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Original Citation

Jones, Benjamin and Ojeda, J. J. (2012) Substrate and material transfer effects on the surface chemistry and texture of diamond-like carbon deposited by plasma-enhanced chemical vapour deposition. Surface and Interface Analysis, 44 (8). pp. 1187-1192. ISSN 01422421

B.J. Jones and J.J. Ojeda **Substrate and material transfer effects on the surface chemistry and texture of diamond-like carbon deposited by plasma enhanced CVD** *Surface and Interface Analysis* **44** (2012) 1187–1192.
Archive Version. Definitive version available at Wiley Interscience or via http://dx.doi.org/10.1002/sia.4871

Substrate and material transfer effects on the surface chemistry and texture of diamond-like carbon deposited by plasma enhanced CVD

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Abstract

Diamond-like carbon (DLC), a thin amorphous carbon film, has many uses in tribological systems. Exploiting alternative substrates and interlayers can enable control of the hardness and modulus of the multi-layer system and improve wear or friction properties. We utilise XPS and AFM to examine DLC concurrently coated on an epoxy interlayer and a steel substrate by plasma enhanced chemical vapour deposition (PECVD). sp^2/sp^3 ratios were calculated both by deconvolution of the XPS C1s line and analysis of the C KLL Auger spectrum. Altering the substrate causes changes in the carbon bonding configuration, evident with the same trend through both analysis methods, though with differing absolute values, related to hydrogen and oxygen content. There is significant variation in the microscale surface texture, exhibited both by average roughness values and size and uniformity of surface asperities. This suggests that alteration to the film surface structure is a factor to be considered in addition to interface adhesion, hardness and elastic modulus, in investigating substrates and interlayers for tribological coatings. Examination of a DLC film separately produced on a steel substrate, in comparison with that produced concurrently with DLC coating of epoxy, shows the possibility of effects on the chemistry of the film through transfer of material from adjacent samples within the plasma deposition, related to heating, out-gassing or sputtering processes. The possibility of such contamination has implications in coating parameter design and coating of multiple samples with PECVD.

1. Introduction

Previous research and development efforts have established that diamond-like carbon (DLC) thin film coatings have the potential to minimise the friction and wear of various moveable devices [1,2]. DLC is an amorphous carbon that contains both sp^2 (graphitic) and sp^3 (diamond-like) bonding, and depending on deposition mechanism, a proportion of hydrogen. DLC films can possess many advantageous properties such as high hardness, low friction, high chemical stability and biocompatibility. The balance of the components, and incorporation additional elements such as silicon, can to an extent be tuned, in order to tailor the coating for a particular application. DLC films have therefore been utilised in many industrial sectors such as medical, manufacturing and aerospace [2-7]. Plasma enhanced chemical vapour deposition (PECVD), in contrast to many other coating systems, does not necessitate or produce substantial substrate heating and can therefore be utilised for coating temperature-sensitive materials. However, high internal stresses within the applied film can limit useful DLC coating thickness to less than 10μm, thus limiting practical application in some areas. To improve substrate-film adherence many groups have utilised thin interlayers, incorporating materials such as titanium [8], tungsten [9] or silicon [2,5,10,11]. An alternative strategy has been developed [7] which utilises a thick epoxy layer with a DLC surface thin film, with applications for aircraft landing gear. Podgoric *et al.* [7] demonstrate that this layered structure has improved wear and friction properties when tested against conventional chromium finish, and against “stand-alone” DLC on steel substrates. This has been related to the hardness and elastic modulus of the substrate, allowing deformation without cracking of the surface layer. This is supported by Borrero-López *et al.* [12] who show differing crack dynamics and delamination mechanisms for DLC films, dependent on the compliance and hardness of the substrate. Here we use surface analytical techniques, XPS and AFM to determine the composition and topography of DLC coated on steel and epoxy resin, and explore the effect of the substrate – or thick interlayer – on the surface structure of the diamond-like carbon film.

2. Experimental

Diamond-like carbon films were concurrently produced on stainless steel (“DLC-S1”) and steel with a layer of epoxy resin (“DLC-E”), applied as described by Podgoric *et al.* [7]; a sample with glass-fibre reinforced epoxy resin was also coated in this deposition. Argon plasma pretreatment and DLC film deposition were conducted by Diameter Ltd (now Renishaw Advanced Materials) utilising a 13.56-MHz rf-powered, capacitively coupled, plasma enhanced chemical vapour deposition (PECVD) reactor (sometimes referred to as plasma assisted, PACVD). The DLC coating, of thickness approximately three-quarters of a micron, was deposited utilising parameters that have been shown to produce good substrate adhesion, wear resistance and low friction coatings for machine tools [2]. An argon plasma pretreatment below 450V was utilised, in order to clean but not restructure the steel surface [10]. Following pretreatment, the bias voltage was adjusted to 450V and a silicated interface layer was formed by adjusting the argon flow rate to 10sccm and introducing tetramethylsilane (TMS) with a flow rate of 25 sccm. This layer has been previously shown to enhance the adhesion of the film to steel substrates [2, 10, 11]. Once the interfacial layer was formed, acetylene gas at 60 sccm was introduced into the chamber. The TMS flow was reduced in stages to prevent an abrupt transition; the argon and acetylene flow rates and bias were maintained for deposition of the final, silicon-free, layer. A similar DLC film was subsequently produced on stainless steel (“DLC-S2”) without the epoxy resin sample in the chamber. Earlier work [7] used pin-on-disc measurements to assess the tribological properties of the layered epoxy/DLC structure. This shows the co-efficient of friction for DLC-E in sliding wear to be 0.07, with no degradation over 1800 s; DLC-S1 exhibited an initial co-efficient of friction of 0.10 degrading to 0.14 over the same period.

Surface texture parameters were assessed utilising a Digital Instruments DI3100 atomic force microscope (AFM) operating in tapping mode with a silicon cantilever operating at approximately 150kHz. The surfaces were examined over multiple 10µm x 10µm and 1µm x 1µm square areas; texture parameters RMS roughness (R_q), skewness, kurtosis and peak count were averaged over five areas for each scan size, the uncertainty values shown are indicative of variation in measurement among areas. The XPS measurements for surface chemistry were made on a VG Escalab 210 Photoelectron Spectrometer. The X-ray source was a non-monochromated Al Kα source (1486.6eV), operated with an X-ray emission current of 20 mA and an anode high tension (acceleration voltage) of 12 kV. The takeoff angle was fixed at 90° relative to the sample plane. The area corresponding to each acquisition was a rectangle of approximately 5x2 mm. Each analysis consisted of a wide survey scan (pass energy 50eV, 1.0eV step size) and high-resolution scans (pass energy 50eV, 0.05eV step size) for component speciation. The binding energy scale was calibrated using the Au $4f_{5/2}$ (83.9 eV), Cu $2p_{3/2}$ (932.7 eV) and $Ag3d_{5/2}$ (368.27 eV) lines of cleaned gold, copper and silver standards from the National Physical Laboratory (NPL), UK. Substrate charging is not countered, for example with an electron flood gun; however, the binding energy shifts within the C 1s envelope are nevertheless valid [13].

3. Results and Discussion

X-ray photoelectron spectroscopy (XPS) survey spectra for the epoxy resin substrate, DLC-S1, DLC-E, and DLC-S2 are shown in figure 1, and quantification of the results is given in table 1 . The epoxy resin contains calcium, nitrogen, and sodium, in addition to carbon and oxygen. These elements are also present in DLC-E, deposited on the epoxy. This may be related to a degree of migration through the deposited thin film; however, sodium and calcium are also present in DLC-S1, concurrently deposited on stainless steel. The presence of these elements in the DLC-S1 sample cannot be related to transfer through the film, and suggests transfer of components to the process gases due to outgassing, heating or the sputtering action of the epoxy substrates within the plasma coating process, and subsequent deposition of these elements within the DLC. This is supported by the absence of these elements in the DLC-S2 sample, produced with no epoxy sample in the chamber.

XPS analysis of the DLC films enabled the assessment of the sp^3/sp^2 ratio and oxygen bonding at the sample surface through a deconvolution of the C1s peak. The C1s peak was fitted with component peaks for sp^2 and sp^3 configurations, along with components for C=O and C-O bonded carbon, as shown in figure 2 a-c. The line shape was assumed to be 70% Gaussian and 30% Lorentzian, and the separation of the sp^2 and sp^3 components was fixed at 0.5eV [10,14,15]. As the sensitivity factor is independent of the chemical state of the atoms [14] the relative fraction of each component was calculated from the areas of the respective peaks. Differences in sp^3/sp^2 hybridization can be determined to a good approximation from this method, which has been previously utilised by many groups [10, 13-16]. However, Mezzi and Kaciulis [17], Leung et al. [14] and Yan et al. [15], among others, have highlighted that the curve-fitting technique based on a binding energy shift in the C1s XPS spectrum may not be absolutely accurate. This may be especially problematic in the case of hydrogenated samples, as the positions of the C-H and C-C signals are in the range between 284.5 and 286.0 eV, which may lead to an erroneous determination of the $sp^2$and sp^3 areas. These groups have utilised the analysis of C KLL X-ray excited Auger spectra (XEAS) as an alternative approach to determine the carbon hybridization. This method consists in the determination of the distance, D, between the most positive maximum and most negative minimum of the first derivative of C KLL spectrum, based on a linear interpolation of D between the diamond (100% sp^3) and graphite values (0% sp^3) [14,15, 17-19].

Therefore, in addition to C1s XPS deconvolution, the sp^2 fraction is also calculated from the D parameter from the C KLL spectrum, as based on the method previously reported by Mezzi and Kaciulis [17] results from both methodologies are shown in table 1. For this set of samples, the bonding configuration calculated by the D parameter shows the same trend as that calculated by deconvolution of the XPS C1s spectrum. The absolute values of sp^2 fraction calculated from the C KLL Auger spectra (12.7% - 20.1%) are similar to those calculated by Mezzi and Kaciulis for DLC [17], but consistently smaller than the values from C1s deconvolution (40.7% - 43.7%). This discrepancy has been previously observed by Leung et al. [14] and Yan et al. [15], who discuss as a possible explanation that the background of the Auger spectrum could be influenced by other effects such as secondary electron emission. It is also important to note that the calculation of sp^2 and sp^3 fractions from the interpolation of the D parameter has been previously employed for samples such as pyrolytic graphite and single-wall carbon nanotubes [17], where the amount of carbon bound to oxygen (C-O, C=O) is low. The influence of surface oxygen on D value measurements has been indicated as an issue for further studies by Lascovich et al. [18], as the important fraction of C-O and C=O components may have an effect in the C KLL Auger calculations. When such other carbon moieties are present in high quantities, the variation of the D parameter might not behave linearly as assumed in the previous model [17, 14], as the high energy shoulder *ca*. 247 eV in the derivative Auger spectrum due to the presence of oxygen [18, 15] could have an effect in assessing the D parameter, resulting in alterations to the sp^2 value calculated via this method. Further studies assessing the variation between the sp^2 and sp^3 fractions are still needed, in order to assess the different sources and likelihood of errors and ambiguities incurred in both the C1s XPS deconvolution and the C KLL Auger calculations. For these DLC samples, the variation trend is consistent using both calculation methods although it is expected that the absolute values may differ due to the high presence of other carbon moieties in these samples.

Figure 2 a-c shows the deconvolution of the XPS C1s line for DLC-E, DLC-S1 and DLC-S2 samples, quantification of the fit is shown in table 1. As can be seen the sample surfaces exhibit differences in the carbon – oxygen bonding components between the DLCs concurrently deposited on steel and epoxy. DLC-E, produced on epoxy, exhibits an increased sp^2 fraction compared to the sample concurrently produced on steel (DLC-S1), calculated both from C1s deconvolution (figure 2 a-c) and analysis of the derivative of the C KLL Auger spectra (figure 2d). This effect of the substrate material or structure on the surface chemistry of the final DLC film, may be related to variations in the initial formation of the a-C:H film due to carbon species penetration, surface diffusion and bonding [10,20]. Similar substrate effects on film chemistry have been previously observed with XPS by altering a stainless steel substrate with plasma treatment [10] and by Raman spectroscopy on metals and PTFE [20]. Raman has also been used to show similar effects with tetrahedral amorphous carbon, a highly sp^3 and hydrogen free a-C, grown on metallic substrates [21].

Comparing DLC-S1 and DLC-S2 shows that there is also evidence of differences in sp^2 fraction and carbon-oxygen bonding configuration between the DLC films, both with steel substrates, that are produced in different deposition batches. This can be related to the removal of material into the plasma from the epoxy substrate, which is co-deposited with DLC concurrently with DLC-S1, and subsequently incorporated into the deposited DLC film, leading to a marked increase in the oxygen concentration from 7.2 at% to 11.0 at%. Although in this case perhaps aiding the wear-rate effect investigation [7], this incorporation of additional material could be considered cross-contamination from adjacent or nearby samples, and the finding therefore has implications for samples in batch coatings. A degree of difference will be expected between coating runs, which is why samples for comparison may at times all be coated in the same deposition batch. However, these results show that this practice may not always be optimal or useful as may not give a true picture due to the potential for cross contamination to affect the film chemistry.

Figure 3 shows AFM images of surface topography of the DLC coated samples, with 10μm x 10μm and 1μm x 1μm areas, calculated texture parameters are detailed in table 2. As can be observed, the underlying substrate surface affects the growth pattern and RMS roughness values. DLC-E forms a nodular growth pattern that has been previously observed in other DLC systems [10,22,23]. The overall roughness contribution from nodularisation and the average nodule diameter have been shown to be a function of substrate pre-treatment process [10] and precursor gas mix [22], related to surface diffusion and subplantation of impinging species [10,23]. Here the DLC grown on epoxy forms large asperities, with an average of 12.4±3.9 peaks per 10μm x 10μm area. The DLC-S1 sample has a more intermittent nodularisation pattern, in areas enhanced or retarded by the machined texture of the underlying substrate. There is a wide range of nodule diameters, contributing to an average of 53±19 peaks over the same area. Over 1μm x 1μm areas, the inherent DLC structure dominates, and the RMS roughness values for each sample show no significant difference. It is clear that the large-scale asperities observed on the DLC-E are formed from clustering of nano-scale nodules, similar in size to those previously observed in amorphous hydrogenated carbon on silicon [22]. These are more defined in the sample on epoxy than that on steel, contributing to the higher kurtosis values, again at this surface area evaluation size there is greater uniformity in DLC-E than DLC-S1, exhibited by tighter standard deviation values. AFM analysis of DLC-S2 again shows the machining texture affects the DLC film growth, the sample shows asperities of a range of sizes with structures similar to those observed in DLC-S1.

The difference in the DLC surface morphology and surface chemistry with different substrates may be a contributing factor to the variation in wear and friction performance observed by Podgoric *et al.* [7], in addition to the substrate stiffness and hardness effects [7,12] and substrate-film interface control [10].

4. Conclusions

Comparing DLC concurrently deposited on steel and an epoxy resin interlayer, we demonstrate that the substrate surface affects the final DLC film surface topographical structure and chemistry. Topography, characterised by RMS roughness values over 10μm square change from 307±43 nm for DLC on epoxy substrate to 53±12 nm for DLC on steel, and the number of asperities increases from 12 to 53 over the same area. DLC on epoxy shows a more uniform structure of larger asperities formed of clusters of small nodules, compared to the range of diameters of asperity exhibited by DLC on steel. Surface chemistry variation is observed in carbon bonding configuration assessed by XPS deconvolution of the C1s line showing variation in carbon-oxygen bonding and the sp^2 fraction. This configuration ratio was also calculated by evaluation of the D parameter from the C KLL Auger spectrum, which showed the same trend in data, but different absolute values related to the various carbon moieties. This substrate effect has implications in process design of PECVD grown thin films, and taken together with mechanical testing on these samples [7], interface modification effects on adhesion [10] and assessment of crack dynamics and failure modes [12] suggests that alteration to the film surface structure is an additional factor for consideration, as well as interface adhesion, hardness and elastic modulus of the substrate, which all need to be taken into account in understanding the mechanisms of wear and friction improvements in multilayer DLC coatings.

Surface structure and chemistry measurements also show variation between two samples of DLC on steel, one deposited concurrently with an epoxy sample and the other independently. The sample of DLC on steel deposited concurrently with a DLC on epoxy substrate contains increased levels of oxygen as well as sodium and calcium. With implications for PECVD parameter design and samples in batch coatings, this finding demonstrates that the presence of a material in the chamber, which can be affected by the vacuum, heating or sputtering action, can cause cross contamination and affect bonding configuration in an adjacent sample.

Acknowledgements

We thank Dr Sander Podgoric (Gulfstream Aerospace), Dr Robert Bulpett (Brunel University and Renishaw Advanced Materials) and Hawker Pacific Aerospace for provision of samples.

References

[1] A. Erdemir, C. Donnet *J. Phys. D: Appl. Phys.* **2006**, *39,* R311

[2] M. Zolgharni, B.J. Jones, R. Bulpett, A.W. Anson, J. Franks *Diamond Relat. Mater.* **2008**, *17,* 1733

[3] A.H. Lettington, *Carbon* **1998,** *36*, 555

[4] B. Jones, T. Anson *Mater. World* **2008,** *16(8)*, 24

[5] P.D. Maguire, J.A. McLaughlin, T.I.T. Okpalugo, P. Lemoine, P. Papakonstantinou, E.T. McAdams, *et al. Diamond Relat. Mater.* **2005**, *14*, 1277

[6] B.J. Jones, A. Mahendran, A.W. Anson, A.J. Reynolds, R. Bulpett, J. Franks, *Diamond Relat. Mater.* **2010**, *19,* 685

[7] S. Podgoric, B.J. Jones, R. Bulpett, G Troisi, J. Franks *Wear* **2009**, *267*, 996

[8] C.W. Moura e Silva, E. Alves, A.R. Ramos, C.S. Sandu, A. Cavaleiro, *Vacuum* **2009**, *83*, 1213

[9] T. Takeno, T. Sugawara, H. Miki, T. Takagi, *Diamond Relat. Mater.* **2009**, *18*, 1023

[10] B.J. Jones, L. Anguilano, J.J. Ojeda *Diamond Relat. Mater.* **2011**, *20*, 1030

[11] W. Jing, L. Gui-Chang, W. Li-Da, D. Xin-Lu, X.Jun, *Chinese Phys. B* **2008**, *17*, 3108

[12] O. Borrero-López, M. Hoffman, A. Bendavid, P.J. Martin *Diamond Relat. Mater.*, **2010**, *19,* 1273

[13] S.T. Jackson, R.G. Nuzzo. *Appl. Surf. Sci*. **1995**, *90*, 195

[14] T.Y. Leung, W.F. Man, P.K. Lim, W.C. Chan, F. Gaspari, S. Zukotynski, *J. Non-Cryst. Solids* **1999**, *254*, 156

[15]X.B. Yan, T. Xu, S.R. Yang, H.W. Liu, Q.J. Xue, *J. Phys. D: Appl. Phys.* **2004**, *37*, 2416

[16]J.F. Zhao, P. Lemoine, Z.H. Liu, J.P. Quinn, J.A. McLaughlin. *J. Phys.: Condens. Matter.* **2000**, *12,* 9201

[17]A. Mezzi, S. Kaciulis. *Surf. Interface Anal.* **2010**, *42*, 1082

[18]J.C. Lascovich, R. Giorgi, S. Scaglione, *Appl. Surf. Sci*. **1991**, *47*, 17

[19]D. Caschera, P. Cossari, F. Federici, S. Kaciulis, A. Mezzi, G. Padeletti,*et al. Thin Solid Films* **2011**, *519*, 4087

[20]I. Ahmed, S.S. Roy, Md.A. Rahman, T.I.T. Okpalugo, P.D. Maguire, J.A. McLaughlin *Current Applied Physics* **2009**, *9*, 937

[21]F-X Liu, K-L Yao, Z-L Liu *J. Non-Cryst. Solids* **2007**, *353*, 2545

[22]B.J. Jones, S. Wright, R.C. Barklie, J. Tyas, J. Franks, A.J. Reynolds *Diamond Relat. Mater.* **2008**, *17*, 1629

[23]X.L. Peng, Z.H. Barber, T.W. Clyne *Surf. Coat. Technol.* **2001**, *138*, 23

	at. %					C1s Deconvolution			C KLL
Sample	**C**	**O**	**Ca**	**N**	**Na**	**sp^2 %**	**C-O %**	**C=O %**	**sp^2 %**
DLC-E	85.4	12.2	0.4	1.2	0.7	43.7	15.9	5.3	20.1
DLC-S1	84.3	11.0	2.1	1.5	0.7	42.2	19.6	2.1	14.1
DLC-S2	91.5	7.2	trace	0.9	trace	40.7	9.7	5.3	12.7

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Table 1. Surface chemistry of DLC on epoxy and steel, calculated from XPS data. sp^2 % (as a proportion of sp^2+sp^3) is calculated both by deconvolution of C1s line [10,13,14] and via D spacing from the C KLL Auger spectrum [17,18], a similar trend is observed, the absolute differences may be related to the range of carbon moieties in these samples.

Sample	**Scan**	**R$_q$ /nm**	**Skewness**	**Kurtosis**	**Pk / 100µm^2**
DLC-E	**10µm**	307±47	-0.41±0.28	3.8±1.7	12.4±3.9
	1µm	25.4±4.4	-0.74±0.16	3.4±0.3	
DLC-S1	**10µm**	53.0±12.2	-0.20±0.23	2.8±0.7	53±19
	1µm	21.9±6.3	-0.29±0.47	2.6±0.7	
DLC-S2	**10µm**	29.4±2.7	1.1±0.4	5.8±1.5	110±22
	1µm	18.2±9.9	0.15±0.49	2.9±0.8	

Table 2. Surface texture parameters for DLC on epoxy and steel, calculated from AFM data over 10x10µm and 1x1µm areas.

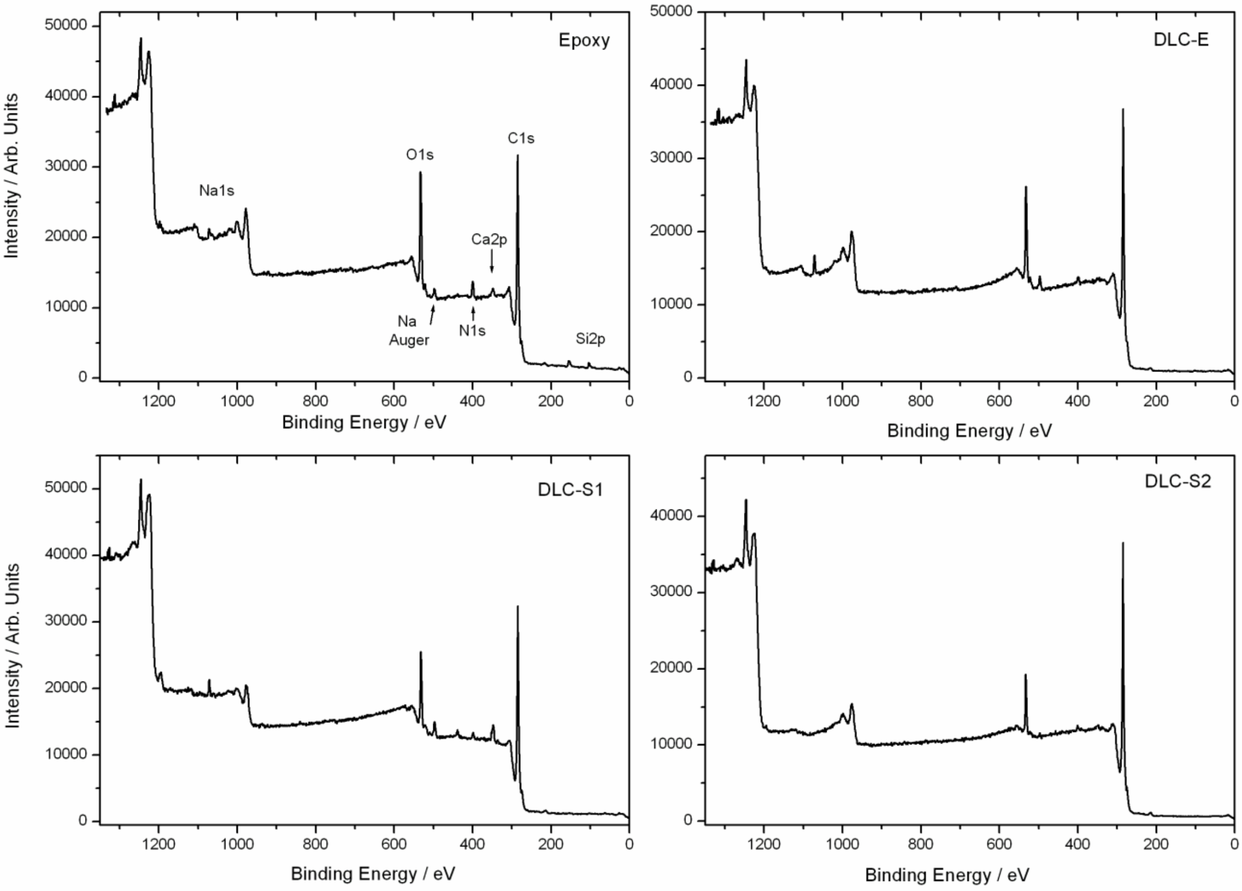

Figure 1. XPS spectra of epoxy and DLC films on epoxy and steel showing variation in film composition with substrate.

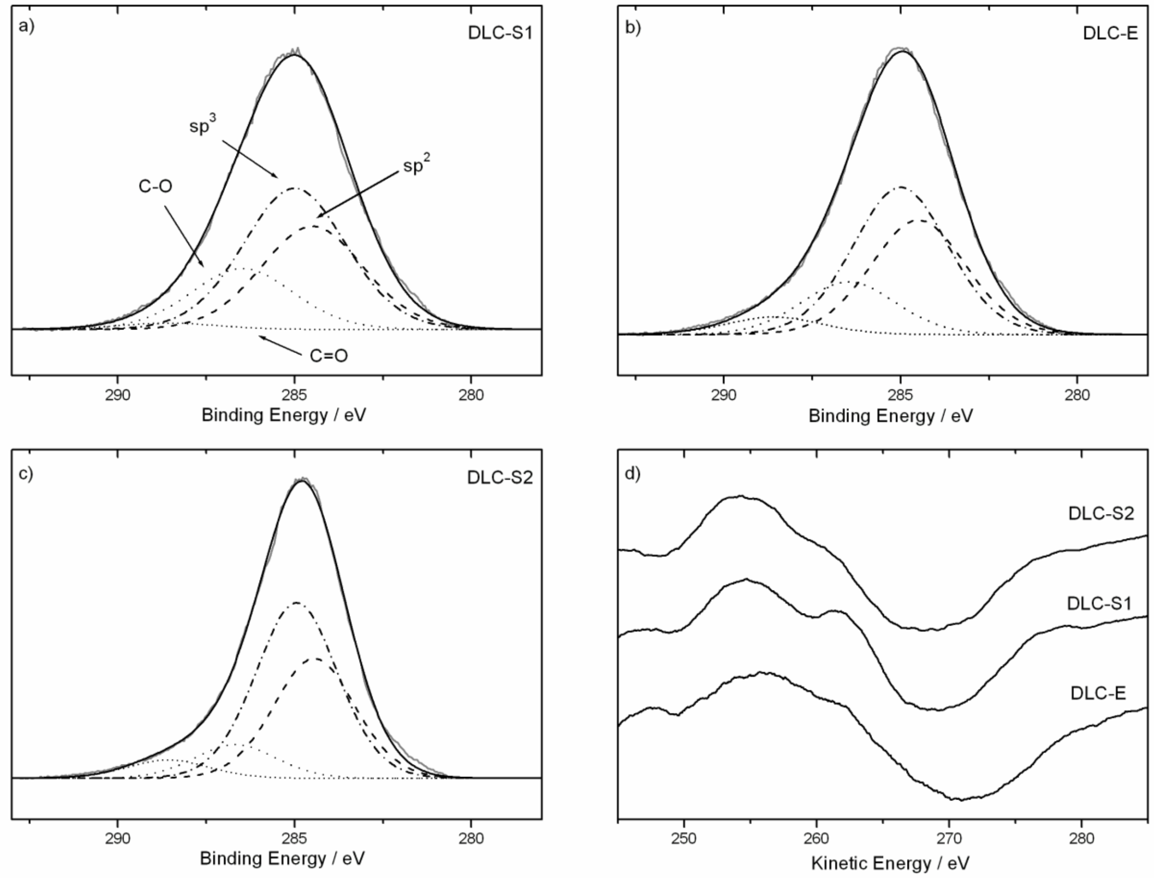

Figure 2. (a–c) Deconvolution of XPS C1s line to sp^2/sp^3 configuration and carbon–oxygen bonding and (d) derivative of C KLL Auger spectra.

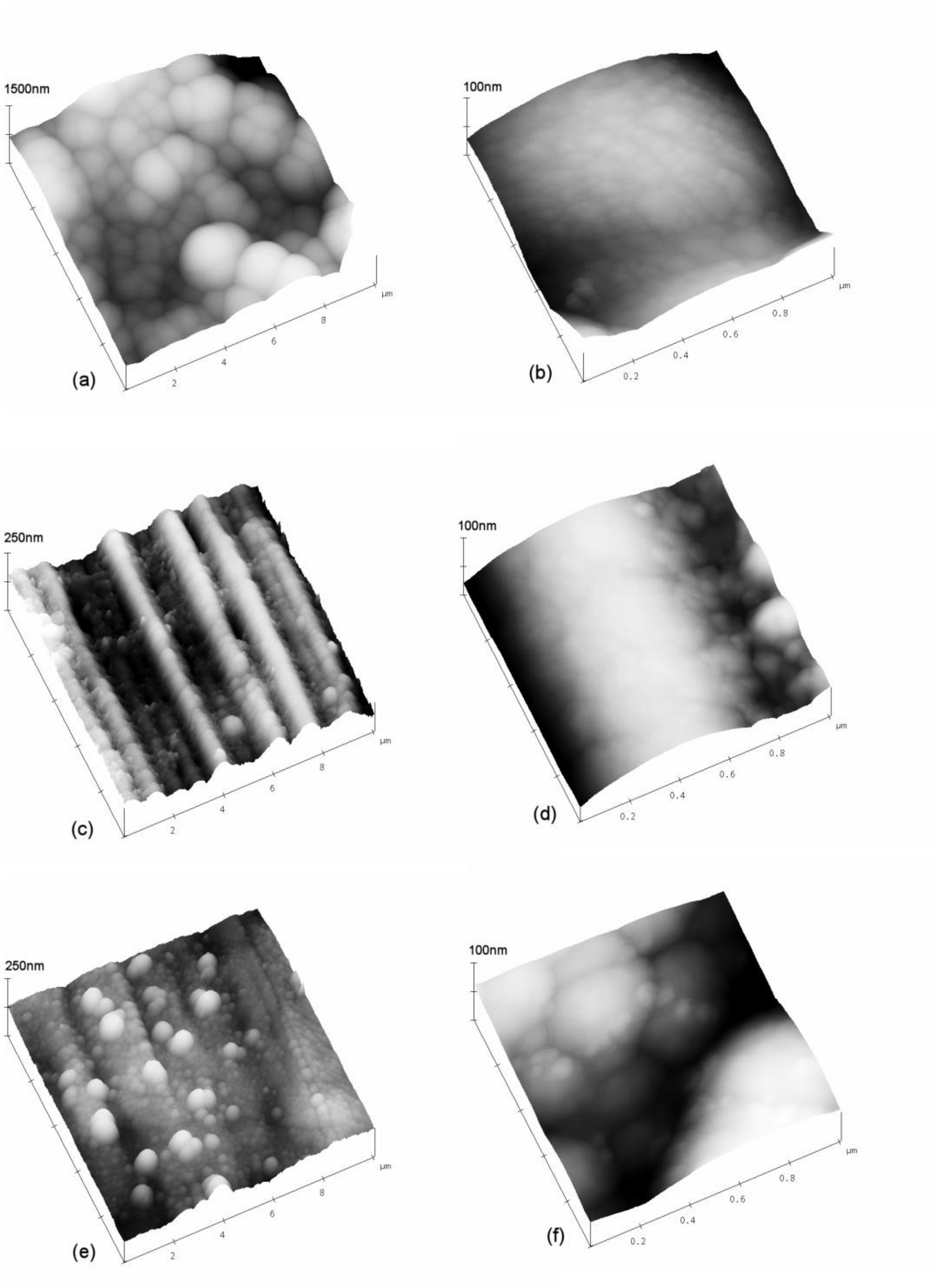

Figure 3. Surface structure of DLC films shown by AFM for (a and b) DLC-E, (c and d) DLC-S1 and (e and f) DLC-S2 over (left) 10 x 10 µm and (right) 1 x 1 µm