ВЛИЯНИЕ НА ВИСОКО ЕНЕРГИЙНО ИМПУЛСНО-ДЪГОВО КАТОДНО РАЗПРАШАВАНЕ ПРИ ОТЛАГАНЕ НА СВОБОДНИ ОТ ВОДОРОД ТЕТРАХЕДРАЛНИ АМОРФНИ ВЪГЛЕРОДНИ ПОКРИТИЯ (ta-C)

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Абстракт: *Физичните свойства на отложени филми на въглеродна основа са силно зависими от съотношението на sp2 (графитоподобни) към sp3 (диамантоподобни) връзки. В “Subplantation model" на Lifshitz et al. и на Robertson, йони с достатъчна енергия при сблъскване проникват под повърхността на растящия филм, и увеличават местната плътност. Йоните с по-ниска енергия няма да могат да проникнат под повърхността и ще образуват sp2 връзки. Следователно структурата на отложените филми се определя главно от енергията на въздействието на въглеродните йони върху субстрата и последващия ефект на релаксация, свързан с температурата по време на отлагането. За това изследване филмите са отложени с помощта на импулсно-дъгова технология. Има ясни факти как скоростта на отлагане влияе върху нанотвърдостта и грапавостта на покритията. Установено е също така, че легиращи елементи могат значително да увеличат скороста на отлагане.*

Ключови думи: *Тетрахедрален аморфен Въглерод (ta-C); Енергийно въздействащи йони; Импулсно-дъгова технология; sp2 (графитоподобни) към sp3 (диамантоподобни) връзки.*

INFLUENCE OF PULSED ARC ENERGETIC CONDENSATION ON DEPOSITION OF ta-C FILMS

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Abstract: *The physical properties of deposited Carbon-based films are strongly dependent on the ratio of* sp^2 *(graphite-like) to* sp^3 *(diamond-like) bonds. In the “Subplantation model” of Lifshitz et al. and of Robertson, incident ions of sufficient energy penetrate the surface of the growing film, enter interstitial subsurface and increase the local density. The ions with lower energy will not be able to penetrate the surface and will form* sp^2 *bonds. Thus, the structure of the deposited films is mainly determined by the energy of the impinging the substrate Carbon ions and the following relaxation effect linked with the temperature during deposition. For this study films were deposited using pulsed arc technic. There are clear facts how deposition rate influences the nano-hardness and roughness of the coatings. It was also found that dopants can significantly increase the deposition rates.*

Keywords: *Tetrahedral amorphous Carbon, ta-C; Energetic impinging ions; Subplantation; Pulsed arc technic;* sp^2 *(graphite-like) and* sp^3 *(diamond-like) bonds.*

1. Introduction

The deposition of hard-amorphous Carbon films requires high energy of all impinging particles for film formation [1,2]. These conditions are met by a cathodic arc plasma deposition process whereby a vacuum arc discharge on the surface of a solid graphite cathode generates positively charged Carbon ions. A hydrogen-free DLC film can then be formed on the surface of a substrate placed under an electrically negative potential. Once the ions arrive at the surface, the Carbon atoms bond together forming a matrix. Normal bonding behavior of molecular orbitals is by bonding in the same orbital type. In comparison with other elements Carbon behaves differently by bonding in form of hybridization [3, 4]. The concept of hybrid orbitals has been hypothesized to give a more complete description of the process of bond formations with the promoted states of Carbon. The result is a mixed state formed out of one *s*-orbital and three p-orbitals, namely $p_x/p_y/p_z$. A sp^3-configuration is a combination of hybrid orbitals forming a tetrahedral assembly with the center of masses in the corners. The characteristic angle between the hybrid orbitals is 109.5° [4]. Likewise, instead of using four orbitals to form hybrids, we can form sp^2 hybrid orbitals by superposition of an *s*-orbital and two *p* -orbitals [4, 5]. The sp^2-hybridization is the combination of one s -orbital with only two *p* -orbitals, namely p_x and p_y. They contribute together to form a planar assembly with a characteristic bond angle of 120°.

In the past two decades, the deposition process of *ta-C* films was analyzed, and good models proposed such as the "Subplantation model" of Lifshitz et al. [1], [2], [6] and of Robertson [7]. Based on these models, it is already known that the formation of *ta-C* films is due to an internal subsurface growth induced by shallow Carbon ion implantation. In subplantation, incident ions of sufficient energy penetrate the surface of the growing film, enter interstitial subsurface and increase the local density [8]. Penetration can occur either by direct entry in the matrix or by knock-on displacement. The ions with lower energy will not be able to penetrate the surface and will form sp^2 *a-C*. The ions with sufficient energy will go further under the surface of the deposited film and increase the density. In case the penetrating ions are with energy above a threshold, the excessive energy rapidly dissipates in form of a "thermal spike", followed by a relaxation in the higher density area. Thus, two processes are playing a major role in the formation of the tetrahedral amorphous Carbon films: i) densification of the regions by the newly arriving energetic Carbon ions, ii) relaxation of density.

The physical properties of the Carbon-based materials are strongly dependent on the ratio of sp^2 (graphite-like) to sp^3 (diamond-like) bonds [9]. The sp^3 fraction can vary from 0 to 90% and is strongly dependent on the deposition method [3]. Higher sp^3 fraction will result in a higher hardness and denser films. Hardness, compressive stress, and the limitation in thickness are parameters promoting instabilities of the film, leading to adhesion problems and to film delamination. From another side mechanical properties of diamond-like Carbon films can be improved by manipulating them with various doping elements like nitrogen, oxygen, silicon, niobium, tungsten, boron, titanium, and others.

Arc plasmas are fully ionized with highly energetic ions, which leads to excellent adhesion, dense deposition and in case *ta-C* films, high content of tetrahedrally oriented Carbon atoms (sp^3). A major drawback is that macro-particles (MP) are ejected onto the deposited films and lead to increased surface roughness.

This work details the deposition of hydrogen-free tetrahedral amorphous Carbon (*ta-C*) films by means of a modified arc evaporation technique. To improve the quality of the applied coatings an installation more effective than a DC arc discharge is employed. The technique utilizes a DC arc power supply that drives an arc discharge plasma and in parallel to it a Pulsed DC Power Supply that generates and overlaps steep voltage pulses onto the DC arc discharge voltage. It has been tested by co-workers from Fraunhofer IWS and INOVAP [10,11] and leads to a high-density plasma as well as increased ion bombardment [13,14,15,16].

To influence the properties of the deposited tetrahedral amorphous films, they can be manipulated by doping them with various elements. Three models are investigated here: *ta-C*, W doped *ta-C*, and B doped *ta-C* with different doping percentages, respectively.

In addition, the influence of the angle of incidence of the impinging Carbon ions on the film properties has been studied as well as the angle of emission from the target and deposition rates.

2. Experimental set up

In this study hydrogen-free tetrahedral amorphous Carbon (*ta-C*) films were obtained by means of an arc evaporation technique using a DC Arc Power Supply (100 A DC, Solvix) that drives an arc discharge plasma and in parallel to it a Pulse Power Supply (Arcus 600, ZPulser) that generates steep voltage pulses superimposed onto the DC arc discharge voltage leading to a high-density plasma as well as increased ion bombardment. Ionbond PVD 350 Tetrabond plus equipment, an industrial scale cathodic arc evaporation system was used as a base of this [12].

The DC arc power supply has a range of 40 to 100A and an intermediate value was selected. Based on specifics of the Pulsed Power Supply (PPS), the charged voltage (U_{ch}) may also be set to values up to 400V. For the tests described in this paper a Voltage charge (U_{ch}) of 150 and 250V were used. During the deposition of the *ta-C* and doped *ta-C* films, the substrate temperature T_s was kept below a threshold, also with fixed power supply parameters.

Here [12] there is more information about the experimental set up, the special substrate fixturing, and the methods adopted for film analysis.

The results from the investigation tests are described in detail below.

3. Experimental Results

3.1. Comparison ta-C DC arc and pulsed arc

Pulsed cathodic vacuum arc has higher current and plasma density than *DC* vacuum arc [13, 14, 15, 16]. Fig. 1a shows current and voltage of a DC arc on a graphite target. The voltage is varying up and down. The mean value is circa -30 Volts (olive line). The Voltage fluctuations are on a millisecond time scale.

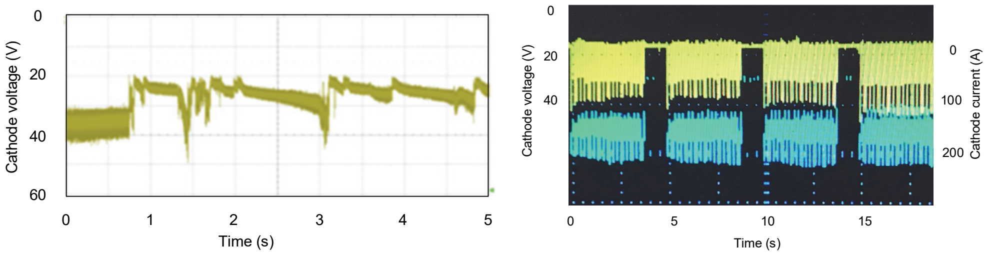

Fig. 1. *Arc voltage on a carbon target;*
a) *DC arc (left);* ***b)*** *DC and pulsed arc (right)*

The Cathode Spot (CS) sequence of ignition and extinction was observed to be very slow. An explanation for this arc behavior is that the thermal electrical resistance coefficient for Carbon up to 900°C is negative and due to this fact, an arc spot tends to remain relatively long time in the same place, therefor digging a hole in the Carbon target making the crater to become deeper and wider. When conditions for extinction of an emission center are met, the arc literally "jumps" to a new spot, causing large fluctuations in voltage. The arc "jump" can be observed, as it is often accompanied by a change of the plasma plume direction and emission of incandescently glowing macro-particles.

Fig. 1b is an example with the pulse train used in this paper for a U_{ch} of 150 V. The current reaches 200A during the pulse. In contrast with the DC arc, the pulsed arc provides a highly reproducible plasma voltage and current during each pulse as well as during the time between the pulses. Shown is the period between 2 pulse trains of 1 ms, but in fact at a timescale of minutes the arc shows the same stability. Thus, the plasma density, which closely follows the arc current curve is also highly reproducible.

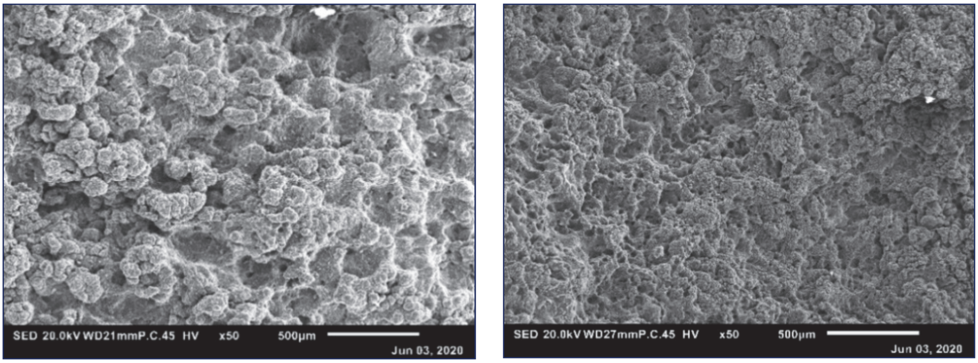

Fig. 2. *SEM image of a graphite target surface eroded after;*
a) *DC arc discharge (left);* ***b)*** *pulsed arc discharge (right)*

Fig. 2a, shows an SEM image of a graphite target surface after a DC arc discharge. It is observed that the Cathode Spots are literally "drilling" holes into the surface of the cathode. Fig. 2b, shows an SEM image of a graphite target subjected to a pulsed arc discharge at a charge Voltage of 150 V. It is observed that the craters are substantially smaller in diameter, and shallower.

3.2. Deposition rate

For the stationary case, the deposition rates were measured with samples that were fastened onto a solid block of Aluminum with monitored temperature. The deposition process was adjusted for both deposition time and cooling time intervals to keep the Aluminum block within ±5°C during deposition.

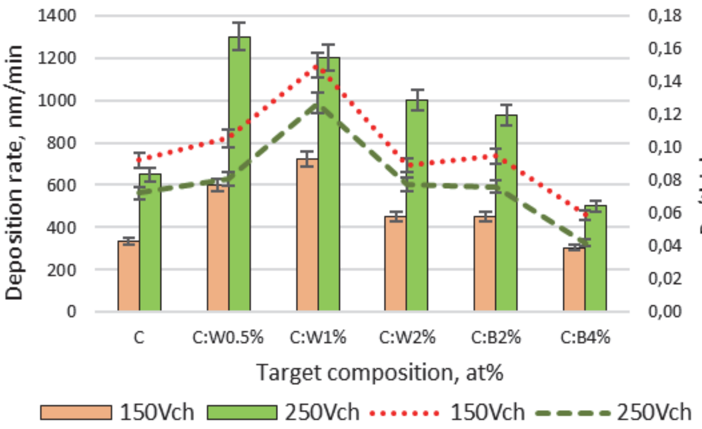

Fig. 3. *Comparison of deposition rates vs. target composition using pulsed arc with samples stationary opposite the cathode at U_{ch} 150 V and 250 V.*

In Fig. 3 deposition rates on samples opposite the cathode are plotted for different target compositions utilizing pulsed cathodic arc at 150 and 250V U_{ch}. The t*a-C* films doped with 0.5% W manifested the highest deposition rate of 1300 nm/min at a charge of 250V. All examined films deposited at 150V U_{ch} had lower deposition rates in comparison with 250V U_{ch}. All doped *ta-C-s* showed a deposition rate higher than pure *ta-C-s*, except the one for *ta-C* doped with 4% Boron. It is also evident that low level dopants (<2%) increase the deposition rate, where higher level of dopants tend to give deposition rates comparable with that of pure *ta-C*.

Film roughness was strongly influenced by the deposition rates. Films deposited with high deposition rates exhibited high R_a roughness, in contrast with the films deposited with low deposition rate which exhibited the lowest R_a roughness (Fig. 3). The comparison between the film's R_a/film thickness function deposited at 150V and 250V U_{ch} shows close to parallel data separation, where the deposited films at 250V U_{ch} exhibited lower roughness. Basically, the R_a/film thickness function for different target compositions follows a similar tendency as the deposition rate versus target compositions, but with one exception, the higher U_{ch} yields a higher deposition rate at a lower roughness.

3.3. Nano-layering with pulsed arc

In our work we were able to obtain nano-layered films deposited by means of pulsed arc discharge on HSS (1.2379) samples. These samples were investigated by Electron Energy Loss Spectroscopy (EELS) and images taken by High-Resolution Transmission Electron Microscopy (HRTEM). Nano-layering was observed on samples manipulated in two-fold rotation only. Two tests were performed, one using pulsed arc discharge technique and the other using DC arc discharge technique. Fig. 4 shows HRTEM images from the film deposited by means of DC arc discharge. Image (a) was taken under magnification of x200 and image (b) under magnification of x2'000. No nano-layering was observed, only a monolithic structure.

In contrast to the deposited films using DC arc discharge the one deposited using pulsed arc technique has clearly observed nano-layers. Fig. 5 shows the HRTEM film images from deposition by means of pulsed arc discharge. Image (a) x200 and image (b) x2,000 magnification. The period of modulation is circa 10nm. Using EELS technique, the amount of sp^2 fractions at several places was measured after cross sectioning of the sample. The sp^2-fraction was obtained from the integrated intensity ratio of C-K edge 1s→π※ peak (Iπ※) at 285.5eV of Carbon. Graphite was used as a reference. Table 1 shows the results from the EELS analyses. The measured points were numbered with the smallest number starting closest to the substrate-coating interface. Higher percentage of sp^2 bonds appeared as a lighter layer and increasing the percentage of sp^3 bonds makes the layers to appear darker. A trend is observed. The sp^2 fraction content inside the film increases with development of the film thickness respectively elevating the substrate temperature. Despite this process the main structure of the film remains unchanged, that is the periodicity, i.e., repetition of dark and light layers respectively, remains evident with different contents of sp^2 hybridizations.

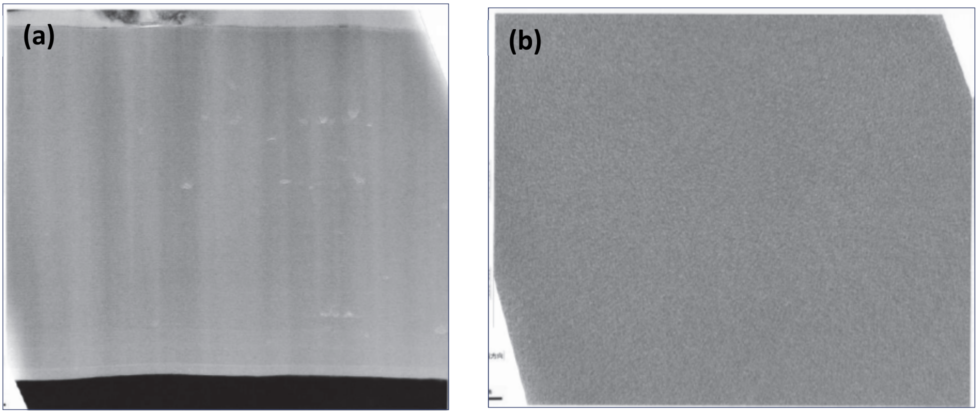

Fig. 4. ***a:*** *HRTEM image of film deposited using DC arc discharge at x200 magnification.* ***b:*** *HRTEM image of film deposited using DC arc discharge at x2.000 magnification.*

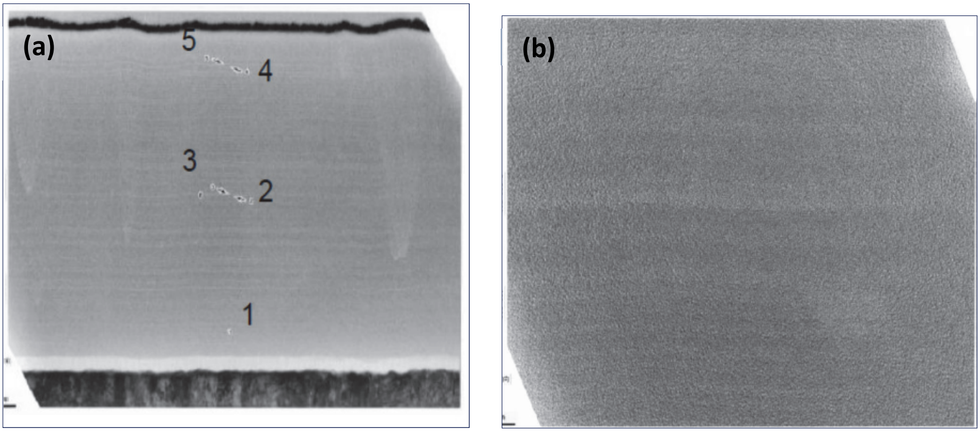

Fig. 5. ***a:*** *HRTEM image of film deposited using Pulsed arc discharge at x200 magnification.* ***b:*** *HRTEM image of film deposited using Pulsed arc discharge at x2'000 magnification.*

Point	**Color**	**EDS-C**	**EELS sp2**
droplet	Light	99.4	63%
1	Dark	99.6	25%
2	Dark	99.6	29%
3	Light	99.6	41%
4	Dark	99.6	33%
5	Light	99.4	48%

Table. 1. Results from EELS done on sample coated using pulsed arc technique.

4. Interpretation of results

4.1. henomena at the target surface

The arc spot of a DC arc discharge on the surface of a Carbon target tends to remain a long time at one location, as the electrical resistivity ***ρ*** of Carbon decreases with an increase in temperature to ~ 750° to 900°C (depending on impurities and type of graphite) and then above this temperature range rises again [17]. Thus, the arc has the tendency to stay longer at one location until the threshold temperature is reached and a new emission spot in the close neighborhood is ignited.

During a pulsed arc evaporation two sub-processes occur:

I. By applying pulsed energy, the arc current increases rapidly. The “arc spot splits” to several simultaneously active emission sites proportional to the arc current value, with a strong repulsion force between the individual sites, forcing them to move fast. This has been observed by the author but also by R. Sangines et al. and T. Schülke et al. [15, 18].

II. In addition, it was observed that by applying a short pulse the cathode Voltage climbs rapidly. For a 250V U_{ch} the cathode Voltage rises to -70V. Therefore, ionized atoms attracted back to the graphite target will deliver more energy per ion, than for a DC arc. Jüttner [19] described this phenomenon for metals. This process results in an increased temperature of the target material in the area around and in close proximity of the cathode spot. Hence, the difference in the electrical resistivity between the cathode spot and the area around it will be less and will support the ignition of a new cathode spot. When the pulse charge On time is over, there is no physical proof that the post-pulse DC arc is at the original arc spot. Further, evidence that supports this conclusion, is that the pulsed arc target utilization is higher in comparison with the DC arc target utilization, as the eroded surface by the pulsed arc discharge covers the whole surface.

Both sub-processes combine to support the formation of smaller craters. The target surface remains smoother, and the *ta-C* film is deposited with less macro-particles leading to a lower film-roughness.

4.2. Plasma related phenomena

The plasma density is much higher with pulsed arc than with DC arc. Our work confirms that films deposited using pulsed arc at 250V U_{ch} exhibit lower roughness than films deposited at 150V U_{ch} (Fig.6). This suggests that the higher plasma density and temperature with the higher charge results in reduction of size and number of particles emitted by the target.

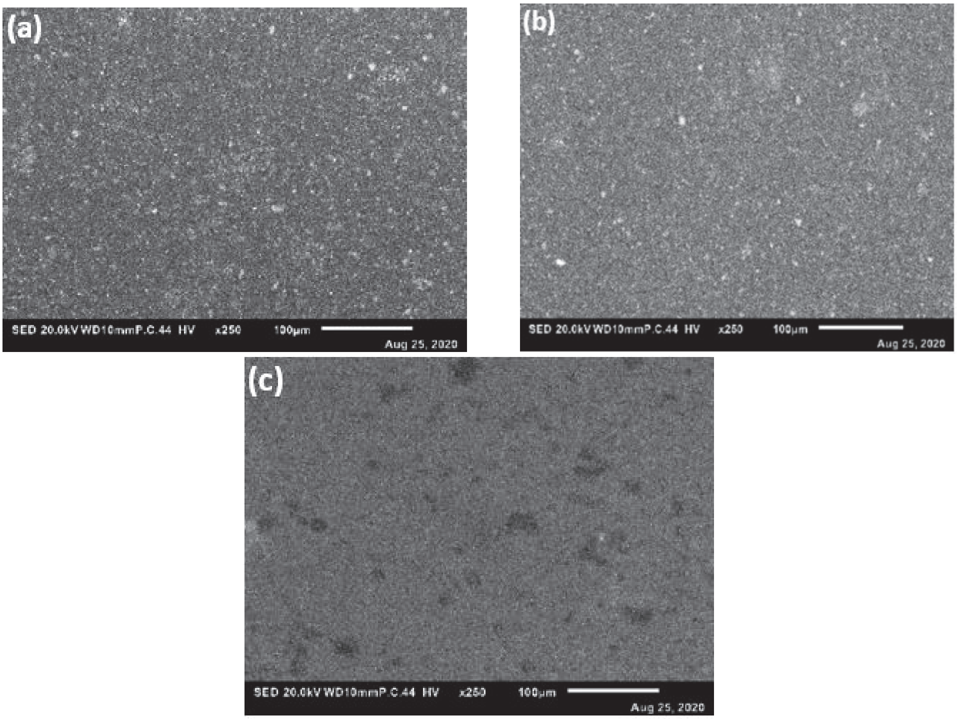

Fig. 6. *SEM images of samples coated using DC and pulsed arc.*
Single fold rotating fixture.
(a) *ta-C film coated by DC arc,* ***(b)*** *ta-C film coated by pulsed arc at 150V* U_{ch}*,*
(c) *ta-C film coated by pulsed arc at 250V* U_{ch}*.*

It has been observed that target dopants up to 1% increase the deposition rate substantially. The dopant elements W and B have a lower ionization energy than C. We assume that two phenomena play a role in the process of forming the plasma; as having lower ionization energy the dopant elements in comparison with Carbon will emit relatively more electrons, and dopant atoms in the plasma will have a higher probability to be ionized. Indeed, for W it has been observed that doubly ionized atoms occur (Fig. 3).

Higher concentration of target dopants does not enhance the deposition rate to a high degree. It is our opinion that the segregation of the dopant element occurs on the surface of the target leading to larger clusters which are not any more involved in the arc discharge process. This will be shown in detail in a future publication of the author.

4.3. Deposition rates

The deposition rate of *ta-C* using pulsed arc technique is clearly high. The growth rate at 250V U_{ch} increases by a factor of two in comparison with the growth rate at 150V U_{ch}. Fig. 7 shows the deposition rate during a pulse when the sample is in a stationary position facing the cathode. Bias current curve has been taken as a representation for the deposition rate close before, during, and close after the pulse, where the DC arc deposition rate is 2.85 nm/s and the deposition rate at the pulse maximum reaches 249 nm/s for 250V U_{ch}, a factor 80 higher.

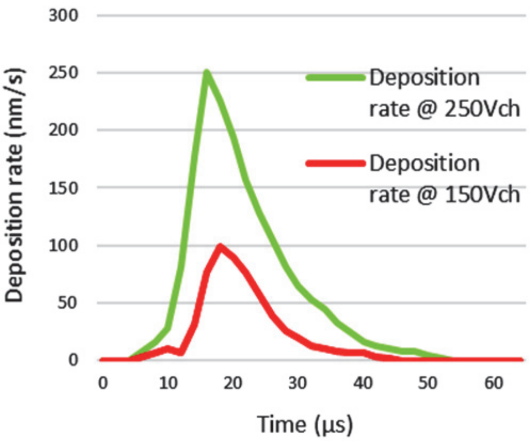

Fig. 7. *Deposition rate of ta-C with sample facing the cathode during a pulse at 150 V U_{ch} and 250 V U_{ch}*

4.4. Energy dissipated in the coating during deposition

The energy dissipated in the coating has been also calculated. The heat released during condensation of C atoms has been taken as 7.4 eV [20,21]. For the calculation it was assumed that the average ionization degree of all atoms was 1. The bias Voltage was 50V.

During a DC arc *ta-C* film deposition with 45 A cathode current, the energy applied to the surface of the growing film with the sample facing the cathode, is only 0.28 W/cm^2. When pulsed arc discharge is applied, the applied energy is greatly increased, as for 150V U_{ch} reaches 0.54 W/cm^2 and even 1.05 W/cm^2 when U_{ch} is 250V.

The deposition rate for doped *ta-C* can reach a factor two higher, which suggests that during the pulse time the applied power reaches up to 2 W/cm^2.

4.5. sp^2/ sp^3 nano layering

As the substrate passes in front of the ion source it is exposed periodically to a dense plasma, as well as to varying angular ion impingements. Schultrich [14] suggests that the periodical *sp^2/sp^3* nano-layering is due to the rotation of the sample. Rotation was indeed found to be a factor in our studies, but films produced by incorporating low deposition rate techniques, such as DC arc discharge technique, did not show any multi-layering. In our experiments a larger angle of incidence results in a lower depth of penetration of the C ions in the growing film [12]. A larger angle of incidence and a larger angle of emission also result in a lower deposition rate. Furthermore, a lower deposition rate is linked with a lower heat load and a lower temperature at the film surface. The internal stress of ta-C is lower for normal incidence than for angles less than 90˚, a tendency we think is linked with the higher heat load for higher deposition rates. The same tendency is also observed for the *ta-C* film hardness, where normal incidence reflects in a lower hardness than at 45˚. To outline, at the 90˚ position, the deposition rate is high and therefore during the pulse the amount of heat transferred to the film is also high, resulting in a decrease of the *sp^3* fraction.

Given that the hardness is lower at 90˚ and that the energy applied to the coating is at its maximum when the substrate faces the ion source perpendicularly, we assume that the *ta-C* film nano-layering is caused by a non-equilibrium heating when the substrate passes through the dense plasma and the angle of incidence is a co-factor. To summarize, the sample enters the cathodic arc plasma with a temperature similar to the aluminum fixture, and while passing through the plasma, the film surface heats up rapidly, resulting in a decrease of the sp^3 phase content.

5. Conclusions and Outlook

1) In contrast with the DC arc, the pulsed arc provides a highly reproducible plasma voltage and current during each pulse as well as during the time between the pulses. From another side, the increased cathode voltage gives the ionized atoms attracted back to the graphite target to deliver more energy per ion, than for a DC arc. The result is that pulsed arc target utilization is higher in comparison with the DC arc target utilization, as the eroded surface by the pulsed arc discharge covers the whole surface and remains smoother. SEM images show remarkably smaller crater diameters and crater depths on the face of the Graphite target when eroded by pulsed arc versus the DC arc.
2) *Ta-C* films deposited with high pulsed arc current in comparison with DC arc current exhibit significantly lower roughness. The higher charge results in reduction of size and number of particles emitted by the target, which suggests that the higher plasma density leads to less macro-particles and a lower film-roughness.
3) The bias current curve has been taken as a representation for the deposition rate close before, during, and close after the pulse, where the deposition rate at the pulse maximum shows to be remarkably higher in comparison with the DC arc deposition rate.
4) Multilayering sp^2/sp^3 within tetrahedral amorphous Carbon (*ta-C*) films in our experiments is a result of an excessive non-equilibrium heating when the substrate passes through a dense plasma.

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