 including friction, adhesion, and wear for small device
580 applications. Thus, these types of films may hold
581 promise for technologies such as MEMS devices, small-
582 scale machining applications, and even nanomechanical
583 data storage.

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