Effect of hydrogen on SiC-C films with AES and XPS analyses

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Abstract SiC-C films with different content of SiC were deposited with r. f. magnetron sputtering followed by argon ion bombardment. These films were then permeated by hydrogen gas under the pressure of 3.23×10^7 Pa for 3h at 500K. AES and XPS were used to analyze chemical bonding states of C and Si in the SiC-C films as well as contaminating oxygen before and after hydrogen gas permeation in order to study the effect of hydrogen on them. Related mechanism was discussed in this paper.

Keywords SiC-C films, Hydrogen permeation, XPS, AES

CLC numbers TQ163, O484.5

1 Introduction

Graphite and SiC have been regarded as plasma facing materials in Tokamaks, for 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 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 between energetic hydrogen and low Z materials has been studied under the conditions of ion energy larger than 0.1keV.[4,5] Few studies were reported with ion energy less than 0.1keV, i.e, under the conditions of hydrogen in atomic or molecular states. In order to study the effects of hydrogen on carbon and carbides, we try to focus on the interaction of hydrogen gas with carbon-carbide films.

AES and XPS analyses give direct information on the composition and bonding type of atoms in solid phases, the line-shape in Auger spectra and the chemical shifts in binding energy of the photoelectron peaks occuring when there is a change in the valence state of the bonding atoms. AES and XPS analyses were used to further understand the chemical sputtering processes of carbon and carbides how to take place due to the hydrogen participation, and to obtain the information on the chemical sputtering processes of the mixture of carbon and carbides.

2 Experimental details

Substrates made of austenitic type stainless steel 1Cr18Ni9Ti were polished and then degreased in benzene using ultrasonic cleaning, rinsed in de-ionized water and finally dried. SiC-C films with the content of 70% and 20% SiC were deposited by r.f. magnetron sputtering on the substrates followed by Ar^+ ion beam bombardment to obtain high density films with an enhanced adhesion strength to the substrate by forming the transition layer between film and substrate. The chamber had a base pressure of 4×10^{-4} Pa but this pressure increased to about 0.5 Pa during deposition due to argon feeding the discharge. The deposited SiC-C films with a thickness of about 30 nm were then bombarded with a 40 keV Ar^+ ion beam to doses of $(1\text{-}5)\times10^{16}$ ions/cm^2 at room temperature. After that, deposition continued to get another layer with thickness of 30 nm on the bombarded surface, followed by Ar^+ beam bombardment under the same condition as in the first sequence. Such a process was repeated until the film thickness of 200 nm for the SiC-C films was achieved. The pressure during Ar^+ ion bombardment was 4×10^{-4} Pa. After samples preparation, some surfaces of them were permeated by hydrogen gas under a pressure of 3.2×10^7 Pa for 3 h at 500K.

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),

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operating at 13 kV×19 mA. Ar^+ ions of 1-3 keV were used to etch surface of the sample in order to remove the top contamination layer and to get the information on inner area of the SiC-C films. The vacuum in the analysis chamber was maintained at better than 1×10^{-6} Pa.

3 Results and discussion

Fig.1(a) shows an Auger spectrum on the surface of the 20% SiC-C sample. It is seen that except for oxygen contamination, only carbon signal was detected. Contamination carbon was also overlapped on that of the films. Fig.1(b) shows the one on the surface of the 70% SiC-C sample, where silicon signal can be seen due to the increase of its content. Based on the wide scan of XPS on the surfaces, natural adsorbed carbon and oxygen or oxidized contamination were found on the top layer within a thickness about 6 nm. Some contaminations like carbon, oxygen 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 were placed in air.[6]

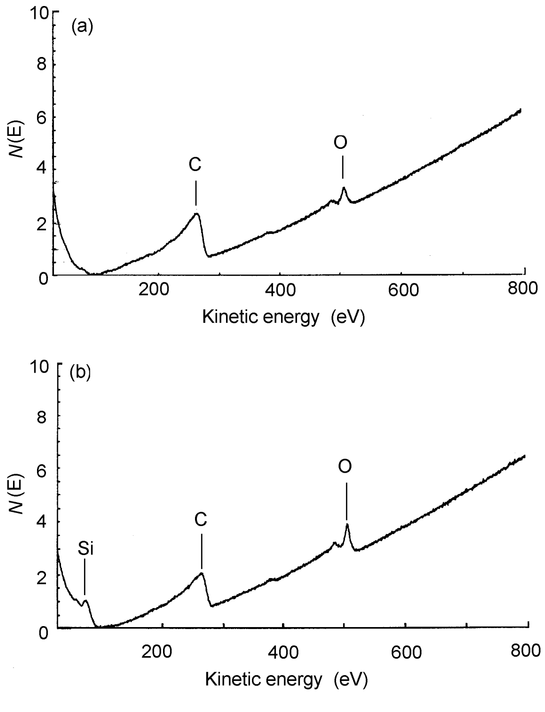

Fig.1 AES spectra on the surface after high pressure hydrogen permpeating. (a)20% SiC-C sample; (b) 70% SiC-C sample.

Fig.2 presents the electron excited Si *LVV* Auger spectra of the ion beam mixed SiC-C films with different SiC concentration after high pressure hydrogen permeating. The line-shape at surface for the 70% SiC-C sample is characteristic of the mixture of SiC with $Si_{1-x}C_x$ (x>0.6) or SiO_y ($y\leqslant2$) and distinguished by the presence of the peaks at the range of 77.0 eV to 87.0 eV. The peak at ~90 eV is close to that for silicon bonded carbon while the peak at ~10eV lower, i.e. about 80eV, is due to the silicon bonded to oxygen.[7] It seems difficult to judge whether silicon in the 20% SiC-C sample belongs to silicon carbides or silicon oxides due to its smaller content. But there are three small dips between 77-90eV in the figure showing SiC, $Si_{1-x}C_x$ or SiO_y, and SiO_2.

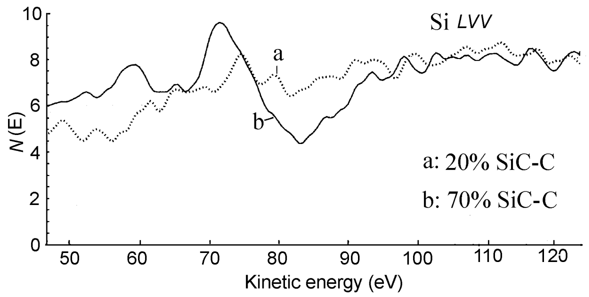

Fig.2 The Si *LVV* electron excited Auger spectra of the SiC-C films.

Fig.3 displays the C *KLL* spectra on the surface of the ion beam mixed SiC-C films after high pressure hydrogen permeating. The line-shape of C *KLL* spectrum for the 70% SiC-C sample shows a peak centered at 271.0 eV being mainly due to SiC compound, while a C *KLL* peak centered at higher energy side is mainly due to element carbon like graphite for the 20% SiC-C sample.

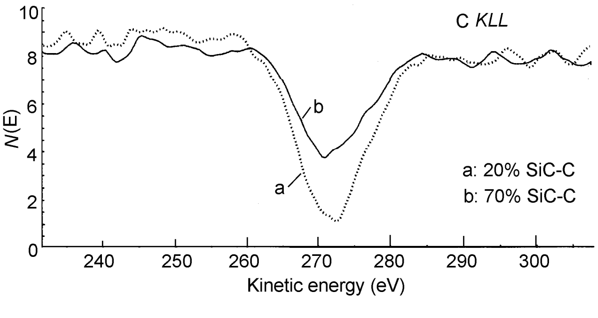

Fig.3 The C *KLL* electron excited Auger spectra of the SiC-C films.

Fig.4 gives the O *KLL* spectra on the surface of the ion beam mixed SiC-C films after high pressure hydrogen permeating. The line-shape of O *KLL* spectrum at high energy side shows a sub-peak at 514.4 eV for the 70% SiC-C sample, while there are two sub-peaks at 499.0 eV and 495.3 eV on the low energy side for the 20% SiC-C sample. These results indicate that the degree of oxidation of silicon seems different.

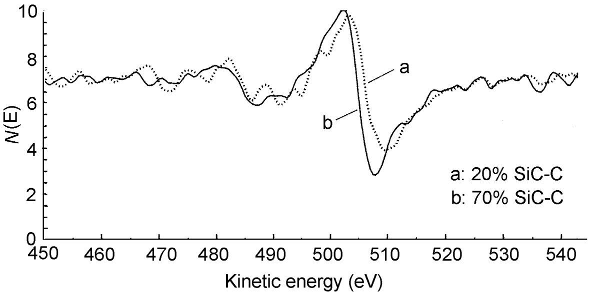

Fig.4 The O *KLL* electron excited Auger spectra of the SiC-C films.

Fig.5(a) shows the C 1*s* pattern on the surface of the ion beam mixed 20%SiC-C films after high pressure hydrogen permeating, which can be resolved into three Gaussion components. The peak located at about 284.8 eV is due to element of carbon, or residual adsorbed carbon or carbon out from SiC. The peak at 286.9 eV[8,9] is due to the bond of carbon related 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] which was confirmed by the fact that the peak disappeared after deleting the oxygen contamination layer. Fig.5(b) shows the C 1*s* pattern on the surface of the ion beam mixed 70%SiC-C films after high pressure hydrogen permeating. It can be resolved into four Gaussion components. Apart from the peaks similar to those shown in Fig.5(a), the peak at 283.4 eV is due to SiC.

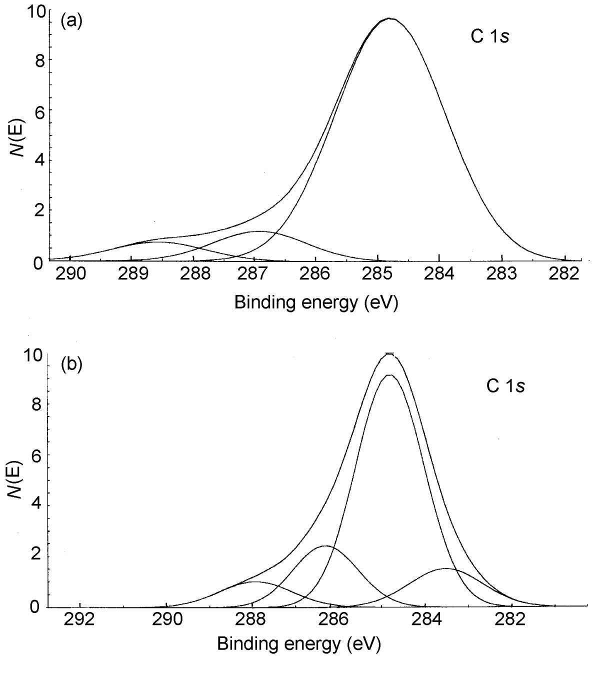

Fig.5 The C l*s* patterns on the surface after high pressure hydrogen permeating. (a) 20%SiC-C sample; (b) 70%SiC-C sample.

Fig.6(a) is the Si 2*p* spectra on the surface of the ion beam mixed 20%SiC-C films after high pressure hydrogen permeating, where the Si 2*p* pattern only has one component located at 101.4 eV due to Si$_{1-x}$C$_x$ or SiO$_y$ (y<2) or C-Si-O configuration.[1] Fig.6(b) shows the Si 2*p* pattern on the surface of the ion beam mixed 70%SiC-C films after high pressure hydrogen permeating, where the Si 2*p* pattern can be resolved into three components. One component located at 100.8 eV is due to SiC. The second at 101.8eV seems due to Si$_{1-x}$C$_x$ or SiO$_y$ (y<2) or C-Si-O configuration. And the last at 103.0 eV is due to SiO$_2$.[12]

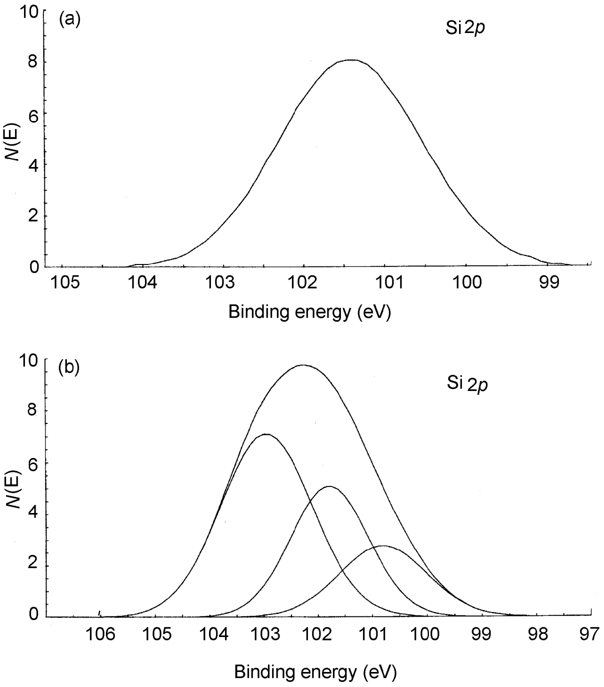

Fig.6 The Si 2*p* patterns on the surface after high pressure hydrogen permeating. (a) 20%SiC-C sample; (b) 70%SiC-C sample.

Fig.7(a) shows the O 1*s* pattern on the surface of the ion beam mixed 20%SiC-C films after high pressure hydrogen permeating, where the O 1*s* pattern can be resolved into three components. The peak located at 530.7 eV is due to SiO$_2$. The one at 531.9 eV seems due to SiO$_y$ or C-Si-O. And the third one at 533.4 eV seems due to oxygen reacting with carbon related hydrogen, possibly, like O-CH$_2$ configuration. It seems that oxygen transferred from SiO$_2$ to SiO$_x$ or C-Si-O and to O-CH$_2$

configuration on the basis of their XPS intensities due to high pressure hydrogen permeating. Fig.7(b) shows the O 1*s* pattern on the natural surface of the ion beam mixed 70%SiC-C films after high pressure hydrogen permeating, where the O 1*s* pattern can also be resolved into three components. The peak located at 531.1 eV is still due to SiO_2. The second at 532.5 eV is still due to SiO_y or C-Si-O. And the third one at 534.0 eV seems due to O-CH_2 configuration.

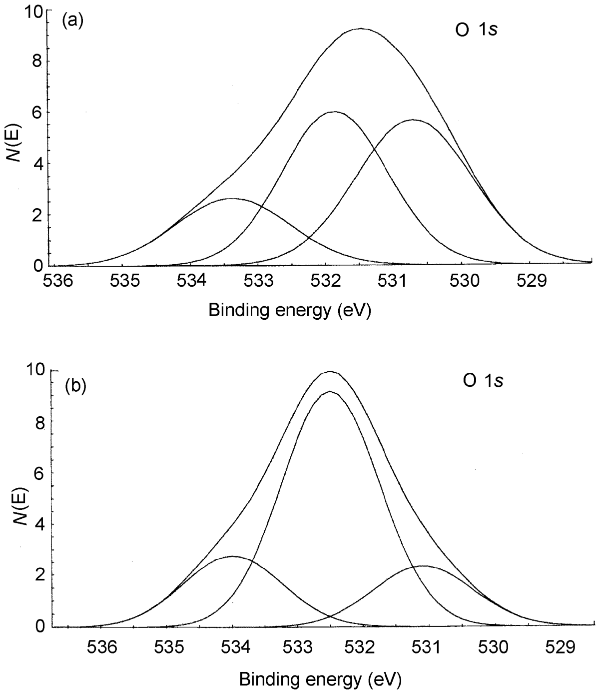

Fig.7 The O 1*s* patterns on the surface after high pressure hydrogen-permeating. (a) 20%SiC-C sample; (b) 70%SiC-C sample.

4 Conclusions

The analyses of AES and XPS have been used for the ion beam mixed SiC-C films with different content of SiC compound after high pressure hydrogen permeating. The following conclusions may be drawn from the study described above:

1. After high pressure hydrogen permeating, hydrogen can react with the elements carbon of the SiC-C films to form hydrocarbon such as CHx group as well as react with oxygen contamination to form such a configuration of O-CH_2.

2. High pressure hydrogen permeating can lead to the formation of silicon oxides. In addition to SiO_2, the XPS analyses of Si 2*p* with C 1*s* confirmed that sub-oxide like SiO_y was also formed.

3. It is difficult to distinguish the behaviors of carbon. Does the carbon belong to element carbon of the film or adsorbed carbon or carbon out from SiC? We do not know. In fact, it is impossible to investigate behaviors of the SiC-C samples with different SiC concentration by XPS and AES analyses only. But it is true that carbon with much high chemical activity seems easy to react with hydrogen, and high pressure hydrogen permeating at high temperature could induce the activity of carbon.

4. Using AES and XPS to check the bonds of silicon with hydrogen seems also very difficult.

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