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# Chemical erosion by deuterium impact on carbon films doped with nanometer-sized carbide crystallites

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## Abstract

The erosion by 30 and 200 eV/D at temperatures between 300 and 1100 K was investigated for magnetron-sputtered films, consisting of carbon and metal (2–7 at.% W, Ti, Zr) present as nanometer-sized carbide crystallites. The total erosion yield was determined from weight-loss measurements and film thickness changes measured by RBS. The chemical erosion yield was obtained from the $CD_4$ signal of mass spectrometry. The total erosion yield of doped films is reduced by a factor of 3–20 compared to pure C films. The $CD_4$ production yield decreases less implying that the distribution of the chemically eroded species was changed by the dopants. Therefore, measuring only $CD_4$ production or its spectroscopic signature could yield to misleading values and interpretations.

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## 1. Introduction

The use of carbon materials together with metallic plasma-facing materials (PFMs) in fusion devices – as planned for ITER with Be, W, and C [1] – will lead to cycles of erosion of the PFMs by hydrogen and subsequent deposition of mixed carbon–metal layers [2]. These layers will be partly on areas subjected to further erosion during the lifetime of the plasma-facing components and partly on hidden areas. Therefore, the erosion behaviour of such mixed layers needs to be investigated, together with their co-deposition with hydrogen (T inventory). Moreover, a reduction of the chemical erosion of carbon by doping has been reported [3,4] but is still not fully understood. Hence, metal-doped carbon films emerge as ideal model specimens for mechanistic investigations of the erosion of doped carbon by hydrogen.

In previous studies, the temperature dependence of the $CD_4$ production yield of doped carbon films was determined for 30 eV deuterium impact [5–7]. The investigated dopants – W, Ti, and V – reduce the maximum in the $CD_4$ production yield, occurring in temperature-dependent measurements. Depending on the concentration of the dopant, the maximum may even be suppressed such that

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the yield monotonically drops from room temperature (RT) to elevated temperatures. On the other hand, the $CD_4$ production yield of doped carbon films increases at RT compared to pure carbon materials, while measurements of the total erosion yield of these films indicate a reduction. As a key question from the latest paper published by our group [7], it arose whether the $CD_4$ emission is a good measure for chemical erosion yields. Other groups spend a lot of effort to detect and quantify heavier hydrocarbons [8–10], and accurate measurement of radicals still remains challenging [11]. Therefore, this paper is devoted to simultaneously quantify both the total erosion yield and the $CD_4$ production yield. In addition, data obtained by 200 eV deuterium impact are presented.

## 2. Experimental

### 2.1. Film production and characterisation

Pure carbon films and films doped with Ti, W, and Zr (a-C:Me) were prepared by magnetron-sputtering using argon as sputtering gas. The mixed films were deposited on silicon and graphite substrates, which were neither biased nor intentionally heated. The ratio of metal to carbon was controlled by varying the power of the two independent magnetron sources. More details about the deposition process can be found elsewhere [12].

The films were characterised in respect to composition, thickness, lateral and in depth homogeneity, surface morphology, crystallinity, chemical state, and the influence of thermal treatment on these properties [7,12–14]. Before the erosion experiments started, all films were annealed to ~1100 K for ~0.25 h, which led to the formation of carbide crystallites of nanometer size [13,14].

The films have a thickness between 0.4 and 1.4 μm. The total amount of carbon and metal in the films was determined by ion backscattering of 1.5 MeV protons and 0.6 to 4.0 MeV $^4$He at a scattering angle of 165°. They show adequate homogeneity of better than ~0.5 at.% across the depths of interest for the erosion experiments. The maximal oxygen content was always below 4 at.%, and less than 1 at.% argon was detected in all films.

### 2.2. Erosion experiment

All erosion experiments were performed at the high current ion source in Garching with 90, 600, and 3000 eV $D_3^+$, i.e., 30, 200, and 1000 eV per deuterium, respectively [15]. The flux density was $\sim 10^{19}$ D/$m^2$ s, and the erosion spot was $\sim 0.5$ $cm^2$. The specimens were heated by electron bombardment from the rear, and the temperature was monitored by an IR-pyrometer. Annealing to ~1100 K for ~0.25 h directly before the erosion experiment served to degas the set-up as well as to stabilize the chemical structure of the films, avoiding temperature-related changes during the erosion experiment [13,14].

The *total erosion yield* was determined from both the accumulated ion fluence onto the specimen and the total amount of carbon and metal eroded measured by two techniques: weight-loss (WL) and ion beam analysis (IBA) on the remaining films across the erosion area. Firstly, WL of the films was usually determined in air (ex situ) as an upper limit of the yield, because the subsequent degassing at 1100 K in the erosion chamber contributed to a loss of weight. The in situ balance, i.e., inside the vacuum chamber after degassing, was in operation only for some measurements, and due to the slight amount of mass lost after each erosion experiment, the uncertainty for the in situ weighing could exceed 50%.

With IBA, the remaining film thickness was determined laterally resolved. Therefore, this technique delivered also the flux distribution of eroding D ions, which was between a Gaussian and a pure rectangular shape along the two main axes of the erosion spot. The uncertainty of the amount of eroded carbon is of ~20% for the most films, but could reach 50% for films with low erosion.

The *chemical erosion yield* was obtained by quadrupole mass spectrometry from the signal of mass 20, i.e., $CD_4$ production yield. The signal was first background-corrected, afterwards normalized to the ion flux and finally scaled with a calibration factor. This factor was gained by setting the background-corrected and normalized signal of mass 20 obtained for pyrolytic graphite bombarded with 1 keV/D at ~800 K equal to 0.1, which is known to be the chemical erosion yield of this graphite at these conditions [16]. This calibration method does not take into account changes in the ratios of radical to molecule or $C_1D_z$ to $C_{x>1}D_y$, which lead to inaccuracy of the absolute obtained values for erosion conditions different from 1 keV/D and 800 K (e.g., energy and temperature) [16].

For the background correction, the mass signals without ion beam before and after the erosion measurement (sometimes also in between) were linearly interpolated and then subtracted. Contributions to the mass 20 signal from the wall due to heating of the surrounding, due to reflected deuterium as discussed in [8,10], and due to ion impact on apertures were neglected. (Especially, no fast increase in the mass signals was observed when the ion beam was turned on onto a fresh specimen.) Also any contribution from deuterated water was disregarded because of the liquid nitrogen cryo pump, realizing a total pressure of $<10^{-6}$ Pa without ion beam, which rose to $\leqslant 10^{-4}$ Pa with ion beam.

For each erosion measurement, a fresh specimen was used. Two kinds of measurements were performed:

> *Fluence-scans (F-scan)*: A fluence of $2–8 \times 10^{23}$ D/m$^2$ was accumulated at fixed erosion parameters (temperature, energy) to assure a sufficient accuracy in the total erosion yield. The $CD_4$ emission was monitored to obtain the corresponding averaged chemical erosion yield and the fluence dependence of the $CD_4$ production yield.
>
> *Temperature-scans (T-scan)*: The $CD_4$ emission was monitored continuously, while the specimen temperature was increased stepwise from room temperature to about 1100 K under continuous impact of deuterium. For each temperature step, the fluence was kept as small as possible, but still large enough to ensure that the emission of erosion products was nearly constant. Specifically, the accumulated fluence per temperature step was always lower than $10^{22}$ D/m$^2$ and for most steps, it was between $4–7 \times 10^{21}$ D/m$^2$. The accumulated fluence for the complete T-scan was always below $10^{23}$ D/m$^2$.

To control the temperature, the emissivity of each specimen was first determined during the annealing to ∼1100 K with a filamentary pyrometer. The emissivity may change during the erosion measurements. For the same heating power, the temperature variation for the different specimen was less than 50 K. Note that the temperature difference of two

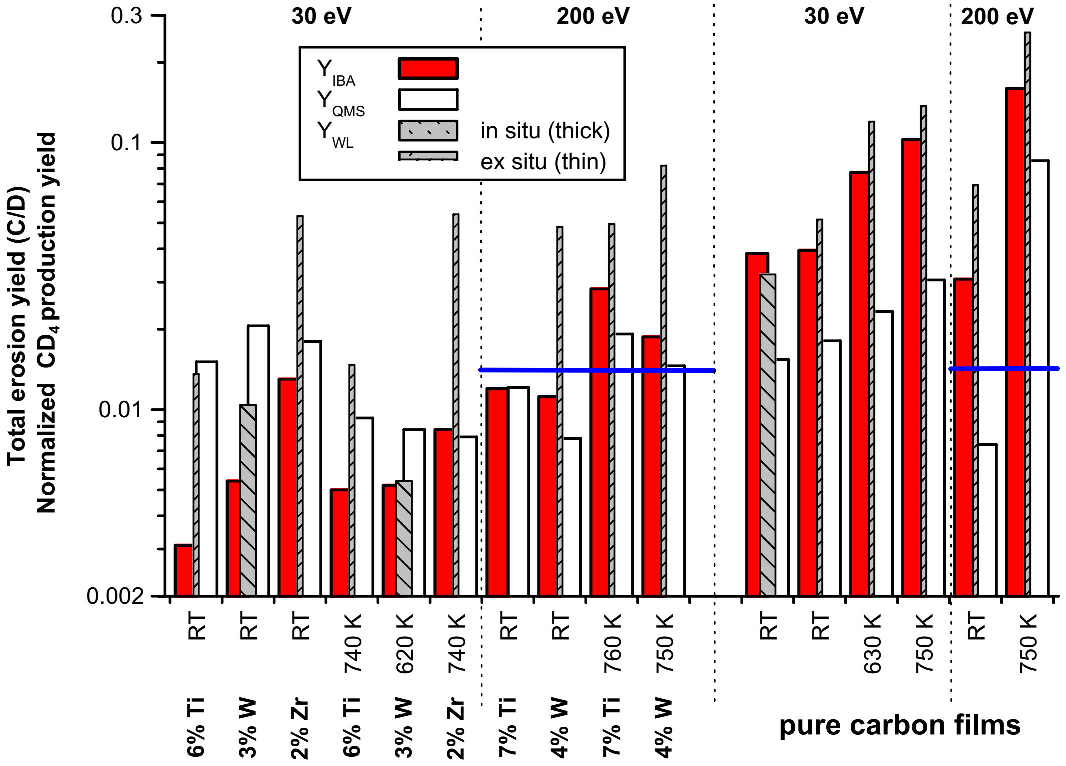

Fig. 1. Total erosion yield obtained from IBA (filled bars) and WL (in situ: thick striped grey bars, ex situ: thin striped grey bars) and chemical erosion yield, i.e., relative $CD_4$ production yield (QMS; white bars) of carbon films doped with Ti, W, and Zr, pure carbon films, and pyrolytic graphite at 30 and 200 eV deuterium impact. Applied fluence is mostly $4–8 \times 10^{23}$ D/m$^2$. Horizontal lines indicate the calculated physical sputtering yield of carbon [15].

neighbouring steps in a T-scan is measured better than ±10 K.

## 3. Results

The total erosion yield gained from IBA and WL, as well as the averaged chemical erosion yield obtained from the $CD_4$ signal for 30 and 200 eV deuterium impact of the *F-scans*, are given in Fig. 1 for pyrolytic graphite, pure carbon films, and carbon films doped with Ti, W, and Zr. In order to see the effect of the doping more clearly, the ratios of the total yield for doped versus undoped carbon obtained from IBA and QMS and the ratio of QMS versus IBA are given in Fig. 2 for the four used erosion conditions: 30 and 200 eV/D in combination with RT and elevated temperatures (600–800 K). Several statements are directly obvious from Figs. 1 and 2:

(i) The doped films have lower total erosion than pure carbon ($Y_{\mathrm{IBA}}$) for all four erosion conditions. The reduction by doping of the total erosion is between a factor of 3 and 20.

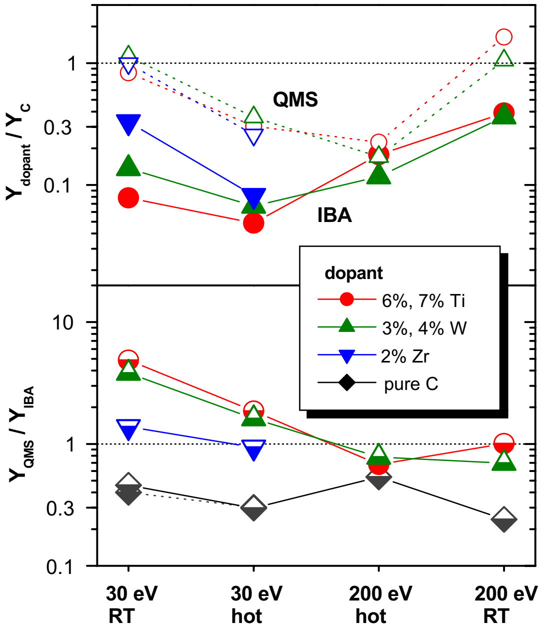

Fig. 2. Top: Ratio of the total erosion yields of doped C film to pure C film (IBA: filled symbols) and ratio of the relative $CD_4$ production yields of doped C film to pure C film (QMS: open symbols); bottom: ratio of the chemical erosion yield obtained from the $CD_4$ signals to total erosion yield (half-filled symbols). The data from Fig. 1 are used.

(ii) Ex situ weight-loss measurements can only be used as an indicator, but does not lead to accurate values, because the mass loss caused by erosion is too low compared to mass loss by degassing. In situ measurements fit quite well with IBA data.

(iii) For the pure C films, the total erosion yield is larger than the chemical erosion yield, i.e., relative $CD_4$ production yield, thus $Y_{\mathrm{QMS}}/Y_{\mathrm{IBA}} < 1$. For the doped films, this turns to the opposite for 30 eV/D at both temperatures and for 200 eV/D at RT. This implies that changes in the distribution of the erosion products occur, which are not described by the calibration [16].

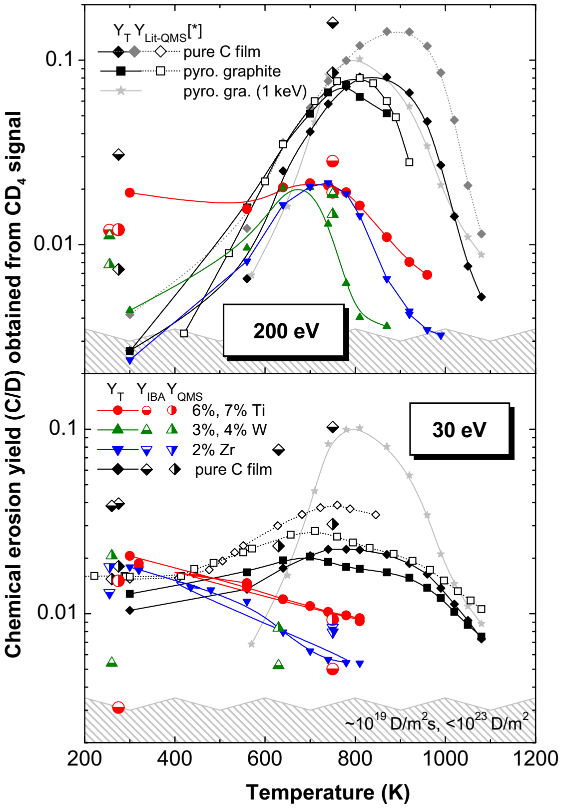

Fig. 3. Chemical erosion yield obtained from the $CD_4$ signals of carbon films doped with Ti, W, and Zr and without doping versus specimen temperature during bombardment with 200 and 30 eV/D. The fluence increases with temperature and is always less than $10^{23}$ D/m$^2$, mostly even less than $5 \times 10^{22}$ D/m$^2$ at the highest temperature of the T-scans. QMS data of lower than 0.003 are doubtful (dashed area). For comparison, data from Fig. 1 (crossed and half-filled symbols), data for pyrolytic graphite (also for 1 keV/D; grey stars) and for pure C film from previous studies [6,16] (marked by $*$) are inserted. *Note*: Physical sputtering is not subtracted for $Y_{\mathrm{IBA}}$ and the data from Fig. 1 at RT are moved to around 280 K for better visibility.

One has to keep in mind that both yields, $Y_{IBA}$ and $Y_{WL}$, include the physical sputtering, which is negligible for 30 eV/D, but not for 200 eV/D, at which the physical sputtering yield is about 0.015 for C, 0.008 for Ti and negligible for W and Zr [15].

Fluence dependencies have not been presented and discussed in this paper even though preferential erosion of the carbon was observed and led to an enrichment of the dopant on the surface [5].

Fig. 3 shows the temperature dependence of the chemical erosion yield gained from $CD_4$ signals from various films for 200 and 30 eV deuterium impact ($Y_T$; *T-scans*). For comparison, data belonging to pyrolytic graphite and pure carbon films from previous investigations [6,16] are included, as well as the total and relative $CD_4$ production yields obtained from the F-scans (Fig. 1). The yield of pure carbon exhibits the well-known maximum at around 800 K and shifts to lower temperatures with decreasing energy [3,9,16]. The enhancement of the maximum yield of the pure C films compared to pyrolytic graphite at around 800 K was explained by differences in their carbon structures [6].

The 30 eV data for doped films are in agreement with the results published in [7]. The 200 eV data show a reduced erosion at elevated temperature and a shift of the maximum to lower temperature. The high $CD_4$ signal for the Ti-doped film at 200 eV/D at RT is not yet well understood and does not only occur in the T-scan, but also occurs in the F-scan. Note, the deviance of the $Y_{IBA}$ data in Fig. 3 (lower-half filled symbols) corresponds to the behaviour described in (iii) the data from pure C films are above the $Y_T$ data and those from the doped films below.

## 4. Discussion and conclusion

The total and chemical erosion of mixed films were investigated for 30 and 200 eV deuterium impact and temperatures between room temperature and 1100 K. As mixed layers, magnetron-sputtered films were produced. They consist of carbon and metal (3 and 4 at.% W, 6 and 7 at.% Ti, 2 at.% Zr). The dopant is mainly present as nanometer-sized carbide crystallites [13,14]. The total erosion yield was determined from weight-loss measurements and changes of film thickness were measured by RBS. The chemical erosion yield was obtained only from the $CD_4$ signal of mass spectrometry. Two different experiments were performed: (i) measuring the chemical erosion yield while stepwise increasing the temperature, for small fluence per step ($<10^{22}$ D/m$^2$) and small total accumulated fluence ($<10^{23}$ D/m$^2$) and (ii) determining the fluence behaviour at room temperature and at elevated temperature (620–760 K) of the total and the chemical erosion yield up to $8 \times 10^{23}$ D/m$^2$.

From these measurements three main statements can be drawn:

(i) The total erosion yield is reduced by a factor of 3–20 for doped films compared to pure C films.

(ii) The $CD_4$ production yield decreases less by doping than the total erosion yield. This implies that the distribution of the chemical erosion species is changed by doping, as was proposed in [7]. In fact, it has already been shown that the distribution for pure C material depends on erosion parameters, like energy and temperature, and on the hydrogen isotope [8,9,16,17]. Therefore, deducing the chemical erosion yield only for the measurement of the $CD_4$ emission or its spectroscopic signature would yield to misleading values and interpretations of the erosion behaviour. Nevertheless, the $CD_4$ signal is usually a good indicator for chemical erosion.

(iii) The temperature dependence of the chemical erosion yield obtained from the $CD_4$ signals at 200 eV/D shows a reduction of the maximum and a shift to lower temperatures with doping. For 30 eV/D, the maximum is even vanished by doping. All data fit to the interpretation that the activation energy of the hydrogen release during ion impact decreases due to the dopants [5,7,18]. Nevertheless, it would be necessary to verify this with more total erosion yield measurements at intermediate temperatures.

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