ИЗСЛЕДВАНЕ ЕФЕКТА ОТ НЕРАВНОВЕСЕН ПРОЦЕС ВЪРХУ ТРИБОЛОГИЧНИТЕ СВОЙСТВА НА ЧИСТИ И ЛЕГИРАНИ ta-C ПОКРИТИЯ ПРИ ПРИЛАГАНЕ НА ИМПУЛСНО-ДЪГОВО КАТОДНО РАЗПРАШАВАНЕ

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Абстракт: *Свободни от водород тетрахедрални аморфни въглеродни покрития (ta-C), легирани с волфрам (W) и бор (B) бяха отложени чрез специална импулсно-дъгова технология, базирана на неравновесен процес. Тяхната структура се определя главно от енергията на бомбардиране с въглеродни йони по субстрата и последващия ефект на релаксация, свързан с температурата на покритието по време на отлагане. В допълнение, дълбочината на имплантиране е силно повлияна от ъгъла на падане на йоните. Скоростта на отлагане беше проверена за импулси с различни характеристики, както за C катоди, така и за C катоди легирани с B и W. Има ясен ефект, че скоростта на отлагане над определена прагова стойност влияе отрицателно върху твърдостта.*

Ключови думи: *Тетрахедрален аморфен Въглерод (ta-C); Нанасяне на филми чрез импулсно-дъгова технология; Легиран тетрахедрален аморфен въглерод (ta-C).*

A STUDY OF PULSED ARC NON-EQUILIBRIUM PROCESS EFFECT ON TRIBOLOGICAL PROPERTIES OF PURE AND DOPED ta-C COATINGS

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Abstract: *Hydrogen-free tetrahedral bonded amorphous Carbon films (ta-C), W doped, and B doped ta-C were deposited by a special pulsed arc technique based on a non-equilibrium process. Their structure is mainly determined by the energy of the impinging the substrate Carbon ions and the following relaxation effect linked with the temperature of the coating during deposition. In addition, the implantation depth is heavily influenced by the angle of incidence of the ions. Furthermore, the deposition rate was checked for various pulse architectures, and for Boron (B) and Tungsten (W) doped C targets. There is a clear effect that a deposition rate above a certain threshold value negatively influences the hardness.*

Keywords: *Tetrahedral amorphous Carbon, ta-C; Pulsed arc deposition; Doped ta-C.*

1. Introduction

It is well known that thin films made of diamond-like Carbon (DLC) exhibit high hardness, low friction, and low wear rate. Due to their excellent mechanical and tribological properties, the DLC films are often used in the form of protective coatings for biomedical implants, magnetic storage devices, automotive parts, cutting tools, watches, and many more real-world applications. Hydrogenated Diamond Like Carbon material has been utilized widely in industry and applied as a coating to increase wear resistance and reduce frictional losses. Typically, hydrogenated DLC has a hardness in the range of 2’500-4’000 HV and maximum application temperature of up to 300°C, which has limited its usage.

In the case of hydrogen-free DLC the coatings are prepared using solid Carbon or graphite targets. Important features of non-hydrogenated films are their higher hardness (>4.000 HV), higher operational temperature (up to 600°C) and large internal compressive stress. Regardless of the applied film growth technique, the deposition of a 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.

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 [3]. The sp^3 fraction can vary from 0 to 90% and is strongly dependent on the deposition method [4]. 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. 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.

The two most applied PVD methods to deposit *ta-C* films with high content of tetrahedrally oriented Carbon atoms (sp^3) are cathodic arc and pulsed laser ablation deposition. The base of each technique is cathodic arc plasma evaporation. Arc plasmas are fully ionized with highly energetic ions, which leads to excellent adhesion and dense films. 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. 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 [5,6] and leads to a high-density plasma as well as increased ion bombardment [7, 8, 9, 10]. This technology provides several advantages, for example, decreased surface roughness and increased deposition rate.

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.

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. During the deposition, the substrate temperature T_s was kept below a threshold. The results from the investigation tests are described in detail below.

2. Experimental details and methods utilized for film analyses

2.1. Experimental set up for deposition

To improve the quality of the applied coatings an installation more effective than just a simple DC arc discharge should be employed. 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 Pulsed 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 installation.

An example of the Arc current and Arc Voltage characteristic is shown in Fig. 1.

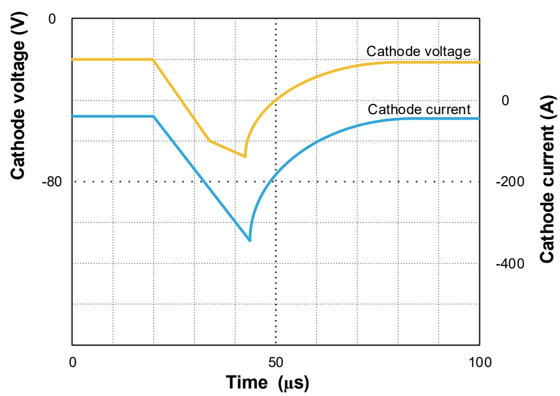


Fig. 1: *Arc voltage and Arc current pulse*

The DC arc power supply has a range of 40 to 100A. 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. The *ta-C* and doped *ta-C* films were deposited with fixed power supply parameters during the deposition step.

The films were deposited by running a cathodic arc discharge on a pure Carbon target or Carbon doped target at $2x10^{-5}$ mbar starting pressure. It was necessary to have a small Ar gas flow to achieve proper ignition and sustainable arc discharge on the target surface. The substrates were negatively biased. The chamber was initially heated through radiant heating elements located on the chamber walls, to approximately 200˚C, measured on the heater. Prior to the deposition, precleaned samples were carefully etched by an Ar glow discharge. There was no metallic ion etching or metallic interface applied.

The machine is capable of working with up to six cathodes (diameter 63 mm), three installed on the door and three installed on the chamber side. For this work we used only one of these installed cathode assemblies, the very bottom one, which faces directly the sample.

Graphite targets were used in different compositions, pure Carbon with purity of 99.7% and doped Carbon with following atomic percentages:

- Carbon 99.7%
- Carbon + Boron 2 at.%
- Carbon + Boron 4 at.%
- Carbon + Tungsten 0.5 at.%

- Carbon + Tungsten 1 at.%
- Carbon + Tungsten 2 at.%

The targets were provided by Avaluxe International GmbH [11], and were composed of Carbon powder, with average grains size 11 µm, where relevant B or W powder had average grain sizes of 5 and 10µm respectively and ash content of all the targets was 0.3%.

2.2. Substrate Fixturing: Stationary vs. Rotating

A massive Aluminum block was used as fixture. The block had a cylindrical shape, diameter 130 mm and 500 mm height, where the front of the fixture side had a machined flat for properly placing the test samples. Two kind of test samples were used, test coupons for measuring roughness and hardness, and Si strips for measuring internal stress. The polished test coupons (HSS 1.2379) had a diameter 15mm, thickness 5 mm, hardness of 747 HV (10 mN) and a roughness R_a of 0.01 µm and R_z of 0.25µm. They were securely tightened with specially designed clamps to ensure good heat transfer from the coupons to the Aluminum block. The strips were Si (100), dimension of 10x30 mm with a thickness of 180 µm. The temperature of the Aluminum block was measured during deposition and remained below 130˚C in all experiments.

Two series of experiments were done: a) stationery and b) rotating substrate table.

In the stationary tests, the Al fixture was kept stable in front of the cathode, at a distance of 150 mm. The samples were mounted opposite the cathode at every 45 mm intervals vertically, covering a range of 180 mm center to center, starting from the center of the bottom cathode, so that the view angle of cathode to sample was nearly perpendicular to the cathode surface. That angle will be indicated as emission angle. To measure the influence of the angle of incidence of the vapor beam including particles on the substrate surface, the Al fixture was mounted at different angles around its axis. The distance between sample and cathode remained nearly the same. The view angle from target to sample remained near perpendicular, only the angle of incidence of vapor beam to the substrate surface varied, see Fig. 2a.

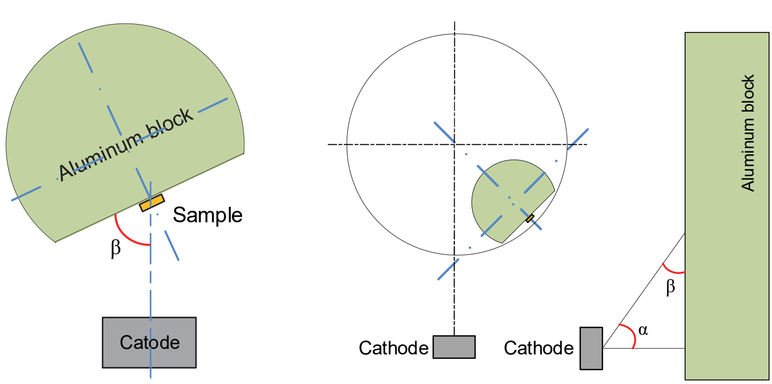


Fig. 2 a: Schematic drawing of stationary fixture block showing angle of incidence. b: Schematic drawing of single fold rotating fixture block showing angle of emission and angle of incidence.

For the second block of tests, the Al block was involved in rotation facing outward. The Al fixture passed the cathode at 8 rpm rotation, see Fig. 2b.

For these experiments the setup of the samples on the Aluminum block was kept the same as previous tests. The samples at different heights on the block representing different angles of incidence on the sample surface, but also different angles of emission from the target surface while substrate is rotating. Small shields were mounted vertically next to the samples to restrict the incidence angle in the horizontal plane. To ensure the same deposition conditions the Si strip for measuring the stress level of films was also situated in between similar shields with 20mm height.

For both cases the prefixed angles of emission of 90˚, 71˚, 58˚, 45˚, 37˚ were chosen. For the first block of tests, the angle of emission remains approx. 90˚ for all angles of incidence.

The Al block temperature was kept below 130 °C [12].

2.3. Methods adopted for film analysis.

A Calo-wear test technique was used to determine the thickness and wear rate of the deposited films. It is a destructive test using the equipment” Kalo MAX NT”.

Nano-indentation is an accepted method for determination of hardness of the deposited coatings avoiding delamination. To minimize the substrate influence, the penetration depth range was kept below 10% of the total film thickness. Nano-indentation equipment manufactured by “Fischer, model Fischerscope H100 was employed to carry out the nano-hardness measurements of the deposited *ta-C* films with a load of 5 and 10 mN depending on the coating thickness and based on the <10% penetration depth rule.

The coated surface roughness was measured using an industrial contact profilometer from **„Taylor Hobson Precision”**, model **FORM TALYSURF 50**. The actual profile is scanned with a stylus, which mechanically measures the topographical profile using a fine diamond tip of radius R_{tip}. We used parameters R_{tip}= 0.002 mm and the λ_c= 0.25 mm and measured R_p and R_a amplitude parameters.

Profilometry can be used to measure substrate bending due to internal stress of the coating. For this purpose, the same contact profilometer was employed to estimate the curvature of the coated silicon wafer. The value of the intrinsic stress of the deposited coating is calculated using Stoney’s equation [13].

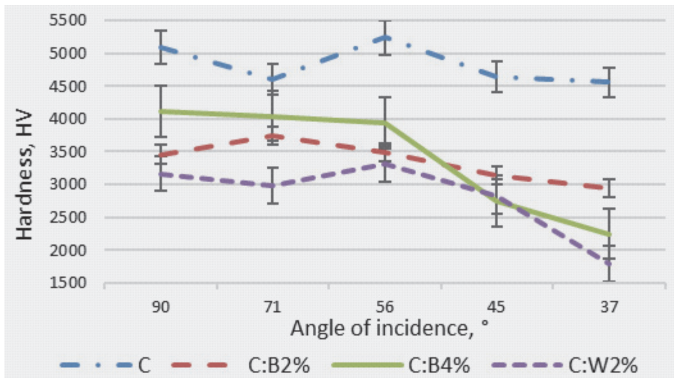
3. Experimental Results

3.1. Tests with a stationary fixturing in front of the ARC source

The stationary experiments were designed to study film properties where the emission angle from the target was constant, the distance target to sample was nearly constant and the angle of incidence of ions on the sample varied, see Fig. 2a. For all tests, the thickness of the deposited films was kept between 1-1.5 µm. The applied charge Voltage (U_{ch}) was 150V and 250V.

3.1.1. Influence of angle of incidence for the stationary case

The hardness versus angle of incidence is shown in Fig. 3a, the internal stress in Fig. 3b. Undoped *ta-C* shows the highest hardness, 2% W doped *ta-C* showed the lowest hardness and had almost half of the hardness value of the pure *ta-C* film. Films deposited under energetic ion bombardment tend to generate high internal stress [14]. At the same time under these conditions the growing films become denser and form more sp^3 clusters. This correlation between density and stress can be explained by the “subplantation theory” in terms of diffusion of the added Carbon atoms within the bulk. It is noted that low temperature annealing can eliminate stress peaks as well [15].



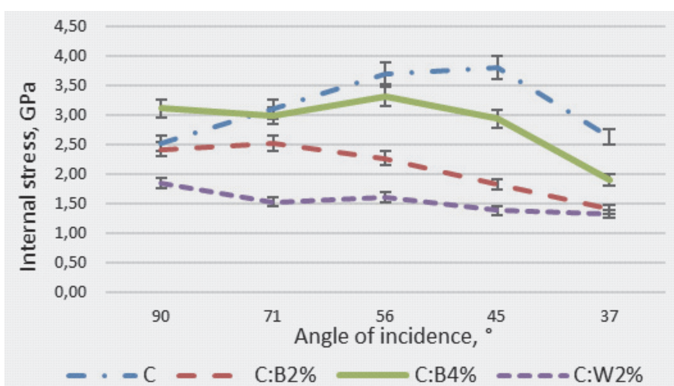
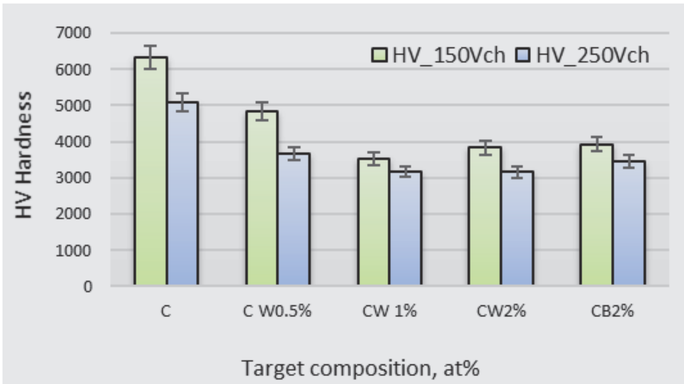


Fig. 3. *Properties of films deposited with pulsed arc at U_{ch} 250 V in front of the cathode as function of angle of incidence of the vapor beam on the substrate for different target compositions: a) hardness, b) internal stress.*

Observing the Internal stress results it is noted that they correlate well with the hardness distribution over different angles. In the preparation of the samples for stress measurement a factor to consider was, that the Si strip starts to bend under the influence of the stress of the film and has consequently a reduced contact with the block, compromising the energy transfer to the fixture. Due to this, the higher stress samples (*ta-C* and doped *ta-C* with 4% B) cannot be excluded from having higher temperature during deposition. Fig. 3b shows the *ta-C* internal stress distribution which is higher for an angle of incidence smaller than 90˚. In the B doped *ta-C* films (both 2% and 4% B) the stress was less affected. W doped *ta-C* showed a near linear stress dependence on the angle of incidence.

Similar tests were run with 150V U_{ch}. The analyzed data was for samples positioned at 90˚, i.e. with normal incidence of the impinging ions. Fig. 4a and Fig. 4b show the comparison between the nano-hardness and the internal stress at 150 and at 250V U_{ch} vs. target composition. It is well noted that the *ta-C* hardness is higher at 150V than at 250V U_{ch}. The block onto which samples were mounted was kept at the same temperature for both experiments. The amount of energy the substrate is facing passing through the plasma is substantially higher at 250 V than at 150 V U_{ch}. With the tight mounting to the solid Al fixture, providing good heat transfer, it indicates that when facing the plasma, at the film surface occurs a non-equilibrium temperature excursion.



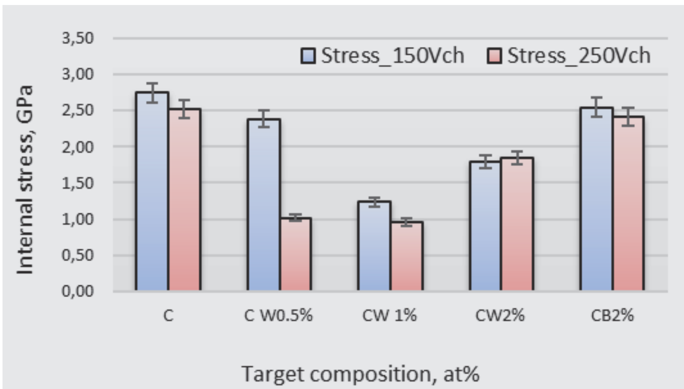


Fig. 4. *Properties of films deposited with pulsed arc at U_{ch} 150 V and 250 V in front of the cathode and a perpendicular vapor beam: a) hardness, b) internal stress.*

W doped *ta-C* films show lower hardness and lower internal stress than undoped. There is a tendency of decreasing hardness and internal stress in the *ta-C* films doped with 1% Tungsten. There is a return of hardness and internal stress for the films doped with 2% W deposited at 150V and 250V U_{ch}.

3.1.2. R_a and R_p roughness results

Fig. 5a and Fig. 5b show the roughness functions R_a/film thickness and R_p/film thickness, respectively. It is noted that the roughness results can be divided into two groups. T*a-C* and *ta-C* doped with 4% B films are in the first group. These films exhibit very low average and peak roughness amplitude (R_a, R_p), except for the 90˚ angle of incidence. *Ta-C* doped with 2% Boron and *ta-C* doped with 2% Tungsten films are in the second group. These films are very similar and exhibit higher average and peak roughness amplitude (R_a/film thickness, R_p/film thickness), which become smoother with a decrease of the angle of incidence. Their internal stress values are within a very similar range. It should be noted that Lifschitz et al. have demonstrated that a higher C ion energy during film growth results in a low roughness but must be emphasized that a high temperature during deposition results in a higher roughness. A value R_a of 70 nm is shown at a deposition temperature of 225˚C [2].

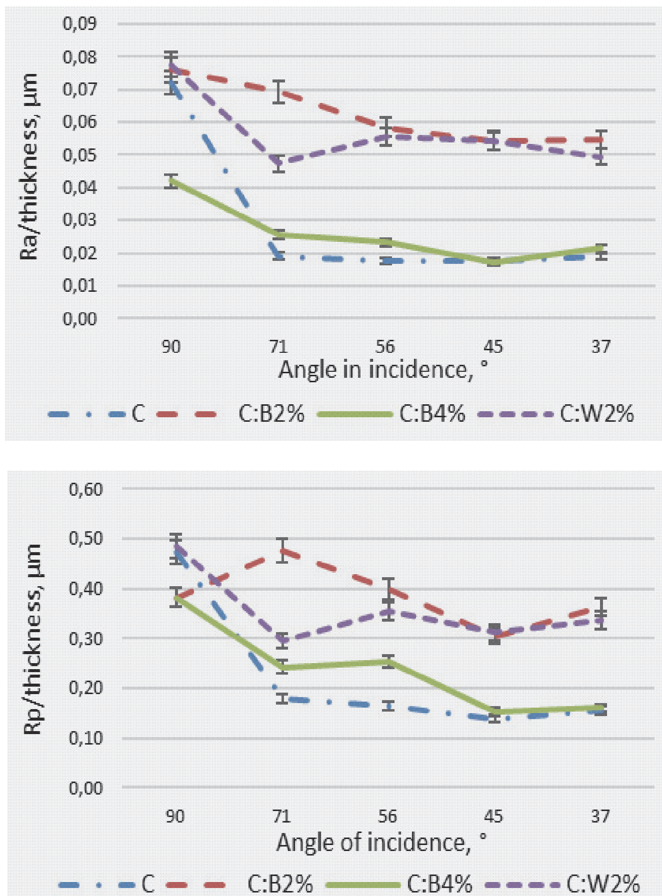


Fig. 5. *Roughness vs. angle of incidence of films deposited with pulsed arc at Uch 250 V in front of the target for different target compositions: a) Ra/film thickness, b) Rp/film thickness.*

The influence of the charge voltage U_{ch} on the roughness was evaluated for different target compositions at angle of incidence of 90˚. The analyzed data are plotted in Fig. 6a and Fig. 6b.

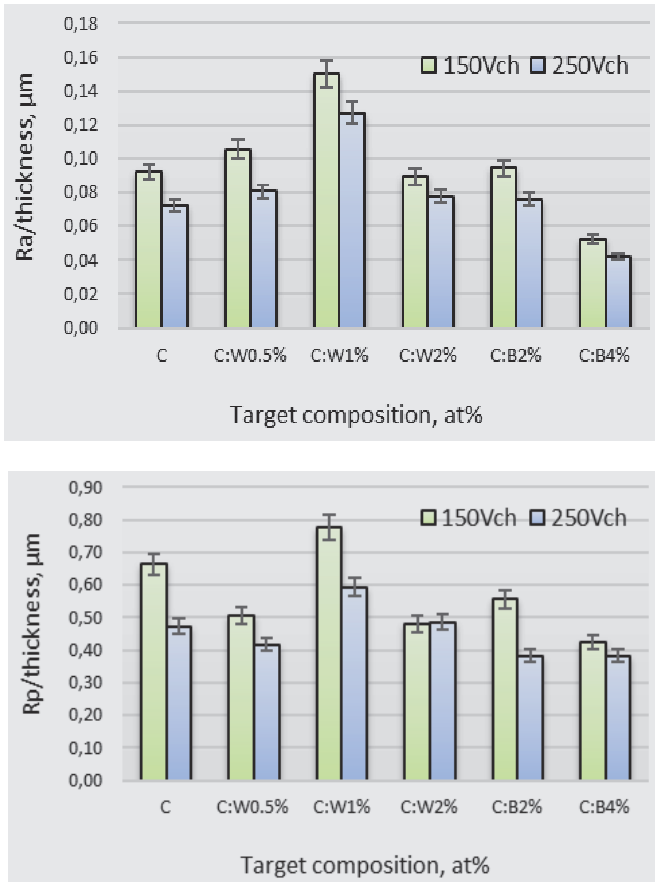


Fig. 6. *Roughness of films deposited using pulsed arc in front of the cathode with perpendicular vapor beam at Uch 150 V and 250 V:*
a) Ra/film thickness, b) Rp/film thickness.

The films deposited at 150 V U_{ch} exhibit higher R_a and R_p roughness than at 250 V U_{ch}. For Tungsten doped *ta-C* films, the roughness increases with increasing target dopant level up to 1 % and then reduces again. Boron doped *ta-C* films showed lower R_a and R_p in comparison with Tungsten doped films.

3.2. Single fold rotation experiment

3.2.1. Influence of angle of emission and incidence

This set of experiments attempts to determine at what degree the angle of emission and the angle of incidence of the impinging ions affects the physical properties of the deposited tetrahedral amorphous films. The fixture was configured for a single fold rotation and this way the samples were facing the cathode. Six different target materials were evaluated C, C-B2%, C-B4%, C-W0.5%, C-W1%, C-W2%. The coating thickness in all tests was kept between 1-1.5 µm. For larger angles, see Fig. 2b, the deposition time was adjusted to keep it between 1-1.5 µm. Fig. 7 shows the hardness results.

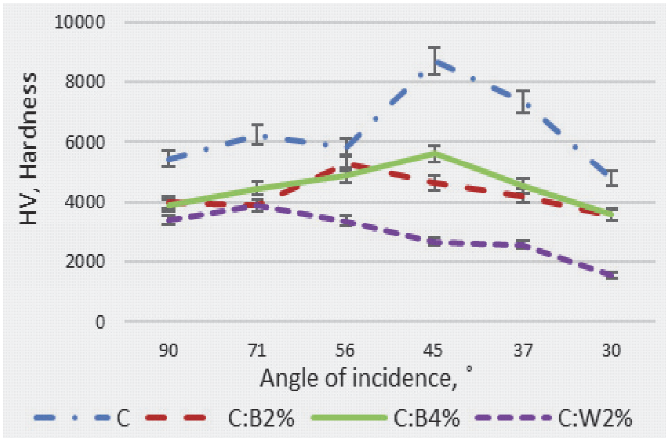
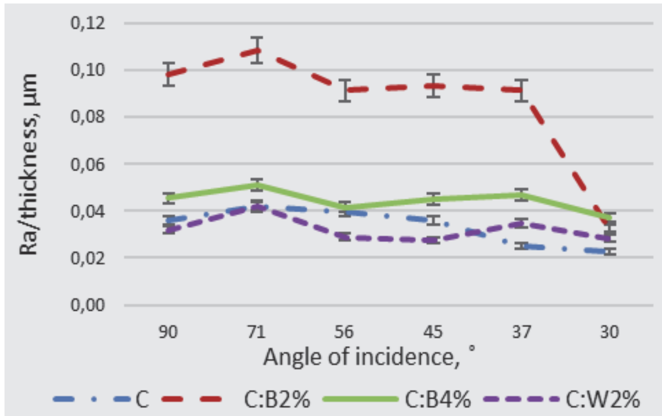


Fig. 7. *Hardness of films deposited using pulsed arc at Uch 250 V and single fold rotation vs angle of emission/incidence for different target compositions.*

Pure *ta-C* and *ta-C* doped with 4% Boron demonstrate the highest hardness values in comparison with the other materials and show a marked increase toward shallower angles up to 45˚. At more shallow angles the hardness decreases rapidly. The other two compositions, *ta-C* doped with 2% Boron and with 2% Tungsten show a constant hardness down to angles of emission/incidence of 56˚ and 71˚ respectively, at shallower angles the hardness decreases in the same manner. The lowest hardness was measured for *ta-C* doped with 2% W. The temperature of the fixture during all the tests remained <120˚C irrespective of deposition time.

3.2.2. R_a and R_p roughness results

Graphs are plotted based on a normalized roughness, R_a/film thickness and R_p/film thickness. Pure *ta-C* and *ta-C* doped with 4% Boron show average roughness R_a values very similar in the range of 40 nm, Fig. 8. *Ta-C* doped with 2% Tungsten had the lowest roughness of all presented models in the range of 30 nm. The highest roughness values were obtained for the *ta-C* doped with 2% Boron. For most dopant levels R_a drops for angles shallower than 45˚. Otherwise, the roughness of the deposited films remains in a narrow range. It should be noted that both, angle of incidence and angle of emission varied simultaneously with the samples mounted above each other to obtain different angles of incidence.



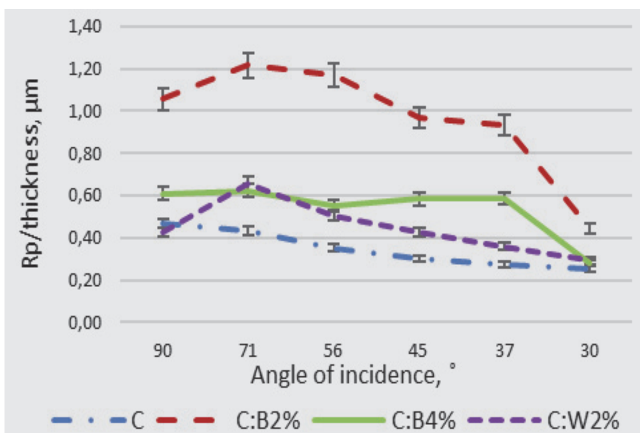


Fig. 8. Roughness of films deposited using pulsed arc at Uch 250 V and single fold rotation vs angle of emission/incidence for different target compositions:
a) Ra/film thickness, b) Rp/film thickness

R_p/film thickness roughness functions (Fig. 8b) are similar to R_a/film thickness roughness functions (Fig. 8a). They show close to a flat distribution in a narrow range up until 45˚, after which the roughness decreases. This trend is observed for all compositions. The roughness R_p of *ta-C* demonstrates the lowest values and almost linearly declines with shallower angle. Here again, the highest roughness values were obtained from the *ta-C* doped with 2% Boron.

To determine the effect of cathode positioning within the chamber on the corresponding film roughness results, we have repeated the experiment described above with a Tungsten doped target placed at a position higher than the sample. No significant differences in roughness were observed when comparing the results of emission angles of +71˚ and -71˚.

3.3. Deposition rate

For the stationary case, the deposition rates were measured and compared.

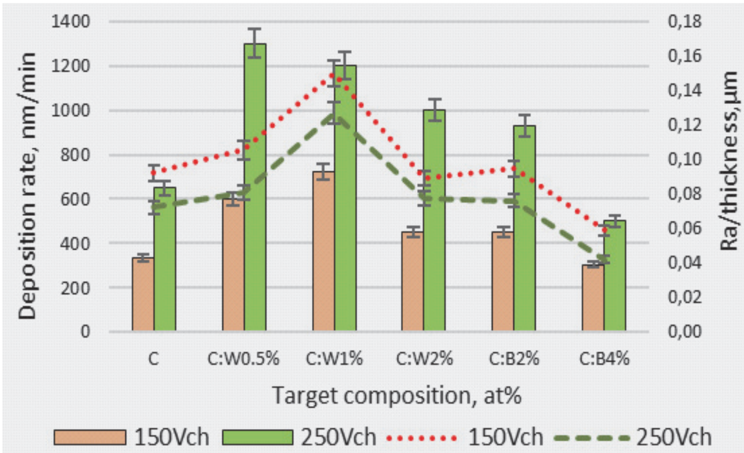


Fig. 9. *Comparison of deposition rates vs. target composition using pulsed arc with samples stationary opposite the cathode at U_{ch} 150 V and 250 V.*

In Fig. 9 deposition rates on samples opposite the cathode are plotted for different target compositions utilizing pulsed cathodic arc at 150 and 250V U_{ch}. The *ta-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. 9). 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.

4. Interpretation of results

4.1. Phenomena 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 [14]. 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 author but also by R. Sangines et al. and T. Schülke et al. [9, 16].

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 [17] 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. Hardness and internal stress

The energy and the angle of incidence of the impinging ions affects greatly the physical properties of the tetrahedral amorphous films.

Based on sub-plantation theory, incident ions penetrate the surface of the film and increase the local density. Ions with insufficient energy to penetrate the film surface just nucleate on the upper surface forming sp^2 bonding. Only ions with sufficient energy can enter interstitial positions below the surface. Schultrich [8] has provided an overview of the influence of angle of incidence, the ion energy, and the temperature on properties of *ta-C*.

However applied deposition conditions can strongly influence the mechanical properties of the deposited *ta-C* and derivatives of *ta-C* films such as doped *ta-C* [18, 19].

In our experiments it was observed:

- Pure *ta-C* films have higher hardness in comparison with doped *ta-C* films.
- Pure *ta-C* as well as doped *ta-C* films deposited at positions with an emission angle and angle of incidence of 19˚ exhibit higher hardness than films deposited at angles of 0˚.
- Pure *ta-C* as well as doped *ta-C* films deposited at 150V U_{ch} show higher hardness in comparison with 250V U_{ch}.
- The deposition rate for films deposited at 250V U_{ch} is much higher than the deposition rate for films deposited at 150V $U_{ch.}$
- The deposition rate of doped *ta-C* films with up to 2% dopant is higher than pure *ta-C*.

In all cases the samples were tightly fastened to an Al block fixture with a temperature measured lower than 100 ˚C. Chhowalla et al. [20] have reported about doped *ta-C* with 2% Boron and have not found a substantial difference in hardness compared to pure *ta-C*.

Analyzing our data, we have observed that there is an inverse correlation between deposition rate and hardness. Our findings were valid for pure *ta-C* as well as for doped *ta-C* deposited at different pulse charge voltages. In case of 250V U_{ch} nearly 60% of the coating is deposited during the pulse. For 150V U_{ch} approx. 33% of the coating is deposited during the pulse. The dissipated power in the pulse is higher for 250V U_{ch} than for 150V U_{ch}.

From this we can conclude, that although the fixture sample has been at a temperature below 100 ˚C, the power dissipated in the outer surface of the sample during the pulse causes a non-equilibrium temperature excursion. That in turn results in a softer coating layer. Increased deposition rate, either by a high pulse U_{ch} or by adding a dopant, results in a softer coating. We would propose to add to the model of Schultrich [8] a term resulting in softening of the coating, when the deposition rate exceeds 10 nm/s.

A strong correlation was found between film hardness and film stress (Fig. 6a and Fig. 6b). Especially for *ta-C* doped with 1% W the stress was clearly lower than expected based on the hardness. The same was observed by Chhowalla [20] for *ta-C* doped with Boron. It is assumed that the dopant is embedded in the amorphous *ta-C* matrix, either evenly distributed or in small clusters. An interface region with lower hardness is formed around the dopant. This results in a stress absorbing region, resulting in a lower compressive stress. Our results concerning nano-hardness of doped films are in agreement with literature for *ta-C* films doped with 2% Boron.

4.3. Roughness

In our experiments was observed:

- Pure *ta-C* as well as doped *ta-C* films deposited at 250V U_{ch} show R_a roughness 20% lower than for films deposited at 150V U_{ch}.
- The roughness increases from pure *ta-C* to doped *ta-C* deposited films with a maximum at a target composition of 1 at% W
- For the stationary case with an emission angle of the vapor being perpendicular, a more shallow angle of incidence results in a reduced roughness
- For an emission angle and angle of incidence changing simultaneously (in case rotation) this effect is not visible.

In our experiments there are a few main factors influencing the roughness of the deposited films:

- Creation of macro particles at the cathode site.
- Pulse influence on number and size of macro particles transported through the dense plasma.
- Sticking of macro-particles to the film
- Roughening of the growing film surface under the influence of ion bombardment and temperature.

The first two factors are clearly understood. For the last one Lifschitz et al. [18] have demonstrated that a higher C ion energy during a *ta-C* film growth results in a lower surface roughness. Nevertheless, a high temperature during deposition results in a higher surface roughness.

There is an observable decrease of roughness when increasing the charge voltage from 150V to 250V of 20% and this can be largely explained by a more uniform erosion of the target and reduction of macro-particles ejected from the target.

The reduction of roughness at shallower angle of incidence we interpret that the sticking probability at shallow angle of incidence is lower than perpendicular.

The variation of roughness for different compositions shows a correlation with the deposition rate, see Fig. 13. This relation suggests that temperature increases at the outer substrate surface caused by high deposition rate result in roughening of the *ta-C* film. As discussed by Lifschitz [18], for a deposition temperature of 225˚C the roughness is in the range of 70 nm. Despite all tests specimens were fastened to an aluminum fixture providing heat transfer, the inverse correlation between deposition rate and hardness indicates that the outer surface film temperature during the pulse raises above 200˚C. Indeed, in our experiments we observed an increase in R_a roughness of 60 nm for 1.5 µm thick film comparing pure *ta-C* with 1% Tungsten doped *ta-C* films.

In conclusion, there are two processes contributing to cause film roughness: macro-particles ejected from the cathode spots reaching the substrate along with the plasma, and roughening generated by increased temperature at the film surface by high density of the impinging ions triggering the sp^3 to sp^2 phase transition.

5. Conclusions and Outlook

In summary, we have deposited hydrogen-free tetrahedral bonded amorphous Carbon films (*ta-C*), W doped, and B doped *ta-C* by DC arc with short, superimposed pulses on top.

Our work was showing that:

1) When the growth rate during the pulse is higher than 10 nm/s, the deposited *ta-C* and doped *ta-C* films tend to become softer despite the efficient heat transfer from the substrate to the fixture. A non-equilibrium temperature excursion at the surface of the growing film causes a decrease of hardness.
2) The excessive energy in the plasma during the pulse has less influence when the sample is at a shallower angle, resulting in an increase of hardness at angles of incidence up to 45˚.
3) *ta-C* films deposited with high pulsed arc current in comparison with DC arc current exhibit significantly lower average (R_a) roughness and peak (R_p) roughness. These results are directly linked to how the Carbon target is eroded.
4) Doped *ta-C* films with Tungsten exhibit lower average and peak roughness in comparison with *ta-C* films doped with Boron.
5) Doping Carbon coatings with Tungsten and Boron results in an increase in deposition rate and a decrease in hardness and internal stress. From all examined films, *ta-C* doped with 0.5% W exhibits the highest deposition rate in the range of 1500 nm/min.

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