



Simultaneous carbon and tungsten thin film deposition using two thermionic vacuum arcs

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ABSTRACT

Carbon and tungsten films were deposited sequentially and simultaneously from two separate plasmas produced by the thermionic vacuum arc (TVA) method. Total film thickness and atomic concentration of C and W were measured for different substrate positions and arc parameters and a comparison between sequential and simultaneous deposition of carbon and tungsten is presented. For the simultaneous case, while keeping the same discharge parameters as in the sequential case, the carbon composition percentage is enhanced despite the presence of the tungsten plasma. When only the carbon deposition rate is increased 10 times, the tungsten atomic concentration drops to a lower level, while the content of carbon becomes dominant for the substrates positioned near the carbon anode.

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1. Introduction

The current design of the plasma facing components of a modern fusion reactor consists of three main elements: beryllium (Be), tungsten (W) and carbon fiber composite [1]. The interaction of these materials with the fusion plasma leads to the formation of mixed material layers that can change fuel retention properties. In order to simulate mixed material formation, an important amount of work is presently dedicated to studying synthesis of metal-carbon films using different methods such as magnetron sputtering [2], chemical and plasma vapor deposition (CVD and PACVD, respectively) [3,4], electron cyclotron resonance (ECR)[5], filtered cathodic vacuum arc (FCVA) [6], and pulsed laser deposition (PLD) [7].

The thermionic vacuum arc method (TVA) has been very efficient for creating pure and composite refractory [8], tribological [9,10] and magnetostrictive materials [11] with industrial applications including coatings on the first wall of the fusion devices [12]. This method offers a large degree of flexibility due to its unique properties, among them being deposition in ultra high vacuum environment and ion energy control during deposition. One of the main advantages of this method is the possibility to evaporate materials from multiple targets (anodes made of specific materials) and deposit them on different substrates. Simultaneous deposition from multiple targets is not necessarily equivalent with a sequential deposition from individual targets, since there are many plasma processes involved which can affect the deposition rates. Control of thickness and composition is a much more challenging task when depositing thin films from multiple targets. In

this paper we investigate the spatial variation of film thickness and composition in a set of two experiments: one with a sequential operation of two targets in which carbon is deposited first and then tungsten is deposited on top of the carbon layer and the second with simultaneous operation involving the two targets of carbon and tungsten.

2. Experimental system

The used method based on TVA for sequential or simultaneous deposition of carbon and tungsten films was described in details elsewhere [10]. It is based on two identical set-ups which produce two separate electron beams emitted by externally heated cathodes. Each cathode is made from a tungsten wire with a diameter of 1 mm. The electron beams are accelerated by high anodic voltages and bombard simultaneously the graphite and tungsten rods of 10 mm diameter and 150 mm length, as shown in Fig. 1. In both set-ups a grounded Wehnelt cylinder focuses the electron beam on a small spot of about 1 mm diameter on the anode.

Two different plasmas were formed in pure carbon and tungsten vapors by applying on each anode–cathode set a high voltage of 1 kV to 2 kV. The deposition chamber was pumped down to $5 \cdot 10^{-4}$ Pa by mechanical and diffusion pumps. The TVA has proved to be a highly efficient tool for obtaining droplet free plasmas in metal vapors due to the efficient heating provided by the electron bombardment and subsequent evaporation at the anode of metals with vaporization temperatures of over 3000 K [8–12].

The currents used to heat the cathode filaments were 58.2 to 59 A for carbon and 52.5 to 63.7 A for tungsten, respectively. The current of the discharge ignited in C vapors was $I_{\text{disch}} = 1$ to 1.8 A at a voltage $U_{\text{disch}} = 1.5$ –1.8 kV. For the discharge ignited in W vapors, the current

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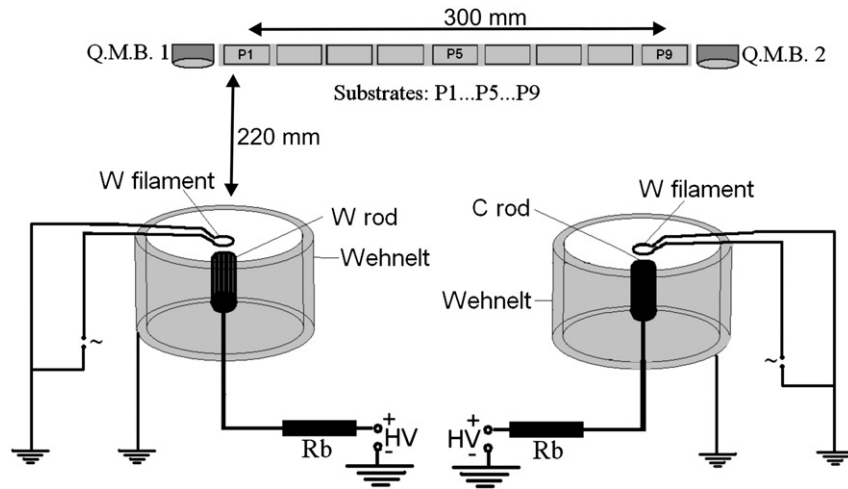


Fig. 1. Experimental system for deposition of thin films with simultaneous operation of two thermionic vacuum arcs: high-voltage sources (HV), ballast resistor $R_b = 800 \Omega$, quartz microbalances (QMB1 and QMB2).

intensity was $I_{\text{disch}} = 2\text{--}2.75 \text{ A}$ and the voltage was $U_{\text{disch}} = 1.6$ to 1.8 kV .

The investigated deposited film samples were located collinearly at P_1 to P_9 , above the two anodes, as shown in Fig. 1. Closest to the tungsten anode was P_1 , while P_9 was closest to the carbon anode. P_5 was located at mid distance between the two anodes. The distance between the tungsten anode and the sample P_1 was 220 mm , equal with the distance between the carbon anode and the sample P_9 , while the distance between the two anodes was 300 mm . The distance between two consecutive samples was not the same but rather varied between 10 and 70 mm . The deposition rates r_d and film thickness d were measured and controlled in situ by two FTM7 quartz microbalances, the first one being positioned near P_1 and the second one near P_9 . Each microbalance was calibrated for measuring the deposition rates of tungsten and carbon, respectively, as if they were placed at the position of P_5 . A small shadowing plate was placed near each microbalance to block as much as possible the flux of ions from the opposite anode while the space to the corresponding anode was left clear. An agreement within a few percents between the deposition rate indicated by the microbalance in a given period of time and the

measured thickness of the deposited layer on a substrate has been confirmed experimentally in both carbon and tungsten discharges.

3. Experimental results and discussions

A thin film of tungsten with thickness of 200 nm was sequentially deposited on top of a 200 nm layer of carbon, with comparable deposition rates of about 0.1 nm/s for both processes. The deposition time was roughly 36 min for a single layer in the sequential case. Total film thickness of the samples is presented in Fig. 2(a), where only measurements of samples P_2 to P_4 and P_6 to P_9 could be made available. In Fig. 2(a) the dots correspond to the x position of the samples relative to positions of the two anodes: tungsten at $x = 0$, and carbon at $x = 300 \text{ mm}$. Each thickness value given for a sample was obtained in the following way: three points were chosen at about $1/4$, $1/2$ and $3/4$ of the 1 cm long samples and at each point three measurements have been carried out using ellipsometry. First, an average value per point was calculated and then the three obtained values were averaged again to provide the film thickness deposited on a sample. As it can be seen the total thickness of the film varies slightly

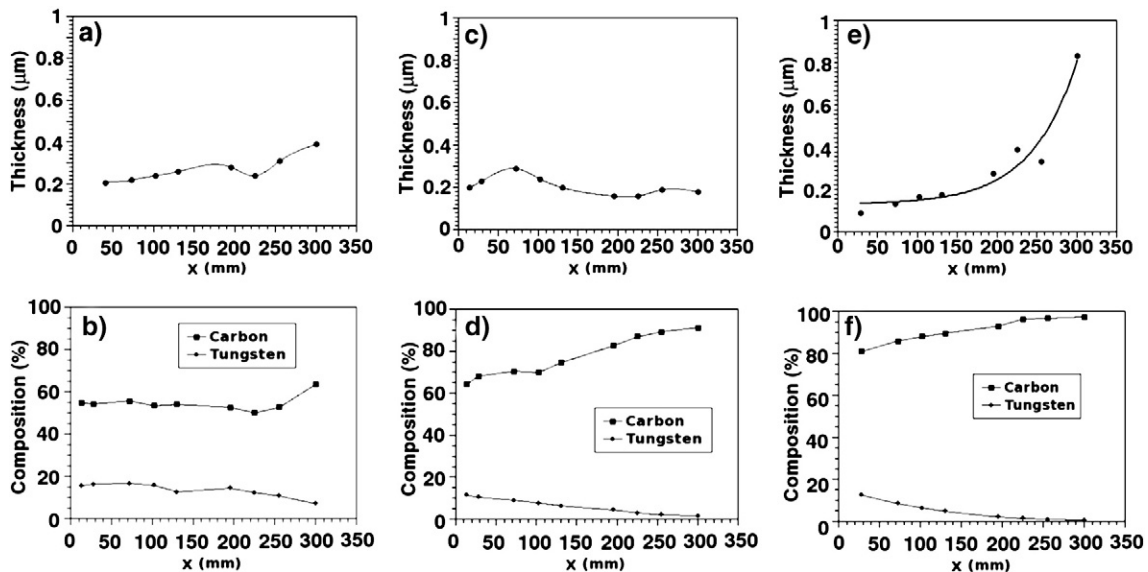


Fig. 2. Total thickness (a, c, e) and atomic concentration of C and W (b, d, f) of film deposited on samples positioned at different distances from the tungsten anode ($x = 0$), for sequential deposition of C and then W (a, b), for simultaneous deposition of C and W with the same deposition rates (c, d); for simultaneous deposition of C and W with the carbon deposition rate $10\times$ the tungsten deposition rate (e, f).

with position, except for P8 and P9 where it increases abruptly. These two samples are placed above the carbon anode. An analysis of the atomic composition of the film using SEM-EDS measurements shows in Fig. 2b) a constant ratio of C to W as expected except for the samples P8 and P9. For these two the ratio increases to about 9:1 from an average of about 3:1 in terms of atomic concentrations.

In the case of simultaneous deposition of carbon and tungsten the results are quite different as compared with the sequential deposition. First, deposition of both materials was carried out with the same rate of 0.1 nm/s. The total film thickness remains relatively constant with a slight increase near both anodes, more pronounced next to the tungsten electrode, as shown in Fig. 2c). However, the ratio in the composition of the materials changes significantly. As it can be seen in Fig. 2d), the percentage of carbon increases steadily the closer the sample is to the carbon anode, while the amount of tungsten decreases to single digit percents. Thus, from a carbon to tungsten ratio of about 5:1 on P1, at P9 carbon dominates at 45:1.

In the next step of simultaneous use of the two targets, the carbon deposition rate was increased 10 times, to about 1 nm/s, while the tungsten deposition rate was kept the same at 0.1 nm/s. This was possible by increasing the current in the carbon discharge from 1 A to about 1.8 A, while the voltage increased only from 1.5 A to 1.8 kV. In this new parameter regime the total film thickness varied strongly among the samples positioned along the 300 mm length which corresponds to the distance between the two anodes, as shown in Fig. 2e). The thickness of the film increases 4 times to about 870 nm for sample P9. The atomic concentrations of carbon and tungsten are shown in Fig. 2f). It is obvious that C deposition is much favored with a presence of about 98% in sample P9, while W deposition is strongly diminished to atomic concentrations below 1%. The C composition is high even in the samples found near the W electrode: 81% for P1, and 86% for P3.

From the experimental data it is clear that the two deposition processes, sequential and simultaneous, differ dramatically in terms of film thickness and layer composition, even if the parameters of the arc discharges are kept approximately the same. In order to understand film grow and its final composition which is particularly important in specific coating applications, we have done a rough evaluation of the layer's relative thickness. We approximated that the films were homogeneous with no holes or defects. Based on film thickness measurements, atomic concentration and deposition rates we estimated the relative thickness of W and C films deposited on each sample among the three sets of experiments, by normalizing to the maximum deposited thickness of each element. In Fig. 3 we can see that the deposited tungsten layers significantly decrease in width when switching from sequential (top fitted curve) to simultaneous deposition (lower fitted curves) of both materials in spite of the fact that tungsten target conditions are similar and so is the vaporization rate in all studied cases. The tungsten film is somewhat thicker near

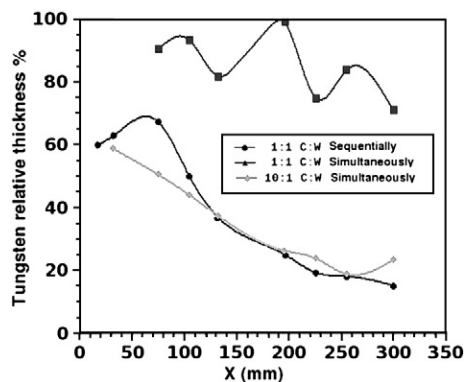


Fig. 3. Tungsten layer thickness relative to the maximum deposited value vs. their position.

the W electrode as expected and thinner on samples near the C electrode. This trend is more noticeably for the simultaneous processes. An interesting observation is that there are no major differences concerning the thickness of the deposited tungsten films for the two simultaneous cases, and closed values were obtained.

On the other hand, from the analysis of carbon depositions in Fig. 4 we see that the relative thickness of the films above the tungsten electrode seems to be comparable for the three cases studied. A large increase is seen in the 1 nm/s deposition rate process especially near the C anode. For the two deposition processes with 0.1 nm/s deposition rates the thickness is comparable over the full distance between the two anodes, regardless of the tungsten plasma.

The effect of increased C composition in the deposited films can be qualitatively explained by considering the features of the plasmas produced by the two set-ups. The ionization potential for C and W atoms are 11.26 and 7.98 eV [18], respectively. Thus, a gas of W atoms would require less electrical power to become ionized. This situation is reflected in the electrical power supplied by the high-voltage sources. At the same voltage applied on the electrodes, of about 1.6 kV, the currents drawn by the discharges are 1 A and 2 A, for C and W plasmas, respectively, owing to the lower ionization potential of W. However, here we have to account for the thermionic current emitted by each cathode. In our case, both materials must be heated to high temperatures (3600 K [13] and 3695 K [14] for C and W in vacuum, respectively) in order to sublimate or vaporize and therefore an intense electron beam is required which deposits its kinetic energy on the targets. The accelerated electrons have a twofold role contributing also to the ionization of atoms in the metal vapors. Once the discharge is ignited, the plasma is at positive potential relative to the ground. The electrical potential of plasma peaks near the anode at about 1 kV and drops quickly with the distance to 100–150 V at about 15–20 cm [15]. It appears that tungsten ions encounter a higher electrostatic barrier set by the potential distribution of the carbon plasma than it is the case for carbon ions in the potential of the tungsten plasma, and are hindered from reaching the samples found next to the carbon anode. Also the tungsten ions have a much lower mobility than carbon ions since their atomic mass is 15 times higher.

During the simultaneous processes we observe that deposition of tungsten does not suffer drastically for a steep increase in the deposition rate of carbon, from 0.1 to 1 nm/s. A higher deposition rate can result from enhanced sublimation of carbon at the anode and further intense vapor deposition on the samples. Since the density of carbon ions does not vary significantly as it is given by the ionization processes which are roughly determined by the electrical input power, vapor deposition becomes dominant and exceeds deposition realized by the carbon ion flux.

A tungsten deposition rate above 0.1 nm/s can be achieved in the present set-up while keeping the rate of carbon constant by increasing the electrical power fed to the tungsten discharge. However, this leads to a large heat dissipation through the electrodes and the focusing

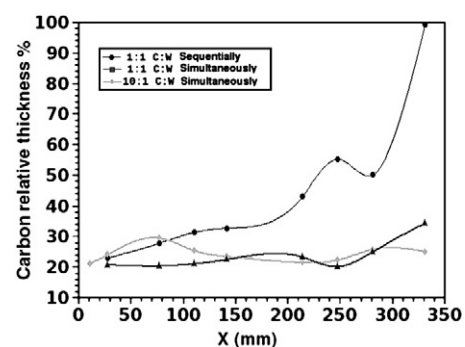


Fig. 4. Carbon layer thickness relative to the maximum deposited value vs. their position.

Wehnelt cylinder which can quickly destroy the set-up. Thus, control of the composition in the thin films can be achieved by carefully setting the deposition rate which is given by the discharge parameters as well as the filament current.

4. Conclusions

Carbon and tungsten films were sequentially and simultaneously deposited from two targets using the TVA method on substrates positioned at different distances from the sources. In the sequential deposition process, the atomic composition of C to that of W was approximately 3 to 1 near the W anode and 9 to 1 in samples near C anode. The plasma parameters were approximately the same and so was the deposition rate of the two materials. Major differences appear in the simultaneous deposition of C and W films, where for the same discharge parameters the atomic composition of C increased above 65% for the whole range of samples exposed to both plasmas and reached 90% near C anode, while that of W slightly decreased and was situated in the range from 13% to 2%. When the deposition rate of C was increased 10 times by introducing more electrical power into the vacuum arc, the atomic composition of C jumped above 80% and reached about 98% near the C anode. The composition of W continued to decrease and was below 12% to almost below 1%.

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References

- [1] K. Sugiyama, M. Mayer, V. Rohde, M. Balden, Th. Dürbeck, A. Herrmann, S. Lindig, A. Wiltner, H.W. Müller, R. Nucl. Fusion 50 (2010) 035001.
- [2] K. Bewilogua, R. Wittorf, H. Thomsen, M. Weber, Thin Solid Films 447 (448) (2004) 142.
- [3] W.-N. Li, Y.-S. Ding, S.L. Suib, J.F. DiCarlo, F.S. Galasso, Surf. Coat. Technol. 190 (2005) 366.
- [4] A. Lamperti, P.M. Oss, Appl. Surf. Sci. 205 (2003) 113, and references therein.
- [5] T. Yajima, S. Umemura, S. Hirano, A. Imoto, R. Kaneko, Surf. Coat. Technol. 169 (170) (2003) 274.
- [6] M. Bilek, M. Chhowalla, M. Milne, W.I., Appl. Phys. Lett. 71 (1997) 1777.
- [7] J. Budai, Z. Tóth, A. Juhász, G. Szakács, E. Szilágyi, M. Veres, M. Koós, Appl. Phys. 100 (2006) 043501.
- [8] C.P. Lungu, I. Mustata, G. Musa, A.M. Lungu, V. Zaruschi, K. Iwasaki, R. Tanaka, Y. Matsumura, I. Iwanaga, H. Tanaka, T. Oi, K. Fujita, Surf. Coat. Technol. 200 (2005) 399.
- [9] C.P. Lungu, I. Mustata, G. Musa, V. Zaruschi, A.M. Lungu, K. Iwasaki, Vacuum 76 (2004) 127.
- [10] C.P. Lungu, A.M. Lungu, P. Chiru, A. Tudor, R. Brescia, Int. J. Surf. Sci. Eng. 4 (2010) 191.
- [11] I. Mustata, C.P. Lungu, A.M. Lungu, V. Zaruski, M. Blideran, V. Ciupina, Vacuum 76 (2004) 131.
- [12] C.P. Lungu, I. Mustata, V. Zaruschi, A.M. Lungu, A. Anghel, P. Chiru, M. Rubel, P. Coad, G.F. Matthews, Phys. Scr. T128 (2007) 157.
- [13] H.O. Pierson, Handbook of Carbon, Graphite, Diamond and Fullerenes, Noyes Publications, New-Jersey, 1993.
- [14] J. Emsley, The Elements, 3rd ed. Oxford University Press, 1998.
- [15] V. Tiron, C. Aniculaesei, G. Popa, J. Autom. Mobile Robot Intell. Syst. 4 (2009) 147.