Environmental stability of oxide-capped Mo/Si mirrors

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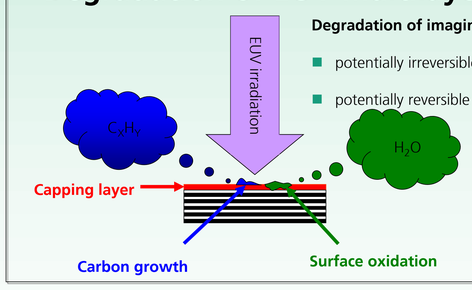
Abstract

The lifetime of Mo/Si multilayer-coated optics is one of the outstanding issues on the road to commercialization of extreme-ultraviolet lithography (EUVL). Without further precautions, oxygen containing species, e.g. residual water, and hydrocarbons can significantly decrease mirror reflectivities under EUV irradiation. It has been recently demonstrated that oxide-capped Mo/Si multilayer mirrors show enhanced radiation stability due to high oxidation resistance [1]. Due to this reason environmental stability tests have to be performed by exposing the oxide-capped Mo/Si multilayers to pulsed EUV with in-band radiation powers comparable to those to be used in the commercial tools. Besides irradiation stability, the oxidic caps should also be tested with regard to characteristic oxidative and reductive treatments.

In order to enhance the oxidation resistance of Mo/Si multilayer stack, various diffusion barriers were involved in the multilayer design between Mo/Si stack and capping layers. The multilayer designs as well as the deposition parameters of the differently capped Mo/Si multilayer coatings enhanced by diffusion barriers were optimized in terms of maximum peak reflectivity at a wavelength of 13.5 nm. To understand capping layer behavior depending on oxidation degree of the environment, characteristic oxidative and reductive gas phase conditions were used for probing the capped multilayers.

[1] S. Yulin et al. Mo/Si multilayers with enhanced TiO_2- and RuO_2-capping layers: SPIE Vol. 6921, 692118, (2008).

Degradation of EUV multilayer coatings



Degradation of imaging optics by two mechanisms:

- potentially irreversible **surface oxidation**: $Si + H_2O \rightarrow SiO_2 + H_2$
- potentially reversible **carbon growth**: $C_xH_y \rightarrow C(s) + H_2 + CH + \ldots$

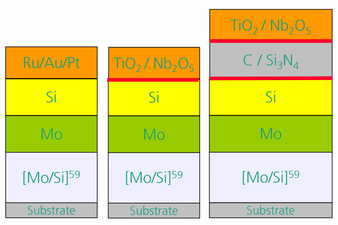
Degradation results in:

- drop of maximal reflectivity
- degradation of reflectivity uniformity

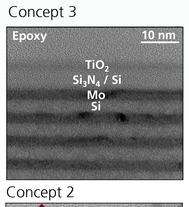
Capping layers for EUVL

Concepts:

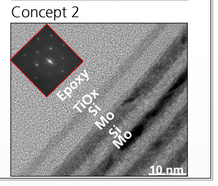
1. Noble metals (Ru, Au, Pt, Pd)
2. Stable oxides (TiO_2, Nb_2O_5, RuO_2)
3. Diffusion barriers (C and Si_3N_4)



Concept 3



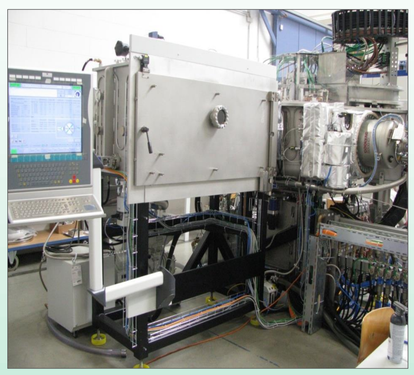
Concept 2



Cap-material requirements:

- chemically inert against O_2
- good optical properties
- amorphous structure

Multilayer deposition at IOF

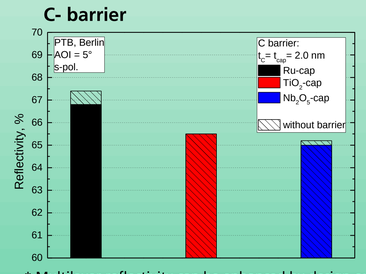


Sputtering system Nessy-3 (2013):

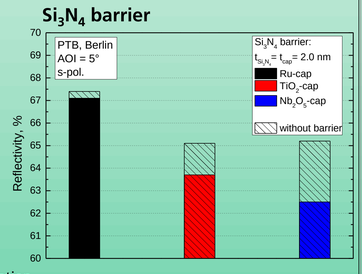
- Base pressure: $1 * 10^{-9}$ mbar
- Work pressure: $6 * 10^{-4}$ mbar
- Optics size: D < 200 mm
- 6- magnetrons: up to 6 materials in multilayer design
- Thickness uniformity: ± 0.1% on 200 mm
- Reflectivity uniformity: ± 0.3% on 200 mm
- Load / unload system

Measured EUV reflectivity @ 13.5 nm*

C- barrier



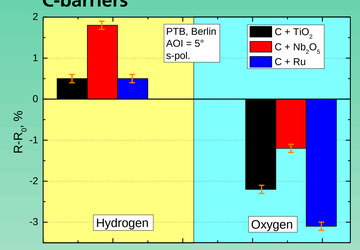
Si_3N_4 barrier



* Multilayer reflectivity can be enhanced by design optimization

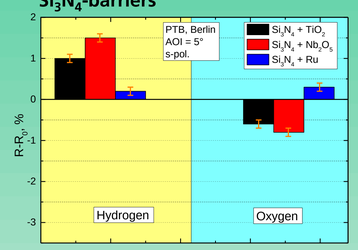
Evolution of reflectivity after treatments

C-barriers



- Treatment by hydrogen: reflectivity increase

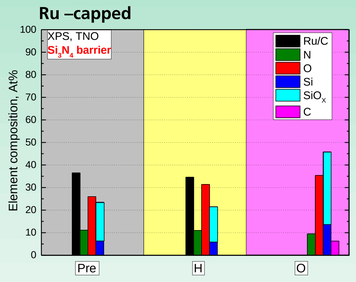
Si_3N_4-barriers



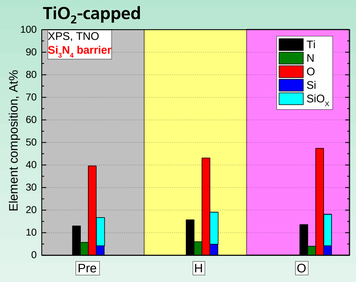
- Treatment by oxygen: reflectivity loss

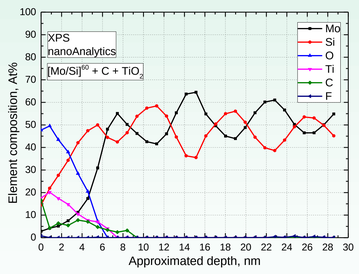
XPS study

Ru –capped



TiO_2-capped



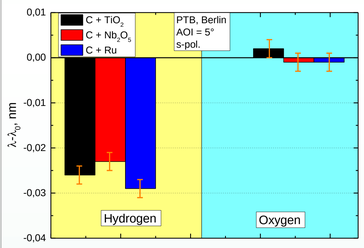


Cap + barrier	Hydrogen	Oxygen
Ru + C		
Ru + Si_3N_4		
Nb_2O_5 + C		
Nb_2O_5 + Si_3N_4		
TiO_2 + C		
TiO_2 + Si_3N_4		

- Priority in stability (H): Ru-TiO_2-Nb_2O_5
- Priority in stability (O): Nb_2O_5-TiO_2-Ru
- Preferable cap material: TiO_2
- Superior barrier: Si_3N_4 (C – is also under study)

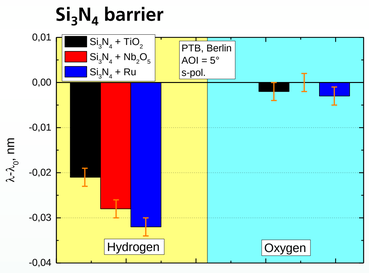
Evolution of peak wavelength after treatments

Carbon barrier



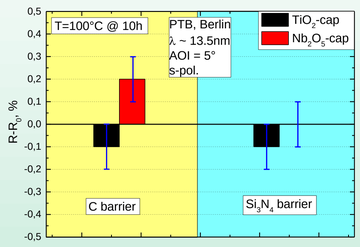
- Treatment by hydrogen: wavelength drop

Si_3N_4 barrier

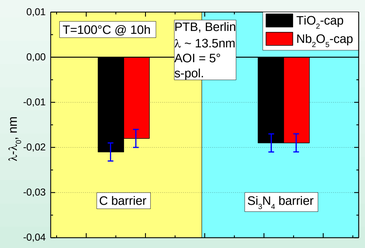


- Treatment by oxygen: no changes

Temperature effect

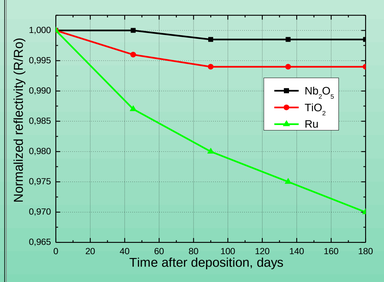


- Reflectivity: no changes



- Wavelength: reduction of 0.02 nm

Temporal stability

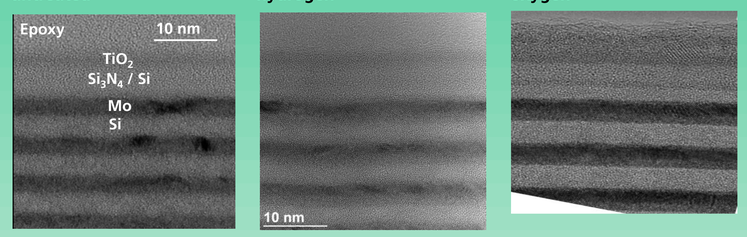


6 months after deposition*:	
Nb_2O_5:	- 0.2 %
TiO_2:	- 0.3 %
Ru:	- 2.6 %*

* S. Yulin et. al, "EUV optics lifetime under pulsed source", EUVL Symposium Kobe 2010

HRTEM

untreated **hydrogen** **oxygen**

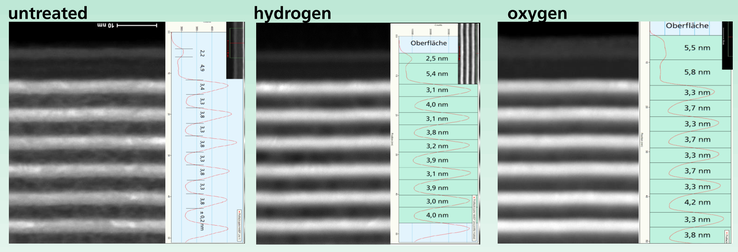


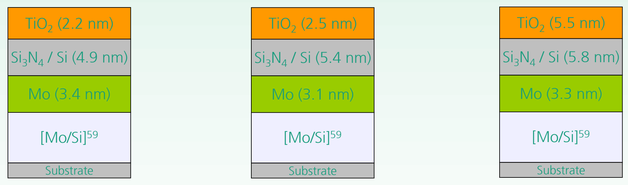
- Mo/Si structure: without noticeable changes
- TiO_2-capping layer: thickness growth after oxygen (from 2.2 nm to 5.5 nm)*

* Thickness increase of TiO_2-capping layer is under study (currently no explanation)

STEM

untreated **hydrogen** **oxygen**

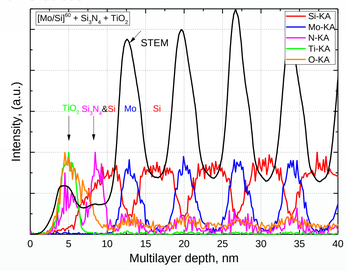




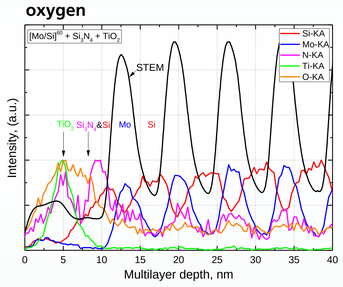
- Thickness of capping layer system (TiO_2+Si_3N_4+Si):
  - untreated: : 7.1 ± 0.2 nm
  - oxygen: 11.2 ± 0.2 nm
  - hydrogen: 7.9 ± 0.2 nm

EDXS

untreated



oxygen



- Oxygen diffusion inside of capping layer system (TiO_2+Si_3N_4+Si) with possible formation of SiN_xO_y-layers
- Presence of two obvious N-peaks even in untreated samples

Summary

- In order to enhance the oxidation resistance of Mo/Si multilayer stack, various diffusion barriers (Si_3N_4 and C) were involved in the multilayer design between Mo/Si stack and oxidic (TiO_2 and Nb_2O_5) capping layers.
- Reflectivity losses at the wavelength of 13.5 nm are currently mitigated up to ~ 0.5% and ~1.5% due to optimization of multilayer design and deposition process in oxide-capped Mo/Si multilayer mirrors with C- and Si_3N_4-diffusion barriers and fixed thickness of 2.0 nm, respectively.
- Different treatments (with hydrogen and oxygen) as well a temporal and thermal studies were performed for stability testing and multilayer design optimization.
- According to our XPS-, TEM- and EUVR- studies the superior stability of internal structure and reflective properties and of Mo/Si multilayer mirrors after various treatments can be achieved by application of TiO_2-cap with Si_3N_4-barrier layer.
- Complete removing of Ru- and partial removing of Nb_2O_5-capping layers were found by XPS-study after treatments in oxygen and hydrogen, respectively.
- Exposing the oxide-capped Mo/Si multilayers to pulsed EUV with in-band radiation powers comparable to those to be used in the commercial tools is currently under realization.

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