Carbon behavior on tungsten surface after carbon and hydrogen mixed beam irradiation

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Abstract

The carbon behavior near the surface layer of tungsten after hydrogen and carbon mixed ion beam irradiation was investigated with XPS. Depth profiles of atomic components near the surface layer depended on the concentration of carbon ions in the beam of 0.1% or 0.8% and beam fluence from 3×10^{22}/m^2 to 3×10^{24}/m^2. Carbon concentration at the local peak increased with increasing beam fluence. Comparison of the experimental results with the simulation results with EDDY code was performed. At the temperature of 653 K, the simulation results qualitatively corresponded to the experimental results except near the top surface. In the simulation at high temperatures, carbon profile drastically expanded into the bulk layer due to thermal diffusion. But in the experiment, such expansion of the carbon distribution with the temperature was not observed for temperature up to 913 K.
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1. Introduction

Tungsten will be used at baffles and side-wall regions of divertor, and carbon will be used at divertor strike points in ITER-FEAT [1]. In the divertor regions, sputtered carbon particles will be ionized and implanted with D and T ions into the surface layer of tungsten. Carbon implantation into the tungsten surface will not only affects to the process of erosion and deposition as reported in Ref. [2–5] but will produce the surface modification such as blistering.

It was made clear that carbon impurity in the hydrogen ion beam affected blister formation on tungsten in our previous studies [6–10]. The beam energy was 1.0 keV, and the fluence was in the range of 10^{24}–10^{25}/m^2. In the case of carbon concentrations in the beam of more than 0.35% at 653 K, a high density of various sizes of blisters (from 1.0 μm to 1.0 mm in diameter) were formed. When the carbon concentration was 0.11%, no significant blisters were observed on the

sample. When the carbon concentration was 2.35%, there was net deposition of carbon and no blisters were observed. Blister formation also depended on the beam fluence, energy and sample temperature.

It is believed that blisters are formed by a large amount of hydrogen gas trapped and containing at the grain boundaries of the bulk layer beyond implanted range. Diffusivity, recombination, permeability and solubility of hydrogen which would affect to the retention and blister formation depend on the surface condition. They can change due to the surface modification by the carbon implantation. It is important to study carbon behavior on the surface of samples in order to understand blister formation. In this study, carbon behavior near the surface layer of tungsten after hydrogen and carbon mixed ion beam irradiation was investigated by changing the carbon concentration in the beam, varying fluence and sample temperature.

2. Experiments

Sintered polycrystalline tungsten samples (Nilaco Co.) were used in the experiment (1.0 mm in thickness,

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sizes of 10×20 mm); all samples were mirror polished for the experiments, and not annealed.

Carbon and hydrogen mixed ion beam irradiation to samples was performed with HiFIT [11]. This device consists of a 2.45 GHz ECR ion source, triode spherical electrodes, a beam chamber, a sample irradiation chamber, an ion mass spectrometer and a thermal desorption spectroscopy chamber (TDS chamber).

Before and after beam irradiation to the sample materials, the ion beam mass spectrum was measured in order to estimate the ratio of ion species, particularly the carbon impurity concentration. Main species in the mixed ion beam were H_3^+ and carbon which was contained in the form of CH_x^+ (>80% in the C impurities) or $C_2H_x^+$ (<20% in the C impurities). Oxygen was also contained in the form of H_xO^+, whose ratio was less than 0.1%. Other species were less than the limit of detection (less than 0.01%). A typical mass spectrum of the mixed beam is shown in Ref. [5,6]. Beam energy and flux are 1.0 keV (mainly H_3^+) and 2.5–4.0×10^{20}/m²s, respectively.

The surfaces of the irradiated parts were analyzed with an X-ray photoelectron spectroscopy (XPS; AXIS 165, Kratos Co.). This device is equipped with an Mg K_α (kinetic energy: 1253.6 eV) monochromic radiation source and argon beam ion gun for etching of samples. Carbon, tungsten, and oxygen peaks were detected on the irradiated part of surface. For example, C-1s (284.5 eV of graphite and 283.2 eV of WC), W-4f (33.4 and 31.4 eV) and O-1s (532.0 eV of O_2 and 530.5 eV of WO_3) were detected. After the irradiation of samples, they were exposed to air when delivering them to the XPS device.

The depth of erosion after mixed beam irradiation or Ar beam etching was measured with the surface profile scanning device (Dektak3, Veeco Co.)

3. Results and discussion

3.1. Dependence of beam fluence

The C impurity concentration in the ion beam was set at 0.1% and 0.8% and the beam fluence was varied from 10^{22}/m² to 10^{24}/m². Sample temperature was maintained at 653 K. Figs. 1 and 2 show the depth distribution of the atomic concentration of W and C as function of the mixed ion beam concentration and beam fluence.

In the case of the C impurity concentration of 0.1% (Fig. 1), a WC layer was partially formed on the surface layer of irradiated parts. The depth distribution of carbon has a peak at the depth of about 15 nm from the top surface. When the beam fluence increased from 3×10^{23}/m² (Fig. 1(a)) to 3×10^{24}/m² (Fig. 1(b)), atomic concentration of carbon at the peak increased from 20% to 40%. Irradiated part was eroded by carbon and oxygen
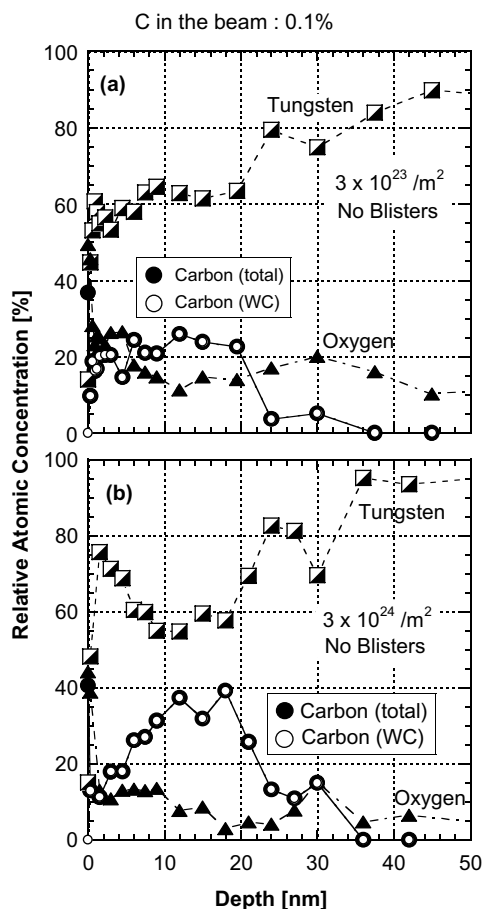

Fig. 1. Depth distribution of W, C and O in tungsten samples with 333 eV H and 1000 eV C irradiation for the C impurity concentration in the beam of 0.1%. Beam fluence is (a) 3×10^{23}/m² and (b) 3×10^{24}/m². Sample temperature is 653 K.

impurities and blisters did not appear on the surface in both cases.

Surfaces were covered by graphite and WC in the cases of C impurity concentration of 0.8% (Fig. 2). As the beam fluence increased from 3×10^{22}/m² (Fig. 2(a)) to 3×10^{23}/m² (Fig. 2(b)), the relative C concentration increased from 30% to 55%. When the fluence increased to 3×10^{24}/m² (Fig. 2(c)), the carbon concentration at the local peak stayed almost the same and carbon distribution slightly expanded into the bulk layer. Blisters were formed on the surface in the cases of fluence of 3×10^{23}/m² and 3×10^{24}/m².

3.2. Dependence of sample temperature

In this experiment, the C impurity concentration in the beam was maintained at about 0.8% and sample temperature was varied from 453 to 913 K.
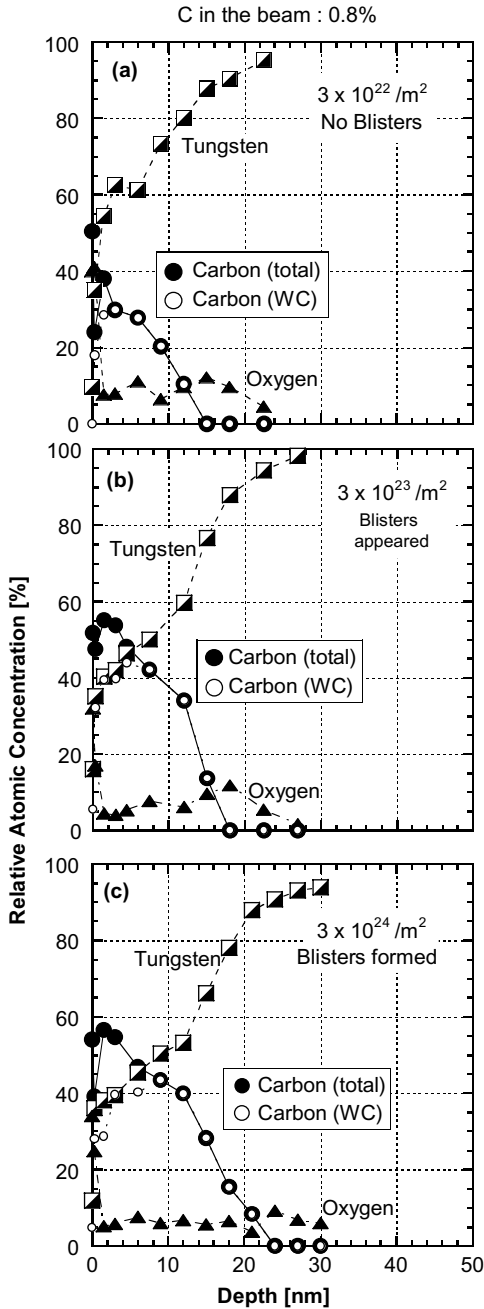
Fig. 2. Depth distribution of W, C and O in tungsten samples with 333 eV H and 1000 eV C irradiation for the C impurity concentration in the beam of 0.8%. The beam fluence is (a) $3 \times 10^{22}/m^2$, (b) $3 \times 10^{23}/m^2$ and (c) $3 \times 10^{24}/m^2$. Sample temperature is 653 K.

Fig. 3 shows the variation in atomic concentration of the irradiated zone with sample temperature. Distribution of carbon near the surface layer depended on surface temperature.
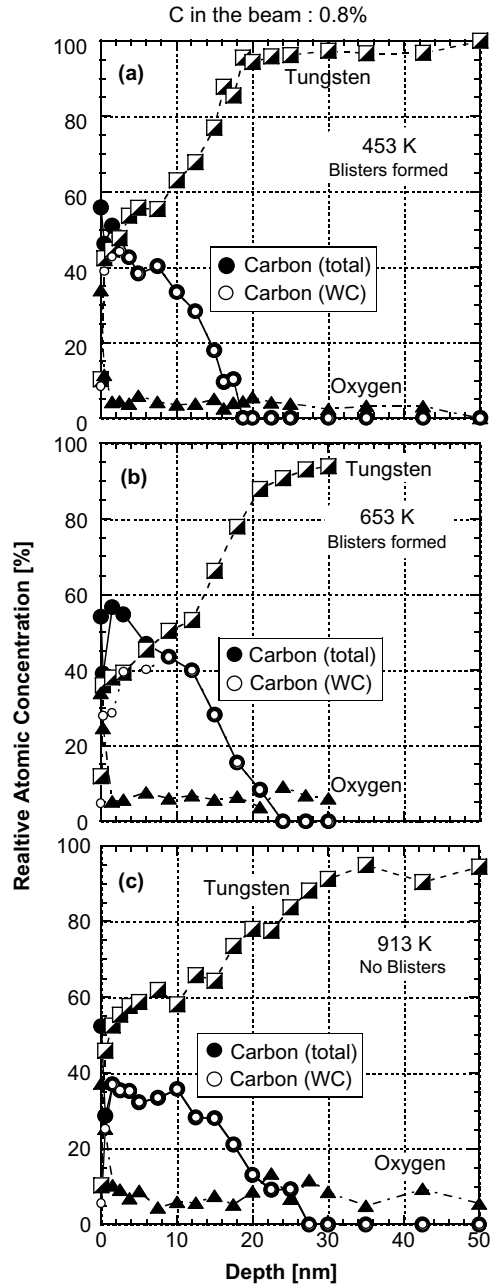
Fig. 3. Depth distribution of W, C and O in tungsten samples with 333 eV H and 1000 eV C irradiation for the C impurity concentration in the beam of 0.8%. Sample temperature is (a) 453 K, (b) 653 K and (c) 913 K. Beam fluence is $3 \times 10^{24}/m^2$.

At 453 K (Fig. 3(a)), graphite and WC co-existed from top surface to the depth of 2–3 nm, which is the implanted range of carbon. Under this layer, WC was found to depth of 5–15 nm. For the sample temperature of 653 K (Fig. 3(b)), the co-existed layer slightly

expanded to the depth of 8 nm and the relative C concentration in the co-existed layer remained at 55%. For the temperature of 913 K (Fig. 3(c)), the distribution of carbon expanded to a depth of about 27 nm. The local peak of the relative C concentration was decreased to about 35%, and graphite existed only near the surface. It is believed that the reason for the decrease of graphite in the graphite/WC co-existing layer around the top surface is the chemical erosion of carbon atoms due to the reaction with implanted H ions in the beam. According to the report of Roth and Garcia-Rosales, chemical erosion of carbon atoms starts at about 600 K, and it is pronounced at 800–900 K [12]. The effect of thermal diffusion was not significant.

The surface conditions of the irradiated area were different depending on the sample temperature. In the case of the sample temperature of 453 K, a high densities of blisters with sizes up to 20–30 μm formed. Large number of blisters with the diameter up to an order of 0.1 μm were formed on the surface at a temperature of 653 K. No significant blisters were formed at 913 K. The dependence of blister formation on sample temperature may be related to the behavior of implanted hydrogen, not the carbon composition on the surface. In all cases, the depth of surface erosion by mixed ion beam irradiation was around 100 nm.

3.3. Comparison with simulation results

The mechanism of mixed layer formation, the dynamic behavior of carbon atoms on tungsten surfaces irradiated simultaneously with H$^+$ and C$^+$ ions have been simulated with the EDDY code. The detail of the EDDY code is described in Ref. [13]. The depth profile of atomic compositions in the target due to collision cascades and thermal diffusion of impurity atoms deposited on the target can be calculated by this code. Thermal diffusion is simulated by using the diffusion equation with the diffusion coefficient, $D = D_0 \exp(-Q/k_B T)$, where D_0 is the material constant, Q is the activation energy, k_B is the Boltzman coefficient and T is the sample temperature. For the diffusion of C impurity deposited on the W target, $D_0 = 3.15 \times 10^{-7}$ m^2/s and $Q = 1.78$ eV, which were measured by other experiment [14]. For hydrogen atoms, any retention process is not taken into account. Hydrogen atoms are assumed to desorb instantaneously after implantation. Chemical erosion is not taken into account.

Fig. 4 shows the simulation results of the fluence dependence with the EDDY code at the sample temperature of 653 K (653 K is essentially diffusion free). For the C impurity concentration in the beam of 0.1% (Fig. 4(a)), the depth distribution of implanted carbon in the tungsten has a peak at 20 nm from top surface. With increasing beam fluence to 3×10^{24}/m^2, concentration of carbon at the peak increased to about 40%, which
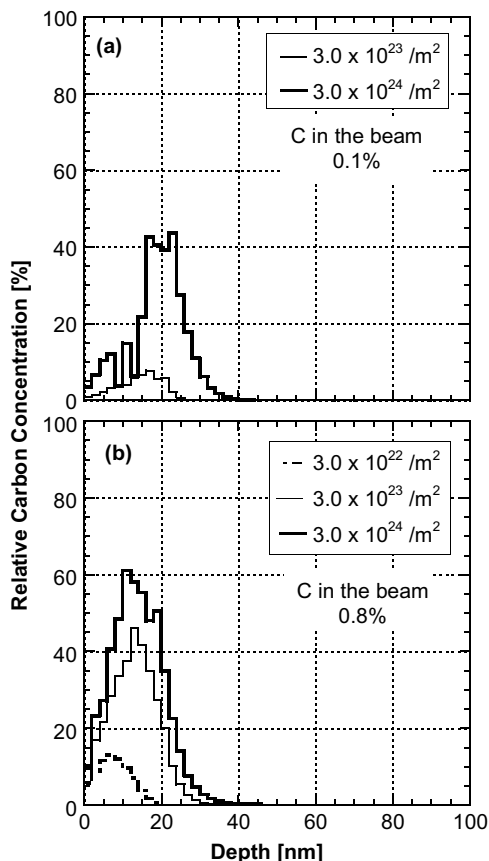

Fig. 4. Dependence of depth distribution of carbon by simulation with EDDY on beam fluence. Beam energy and sample temperature were set at 1.0 keV and 653 K (essentially diffusion-free), respectively. C impurity concentration in the beam was (a) 0.1% and (b) 0.8%.

quantitatively corresponded with the experiment and the distribution of carbon expanded to a depth of 35 nm. For the C impurity concentration of 0.8% (Fig. 4(b)), the local peak of carbon was about 10 nm from the top surface at 3.0×10^{22}/m^2. The local peak moved to a depth of 15 nm with increase in the beam fluence to 3.0×10^{23}/m^2. At the beam fluence of 3.0×10^{24}/m^2, the position of the local peak stayed at 15 nm, but the relative C concentration increased to about 60%. The detailed results and discussions of simulation concerning fluence dependence are shown in Ref. [15].

Fig. 5 shows the simulation results of the sample temperature dependence for the C impurity concentration in the beam of 0.8%. With increasing the surface temperature from 653 K, carbon distribution drastically expanded into the bulk layer, beyond at least 100 nm, and the relative C concentration decreased to less than 10% due to the thermal diffusion. Such a drastic diffusion of carbon was not observed in the experimental
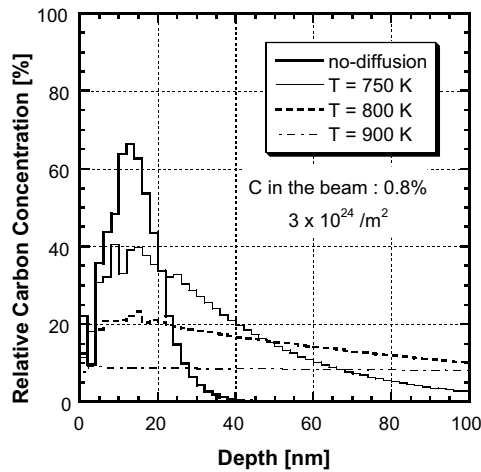
Fig. 5. Dependence of depth distribution of carbon by simulation with EDDY on sample temperature. C impurity concentration in the beam was 0.8%. Beam energy and were set at 1.0 keV and $3 \times 10^{24}/m^2$, respectively.

results. Some effects such as chemical erosion of carbon would release carbon atoms from the tungsten surface before diffusing into the bulk. Thermal diffusion of C in the C/W mixed layer or WC layer under the simultaneous implantation of hydrogen and carbon will have to be investigated. Diffusion coefficient of carbon would depend on the carbon concentration in C/W layer as Schmid describes in Ref. [16], and diffusion coefficient of C in the WC layer would be different from that in the W layer.

4. Summary

The study of carbon behavior near the surface layer of tungsten after hydrogen and carbon mixed ion beam irradiation was investigated. At the temperature of 653 K, a graphite/WC layer co-existed in the case of the C impurity concentration in the beam of 0.8%. The relative C concentration at the peak depth also increased from 40% to 55% with increasing beam fluence. In the cases of the carbon concentration of 0.1%, WC was partially contained in the top layer to a depth of about 30 nm. The relative C concentration at the local peak increased from 20% to 35% with increase in the beam fluence to $10^{23}/m^2$.

Sample temperature dependence of the carbon behavior was also studied for the impurity C concentration of about 0.8%. With increasing sample temperature, the profile of carbon concentration slightly expanded into the bulk layer. Graphite/WC co-existed

layer formed at the implanted range, 2–3 nm from the top surface, and the relative C concentration at the peak was 50–55% at the temperature of 453 K. Graphite/WC co-existed layer also formed at the temperature of 453 and 653 K. For irradiation at 913 K, graphite existed only near the top surface. Chemical sputtering of carbon would enhance carbon erosion at the temperature.

Comparison of the experimental results with the simulation results from the EDDY code was performed. With increase in the beam fluence at 653 K, the local peak of carbon distribution moved to bulk layer and carbon concentration at the peak increased. In the higher temperature cases, the carbon distribution drastically expanded into the bulk and the concentration at the local peak decreased due to thermal diffusion. Such an expansion of carbon distribution was not observed in experimental results.

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