Deuterium retention in tungsten-doped carbon films

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Abstract

Measurements on deuterium retention in tungsten-doped carbon films were performed and compared to measurements on pure carbon films and pyrolytic graphite. Deuterium has been implanted with a 200 eV D beam at 300 K substrate temperature. The total amount of retained deuterium was obtained by $D(^3He,p)^4He$ nuclear reaction analysis at 800 keV. Implantations were performed at different fluences below 10^{24} D/m^2, dopant concentrations below 15 at.%, and pre-annealing temperatures below 1300 K. The two latter parameters influence the structure of the carbon matrix and the formation of tungsten carbide crystallites. Pure carbon films show a slight increase of D retention with fluence as previously observed for pyrolytic graphite. This indicates that the carbon structure does not have influence on the retention. The doped films exhibit a lowering of the increase with fluence by a factor of two compared to pure carbon. Pre-annealing does not show any effect on retention.

1 Introduction

Carbon erosion due to hydrogen impact at the strike point of the ITER divertor, made of carbon-fibre composite, will lead to co-deposited layers with a high tritium inventory [1]. Tungsten (W) and beryllium (Be) will be used elsewhere in the machine as plasma-facing components. Sputtering and migration processes will lead to the formation of mixed materials [2]. Therefore, metal containing co-deposited layers and their deuterium (D) retention behaviour are of major interest.

In order to gain basic knowledge of the retention processes of deuterium in mixed materials, well characterized model system for mixed materials were investigated using certain experimental conditions of deuterium implantation (energy, flux of incident D-beam, specimen temperature) [3]. This study is restricted to tungsten-carbon mixtures with W concentration below 20%, which allows a quite limited extrapolation to ITER.

The tungsten-doped amorphous carbon films (a-C:W) produced by magnetron sputtering consist of a amorphous carbon matrix with tungsten carbide-like nanometre-sized inclusions [4]. The structure of the carbon matrix of doped (a-C:W) and pure amorphous carbon films (a-C) has been analyzed by Raman spectroscopy. Heating of a-C films leads to differences in the ratio between aromatic clusters and amorphous chains. Similar differences are induced by adding dopants. Heating up to 1300 K vanishes the differences, i.e., pure and doped C films have the same carbon structure. After deposition tungsten is atomically dispersed in the carbon matrix, leading to a chemical interaction between W and C [4]. Heating to temperatures around 1300 K leads to a formation of the W_2C phase, while the WC phase was observed then at temperatures around 1700 K [4].

For a wide variety of graphite materials (CFC, pure graphites, carbide-doped graphites), diffusion over the implantation zone into the bulk was shown [5–7], observable in an increase of the deuterium inventory for increasing fluences above the saturation level. I.e.,

the bulk is not saturated with D [5–7]. In principal, this behavior can be expected for carbon films too, even if they exhibit a different carbon matrix structure and finely dispersed nm-sized carbon crystallites [4]. Therefore, the fluence dependence of the deuterium retention of pure and W-doped films and the effect of annealing was investigated.

2 Experimental

2.1 Specimens

In order to perform deuterium implantation experiments and to analyze the deuterium retention, thin films were deposited by magnetron sputtering on Si (100) wafer fragments of 12x15 mm^2 size. It was shown that the silicon substrate has no influence on the structure of the carbon matrix and the W-C-chemistry inside the film for temperatures below 1300 K [4].

The tungsten concentration was adjusted by selecting a low power between 2 W and 10 W for the DC discharge, compared to 500 W applied to the RF discharge at the carbon cathode. Film thickness and tungsten concentrations were determined by Rutherford backscattering (RBS) with 4 MeV ^{4}He. The film thickness varied between 0.6 and 1.2 μm. Specimens with 2.5, 7.5 and 15% tungsten were selected for implantation. Tungsten concentrations are given in atomic percent throughout the paper.

In order to study differences in the retention behavior between unheated and pre-heated samples, tungsten-doped films (a-C:W) were pre-annealed in a high vacuum furnace to 700 K and 1300 K. Undoped carbon films (a-C) were produced and analyzed in the same manner.

As reference material, pyrolytic graphite was used (Grade HPG, Union Carbide). The graphite planes show a mosaic spread of 30°. Plates of 12x15 mm^2 size with 1 mm thick-

ness were cut with their surface aligned parallel to the graphite planes. The surface was polished with a diamond paste and cleaned in ultrasonic bath.

2.2 Deuterium implantation and analysis of the retained deuterium amount

Deuterium was implanted in the Garching high current ion source facility at room temperature for different fluences up to 10^{24} D/m^2. A monoenergetic and mass-separated D$_3^+$ ion beam with a flux of 10^{19} D/m^{2}s and energy of 200 eV per deuterium atom was used. The erosion spot has a size of 70 mm^2 (see 2.3.).

The total amount of retained deuterium per unit area was obtained using the D(^{3}He,p)^{4}He nuclear reaction analysis (NRA) with 800 keV ^{3}He at the tandem accelerator facility. At this analyzing energy, the information depth is about 1 μm. The analysing spot size was 0.5x1 mm^2. Protons emitted from the nuclear reaction were detected by a large angle proton counter. Depth profiles of D were simultaneously obtained with the same nuclear reaction from the energy spectrum of the ^{4}He particles at a scattering angle of 102.5°. The profiles indicate that more than 95% of the retained deuterium even for fluences up to 10^{24} D/m^2 is located in the upper 500 nm. Therefore, the diffusion into bulk is low and the thickness of the films is sufficient for determining the D retention behaviour of a-C:W. The position of the specimen was controlled by aligning the same edge of the specimens in the erosion experiment and in the analysing facility. Therefore, it was possible to hit the reference zone with the NRA beam. The deuterium implantation was performed at a fixed position, while during the NRA analysis the manipulator was moved one-dimensionally in order to obtain a scan over the specimen across the implantation spot. The incident angle of the ^{3}He and the D$_3^+$ beam was held fixed, perpendicular to the surface.

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2.3   Beam profile characterization

In order to investigate the beam profile, hydrogenated amorphous carbon layers produced by plasma-enhanced chemical vapour deposition with CH_4 precursor gas were used. Fig. 1 shows an erosion spot on an a-C:H layer after deuterium beam exposure with an accumulated ion charge of 0.6 C. The erosion spot is clearly distinguishable by changes in the interference color of the transparent a-C:H layer. Here, the red color from the original film changes to yellow and near violet. The wavelength difference between red and near violet is about 150-200 nm, corresponding to a maximal change in layer thickness of about 75-100 nm [8]. At the edge of the spot (marked by arrows in Fig. 1) the sharp transition from yellow to red indicates a steep slope. Inside the erosion spot inhomogeneities in thickness of about 25 nm are observed.

The erosion depth was determined by ellipsometry. A laser spot of 10x30 μm^2 size was scanned two dimensionally over the specimen area with a rectangular grid of 0.3 mm step width. The layer thickness of each pixel was calculated as described in [9].

Five specimens were exposed at the same conditions up to the same fluence and analyzed with ellipsometry to check the reproducibility of the beam profile over the measurement campaigns (Fig. 1). Two specimens were eroded at the same day, the third one after a week and a fourth one after two weeks. During this campaign the high current ion source was continuously running over two weeks at the same settings. The fifth one was eroded in a second campaign, two weeks after the first campaign. Between these two campaigns, the machine was running in different settings. By simple optical inspection only slight variations between the five erosion spots could be detected, mainly between the fifth specimen and the four other ones.

Comparing equivalent pixels with each other, the average thickness, the standard derivation and the relative error was calculated. This value gives a position dependent measure

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of the reproducibility of the beam profile. At areas exposed to high fluences in the central region of the erosion spot, according to colors between turquoise and violet, the relative error is not higher than 15%.

The area with a reproducible spot profile has a size of 30 mm^2, while the area surrounded by the steep gradient is about 70 mm^2. In three zones of the reproducible area a higher erosion depth is observed (erosion depths between 70 nm and 90 nm, corresponding to colours between blue and violet). Inside each of the three zones the lateral variation of the erosion depth is not bigger than 10%. The largest of these zones had an area of 6 mm^2. In each campaign, this zone was analyzed and selected as reference zone for data evaluation (Fig. 1).

2.4 Fluence distribution

Using the following considerations, the lateral fluence distribution can be derived from the erosion depth of the beam spot.

Erosion processes lead to a decreased film thickness, as carbon atoms are removed by the incident deuterium particles [10]. The decrease in film thickness is proportional to the number of removed carbon atoms. The number of removed carbon atoms depends on the number of incident particles and the erosion yield. Under the assumption of a constant erosion yield (D fluxes in the range of $(1\text{-}8)\cdot10^{19}$ D/m^{2}s [11], homogeneous a-C:H layer and incident angle), the number of removed carbon atoms per unit area is directly proportional to the number of incident particles per unit area, namely the fluence.

For the accumulated charge of 0.6 C averaging the erosion depth over the reference zone, an average fluence of $2\cdot10^{23}$ D/m^2 was determined with an accuracy of 8%. This leads to a calibration factor of $3.3\cdot10^{23}$ D/m^{2}C for the accumulated charge in the deuterium retention experiment of a-C and a-C:W.

2.5   Data evaluation: Deuterium amount and fluence dependences

As the beam profile is reproducible and specimens are adjusted well during implantation, the reference zone can be allocated on each implanted a-C:W film. To determine the deuterium amount in the pure and W-doped films, a one-dimensional scan was performed parallel to the 12 mm edge with the rectangular NRA beam spot of 0.5x1 mm^2 size, crossing the reference zone (Fig. 1). Data points generated on a part of the scan overlapping with the reference zone were averaged, resulting in an averaged amount of trapped deuterium per unit area.

Positioning of the analysing area in the NRA experiment influences directly the accuracy of the fluence value. Using the known distribution of the fluence (chapter 2.4) and assuming a half millimeter positioning error, the accuracy of the fluence value increases to 16%.

3   Results and discussion

For pure as well as for doped carbon films, each deuterium depth profile shows that more than 95% of the retained D is located in a surface near layer of a thickness below 0.5 μm. Inside this subsurface layer, the shape of the depth profile depends on the properties of the carbon film.

Figure 2 shows the amount of retained deuterium n_D as function of the fluence Φ of incident deuterium for different dopant concentrations and pre-annealing temperatures. The implantation zone is saturated at a fluence of about $5 \cdot 10^{20}$ D/m^2. Below this fluence, the amount of retained deuterium follows the dotted line, which represents the 100% reten-

tion line of the nonreflected part (about 85%) of the incoming beam. Above 10^{21} D/m^2, results are compared by the magnitude of X in the power law Φ^X.

Unheated as well as pre-heated a-C films exhibit about the same fluence dependence as pyrolytic graphite (Fig. 2a). This indicates that the deuterium retention is independent of the carbon bonding structure.

Doping with 2.5% tungsten does not change retention behaviour significantly up to a fluence of 10^{23} D/m^2. Above, the deuterium amount rises to higher values compared to pyrolitic graphite and a-C films. This effect is reproducible, but no explanation has been found yet. In contrast, the increase of the inventory with fluence is lower for tungsten-doped films with concentrations of 7.5%. This leads to a maximal reduction of the retained deuterium by a factor of two at a fluence of 10^{24} D/m^2 compared to pure carbon.

In a further step, the dopant concentration was increased and the samples were pre-heated to different temperatures. Figure 2b shows a magnification including all data points of doped and pre-annealed samples. Concerning the power over the fluence, the highest value is 0.057 and the lowest is 0.048, which can not be distinguished from each other, as the uncertainty of the data is ± 0.018. In consequence, it is assumed that the influence of parameter variation is negligible for concentrations of 7.5% and above.

In general, tungsten doping reduces the increase of the retained amount of deuterium with increasing fluence.

In literature [12], fluence dependences of deuterium retention of graphite materials are compared with that for HOPG standard material with the graphene planes parallel to the surface and perpendicular to the D beam. While HOPG shows saturation in the inventory for high fluences, other graphites, e.g. CFC materials, show a significant increase with fluence [6,7,13]. This difference in fluence behavior is often attributed to differences in the extent of diffusion deeper into the bulk. The investigation of deuterium depth profiles of the a-C and a-C:W films indicates that the deuterium does not diffuse dominantly beyond

500 nm for a fluence up to 10^{24} D/m^2. A more detailed analysis of the depth profiles could reveal more information about diffusion processes beyond the thin implantation zone and the effect of the doping.

Chemical carbon bondings are changed in the vicinity of a W-C-bonding. These changes might result in an altered trapping behavior inside the bulk. Further on, changes of trapping energies might be reflected in the trends observed for fluence dependences of the deuterium retention. In consequence, measuring trapping energies should give an explanation for the lowered increase of the deuterium amount with fluence after doping.

4   Conclusions

Tungsten-doped amorphous carbon films were used as model system to study the deuterium retention behavior of metal containing co-deposited layers. Fluence dependence measurements of the deuterium retention in pure and doped carbon films aimed to investigate the influence of the carbon matrix structure and the W-C chemistry. While the retention behavior of pure films does not depend on the carbon matrix structure, doping reduces the power over the fluence by a factor of two compared to pure carbon films and graphites. Variations in dopant concentration and annealing temperature show that the reduction of deuterium inventory in pre-annealed a-C:W is insensitive on changes in the structure of the carbon matrix and on the formation of W$_2$C around 1300 K.

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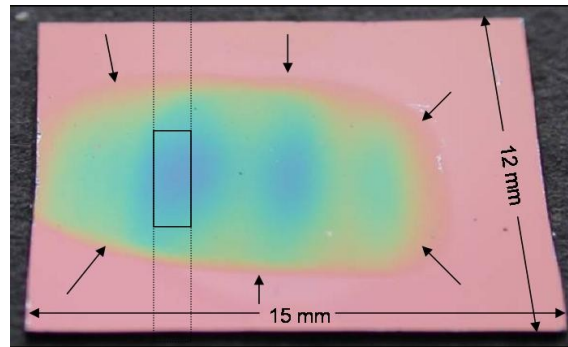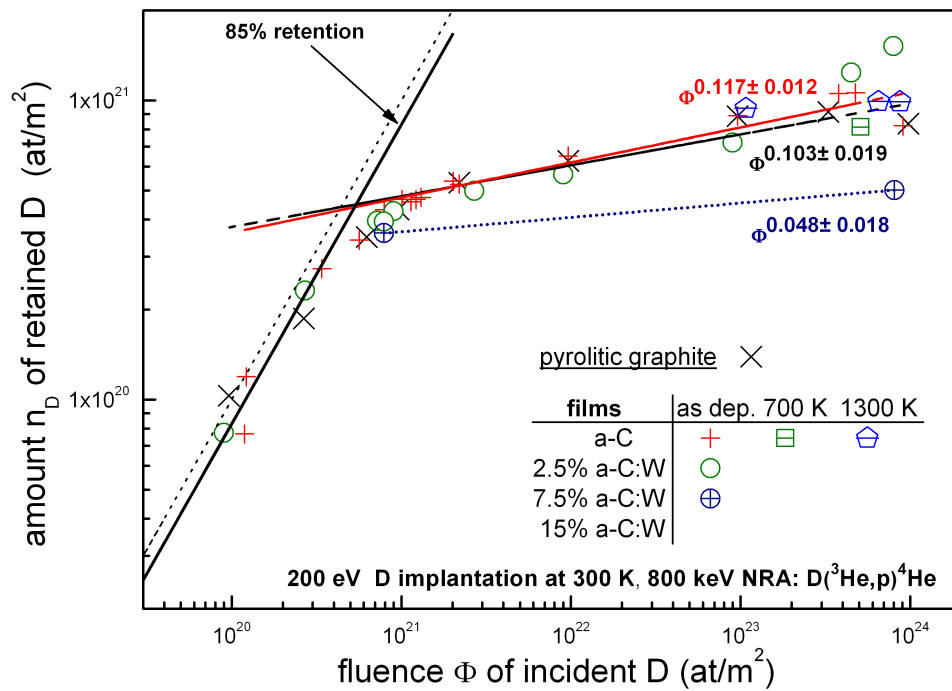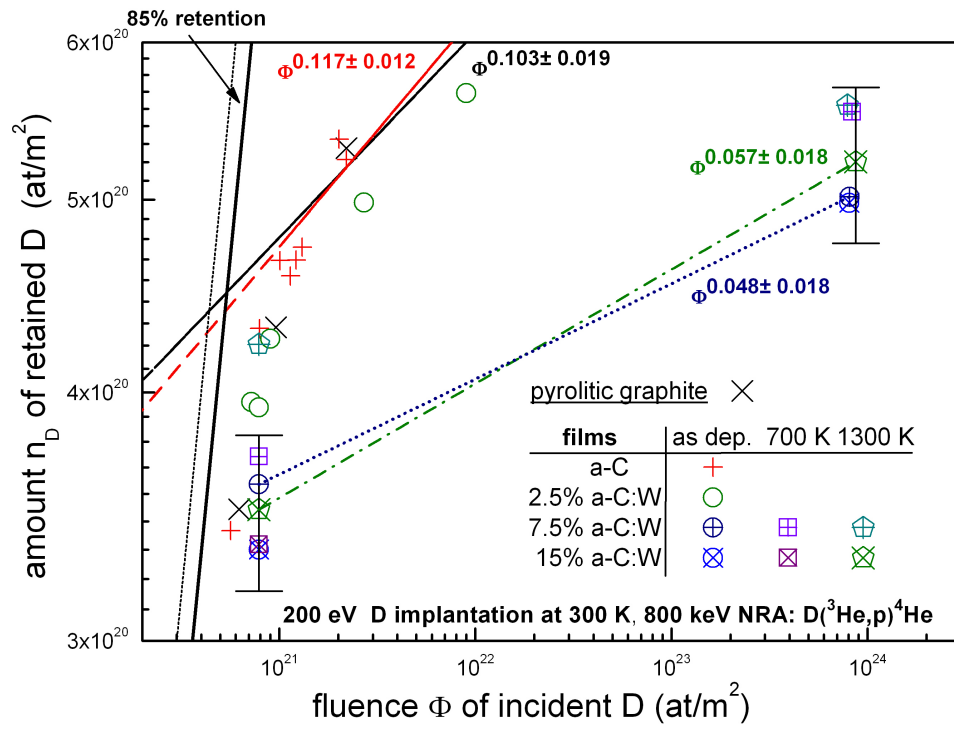
figures

Fig. 1

Fig. 2a)

Fig. 2b)

200 eV D implantation at 300 K, 800 keV NRA: D(^{3}He,p)^{4}He

Figure captions

Fig. 1:

Eroded a-C:H layer with a hydrogen content of 30% on Si plate of 12x15 mm^2 size is imaged on a dark background. The erosion spot covers a colour spectrum between yellow and near violet and is distinguishable from the outer, red areas of the specimen. The boundary of the erosion spot is marked by arrows and the area analysed by NRA by the dotted rectangle (1D scanned area of 1 mm width: dotted; reference area: solid). The reference zone is depicted by the solid rectangle.

Fig. 2):

Amount of retained deuterium implanted to room temperature versus the fluence of incident 200 eV deuterium: a) Pure and doped films (2.5%, 7.5%) after deposition are compared to pyrolytic graphite reference material. Comparisons are drawn out of a power law Φ^X. 2b): A magnification including all data points of doped and pre-annealed samples is shown. Error bars are included for the data pairs of the 15% a-C:W specimen, pre-heated to 1300 K. Power over the fluence lies between 0.057 (dash-dotted) and 0.048 (short dotted). This difference is smaller than the error in the power of ± 0.018.