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METALLURGICAL AND PROTECTIVE COATINGS

EROSION BEHAVIOUR OF PHYSICALLY VAPOUR-DEPOSITED AND CHEMICALLY VAPOUR-DEPOSITED SiC FILMS COATED ON MOLYBDENUM DURING OXYGENATED ARGON BEAM THINNING

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The erosion behaviour during bombardment with a 5 keV argon beam at room temperature was studied for silicon carbide (SiC) films of thickness of about 10 μm coated on molybdenum by physical vapour deposition (PVD) and chemical vapour deposition (CVD). The PVD SiC (plasma-assisted ion plating) exhibited a greater thinning rate than the CVD SiC film. Electron probe X-ray microanalysis revealed that the chemical composition of PVD SiC was changed to a composition enriched in silicon by the bombardment, and there was a notable change in its surface morphology. The CVD SiC retained its initial chemical composition with only a small change in its surface morphology. Auger electron spectroscopy indicated that silicon oxide was formed on the surface of PVD SiC by the bombardment. The greater thinning rate and easier change in chemical composition in PVD SiC could be attributed to its readier chemical reaction with oxygen due to its more non-uniform structure and weaker chemical bonding. Oxygen was present as one of the impurities in the argon beam.

1. INTRODUCTION

The first wall in a tokamak-type nuclear fusion reactor is expected to be coated with some materials with low Z (Z is the atomic number) to minimize the contamination of a confined fusion plasma with high Z impurities[1]. The coating materials are required to have a high resistivity to surface irradiation, stability under thermal cycling, a high heat shock resistance and a low evaporation rate as well as good adherence between the coating films and the substrate metals.

The system consisting of silicon carbide (SiC) as a coating material and molybdenum as a substrate satisfies many of the above-mentioned conditions[2,3]. Some characteristics of deposited SiC are expected to depend on its microstructure, which in turn would depend on the coating methods and conditions used. There are several coating methods for SiC on molybdenum, including chemical vapour deposition (CVD) techniques and physical vapour deposition (PVD) techniques; each method has its advantages and disadvantages for application to a nuclear fusion reactor. In general, PVD techniques have lower substrate temperatures than CVD techniques, which helps to prevent deterioration of the mechanical properties

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of the substrate. In addition, PVD techniques can be used for an *in situ* coating process of first-wall components. In turn, CVD techniques can yield more thermally stable films[2].

Extensive studies[4–7] of the surface erosion of metals and composites by energetic particle bombardments have been carried out. Some papers concerning the erosion behaviour of SiC by low energy ions have been published[7–16]. The dependence of the erosion behaviour on the coating conditions or methods was described in only a few papers[13–15]. We selected two representative coating methods; one is activated ion plating (one of the PVD techniques) and the other is a conventional CVD technique. We studied the erosion behaviour under argon beam bombardment of SiC deposited by various methods.

2. EXPERIMENTAL PROCEDURES

Details of the activated ion plating (one of the PVD techniques) used in the present study can be found elsewhere[3]. The sintered molybdenum substrates were polished on emery paper and ultrasonically cleaned in acetone. The silicon vapour, which was obtained from an electron-beam-melted silicon pool, and the introduced acetylene (C_2H_2) were glow discharged by an r.f. coil. The total pressure of the reactant gases was varied between 0.5 and 1.0 Pa. The substrate was heated to 500–1300 K. The chemical composition of activated ion-plated SiC depends strongly on the substrate temperature during deposition. By controlling the substrate temperature, three different chemical compositions, *i.e.* $Si_{0.25}C_{0.75}$ (at 1300 K), $Si_{0.45}C_{0.55}$ (at 1070 K) and $Si_{0.55}C_{0.45}$ (at 879 K), could be obtained. Most of the experiments were conducted on the $Si_{0.45}C_{0.55}$. The thickness of the PVD SiC coatings was about 10 μm.

The CVD coating used in the present study was described elsewhere[2] in detail. SiC was deposited by the hydrogen reduction and/or thermal decomposition of ethyltrichlorosilane ($C_2H_5SiCl_3$). The substrate temperature during deposition was between 1320 and 1570 K. The chemical composition of the deposits was nearly stoichiometric, *i.e.* $Si_{0.5}C_{0.5}$. The thickness of deposited SiC was about 20–30 μm.

Results of detailed characterization of the PVD and CVD SiC were reported elsewhere[2,3]. The PVD and CVD SiC was found to consist of α- and β-SiC. The CVD SiC was found by X-ray diffractometry, IR spectroscopy and ion mass microanalysis (IMMA) to be contaminated with a small amount of oxygen and to contain an SiO_2 phase. The contamination of deposits with hydrogen and the formation of Si—H bonds were not detected by IR spectroscopy and IMMA on either the CVD SiC or the PVD SiC. Gravimetry indicated that both the CVD SiC and the PVD SiC had nearly the theoretical density of 3.12 to an accuracy of 10%.

The chemical composition and surface morphology of the deposited SiC films were determined by Auger electron spectroscopy (AES), electron probe X-ray microanalysis (EPMA) and scanning electron microscopy before and after irradiation. Here we obtained the averaged chemical composition from the surface down to a depth of about 5 μm by EPMA using 15 keV electrons as a probe.

The deposited films were bombarded with a beam of 5 keV argon at room temperature using a saddle-field type of gun. The pressure was about 3×10^{-3} Pa

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during irradiation with a base pressure of about 5×10^{-4} Pa pumped by an oil diffusion pump with a liquid nitrogen cold trap. The ion beam current was about 0.1 mA and approximately equal amounts of the neutral argon beam irradiated the specimen surface. The beam spot diameter was 2 mm. The beam intensity was about 1×10^{15} atoms mm^{-2} s^{-1}.

The amount of erosion caused by the argon bombardment was estimated by measuring the step height at the boundary between the irradiated and unirradiated area with a surface roughness monitor. A step height of about 0.5 μm was detectable, being distinguishable from the surface roughness.

3. RESULTS

The surface morphology change caused by the irradiation is shown in Figs. 1 and 2 for PVD SiC and CVD SiC respectively. Here the PVD SiC has the chemical composition $Si_{0.45}C_{0.55}$. Before irradiation, the PVD SiC had a rather flat surface morphology with many small bumps (Fig. 1, region e). The morphology was smoothed by the irradiation to give many small and shallow hollows. Some local attacks were observed and pits, which penetrated to the molybdenum substrate, were noticed at the centre of shallow hollows on the films irradiated for more than 100 min.

The surface morphology of CVD SiC was also smoothed by the irradiation. Before irradiation, large nodules with small bumps on them were observed (Figs. 2(a)–2(c)). The small bumps on the large nodules were removed by the irradiation and the undulations of the large nodules were smoothed (Figs. 2(d)–2(f)). There was far less modulation of the surface morphology in the CVD SiC than in the PVD SiC. No local attack was observed on the CVD SiC irradiated for up to 200 min.

The thinning rate caused by the irradiation of the deposited films is depicted in Fig. 3. It was found that the thinning rate of PVD SiC was about twice as large as that of CVD SiC. The erosion rate or sputtering rate could be estimated roughly to be about $(1–2.5) \times 10^{-1}$ atoms (incident Ar atom)$^{-1}$ and $(6–8) \times 10^{-2}$ atoms (incident Ar atom)$^{-1}$ for the PVD SiC and CVD SiC respectively, assuming that both have a theoretical density of 3.12. The thinning rate of PVD Si_xC_{1-x} $(0.25 \leqslant x \leqslant 0.55)$ was found not to depend on their chemical composition.

Figure 4 shows the chemical composition change of the irradiated films. The argon irradiation did change the chemical composition of PVD Si_xC_{1-x} but did not change that of CVD SiC. EPMA revealed that the irradiation yielded the same chemical composition of about $Si_{0.57}C_{0.43}$ for PVD Si_xC_{1-x} $(0.25 \leqslant x \leqslant 0.55)$, regardless of its initial composition (Fig. 5).

AES revealed an SiO_2 film about 100–200 Å thick on the irradiated PVD SiC (Fig. 6), although no oxygen contamination was detected by EPMA (Fig. 5). Silicon in SiC gave different Auger electron spectra from those of silicon in SiO_2. After the oxidized layer of thickness 100–200 Å was sputtered off, the spectra of silicon in SiO_2 disappeared and we obtained clear SiC spectra (Fig. 6(e)). AES also revealed the change in chemical composition of PVD SiC to the side enriched in silicon. The estimated chemical composition from AES was about $Si_{0.6}C_{0.4}$ after the bombardment of the $Si_{0.45}C_{0.55}$.

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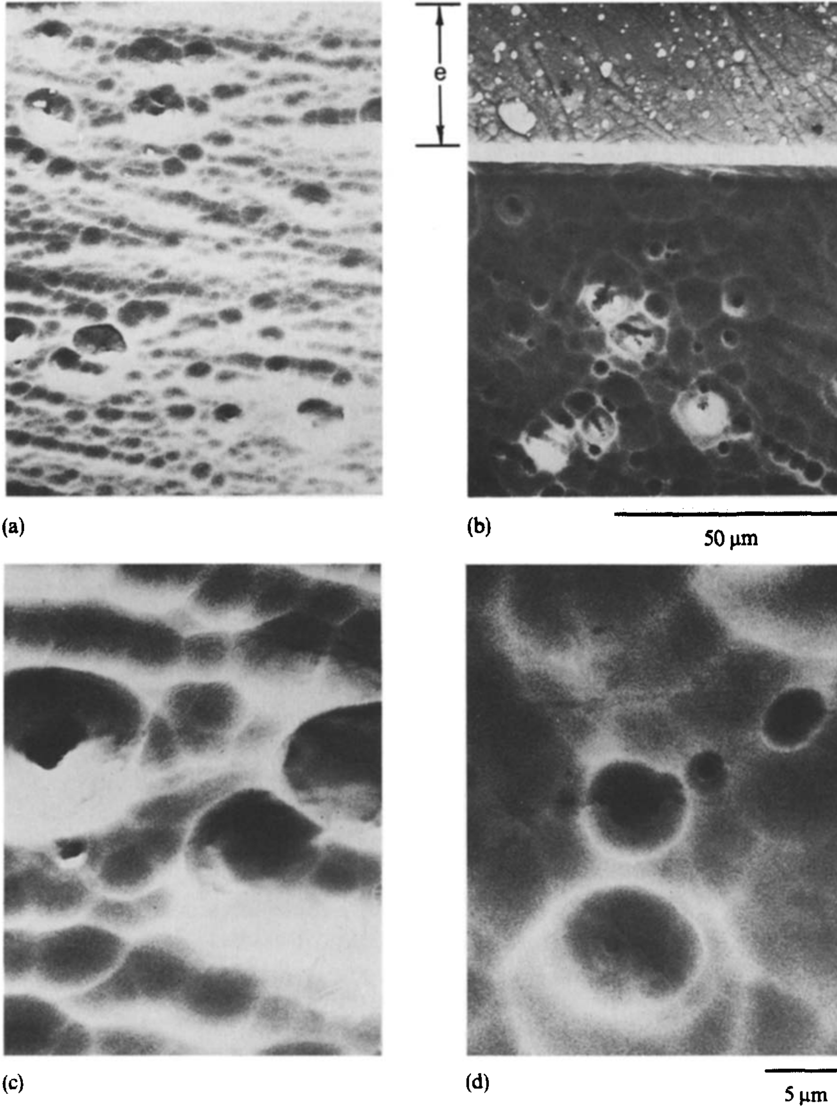

Fig. 1. Scanning electron micrographs of bombarded and unbombarded PVD $Si_{0.45}C_{0.55}$: (a) bombarded for 60 min (low magnification); (b) bombarded for 100 min (region e, unbombarded (masked)) (low magnification); (c) bombarded for 60 min (high magnification); (d) bombarded for 100 min (high magnification).

4. DISCUSSION

The Auger electron spectra (Fig. 6) revealed that the thin SiO_2 film was formed on the PVD SiC by the argon bombardment. This indicated that the oxygen was present as an impurity during bombardment. The presence of oxygen during surface irradiation is known to have profound effects on the irradiation behaviour of carbide ceramics, which was well reviewed by Rye[16] for SiC. As the physical

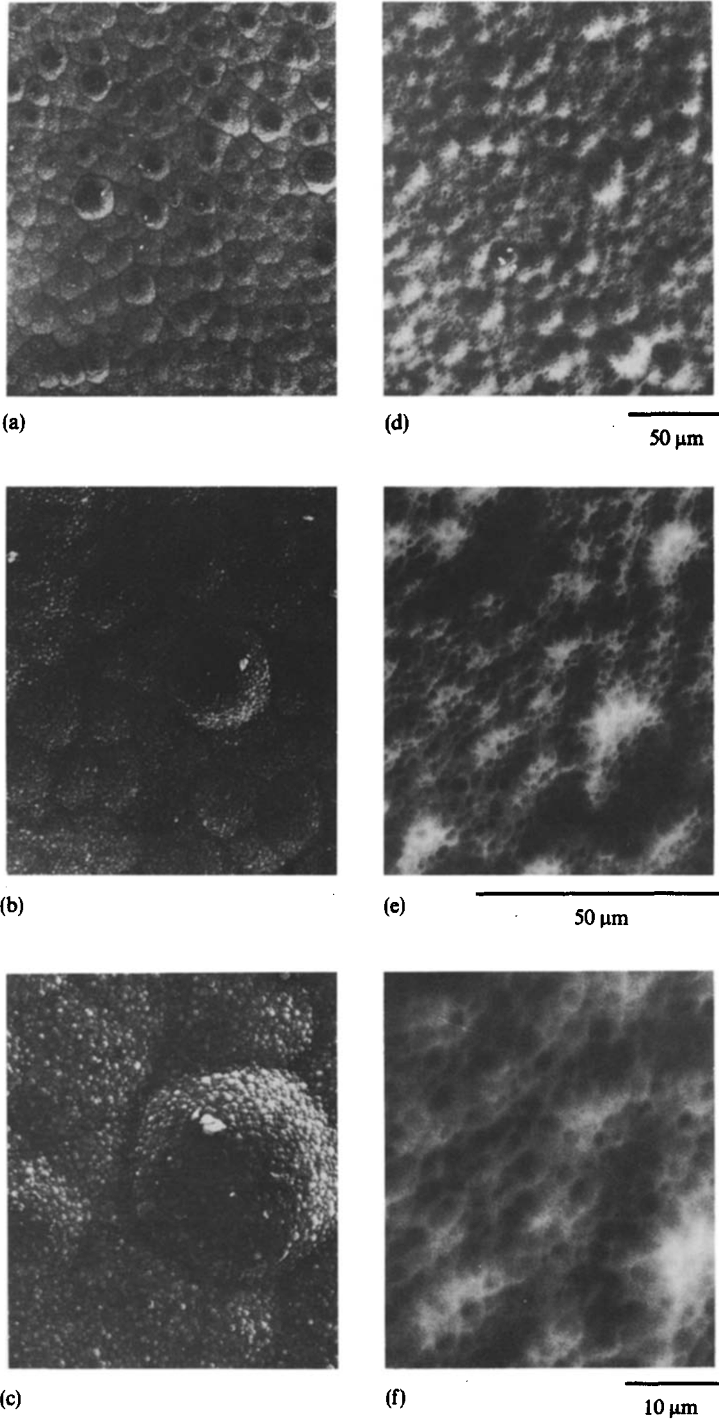

Fig. 2. Scanning electron micrographs of bombarded and unbombarded CVD SiC surfaces: (a)–(c) unbombarded; (d)–(f) bombarded.

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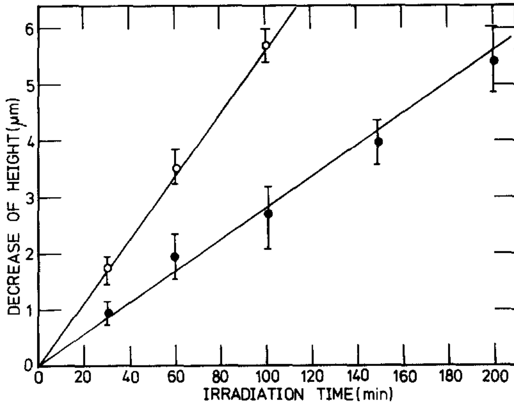

Fig. 3. Thinning rate of PVD SiC and CVD SiC caused by 5 keV argon beam bombardment as a function of bombarding time: ○, PVD $Si_{0.45}C_{0.55}$; ●, CVD SiC.

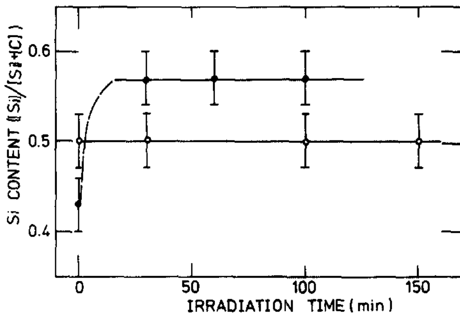

Fig. 4. Chemical composition change determined by EPMA of PVD SiC and CVD SiC caused by 5 keV beam bombardment as a function of bombarding time: ●, PVD SiC; ○, CVD SiC.

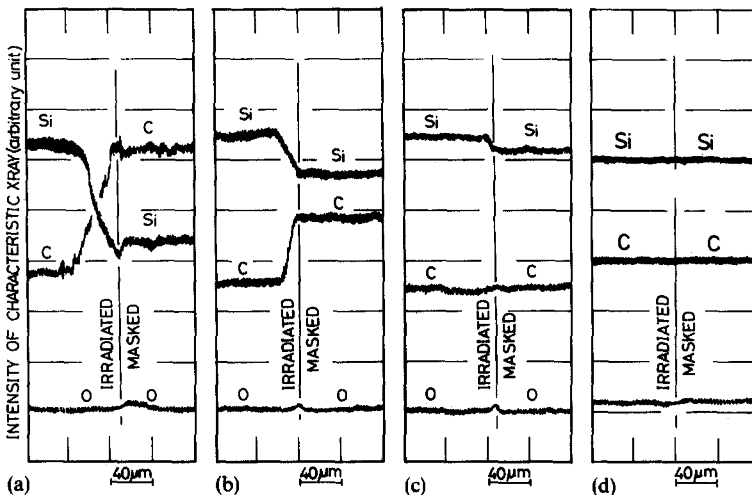

Fig. 5. Chemical composition change determined by EPMA of PVD SiC and CVD SiC after bombardment for 60 min: (a) PVD $Si_{0.25}C_{0.75}$; (b) PVD $Si_{0.45}C_{0.55}$; (c) PVD $Si_{0.55}C_{0.45}$; (d) CVD $Si_{0.5}C_{0.5}$.

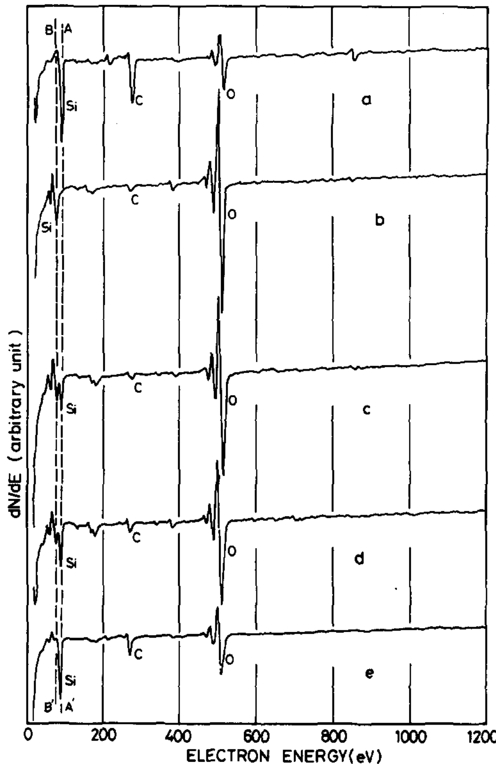

Fig. 6. Auger electron spectra of unbombarded and bombarded PVD $Si_{0.45}C_{0.55}$ (A–A′, position of the AES signal from silicon in SiC; B–B′, position of the AES signal from silicon in SiO_2): spectrum a, unbombarded; spectrum b, as bombarded; spectrum c, bombarded and etched by 3 keV argon for 20 min; spectrum d, bombarded and etched by 3 keV argon for 60 min; spectrum e, bombarded and etched by 3 keV argon for 110 min.

sputtering with argon ions removes both silicon and carbon from SiC at an equal rate[5,10], the observed change in the chemical composition of PVD SiC must be due to the oxygen impurity.

The oxygen will interact with SiC to form SiO_x and CO_y, resulting in preferential removal of carbon. Sproul and Richman[17] reported preferential removal of carbon and the formation of titanium oxycarbide when titanium carbide (TiC) was sputtered by argon ions in the presence of oxygen.

The interaction of PVD SiC with oxygen in the argon beam was quite different from that of CVD SiC. The results indicated that the PVD SiC was far more severely chemically eroded by the oxygen than the CVD SiC. The thin SiO_2 film was formed on the bombarded PVD SiC and the chemical composition of the PVD SiC was altered to the side enriched in silicon by the argon beam bombardment. In contrast, the presence of oxygen in the argon beam did not seem to affect the erosion behaviour of CVD SiC, where the physical sputtering seemed to be dominant. The estimated sputtering rate of CVD SiC was (6–8) $\times 10^{-2}$ atoms (incident Ar atom)$^{-1}$, which agreed well with that reported by Mohri *et al.*[8]

The difference in reactivity with the oxygen is due to the difference in

characteristics between the PVD SiC and the CVD SiC. The PVD SiC, being deposited at a relatively low temperature and with a high deposition rate, probably has some chemically unbound silicon and carbon. The chemically unbound silicon and carbon will react easily with oxygen, resulting in a much higher erosion rate than that for the CVD SiC with the oxygenated argon beam.

The unbound silicon easily forms an SiO_2 film as observed by AES. The SiO_2 film was reported to passivate silicon in SiC to chemical attack but not to passivate carbon in SiC [9,12,16]. On this partially passivated surface the oxygen will react with carbon and remove it from SiC preferentially, shifting the chemical composition to the side enriched in silicon. The observed local attack may be due to the non-uniform structure of PVD SiC.

The as-deposited CVD SiC was found to contain more oxygen and less chemically unbound silicon and carbon than the PVD SiC by the previous analyses[2,3,15]. The chemically well-bound silicon and carbon resist reaction with oxygen. Also, the oxygen contained in the CVD SiC makes the SiC passive to chemical erosion[15].

5. CONCLUSION

The PVD and CVD SiC films deposited onto molybdenum were compared in terms of their resistivity to surface bombardment with a 5 keV argon beam at room temperature. The PVD SiC changed its surface morphology remarkably and its chemical composition was shifted to the side enriched in silicon by the bombardment. The chemical composition of CVD SiC was changed little by the irradiation and the degree of change in its surface morphology was far less than that of PVD SiC. The erosion rate of PVD SiC was estimated to be $(1–2.5) \times 10^{-1}$ atoms (incident Ar atom)$^{-1}$, which was about twice as large as that of CVD SiC ($(6–8) \times 10^{-2}$ atoms (incident Ar atom)$^{-1}$).

Oxygen was one of the impurities in the argon bombardment environment and it played an important role in eroding the PVD SiC.

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