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ABSTRACT

Since the introduction of extreme ultraviolet (EUV) lithography (EUVL), the inevitable presence of EUV-induced plasmas inside the lithography tools impacts the operation of EUV optical components. EUV-induced plasmas are created everywhere in the optical path due to the ionizing interaction between the high energy (92 eV) EUV photons and the tools’ background gas, which typically is hydrogen gas at a pressure of 1–10 Pa. From a physical point of view, the main impact of the plasma is due to the presence of ions that impinge the plasma-facing surfaces. Experimental research into the fluence and energy distribution functions (IEDFs) of ions from EUV-induced plasmas has been limited to time-averaged measurements. In this Letter, we present time-resolved measurements of IEDFs for H\(^{+}\), H\(_2\)\(^{+}\), and H\(_3\)\(^{+}\) ions from an EUV-induced plasma in pure hydrogen gas. To this end, an electrostatic quadrupole plasma (EQP) analyzer has been used. The measurements pinpointed momentary fluxes up to three orders of magnitude higher than earlier reported average ion fluxes. In addition, the mean ion energy was unexpectedly found to remain elevated up to 50 µs after the gas had been irradiated with EUV photons. Also, it was shown that the EQP detects H\(_2\)\(^{+}\) ions on timescales much larger than expected. The presented results are valuable not only for the understanding of elementary processes regarding EUV-induced plasmas interacting with surfaces but also for simulating and predicting the impact of EUV-induced plasma on the lifetime and stability of optical components in EUVL.

With the introduction of extreme ultraviolet lithography (EUVL), i.e., lithography using 13.5 nm extreme ultraviolet (EUV) photons, the industry and related scientific fields have shown major interest in EUV-induced plasmas; a peculiar type of plasma inevitably experienced during the operation of EUVL tools. EUV-induced plasmas have been observed in the optical path of such tools where they are the result of the ionizing interaction of the high energy photons (92 eV) with the low pressure (1–10 Pa) hydrogen (H\(_2\)) background gas. Since the photolithographic process is conducted in a repetitive manner, the induced pulsed plasma is highly transient with an initial electron energy distribution function (EEDF) that is non-Maxwellian. EUV-induced plasmas are recognized by the field to impact the long term operation of multilayer EUV optical components. Optimization of the plasma conditions can lead to improvement of operation, e.g., in terms of cleaning EUV optical surfaces.

Over the last few years, EUV-induced plasmas have been characterized from their optical emission and from an electron dynamics point of view using numerical simulations and experiments such as those using Langmuir probes and microwave cavity resonance spectroscopy (MCRS) not only in H\(_2\) but also in argon environments. Also, the ionic components have been experimentally characterized using retarding field energy analyzers (RFEAs) and electrostatic quadrupole plasma (EQP) analyzers in pure H\(_2\) and recently in H\(_2\) diluted with a small fraction of nitrogen. Until now, these measurements have always been time-averaged.

In this Letter, we present EQP measurements of species-resolved and energy-resolved ion energy distribution functions (IEDFs) for ions produced in EUV-induced plasmas in H\(_2\) which are temporally resolved. As a complementary tool—not resolving ionic species but having a higher temporal resolution—an RFEA is used in addition to interpret and verify the findings. The results pinpoint momentary fluxes up to three orders of magnitude higher than earlier reported average ion fluxes and reveal some unexpected plasma physical features. As such, they are valuable not only for a better understanding of EUV-induced plasmas in general but also for modeling and predicting (long-term) impact of EUV-induced plasmas on EUV optical components in EUVL tools.

The used experimental configuration is similar to that in our previous works, with the difference that the readout electronics of the
The used EQP1000, Hiden analytical Ltd., and its application to EUV-induced plasmas with similar geometry and conditions are extensively discussed in our previous works.\textsuperscript{25–27} Here, we suffice with only the main features.

The EQP1000 samples ions that enter the device through an orifice in its ruthenium-coated stainless steel front-cap, which in turn was sunken in the plasma-facing back-end closure of the measurement cylinder. An orifice diameter of 20 µm was chosen because it is sufficiently small compared to the Debye length (~40 µm for typical values for the electron temperature (1 eV) and the electron density ($3 \times 10^{16} \text{m}^{-3}$) in these kinds of plasmas\textsuperscript{25}) to prevent plasma to enter and disturb the EQP. Before being detected by the secondary electron multiplier (SEM), which had a dynamic range of 7 orders of magnitude, the ions were energy and mass (range 1–50 amu) filtered by 15 individually adjustable electrostatic lenses inside the EQP (see Refs. 25 and 26 for the optimization of the lens settings). In essence, the EQP1000 was already equipped with the possibility to gate the detector relative to an externally provided trigger signal and hence able to measuring time-resolved. However, it would have taken several hours to map a plasma dynamic process of 2 ms (such as here) with microsecond resolution. To prevent issues with source stability on these time scales, a custom field programmable gate array (FPGA) multiscanner scaler was used to measure directly the output of the SEM ion detector. With that, the measurement time per setting was reduced by almost two orders of magnitude. Although the EQP contained an ion detector that was as fast as 50 ns, the bandwidth of the energy filter limited the overall time resolution to 5–10 μs (extensively explained in Ref. 26).

Figure 2 shows the temporal evolutions of IEDFs for H\textsuperscript{+}, H\textsubscript{2}\textsuperscript{+}, and H\textsubscript{3}\textsuperscript{+} ions from the afterglow of a plasma induced by irradiating pure H\textsubscript{2} gas at 5 Pa (typical pressures used in EUVL tools) with a pulse $(121 \pm 7 \mu l)$ of EUV-radiation.

These measurements indicate that the maximum momentary fluxes of roughly $10^{7}$ c/s for H\textsubscript{2}\textsuperscript{+} (and $10^{6}$ c/s for H\textsuperscript{+} and H\textsubscript{3}\textsuperscript{+}) are two to three orders of magnitude higher than the time-averaged values in similar plasma configurations reported in our earlier works.\textsuperscript{25,27}
Furthermore, the shapes of the IEDFs establish over the first 5–10 μs after irradiation of the gas. This can—as discussed earlier and elaborated on in Ref. 26—be attributed to the limited temporal resolution of the EQP. The fact that this feature represents the time response of the EQP rather than “real” plasma dynamics is verified by temporally resolved measurements at identical configurations by an RFEA; see Fig. 3 where the shape of the energy distribution function (for all ions together) establishes at much shorter timescales. A detailed description of the RFEA and the manner in which it is applied to the EUV-induced plasmas in our configuration can be found in Ref. 25.

From a plasma dynamics point of view, the main results [Figs. 2(a)–2(c)] show two peculiarities.

I: Once the shapes of the IEDFs have developed, they remain roughly unaltered over the course of the plasma decay.

This is in contrast to what would be expected from earlier experiments mapping the electron dynamics in comparable decaying EUV-induced plasmas.24,29 Considering that the energy of the incoming ions (into the EQP) is only determined by the potential drop over the developed space charge region (which in its turn is determined by the electron temperature), ion energies are expected to have decreased down to a few times room temperature within the first 1–10 μs. On this timescale, electron thermalization to room temperature was observed.24,29 The measurements here, however, indicate elevated ion energies up to 50 μs after irradiation of the gas. Note that a similarly elevated ion mean energy (2 eV) was found in the late afterglow (600 μs after the plasma was switched off) of a pulsed inductively coupled hydrogen plasma by Osiac et al.29

II: H2⁺ is unexpectedly detected up to 50 μs in the afterglow phase.

This is in contrast to what would be expected when considering the highly efficient proton-hop collision reaction:

\[
H_2^+ + H_2 \rightarrow H_3^+ + H. \tag{1}
\]

This reaction has a very large cross section resulting from the (Langevin collision) mechanism where the H₂⁺ ion induces a dipole moment in the H₂ molecule, leading to an attracting potential. The reaction in Eq. (1) has a rate constant of \(2 \times 10^{-12} \text{cm}^3 \text{s}^{-1}\),10 which means in this case that H₂⁺ created by photoionization during the EUV pulse will be converted into H₃⁺ on time scales of 0.1–1 μs typically.

Starting with the observation of elevated mean ion energies, apparently, even after the irradiation of the H₂ has stopped, and thus no external energy was supplied to the system anymore, the temperature of the electrons remains high for a significantly longer time than expected. To give a first order approximation of the desired electron energy to explain observation I (ion energies of roughly 2.5–3 eV over the course of the plasma decay), we approximate the developed space charge region in front of the front-cap of the EQP as a traditional collisionless plasma sheath,26 i.e., on these relatively long time scales, the afterglow of such an EUV-induced plasma can be approached as steady-state since the plasma’s highly transient characteristics are present during the first 0.1–1 μs after initiation only. The potential drop \(\Phi_w\) over the collisionless plasma sheath—over which the ions are accelerated to the front-cap of the EQP device—can be computed as

\[
\Phi_w = -T_e \ln \left( \frac{m_i}{2\pi m_e} \right)^{1/2}, \tag{2}
\]

with \(T_e\), \(m_o\), and \(m_i\) being the electron temperature, the electron mass, and the mass of the involved ion, respectively. For the most dominant ion in the system, H₂⁺, \(\Phi_w = -3.4T_e\). This means that \(T_e \approx 0.7–0.8\) eV to have H₂⁺ ions being accelerated to 2.5–3 eV. Although this value for \(T_e\) is a rough estimate that also depends on the applied sheath model, it indicates electron temperatures significantly higher than room temperature (~2.5 × 10⁻² eV).

To explain the presence of electrons with elevated temperatures, there must be a continued supply of energy to the system. Corresponding to the explanation for elevated mean ion energies in afterglows of inductively coupled H₂ plasmas,30 this energy might be provided to the electrons by superelastic collisions with vibrationally excited hydrogen molecules. During the formation of the EUV-induced plasma (and in its early afterglow before the bulk of the electrons have cooled down to room temperature), H₂ molecules become excited by collisions with electrons. During a long period in the afterglow, even when the bulk of the electrons has cooled down to near room temperature, these long-living vibrational states give additional energy to superelastically colliding electrons and hence these can be pinpointed as the “system’s battery.”

With the current experimental data at hand, it is not possible to give a fully substantiated explanation for the fact that H₂⁺ ions are detected such long after the gas was irradiated. However, this effect is most likely coupled to the elevated electron energies far in the afterglow phase. Apparently, taking into account the high loss rate of H₂⁺ [see Eq. (1)], there must be a continued production term for H₂⁺. Since the gas is irradiated with EUV photons only during the first 100 ns, production must be governed by other processes such as asymmetric charge transfer, electron impact dissociation of H₂⁺ to H₂⁺, and/or electron impact ionization. A global model of Mendez et al.33 and simulations by van de Ven.34 indicate that starting from \(T_e \approx 1 \text{ eV}\), the contribution of H₂⁺ to the total ion density becomes larger with increasing electron temperature. However, more sophisticated modeling efforts for these conditions are needed to explain the observations in Fig. 3(b).

The findings of the current work [elevated electron energies for a considerable amount of time (~50 μs) after EUV irradiation] can only be fitted with earlier findings that the electron population thermalizes to room temperature on much shorter time scales (1–10 μs) when the electron energy distribution function (EEDF) has two components. In that case, the EEDF is made up by a thermal region around room temperature (governing the observed ambipolar flow) and a high energy
tail determining the plasma potential with respect to its surroundings and, hence, the mean energy of the ions in the afterglow.

In conclusion, the results presented in this Letter are measurements of IEDFs of ions from EUV-induced plasmas that are temporally resolved. The main conclusions are that the ion energy unexpectedly remains high (a few electron-volts) for a considerably long time (tens of microseconds) after EUV irradiation of the gas and that—most likely coinciding with that—the contribution of H$_2^+$ to the total ion flux remains significant on much longer time scales (again tens of microseconds) than expected. These results provide more insight into the dynamics of EUV-induced plasmas and provide valuable input with respect to predicting and simulating the impact of EUV-induced plasma on EUV optical components.

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