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Compositional depth profiling of diamond-like carbon layers by glow discharge optical emission spectroscopy

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This article describes the compositional depth profiling (CDP) of diamond-like carbon (DLC) layers by Glow Discharge-Optical Emission Spectrometry (GD-OES). The DLC layers were deposited on flat steel samples. Analysis by using a Charge Coupled Device (CCD) GD-OES instrument revealed saturation effects of the carbon lines at 156 nm and 165 nm. Therefore, the application of these lines for CDP of DLC layers is not possible. A third line at 193 nm was not affected by this saturation effect and is therefore a good choice for calibration. A second effect was observed as a non-flat crater in combination with large differences of the sputtering rate factor of the substrate (1.1) and the DLC (0.032) led to an unusual behaviour at the interface between the DLC layer and substrate. Both measurements of the crater shape and of the sputtered coating weight up to the interface and just behind it showed clearly that about 30% of the DLC layer remains at the crater edge, once the crater centre reaches the interface. This was found to be the main reason for the incorrect DLC-layer thickness, if the intersection between the carbon and iron concentration was used as a measure for the end of the DLC layer.

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1 Introduction

The requirements for higher performance of powertrain and engine systems in the automotive sector are steadily increasing. The parts inside these components keep getting smaller and are exposed to higher pressure during operation. These functionally stressed areas of the components are protected by coatings which increase their durability. This is one reason why more and more coatings are being used in such environments. High hardness, low friction, and high wear resistance are the advantages of diamond-like carbon (DLC) coatings. These coatings are useful for small parts. It is crucial to ensure a sufficient DLC-layer thickness to withstand the high pressure and increasing temperatures. The layer thickness needs to be within the certain range. A low layer thickness leads to a decrease in durability, while a larger layer thickness is not as critical. However, it can lead to chipping and impair functionality as well. The investigated

DLC layers here are amorphous hydrogenated carbon (a-C:H).

In general, the thickness of the DLC layer is determined by infrared spectrometry. However, with each change in the coating parameters, the determination of a new refractive index becomes necessary.

A depth profile approach using Glow Discharge Optical Emission Spectrometry (GD-OES) is another means to analyze the thickness. GD-OES can be used for production control as a fast finger print method and difference detection, *e.g.* substrate roughness and interface structure become visible immediately even without quantification. Additionally, GD-OES can be used quantitatively in order to assess the composition and thickness of the DLC layer and the adhesion layer. For such an analysis, a calibration method and a density model are necessary. The quantification model used in the software of all commercial GD-OES systems is based on the concept of constant emission yields reviewed by Bengtson and Nelis.¹

In this multi-matrix calibration, the intensity of an element is presented in relation to the concentration multiplied with the sputtering rate (SR), defined as mass loss per time. In practice, the so-called sputtering rate factors (SRFs) are used, which represent the ratio of the sample sputtering rate to the SR of pure Fe.

$$\text{SRF} = \frac{\text{SR}_{\text{sample}}}{\text{SR}_{\text{Fe}}} \quad (1)$$

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The SR of bulk samples is calculated from crater volume measurements, density of the samples, and sputtering times.² The SR of a layer is calculated from the layer thickness, crater diameter, sputtering time, and layer density. However, this requires flat craters with sharp transitions between the layer and substrate and the knowledge of the layer density.

At this point, it has to be mentioned that the SRF sometimes is also determined in an indirect way. If the curve for a multi-matrix calibration is defined by a number of well characterized bulk samples, the SRF of any sample can be calculated in such a manner that the corresponding point appears exactly on the calibration curve. If there are several elements in this sample of a known concentration, this method is very reliable because the calculated SRF must be the same for all elements and even all lines. Nevertheless, this factor is not identical to the SRF as defined in eqn (1). It is a proportionality factor which satisfies the applied model.³ In most cases, both factors agree very well. The layer density is used additionally for quantification when the sputtered mass of the element is converted into a layer thickness. Different density models are used, which are all based on the density of the pure elements.⁴ The results using these models differ; nevertheless, for more or less pure materials the key parameter for this conversion is the density of the pure element.

The density of DLC can be estimated in the range between diamond (3.5 g cm^{-3} , close packing of carbon) and long chain hydrocarbon polymers.⁵ Hydrogen is proven to be a crucial factor for the density. Koidl *et al.* found a correlation between the hydrogen content (27–50 at%) and the DLC-layer density ($1.9\text{--}1.3 \text{ g cm}^{-3}$).⁶ Heteroatoms (*e.g.* W, Si, and N) also contribute to density, with densities reaching up to 6.0 g cm^{-3} .⁷ Therefore, the determination of the DLC-layer density is one of the key questions for further quantification. The density of similar bulk materials may differ remarkably from that of a layer. The determination of the density of a layer as the ratio of its weight to volume is very demanding and therefore often indirect methods are used. X-ray reflectivity (XRR) was used by Robertson to investigate the density of DLC layers.⁸ LiBassi *et al.* described the density determination of DLC by XRR and Electron Energy Loss Spectroscopy (EELS).⁹ Also Thomas *et al.* presented a method to determine the density of layers by EELS.¹⁰

Charitidis showed that the density increases with hardness.¹¹ This is due to the structural composition of DLC. Hence, the density mainly depends on the sp^2/sp^3 bonding ratio of carbon. Robertson asserts that the hydrogen concentration is a significant factor in this respect.⁸ Hydrogen is bonded in CH_x groups. The higher the hydrogen content of the layer, the more it becomes like a polymer layer. The hydrogen concentration in the a-C:H layer usually varies between 10 and 40 at%.⁸ A method to analyze the hydrogen concentration by using GD-OES is given by Takahara *et al.*¹² Koidl *et al.* also list some kinds of methods and describe two of them.⁶ They also show the relationship between the sp^2/sp^3 bonding ratio to the hydrogen concentration and the layer density.

2 Experimental

The samples were prepared by first applying an adhesion layer of chromium of several hundred nanometre thickness on a steel

plate (1.3505 steel) by Physical Vapour Deposition. The DLC layer was deposited on the adhesion layer by using the Plasma-Enhanced Chemical Vapour Deposition method (Fig. 1).

To determine the DLC-layer thickness, an infrared reflectivity method was used (Bruker Hyperion). The relative standard deviation was within a range of 0.8%. To obtain the IR data, a Focused Ion Beam (FIB)-cut and subsequent scanning electron microscopy (SEM) imaging were conducted.

Prior to the chemical analysis, all surfaces were cleaned with *n*-heptane to remove any residual contaminants. For analysis of the DLC-composition, the samples were examined using a Charge Coupled Device (CCD) spectrometer (GDA650, Spectrums). The spectral range is from 120 nm to 550 nm and the spectral resolution is 20 pm. The time of measurement was 20 ms and one spectrum is saved per second. A DC-source with a 2.5 mm diameter anode was used in the device. The measurement parameters were 900 V and 15 mA for the calibration and also for the measurement. In this mode, voltage and current are kept constant by regulation of the pressure. For analysis, wavelengths at 156.143, 165.701, 193.091 (all three carbon lines) and 283.200 nm (iron) were used (please note, in the upcoming sections only integer values of these are used). Additionally, secondary ion mass spectrometry (SIMS) [primary ion: Cs^+ , 5 kV, 100 nA, secondary ion: CsM^+ ($\text{M} = \text{H}, \text{C}, \text{N}, \text{O}, \text{Ar}, \text{Cr}, \text{Fe}, \text{W}$), scanned area $250 \times 250 \mu\text{m}^2$, charge compensation] was used as a second method for the layer characterization.

Table 1 shows the calibration samples, which were used. A selection of these samples was used for recalibration.

Images of the crater topography were obtained using a confocal profilometer (MicroProf, FRT GmbH), scanning an area of $7 \times 7 \text{ mm}^2$ at a lateral resolution of 10 microns and

Fig. 1 Sample structure.

Table 1 Calibration and DLC samples

Sample	Producer	SRF	Fe in m%	C in m%
1761	NIST	1.000	95.0846	1.03
1762	NIST	1.053	94.0929	0.337
1763	NIST	1.042	95.0192	0.203
1764	NIST	1.020	95.4882	0.592
1765	NIST	1.010	99.6122	0.006
TRP 1043-2	TKS	1.000	99.9974	0.0002
DLC	Continental	0.032		98.2
65	ASMW	1.835	69.4	0.82
244	CKD	0.900	92.9712	2.6
249A	CKD	0.892	92.359	3.75

a depth resolution of 20 nm. Crater volumes were determined based on these measurements. The SRFs of the calibration bulk samples were calculated from crater volume measurements of the samples (Table 1) and of NIST 1761 under standard conditions for a 4 mm source (700 V, 20 mA), density of the samples and sputtering time.²

3 Results and discussion

In the DLC layer, a hydrogen concentration of 18 at% was measured by SIMS. Therefore, the DLC layer can be classified into the group of a-C:H. Due to the low sputtering rate of DLC at low H-concentrations, it is difficult to measure this hydrogen concentration with a 4 mm source.¹²

At first, a PMT (photo multiplier tube) based GDA750, using the 156 nm carbon line, was applied for depth profiling of DLC. Using a 2.5 mm source, the H-signal was near the background and H could not be included in the quantification procedure. Additionally, the DLC-layer thickness determined by GDA750 did not match the thickness obtained by IR measurement. The calculated thickness was much too thin. With the GDA650, all suitable analytical carbon lines can be measured, but with CCD detection, 2.5 mm source, and 20 ms integration time no hydrogen signal is detectable with the GDA650. Therefore, we focused our work on the quantification of carbon and calibrated the GDA650 for iron and different carbon lines. The performance of the carbon lines of course also has an impact on the quantification of hydrogen, which had to be excluded in this investigation, due to low sensitivity.

3.1 Intensity-time profile

Fig. 2 shows the intensity-time profile of three carbon lines (156 nm, 165 nm and 193 nm) for the DLC layer and one iron line (238 nm) for the substrate. This profile has three parts. Part a is the DLC layer, part b is the interface between DLC and steel and part c is the substrate, 1.3505 steel with about 0.9 m% carbon. For an easier interpretation, all carbon lines were normalized to the carbon intensity in the steel substrate. The

156 nm and 165 nm carbon lines show the same trend in all three parts. As far as the resolution allowed, this was also confirmed for the other lines of the triplet at 156 nm and the quintet at 165 nm. Whereas the level of these lines is the same in parts a and c, the 193 nm carbon line shows a doubled intensity in part a. The high carbon intensity at the interface is caused by the crater shape and by the high SR difference between the DLC layer and the steel substrate. In part a, the carbon is excavated evenly, in a concave shape. The release of carbon atoms from the surface is quite low compared to the iron atoms (different SRs). When the center of the crater touches the substrate a huge amount of iron atoms (compared to carbon) is released from the surface. It's like an explosion just beneath the carbon. During part b the remaining DLC layer is removed from the bottom upwards by the iron atoms being excavated. Thus the carbon intensity of this part is significantly increased. In part c, the remains from the DLC layer are gone. Any carbon signals detected here are from the carbon in the steel substrate.

The crater forms a little circular region during sputtering at the interface between the DLC layer and steel. The breakthrough is in the middle of the crater (see Fig. 3). The rest of the DLC layer (about 25%) remains at the crater edge and will be sputtered later during part b. At this point the increased carbon peak appears.

3.2 Calibration curve

The calibration curve is an important basis for quantification. If a sample with known concentration and sputtering rate deviates from the calibration curve, the quantification of concentration and thickness will be wrong.

All samples were measured three times and the average intensity over 20 s was determined. A new crater was used each time. The intensity value is the average of a period of time from 40 to 60 s. Fig. 4 shows the calibration curves of the different carbon lines. On the ordinate the product of concentration times SRF is shown. For the DLC layer, a SRF of 0.032 was used, which is obtained as result of quantification using the 193 nm carbon line (see 3.3 and Fig. 6).

Fig. 2 Intensity-time profile of the DLC layer on steel, 90 s = 1 μ m, 120 s = 4 μ m in Fig. 6, CCD spectrometer GDA650, 900 V, 15 mA.

Fig. 3 Crater at 95 s sputter time, interface already penetrated, remaining carbon at the edge of the crater.

Fig. 4 Calibration curves of the different carbon lines.

The carbon line intensities of the DLC layer at 156 nm and 165 nm differ significantly from the corresponding calibration curve, when the SRF of 0.032 is used. As both lines have the same intensity in the steel substrate ($c(\text{C}) = 0.9 \text{ m\%}$, $\text{SRF} = 1.1$) and in the DLC layer ($c(\text{C}) \approx 100 \text{ m\%}$, $\text{SRF} = 0.032$), it is assumed that there is a saturation of the light emission at this level, when DLC is sputtered.

From the literature it is known that the effect of self-absorption depends on the distribution of the emitting and absorbing species and thus, self-absorption is one of the possible processes, which can be responsible for this effect. Small absorption coefficients usually reduce the intensities and this leads to non-linear curves, which normally can be described in GD-OES by quadratic polynomials. Larger absorption coefficients and special element distributions can lead to self-reversal of the lines and after saturations the intensities may even reduce again. Under certain conditions of the absorption coefficient and element distribution, even flat top line profiles and saturation of the intensity are reported.¹³

The different behavior of the different lines may be explained by the fact that the lines at 156 nm and at 165 nm correspond to transitions to the ground state (so-called resonance lines) and the line at 193 nm ends in an excited state and less self-absorption will occur (Fig. 5).¹⁴ The different behavior of DLC in comparison to all the calibration samples may be due to the extremely low sputtering rate of DLC, which may cause a different element distribution in the discharge volume. Further experiments in order to study the effect of self-absorption are conducted using a high resolution Fourier transform spectrometer.

Takahara *et al.* present a graph, where the intensity of the 156 nm carbon lines does not vary, even if the concentration of hydrogen increases from 17 to 35 at%.¹² A higher concentration of hydrogen also means a lower SR, but both effects will never compensate totally and our observation of saturation explains this result, too. In contrast to this, the 193 nm carbon line

Fig. 5 Term scheme of the optical transition of carbon.¹⁴

Fig. 6 Concentration–depth-profile using the 193 nm carbon line, the 238 nm Fe line and a carbon density of 2.94 g cm^{-3} (the value of the SRF is also presented).

Table 2 Quantification of the DLC-layer thickness

Carbon line in nm	Sputtered mass of carbon up to the intersection C/Fe in g m^{-2}	Calc. thickness in μm	Complete coating mass of carbon in g m^{-2}	Calc. thickness in μm	Ratio from the calc. thickness at the intersection C/Fe to real thickness in %
156	1.56	0.60	2.58	0.9	60
165	2.03	0.72	2.91	1.0	70
193	2.97	1.05	4.42	1.5	67

intensity of the DLC layer matches the calibration curve. All calibration curves are not totally linear, which points to some self-absorption at all lines.

3.3 Quantification procedure

The SRF of DLC is a direct result of the quantification procedure using the carbon 193 nm and iron 238 nm lines. This factor is 0.032 and results when calculating the concentration of all elements from their sputtered masses per time. This SRF was used in Fig. 4 in order to show the position of the DLC layer in the calibration graphs of the different carbon lines.

Another direct result of the quantification is the coating weight of carbon (4.42 g m^{-2}), which is calculated by integration of the sputtered mass per time until the substrate is reached (120 s). It is essential to note that the coating weight determined up to the beginning of the adhesion layer (92 s) is only 2.97 g m^{-2} and this is 67% of the complete DLC layer.

The error of the contamination was calculated with the software. For this measurement, the error was determined to be 0.16 g m^{-2} within the first three seconds, which corresponds to a relative error of 3%.

If the well-known DLC-layer thickness ($1.5 \mu\text{m}$) and the crater diameter (2.5 mm) are used, the total coating weight of carbon can be directly transformed into a DLC-layer density of 2.94 g cm^{-3} .

At this density of 2.94 g cm^{-3} for carbon, the correct layer thickness of $1.5 \mu\text{m}$ is reproduced by the quantification software. For this approach, it is necessary to quantify the carbon signal up to the transitions into the substrate (120 s). Due to the much higher SR and correspondingly higher erosion rate (ER) of Fe, the total depth after 130 s is already $5.0 \mu\text{m}$ (see Fig. 6). The application of such depth quantification includes the assumption that other elements are not present in the DLC layer to a remarkable content and therefore do not contribute to the layer thickness. Also changes of the emission yield of the C 193 nm line or of the density of carbon must be excluded. Corresponding correction terms may be included, if the concentration of hydrogen can be measured.

Fig. 6 shows the quantified profile of Fig. 2 for 130 s including the calculated SRF as a function of the depth. The SRF of DLC is 0.032 and becomes 1.1 at the substrate. The quantification using the 193 nm carbon line shows a nearly correct DLC-layer thickness.

For an accurate quantification, only the carbon 193 nm line should be used, which is shown in Fig. 2 and 6. About 30% of

the DLC-layer mass is located in the crater edge and will only be removed gradually while sputtering into the substrate (center of the crater). Therefore, about 30% of the carbon atoms appear after the intersection between the carbon and iron concentration. So the thickness at this intersection will also be incorrect. Table 2 shows that effect.

4 Conclusions

The quantified depth profiles of the DLC sample show different results when different carbon lines are used. The carbon lines at 156 nm (triplet) and 165 nm (quintet) show a saturation effect. These lines correspond to transitions to the ground state (so-called resonance lines) and strong self-absorption must be expected. The line at 193 nm ends in an excited state and so less self-absorption will occur.

The correct quantification of carbon in DLC is the base for specifying other elements like hydrogen. Any additional carbon incorporated into the adhesion layer or interface is critical for the quantification and must be accurately known or reduced. Additionally, care must be taken regarding the contribution of carbon from surface contaminations and from the substrate.

Thickness calculations using the 193 nm carbon line are nearly correct if a density of 2.94 g cm^{-3} is used. The density can be calculated using the known layer thickness and coating weight; however, for this approach the calibration must be exact. *Vice versa*, the layer thickness of DLC can be calculated if the carbon density is known.

The results of the DLC-layer thickness determination (Table 2) demonstrate what happens when the saturation effect is disregarded. The DLC thickness quantification using the 156 nm carbon line is considerably smaller compared to the real layer thickness. The same effect can be seen with the 165 nm carbon line.

The SRF dependence on time is another important aspect of quantification and may be used in the future to characterize the DLC layer, with respect to its density or its hydrogen concentration. These investigations will be continued with a PMT instrument which can detect the 193 nm carbon line and intense hydrogen lines.

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