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LIF Velocity Measurement of Sputtered Boron Atoms from Boron Nitride Target

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Details of the boron nitride (BN) sputtering process are of interest for diagnostics and modeling of Hall thruster erosion. This contribution presents velocity distributions of sputtered boron atoms from BN targets. Measurements were performed for normally incident argon ions at energies of 300, 800, and 1200 eV, and xenon ion at 1200 eV. The velocity distributions were found using laser induced fluorescence (LIF) spectroscopy of boron with a tunable diode laser system in the vicinity of 250 nm. The LIF velocity profiles for sputtered boron from BN were fitted with Thompson distributions giving surface binding energy of E_b=4.8±0.2 eV. Measurements were validated with a pure boron target giving a binding energy of E_b=5.7±0.3 eV in agreement with published values.

Nomenclature

c	=	speed of light
E_b	=	surface binding energy
f	=	focal length
m	=	energy-dependent parameter in Sigmund-Thompson distribution
M	=	atomic mass
u	=	velocity component of particles along the laser beam
v_b	=	corresponding atomic velocity for E_b
Z	=	the distance from the detection point to the target surface
$h\upsilon$	=	photon energy
ν_0	=	resonance frequency
ν_L	=	laser frequency
$\Delta\nu$	=	frequency shift of the fluorescence signal
λ_0	=	the transitional wavelength

I. Introduction

Boron nitride (BN) is the most widely used material for the acceleration channel wall that protects the magnetic circuitry from the discharge plasma in a Hall thruster[1-3]. The major mechanism limiting the lifetime of Hall thrusters is sputter erosion of the BN wall due to bombarding of ion fluxes (~ 100 eV and below) having non-axial trajectories. Hall thruster reliability is critical for applications requiring prolonged operation. Currently, in procedures referred to as ground-based tests, Hall thrusters are operated beyond their expected total thrust duration in a vacuum chamber[1-3]. This is the primary method to verify sufficient life of a Hall thruster for its mission. The method allows only *post facto* analysis and becomes increasing impractical and expensive for proposed future thrusters with missions of 5-10+ years. It also provides limited understanding of the erosion mechanisms, for example the dependences of erosion rate on operation conditions. The low sputter erosion rates of BN combined with the need for *in situ* measurements severely limit the available diagnostic methods.

Previous research efforts at the Laser Plasma Diagnostics Laboratory (LPDL) at Colorado State University have developed cavity ring-down spectroscopy (CRDS) sensors for electric propulsion applications, including erosion monitoring, as well as for industrial ion beam etch systems[4-10]. We have demonstrated the use of a CRDS sensor to monitor sputter eroded manganese from a steel channel within an anode layer thruster[10]. Furthermore, a CRDS sensor for *in situ* BN sputter erosion measurements has been developed for Hall thrusters and has been used to

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obtain a demonstrative spectrum of sputtered boron atoms from BN target[9]. The sensor has a minimum detectable absorbance of 0.6 ppm in 20 s measurement time, which should be very adequate for erosion studies of Hall thrusters.

CRDS directly measures the path-integrated number density of particles along the optical axis. However, computation of the corresponding BN erosion rate requires the flux density of the sputtered particles, which depends on both the number density and velocity of sputtered particles. Therefore, the velocity (distribution) of sputtered boron atoms (from BN materials) is a critical parameter for interpretation of measurements from BN CRDS erosion sensors. While ejection velocities and binding energies are generally known for single-component targets, the situation is more difficult for multi-component targets, and we are unaware of past measurements for BN. Additionally, velocity spectra of sputtered atoms give direct and detailed insight into the basic sputtering mechanism[11,12]. The velocity (energy) distribution of sputtered boron allows determination of the surface binding energy E_B and, when combined with angular (differential) sputter yield data, provides a rich description of the BN sputtering process. For these reasons, velocity measurements of sputtered boron from BN targets are needed in Hall thruster research.

In this paper, we report LIF measurements of velocity distributions of sputtered boron atoms due to ion beam bombardment of a BN target. The LIF technique provides *in situ* non-intrusive velocity resolved measurements. Similar experiments for sputtered boron atoms from different materials have been done for applications in fusion[13-15]. We follow their approach including the use of opto-galvanic spectroscopy to provide a frequency reference for the LIF measurements. The layout of this paper is as follows. The diagnostic technique and experimental apparatus are described in Section II. The analysis of experimental results is presented in Section III. Finally, in Section IV, we present conclusions.

II. Experimental

A. LIF Measurement of Velocity Distribution

LIF is widely used technique for non-intrusive velocity distribution measurements of sputtered atoms or molecules vacuum (collisionless) conditions[12-18]. A tunable laser with frequency ν_L illuminates the targeted species. The transition frequency of a stationary atom is ν_0, whereas the atoms with a velocity component u away from (and parallel to) a laser beam can only absorb photons if they satisfy the Doppler shift condition. The magnitude of frequency shift $\Delta\nu$ is:

$$\Delta\nu = \nu_L - \nu_0 = \frac{u}{c}\nu_0 \qquad (1)$$

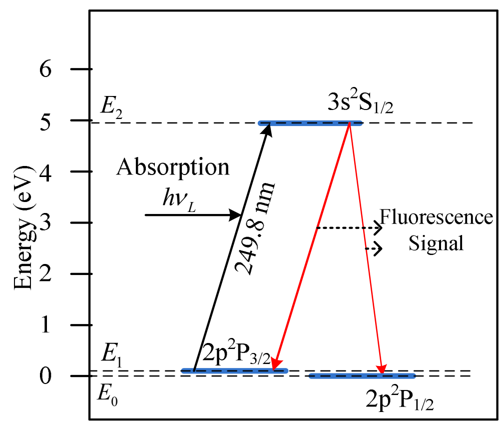

Figure 1. Selected boron transitional lines.

The subsequent fluorescence emission from excited atoms is detected and recorded as a function of the laser frequency. By scanning a laser near a known transition, the wavelength distribution of the fluorescence intensity is broadened based on the velocity distribution of the absorbing species along the path of the laser. Note that owing to the collisionless environment, thermal and pressure broadenings do not come into play. Thus the velocity distribution can be derived from the fluorescence spectrum. Figure 1 shows the selected boron atomic transition line and the fluorescence signal. The ground state for this species has two distinct levels: $2p^2P_{1/2}$ (at 0 eV) and $2p^2P_{3/2}$ (at 0.00189 eV). In this work, boron atoms were pumped from ground state $2p^2P_{3/2}$ to excited state $3s^2S_{1/2}$ by a laser at $\lambda_0 = 249.8$ nm. The fluorescence signal comes from the de-excitation of the excited atoms with a radiative lifetimes of 4 ns[19].

B. Apparatus

The tunable laser used to excite sputtered boron atoms was a frequency-quadrupled external cavity diode laser (ECDL) system (Toptica TA-FHG110) with ~10 mW power output and ~5 MHz linewidth. The ECDL system used a 1 μm laser diode as the laser source. The 1 μm laser beam was amplified by a tapered amplifier and then passed though two (actively locked) frequency-doubling cavities. A test beam at 1 μm from the ECDL system was used along with a wavemeter (Coherent Wavemaster) to check the frequency (wavelength) of the laser. The laser frequency measurement resolution was 0.1 GHz which corresponds to a resolution of 0.4 GHz (100 m/s) for the 250 nm UV beam. The absolute frequency ("zero" of the distribution) was also checked with a hollow cathode lamp (HCL) as will be described below. The UV laser beam was capable of continuously tuning approximately 150 GHz around λ_0 by changing both the voltage of the piezo-electric stack in the external cavity and the temperature of the laser diode. In the present experiments, the laser was manually tuned to scan through the targeted wavelength range (at a series of discrete wavelength steps). During the scan, the output power was monitored and adjusted to maintain a constant level of 3.5 mW.

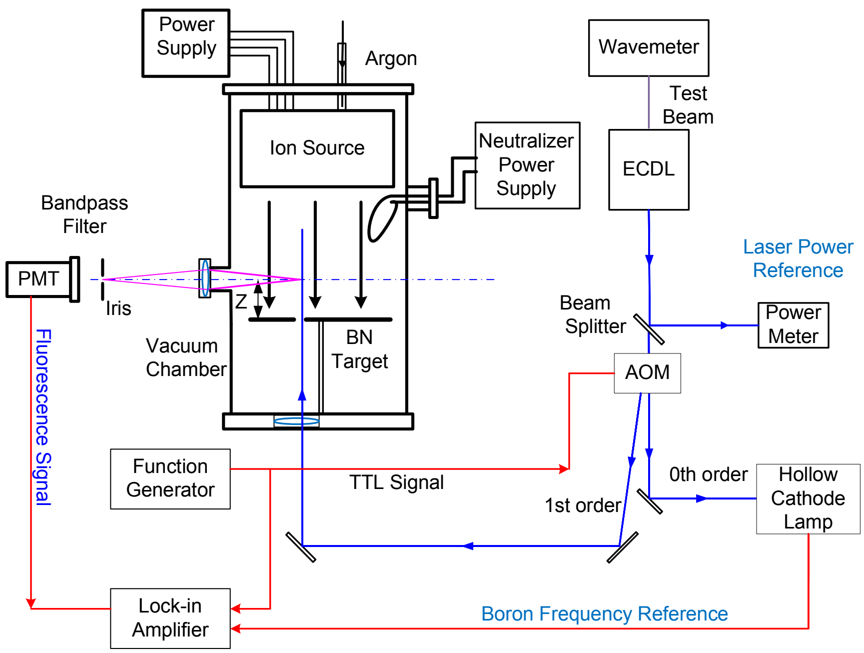

Figure 2. Experimental setup for boron LIF measurements.

Figure 2 shows a diagram of the experimental set-up for boron LIF measurements. Initial measurements failed to detect the LIF signal against the strong light background so, as will be described below, a modulated beam with lock-in amplifier detection was used. At the exit of the ECDL, a beam splitter directed ~10% of the beam into a power meter to monitor the laser power output. The remainder of the beam was directed to an acousto-optic modulator (AOM) which was used as a fast optical switch and controlled by a function generator. The zero'th order beam from the AOM was directed to a commercial boron hollow cathode lamp (HCL) for frequency reference, whereas the first order beam was delivered into the vacuum chamber with a fused silica window and focused loosely in front of the target. The beam passed through a small (~4 mm) circular hole in the target center. Roughing and turbo pumps (Turbo-V550) were used to bring the pressure to approximately 0.1 mPa under no-flow conditions and to approximately 1 mPa under a small feeding flow for the ion source. At these conditions, the sputtered atoms were in a free-molecular regime (Knudsen number << 1). A Kaufman type ion source generated an ion beam to bombard the target and produce sputtered particles. The ion source operated with an IonTech power supply (MPS 3000), with typical beam currents and voltages of about 10-40 mA and 300-1200 V respectively. High-purity argon (Ar) and xenon (Xe) gases were used as the working gas with thermal mass-flow controllers. The ion beam was normally incident upon the target. A 14 mm by 14 mm sputter target with a ~4 mm diameter center bore for the beam to pass though was held by an adjustable post. The fluorescence light was collected by a 2.53 cm diameter fused silica lens with f =150 mm at position Z=55 mm above the target. The light was imaged onto a photomultiplier tube (PMT, Hamamatsu R3896) with a dielectric interference filter (center wavelength at 250 nm and a transmission bandwidth of 30 nm). The PMT was operated at 1000 V with a 8 kΩ transimpedance resistor connected to its output.

When the ion source was on, there was strong background light from both the neutralizer filaments and the ion beam. On the other hand, BN has a low sputter yield and our laser has relatively low power, so that the resulting fluorescence signal was much weaker than the background noise (and undetectable). Therefore, a lock-in detection technique with a chopped laser beam was used to detect the fluorescence signal and improve the signal-to-noise ratio (S:N). A function generator produced a 500 Hz TTL square-wave signal to modulate the AOM to chop the laser beam. The PMT's voltage signal across the transimpedance resistor (30 μV range) was filtered and amplified by a dual phase lock-in amplifier (EG&G 5210) with a reference TTL signal and a time constant of 10 s. The lock-in time constant was selected to be slow enough to achieve high S:N. The use of the lock-in configuration resulted in a final S:N ratio of ~150.

C. Boron Reference Spectrum from Hollow Cathode Lamp

The LIF velocity measurements require accurate determination of the frequency shifts shown in Eq. (1) including properly locating the zero of the frequency axis (i.e. the frequency corresponding to stationary atoms). In this study, a reference spectrum of boron atoms was measured through the opto-galvanic effect and used to set (or "zero") the absolute frequency and velocity axes. The opto-galvanic technique can be considered as an alternative to absorption or fluorescence technique[20]. The opto-galvanic effect is observed as a perturbation in the conductivity of a self-sustained gaseous discharge, when the discharge is illuminated by radiation resonant with an atomic or molecular transition of the elements within it. It gives a simple and economical way to obtain an atomic or molecular spectrum and can be used in a wide range of applications including spectroscopy, small-concentration detection, isotopic analysis, laser calibration, and laser stabilization[20]. The pressure and mean free path of boron in the HCL ensure that its spectrum is centered at the zero velocity position.

A commercial hollow cathode lamp (HCL) with boron on the cathode provided a glow discharge of boron with an enlargement of the negative glow region. The HCL was filled with 133 Pa of Ne gas. When connected to a DC power supply, a gaseous discharge of Ne occurs within the HCL and produces Ne ions that bombard the cathode surface and sputter a portion of the cathode material (boron) to the gas phase. Figure 3 shows the detailed diagram of HCL setup. About 5 mW of laser power from the AOM was directed into the negative glow region of the HCL though a fused silica window. The HCL was operated at 6 mA of discharge current. Opto-galvanic signals were detected across the ballast resistor of 30 kΩ with a 0.47 mF capacitor. The lock-in amplifier filtered and amplified the signal. The beam (AOM) and lock-in were modulated with a TTL frequency reference signal from a function generator. A digital oscilloscope was used to record the signal. Modulation and lock-in parameters were similar to those used in the LIF experiments.

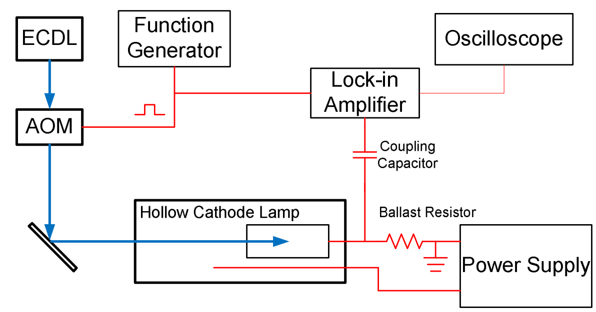

Figure 3. HCL frequency reference.

III. Results and Analysis

The sputtered boron from the BN target has a somewhat under-cosine angular distribution (differential sputter yield profile)[21], with a significant number of particles ejected normal to the target surface. The distance *Z* in the experiments was chosen to be much larger than the dimension of the target. As a result, the target can be considered a point source in the model for fitting the experimental data. The point source assumption is quite valid as a result of the small half apex angle (10° maximum) from the detection point to the target boundary (giving at worst 98% alignment of the velocity vector with the optical axis). In this case, the (flux based) velocity distribution $f(u)$ of sputtered boron atoms along the laser beam follows a Sigmund-Thompson distribution[11,12]:

$$f(u) \propto \frac{u^3}{(u^2 + v_b^2)^{3-2m}} \qquad (2)$$

where v_b is the atomic velocity corresponding to E_b ($\equiv M v_b^2/2$), and m is an energy-dependent parameter in the differential cross-section relating to the screened Coulomb potential. Specification of the velocity distribution requires both m and v_b (E_b). The value of m varies from approximately 0-0.3 for low ion energies (<~ 1 keV)[11,12]. In the present work, the measured profiles were fitted with m and v_b both as free parameters (least-squares method). The strong sensitivity to m is discussed in following paragraph.

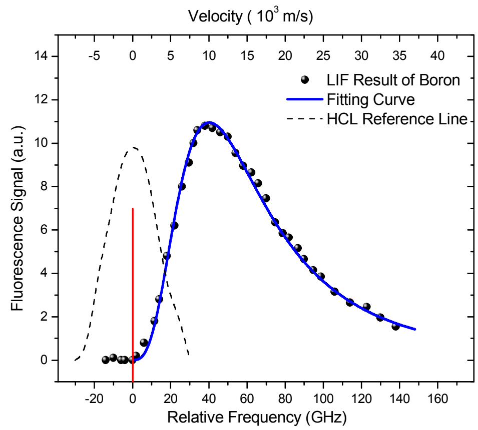

Figure 4. Boron LIF spectrum and fit for Ar ions at 1200 eV.

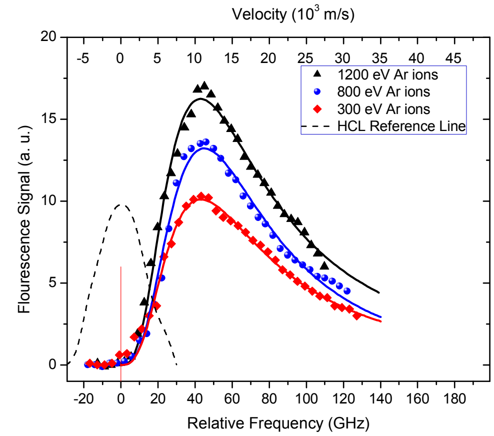

Figure 5. BN LIF spectra and fits at different Ar ion energies.

Prior to BN measurements, velocity profiles were performed for a boron target (~99.9% purity) to validate the experiment setup and method. Figure 4 shows the LIF spectrum from pure boron sputtered by an argon ion beam (1200 V, 30 mA) as well as the wavelength reference signal of the boron opto-galvanic HCL spectrum. The HCL spectrum has a full width at half maximum of ~20 GHz. The peak of the spectrum was used as the reference ("zero") for the LIF spectra and was located within ±0.01 GHz uncertainty (approximately 40 times better precision than is possible with our wavemeter for the UV beam). A Sigmund-Thompson profile, which best fits the experimental LIF curve, gives m=0±0.02 and v_b=10,000±300 m/s (E_b=5.7±0.3 eV). The error bars are based on 95% confidence bounds from fitting. The measured E_b agrees with the sublimation energy of boron (5.73 eV) from the computer code Srim and Trim[22] and the experimental result of Ito, Y. *et al.* (6 eV)[15].

The LIF spectra of sputtered boron from a BN target (grade HBR, obtained from GE Advanced Materials) have been measured with both Ar and Xe ions. Three tests were done with an Ar ion beam at energies of 300, 800, and 1200 eV, all at current of 30 mA. Figure 5 shows the three LIF spectra along with the corresponding fitted profiles. Additionally, one test was performed with a Xe ion beam at 1200 V (30 mA), the results for which are shown in Fig. 6. The best fit values of m and v_b (E_b) for all four measurement conditions are listed in Table 1. All values of m are close to 0.2 and in the expected range of 0-0.3 for low energy ions. It is noteworthy that there is a large influence of m on the associated best fit value of v_b. To illustrate this, Figure 7 shows best fit profiles for the BN experimental data for 800 V Ar ion beam for different cases where m is fixed and v_b treated as the sole fit parameter. The best-fit values of v_b change from 11,300 m/s (E_b=7.2 eV) to 8,200 m/s (E_b= 3.9 eV) as m varies from 0 to 0.3.

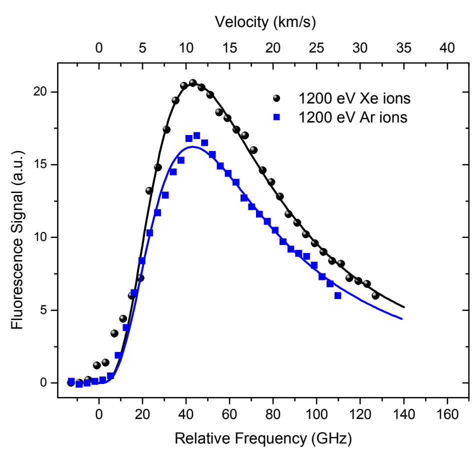

Figure 6. BN LIF spectra and fits for Xe and Ar ions at 1200 eV.

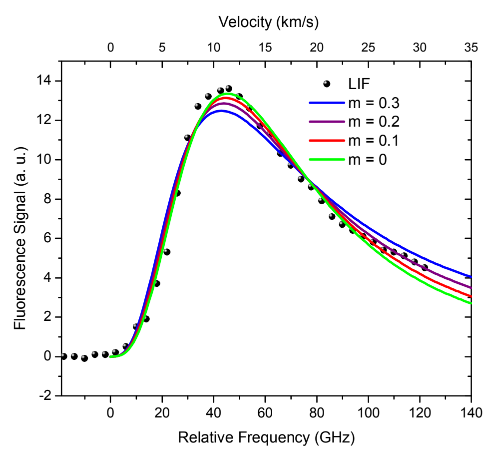

Figure 7. Best fit profiles for several values of *m* for Ar ions at 800 eV.

Ion beam condition	m	v_b (m/s)	E_b (eV)
300 V, Ar	0.20±0.04	9,200±300	4.8±0.3
800 V, Ar	0.19±0.02	9,200±400	4.8±0.4
1200 V, Ar	0.22±0.05	9,100±400	4.7±0.4
1200 V, Xe	0.17±0.05	9,500±500	5.0±0.5

Table 1. Best fit parameters for boron velocity profiles for sputtered BN as found from LIF.

In Hall thrusters, the ions that erode the BN wall material have typical average energy of ~100 eV[23]. On the other hand, the lowest ion energy we have measured at (owing to stability of the ion source used) is 300 eV; however, the theoretical expectation, consistent with our measurement results, is that the binding energy is material (target) dependent and thus does not (strongly) depend on the ion energy, species, or incidence angle[11,12]. Indeed, the measured binding energies due to Ar ions at different energies, as well as the Xe ion measurement, all appear self-consistent and give a surface binding energy of boron (from BN target) of E_b=4.8±0.2 eV (based on averaging the measured data). Some past research, with other species and target materials, has shown weak dependences of the ejected velocity profiles on ion energy and incidence angle[11,12,16-18,24], but the variations are relatively small compared to our experimental uncertainty and the accuracy needed for electric propulsion engineering analyses.

IV. Conclusion

We have performed LIF measurements to determine the velocities of sputtered boron atoms from BN targets. The illumination source was a frequency-quadrupled continuous-wave ECDL system in the vicinity of 250 nm. Opto-galvanic spectroscopy has been applied to obtain the boron thermal absorption spectrum which acts as a frequency reference for the LIF spectra. The weak fluorescence signals from excited boron atoms have been amplified and measured with a lock-in amplifier. Boron LIF spectra due to argon ions incident on a pure boron target, as well as due to argon and xenon ions incident on a BN target, have been measured and fitted with Sigmund-Thompson distributions. The measured surface binding energy of pure boron was E_b=5.7±0.3 eV, which agrees with previous measurement results. The surface binding energy of boron from BN has been studied in four different conditions yielding an averaged surface binding energy of E_b=4.8±0.2 eV. The binding energy (along with m parameter) provides a convenient means to characterize the overall velocity (energy) profile. Binding energies generally depend on the target material but not (strongly) on the ion species, energy, or incidence angle, so that the value reported above should be applicable to ion sputtering conditions of the BN channel in Hall thrusters. Therefore, these results will benefit diagnostics and modeling of the Hall thruster erosion process. In particular, our group is conducting ongoing work to develop CRDS based laser sensors for Hall thruster erosion, and the results presented here will help provide the needed link between number density (measured by the CRDS sensor) and flux of sputtered particles and corresponding erosion rate.

Acknowledgments

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