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Deuterium-induced chemical erosion of carbon-metal layers

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Abstract

Magnetron-sputtered layers consisting of carbon and metal (W, Ti, V) were produced with 0–20 at.% metal concentration. The mixed layers were characterised by RBS, SEM, XRD and XPS, and exposed to D_3^+ ions of 30 eV/D at temperatures between 77 and 1100 K. The chemical erosion yield was investigated by mass spectrometry and RBS. Above RT (∼300 K), the CD_4 production yield for pure C layers exhibits a maximum around 750 K, which decreases with increasing metal concentration. For more than ∼3 at.% W, ∼6 at.% V and ∼7 at.% Ti, the maximum vanishes and the CD_4 yield continuously diminishes with temperature. A decrease of the activation energy for ion-induced hydrogen release by adding dopants is responsible for the decrease. The CD_4 yield at RT increases depending on metal and concentration, because the distribution of the erosion products is changed. Enrichment of metal on the surface with ion fluence is observed.

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Keywords: Amorphous films; Carbon-based materials; Chemical erosion; Erosion & deposition; Hydrocarbons

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1. Introduction

The usage of carbon materials together with metallic plasma-facing materials in fusion devices – as planned for ITER with Be, W, and C [1] – will lead to the deposition of mixed layers [2]. These layers, containing carbon and metals in different ratios, could be re-eroded by hydrogen. Therefore, the chemical erosion behaviour of such mixed layers should be investigated and clarified to improve estimations for re-erosion of mixed layers. Additionally, the co-deposition with hydrogen and the hydrogen inventory (T inventory) of the mixed materials have to be examined, too.

From studies of doped carbon materials it is known that metal-doping in carbon materials influences the processes of chemical erosion of carbon by hydrogen impact [3–5]. Therefore, the aim of this investigation is to obtain erosion data for metal-containing C layers and correlate them with the mechanisms of chemical erosion, as done in earlier studies [6–8]. Some of the interactions between carbon and hydrogen involved in the erosion process, such as the H–C bonding, determine the hydrogen inventory and the release of hydrogen from these layers.

The mixed layers were produced by magnetron-sputtering in order to simulate the deposition process that takes place in a fusion plasma environment. In both cases, material arrives at the substrate (wall) mainly as single atoms. Furthermore, hydrocarbons contribute to the growth of mixed layers in fusion plasma devices [9]. The difference due to the H content will vanish during the erosion with hydrogen [10].

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To obtain the strongest influence of dopants on the chemical erosion, the distribution of dopants should be as fine as possible, i.e. atomically dispersed [3]. Therefore, it is important for this work to characterise the layer growth and clustering of dopant atoms during deposition and thermal treatments.

Such nano-structured carbon layers enjoy great popularity because of their excellent tribological properties [11–17]. Nano-structured carbon has shown promising properties for a wide range of applications in microelectronics, electrochemistry, catalysis, gas-sensing and hydrogen storage [18]. Additionally, these layers are an ideal test system for diffusion and reaction studies [19,20], as well as for investigations of the catalytic effect of some metals on the graphitization during production of doped graphites [16,21,22].

In this paper the investigation is focused on the chemical erosion by 30 eV deuterium impact on magnetron-sputtered carbon layers doped with Ti, W and V. This study continues and extends the previous one on hydrogenated carbon films doped with Ti [7].

2. Experimental

2.1. Layer production and characterisation

Pure carbon layers and layers doped with Ti, W and V were prepared by magnetron-sputtering. The mixed films were deposited on silicon and graphite substrates using two different types of discharges in two independent sources of a commercial device (DC: metal cathode; RF: graphite cathode). The specimen holder, which rotated during deposition, was neither biased nor intentionally heated. Argon was used as sputtering gas with a working pressure of ~0.45 Pa, which was stabilised by controlling the Ar influx. The metal concentration in the carbon layers was controlled by varying the DC power, and it ranges from 0 to 20 at.%, the lowest concentrations (<2 at.%) being the most difficult ones to obtain. More details about deposition and layer properties can be found elsewhere [5,8,23].

Composition, thickness, and homogeneity in depth of the layers were determined by ion backscattering of 0.8–4.0 MeV ^{4}He at a scattering angle of 165°. The total C content was measured by backscattering of 1.5 MeV protons. The lateral homogeneity and the growth morphology of the layers were studied by SEM and their crystallinity by XRD. The chemical state for the outermost atomic layers was determined by XPS. The layer thickness was also obtained by profilometry.

The mixed layers have a thickness between 0.4 and 1.4 μm and show adequate homogeneity of better than ~1 at.% across the depths of interest for the erosion experiments (<100 nm). The maximal oxygen content is kept below 4 at.%, and in all cases less than 1 at.% argon is detected.

The surface morphology of the layers, i.e. the natural roughness, looks like small spheres with a lateral extent of around 25 nm and a height of significantly less than 10 nm for a layer thickness of several hundred nanometres. Defects, i.e. roughness of the substrate (graphite), enlarge the spherical structures by up to one order of magnitude. Such spherical structures are typical for columnar growth [11].

Heating at 1100 K for ~0.25 h prior to the erosion experiments removes all argon, promotes atomic order, and increases the crystallite size of the carbide clusters above the detection threshold of XRD [23]. This implies that, even if there would be no mobility and clustering during the deposition process, the dopant atoms are at least partly clustered to a few nanometer large carbide grains by the heating process. The C phase stays amorphous. No other changes are observed after heating.

2.2. Erosion experiment

All erosion experiments were performed at the high current ion source in Garching [8,24] with 90 eV D_3^+, i.e. 30 eV per deuterium. The ion flux was around 10^{19} D/m^{2}s, and the erosion spot was ~0.4 cm^2. The specimens were heated by electron bombardment from the rear and their temperature was monitored by an IR-pyrometer. Before the erosion experiment, the specimens were heated up to ~1100 K for ~0.25 h to degas them and their surrounding. During the erosion experiment, the specimen temperature was increased in steps. It was assured that a nearly constant emission of erosion products was reached at each step. The accumulated fluence per temperature step was usually between 2 and 8×10^{21} D/m^2.

The chemical erosion yield was determined by quadrupole mass spectrometry. The time evolution of the emission rates of masses 2 to 40 was recorded. The signal of deuterated methane (CD_4), i.e. mass 20, is predominately evaluated. The mass signals without ion beam were recorded before the heating ramp, at the end of it, and after cooling down. Then they were used to linearly interpolate the background. The linearity was checked at some intermediate temperatures.

Once the background was eliminated, the CD_4 signal was scaled in the same way as reported in [24]. The CD_4 signal of pyrolytic graphite bombarded with 1 keV/D at around 800 K was set equal to a chemical erosion yield of 10%. This calibration does not take into account variations in the ratios of radicals to molecules and of C_1D_z to $C_{x>1}D_y$ for different impact energies. For example, the CD_4 production yield at ~300 K for 30 eV/D is 1.5% CD_4/D, while the total carbon erosion yield gained by weight loss measurements is ~4% C/D [24].

With another specimen holder, temperatures down to 77 K, i.e. liquid nitrogen, were achieved. The temperature was measured by a thermocouple (K type). Degassing was performed by heating for 1 hour at 410 K, which is the maximum achievable temperature for this holder. The size of the erosion spot for this set-up was ~0.8 cm^2. The calibration of the CD_4 signal, as described above, is not absolutely valid because the pumping conditions, e.g. additional cryo trap, were altered by changing the specimen holder. Therefore, the yield for a pyrolytic graphite specimen at ~300 K (RT) acquired with the high temperature holder is used to scale all data obtained with the low temperature holder.

3. Results and discussion

Fig. 1 shows the temperature dependence of the CD_4 production yield of carbon layers doped with different concentrations of V, Ti and W. For comparison, data belonging to pure carbon layers and pyrolytic graphite are included. The yield of pure carbons exhibit the well-known maximum at ~750 K [4,24,25].

The enhanced maximal yield of the pure C layer compared to pyrolytic graphite around 750 K is explained by differences in the C structure [5,8], even though the CD_4 yield remains the same at RT. The yield below RT is found to be independent of temperature for both, pyrolytic graphite and carbon layers [5,8].

All modifications of the yield-temperature dependence by doping compared to pure carbon can be summarised as:

(i) the CD_4 production yield is increased at RT and
(ii) the CD_4 production yield around the maximum (~750 K) is strongly reduced.

For *vanadium-doped* layers, the CD_4 production yield at RT increases with V concentration; nearly by a factor of 2 for 18 at.% V-doped layers. In contrast, the yield at higher temperatures, e.g. around 750 K, drastically decreases in the same V concentration range (0.5–18 at.% V), and above 6 at.% V the yield only diminishes above RT.

The temperature dependence of the specimen doped with 7 at.% V shows a pronounced shoulder above 800 K. The signal of mass 19, e.g. CD_3H or HDO, exhibits a peak at the same temperature. Similar shoulders and peaks, but less pronounced, are also visible in other data sets (Fig. 1). It is not clear whether these shoulders truly originate from erosion or are experimental artefacts.

For *titanium-doped* layers, the yield decreases with Ti concentration over the whole temperature range. For a concentration of ~7 at.% Ti, the maximum already vanishes. The yield at RT shows an astonishing behaviour: it increases by ~60% compared to pure carbon, and it does so already for the lowest achieved Ti concentration of 1.5 at.% Ti. It would be interesting to investigate even lower Ti concentrations.

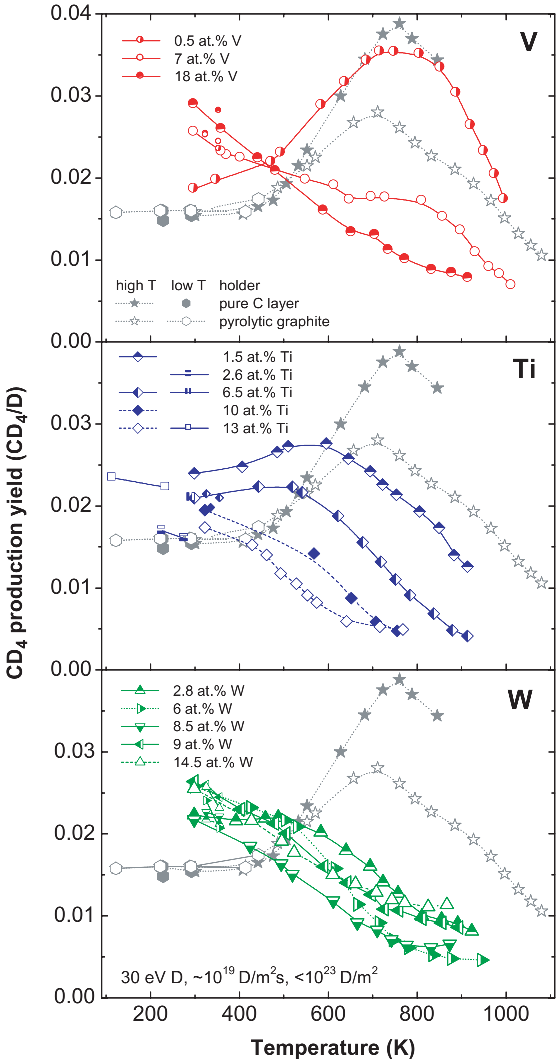

Fig. 1. Methane production yield of C layers doped with V, Ti and W versus specimen temperature during bombardment with 30 eV/D and a flux of ~10^{19} D/m^2 s. The accumulated fluence is always less than 10^{23} D/m^2 and mostly less than 5×10^{22} D/m^2 at the highest temperature. The yield after cooling down to nearly 300 K is given as small symbols. For comparison, data for pyrolytic graphite and pure C layers from previous studies are inserted [8]. Additionally data measured at low temperatures and on hydrogenated carbon layers doped with 10 and 13 at.% Ti (dashed lines) are added for completeness [7,8].

For *tungsten-doped* layers, a similar trend is not evident in Fig. 1. The variation in the yields is smaller than for the two other dopants in the same concentration range. For the lowest W concentration (2.8 at.% W), the maximum above RT has already disappeared.

To highlight the dependency on metal concentration, some data from Fig. 1 are plotted in Fig. 2 versus the bulk concentration. Around 600 K, the CD_4 production yield decreases with concentration for the three metals. At RT, the yield shows a maximum whose location depends on the dopant type. The maximum is below 1.5 at.%, around 10 at.% and above 18 at.% for Ti, W and V, respectively. Note that the concentration values given above will depend on the cluster size of the dopant.

Published data for Ti-doped specimen, which were only pre-heated at 410 K, are also introduced in Figs. 1 and 2 (squares [8]). The two data sets for Ti-doping in Fig. 2 are not consistent, even though the layer production and erosion measurements are nearly the same. The main difference between both measurements is the heat treatment in the two different holders and, therefore, the thermally induced changes in the layers, e.g. the cluster size of the dopant.

It was previously discussed [7], that disturbing contributions to mass 20, i.e. CD_4, come from the background gas, from CD_3 reacting with D on the walls, and from ion-induced desorption of CD_4 and D_2O by reflected ions. Cracking of heavier hydrocarbons can be neglected [7]. At higher temperatures (>800 K), the background reaches in some cases more than 50% of the raw signal. The uncertainties introduced by background subtraction, together with fluctuations in the ion current, restrict the accuracy for the reduction factor of the yield at ~750 K, which is roughly a factor of 10 for all three dopants with ~15 at.%.

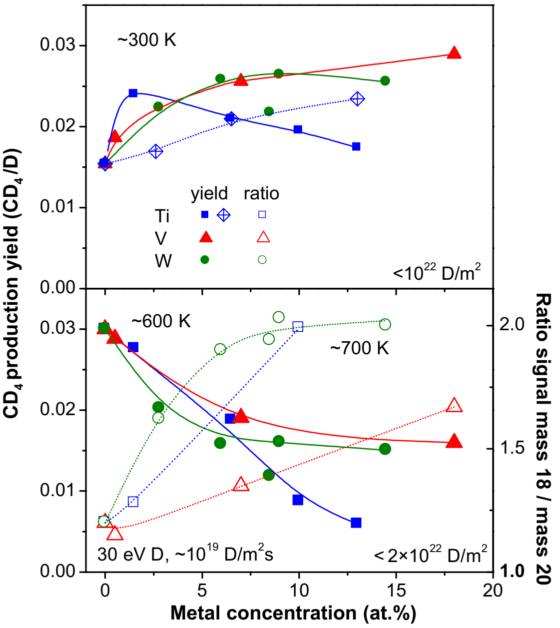

Fig. 2. Methane production yield by 30 eV/D bombardment at 300 and 600 K (filled symbols) and ratio of the signals of mass 18 to mass 20 at 700 K (open symbols) of C layers doped with V, Ti and W versus bulk metal concentration. The data at 300 K and elevated temperatures have an accumulated fluence of less than 1 and 2×10^{22} D/m^2, respectively. Previously published yield data for Ti-doped layers are inserted (crossed symbols [8]). The lines are only to guide the eyes.

The data at RT could all be systematically to low, because constant emission of the erosion products was not achieved. For this, higher fluences would have been needed. On the other hand, the accumulated fluence should be minimised for measuring a complete temperature dependency to avoid strong enrichment of the metal. For all shown temperature dependencies (Fig. 1), the accumulated fluences are below 10^{23} D/m^2 and for the majority even below 5×10^{22} D/m^2. The effect of dopant enrichment is checked by measuring the yield after cooling down to RT (small symbols in Fig. 1). For layers doped with W and V, these values are slightly higher (<10%) than the starting ones, while for the Ti-doped layers these values are decreased [7].

From RBS measurements it has been proven that the metal enriches near the surface for all three metals.

Additionally from RBS, the total carbon loss is determined for a 6.5 at.% Ti-doped layer exposed to high fluences (2.4×10^{23} D/m^2) at temperatures below 350 K. The result is a total carbon erosion yield of 1.5% ± 0.5% C/D, which is less than the half the value of pure carbon (~4% C/D [24]), i.e. a reduction by more than 50%.

From another point of view, the ratio of C erosion detected as CD_4 to the total erosion yield is for pure carbon ~40%, while it is for the 6.5 at.% Ti-doped layer about ~70% (~0.01 CD_4/D [8]). This implies that the amount of heavier hydrocarbons and of high-sticking erosion products is reduced relative to CD_4 by the presence of metal.

As reported previously [7], the ratios of the signals of masses 18 (CD_3) and 20 of Ti-doped layers show different temperature dependencies than those for pyrolytic graphite. For pyrolytic graphite as well as for the pure carbon layer, the ratio is nearly constant between RT and ~800 K, while for all doped layers it increases with temperature and dopant concentration. Tungsten-doping exhibits the strongest increase, which seems to saturate with concentration (Fig. 2, open symbols). Unfortunately, the mass signals for the heavier hydrocarbons are still not suitable for data evaluation.

It would be helpful for the mechanistic interpretation to measure also for the V-doped layers the temperature dependence below RT. For Ti-doping it is reported that the yield is constant below RT [8]. From the slope of the temperature dependence close to RT at higher V concentrations, it could be expected that the CD_4 production yield increases for V-doped layers with further decreasing temperature.

4. Conclusion

The temperature dependence of the CD_4 production yield of mixed layers containing carbon and metals is investigated for bombardment with a D_3^+ beam of 30 eV/D. For all three metals, V, Ti and W, a strong reduction of the well-known maximum in the yield-temperature dependence of pure carbon is observed. The reduction depends on the metal concentration and the yield diminishes continuously above RT for 3 at.% W, 6 at.% V and 7 at.% Ti. This reduction of the CD_4 yield at elevated temperatures could be explained as a decrease of the activation energy for the hydrogen release during ion impact of these dopants, as previously reported for B and Ti [6,7]. It could be speculated that this lowered activation energy causes lower desorption temperatures for retained hydrogen in such mixed layers. This would of course be of interest for the estimation of tritium inventory in deposited mixed material.

The CD_4 production yield for all doped layers is enhanced at RT compared to pure C. This enhancement depends on the metal concentration showing a maximum. This maximum is found at concentrations below 1.5 at.%, around 10 at.% and above 18 at.% for Ti, W and V, respectively. The enhanced CD_4 yield implies that the distribution of the erosion products is changed to an increased CD_4 production. A proof for this interpretation is provided by total erosion yield measurements, e.g. by RBS.

The key question for the impact of this study is whether the CD_4 yield is still a good proof of the total erosion yield at all temperatures or not. At RT this has been proven here. At ~600 K the reduction in CD_4 yield results in a reduction of the total erosion yield, as it is already shown in an earlier paper [7], where the erosion yield was determined to be 2.5% ± 1.5%. If this yield is compared with the one corresponding to pyrolytic graphite under the same conditions at 600 K, which is reported to be 8.5% [24], a reduction of the total erosion yield by a factor of more than 3 is observed, even without taking into account that disordered carbon has a higher erosion yield than graphite [25]. Nevertheless, it has already been planned to erode at a fixed temperature differently doped layers and determine the total erosion yield by means of RBS. Additionally, the expected increase of the CD_4 yield with fluence due to enrichment of the dopant by preferential erosion of C for layers with concentrations below the maximum can also be experimentally investigated. The final data of the measurement series taken after returning to RT in Fig. 1 support this expectation.

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