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Tribochemistry of silicon and oxygen doped, hydrogenated Diamond-like Carbon in fully-formulated oil against low additive oil

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Abstract

Diamond-like Carbon (DLC) coatings are increasingly used to reduce wear and lower friction in many applications. Doped DLCs are being produced with the goal of further enhancing the friction and wear profile as well as increasing the coating reliability.

Silicon is often incorporated into DLC as it is known to affect the sp^2/sp^3 ratio which in turn can affect the hardness of the film. It can also improve adhesion of the DLC coating to the substrate and lower internal stress.

In this study, investigations into the wear behaviour, tribochemistry and oil-formulation dependence of Si, O-doped DLC (Si-DLC) were conducted. The oxidative stability of Si-DLC was also examined.

Silicon-doped DLC is able to form a protective tribofilm when a fully-formulated lubricant is used. The tribofilm is composed of; S, P, Ca and Zn which are widely recognised as being important to wear reduction.

A mechanism of wear repression facilitated by oil additives is proposed.

Keywords: DLC-Coatings, Boundary-Lubrication, Oil Additives, Wear Mechanism,

1 Introduction

Diamond-like Carbon (DLC) coatings are widely used to reduce both friction and wear in a variety of applications. Diamond-like carbon coatings are often used on automobile parts and are now finding wider use in items that benefit from friction reduction such as razor blades [1]. DLC has been doped with both metal and non-metal elements to improve its characteristics. Dopants may increase the affinity of DLC for lubricant additives by increasing overall reactivity [2].

DLC doped with silicon is commonly used as silicon can reduce internal stress and reduce friction when included in DLC [3-5]. Silicon incorporation can also affect chemical reactivity of the film [6]. Silicon incorporation also affects the film's sp^2/sp^3 ratio as silicon does not readily take part in sp^2 hybridised bonding.

Addition of silicon into DLC films can most easily be achieved by using a siloxane compound, a stable silicon and oxygen containing precursor [7]. If siloxanes are employed the film produced will have a noticeable oxygen content which will further affect the film. Si-DLCs can be prepared from silanes, exclusively silicon and hydrogen-containing compounds, if oxygen content is not desirable. Thus the coating investigated herein must be regarded as a Si, O–doped DLC.

Many authors report Si-DLC has improved friction characteristics when compared with non-doped DLC. This finding is usually when Si-DLC is tested with dry-sliding or with water as a lubricant [8, 9]. It is often noted that trace water or humidity drastically affect the friction and wear profile of this system. The mechanism of reduced friction for Si-DLC is still not fully understood. However, several authors report the formation of important Si-O compounds at the sliding interface that are often commented on as being able to reduce friction and wear [4, 9, 10]. These compounds include SiO_2 and silanols. Far less research has focused on Si-DLCs performance when in a fully-formulated oil.

There is also no current consensus on the optimum amount of silicon to incorporate into Si-DLCs for best performance. In one study when various % doping of silicon were tested an optimum of 6.6 at% was found to be best for wear resistance [11]. However to best reduce internal stresses of the DLC an optimum of 1-2 at% was established. In this study the silicon content exceeds both of these; however, a large amount of oxygen is also incorporated which could further change characteristics of the DLC.

The main objectives of this work were to investigate the tribological dependence and behaviour of silicon doped DLCs with formulated oil. The focus is on the role silicon specifically plays in mediating tribological interactions with the oil and whether this is beneficial under the conditions studied.

Formation of silicon oxides in a fully lubricated contact may not be as pronounced, or as beneficial, when compared with the effect imparted on dry sliding contacts. The

effect of other additives present in fully formulated oils could interfere with the reported role of silicon oxides.

1.1 Si-DLC in the literature

A dichotomy exists in the literature on silicon doped DLCs in that Si,O doped and Si DLCs would both be considered Si-DLC but can have quite different chemical compositions. Si, O doped DLCs, predominately made from siloxanes, appear to maintain the siloxane backbone even through the PVD process and overall have a higher amount of oxygen in the coating. Si-DLCs can have a very low, or almost-zero oxygen, content and will have a greater amount of Si-C bonding which can influence the DLC's structure. Table 1 (below) shows a summary of research on Si doped DLC and its tribological properties.

Table 1 Overview of current literature on Si-DLC

Author	Deposition method	Precursor	Friction	Wear	Si-O species	sp^2/sp^3
Iseki [12]	PACVD	TMS/ Methane/ H_2	Not tested	Not tested	Non detected	High % Si inhibits sp^2 clustering
Kato [13]	PACVD	TMS/ H_2	Not tested	Not tested	Silanol (Si-OH)	Si content increases sp^3 content
Kim [9]	RF PACVD	Benzene/ Silane/H_2	(air) Friction coefficient decrease with increasing silicon content	Wear increased with Si content	Low friction attributed to silicon-rich oxide debris	Not given
Oguri [14]	PACVD	$SiCl_4$ / Methane / H_2	Friction (air) $\mu = 0.06$, (N_2) $\mu = 0.03$	Not given	Silicon oxide/ silica sol	Not given
Pham [6]	RF PACVD	Composite; Silane upper layer	(air) $\mu = 0.02$, 1/3 of un-doped DLC	Higher wear rate that un-doped DLC	Si-O containing tribofilm	Not given
Moolsradoo [15]	Plasma based Ion implantation	Acetylene/ TMS/ O_2	(air) 34% at. Si $\mu = 0.04$, 25% at. Si exhibited greater μ	Wear increases with annealing in argon/air	Silicon oxide layer	Not given
Veres [16]	RF CVD	Methane or TMS or HMDSO	Not given	Not Given	O sequesters Si from the coating	Graphitic clusters detected

Source gas chemistry has been identified as highly influential in terms of the DLC produced. Iseki [12] notes that when Si-DLC is prepared from silanes exclusively there is a large fraction of both Si-C and Si-H bonding. Also established was that hardness increased as Si

content increases. Also, increasing Si content resulted in decreased sp^2 clustering within the film. Kato [13] compares silane based Si-DLC and non-doped DLC, with a range of 4 – 17% Si content. On the Si-DLCs silanol was detected on the surface. It was noted that there is no absorbed water on the non-doped DLC's surface, however for all Si-DCLs there is an adsorbate layer present. Additionally, Kim [9] examined Si-doped DLC created from a silane precursor and tribotested it under ambient conditions. Low and stable friction was observed and was attributed to the formation of silicon-rich oxide debris. Finally, Pham [6] investigated a silane based DLC and found that when tested in ambient conditions evidence of both Fe and Si oxides were noted and that the Si-DLC had higher wear than non-doped DLC.

However, when Si, O containing precursors are used a change in the coating structure occurs. FT-IR suggests that the dominant form of Si in the film is as a Si-O network with a smaller fraction coming from Si-C bonds thus affecting the coatings microstructure [15]. This trend was also identified by Veres *et al* [16], in that the presence of oxygen decreased the amount of Si in the carbon matrix.

A comparison of Si-DLC sliding in both dry and ambient environments appears to have very different outcomes in terms of noted species in the worn area. When sliding in humid environments Si and O are detected in the worn area which FT-IR attributes to the presence of a silica-sol layer. However, when sliding in a dry atmosphere the debris is mainly noted to be carbonaceous [14]. This appeared to have little effect on the friction coefficients which were recorded as comparable, differing only by mechanism.

Very few papers appear that investigate the influence fully-formulated oil has on the tribology of Si-doped DLCs. Due to Si-DLC's potential ability to self-lubricate it could be that novel oil formulations are required to best facilitate this effect.

2 Experimental

2.1 Materials

The DLC coating used in this project was a commercial sample produced using PACVD technique. The coating is produced using lower temperature plasma; the substrate is negatively biased by 500 V with the chamber acting as the electrode. A hot cathode auxiliary system is also employed to enhance plasma generation. The process typically takes place at 10^{-3} mbar. The coatings can be viewed as multi-layered as there are interlayers employed to improve coating adhesion to the substrate. The substrate is first cleaned with argon ion etching before any deposition commences. Then a titanium layer is deposited, followed by a silicon based interlayer. After interlayer deposition the bulk DLC is deposited. Elastic recoil detection analysis (ERDA) of the coating (table 2) shows the total composition of elements, including hydrogen.

Table 2 coating composition

Coating	%C	%H	%O	%Si	%Ar
Si-DLC	44.6	34.0	7.0	14.0	0.4

As shown above the silicon-doped coating also includes oxygen (as well as trace amounts of argon) in the coating and there is twice as much silicon within the coating as oxygen. As such it can be considered dually doped as it is highly likely that incorporation of additional oxygen into the film will affect the performance. Coating thickness is reported as 2.4 µm.

Si-DLC was deposited on 52100 AISI steel plates of dimensions 7*7*3 mm with a maximum roughness of R_a = 0.08 µm. Pins were of AISI 52100 steel with semi spherical ends of 120-150mm, 44-46 HRC and a max R_a of 0.3 µm. Coating hardness is reported as 17.9 GPa.

2.1.2 Lubricants

The lubricants used for this investigation include a bespoke lubricant which is a version of a commercially available heavy duty diesel engine oil (10w40 viscosity grade) blended with additional GMO, an organic friction modifier. The second lubricant is an oil blended to contain minimal additives. Full details of the oil formulation are not given as they are commercially sensitive samples. ICP analysis however is available for the fully-formulated oil and is shown in table 4. The fully-formulated oil contains Ca, P, S and Zn elements as well as anti-oxidants, detergents and dispersants.

Table 3 ICP analysis of formulated oil

ICP analysis (ppm)	
Ca	2391
Mg	81
P	761
S	2064

Si	**4**
Zn	**833**

The low additive oil was viscosity matched to the formulated oil and contains only detergent species and viscosity modifiers.

2.1.3 Thermal effects of gas absorption upon the coating

Due to the fundamental role oxygen plays, as identified within the literature on Si-doped DLCs, a study was undertaken to investigation the ease of which the coating's microstructure changes when exposed to oxidative conditions. As such, samples of Si-DLC samples were submerged in the low additive oil and placed in flasks. One was flushed through with nitrogen for twenty minutes and then sealed; the other was kept open to air. Both samples were heated at 80 °C for 600 hours. The samples were then washed in heptane and analysed, along with an un-heated sample.

2.1.4 Tribometer testing procedure

The TE77 platform (figure 1) allows for tribological investigations under different heating and load conditions to simulate various conditions observed in the engine. In this case boundary lubrication as the lambda value for the system was calculated to be $\lambda= 0.0040$. Before experimental set-up all parts are sonically cleaned in acetone for twenty minutes. Heating is controlled by a thermo-couple that regulates the oil temperature according to a user defined value. The heater plate is positioned below the sample holder. The load cell is able to measure the frictional force and converts this to a digital signal, using an analogue to digital converter. This is then processed by Labview. An initial Hertzian contact pressure of 0.15 GPa was chosen to emulate the conditions of a piston ring contact, in which DLC coatings can be employed [17]. The frictional force is the average of 1000 measurements read at five minute intervals for seven hours. Once finished the pin and plate are rinsed in heptane to remove excess oil. Steel/steel data was not sought in this instance as the benefits of steel/DLC tribopairs over steel/steel are reported in the literature [18]. Experimental set-up detailed below (table 4):

Table 4 Tribometer running conditions

Running Conditions	Value
Load	28N
Maximum Hertzian Pressure	0.15 GPa
Average Running Speed	0.2 m/s
Temperature	100 °C
Frequency	20 Hz
R_a	0.08 µm
Volume of oil	4 mls
Pin radius	150 mm

After testing, wear is then calculated from profilometry data to obtain dimensional wear coefficients. The dimensional wear coefficient is the volume worn (m^3) divided by the sliding distance (m) multiplied by the unit of load (N).

2.2 Surface analysis

The coating was characterised both prior to and post wear-testing to gain insight into surface composition. Before any post wear testing was undertaken samples were carefully cleaned by rinsing excess oil from the surface using high-purity heptane. Post wear analysis was conducted using scanning white light interferometry on a Bruker NP FLEX interferometer. All measurements were taken using vertical scanning interferometry mode, scan speed of 1, magnification of x2.5. In addition to this areas of the plate and pin head were optically imaged to identify any surface changes.

Static Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) chemical maps were obtained for worn samples to confirm the presence of a tribofilm. The technique used employs a primary ion beam source of Bismuth, in the form of a liquid metal ion gun. The primary ions are fired at the worn area and impact on the surface provokes ejection of secondary ions from the surface of interest. A cluster ion beam was used Bi_3+ with an energy of 2 KeV for static SIMS. The target current was 1 Pico Amp (or within in the range 0.1 -3 Pico Amps), from the flood gun to compensate for charge build-up. Depth profiles were undertaken using a C_{60} source to allow for slower profiling with a maximum time of 800 seconds. All sample spectra were examined for the presence of: Ca, P, S, Zn, O species along with various Si, C, H, O, Fe species. Spectra obtained were analysed using ION-TOF software. Individual spectra were calibrated to the H, C, CH, O and OH signals for the negative spectra and a deviation limit of 70 ppm was used to ensure accuracy.

XPS was carried out using a VG ESCALAB 250 X-ray Photoelectron Spectrometer which uses monochromatized X-rays from an aluminium K alpha source. The system also employs high transmission electron optics and a multi-channel detector. An approximate area of 500 μm^2 was analysed in the worn area. XPS is surface specific in that it can only penetrate the upper few nanometres of the sample. A short survey scan with an energy of 150 eV was carried out at first to determine which elements were present. Longer scans (20 eV) of the selected peaks were carried out to fully resolve any peaks present. CasaXPS software was used to analyse the data. Reported literature precedents for C1s calibrations for various DLC and Si-DLC samples were in agreement on the calibration reference value of 284.4 eV for the main peak. [16, 19]. Evaluation of Si2p position and oxygen components were also verified from literature values [16, 20-22]. CasaXPS software was used for performing the curve fitting procedures on XPS peaks obtained, using the Shirley algorithm to construct a background. Peak area and full-width at half-maximum (FWHM) were constrained in order to obtain information with the most appropriate chemistry associated with the system [23]. The value of FWHM of XPS peaks herein are a convolution of analyser resolution and of natural FWHM of the peaks [21, 24].

Transmission Electron Microscopy (TEM) was employed to image any tribolayers present. Energy-dispersive X-ray analysis was used to identify elements within the film. A Philips CM200 FEGTEM Field emission gun TEM/STEM with Supertwin Objective lens and cryoshielding, was used to obtain the TEM image. Oxford Instruments INCA EDX system and Gatan Imaging Filter were used to produce high resolution TEM images, microanalysis and mapping.

3.0 Coating characterisation pre-wear

3.1 Dynamic SIMS data of unworn sample

Dynamic profile data (Figure 2a and b) confirm an inverse relationship of certain species within the DLC. It appears that hydrated carbons, silicon oxides and hydroxyl groups are at greatest concentration at the surface, however with profiling these species deplete.

In comparison the unsaturated carbon chains and less oxidised silicon species, appear to increase in concentration with etching; the main fragments being Si:O 1:1, compared with the surface.

This shows that there is indeed a rich oxide layer at the upper surface of the DLC and that this is not maintained in the bulk of the material. The dynamic profile is not directly calibrated to depth; however combining the SIMS data with XPS data, an approximate depth of the presence of the Si oxide layer would suggest a minimum of 10 nm if not greater based on XPS penetration depth.

3.2 XPS pre-wear

XPS profile of the coating surface (figure 3) shows that oxygen makes up 12% of the spectrum and silicon makes up 15%. ERDA data (table 2) suggests there should be approximately twice as much silicon compared to oxygen when the coating is analysed as a whole.

Again, this shows a higher than expected amount of oxygen is present at the surface when compared with the whole coating This suggests that additional oxygen is being incorporated into the upper layer of the coating even prior to testing and could be of most importance during the initial period of friction and wear testing.

Various types of silicon and oxygen containing species have been shown to influence the friction and wear of silicon doped DLCs. Therefore their prevalence at the surface prior to testing is noteworthy.

4.0 Results

4.1 Friction results from Si-DLC tested over 7 hours

Early stage friction (figure 4a), up to the two hour time interval, shows fully-formulated oil giving a slight reduction in friction when compared to low additive oil. However the reduction observed is small; recorded as a maximum reduction of 10%.

The respective coefficients of friction appear to merge (figure 4b) after longer testing in that; the friction coefficient of the sample tested in low additive oil continues to reduce, whereas the fully formulated oil affects no such gradual decline in friction.

The initial slightly lower friction with the fully-formulated oil could be attributed to the friction modifier contained in the fully-formulated oil. The absence of a more pronounced difference between the two could be due to the well reported ability of Si-DLC's to self-lubricate (figure 5) when trace water is present, as is inevitable in, non-vacuum, laboratory conditions [14].

The presence of both Si and O within the DLC coating allow for formation of Si-O species and Si-OH species. These species are polar and able to interact well with other hydroxide and oxide species that may be present on the counter body.

However, as the friction appears to be the same in low additive oil as it is for fully formulated oil toward the end of the test duration, this indicates another factor affecting friction reduction for the sample tested in low additive oil.

Optical images of the pin (figure 6) from the sample tested in low additive oil show a black layer on the pin. XPS of this layer identifies the presence of a Si-O type species. This layer is not present on the pin that was tested in fully formulated oil. It would appear that this layer is the reason for reduced friction in low additive oil and represents a transfer layer from the Si-DLC that maintains lower friction.

It is unclear whether the friction modifier works in synergy with any silicon oxide species at the surface or whether this interrupts the inherent self-lubricating ability of the DLC. It is most likely that Si-OH type groups maximise the adsorption of friction modifiers to the DLC and therefore potentiate the friction modifiers affects, however the friction data is not conclusive on this.

4.2 Wear results

Wear of coatings (table 5) recorded after seven hours of testing shows greater total wear of the Si-DLC when tested in low additive oil as predicted. Dimensional wear coefficients (k) were used to compare wear of the samples in the different oils. For the samples tested in fully-formulated oil is recorded as $3.7E^{-18} \pm 1.4E^{-18}$ m³/Nm. The sample tested in low additive oil has a k value of $9.0E^{-17} \pm 6.2E^{-18}$ m³/Nm. This clearly indicates fully-formulated oil works synergistically with the coating to reduce wear.

Wear of the coating was also measured at the point of maximum depth loss (table 5) to gauge loss of coating thickness. The depth lost (2.2 µm ± 0.16 µm) when tested in the low additive oil suggests the coating, total thickness 2.4 µm, has been completely removed by wear in certain places. This can be further validated by inspection by eye as steel substrate has been clearly revealed in specific sections of the sample. Following the wear progress, it would appear that some of the more severe wear, where steel is revealed, takes place earlier on ~ 2 hours into testing. However the coating is not completely removed by the end of the test. This is not the case for fully formulated oil which undergoes a loss in thickness of only 0.6 µm ± 0.09 µm.

Wear of the pin was quantified (table 5); again using the dimensional wear coefficient, the wear for the pin tested in low additive oil is higher than that tested in formulated oil. Both pin wear values are higher than those of the DLCs tested.

Table 5 Quantified pin wear

	Wear of plate (m³/Nm)	Max. Thickness lost (µm)	Wear of pin (m³/Nm)
Low additive oil	$9.0E^{-17} \pm 6.2E^{-18}$	2.2 ± 0.16	$4.12E^{-15} \pm 5.53E^{-16}$
Formulated oil	$3.7E^{-18} \pm 1.4E^{-18}$	0.6 ± 0.09	$1.29E^{-15} \pm 3.01E^{-16}$

5.0 Thermal effects of gas absorption upon the coating

The importance of oxides on the surface of Si-DLC is made obvious from the literature. It is important to establish the tendency of which the silicon in the coating has to oxidise and whether this depends on tribological effects. XPS spectra of the sample were obtained after different treatments (figures 7a, b and c).

Heating the sample (figure 7b) in an atmosphere of nitrogen induces a small change in the coating; an additional peak appears that is indicative of the higher oxide of Si.

The sample heated in air (figure 7c) produces a clearly visible shoulder to the Si 2p region. The emerging peak at 102.4 eV is indicative of silicon bonded to, proportionally, more oxygen; the inclusion of additional oxygen atoms raises the eV for the environment at silicon [22].

The oxygen signal for the sample heated in air is 533.34 eV again confirming the presence of SiO_2 type species. Therefore it can be observed that silicon doped DLC does oxidise when heated in air without the need for any tribological influence.

6.0 Post wear analysis results

6.1 XPS results for Si-DLC in low additive oil

The upper surface of the sample tested in low additive oil, as examined by XPS (figure 8), shows the presence of nitrogen which could be from trace organic additives in the base-oil. XPS peak component break-down (figure 10b) shows two distinct peaks, one at 102.8 eV, in the Si-DLC spectrum indicative of silicon at a higher oxidation state [22]. Oxygen peak components are in agreement with this.

This shows that the silicon in the coating is being severely worn and exposed to oxygen. The rise in eV value of the Si2p peak echoes the spectra of the sample that was heated in air. Both samples appear to be oxidised quite severely.

6.2 XPS results for Si-DLC in formulated oil

Unlike in the low additive oil, fully-formulated oil appears to suppress the emergence of a peak at a higher eV value in the Si-DLC spectrum (figure 10a). The two components of the peak are at 100.4 eV and 101.4 eV, indicating C-Si and C-Si-O respectively.

The sole presence of these two components for the Si 2p peak suggests that the coating resists most wear based changes to its microstructure. In addition to this calcium, zinc, phosphorous and sulphur peaks are present in the spectrum (figure 9); evidence of the formation of a tribofilm.

6.3 XPS results for counter bodies

XPS analysis of the pins reveals a tribofilm on the counter bodies (table 6):

Table 6 XPS analysis of counter bodies

Element (%atomic conc.)	Formulated Oil	Low additive oil
O	25.5	23.8
C	54	63.1
N	1.5	2.4
Zn	0.3	0.0
Fe	1.1	0.8
Ca	1.5	0.6
Mg	12.5	7.3
S	2.0	0.0
P	1.6	0.0
Cr	0.0	0.3
Si	0.0	1.7

XPS analysis identifies Zn, S and P present on the pin tested in formulated oil but not on the pin tested in low additive oil, suggesting formation of a Zn based protective tribofilm. The pin tested in low additive oil shows the presence of Si and Cr that are not observed in formulated oil. This is indicative of increased wear as both Si and Cr are components of the tribopairs. The Si signal appears at 102 eV and is indicative of an Si-O type compound [24]. It is notable that Si is lacking from the formulated oil spectrum.

6.4 TEM/EDX data from Si-DLC in formulated oil:

A Transmission Electron Microscope image (TEM) was obtained of a cross section (figure 11), prepared using a focused ion beam, of the surface of the Si-DLC. A tribofilm is evident for Si-DLC when tested in fully-formulated oil. The tribofilm pictured appears to be unevenly distributed and thicker in certain areas. Maximum film thickness was recorded as 15.0 nm.

EDX spectra (not shown) were obtained of the DLC, as background, and the tribolayer. Zinc, sulphur and calcium are all identified to be present in the tribofilm. The silicon signal appears to be far less intense in the tribolayer than in the DLC, in contrast the carbon peak intensity does not appear to change between the two.

6.5 SIMS chemical map data, low additive oil tested

Secondary-ion mass spectrometry was conducted on both samples post-wear. Chemical maps were obtained.

The chemical map of the sample tested in low additive oil (not shown) shows that, across the worn area; O-, CNO- and similar carbonaceous species are present. Silicon species (Figure 12) are present on the plate but they are present as the oxides and no longer appear to be fragments of a carbon chain. Silicon is now mainly present as smaller ion fragments including $SiHO_2$ and SiO_2. The lack of ions where silicon is within a carbon matrix is evidence of the severe wear the coating has undergone, suggesting that silicon has been actively sequestered from the coating during the wear process.

6.6 SIMS chemical map data, formulated oil tested

Chemical map data (figures 13) of the sample tested in fully formulated oil here shows a well-defined, constrained wear track in which several trends are present. There is a pronounced difference from within the wear track when compared with the unworn section of the film. The worn area shows depletion of O- ions when compared to the whole plate. As well as loss of the higher oxides of silicon, where silicon: oxygen ratio is 1:2 or higher. An opposite trend is observed with sulphur and phosphorous species. The worn area contains a far larger amount of PO_3-, PO_2- and SO_2- species. In addition to this there appears to be great concentration of silicon maintained in a carbon matrix, in that the signal for Si-C type compounds appear richer in the worn area.

It would appear that build-up of P and S compounds, most likely originating from Zn-type additive molecules, in the worn area are able to reduce oxygen concentration. They also appear to help maintain the DLCs microstructure; with more silicon incorporated with carbon.

The reduction in amount of the more oxidised silicon species appearing in the worn area may explain why the friction for the fully-formulated oil was not quite as low as might be expected. Many authors comment on the role of silicon oxides and silica-sol layers and their improved lubricity [10, 14]. Having silicon protected from oxidation in the worn area will limit the formation of these species and thus reduce their effect on friction.

6.7 Dynamic SIMS profile data

Dynamic SIMS profile data (figure 14) was obtained for the sample tested in fully-formulated oil in order to investigate the relationship of P and S ions with the Si-C type species. A C_{60} source was used to etch into the samples.

The profile obtained shows a definite pattern emerge whereby the immediate surface layer is markedly different to the bulk material, further in.

Present at the immediate surface are oxygenated species including hydroxides and oxides of sulphur and phosphorous. In addition to this there are also trace amounts of highly oxidised silicon type species at the surface, however these tail off very steeply; unlike the signal for both P and S which is prominent for longer. Presence of these species at the upper surface is clearly indicative of tribofilm formation.

Once these species are uncovered by profiling, new signals emerge that account for the further bulk of the DLC. These include carbon chains, and species including silicon bonded to hydrogen and carbon as well as some oxygen, as expected. Si within the bulk of the film appears largely to be present as the hydride or bonded to carbon, along with some oxygen.

Profiling data appears to confirm that presence of P and S at the upper surface reduces the amount of silicon oxides formed. Dynamic profiles of the samples tested in low additive oil were not obtained.

7.0 Discussion

7.1 Coating analysis pre-wear

Spectral analysis combined with known atomic compositional data of the coating enables a large portion of the DLCs substructure to be elucidated. It is evident from XPS and SIMS data that at the surface of the DLC there are a large number of oxide rich silicon species whereas further into the coating these species are less prevalent. XPS (figure 3) indicates a ratio of Si:O as one to one whereas ERDA data (table 2) indicates it is actually two to one; this is clearly indicative of oxidation of the surface. Using XPS' penetration depth as a gauge, it would appear that the depth of the oxide layer could be up to 10 nm.

This dichotomy can be explained as an artefact of production, dangling bonds from synthesis of DLC coatings at the upper most surface react with species present in the air upon release of vacuum [25]. This causes a higher than normal amount of –H and –OH terminated species at the upper-most surface. Dynamic SIMS data (figures 2 a and b) is in agreement with XPS results in that the predominant form of silicon within the coating is as the silicon-carbide hybrid, Si-O-C.

7.2 Proclivity of the coating to oxidise when heated in different environments

XPS results (figure 7) confirm that the surface silicon atoms have a tendency to oxidise when heated in air without the need for tribological influence. Therefore it is reasonable to assume that the silicon in the coating will also tend toward oxidation when heated during tribological testing.

This surface oxidation will influence the coatings performance in terms of both friction and wear. Formation of oxides on the surface will increase the coatings polarity, making it more able to interact with the polar head groups of lubricant additives.

This oxidation also represents the beginning of the coating degradation as Si-O bonds form at the expense of Si-H and Si-C bonds, sacrificing some of the diamond-like nature of the coating. Some surface oxidation may be beneficial to the coating, formation of surface oxides in metal systems have been reported to enhance surface wear resistance in certain cases [26]. Additionally, the role of oxides and silicon-oxygen compounds are widely reported as being useful to reduce friction within Si-DLC systems [14].

7.3 Friction analysis

Several factors appear to affect the friction profiles (figures 4a and b) of the systems tested. These include the presence of the friction modifier, GMO, the formation of Si-O containing compounds and the possible antagonistic effect on friction of an anti-wear film. Also, uniquely to the low additive oil tested system is the presence of a dark transfer layer on the pin (figure 6) that appears to affect friction.

Presence of Zn, S and P containing groups on both the DLC and counter body tested in formulated oil indicate the presence of a protective tribofilm. Zn type tribofilms are known to raise friction values; this could indicate why the friction is higher than may be expected for a system involving DLC.

It would appear that the formation of the transfer film on the counter body for the low additive oil tested sample does reduce friction and this affect is continued after severe wear of the coating. The transfer layer contains Si-O type moieties as identified XPS. These species are thought to reduce friction [9, 11, 14]. This species is not observed when the pin tested in formulated oil is examined.

7.4 Wear track analysis

Fully-formulated oil reduces overall wear of Si-DLC as tested in this study. TEM imaging (figure 11) of the cross section show the formation of an uneven tribofilm with a maximum thickness of 15 nm. EDX analysis confirms presence of Zn, Ca and S within this tribolayer. It is unclear whether this is a transfer layer from the steel pin or if the tribolayer is produced on the DLC.

SIMS data (figure 13) identifies several trends that appear. It becomes apparent that, when tested in fully formulated oil, the area outside the wear scar contains highly oxidised silicon compounds. These ion fragments have a higher ratio of silicon to oxygen, either 1:2 or 1:3; this includes SiO_2, $SiHO_3$, $SiHO_2$ and $SiCH_3O_2$. There is a noticeable depletion of these compounds in the worn area suggesting that silicon within the wear scar is protected from further oxidative-damage.

When examining the bulk of the DLC (figure 2b); made apparent by the type of ions observed and consistency with chemical precursors, it is obvious that less oxidised silicon compounds also exist in the film. These fragment ions; SiH_5O SiC_2HO, SiC_2H_5O, Si_2H_4O can all be regarded as less oxidised silicon, 1:1 Si:O, compounds. The chemical map also indicates a slight build-up of un-oxidised DLC in the wear scar. These less oxidised silicon species are suggestive of survival of a siloxane, C-Si-O, backbone during the PACVD deposition, as has been noted elsewhere [5, 15].

The chemical map data (figure 13) clearly shows that classical anti wear elements are accruing in the worn area including species like HS-, PO_3-, SO_2 -. In addition to this the map of O- ions is noticeably depleted in the worn area. This suggests fewer oxygen-containing compounds are present in this area compared to the rest of the plate. Oxidation appears to be inhibited in the worn area.

There is no corresponding trend with silicon from the chemical map data of the Si-DLC tested in the low additive oil (figure 12). There is widespread presence of highly oxidised silicon compounds ($SiHO_3$) across the entire plate and very little evidence of less or un-oxidised silicon preserved from the DLC. There is some evidence of interlayers being revealed as part of the wear process.

Common oil formulations contain both anti-oxidants and anti-wear compounds like ZDDP, which is also know to act as an anti-oxidant. It appears to be the case that the silicon within the coating is highly oxidised at the surface. SIMS profiles (figures 2a and b) show species like SiO_2 in high concentration at the very top layer and following C_{60} depth profiling this is replaced by longer SiC_xH_nO chains. XPS data (figure 3) also confirms presence of silicon oxides and generally more oxygen at the upper surface that is consistent with the bulk of the coating.

7.5 Putative wear mechanism

Due to the large difference in wear for the samples it is demonstrable that Si, O-DLC shows high dependency on oil formulation; the low additive oil contains no anti-wear or anti-oxidant additives whereas the fully-formulated oil can be regarded as rich in these compounds. Well-established chemical thermodynamics can help to illustrate the wear process occurring at the DLC interface.

Table 7 Dissociation energy of key bonds

Bond	Disassociation Energy (kJ/mol) [27]
H-Si	298
H-C	337
C-O	377
C-Si	435
O-SI	798

There is a large bond disassociation energy, 798 KJ mol^{-1} associated with the O-Si bond. This is indicative of how strong the bond that forms is and the thermodynamic driving force for its production. When Si is incorporated to the DLC matrix it can only make certain bonds (table 7): Si-H, Si-Si, Si-O and Si-C bonds. The oxidation of C-Si and Si-H bonds are thermodynamically favourable and as such can proceed via oxidation from atmospheric species [7, 28].

Oil additives like ZDDP and similar compounds are able to inhibit oxidation. They do this by themselves being oxidised. It is interesting to note the large build-up of PO_3 and SO_2 in the worn area, indicative of oxidation of sulphur and phosphorous compounds. The area they accrue in corresponds to the worn area on the chemical map where highly oxidised silicon species are lacking. Preferential oxidation has taken place, protecting the Si-DLC from further oxidative wear.

As well as these oxidised species the wear scar also contains HS-. This corresponds to sulphur at its lowest oxidation state which is also present mainly in the worn area. It would seem that certain additives in the oil are accruing in the wear scar. Here they are able to protect the Si-coating from further oxidative wear by themselves being oxidised.

As the low additive oil does not contain the anti-oxidant species required to inhibit oxidation the process is allowed to proceed unfettered. This facilitates chemical break down of the coating and results in the observed higher wear.

Chemical deterioration of the coating is facilitated by mechanical wear. The reciprocating pin, cleaves apart bonded elements that make up the DLC coating. As the coating is predominately made up of C-H, C-C, C-Si, Si-H and Si-O bonds this bond breakage, in most cases will leave a reactive carbon, or carbon centred dangling bond, or the analogous reactive silicon [29, 30].

If the bond cleavage results in a carbon centred dangling bond being formed several reactions can then take place. Both the formation of a C-H and C-O-(H) bonds are thermodynamically favourable. Hydrogen for abstraction can be provided by anti-oxidants or

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other sources of H in the system. As such these species can passivate the dangling bonds effectively, thus terminating the radical species.

However, if a silicon dangling bond is created it is not thermodynamically favourable for a Si-H bond to form and remain stable. A Si-C bond would not represent the thermodynamic minimum for this system either and is also less likely to form as freely-available sources of reactive carbon are scarce. Sources of oxygen are abundant in various forms from both oxygen in the air and oxygen containing chemical moieties in the oil.

As such the formation of Si-O bonds are favourable in these conditions (figure 15) and can be seen to form when allowed. The presence of the anti-oxidants and anti-wear additives in the fully formulated lubricant can sharply reduce the oxidation of the silicon in the coating. This is achieved by out-competing the silicon for sources of oxygen. This results in the formation of a layer of POx and SOx compounds, instead of the more oxidised silicon species identified at the upper surface of the DLC.

These compounds then build-up in the worn area forming a protective tribofilm. This film is able to reduce the rate of oxidation of silicon within the coating resulting in reduced total wear when compared with the low additive oil.

8 Conclusions

Characterisation of Si, O containing Diamond-like Carbon has been achieved both prior to and following wear testing. Chemical composition of the film can be seen to alter upon wear, depending on conditions. Chemical states at silicon show the most discernible change upon either exposure to oxygen or wear-processes.

Si, O –doped, hydrogenated DLC has been tested in two different oils and analysed in terms of friction and wear profiles. Using a variety of spectral techniques elements important to wear protection were identified in the worn area including P, S, Zn and Ca species.

- The role of oxygen in the wear of the coating is shown.
- The DLC shows high dependence on oil formulation for improved-wear performance when tested over seven hours.
- A mechanism is proposed whereby sequential oxidation of silicon within the coating accelerates degradation of the DLC.
- Inclusion of anti-oxidant species within fully-formulated oils are proposed as the major factor limiting the wear of Si,O-DLC.

In future, additional organic additives could be incorporated in to oil formulations to further guard against oxidative damage of Si,O-doped DLCs. DLCs doped solely with silicon, omitting oxygen, may behave differently to those with both Si and O. However, the tendency of silicon within the coating to oxidize will be maintained and could be potentiated by the lack of oxygen in the bulk coating.

References for: Comparison of the performance and tribochemistry of Silicon and Oxygen doped, hydrogenated Diamond-like Carbon in fully-formulated oil against low additive oil

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Figure 1. TE77 reciprocating pin-on-plate schematic:
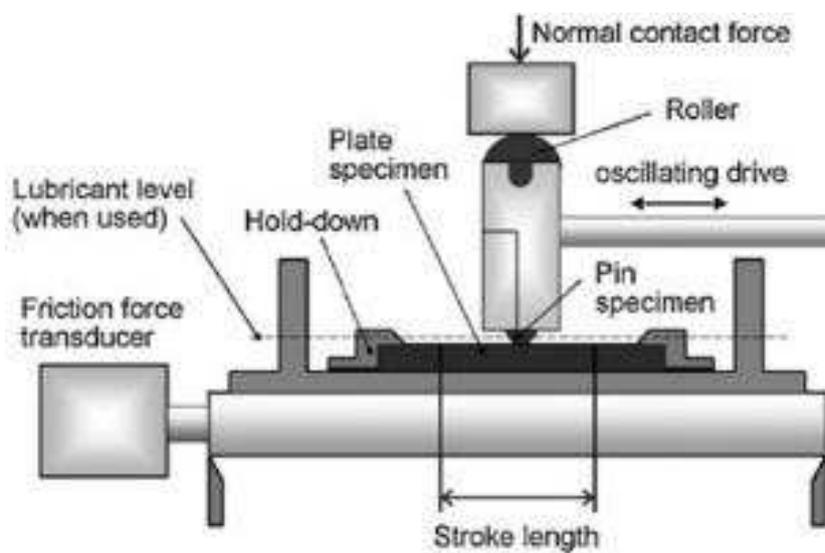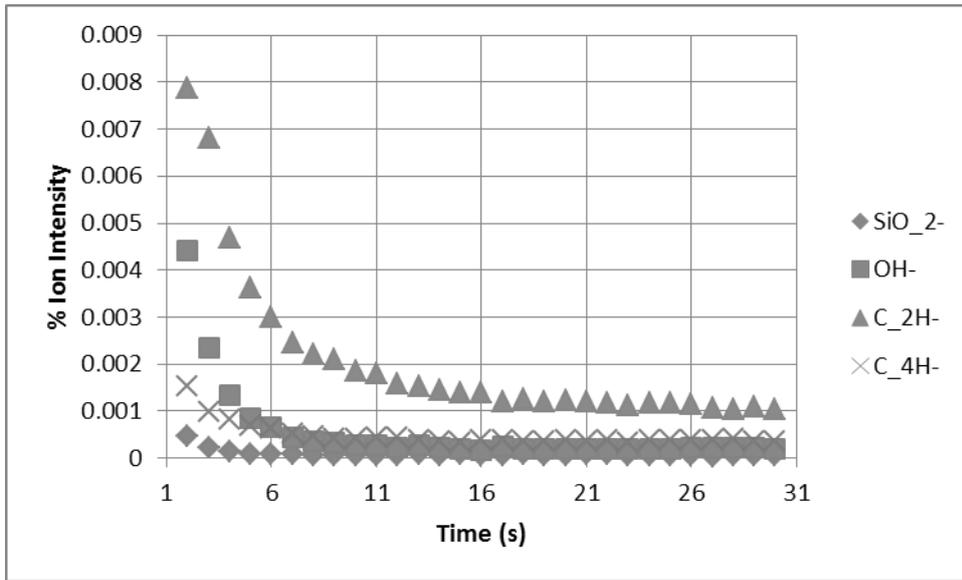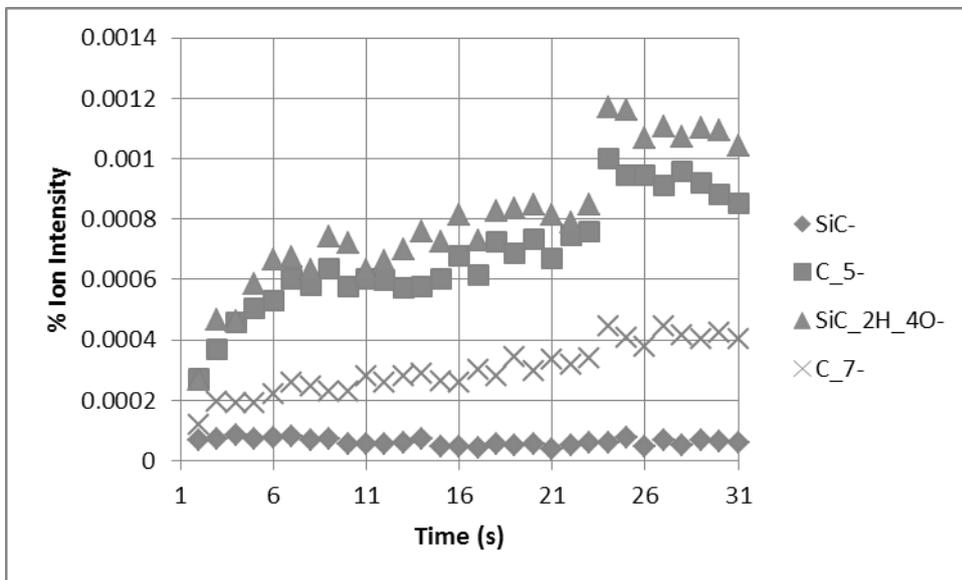
Figure 3: XPS of virgin DLC
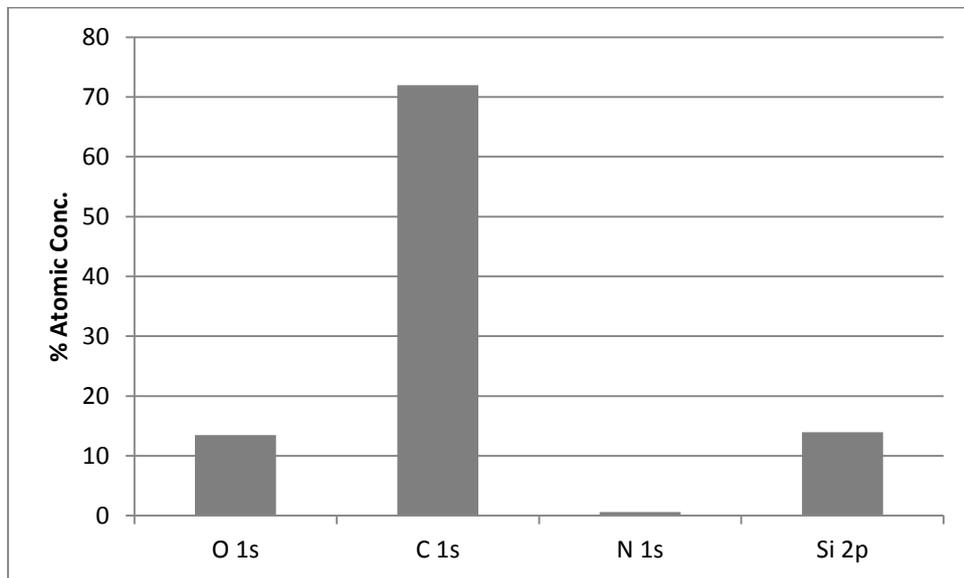
Figures 4: Friction coefficients by oil

a) 2 hours lubricated tests
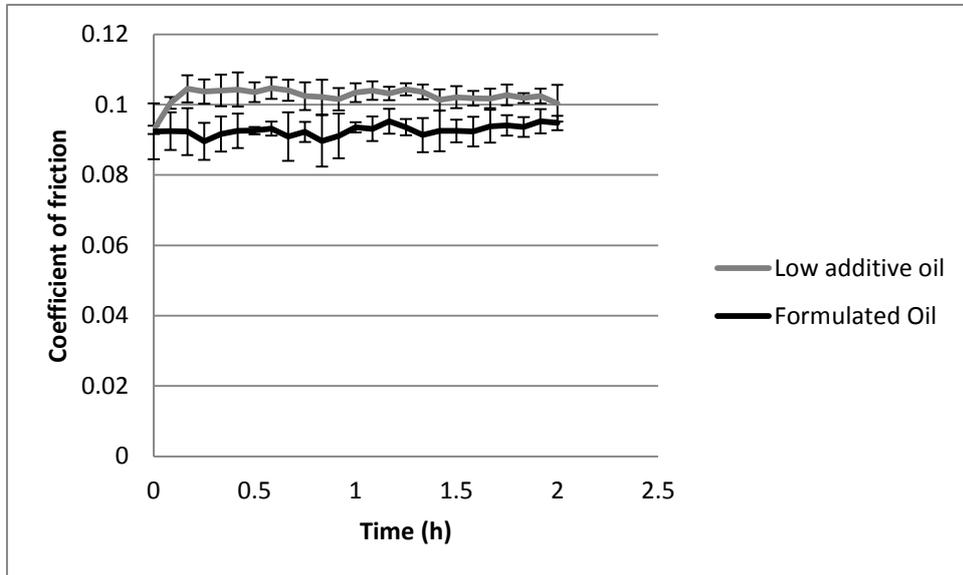
b) 7 hours lubricated tests
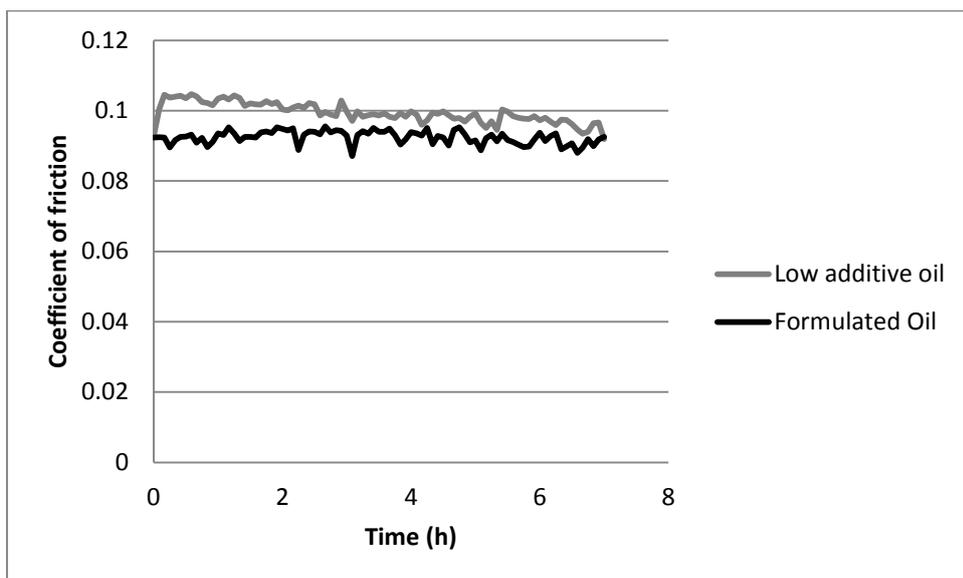
Figure 5: Possible representation of silicon's self-lubricating mechanism

Silica-sol debris layer

DLC film
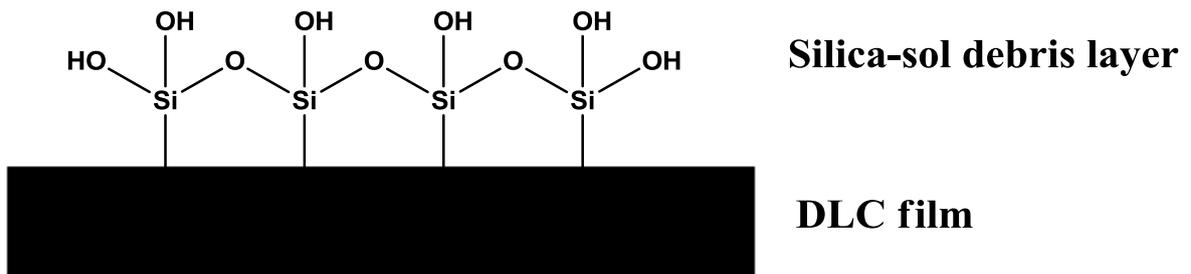
Figure 6: Optical images of worn areas on pins (right) and plates (left), low-additive oil (top) formulated oil (bottom).
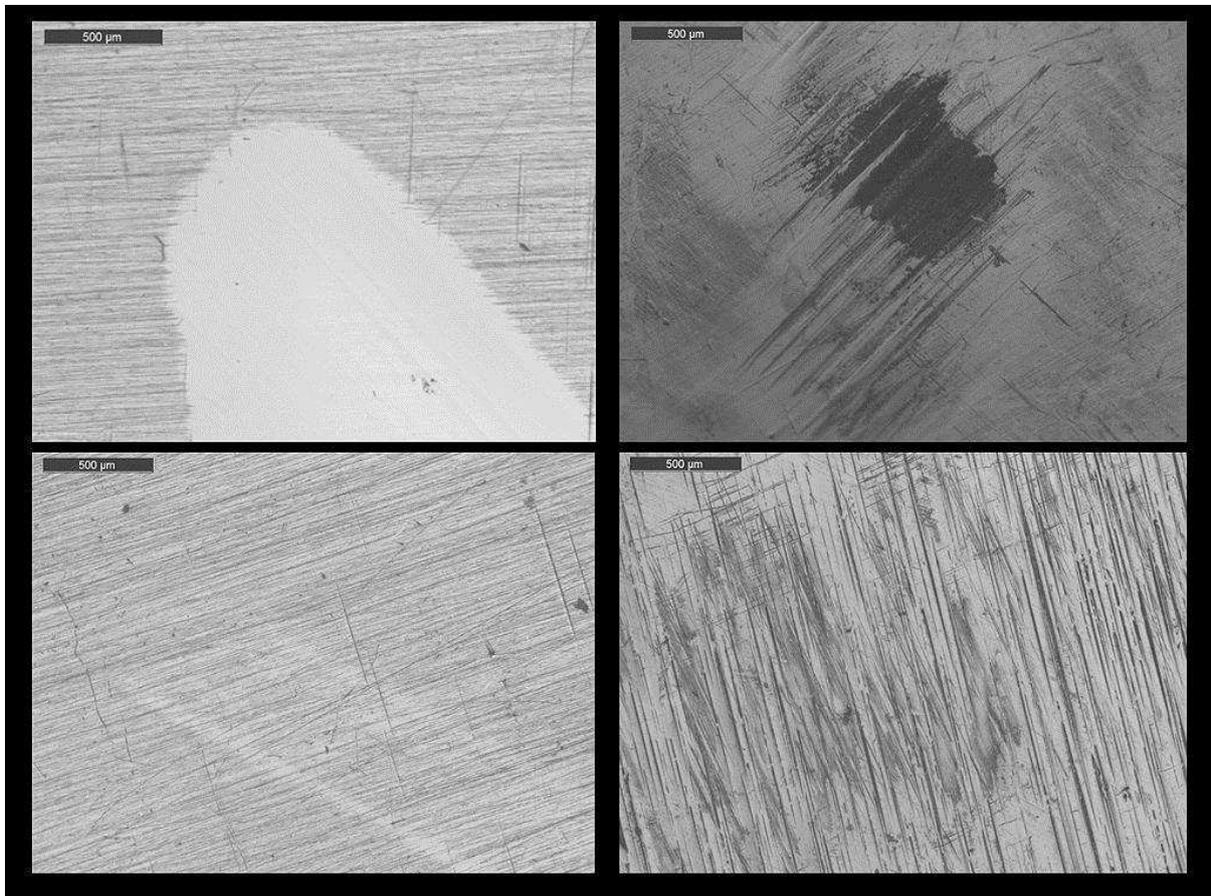
Figure 7: XPS analysis of Si peaks from Si-DLC heated under different conditions:
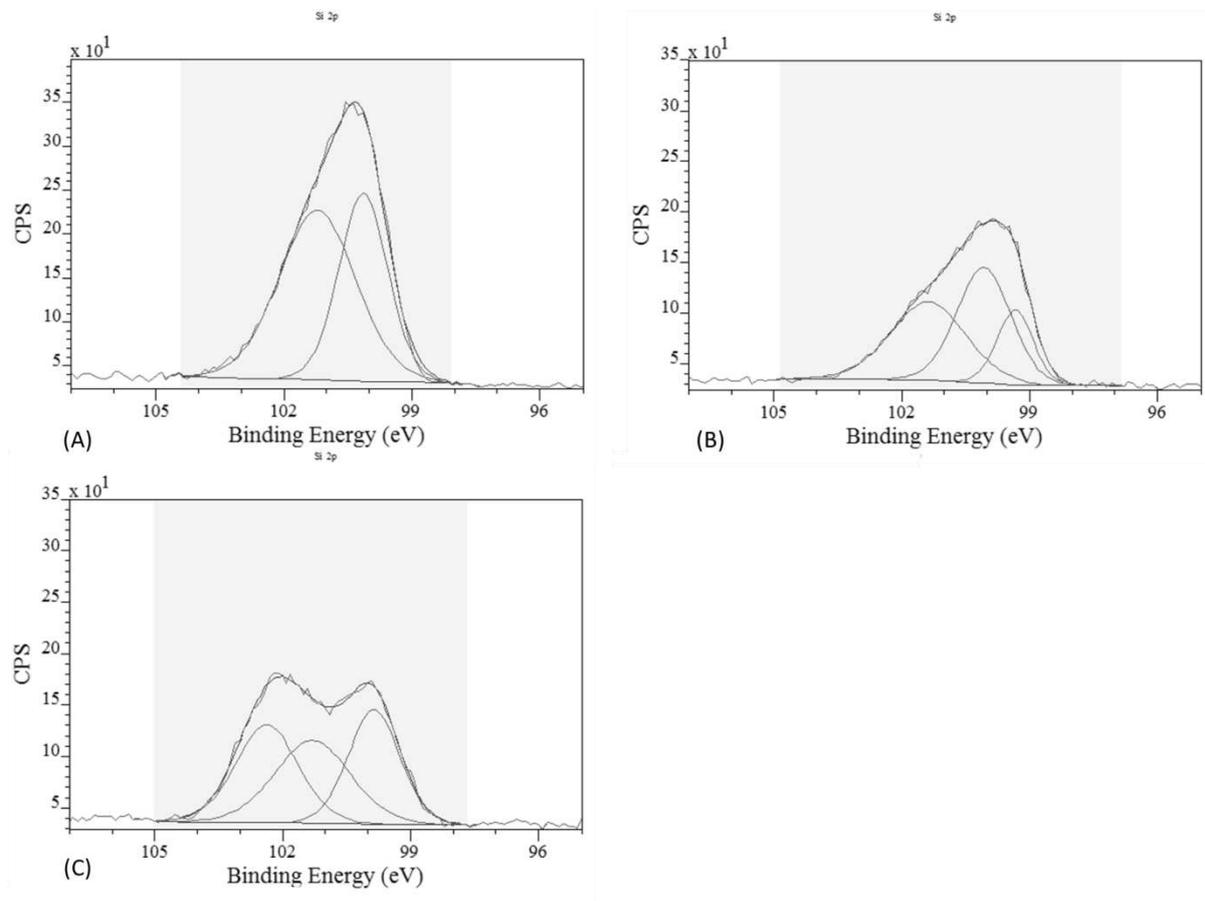
A) Si-DLC untreated, (B) Si-DLC heated under N_2, (C) Si-DLC heated under O_2.

Figure 8: XPS analysis showing %Atomic concentration of elements on Si-DLC tested in low additive oil
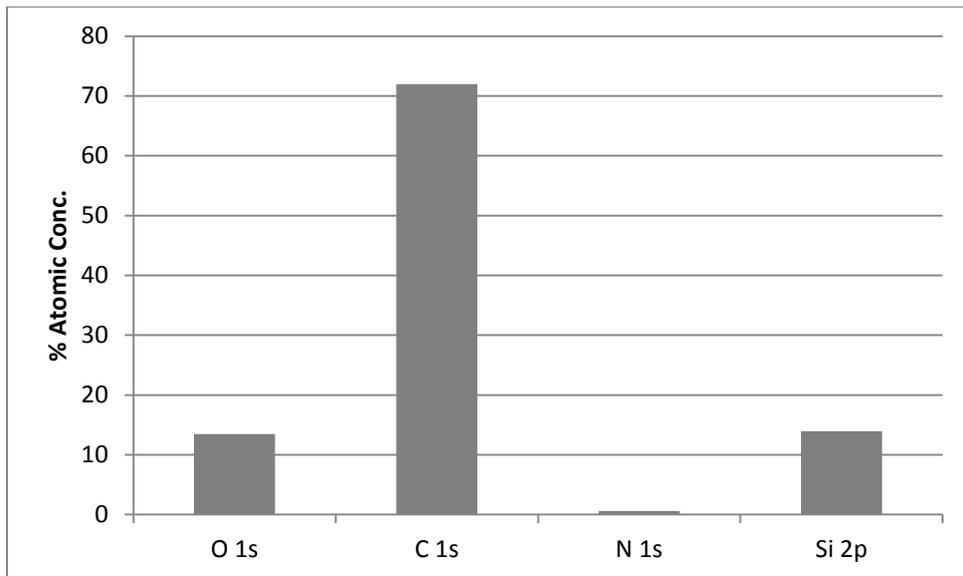
Figures 9: Elements in the tribofilm of formulated oil and Si2p peak
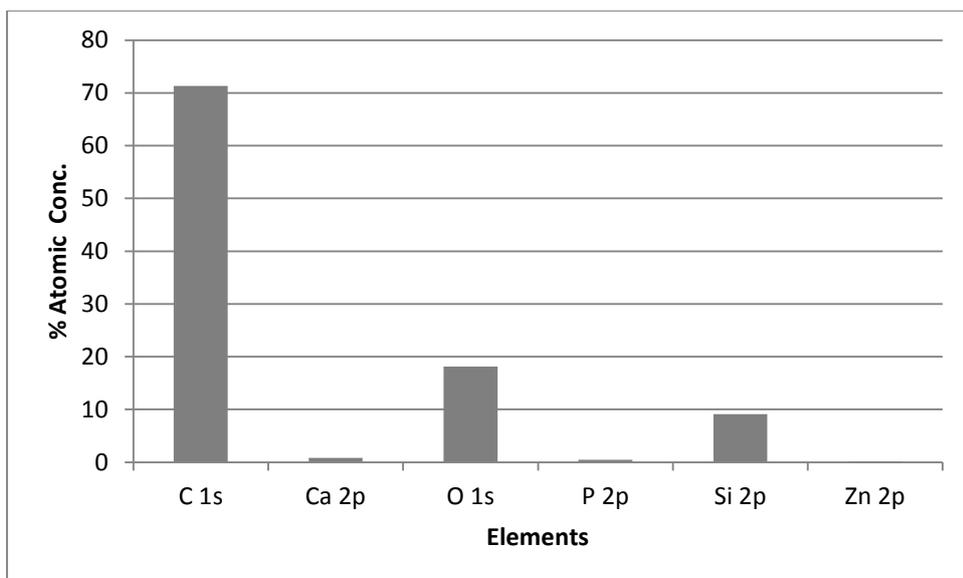
Figure 10: XPS analysis of Si peak when tested in and formulated oil (a) low additive oil (b):
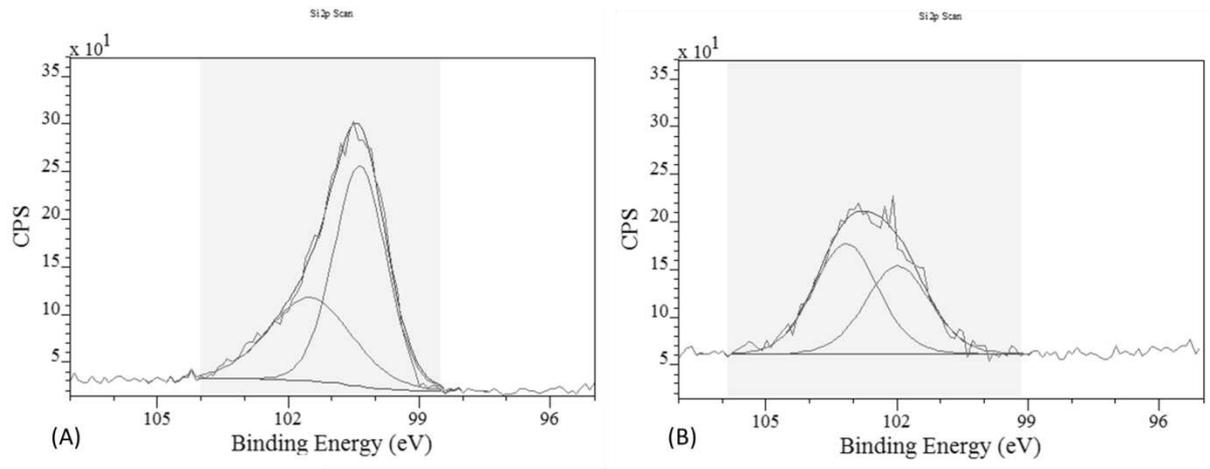
Figure 11: TEM image of showing tribofilm:
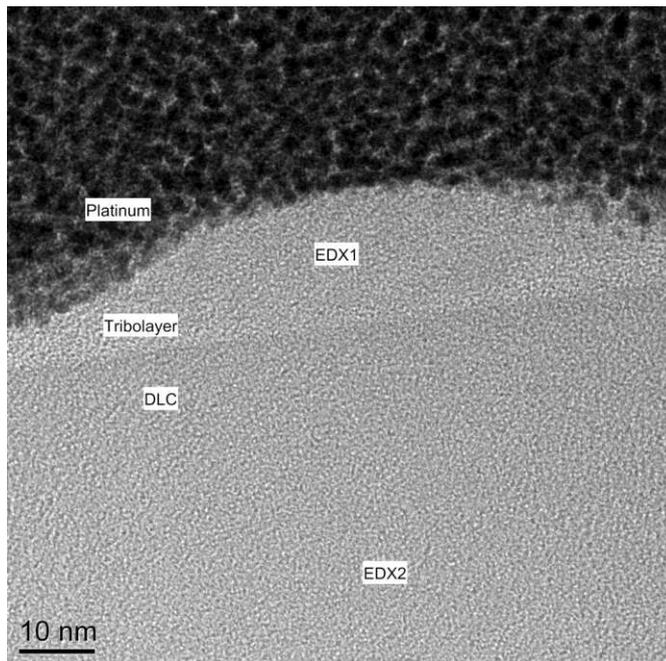
Figure 12: SIMS chemical map of sample in low additive oil showing widespread oxidation of coating constituents
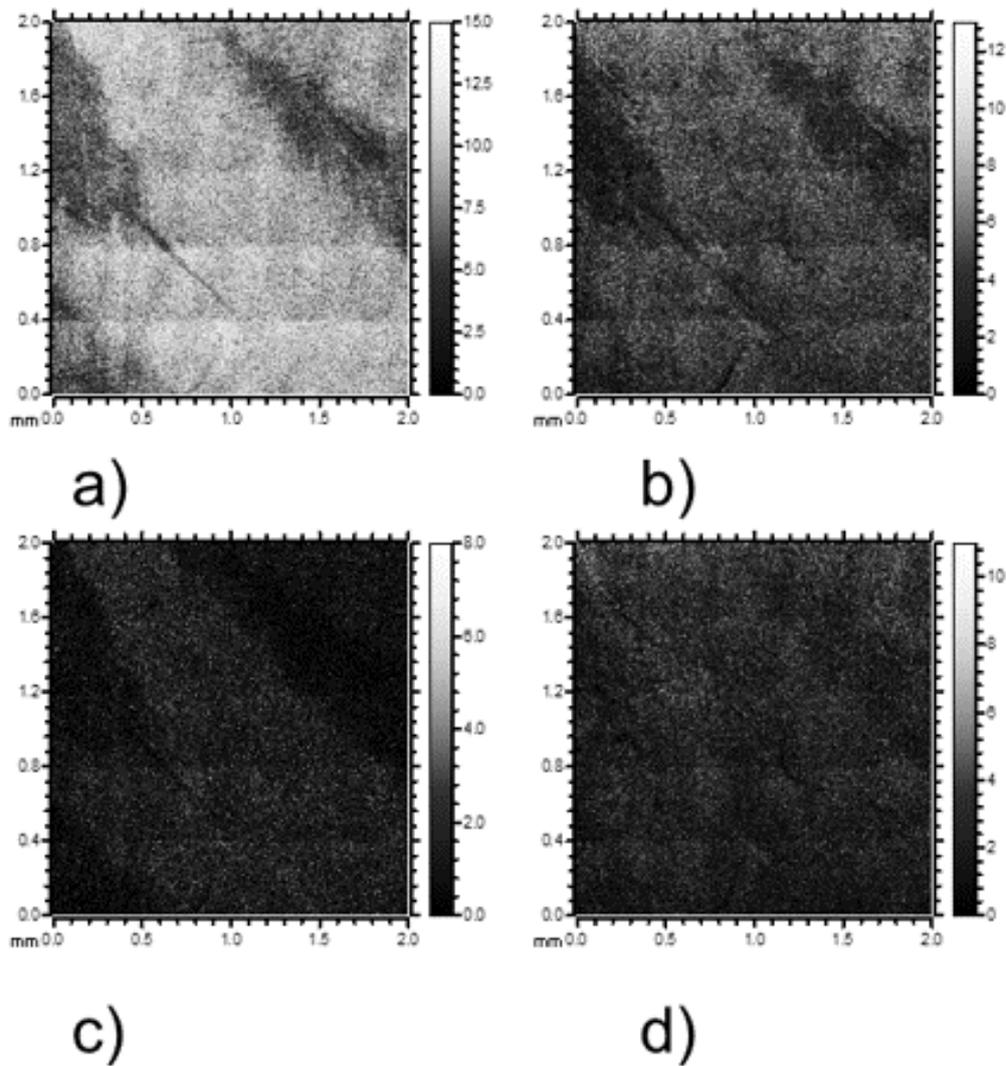
Negative ion ToF-SIMS map of Si-DLC tribotested in low additive oil. a) C_4H b) $SiHO_2$ c)C_6 d) SiO_2. Lighter areas indicating greater concentration of ions.

Negative ion ToF-SIMS map of Si-DLC tribotested in formulated oil. a) CH_2 (b) O (c)PO_3 (d) HS. Boxed area showing reduction in amount of O- in wear scar. Lighter areas indicating greater concentration of ions.
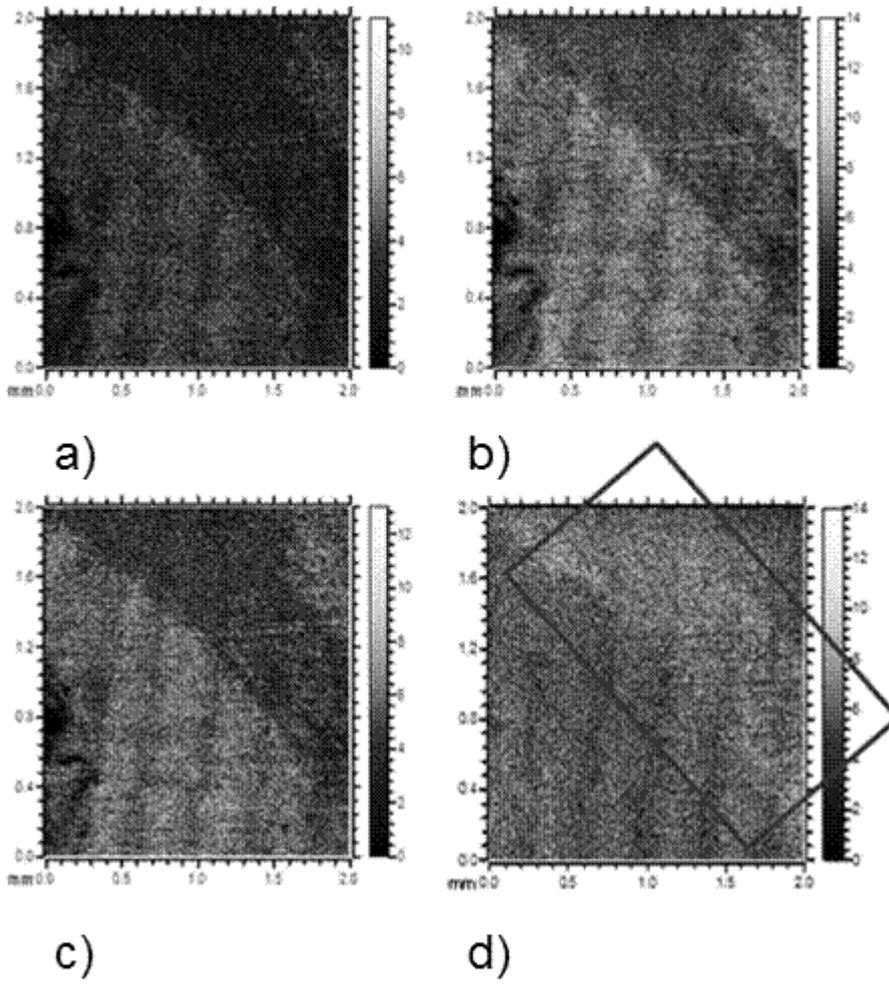
Negative ion ToF-SIMS map of Si-DLC tribotested in formulated oil. a) SiO_2 b) $SiHO_3$ c) $SiHO_2$ d) SiC_2H_5O. Boxed area showing increase in amount of SiC_2H_5O in wear scar. Lighter areas indicating greater concentration of ions.

Figures 14 dynamic SIMS profile of Si-DLC tested in formulated oil showing presence tribofilm on the DLC, Si oxides and bulk DLC

Surface rich/ anti wear compounds
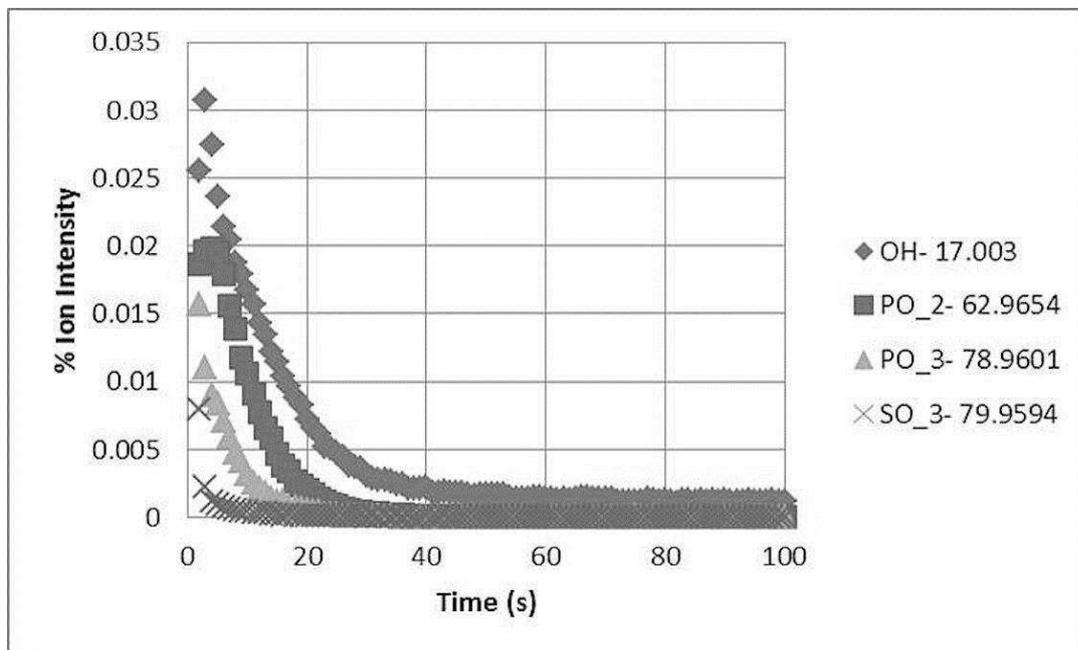
**Oxygen rich Si species**
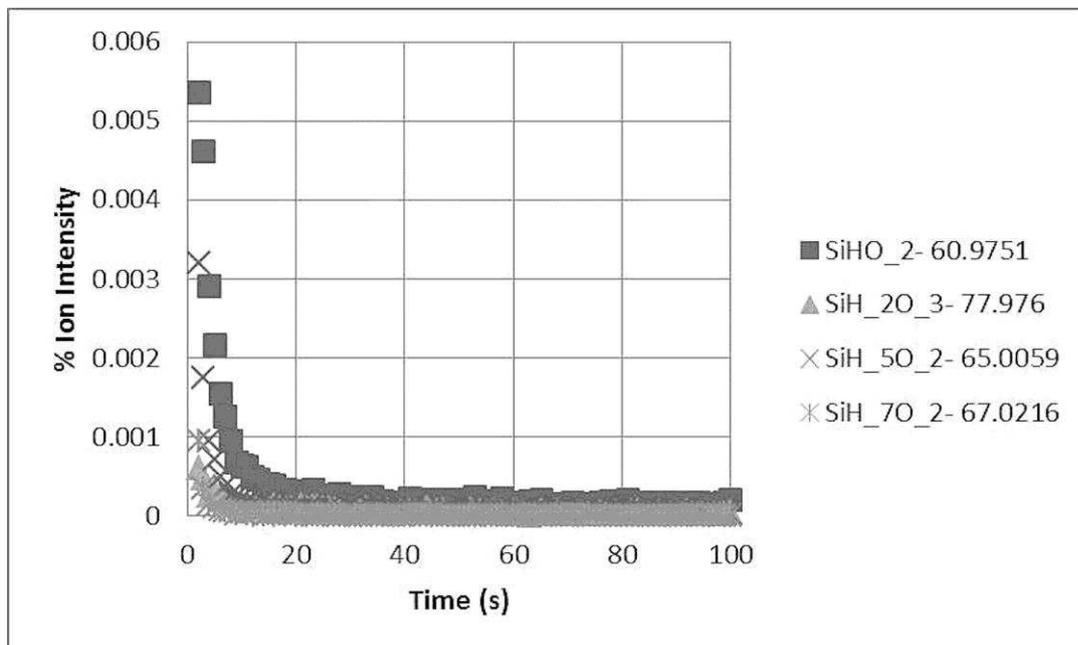
Bulk DLC compounds
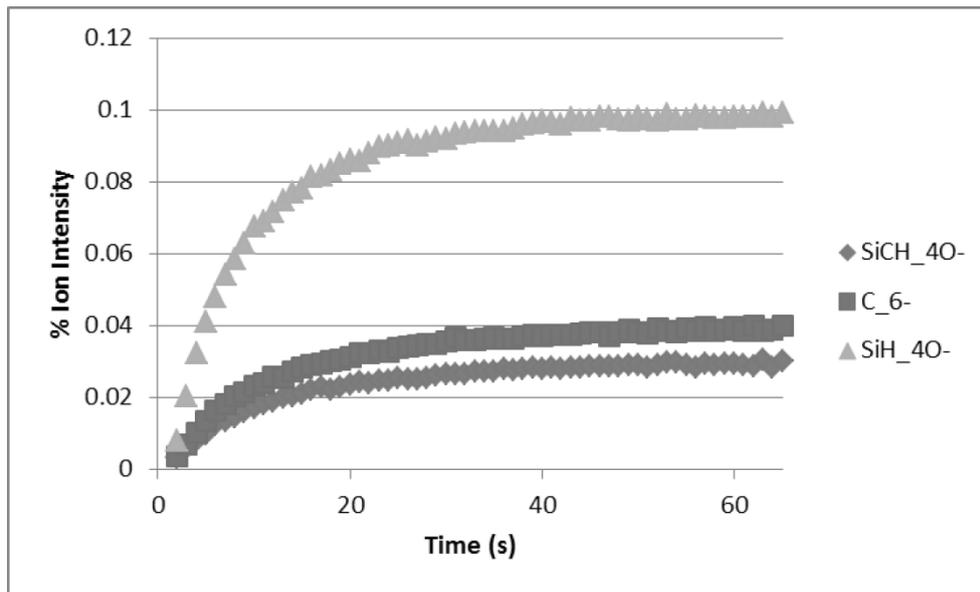
Figure 15: showing oxidation of Si within the coating. Thermodynamic driving force favours oxidation at Si.
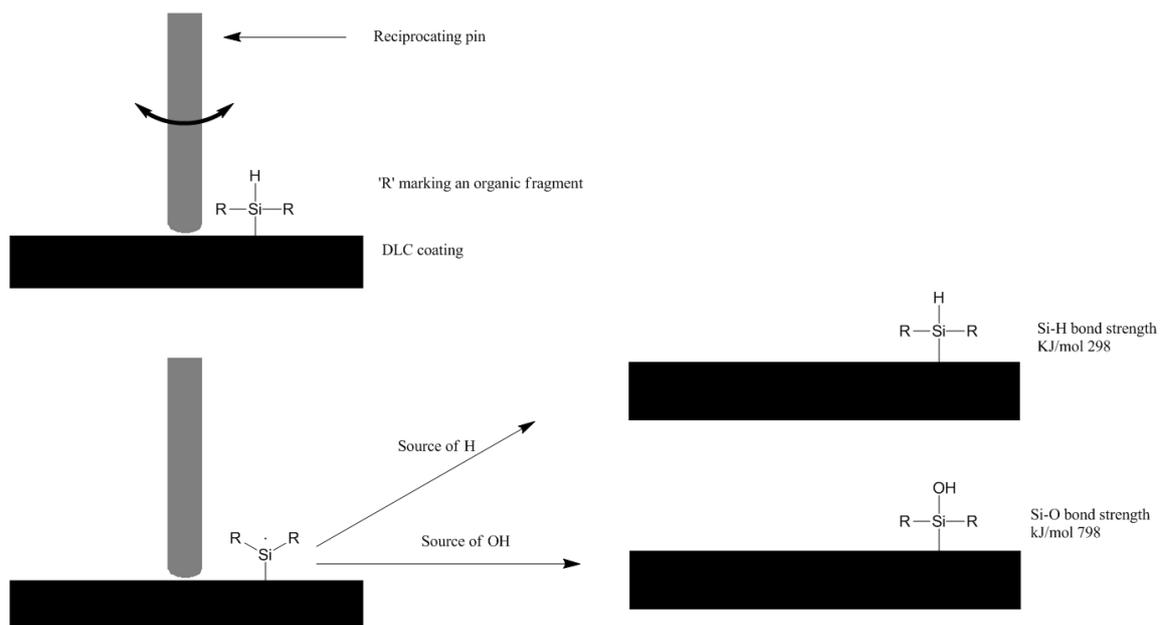
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