Plasma cleaning of lithium off of collector optics material for use in extreme ultraviolet lithography applications

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Abstract. One of the critical issues within extreme ultraviolet lithography is mirror lifetime and the degradation due to debris from the pinch. This research investigated and showed the efficacy of using a helium secondary plasma and heat for removal of Li debris from collecting on the surface of collector optics. A He helicon plasma, which minimizes self-biasing and sputtering, has good extreme ultraviolet (EUV) photon wavelength transmission and preferential sputtering of lithium compared to other collector optics material. Through the combined use of heating and a He secondary plasma, EUV collector sample surface roughness and surface composition was able to be maintained near as-received status. The use of the He secondary plasma while the collector optics sample is exposed to Li debris shows promise as an *in situ* cleaning process for collector optics and can extend the lifetime of collector optics. © *2007 Society of Photo-Optical Instrumentation Engineers.*
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1 Introduction

According to the International Technology Roadmap for Semiconductors (ITRS), the 32-nm node will require next-generation lithography for semiconductor productions with a light wavelength of 13.5 nm, which is termed extreme ultraviolet lithography (EUVL).[1–3] Currently, there are several processes under development to produce EUV photons at this wavelength including laser produced plasma pinches (LPP), gas discharged plasma pinches (GDPP), and vacuum arcs.[4] Some drawbacks of the various schemes include a low collection efficiency, the degradation of the electrode system, and the limited lifetime of the collector optics.[4,5]

The initial choice of a target material for the EUV pinch was xenon, as it yields a modest series of line transitions in the 13.5 ± 0.2-nm range with a 1% conversion efficiency.[4] Now that EUV source power requirements are approaching 200 W, assuming a $10\ \mathrm{mJ/cm^2}$ resist, xenon is becoming increasingly untenable as this exposes the plasma-facing collector mirror optics to conditions that are extremely harsh and damaging.

As such, alternative target materials, such as Li and Sn, have been identified to have a higher electrical conversion efficiency and yield a broader band spectra at 13.5 ± 0.2 nm for Sn and a narrow line spectrum at 13.5 nm for Li and both of these target materials have a higher EUV conversion efficiency, on the order of 1 to 4%.[4] However, both Sn and Li are condensable metal vapors and can coat the mirror collection optics, which will degrade the mirror's reflectivity. Output power, imaging capability, wafer throughput, and overall cost of ownership are important factors in determining which of the sources tool suppliers and chip manufacturers will select, but one commonality with all EUVL sources is that the collector optics must be robust and have a long lifetime.

Although GDPP, LPP, and vacuum arc convert about 1 to 4% of net deposited plasma energy into EUV photons, the remaining energy generates out-of-band radiation and produces highly energetic ions and neutrals in the dense hot plasma that move outward in all directions. A fraction of these ions strike electrode surfaces, injection nozzles, and the vacuum chamber producing low-energy sputtered atoms, and another fraction will reflect and create a source of medium-energy gas atoms. Highly energetic ions will also travel the same line of sight path as the desired photons into the collector optics.[6] These sources of ion and low-energy sputtered atoms are collectively labeled "debris," and mitigation techniques are the subject of ongoing efforts to block this debris from reaching the collector optics. Various mitigation techniques include foiltraps and E and B repulsions fields.[6,7] Foiltraps are the industry standard technique and are effective, but they still allow debris to reach the collector optics. For high-volume manufacturing operation (100 wafers per hour), the collector optics must not lose more than 10% of absolute EUV reflectivity over 10^{11} pulses or 30 000 h.[8]

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However, even as effective as these mitigation techniques are, there are limitations, and some debris will still reach the collector optics. The use of condensable fuels, such as Sn and Li, are especially difficult because of the vapor deposition and coating on materials. Lithium is especially difficult to deal with because of its chemical reactivity and compound formation. However, Li is advantageous to use over Sn because it is lightweight and has a low vaporization point, allowing it to vaporize off of the optical surface during operation when the optics are kept at an elevated temperature. Also, Li forms lower energy debris so it causes less damage to the collection optics compared to the heavier and higher energy debris formed with the use of Sn. Thus, the use of Li as a potential fuel in an EUVL source has attracted considerable interest.

Prevention and removal of Li debris from the collector optics is an important area of study so as to develop long lasting collector optics and operating regimes in addition to expanding the knowledge base about Li transport and interaction. This investigation was designed to study a secondary plasma interaction with EUV collector optics for use in subsequent removal of the Li debris from the optics surface.

2 EUV Collector Optics Degradation Mechanism

Normal-incident EUV mirror optics, typically used for LPP sources, consist of a smooth Si substrate that is covered with alternating layers of high and low absorbance thin films, such as Mo and Si, each with a layer thickness of $\sim$3.5 nm.[4] These multilayer mirror layers work as Bragg reflectors adding weak reflections from many surfaces in phase. For high-volume manufacturing operation (on the order of 100 wafers per hour), the collector optics must not lose more than 10% of absolute EUV reflectivity over about 1 year of operation, which is on the order of 10^{11} pulses for an average repetition rate of 5 kHz.[8] Therefore, erosion of the bilayers and surface scattering of the incident photons must be kept to a minimum.

EUV mirror optics are subjected to degradation through four main pathways.[9] The first is buildup of low-energy neutral debris on the surface of the mirror optics. If this buildup is substantial such that the thickness of the buildup is on the order of a few wavelengths of 13.5 nm, this will disallow EUV reflection due to scattering and can act to scatter the incident EUV photons away from the desired focal point. This effect only comes into play if there is a large substantial amount of deposition on the surface of the mirror and is not significant if the debris buildup is on a small order of magnitude in comparison to 13.5 nm. This buildup of debris on the surface along with implantation of debris leads to a second pathway of mirror optics destruction coming from diffusion of debris material into the optics material that acts to change the mirror composition, blurring the defined layer boundaries, and changing the indices of refraction, which leads to a decrease in EUV reflection to the intermediate focal point.

A third pathway of mirror degradation comes from the sputtering of the optics by higher energy incident ions from the plasma pinch. Debris generation can be limited to a certain extent, but this production cannot be eliminated in its entirety.[5,10,11] Optical mirror surfaces for Li-based EUV systems must be engineered to withstand a continuous bombarding flux of sub-kilo electron volt Li ions for a commercially viable high-volume manufacturing component.

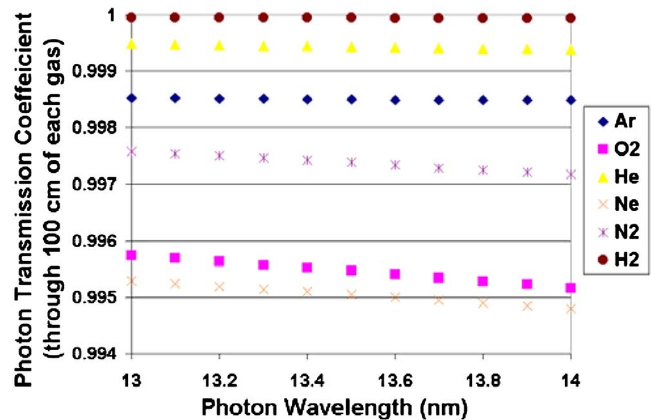

Fig. 1 Transmission coefficients for 6-eV photons in the EUV spectrum through various gases at 78 mTorr through 100 cm (see Ref. 14).

The fourth degradation mechanism is due to elevated temperatures of more than 200°C. Such products may also diffuse to the substrate, in principle, increasing substrate roughness if the substrate acts as a diffusion barrier. Enhanced thermal interdiffusion of the high and low index materials, such as Si and Mo, within the mirror structure, can occur.[12] This necessitates the development of mirror optics that maintain their stability at elevated temperatures. There is also a need for effective diffusion barriers with low EUV absorption that can resist the diffusion of debris within the mirror matrix.

Various leading mitigation techniques to limit the amount of debris that reach the collector include the use of mass-limited droplet targets, tape targets, ambient gas buffer, electrostatic repulsion fields, and permanent and pulsed magnetic fields.[13] Foiltraps, in which a set of thin plates are placed parallel to the light rays to catch the Brownian motion of debris in an ambient buffer gas, have proven particularly effective. However, none of these techniques are yet able to reach a mirror lifetime of 10^{11} shots, necessitating the development of *in situ* mirror cleaning techniques.

Investigation into such techniques has been somewhat limited. One idea is to use oxygen, as high energy oxygen ions can mechanically break the molecular bonds of the surface molecules and remove some species from the surface. Atomic oxygen present in the plasma also readily reacts with the debris on the surface of the mirror optics and can form more volatile compounds that can be more easily evaporated or removed. However, oxygen species are effective predominately on hydrocarbons and not on condensable metal vapor debris. Oxygen species are also very reactive with the mirror optics itself. In the case in which the debris load is so severe that cleaning must happen while the source is on, oxygen has the disadvantage of being highly absorptive of EUV photons in comparison to other gases, as shown in Fig. 1, which shows transmission coefficients of various gases from 13 to 14 nm, gas pressure of 78 mTorr, and gas energy of 6 eV.[14] A gas energy of 6 eV and 78 mTorr were chosen to illustrate this point because this is

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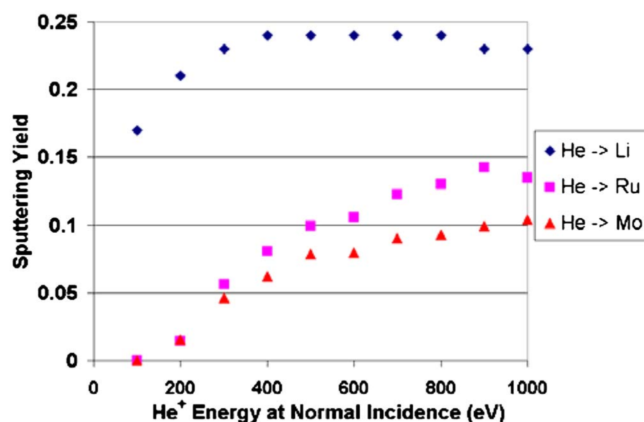

Fig. 2 Theoretical sputtering coefficients for He+ ions normal incidence on Li, Ru, and Mo (see Refs. 15 and 16).

the range in which experimental investigation was undertaken and commercial operation around the collector optics could be undertaken, but the relative comparison of transmission coefficients for the various gases holds true at a wide range of gas pressures and energies for this photon wavelength range.[14]

Therefore, cleaning through oxidation is unlikely to be effective. This work concentrates on the use of He as a plasma species for secondary plasma source for cleaning. Figure 1 shows He is a good choice from the standpoint of EUV photon transmission through He gas. In addition, He has a better theoretical preferential sputtering yield for Li versus the mirror capping layer of Ru and Mo at lower energies, as shown in Fig. 2.[15,16] This indicates that He ions can be directed to preferentially sputter Li debris from the surface of the mirror while minimizing damage to the mirror itself.

3 Experiment Facility

A new facility, the Surface Cleaning of EUV Optics by Plasma Exposure (SCOPE) at the University of Illinois, has been constructed for the purpose of studying plasma cleaning of optics materials for use in EUV applications. The SCOPE facility is a multifunctional device that is capable of creating Li debris conditions incident upon EUV optics materials so as to develop a model of Li transport and operating regimes that will aid in the advancements of EUV mirror lifetime optics. SCOPE is composed of a unique sample holder, magnetron, and a secondary plasma source.

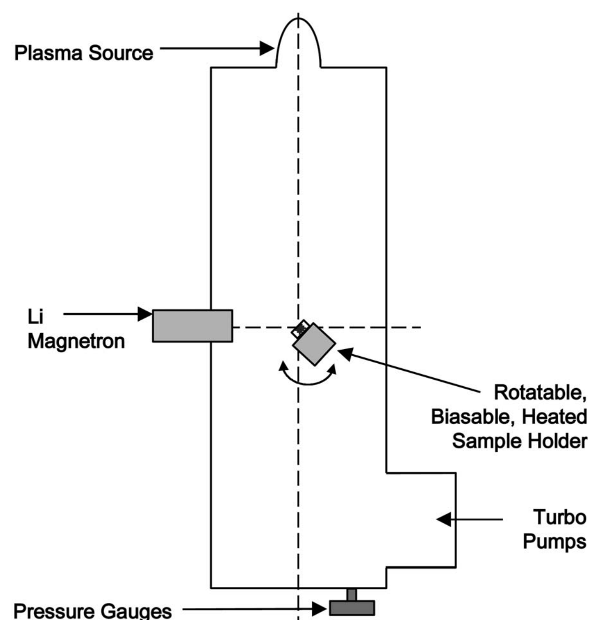

Fig. 3 Schematic of SCOPE facility.

A 3-in. magnetron with a Li target and a He plasma is used to sputter Li off of the target and deposit a Li film on mirror optics samples that are ~6 cm away. For the plasma cleaning portion of SCOPE, a helicon plasma source is employed at 13.56 MHz from 0 to 3 kW. The antenna employed in SCOPE is an $m=0$ helicon plasma stabilized with external magnetic fields. Helicon plasmas have been shown to work well as secondary plasma sources while avoiding the production of debris through self-sputtering.[17] This setup is illustrated in Fig. 3.

4 Experimental Investigation

Experiments with the use of a He secondary plasma were performed to study the mitigation and removal of Li debris from EUV mirror optics, as laid out in Table 1.

Atomic force microscopy (AFM) and scanning electron microscopy (SEM) surveys of the experimental samples are

Table 1 Experimental matrix and resulting RMS roughness.

	He Background Pressure	Bias Voltage on Sample	Magnetron Plasma	Helicon Plasma	Sample Temperature	RMS Roughness
Sample 0			Control sample			2.94 nm
Sample 1	78 mT	0	Yes	No	50°C	56.9 nm
Sample 2	78 mT	−100	Yes	No	50°C	30.5 nm
Sample 3	78 mT	−100	Yes	Yes	50°C	27.4 nm
Sample 4	78 mT	0	Yes	No	400°C	26.4 nm
Sample 5	78 mT	−100	Yes	Yes	400°C	1.03 nm

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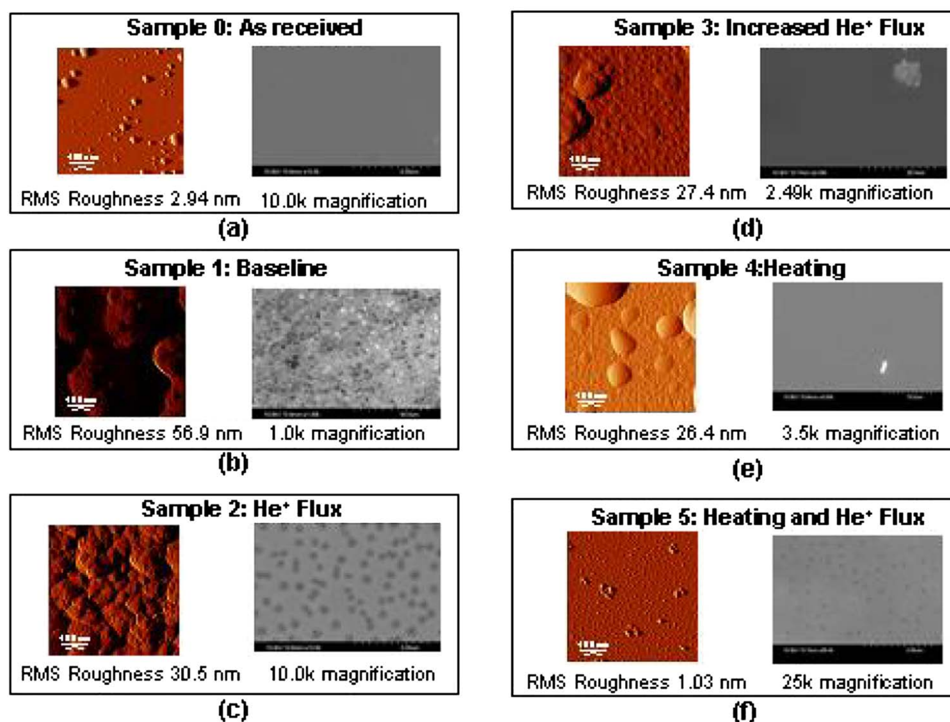

Fig. 4 (a) Sample 0, (b) sample 1, (c) sample 2, (d) sample 3, (e) sample 4, and (f) sample 5.

shown in Fig. 4. When looking at the as-received mirror samples in Fig. 4(a), it should be noted that the SCOPE facility is not in a clean room; as can be seen in Fig. 4(a), there was a certain amount of contamination or existing debris on unexposed mirror optics samples. This was considered the control for the remainder of the experiments.

For the first experiment, sample 1 was kept at 50°C and 0 V with the magnetron on. At this temperature, the vapor pressure and hence evaporation of Li from the surface is negligible.[18] Because of the location of the sample with respect to the magnetron, the He plasma used to sputter Li from the magnetron overlaps at the sample. Hence, with just the magnetron plasma, this can be thought of as a secondary plasma source on the mirror optics that would not normally be present in an EUVL source. From Langmuir probe measurements at the sample surface with just the magnetron plasma on, the electron density, n_e, was determined to be $1\times10^{10}\ \mathrm{cm}^{-3}$ and T_e of 4.7 eV. However, sputtering of the Li debris from the mirror sample can also be deemed as negligible because at 0-V bias, this is in the electron saturation region and no ion current is being drawn to the sample. From a profilometry measurement of the debris thickness on the sample, as shown in Fig. 5, the deposition rate on the mirror optics was $3.33\pm.5$ nm/min. Figure 4(b) shows the AFM survey and SEM survey of sample 1 and show the Li film on the surface of the mirror optics to be very rough and to vary widely across the sample. In this condition, the EUV reflectivity would be minimal.

Sample 2 was run under the same conditions but this time a −100-V bias was applied so as to draw He^+ ions in from the magnetron He plasma and sputter Li from the surface of the mirror optics. This lowered the rate to 1 ± 0.5 nm/min as shown in the resulting profilometry result in Fig. 6. Figure 4(c) shows the AFM and SEM results for sample 2. Again, notice the roughness and the clumping nature of the debris left on the surface of the mirror optics. This mirror would also not be reflective.

Sample 3 repeats the conditions of sample 2, but with the added He^+ flux from the secondary helicon plasma source. Again, the magnetron was operated under the same conditions. From Langmuir probe analysis, the new n_e, with both plasma sources in operation, was $3\times10^{12}\ \mathrm{cm}^{-3}$, a factor of more than 100 times the density from the magnetron plasma alone, and T_e is 6 eV. The debris film is less than the resolution of the profilometer, but an AFM survey, in Fig. 4(d), clearly shows that there is still debris present on the surface of the mirror optic.

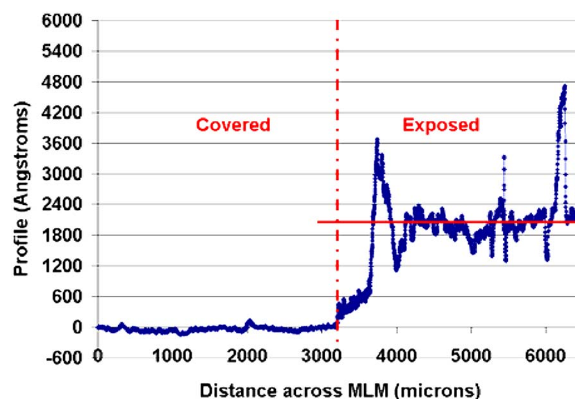

Fig. 5 Profile of sample 1, run for 60 min at 78 mTorr with the magnetron He plasma and the mirror optics at 50°C and 0 V.

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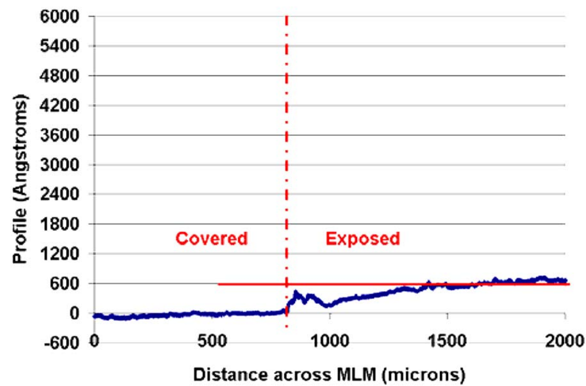

Fig. 6 Profile of sample 2, run for 60 min at 78 mTorr, with the magnetron He plasma and the sample at 50°C and −100 V.

This illustrates that although there is still debris on the surface of the mirror optics, for everything else being held constant, the increase in He^+ ion flux to the mirror surface acts to enhance removal of debris. The important illustration here, though, is that with the addition of the added He^+ ion flux, there is significant enhanced sputtering of debris from the surface of the mirror optics. However, the coating is still too thick to allow effective EUV reflectivity.

The next mirror sample, sample 4, was kept at the same operating parameters of the magnetrons before, but the sample temperature was elevated to 400°C on the surface, and there was no secondary He plasma from the helicon source. The elevated temperature was chosen to increase the Li evaporation rate; in addition, the multilayer coating of these samples were specifically engineered to withstand this elevated temperature.[19] The profilometry measurement is shown in Fig. 7. From this profilometry measurement, the net deposition rate is 0.33 ± 0.2 nm/min. This can be difficult to discern because of the dust and contamination on the surface, but there is a sharp line from where the coverslip was at ~ 3400 μm in Fig. 7. Figure 4(e) is an AFM and SEM survey of sample 4 showing that there is debris on the optics surface, but much reduced. The RMS roughness would still preclude effective focused EUV reflectivity, though.

Lastly, sample 5 was processed with the magnetron He plasma at the same conditions, sample bias voltage of

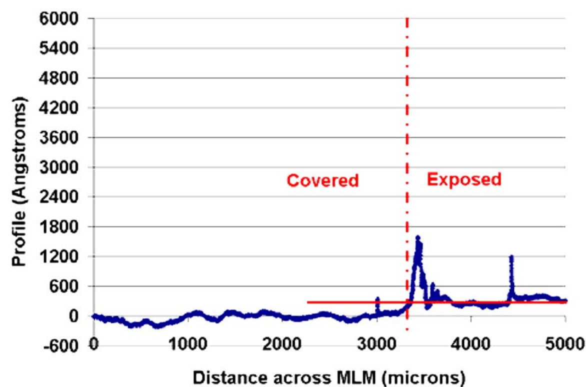

Fig. 7 Profile of sample 4, run for 60 min at 78 mTorr with the magnetron He plasma and the mirror optics at 400°C and −100 V.

−100 V, the sample temperature was elevated to 400°C on the surface, and there was a secondary He plasma from the helicon source. The resultant Li debris film thickness was less than the resolution of the profilometry and indicates that there was not a Li film, but rather localized regions of Li deposition. This is further confirmed by the AFM and SEM surveys of this sample, as shown in Fig. 4(f). From these results, it is clearly shown that the sample resembles the as-received sample in Fig. 4(a). This clearly shows the Li debris is both prevented from and effectively removed from the mirror sample. Hence, reflectivity should be maintained. The buildup and incidence of Li debris on the sample surface was minimal such that diffusion into the mirror matrix was minimized. The important result shown here is that through the combined use of heating and a secondary He plasma source, mirror optics can be maintained in an as-received state. This process, combined with other industry standard mitigation techniques, can provide a way to further increase the protection and extend the lifetime of the collector optics with minimal loss of EUV photon collection at the intermediate focus. The use of a secondary plasma and heating could be a viable *in situ* collector mirror optics cleaning and debris prevention technique.

5 Conclusion

The addition of heating and a secondary plasma act together to keep the EUV optics sample near as-received state with regards to surface roughness and debris buildup on the surface. This combination of heating and sputtering from the secondary plasma cannot be thought to be independently exclusive of each other, though. Evaporative loss of Li has been shown to be enhanced through ion sputtering.[20–22] However, when the collisions near the surface are not of a binary nature or when the target atoms are no longer stationary, the resultant collision involves a volume with a high number of moving atoms near the surface. The result is a temperature dependence of sputtering rate.[22] In this same vein, ion irradiation of the mirror optics sample can increase the evaporative loss that would not normally be expected. To be liberated from the surface of the mirror optics sample, the Li atoms must overcome the binding energy holding it in place. This can be accomplished through the transfer of energy thermally or physically. That is, Li at an elevated temperature can be sputtered at a higher rate because the threshold for escape energy from sputtering alone has been lowered due to the additional energy supplied by thermal transfer. Li evaporation can occur at a higher rate because of the contribution of the kinetic energy from the He^+ ion, which contributes to overcoming the binding energy of the Li atom.[21,23]

These results show that the combination of heating EUV optics and exposure to a relatively low-density secondary He plasma that can minimize or even reverse the buildup of surface roughness and debris while maintaining minimal EUV photon absorption during exposure to EUV Li debris-like conditions can maintain the surface roughness and minimize debris buildup on the optics surface as that of an as-received state and provides a potentially viable *in situ* mechanism for extending the lifetime of EUV optics.

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