

DETERMINATION OF SP³ FRACTION IN ta-C COATING USING XPS AND RAMAN SPECTROSCOPY

*V. Zavaleyev^a, J. Walkowicz^a, M. Sawczak^b, M. Klein^{b,e}, D. Moszyński^c,
R. Chodun^d, K. Zdunek^d*

*^aFaculty of Technology and Education, Koszalin University of Technology,
Koszalin, Poland;*

*^bThe Szewalski Institute of Fluid-Flow Machinery, Polish Academy of Sciences,
Gdansk, Poland;*

*^cInstitute of Chemical and Environment Engineering, West Pomeranian University
of Technology, Szczecin, Poland;*

^dFaculty of Materials Science, Warsaw University of Technology, Warsaw, Poland;

*^eFaculty of Applied Physics and Mathematics, Gdansk University of Technology,
Gdansk, Poland*

E-mail: viktor.zavaleyev@tu.koszalin.pl, zavaleyev@list.ru

The paper presents results of studies on the structure of tetrahedral amorphous carbon films (ta-C) with a thickness in the range from 20 to 280 nm, deposited using pulsed vacuum arc technique with an electromagnetic Venetian blind plasma filter. The results of the phase structure analysis, obtained using visible Raman spectroscopy and UV Raman spectroscopy methods, showed a strong dependence of the results on the presence, on the surface of synthesized thin carbon films, even of a minimum number of microparticles. The presence of microparticles in the deposited coatings strongly affects the accuracy of the measured data, used next for calculation the I_D/I_G , I_T/I_G ratios and determination of the G-peak dispersion, for all coating thicknesses, which pointed to significant diversification in sp³-bonds content in deposited films.

INTRODUCTION

Hard diamond-like carbon coatings ta-C are characterized by high strength and good frictional properties that determine their extensive utilization. It is known that the physico-mechanical properties of amorphous ta-C thin films depend on the content of sp³-bonds [1–5]. Experimental studies of amorphous carbon coatings deposited by Physical Vapour Deposition (PVD) method, carried out by Iijima with the use of high resolution electron microscopy [6], showed that the amorphous carbon films formed by vacuum deposition contain fine particles of the diameter less than 100 Å, which have a graphite-like structure and contain in their centers highly strained carbon-carbon bonds, dangling bonds and a certain number of tetrahedral bonds. Therefore, determination of the structure of amorphous carbon coating is quite a complicated problem. Raman spectroscopy has been widely used to date for structural studies of ta-C thin films. However most of the scientific works that concern Raman spectroscopy and XPS studies of the ta-C coatings describe the amorphous carbon thin films synthesized using various designs of plasma filters. The review of the literature has shown that the form of Raman spectra of amorphous carbon coatings is affected by numerous parameters, such as: energy of ions bombarding the substrate, the value and the pulse width of the substrate bias potential, the substrate temperature during deposition, and the size of crystallites of various forms of carbon formed during the synthesis [1–5, 7–18]. Raman spectra of these coatings contain bands due to the presence of graphite crystallites, as well as other phases of disordered carbon. The Raman spectrum excited with photons of visible light is dominated by scattering of sp²-bonded

graphitic carbon, due to resonance enhancement of the Raman scattering cross section. Two broad bands appear at about 1550...1560 cm⁻¹ (G-peak) and at about 1350...1360 cm⁻¹ (D-peak). Although the visible Raman spectrum depends fundamentally on the ordering of the sp²-bonded carbon and only indirectly on the sp³-content, it can also be used in a restricted range of conditions to derive information about the sp³/sp² ratio. In the last few years several studies, with UV excitation used for evaluation ta-C thin films, have shown that the D and G Raman bands are significantly reduced compared to the sp³ bands. A Raman band was observed at about 1060...1100 cm⁻¹. It can be attributed directly to sp³-bonded carbon (T-peak) [3]. But there is no scientific papers on the influence of graphite microparticles embedded in the synthesized ta-C thin films on the interpretation of the I_D/I_G and I_T/I_G ratios and on the determination of the G-peak dispersion.

The present paper reports on the results of the series of experiments on the deposition of amorphous carbon coatings with the thickness from 20 up to 280 nm, with minimal amount of microparticles on the surface, by pulsed vacuum arc method using a water-cooled electromagnetic Venetian blind plasma filter. Particular attention was paid to the comparative research of the influence of a minimum amount of microparticles in amorphous carbon ta-C coatings of different thickness on the phase structure and the relative amount of sp³/sp²-bonded carbon atoms determined using Raman spectroscopy and XPS.

MATERIALS AND METHODS

Experiments were performed on a customized industrial vacuum-arc device C55CT produced by the

German company INOVAP GmbH for diamond-like carbon (DLC) coatings deposition. Customization included the installation of water-cooled electromagnetic Venetian blind plasma filters in front of the metal and carbon cathodes, as well as the installation of water-cooled electrodes of Arc Enhanced Glow Discharge (AEGD) substrate cleaning system (Fig. 1).

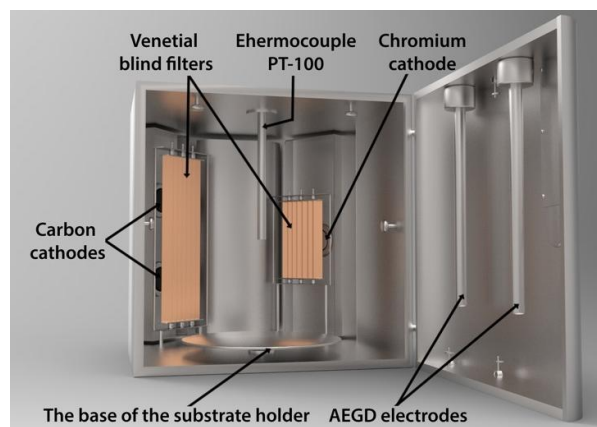


Fig. 1. Arrangement of additional elements in the vacuum chamber of modified vacuum arc device C55CT

The cathodes of the arc sources used in the experiments for ta-C coatings deposition, 70 mm in diameter, were made from pure carbon and chromium. Two graphite cathodes, with a DC-arc current of 50 A with superimposed high-current arc pulses of 1400 A, were used for carbon deposition. The pulse duration was set to 300 μ s and the repetition rate was 100 Hz. Argon gas (99.999% purity) was used to improve working stability of the used vacuum arc plasma sources. The silicon plates with crystallographic orientation (100) of the dimensions of 5 \times 30 \times 0.5 mm were used as the substrates.

Previous study [14] showed that the substrate temperature during synthesis of the carbon coatings is one of the key parameters, which determine the coatings properties, i. e. the content of sp³-hybridized carbon atoms, the level of compressive stresses, as well as coating adhesion and microhardness. Since the planetary substrate holder had no additional cooling, in the present experiments the substrate cooling step (to the temperature of 40 °C) was inserted after adhesive metal sublayer deposition. During the phase of amorphous carbon ta-C coating deposition the substrate temperature limit of 45 °C was set. The substrate rotation speed was 5 rpm. All stages of the present experiments were identical and the thickness of the ta-C coatings (Table 1) was adjusted by the number of steps in the deposition stage.

Because of the specificity of our technology of thin ta-C films deposition, i. e. high intensity of the substrate etching method (AEGD) and the presence of the microparticles on the coating surface, the thickness measurements using profilometer and ellipsometer were affected by significant errors. Also the use of the interferometer for measuring the thickness of the coating is difficult – there are disturbances in the amorphous carbon thin film itself, as it is reported in [19]. Thus thickness of the synthesized ta-C thin films was evaluated according to the data published by

T.J. Moravec [20]. This method is based on a comparison of the coating interference color with standard colors for a diamond-like carbon coating with a known refractive index. The verification measurements were made using scanning electron microscope Hitachi SU-70. In Fig. 2 the SEM image of the cross section of ta-C coating deposited on the silicon substrate is presented.

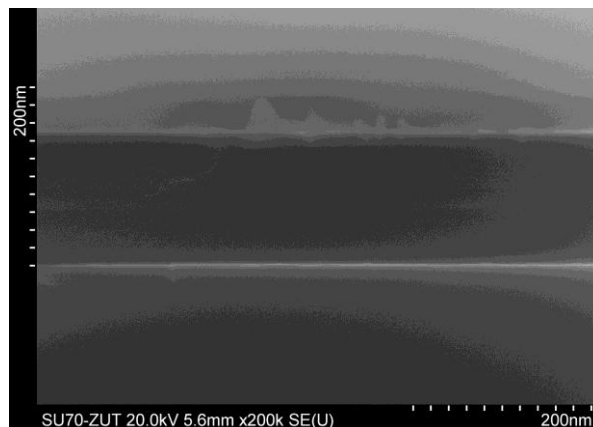


Fig. 2. The cross section of the ta-C coating 150 nm thick

The comparison of the thicknesses of deposited ta-C coatings, measured using SEM, with the data published by Moravec showed good correlation, within an accuracy of 5 nm, for all synthesized coatings.

All measurements of Raman spectra were carried out in three different locations on each of the tested samples using the device Renishaw inVia, the Raman scattering spectrometer working at the wavelengths of 514 and 785 nm in the geometry of the reverse scattering. Raman spectra were stimulated by radiation of an argon-ion laser with the power of 50 mW and energy equal to 2.41 eV (514 nm) focused on a sample in a spot with the diameter of \sim 1 μ m. The use of the maximal power resulted in essential local overheating of the sample and changed the spectra, that's why reproducible results were obtained at decreased power of the incident radiation to 1.5 mW.

The ta-C films were also examined by UV Raman spectroscopy. We measured the Raman spectra using 4.66 eV (266 nm) excitation energy. As the source of UV light the Crylas FQCW266-50 crystal laser system was used, employing a 1064 nm line of Nd:YVO₄ laser converted to 266 nm in the fourth harmonic generator. The scattered light was dispersed by a JASCO NRS 5100 spectrometer working in backscattering geometry. The laser beam was focused onto spot 10 μ m in diameter by 40x objective. To achieve a satisfactory signal to noise ratio of obtained spectra the parameters of acquisition were optimized. The spectral resolution of measurements was 5.7 cm⁻¹, while the exposure time for 10 mW laser was 30 min. Under this conditions we have not detected any visible damage of the sample surfaces, as well as ranging the laser power from 5 mW (which is minimum for used Crylas device) to 10 mW did not change the measured signals. In order to analyze the position, intensity, and line width of the peaks, of visible and UV Raman spectrums were fitted two Gaussian peaks. For consistency with the published

literature, we define these two peaks as G and D for visible and G and T for UV respectively [11–15, 21].

The X-ray photoelectron spectra were obtained using Al K α ($h\nu = 1486.6$ eV) radiation with the use of a Scienta SES 2002 spectrometer operating at constant transmission energy ($E_p = 50$ eV). The spectrometer was calibrated using the photoemission line (with reference to the Fermi level): E_B Ag 3d $_{5/2} = 368.3$ eV. The analysis chamber during experiments was evacuated to the vacuum better than $1 \cdot 10^{-7}$ Pa. The spectra were recorded at room temperature. The samples were clamped by springs onto a sample holder. The size of the analyzed area was approx. 1×4 mm. An area of 10 mm in diameter of each sample was sputter-cleaned with 3 keV Ar $^+$ ions. Charging effects were corrected using the C 1s peak due to adventitious carbon with E_B fixed at 284.6 eV. The surface composition of the samples was obtained on the basis of the peak area intensities using the sensitivity factors from CasaXPS software and homogeneous spatial distribution of the elements. Data processing involved background subtraction by means of a “Shirley-type” integral profile and a curve-fitting procedure (a mixed Gaussian–Lorentzian function was employed) based on a least-squares method.

RESULTS AND DISCUSSION

VISIBLE AND UV RAMAN SPECTROSCOPY

Determination of sp 3 -bond content in the investigated ta-C films plays a key role, since the amount of sp 3 -bonds influences physical properties of the films. To investigate the ratio of sp 3 /sp 2 -bonds in ta-C films Raman scattering, with different excitation wavelengths – visible $\lambda = 514$ nm and UV $\lambda = 266$ nm, is commonly used. It is known that Raman spectroscopy in the visible wavelength range of excitation (514 nm) is more sensitive to sp 2 -bonds than to sp 3 ones, as the photons in the visible range resonantly enhance the π states, formed by sp 2 -hybridized carbon atoms, but not the σ states, formed by sp 3 -hybridized carbon [22–24]. The Raman spectrum in the visible wavelength range is characterized by two spectral signals: the D-peak, which is a breathing mode of A $_{1g}$ symmetry, and the G-peak corresponding to the E $_{2g}$ symmetry [24–26]. In Raman spectroscopy with UV wavelength range of excitation (266 nm) and higher photon energies, both the π states and the σ states are effectively excited [21, 27]. Moreover in the Raman spectrum in the UV wavelength range an additional T-peak appears, which is due to the C–C sp 3 vibrations and is visible only for UV excitation. The simulations confirmed that it corresponds to the peak in the C–C sp 3 vibration density of states (VDOS) of ta-C, which conform with a large amount of sp 3 -hybridized carbon atoms [28–30].

Fig. 3 shows the spectra of visible and UV Raman scattering in the ranges of 800...2000 and 600...2000 cm $^{-1}$ respectively, measured for ta-C films, with the thickness of 20...280 nm, deposited on a silicon substrate using a water-cooled electromagnetic Venetian blind plasma filter. As can be seen from Fig. 3,a all the spectra obtained at the visible range of excitation contain almost symmetrical band centered

around 1575 cm $^{-1}$ (the G-peak) and the band located at 1350 cm $^{-1}$ (the D-peak), as well as the peak visible at 960 cm $^{-1}$, which occurs as a consequence of the second order phonon scattering from the silicon substrate. The intensity of this peak is a measure of the transparency of ta-C films near the laser wavelength (514 nm).

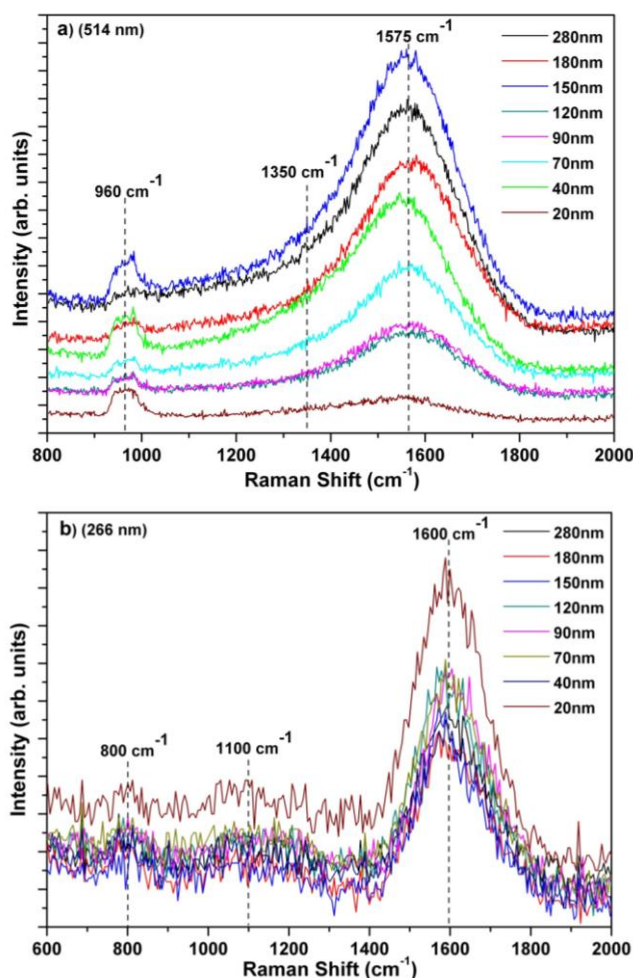


Fig. 3. Raman spectra obtained at visible (a) and UV (b) excitation wavelength for ta-C films with the thickness of 20...280 nm

The spectra obtained at UV excitation wavelength show that the G-peak is shifted toward higher frequencies and is located at 1600 cm $^{-1}$, besides, T-peak appears at lower frequency of 1100 cm $^{-1}$. Moreover, the additional peak is visible at low frequency region (around 800 cm $^{-1}$), which is due to vibrations of sp 3 -bonds of amorphous carbon film (see Fig. 3,b) [30], but it will not be discussed in this work. The disagreement may result from the use of different dielectric multi-layers filters, which influence the spectral range and were used to reject the Rayleigh scattering [31–32].

As suggested by A.C. Ferrari [33], the calculated ratio I_D/I_G can be used for qualitative determination of the amount of sp 3 - and sp 2 -bonds in the deposited amorphous tetrahedral ta-C thin films. The lower the ratio I_D/I_G the higher the amount of sp 3 -bonds in the deposited ta-C coating. The changes of the ratio I_T/I_G with sp 3 content are not linear, nevertheless, together with the T-peak position, it can be used as the measure of sp 3 fraction in ta-C films [25, 34]. K.W.R. Gilkes et

al. [34] showed that the ratio I_T/I_G equal to about 0.4...0.42 indicates the content of sp^3 -bonds in ta-C coatings of ~80%. Reduction in the value of the ratio I_T/I_G to 0.3...0.4 still indicates a high content of sp^3 -fraction of 60...80%, but the content of sp^2 clustering makes an accurate estimation difficult. But the value of the ratio I_T/I_G lower than 0.2 indicates that the sp^3 content is less than 20...30%.

Fig. 4 shows the variation of the average calculated values of the ratios I_D/I_G and I_T/I_G , and the position of the T-peak for non-hydrogenated ta-C coatings with the thickness in the range 20...280 nm. Dependence of the ratio I_D/I_G on the coating thickness (see Fig. 4,a) is not uniform and varies from 0.95 to 0.35 when the coating thickness is changing from 20 to 90 nm.

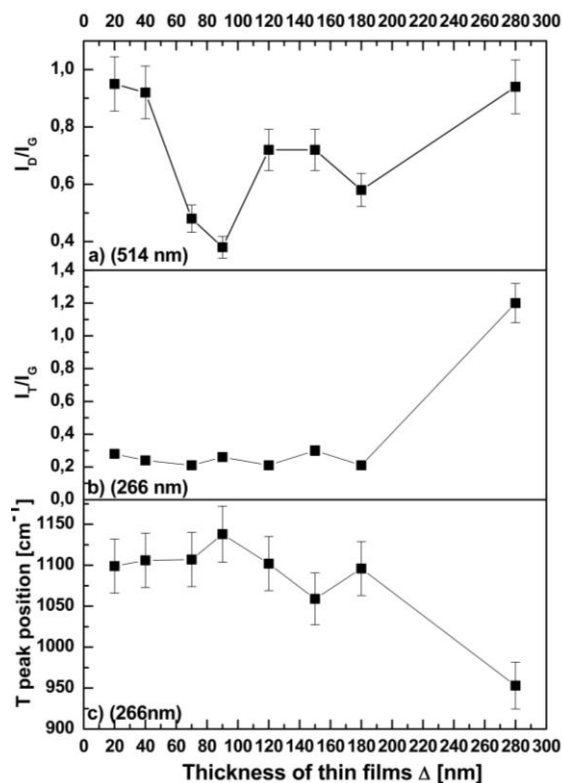


Fig. 4. The ratio I_D/I_G (a), I_T/I_G (b) and the T-peak position (c) for ta-C coatings with the thickness in the range from 20 to 280 nm

For the coating thickness of 120 and 150 nm, the ratio I_D/I_G is equal to 0.7. With the thickness increase to 180 nm, the ratio I_D/I_G decreases to 0.6 and then again increases to 0.9 at the coating thickness of 280 nm. The dependence of the ratio I_D/I_G indicates to the highest content of sp^3 fraction in the ta-C coating 90 nm thick, and the lowest sp^3 -bond content in the coating 280 nm thick. More uniform is the dependence of the ratio I_T/I_G on the coating thickness (see Fig. 4,b). Within the range of 20...180 nm of the coating thickness, the ratio I_T/I_G is contained within the range from 0.20 to 0.28 and then increases to 1.20 at the thickness of 280 nm. Comparing our estimates with the data obtained by K.W.R. Gilkes et al. [34] we see that in almost all of our coatings the content of sp^3 -phase is less than 20...30%, and only the

coating 280 nm thick contains more than 80% of sp^3 -phase.

Therefore, because of substantial discrepancy between the estimated contents of sp^3 fraction made using the relations I_D/I_G and I_T/I_G , we cannot reliably determine the actual content of sp^3 -phase in deposited ta-C films based on the results of Raman spectroscopy. In our opinion, such a large scatter in the calculated values of the relations I_D/I_G and I_T/I_G is likely to be the results of the presence of graphite microparticles on the surface of the synthesized ta-C thin films, which can have a size from several nanometers to several tens of micrometers [35, 36]. That is, during measurement of Raman spectra, laser spot can randomly cover the surface of the microparticle. The dependence of the T-peak position on the coating thickness shown in Fig. 4,c can confirm our hypothesis. The presented diagram shows that for the coating thickness in the range 20...120 nm and equal to 180 nm, the T-peak is located at the higher frequency of about 1100 cm^{-1} and above, while for the thickness of 150 and 280 nm the T-peak shifts towards lower frequencies of 1060 and 940 cm^{-1} respectively. The presented change in the T-peak position correlates well with the data described in [25], where the authors investigated the amorphous carbon ta-C films and showed that the higher the frequency of the T-peak, the smaller the amount of sp^3 -phase and higher clustering of sp^2 -phase in the amorphous carbon thin films.

Based on the above and taking into account the results obtained for different wavelengths Raman spectrometry, it was decided to determine the dispersion of the G-peak, which also allows to assess the extent of sp^2 -phase clustering. By the Raman spectrometry, using different excitation wavelength, it becomes available to receive additional important information about the internal structure of the carbon coatings. A.C. Ferrari and J. Robertson, based on multi-wavelength Raman scattering, introduced important parameter – the dispersion of the G-peak position [25, 33], which is associated with sp^2 clustering and ordering [37]. They also show that the G-peak dispersion is observed only in the disordered structures of carbon, and the dispersion is proportional to the degree of disorder [33, 37]. The dispersion rate also increases with disorder. Accordingly, this means that the larger the G-peak dispersion the higher disorder of the sp^2 clusters [38]. The G-peak dispersion, for deposited ta-C coatings, was determined as the rate of change of the G-peak position, as a function of the excitation wavelength, using empirical formula proposed by A.C. Ferrari and J. Robertson [25]. Fig. 5 shows the dependence of the G-peak dispersion and full width at half maximum (FWHM) of the G-peak for coatings with the thickness from 20 to 280 nm. From the presented diagram it follows that the largest G-peak dispersion of 0.22 occurs for the coating with a thickness of 40 nm, and the lowest G-peak dispersion of 0.08 was determined for the coating 90 nm thick.

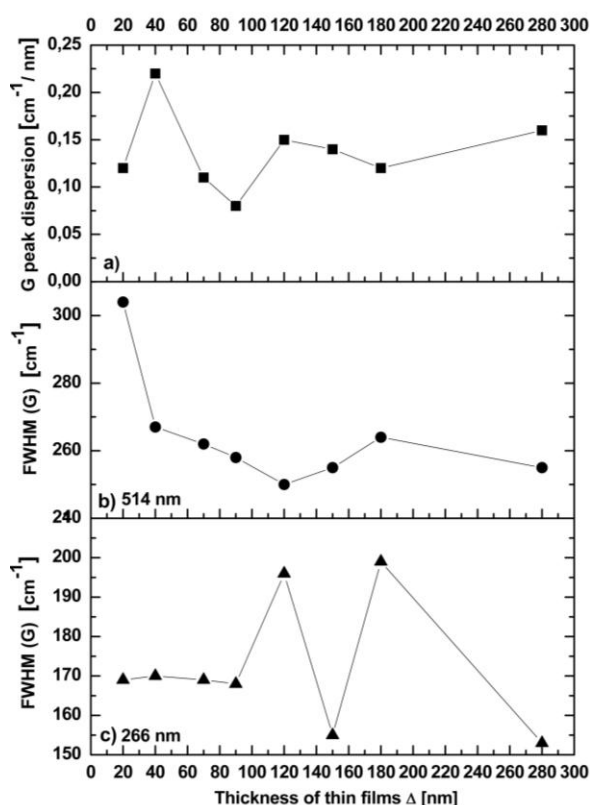


Fig. 5. The dependence of the G-peak dispersion and the full width at half maximum (FWHM) of the G-peak for ta-C coatings with the thickness from 20 to 280 nm for excitation wavelengths of 514 nm and 266 nm

The dispersion of the G-peak of the remaining coatings varies from 0.12 to 0.16. This shows that the ta-C layer with a thickness of 40 nm contains the lowest amount of sp^2 clusters and the highest amount of sp^3 -phase, while the coating with a thickness of 90 nm contains the highest amount of sp^2 clusters. Fig. 5 presents the dependence of the full width at half maximum (FWHM) of the G-peak on the coating thickness for both wavelengths: visible of $\lambda = 514$ nm and UV of $\lambda = 266$ nm. The presented graphs show, that for the visible wavelength of $\lambda = 514$ nm, the FWHM of the G-peak decreases almost linearly with increasing coating thickness and varies from 304 to 255 cm^{-1} (see Fig. 5,b). The FWHM values of the G-peak for UV wavelength of $\lambda = 266$ nm change quite differently – they are lower and their changes with the coating thickness do not correlate with the changes obtained for a wavelength of 514 nm (see Fig. 5,c). As it was shown in [21, 25, 33, 37], thin amorphous carbon coatings having the minimal sp^2 content have the largest FWHM of the G-peak, as they are more disordered. This is in agreement with the fact that the linewidth of G-peak at any excitation wavelength increases as the disorder increases [33, 37]. The obtained results of the dependence of the G peak dispersion and the FWHM of the G-peak on the coating thickness (see Fig. 5) also support our hypothesis that during measurement by Raman spectrometry the laser spot could possibly be located either on the film itself or on the graphite microparticle surface, which in turn have a profound effect on results of the experimental data processing. However, the large values of the FWHM of the G-peak

obtained for the wavelength of $\lambda = 514$ nm indicate, that all our synthesized thin films should have a high content of sp^3 -bonds. Given the ambiguity of the results described above, obtained by Raman spectroscopy for the two laser wavelengths of 514 and 266 nm, we have conducted additional research using XPS spectroscopy to reliably determine the content of sp^3 -bonds in the films, and to confirm our hypothesis.

XPS STUDIES OF ta-C FILMS OF DIFFERENT THICKNESS

Fig. 6 shows the typical XPS survey spectra of thin ta-C films deposited by pulsed vacuum-arc method using a water-cooled Venetian blind plasma filter.

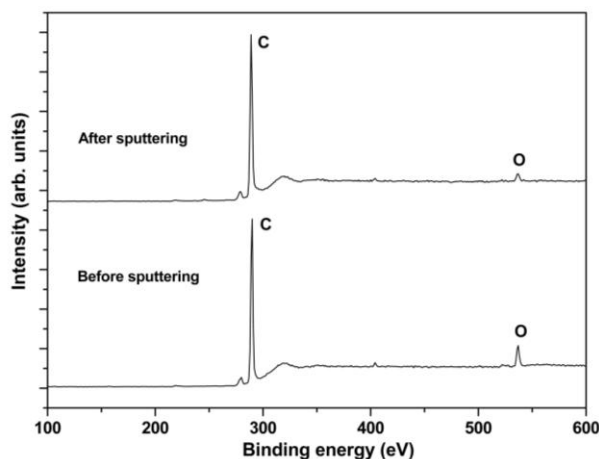


Fig. 6. Typical XPS spectra of ta-C films deposited by pulsed vacuum arc method with plasma filtering, before and after sputtering with Ar^+ ions

In the XPS spectra of ta-C films the carbon peak (C) prevails, and a weak oxygen peak (O) coming from surface impurities is also visible. The surface of the amorphous carbon coating was cleaned by sputter etching with argon ion beam with the energy of 3 keV, at the pressure 10^{-5} Pa for 2 min. After etching the oxygen peak was detected again, but its intensity was lower, which indicate that oxygen is present only on the surface and not throughout the entire volume of the film. In order to completely remove the oxygen impurity the duration of surface ion etching with argon ions should be increased, but this could lead to the increase of the sample temperature, and possibly to their partial graphitization. Therefore, we decided not to increase the ion cleaning duration to be able reliably assess the content of sp^3 -bonds in the synthesized coatings. Fig. 7 shows the C 1s spectra of ta-C thin films with a thickness from 20 to 280 nm deposited by pulsed vacuum-arc method, using a water-cooled Venetian blind plasma filter.

The maximum of C 1s peak for every sample is located at the energy of $(285 \pm 0,1)$ eV. Since in the process of surface cleaning with argon ions, we could not completely remove the oxygen impurity from the coating surface, therefore a small peak at the energy of (288.5 ± 0.3) eV is also observed. It corresponds to the C=O bonding [39]. Further a deconvolution of C 1s peak of ta-C coating was carried out assuming the presence of three components.

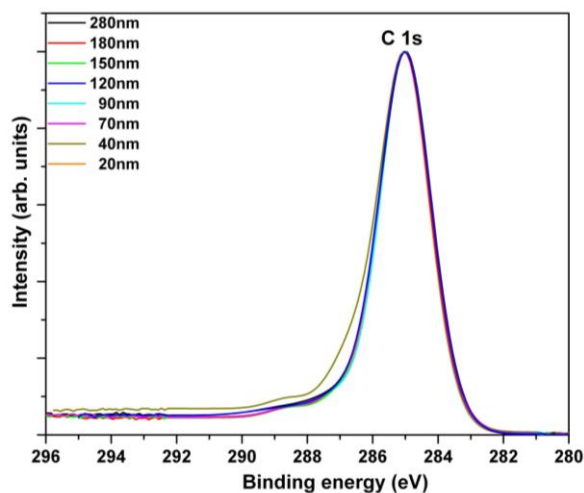


Fig. 7. XPS C 1s spectra of ta-C thin films deposited by pulsed vacuum-arc method using a water-cooled Venetian blind plasma filter

The first component is located at the energy of (284.5 ± 0.1) eV, and corresponds to sp^2 -hybridization between the adjacent carbon atom. The second peak located at the energy of (285.0 ± 0.1) eV corresponds to sp^3 -hybridization of carbon atoms. The third peak, of much lower intensity, is located at energy of (288.5 ± 0.2) eV and corresponds to the C = O bonding between carbon and oxygen atoms, considered as a contamination of the surfaces exposed to the air. The energy values of sp^2 and sp^3 components of C 1s spectra of ta-C coatings are consistent with the binding energies of 284.5 and 285 eV, measured for the C 1s peak of graphite and diamond, respectively [40–42].

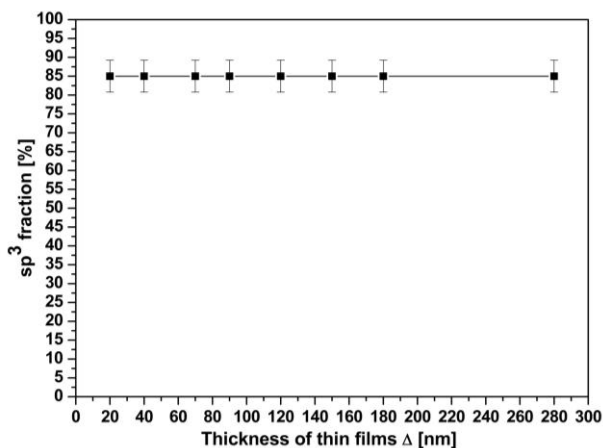


Fig. 8. The content of sp^3 carbon bonds in ta-C coatings with the thickness from 20 to 280 nm based on XPS results

Fig. 8 shows the dependence of the content of sp^3 -bonds on the ta-C films thickness, determined using XPS method. High, constant content of sp^3 carbon bonds of $\sim 85\%$ is observed in deposited ta-C films, within full range of their thickness from 20 to 280 nm. A study conducted by XPS showed that the presence of some amount of micro-particles on the surface of ta-C coatings, deposited by pulsed vacuum-arc method using a water-cooled Venetian blind plasma filter, do not influence the content of sp^3 -bonds in the coating.

The presented results of our research on the structure of ta-C films using Raman spectroscopy (with two excitation wavelengths: visible $\lambda = 514$ nm and UV $\lambda = 266$ nm) and XPS are mutually inconsistent. We have proposed the hypothesis that during measurements using Raman spectrometry, laser spot can possibly be located either on the surface of the microparticles or on the coating, what distorts the obtained results. Our hypothesis is consistent with the results obtained in [43]. Y.X. Leng et al. deposited ta-C coatings by pulsed vacuum-arc method using a magnetic 45°-knee plasma filter, which by its design features also cannot completely remove microparticles from the plasma stream. In their studies, the authors obtained a high value of the ratio $I_D/I_G = 0.8$, but the study by XPS spectrometry showed a high content of sp^3 carbon bonds of around 80%. Another confirmation of our hypothesis was found in the papers [44, 45], in which the authors synthesized amorphous carbon coatings, with microparticles on the surface, by pulsed laser deposition. In the studies of coatings deposited at room temperature, they also received high value of the ratio I_D/I_G equal to 0.8 [44] and 1.4 [45], but the XPS studies showed a high content of sp^3 carbon bonds of about 50%. The quoted data of different authors once again confirm our hypothesis that the presence of microparticles, deposited on the surface of amorphous carbon coatings, can greatly affect the values calculated based on Raman spectroscopy measurements. This in turn leads to erroneous estimation of the ratio of sp^3/sp^2 -bonds in ta-C thin films.

CONCLUSIONS

The results of the research carried in our work for the first time present the effect of the presence of microparticles on the surface of the ta-C thin films on the parameters values calculated based on the Raman spectroscopy measurements carried out with different excitation wavelengths: visible $\lambda = 514$ nm and UV $\lambda = 266$ nm. The ratios I_D/I_G , I_T/I_G and the dispersion of the G-peak position estimated for ta-C films with the thickness from 20 to 280 nm showed a significant mutual discrepancy. In our opinion, the reason for such a disagreement in the obtained results is random location of the laser spot in the course of measurements by Raman spectroscopy either on the surface of the ta-C thin film or on the surface of the microparticles, which in turn leads to a scatter of the received results, and can lead to erroneous estimation of the ratio of sp^3/sp^2 -bonds in ta-C thin films. In order to avoid false results, additional investigations using XPS spectroscopy are necessary, which can help to evaluate objectively the content of sp^3 -bonds in the structure of the synthesized amorphous carbon thin films. The data obtained by XPS spectroscopy have shown that the presence of microparticles on the surface of the ta-C coating has no significant effect on the determined content of sp^3 -bonds. A high, constant amount of sp^3 carbon bonds of $\sim 85\%$ was found in all deposited ta-C thin films with the thickness from 20 to 280 nm. XPS spectroscopy results are in good agreement with the FWHM values of the G-peak obtained for visible wavelength of $\lambda = 514$ nm, which point to the importance of the

determination of the G-peak FWHM in the estimation of the content of sp^3 -bonds in thin ta-C coatings. Results obtained with the use of XPS spectroscopy demonstrate the possibility to synthesize by pulse vacuum arc method, using a water-cooled Venetian blind plasma filter, the ta-C thin films with a high content of sp^3 fraction.

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REFERENCES

1. V.E. Strel'nitskij and I.I. Aksenov. *Diamond-like carbon films*. Kharkov: NSC "Kharkov Institute of Physics and Technology", 2006.
2. I.I. Aksenov, A.A. Andreev, V.A. Belous, V.E. Strel'nitskij, V.M. Khoroshikh. *Vacuum arc*. Kiev: "Naukova Dumka", 2012.
3. J. Robertson. Diamond-like amorphous carbon // *Mater. Sci. Eng.* 2002, R 37, p. 129-281.
4. Y. Lifshitz. Diamond-like carbon-present status // *Diam. Relat. Mater.* 1999, v. 8, p. 1659-1676.
5. D.R. McKenzie. Tetrahedral bonding in amorphous carbon // *Rep. Prog. Phys.* 1996, v. 59, p. 1611-1664.
6. S. Iijima. Direct observation of the tetrahedral bonding in graphitized carbon black by high-resolution electron microscopy // *Jour. Crys. Grow.* 1980, v. 50, N 3, p. 675-683.
7. N. Wada, P.J. Gaczl, and S.A. Solin. Diamond-like 3-fold coordinated amorphous carbon // *J. Non-Cryst. Solids*. 1980, v. 35-36, p. 543-548.
8. R.O. Dillon and John A. Woollam. Use of Raman scattering to investigate disorder and crystallite formation in as-deposited and annealed carbon films // *Phys. Rev.* 1984, v. B 29, N 6, p. 3482-3489.
9. F. Li, J. Lannin. Radial distribution function of amorphous carbon // *Phys. Rev. Lett.* 1990, v. 65, N 15, p. 1905-1908.
10. N.H. Cho, D.K. Veirs, J.W. Ager III, M.D. Rubin, C.B. Hopper, D.B. Bogy. Effects of substrate temperature on chemical structure of amorphous carbon films // *J. Appl. Phys.* 1992, v. 71, N 5, p. 2243-2248.
11. F.-X. Liu, K.-L. Yao, Z.-L. Liu. Substrate bias effect on structure of tetrahedral amorphous carbon films by Raman spectroscopy // *Diam. Relat. Mater.* 2007, v. 16, p. 1746-1751.
12. B.K. Tay, X. Shi, H.S. Tan, H.S. Yang, Z. Sun. Raman studies of tetrahedral amorphous carbon films deposited by filtered cathodic vacuum arc // *Surf. Coat. Technol.* 1998, v. 105, p. 155-158.
13. M.A. Rahman, P. Maguire, S.S. Roy, R. McCann, F. McKavanagh, J.A. McLaughlin. Sp^3 content in ta-C films vs pulse bias width to the substrate: A correlative structural analysis // *Diam. Relat. Mater.* 2009, v. 18, p. 1343-1347.
14. V. Zavaleyev, J. Walkowicz, G. Greczynski, L. Hultman. Effect of substrate temperature on properties of diamond-like films deposited by combined DC impulse vacuum-arc method // *Surf. Coat. Technol.* 2013, v. 236, p. 444-449.
15. M. Chhowalla, A.C. Ferrari, J. Robertson, and G.A.J. Amaratunga. Evolution of sp^2 bonding with deposition temperature in tetrahedral amorphous carbon studied by Raman spectroscopy // *Appl. Phys. Lett.* 2000, v. 76, N 11, p. 1419-1421.
16. M.C. Polo, J.L. Andujar, A. Hart, J. Robertson, W.I. Milne. Preparation of tetrahedral amorphous carbon films by filtered cathodic vacuum arc deposition // *Diam. Relat. Mater.* 2000, v. 9, p. 663-667.
17. J. R. Shi, X. Shi, Z. Sun, S.P. Lau, B.K. Tay, H.S. Tan. Resonant Raman studies of tetrahedral amorphous carbon films // *Diam. Relat. Mater.* 2001, v. 10, p. 76-81.
18. W.G. Cui, Q.B. Lai, L. Zhang, F.M. Wang. Quantitative measurements of sp^3 content in DLC films with Raman spectroscopy // *Surf. Coat. Technol.* 2010, v. 205, p. 1995-1999.
19. P. Lemoine, J.P. Quinn, P.D. Maguire, J.A.D. McLaughlin. Measuring the thickness of ultrathin diamond-like carbon films // *Carbon*. 2006, v. 44, N 13, p. 2617-2624.
20. T.J. Moravec. Color chart for diamond-like carbon films on silicon // *Thin Solid Films*. 1980, v. 70, p. L9.
21. K.W.R. Gilkes, S. Prawer, K.W. Nugent, J. Robertson, H.S. Sands, Y. Lifshitz, X. Shi. Direct observation of sp^3 -bonding in tetrahedral amorphous carbon using ultraviolet Raman spectroscopy // *Appl. Phys. Lett.* 1980, v. 70, p. 1980-1982.
22. S. Prawer, K.W. Nugent, Y. Lifshitz, G.D. Lempert, E. Grossman, J. Kulik, I. Avigal, R. Kalish. Systematic variation of the Raman spectra of DLC films as a function of $sp^2:sp^3$ composition // *Diam. Relat. Mater.* 1996, v. 5, N 3-5, p. 433-438.
23. S. Gayathri, R. Krishnan, T.R. Ravindran, S. Tripura Sundari, S. Dash, A.K. Tyagi, B. Raj, M. Sridharan. Spectroscopic studies on DLC/TM (Cr, Ag, Ti, Ni) multilayers // *Materials Research Bulletin*. 2012, v. 47, p. 843-849.
24. S. Neuville. *Carbon Structure Analysis with Differentiated Raman Spectroscopy: Refined Raman Spectroscopy Fundamentals For Improved Carbon Material Engineering*. LAP Lambert Academic Publishing, 2014.
25. A.C. Ferrari and J. Robertson. Raman spectroscopy of amorphous, nanostructured, diamond-like carbon, and nanodiamond // *Philos. Trans. R. Soc. London*. 2004, v. A 362, p. 2477-2512.
26. T.R. Ravindran, B.R. Jackson, and J.V. Badging. UV Raman Spectroscopy of Single-Walled Carbon Nanotubes // *Chem. Mater.* 2001, v. 13, p. 4187-4191.
27. J. Schwan, S. Ulrich, V. Batori, H. Ehrhardt. UV Raman spectroscopy on amorphous carbon films // *J. Appl. Phys.* 1996, v. 80, N 1, p. 440-447.

28. V.I. Merkulov, J.S. Lannin, C.H. Munro, S.A. Asher, V.S. Veerasamy, and W.I. Milne. Studies of Tetrahedral Bonding in Diamondlike Amorphous Carbon // *Phys. Rev. Lett.* 1997, v. 78, p. 4869-4872.
29. Th. Kohler, Th. Frauenheim, and G. Jungnickel. Stability, chemical bonding, and vibrational properties of amorphous carbon // *Phys. Rev.* 1995, v. B 52, N 16, p. 11837-11844.
30. D. Drabold, P.A. Fedders, Petra Stumm. Theory of diamondlike amorphous carbon // *Phys. Rev.* 1994, v. B 49, N 23, p. 16415-16422.
31. M. Profeta, F. Mauri. Theory of resonant Raman scattering of tetrahedral amorphous carbon // *Phys. Rev.* 2001, v. B 63, p. 245415-245415.
32. V. Pajcini, C.H. Munro, R.W. Bormett, R.E. Witkowski, and S.A. Asher. UV Raman Microspectroscopy: Spectral and Spatial Selectivity with Sensitivity and Simplicity // *Appl. Spectroscopy.* 1997, v. 51, N 1, p. 81-86.
33. A.C. Ferrari and J. Robertson. Interpretation of Raman spectra of disordered and amorphous carbon // *Phys. Rev.* 2000, v. B 61, p. 14095-14107.
34. K.W.R. Gilkes, S. Praver, K.W. Nugent, J. Robertson, H.S. Sands, Y. Lifshitz, X. Shi. Direct quantitative detection of the sp^3 bonding in diamond-like carbon films using ultraviolet and visible Raman spectroscopy // *J. Appl. Phys.* 2000, v. 87, N 10, p. 7283-7289.
35. V. Zavaleyev. *Optimization of device construction and deposition technology of ta-C coatings using Taguchi method of experiment design*: Dissertation, Lodz University of Technology. Lodz, 2015.
36. V. Zavaleyev, J. Walkowicz. Application of the Taguchi approach of the design of experiments for determination constructional and working parameters of the linear Venetian blind microdroplet filter // *Vacuum.* 2012, v. 86, p. 1248-1254.
37. C. Ferrari, J. Robertson. Resonant Raman spectroscopy of disordered, amorphous, and diamond like carbon // *Phys. Rev.* 2001, v. B 64 p. 075414-1-075414-13.
38. A.C. Ferrari, S.E. Rodil, J. Robertson. Resonant Raman spectra of amorphous carbon nitrides: the G-peak dispersion // *Diam. Relat. Mater.* 2003, v. 12, p. 905-910.
39. S. Neuville, A. Matthews. A perspective on the optimisation of hard carbon and related coatings for engineering applications // *Thin Solid Films.* 2007, v. 515, p. 6619-6653.
40. J. Diaz, G. Paolicelli, S. Ferrer, and F. Comin. Separation of the sp^3 and sp^2 components in the C1s photoemission spectra of amorphous carbon films // *Phys. Rev.* 1996, v. B54, p. 8064-8069.
41. P. Merel, M. Tabbal, M. Chaker, S. Moisa, J. Margot. Direct evaluation of the sp^3 content in diamond-like-carbon films by XPS // *Appl. Surf. Sci.* 1998, v. 136, p. 105-110.
42. Namwoong Paik. Raman and XPS studies of DLC films prepared by a magnetron sputter – type negative ion source // *Surf. Coat. Technol.* 2005, v. 200, p. 2170-2174.
43. Y.X. Leng, J.Y. Chen, P. Yang, H. Sun, G.J. Wan, N. Huang. Mechanical properties and platelet adhesion behavior of diamond-like carbon films synthesized by pulsed vacuum arc plasma deposition // *Surf. Sci.* 2003, v. 531, p. 177-184.
44. A. De Bonis, J.V. Rau, A. Santagata, R. Teghil. Diamond-like carbon thin films produced by femtosecond pulsed laser deposition of fullerite // *Surf. Coat. Technol.* 2011, v. 205, p. 3747-3753.
45. J.V. Rau, R. Teghil, A. De Bonis, A. Generosi, B. Paci, R. Generosi, M. Fosca, D. Ferro, V. Rossi Albertini, N.S. Chilingarov. Pulsed laser deposition of hard and superhard carbon thin films from C60 targets // *Diam. Relat. Mater.* 2010, v. 19, p. 7-14.

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ОПРЕДЕЛЕНИЕ ФРАКЦИИ SP^3 В ta-C-ПОКРЫТИИ С ИСПОЛЬЗОВАНИЕМ XPS И РАМАН-СПЕКТРОСКОПИИ

В. Завалеев, Ж. Валкович, М. Савчак, М. Клейн, Д. Мозинский, Р. Шодун, К. Зденек

Представлены результаты исследования структуры тетраэдральных аморфных углеродных пленок (ta-C) толщиной в интервале 20...280 нм, осажденных методом импульсной вакуумной дуги с электромагнитным жалюзи плазменного фильтра. Результаты фазово-структурного анализа, полученные методами спектроскопии комбинационного рассеяния света в видимом и УФ-диапазонах, демонстрируют сильную зависимость результатов от наличия на поверхности тонких углеродных пленок микрочастиц даже в минимальном количестве. Присутствие микрочастиц в осажденных покрытиях сильно влияет на точность измеренных данных, используемых далее для вычисления соотношений I_D/I_G , I_T/I_G и определения дисперсии G-пика для покрытий всех толщин, что приводит к значительному разбросу данных при оценке связей в осажденных пленках.

ВИЗНАЧЕННЯ ФРАКЦІЇ SP^3 У $ta-C$ -ПОКРИТТІ З ВИКОРИСТАННЯМ XPS І РАМАН-СПЕКТРОСКОПІЇ

В. Завалев, Ж. Валкович, М. Савчак, М. Клейн, Д. Мозинський, Р. Шодун, К. Зденек

Представлені результати дослідження структури тетраедральних аморфних вуглецевих плівок ($ta-C$) завтовшки в інтервалі 20...280 нм, осаджених методом імпульсної вакуумної дуги з електромагнітним жалюзі плазмового фільтра. Результати фазово-структурного аналізу, що отримані методами спектроскопії комбінаційного розсіяння світла у видимому і УФ-діапазонах, демонструють велику залежність результатів від наявності на поверхні тонких вуглецевих плівок мікрочасток навіть у мінімальній кількості. Присутність мікрочасток в осаджених покриттях дуже впливає на точність виміряних даних, що використовувалися для обчислення співвідношень I_D/I_G , I_T/I_G і визначення дисперсії G -піка для покриттів усієї товщини, що призводить до значного розкиду даних при оцінці зв'язків в осаджених плівках.