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Chemical erosion of atomically dispersed doped hydrocarbon layers by deuterium

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Abstract

The chemical erosion of atomically dispersed Ti-doped (~10 at.%) amorphous hydrocarbon layers (a-C:H:Ti) was investigated in the temperature range of 300–800 K for 30 eV deuterium impact. Compared to pyrolytic graphite, the methane production yield is strongly reduced at elevated temperatures. This reduction starts from temperatures just above room temperature and is even larger than for B-doped graphite. The reduction of the activation energy for hydrogen release may be the dominant interpretation for the decreased hydrocarbon formation. The ratio of emitted CD_3 to CD_4 increases with temperature for pyrolytic graphite and even stronger for the doped layers. The fluence dependence of the chemical erosion yield was determined, which is explained by enrichment of the dopant due to the preferential erosion of C.

Keywords: Chemical erosion; Carbon; Plasma-wall interaction; Hydrogen; Doping

1. Introduction

For an evaluation of carbon-based materials in fusion devices, i.e. hydrogen surrounding, the chemical erosion of carbon by hydrogen isotopes and especially the correlated tritium co-deposition with C have to be taken into account [1]. In order to reduce the high chemical reactivity, metal-doped carbon materials have been investigated in the last decade [2–5]. Various doped carbon-based materials show a reduced erosion yield.

The processes involved in the chemical erosion of pure carbon materials have been investigated in great detail by several groups [5–9]. A model for the involved physical and chemical processes has been established [5–9]. There are two distinct erosion regimes: (i) thermally activated erosion of hydrocarbons, in which the maximum in the erosion is caused by a competition of the thermally activated release of hydrocarbon radicals and hydrogen atoms, and (ii) chemically enhanced sputtering of hydrocarbons, which dominates only at low impact energies and near room temperature [8]. But there are still some observations not implemented in this model, like the conversion step from radical to molecule, the change in the ratio of radical to molecule and methane to heavier hydrocarbons with impact energy, the drastic shift of the temperature of the maximal erosion with impact energy, or the flux dependence [5,10].

Until now only for boron-doped carbon-based materials the driving mechanism for the observed reduction of the thermally activated erosion has been elucidated: the activation energy for the hydrogen release is reduced from 1.8 eV for pure C to 1.2 eV for B-doped C [5]. For other dopants the mechanism which leads to the observed reductions of the erosion yield is unclear. For the parameter range of the chemically enhanced sputtering (low impact energy, low temperature), the only obvious effect explaining the reduction is the preferential erosion of one component of these multi-component materials [11], in

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this case C, and the enrichment of the other component at the surface. Combined with this enrichment, the surface morphology of the investigated granular materials is changed: rough surface morphologies are created [12–15]. This effect, together with the correlated reduction in the erosion yield, seems to be the dominant mechanism for the observed reduction of the chemical erosion.

In recent studies it was shown that the enrichment and the roughened surface morphology are not sufficient to explain the observed reduction by more than one order of magnitude for the erosion of carbide-doped fine-grain graphites bombarded with 30 eV deuterium at room temperature [15]. In order to gain such reductions high fluences in the order of 10^{25} D/m^2 were necessary. Such high fluences are still more difficult to achieve for mono-energetic/mass separated ion (atom) beams with very low energies (<10 eV).

From the present understanding it is proposed that the fluence necessary to reach the steady state enrichment should be the lower the finer the dopant is distributed in the C matrix [3]. Therefore, atomically dispersed doping in C is suggested to study the influence of doping on the chemical erosion processes of C with hydrogen. Ti- and Mo-doped magnetron-sputtered amorphous hydrocarbon layers were produced [16]. This manufacturing is one of the best approaches for atomically dispersed doping. In this paper the first results of erosion experiments for conditions of both chemical erosion regimes of these layers are presented.

2. Experimental

The layers were produced in a co-operation with the University of Greifswald, Germany. The metal-doped layers were deposited by means of magnetron sputtering [16] on silicon wafers as substrate. The doping material was sputtered in a reactive gas atmosphere consisting of a mixture of Ar and CH_4. Methane contributes to the layer growth, while the sputtered dopant atoms are expected to be homogeneously dispersed in the layer on the atomic level.

The averaged layer composition and thickness were determined by ion beam analysis (IBA). Backscattering of 1.5 MeV protons with a scattering angle of 165° and elastic recoil detection using 2.6 MeV ^{4}He were used to determine the C, O, Ti, and Mo amount and the hydrogen content, respectively. The enrichment of the dopant due to preferential erosion of C from the surface, the depth profile and the chemical state for the outermost atomic layers were measured with X-ray photoelectron spectroscopy (XPS) inside and outside the erosion spot. The averaged concentrations of dopants are in the range of 6–50 at.% in these layers. The hydrogen content is neglected in the concentration calculations. Measurements for four layers are presented. These unbombarded C layers contain 10 at.% Ti with 3 and 5 at.% O, 13 at.% Ti with 6 at.% O, and 50 at.% Mo without any detectable O.

The erosion experiments were performed at the Garching high current ion source. The source was adjusted to produce 30 eV D (90 eV D_3^+) with fluxes around 10^{19} D/m^2 s. The specimens were heated with electron bombardment from the rear up to 900 or 1200 K for several minutes. The temperature was monitored by an IR-pyrometer, which was calibrated with an optical filament pyrometer. The total erosion yield and the chemical erosion were determined by weight-loss measurements and quadrupole mass spectrometry, respectively. The mass spectrometer is in line-of-sight to the specimen. The advantage of this configuration is the possibility to detect radicals, which do not survive many wall collisions, and to separate the background by comparing measurements with and without blocked line-of-sight. Blocking was not available for this study.

The emission rates of the eroded species between mass 2 and 40 were measured as a function of time. The signal for the deuterated methane (mass 20) was predominantly evaluated. The mass signals without ion beam, before and after the erosion measurement, were used for background correction. To calibrate roughly the CD_4 signal, pyrolytic graphite was bombarded with 1 keV D at around 800 K. The CD_4 signal measured under these conditions is set equal to a chemical erosion yield of 0.1. This calibration does not take into account variations in the ratios of radicals to molecules and C_1D_z to $C_{x>1}D_y$ for different impact energies. For a more detailed discussion of this calibration see [10].

3. Results

The fluence dependence of the methane production rate of a 10 at.% Ti-doped layer at 620 K is shown in Fig. 1 for three fluence scales. The increasing rate at very low fluences ($<0.3 \times 10^{22}$ D/m^2) is due to a delayed CD_4 production until the precursor for the hydrocarbon emission is formed [17,18]. Beyond 0.3×10^{22} D/m^2 the CD_4 production rate decreases and by $\sim 4 \times 10^{22}$ D/m^2 the rate falls to 50% of the maximal amount. A further decrease is expected beyond the highest applied fluence of 40×10^{22} D/m^2. From correlated weight loss measurements, interrupting the bombardment, the average total erosion yield from 0 up to 7.4×10^{22} D/m^2 is 2.5% ± 1.5%. At higher fluences the total yield decreases below the detection limit. The temperature dependence of the chemical erosion yield (CD_4) is determined (Fig. 1) at even higher fluences. Nearly no variation of the yield with temperature is found. After the erosion experiments the layer thickness of 2.7×10^{22} (C + Ti + O)/m^2 is reduced by less than 10%, which is just the accuracy of the ion beam measurement.

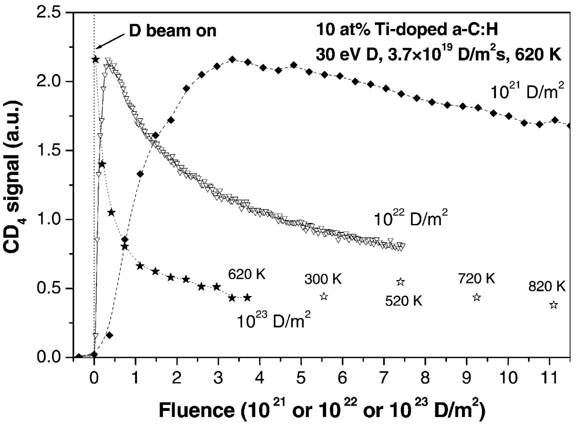

Fig. 1. Methane production vs. fluence of a 10 at.% Ti-doped a-C:H layer eroded at 620 K with 3.7×10^{19} D/m^{2}s of 30 eV. The same data are shown for three different fluence scales. At the highest fluences the temperature was changed as labelled. This layer was degassed at 900 K for >10 min.

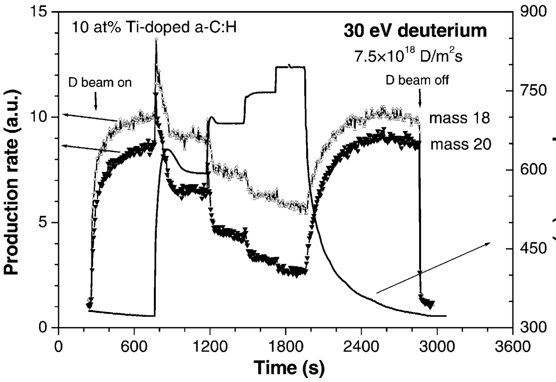

Fig. 2. Temperature evolution and time-resolved mass spectrometer signals of mass 18 and 20 of a 10 at.% Ti-doped a-C:H layer.

The averaged composition of this layer and its surface composition with and without bombardment are measured: the titanium enriches at the surface due to preferential erosion of C by a factor of 4 to a value of 0.44 Ti atoms per C atom after a fluence of 1.1×10^{24} D/m^2. The methane formation rate is reduced by a correlated factor to less than a fourth of the maximum rate. Before bombardment only a few percent of the Ti forms carbide. This is increased to about 20% after bombardment. The largest amount of the Ti is metallic or oxidised. The concentration of oxygen from the XPS analysis is overestimated because of the in-situ absorption and oxidation. The averaged composition obtained by IBA is still 85 at.% C, 10 at.% Ti, and 5 at.% O.

In order to obtain a more detailed temperature dependence of the chemical erosion yield, virgin layers were continuously bombarded with 7.1–8.6×10^{19} D/m^{2}s of 30 eV D, while the temperature was increased in steps. The time evolution of the temperature and the mass spectrometer signals of mass 18 and 20 are shown in Fig. 2. By changing the temperature abruptly, transient peaks in the CD_4 emission are observed, analogous to previously reported transient behaviours [19,20]. Each temperature step was held until the mass 18 and mass 20 signals were nearly constant.

Disturbing contributions to mass 18 could come from CD_2H_2, H_2O, and DO from cracked D_2O. Deuterated water itself contributes to mass 20 as well as CD_4 in the background gas and from recombination of CD_3 with D on the walls. Deuterated heavier hydrocarbons do not crack into mass 20 and cracking into mass 18 is less than 4% [21,22]. The contribution of the background gas was always determined in the measurements (Fig. 2) and used for the background correction. Heating without ion beam or measurements after switching off the ion beam, while the specimen was still heated, indicate that contributions coming from heating the specimen surrounding can be neglected. Thus the outgassing before erosion experiments was sufficient. The contribution of the beam-induced background originated at the apertures of the beam or by reflected D at the wall could be estimated from measurements on specimens without chemical erosion of C, e.g. Si or W. In such measurements the signals of mass 18 and 20 during the D bombardment have small nearly constant values above the background gas level. These values vary from measurement to measurement. The contribution of the beam-induced background is between half and twice of the background gas and is not taken into account in the background correction.

The erosion yields derived from mass 20 are plotted in Fig. 3 (upright triangles) after background correction against the temperature. Data for pyrolytic graphite (Union Carbide, USA) and a TiC-doped fine-grain graphite (CEIT, Spain) [15] are inserted for comparison.

Two similar Ti-doped layers show the same steadily decreasing CD_4 production rate with temperature, which demonstrates a strong reduction of the chemical erosion at elevated temperatures compared to pyrolytic graphite. This behaviour is only slightly affected by enrichment as indicated by the same CD_4 production yield after returning to room temperature and by a similar temperature dependence by repeating this experiment on one layer (Figs. 2 and 3). After bombarding with a total fluence of 3×10^{22} D/m^2, the surface composition of this layer and its thickness are checked. No enrichment is observed and the expected reduction of the layer thickness is below the ac-

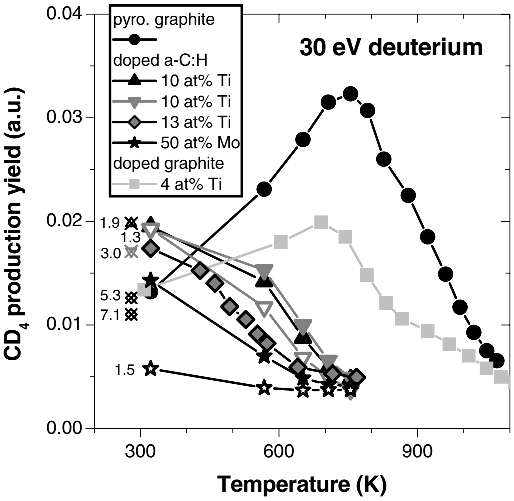

Fig. 3. Comparison of CD_4 production yield vs. specimen temperature for four layers, pyrolytic graphite, and a TiC-doped fine-grain graphite. Open and crossed symbols indicate data of a second measurement and data after cooling down to 300 K (moved to 280 K), respectively. The accumulated fluences are labelled in 10^{22} D/m. The used fluxes were 7.1–8.6 × 10^{18} D/m^2 s. All layers were degassed at 1200 K for >10 min.

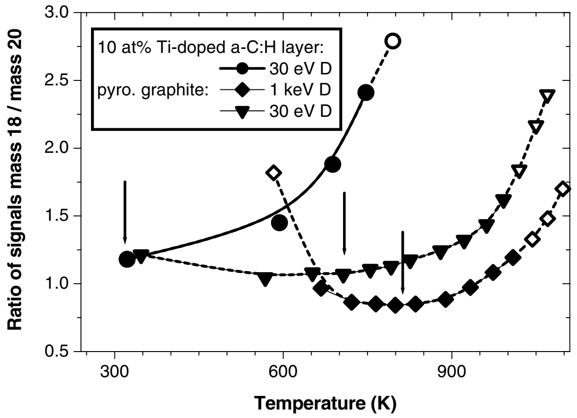

Fig. 4. Ratio of mass spectrometer signals of mass 18 to mass 20 vs. temperature. The arrows mark the temperature of the maximal observed yields. Open symbols (respective dashed lines) indicate ratios obtained from mass signals small compared to the background signal after background subtraction.

curacy of the ion beam measurement of 10% of the initial film thickness.

On the 13 at.% Ti-doped layer (Fig. 3) higher fluences were accumulated due to performing more temperature steps at low temperatures and because the measurement was continued after cooling down to room temperature in order to check the fluence dependence observed in Fig. 1. A calibration for this measurement is not available, so a previous calibration factor is used. The CD_4 production rate decreases monotonically with temperature. The CD_4 production yield of this layer is already influenced by Ti enrichment as indicated by CD_4 production after cooling down to 300 K.

An a-C:H:Mo layer with a Mo to C ratio of 1 was also investigated with a stepwise increasing temperature. A strong reduction in the CD_4 production yield is observed for this layer (Fig. 3). But the Mo surface concentration is increased at the surface as is indicated by the increasing Mo signal in the XPS measurement with decreasing take-off angle for the photo electrons.

The background corrected signal at mass 20 is correlated with the CD_4 molecules, while the signal at mass 18 is correlated with the cracking from CD_4 but also with emitted CD_3 radicals. The ratio of mass 18 to mass 20 is shown in Fig. 4. Due to the uncertainties in the background correction, ratios calculated from small mass signals are specially marked or even not shown. The ratio changes with temperature, but with a contrary dependence as reported for simultaneous incidence of thermal H^0 and energetic Ar ions [23]. The cracking from CD_4 increases slightly with the thermal energy of the particle [24], but it is not strong enough to explain all the observed increase. Remarkably, the ratio at elevated temperatures is always larger for the doped layers than for the graphites. For graphite (30 eV and 1 keV D) the ratio shows a minimum at the temperature of the maximum erosion yield (Fig. 4, arrows). In conclusion, more CD_3 radicals are emitted at elevated temperatures and this increase is even stronger for the doped layers.

The mass signals of C_2D_y species are small and partly covered by contribution of CO. These signals increase with temperature but without correlation to the stepwise increasing temperature. Also transient peaks are not observed. In future measurements more effort has to be dedicated to these species.

4. Discussion and conclusion

The chemical erosion of atomically dispersed Ti-doped amorphous hydrocarbon layers was investigated in the temperature range 300–800 K for 30 eV D bombardment. The methane production yield decreases monotonically for temperatures just above room temperature. The strong reduction of the chemical erosion yield at elevated temperatures compared to pyrolytic graphite may be attributed to a reduction of the activation energy for hydrogen release. Two questions arise: (i) Is there a maximum in the CD_4 emission around room temperature? (ii) Is the increased CD_4 emission at room temperature correlated with an increased erosion or is it an artefact of the assumptions of the calibration?

To solve the first question, measurements with finer temperature steps were done (Fig. 3), but due to the slight fluence dependence it is still questionable if a maximum exists above room temperature. Experiments with a cooled target below 300 K would be very interesting, especially to separate the effect of the two erosion regimes. Such separation is not possible with the existing data. However, we can conclude that the temperature of the maximum CD_4 yield is shifted by about 300 K for the atomically dispersed Ti-doped amorphous hydrocarbon films compared to usual graphite. This shift is even stronger than for B-doped graphites (200 K [5]).

The maximum CD_4 yield of the C films is reduced by about a factor of 2 compared to pyrolytic graphite but has about the same amount as for 4 at.% TiC-doped fine-grain graphite. The CD_4 yield at room temperature is enhanced compared to the graphites. This enhancement and the observed shift in temperature could be explained in the frame of the model understanding of the thermally activated regime [5], if for the Ti-doped layers not only the activation energy of the D release is reduced, like for B-doped graphites, but also the activation energy of the hydrocarbon formation. Both activation energies have to be strongly decreased (below 1 eV) from the best fit values for pyrolytic graphite (1.8 and 1.7 eV, respectively) to confirm the erosion yield derived from mass 20.

Two reasons exist to have doubts about the increased erosion yield at room temperature: (i) In the literature [7], data are shown that the starting state of the carbon in the target affects the yield. Definitely, the layers and the pyrolytic graphite consist of C in different binding states, even if the differences are reduced due to the amorphization and hydrogenation by the ion bombardment [7]. Nevertheless, a comparable undoped C layer should be measured. (ii) The ratio between single carbon-containing species to heavier hydrocarbons (C_1D_z to $C_{x>1}D_y$) may be changed by the doping. This ratio is assumed to be constant for the calibration of the chemical erosion yield from the CD_4 emission rate. A hint for an influence of the doping on this ratio ($C_1D_z/C_{x>1}D_y$) is given by the changed CD_3/CD_4 ratio for the doped layers with temperature (Fig. 4). If the increase in the yield is not taken into account, then only the activation energy for hydrogen release must be reduced from 1.8 eV for pyrolytic graphite to 0.9 eV, which is even lower than for the boron-doped graphite (1.2 eV).

The fluence dependence of the chemical erosion yield is determined, which can be explained by enrichment of the dopant due to the preferential erosion of C. Unfortunately, the contribution of the varying dopant enrichment could not be completely eliminated from the chemical erosion yield because a certain fluence is necessary for reaching steady state during each temperature step of the experiment. This enrichment covers the temperature dependence of the CD_4 production for fluences beyond 40×10^{22} D/m^2 (Fig. 1).

Even if this fluence dependence and the transient behaviour after changing the erosion conditions [19,20] admit only a small scope for experiments, layers of this type are excellent test materials for fundamental investigations of the influence of different dopants on the processes of the chemical erosion and their impact with respect to their concentrations. Especially for flux limited experiments with atomic and very low energy hydrogen (<10 eV), this type of material could be very helpful.

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