

Study in Mechanism of Hydrogen Retention by C-SiC Films with IR

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Abstract

C-SiC films with different content of SiC on stainless steel substrate were prepared with ion beam mixing. It was found that hydrogen concentrations in C-SiC coatings was higher than that in stainless steel after H⁺ ion implantation followed by thermal annealing. Infrared (IR) transmission measurement was used to study the mechanism of hydrogen retention by C-SiC films. The vibrational features in the range between 400 and 3200 cm⁻¹ in IR transmission spectra show the Si-CH₃, Si-CH₂, Si-H, CH₂, and CH₃ bonds, which are responsible for retaining hydrogen.

1. Introduction

For operating fusion devices or the future power reactors, plasma-facing materials are subjected to high-flux particle bombardment including ions and neutrals of fuel hydrogen isotope and helium ash [1]. As a result hydrogenation leads to brittleness of stainless steel of which are made the limiters and diverters. C-SiC coating materials are adopted as candidates for plasma-facing component to protect stainless steel from hydrogen brittleness. In order to study hydrogen behavior in plasma-facing coating materials, there have been developed several techniques to measure it. Infrared (IR) spectroscopy is widely used since it is nondestructive and easily performed and yields information about hydrogen content and also bonding configuration. In this paper we give information on the behaviors of hydrogen in C-SiC films with IR analyses, and try to study the mechanism on retaining hydrogen in C-SiC films prepared with ion beam mixing [2].

2. Experimental

Substrates of 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 is used to prepare C-SiC films with high density and enhanced strength of adhesion to substrates by forming the transition layer between film and substrate. C-SiC films with different content of SiC were deposited by r. f. magnetron sputtering on the substrates of stainless steel or NaCl crystal at room temperature. 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 for the discharge. The deposited C-SiC films with a thickness of about 30 nm were then bombarded with 40 keV Ar⁺ ion at a dose of $1 \sim 5 \times 10^{16}$ ions · cm⁻² at room temperature. After that, deposition was continued to get another layer with thickness of about 30 nm on the bombarded surface, and followed by Ar⁺ bombardment under the same condition as the first. Such a process was repeated up to that the thickness of C-SiC films was about 200 nm at last. The base pressure during ion bombardment was 4×10^{-4} Pa. After sample preparation, some surfaces of them were vertically implanted by H⁺ ion beam with

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an energy of 5 keV at a dose of 1×10^{18} ions cm^{-2} , while the hydrogen ion current densities were maintained at less than $9 \mu\text{A}/\text{cm}^2$. In order to decrease the sample temperature during ion beam implantation, a limited ion current as low as possible was used, and at the same time, a method of ion implantation with interruption was used, where the ion implantation was about 20 minutes and the rest time was also 20 minutes. This processes continued to arrive the dose of 1×10^{18} ions $\cdot \text{cm}^{-2}$. The vacuum during hydrogen ion implantation was about 4×10^{-4} Pa. Some of hydrogen ion implanted samples were annealed at 373 K for 1h in the vacuum furnace, where the vacuum was about 4×10^{-3} Pa.

Infrared (IR) transmission measurements over the region 400 to 3200cm^{-1} were made using Fourier transformed infrared spectroscopy (FTIR) with a Nicolet FTIR spectrometer.

3. Results and Discussion

The samples of stainless steel 1Cr18Ni9Ti with or without C-SiC coatings were implanted by hydrogen ion beam and followed by thermal annealing at 373 K for 1 h. SIMS depth profiles for the resulting samples showed that much more adsorbed hydrogen species are piled on the top surface of the C-SiC coated stainless steel, while there is no such a phenomenon in the stainless steel without C-SiC coating [3]. This indicates that C-SiC coatings can play a role of a hydrogen barrier. In other words, C-SiC coatings can prevent hydrogen from entering stainless steel substrate.

In order to study the mechanism of hydrogen retention in C-SiC coatings, infrared spectroscopy analysis was used. In this situation, we focused on the relationship between hydrogen and components of the bulk of C-SiC coatings, i. e., between hydrogen, C and Si elements of the coatings. NaCl substrates were selected because IR transmission spectra are easier to obtain. Fig.1 shows the IR transmission spectra of the ion-beam-mixed C-SiC films with different SiC content before H^+ ion implantation.

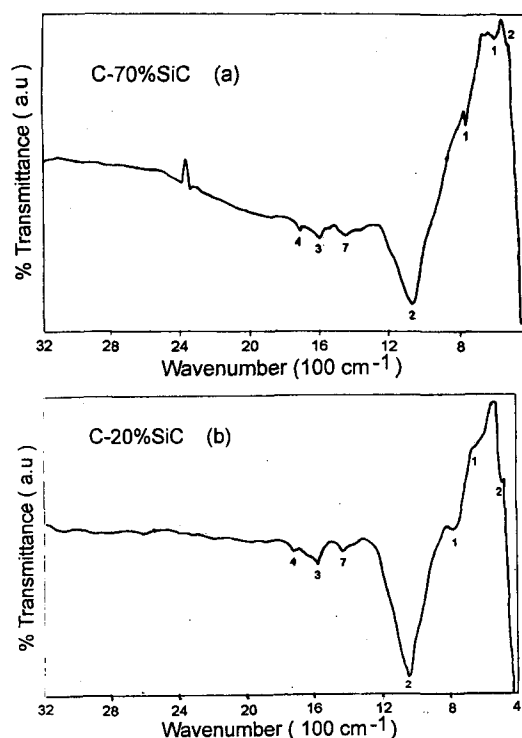


Fig. 1. Infrared spectra for the C-SiC films before H^+ ion implantation: (a) the C-70%SiC film (b) the C-20%SiC film.

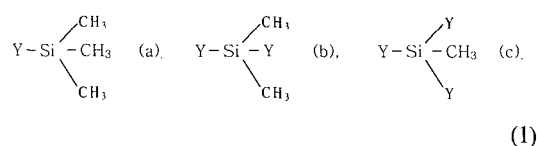
It is found in Fig.1(a) for the sample with 70%SiC component that the bonds related to oxygen at 528 and 1080cm^{-1} are due to the SiO_2 [4]. The absorption at 1720cm^{-1} indicates the presence of C=O bonds. The band at 1445cm^{-1} which is attributed to Si-CH₂ scissoring or bending modes appeared in Fig.1(a) for the sample before H^+ ion implantation. The situation in Fig.1(b) for the sample with 20%SiC component is similar to those in Fig.1(a) for the sample with 70%SiC component. It is known that the residual gases such as CO, CO₂, H₂O, and etc. are always present in the vacuum chamber during sample preparation. Such substances may be dissociated due to energetic ion bombardment, active oxygen and hydrogen may move into the film to form those bonds mentioned above [5]. The main components of SiC can be seen at the bands of 752cm^{-1} in Fig.1(a), which is assigned to the Si-C stretching mode. In Fig.1(b), the band at 766cm^{-1} showing Si-C stretching

shifts to higher energy side due to the increase of carbon content [6] in comparison with that in Fig.1(a). The bands at 1598 cm^{-1} in Fig.1(a) for the C-70%SiC films and at 1577 cm^{-1} in Fig.1(b) for the C-20%SiC films are due to C=C stretching mode [7].

The samples of C-SiC films with different content of SiC component after H^+ ion implantation at 5 keV with a dose of 1×10^{18} ion. cm^{-2} and annealing at 373 K for 1 h were also analyzed with infrared spectroscopy, and the result is partly shown in Fig. 2. We can find in the IR transmission spectra that the bands in the Fig. 1 also exist in the infrared spectra of C-SiC films after H^+ ion implantation, i.e. contamination from residual gases still exist in the films. There was a certain decrease in the intensities of Si-O bonds and increase in the intensities of Si-CH₂ scissoring or bonding modes due to H^+ ion implantation. In addition, the intensities of C=C stretching mode for the C-20%SiC films are still higher than that for the C-70%SiC one, showing the different carbon content in the films.

Now let us focus on the bands related to hydrogen in the films due to H^+ ion implantation.

Figure 2 shows the main bands related to hydrogen in the infrared spectra for the C-SiC films with different SiC content after H^+ ion implantation and annealing at 373K for 1h. The bands at 924 cm^{-1} for C-70%SiC films is due to rocking or wagging vibrations of CH₃ groups attached to silicon [8]. The possible groups giving rise to the Si-CH₃ rocking vibration are



where Y is either Si or C not attached to three hydrogen atoms. The band at 904 cm^{-1} for the C-20% SiC films shifts to lower wave number compared with that for the C-70%SiC films. This phenomenon is consistent with the shift in frequency according to the electro-negativity of C atom [9]. The symmetric bond-bending mode of Si-CH₃ configurations is observed at 1246 cm^{-1} for the C-70%SiC films and at 1241 cm^{-1} for the C-20%SiC ones [9]. The bands at 2000 cm^{-1} for the C-70%SiC and at 2058 cm^{-1} for the C-20%SiC films are due to Si-H stretching mode. The configurations are:

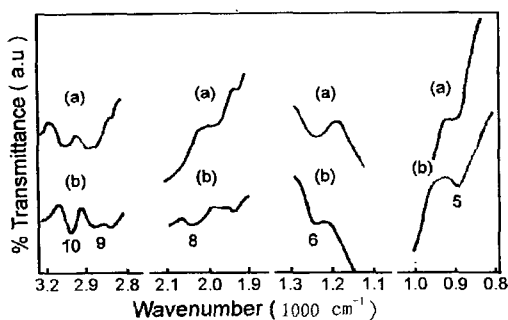
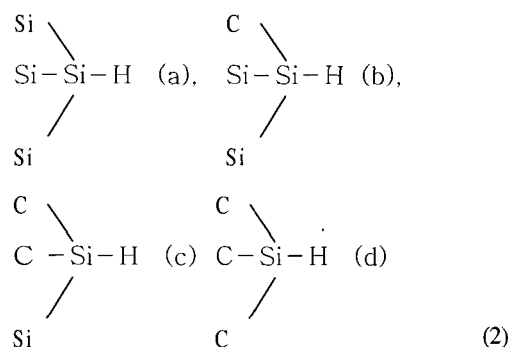


Fig. 2. Selected bands in the infrared spectra for the C-SiC films after H^+ ion implantation: (a) the C-70%SiC films (b) the C-20%SiC films

The band at 2000 cm^{-1} is due to Si-H stretching mode with no carbon attached to the silicon, while a shift of Si-H stretching mode to 2058 cm^{-1} is due to inductive effects of carbon atoms on the Si-H bond. In other words, the stretching frequencies of the three types of Si-H bonds depicted in (2)(b)(c)(d), seem to be degenerate. The bands at 2852 cm^{-1} for the C-70%SiC and at 2838 cm^{-1} for the C-20%SiC are attributed to CH₂ symmetric stretching modes [10]. The bands at 2928 cm^{-1} for the C-70%SiC and at 2922 cm^{-1} for the C-20%SiC are due to CH₃ anti-symmetric stretching

Table 1 Assignment of the IR bands in Fig. 1. and Fig. 2.

| Number | Wavenumber (cm ⁻¹) | C-20%SiC films | | C-70%SiC films | | Vibration mode |
|--------|-----------------------------------|---------------------------------------|--------------------------------------|---------------------------------------|--------------------------------------|---|
| | | Before H ⁺ implantation | after H ⁺ implantation | before H ⁺ implantation | after H ⁺ implantation | |
| 1 | | 766 | 727,746 | 752 | 704,754 | Si-C stretching |
| 2 | | 568 | 570 | 528 | 560,576 | SiO ₂ |
| | | 1045 | 1038 | 1080 | 1041 | |
| 3 | | 1577 | 1599 | 1598 | 1572 | C=C stretching |
| 4 | | 1721 | 1723 | 1720 | 1722 | C=O stretching |
| 5 | | 0 | 904 | 0 | 924 | Si-CH ₃ rocking or wagging |
| 6 | | 0 | 1241 | 0 | 1246 | Si-CH ₃ symmetric bond bending |
| 7 | | 1435 | 1439 | 1438 | 1445 | Si-CH ₂ scissoring or bending |
| 8 | | 0 | 2058 | 0 | 2000 | Si-H stretching |
| 9 | | 0 | 2838 | 0 | 2852 | CH ₂ symmetric stretching |
| 10 | | 0 | 2922 | 0 | 2928 | CH ₃ antisymmetric stretching |

modes [8,11].

The band assignments which are discussed above are given in Table 1.

4. Conclusions

IR spectroscopy was used to study the mechanism of hydrogen retainment by C-SiC films. The main conclusions of this study are given below.

- (1) Hydrogen species could be bound by Si or C in C-SiC films. It is found that there are stretching bands of Si-H, CH₂, CH₃, bending bands of Si-CH₃, wagging or rocking bands of Si-CH₃, and scissoring or bending bands of Si-CH₂. All of these bands show the dynamic behavior of hydrogen incorporation in C-SiC films. These bands are responsible for tying hydrogen in C-SiC films.
- (2) The bands are a little shifted in frequency with different content of carbon in C-SiC films. It seems that the bond frequencies are affected by composition of the C-SiC films.
- (3) Apart from the component elements of the C-SiC films, oxygen contamination from residual gases in the work chamber entered the films during film preparation. Hydrogen contamination entered the film to mainly form the bonds of Si-CH₂ scissoring

or bending mode.

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