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Sputtering and codeposition of silicon carbide with deuterium

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Abstract

Due to its excellent thermal properties, silicon carbide is being considered as a possible plasma-facing material for fusion devices. If used as a plasma-facing material, the energetic hydrogen isotope ions and charge-exchanged neutrals escaping from the plasma will sputter the silicon carbide. To assess the tritium inventory problems that will be generated by the use of this material, it is necessary that we know the codeposition properties of the redeposited silicon carbide. To determine the codeposition properties, the deuterium plasma experiment at Sandia National Laboratories in Livermore, California has been used to directly compare the deuterium sputtering and codeposition of silicon carbide with that of graphite. A Penning discharge at a flux of 6×10^{19} D/m^2 and an energy of $\approx$300 eV was used to sputter silicon and carbon from a pair of 0.05 m diameter silicon carbide disks. The removal rate of deuterium gas from the fixed volume of the system isolated from all other sources and sinks was used to measure the codeposition probability (probability that a hydrogen isotope atom will be removed through codeposition per ion striking the sample surface). A small catcher plate used to capture a fraction of the codeposited film was analyzed using Auger spectroscopy. This analysis showed the film to begin with a high carbon to silicon ratio due to preferential sputtering of the carbon. As the film became thicker, the ratio of the depositing material changed over to the (1:1) value that must eventually be attained.

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1. Introduction

Silicon carbide is one of many materials being considered for use as a plasma-facing material for fusion reactors. Having a moderately low effective atomic number and excellent thermal properties makes silicon carbide a serious candidate for this application. As a plasma-facing material, silicon carbide will have its silicon and carbon atoms sputtered by the energetic hydrogen isotope ions and neutrals escaping from the plasma. If the silicon and carbon atoms codeposit with the hydrogen isotopes from the plasma, a large inventory of these isotopes will build up on the walls of the plasma chamber. If part of the hydrogen fuel is tritium, safety issues will result from the inventory.

The erosion rate of silicon carbide by energetic hydrogen isotopes has been investigated by several groups [1–5]. While there is some deviation in the various experimental results, the erosion rate of silicon carbide is very similar to that of carbon. Balden et al. [6–8] has examined the codeposition rate of hydrogen isotopes with silicon-doped graphite and found that the concentration of hydrogen isotopes in the codeposited films depends on the fraction of silicon in the redeposited film. For an equal amount of silicon and carbon, the H/(Si + C) ratio was determined to be $\approx$0.7 at room temperature. With the silicon carbide codeposited layer containing this quantity of hydrogen isotopes, it would appear that erosion of silicon carbide would generate an inventory of these isotopes equal to or greater than that of graphite. The purpose of this paper was to provide a

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direct comparison of the codeposition rates of silicon carbide with that of graphite for a specific exposure condition. The direct comparison was performed by first striking a Penning discharge between two parallel graphite plates in a vacuum chamber backfilled with deuterium gas. Energetic deuterons striking the graphite plates sputtered atoms from the plates out onto the vacuum vessel walls where they were codeposited with the deuterium. The experiment was then repeated with the graphite plates replaced by silicon carbide plates. While the conditions necessary to permit a Penning discharge limit the measurements to a single incident energy, and require gas pressures greater than that typical of accelerator experiments, the experiment did allow a direct comparison of the codeposition properties of the two materials.

2. Experiment

The silicon carbide and graphite samples were both POCO products. The graphite was POCO AXF-5Q, the same material as that used in the TFTR reactor. The silicon carbide (converted from graphite) was a high purity material (<5 appm impurities) with a density of 1.77 g/cm^3. The plasma used in this experiment was generated by a Penning discharge. The configuration consists of two parallel plates at equipotential that serve as cathodes. Along the rims of the plates are electrically isolated concentric shields that serve as anodes. There is a solenoid magnetic field perpendicular to the set of electrodes (see Ref. [9] for a more detailed description of the system). A small stainless steel catcher plate was located ≈5 cm from the plasma, and collected only a minor fraction of the sputtered atoms. A majority of the sputtered atoms were deposited on the walls of the vacuum vessel. The total volume of the deuterium plasma experiment as determined by pressure rise during the addition of a fixed amount of gas was 59.2 l.

During a typical experiment, the vacuum vessel was first pumped down to its base pressure ($\sim 6 \times 10^{-5}$ Pa), isolated from the pump, and then backfilled with deuterium gas to a pressure of ≈6.6 Pa. Upon initiation of the discharge, the pressure inside the chamber was monitored using a capacitance manometer. Once the pressure in the chamber was reduced by codeposition down to a pressure of ≈3.3 Pa, the discharge was terminated. The gas was then slowly pumped out of the vessel through a connecting mass spectrometer. The mass spectrometer was used to measure the impurities that had accumulated in the chamber during the discharge. In all cases, the only significant impurity in the deuterium gas was protium. Typically, the fraction of the remaining gas that was protium varied from about 20% to 40%. This recorded gas fraction was used in the data analysis to correct for the total hydrogen isotope removal rate by the plasma. It is believed that the protium was generated primarily by the decomposition of water vapor by the plasma. It must be remembered that the vacuum vessel was backfilled with deuterium, and disconnected from the pumping system for times greater than 30 min. In earlier trial experiments, the protium production had been even greater. It was only through extended baking of the vacuum vessel along with glow discharge cleaning that the protium production was lowered to these reported values. While it is believed that the protium was generated primarily by decomposition of water vapor, the ratio of hydrogen to water in the system at the end of an experiment was measured to be 200 to 1. This ratio would suggest that water vapor (or oxygen) did not play an important role in the erosion of the graphite and silicon carbide.

For all experiments, a discharge current density of either 1 mA/cm^2 or 2 mA/cm^2 was used. With the ions being primarily D_2^+ [10], the particle flux to the cathodes was either 1.3×10^{16} or 2.6×10^{16} D/cm^2 s (not including neutrals, if present). The power supply for the Penning discharge was used in the current regulated mode, but some deviation above and below the average current still occurred. As part of the data analysis, the current was averaged over the total plasma exposure time to correct for the noted deviations. During a typical experiment, the bias voltage required to maintain the set current started at ≈700 V and dropped to about 600 V by the end of the experiment. This implies an average energy of the D atoms to be ≈325 eV/D. The voltage decrease was thought to be at least partially due to the pressure decrease in the chamber during the experiment. During an experiment at the higher 2 mA/cm^2, the cathode temperature would increase from room temperature up to a maximum of ≈500 K during a typical 30 min plasma exposure. The maximum temperature was ≈100 K lower for the 1 mA/cm^2 samples.

At the end of the silicon carbide plasma exposure, the catcher plate with the collected film was removed from the system and transferred in air to a sputter Auger analysis system. Auger analysis was used to determine the relative concentrations of the elements in the redeposited film as a function of depth.

3. Results and discussion

Figs. 1 and 2 show data on pressure versus time for the graphite and silicon carbide samples. There are two curves per plot, one for each current density. Several steps were required to convert this raw pressure data into the desired hydrogen isotope removal rate versus particle fluence. The first step was to integrate the current (collected by the data acquisition system) over time to allow time on the *x* axis to be converted to particle fluence. Next, the mass spectrometer data was used to

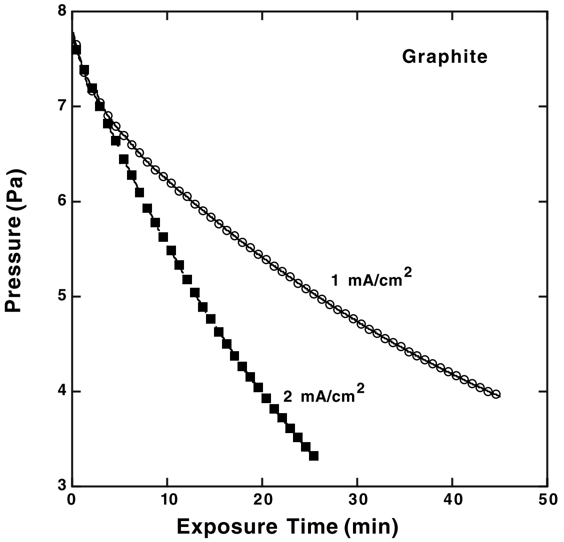

Fig. 1. Deuterium pumping by codeposition due to the erosion of graphite.

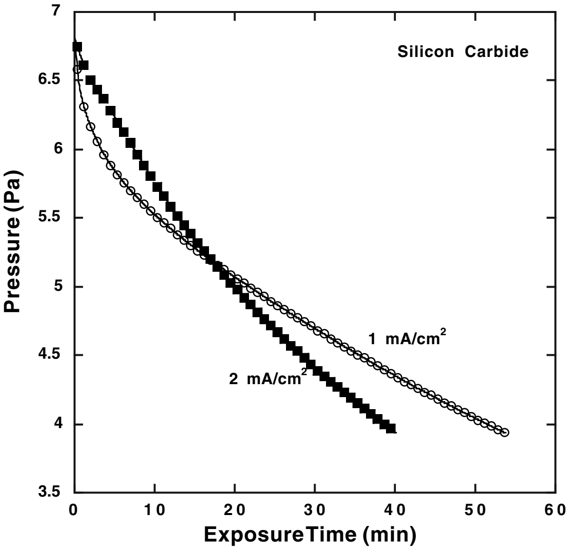

Fig. 2. Deuterium pumping by codeposition due to the erosion of silicon carbide.

calculate the fraction of the gas remaining in the chamber at the end of the experiment that was actually deuterium. Under the assumption that the sensitivity of the mass spectrometer to mass 2, 3, and 4 were all the same, measurements showed 60–80% of that gas to be deuterium. The remaining 20–40% of the gas was almost entirely protium. Because protium entered the system more or less uniformly with time during the experiment, the codeposition process also pumped some of the protium. To calculate the total amount of hydrogen isotopes pumped during the experiment (both deuterium and protium), it was necessary to solve the first order differential equation for the amount of protium in the system as a function of time. Using the slope of pressure versus time at the midpoint of the experiment to estimate the codeposition rate (estimate of the removal rate for the first order differential equation), it was possible to calculate the production rate of protium during the experiment. As an example, for the lower current experiment shown in Fig. 1, mass spectrometry showed that of the 3.95 Pa of gas pressure remaining in the chamber at the end of the experiment, 0.95 Pa was due to the addition of protium. From the solution of the differential equation, it was determined that another 0.26 Pa of protium was pumped away during the experiment by the codeposition process. Cumulatively, 0.03 Pa of protium pressure was added to the system for each minute of plasma exposure. The protium correction was applied individually to each experiment based on the mass spectrometry data for that experiment. Finally, conversion of pressure to atoms using the system volume (59.2 l) allowed the calculation and plotting of atoms removed versus fluence. The data from above is shown in converted form in Figs. 3 and 4.

The slopes of the lines in Figs. 3 and 4 are the codeposition probability of the two different materials (probability that a hydrogen isotope atom will be removed through codeposition per ion striking the sample surface). It can be seen in these figures that some of the experiments began with enhanced pumping at the onset due to additional wall pumping effects. Several of the experiments were immediately preceded by helium glow discharge cleaning of the chamber walls. A side effect of this cleaning was removal of the hydrogen from the

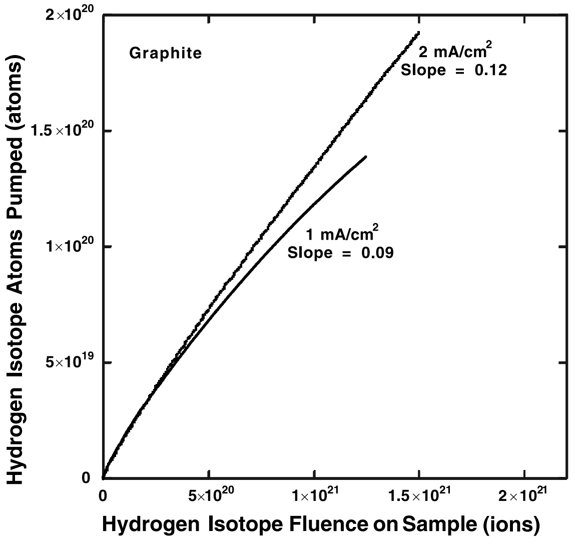

Fig. 3. Codeposition probability due to the erosion of graphite.

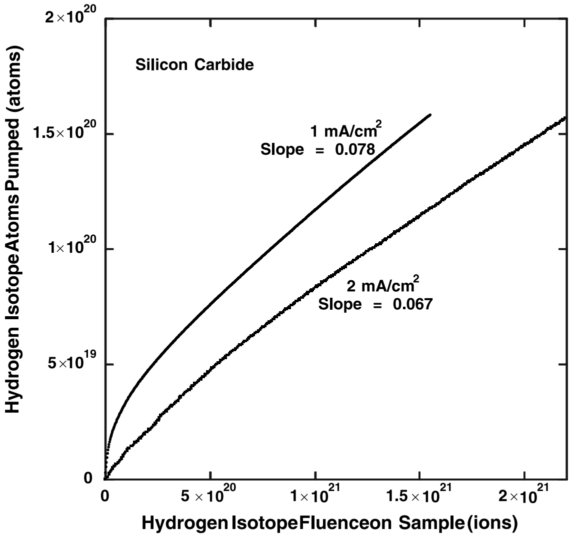

Fig. 4. Codeposition probability due to the erosion of silicon carbide.

near-surface of pre-existing codeposited layer on the walls. Once the actual experiment began, a sizable fraction of the deuterium ions striking the cathode samples were reflected out onto the walls. A carbonaceous layer depleted of hydrogen has a very high sticking coefficient for impinging hydrogen ions or neutrals. After saturation of the near surface of these layers, further pumping would occur only with additional carbon deposition. For that reason, the recorded slopes were based only on the data in the second half of each experiment.

Averaging the values of the slopes shown in Figs. 3 and 4, the codeposition probability is 0.072 ± 0.006 for silicon carbide and 0.106 ± 0.015 for graphite. The ratio of the average codeposition probability for silicon carbide to that for graphite is 0.68 ± 0.14. The implication of these results is that silicon carbide used as a plasma-facing material in a next-step fusion device will generate only about 2/3 as much tritium inventory in the codeposited layer as that for graphite under plasma conditions similar to those used in these experiments.

Prior to a discussion on the comparison of the codeposition probabilities of the two materials, the magnitudes of the codeposition probabilities themselves require consideration. By definition, the codeposition probability is the sputtering coefficient times the hydrogen to carbon ratio in the codeposited film. According to the studies of Balden and Roth [11] and Roth [12], the sputtering coefficient for 325 eV deuterium on graphite at 500 K is ≈0.03. Multiplying the sputtering coefficient by 0.4 [13–15] (the expected D/C ratio in the carbon codeposited film), a codeposition probability of 0.012 is calculated. This calculated probability is a factor of 8.8 less than the value of 0.106 determined in these experiments. While the absolute determination of sputter or codeposition rates was not the intent of this study, this difference must be addressed. In an almost identical experiment by Hsu and Causey [9], a catcher foil that subtended most of the solid angle for the sputtered carbon was placed around the Penning device. The authors used nuclear reaction analysis of the film to account for a codeposition probability of ≈0.083. Rutherford backscatter was used to verify that sufficient carbon was present on the foil to account for this amount of deuterium codeposition. Based on films found outside the catcher foil at the ends of the vacuum vessel, the authors speculated that some sputtered carbon had also escaped from around the catcher foil. Additional deposition outside of the catcher foil could easily bring the codeposition probability up to the newly measured value of 0.106. From the combination of experiments, it appears that enhanced sputtering occurs under the conditions used in these experiments. The logical explanation is that the enhanced erosion and codeposition is due to the higher gas pressures used in the experiments. Operation of a plasma in a gas at this pressure is certain to produce a significant quantity of atomic hydrogen in and around the plasma. As shown by Haasz et al. [16], the erosion rate of graphite is significantly increased when atomic hydrogen is present during hydrogen ion implantation (chemical erosion dominates the erosion process). For a [H^o/H^+] ratio of 10, the graphite erosion rate was seen to increase by an order of magnitude over that due to ions alone. While the 500 K temperature used in the experiments reported here is below the temperature for the peak production of methane, methane is still the likely hydrocarbon produced by the chemical erosion. Due to interference by OH, H_2O, HDO, and D_2O, no attempt was made to detect deuterated methane in the chamber at the termination of the plasma discharge.

As stated above, the measured sputtering coefficient for carbon is ≈0.03 [11,12]. From the work of Plank et al. [2] and Balden et al. [1], the sputtering yield of silicon carbide for the same conditions is also ≈0.03. Balden et al. [8] and Balden and Mayer [7] examined the codeposition of deuterium with silicon doped carbon. The ratio of D/(Si + C) in the collected films varied from about 0.4 to about 0.75 depending on the Si/(Si + C) ratio in the film. A value of 0.7 was determined for the case of Si/C = 1. Based on these results, silicon carbide should be sputtered and codeposit with deuterium at a rate equal to or greater than that for graphite. This calculated ratio of 1.0 or greater for silicon carbide codeposition to that of graphite does not agree with the ratio of 0.68 determined in these experiments. It is perhaps not meaningful to even compare the results of these experiments to those performed under other conditions. If one accepts the premise that enhanced sputtering is

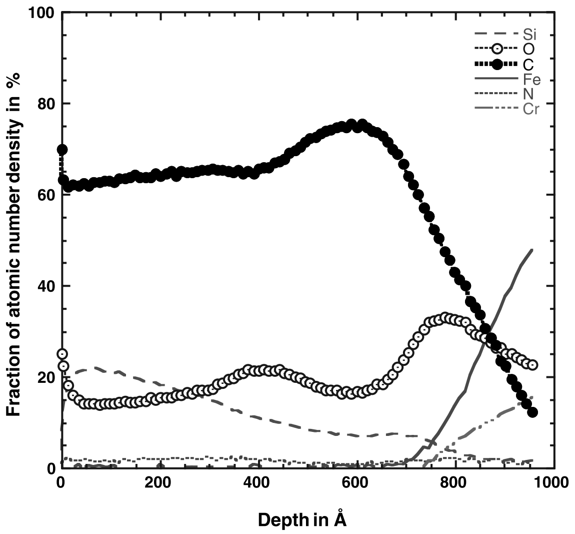

Fig. 5. Auger spectroscopy of the collected codeposited layer after the plasma erosion of silicon carbide.

occurring in these experiments, then a comparison to sputtering results dominated by physical sputtering does not make sense. Still, it is quite possible that the effective sputtering coefficients of graphite and silicon carbide by deuterium are similar when the sputtering first begins. If the surface composition of the silicon carbide changes during the experiment, then a change in the erosion rate may also occur. The sputter Auger results (see Fig. 5) suggest this did occur. In this figure, the interface between the film and the steel substrate can be identified as the area where the iron concentration drops and the carbon concentration increases. As the experiment proceeded (moving from right to left on the plot), the ratio of silicon to carbon increased. This would suggest that a similar increase in the silicon to carbon ratio occurred on the silicon carbide cathode surfaces as the experiment proceeded. The codeposition probabilities were only determined for longer times where the erosion rate of the silicon carbide had already been slowed by the buildup of silicon. The buildup of silicon on the surface is further evidence that chemical erosion is the cause or enhanced erosion, not self sputtering that would have resulted in minimal changes in the surface concentrations of the carbon and silicon.

4. Conclusions

For the conditions of 650 eV D_2^+ ions, a substrate temperature of ≈500 K, a particle flux of 1 to 2 mA/cm^2, and background deuterium gas pressures of 3.3–6.6 Pa, the codeposition probability of deuterium with silicon carbide is only 68 ± 14% that of deuterium with graphite. The measured codeposition probabilities (and the implied sputtering coefficients) for both materials are almost an order of magnitude greater than those determined at lower background gas pressures by other experimenters. It is proposed that the enhanced erosion and redeposition is due primarily to the production of atomic deuterium in and around the plasma. It is also proposed that the codeposition probability of the silicon carbide is less than that of graphite due to the buildup of silicon on the silicon carbide surface, decreasing the chemical erosion rate.

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