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Journal of Nuclear Materials 321 (2003) 152–157
journal of nuclear materials
www.elsevier.com/locate/jnucmat

Study in chemical bonding states of SiC films before and after hydrogen ion irradiation

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Received 20 January 2003; accepted 14 April 2003

Abstract

SiC films on stainless steel prepared by ion beam mixing were irradiated by hydrogen ion beam with an energy of 5 keV and a dose of 1×10^{22} ions/m^2. The X-ray photoelectron spectroscopy (XPS) was used for characterization of chemical bonding states of C and Si elements in SiC films before and after hydrogen ion irradiation in order to study the effect of hydrogen ion irradiation on SiC films and to understand how the chemical sputtering processes of carbon in SiC films takes place.

1. Introduction

The conditions existing in a fusion reactor provide the materials engineer with a great challenge. Some of the conditions include high heat fluxes and high erosion rates due to energetic hydrogen isotope ion fluxes. SiC is a candidate material for the first wall of magnetic confinement fusion devices since it is a refractory material with good thermal conductivity and thermal shock resistance. As a first wall material, SiC would be subjected to bombardment with energetic particles from the plasma [1–3].

Although low atomic number (Z) assures that radiation losses would be minimized if Si or C particles entered the plasma, there is still a problem. It is hoped that the erosion problem can be minimizes by selecting materials that have low hydrogen solubility and that do not chemically react with hydrogen isotope or at low rate if do. In our work, we prepare SiC films on stainless steel as plasma facing coatings. Therefore it is of interest to study the process of hydrogen behaviors in SiC and to understand the effects of H particles bombardment on SiC. In this paper, we report the study in chemical bonds between the elements in the prepared films before and after hydrogen ion irradiation.

It is found that the damage induced in SiC by hydrogen ion irradiation could trap H [4–7]. Several authors conclude according to the results of desorption and Raman spectroscopy that H is bonded chemically to Si as well as C. In addition, it is also found that carbides exposed to the energetic hydrogen are more easily sputtered than those of metals by chemical reaction, where low Z materials that contain carbon atoms are known to produce methane by bombardment with hydrogen ions. But, up to now, the procedural details of chemical sputtering for carbides are still not clear. There are two viewpoints, one is that hydrogen ion bombardment may bring about preferential sputtering of silicon atoms for SiC, hence chemical sputtering of carbon then happen where activated carbon species react with hydrogen to form hydrocarbon species like methane. This means that physical sputtering of silicon for SiC happens first, chemical sputtering of carbon then takes place. The changes of the surface composition by hydrogen ion bombardment lead to chemical sputtering of carbon for carbides [8]. Another viewpoint is that hydrogen ions transfer sufficient energy to carbide

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doi:10.1016/S0022-3115(03)00238-1

molecules to decompose them by bombardment, and the liberated carbon atoms then react with hydrogen to form hydrocarbon molecules on the surface [9].

XPS analyses give direct information on the composition and the bonding type of the atoms in solid phases, showing chemical shifts in the binding energy of the photoelectron peaks occur when there is a change in the valence state of the bonding atoms. In order to further understand the chemical sputtering processes of carbides due to the hydrogen ion bombardment, XPS analyses were used to try to distinguish the processes described above by obtaining the composition and the shifts in binding energies of the elements on the surface of carbide films.

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. Ion beam mixing technology was used to prepare SiC films of high density and enhanced adhesion strength to the substrate by forming the transition layer between the film and substrate. SiC films were deposited by r.f. magnetron sputtering on the stainless steel substrates. 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 films with a thickness of about 30 nm were then bombarded at room temperature with 40 keV Ar^+ ion and a dose of $(1–5) \times 10^{16}$ ions/m^2. After that, deposition was continued to get another layer with thickness of 30 nm on the bombarded surface, and followed by Ar^+ bombardment with the same condition as first. Such a process was repeated until the thickness of SiC films was about 200 nm [10]. The pressure during ion bombardment was 4×10^{-3} Pa. After sample preparation, some of the samples surfaces were vertically bombarded by H^+ ion beam with an energy of 5 keV and a dose of 1×10^{18} ions/m^2, while the hydrogen ion current densities were maintained at less than 9 μA/cm^2. The low ion current was used to minimize the temperature increase. At the same time, a method of ion bombardment with interruption was used, where the ion bombardment was about 20 min, and the rest time was also 20 min. This process was continued to arrive at the dose of 1×10^{18} ions/m^2.

X-ray photoelectron spectra of the surface composition were obtained using KRATOS-XSAM800 surface analysis system with mono-chromatic Al Kα radiation (1486.6 eV) operating at 13 kV × 19 mA. Ar^+ ion with 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 SiC films. The vacuum in the analyzer chamber was maintained at better than 1×10^{-6} Pa.

3. Results and discussion

Fig. 1 shows the wide scan on the surface of deposited SiC film with ion beam mixing technique. This pattern was obtained for the natural surface before ion-etching, where natural adsorbed or oxidized contamination was found on the top layer within about 6 nm thickness. Some contaminations came from the residue gases such as CO, CO_2, H_2O etc. in the vacuum chamber during film deposition [11] and some from air when the samples were placed in air. It is found that apart from those contaminations, elements of the film such as C, Si as well as bombarding argon can be seen in Fig. 1. The pattern after deleting top layer by ion-etching is shown in Fig. 2. Contamination of oxygen still existed but its

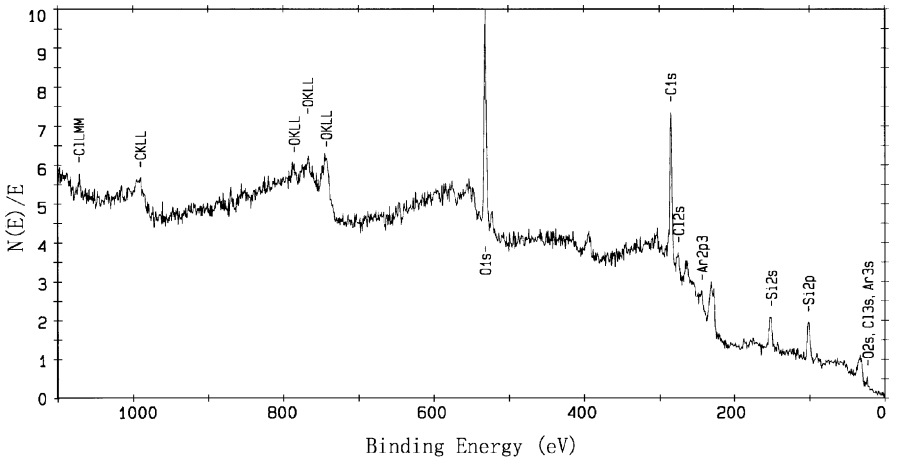

Fig. 1. XPS spectra over a wide energy range for the surface before ion-etching.

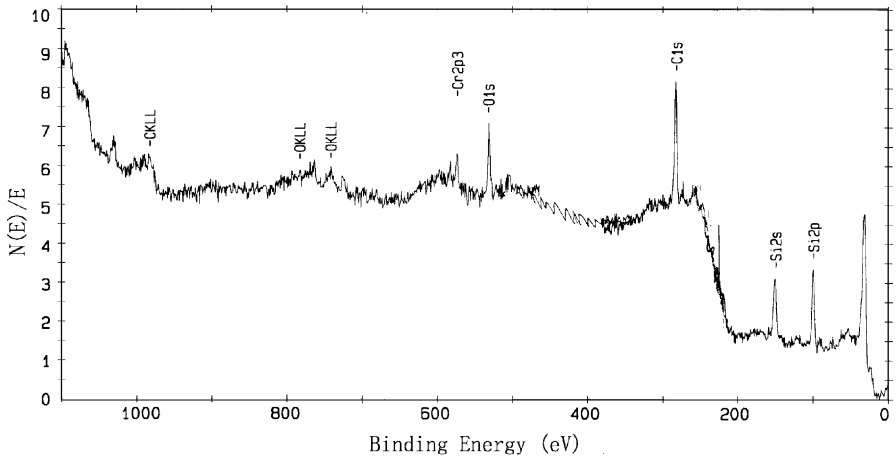

Fig. 2. XPS spectra over a wide energy range for the surface after ion-etching.

intensity was greatly decreased. The situation (not shown here) of the samples after hydrogen ion irradiation was similar to those above. But we found that after ion-etching with the same parameters and time, the intensities of oxygen on the surfaces were higher for the sample after hydrogen ion irradiation than that for the one before hydrogen ion irradiation. This means hydrogen ion bombardment induced oxygen to deeper layer in the film, or activated oxygen by hydrogen ion bombardment reacted with other element to form some oxide, which is more difficult to etch than adsorption oxygen.

Fig. 3 shows the narrow scan for C 1s on the natural surface of the SiC films prepared with ion beam mixing technique. The XPS spectrum of C 1s was resolved into three Gaussian components after subtracting the background using the conventional method as shown in Fig. 3. A peak located at 282.9 eV is due to SiC [12,13], the second one at 284.8 eV is due to adsorbed carbon or element carbon [12], the third one at 286.5 eV is due to hydrocarbon contamination [12]. In order to check the hydrocarbon, we analyzed the sample with XPS after ion-etching the contamination layer on its surface. Fig. 4 shows the C 1s pattern on the cleaned surface for SiC films prepared with ion beam mixing technique before hydrogen ion irradiation, i.e., the top contamination layer on surface was ion sputtered away. The XPS spectrum of C 1s was resolved into two Gaussian components. A peak located at about 286.5 eV disappeared. The peak located at 284.8 eV shown in Fig. 3 shifted to lower energy side at about 284.4 eV. This is really due to carbon in graphite state, and the intensity of this peak was decreased quickly due to remove of absorbed carbon. The peak at 282.9 eV in Fig. 4 is due to SiC.

Fig. 5 shows the C 1s spectra on the cleaned surface for the SiC film after hydrogen ion irradiation. This

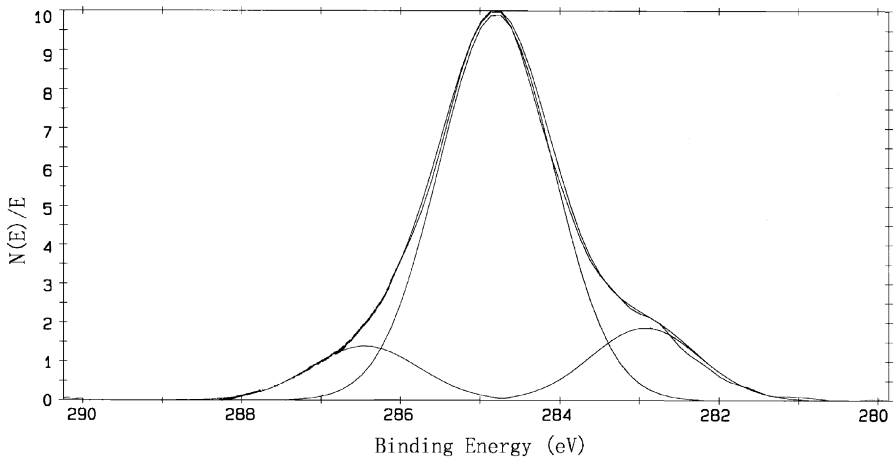

Fig. 3. C 1s patterns on the natural surface of SiC films.

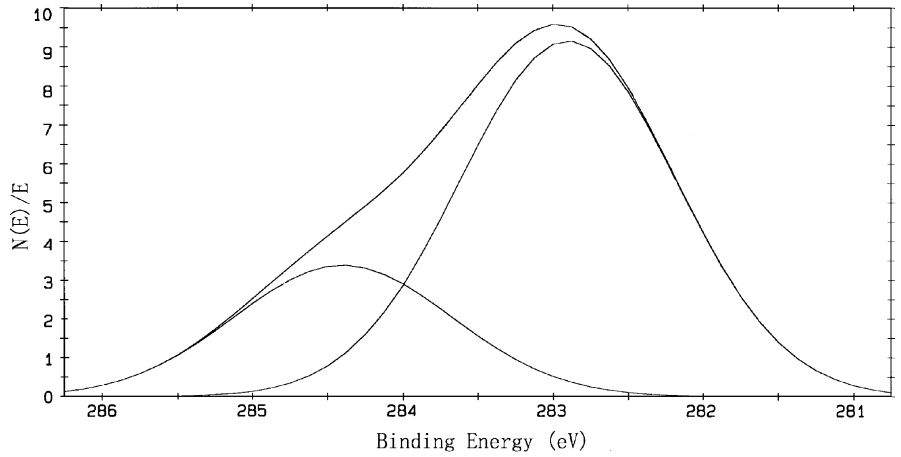

Fig. 4. C 1s patterns on the cleaned surface of SiC films.

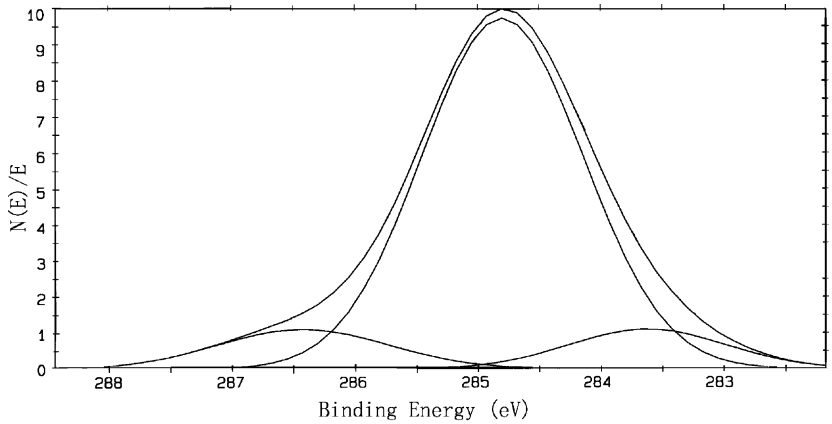

Fig. 5. C 1s patterns on the cleaned surface of SiC films after hydrogen ion irradiation.

pattern can also be resolved into three components. The one located at 283.6 eV is assigned to $Si_{1-x}C_x$ ($x > 0.6$) [13], the one at 284.8 eV to adsorbed carbon-like, possibly, to liberated element carbon with activity. And the one at 286.5 eV representing the bonds of carbon to hydrogen appeared again, signifying the presence of hydrocarbon. Based on the results shown above, it can be found for the cleaned surface before and after hydrogen ion irradiation that SiC was changed to $Si_{1-x}C_x$ ($x > 0.6$) on the surface, and the shift of binding energy for element carbon was shifted from 284.4 to 284.8 eV due to hydrogen ion irradiation.

Fig. 6 shows the Si 2p pattern on the cleaned surface of SiC films with ion beam mixing technique before hydrogen ion irradiation. It is found that the Si 2p pattern can be resolved into three components, one located at 100.7 eV is due to SiC, the other one at 102.0 eV combining with the C 1s component at 283.6 eV seems due to $Si_{1-x}C_x$ ($x > 0.6$) or C–Si–O [14] configuration. Usually, binding energy of the core-levels of atoms is sufficiently affected by their chemical environment to cause a detectable shift in the measured photoelectron energy. The binding energy of Si 2p shifted to higher energy side was due to the charging effect by defects surrounding silicon. And the third one at 103.3 eV was due to SiO_2 [15]. This means that oxygen contamination reacted with silicon to form SiO_2. Fig. 7 shows the Si 2p spectra on the cleaned surface of SiC film after hydrogen ion irradiation. It is found that this pattern can only be resolved into two components. The one located at 102.1 eV is, obviously, due to $Si_{1-x}C_x$ or C–Si–O [14] configuration like above, and another one at 103.2 eV is due to SiO_2. It seems no stoichiometrical SiC on the surface after hydrogen ion irradiation. Based on the results of Si 2p analyses, it can be found for cleaned surface before and after hydrogen ion irradiation that SiC disappeared, and the relative intensity of SiO_2 increased after hydrogen ion irradiation.

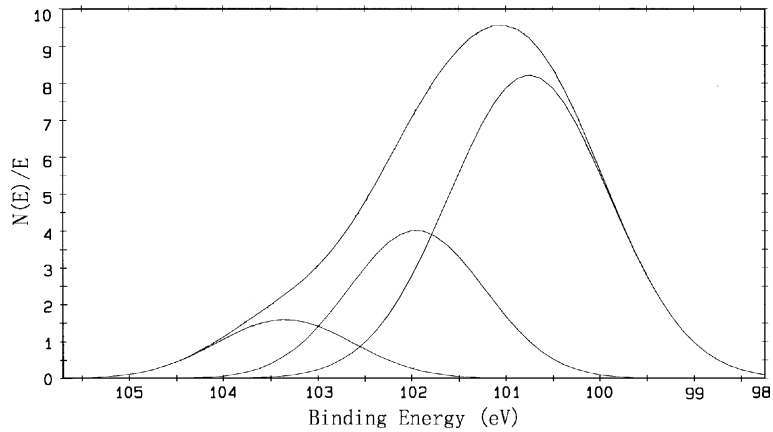

Fig. 6. Si 2p patterns on the cleaned surface of SiC films.

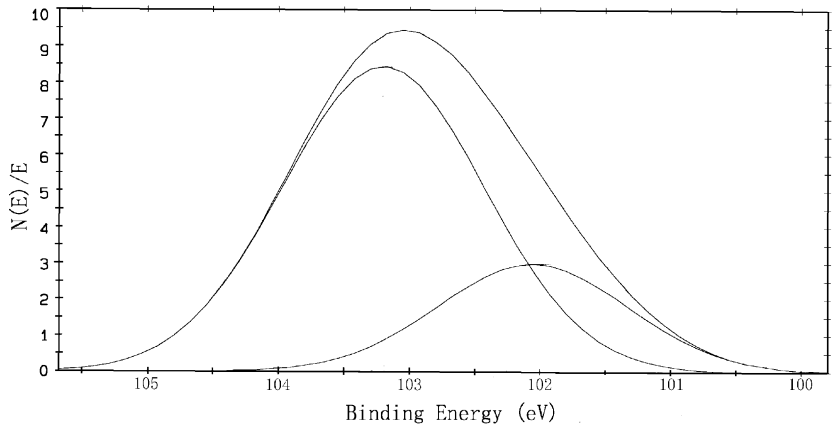

Fig. 7. Si 2p patterns on the cleaned surface of SiC films after hydrogen ion irradiation.

Now let us compare with the two samples before and after hydrogen ion irradiation. Several features can be concluded as follows:

(1) Instead of SiC, the component of $Si_{1-x}C_x$ which is a non-stoichiometric silicon carbide, appeared on the cleaned surfaces due to argon or hydrogen ion irradiation. This implies that ion bombardment can change the chemical composition on the surface of SiC films due to silicon sputtered out.
(2) The shift to 284.8 eV in binding energy of C 1s after hydrogen ion irradiation (its intensity shown in Fig. 5 is higher than that one shown in Fig. 4) means that the concentration of activated carbon increased rapidly due to hydrogen ion irradiation.
(3) For the cleaned surfaces of SiC films by ion-etching with almost the same ion sputtering parameter and time, the intensity of SiO_2 on it after hydrogen ion irradiation is much higher than that one before hydrogen ion irradiation. This means that, on one hand, more oxygen was introduced or retained during hydrogen ion irradiation, on the other hand, the liberated silicon atoms sputtered out from SiC increased due to hydrogen ion irradiation. Hence, the intensity of the peak representing SiO_2 shows the degree of the sputtered silicon atoms.

4. Conclusions

The analyses of XPS have been used for the ion beam mixing prepared SiC films on stainless steel substrate before and after hydrogen ion irradiation. The following conclusions may be drawn from this study described here:

(1) Hydrogen ion bombardment at 5 keV can cause preferential physical sputtering of silicon atoms from the surface, changing the composition on the surface of SiC films

(2) The liberated silicon atoms can easily react with oxygen forming silicon oxides, and chemical reaction between activated carbon and hydrogen form hydrocarbon species such as methane which can escape from the surfaces. This result shows that hydrocarbon species such as methane can be decreased if the activated carbon decreases. In other words, we try to decrease the sputter of silicon from SiC by energetic hydrogen ion bombardment.

Acknowledgements

This work has received financial support from the National Natural Science Foundation of China, and Foundation of the Institute of Engineering Physics of China.

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