

Erosion of a-C:D thin films by low energy D^+ , D_2^+ , and D_3^+ ion beam irradiation*

F.W. Meyer^{1*}, P.R. Harris¹, H. Zhang¹, W. Jacob², T. Schwarz-Selinger²
and U. von Toussaint²

¹*Physics Division, Oak Ridge National Laboratory, Oak Ridge, TN 37831-6372 USA.*

²*Max-Planck-Institut für Plasmaphysik, EURATOM Association, Boltzmannstr. 2, 85748 Garching, Germany.*

We report measurements of total C sputtering yields for amorphous deuterated carbon thin films irradiated by equal velocity D^+ , D_2^+ , and D_3^+ beams in the energy range 30 – 200 eV/D. The C sputtering yields were deduced from crater volumes determined from 2-D ellipsometry scans, the known thin film C density, and the measured total number of incident D particles during the beam exposures. While our results for incident D_3^+ ions are in good agreement with mass loss measurements for D_3^+ , our results for D_2^+ and D^+ incident ions fall systematically below the D_3^+ results, indicating a significant molecular size effect. A molecular size effect has been previously found for CD_4 production during low energy impact of same-velocity D^+ , D_2^+ , and D_3^+ ions incident on ATJ graphite, which, however, was smaller in magnitude. The total C sputtering yields obtained from ellipsometry are in reasonable agreement with recently deduced total C production yields based on a mass spectroscopy approach.

JNM keywords: C0100 Carbon, C0400 Chemical Reactions, D0500 Divertor Materials, I0400 Ion Irradiation, S1300 Surface Effects.

PSI-19 keywords: Carbon-based materials, Chemical erosion, Erosion and deposition, Sputtering

PACS: 34.35.+a, 52.20.Hv, 79.20.-m, 79.20.Rf

Published in:

Journal of Nuclear Materials **415**, S125–S128 (2011).

doi:10.1016/j.jnucmat.2010.08.037

*Corresponding author address: Physics Division, ORNL, Oak Ridge, TN 37831-6372 USA

*Corresponding author e-mail: meyerfw@ornl.gov

1. Introduction

Carbon-based materials are important constituents of plasma-facing components of present and future fusion devices [1]. For this reason, the physical and chemical sputtering behavior of carbon materials has been extensively studied [2]. One area still largely unexplored is the possible difference in low energy sputtering behavior between atomic and molecular incident ions. A commonly made assumption is that the sputtering yield per atomic constituent for molecular incident projectiles at energy E is the same as that for atomic incident projectiles at energy $E/2$ and $E/3$ (for the diatomic and triatomic incident molecular ion, respectively) [2]. To test this assumption we recently compared CD_4 production per D from ATJ graphite for atomic and molecular species of the same velocity using a quadrupole mass spectrometer (QMS) approach [3]. Below ~ 60 eV/D, we found that the methane yield for incident D_3^+ ions exceeded by more than a factor of three the yield for incident D^+ ions at the same energy/D. This effect increased with decreasing energy and amounted to about a factor of two at 10 eV/D. In [3] we referred to this enhancement as a molecular size effect. For clarity, we will use the same term in this paper to denote those cases where, at the same energy/D, the sputtering yield for an incident molecular ion with “ n ” atomic constituents exceeds that for the corresponding incident atomic ion by more than a factor of “ n ”. In addition to begin observed experimentally, such enhancements have been seen in molecular dynamics simulations both for methane as well as total carbon production [3,4].

To ascertain if such molecular size effects could be observed in total C yields, we recently initiated measurements of C erosion of amorphous deuterated carbon thin films irradiated by equal velocity D^+ , D_2^+ , and D_3^+ beams in the energy range 30 – 200 eV/D. The determination of the molecular size effect in total C erosion is of significant practical interest. As divertor temperatures continue to decrease, molecular instead of atomic ions will eventually be the dominant divertor species and their collisional interactions both in the gas phase and at the divertor walls need therefore to be accurately assessed. Molecular-size-enhanced chemical-sputtering interactions could significantly impact lifetimes of C-based plasma facing materials and may have detrimental implications on T retention.

2. Experimental Approach

The experimental apparatus used in this work has been described previously [5,6]. All measurements were performed in a floating potential ultra-high vacuum chamber with base pressures in the 10^{-8} Pa range, into which decelerated ion beams from an ECR ion source were directed, as previously described [7]. The beams were well defined both spatially, as verified by a wire scanner that could be positioned in the sample plane, and in energy, as determined by auxiliary measurements of sample current vs. chamber deceleration voltage [8]. Fluxes in excess of 1×10^{15} D/ (cm²·s) were obtained at all energies in the investigated range. The deuterium ion beams impacted the sample at normal incidence.

As a model system for hydrocarbon surfaces plasma-deposited amorphous deuterated carbon thin films (a-C:D) were used. a-C:D films were deposited on 400 μ m thick, polished single crystalline silicon wafers (Si(001)) mounted at the driven electrode of an asymmetrical, capacitively coupled discharge (13.56 MHz). Film growth was monitored in-situ with interferometry. Pure CD_4 (isotope enrichment 99.5%) was used for film deposition. A gas pressure of 2 Pa and a total CD_4 gas flow of 20 sccm were used. An applied rf power of 26 W leads to a dc self-bias voltage of -300 V. Properties of a-C:H films deposited in a similar fashion have been described by Schwarz-Selinger et al. [9]. Using CD_4 as feed gas,

films with a deuterium content ($D/(D+C)$) of 35 %, refractive index $n = 2.12 - 0.12i$ at 632.8 nm and carbon number density of $8 \times 10^{22} \text{ cm}^{-3}$ are produced. Layers used in this study had an initial thickness of about 60 nm which varied across the sample by less than 2 nm. To obtain layers with identical properties, films were initially deposited on 10 cm diameter wafers that were subsequently hand cut into pieces 25 mm x 25 mm in size.

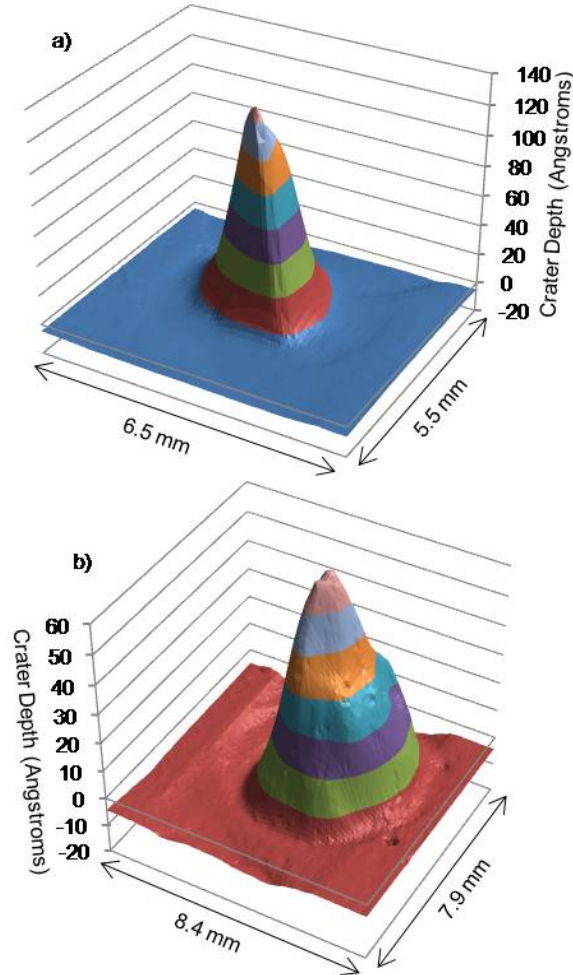


Figure 1: 2-D ellipsometry post- and pre-exposure scan differences for (a) 80 eV/D D^+ exposure and (b) 80 eV/D D_2^+ showing typical crater depth distributions; note effect of film swelling of 6-8 Å which displaces film surface to slightly negative depths, and rim at slightly negative depths resulting from surface modification by incident beam (see text).

The lateral film thickness distribution on each sample was analyzed before and after exposure to the ion beams with ellipsometry ex-situ. A Jobin Yvon PZ 2000 equipped with an automated sample stage was used to map the surface with a micro spot size of $10 \times 30 \mu\text{m}$ and a step width of 0.1 mm. An optical model consisting of three layers was applied to convert the ellipsometric angles into thickness. The model consisted of the Si substrate, a 2 nm thick SiO_2 interface layer and a homogenous a-C:D layer on top with constant optical properties given above. Those changes in the thin film that were related to the actual erosion were deduced by point wise subtraction of the 2D thickness distributions before and after ion beam exposure. As can be seen in Fig. 1 the ion beam produces isolated craters on the homogenous flat background surface. A feature evident in all the difference scans was a noticeable uniform swelling of the thin film. It is attributed to a slight relaxation of the film which presumably occurred during the chamber bake at about 100°C for 4 days. This standard

procedure was applied to return to a 10^{-8} Pa scale base pressure after introducing the thin film samples into our scattering chamber for the beam exposure measurements. The swelling amounted typically to 0.6-0.8 nm, compared to total film thicknesses of around 60 nm. The corresponding $<2\%$ decrease in C density was neglected in the subsequent analysis. The total eroded carbon amount of the individual crater was determined by converting the integrated crater volume with the known carbon density given above. In addition to the erosion the ion beam exposure modifies the top surface within the ion penetration range [10]. Depending on the ion energy during growth and during erosion, deuterium in the top surface can either be depleted or added which changes the optical properties. For the films used we expect an increase of the deuterium content during exposure and a top layer with a reduced refractive index compared to the bulk material. Although this leads to an apparent increase of the film thickness and therefore to an error in the absolute value of film thickness when not incorporated into the optical model, this effect can be neglected in the present analysis. Instead of using the flat surface as reference the very edge of the erosion features is used, where the ion beam intensity was still sufficient to modify the near-surface-region yet not sufficiently high to lead to appreciable erosion. This can be seen in Fig. 1 (b) as a rim-like structure around the erosion crater of slightly increased apparent film thickness. Assuming this modification occurs homogeneously throughout the crater in proportion to the local beam intensity, the error due to the modified D content then cancels out.

The measured beam currents incident on the a-C:D thin films were corrected for secondary electron emission only at the highest investigated energy of 200 eV/D, where secondary electron emission coefficients of 0.03, 0.06 and 0.1 were assumed for the D^+ , D_2^+ , and D_3^+ beams, based results for HOPG targets by Cernusca et al. [11]. All beam exposures were carried out to total accumulated D fluences of at least 10^{19} cm^{-2} . This assured that the dominant part of the erosion occurred during steady state chemical sputtering conditions. Our previous measurements of CD_4 production as function of beam fluence [5] showed that for virgin ATJ graphite, i.e. for zero initial D content, typical fluences of not more than 10^{18} cm^{-2} were required to reach steady-state near-surface D enrichment, where methane production became fluence independent. Since the present thin films were already deuterated to 35%, the beam fluences required to reach steady state conditions are expected to be substantially less than 10^{18} cm^{-2} .

The thickness information provided by the evaluation of the ellipsometry measurements before and after exposure was used to determine the net change in thickness. Before the crater volume was calculated isolated outliers were removed using a 5x5-pixel-median filter applied to the height-fields of the unexposed and exposed sample. The crater area is given by the product of the known pixel area and the number of pixels of each crater, and the crater volume correspondingly by the sum of the product of the crater pixels, the pixel area and the corresponding eroded material depth of each pixel.

A sensitive quadrupole mass spectrometer (QMS) was installed in the scattering chamber to detect the emission of deuterium, methyl radicals, and CD_4 , C_2D_2 , C_2D_4 , C_2D_6 , C_3D_6 , and C_3D_8 hydrocarbons. Using a procedure previously outlined [5], absolute production yields for these hydrocarbons could be determined by the use of calibrated leaks, and appropriately summed to provide an estimate of total carbon production yields, and compared to total carbon yield results obtained by ellipsometry or mass loss methods. Such total C sputtering yields have been previously reported [12] for D_2^+ projectiles incident on a variety of different carbon targets.

3. Results

Figure 2 shows the total carbon chemical sputtering yields determined in the manner outlined above for D^+ , D_2^+ , and D_3^+ beams incident on the a-C:D thin films in the energy range 30 – 200 eV/D. The results are also summarized in Table I. As can be seen from the figure, the present results for incident D_3^+ are in good agreement with the mass loss results of Balden and Roth [13] for the same projectile incident on pyrolytic graphite. Also evident from the figure is that, with exception of the higher energy measurement at 200 eV/D, the results for incident D_2^+ and D^+ beams are all smaller than those for D_3^+ , indicating a significant molecular size effect. Table I makes clear that, with exception of the 200 eV/D yields, the D_3^+ and D^+ sputtering yields differ by significantly more than the combined experimental error. Balden and Roth [13] showed one measurement of the chemical sputtering yield obtained using D^+ instead of D_3^+ at 60 eV/D, which gave a slightly smaller yield than any of their three D_3^+ based measurements at the same energy/D. Compared to the spread in the D_3^+ beam-based results at that energy the smaller D^+ beam-based yield was judged not to be significant, and it was concluded, on the basis of that single measurement, that there was no molecular size effect. However, when assigning an similar uncertainty to the D^+ beam induced yield as can be inferred for the D_3^+ beam induced yields\ from the spread of repeated measurements at the same energy, it could be argued that, within the combined uncertainties of their D_3^+ and D^+ results, the result of Balden and Roth for the molecular size effect at 60 eV/D is consistent with ours.

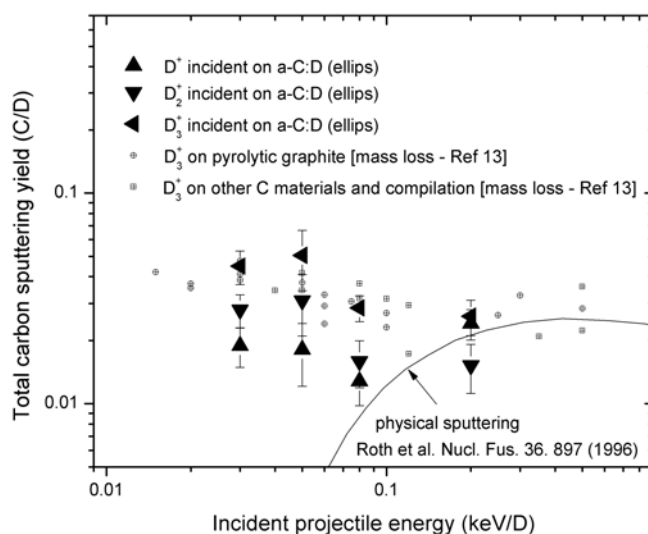


Figure 2: Total C erosion yields for D^+ , D_2^+ , and D_3^+ ions incident on a-C:D thin films as function of the energy/D; square and round crosses: total mass loss results of Balden and Roth [13] for D_3^+ incident on pyrolytic graphite. Also shown is the contribution of physical sputtering at the higher energies, as determined using the modified Bohdansky formula [13].

In Figure 3 a comparison is shown between the total C sputtering by D^+ , D_2^+ , and D_3^+ ion beams deduced for a-C:D thin films by the present ellipsometry approach and a determination of the total C sputtering by the same three ions but for ATJ graphite, using a mass spectrometry approach. The mass spectrometry results are an extension of previously reported measurements for D_2^+ [12], and were obtained after complete renormalization of our

quadrupole mass spectrometer, and re-evaluation of the relevant cracking pattern matrix required for the deconvolution analysis of the measured hydrocarbon species. The present mass spectrometry-based results for D_2^+ are in good agreement with our previously published values [12]. Equally important, and in contrast to an earlier comparison of the two approaches [13], the results for the three different D beam species are consistent with the present ellipsometry-based yields to within the $\pm 50\%$ uncertainty of the present mass spectrometry-based measurements.

Table I: Total Carbon sputtering yields for D^+ , D_2^+ , and D_3^+ ions incident on a-C:D thin films; total uncertainty contains 10% systematic uncertainty in C density determination and 5% in ion fluence determination combined in quadrature with the random uncertainty in the crater volume determination.

Ion	D^+	D_2^+	D_3^+
Energy			
30 eV/D	0.019 ± 0.004	0.028 ± 0.005	0.045 ± 0.008
50 eV/D	0.018 ± 0.006	0.031 ± 0.010	0.050 ± 0.016
80 eV/D	0.013 ± 0.003	0.016 ± 0.004	0.029 ± 0.004
200 eV/D	0.024 ± 0.005	0.015 ± 0.005	0.026 ± 0.005

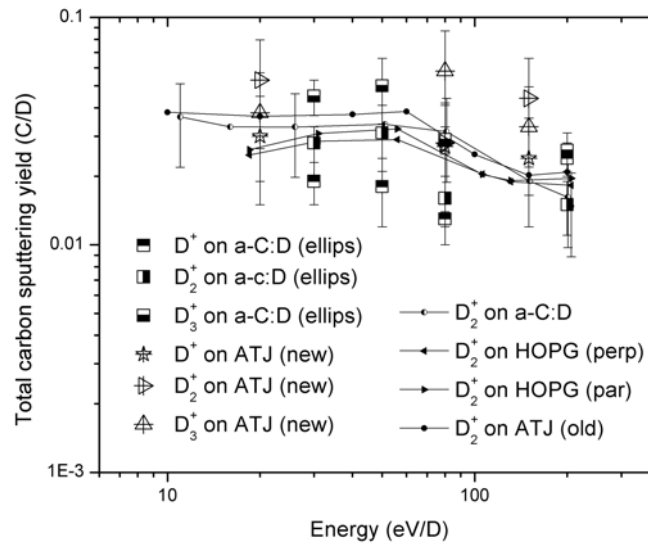


Figure 3: Comparisons of total C sputtering yields for a-C:D thin films deduced by ellipsometry and total C sputtering yields for atomic and molecular D projectiles incident on ATJ graphite based on mass spectroscopy measurements of the constituent hydrocarbons. Also shown are earlier reported mass spectroscopy measurements [12] of total C sputtering yields for D_2^+ incident on a range of different C materials: ATJ graphite, HOPG (basal planes parallel to surface), HOPG (basal planes perpendicular to surface), and a-C:D thin films.

4. Discussion

Since the chemical sputtering yields are quoted per number of incident D atoms, i.e. already divided by either 2 or 3 for incident D_2^+ and D_3^+ projectiles, respectively, the yield enhancement for incident molecular beam species at energies below 200 eV/D is significant

and noteworthy. These observed enhancements suggest that at these energies, the molecular species either survive intact, or the atomic fragments remain spatially correlated, over a substantial part of their total range in the thin films. This suggestion is supported by recent Raman measurements comparing surface damage production in room temperature ATJ graphite by low energy, same velocity atomic and molecular D projectiles [14]. By virtue of their larger mass or higher deposited energy density, the intact molecules or spatially correlated dissociation fragments are more effective in transferring energy to hydrocarbon precursors produced in the carbon target by the cumulative beam exposure, resulting in their kinetic release in room temperature targets. Thermally activated hydrocarbon release is expected to become increasingly important at elevated target temperatures [2]. If the enhanced kinetic ejection by intact molecules or spatially correlated fragments is the mechanism behind the molecular size effect, then the decreasing role of kinetic ejection processes at elevated target temperatures may reduce the molecular size effect under such conditions. Additional measurements at elevated sample temperatures are planned to further elucidate this question.

As already noted in the Introduction, the molecular size effect in the total carbon chemical sputtering yield evident in the present results is significantly larger, and extends to higher energies, than that previously observed for CD_4 production in ATJ graphite using a mass spectrometry approach. Since, as is shown in Figure 3, the mass spectrometry approach gives estimates of total C production in ATJ graphite by atomic and molecular D beams which are consistent, within the combined experimental uncertainties, with the present ellipsometry results, a plausible explanation of this apparent discrepancy is that the ejected hydrocarbon species distribution shifts to heavier hydrocarbons with increasing molecular size of the incident projectile. More detailed measurements for the complete characterization of the ejected hydrocarbon mass distributions are planned in the near future using a line-of-sight TOF system in conjunction with a more sensitive line-of-sight quadrupole mass spectrometer, in order to reduce the effect of wall collisions on the measured distributions.

The reasonable agreement between the ellipsometry and mass spectrometry results suggests that, within the combined experimental uncertainties, little significant sticking of ejected hydrocarbons appears to occur on the chamber walls prior to detection by the quadrupole mass spectrometer. This statement of course must be qualified somewhat by the fact that the ellipsometry and mass spectrometry results are for two different carbon targets. However, from inspection of Figure 3 it is evident that the steady-state yields for ATJ graphite, HOPG, and a-C:D thin film targets are quite similar ($\pm 30\%$). Subject to this qualification, from the low inferred sticking, it thus appears that stable hydrocarbon production may dominate the room temperature chemical sputtering process at low energies, and that sticking to well-passivated stainless steel chamber walls may be a smaller effect than inferred by Balden and Roth [13]. Observation of stable hydrocarbon production has been reported by Zecho et al. [15], albeit for chemical erosion of a-C:H thin films during thermal H exposure. Nevertheless, we are in full agreement with Balden and Roth's stated conclusion of the importance of line-of-sight measurements to clarify the above issues.

At the highest investigated energy of 200 eV/D, the carbon production yields for all three atomic and molecular D beams agree within the experimental uncertainties. At this energy, physical sputtering should dominate the total carbon production, as suggested by the comparison shown in Figure 2 of the measured yields and the modified Bohdanský formula [from Ref. 13]. The interpretation is therefore simplified: for the incident molecular species dissociation and rapid loss of spatial correlation of the fragments occurs very early in the total projectile ion range. This is consistent with Raman measurements of surface damage by atomic and molecular D beams, which showed no difference between D^+ and D_3^+ beams already at 125 eV/D [14]. Since the fragments separate rapidly and lose spatial correlation at

high energy, they interact with the carbon target independently via their own collision cascade; the total carbon production is thus just due to the combined sputtering of two or three separate D projectiles with the same initial velocity as the incident molecular D_2^+ or D_3^+ ion.

Acknowledgements

PRH and HZ were appointed through the ORNL Postdoctoral Research Associates Program administered jointly by Oak Ridge Institute for Science and Education and Oak Ridge National Laboratory. This research was sponsored by the Office of Fusion Energy Sciences and the Office of Basic Energy Sciences of the U.S. Department of Energy under contract No. DE-AC05-00OR22725 with UT-Battelle, LLC.

[#] Present address: Star Engineering, New Paltz, NY 12561

References

- [1] G. Federici, Physica Scripta T124 (2006) 1.
- [2] W. Jacob and J. Roth, in *Sputtering by Particle Bombardment: Experiments and Computer Simulations from Threshold to MeV*, R. Behrisch and W. Eckstein, eds., Springer, Berlin, pp. 329 – 400, 2007.
- [3] L.I. Vergara, F.W. Meyer, H.F. Krause, P. Träskelin, K. Nordlund, and E. Salonen, J. Nucl. Mater. 357 (2006) 9.
- [4] P. S. Krstic, C. O. Reinhold and S. J. Stuart, Europhys. Lett. 77 (2007) 33002
- [5] L.I. Vergara, F.W. Meyer, and H.F. Krause, J. Nucl. Mater. 347 (2005) 118
- [6] F.W. Meyer, H. Zhang, L.I. Vergara, H.F. Krause, Nucl. Instr. Meth. Phys. Res. B 258 (2007).
- [7] V.A. Morozov, F.W. Meyer, Rev. Sci. Instrum. 70 (1999) 4515.
- [8] P.R. Harris and F.W. Meyer, Rev. Sci. Instr. 81 (2010) 02A310.
- [9] T. Schwarz-Selinger, A. von Keudell, W. Jacob, J. Appl. Phys. 86, (1999) 3988.
- [10] W. Jacob, Thin Solid Films 326, (1998) 1-42.
- [11] S. Cernusca, HP. Winter, F. Aumayr, R. Díez Muiño, and J.I. Juaristi, Nucl. Instr. Meth. Phys. Res. B 203 (2003) 1.
- [12] H. Zhang and F.W. Meyer, J. Nucl. Mater. 390-391 (2009) 127.
- [13] M. Balden and J. Roth, J. Nucl. Mater. 280 (2000) 39.
- [14] H. Zhang, F.W. Meyer, H.M. Meyer III, M. J. Lance, Vacuum 80 (2008) 1285.
- [15] T. Zecho, B.D. Brandner, J. Biener, and J. Küppers, J. Phys. Chem. 105 (2001) 6194.