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ENHANCED SPUTTERING OF GRAPHITE AT HIGH TEMPERATURE

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ENHANCED SPUTTERING OF GRAPHITE AT HIGH TEMPERATURE*

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The enhanced sputtering of graphite at temperatures above 1000 K has been investigated for a variety of incident ion species and energies. Papyex graphite strips were irradiated with 35 to 150 keV H, C, O, and Ar ions in the temperature range from 300 to 1800 K, and with 0.13 to 5 keV H ions at 1800 K. Sputtering yields were determined by weight change measurements, and were compared in many cases with yields determined by in-situ ion beam analysis of collector probes. For temperatures above 1000 K, enhanced sputtering yields are found which increase with temperature to 6 to 20 times room temperature values at 1800 K. At a given temperature, measured yields for all species and energy combinations scale with the nuclear deposited energy at the surface and do not correlate with electronic losses. The low energy H measurements indicate a transferred energy threshold of ~ 5 eV for the enhanced erosion process, significantly lower than the displacement threshold energy in graphite of 30 eV. The enhanced erosion is characterized by an activation energy which varies from 0.5 to 1.1 eV with decreasing incident particle mass. The overall results, together with recently reported velocity and mass spectra of the sputtered particles, suggest a radiation-enhanced sublimation mechanism.

1. INTRODUCTION

Recent measurements (1-3) of the sputtering yield of graphite under keV ion bombardment have revealed an enhanced erosion above 1000 K which increases to 10 - 20 times the room temperature value at 2000 K. This enhanced erosion occurs for a variety of incident ion species and is not associated with the release of volatile compounds characteristic of the reactive or chemical sputtering (4) of graphite under H bombardment at 700 - 1000 K. The resulting high erosion rates seriously limit the usefulness of graphite as a high-temperature plasma-side material in fusion reactors. In this paper, we report sputtering yield measurements for H, C, O, and Ar ions at various energies between 0.13 and 150 keV on graphite targets at temperatures ranging from 300 - 1800 K. The results are compared with calculations of elastic and inelastic energy losses for the various incident conditions, and with possible models for the enhanced erosion process.

Previously reported results (2, 3) of the mass and energy spectra of the sputtered particles indicate that the enhanced erosion process above 1000 K is characterized by the near-thermal release of individual C atoms. The angular distribution of sputtered particles for grazing incidence bombardment also suggests thermal release (1). Accordingly, we refer to this process in the following as radiation-enhanced sublimation.

2. EXPERIMENTAL

The erosion measurements were performed using 35 to 150 keV H, C, O, and Ar ions from an ion implantation accelerator and 0.13 to 5 keV H ions from a high current ion source. Papyex (5)

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graphite samples approximately 4 x 20 x 0.5 mm^3 were mounted on electrical leads in a vacuum chamber and heated resistively. Sample temperature was monitored using an optical pyrometer with an absolute accuracy of ~ 20° C and a relative reproducibility of < 10° C. Each erosion measurement typically resulted in the removal of more than 100 monolayers of carbon. Ordinary thermal sublimation accounts for less than 1 % of the carbon loss for the temperature and conditions of these experiments.

For the high energy implantations, samples were annealed at 1900 K for ten minutes in 10^{-6} Torr vacuum, weighed in air using a microbalance with an accuracy of 1 ug, and sputtered at normal incidence with H, C, O, and Ar ions from an ion implantation accelerator at Oak Ridge National Laboratory. Sample temperatures varied from 300 to 1800 K and irradiation conditions were typically 1 to 10 hours at ~ 0.1 mA/cm^2 and 10^{-5} Torr. Relative erosion yields were determined in-situ from the analysis of C atoms collected on Si catchers in front of the sample using resonant backscattering (6) of 1.75 MeV H^+ ions from a Van de Graaff accelerator. The experimental geometry for these measurements is indicated in Fig. 1 and some typical resonant scattering curves are shown in Fig.2. Absolute erosion yields were determined from the weight change of the samples. Where appropriate, the weight gain associated with the implanted species was included.

At lower energies, erosion yields were determined from the weight change of samples irradiated at the high current ion source at IPP Garching (7). Samples were irradiated with H-ions at normal incidence at 1800 K for energies varying from 0.13 to 8 keV in order to investigate threshold effects in the enhanced erosion process. Irradiation conditions were generally similar to the high energy implants.

For the relative erosion measurements, uncertainties in target temperature and back-

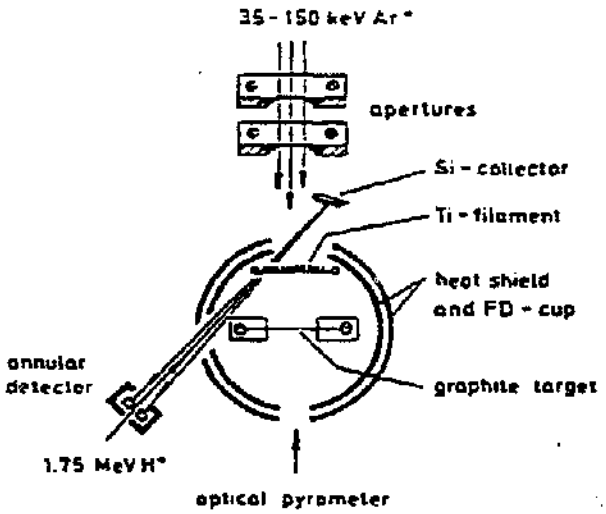

FIGURE 1

Schematic of the experimental apparatus used for the high-energy erosion measurements. The target and shield assembly could be rotated to allow in-situ ion beam analysis of the target surface as well as the collector. The Ti filament was located below the ion beams and was used to continuously evaporate Ti on a surface in another experiment.

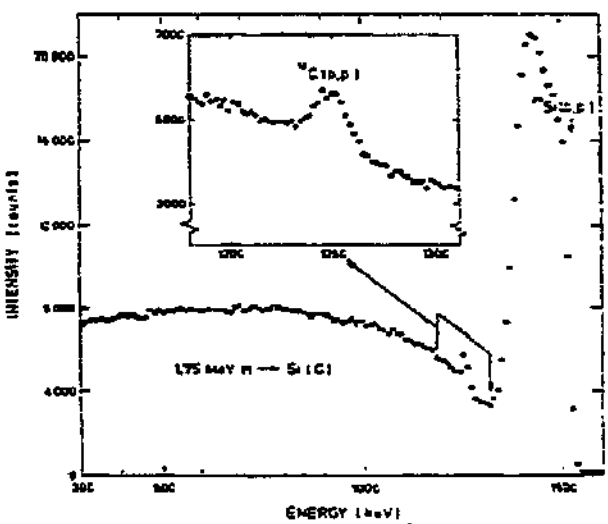

FIGURE 2

Backscattering intensity vs. energy for 1.75 MeV H ions incident on Si with approximately 10 monolayers of deposited C on the surface. The C and Si proton resonances are clearly seen. The data were taken in the geometry of Fig. 1 following 150 keV Ar sputtering of graphite.

scattering statistics or weight changes contribute to an estimated relative error of ~ 30 %. Absolute yields are determined within a factor of two. For the case of 100 keV H irradiation at 1800 K, the weight change was larger than expected from the amount of C deposited on the collector. This is attributed to the possible flaking of the graphite surface under these high energy, low erosion conditions. The radiation enhanced sublimation yield in this case was taken from the collected amount. The correspondence between collected amount and weight change was excellent for the other irradiations.

3. RESULTS

Temperature-dependent erosion yields determined in this study and in our previous related work (1) are summarized in Table I. These data indicate erosion yields for graphite at 1800 K which vary from 6 to 20 times room temperature values. The yield enhancement at 1800 K is largest for incident light ions, and exceeds the reactive sputtering peak at 900 K for hydrogen ions (1).

In Fig. 3, erosion yields are plotted vs. 1/T for incident Ar, O, C, He, and H ions. These data are consistent with activation energies for the enhanced erosion process which vary from 0.5 eV for heavy ions to 1.1 eV for low-energy light ions. Such activation energies would lead to significant thermal evaporation at temperatures well below 1000 K, assuming normal pre-exponential factors. This suggests that additional steps may be involved in the erosion process. For comparison, the activation energy for ordinary thermal sublimation of graphite is ~ 8 eV (8).

Erosion yields at 1800 K are plotted against the nuclear deposited energy at the surface for various ion and energy combinations in Fig. 4. The nuclear deposited energy represents elastic energy losses which result in atomic displacements and is proportional to the sputtering yield

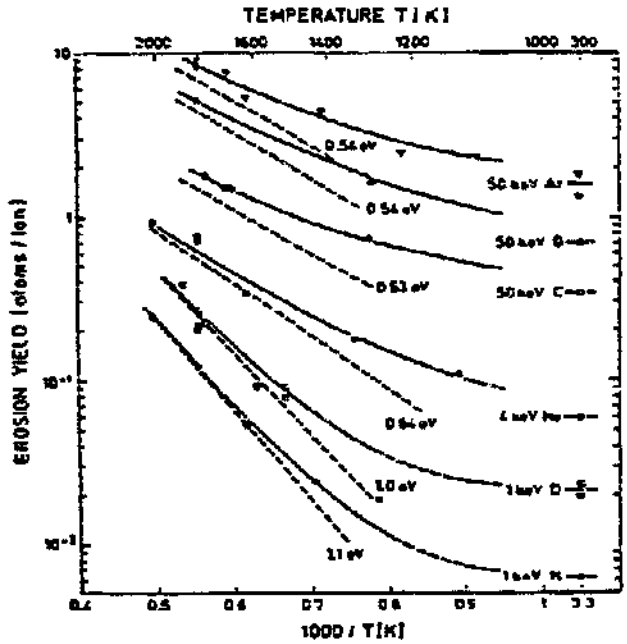

FIGURE 3

Graphite erosion yields vs. inverse temperature for several incident ion-energy combinations. Arrhenius plots and activation energies derived from subtracting the room temperature yields are also shown. The He and D data are from ref. 1.

in the cascade theory of sputtering (9). The nuclear deposited energies for Fig. 4 were calculated using the TRIM code (10) with Lindhard parameters (11) and 5 eV and 30 eV displacement thresholds. The data scale linearly with the nuclear deposited energy over a wide range of incident particle masses and energies for a 5 eV threshold. This suggests a collisional contribution to the enhanced erosion.

The same yield data are plotted in Fig. 5, this time versus the inelastic or electronic losses. This is the energy which is lost to electronic excitations including bond breaking. Again, the calculated energy losses are from TRIM with Lindhard parameters. Unlike the case of the nuclear deposited energy, there is no correlation between the erosion yield at 1800 K and inelastic energy losses.

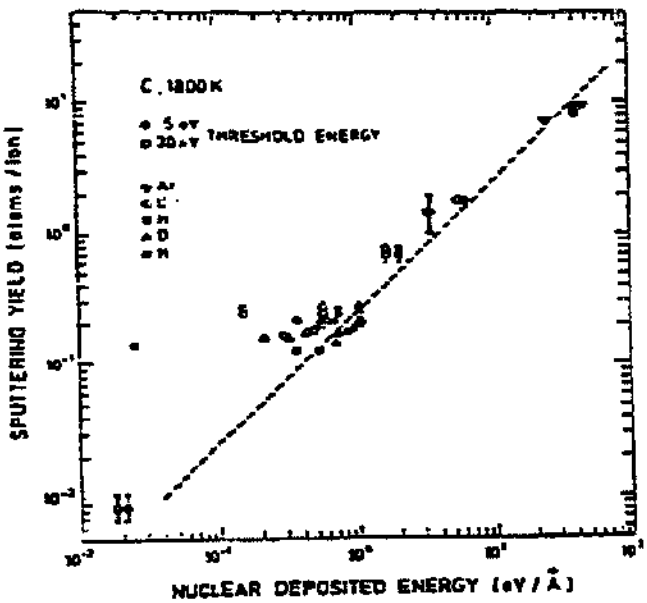

FIGURE 4

Graphite erosion yield at 1800 K for a variety of incident ions and energies vs. nuclear deposited energy at the surface. The yields scale linearly with the deposited energy for a 5 eV transferred energy threshold. The H and D data are from ref. 1.

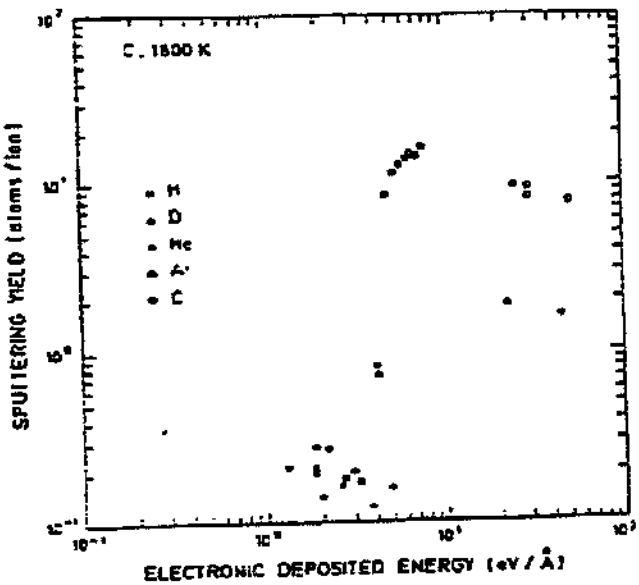

FIGURE 5

Graphite erosion yield at 1800 K for a variety of incident ions and energies vs. electronic deposited energy at the surface. There is no apparent correspondence between the electronic stopping and the measured yields. Data from refs. 1 and 2 are included.

The threshold behavior of the erosion yield at 1800 K is indicated in Fig. 6 for incident H ions. The solid and dashed curve in Fig. 6 are TRIM calculations of the nuclear deposited energy at the surface for the incident conditions assuming a 5 eV and 30 eV displacement threshold, respectively. Also shown in figure 6

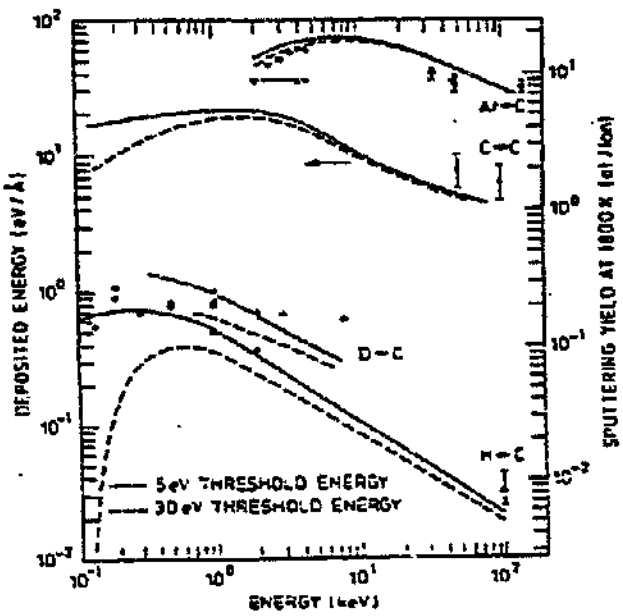

FIGURE 6

Energy dependence of the erosion yield and the calculated nuclear deposited energy for H, D, C and Ar on graphite at 1800 K. The deposited energy curve most closely reproduces the low energy data for a 5 eV transferred energy threshold. The D data are from ref. 1 and the low energy Ar data are relative yields from ref. 2 which have been normalized to the deposited energy curve in order to compare the energy dependences.

are similar data and calculations for Ar, C and D ions on graphite. All of the energy-dependent data scale approximately with the deposited energy. The low-energy H measurements clearly suggest that the enhanced erosion process is characterized by a displacement threshold near 5 eV, comparable to the threshold for room temperature sputtering of graphite (7).

Additional measurements were made of the Ar sputtering of graphite at 1800 K in the presence of an evaporated Ti flux. Preliminary results indicate that the erosion yields were not significantly affected until steady-state coverage reached approximately one monolayer. At this point, yields increased somewhat perhaps due to the increased nuclear stopping at the surface associated with the Ti atoms and then eventually fell to levels expected for TiC at higher coverages. These results are presently being interpreted and will be included in a future publication (12).

Many of the graphite samples used in these studies were examined in the scanning electron microscope following irradiation. These examinations revealed surface morphologies which were consistent with the accumulated nuclear deposited energy for a particular sample. For the highest damage levels, these morphologies were strongly convoluted with sufficient surface roughness to blacken the irradiated spot. There is no evidence that this accumulated damage influences the radiation-enhanced sublimation process.

4. DISCUSSION

There is a considerable body of evidence which suggests that the enhanced erosion of graphite under ion bombardment above 1000 K is a radiation-enhanced sublimation process. Previous studies have found that the released particles are individual C atoms (2) with a near-thermal velocity distribution (3) and an emission spectrum which is approximately cosine for bombardment at grazing incidence (1). Sputtered particles would have energies in the 5 eV range, and a sputtered flux would peak in the forward direction for grazing incidence bombardment. On the other hand, thermal evaporation is characterized by the release of carbon dimers and trimers with approximately ten times more relative abundance than the radiation enhanced process (2). These results point to a radiation enhanced sublimation process which is different from normal evaporation.

The present results further clarify the importance of radiation damage in the process. The enhanced yields are proportional to the nuclear deposited energy at the surface over a wide spectrum of incident ion energies and masses. Such a correspondence does not exist between the enhanced yields and inelastic losses. The displacement of near surface atoms is therefore a critical step in the process.

The energy dependence of the enhanced erosion at low energies indicates a transferred energy threshold for the process of $\sim$ 5 eV. This is much lower than the generally accepted displacement threshold energy in bulk graphite of 30 eV (13). This suggests the formation of a surface defect with a much lower threshold energy than would be characteristic of bulk interstitials. The relatively low activation energy of the enhanced erosion process in comparison with its high initiation temperature suggests that the C release may be controlled by the difference in activation energies for the release and annealing of this surface defect (1). Such a model can reproduce the observed yields using reasonable pre-exponential factors and surface defect densities.

5. SUMMARY

The enhanced erosion of graphite above 1000 K has been investigated for a wide variety of incident ion masses and energies. Erosion yields up to 20 times room temperature values have been observed at 1800 K. The results clearly indicate a collisional origin for the erosion with a transferred energy threshold near 5 eV. The temperature dependence of the erosion process is characterized by an activation energy of 0.5 to 1.1 eV. These results, taken together with earlier measurements, suggest a radiation-enhanced sublimation mechanism.

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Table I Temperature dependence of the erosion yield of graphite for various incident ions and energies. Yields for H, D, and He ions are from previous measurements (1).

	H → C (1 keV)	D → C (1 keV)	He → C (4 keV)	C → C (50 keV)	O → C (50 keV)	Ar → C (50 keV)
300 K	0.006	0.02	0.06	0.34 (0.16, 100 keV)	0.7	1.3, 1.6 (1.0, 150 keV)
770 K					1.1	
1100 K	0.023		0.11			2.3
1300 K	0.019		0.18	0.75	1.67	
1400 K	0.024					4.3
1500 K		0.09, 0.08				
1600 K	0.054		0.34			5.2
1700 K				1.5, 1.5		
1800 K	0.12 (0.008, 100 keV)	0.20	0.72	1.6 (1.8, 100 keV)	5.2	8.1, 9.1 (7.5, 150 keV) (5.2, 35 keV)
1870 K		0.38				
2010 K	0.25		0.93			

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