Retention and erosion behavior of oxygen implanted in different Si/C-materials

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Abstract

Different Si/C-materials like plasma deposited thin a-Si/C:H films, bulk Si doped graphites (SiC30) and pure silicon have been irradiated with an oxygen ion beam of the isotope ^{18}O at energies between 1 and 5 keV and at target temperatures up to 1700 K. The release of oxygen and oxygen containing molecules during irradiation and during subsequent thermal desorption has been analyzed by means of quadrupole mass spectrometry in both the residual gas and direct 'line-of-sight' detection. All investigated materials show an enhanced oxygen retention compared to pure graphite and a markedly reduced chemical erosion in the form of CO and CO_2 depending on the silicon content of the sample. Furthermore, the oxygen impact onto such substrates gives rise to a build up of a silicon oxide layer at the near surface. This leads to an additional release of SiO during irradiation at elevated temperatures as well as during subsequent thermal desorption.

Keywords: Chemical erosion; Desorption; Oxygen retention; Low Z wall material; Mass spectrometry

1. Introduction

Carbon materials are used as plasma facing components in most of the existing fusion devices. Along with it goes the problem of surface erosion from exposed components due to high particle and heat fluxes from the plasma. This leads to an increase of the impurity contamination (main impurities are carbon and oxygen, both some %), a dilution of the fuel and a reduction of the lifetime of plasma facing components. Therefore erosion of those first wall materials is one of the main problems in plasma wall interactions. The high erosion behavior of carbon materials is, besides unavoidable physical sputtering of carbon atoms mainly caused by chemical erosion of the material due to the impact of energetic hydrogen or oxygen and the formation of volatile carbon molecules [1]. In contrast to hydrogen impact, the chemical erosion due to oxygen in form of CO and CO_2 reaches an erosion yield of around unity with no pronounced temperature and energy dependencies in the range up to 1800 K and 250 eV–5 keV respectively [2,3].

Therefore one of the main emphasis in developing appropriate materials for fusion application is to reduce the high chemical erosion yields especially due to energetic oxygen. For this reason materials exhibiting a high oxygen gettering capability like boron, beryllium and silicon have been used in different forms as first wall coatings or bulk limiter/divertor tiles [4]. Since the boronization technique was successively developed at TEXTOR [5], boronization, which means the plasma deposition of a thin amorphous hydrogenated carbon/boron layer (a-C/B:H), is nowadays widely used as a standard protective coating for the first wall in fusion devices. Together with other advantages, this conditioning has mainly reduced the oxygen and carbon impurity concentration in the plasma. Investigations of these films due to energetic oxygen impact have shown that this behavior arises from a high oxygen retention capability and a clearly reduced chemical erosion of this material which goes along with the formation of stable boron oxides [3,6]. These boron oxides are not released thermally until temperature rises about 1200 K.

Silicon carbides are expected to have an oxygen gettering capability as high as boron carbides. Since silicon is also known to establish a radiative plasma boundary by line radiation like in the case of radiation cooling with

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neon, which has been lead to improved plasma performance in TEXTOR [7,8], silicon containing graphites are of special interest for their application as first wall material in future fusion devices.

For this reason, first wall conditioning with silicon containing carbon layers (a-Si/C:H) has been done, in 1993, using the 'siliconization' procedure developed and applied for the first time in the TEXTOR tokamak. Compared to boronized wall conditions this has lead to a further improvement of the plasma performance due to reduced low Z impurities (B, C and O), as well as a high radiation level within the edge plasma and improved plasma confinement [9]. The characterization of those films in lab experiments have shown that the chemical erosion yields of a-Si/C:H films by H^+ impact are reduced by up to a factor of 30, that they exhibit a strong oxygen gettering and are almost inert to molecular oxygen [10]. Therefore it should be of special interest to investigate in more detail the chemical erosion behavior of those silicon containing films and other bulk doped silicon carbides due to the impact of energetic oxygen ions, which we deal with in this paper.

2. Experimental

To investigate the chemical erosion and retention behavior of different Si/C-materials due to energetic oxygen the samples were bombarded with an oxygen ion beam and the reaction products during irradiation and thermal desorption were analyzed by means of mass spectrometry. In both systems a mass separated oxygen ion beam of the isotope ^{18}O with a beam current of several μA was used for the irradiation experiments. The beam is focused onto the samples with normal incidence to the target surface at an area of around 2 mm^2 and an ion flux density of $1–3 \cdot 10^{14}$ O^+/cm^2 depending on the beam energy (1.5–3 keV O^+). The reaction products were detected by a quadruple mass spectrometer either in the residual gas or directly without hitting the chamber wall (LOS) at 45° with respect to the incident ion beam. The samples can be ohmically heated up to about 2000 K during irradiation and the temperature is controlled by infrared pyrometers. After implantation the retained oxygen was thermally desorbed with a linear heating ramp of around 5–10 K/s.

More detailed information about the experimental set-up of the ion beam apparatus and detection systems used for both residual gas analysis (RGA) and 'line-of-sight' detection (LOS) have already been given in previous papers [3,11].

Materials investigated were bulk silicon doped carbon SiC30 (Schunk), a composite C/SiC/Si with SiC content of about 62 wt% and 3 wt% pure Si [13], a-Si/C:H films with different C content as deposited as wall coating at the first time onto the plasma facing components in the TEXTOR tokamak [10] and pure silicon substrates.

3. Results and discussion

3.1. Reactions of O^+ on SiC30

3.1.1. T-dependence of the reemission behavior

The main reaction products reemitted during bombardment of SiC30 with energetic oxygen were CO and CO_2 both indicating only a slight temperature dependence. At room temperature (RT) the reemission of these products shows the same transient behavior as in the case of oxygen impact on pure graphite and B/C-materials [6]. At the start of the implantation the incoming oxygen is almost completely retained within the substrate up to a fluence of around $1 \cdot 10^{16}$ O^+/cm^2. By further bombardment the reemission increases continuously and reaches a steady state value after saturation of the sample for fluences above $1 \cdot 10^{16}$ O^+/cm^2. Compared with graphite the CO + CO_2 erosion yield ($Y \approx 0.32$) is reduced by a factor of two.

The release rate of all emitted particles in the LOS-configuration as a function of target temperature during irradiation with 1.5 keV O^+ is shown in Fig. 1. CO and CO_2 exhibit a qualitative similar behavior as from graphite, with a small minimum of the CO yield around 500–600 K and a corresponding maximum of the CO_2 reemission. Above 1000 K the CO_2 yield decreases further with increasing temperature whereas CO remains the main reaction product with an almost constant yield of around 0.35. In the whole temperature range SiO was the only silicon oxide observed although we have operated the QMS up to a mass of 92, corresponding to Si_2O_2. The chemical erosion rate of SiO shows a strong temperature dependence and increases from 0.005 Si/O at RT up to 0.16 Si/O at 1700 K. The relative small release rate of SiO at RT–800 K as well as the fact of its thermal stability within this temperature range give rise to the assumption of a molecule sputtering process at low temperatures as mechanism for the SiO release, like in the case of boron oxide reemission from B/C-materials [3,12]. To support this thesis additional time-of-flight measurements have to be performed to investigate the energy distribution of the SiO molecules. The significant increase of the SiO release above 1000 K is due to an enhanced thermal reemission at these elevated temperatures.

Besides the molecular chemical erosion products, the physical sputtered carbon and silicon atoms have been observed with yields of 0.2 C/O^+ and 0.16 Si/O^+ respectively at RT. Above 1200 K the release of Si atoms increases steeply due to the onset of thermal sublimation from the bulk. In contrast to oxygen bombardment of graphite the implanted oxygen was also released in form of atomic as well as molecular oxygen. However, these reemissions show a small temperature dependence with yields in the range of 0.01–0.03 O/O^+ in the case of atomic and $< 10^{-2}$ O_2/O^+ for molecular oxygen when thermal energies have been assumed.
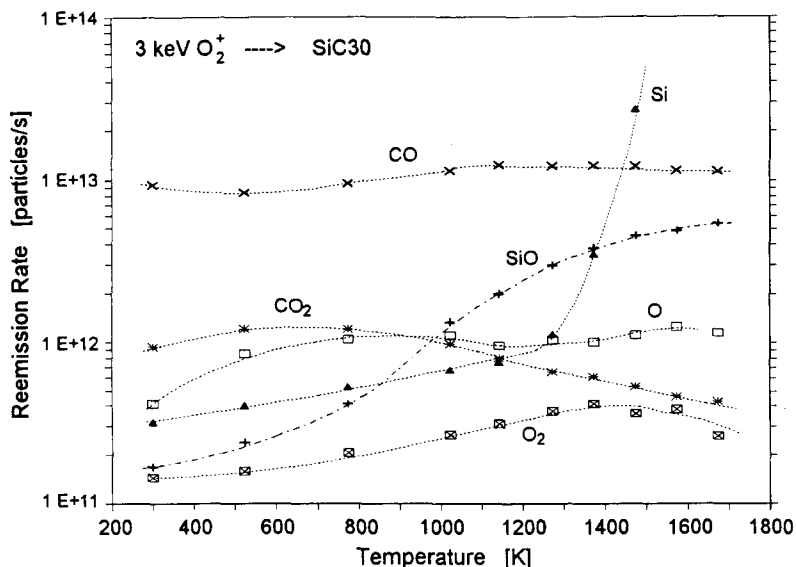
Fig. 1. Reemission spectrum as a function of target temperature during irradiation of a SiC30 sample with 1.5 keV O^+. The implanted oxygen flux was about $3.25 \cdot 10^{13}$ O^+/s.

3.1.2. Oxygen retention and thermal desorption

At the beginning of the irradiation most of the implanted oxygen accumulates within the implantation region of the irradiated area until saturation of the sample is reached. This retained oxygen is then released by a subsequent thermal desorption procedure where the sample is heated up with a linear temperature ramp. Fig. 2 shows a typical thermal desorption spectrum from SiC30 after irradiation with 1.5 keV O^+ at RT up to saturation ($\approx 3 \cdot 10^{18}$ O^+/cm^2) and a ramp rate of 5 K/s. Most of the retained oxygen desorbs in form of SiO with a peak maximum at 1500 K. As a confirmation of the detected SiO signal measured at $M = 46$ ($^{28}Si^{18}O$) which is also identical with $C^{16}O^{18}O$ we have checked the ratio of the silicon isotopes
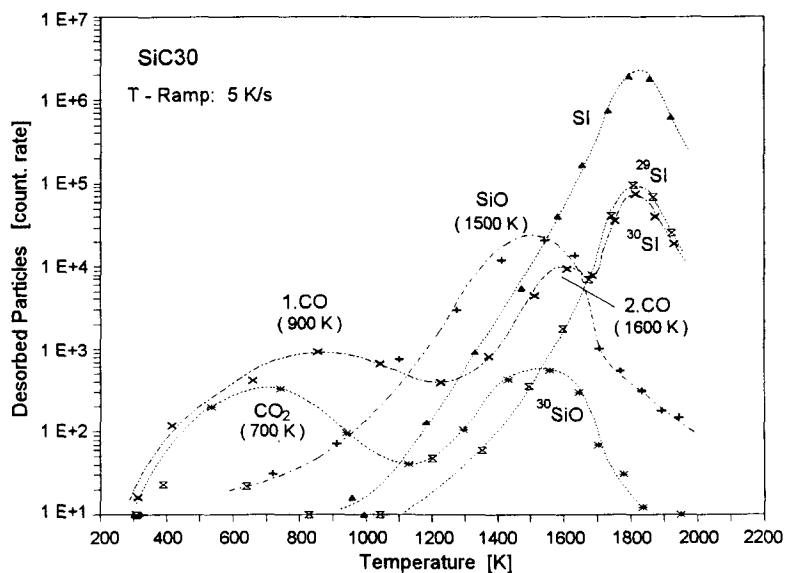

Fig. 2. Thermal desorption spectrum of SiC30 after implantation with 1.5 keV O^+ at RT up to saturation ($\approx 3 \cdot 10^{18}$ O^+/cm^2). For quantitative analysis the counting rate shown in this spectrum have to be weighted with the sensitivity of the QMS.

at $M = 47$ (^{29}SiO) and $M = 48$ (^{30}SiO). Except for SiO, no other silicon oxides have been observed in contrast to the desorption from B/C-materials where different boron oxides were formed up to B_2O_3 [6].

The desorption peaks of CO and CO_2 occur as in the case of graphite with peak temperatures at 900 K and 700 K respectively. In addition to the CO desorption peak at 900 K most of the CO (up to 90%) is released in a second desorption peak at about 1600 K just after the desorption of SiO. For a quantitative analysis this second CO desorption peak has to be cautiously interpreted because it is detected at $M = 30$ where in this temperature range the $C^{18}O$ signal is overlaid by the additional thermal sublimation of the silicon isotope ^{30}Si. This is evident from Fig. 2 where the thermal sublimation of the Si isotopes ^{28}Si (92.2%), ^{29}Si (4.7%) and ^{30}Si (3.1%) are also shown. The $M = 30$ peak around 1850 K is clearly due to Si-sublimation whereas part of the $M = 30$ peak at 1600 K is dominated by the additional CO desorption. The real occurrence of the second CO peak is supported by the fact that this behavior is qualitatively the same as in the case of B/C-materials, where the desorption of the different boron oxides is also accompanied by a second CO peak within this temperature range [3,6].

A quantitative analysis of the desorption spectrum as well as from the reemission measurements yield a total retention of up to $1 \cdot 10^{17}$ O/cm^2. Related to the implantation depth of 1.5 keV O$^+$ into SiC30 (≈ 4.2 nm ± 1.8 nm from TRIM-calculations) this corresponds to a saturation value of about 1.9 O/Si + C. These results are in good agreement with lab experiments on chemical erosion of a-Si/C:H films due to 150 eV oxygen ion impact from a glow discharge where the incoming oxygen was partly released in form of CO or retained in the coating to build a

passivating oxide layer (≈ 5 nm) of SiO_2 at the surface [9,10].

3.2. Reactions on different a-Si / C:H films

3.2.1. CO reemission behavior

The investigated samples were thin amorphous layers of about 100 nm thickness deposited onto EK98 graphite during the 'siliconization' of the TEXTOR tokamak. The C/Si ratio of these layers varies from unity to zero depending on the gas mixture (SiH$_4$, CH$_4$, He) used during the deposition process. With increasing amount of Si the reemission of CO and CO_2 is more and more delayed and decreases to less than 10^{-2} C/O$^+$ in the case of a pure a-Si:H layer at RT. Fig. 3 shows the CO reemission as a function of the implanted oxygen fluence detected in the residual gas during the irradiation of a pure a-Si:H layer from the first TEXTOR-Siliconization with 3 keV O$^+$ at RT. Before each measurement the sample was annealed for 1 min at different temperatures. For annealing temperatures up to 1000 K the CO reemission is strongly delayed and the implanted oxygen is almost completely retained up to a fluence of around $1.25 \cdot 10^{17}$ O$^+$/cm^2. This corresponds to a total oxygen retention in the layer of $\approx 4 \cdot 10^{17}$ O/cm^2 (> 0.9 O/Si). Above this temperature the CO reemission starts already at fluences $> 1 \cdot 10^{16}$ O$^+$/cm^2. Moreover, the reemission rate of CO in the steady state increases from 0.05 CO/O$^+$ at 1100 K up to 0.55 CO/O$^+$ at 2100 K. This behavior is due to diffusion of C-atoms from the graphite substrate into the Si-layer at elevated temperatures. After an annealing procedure at 2100 K the Si-atoms are almost completely sublimed from the layer (Fig. 2) so that the total chemical erosion yield reaches $Y_{chem} \approx 0.7$ (CO + CO$_2$)/O$^+$ like in the case of pure graphite.
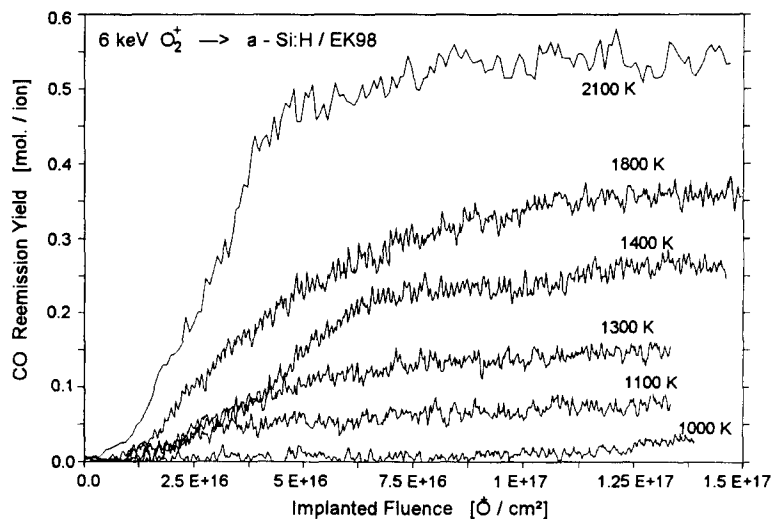

Fig. 3. CO-reemission as a function of the incident oxygen fluence during irradiation with 3 keV O$^+$ at RT. Before each measurement the sample was annealed for about 1 min at different temperatures.

3.2.2. T-dependence of the reaction products

A spectrum of all reaction products during irradiation of an a-Si/C:H layer (Si/C $\approx$ 1:1) with 1.5 keV O^+ at RT up to 1300 K is shown in Fig. 4. The sample was irradiated at all temperatures up to saturation. The main reaction products are again CO and CO_2. Compared with SiC30 the chemical erosion yield due to CO + CO_2 at RT ($\approx$ 0.41 C/O^+) is slightly enhanced. Above 1000 K the CO reemission increases further and the chemical erosion yield reaches $\sim$ 0.7 C/O^+ at 1300 K which is comparable to pure graphite. Silicon oxides are released in form of SiO only. The erosion yield of SiO starts at relatively small values of around $1 \cdot 10^{-2}$ Si/O^+ at RT slightly increasing up to $5 \cdot 10^{-2}$ Si/O^+ at 1000 K. Above this temperature the SiO yield rises more steeply and reaches again 0.17 SiO/O^+ at 1300 K.

In case of a pure a-Si:H layer the reemission behavior is more transient. As long as the layer is not eroded during ion bombardment or due to thermal sublimation at elevated temperatures the chemical erosion yield of CO + CO_2 remains in the range of 10^{-3} at RT. Even the release of SiO yields only some 10^{-3} SiO/O^+.

Physically sputtered carbon atoms from all a-Si/C:H layers exhibits roughly the same yield of around 0.2 C/O^+ independent of the carbon content, whereas the sputtering yield of silicon atoms increases from 0.16 Si/O^+ (C/Si $\approx$ 1) up to 0.34 Si/O^+ (C/Si $\to$ 0) at RT when assuming binding energies of 7.4 eV (C) and 4.7 eV (Si). The release rate of atomic oxygen due to subsequent sputtering of already implanted oxygen ions was determined to some 10^{-2} O/O^+ nearly independent on temperature and Si-content of the layer, whereas the yield of molecular oxygen increases slightly with both temperature

and Si-content from $4 \cdot 10^{-3}$ (Si/C = 1, RT) to $2 \cdot 10^{-2}$ (Si/C = 1, 1300 K) and $8 \cdot 10^{-2}$ O/O^+ (a-Si:H, RT) respectively.

3.2.3. Thermal desorption of the retained oxygen

The thermal desorption behavior of the a-Si/C:H layers is qualitatively similar to that from bulk silicon doped SiC30. The retained oxygen is released in form of SiO, CO and CO_2 only. The desorption of CO and CO_2 appears at the same desorption peaks as from other graphitic materials (CO_2: 700 K, CO: 900 K) and exhibits a second CO-desorption peak around 1550 K. The second peak containing most of the total desorbed CO occurs again after the desorption of SiO which is centered around 1450 K. Depending on the Si/C ratio of the sample, the CO and CO_2 desorption is more or less pronounced. It contains only 10–20% of the retained oxygen (pure a-Si:H) and 40% (Si/C = 1) respectively. The SiO desorption peak contains, for all layers, most of the retained oxygen. Although the desorption peaks at their height and width are all comparable, the peak temperature is shifted slightly with increasing silicon content from 1450 K (a-Si/C:H) to 1250 K (pure a-Si:H).

3.3. Reactions on pure silicon

Since the a-Si/C:H layers were all deposited onto a graphite substrate it was desirable to investigate the influence of the silicon erosion from a pure Si sample. For these experiments we used a tile from a Si-wafer which due to its high conductivity could not be heated up ohmically for thermal desorption. The fluence dependent reaction spectrum from such a Si-sample during irradiation
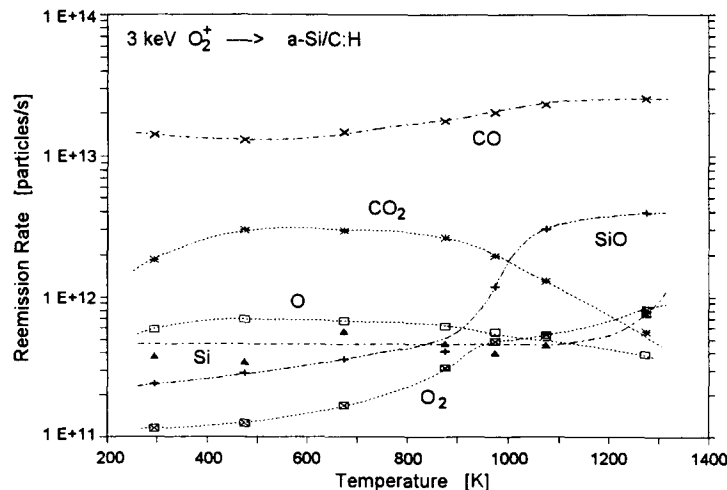

Fig. 4. Reemission spectrum as a function of target temperature during irradiation of an a-Si/C:H layer with 1.5 keV O^+. The oxygen ion flux was about $3.6 \cdot 10^{13}$ O^+/s.
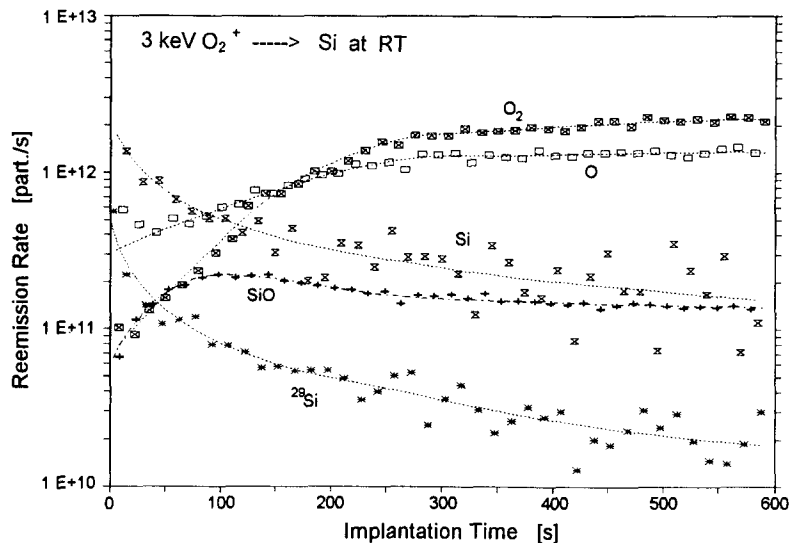
Fig. 5. Reemission spectrum as a function of implantation time during irradiation of a pure Si sample with 1.5 keV O^+ at RT. The oxygen ion flux was about $2.4 \cdot 10^{13}$ O^+/s.

with 1.5 keV O^+ at RT is shown in Fig. 5. All detected species exhibit a transient behavior, presumably due to the formation of a protective SiO_2 layer at the surface. SiO is the only silicon oxide observed to be released during oxygen bombardment. Its erosion yield increases at the beginning up to a maximum of $7 \cdot 10^{-3}$ and then decreases slightly to a steady state value of $5 \cdot 10^{-3}$. The formation of a stable oxide layer is also seen from the continual decrease of the sputtered Si-atoms from 0.6 Si/O^+ down to $< 10^{-2}$. Along with this behavior goes the increase of the oxygen release in form of both atomic and molecular oxygen with a total release rate of ≈ 0.18 O/O^+. The obvious lack in the oxygen balance (up to a factor 4–5) is assumed to be due to the strong gettering of oxygen from the pure silicon and the formation of a stable oxide layer at the surface.

4. Summary and conclusions

Reemission and thermal desorption experiments with different silicon containing graphitic materials and thin layers have shown that these Si/C-materials exhibit an enhanced oxygen retention which is attributed to their high oxygen gettering capacity in comparison to graphite. The total retention increased with increasing Si content of the sample up to $> 4 \cdot 10^{17}$ O/cm^2 (> 0.9 O/Si) in case of an a-Si/H layer from the TEXTOR-Siliconization. The chemical erosion yield of Si/C-materials due to CO- and CO_2-release is reduced by roughly a factor of 2 (SiC: $Y \approx 0.3$) at RT. Silicon films deposited onto graphite show a gradually increasing CO-reemission after annealing above

1100 K. This behavior is probably due to the diffusion of carbon atoms from the substrate into the layer at these elevated temperatures which leads to the formation of SiC and a subsequent release of CO and CO_2. At temperatures above 1300 K the chemical erosion due to $CO + CO_2$ is therefore clearly enhanced and reaches values around 0.7 C/O^+ which is similar to pure graphite.

From all Si/C-samples the reemission of silicon oxides has been observed over the whole temperature range in form of SiO only. The SiO erosion yield exhibits a pronounced temperature dependence. From room temperature ($Y \sim 10^{-3}$ SiO/O^+) it increases slowly up to some 10^{-2} in the range of 1000 K, whereas above this temperature it increases more steeply up to 0.17 SiO/O^+ at $T > 1400$ K. Due to the high thermodynamical stability of the silicon oxide layer formed during irradiation the release of SiO at RT is presumably due to molecule sputtering with over-thermal energies, whereas the increase at elevated temperatures is dominated by a thermal release of SiO.

This is confirmed by thermal desorption in which most of the retained oxygen desorbs in form of SiO at 1500 K. Again no other silicon oxides have been observed. Only 10–40% (depending on the Si-content) desorbs in form of $CO + CO_2$, whereby most of it appears in a second CO-desorption peak at 1600 K just after the desorption of SiO.

Even taking into account the desorbed oxygen, there is still a small lack in the total oxygen balance, which might be attributed to a retention of some oxygen in a highly stable formation up to 1800 K and a possible overthermal release of some species like SiO, CO, and O thus resulting in a slightly enhanced reemission yield, since all those particles were assumed to be released thermally.

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