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Mechanism of chemical sputtering of graphite under high flux deuterium bombardment

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Abstract

Chemical sputtering of graphite materials (isotropic graphite and carbon fiber composite) was studied by irradiation of 5 keV D_3^+ beam with a flux up to 4×10^{21} m^{-2} s^{-1}, which is more than one order magnitude higher than previous low flux beam experiments ($<10^{20}$ m^{-2} s^{-1}). The chemical sputtering yield was obtained from measurements of the released methane signal with a quadrupole mass analyser. It was found that the methane yield at peak temperatures is almost independent of flux from 5×10^{20} to 4×10^{21} m^{-2} s^{-1}. Peak temperatures range between 900 and 1000 K, which is higher than those of the previous low flux experiments (<900 K, $< 10^{20}$ m^{-2} s^{-1}). By comparing our experimental results with calculation results based on Roth's model, the annealing effect of radiation damage to prevent methyl group formation appears to be unimportant. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

Carbon-based materials are commonly used for plasma facing components (PFCs) in large tokamak experiments because of their good thermomechanical properties at elevated temperatures and much lower radiation losses than high-Z metals when entering core plasmas. However, it is well known that graphite materials have unique erosion processes other than physical sputtering, such as chemical sputtering, under hydrogen ion bombardment. Recent studies suggested that the chemical sputtering could play a major role in erosion of carbon-based materials under low edge electron temperature ($T_e < 50$ eV) environments [1]. A lifetime estimation of divertor plates and impact of the erosion on plasma performance depend on the importance of chemical sputtering under these plasma conditions.

Chemical sputtering of carbon-based materials has been studied intensively by using ion beams in the energy range between 10 keV and 10 eV with irradiation fluxes less than 10^{20} m^{-2} s^{-1} [2]. In actual edge plasma conditions, the impinging ion flux onto PFCs exceeds 10^{22} m^{-2} s^{-1}, much larger than that in these ion beam experiments. In order to evaluate erosion yield of chemical sputtering under edge plasma conditions characterized by high ion flux, comprehensive models for chemical erosion applicable for high flux condition must be constructed.

In recent years, understanding of chemical sputtering mechanisms has been greatly advanced by detailed studies on elementary chemical processes in amorphous C/H films [3]. Roth et al. [4,5] made an analytical model based on these results to cover a wide range of ion energy and flux, which seems to give a key to understanding experimental data under high flux conditions. Dependence of the chemical erosion yield of carbon-based materials on ion flux by this model shows some correspondences with experimental data in ASDEX-U and TEXTOR. However, under tokamak edge plasma conditions, neutrals and electrons as well as ions, flow

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into PFCs and it is not clear whether the variation of chemical erosion yield are ascribed to only the ion flux change.

In addition, in high flux regime the behavior of dynamically retained hydrogen in graphite, which is instantaneously released after ion irradiation stops, would be also a matter of concern. The density of this dynamic hydrogen in the graphite materials can be comparable with that of trapped hydrogen in high flux regime and it could play an important role in chemical reaction. It is not obvious, however, that the density of dynamic hydrogen is simply proportional to ion flux under these conditions. To establish a more comprehensive theoretical basis of chemical sputtering in terms of flux dependence, more experimental data by high flux irradiation under controlled experimental conditions are necessary.

In this study, we irradiate pure graphite (isotropic graphite and carbon fiber composite) with high flux beams (5 keV D_3^+, up to 4×10^{21} m^{-2} s^{-1}) to obtain a useful database for the modeling of chemical sputtering. So far, there are no chemical sputtering measurements for this energy under irradiation flux over 10^{20} m^{-2} s^{-1}. We will also make a comparison between our experimental results and calculation results based on Roth's model.

2. Experiments

Fig. 1 shows the schematics of our experimental system. A high flux beam irradiation device for this study has a bucket-type ion source equipped with multi-aperture triode extractor, consisting of positive, negative, and ground electrodes [6]. The multi-aperture spherical electrodes have an effective diameter of 14 cm and a radius of curvature of 50 cm. This beam irradiation device is operated in pulsed mode with a maximum pulse length of 4 s. In the case of deuterium discharge at a gas pressure of 15 m Torr and an extraction voltage of 5 keV, the extracted ion of D_3^+ was dominant. When this ion beam interacts with materials, the 5 keV D_3^+ molecular ions can be considered as three 1.7 keV D atoms. The atomic concentration of this 1.7 keV deuterium species is about 80%. Secondly dominant species is 5 keV D^+ and dominant impurity species is oxygen extracted as D_3O^+ with atomic concentration of about 2%.

Irradiation samples were set at an angle of 45° with respect to the beam axis. Samples were changed in a load lock chamber which was differentially pumped. Graphite samples used in this study were isotropic graphite (IG430U, Toyo Tanso) and carbon fiber composite (CX2002, Toyo Tanso). Methane molecules ($M/e = 20$, CD_4) released from the graphite samples during irradiation were observed by a quadrupole mass analyser installed in a detector chamber. In order to differentiate the chemically sputtered methane signal from the background one, a shutter was set in front of a double entrance slit located between the samples and the detector chamber, as shown in Fig. 2. In the case when the shutter was open, methane signals from the sample surface and background were observed. On the other hand, only background methane was observed with the shutter closed. Therefore, the difference of these methane signals corresponds to chemically sputtered methane from the samples only. The double slit configuration has a large opening between two apertures so that the background gas mainly flows into the detector chamber through this opening and the background gas flow is not affected by the position of the shutter very much. For a detailed calibration, the variation of background signal between the cases of 'shutter open' and 'shutter closed'

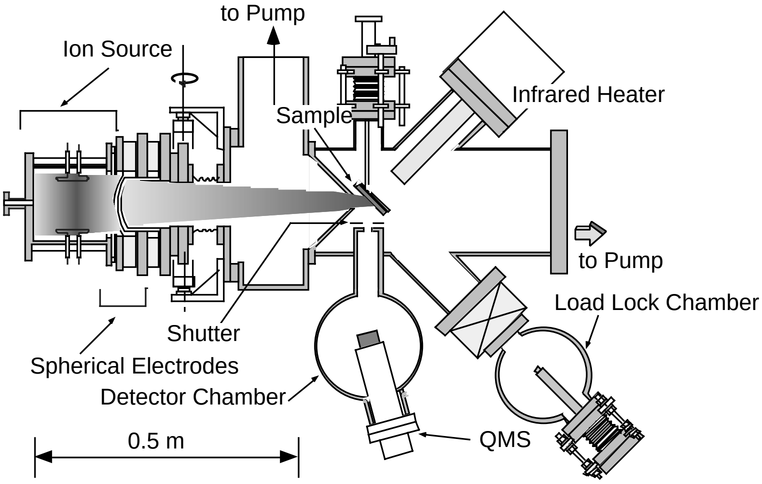

Fig. 1. Schematic of the experimental device. High flux beam generator and sputtered particle measurement system are shown.

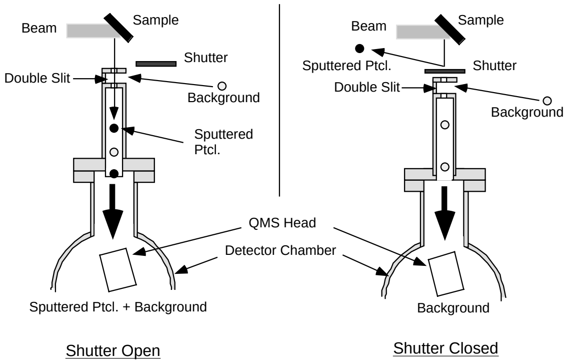

Fig. 2. Method of eliminating the background methane signal from that of sputtered methane directly flowing into detection chamber with QMS installed.

was measured by flowing methane gas only was observed. In this case, the methane signal for 'shutter open' was higher than that for 'shutter closed' by a factor of 1.10. By taking this calibration, the background can be completely cancelled and time evolution of methane release from the samples can be analysed in detail, especially in the decaying phase after beam termination. The time evolution of these signals is shown in Fig. 3.

In this experiment, the signal of $M/e = 20$ (CD_4) was observed by QMS. Since our irradiation beam contains oxygen impurity, not only CD_4 but also D_2O could be included in the signal at $M/e = 20$. Contribution of D_2O to the $M/e = 20$ signal was evaluated by referring to Chen et al. [7]. In this reference, H_2O yield under simultaneous O^+ and H^+ bombardment to graphite was observed experimentally. The H_2O yield, defined as released H_2O flux divided by O influx, is about 0.25 for the flux ratio of oxygen to hydrogen of 0.1 at the temperature of about 800 K. The ratio of D_2O to CD_4 in our experiments was estimated to be only about 5% based on the assumption that the above-mentioned H_2O yield is the same as the D_2O yield in our experiments and that CD_4 is about 0.12 (2 keV and 550°C) [8]. Therefore, the effect of D_2O inclusion in the signal of $M/e = 20$ is thought to be small.

Heating of the samples was done by an infrared heater from the rear side of the samples and surface temperatures were measured by a two-color infrared pyrometer. Response time of the pyrometer is about 20 ms, which is fast enough for our experiments. The calibration of the pyrometer was done by using thermocouples embedded in a graphite sample. As the graphite sample was heated by the infrared heater, it was confirmed that the difference of the temperatures indicated

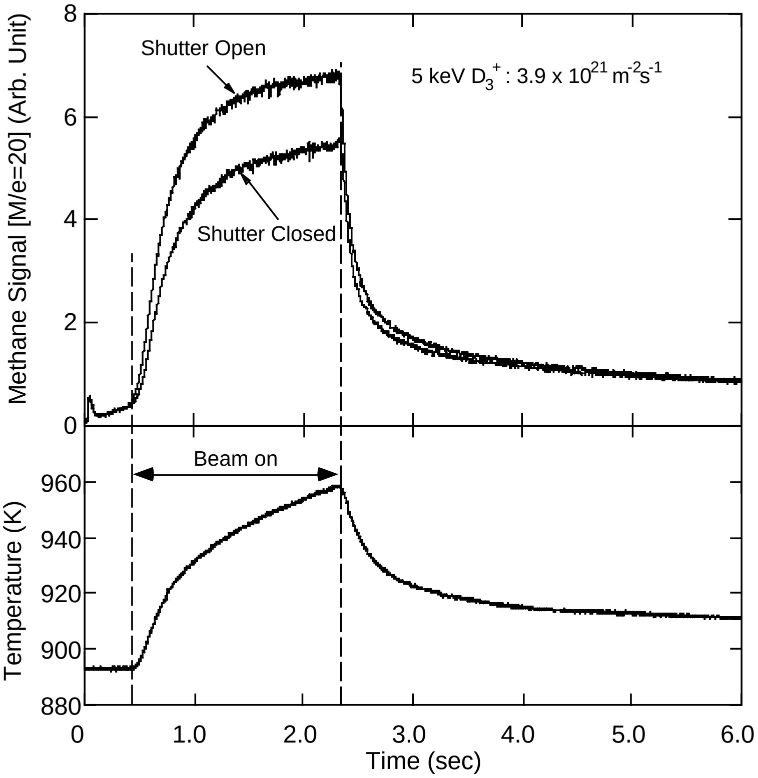

Fig. 3. Time evolution of methane signal with the shutter open and the shutter closed, and evolution of the surface temperature.

by the pyrometer and the thermocouples was less than 5 K in the temperature range between 650 and 1100 K.

Deuterium ion beams with fluxes from 5×10^{20} to 4×10^{21} m^{-2} s^{-1} were used in the experiments. Surface temperature of the samples increased by about 65 K during irradiation in the case of the highest flux (Fig. 3). For all cases, chemically sputtered methane signals increased with time for about 1 s after the initiation of the irradiation until they reached almost saturated values. The data presented in this paper were these saturated values (just before the beam was turned off). The lowest irradiation fluence of deuterium for the flux of 5×10^{20} m^{-2} s^{-1} (the lowest flux in this study) was about 2×10^{21} m^{-2}, which was almost the same as the saturated retention of 1.5 keV D irradiation into graphite at room temperature [9]. Since the retained deuterium decreases over the temperature of about 400 K, the deuterium retention was saturated for all experimental conditions in our study.

3. Experimental results

Fig. 4 shows methane signals from isotropic graphite (IG430U) as a function of temperature with irradiation flux as a parameter. For all irradiation fluxes, the methane signals have a maximum between 900 and 1000 K. In the past, peak temperatures for low flux ($<10^{20}$ m^{-2} s^{-1}) were from 750 to 850 K and our results clearly show higher peak temperatures. For carbon fiber composite (CX2002), similar results were obtained except that a higher methane signal than that of IG430U was observed for low fluence irradiation; however, the methane signal became similar to that of IG430U as the fluence exceeded 10^{24} m^{-2}.

Fig. 5 shows methane yields (methane signal divided by flux) at the peak temperatures as a function of irradiation flux. In this figure, previous low flux results (Davis et al. [10]) are also shown. Our experimental data indicate that no clear flux dependence was observed in the high flux regime for both IG430U and CX2002. This tendency is similar to that of Davis et al. for low flux irradiation (10^{18} to 10^{20} m^{-2} s^{-1}) [10]. Therefore, it is suggested that methane yields have very weak flux dependence for a wide flux range, from 10^{18} to 10^{22} m^{-2} s^{-1}. Although beam energy and species are different between our experiments (1.7 keV D) and those of Davis et al. (1 keV H), it could be considered that the effect of these differences on the flux dependence of methane yields are not significant [1] and it makes sense to compare our results with those of Davis et al.

From the viewpoint of the temperature at which the peak methane yield occurs, our data points are in a different regime compared with those of the low flux data, see Fig. 6. It was found that peak temperatures have a tendency to increase with flux over the wide flux range including our data and the previous low flux data [4,10–12]. Roth [4] claimed that peak temperatures of all of the chemical sputtering data did not exceed 900 K. Therefore, our data with the peak temperatures over 900 K are unique in this respect and can provide important information for the construction of a comprehensive model of chemical sputtering. Solid and broken lines in Fig. 6 denote calculations based on Roth's model with different assumptions on methyl group formation in graphite. The details will be discussed in the next section.

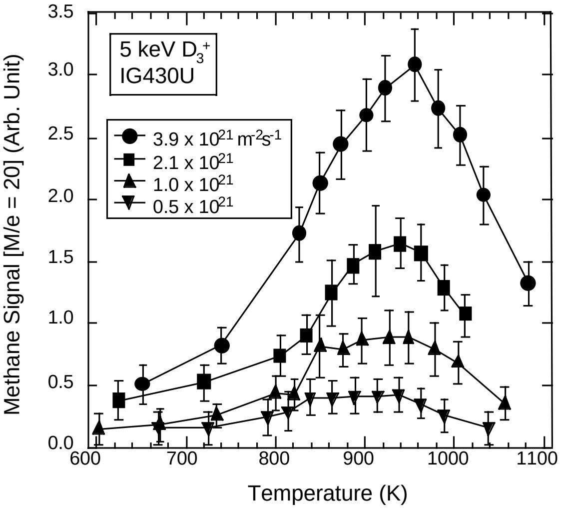

Fig. 4. Temperature dependence of methane signal ($M/e = 20$) for isotropic graphite (IG430U) with irradiation fluxes as a parameter.

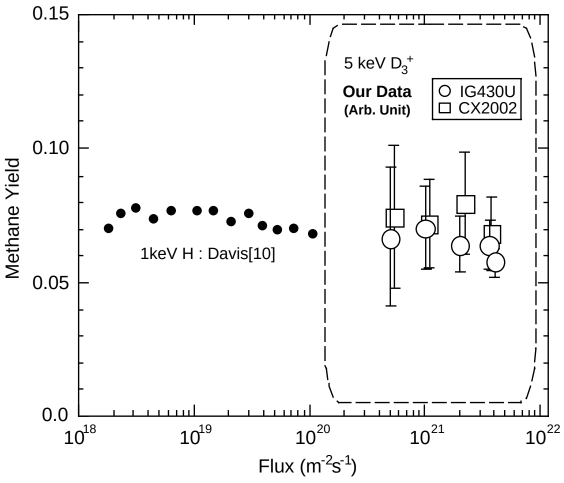

Fig. 5. Flux dependence of methane yield for isotropic graphite (IG430U) and carbon fiber composite (CX2002). The previous data by Davis et al. is also shown. The methane yield of our data is in arbitrary units.

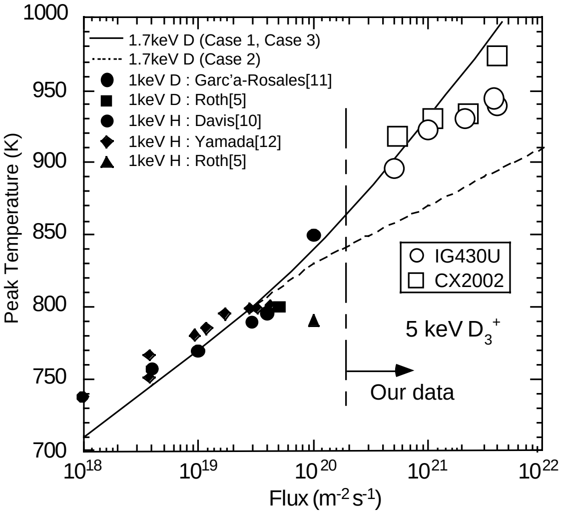

Fig. 6. Peak temperatures as a function of flux for our data and the previous low flux beam irradiation data.

The reason why the peak temperatures increase with flux is considered as follows. The chemical reaction process for chemical sputtering can be divided into two reaction chains: one is hydrogenation (forming methyl group); the other is erosion (releasing methyl group) [3]. The activation energy for hydrogenation process is very low and hydrogenation takes place even at room temperature. However, at higher temperatures, more than 600 K, hydrogen atoms combined with carbon atoms in radical states (denoted as sp^x [4,5,13]) are thermally released to prevents methyl group formation (density of methyl groups decreases with temperature). On the other hand, the release of methyl groups takes place thermally and its reaction rate increases rapidly with temperature. Therefore, the methane yield has a maximum at a certain temperature. By increasing the flux, the density of methyl groups is increased in the high temperature region because the active hydrogen density contained in graphite increased. Consequently, the peak temperature shifts upward with flux.

4. Comparison with model calculation

There are several important points for modeling of chemical sputtering:

1. considering the appropriate chemical reaction;
2. considering the effects of ion irradiation (defect formation, recoil of hydrogen, and so on);
3. appropriate evaluation of active (free) hydrogen density in graphite.

In the 1990s, detailed studies on bonding of hydrogen and carbon in amorphous C/H films was intensively carried out. These data provided a reliable picture of chemical reaction in the C–H system [3]. By taking this chemical reaction into consideration, new chemical sputtering models were proposed [4,5,13]. In this section, we make comparisons between one of the typical models made by Roth [5] and our results. In his model, the sputtering yield Y_{tot} is expressed as

$$Y_{\text{tot}} = Y_{\text{phys}} + Y_{\text{therm}}\left(1 + DY_{\text{phys}}\right) + Y_{\text{surf}}, \tag{1}$$

where the first term on the right hand side, Y_{phys}, denotes physical sputtering yield and the second and the third terms relate to chemical sputtering. The third term relates to surface sputtering, which occurs in the energy range less than 100 eV and can be neglected in our experimental condition. The second term contains a thermal chemical erosion yield Y_{therm} and a parameter D depending on hydrogen isotopes. Thermal erosion yield Y_{therm} is expressed as

$$Y_{\text{therm}} = C^{\text{sp}^3}\left[0.033\exp\left(\frac{-E_{\text{therm}}}{kT}\right)\right] \Big/ \left[2\times 10^{-32}\Phi + \exp\left(\frac{-E_{\text{therm}}}{kT}\right)\right] \tag{2}$$

with methyl group density C^{sp^3} as

$$C^{\text{sp}^3} = C\left[2\times 10^{-32}\Phi + \exp\left(-\frac{E_{\text{therm}}}{kT}\right)\right] \Big/ \left\{2\times 10^{-32}\Phi + \left[1 + \frac{2\times 10^{29}}{\Phi}\exp\left(-\frac{E_{\text{rel}}}{kT}\right)\right]\exp\left(-\frac{E_{\text{therm}}}{kT}\right)\right\}. \tag{3}$$

In Eq. (3), C is a correction term, which modifies C^{sp^3} effective only under high flux condition.

The choice of C is a determining factor for the flux dependence of chemical erosion yield especially in high flux region. Roth proposed two expressions for the term C such as

$$C = 1 \Big/ \left[1 + 3\times 10^{7}\exp\left(-\frac{1.4}{kT}\right)\right] \tag{4}$$

and

$$C = \frac{1}{1 + 3\times 10^{-23}\Phi}. \tag{5}$$

The annealing effect of radiation damage was considered in Eq. (4), while the effect of hydrogenation time was considered in Eq. (5).

By applying these formula to our experimental conditions (1.7 keV D), the temperature dependence of methane yield under three different assumptions with irradiation flux as a parameter is shown in Fig. 7. The assumptions are $C = 1$ for Case 1, Eq. (4) for Case 2, and Eq. (5) for Case 3. For Case 1, in which only thermal chemical erosion is considered, the peak temperature continues to shift upward from a flux of 10^{19} to

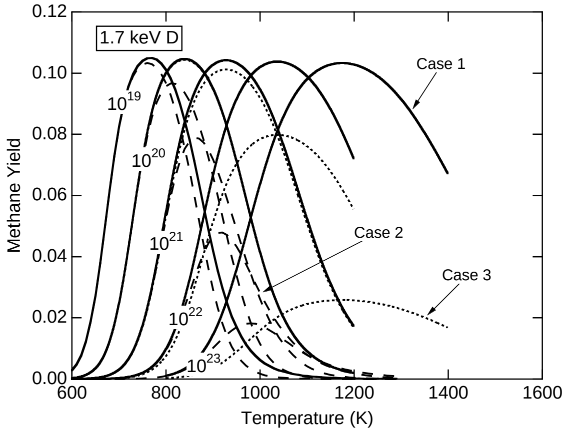

Fig. 7. Calculation results of methane yield based on Roth's model. Case 1, 2, and 3 correspond to the cases with $C = 1, C$ in Eq. (4), and C in Eq. (5), respectively.

10^{23} m^{-2} s^{-1} and the peak methane yield does not change significantly with the flux. For Case 2, the peak temperature also shifts to high temperature, but the rate of increase is lower than that of Case 1. These trends are also shown in Fig. 6. From Fig. 6, the annealing effects (expressed by Eq. (4), Case 2) reveal themselves over a flux of about 10^{19} m^{-2} s^{-1}, which corresponds to a temperature of about 800 K. In this flux range, the peak yield for Case 2 decreases rapidly with flux, as shown in Fig. 7. For Case 3, the peak yield decreases rapidly over a flux of 10^{20} m^{-2} s^{-1}, though the peak temperature is the same as that of thermal chemical sputtering only (Case 1).

By comparing our experimental data with the above-mentioned calculation results, it was found that the peak temperature of our experimental data has a good correspondence with that of Case 1 and 3 (solid line), see Fig. 6. In these cases, the peak temperatures are the same as those of thermal chemical erosion yield Y_{therm} and it is inferred that the annealing effect (Eq. (4)) is unimportant in our experimental conditions. In addition, from the viewpoint of flux dependence of methane yield at peak temperatures, experimental yields are very weak regardless of flux range shown in Fig. 5, which also supports the above-mentioned inference. To refer to the validity of the assumption in Case 3 (hydrogenation effect, Eq. (5)), the yield data over 10^{22} m^{-2} s^{-1} would be needed since apparent decrease of peak yield shows up over the flux of 10^{22} m^{-2} s^{-1}. It could be difficult to compare our data with the calculation results of Case 3 due to limited flux range and errors of our experiments. So far, the reason why the annealing effects do not reveal themselves in our experimental conditions is unclear. One of the conjectures for this is that high density active deuterium in graphite prevents graphitization to some degree. However, more study is needed to investigate what really happens in graphite under high flux conditions.

5. Transient release of methane

In hydrogen beam irradiation experiments by Chiu et al. [14] and Haasz et al. [15], transient methane emission 'spikes' at the termination of irradiation were observed. According to these papers, this effect was attributed to methane breakup by incident beam ions. In their experiments, the maximum flux was in the 10^{19} m^{-2} s^{-1} range, which is two orders of magnitude lower than that of our beam. Therefore, in order to examine whether flux-dependent phenomenon is observed or not, the transient behavior of methane release just after beam termination was also investigated.

The results are shown in Fig. 8, in which time evolution of methane release is illustrated with irradiation flux as a parameter. It was found that the transient spikes observed by Chiu et al. [14] and Haasz et al. [15] were not observed in our experiments. The reason could be ascribed to difference of samples and energy range between our experiments and theirs. They irradiated pyrolytic graphite, while our samples were isotropic graphite and carbon fiber composite. They claimed that methane molecule diffusion was slower in ion-created microchannels than in inherent channels. Once the ion-created microchannels were formed, the transient spikes appeared. In our case, many micropores (inherent channels) were already present in as-received samples and the effects of ion-created microchannels might be small. In addition, they showed the existence of an energy threshold over which the transient spikes occurred. This threshold energy was more than 2 keV in their

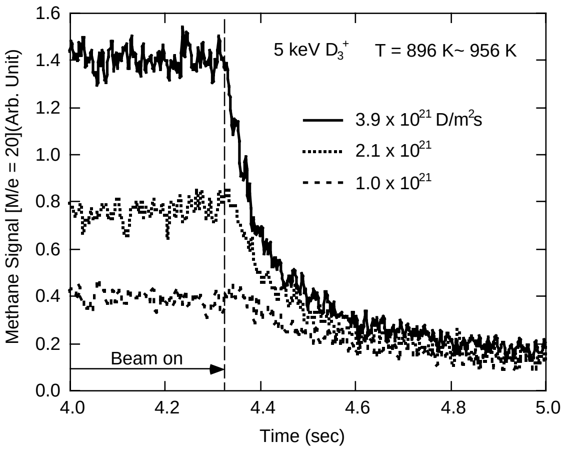

Fig. 8. Evolution of methane signals for different irradiation flux in the temperature from 896 to 956 K at the beam termination.

experiments. Although this threshold was dependent on irradiation flux, our beam energy could be too low to cause the transient (1.7 keV/ion).

From Fig. 8, it was found that the decay behaviors are clearly flux dependent. As the irradiation flux becomes higher, the methane signal decays faster after beam termination. Eventually, the methane signals for different fluxes approached almost the same value after a time of 4.6 s. This phenomenon could relate to the behavior of dynamic retained methane molecules in graphite. In the case of the highest flux (3.9×10^{21} m^{-2} s^{-1}), large amounts of methane molecules existed within the ion range and were desorbed during this fast decay period. From decay data in Fig. 8, the diffusion time of these free methane molecules would be less than 0.3 s. It could be considered that dynamic retained deuterium in graphite was also released during this transient according to Emmoth et al. [16], in which it was described that dynamic retained deuterium was released within 60 ms (ion energy 120–140 eV, temperature 100–500°C). After this transient, the methane signal decayed with a decay time on the order of more than 1 s, which was almost independent of flux. This decay time would be determined by thermal chemical reaction including hydrogenation and erosion of methyl group.

6. Conclusion

In order to study chemical sputtering mechanism of graphite under high flux conditions, two kinds of graphite samples were irradiated by 5 keV D_3^+ ion beams with a flux of 5×10^{20} to 4×10^{21} m^{-2} s^{-1} and the released methane (CD_4) was observed. Methane yields (methane signal per flux) of isotropic graphite (IG430U) and carbon fiber composite (CX2002) at peak temperatures are almost independent of the irradiation flux, similar to observations for low flux beam experiments ($<10^{20}$ m^{-2} s^{-1}). Peak temperatures of chemical sputtering increase with flux and range between 900 and 1000 K, which are higher than those of the low flux experiments. By comparing our data with calculation results based on Roth's model, it was found that the annealing effect to prevent methyl group formation could be unimportant in our high flux range (5×10^{20} to 4×10^{21} m^{-2} s^{-1}). Rapid decrease of methane release just after beam stopped was observed over the flux of about 1×10^{21} m^{-2} s^{-1}.

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