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Hydrogen Behaviors with different introduction methods in SiC-C Films

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Abstract

SiC-C films were deposited with r. f. magnetron sputtering on substrates followed by argon ion bombardment. These films were then permeated by hydrogen gas under the pressure of 3.23×10^{7} Pa for 3 hours at temperature of 500K or bombarded with hydrogen ion beam at 5 keV and a dose of 1×10^{18} ions/cm^{2}. SIMS, AES and XPS were used to analyze hydrogen related species, chemical bonding states of C, Si as well as contamination oxygen due to hydrogen participation in the SiC-C films in order to study the different behaviors of hydrogen in carbon-carbide films due to different hydrogen introduction. Related mechanism about the effects of hydrogen on the element of the SiC-C films was discussed in this paper.

Keywords : SiC-C films, hydrogen behaviors, magnetron sputtering

1. Introduction

Graphite and SiC regard as plasma facing materials in tokamaks since they are refractory materials with good thermal conductivity and thermal shock resistance. In addition, their low atomic number (Z) assures that radiation losses would be minimized if Si or C particles entered the plasma [1-3]. But the graphite and carbides are susceptible to chemical sputtering, resulting in production of methane and other hydrocarbon species under hydrogenic plasma exposure, which may limit their uses. The interaction of hydrogen with low Z materials has been studied at its charged state [4-5]. Few reports on it were studied at its atomic or molecular states. In this paper, we try to compare the effects of hydrogen on carbon and carbides at its different states, i.e., at charged or non-charged states.

SIMS is widely used to detect hydrogen distribution in depth and species related hydrogen. AES and XPS analyses could give direct information on the composition and the bonding type of the atoms in solid phases, line-shape in Auger spectra and chemical shifts in binding energy of the photoelectron peaks occur when there is a change in the valence state of the bonding atoms. In this paper information of microanalyses on the hydrogen introduced SiC-C films is reported to study the behaviors of hydrogen with different introduction methods.

2. Experimental details

70% SiC-C films were prepared with ion beam mixing in our equipment [6], where films were deposited by r.f. magnetron sputtering on stainless steel and then by Ar^{+} ion beam bombardment. The base pressure in chamber was 4×10^{-4} Pa and increased to about 0.5 Pa during r.f. magnetron sputtering deposition, while it became 3×10^{-3} Pa during argon or hydrogen ion

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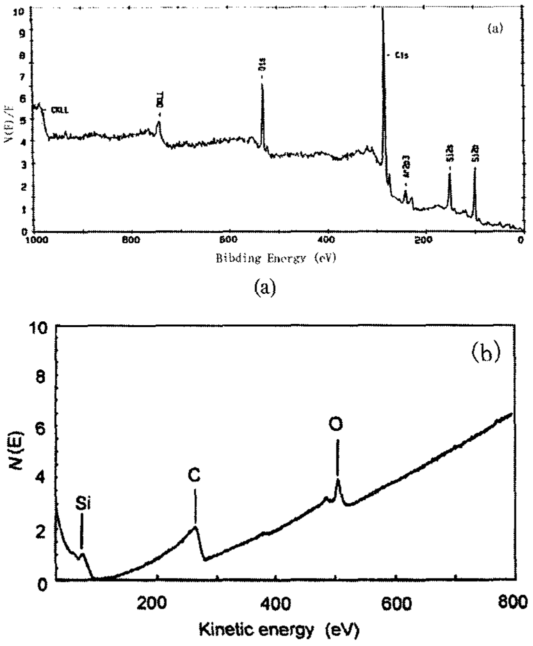
bombardment. The 70% SiC-C films were prepared as follows: 70% SiC-C films deposited with a thickness of about 30 nm were bombarded at room temperature with 40 keV Ar^+ ion beam and doses of $(1\text{-}5)\times 10^{16}$ ions/cm^2. After that, deposition was continued to get another layer with a thickness of 30 nm on the bombarded surface, and followed by Ar^+ beam bombardment with the same condition as first. Such a process was repeated up to that the thickness of 70% SiC-C films was about 200 nm at last. After samples preparation, some surfaces of them were permeated by hydrogen gas with a pressure of 3.2×10^7 Pa for 3 hours at the temperature of 500 K. Some were vertically implanted by H^+ ion beam with an energy of 5KeV and a dose of 1×10^{18} ions cm^{-2}, the hydrogen ion current densities were maintained at less than 9 μ A/cm^2. In order to decrease the sample temperature during ion beam implantation, a limited ion current as low as possible was done, and at the same time, a method of ion implantation with interruption was used, where the ion implantation was about 20 minutes, then rest time was also 20 minutes until this processes continued to arrive at the dose of 1×10^{18} ions · cm^{-2}.

Auger electron spectra (AES) and X-ray photoelectron spectra (XPS) of the surface composition were obtained using KRATOS-XSAM800 surface analysis system with mono-chromatic Al K_α radiation (1486.6 eV) operating at 13 kV × 19 mA. Ar^+ ion with 1-3 keV was used to etch the surface of the sample in order to delete the top contamination layer and to get the information on inner area of the 70% SiC-C films. The vacuum in the analyzer chamber was maintained at better than 1×10^{-6} Pa. And secondary ion mass spectra (SIMS) with a PH-650 system were used to measure formation of hydrogen related species in the 70% SiC-C films. During SIMS measurement, the vacuum in chamber was about 3×10^{-6} Pa.

3. Results and discussion

Fig. 1 shows the element composition on the surface of ion beam mixed 70% SiC-C films. Fig. 1(a) shows the XPS wide scan spectrum, and Fig. 1(b) shows the Auger one. Adsorbed or oxidized contamination was found on the top layer about 6 nm thick. Some contaminations like oxygen and carbon came from the residue gases such as CO, CO_2, H_2O etc. in the vacuum chamber during film preparation and some from air when the samples was placed in air [7]. Apart from oxygen, elements of the films like C and Si and bombarding argon can also be seen. Contamination carbon was overlapped on carbon signal from the films. It can be found that the intensity of oxygen on the surface measured with XPS was great decreased, but that measured with AES was no obvious change after ion-etching contamination top layer. Obviously, the sensitivity to detect oxygen with XPS is better than that with AES.

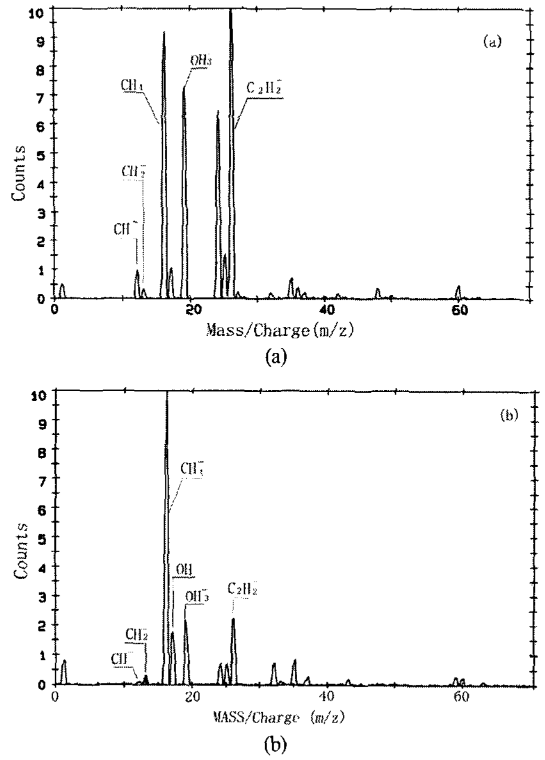
Fig. 2 shows mass spectra of the negative species for 70% SiC-C films introduced hydrogen by high pressure permeation (a) or by ion implantation (b). The negative



(a)

(b)

Fig. 1 Spectra on the surface of 70% SiC-C films : (a) XPS spectrum, (b) AES spectrum.



(a)

(b)

Fig. 2. Mass spectra of the negative species for the surfaces of 70% SiC-C films (a) Due to high pressure hydrogen permeating, (b)Due to hydrogen ion irradiation.

species related hydrogen like CH$^-$, CH$_2^-$, CH$_4^-$, and OH$^-$, OH$_3^-$, C$_2$H$_2^-$ etc. can be seen in both of Fig. 2(a) and Fig. 2(b). The results manifest that the formation of hydrogen related species are the same irrespective of hydrogen introduction by high pressure permeation or by ion implantation, and the amount of species CH$_4^-$ was particularly high. Only a difference is that the amount of some species such as OH$_3^-$ and C$_2$H$_2^-$ were relatively higher due to high pressure hydrogen permeation than those due to hydrogen ion implantation. It seems that hydrogen permeation under the high pressure condition at 500 K was easier to induce the formation of C$_2$H$_2^-$, and to introduce much more oxygen leading to the formation of OH$_3^-$. While, preferential sputtering of oxygen due to hydrogen ion bombardment led to a decrease in OH$_3^-$.

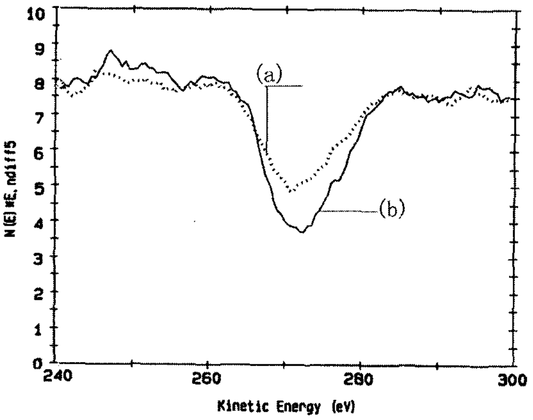


Fig. 3. C KLL electron excited Auger spectra of the 70% SiC-C films(a) Due to high pressure hydrogen permeating, (b) Due to hydrogen ion irradiation.

Fig. 3 displays the C KLL spectra on the surface of the ion beam mixed 70% SiC-C films after high pressure hydrogen permeating (a) or hydrogen ion implantation (b). The line-shape of C KLL spectrum in Fig. 3(a) shows a peak centered at 271.0 eV being mainly due to SiC, while a C KLL peak in Fig. 3(b) moved to a higher energy side at 272.3 eV with a shoulder at higher energy side due to $Si_{1-x}C_x$ (x>0.6). This is due to preferential physical sputtering of silicon by hydrogen ion bombardment [8].

Fig. 4 shows the electron excited Si LVV Auger spectra of the same films above after high pressure hydrogen permeating (a) or hydrogen ion implantation (b). The line-shape in Fig. 4(a) is characteristic of the mixture of SiC with $Si_{1-x}C_x$ (x>0.6) or SiO_y ($y \leq 2$) and distinguished by the presence of the two shoulders at 77.0 eV and 87.0 eV. While these shoulders became peaks at the almost same positions in Fig. 4(b) which confirmed the existence of $Si_{1-x}C_x$ (x>0.6) and SiO_y ($y \leq 2$). The peak at ~90 eV is close that for silicon bonded carbon while the peak at ~10 eV lower is due to silicon bonded to oxygen [8].

Fig. 5 shows the O KLL spectra on the surface of the same films after high pressure hydrogen permeating

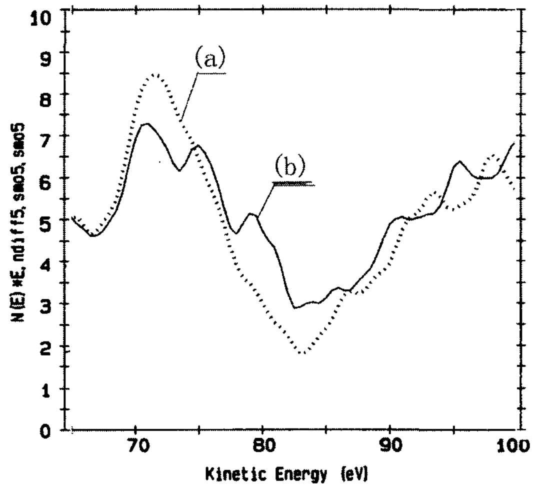


Fig. 4. Si LVV electron excited Auger spectra of the 70% SiC-C films : (a) Due to high pressure hydrogen permeating, (b)Due to hydrogen ion irradiation.

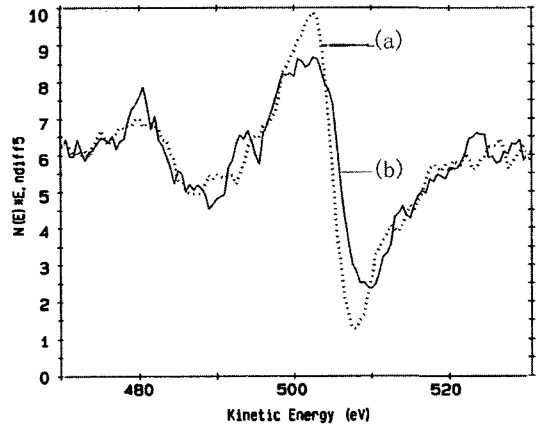
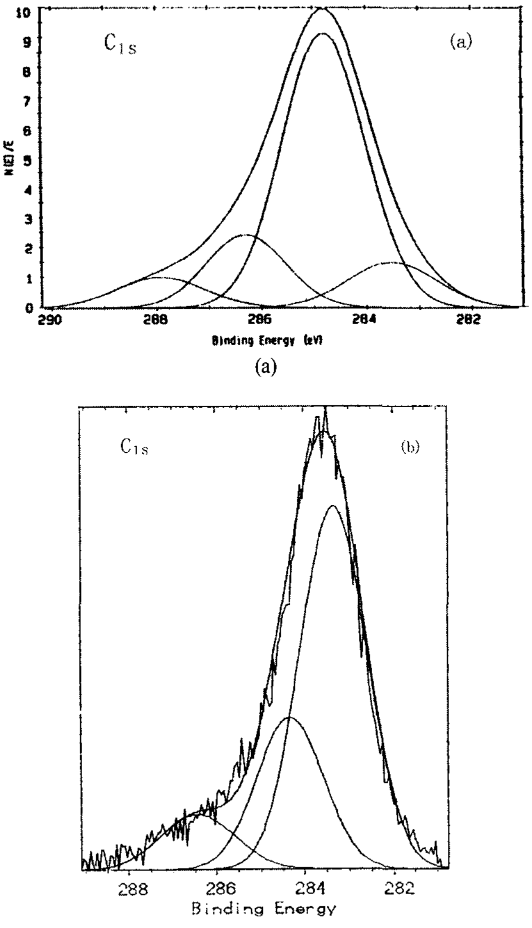


Fig. 5. O KLL electron excited Auger spectra of the 70% SiC-C films(a) Due to high pressure hydrogen permeating, (b)Due to hydrogen ion irradiation.



(a)

(b)

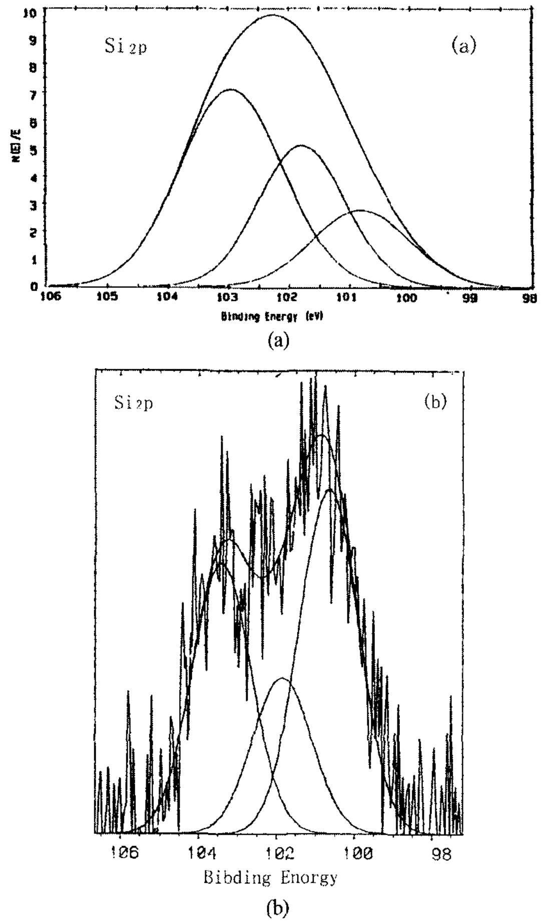
Fig. 6. C1s patterns on the surface of the 70% SiC-C films, (a) Due to high pressure hydrogen permeating, (b) Due to hydrogen ion irradiation.

(a) or hydrogen ion implantation (b). The line-shape of O KLL spectrum at 507.5 eV in Fig. 5(a) is due to SiO_y ($y \leq 2$) or C-Si-O [1] after high pressure hydrogen permeating. And it moved to a higher energy side at 510.2 eV shown in Fig. 5(b) after hydrogen ion implantation. In comparison with 509.0 eV for SiO_2 [1], it is due to SiO_y ($y \leq 2$) related to hydrogen. It seems that hydrogen in charged states is easier to react with C, O, and Si than in non-charged states.

Fig. 6 shows the C1s pattern on the surface of the ion beam mixed 70% SiC-C films after high pressure hydrogen permeating (a) or hydrogen ion implantation (b). The spectrum C1s in Fig. 6(a) can be resolved into four Gaussion components. The peak located at 283.4 eV is due to $Si_{1-x}C_x$ ($x>0.6$), the peak at about 284.8 eV is due to element of carbon like graphite or adsorbed carbon, the peak at 286.5 eV [9] is due to bond of carbon with hydrogen, possibly, CH group,

[10] and the peak at 288.6 eV is due to oxygen reacting with carbon related hydrogen, possibly, O-CH_2 configuration [11]. This was confirmed that the peak disappeared after deleting the oxygen contamination layer. The spectrum C1s in Fig. 6(b) can be resolved into three Gaussion components including peaks at about 283.3 eV, 284.3 eV and 286.1 eV. The results show that hydrocarbon like species were formed in 70%SiC-C films by hydrogen introduction of both metnods. And the fact that there was no peak at 288.6 eV in Fig. 6(b) confirms the preferential sputtering of oxygen due to hydrogen ion bombardment.

Fig. 7 shows the Si 2p spectra on the surface of the same films above after high pressure hydrogen permeating (a) or hydrogen ion implantation (b). The Si2p pattern in Fig. 7 (a) can be resolved into three components. One component located at 100.8 eV is due to SiC. The second at 101.8 eV seems due to $Si_{1-x}C_x$ or SiO_y (y<2) or C-Si-O configuration [1]. And the third at 103.0 eV is due to SiO_2 [12]. In Fig. 7(b), there were also three components, one at 100.6 eV, one at 101.8 eV and the other at 103.4 eV. The binding energies of two components shifted a little in the situation of hydrogen ion implantation in comparison with that of hydrogen permeation.

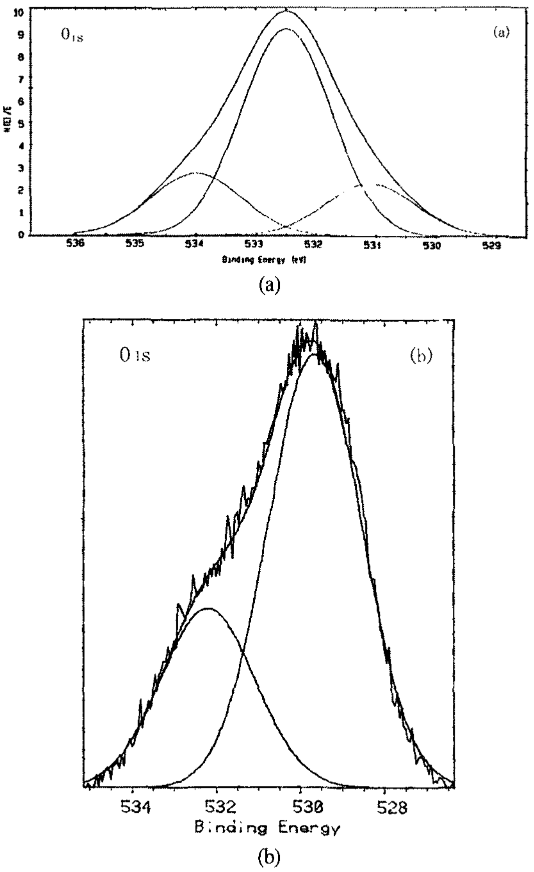


(a)

(b)

Fig. 7. Si2p patterns on the surface of the 70%SiC-C films, (a) after high pressure hydrogen permeating, (b)after hydrogen ion irradiation.

Fig. 8 shows the O1s pattern on the surface of the same films above after high pressure hydrogen pert



(a)

(b)

Fig. 8. O1s patterns on the surface of the 70%SiC-C films, (a) after high pressure hydrogen permeating, (b) after hydrogen ion irradiation.

meating (a) or hydrogen ion implantation (b). The O1s pattern in Fig. 8(a) can be resolved into three components. The peak located at 531.1 eV is due to SiO_2. The one at 532.5 eV is due to SiO_y or C-Si-O. And the third one at 534.0 eV seems due to O-CH_2 configuration. The O1s pattern in Fig. 8(b) can be resolved into two components at 529.6 eV and 532.2 eV. It confirms again the preferential sputtering of oxygen due to hydrogen ion bombardment.

4. Conclusions

The analyses of SIMS, AES and XPS have been used to study hydrogen behaviors in the ion beam mixed SiC-C films after high pressure hydrogen permeating or hydrogen ion irradiation. The following conclusions may be drawn from this study described here:

1. Hydrogen related species were formed in the SiC-C films by hydrogen introduction of both methods. The amount like OH_3^- and $C_2H_2^-$ were larger with high pressure hydrogen permeating than with hydrogen ion irradiation.
2. Based on the results from XPS and AES analyses, decomposition of SiC compound seems easier to happen due to hydrogen high pressure permeation at 500K, while preferential physical sputtering of silicon in SiC easier to happen due to hydrogen ion irradiation. And hydrogen in charged states is easier to react with C, O, and Si than in non-charged states.
3. Preferential sputtering of oxygen due to hydrogen ion irradiation can decrease the products of contamination oxygen reacting with Si and carbon of SiC-C films.

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