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Removal of deuterium from co-deposited carbon–silicon layers

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Abstract

The composition of co-deposited carbon–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 ion-induced release of D due to the analysing beam (1.2 MeV ^{3}He) was determined. 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 larger than 0.2 $\mathrm{Si}/(\mathrm{Si}+\mathrm{C})$. The C removal rate is always lower than the D removal rate. Si is not removed by this method. The observed properties of the layers are compared with those of hard and soft a-C:D films. © 2000 Elsevier Science B.V. All rights reserved.

1. Introduction

The successful operation of future fusion devices depends on the selection of appropriate plasma facing materials. These materials have to be compatible with the particle and power loads during normal and off-normal operating conditions, the hydrogen recycling of the walls, the neutron radiation, and low tritium inventories in the devices [1,2]. The exact requirements for the materials differ and depend upon location and function of the plasma facing component in the chamber [2,3]. Therefore, a variety of materials (and elements) is planned, e.g. for ITER [1,4]. For the surfaces with the highest heat loads, such as the divertor plates and protection limiters, carbon-based materials offer the best possibility to withstand these heat loads [1,4,5], despite other disadvantages of carbon.

The major disadvantages of carbon are its high-chemical reactivity with hydrogen (and oxygen), and the ability to trap large amounts of hydrogen. The chemical reactivity results in high erosion yields, which have to be taken into consideration for lifetime estimates. Carbon eroded at one place of the device may be re-deposited elsewhere and trap large amounts of hydrogen by co-deposition. The tritium inventory in these co-deposited layers is a safety problem [4]. A large inventory is not tolerable in the device, and strategies either to avoid or to remove these layers are necessary [4,6].

The deposition of amorphous hydrogenated carbon (a-C:H) layers has been studied for many years [7]. Removal of hydrogen from a-C:H layers was investigated by heating in vacuum, air or oxygen [8–14], and by exposure to different plasmas [4,6]. Unfortunately, co-deposited layers in a fusion device may also contain other elements present in the torus, especially dopants if doped carbon materials are used. For the ITER-divertor target plates, a silicon-doped 3D carbon–carbon fibre composite (CFC) has been recommended and is the current reference material (NS31) [15]. The influence of dopants or impurities on the amount of hydrogen trapped in the co-deposited layers and on the removal of hydrogen is not well known. Only some work has been performed on Si containing a-C:Si:H films [16–20].

We have analysed the composition and deuterium content of co-deposited layers with varying concentrations of C and Si using MeV ion beam techniques. The temperature dependence of the deuterium removal from these layers as well as the removal of the whole layer was investigated by heating in air up to 800 K. The experimental results obtained are compared with the properties of hard and soft a-C:D films.

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2. Experimental

The co-deposited layers were produced by collecting the material sputtered by D ions from targets with varying Si/C ratio together with the reflected D atoms on collector plates [20]. Pieces of these plates were used as samples for the investigation of the removal behaviour of D. The samples were of three types: Deposited layers containing only D and C, layers containing low amounts of Si ($c_{Si} < 10\%Si/(C+Si)$), and layers containing large amounts of Si ($c_{Si} > 20\%Si/(C+Si)$). The D content and the composition (C, Si, O) of these samples were determined using MeV ion beam analysis techniques before and after heating in air at chosen temperatures.

2.1. Production of the co-deposited layers

A detailed description of the experimental set-up and results about the D content in the layers can be found in [20,21].

Pyrolytic graphite, fine-grain graphites covered with Si dots of various size, Si wafers, and the Si-doped CFC NS31 were used as sputtering targets [20]. The targets were bombarded with a mass-separated beam of 3 keV D_3^+ ions at normal incidence (corresponding to 1 keV per D) [21]. The eroded material was deposited together with reflected D on circular collector plates (2.5 cm radius). Strips of papyex graphite (Le Carbon–Lorraine, ref. no. 497-30121, France) with a gold layer of about 110 nm thickness on top were used as collectors. The purpose of the gold layer was to separate the low-Z components (C, O, Si) from the carbon substrate in the ion beam analysis spectra.

The flux of the sputtered particles is approximately a cosine distribution and, therefore, the layer thickness varied along the collector plates due to variations of the scattering angle [20,22]. This was taken into account by analysing several positions along a line. The reflected deuterium is implanted into the layer and partly re-eroded the layer. Only at the beginning of the layer growth, some D came to rest in the Au and diffused out. The flux and the energy distribution of the reflected D depend on the scattering angle and target composition [20,22]. For each re-deposited target atom, more than one reflected D atom hit the collector. For all used layers, the final layer thickness was above 10^{21} atoms/m^2.

The collector plates could be heated up to a temperature of 1000 K [20]. All co-deposited layers used for the removal investigation by heating in air were deposited at about 300 K.

2.2. Ion beam analysis

For analysing the composition and thickness of the deposited layers, MeV ion beam techniques were used. A beam of 1.2 MeV ^{3}He was collimated to 1 × 0.5 mm^2 (or 1 × 1 mm^2) on the sample. The amount of D was determined with the $D(^3He,p)\alpha$ nuclear reaction (NRA), using a large solid angle proton counter at a scattering angle of about 145°. (The amount of H was not measured.) The ion-induced release of deuterium from the co-deposited layers due to detrapping by the analysing beam [23,24] was determined to be less than 3% of the initial D amount for the used fluence of 1 μC (1.25 or 0.625×10^{19} ^{3}He/m^2, see also below). The absolute error in the measurement of the amount of D was about 5%.

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

In order to avoid loss of D and changes in the layer and, therefore, in the removal behaviour due to the analysing ion beam [23,24], the measurements after the heating were performed at previously analysed and fresh sample positions along a line. An ion-induced release was found for all samples (see Section 3.2., Fig. 1). An

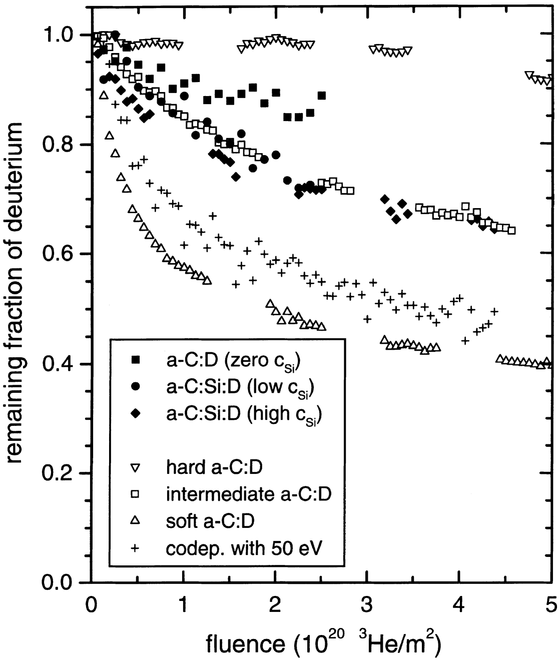

Fig. 1. Fluence dependence of the ion-induced release of D for co-deposited layers with no additional Si, low (0.07) and high Si concentration (0.23 Si/(C + Si)) (solid symbols). The initial ratios D/(C + Si) are 0.5, 0.5 and 0.7, respectively, measured with 1.2 MeV ^{3}He ions. For comparison, the fluence dependence for a hard (D/C ~0.5), an intermediate (~0.7) [26] and a soft (~1.0) a-C:D film deposited in a RF glow discharge (open symbols) [25], and for a layer produced with low incident energy of 150 eV per D_3^+ ion (D/C ~0.5) [27] (crosses) are shown.

influence on the removal behaviour was only observed for samples with a high Si concentration (c_{Si}). For those samples, where data exist only from previously analysed positions (NRA), the D content was corrected by 10% (590, 610 K).

2.3. Heating of the layers in air

The samples were heated for 1 h in air at a chosen temperature between 525 and 800 K. Only one sample (low c_{Si}) was successively heated at 525, 580 and 630 K. At the temperatures 590, 610 and 650 K, one sample from each of the three types was heated simultaneously. The temperature inside the oven fluctuated by about 30 K around the set temperature in a cycle of about 15 min due to the controller of the oven. The accuracy of the set temperature was about 20 K.

3. Results and discussion

3.1. Dependence of D concentration on composition

Detailed results about the D concentration as a function of layer composition were published earlier [20] and will only be summarised here. The amount of D trapped in the co-deposited layers depends weakly on the Si content of the layer, with a maximum of about $0.7\text{D}/(\text{Si}+\text{C})$ at $\text{Si}/\text{C} \approx 1$. For layers containing only C or Si, the D ratio was about 0.45 D/C and 0.5 D/Si at room temperature, respectively. With increasing deposition temperature, the concentration of trapped D is nearly constant up to 600 K. At higher temperatures the D concentration decreases and reaches, at 1000 K, about 20–30% of the room temperature concentration.

3.2. Release of D due to ion-induced desorption

For layers containing only D and C, the determined D/C ratio of 0.45 suggests a similarity to hard a-C:D films (typical: 0.43 D/C for hard films and 1.0 for soft ones) [7]. This similarity is supported by the relatively high energies of the reflected deuterium. Fig. 1 shows the ion-induced release of D from the co-deposited layers as a function of 1.2 MeV ^{3}He ions fluence for the three types of layers (zero, low, high c_{Si}) and, for comparison, for four other layers: three of them were deposited in a RF glow discharge [25] and characterised as hard, intermediate (D/C ~0.7) [26] and soft a-C:D films. For the co-deposited layers used here, the ion-induced release of D is not like that for hard films, but it is more like that for the intermediate one. The fourth layer was produced in the same manner as the samples used here, but with an energy of 150 eV per incident D_3^+ ion [27], instead of 3 keV. The energy of the reflected D now should be low enough to produce a soft a-C:D film [7]. However, this film has only a D to C ratio of 0.5, and is, therefore, closer to the hard films. In contrast to the D/C ratio, the release behaviour resembles the soft films. Combining both observations, neither the D energy nor the ratio of D to C alone are sufficient parameters to characterise co-deposited layers [7].

The Si containing C layers show an enhanced loss of D by ion-induced desorption, compared to layers containing only C (Fig. 1). This enhancement may be due to the presence of Si in the layers: Si atoms increase the electronic energy loss of the high energetic ^{3}He ions, which is 31.2 and 53.7 eV/10^{19} atoms/m^2 in C and Si, respectively. Electronic excitations are responsible for detrapping of bound hydrogen atoms [28]. The higher energy loss may result in an increased detrapping. Another possible explanation is that the presence of Si atoms in the layers result in a lower binding energy of the trapped D [16]. Both effects would influence hydrogen recycling in a fusion device. However, also a change of the deposition conditions, such as the variation of the energy distribution of the reflected D by the target composition or the layer thickness cannot be ruled out as explanation for this observation. Further, investigations are necessary to distinguish between these explanations.

3.3. Removal of D by heating in air

The removal of D and C from the layers by heating in air is shown in Fig. 2 as a function of the Si concentration (c_{Si}) before heating. Following a data set for one

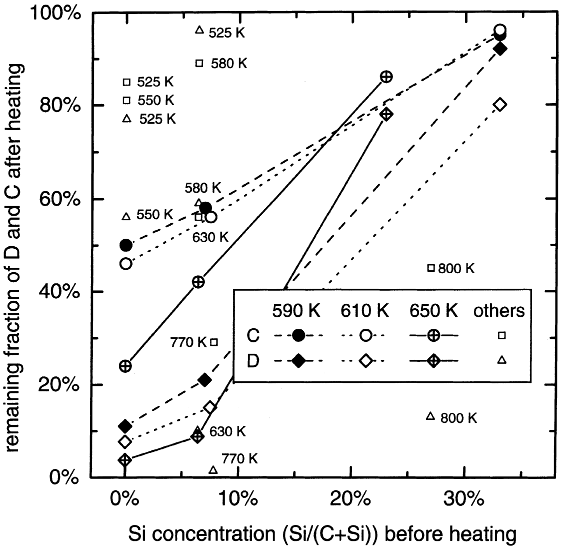

Fig. 2. Remaining fraction of the initial D (diamonds) and C amounts (circles) after heating of co-deposited layers in air at different temperatures for 1 h as a function of the Si concentration before heating.

heating temperature, e.g. 590 K, it is clearly visible that the removed fraction and the removal rates for D and C decrease with increasing c_{Si}. For the layers with zero or low c_{Si}, the mean removal takes place already at temperatures around 600 K, at which the D content is decreased to values below 20% of the initial amount by heating for 1 h. A comparison of the data for D and C shows that the erosion rate of C is lower than that of D.

The amount of Si in the layer was never changed by heating in air: Si is not removed. Rather, the Si is oxidised as the increase of O implies: The ratio of O to Si increases due to the heating in air from around 1 to above 2 for the samples containing small amounts of Si and from below 1 to around 1.5 for samples containing large amounts of Si. The initial O content depends on the initial layer thickness [20].

In order to obtain the dependence of the removal rates of D and C on the heating temperature, the data are grouped by their Si concentration (zero, low, high c_{Si}) and are presented as a function of heating temperature in Fig. 3. An increase in the removal rate with temperature is indicated by the slope of the curve.

For the layers without Si, the major change of the D removal rate with temperature takes place in a small temperature range around 550 K. For C, the temperature dependence of the erosion rate becomes weaker above 600 K, where the remaining fraction of D is below 20% and about half of the C content is eroded. Such an evolution of the temperature dependence was previously reported for the erosion of soft a-C:D films by heating in air [8]. With the reported removal rate, our layers should be completely eroded after heating for 1 h at 550 K. Our rates seem to be a factor of 10 lower $(4 \times 10^{20}\ \mathrm{D\,m^{-2}\,h^{-1}}, 3 \times 10^{20}\ \mathrm{C\,m^{-2}\,h^{-1}})$. In order to determine absolute values of the rates and possible influences of the layer structure [4] and thickness [9], further experiments have to be performed investigating the time dependence of the removal of films with different thickness.

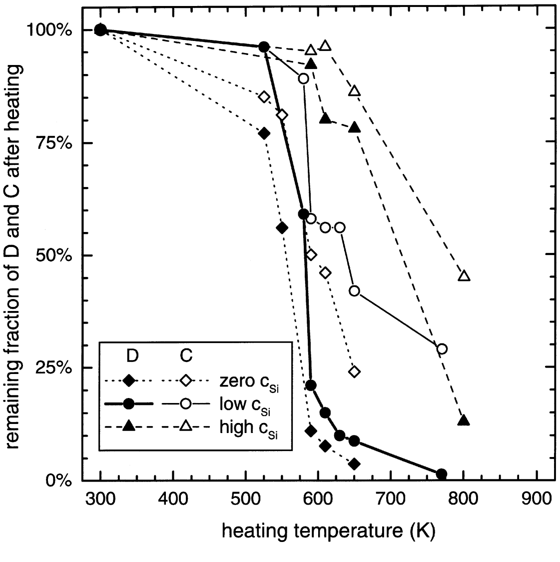

Fig. 3. Remaining fraction of the initial D (solid) and C amounts (open symbols) after heating of co-deposited layers in air for 1 h as a function of heating temperature for layers containing no additional Si (diamonds), low (circles), and high-Si concentrations (triangles).

For the layers with low Si concentration, the temperature dependencies of the removal behaviour of D and C are comparable to the layers without Si. However, the necessary temperatures to achieve similar removal of D and C increase by about 50 K. With increasing Si concentration this shift increases. For the layers with Si concentrations larger than $0.2\ \mathrm{Si}/(\mathrm{Si}+\mathrm{C})$, the necessary temperatures are shifted by more than 100 K. At 650 K, more than 75% of the initial D and C still remain in the layers after 1 h.

No apparent explanation for that shift with Si concentration can be given due to the complexity of the oxidation processes. Beside the thermodynamics and reaction kinetics between D, C, O and Si, the layer morphology, such as porosity, or diffusion (effect of the oxidised Si as a diffusion barrier) may play a significant role in the removal behaviour.

4. Conclusion

We have analysed the composition of co-deposited 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 layers were produced by collecting eroded material from C and Si containing targets together with the reflected D.

An ion-beam-induced release of D due to the analysing MeV ion beam (1.2 MeV ^{3}He) was observed. Compared to a-C:D layers [7,25,26], the determined release is comparable to intermediate a-C:D layers, with a D concentration between that of hard and soft layers. The release rates increase with increasing Si concentration in the layers. It should be kept in mind that the hydrogen concentration is not sufficient to characterise the co-deposited layers, if the deposition conditions are different.

The removal rates of D and C by heating the co-deposited layers in air increase strongly at temperatures around 550 K for a-C:D layers. The removal rates of C are always lower than those of D. For Si containing layers, the shapes of the temperature dependencies of the removal rates are similar, however, the influence of the Si expresses itself in a shift of the removal rates by more than 100 K for layers with Si concentrations larger than $0.2\ \mathrm{Si}/(\mathrm{Si}+\mathrm{C})$. Si is not eroded by heating in air. Rather, the Si is oxidised.

The addition of Si to co-deposited hydrogen–carbon layers influences the concentration of hydrogen in the co-deposited layer [20], the ion-beam-induced detrapping by incident high-energy beams, and the hydrogen and carbon removal rates by heating in air. This shows the importance of the investigation of mixed co-deposited layers. Co-deposited layers created in today's nuclear fusion plasma experiments show higher hydrogen removal rates by heating in air than layers created in laboratory experiments [9–11]. Metal impurities or a different morphology (higher porosity) may be the reason for these differences. From the viewpoint of hydrogen trapping [20,29] and removal, e.g., by oxidation, the impact of silicon is mostly negative by increasing the trapped hydrogen concentration and the necessary removal temperatures. However, it cannot be excluded that other impurities have beneficial effects and act as promoters for the cleaning procedure. More work is necessary on the composition, structure and creation conditions of mixed co-deposited layers in plasma devices.

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