



Dramatic reduction of chemical sputtering of graphite under intercalation of lithium

H. Yagi, H. Toyoda *, H. Sugai

Department of Electrical Engineering, Nagoya University, Furo-cho, Chiksa-ku, Nagoya 464-8603, Japan

Abstract

In previous studies, in situ deposition of a lithium thin layer onto graphite was found to considerably suppress *physical sputtering* of graphite, owing to rapid diffusion of Li into graphite bulk (so-called intercalation). This paper reports that the Li intercalation dramatically reduces graphite *chemical sputtering* as well, once the Li-deposited surface is cleaned by hydrogen plasma. This is evidenced in a small-scale plasma experiment on the Li-deposited graphite in hydrogen glow, comparing with an ultra-high-vacuum beam experiment. In the latter experiment, energy-controlled H_2^+ beam is irradiated on a Li-deposited graphite sample where methane yield is measured together with in situ surface analysis of graphite by X-ray photoelectron spectroscopy. Both the plasma experiment and the beam experiment showed similar temporal variations of methane yield after the hydrogen exposure of the Li-deposited graphite. Namely, the methane yield gradually decreases down to a negligible level compared with the pure graphite case. The XPS analysis of surface atoms (O, C, Li) suggests that the hydrogen plasma exposure gives rise to removal of Li-containing impurities on the graphite surface. As a consequence, the hydrogen glow conditioning results in an almost complete suppression of chemical erosion of graphite below 500 K.

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PACS: 52.40.Hf

Keywords: Lithium coating; Lithium; Graphite; Chemical sputtering; Carbon impurity

1. Introduction

To date, graphite is the main material used for protection of high flux of heat and particles due to its favorable thermomechanical properties. However, carbon has the drawback, of high chemical reactivity with hydrogen, which induces serious erosion of graphite and carbon impurities in high flux fusion devices. Namely, *chemical sputtering* of graphite is presently one of major carbon impurity sources in high flux divertor machines [1]. Thus, suppression of the graphite chemical sputtering has been a great challenge from the material life and impurity control point of view.

On the other hand, graphite wall conditioning by in situ lithium deposition has been observed to induce significant suppression of carbon impurities in TFTR [2]: In this limiter machine, the *physical sputtering* of graphite has been believed to be the main impurity source. Previous laboratory experiments [3] demonstrated that the Li conditioning gives an order of magnitude less physical sputtering of graphite. Subsequent measurements [4] of Li dynamics by Rutherford backscattering spectrometry clearly revealed a rapid diffusion of Li into graphite bulk, so-called *graphite intercalation*.

Preliminary experiments [5] on the chemical sputtering of graphite have shown only 25% reduction of the sputtering yield by Li deposition. In this paper, we point out that such small Li effects are caused by surface impurities formed by Li deposition. In order to obtain a full effect of Li intercalation, one should make pre-conditioning of Li-deposited surface, which in turn

* Corresponding author. Tel.: +81-52 789 4698; fax: +81-52 789 3152.

E-mail address: toyota@nuee.nagoya-u.ac.jp (H. Toyoda).

suppresses chemical erosion of graphite almost completely.

2. Plasma experiments

2.1. Experimental

The plasma experiment was carried out in a stainless steel cylindrical vessel (30 cm in diameter and 60 cm in length) used in the previous experiment [5]. The vessel was slightly modified in order to introduce a large diameter (24 cm in diameter) graphite sample at the vessel top through a load-lock chamber. Three kinds of graphite materials were tested; flexible graphite sheet of 0.38 mm in thickness (Toyo Tanso Co., perma-fiol PF38-UHPL), isotropic graphite (IG) of 1 mm in thickness (Toyo-Tanso Co., IG-110), carbon fiber-reinforced carbon composite (CFC) of 8 mm in thickness (Toyo-Tanso Co., CX-2002U). The graphite sample is cleaned by a hydrogen DC glow discharge (~ 200 V, 0.3 A, 2.7 Pa) at ~ 300 °C for ~ 60 min, and after cooling down to room temperature, lithium in an oven 25 cm below the sample is evaporated at $\sim 3 \times 10^{-4}$ Pa. The amount of Li deposited on the sample is monitored by a quartz microbalance. In this paper, the Li amount is presented in terms of “equivalent lithium thickness”, since a clear Li layer is not observed on the graphite surface because of the intercalation. After Li deposition, the DC glow discharge is ignited in H_2 at 2.7 Pa between an anode and the grounded vessel (cathode). The graphite sample is also grounded, so that it is bombarded by hydrogen ions (current density ~ 0.4 A/m²) at the incident energy of ~ 200 eV. The methane (CH_4) yield from the sample is measured by a quadrupole mass analyzer (QMA), using the mass peak at $M/e = 15$ (CH_3^+).

2.2. Temporal variation of methane yield from graphite surface

The hydrogen DC glow discharge is turned on at 2.7 Pa at the time $t = 0$ immediately after the Li deposition, and the methane yield from the graphite sample is monitored by the QMA. Fig. 1(a) shows examples of the measured time dependence of CH_4 yield from the CFC sample at room temperature. For reference, the yield without Li deposition (pure graphite) is indicated by the dashed line in the figure, while the top horizontal scale indicates the time-integrated ion incident flux, i.e., the hydrogen ion fluence. Methane is desorbed from not only the graphite sample but also the vessel wall which is covered with thin carbon layers due to redeposition effect during the discharge. In order to eliminate such background signal in both Li-free and Li-deposited cases, we subtracted, from the total signal intensity, the background signal intensity ($\sim 1 \times 10^{17}$ molecules/m² s), which was measured in the hydrogen discharge after

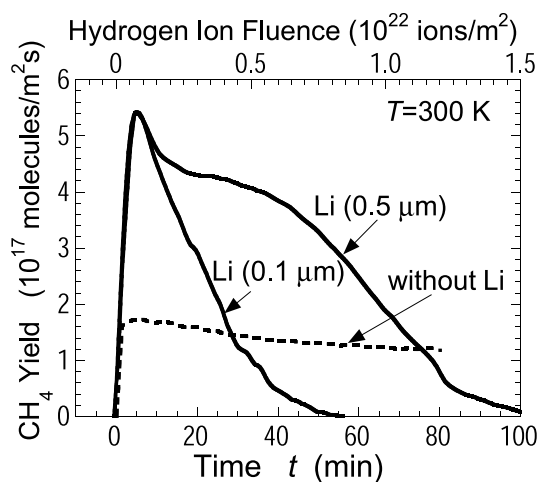


Fig. 1. Time evolution of CH_4 yield from CFC at 300 K after hydrogen glow ignition.

withdrawing the graphite sample to the load-lock chamber.

The existing data of chemical erosion yield of pure graphite for 100–600 eV H^+ incidence around room temperature scatter from 10^{-3} to 10^{-1} C-atoms/H-ion. The CH_4 yield without Li deposition in Fig. 1(a) is $\sim 1.5 \times 10^{17}$ molecules/m² s, which allows us to estimate the order of erosion yield to be $\sim 2 \times 10^{-2}$ C-atoms/H-ion, assuming the dominant ion species to be H_3^+ and neglecting thermal hydrogen atoms.

Although the CH_4 yield from the Li-free graphite is almost constant in time, the Li-deposited CFC shows the strong time dependence as seen in Fig. 1: The initial CH_4 yield exceeds the Li-free level, however it gradually decreases and finally vanishes in the back ground level after 60 and 100 min for 0.1 and 0.5 μm thick Li deposition, respectively. Almost the same result was obtained for IG and graphite sheet (PF-UHPL). The beam experiment described later suggests that such temporal decrease is related to the surface cleaning by the hydrogen glow. After sufficient cleaning, the methane yield is almost completely suppressed.

Focusing on the CH_4 yield from CFC in steady state, the dependence on the graphite temperature T is plotted in Fig. 2 where the CH_4 yield after the hydrogen glow conditioning is normalized by the value for the pure CFC without Li deposition. The chemical erosion is completely suppressed at $T = 300$ K even for a small Li deposition of 0.1 μm in thickness. With increasing the temperature, only 10% of CH_4 yield is observed for $T < 450$ K and at $T > 500$ K, the reduction rate decreases to $\sim 50\%$ for the 0.1 μm thick Li case. In high temperature range, there still remains a possibility to enhance the Li effect by increasing the Li amount, as indicated the point in Fig. 2 at $T = 550$ K for 1 μm thick deposition.

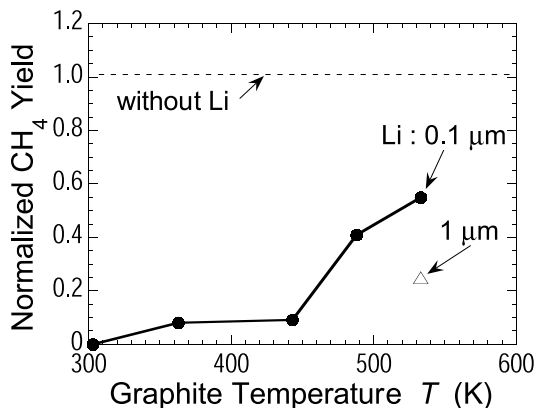


Fig. 2. Temperature dependence of normalized CH₄ yield after conditioning of Li-deposited CFC.

3. Beam experiments

3.1. Experimental

The plasma experiments described above suggested an important role of hydrogen glow conditioning after Li deposition. In order to elucidate the conditioning mechanism in a well-defined condition, a beam experiment is carried out using an ultra-high vacuum ($\sim 2.5 \times 10^{-7}$ Pa) apparatus shown in Fig. 3. A mass-selected energy-controlled ion beam of H₂⁺ (50–400 eV, <80 nA) is irradiated on a 2×2 cm² graphite sample at 3 °C (due to liquid N₂ cooling baffle) with an incident angle of the surface normal. The H₂⁺ fluence (Φ) given by the beam current density times the irradiation time is 10^{21} ions/m² at maximum. During the beam irradiation, methane desorbed from the graphite is introduced to an

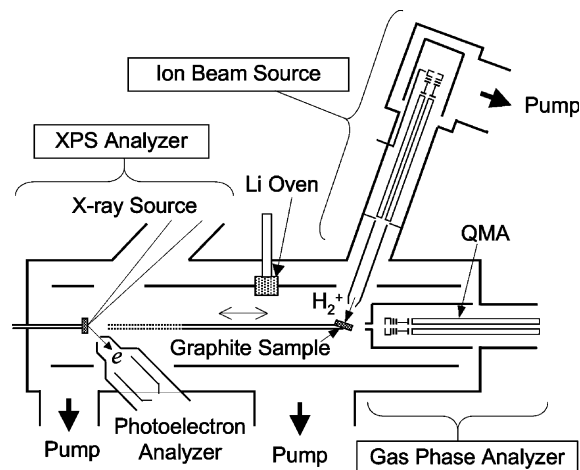


Fig. 3. Schematic of the apparatus for beam experiment, consisting of ion beam source, gas phase analyzer (QMA) and surface analyzer (XPS).

orifice of QMA, ~ 2 cm apart from the sample. The QMA allows us to monitor the temporal variation of chemical sputtering by the signal intensity at $M/e = 15$ (CH₃⁺).

Highly-oriented pyrolytic graphite (HOPG) was selected as the most suitable material owing to the well-defined clean surface. Lithium is deposited in vacuum onto the graphite set on an axially movable sample stage. Then the Li-deposited sample is transferred to the position where the H₂⁺ ion beam is continuously irradiated. The remarkable feature of the present experiment is that in situ surface analysis by X-ray photoelectron spectroscopy (XPS) can be made by transferring the sample in vacuum at desired time.

3.2. H₂⁺ beam irradiation to HOPG

Firstly, we checked the time scale of Li intercalation (the time for Li to diffuse into graphite bulk), using the XPS which gives information on atomic composition of a surface layer of ~ 2 nm in depth. In case of $0.5 \mu\text{m}$ thick Li deposition, the surface Li composition was >80 at.% at 1 min after deposition. At ~ 5 min, however it significantly decreased and at ~ 10 min it reaches the stationary value of ~ 20 at.% which corresponds to Li₂O formation from the measured atomic ratio of Li/O ~ 2 . Thus, the intercalation time scale is ~ 5 min for $0.5 \mu\text{m}$ in thickness, which is consistent with the previous RBS data [4] of ~ 20 min for $2 \mu\text{m}$ in thickness. Similar measurements for the IG sample showed two times faster intercalation in comparison with the HOPG. Accordingly, one may consider that, in the plasma experiments, most of deposited Li atoms have already diffused into the graphite bulk, leaving thin Li₂O layers on the surface, before the hydrogen glow discharge.

Secondly, the H₂⁺ ion beam is continuously irradiated to the HOPG sample, and the CH₄ yield was monitored as a function of time (or H₂⁺ ion fluence). Fig. 4(a) shows the results for $0.5 \mu\text{m}$ thick Li deposition, for different beam energies, where the vertical scale is normalized by the CH₄ yield from the Li-free pure HOPG. The ion beam current at 50 eV was so small that the data at the high fluence ($\Phi > 10^{20}$ ion/m²) were not available. It can be seen in the figure that, irrespective of the beam energy, the maximum CH₄ yield appears at $\Phi \sim 10^{20}$ ion/m² with almost same yield as the pure graphite case.

Fig. 4(b) shows the surface atom compositions measured by the XPS before the beam incidence ($\Phi = 0$), after 50 eV injection ($\Phi \sim 1.5 \times 10^{20}$ ion/m²), 300 eV ($\sim 6 \times 10^{20}$ ion/m²), and 400 eV ($\sim 9.5 \times 10^{20}$ ion/m²). It should be noted before H₂⁺ incidence (~ 10 min after Li deposition) that the Li/C atomic ratio is ~ 2 , suggesting Li₂O formation. Namely, in spite of ultra-high vacuum, Li deposition gives rise to a thin impurity layer composed of Li, O and C atoms. When the hydrogen beam is continuously injected to the surface, O and C atoms are removed from the surface as H₂O and CH₄, respectively,

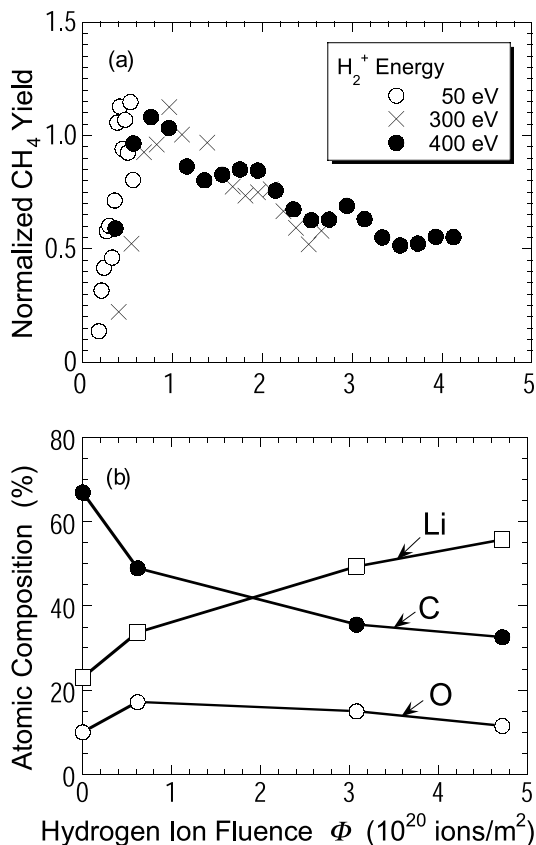


Fig. 4. (a) CH₄ yield for different ion energies and (b) surface atom composition as a function.

and hence the Li percentage gradually increases as seen in Fig. 4(b). As the surface is cleaned with increasing the hydrogen fluence, the CH₄ yield is gradually suppressed as seen in the figure. At a limit of high fluence, one may expect a complete suppression of CH₄ yield as observed in the plasma experiments where the fluence is at least twenty times higher than in the beam experiments.

4. Discussion

Since lithium atom strongly reacts with water vapor and most of the molecules get adsorbed on the graphite surface, Li-containing impurity layers will be formed during the Li deposition although most of Li atoms rapidly diffuse from surface to bulk of graphite due to intercalation effect. The thickness of impurity layer will depend on the background pressure, the Li deposition time, the graphite temperature and so on. In Fig. 1, for example, the 0.5 μm thick Li deposition gives higher CH₄ yield and longer cleaning time than the 0.1 μm thick case, probably due to thicker impurity layer. The cleaning time in actual fusion devices having the hy-

drogen ion flux of $\sim 10^{24}$ ions/m² s will be as short as ~ 50 ms for the same impurity layer thickness as in the present plasma experiments.

The CH₄ yield below 450 K is almost completely suppressed after sufficient hydrogen glow conditioning. Such strong suppression of chemical erosion has been reported in case of boron doped graphite, however it is limited to the graphite temperature higher than 650 K [6] and below this temperature the suppression effect is significantly lost. On the other hand, combination of CFC with B₄C enables us to reduce the sputtering yield by 60% at the temperature from 400 to 1000 K [7]. Further studies of Li effects are needed for temperatures higher than 600 K.

The hydrogen glow conditioning removes oxygen impurities from the graphite surface, which is in turn covered with intercalated Li atoms diffusing toward the surface. In addition, the hydrogen glow inserts H atoms in a shallow graphite layer, so that chemical interaction may take place between the H atom and the intercalated Li atom. Although the mechanism of Li-induced suppression of chemical erosion is not understood yet, possible reasons will be the surface coverage with intercalated Li atoms, and the simultaneous presence of Li and H atoms in the graphite which may prevent CH₄ formation inside the graphite.

5. Conclusion

The results obtained in the laboratory plasma experiments and the beam experiments suggest that the chemical sputtering of graphite can be strongly suppressed by a small amount of Li deposition once the hydrogen glow conditioning is done after Li deposition. As a consequence, the chemical erosion is reduced by a factor of 9 or more at the temperature below 450 K for 0.1 μm thick Li deposition, and by a factor of ~ 4 at 550 K for 1 μm thick Li deposition. In order to understand the suppression mechanism, further investigations are needed on the temperature dependence above 600 K and a dependence on an amount of Li deposition.

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