

Auger analysis of plasma treated ultrananocrystalline diamond films

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Ultrananocrystalline diamond films have attracted great research interest due to their properties approaching those of diamond. In a cycle of works we study the treatment of such layers in oxygen or ammonia plasma. In the first case the treatment time is tracked; and in the second one we monitor the influence of different additions (fluorophore, maleimide, etc.). In the current work the accent falls on the Auger analysis (AES). With a view to the electronic spectroscopies, this is a research of the partial monoatomic overlayer. Since there is more than one adsorbate, it suggests a solution for the general case of n adsorbed elements giving their fractional monolayer coverage. This solution is an approximation for energy above 150 eV, however, it is exact in respect of the magnitude of the fractional monolayer coverage.

The research showed a significant surface modification of the ultrananocrystalline diamond films in oxygen and ammonia plasma. The fractional monolayer coverage is in the range of dozens of percentages. The monolayer coverage model gives values for the adsorbed quantities about 1.9 times higher as compared to the values, obtained by the homogeneous one. The comparison between AES and X-ray photoelectron spectroscopy (XPS) results for the coverages, shows qualitative similarity.

The usage of realistic model of the adsorbed layer is crucial for the quantification.

Key words: ultrananocrystalline diamond films, Auger analysis, monolayer coverage

INTRODUCTION

All types of diamond films (single-, poly- (PCD), nano- (NCD), and ultrananocrystalline (UNCD) [1, 2]) have recently attracted an increasing interest for applications in biotechnologies, especially as a template for the functionalization with biomolecules, e.g. for biosensors or DNA chips [3–5]. Besides the intrinsic extreme properties of the diamond films such as the high hardness, the chemical inertness, the high thermal conductivity, and the high optical transparency which are to a large extent preserved in the diamond films, and their general bioproperties such as biocompatibility, bioinertness, and non-fouling character, there are a number of surface properties making the diamond films extremely attractive for such applications. They can be prepared either H- or O-terminated, giving a way to either hydrophobic or hydrophilic chemistries. Almost all diamond surfaces are H-terminated after the growth, and these surfaces are

rather stable [3, 4, 6], i.e. they can not be easily modified by simple chemical treatment in order to achieve, for example, O- or NH₂-termination, but require photo-, thermo- or electrochemical processes. Another possibility is the application of plasmas, making use of their non-equilibrium character, and the presence of highly excited species.

In a cycle of works we report on the investigation of the surface modification of UNCD films by oxygen and ammonia plasmas by means of surface sensitive analytical techniques, namely Auger electron spectroscopy (AES) and X-ray photoelectron spectroscopy (XPS). With a view to the electronic spectroscopies, this is a research of the partial monoatomic overlayer. In the current work the accent falls on the Auger analysis.

Theory

Seah [7] is the first to give accurate expressions for the Auger signals in the monolayer coverage. The model for substrate from element B with coverage from the element A, considers Auger signal from the substrate with two components: the first from the non-covered ($1 - \Phi_A$) part and the

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second from beneath the covered part, Φ_A . Analytic expression binds the fractional monolayer coverage, Φ_A , with the Auger intensities I_A and I_B .

For Φ_A the equation [7, 8] is obtained:

$$\frac{\Phi_A \{1 - \exp[-a_A / \lambda_A(E_A) \cos \theta]\}}{1 - \Phi_A \{1 - \exp[-a_A / \lambda_A(E_B) \cos \theta]\}} = \left[\frac{1 + r_A(E_A)}{1 + r_B(E_A)} \right] \frac{I_A / I_A^\infty}{I_B / I_B^\infty} \quad (1)$$

in which a_A means characteristic linear size of the atom A ; $\lambda_M(E_i)$ and $r_M(E_i)$ – respectively, the length of the attenuation and the back-scattering term of the electrons with energy E_i in matrix M ; I_i^∞ – the Auger signal from a pure sample of the element i , and $\cos \theta$ has typical value of 0.74 for the cylindrical mirror analyser. For energy above 150 eV and if Φ_A is small, Eqns. (1) is reduced to:

$$\Phi_A = Q_{AB} \frac{I_A / I_A^\infty}{I_B / I_B^\infty} \quad (2)$$

with a symbol Q for the matrix factor of the monolayer coverage:

$$Q_{AB} = \left[\frac{\lambda_A(E_A) \cos \theta}{a_A} \right] \left[\frac{1 + r_A(E_A)}{1 + r_B(E_A)} \right] \quad (3)$$

We will point out that Eqns. (1), (2) and (3) are relevant for quantification of XPS data too, with the only difference that in this case $r_M(E_i) = 0$.

EXPERIMENTAL

The ultrananocrystalline diamond films were prepared by microwave plasma chemical vapor deposition from CH_4/N_2 gas mixture with 17% methane. UNCD films consist of diamond nanocrystallites with diameters of 3–5 nm, embedded in an amorphous carbon matrix with grain boundary width of 1–1.5 nm. The volume ratio between the two phases, the crystalline and the amorphous, is close to one.

In the experiments with oxygen-plasma treatment it changes the exposition time. In the others we examine the influence of the combination of O_2 - and NH_3 -plasma treatment with several technologies. 1. NH_3/N_2 -plasma treatment (for 10 min.), marked in the text as “ NH_3 ” (gas flows of 50 sccm of NH_3 and 950 sccm of N_2); 2. SAMSA attachment (SAMSA concentration of 2 mM, for 15 h), marked in the text as “FI” (the thiol-bearing SAMSA fluorescein is prepared from 5-((2-(and-3)-S-(acetylmercapto)succinoyl) amino) fluorescein, A-685, Invitrogen, dissolved in NaOH , neutralized with concentrated HCl , and buffered with sodium phosphate); 3. Mitsunobu reaction after O_2 -plasma

treatment, marked in the text as “ $\text{O}_2 + \text{M}$ ” (Triphenylphosphane Ph_3P was diluted with tetrahydrofuran (anhydrous) THF. Di-isopropyl-azodicarboxylate DIAD was added at 0 °C and the samples with oxygen terminated UNCD/a-C composite films were immersed into the mixture for 1 min, and stirred for 5 min. Then, N-substituted maleimide (0,029 g) was added as a solid to the reaction mixture. It was kept for about 5 min at low temperature for maleimide dissolving. The reaction mixture was stirred overnight at ambient temperature); 4. Mitsunobu reaction and SAMSA attachment after O_2 -plasma treatment, marked in the text as “ $\text{O}_2 + \text{M} + \text{FI}$ ”; 5. SSMCC attachment after NH_3/N_2 -plasma treatment (1.5 mM SSMCC solution, for 24 h), marked in the text as “ $\text{NH}_3 + \text{SSMCC}$ ” (SSMCC (sulfosuccinimidyl 4-(N-maleimidomethyl) cyclohexane-1-carboxylate) dissolved in TEA solution (150 nM solution of triethanolamine (TEA) in deionized water)).

More details for the experiment and for the results from it can be found in our work [9].

The Auger analysis was performed in the differential mode at primary electron energy $E_p = 3$ keV ($I_E = 0.07 \mu\text{A}$, $V_{\text{mod}} = 4 V_{\text{ptp}}$, $\Delta E/E = 0.3\%$). The most intense Auger peaks of C (272 eV), N (381 eV), and O (510 eV) were monitored, as well as those of Si (92 eV), S (152 eV), and F (650 eV); the concentration of the last 3 elements was below the sensitivity of our analysis. (Ion milling of the surface was not performed in order to prevent its amorphisation and/or graphitisation.) The analyzed area is with a spot size of $\sim 5 \mu\text{m}$. Usually, the analysis is performed in 5 points from the sample surface, after which the values of the measured intensities are averaged, if there are not any major differences between them. Otherwise, more analyses are made, up to 20. The intensity is measured “peak to peak”. The quantification is made by comparison with the standard samples of SiO_2 , AlN , and graphite.

RESULTS

Generalized formulae for monolayer coverage in the case of several adsorbates

In the case of n adsorbates of the elements A_k , covering the substrate (B), analogically to the reasoning [8] behind the deduction of Eqns. (1), we reach a system of N equations for the degree of coverage Φ_k . For energy above 120 eV, the system becomes linear. Its solution is:

$$\Phi_{A_k} = \left[\frac{\lambda_{A_k}(E_{A_k}) \cos \theta}{a_{A_k}} \left[\frac{1+r_{A_k}(E_{A_k})}{1+r_{B_k}(E_{A_k})} \right] \frac{I_{A_k}/I_{A_k}^\infty}{I_B/I_B^\infty} \left\{ 1 + \sum_i \frac{\lambda_{A_i}(E_{A_i})}{\lambda_{A_i}(E_B)} \cdot \frac{1+r_{A_i}(E_{A_i})}{1+r_{B_k}(E_{A_i})} \cdot \frac{I_{A_i}/I_{A_i}^\infty}{I_B/I_B^\infty} \right\}^{-1} \quad (4)$$

Here Φ_k is the fractional monolayer coverage of the element A_k , while the other symbols are as in Eqns. (1), juxtaposed to the element with the corresponding index.

In our case of three elements (O and N above C), the common denominator in the matrix factor of Eqns. (4) is:

$$Q' = \left[1 + \frac{\lambda_O(E_O)}{\lambda_O(E_C)} \cdot \frac{1+r_O(E_O)}{1+r_O(E_C)} \cdot \frac{I_O/I_O^\infty}{I_C/I_C^\infty} + \frac{\lambda_N(E_N)}{\lambda_N(E_C)} \cdot \frac{1+r_N(E_N)}{1+r_N(E_C)} \cdot \frac{I_N/I_N^\infty}{I_C/I_C^\infty} \right]^{-1} \quad (5)$$

Experimental Auger data

The measured relative intensities from the experiments with an oxygen-plasma treatment are shown in Fig. 1, while those with an NH_3 -plasma treatment in Fig. 2.

Quantification

The data from Fig. 1, quantificated by Eqns. (2) and (3), are presented in Table 1, while those from Fig. 2, quantificated by Eqns. (4) and (5), are presented in Table 2. In the tables Φ_k is a symbol for the degree of coverage with the element k , normalized to the area of the atom (In terms of the model, this is the square of his covalent diameter.). The symbol $\Phi_{k/C}$ is for degree of coverage, defined as ‘number of adsorbed atoms on atom from the substrate’.

The data from the XPS analysis are presented in the last column of Tables 1 and 2.

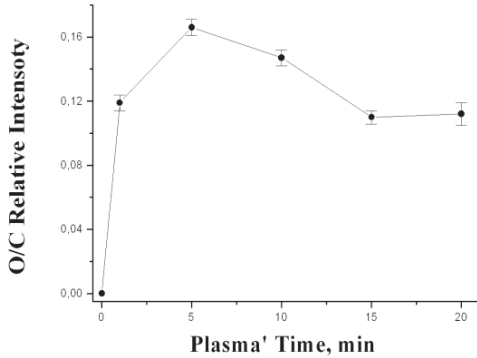


Fig.1. Dependence of the relative intensity of the oxygen Auger signal (towards the carbon) from the time of treatment with oxygen plasma.

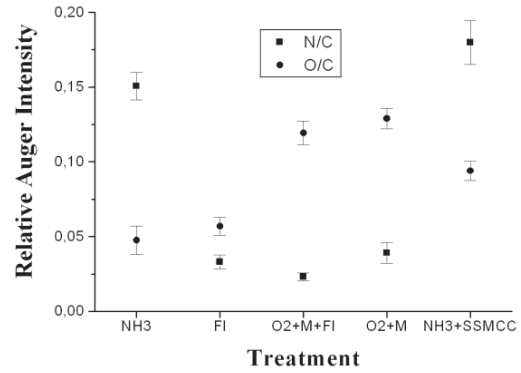


Fig. 2. Relative intensity of the oxygen and nitrogen Auger signal (towards the carbon) for different treatments with ammonium plasma.

The attenuation lengths, appearing in the formulas, are obtained from a predictive formula of TPP-2M in the database [10]. The covalent atomic radiuses of oxygen and nitrogen are taken from the NIST database. The back-scattering term calculation, necessary for the matrix correction, is done according to [11]. More procedure details are presented in section ‘Discussion’.

Table 1. AES data quantification of the oxygen-plasma experiments (The notation is in the text).

Time, min	Φ_O , %	C_O , at. %	O/C-atom	OIS, at. % (XPS)
1	7.6	4.5	0.14	15.45
5	10.6	6.2	0.20	14.10
10	9.4	5.5	0.18	15.07
15	7.1	4.2	0.13	16.00
20	7.2	4.2	0.14	15.02

Table 2. AES data quantification of the experiments combined O_2 - and NH_3 -plasma treatment with several technologies (The notation is in the text).

Treatment	Adsorbed Oxygen				Adsorbed Nitrogen			
	Φ_{O_s} , %	C_{O_s} , at. %	O/C-atom	$O1s$, at. % (XPS)	Φ_{N_s} , %	C_{N_s} , at. %	N/C-atom	$N1s$, at. % (XPS)
NH_3 PI (10 min)	2.8	1.8	0.05	3.12	10	4.8	0.17	7.39
FI	3.5	2.2	0.07	5.97	2.4	1.1	0.04	1.35
O_2 PI + M + FI	7.2	4.5	0.14	12.30	1.6	0.74	0.03	1.21
O_2 PI (10 min) + M	7.7	4.8	0.14	–	2.7	1.3	0.04	–
NH_3 PI + SSMCC	5.5	3.4	0.10	8.18	12	5.6	0.20	7.34

DISCUSSION

Although it remains semi-quantitative, the surface evaluation, done by this method, is much more accurate compared to that of the homogeneous model of the surface (where the matrix correction is disregarded). The obtained numerical result of the surface is 2 to 8 times bigger [7] (we have an average of 1.9 in our case). By reason of interpretation through ‘the common’ Auger quantification, the atoms from the monolayer coverage are looked at as distributed in greater volume (determined from the information depth), apparently their concentration is lower.

We would like to highlight, that the formula derivation (4) is not linked with the magnitude Φ_i , i.e. Eqns. (4) are always valid, and are not approximated to Φ_i . This is important because in the case of heterogeneous coverage, it can turn out that the total degree of the coverage is not small, although every of its components is small (i.e., $\Phi_i \ll 1$, but not $\sum \Phi_i \sim 1$).

The used model suggests covering the substrate with the material from the standard sample (‘overlayer’ experiment). The calculated degree of coverage measure is the average atom size from the standard, a . All of this is clearly defined in the deposition of metal over metal. The adsorption of an element, for which there is no elemental standard (usually metalloid or gas), requires a comment. The formal approach is to assume coverage of hypothetical substance which has the same structure as the standard but consists of adsorbate atoms only. However, we now have Φ depending on the standard which is disturbing at first sight. But if we take in consideration that in the case of other standard we have to introduce matrix

correction too, the detailed deduction according to the model gives us that $\Phi \sim a^2$. a reflects the atom density (in the volume a^3 there is one atom). The actually covered area a^2 (‘occupied’ by single adsorbed atom), is the S/a^2 -part, where S the actual size of the atom, calculated with the corresponding atom radius. That is to say that in such normalization of the atom area, Φ depends on the type of the adsorbed atom only, but not on the used standard.

In the discussed case (of adsorption of an element, which does not have elemental standard), the maximum degree of coverage depends on the system (A, B) and the conditions, in which the process takes place. Maximum coverage is attainable in the case of chemisorption, and it could be less than the determined coverage through the atomic radius (considered as 100%). If the object of the experimental study is not the adsorption itself, additional data for the physical chemistry of the surface are necessary for the determination of Φ_{max} [12]. It may turn out to be more useful if the result is presented as a ‘number of adsorbed atoms on atom from the substrate’. In the studied case, the adsorption of non-activated gas (oxygen or nitrogen) is not present even in the case of atmospheric pressure. Apparently, the plasma activates the chemi-sorption. But a C-atom from the surface has one free valance bond with which it can connect to the adsorbed species. The maximum degree of coverage can be achieved if every atom from the surface joins one adsorbed particle. For example, for the last sample in Table 2 there is a particle at three of every 10 surface atoms (two particles, including oxygen atom and one, including nitrogen atom).

Main requirement for the accuracy in the determination of degree of coverage is to know the attenuation length of the electrons, λ . It would be best if reliable experimental data are used. The lack of such for the nitrogen standard used by us, made us use the both standards with the same priority, i.e. predictive formulae. (For instance, in [13] through Elastic peak and reflected electron loss spectrum (REELS) measurements 1.75 nm are obtained for SiO₂; and 1.77 nm are obtained through TPP-2. For Si₃N₄; however, the respective figures are 1.12 nm and 1.41 nm). In the case of metal over metal deposition, λ can be determined by overlayer experiment, too.

The comparison between AES and XPS results on the coverages shows similar quality behavior. The quantity difference in the results suggests for a systematical error. The probable reason for this is the difference in the readings of the surface carbon contamination of both of the spectroscopic methods [8]. The different composition of standards, as well as the area and the place of the analysis, may have significant contribution. (In the case of XPS, the area is 400 × 700 μm but the analysis is in three points).

CONCLUSIONS

The research showed a significant surface modification of the ultrananocrystalline diamond films in oxygen and ammonia plasma. Chemisorbed oxygen and nitrogen are observed. The fractional monolayer coverage is of order of about ten per cent. The comparison between AES and XPS results for the coverages shows qualitative similarity.

Oxygen and nitrogen content, calculated by the model of the monolayer coverage, is about 1.9 times bigger, compared to the same obtained by using homogeneous model of the surface.

The usage of realistic model of the adsorbed layer is crucial for the quantification.

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ОЖЕ-АНАЛИЗ НА ПЛАЗМЕНО ТРЕТИРАНИ УЛТРАНАНОКРИСТАЛНИ ДИАМАНТЕНИ СЛОЕВЕ

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(Резюме)

Ултра-нанокристалните диамантени слоеве привличат голям изследователски интерес, поради свойствата им, близки до тези на диаманта. В цикъл научни трудове изследваме третирането на такива слоеве с кислородна и амонячна плазма; в първия случай – от продължителността на третирането, а във втория – влиянието на различни добавки (флуорофор, малеимид и т.н.). В настоящата работа ударението пада на Оже анализите. От гледна точка на електронните спектроскопии, това е изследване на частично покритие от моно-атомен слой. Тъй като присъстващите адсорбати са повече от един, се предлага решение за общия случай за n адсорбирани химични елемента, даващо тяхното частично от моно-слоино покритие. Решението е в сила за енергии на следените Оже пикове над 120 eV, но то е точно спрямо степента на покритие.

Изследванията показаха значително повърхностно изменение на ултрананокристалните диамантени слоеве в кислородна и амонячна плазма. Частичното моно-слоино покритие е от порядъка на десетия процента. Този резултат (пресметнат по модела за моно-слоино покритие) е около 1.9 пъти по-голям в сравнение с резултата, използващ хомогенен модел на повърхността. Сравнението между Оже резултатите за покритията и тези от Рентгенова Фотоелектронна Спектроскопия (РФС) показва качествено подобие.

Използването на реалистичен модел за адсорбиран слой е решаващо за количествения анализ.