ABSTRACT

Removal of hydrogenated carbon from mixed W-C films was studied for two different initial compositions (approx. 20 and 50 at.% of W). The deposits were prepared by sputter deposition in a mixture of Ar and C$_2$H$_2$. Samples were exposed to oxygen plasma created in a quartz tube by a microwave discharge at the power of 1000 W. The evolution of the coating composition was monitored versus plasma treatment time by AES depth profiling. Furthermore, SEM characterization was performed to observe morphological differences. The results showed that at low tungsten concentration (20 at.% of W) almost entire hydrogenated carbon was removed from the mixed W-C films. At high tungsten concentration (50 at.% of W), a compact passive WO$_3$ layer was formed on the surface of the samples. This compact layer prevented interaction with hydrogenated carbon even after prolonged plasma treatment as proved by SEM analysis. XRD characterization revealed that the oxide film was highly crystalline. In the case of a sample with the low tungsten content (20 at.% of W), WO$_3$ layer was more porous with many cracks and thinner. Successful removal of carbon from W-C films with low tungsten content was explained by migration of particles through the porous films.

1 INTRODUCTION

The first choice of material for plasma facing components in ITER is beryllium, carbon, and tungsten. A part of the divertor will be made from carbon fiber/carbon composite and another part from tungsten. The carbon materials will be later replaced by metals or their compounds. Although it is foreseen that carbon will not be used in future tokamaks, it is still important to address interaction of carbon with hydrogen plasma and to develop method for removal of hydrogenated carbon deposits. Namely, the first configuration of ITER will contain carbon materials and it is likely that it will not be limited to details of the divertor due to the chemical erosion as exposed to deuterium plasma.
Several techniques have been proposed for the removal of hydrogenated deposits. The techniques include mechanical treatment, laser or flash light removal, and chemical methods [1-8]. Among the chemical methods, the application of neutral reactive particles seems to be particularly popular. The neutral reactive particles should be rather reactive at the operating temperature of the divertor and should not remain in the system after successful removal of hydrogenated carbon deposits. One of the most reactive neutral particles is atomic oxygen [9, 10]. It can be created by dissociation of parent molecules using an appropriate electrodeless discharge. Neutral oxygen atoms are perfectly stable in vacuum and their life time in real systems is long enough to be carried far away from the origin. This property encourages development of devices as remote sources of O-atoms [10]. Although many authors showed the possibility of removal of hydrogenated carbon by neutral oxygen atoms created in glow discharge [11-14], much less work has been performed on removal of mixed material [3,15-16]. Since both C and W will be presented in the first configuration of ITER divertor, one can expect formation of mixed W-C films, probably also with the small addition of beryllium. The concentration of W in the amorphous hydrogenated carbon films is expected to be low. On the other hand when carbon is omitted and replaced by tungsten or another suitable metal, traces of carbon are likely to remain in the remote parts of the divertor, so the deposits that might form in the secondary phase may be rather rich in tungsten. The aim of the present paper is to demonstrate huge differences in the oxygen atom chemistry between the deposits with low and high tungsten concentration.

2 EXPERIMENTAL

Hydrogenated carbon deposits with addition of tungsten were prepared by sputter deposition of tungsten in acetylene atmosphere. A simple device allows for tailoring the composition of deposited films [17-18]. In the case of no target biasing, the deposit is practically pure amorphous hydrogenated carbon. When biasing is added, tungsten target is exposed to energetic ions, so the deposited film contains also tungsten. Almost pure tungsten could be deposited using pure argon instead of acetylene as a gas in the deposition device. The concentration of tungsten in the film obviously depends on the target biasing and, predominantly on the flow rate of acetylene in the deposition system. In order to study the influence of concentration of tungsten on the properties of the films, we prepared two samples with approx. 20 at.% of tungsten and with approx. 50 at.% of tungsten.

In the case of a sample with low W content, a thin layer of pure carbon was deposited above W-C layer as well in order to simulate uneven sample structure which is more probable to occur in fusion reactors. Since the erosion rate of carbon in fusion reactors is much higher than for high-Z materials like tungsten, the deposits formed in fusion reactors are likely to contain only small amounts of tungsten. Nevertheless, we wanted to simulate also the worst case i.e. a sample with a high W content, with a structure similar to tungsten carbide. Here we should also mention that hydrogen content in our samples is unknown due to the fact that most analysis techniques cannot detect hydrogen.

Samples were exposed to oxygen plasma, at a total pressure of 70 Pa, created in a quartz tube with a diameter of 5 cm. The glowing plasma appeared inside a microwave cavity. The cavity was powered with a MW generator at the standard frequency of 2.45 GHz and the nominal power of 1000 W. Characteristics of oxygen plasma created in such a device have been elaborated recently [19] so only major parameters are stated here. The major reactant in such plasma is atomic oxygen. The neutral oxygen atom density has been measured by a calibrated catalytic probe and a value is $6 \times 10^{21} \text{ m}^{-3}$ so the corresponding flux to the surface is $9.5 \times 10^{23} \text{ m}^{-2} \text{ s}^{-1}$ [19]. The ion density in such plasma is at least four orders of magnitude
lower. Samples are kept at floating potential so the contribution of ions to the surface chemistry is neglected on the account of neutral oxygen atoms. The temperature of the sample during plasma treatment was about 850 K. This temperature is slightly higher than operating temperature expected for ITER. Nevertheless, the intensity of surface reactions (cleaning) is normally enhanced at higher temperatures and also the walls of ITER reactor can be additionally heated during plasma cleaning in order to accelerate degassing of reaction products.

The samples were characterized by Auger electron depth profiling (AES). We used standard conditions [15]. The depth profiling was obtained by etching of the films with two Ar ion guns at the energy of 3 keV and the incident angle of 47°. The estimated etching rate for a mixture of tungsten and carbon was about 2 nm/min. Sensitivity factors for W and C were measured on a standard tungsten carbide sample. The concentration of other elements was calculated by taking into account sensitivity factors from the manufacturer handbook.

Surface morphology of the samples after oxygen plasma treatment was analysed with Scanning Electron Microscope (SEM) while chemical composition of the surface was determined by X-ray photoelectron spectroscopy (XPS). The samples were irradiated with monochromatic AlKα radiation over a size of 500 μm. High-resolution spectra of W4f were measured at a pass energy of 29.35 eV and 0.1 eV energy step. More details are given in Ref [15].

3 RESULTS AND DISCUSSION

Both types of samples have been treated by oxygen plasma and characterized by AES. The most significant results are summarized in Figures 1 and 2. Figure 1 represents the evolution of the depth profiles for the case of samples with about 20 at.% of W coated with a thin layer of pure carbon (Figure 1a), while Figure 2 corresponds to 50 at.% of W. Slight variations of the W/C ratio on as-deposited sample in Figure 1a are due to the pressure instabilities of argon and acetylene gases during sample preparation by a sputter deposition. When comparing Figures 1 and 2, a huge difference is readily observed. In the case of the sample with low W content, pure carbon layer is removed in less than 5 min (Figure 1b). Furthermore, also removal of carbon from W-C layer began. This carbon is almost perfectly accomplished even after 10 min of plasma treatment (Figure 1c). Contrary to this sample, the original composition of the film for the case of the sample with 50 at.% of W still persists after prolonged plasma treatment. In fact, the depth profile shown in Figure 2b is practically the same as depth profile shown in Figure 2d. Comparable depth profiles for the case of 20 at.% of W are shown in Figures 1b and 1d. Another difference between samples with low and high concentrations of tungsten in the as-deposited films is the thickness of the interface film between deposits and the substrate. In the case of high tungsten concentration, the interface remains practically intact even after 15 min of oxygen plasma treatment, while it broadens for the case of deposits with 20 at.% of W.

A huge difference in oxidation behaviour between samples with different concentration of tungsten deserves a decent discussion. The oxidation of any material often occurs in two different mechanisms. One is called active oxidation and the other one passive oxidation. Passive oxidations means that the oxide film formed on the surface of a material prevents further oxidation because it serves as a protective barrier. A good example is oxidation of aluminium. The active oxidation, however, does not allow for forming of the protective film, as for example active oxidation of silicon carbide [20, 21]. Using these two terms we can conclude that the oxidation of amorphous hydrogenated W-C film with a high W
concentration follows the passive mechanism, while the oxidation of the material with a low W concentrations follows the active one.

Figure 1: AES depth profiles of amorphous hydrogenated carbon films with about 20 at.% of initial tungsten concentration: (a) as deposited, (b) after 5 min of O-plasma treatment, (c) after 10 min of O-plasma treatment and (d) after 15 min of O-plasma treatment
Figure 2: AES depth profiles of amorphous hydrogenated carbon films with about 50 at.\% of initial tungsten concentration: (a) as deposited, (b) after 5 min of O-plasma treatment, (c) after 10 min of O-plasma treatment and (d) after 15 min of O-plasma treatment
More difficult, however, is the explanation of this difference for our particular case. Namely, in both cases a tungsten oxide film appears on the surface of the material. Since AES is regarded as a semi-quantitative method and cannot give the answer about the oxidation state of tungsten due to unknown sensitivity factors, we performed XPS measurements which are shown in Figure 3. The oxide in Figure 3 was attributed to WO$_3$ according to the binding energy of the XPS peak of tungsten W4f, which is positioned at the energy of 35.6 eV and 37.6 eV [15]. In the case of deposits with a high tungsten concentration (Figure 2), the oxide film prevents degradation of hydrogenated carbon deposits, while in the other case (Figure 1) the “same” oxide film does not prevent the degradation. One possible explanation of this paradox takes into account the porosity of tungsten films created after the removal of hydrogenated carbon and oxidation of the surface film. The AES depth profiles, of course, cannot distinguish the samples from their roughness and porosity. Namely, AES only gives information on the composition of a thin film. Still, a person with a common sense would suppose that the oxide film formed on the surface of a material originally rich with tungsten would be more compact than the same film formed on the surface of a material with a low concentration of tungsten. The surface film that evolves in the first few minutes of oxygen plasma treatment, is probably rather compact and prevents migration of oxygen inside where it would interact with hydrogenated carbon. This is probably the reason why the depth profiles shown in Figures 2b, 2c, and 2d are practically equal. On the other hand, the tungsten oxide film that forms on the surface of the material with originally low concentration of tungsten is porous enough to allow for further interaction between atomic oxygen from gaseous plasma and hydrogenated carbon left between the oxide film and the substrate. The migration of oxygen through the tungsten oxide film presented in Figure 1b is definitely not diffusion. It is rather movement through gaps generated by the carbon consumption between the tungsten oxide grains.

This migration is obviously sufficient enough to remove almost entire hydrogenated carbon from the layer already in 10 min of plasma treatment (Figure 1c). In order to prove the theory stated above we recorded SEM images of the surface as well. They are shown in Figure 4. We can observe very porous structure for the sample with low W content, while in the case of the sample with higher W-content the surface looks much more compact. So this result proves that porosity of the oxide film is responsible for sufficient removal of hydrogen from a sample with low W content.

![Figure 3: High-resolution XPS spectra of tungsten for untreated (in both cases we observe metallic tungsten) and for both plasma treated samples where tungsten is oxidized to WO$_3$.](image-url)
Another difference between depth profiles presented in Figures 1 and 2 is worth discussing: it is the thickness of the interface between the deposit and the substrate. Substrates were highly polished pieces of stainless steel. Although the coatings of hydrogenated tungsten-carbon deposits are almost 1 μm thick, the interface as revealed from Figures 1a and 2a is very sharp. This sharpness indicates no migration of atoms in the thin films. In fact, there are little reasons for migration. As samples are exposed to oxygen plasma, the situation becomes different. Comparison of Figures 1c and 2c reveals a rather thick interface in the case of samples with a low initial concentration of W. The effect is perhaps even more pronounced after 15 min of oxygen plasma treatment (Figures 1d and 2d). Obviously, a reason for atom migration at interfaces should appear in the case with deposits with low W concentration. The most usual reason for elemental diffusion is elevated temperature. The compact tungsten oxide film developed on the samples (Figures 2b and 2d) represent a barrier for oxygen atoms. The probability for heterogeneous surface recombination on flat metal oxides is rather low, so materials are not heated by this process. On the other hand, the probability for recombination for very rough materials could be higher even though the corresponding value for flat material is very low [22]. Since oxygen atoms can reach the hydrogenated carbon film through the tungsten oxide film, we can conclude that this material has numerous gaps so the recombination coefficient should be much larger than the corresponding value for flat material. A larger recombination coefficient causes additional heating and this in turn causes migration of elements at interfaces. Here, it is maybe also worth mentioning that oxidation of hydrogenated carbon films itself is an exothermic reaction.
4 CONCLUSION

A huge difference in the behavior of hydrogenated carbon films with two different concentrations of tungsten and different structure upon exposure to highly reactive oxygen plasma was observed. In the case of deposit with about 50 at.% of W, the exposure to oxygen plasma resulted in the formation of a thin passive layer that prevented interaction between reactive oxygen particles and hydrogenated carbon below the oxide film. The thickness of the oxide film remained unchanged even after prolonged plasma treatment. The removal of hydrogenated carbon from deposits with about 20 at.% of W was accomplished successfully in about 10 min of plasma treatment. The fact that the hydrogenated carbon was oxidized although the film of tungsten oxide appeared on the surface was explained by a porous structure of the tungsten oxide film due to the carbon consumption in the case of a low initial concentration of tungsten. The porosity is obviously high enough to allow for a contact between reactive oxygen particles and the hydrogenated carbon film between the tungsten oxide layer and the substrate. The reactive oxygen particles that are capable of interaction with hydrogenated carbon below the oxide film are most probably neutral oxygen atoms. Namely, charged particles neutralize at very high probability at the first collision with a solid material and any metastable particles are also likely to de-excite on the way through the porous tungsten oxide film.

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