FORMATION AND EROSION OF WC UNDER W^+ IRRADIATION OF GRAPHITE

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ABSTRACT

The bombardment of C with 100 keV and 1 MeV W at normal incidence is studied as a function of the incident W fluence experimentally and by computer simulation with the program TRIDYN. Calculated oscillations in the amount of retained W and in the target weight change are confirmed experimentally for 100 keV at room temperature. XPS investigations show W_2C formation during ion implantation already at room temperature. RBS depth profiles for 1 MeV bombardment show W mobility and surface segregation even at liquid nitrogen (LN_2) temperatures. At elevated temperatures W clusters to form nano-particles at the surface and the oscillations in the retained amount of W disappear.

INTRODUCTION

In a future large fusion machine, ITER [1], three elements have been proposed to serve as first wall materials in different locations; Be for the main vessel wall, and C and W in the divertor. These materials will interact on plasma-facing surfaces due to erosion and re-deposition. As shown earlier [2], in the case of bombardment of W with C, erosion occurs at small ion fluences followed by net deposition as C covers the W surface. Recently it has been found in computer simulations, that oscillations in the sputtering yield as a function of fluence can occur [3]. Due to the strong implications of these kinds of effects in fusion plasma machines, it is the aim of this paper to show that these oscillation effects can also be observed experimentally. At temperatures of 100°C and above the oscillations disappear.

EXPERIMENTAL PROCEDURE

The substrates used in this work were 12 x 15 x 0.5 mm^3 rectangles of oriented high purity pyrolytic graphite supplied by Union Carbide Corp. that were cut with the graphite planes either parallel or perpendicular to the sample surface. The blanks were mechanically polished to produce a mirror finish on the active surface.

Bombardment with 100 keV W ions was carried out on an Extrion model 200-1000 ion implantation accelerator at room temperature and elevated temperatures up to 700°C. 1 MeV implantations were performed on a 1.7 MeV General Ionics Tandetron at room temperature and at liquid-nitrogen (LN_2) temperature. Temperatures were monitored by chromel-alumel thermocouples mounted in the sample holders. The vacuum in the chamber was typically in the low 10^{-7} mbar range during operation. For all implants the beam was rastered so that the beam was reduced from its unrastered value by approximately 30% in each direction to give reasonable uniformity over the implanted region.

The samples were weighed before and after each implantation using a Mettler micro-balance with a sensitivity of 1 microgram. The balance was zeroed before and after each measurement, but drift could not be totally eliminated and the error in the measured masses was estimated to be ±3 micrograms. The amount of W retained in the samples was measured quantitatively after each dose using Rutherford backscattering spectrometry (RBS) with 2.3 MeV ^4He ions at a detector angle of 160°. The sample was tilted at 60° to the incident beam in the

direction of the detector to improve the depth resolution. Accurate depth profiles were extracted from the raw data using Bayesian statistics as described in ref. [4].

XPS analysis was done in a commercial Perkin-Elmer ESCA 6000 Chamber.

SIMULATION

The Monte Carlo program TRIDYN [5,6] is used for the calculations. It is based on the static Monte Carlo program TRIM.SP [6,7], but takes dynamic target changes into account. A randomized target structure is assumed, and the atomic interactions are treated as a sequence of binary collisions. In all calculations the WHB (Kr-C) potential [8] is applied. The inelastic energy loss is described by an equipartition of the continuous Lindhard-Scharff [9] and the local Oen-Robinson [10] models.

A pseudo-projectile corresponds to an incoming fluence. After the collision cascade of each pseudo-projectile is finished, the target composition and density are updated [5]. The surface binding energy is chosen according to the surface composition as given in ref. [11], where the surface binding energy is linearly interpolated between the corresponding values of the pure elements. TRIDYN allows the determination of sputtering yields, reflection coefficients, composition, depth profiles of the implanted species, and related values as a function of the incident fluence. The target weight changes according to the difference between the implanted amount and the amount removed from the target.

RESULTS AND DISCUSSION

100 keV W^+ implantation at different temperatures

Room temperature

The retention of W at 100 keV increases linearly at low fluences with a slope close to 100%. At high fluences it reaches a steady state as the selfsputtering yield of W is larger than unity and no solid W layers can build up. The transition from the linear increase to steady state proceeds through a number of oscillations which have been predicted in computer simulations [3] and demonstrated experimentally [4] (Fig. 1a).

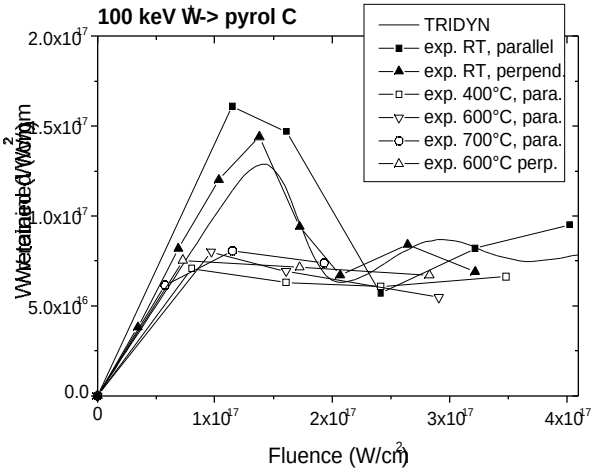

Fig. 1a: Retained W at different target temperatures

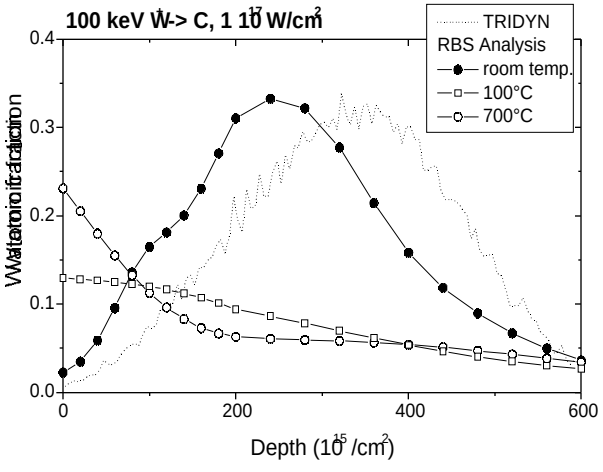

Fig. 1b: W depth profiles at $1x10^{17}$ W/cm^2 for different target temperatures

These oscillations can best be understood from the implantation profiles of W at different fluences. Experimental and calculated profiles show good agreement at the lowest fluences for

the implantation profile of W into the pure carbon substrate. The mean range is about 40 nm and the width of the distribution at 10 nm is much smaller than the mean range. This is typical for heavy ion implantation into low-Z substrates, as the heavy ions cannot be scattered by angles larger than $\arcsin(M_2/M_1)$. With increasing fluence carbon surface atoms are sputtered, bringing previously implanted W atoms closer to the surface. In the present case the carbon sputtering yield, Y_C, due to 100 keV W ions is on the order of 2, increasing to values around 4 due to the accumulation of W near the surface [3]. With continuous sputtering the resulting W profile flattens and the maximum concentration in the bulk gets close to 20 at%. At a fluence of 1×10^{17} atoms/cm^2, the erosion has brought the distribution close to the surface and the W surface concentration increases. In addition to carbon sputtering, W sputtering also has to be considered. As the self-sputtering yield of pure W, Y_W, is about 3, the same amount of W is eroded as implanted for a surface concentration of $1/Y_W$, i.e., at 33 at%. In order to reach steady state conditions, preferential sputtering of carbon atoms will increase the W concentration within the first monolayers to 33%. The concentration within the ion range is determined by the total sputtering yield to be $1/Y_{tot} = 0.2$. These features are clearly seen in the calculated steady state W profiles and are reproduced experimentally [4].

These zero-order processes alone would lead to a continuous increase of the implanted amount of W with fluence until steady state is reached. However, the different locations of W deposition, at the end of range, and W erosion, at the surface, lead to a non-monotonic approach to saturation. Initially, with no W near the surface, sputtering proceeds slowly and high W concentrations build up within the ion range while W sputtering is still negligible. This over-saturation of W leads transiently to an implanted amount much larger than in saturation. As soon as this high W concentration reaches the surface, self-sputtering rapidly reduces the W amount until a surface concentration of 33% is reached. At this stage, the narrow W profile contains fewer W atoms than in steady state. During further implantation, the profile broadens due to the lower electronic stopping and the steady state W concentration is reached after several successively smaller oscillations. The calculated and measured dependences of the implanted W amount with fluence at room temperature are compared in Fig.1a and show excellent agreement.

Another quantity, which gives direct information about the erosion of the carbon substrate, is the weight change of the probe. As W atoms are about 15 times heavier than carbon atoms, the probe will initially gain weight in oscillations similar to those of the implanted amount of W. Once steady state is reached and the implanted W amount stays constant, the additional weight loss becomes a measure of the carbon sputtering yield [4]. From the weight decrease with fluence at saturation a carbon sputtering yield of 3.5 is deduced.

Elevated temperatures

At elevated temperature diffusional effects may alter the implantation profiles and the erosion behavior without being predictable using the TRIDYN code. Figure 1a shows the fluence dependence of the W retention at 400, 600, and 700°C in comparison with the calculated retention curve. Clearly, at elevated temperatures, the oscillations in the retained W amount have disappeared, and a monotonic increase and smooth transition toward the steady state value are observed. Data at 600°C show that this behavior is independent of the direction of the crystal lattice in the pyrolytic graphite, as damage due to the W implantation amorphises the carbon material [12].

The change in the retention behavior must reflect in the depth profiles at room temperature and elevated temperatures. While at room temperature a W implantation profile is found with a maximum correlated to the ion range and negligible surface concentration, the profile at 700°C

has its maximum at the surface (Fig.1b). Already at 100°C the profile broadens towards the surface and the oscillations disappear. Evidently, diffusional effects and surface segregation tend to broaden the profile. As literature values for carbon self-diffusion and diffusion of carbon in W at room temperature are much too low to explain these effects, ion-enhanced diffusion of displaced carbon atoms must be responsible for the observed mobility [13].

The mobility of implanted W atoms not only leads to segregation at the surface as revealed by the depth profiles, but also to clustering of W atoms into particles of sizes up to 100 nm. Fig. 2a shows the surface topography after 1 x 10^{17} W/cm^2 implantation at 600°C.

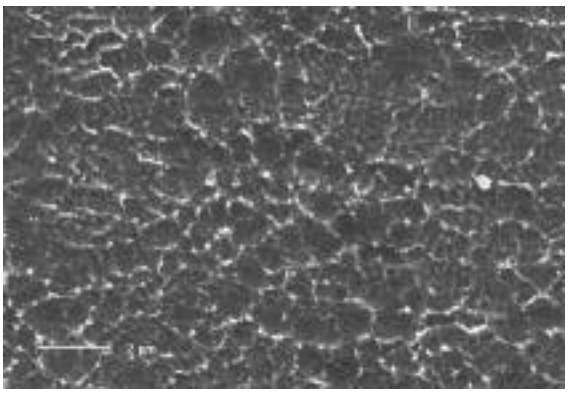

Fig. 2a: Surface topography after 3x10^{17} W/cm^2 at 100 keV and 600°C

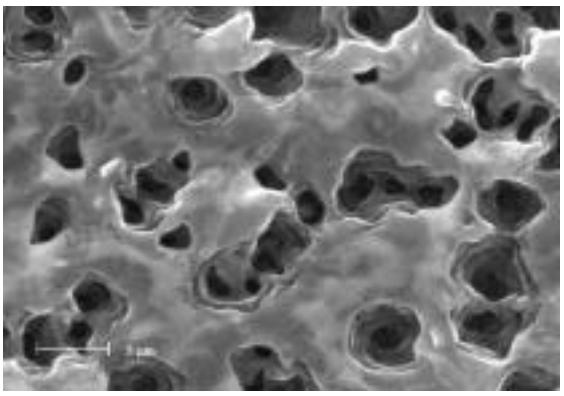

Fig. 2b: Surface topography after 1.3x10^{18} W/cm^2 at 1MeV and room temperature

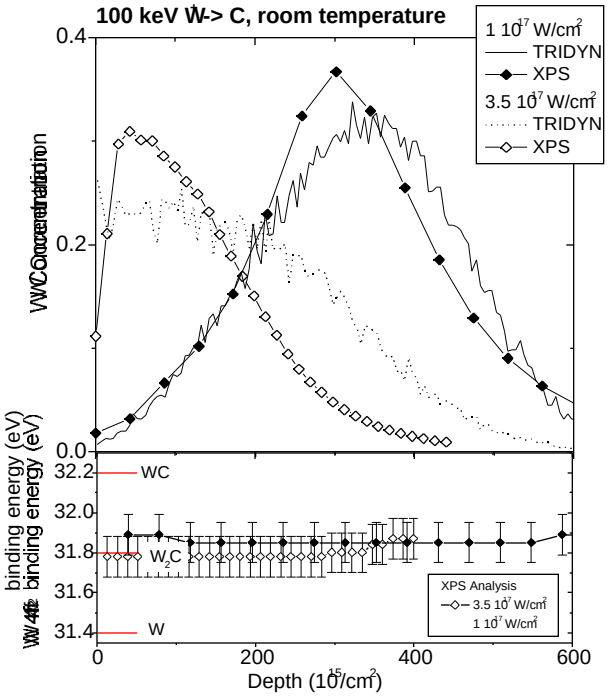

Fig. 3: Depth profiles of W concentration and W 4f$_{7/2}$ electron binding energy at 20°C

A network of small clusters decorates the grain structure of the pyrolytic graphite. The Z-contrast of backscattered electrons reveals the high W content of most of these particles. Depressions between clusters due to erosion indicate that W rich clusters, most probably W_2C, protect the surface from erosion, while unprotected graphite is preferentially sputtered.

Chemical phase investigation using X-ray photoelectron spectroscopy (XPS) demonstrates that evaporated carbon layers on W transform quantitatively to W_2C or WC at temperatures of 700°C [14,15]. The present investigations show that during ion implantation tungsten carbide is formed already at room temperature. In fig. 3 the depth profiles of W at room temperature for fluences of 1 x10^{17} W/cm^2 and in saturation are shown as obtained from 5 keV Ar sputtering of the sample after transfer to the XPS system. From the shift of the binding energy of the W4f$_{7/2}$ electrons, the carbide can be identified as W_2C (Fig. 3). This result is in agreement with arguments that carbide formation in the W-C system occurs

endothermically as soon as C and W atoms come into contact, and enhanced temperatures are only necessary in layered systems requiring atom mobility [13].

1 MeV W^+ implantation at 20°C and LN_2 temperatures

Room temperature

At 1 MeV the W range is about 10 times longer and the sputtering yield is lower than at 100 keV. Consequently, predicted oscillations occur at much higher fluences and are more pronounced. However, already at room temperature no such oscillations are observed (Fig. 4a). At the same time, depth profiles of W show a broad indistinct distribution already at fluences of $5x10^{17}$ W/cm^2.

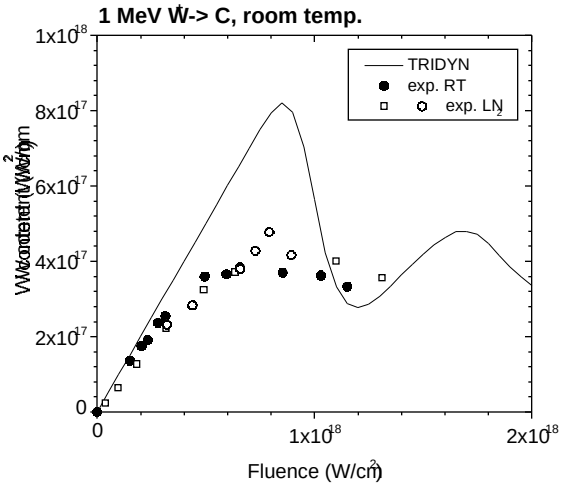

Fig. 4a: Fluence dependence of retained W

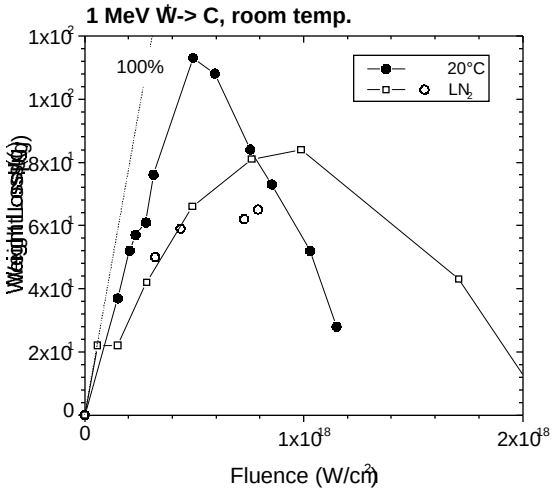

Fig.4b: Fluence dependence of weight loss

Scanning electron micrographs (SEM) of the implanted surface at a fluence of 1 $x10^{18}$ W/cm^2 show strong non-uniform erosion of the surface. Parts of the surface are covered with a W-rich layer, as revealed by backscattered electron imaging, while unprotected parts show deep holes of about 1 μm diameter (Fig. 2b). Evidently, in contrast to the case of 100 keV implantation, for 1 MeV bombardment at room temperature, W mobility leads to surface accumulation and clustering.

Liquid nitrogen temperatures

In order to reduce the W mobility the same implantation sequence was performed at LN_2 temperatures. The retention of W increases further than at room temperature, but there is only a vague indication of an oscillation (Fig 4a). At LN_2 temperatures, SEM shows no surface roughening or W clustering. However, the depth profile of W as determined from RBS shows a very distinct change (Fig. 5). At fluences up to 1 $x10^{17}$ W/cm^2, the profile still agrees well with TRIDYN calculations. At higher fluences, however, the W profile stretches toward the surface and at 2 $x10^{17}$ W/cm^2 a sharp, narrow surface peak develops, indicating a uniform surface coverage of about 10 monolayers of segregated W atoms. As this fluence is reached, W sputtering sets in and prevents the development of a pronounced oscillation peak. This behavior is clearly reflected in the development of the weight change of the sample. At 2 $x10^{17}$ W/cm^2 the linear increase due to W implantation deviates from the predicted 100% line (Fig. 4b).

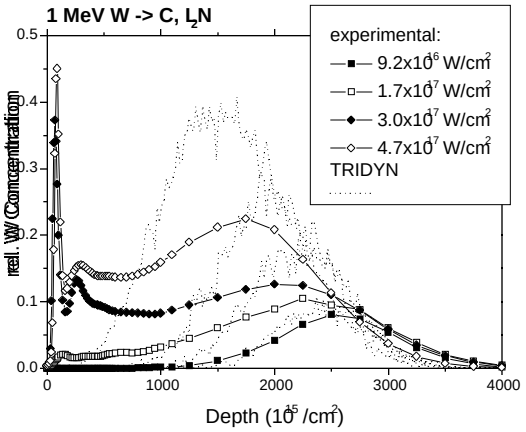

Fig. 5: Comparison of measured depth profiles at LN_2 temperature with corresponding TRIDYN calculations

CONCLUSION

For 100 keV W bombardment of graphite, the W implantation profiles in carbon, the retained amount of W, and the carbon erosion at room temperature can be reproduced well by dynamic implantation codes such as TRIDYN. Since the self-sputtering of W above an energy of 1 keV is larger than unity, a saturation in the implanted amount is reached at high fluences. The oscillatory behavior in approaching this steady state is due to changes in the implantation profile during the implantation and erosion process. At temperatures slightly above room temperature, ion induced mobility and carbide phase formation move the implantation profile toward the surface, and SEM imaging reveals surface clustering of W_2C precipitates. The steady state is reached smoothly without oscillation.

At 1 MeV, the larger separation of the range profile from the surface facilitates the detection of surface segregation effects. Indeed, it has been shown that, even at LN_2 temperatures, several monolayers of W segregate uniformly at the surface without drastic changes of the surface topography. At room temperature this segregated layer clusters into non-uniform W_2C particles leading to a strongly non-uniform erosion and leaving, at fluences above 1 $x10^{18}$ W/cm^2, a porous surface with deep holes.

ACKNOWLEDGEMENT

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