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# Co-deposition of deuterium with silicon doped carbon

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## Abstract

The co-deposition of deuterium with silicon doped carbon for silicon concentrations between 0–100 at.% in the temperature range from room temperature to 1000 K has been investigated. The eroded material from various different targets was caught on collectors together with the reflected D to build up the co-deposited layers, which were analysed with MeV ion beam techniques. The amount of trapped D per re-deposited target atom depends weakly on the Si concentration. The maximum of about 0.7 D/(Si + C) was found at Si/C  $\approx$  1. For pure C and pure Si the D concentration is about 0.45 and 0.5 D atoms per re-deposited target atom at room temperature, respectively. For increasing deposition temperature the D concentration does not decrease significantly until about 600 K. At about 1000 K the D concentration for pure carbon layers is still about 30% of the concentration at room temperature. Also, co-deposited layers of stainless steel and of titanium-carbon mixtures were investigated. © 1999 Elsevier Science B.V. All rights reserved.

*Keywords:* Co-deposition; Deuterium inventory; Ion beam analysis; a-Si:C:H; Thin film composition

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## 1. Introduction

The successful operation of future fusion reactors will depend on the ability of the plasma facing components to handle enormous particle and power loading [1,2]. These loadings differ significantly with the position of the component in the reactor vessel [2,3]. The component lifetime [4] and the contamination of the plasma will be determined by the erosion mechanisms (e.g. physical sputtering, chemical erosion, sublimation) and their rates [5], as well as by the transport and re-deposition of eroded material [6]. Additional, off-normal conditions (e.g. disruptions) and slow high power transients cause mechanical stress and extreme heat loads [1]. Therefore, they have to be taken into account as additional requirements [4]. In conclusion, for ITER the use of a combination of carbon, beryllium, and tungsten is planned [1,7].

The major disadvantage of pure carbon as plasma facing material (PFM) is its chemical reactivity with

hydrogen (and oxygen) producing volatile or weakly bonded compounds, resulting in large erosion yields due to chemical erosion and in the ability to trap large amounts of hydrogen in the implantation zone and, in particular, in co-deposited layers [8,9]. This co-deposition may result in large tritium inventories trapped in the vessel walls of future fusion experiments, when tritium-deuterium mixtures will be used as fusion fuel [10].

In order to reduce the chemical erosion yield of carbon-based materials, a considerable effort has been undertaken to modify these materials by the addition of other elements such as B, Si, Ti or W [11–16]. The influence of these dopants on the hydrogen saturation concentration due to ion implantation is, however, only little investigated. The existing experimental results support, that changes in the structure of the carbon materials evoke larger variations in the hydrogen retention due to an enhanced migration into the bulk than due to changes in the saturation concentration in the implantation zone [9,17].

In the case of using doped carbon-based materials in a fusion experiment, the eroded material re-deposited at another place in the machine will contain the dopant and carbon together with deuterium and tritium (and

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impurities like oxygen). The influence of dopants on the amount of hydrogen trapped in co-deposited layers is not well known. For silicon, some work on a-C:Si:H films were done in laboratory experiments as well as in TEXTOR [18–21].

Because a silicon doped 3D CFC material (NS31) with about 8–10 at.% Si has been recommended as the ITER reference material for the divertor target plates [16,22], we studied the influence of silicon concentration in re-deposited carbon on the amount of trapped deuterium. Also, the dependence of the amount of trapped deuterium on the deposition temperature was investigated.

## 2. Experimental

### 2.1. Production of the co-deposited layers

The experimental set-up for the co-deposition experiments is shown in Fig. 1. The experiments were performed at the high current ion source at Max-Planck-Institut für Plasmaphysik, Garching [23]. Different targets were bombarded with a mass separated beam of 3 keV  $D_3^+$  ions at normal incidence (corresponding to 1 keV per D). The beam spot had a size of about  $6 \times 10 \text{ mm}^2$ . The target current was about 0.1 mA. For each co-deposition experiment a dose in the range of  $1.3\text{--}2.5 \times 10^{20}$  D atoms was accumulated. The pressure in the vacuum target chamber was about  $1 \times 10^{-5}$  Pa during irradiation. The targets could be heated up to 1000 K.

As targets, the following materials were used: pure carbons (pyrolytic graphite, Union Carbide, USA, and CFC N112, SEP, France), pure silicon (wafer (1 1 1), Aurel GmbH), silicon doped CFC (NS31, SEP, France), and specially prepared multicomponent targets. These

special targets consist of pure silicon or fine grain graphite (EK98, Ringsdorf, Germany) covered with a dot pattern produced by vapour deposition of carbon or silicon, respectively. The oxygen concentration in the Si dots was below 10 at.%. Small and big dots covered about 10% and 50% of the surface, respectively. For C and Si the dots were about 250 and 400 nm thick, respectively. Due to the limited thickness, four special targets were bombarded sequentially to reach the accumulated dose and the required layer thickness. For comparison, stainless steel (1.4970, German DIN standard) and specially prepared targets with small and big titanium dots (1100 nm) with an oxygen concentration less than 25 at.% on fine grain graphite were used.

In order to create the co-deposited layers, the eroded material was caught on two collector plates, A and B (Fig. 1). Due to the variation in the scattering angle the fluence of the sputtered particles (about cosine-distributed) and therefore the layer thickness varies across the collectors [24,25]. The reflected deuterium is implanted into the layer and re-erodes partly the layer. The fluence and the energy distribution of the reflected D depend on the scattering angle and the target composition [25,26]. For carbon targets the estimated fluences on the collectors are in the order of  $10^{18}$  D/cm<sup>2</sup>. So, for each re-deposited target atom more than one reflected D atom hit the collector. The penetration depth of the D is in the order of the half of the final layer thickness. For all target materials, pyrolytic graphite (Union Carbide, USA) and papyex graphite (Le Carbon-Lorraine, Ref. no. 497-30121, France) with a gold layer of about 110 nm thickness were used as collector A and B, respectively. The gold layer was used to separate in the ion beam spectra the low-Z components, such as C and O, from the carbon substrate. For stainless steel also a Si plate was used as collector A. Collector A could be heated through thermal contact with the target to a maximum temperature of about 1000 K. The temperature of the collector and target was measured with an infrared pyrometer controlled with incandescence pyrometer. The uncertainty in the temperature measurement was about 30 K.

### 2.2. Analysis

The layers deposited on the collectors were transported through air to the analysis chamber and were analysed with MeV ion beam techniques. The analysing beam was collimated to  $1 \times 0.5 \text{ mm}^2$ . Several spots along a line between the position 1 and 2 on both collectors of each target material were measured (Fig. 1). The amount of deuterium was determined with the  $D(^3\text{He},p)\alpha$  nuclear reaction with 0.79 MeV  $^3\text{He}$  using a large solid angle proton counter at a scattering angle of about  $145^\circ$ . Release of deuterium due to the analysing beam for a-C:D layers [27] has been observed to be less

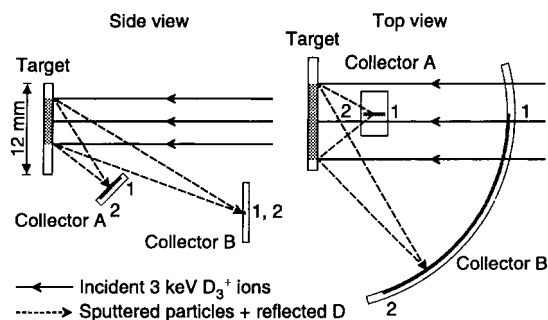


Fig. 1. Experimental set-up: The  $D_3^+$  beam spot on the target is marked in gray. The analysing positions on both collectors are lying along a line between the position 1 and 2 (marked black). The dashed arrows are drawn to illustrate the variation in the scattering angle of the sputtered particles and reflected deuterium for one position on each collector.

than 3% of the D amount for the used fluence of  $1 \mu\text{C}$ . The absolute error in the measurement of the amount of D is about 5%.

The deposited C, Si and O were detected with 2.0 MeV  $^4\text{He}$  backscattering at a scattering angle of  $165^\circ$ . Fig. 2 shows a typical spectrum of a co-deposited layer of NS31 as target material. The amount of C, O, and Si were determined by using the fluence, the area of the respective peak in a spectrum after background subtraction, the solid angle of the detector and the Rutherford cross-sections. The absolute error in the measurement of the amount of C and Si is in the range 5–20% and about 20% for O.

### 3. Results and discussion

#### 3.1. Dependence of D concentration on composition

Fig. 3 shows a typical result for the amount of D, C, and Si versus the amount of re-deposited target atoms, here for a NS31 target. Due to the variation in the fluences of sputtered material from the target, the thickness of the deposited layer differs with the position. Deuterium implantation, D detrapping as well as re-erosion of C and Si take place. The ratio of the re-deposited C and Si atoms is in good agreement with the ratio in the target materials. The co-deposited D atoms, stored in the layers, are proportional to the total amount of re-deposited target atoms.

Due to the different targets, layers with Si concentrations between 0% and 100% in the co-deposited layer were produced. In Fig. 4 the ratio of co-deposited D atoms to re-deposited target atoms is plotted versus the Si concentration in the co-deposited layers. Additional-

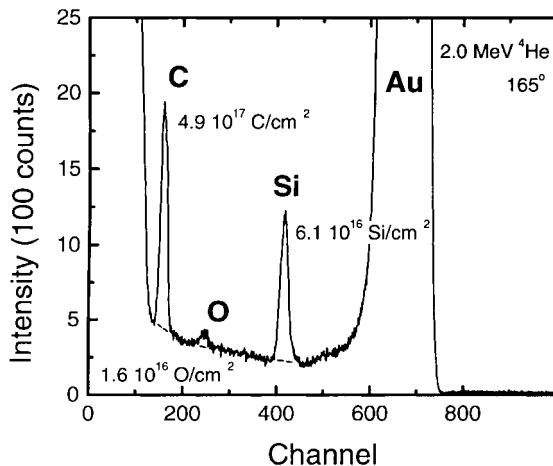


Fig. 2. Averaged backscattering spectrum over the collector A of the co-deposited layer of NS31 as target material. The layer was deposited at room temperature.

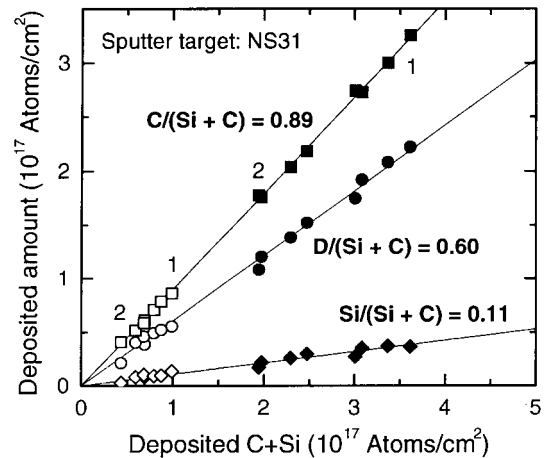


Fig. 3. Amount of D (circles), C (squares), and Si (diamonds) versus total amount of re-deposited target atoms of a NS31 target. The lines results from a linear fit through the data point of the collectors A (closed symbols). The small numbers indicate the position 1 and 2 on the collector A (closed) and B (open). The layers were deposited at room temperature.

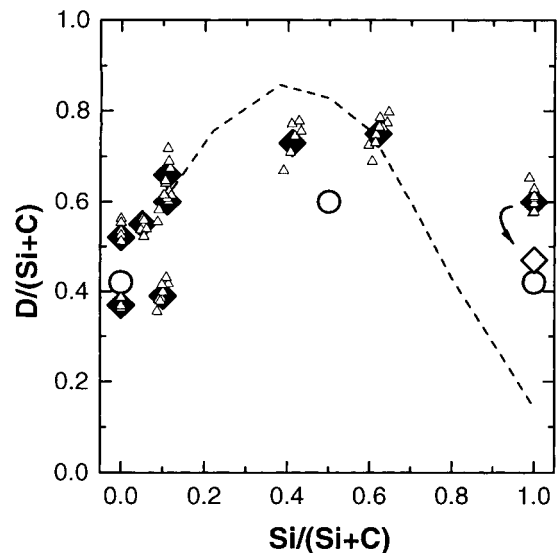


Fig. 4. Ratio of deuterium atoms to re-deposited target atoms versus the Si concentration in the co-deposited layers for each single analysing position (triangles) and the average values over each layer of the collectors A (closed diamonds). An underground correction due to D implantation in Au (more details see text) was applied for one layer (open diamond). All layers were deposited at room temperature. For comparison, the saturation concentration for 8 keV D implantation in C, SiC [9], and Si [28] (circles) and the hydrogen densities of glow discharge a-Si:C:H films taken from [18] scaled with an atomic density of  $0.7 \times 10^{15}$  atoms/cm<sup>3</sup> [19] (dashed line) are shown.

ly, the saturation concentration for 8 keV D implantation in C, SiC [9], and Si is shown [28]. Both, the ratio and the saturation concentration show a maximum around 50% Si. A similar qualitative dependence was observed in a-Si:C:H films created by glow discharges [18,19].

The absolute values of the ratio could be systematically smaller due to D implantation in the collector material. Because of the small thickness of the co-deposited layers, it is not possible to distinguish between D trapped by re-deposited target atoms or by collector material. Deuterium trapping in Au is not well investigated [25,29], in particular at the low energies occurring in our experiment. The amount of trapped D in Au will depend on implantation energy and fluence, which both are varying with the position on the collectors. If the permanently retained D amount in Au is saturated at the obtained fluences and the influence of the energy variation and distribution of D is small, an off-set in the linear extrapolation of the data at zero re-deposited target atoms would exist. For the stainless steel target, the amount of D is nearly constant versus the amount of re-deposited target atoms at about  $1.5 \times 10^{16}$  D/cm<sup>2</sup>. Within the accuracy of the measurements for all layers on Au, such a small off-set could be neglected and is set to zero, except for the layers from stainless steel and pure Si targets. So, only for the pure Si data a constant amount of D was subtracted before the ratio and the average was built. This data point is specially marked in Fig. 4.

In the case of the co-deposited layer of stainless steel targets on Si collectors, the amount of D is independent of the amount of re-deposited target atoms and of the time interval after irradiation. Thus, all the deuterium is trapped in the Si collector, as was also observed for tungsten earlier [26].

Another possibility for a systematic error is the release of deuterium with time after deposition. We controlled the lasting of the D amount for different layers for time intervals between less than one day and a few months after deposition. No release of D with time was observable.

The oxygen impurities in the co-deposited layers possibly influence the ratio of D and re-deposited target atoms. For Be [26,30] and Ti containing layers the amount of O increase linearly with the amount of Be and Ti with a ratio of about 1 and 2, respectively. This corresponds with stoichiometric BeO and TiO<sub>2</sub>. So, the results could be interpreted as co-deposition of deuterium with BeO [26,30] or TiO<sub>2</sub>. For titanium containing layer with Ti/C  $\approx$  0.4 the ratio of D atoms to re-deposited target atoms is 0.42.

For Si containing layers a fixed ratio between the amount of O and Si was not observable. In particular, for layers with a high content of Si (Si/C  $\approx$  1) the amount of O is constant above a certain layer thickness.

The amount of O was always far below the value for stoichiometric SiO<sub>2</sub>, for several analysing positions even below a quarter of the Si amount (Fig. 2). The amount of O does not increase after the first analysis a few days after deposition. It is not possible to distinguish whether the oxygen enters the layers during the deposition, as suggested for Be containing layers [26,30] or during the transport through air. Without a depth profile it could be only speculated that the constant amount of O above a certain layer thickness results due to the passivation by a thin oxidized layer. Overall, no correlation between the O content and the ratio of D and re-deposited target atoms was observed. The reason for the variation in the data at low Si concentration (Fig. 4) between the layers of repeated measurements is still unclear.

### 3.2. Temperature dependence of D concentration

In order to obtain the temperature dependence of the D concentration in co-deposited layers, the target and the collector A were heated to about the same temperature. Fig. 5 summarises the decrease of the ratio of D atoms to re-deposited target atoms with increasing temperature for special targets with big Si dots, N112, and NS31 targets. For comparison, data taken from [8] for D implantation in C at room temperature with subsequent annealing and for D implantation in C at elevated temperatures are shown. For the co-deposited layers the D concentration is always much lower than the value found for room temperature implantation in C

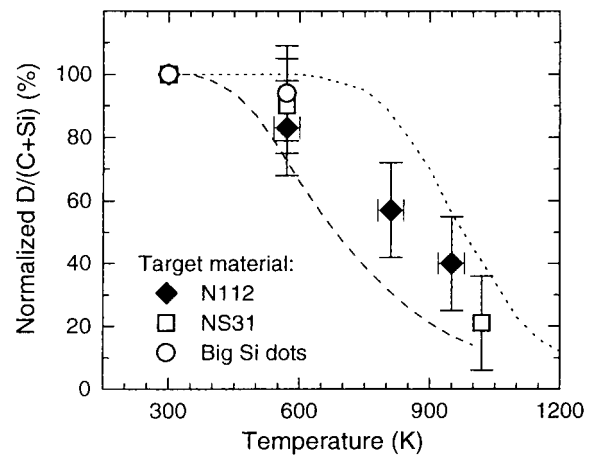


Fig. 5. Ratio of D atoms to re-deposited target atoms for special prepared targets with a pattern of big Si dots (circles), N112 (diamonds), and NS31 targets (squares) versus the temperature of the collector A. The ratios are normalised to the ratio at room temperature. For comparison, data taken from [8] for D implantation in C at the temperature (dashed line) and D implantation in C at room temperature with a subsequent annealing to the temperature (dotted line) are shown.

and subsequent annealing, indicating an ion enhanced release during deposition. However, the values are higher than expected from implantation at elevated temperatures. This may be due to the large contribution of reflected D atoms with energies much lower than the primary ion energy.

In spite of the increasing chemical erosion at higher temperatures, the layer thickness standardized to the impinging D fluence on the target is independent on the target temperature. The product of the chemical erosion for the used D energy is mainly CD<sub>4</sub> with neglectable sticking probability. The probability of the creation of radicals must be small.

#### 4. Conclusion

From the above presentation, the following conclusion can be drawn: The amount of trapped D per re-deposited (Si + C) atom depends weakly on the Si concentration. At Si/C  $\approx$  1 a maximum of about 0.7 D atoms per re-deposited (Si + C) atom was observed. The D concentration is similar to the saturation concentration observed for high fluence D implantation. For titanium containing layers with Ti/C  $\approx$  0.4, the ratio of D atoms to re-deposited target atoms is 0.42.

For both materials, Si and C, the co-deposition follows closely the values observed for ion implantation into bulk materials. This suggests for the applied parameters, like the D implantation energies due to reflection (up to several hundred eV) and the ratio of layer growth rate to impinging D flux on the collector, that the co-deposition is commensurable to implantation of reflected D into the deposited film to saturation. So, this process is better called co-implantation [26]. For implantation energies below about 40 eV the D concentration may be even higher [31].

The D concentration co-deposited (co-implanted [26]) at an elevated temperature above room temperature for the produced layers is between the saturation concentration due to D implantation at the temperature and the remaining D concentration after implantation at room temperature and a subsequent heating to the temperature.

The saturation levels for D implanted in stainless steel [32] result in a much lower concentration of D permanently retained in the surface layer, while more of the implanted deuterium diffuses to the surface, recombine, and desorb. Therefore, much less co-deposition of D with stainless steel is expected. Within the sensitivity of the present experiments co-deposition of D with stainless steel is zero.

In order to predict the tritium inventory in co-deposited layers in fusion reactors, more investigations on mixed materials have to be done, because superposition from pure elemental materials will fail.

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