Cleaning of Condensable Fuels from EUV Optics

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Abstract

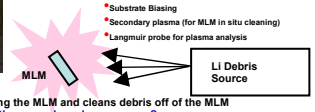
A critical issue leading to decreased mirror lifetime is the buildup of debris on the surface of the primary mirror optics that comes from the use of both Sn and Li in GDPP or LPP. As shown by Cymer at the last symposium, lithium can easily evaporated from the optic surface with heating leading to a viable of high volume EUV source, but as observed experimentally, long duration build up of lithium contaminants leads to overall mirror degradation. Consequently, an in situ cleaning process is needed so as to remove and limit the surface contamination on the optics so as to extend the lifetime of the optics. The Surface Cleaning of EUV Optics by Plasma Exposure (SCOPE) experiment was developed to study the mechanism of lithium deposition and the resulting diffusion to the end goal of using a secondary plasma source to preferentially remove the lithium surface contamination while leaving the underlying optic matrix in tact. Results have shown preferential lithium removal from the surface of the optic materials. Furthermore, work as been done into directed lithium diffusion. Reactive ion etching (RIE) with halide gases is one potential solution to the problem of Sn debris removal. The preliminary results by the group showed that at low sample bias tin could be etched at a rate of about 300 nm/min with a high selectivity of Sn to SiO_2, which is used for capping layer of the mirror. This work presents results for etch rate and selectivity for halide etching of Sn in the Plasma-Material Interaction Group's new reactive ion etching experiment where we have control over important parameters such as gas mixture, RF power, sample bias, and sample temperature; as well as overall system cleanliness. The effect of these parameters on etch rate and selectivity will be presented.

Surface Cleaning of EUV Optics with Plasma Exposure (SCOPE)

SCOPE is a multifunctional tool that simulates LPP/GDPP Li debris interactions with EUV Optics.

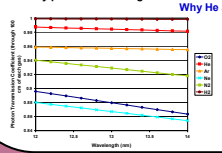
SCOPE consists of:

- **Li ion beam (for Li ion debris)**
- **Li magnetron (for Li neutral debris)**
- **QCM**
- **Substrate Heating**
- **Substrate Biasing**
- **Secondary plasma (for MLM in situ cleaning)**
- **Langmuir probe for plasma analysis**



Secondary plasma both mitigates debris reaching the MLM and cleans debris off of the MLM

Why He as the secondary plasma source?



- **He provides a high transmission coefficient for EUV photons**
- **He does not lead to hydrocarbon formation**
- **He preferentially sputters Li off the MLM while not damaging the MLM**

Factors affecting Li debris deposition on MLMs

- **A: Deposition from the Magnetron**
  - The Magnetron ejects a finite number of Li atoms. This is calculated knowing the current to the magnetron, the sputtering yield and the geometry.
- **γ_M: Fraction of Li debris mitigated by the He plasma in front of the Magnetron**
  γ_{MH}: Fraction of Li debris mitigated by the He plasma in front of the Magnetron and the Helicon plasma present
  - The He plasma between the source of the sputtered Li atoms from the magnetron target and the MLM will act to mitigate Li debris from reaching the MLM, as noted in *"Origin of Debris in EUV Sources and Its Mitigation," by D. N. Ruzic in forth coming EUV book by Sematech.*
  - This is very relevant for commercial tool development
- **C: Sputtering of Li off of MLM**
  The He ions will sputter off Li deposition on the MLM. Again, knowing the current and the sputtering yield, this number can be calculated.
- **D: Thermal Desorption of Li off of MLM at elevated temperature**
  - **Estimated from measurements.**
- **R: Measured Li deposition rate on the MLM.**

R= γ_M(A) – C – D for the Magnetron plasma alone

R= γ_{MH}(A) – C – D for the Magnetron and Helicon plasma

	He background pressure	Bias Voltage of MLM	Magnetron Plasma	Helicon Plasma	MLM Temperature
Sample 1	78 mT	0	Yes	No	50 C
Sample 2	78 mT	-100	Yes	No	50 C
Sample 3	78 mT	-100	Yes	Yes	50 C
Sample 4	78 mT	0	Yes	No	400 C
Sample 5	78 mT	-100	Yes	Yes	400 C

	A	Y	C	D	R
Sample 1	13.25 nm/min	γ_M = 0.25	0 nm/min	0 nm/min	3.3 nm/min
Sample 2	13.25 nm/min	γ_M = 0.60	7 nm/min	0 nm/min	1 nm/min
Sample 3	13.25 nm/min	γ_{MH} = 0.60	7.9 nm/min	0 nm/min	< 0 nm/min
Sample 4	13.25 nm/min	γ_M = 0.25	0 nm/min	2.9 nm/min	0.33 nm/min
Sample 5	13.25 nm/min	γ_{MH} = 0.60	7.9 nm/min	0.9 nm/min	< 0 nm/min

Secondary Plasma Mitigation Conclusions

- The secondary He plasma acts to both mitigate Li debris that is on the MLM in situ and to clean off Li debris that is on the MLM in situ.
- Plasma Mitigation + He ion sputtering removal + thermal desorption is sufficient to remove Li debris from the MLM mirror. This was confirmed with profilometry, SEM, and AFM.
- Ultimate proof of plasma mitigation to be determined by measuring reflectivity of samples.
- Next steps will be to investigate the use of carbon traps to remove Li.

Acknowledgements

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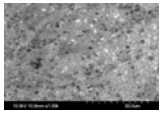
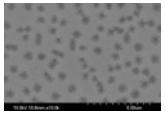
SEM Results of Li Debris Mitigation

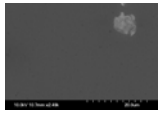
Reference MLM, RMS roughness of 2.946 nm



Sample #1: 50° C, 78mTorr, 0 V, Magnetron plasma, RMS roughness of 56.878 nm



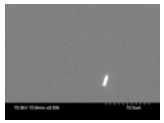
Sample #2: 50° C, 78mTorr, -100 V, Magnetron plasma, RMS roughness of 30.504 nm



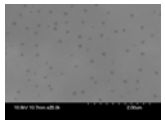
Sample #3: 50° C, 78mTorr, -100 V, Magnetron and Helicon plasma, RMS roughness of 27.376 nm

Notice the clumping and the subsequent balling up of Lithium due to surface tension.

The secondary plasma acts to both mitigate debris from reaching the MLM and sputters it from the surface.



Sample #5: 400° C, 78mTorr, 0 V, Magnetron plasma, RMS roughness of 26.407 nm

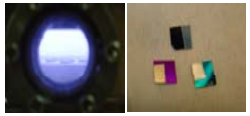


Sample #6: 400° C, 78mTorr,-100 V, Magnetron and Helicon plasma, RMS roughness of 1.034 nm

Notice that the clumping is not as extensive, but still present, on the samples that were processed at temperature. RMS roughness, though, approached the value of the original unprocessed MLM.

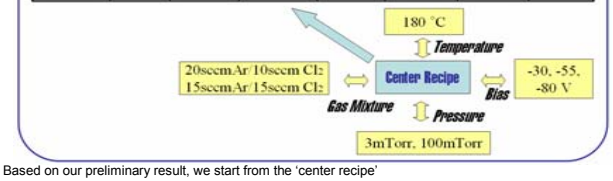
Plasma cleaning/mitigation works!

The recipes for high selectivity between Sn and SiO_2



By covering the samples with a piece of SiO_2 wafer and etching for certain amount of time then measuring the depth change with a profiler, the etch rate of sample was obtained.

Ar/Cl2	RF bias	Pressure	Temperature	ICP Power	ER_{Sn}	ER_{SiO_2}	Selectivity
10sccm/ 20sccm	-70 V	10mTorr	25 °C	500 W	274 [nm/min]	<0.3 [nm/min]	913



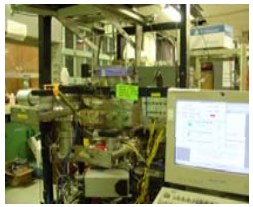
- Based on our preliminary result, we start from the 'center recipe'
- We changed the conditions such as sample temperature, chuck bias, processing pressure and gas mixture ratio.
- Sn etched very fast whereas SiO_2 etched slowly with Cl_2/Ar plasma. Therefore, the etch time for Sn and SiO_2 was considerably different. We set the time 2 minutes for Sn and 30 min for SiO_2.
- In terms of uncertainty of the etch rate results, there was difficulty when reading the depth change due to the intrinsic sample roughness and small etched depth especially for SiO_2 samples.
- For better analysis of the reading error, we need to etch more samples
- The average depth change of SiO_2 samples for 30 min with center recipe was less than 10nm.

Ar/Cl2	RF bias	Pressure	Temperature	ER_{Sn}	ER_{SiO_2}	Selectivity
10sccm/ 20sccm	-70 V	10mTorr	180 °C	343 [nm/min]	0.6 [nm/min]	572

Ar/Cl2	RF bias	Pressure	Temperature	ER_Sn	ER_SiO2	Selectivity
20sccm/ 10sccm	-70 V	10mTorr	25 °C	333 [nm/min]	2.3 [nm/min]	145

- The selected results with other recipes than the center one showed the increased etch rate for the SiO_2
- High temperature will enhance the SiO_2 etching because of less energy necessary to break the bond.
- Also, larger fraction of Ar will enhance the SiO_2 etching because of more physical etching

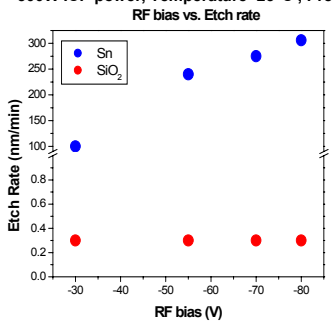
Sn Cleaning by Etching with Cl_2/Ar



- Modified etcher
- 2-turn internal ICP coil insulated with glass cloth tape
- Independent RF power for the chuck bias to control the ion bombardment energy
- Pumping systems including turbo molecular pump, Cryogenic pump and Dry pump for using corrosive halogen gas-Cl_2
- Computer controlled Mass Flow Controllers for Cl_2 and Ar
- Heater and cooling water for the samples
- RGA mounted to monitor the water vapor pressure
- Covered with glass to minimize the contamination and for the etchant not being depleted by the metal parts of chamber wall

Etch rate results for Sn and SiO_2 & selectivity

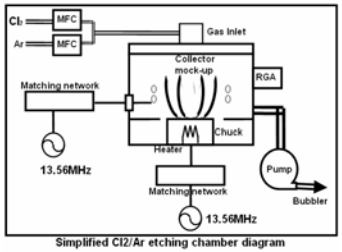
500W ICP power, Temperature=25°C , Pressure = 10mTorr, Ar (10 sccm) ,Cl_2 (20 sccm)



** Error~ ±0.3nm/min for SiO_2 due to the reading difficulty*

- The above figure shows the etch results with different RF bias to the chuck. Other conditions remained same as the center recipe's.
- The etch rate of Sn increased almost linearly with the bias voltage. However, the etch rate of SiO_2 was less than 0.3 nm/min in every case.
- The result for Sn shows well ion enhanced mechanism of Sn etching with Cl_2/Ar plasma.
- Assuming the etch rate of SiO_2 has the highest value-0.3nm/min, the selectivity was shown as above.
- Although the real biased voltage might be little different with the measured one, the maximum voltage was not enough to break the SiO_2 bond and etch away as much as we can see the depth change for 30 minutes.

Sn Conclusions and Future work



Simplified Cl2/Ar etching chamber diagram

The 2-shell collector mock-up by the group

** Real collector optics for EUV lithography from ZEISS*

- Confirmation of preliminary results with our own chamber to give high selectivity between Sn and SiO_2.
- Sn etches more ion-enhanced chemically with Cl radical while SiO_2 etches more physically by ion bombardment.
- Therefore, lower temperature and higher density of Cl radical on the surface of Sn will produce higher selectivity.
- While we are etching more samples with other conditions than only bias and reproducing the etch rate, we will study the etching with a collector mock up we made.
- We will investigate the plasma distribution and see if the etching really works for cleaning.

** From the poster "Collector optics for EUV lithography", SPIE Microlithography, 2004*