Weak adhesion and delamination of hydrogenated diamond like carbon coating on a rough surface of tappet valve substrate

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Abstract. DLC(a-C:H) film are known for their excellent tribological properties however, possess poor adhesion on metallic substrate causing film delamination. Introduction of adhesive silicon interlayer has showed improvement in the adhesion of DLC-H on metallic substrate. In the present study DLC-H was deposited on tappet valve and silicon wafer using PECVD. The as-deposited DLC-H was characterized using XRD, EDS and Raman spectroscopy. SEM was also used to measure the thickness of the DLC-H coating and the average surface roughness (R\(^s\)) was measured using 3D Profilometry. Scratch test was used to determine the COF, adhesion and hardness of the DLC-H coating. The DLC-H coating on tappet valve had weak adhesion compared with DLC-H coating deposited on silicon substrate, which had good adhesion. The result of the Raman spectroscopy revealed a sp\(^3\) fraction of 0.43 for the DLC-H deposited on silicon substrate. The thickness of the as-deposited DLC-H film was 1.78 \(\mu\)m, which was measured using SEM to view the cross-section of the as-deposited DLC-H coating on the silicon substrate. The surface roughness of the as-deposited DLC-H coating on silicon substrate was 26.59 nm. Silicon substrate coated with DLC-H had the lowest COF, ranging from 0.06 to 0.09.

1. Introduction
In the past two decades DLC coatings has become very attractive due to their wide range of applications in various fields (mechanical, electrical, tribological, biomedical and optical fields) [1-2]. Friction and wear are the main cause of high energy consumption in automotive engine parts, making most processes inefficient. However, using DLC coatings helps in lowering friction and wear rate [3-4]. Tribological characteristics of DLC coatings can be affected by adhesion promoter intermediate layer, substrate surface roughness, hydrogen incorporation or hydrogen non-involvement and coating deposition parameters (bias voltage, etching, current, precursor gas, time and substrate temperature) [5]. DLC(a-C:H) film are known for their excellent tribological properties, but has low chemical affinity with metallic alloys and high intrinsic stress, leading to poor adhesion on substrate leading to film delamination. Introduction of adhesive silicon interlayer deposited at different temperatures and
times by electrostatic confinement plasma enhanced chemical vapour deposition (EC-PECVD) has showed an improvement in adhesion on metallic substrate [6]. Results have showed that the adhesive interlayers produced from tetramethylsilane are chemical structured as (a-SiC$_x$:H). Also, the structure, chemical composition and thickness are all dependent on deposition conditions [6]. The thickness of the interlayers increases with deposition time and decreases with deposition temperature. The interlayer contains less hydrogen and silicon atoms at higher deposition temperature, with enhanced formation of Si-C bonds, which relates to the rise in the critical load values found for a-C:H film delamination when the a-SiC$_x$:H interlayers are deposited within 573K to 823K. While, the interlayers are containing less carbon atoms at higher deposition times, decreasing the critical load values of a-C:H film leads to delamination when the a-SiC$_x$:H interlayers are deposited from 5 to 10 minutes [6]. Weak adhesion and delamination from substrates, arising from high tangential stress and high internal compressive stress of a-C:H films, are main factors that limit the film thickness and their durability over time [7]. Hydrogen passivates the dangling bonds in the hydrogenated DLC films and permits only weak interactions between DLC and the sliding partner [8]. In this work, silicon interlayer followed by hydrogenated DLC was deposited on silicon wafer and rough surface of AISI 52100 steel substrate (tappet valve) using PECVD and characterized using XRD, SEM, Raman spectroscopy, 3D Profilometry and scratch test.

2. Experimental methods

2.1. Deposition of hydrogenated DLC on unpolished tappet valve

The tappet valve (AISI 52100) as seen in Figure 1, was first cleaned in an ultrasound water bath by placing the tappet valve into a beaker thereafter, liquid detergent and distil water were added and placed into the ultrasound water bath for a period of 10 minutes, then followed by alcohol for another 10 minutes. This was done in order to remove all contaminations like erase or particles that might affect the deposition of DLC-H on the tappet valve.

![Figure 1. Image of tappet valve for GM Buick Chevrolet Daewoo.](image)

Hydrogenated DLC coatings was deposited on an unpolished tappet valve and silicon wafer using Plasma Enhanced Chemical Vapour Deposition in an Ar/C$_2$H$_2$ atmosphere. The tappet valve and silicon wafer were placed in the PECVD reactor, argon was first used to clean using the following parameters: fixed Ar flow rate was 10 sccm, bias voltage applied to substrate 600 V, current 0.1 A for a duration of 10 minutes. Thereafter, silicone interlayer (SiH$_4$) was deposited to improve the adhesion (approx. 250 nm thick), two pure graphite targets were placed into the erosion zone. Silicone flow rate was 3 sccm, bias voltage applied to substrate 750 V, current 0.05 A for a duration of 10 minutes. DLC-H deposition flow rate was 3 sccm, bias voltage applied to substrate 700 V, current 0.05 A for a duration of 2 hours, hydrogen content (approx. 19% H$_2$). Standard tappet valve from a commercial GM Buick Chevrolet Daewoo (see Fig. 1). The tappet valve had an original roughness, Ra (5 μm), hardness, 4.2 GPa (~427.6 HV 0.05).

2.2. Coating characterization

XRD analyses was used for crystalline phases identification within the quantitative analysis using Rietveld. Philips - X’Pert PRO PW 3040/00 X-ray diffractometer with a Cu-anode, a generator voltage of 45 kV and a current of 40 mA with the goniometer 20 values varying from 10 to 110° with an angular pitch of 0.02° at a scan rate of 100.0 s/step. High Score Plus software was used for the phase identification of the constituent of all the crystalline phases. The particle size was estimated using Debye Scherrer equation.
\[ L = \frac{K\lambda}{\beta \cos \theta} \]  

where \( L \) is particle size, \( \lambda \) is the X-ray wavelength in nanometer (nm), \( \beta \) is the peak width of the diffraction peak profile at half maximum height resulting from small crystallite size in radians, and \( K \) is a constant related to crystallite shape, normally taken as 0.9. The value of \( \beta \) in 2\( \theta \) axis of diffraction profile must be in radians. The wavelength used for the samples was \( \lambda \text{CuK}_\alpha = 0.154178 \) nm.

2.3. Scanning electron microscope (SEM)
The microstructure, morphology, thickness of the films, topography, backscattered electron images and EDS composition were obtained using Scanning electron microscope with field effect cannon - FEG - Inspect 50, with secondary electron detectors, backscatter, EDS X-ray spectrometer and EDAX backscattered electron diffraction chamber EBSD.

2.4. Raman spectroscopy
Raman spectroscopy, (Horiba scientific LabRAM HR Evolution system) having 633 nm excitation wave length laser source with a resolution of 1\( \mu \text{m} \) was used to analyse the DLC-H coating structure with respect to sp2/sp3 ratio. The extended and static modes were used to detect chemical compound formation and the carbon peaks (disorder, D and amorphous graphitic, G peaks) for the coating structure on the silicon substrate. The scan range for the identification of the carbon peaks were, 400 to 2400 cm\(^{-1}\). Data was fitted with a Gaussian line shape in order to show the G and D peaks positions and the ratio of peak intensities. The ratio ID/IG was considered as an indicator of the carbon sp2/sp3 structure.

2.5. Surface profilometry
The surface roughness of silicon substrate and tappet valve both coated with DLC-H, were analysed using Profilometry 3D CCI, Taylor Hobson. Surface roughness data was analysed to the least square line, with Gaussian filter, 0.25 mm upper cut off and bandwidth.

2.6. Scratch test
Adhesion was analyzed for the coated tappet valve and silicon substrate through a critical load measurement, using a CETR UMT-2M-110 tribometer in linear reciprocated mode and the classic scratch test with a diamond tip, in which the applied load varied from 1 to 50 N, with a sliding speed of 0.1 mm/s for 90 secs. The load at which the coating was stripped from the substrate determined the critical load value. The hardness of the coating was also determined using:

\[ HS = \frac{K \times F_N}{W^2} \]  

Where \( K \) is a constant referring to the known geometry of scratching tip (Berkovic indenter \( k=2.31 \)), \( F_N \) is applied normal (vertical) force, \( W \) is the width of scratch.

3. Results and discussion
The image in Figure 2a shows tappet valve coated with hydrogenated DLC, immediately after deposition while, Figure 2b shows the same tappet valve coated with hydrogenated DLC after 24 hours of deposition. It can be seen from Figure 2b that the hydrogenated DLC coating had weak adhesion to the tappet valve substrate, leading to delamination within 24 hours. The weak adhesion was as a result of the surface roughness of the tappet valve substrate. The surface roughness at the top of the tappet valve was different from the circular part of the tappet valve.
Figure 2. Image of tappet valve coated with hydrogenated DLC (a) immediately after deposition (b) 24 hours after deposition.

3.1. Characterization of hydrogenated DLC coating
The XRD diffractogram in Figure 3, shows result of the DLC-H coating on silicon substrate at 69.5°, a single peak was identified at 2theta, this indicates that it is a single crystal. The crystal size was calculated to be 23.04 nm, using Debye-Scherer equation (section 2.2). The EDS result (Table 1) revealed the elemental composition of the silicon substrate coated with DLC-H, tappet valve (upper, middle and lower sections) coated with DLC-H. The chemical composition for the tappet valve showed some variation depending on the part of the tappet valve having different surface roughness. The top, upper, middle and lower sections of the tappet valve had very little carbon content, which was as a result of delamination as seen in Figure 2.

![XRD diffractogram for silicon substrate coated with DLC-H.](image)

3.2. Morphology and thickness of DLC-H coating
The upper section of the tappet valve shows very little DLC-H covering (circled red in Figure 4b). The middle section of the tappet valve had a better coverage of DLC-H, but shows poor adhesion to the tappet valve (Figure 4c). However, the lower section of the tappet, revealed that the DLC-H coating had good adhesion to the tappet valve (Figure 4d). The images in Figure 4b, c & d correlates to the carbon content as revealed from the EDS results (Table 1). Figure 5a, shows the SEM image of the top part of the tappet valve coated with DLC-H, it revealed that the top part had very low DLC-H content, thereby exposing the tappet valve (leading to high Iron (Fe) content) from the EDS result. While, Figure 5b, shows the SEM image for silicon substrate coated with DLC-H coating, which showed a good coverage due to strong adhesion of the DLC-H to the silicon substrate. Figure 5c, is the cross-section of the DLC-H coating, which has an average thickness of 1.79 µm as indicated in the SEM image, the light area of the image is the silicon substrate, while the dark area pointed by the red arrow is the thickness of the DLC-H coating.

Table 1. Chemical composition of various sections of DLC-H coated tappet and silicon substrate.

| Substrate                  | C   | Mn | Cr  | Si  | Ar  | Fe  |
|----------------------------|-----|----|-----|-----|-----|-----|
| Silicon substrate          | 81.07 | -  | -   | 18.27 | 0.30  | -  |
| Top of tappet              | 2.30 | 0.52 | 1.02  | 7.47 | -   | 85.43 |
| Tappet upper section       | -   | 0.62 | 1.10  | 1.20 | -   | 97.08 |
| Tappet middle section      | 4.38 | 0.42 | 1.21  | 5.96 | -   | 88.04 |
| Tappet lower section       | 82.23 | -  | -   | 2.06 | 0.32 | 11.72 |
Figure 6, shows the SEM image of the scratch track on tappet valve coated with DLC coatings. The image reveals the track due to the scratch on the DLC coating on silicon substrate by the diamond tip.

Figure 4. Tappet valve coated with DLC-H (a) image of coated tappet (b) SEM image of upper section (c) SEM image of middle section (d) SEM image of lower section.

Figure 5. SEM image (a) top of tappet valve coated with DLC-H (b) silicon substrate coated with DLC-H (c) cross-section of DLC-H coating on silicon substrate.

Figure 6. SEM image of scratch track for tappet valve with DLC coating.

3.3. Structure and Surface roughness of DLC-H
Raman which is the best and effective way to characterize the detailed bonding structure of DLCs. Graphite is a single crystal, having a Raman active mode at 1580 cm$^{-1}$, zone centred at E$_{2g}$ symmetry labelled ‘G’ for graphite. Diamond also has a single Raman active mode at 1322 cm$^{-1}$, zone centred at T$_{2g}$ symmetry. Graphite has a second mode at around 1350 cm$^{-1}$ of A$_{1g}$ symmetry labelled ‘D’ for disorder, which corresponds to the breathing vibrations of rings at the K zone boundary (Robertson, 2002). The G mode is actually the stretching vibration of any pair of sp$_2$ sites, for both carbon chains or aromatic rings. G does not only mean graphite, the D mode is the breathing mode of those sp$_2$ sites only in rings, not in chains [9].

Also, the ratio of intensity of D/G peaks is a measure of the defects present on carbon nanomaterials structure. D/G ratio is related to sp$_3$/sp$_2$ carbon ratio, if carbon material is fully oxidized, i.e., all carbons are sp$_3$. If D peak is higher, it means that the sp$_2$ bonds are broken which in turn means that there are more sp$_3$ bonds and more transition from sp$_2$ to sp$_3$ material, and there will be a maximum D/G ratio [10]. The Raman spectra plot in Figure 7 below has a Raman active mode at 1369 and 1570 cm$^{-1}$ with intensity of 3970 and 5352 representing the D peak and G peak respectively. The Raman spectra for the DLC-H coating on silicon substrate has a I(D)/I(G) ratio of 0.74, comparing with the work of Ferrari and Robertson, 2000 [10], using the G position and I(D)/I(G) ratio vs sp$_3$ fraction for
as-deposited a-C:H we obtained a sp3 fraction of 0.43. The C-C network of a-C:H depends strongly on its hydrogen content, which links the sp2 and sp3 phases together. The average surface roughness (Ra) for the top of tappet valve and side of tappet valve and silicon substrate all coated with DLC-H were 405.90, 821.40, 26.59 nm respectively, the result shows that the silicon substrate coated DLC-H had the least surface roughness, which indicates proper adhesion to the silicon substrate.

Figure 7. Raman spectra of the DLC-H coating on silicon substrate.

Figure 8. 3D Profilometry image (a) top of tappet valve (b) side of tappet valve (c) silicon substrate.

3.4 Adhesion and delamination of DLC coating
The coefficient of friction (COF) for tappet valve and silicon substrate coated with DLC can be seen in the plot (Figure 9). The COF for the tappet valve was measured at three different points having a range of 0.12 to 0.23, while that of the silicon substrate was 0.06 to 0.09. The silicon substrate fractured at
68 seconds, leading to an increase in COF. Small radial cracking of the DLC-H coating was observed on the surface, leading to tiny peaks at short intervals. The COF shows that the DLC-H coated silicon substrate had better adhesion than that of the tappet valve coated with DLC-H, this is as a result of the high roughness associated with the tappet valve substrate. Hardness value was determined to be 8.5 GPa, using equation 2 (section 2.6).

Figure 9. Coefficient of friction for tappet valve and silicon substrate coated with DLC.

4. Conclusion
In conclusion, hydrogenated DLC coating on tappet valve (AISI 52100) with high surface roughness possess weak adhesion, due to high compressive stress. However, for the DLC-H coating deposited on silicon substrate at the same conditions had a good adhesion. The result of the Raman spectroscopy revealed a sp3 fraction of 0.43 for the DLC-H deposited on silicon substrate. The thickness of the as-deposited DLC-H film was 1.78 µm, which was measured using SEM to view the cross-section of the as-deposited DLC-H coating on the silicon substrate. The surface roughness of the as-deposited DLC-H coating on silicon substrate was 26.59 nm. Silicon substrate coated with DLC-H had the lowest COF, ranging from 0.06 to 0.09 while, the tappet valve coated with DLC-H ranging from 0.12 to 0.23. This research work shows that the silicone interlayer improved the DLC-H adhesion on silicon substrate, however, it was not the same case for the tappet valve, due to high surface roughness.

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References
[1] Ladwig A M, Koch R D, Wenski E G, Hicks R F 2009 Diamond & Rel. Mat. 18 1129.
[2] Suzuki M, Saito T, Tanaka A 2013 Wear, 304 83.
[3] Mobarak H M, Chowdhury M 2014 Tribol. in Indus. 36 163.
[4] Erdemir A, Holmberg K 2015 Coating technology for vehicle applications. Cham, Switzerland, Springer International Publishing AG 10-11.
[5] Al Mahmud K A H, Kalam M A, Masjuki H, Mobarak H M, Zulkifli N W M 2014 J. rev. in solid state & mat. sci. 40 90.
[6] Cemin F, Bim L T, Menezes C M, Maia da Costa M E H, Baumvol I J R, Alvarez F, Figueroa C A 2015 Surf. & Coat. Techn. 283 115.
[7] Sheeja D, Tay B K, Leong K W, Lee C H 2016 Diamond & Rel. Mat. 11 1643.
[8] Grill A 1993 Wear 168 143.
[9] Robertson J 2002 Mat. Sci. & Eng. R37 129.
[10] Ferrari A C, Robertson J 2000 Phys. Rev. B, 61 14095.