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Static and dynamic erosion behavior of TiC coated graphite in high heat flux plasma

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Abstract

A high heat flux helium plasma has been used to irradiate TiC-coated graphite samples with a high substrate temperature up to 1800°C. A new technique of pulse biasing on the target with in situ optical spectroscopy gives dynamic erosion characteristics. The emission intensity of TiI spectral line corresponding to sputtered particle flux was observed to decrease as the temperature increases up to 1300°C. This behavior is explained in terms of self-sustaining coverage of the TiC surface with segregated carbon. Over 1300°C, the emission intensity increases with temperature. Pulse biasing gives also remarkable time evolution of TiI line emission intensity, which is strongly temperature-dependent. It is typically characterized by two time scales. These are discussed using the analysis of mass balance equations for carbon atoms. In addition, an initial overshoot of Ti erosion observed at very high temperature is modelled by a stoichiometric change of the TiC layer. © 1998 Elsevier Science B.V. All rights reserved.

1. Introduction

Carbon materials are extensively used in magnetically confined fusion devices. Their use has provided significant improvements in fusion plasma performance. Carbon materials, however, have several drawbacks. These are: enhanced erosion due to chemical sputtering, radiation enhanced sublimation, and high retention of hydrogen causing loss of control over the plasma parameter. Recently, composite carbon materials have shown good performance [1] because of reduction of oxygen impurities in the plasma. However, the reduction of carbon erosion is not sufficient [2]. Thus, it is of crucial importance for the design of future fusion devices to consider the concept of suppression of wall material erosion.

In laboratory experiments, refractory metal carbides, such as TiC and WC, have shown desirable properties concerning high-temperature sputtering. Suppression of radiation enhanced sublimation, and suppression of Ti or W sputtering by self-sustaining coverage of the TiC or WC surface with segregated carbon atoms supplied from the graphite substrate can be realized, although the total erosion of carbon due to physical process might not be reduced. This behavior has been shown under relatively low particle flux conditions by using ion beams [3,4].

When a high Z metal and graphite are used for the divertor target plate, the baffle plate, and the first wall at the same time in a device, the redeposition of each sputtered material modifies the surface layers. For long-term operation with sufficiently high surface temperatures, the carbon surface may be modified into a metal carbide. Therefore, it is of essential importance to investigate the sputtering behavior of refractory metal–carbon composite materials by bombardment with high particle plasma flux sources at high material temperatures.

In this paper, we report on the dynamic characteristics of Ti sputtering yield form TiC layer deposited on graphite bombarded with a low-energy helium plasma at a high particle flux of $\leqslant 10^{22}$ m^{-2} s^{-1} in the wide temperature range from 700°C up to around 1800°C.

2. Experimental device

The TiC overlayer on Poco-graphite was prepared by chemical vapor deposition. The dimension of a graphite

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substrate is $60 \times 6 \times 1$ mm^3 in size, and the thickness of the TiC layer is about 300 nm. The chemical composition of the TiC layer was analyzed by both Electron Probe Micro Analysis (EPMA) and Rutherford Back-Scattering (RBS), which give 1.0 and 0.94, respectively, for the compositional ratio of C to Ti.

The substrate was mounted on a graphite holder in a linear plasma device NAGDIS-I (Nagoya University Divertor Simulator) [5] for in situ optical measurements, as shown in Fig. 1. The plasma density is up to 5×10^{18} m^{-3} in steady state, and the plasma has a large diameter of 10 cm. The electron temperature is around 7 eV. The substrate was irradiated with low energy helium plasma of around 100 eV and 10^{22} m^{-2} s^{-1}. It was heated by passing an ac current through the sample, coupled with a conventional transformer. The width and thickness of substrate were carefully adjusted to have a uniform temperature distribution over the surface. In order to enhance the uniformity, the substrate edge near the graphite holder was shadowed from plasma irradiation by BN plates. The insulating plates were also used to cover the plasma-facing surface of the graphite holder. The important temperature measurement was performed with a calibrated optical system composed of a mirror, a window and an IR thermometer, as shown in Fig. 1.

A new technique of pulse biasing on the target has been employed to observe the dynamic erosion. The

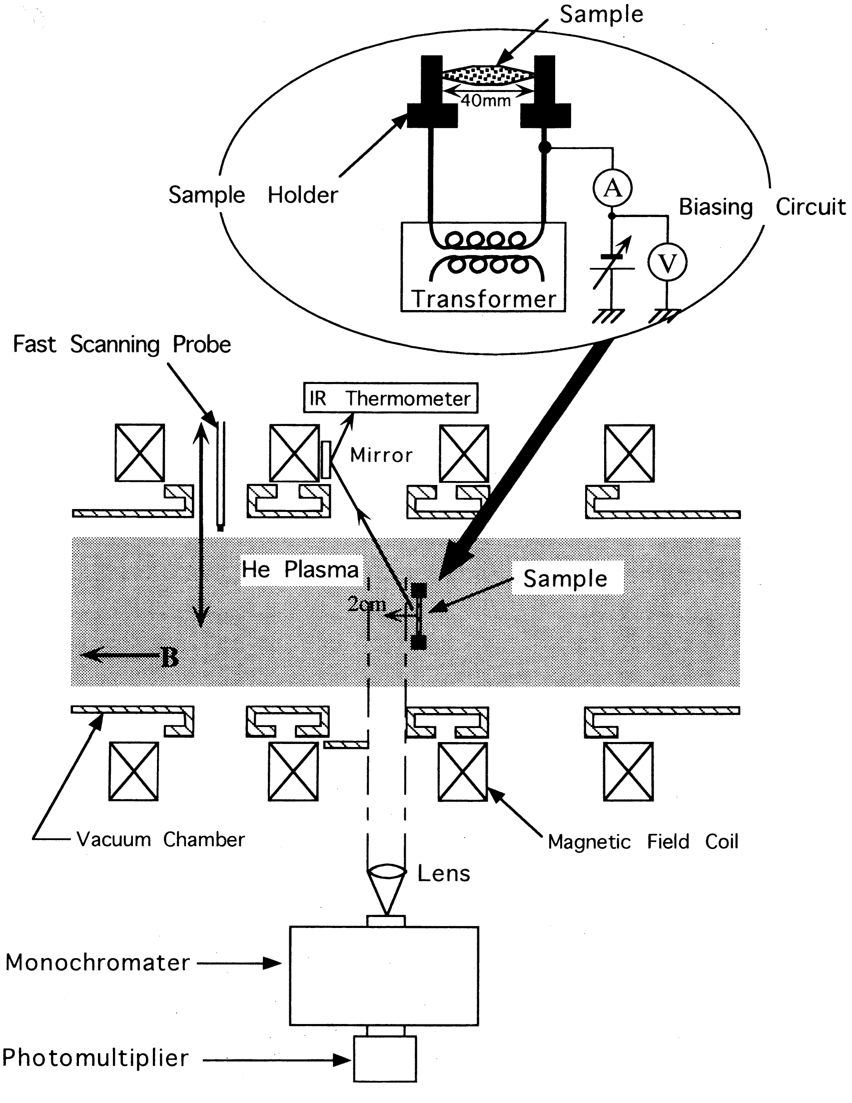

Fig. 1. Experimental arrangement of NAGDIS-I linear plasma device for in situ optical spectroscopy measurement of metal sputtering yield.

incident ion energy is uniquely determined by the sheath voltage owing to a very low ion temperature. The time evolution of the titanium atomic line (364.3 nm), which is proportional to the sputtered titanium atomic flux from the substrate, were observed.

3. Experimental results

In order to validate the pulse biasing technique, the TiI line intensity as a function of incident ion energy in the case of a pure Ti target was compared with the sputtering yield, as shown in Fig. 2. Data on the energy dependence of TiI intensity coincide well with published data on Ti sputtering [6]. This also shows that the effect of oxygen impurities in the plasma (estimated to be a few per cent in ion concentration) is negligible.

The intensities of the TiI line from TiC-coated graphite target irradiated with the helium plasma at different target temperatures are shown as a function of irradiation time in Fig. 3, where the energy and the ion flux were 87 eV and 8.7×10^{21} m^{-2} s^{-1}. It is clearly seen that the rate of increase of the intensity has two stages. A prompt stage is followed by a slow increase in the intensity. The saturation level becomes lower as the temperature increases up to 1300°C. The steady state TiI line intensities at different ion fluxes are shown as a function of target temperature in Fig. 4, where they are normalized to the intensity at 700°C. We see that the lower particle flux gives a wider range of target temperature over which Ti sputtering is suppressed. In addition, we changed the incident ion energy from 83 to 141 eV, under the same ion flux of 3.2×10^{21} m^{-2} s^{-1}. It was observed, not shown here, that the energy increase makes the starting temperature from which the suppression of Ti sputtering is observed to shift upward. These observations suggest that the behavior is described by the product of the sputtering cross section σ and the ion flux ϕ.

Above 1300°C, Ti sputtering increases with temperature. The background Ti spectral line intensity is negligible below 1450°C. However, it appears at 1500°C and increases dramatically with temperature. It may be attributed to Ti sublimation. However, this seems to be too large because the observed rate at 1700°C corresponds to roughly the normal sublimation rate at 2500°C. Ion induced effects could enhance sublimation. Above 1350°C, initial overshooting appears, and it becomes very strong around 1600°C as shown in Fig. 3. The overshooting is enhanced by the increase in ion flux.

4. Modeling and discussion

The reduction of the sputtering yield with temperature is explained in terms of self-sustaining coverage of the TiC surface with segregated carbon atoms, supplied from the graphite substrate (see Fig. 5). If diffusion is very fast, we can assume that the carbon atom density in the TiC layer is constant in space. The volume concentration of solute atoms in the bulk $C_b(t)[m^{-3}]$, and the surface concentration at the top surface $C_s(t)[m^{-2}]$ can be represented by the following equations [7,8]:

$$\dot{C}_s(t) = -k_1 C_s(t) + k_2 a C_b(t) - \sigma\phi C_s(t), \qquad (1)$$

$$a\dot{C}_b(t) = k_1 C_s(t) - k_2 a C_b(t) - k_3 a C_b(t) + k_4 C_g, \qquad (2)$$

where the dot is for time derivatives. The rate constants of dissolution and segregation k_1 and k_2 are given in the unit of s^{-1}, and a[m] is the atomic spacing. k_3 and k_4 are the rate constants of segregation and dissolution, and C_g is the surface number density of carbon atoms in graphite.

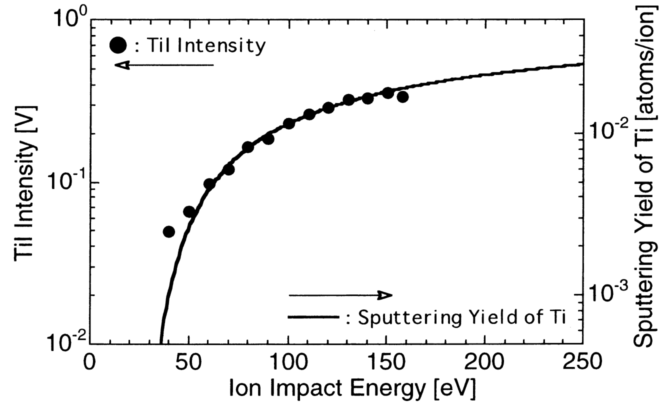

Fig. 2. Dependence of the steady state TiI line (364.3 nm) intensity from helium plasma bombarding the Ti target on ion impact energy. The solid curve represents the sputtering data of Ti by He^+ bombardment [6].

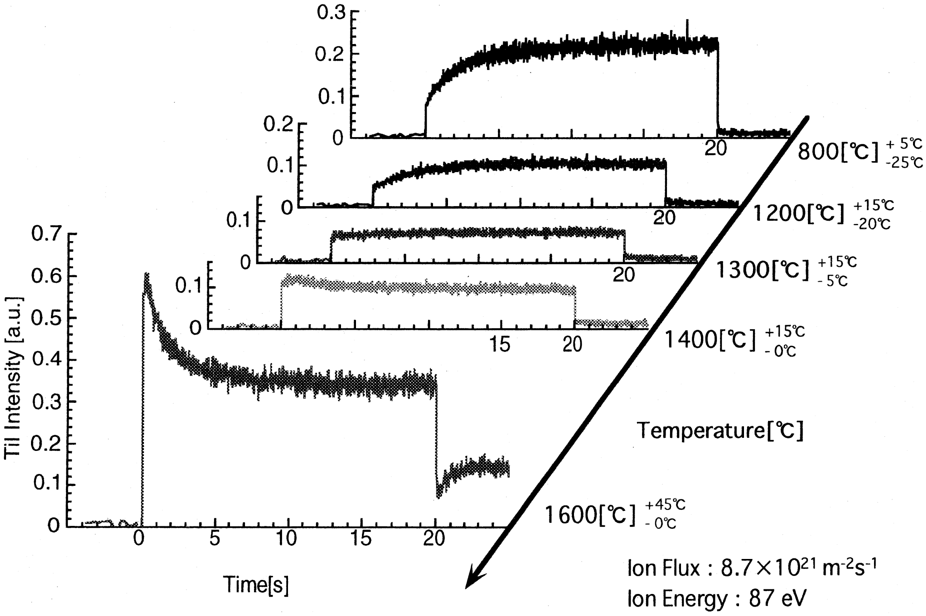

Fig. 3. Time evolutions of TiI line intensity for the TiC coated graphite target irradiated with helium plasma at different target temperature. The ion impact energy is 87 eV, and the ion flux is 8.7×10^{21} m^{-2} s^{-1}.

From Eqs. (1) and (2), we can obtain the time dependent equation for $C_s(t)$,

$$\ddot{C}_s(t) + b\dot{C}_s(t) + dC_s(t) = k_2k_4C_g, \qquad (3)$$

where $b = k_1 + k_2 + k_3 + \sigma\phi$, and $d = k_1k_3 + \sigma\phi(k_2 + k_3)$. It is clear from Eq. (3) that the dynamic surface coverage could be described by two time constants, suggesting a two-stage evolution of TiI line intensity. We assume here that $k_2 = k_3$ [9]. We obtain the steady-state surface coverage $C_s(t \to \infty)$ by putting $\dot{C}_s(t \to \infty) = 0$.

$$C_s(t \to \infty)/C_g = k_4/(k_1 + 2\sigma\phi). \qquad (4)$$

Eq. (4) indicates that the Ti sputtering yield Y_{Ti} can be numerically calculated from the self-sustaining coverage of the TiC surface with segregated carbon atoms, when the sputtered atoms are assumed to come out from the topmost surface. The relationship between the surface coverage of carbon on the TiC sample and the erosion rate is given by $Y_{Ti}(\text{at } T) = Y_{Ti}(\text{at RT})(1 - C_s(t \to \infty)/C_g)$.

The activation energy E_1 of the dissolution rate k_1 at the topmost surface is, in general, larger than that of k_4 at the interface due to the different nature of the interface characteristics for dissolution [10]. Thus, the tem-

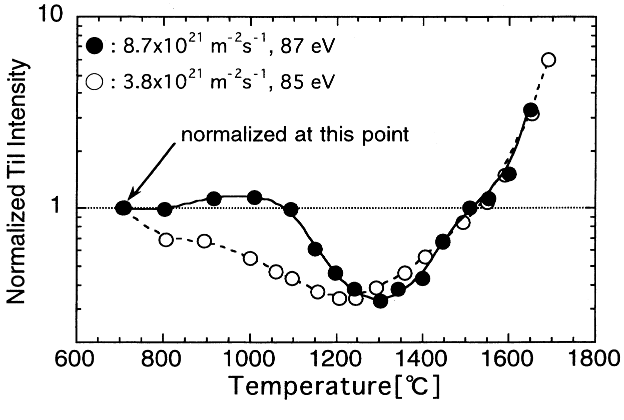

Fig. 4. Temperature dependence of the steady state TiI line intensity for different ion fluxes. The intensities are normalized with those at 700°C.

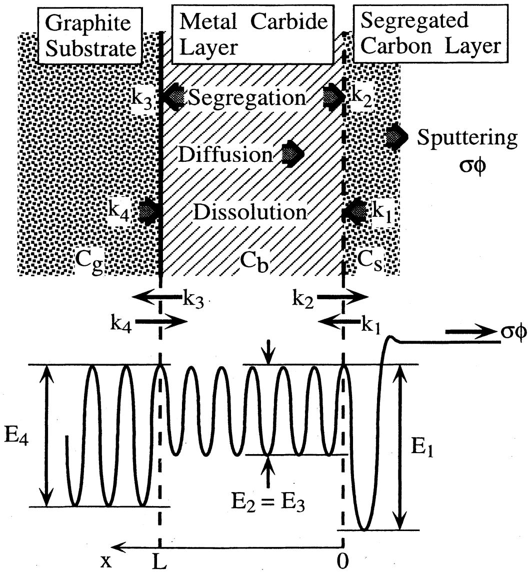

Fig. 5. Schematic of carbon transport in the TiC overlayer on graphite under ion irradiation. Potential structures for the rate constants of each reaction are also shown.

perature dependence of the surface coverage C_s/C_g and the normalized sputtering yield were calculated by fitting parameters of the pre-exponential factors k_1^0 and k_4^0 in k_1 and k_4. The activation energies and pre-exponential factors have been inferred from experiments on the temperature dependence of erosion [3,4,7–9,11,12] and the time evolution of Ti sputtering [7,8]. We should note that these are fitted with the experiments, and are not unique. The curves of C_s/C_g and $Y_{Ti}(\text{at } T)/Y_{Ti}(\text{at RT})$ for $k_1^0(1.1 \times 10^5\ s^{-1}) \gg k_4^0(2.0 \times 10^3\ s^{-1})$ are shown in Fig. 6 and those for $k_1^0 = k_4^0$ are also calculated but not shown here. It was assumed that Ti sputtering takes place when C_s/C_g is less than unity. The latter result, that the surface coverage is always larger than unity, is realized by the radiation-induced effect; namely the radiation-induced multi-layer segregation [10]. One can see clearly that the calculated curve of the sputtering yield in Fig. 6 reproduces well the experimental one. This fact indicates that the increase in the Ti sputtering yield above 1300°C can be explained in terms of thermal equilibrium segregation of carbon atoms at the TiC surface. But above 1500°, titanium sublimation should contribute to a sharp increase in Ti erosion with temperature. One can also see that there is no increase in the Ti sputtering yield in the high temperature region when $k_1^0 = k_4^0$, which is the most preferable property for plasma facing components of fusion devices. This fact indicates that the data on segregation and dissolution of carbon atoms at the carbide surface are very necessary for evaluation of plasma facing components.

Concerning the initial overshooting of dynamic erosion behavior of titanium, we have been considering a titanium rich layer near the surface in the high temperature range. Such a layer could be associated with titanium sublimation.

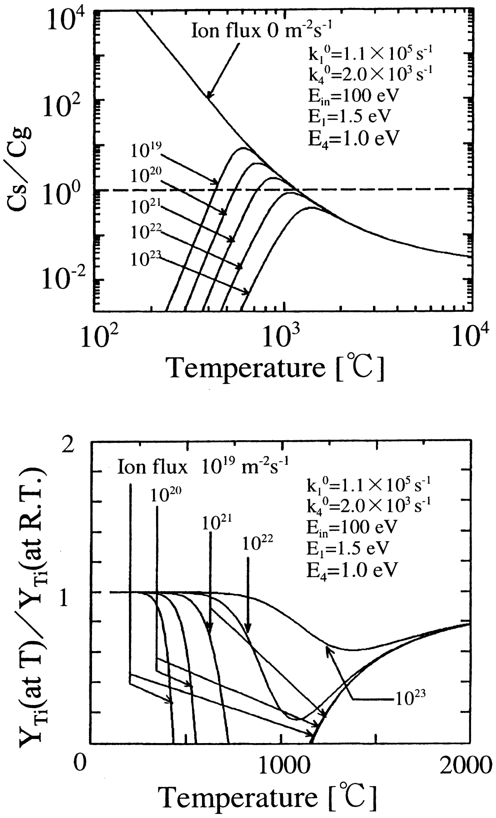

Fig. 6. Temperature dependencies of C_s/C_g and the Ti sputtering yield calculated using Eq. (4) in the case of $k_1 \gg k_4$.

5. Conclusions

The reduction of Ti sputtering from TiC-coated graphite was observed under a high ion flux, close to 10^{22} ions/(m^2 s), and is explained in terms of self-sustaining coverage of TiC surface with segregated carbons. The analysis of mass balance equations for carbon atoms to explain the experimental behavior of Ti erosion is given for dynamic as well as static situations. An initial transient overshooting of Ti erosion observed at very high temperature has been modeled by a stoichiometric change of the TiC layer.

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