Methodology and Feasibility of *In Situ* Erosion Measurements in Carbon-Based Ion Thruster Grids by Laser-Induced Fluorescence

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Abstract

Carbon-based thruster grids offer erosion resistance superior to molybdenum grids. Laser-induced fluorescence (LIF) has shown promise for rapidly measuring erosion of molybdenum thruster grids *in situ*. Carbon sputtering and consequent LIF is more complicated than that of molybdenum due to two main factors: (1) carbon sputters clusters more readily than molybdenum and (2) viable atomic carbon transitions are located in the vacuum ultraviolet. Possible methods of determining carbon erosion by LIF are presented in this paper, the most promising being the excitation of the 156.1 nm carbon line via an anti-Stokes Raman shifted argon fluoride laser.

Introduction

Grid erosion is one of the primary lifetime determining factors in ion thrusters. Carbon graphite and carbon-carbon composite [1,2] have been shown to have superior erosion resistance to molybdenum grids. A real-time *in situ* erosion diagnostic for molybdenum with an absolute density calibration is currently under development at NASA Glenn Research Center [3-5]. A similar diagnostic for carbon-based grids would allow for rapid erosion-testing of carbon grids as well as direct comparison with molybdenum grids.

For molybdenum thruster grids, the erosion product is primarily ground-state molybdenum atoms [6]. The density of molybdenum atoms in the thruster plume can be measured by laser excitation at 345.6 nm followed by fluorescence emission at 550.6 nm [4,7]. Absolute numbers of molybdenum atoms can be obtained by using a resistively-heated molybdenum tube which provides a well-known number density of atoms based on the temperature of the tube.

Comparison of the fluorescence from the tube with the signal from the plume then provides a rigorously quantifiable erosion rate. There has been success by other groups in performing a relative calibration of LIF signals [8] based on known operating conditions of a well-characterized thruster; however, having an absolute rather than relative calibration allows comparison across different thruster designs and materials.

Atomic carbon transitions suitable for LIF are much more difficult to reach than is the case for molybdenum. Molybdenum starts to have suitable transitions in the UV at 390.2 nm [6], which is comfortably within the reach of a frequency-doubled dye laser; the first accessible carbon transition is 165.7 nm, well beyond the reach of simple commercial laser systems. The fluorine excimer laser is tantalizingly close to a carbon transition, but there is no tuning capability in the laser transition whatsoever. The best methods of reaching these transitions by laser is either Raman shifting a UV laser beam [9] or frequency

tripling a laser beam in a xenon gas cell [10]. Neither process is efficient, producing little power of the desired frequency. However, each referenced technique has been exploited to measure carbon sputtering by groups interested in erosion processes in Tokamak-type reactors.

Further complications arise in developing a temperature-based calibration cell for carbon comparable to the molybdenum cell. Carbon is well known [11,12] for producing dimers (C_2) and trimers (C_3) in the gas phase. In addition, the relative proportion of singles, dimers, and trimers varies with temperature and the gas-phase VUV behavior of the dimers and trimers leaves questions such as the exact dissociation energy of each species unanswered or disputed [13-16].

Most importantly, the proportion of each sputtered species (C, C_2, C_3) has not been measured when graphite is impacted by noble gas ions. Although a large number of measurements have been made to determine the sputter yield for carbon graphite [17,18] and recently for composites [19], very few works have examined the type of species that is sputtered. The conventional wisdom for metals has been that mostly ground state atoms are sputtered; however, in an experiment performed by Ahmad, *et al.* [20], measurements from impact of 40 keV argon ions showed evidence of C_2, although that group was unable to quantify the amount. Quantifiable measurements have been made for 2.5 keV cesium ion impact on graphite [21] showing greater than 1 in 10 sputtered species is a cluster. Because clusters are heavier than lone atoms, a very substantial portion of the mass lost during sputtering may be in the form of clusters even if clusters are a minority species in terms of numbers. In spite of this evidence, computer models of sputtering in graphite have allowed only for the possibility of atoms ejected from the surface [22, 23] and previous LIF measurements have assumed atomic ejection only [9,10].

This paper describes the ongoing work to determine what LIF techniques might be feasible for providing an erosion diagnostic for carbon-based thruster grids. This consists of three parts: 1) A method to quantify the relative proportion of clusters sputtered from graphite by noble gas ion impact. 2) The development of an absolute-density calibration cell for carbon so that comparisons can be made with molybdenum. 3) An evaluation of possible LIF transitions that may be used in the diagnostic tool.

Quantification Method to Determine the Relative Proportion of Clusters Sputtered from Carbon

Because the number densities of sputtered species in the ion plume are close to the absolute limits of LIF detection, determination of the relative proportion of clusters sputtered from graphite is important in terms of determining the feasibility of a carbon LIF diagnostic as well as accurately calibrating that diagnostic. Significant erosion of ion accelerator grids occurs by charge exchange ions in a relatively low energy range [24, 25]. However, the only measurements addressing clusters have occurred in the 40 keV range for Ar ions [20] and 2.5 keV for Cs+ [21], neither of which may accurately represent the behavior of Xe+ or Kr+ bombardment in an ion thruster.

In order to measure the relative proportion of each species, a test cell was constructed in which a Kr or Xe fed ion gun directly bombards a graphite sample. The sputtered species is ejected directly into a quadrupole mass-spectrometer. Although the number density of sputtered species is low for quadrupole detection, it is expected that the background would be low enough since there should not be any competing species at m/z =12 or 24. Quadrupole mass-spectroscopy is more straightforward to apply and calibrate than SNMS (Secondary Neutral Mass Spectrometry), which is the variant of SIMS (Secondary Ion Mass Spectrometry) time-of-flight spectrometry used for the cesium work [21]. The SNMS generates negative ions from the neutral species by relying on a collision of the sputtered species with a low work function metal. In any case, calibration is essential as the ionization of any cluster may lead to its fragmentation.

Three steps are necessary. 1) Determine if a quadrupole is capable of detecting the relevant species. 2) Calibrate the quadrupole for each species. 3) Determine the relative proportion of each sputtered species for a variety of energies, angles, and temperatures.

To determine if the relevant species could be detected, mass spectra were obtained at the U.S. Department of Energy Pacific Northwest National Laboratory using

an ABB Extrel 100 MHz quadrupole mass-spectrometer whose entrance aperture was located 7.5 cm from a 2.5 cm square of carbon graphite (99.98% pure). The target was bombarded with 20 µA of 3 keV krypton from an EX-03 ion gun producing a 1 cm beam diameter. Figure 1 shows a typical spectrum taken after the sample had been in place, sputtered for 6 hours, received an overnight partial bakeout at 180 $^{\circ}$C and subsequently cleaned again by 12 hours of sputtering. The test was performed on a shared facility which did have hydrocarbon contamination, producing a peak at m/z = 26 corresponding to C_2H_2. The fairly large background in the chamber required operation of the electron multiplier at very modest voltages and the use of analog rather than counting electronics. The carbon sample was replaced with a clean 2.5 cm square of boron-doped silicon which was used as a control. The control species showed a reduction in both m/z =24 and m/z = 26, making the origin of the C_2 peak at m/z = 24 at least partially due to hydrocarbons. The quadrupole has since been moved to a dedicated vacuum facility, where along with improvements in the ion gun optics we hope to see definitive results. Otherwise, SNMS can be carried out at PNNL to make measurements similar to those made with cesium bombardment [21]. Optical measurement of the relative ratio of each species is possible and will be discussed later in this paper.

14000
12000
10000
8000
6000
4000
2000
0

Intensity (Arb.)
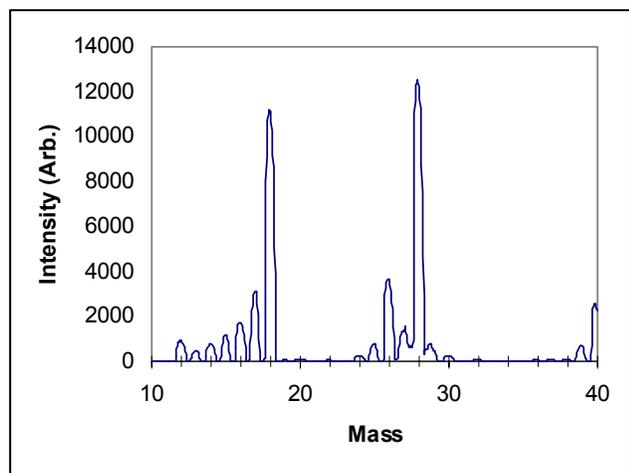
10   20   30   40

Mass

Figure 1 – Quadrupole mass spectra of graphite sputtered by 3 keV Krypton.

The calibration of the quadrupole will be made by a mixed beam of known proportions coming from a small carbon oven that was developed to emit carbon vapor through a circular aperture. The relative proportion of C, C_2 and C_3 is documented as a function of temperature [11,12] for a closed system in equilibrium. The background vacuum (10^{-8} torr) allows escaping vapor to transit the quadrupole without collision, preserving the relative proportion of clusters. Using a variety of temperatures, and thus a variety of proportions of clusters, one can determine the relative detection efficiency of each cluster and the fraction of fragmentation products produced in the ionizer of the quadrupole.

Once calibration of the quadrupole has been achieved, it is relatively straightforward to determine the relative proportion of clusters sputtered from the graphite sample.

Absolute Density Calibration Cell for Carbon

For absolute density calibration, a resistively heated carbon cell, similar to the cell used for molybdenum [3], has been developed. Flexible graphite 0.1 mm thick purchased from Goodfellow was found to be an excellent material for construction of the thermal cell. It can easily be rolled into a cylindrical shape and is quite simple to cut and shape by hand. All attempts at cell construction from rigid graphite, including the use of a graphite oven from a Perkin-Elmer atomic absorption spectrometer, resulted in failures due to stress fractures. Carbon coated metals could also be used to create an oven, but are not as straightforward to construct as ovens made with flexible graphite.

As is the case in molybdenum, the number density of carbon atoms inside an oven at equilibrium is documented. Unlike molybdenum, clusters far outnumber lone atoms in the vapor phase at the temperatures of interest. However, the ability to control the relative composition of the species in question can be put to advantage; by exploring a range of temperatures and comparing the strength of any observed spectroscopic feature with the number of each species at a given temperature, one may determine which species that feature is associated with.

An Evaluation of LIF possibilities for Carbon

Based on the 8200 hour wear test, the maximum calculated Mo density on centerline is 5 × 10^8

atoms/cm^3 [4]. Data are not available for the number density downstream of a carbon grid thruster. It is expected that carbon erosion will be significantly less than molybdenum erosion in any given thruster design. In addition, although atoms are a minority species in carbon vapor [11,12] and laser-ablated carbon [26, 27], work by Abdullaeva [21] suggests that carbon atoms are the majority species produced by sputtering. However, clusters produced during sputtering will no doubt reduce the effective number density of atoms in the plume of an ion thruster.

Other authors [10,11] have used LIF to measure both densities and velocity distributions of sputtered atoms from graphite and TiC. Two separate techniques were tried by those researchers. Frequency tripling in a xenon gas cell [10] produced 200W (0.8 µJ energy in a 4 ns pulse) output from a 4 MW input pulse at the carbon lines at 115.8 nm and 127.7 nm. This power was not enough to saturate either transition. The authors estimated the detection limit of carbon atoms in their specific experimental arrangement to be 2 × 10^8 atoms/cm^3. The second method involved the 8th order anti-Stokes Raman shift [9] of 4 MW of 368.8 nm light to produce approximately 500W (2 µJ energy in a 4 ns pulse) at 165.7 nm. The method of calibration was a glow discharge in CO; however, CO produces interfering fluorescence at this wavelength, obscuring the carbon atoms. An attempt was made by these authors to use the 9th order anti-Stokes Raman shift to reach the 156.14 nm carbon line, but the output proved too unstable to produce reliable results. The authors of these works did not account for the possibility of cluster emission from sputtering, photodissociation of C_2 by the vacuum UV light, or the absorption bands of C_3 in the VUV region.

Recent acquisition of a narrow-band (less than 1 pm) 750 Hz argon fluoride laser provides an opportunity for this author to explore the 156.14 nm carbon line through the third anti-Stokes Raman shift of the laser with a hydrogen Raman cell. The lower order shift should provide at least an order of magnitude more power, two orders of magnitude increase in repetition rate, and a substantial increase in stability at the wavelengths of interest when compared to previous attempts by other groups. The 156.1 nm line should prove to be less susceptible to background CO in the vacuum facility compared to 165.7 and thus is the most likely candidate line. The use of a photon-

counting PMT should enhance the signal-to-noise over the analog boxcar-PMT arrangement used by Bogen [9]. The cumulative effect of these improvements should provide at least an order of magnitude increase in sensitivity over previous LIF detection methods. This LIF method will be tested above a carbon graphite sample bombarded by Kr and Xe ions to produce number densities in the 1×10^7/cm^3 range, and thus should determine if this method is a feasible diagnostic for carbon thruster plumes operating under NSTAR conditions.

The dissociation energy of C_2 corresponds closely with a 193 nm photon energy, and it is still a matter of debate [14] if this dissociation would favor 2 metastable ^1D carbon atoms or a ^3P ground-state and a ^1S excited state carbon atom. If C_2 is present in substantial quantities in the thruster plume, allowing the unshifted portion of the 193 nm beam to enter the chamber with the 156.14 nm beam may increase the sensitivity of atomic LIF by dissociating C_2. Likewise, as C_3 strongly absorbs 193 nm, the presence of the ArF beam may also liberate carbon atoms from C_3 that can then be detected by the 156.14 nm beam. In other words, as long as the unshifted excimer light is far from the metastable C atom line at 193.1 nm, any change in signal by allowing that light into the cell could be attributable to clusters and would provide another measurement of relative proportion of clusters sputtered. In addition, since carbon seems to defy the general rules for metal sputtering, it is ambiguous what proportion of sputtered atoms are in the ground-state. Use of a tunable ArF laser will also allow LIF exploration of the ^1D carbon metastable state at 193.1 nm to see if these atoms are produced in quantity or may be produced in quantity by dissociating C_2 or C_3. This VUV spectral region for examining carbon is particularly attractive due to the low background expected from Xe or Kr. There are no Xe lines from 146.9 nm to 266.8 nm and only two very weak Kr^{++} lines at 163.8 nm and 191.3 nm in the region from 150 nm to 230 nm [28].

Other possibilities exist for carbon atom, dimer, and trimer LIF. These include the following: two-photon transitions at 208 nm leading to carbon atom emission in the infrared [29], Swan-band emission of C_2, and the band system of C_3 at 405 nm. These possibilities seem less promising candidates because of the rotational and vibrational molecular states in the

molecules would dilute any individual LIF line and atomic emission in the infrared would encounter much more interference due to the thruster background and inherent noise in infrared PMTs.

Conclusions

The most viable option for carbon LIF appears to be the 156.14 nm line reached by anti-Stokes Raman shifting a narrow-band tunable argon-fluoride laser, with possible use of 193 nm light to dissociate sputtered clusters. The outcome of several measurements currently being conducted will determine the ultimate viability of carbon LIF as an erosion diagnostic for carbon-based thruster grids. Clusters may represent a significant portion of the sputtered species; we expect to soon quantify the proportions of each cluster species with respect to carbon atoms. Laser spectroscopy performed on a carbon thermal cell will allow the determination of the states of carbon atoms dissociated from clusters at 193 nm.

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