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Deuterium in re-deposited silicon-doped carbon layers and its removal by heating in air

M. Balden *, M. Mayer

Max-Planck-Institut für Plasmaphysik, Euratom Association, Boltzmannstr. 2, 85748 Garching, Germany

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Abstract

The composition of co-deposited hydrocarbon-silicon layers (a-C:Si:D) with varying Si concentrations and their removal by heating in air were investigated using MeV ion beam techniques. The amount of trapped D per re-deposited target atom depends weakly on the Si concentration. For pure C and Si, the D concentrations are about 0.45 and 0.5 D atoms per re-deposited target atom at room temperature, respectively. A maximum of about 0.7 D/(Si+C) was found at $Si/C \approx 1$. For increasing deposition temperature the D concentration does not decrease significantly until about 600 K. At about 1000 K the D concentration for pure C layers is still about 30% of the concentration at room temperature. The removal rates of D and C by heating in air increase strongly at temperatures around 550 K for a-C:D layers. With increasing Si content, these temperatures rise to above 650 K for layers with Si concentrations higher than 0.2 Si/(Si+C). The C removal rate is always lower than the D removal rate. Si is not removed by this method. For comparison, the composition of co-deposited stainless steel layers and Ti–C mixtures were investigated. © 2001 Elsevier Science B.V. All rights reserved.

1. Introduction

The selection of the plasma facing materials for future fusion devices is still an open question. A broad variety of material properties has to be taken into account for the different locations in the machines and operating conditions of the devices: high particle and power loads in the divertor, plasma compatibility of the main chamber wall material, mechanical properties and their degradation due to neutron irradiation, and last but not least radiological aspects of activation and afterheat. Some properties are related to the bulk material, while some other are related only to a thin surface layer, such as erosion and hydrogen recycling by hydrogen impact.

For the surfaces with the highest particle and heat loads, carbon-based materials are under discussion. Their major disadvantage is the chemical reactivity of carbon with hydrogen and oxygen resulting in large erosion yields due to chemical erosion [1] and in the ability of carbon to trap large amounts of hydrogen in the implantation zone and, in particular, in co-deposited layers [2]. The chemical erosion yield of carbon can be reduced by dopants such as boron, silicon or titanium [3]. But the influences of dopants on the amount of hydrogen trapped in the implantation zone and in co-deposited layers as well as on the removal behavior of hydrogen from these co-deposited layers are not well known.

In addition to the influence of the intentionally introduced dopants, also the influence on trapping and H-recycling of other elements present in the device has to be investigated, especially for the suggested mix of materials for ITER [4]. Because an Si-doped carbon–carbon fiber composite (CFC) is envisaged as an alternative divertor material for ITER [5], we focus on the silicon–carbon system as a starting point. We have analyzed the composition and deuterium content of co-deposited layers with varying concentrations of C and Si and varying deposition temperatures using MeV ion beam techniques. The temperature dependence of the

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* Corresponding author. Tel.: +49-89 3299 1688; fax.: +49-89 3299 1212.

E-mail address: martin.balden@ipp.mpg.de (M. Balden).

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deuterium removal from these layers as well as the removal of the whole layer was studied by heating in air up to 800 K.

2. Experimental

The co-deposited layers were produced by collecting the material sputtered by D ions from different targets on collector plates together with the reflected D atoms.

Carbon (pyrolytic graphite, Union Carbide, USA, and CFC N112, SEP, France), silicon (wafer(1 1 1), Aurel GmbH, Germany), silicon-doped CFC (NS31, SEP, France), fine grain graphite (EK98, Ringsdorf, Germany) covered with Si dots of various size (0.5 and 1 mm diameter covering 10% and 50% of the surface, respectively), and silicon covered with C dots (1 mm diameter) were used as targets. They were bombarded generally with a mass separated beam of 3 keV D_3^+ ions at normal incidence (corresponding to 1 keV per D). For pure C, some layers were also produced with an impact energy of 50 eV per D atom. The accumulated doses for the different target materials were in the order of 10^{20} D atoms. For comparison, also layers produced from stainless steel targets (1.4970, German DIN standard) and targets consisting of titanium dots on graphite were analyzed.

The eroded material was deposited together with reflected D on two collector plates, one circular (25 mm radius) and one flat (distance about 10 mm). These plates consist of a 110 nm gold layer on top of a carbon substrate (pyrolytic graphite, Union Carbide, USA and papyex graphite, Le Carbon-Lorraine, ref. no. 497-30121, France). The purpose of the gold layer is to avoid peak overlapping in the ion beam spectra. For stainless steel also Si was used as collector plates.

The flat plate 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 and controlled with an incandescence pyrometer. The uncertainty in the temperature measurement was about 30 K.

Due to the geometrical combination of the target and collector positions and the size of the sputtering spot, the scattering angle for the flat (circular) collector is averaged over about 30° (10°). Across the flat collector from one end (position 1) to the other end (position 2), the mean scattering angle decreases from about 145° (1) to 120° (2), respectively. Across the circular collector from one end (position 3) to the other end (position 4), the scattering angle varies from 155° (3) to 115° (4), respectively. For a smooth surface, the angular distribution of the reflected particles, at normal incidence as well as the angular distribution of sputtered particles is about a cosine distribution. The sputtered particles have low energies in the eV-range. For the reflected particles the maximum energy and the energy distribution depend on the scattering angles [6,7]. Additionally, the surface roughness will modify the energy and angular distribution [7,8], but is neglected for the values given below.

The particle reflection coefficient of 1 keV deuterium on C and Si is 0.093 and 0.185, respectively. The mean energy of the reflected D from C and Si is 328 and 390 eV, respectively [9]. The maximum energy of the reflected D varies from 521 to 654 eV for C (from 758 to 835 eV for Si) for the scattering angle from 160° to 105°. For other target compositions, the effective reflection coefficient could be obtained by using the partial reflection coefficients. Using the geometry and a cosine distribution for the reflected deuterium from a C target, the highest estimated fluence of $2–4 \times 10^{22}$ D/m^2 for the used doses is reached at position 1 of the flat collector. The fluence decreases by 60% across the flat collector to position 2. For the circular collector the corresponding variation of the fluence is from 20% (position 3) down to 10% (position 4).

The reflected deuterium is implanted into the layer and re-erodes partly the layer. For all used layers, the final layer thickness was of the order of 10^{21} atoms/m^2. Therefore, for each remaining re-deposited target atom more than one reflected D atom hits the collector. The penetration depth of the D is about half of the final layer thickness. The amount of implanted D in the Au-coated C collectors could be neglected, while for the Si collectors a constant amount was found. Several spots along a line (corresponding to different layer thickness) on both collectors of each target material were measured.

For analyzing the composition and thickness of the deposited layers, MeV ion beam techniques were used. The samples were transported through air to the analyzing chamber. The amount of deuterium was determined with the D(^{3}He, p)α nuclear reaction (NRA) with 0.79 and 1.2 MeV ^{3}He using a large solid angle proton counter at a scattering angle of about 145°. The ion-induced release of deuterium from the co-deposited layers due to de-trapping by the analyzing beam [10–12] was determined to be less than 3% of the initial D amount for the used fluence.

The amounts of the heavier deposited elements (e.g., C, O, Si) were measured by detecting the backscattered ^{4}He (RBS) of the 2.0 MeV ^{4}He ion beam at a scattering angle of 165°. The 1.2 MeV ^{3}He ions were also used for RBS in the removal experiment. A fluence of about 30–40 μC ($3.8–5 \times 10^{19}$ ^{3}He/m^2) was accumulated for each spectrum. The absolute error in the measurement of the amounts of C, O and Si was in the range 5–20%.

The pieces of the circular collectors were used as specimens for the removal experiment. They were heated for 1 h in air at a chosen temperature between 525 and 800 K. Generally, they were heated once and analyzed before and after that heating. Only one sample was successively heated and analyzed at several temperatures.

The accuracy of the chosen temperature was about 20 K with fluctuations of about 30 K around the achieved temperature due to the controlling procedure of the furnace.

Due to the high incident fluences necessary for RBS, a significant amount of D was released by the analyzing beam [12]. Therefore, the D amount after the heating in air was cross-checked with previous un-irradiated specimen areas. An influence on the removal behavior was only observed for samples with a high Si concentration. The absolute error in the measurement of the amount of D was about 15%. More details to the experiment can be found in [12,13].

3. Results and discussion

3.1. Composition and deuterium content

Fig. 1 shows the results for the amount of trapped deuterium versus the amount of re-deposited target atoms for C, Si, C–Si, and stainless steel targets. In addition, published data for similarly produced re-deposited layers of W and BeO are shown [8,14]. A linear increase of the amount of trapped D with the amount of deposited target atoms shows co-deposition, the slope of the linear increase is determined by the ratio of trapped D-to-target atom. The offset is created by implantation of D into the collector material (e.g., Si) at the start of layer growth. For stainless steel and W [8], co-deposition is not observed, and all D is trapped in the collector substrate. Both C and Si and all C:Si mixtures show co-deposition, as well as BeO [8,14]. Pure, almost oxygen-free Be co-deposits also with D, but with smaller D concentrations than BeO. At 373 K the D-concentration is only about 0.15 D/Be [15].

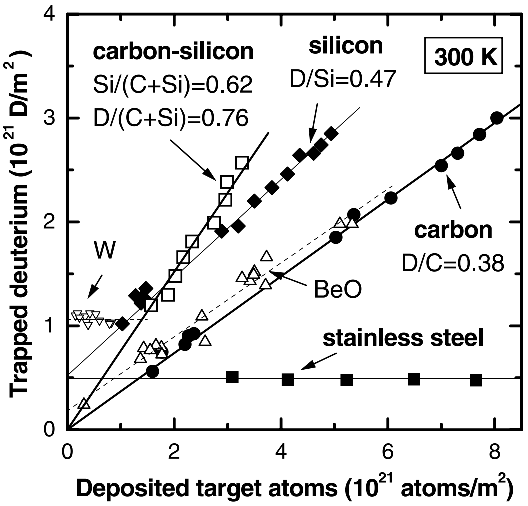

Fig. 1. The amount of trapped D versus the total amount of re-deposited target atoms of C, Si, C–Si, and stainless steel targets. The lines results from a linear fit through the data. The layers were deposited at room temperature. Published data of similar experiments with W and BeO are included [8,14].

Also, the deuterium amount in co-deposited titanium–carbon mixtures and stainless steel layers was determined. The ratio of D atoms to re-deposited target atoms is 0.42 for layers with $\mathrm{Ti/C} \approx 0.4$. But the Ti-containing layers are always completely oxidized to TiO_2. The saturation levels for D implanted in stainless steel [16] result in a much lower concentration of D permanently retained in the surface layer, while the vast majority of the implanted deuterium diffuses to the surface, recombines, and desorbs. Therefore, much less co-deposition of D with stainless steel is expected at a level of the defect density in the deposited material. Within the sensitivity of the present experiments co-deposition of D with stainless steel is zero.

The ratio of co-deposited D atoms to re-deposited target atoms is plotted versus the Si concentration in the co-deposited layers in Fig. 2. Additionally, the saturation concentration for 8 keV D implantation in C, SiC [17], and Si is shown [13]. Both, the ratio and the saturation concentration result in a maximum around $\mathrm{Si/C} \approx 1$. A similar qualitative dependence was observed in a-Si:C:H films deposited from glow discharges

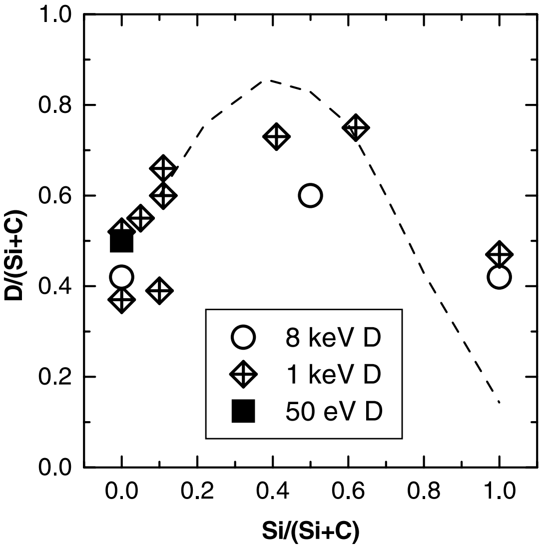

Fig. 2. Ratio of deuterium atoms to re-deposited target atoms versus the Si concentration in the co-deposited layers (◈). In a similar experiment [20] 50 eV D impact energy (■) on the target were used instead of 1 keV in this paper. All layers were deposited at room temperature. For comparison, the saturation concentration for 8 keV D implantation in C, SiC [17], and Si [13] (○) and the hydrogen densities in glow discharge a-Si/C:H films [18,19] (–) are shown.

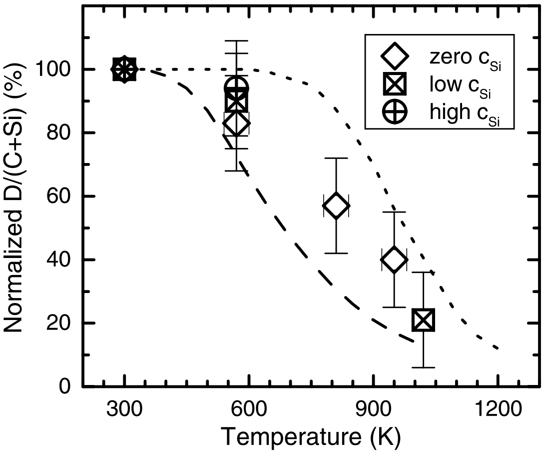

Fig. 3. The normalized ratio of D atoms to re-deposited target atoms for three different Si concentrations: zero, low ($\sim$10% Si/(C+Si)), high ($\sim$30%), versus the collector temperature. Data for D implantation in C at the temperature (dashed line) and D implantation in C at room temperature with a subsequent annealing to the temperature (dotted line) [21] are shown for comparison.

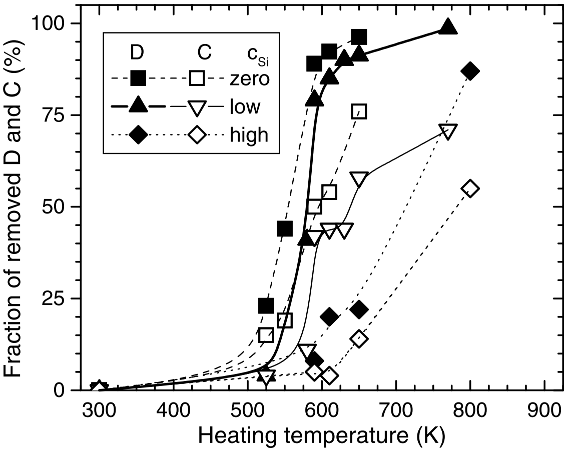

Fig. 4. Fraction of removed D (solid) and C amounts (open symbols) after heating of co-deposited layers in air for 1 h as a function of heating temperature for layers with zero ($\square$, $\blacksquare$), low ($c_{Si} < 15\%$ Si/(C + Si)), (∇, $\blacktriangle$), and high Si concentrations ($20\% < c_{Si} < 40\%$, ($\diamond$, $\blacklozenge$) deposited at room temperature.

[18,19]. No difference in the ratio D/C is observed in pure C layers for 50 eV [20] and 1 keV D impact energy.

The temperature dependence of the D concentration in co-deposited layers was measured by heating the target and the flat collector plate. Fig. 3 summarises the decrease of the ratio of D atoms to re-deposited target atoms with increasing temperature for zero, low, and high Si concentrations. For comparison, data are shown for D implantation in C at room temperature with subsequent annealing and for D implantation in C at elevated temperatures [21].

For the co-deposited layers the D concentration is always lower than the value found at room temperature implantation in C 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.

3.2. Removal by heating in air

The removal of D and C from the layers by heating in air are investigated as a function of the heating temperature for layers with zero, low, and high Si concentration (c_{Si}). The amount of Si never changed in the layer by heating in air. Si is not removed; rather, Si is oxidized as the increasing O/Si ratio implies. The removal rate is indicated by the slope of the fraction of removed D and C versus the heating temperature (Fig. 4). A comparison between D and C shows that the erosion rate of C is lower than that of D, i.e., D is removed first [12].

The major D removal takes place in a small temperature range around 550 K for the pure C layers. The temperature dependence of the removal rate of C becomes weaker above 600 K, where more than 80% of the D is removed while only about half of the C is eroded. Such a temperature dependence was previously reported for the erosion of soft a-C:D films by heating in air [22]. But with their removal rates [22], our layers should be completely eroded after heating for 1 h at 550 K. Our rates (4×10^{20} D/m^2/h, 3×10^{20} C/m^2/h) are a factor of 10 lower. Further experiments are necessary to determine the influences of the layer structure [2] and thickness [23].

For the Si-containig layers, the temperature dependence of the removal of D and C is comparable to the layers without Si. However, the necessary temperatures to achieve a similar fraction of removal of D and C increase by about 50 K for layers with low Si concentration. This shift increases with increasing Si concentration. The necessary temperatures are shifted by more than 100 K towards higher temperatures for the layers with Si concentrations larger than 0.2 Si/(Si+C). After heating for 1 h at 600 K, the carbon still remains in the layers and only 20% of the initial deuterium is removed.

Due to the complexity of the oxidation processes, no explanation can be given for that shift with Si concentration. Besides the thermodynamics and reaction kinetics between D, C, O and Si, the layer morphology, such as porosity, or diffusion (diffusion barrier by oxidized Si) may play a significant role in the removal behavior.

4. Conclusion

We have analyzed the composition of co-deposited deuterium-rich layers with varying concentrations of carbon and silicon (a-C:Si:D) and their removal by heating in air using MeV ion beam techniques. The material eroded from various targets by deuterium impact was caught on collector plates together with the reflected deuterium to build up the co-deposited layers. Deposition temperatures up to 1000 K were investigated.

The amount of trapped deuterium per re-deposited target atom depends weakly on the silicon concentration with a maximum of about 0.7 D/(Si+C) at $\mathrm{Si/C} \approx 1$. For pure carbon and pure silicon the deuterium concentration is about 0.45 and 0.5 D atoms per re-deposited target atom at room temperature, respectively. The amount of trapped D in the co-deposition follows closely the values observed for ion implantation into bulk materials. This suggests that the co-deposition is commensurable to implantation of reflected D into the deposited film to saturation. Therefore, this process should be called co-implantation [8], at least at sufficiently high particle energies.

For elevated deposition temperatures the D concentration is nearly constant up to 600 K. At higher temperatures the amount of trapped D decreases, at about 1000 K the D concentration for pure carbon layers is 20–30% of the room temperature concentration. The D concentration is between the saturation concentration due to D implantation at the temperature and the remaining D concentration after implantation at room temperature and subsequent heating to the temperature.

The removal behavior was investigated by heating the co-deposited layers at temperatures up to 800 K for 1 h in air. The removal rates of D and C increase strongly at temperatures around 550 K for a-C:D layers. With increasing silicon content, these temperatures rise to above 650 K for layers with Si concentrations larger than 0.2 Si/(Si+C). The carbon removal rate is always lower than the deuterium removal rate. The silicon of the re-deposited layer, however, is not removed but oxidized during the heating in air, resulting in increased oxygen contents.

The concentration of hydrogen in co-deposited hydrogen-carbon layers is influenced by the addition of Si into these layers. Also influenced by the Si are the hydrogen and carbon removal rates by heating in air and the ion-beam-induced de-trapping by incident high-energy beams [12]. This shows the importance of the investigation of mixed co-deposited layers. More investigations on mixed materials have to be performed to predict the tritium inventory in co-deposited layers in fusion reactors, because a linear superposition from pure elemental data may fail.

Higher hydrogen removal rates by heating in air were measured for co-deposited layers found in the present nuclear fusion plasma experiments than for layers created in laboratory experiments [23–25]. Metal impurities or a different morphology (higher porosity) may be the reason for these differences. From the viewpoint of hydrogen trapping [13,17] and removal, e.g., by oxidation [12,22], the impact of silicon is positive by increasing the trapped hydrogen concentration and the necessary removal temperatures. That means the introduction of Si worsens the tritium problem [2]. Hopefully, other impurities have beneficial effects and act as promoters for the removal procedure. More work is necessary on the composition, structure and creation conditions of mixed co-deposited layers in plasma devices.

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