Gibbsian Segregating Alloys Driven by Thermal and Ion Flux Gradient

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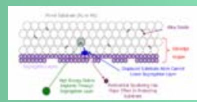
Introduction

A critical issue for EUVL is the minimization of collector degradation from intense plasma erosion and debris deposition. Collector optic reflectivity and lifetime is heavily dependent on surface chemistry interactions between fuels and various mirror materials in addition to high-energy ion and neutral particle erosion effects. An innovative Gibbsian segregation (GS) concept has been developed for being a self-healing collector optic. A Mo-Au GS alloy has been developed on silicon using a DC dual-magnetron co-sputtering system in order for enhanced surface roughness properties, erosion resistance, and self-healing characteristics to maintain reflectivity over a longer period of mirror lifetime. A thin Au segregated layer is maintained through segregation during exposure, even though overall erosion is taking place. When looking at pre and post exposure analysis of a GS Mo-0.56%Au alloy at 20° grazing incidence and 28 cm away from the plasma pinch after 2.2 million shots from a SnCl4-fueled DPP, it was seen that the while the surface roughness went from 1.8 to 7.9 ± .5 nm, there were actually islands formed on the surface with surrounding areas to be very smooth. These islands were from contamination in the system and not from the ion impact damage as the bulk concentration of Au in Mo-Au alloy is ~ 0.56%, while ~ 40% Au was found at the film surface even after being eroded by ~ 20 nm. This illustrates that Au is segregating to the surface faster than it is being eroded. The reflective material Mo underneath the segregated layer was protected by this sacrificial layer. This phenomenon is useful in the design of a collector optics surface and provides insight into plasma-facing optics lifetime as high volume manufacturing tool conditions are approached. The two dominant driving forces, thermal and ion flux gradient are focused in this work. Both theoretical and experimental efforts were undertaken in this study to prove the effectiveness of the GS alloy used as EUV collection optics, and the underlying physics behind it with respect to the segregation diffusion, surface balance, and erosion will be investigated both qualitatively and quantitatively. An in-situ reflectivity measurement has been setup to investigate the GS process during EUV exposure in a DPP environment.

Gibbsian Segregating Alloy Concept

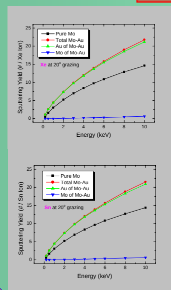


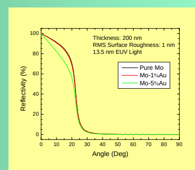
High-reflection Mo could be alloyed with a massive segregating material Au ~ 0.5%, to form a shallow layer to protect the reflection layer

Mo-Au GS alloy

- Gibbsian configuration is to alloy the optical material with a preferential sputtering solute that would be displaced (self-healing) under enhanced surface segregation due to radiation energetic bombardment
- The high reflectivity of the mirror is protected due to the sacrificial sputtering of the segregated layers and the smoothing effect of the segregated material coming to the surface

There is only a slight reduction in reflectivity due to the presence of the surface segregated layer. E.g., ≤ 2.8% reduction for Mo-1%Au at 20°





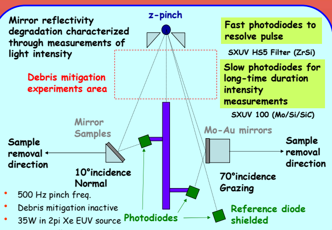
Ion Energy (keV)	Sputtering Yield Reduction from Pure Mo	
	Xe	Sn
0.2	100 %	100 %
0.5	99.9 %	99.9 %
1	99.7 %	99.6 %
2	99.1 %	98.9 %
3	98.5 %	98.3 %
4	97.9 %	97.8 %
5	97.5 %	97.3 %
6	97.0 %	96.9 %
8	96.4 %	96.2 %
10	95.8 %	95.7 %

- Mo-Au GS alloy showed a significant (≥ 95.8% for Xe and ≥ 95.7% for Sn) reduction in Mo erosion over the pure Mo film, reducing the Mo sputtering yield to about only 4% of its initial value even at 10 keV incidence

Solute / Host	Cu	Ag	Au
Mo	-1.16	-1.75	-1.94
Ru	-1.21	-1.72	-1.62

GS candidates and their surface segregation energies [eV]

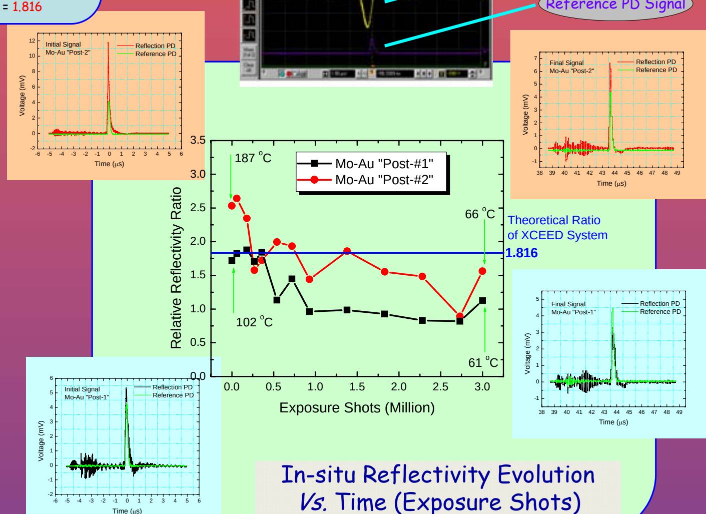
DPP Exposure Configuration



- 500 Hz pinch freq.
- Debris mitigation inactive
- 35W in 2pi Xe EUV source
- Up to 3 million shots with 200 minute exposure
- 2 mTorr operation with Xe feed gas and no carrier and buffer gas

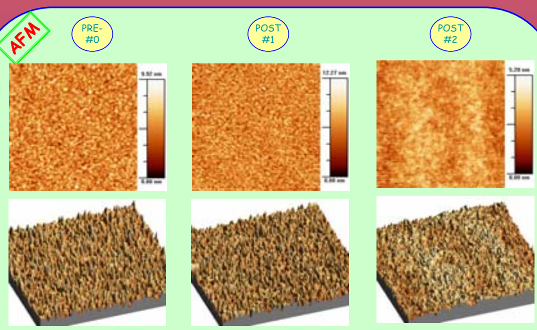
In-Situ Reflectivity

- There is a "theoretical" reflectivity ratio between the reflection PD and the reference PD signals for our XCEED exposure system.
- Assumptions:
  - ✓ Reflection PD: 59.175 cm from the pinch with a ~ 60% reflectivity
  - ✓ Reference PD: 88.7 cm from the pinch after reflected by a multilayer (to save the lifetime of the PD) with a ~ 73% reflectivity at the setup angle
  - ✓ Roughly applying a r^2 estimate
- Theoretical Ratio = Reflection / Reference = [0.6/(59.175^2)] / [0.73/(88.7^2)] = 1.816



In-situ Reflectivity Evolution *Vs.* Time (Exposure Shots)

Surface Roughness



- Post - #1 just got x1.1 increase of the RMS roughness, while Post - #2 became even smoother than its original RMS roughness, after 3 million shots (200 minutes) Xe exposure without any debris mitigation
- GS Mo-Au has impressively small roughness change, due to segregation effect
  - ✓ to protect the mirror material (Mo) underneath the surface Au layer by sacrificial sputtering
  - ✓ to repair the surface damage due to the bombardments by ion debris, especially under higher temperature condition
- It's quite useful for EUV optics, in particular for the grazing incidence since roughness reduction is critical to their reflectivities

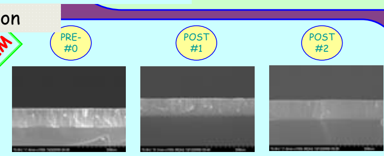
AFM RMS Roughness (nm)

Mo-1.08%Au	RMS Roughness [nm]	Change (Post / Pre)
Pre - #0	1.100	-
Post- #1	1.233	**1.1**
Post- #2	0.539	**0.5**

SEM Thickness and Erosion (nm)

Mo-1.08%Au	Thickness [nm]	Erosion [nm]
Pre - #0	200.99	-
Post- #1	185.15	**15.84**
Post- #2	200.00	**0.99**

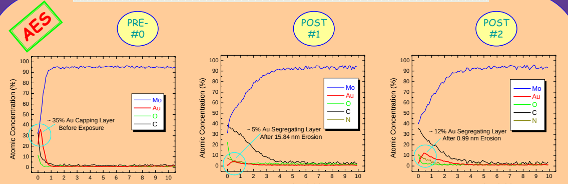
Erosion



- Post - #2 was eroded only 0.99 nm which is hard to accurately measure, however, its RMS roughness did large lessen which could be the contribution of GS mechanism to self-repair the surface by the segregating
  - ✓ The contribution of the segregation effect
  - ✓ Au may indeed act as a sacrificial layer protecting the active mirror component
- ✦ A further look at this small erosion and smoother is necessary to find the physics behind it

- Heated sample has higher initial reflectivity due to smoothing effect of segregated layer
- If sample temperature had not dropped, reflectivity may have remained higher
- Reflectivity degrades with exposure time due to roughening from ion bombardment

Film Composition and Segregation Evidence



- Au component is higher than the bulk AC in the initial few nm of the eroded Mo-Au film
  - ✓ Bulk concentration of Au: ~ 1.08 ± 0.16%
  - ✓ Surface concentration of Au: ~ 5-12% (or higher if a smaller sputtering interval was used) even after eroded by ~ 16 nm
  - ✓ Proved our Gibbsian segregation idea!
- Note that the Au component should segregate and enrich on the surface more strongly than measured here. More segregation is possible to obtain through increased heating and encouraging diffusion along grain boundaries, in order to obtain better GS performance

Future Work

- Time-dependence of erosion
- In-situ reflectivity changes
- XPS measurements for Gibbsian segregated mirrors
- Thermal effects on the GS performance

Conclusions

- In-situ reflectivity measurements have been achieved, and the evolution of a GS-alloy mirror can now be investigated
- Erosion investigation is underway and will be related to the reflectivity degradation
- GS Mo-Au alloy was eroded, but its roughness change was minimal, due to self-healing by refreshing and repairing damaged surface with the segregating layer.
- A thin Au layer is maintained during exposure, even though overall erosion is taking place. This phenomena could be very useful in the design of a collector optics surface

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