EUV multilayer coatings: potentials and limits

2012 International Workshop on EUV Lithography

Sergiy Yulin, Torsten Feigl, Viatcheslav Nesterenko, Mark Schürmann, Marco Perske, Hagen Pauer, Tobias Fiedler and Norbert Kaiser

Fraunhofer-Institut für Angewandte Optik und Feinmechanik Jena, Germany

Thursday, 7 June 2012, Maui, Hawaii

Outline

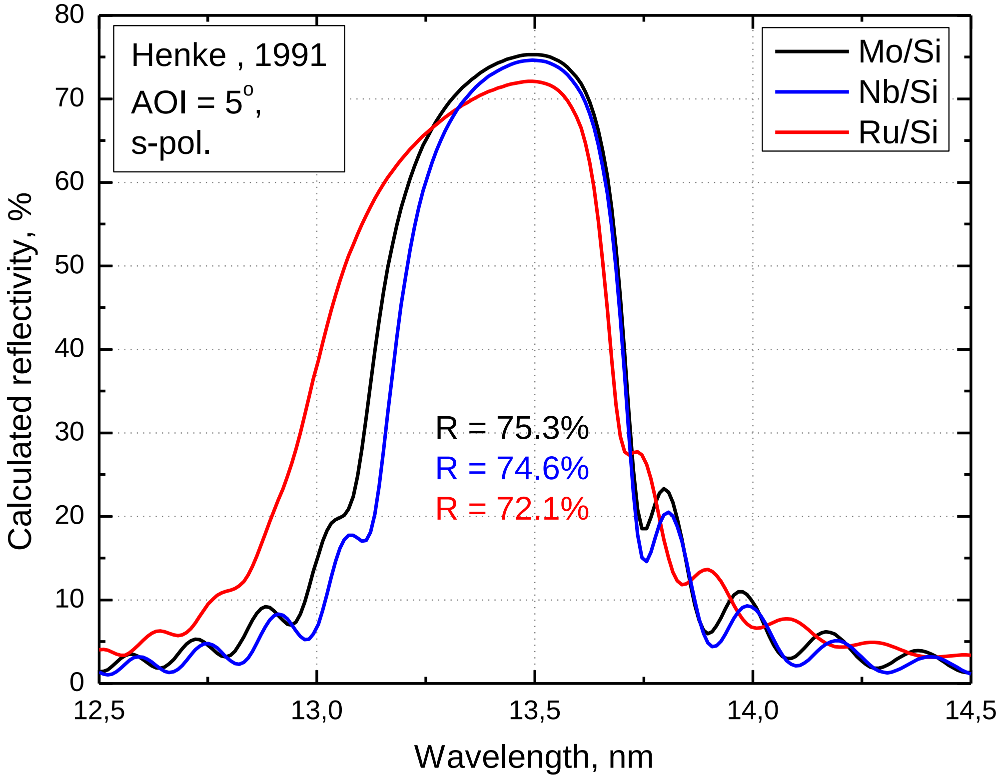
- Introduction
- High-reflective Mo/Si MLs
- High-temperature Si-based MLs
- Radiation stable Mo/Si MLs
- B-based MLs for future generation of EUVL
- Summary and outlook

Some highlights of R&D for EUVL @ Fraunhofer IOF

1999	First R&D work on interface engineering
2002	Transfer of Mo/Si technology to *Schott Lithotec AG*
2003	Design and realization of NESSY-1 system for EUVL optics
2004	Development of high-temperature MLs for *Cymer Inc.*
2005	First high-temperature collector with ∅ 320 mm for *Cymer Inc.*
2006	Development of TiO_2 and Nb_2O_5 capping layers for *Intel Corp.*
2007	Development of optics cleaning technologies for *Intel Corp.*
2008	Development of new capping layer strategy for *Intel Corp.*
2008	First collector with ∅ 660 mm for *Cymer Inc.*
2010	Design and realization of NESSY-2 system for EUVL optics
2012	Design and realization of NESSY-3 system for R&D

High-reflective Si-based multilayer mirrors at 13.5 nm

D.G. Stearns and R.S. Rosen: *High-performance multilayer mirrors for soft-X-ray projection lithography:* Proc. SPIE 1547 , 1991

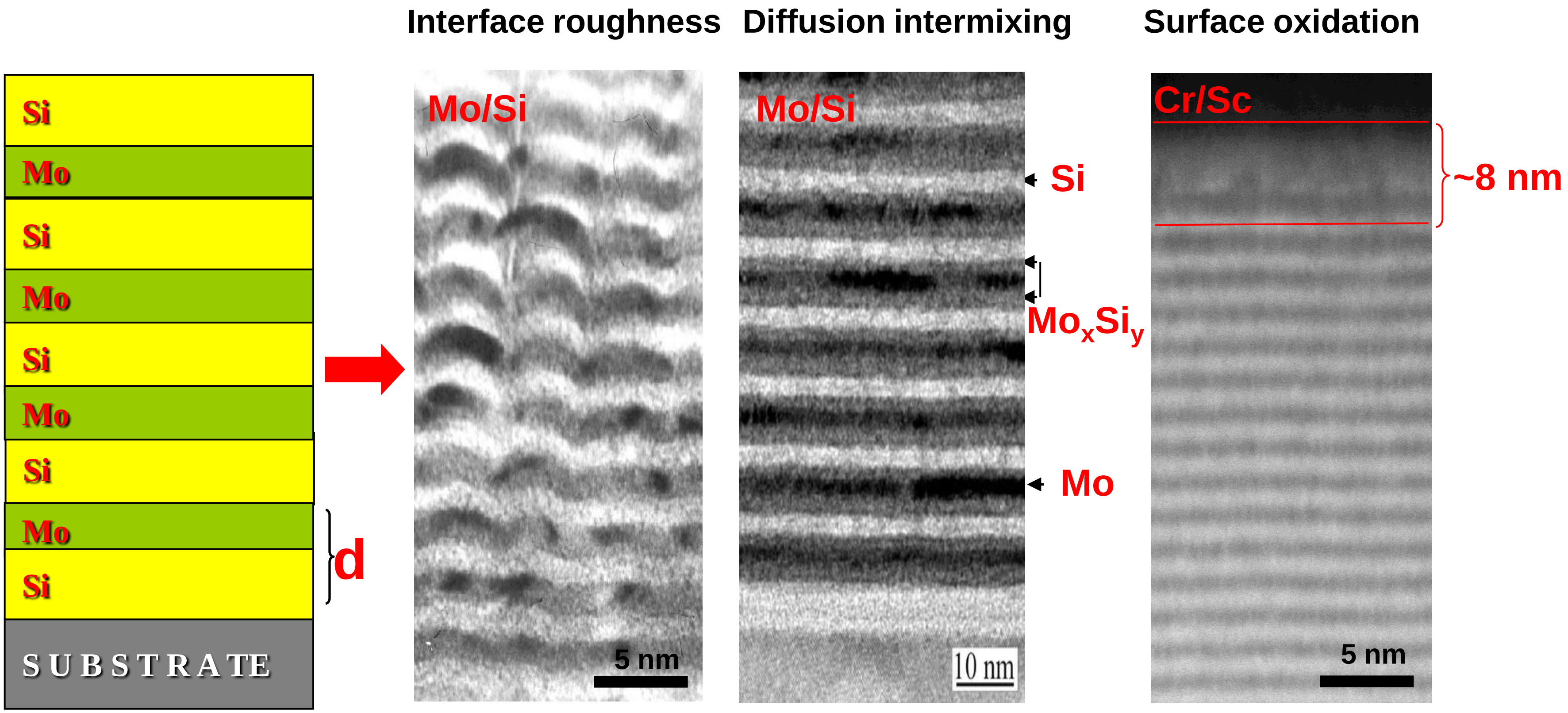


System	$R_{13.5}$, %	FWHM, nm
Mo-Si	75.4	0.58
Nb-Si	74.6	0.53
Ru-Si	72.1	0.69

Mo/Si couple was selected due to:

1) Max. theoretical optical performance
2) Minimum structural defectiveness

Main imperfections in Mo/Si multilayer mirrors



Interface roughness

Diffusion intermixing

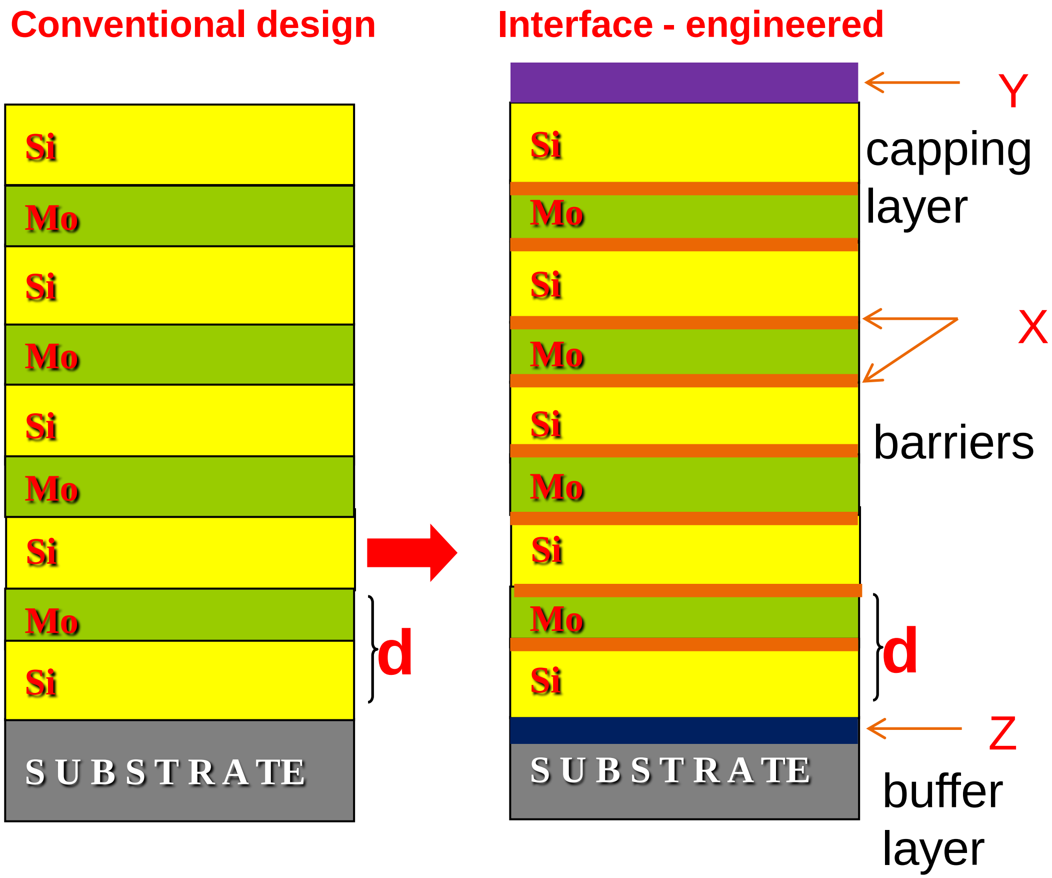
Surface oxidation

The gap between theoretical and experimental reflectivity is integrated effect of all multilayer defects. Internal and surface defects should be mitigated.

Defect mitigation strategy for Mo/Si mirrors at the IOF

Mitigation strategy for multilayer defects includes:

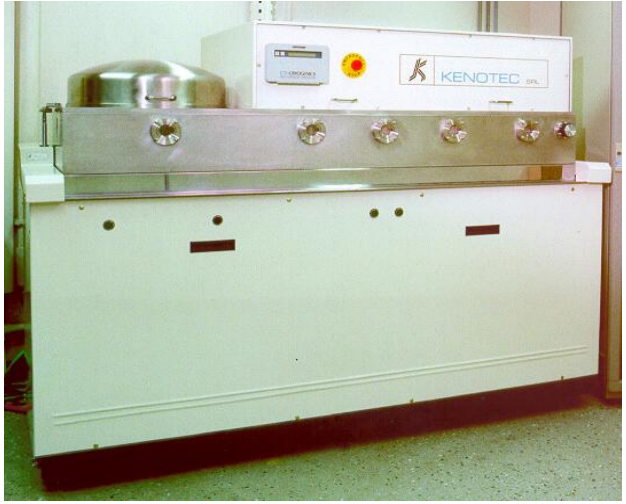
- Interface-engineering:
  - diffusion barriers (X)
  - capping layer (Y)
  - buffer layer (Z)
- Optimized deposition process:
  - deposition parameters
  - deposition tools



Transition from conventional (2-materials) to interface-engineered design (at least 5 materials) is general mitigation strategy of multilayer defects used at IOF.

Magnetron sputtering systems at the IOF

2 X MRC (1998): R&D system



NESSY 1 (2003): 3 x ∅ 300mm (with load lock)

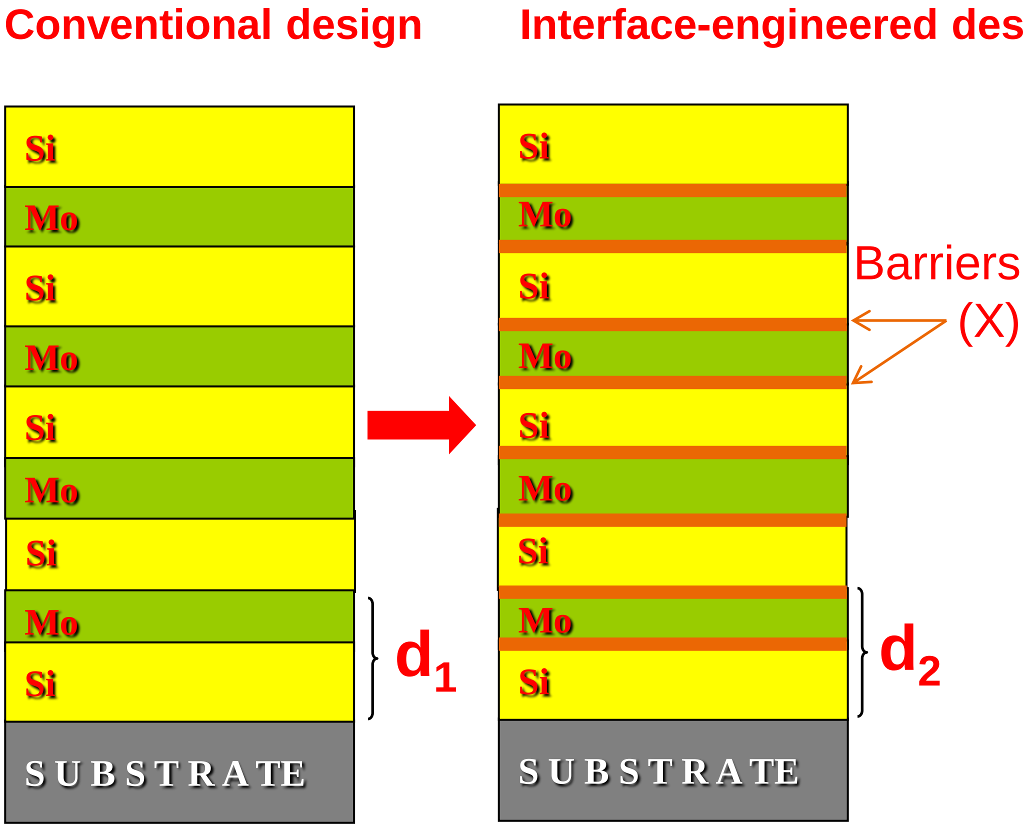
NESSY 2 (2010): up to ∅ 650mm

NESSY 3 (2012): R&D system

Outline

- Introduction
- High-reflective Mo/Si MLs
- High-temperature Si-based MLs
- Radiation stable Mo/Si MLs
- Broadband / narrowband Mo/Si MLs
- B-based MLs for future generation of EUVL
- Summary and outlook

Enhanced reflectivity with diffusion barriers



Main material requirements:

- Minimum absorption at 13.5 nm
- Low diffusion mobility
- Continuous film growth

Currently used barrier materials:

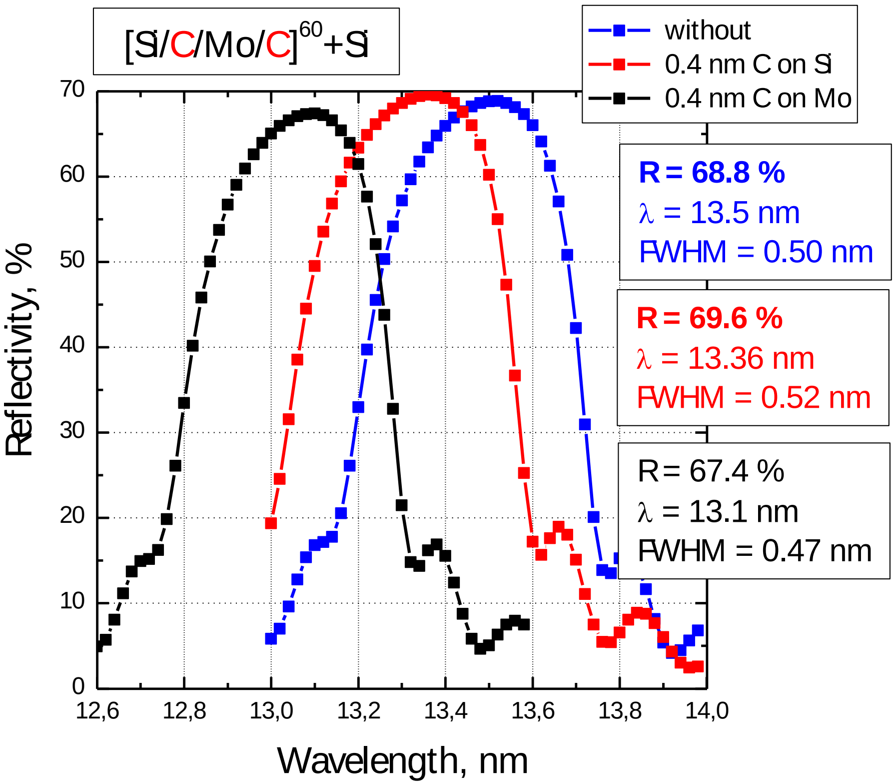
Boron carbide	(B_4C)
Carbon	(C)
Silicon carbide	(SiC)

Typical thickness: 0.2 – 0.5 nm

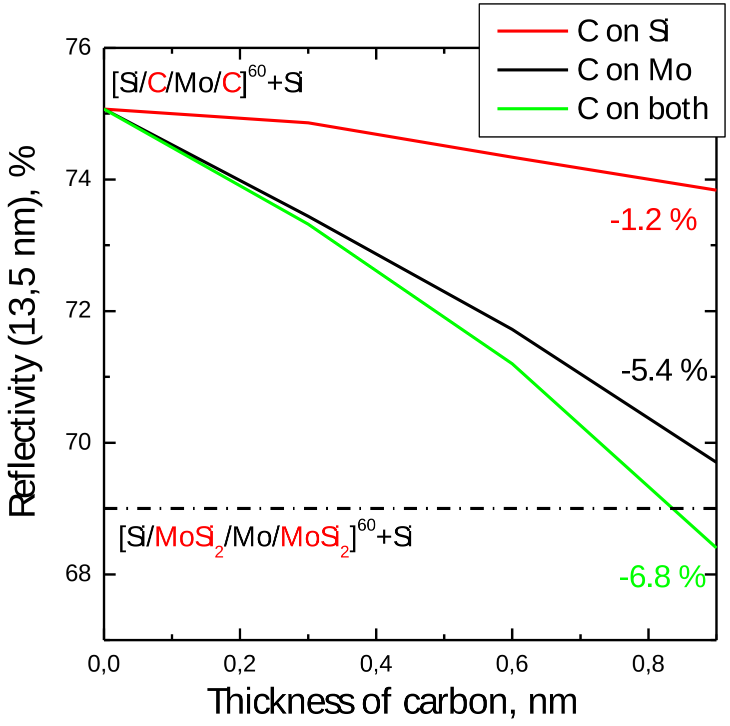
Maximum reflectivity benefit: < 2.0%

S. Bait et al. *Improved reflectance and stability of Mo/Si multilayers*: Opt. Engin., 41(8), pp. 1797 – 1804 (2002).

Enhanced reflectivity of Mo/C/Si/C multilayer mirrors



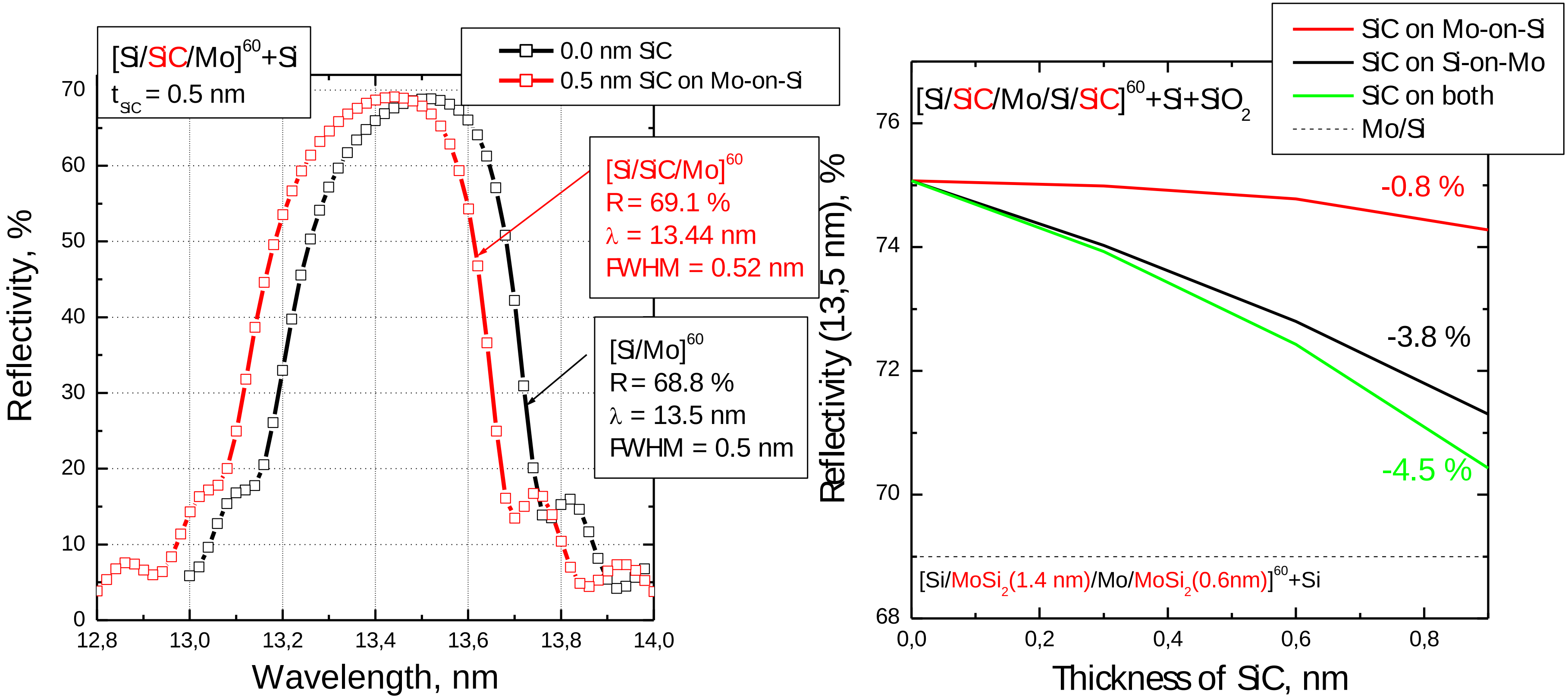
calculation



[Mo/Si]^{60} → [Si/C (0.4 nm)/Mo]^{60}+Si → + 0.8%

Enhanced reflectivity of Mo/SiC/Si/SiC multilayer mirrors

calculation

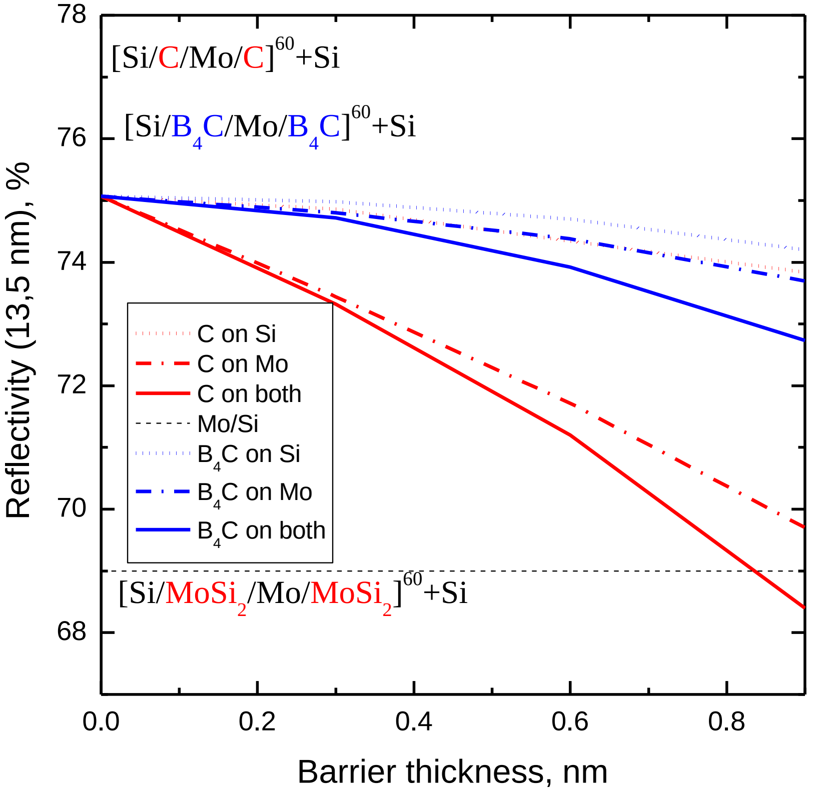


$[Mo/Si]^{60}$ → $[Si/SiC(0.5\ nm)/Mo]^{60}+Si$ → + 0.3%

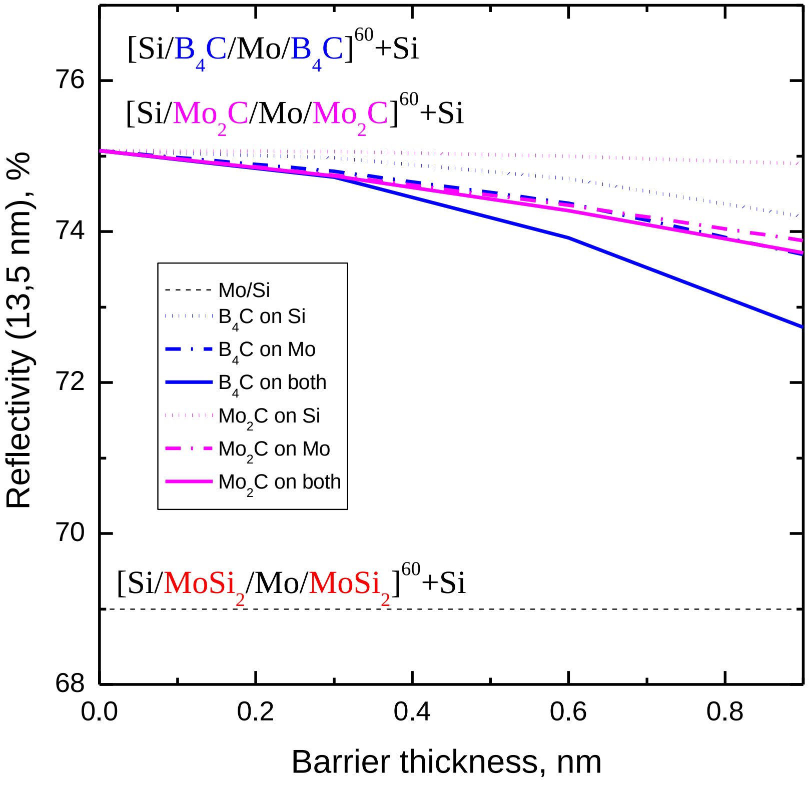
Material selection for diffusion barriers (C, B_4C, Mo_2C...)

calculation

Carbon or B_4C ?



B_4C or Mo_2C ? **Or ... ?**



B_4C is more preferable than carbon. Mo_2C is more preferable than B_4C.

Current state and prospects for reflectivity enhancement

The highest reflectivity at 13.5 nm & AOI ≤ 5:

System	$R_{exp.}$ %	FWHM, nm	Ref.
Mo/X/Si/X	70.15	0.54	FOM
Mo/B_4C/Si/B_4C	70.0	0.53	LBLL
Mo/B_4C/Si/C	69.9	0.54	IWS
Mo/Si/C	69.6	0.53	IOF

Further prospects:

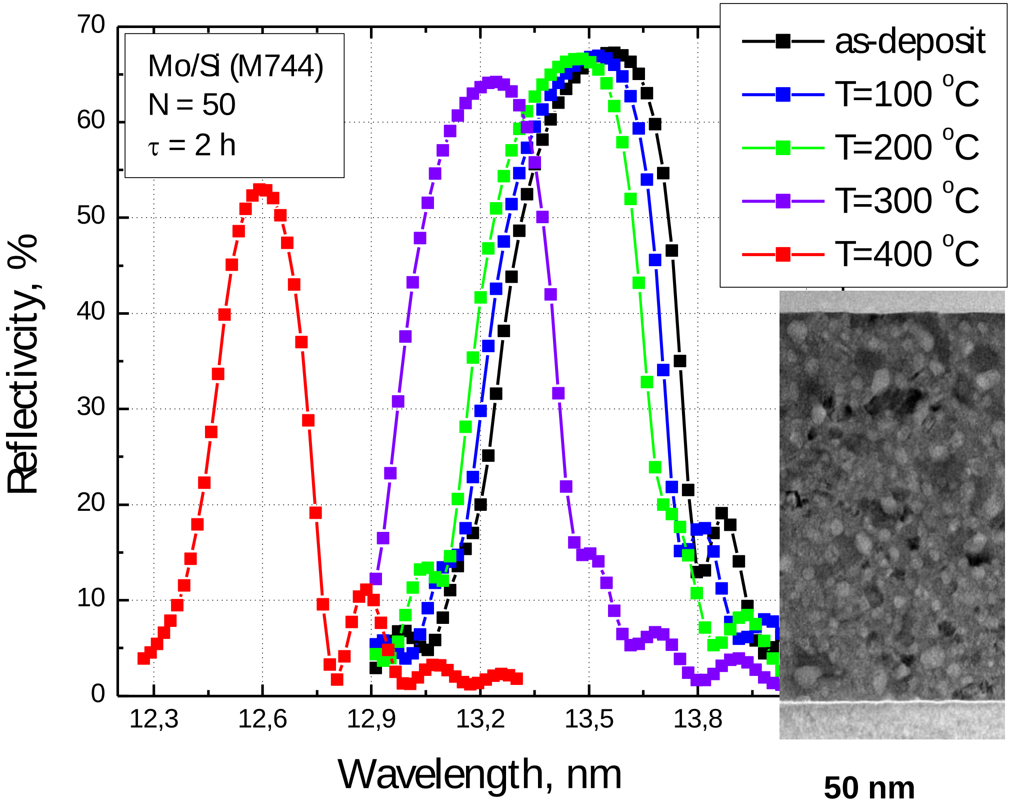
- Transition from Mo/Si to Nb/X/Si/X, Ru/X/Si/X …. multilayer mirrors
- Application of new promising diffusion materials
- Application of new oxidation resistant capping layers

Maximum reflectivity benefit is 1.0 - 2.0%...

Outline

- Introduction
- High-reflective Mo/Si MLs
- High-temperature Si-based MLs
- Radiation stable Mo/Si MLs
- B-based MLs for future generation of EUVL
- Summary and outlook

Thermal stability of conventional Mo/Si multilayer mirrors



Mo/Si multilayer mirrors:

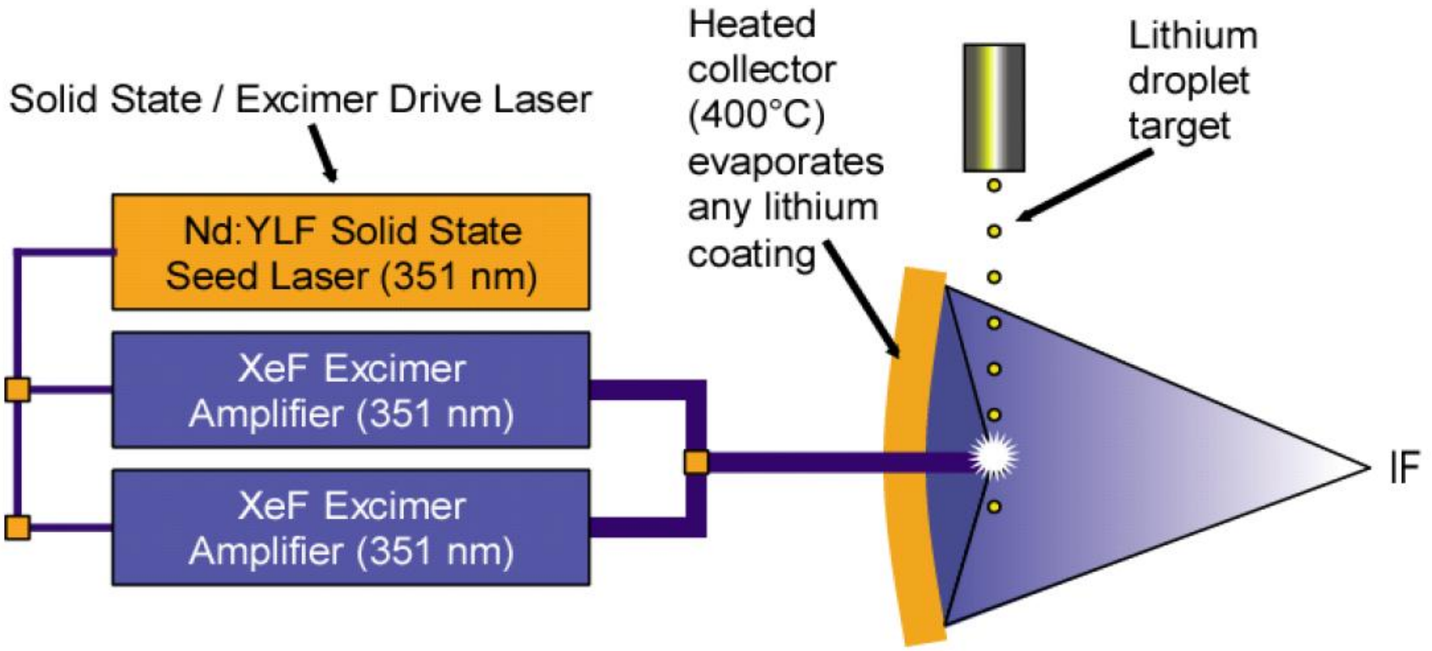
Max. reflectivity:	~ 69.0%
Max. temperature:	~ 100°C
Structure damage:	~ 700°C

V.V. Kondratenko et al: *Thermal stability of soft X-ray Mo/Si and* ***MoSi$_2$/Si*** *multilayer mirrors*, Appl. Opt, 1993.
H. Takenaka et al.: *Thermal stability of* ***Mo/C/Si/C*** *multilayer soft X-ray mirrors*: J. Elect. Spectroscopy, 1996.

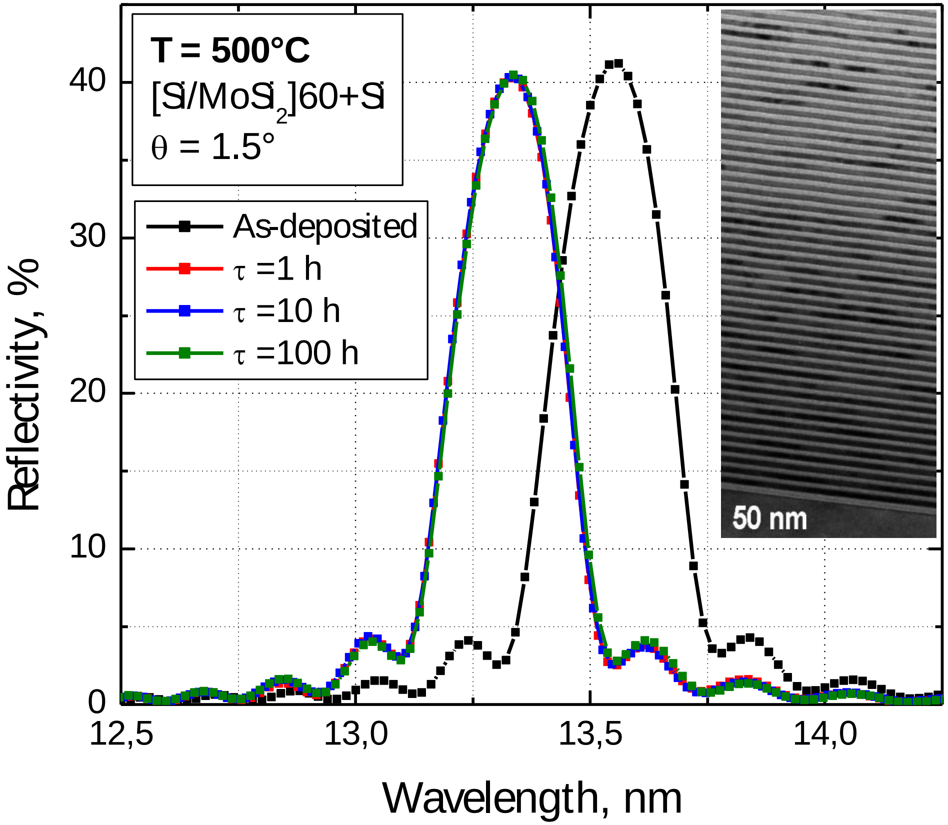
Mo/Si multilayers with enhanced thermal stability

First request: Cymer Inc. @ EUVL Symposium in Miyazaki (2004)
Requirements: R > 60% @ 13.5 nm and T ≤ 500°C
Application: Collector EUVL optics (lithium cleaning: Tm = 108°C)

Excimer Laser Combined with Lithium Droplets



Enhanced thermal stability of $MoSi_2$/Si mirrors



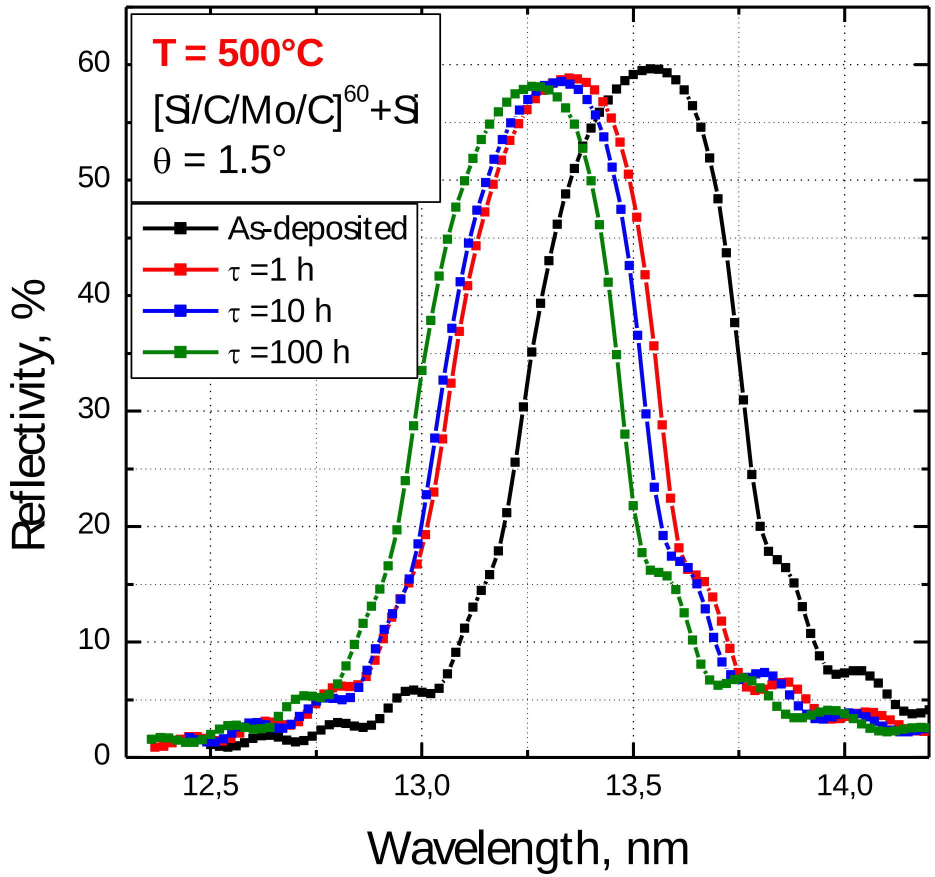
$MoSi_2$/Si multilayer mirrors:

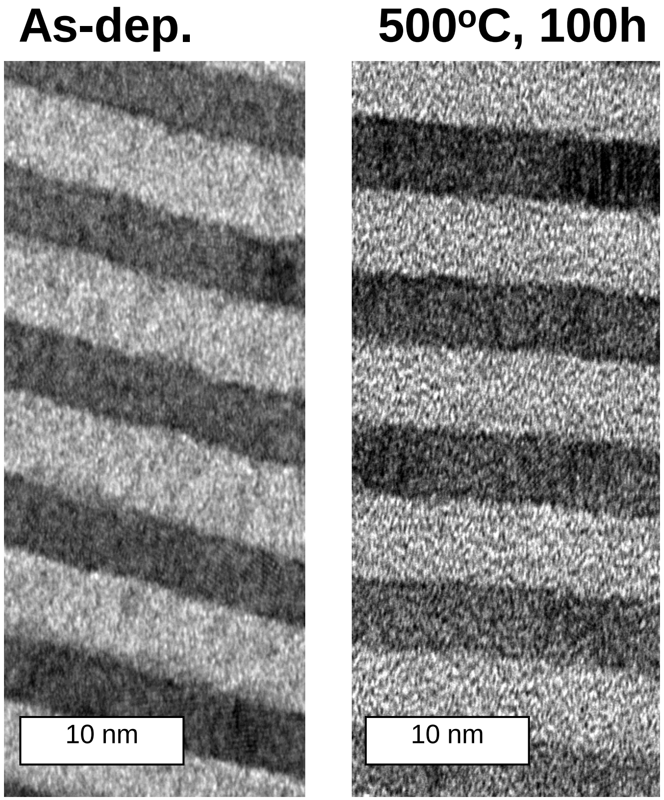
Temperature:	20 - 600°C
Reflectivity:	41.2%@13.5 nm
FWHM:	0.26 nm

V.V. Kondratenko et. al: *Thermal stability of soft X-ray Mo/Si and* ***$MoSi_2$/Si*** *multilayer mirrors*, Appl. Opt, 1993.

Enhanced thermal stability of Mo/C/Si/C mirrors

[Mo/C(0.8 nm)/Si/C(0.8nm)]^{60}



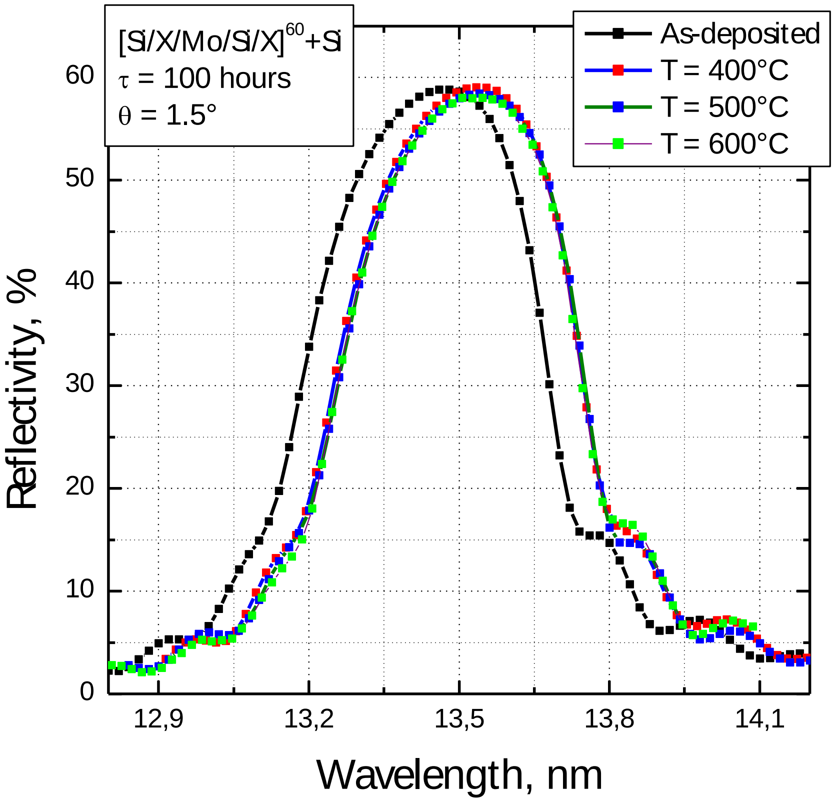


[Mo/C(0.8)/Si/C(0.8)]^{60}

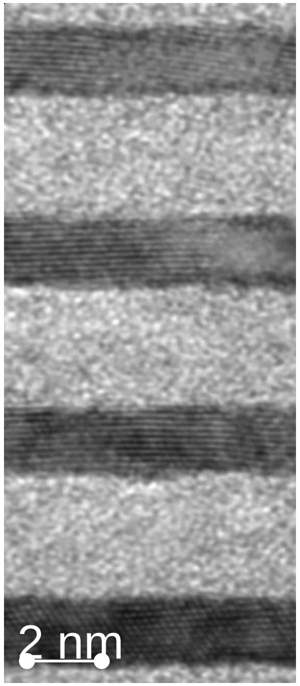
R = 60% @ 13.5 nm but… T < 400ºC

Mo/Si multilayers with enhanced thermal stability

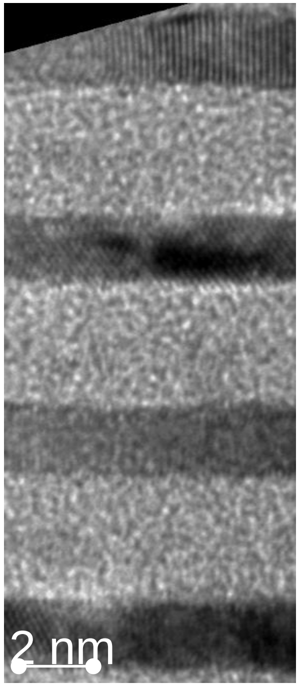
$[\mathrm{Mo}/\mathrm{X}/\mathrm{Si}/\mathrm{X}]^{60}$



As-deposited



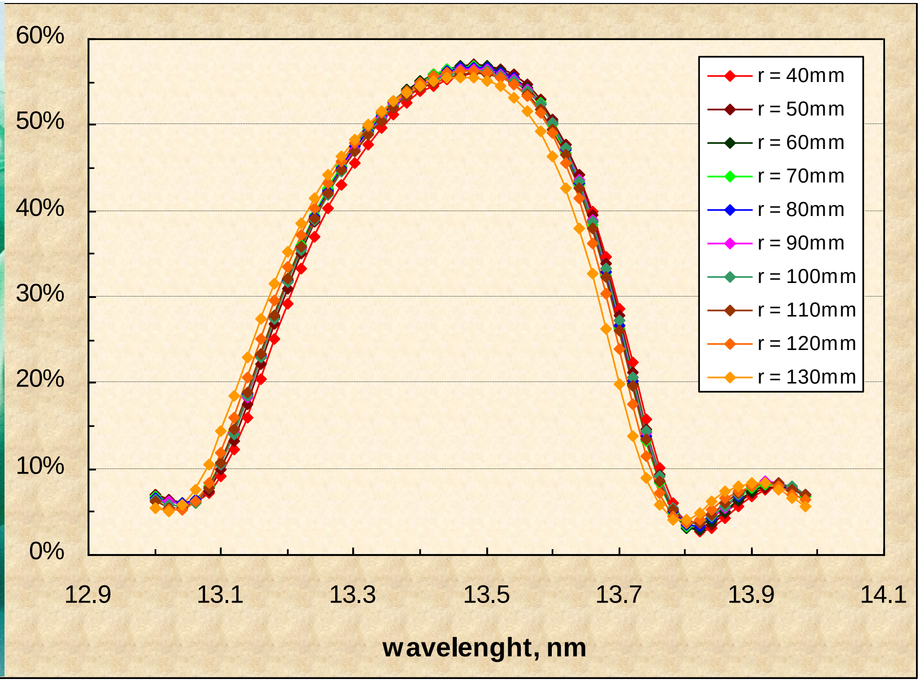
600ºC, 100h



Combination: R ≥ 60.0% @ 13.5 nm & T ≤ 600ºC

Reflectance of the first high-temperature collector optics

2005



Combination: R ≥ 56.0% @ 13.5 nm & T ≤ 600ºC

Current LPP collector coating challenges 2012

Rs > 65 %

$\lambda = (13.5 \pm 0.03)$ nm

→ $\Delta d = 0.015$ nm = 15 pm

Diameter:	> 660 mm
Lens sag:	> 150 mm
Tilt:	> 45 deg
Weight:	> 40 kg

Current state and prospects for enhanced thermal stability

Experimental reflectivity & thermal stability of Si-based multilayers:

System	T_{max}, ^oC	R $_{max}$, %	FWHM, nm
Mo/Si	< 100	69	0.51
Mo_2C/Si	≤ 350	67	0.48
Mo/C/Si/C	≤ 400	60	0.50
$MoSi_2/Si$	≤ 600	42	0.26
Mo/X/Si/X	≤ 600	60	0.47

Further prospects:

- Development of HT multilayers mainly focuses on the improvement of optical performance.

Our limits:

- Development of HT- multilayers with T_{max} > 600^{o}C is limited by temperature of crystallization of Si-layers (T cryst. ~ 650^{o}C).

Outline

- Introduction
- High-reflective Mo/Si MLs
- High-temperature Si-based MLs
- Radiation stable Mo/Si MLs
- B-based MLs for future generation of EUVL
- Summary and outlook

Degradation of Si-capped Mo/Si multilayer mirrors

Industry goal (imaging optics):

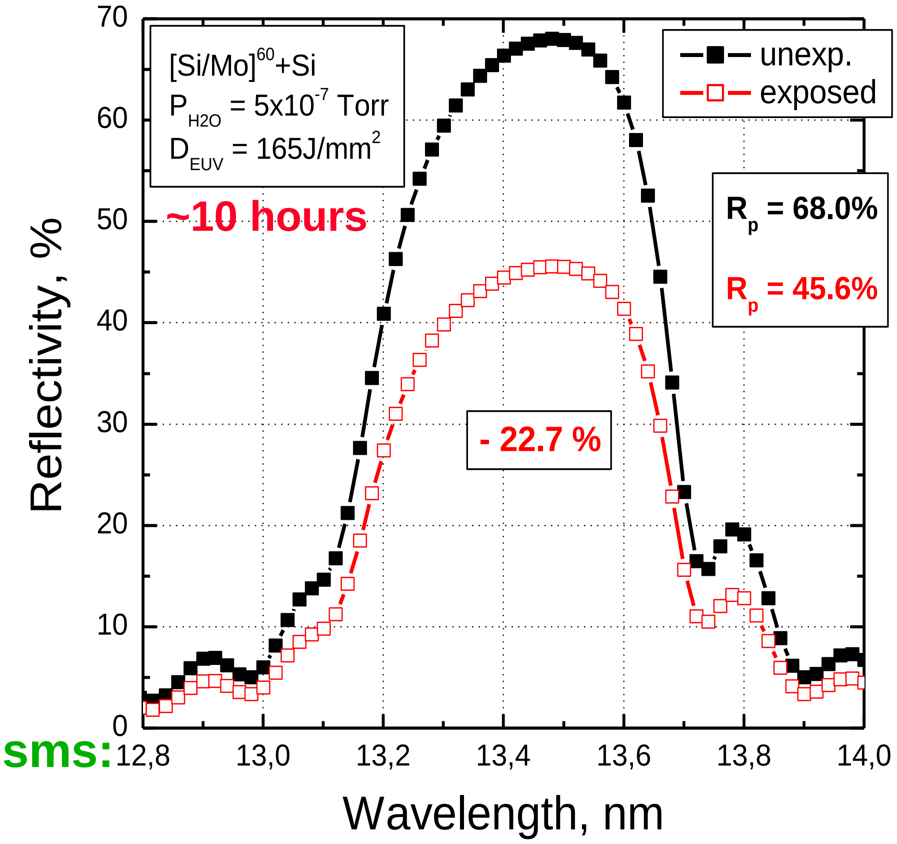
EUV intensity: **I_{EUV} ~ 10 mW/mm²**

Pressure: **P_{H2O} < 10^{-7} Torr**

P_{HC} < 10^{-9} Torr

Reflectivity loss: **Δ R < 1%**

(over 30.000 hours)



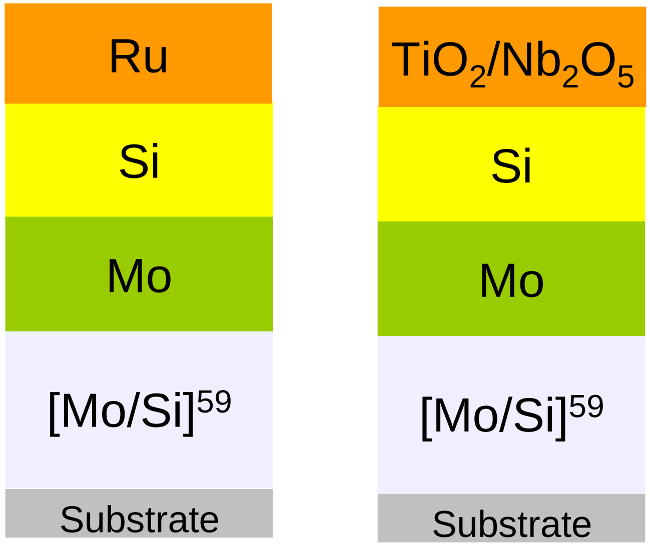
Damage caused by two main mechanisms:

- potentially irreversible **surface oxidation**
- demonstrably reversible **surface contamination** **(mainly carbon growth)**

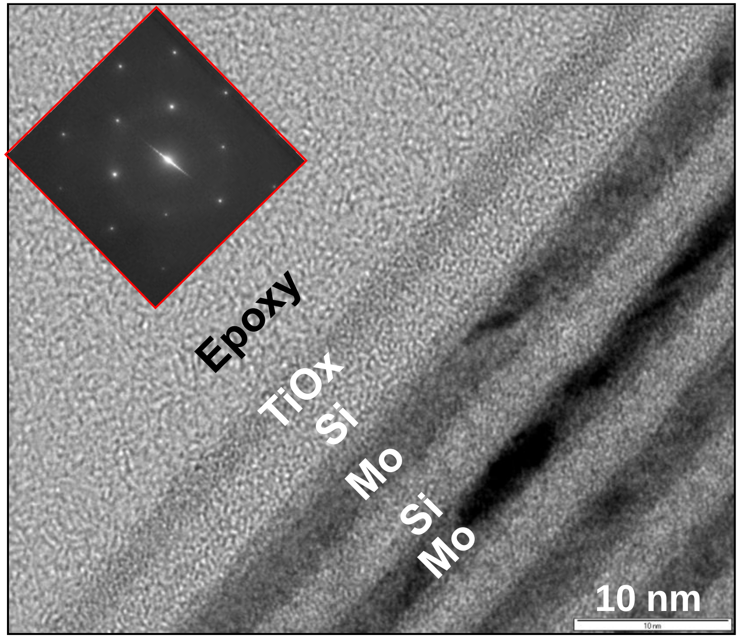
NIST Physics Laboratory

Fraunhofer IOF

Development of oxidation resistant capping layers



1999 - 2005	**2005 - 2010**
Ru	TiO_2/Nb_2O_5
Si	Si
Mo	Mo
$[Mo/Si]^{59}$	$[Mo/Si]^{59}$
Substrate	Substrate
$\sim 10^3$	**$\sim 10^4$**

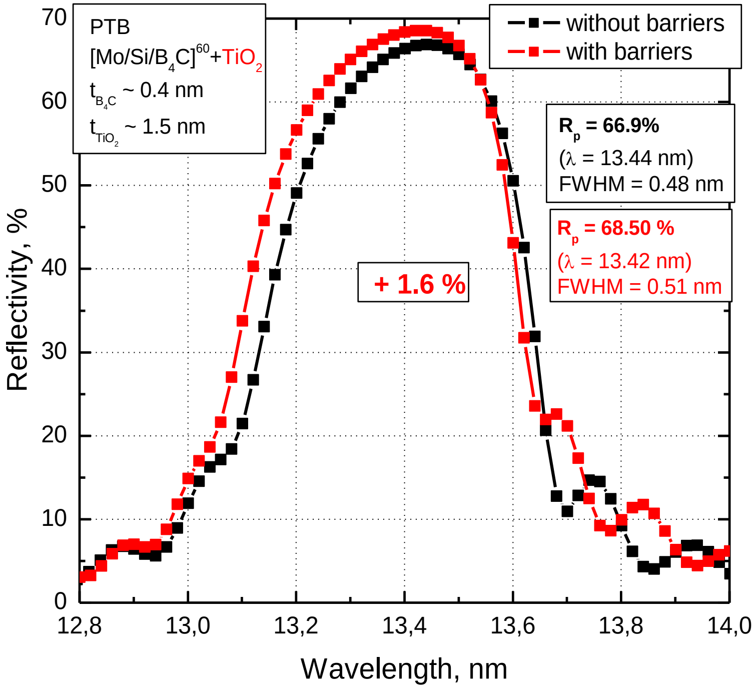


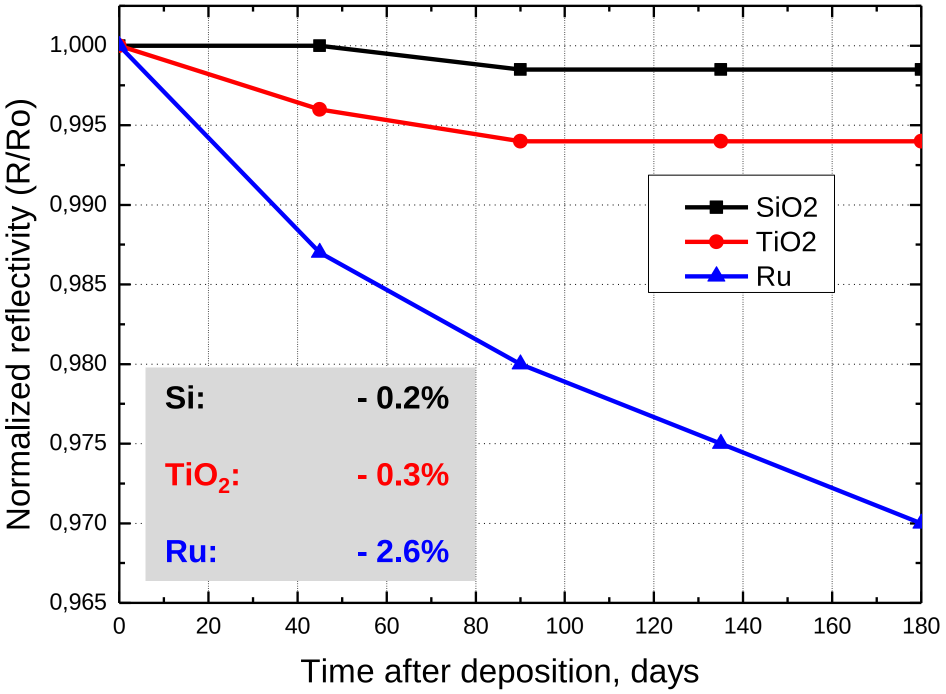
Three capping layer conceptions:

1) Low-oxidation materials: (Ru, Au, Pt …)
2) Stable oxides: (TiO_2, Nb_2O_5, ZrO_2…)
3) Multilayer conception: more than two layers

- Thickness < 2.0 nm
- Good optical properties
- Chemically inert to oxygen
- Amorphous structure
- Compatible with Mo/Si stack

Reflectivity and temporal stability of TiO_2-capped mirrors





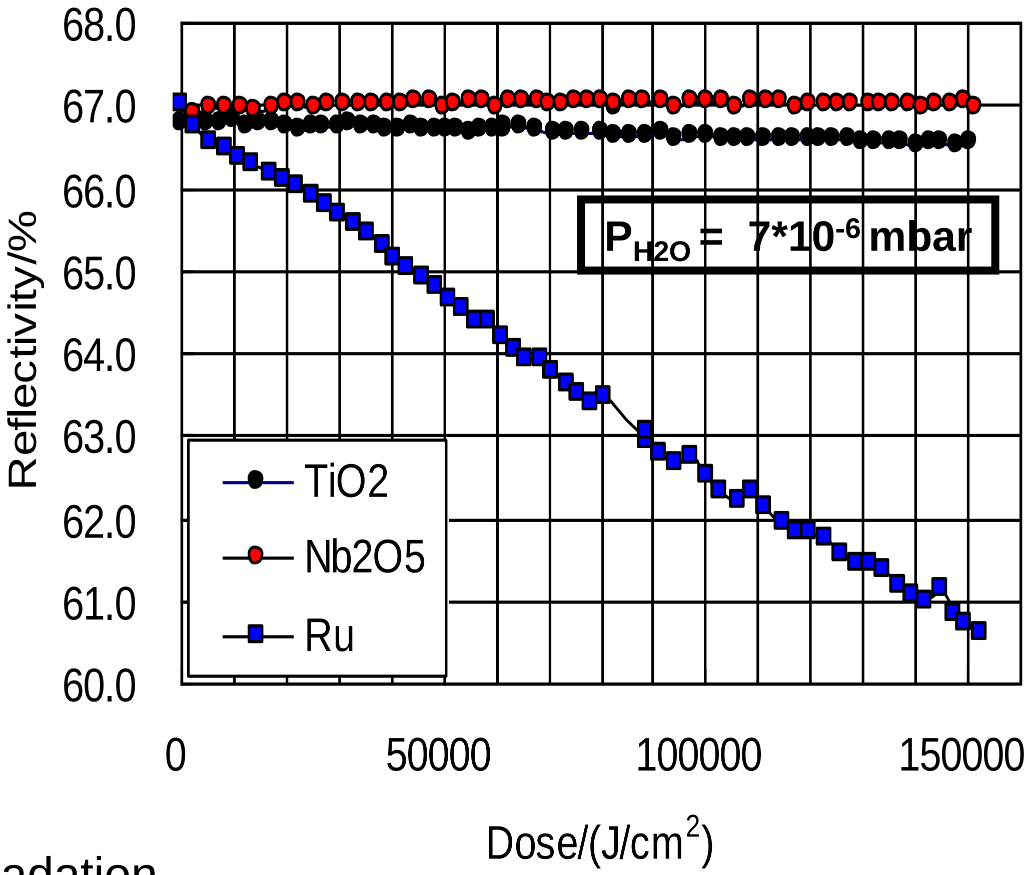
R = 68.5 % @ 13.42 nm

Reflectivity loss of 0.3% within 6 months

Enhanced radiation stability of TiO_2- and Nb_2O_5-capped mirrors

Synchrotron exposure set-up:

Synchrotron:	SAGA-LS BL18
Water pressure:	$7*10^{-6}$ mbar
EUV intensity:	~ 8.0 W/cm^2
Total dose:	150 kJ /cm^2



- Nb_2O_5 and TiO_2: no degradation
- Ru: degradation by surface oxidation

S. Yulin et al., EUVL Symposium, Prague, 2009

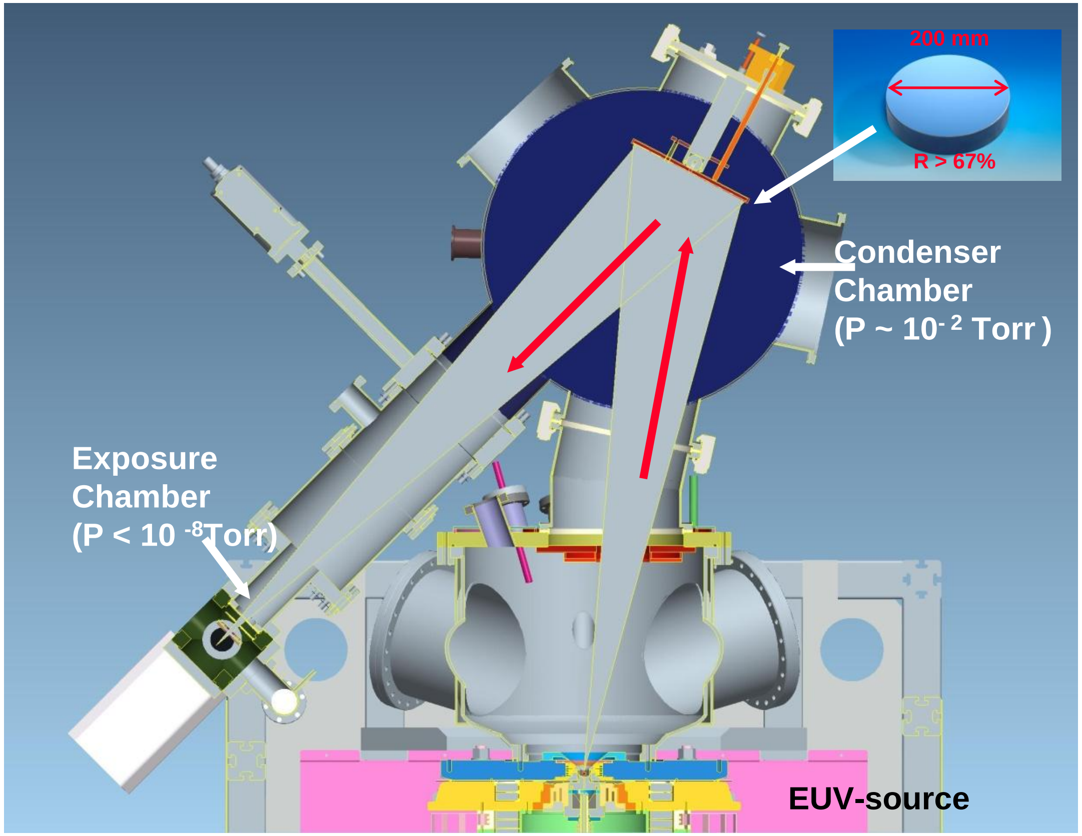
New Exposure Test Stand (ETS) & Xe-gas discharge

ETS requirements:

- Source: DPP / Xe
- Repetition rate: 4 kHz
- In-band power: $\leq 50\mathrm{W}/\mathbf{2}\pi$

- Background pressure $\leq 10^{-8}$ Torr
- Contaminant inlet $\leq 10^{-2}$ Torr
- Pressure control in-situ
- EUV-intensity > 25 mW/cm^2
- Irradiation area > 15x15 mm^2
- EUV intensity ± 5%

Simultaneous exposure up to 4 samples is possible with similar dose (± 5%)



Further prospects for enhanced radiation stability

Currently developed capping layers (for imaging optics):

Material	Rmax, %	Oxidation resistance		Carbon cleaning by EUV	
		Synchrotron	Pulsed	O_2	H_2
Ru	68.7	☹	☹	😐	😐
TiO_2	68.5	☺	☺	☺	😐
Nb_2O_5	68.5	☺	☺	☺	😐

Further studies/prospects:

- Developed capping layer materials should be tested for EUVL optics
- Application of new multilayer capping layer systems

Our limits:

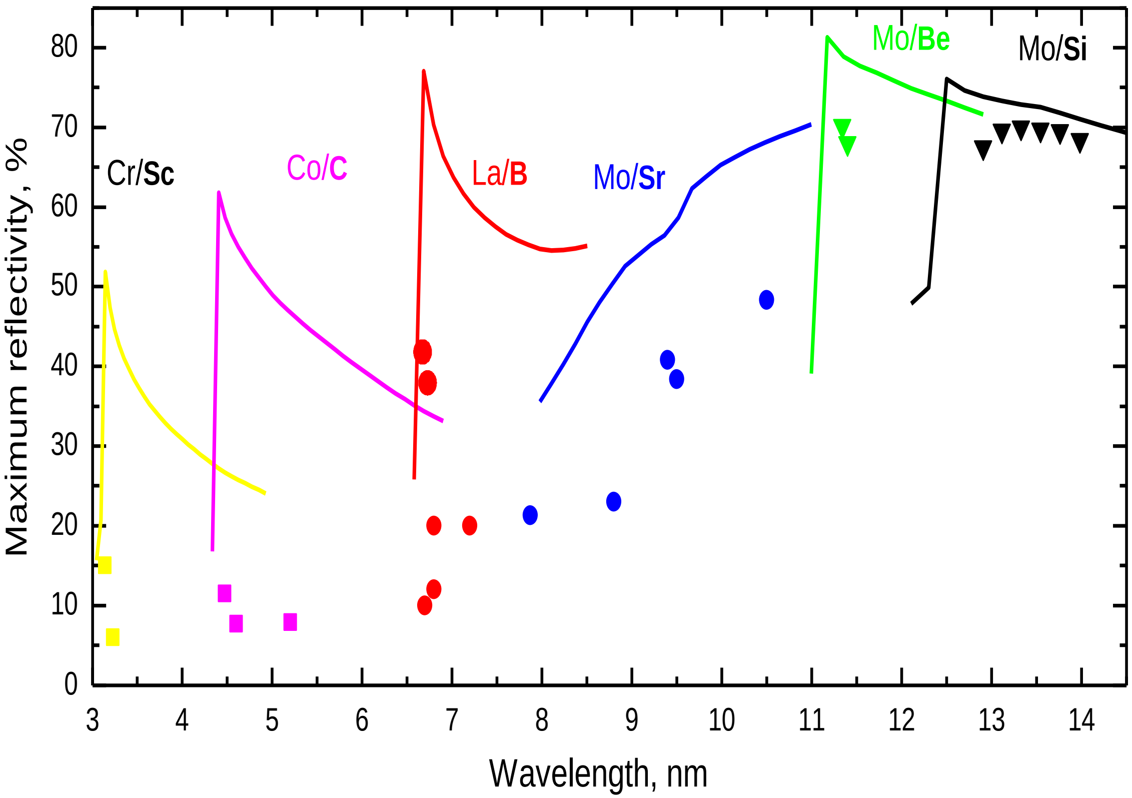
- Considerable reflectivity losses of EUVL optics due to application of oxide capping layer with d >> 2.0 nm (collector optics)
- Capabilities for lifetime studies with high-radiation power are still limited

Outline

- Introduction
- High-reflective Mo/Si MLs
- High-temperature Si-based MLs
- Radiation stable Mo/Si MLs
- B-based multilayers for future generation of EUVL
- Summary and outlook

Next generation of lithography (NGL)

Wavelength selection



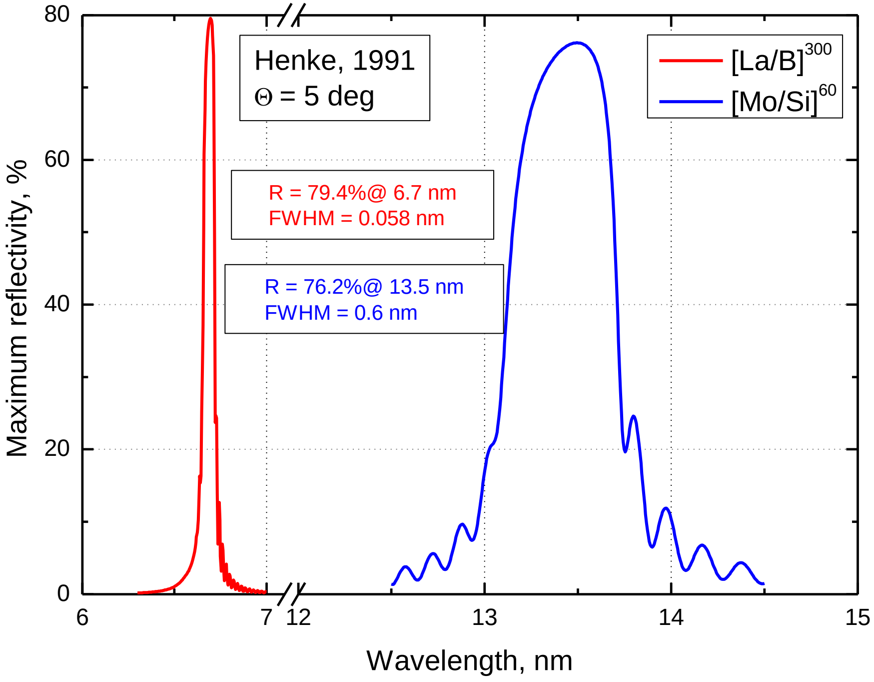
Reflectivity requirements:
(R > 70%)

Mo/Si	12.4 nm
Mo/Be	11.4 nm
La/B	6.67 nm

Fraunhofer
IOF

Theoretical reflectivity at 6.7 nm

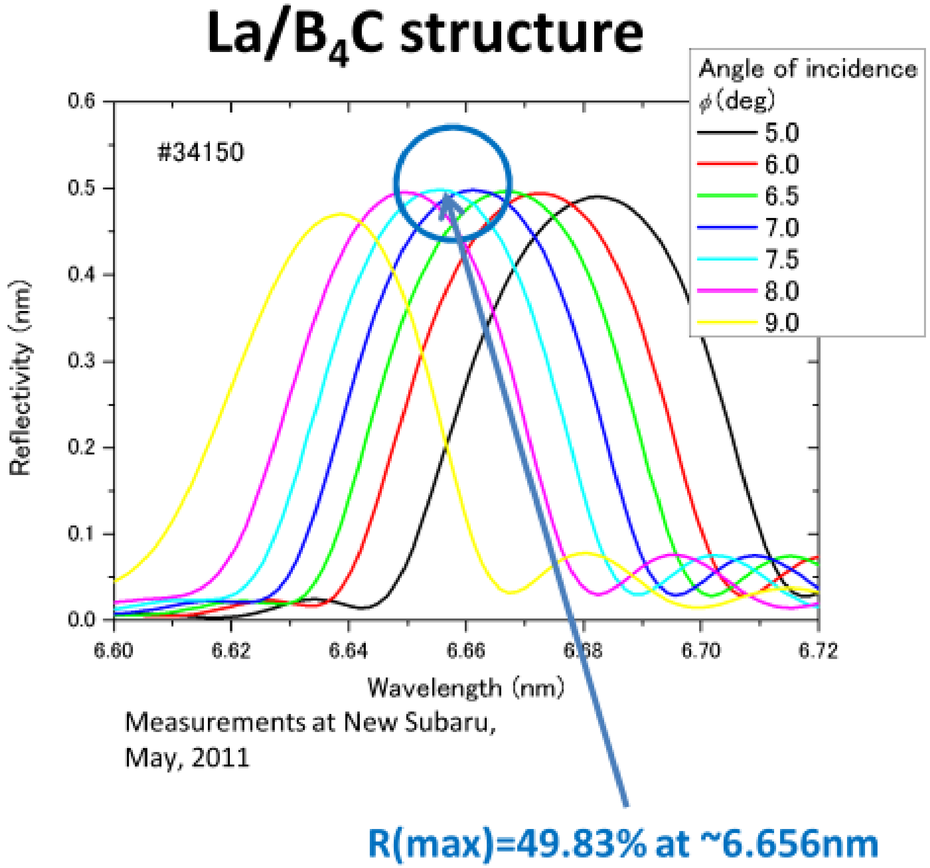
Reflectivity of La/B vs Mo/Si multilayers



	Mo/Si	La/B	Issue
R,%	76.1	79.5	~
d, nm	6.95	3.4	x 2
N	60	≥ 200	x 3
Δλ, nm	0.60	0.07	x10

- La/B multilayer mirrors are extremely narrowband (FWHM = 0.07 nm)
- Higher reflectivity losses can be predicted due to interface defects (d = 3.4 nm)

Experimental reflectivity at 6.7 nm (2012)


La/B_4C structure

Measurements at New Subaru,
May, 2011

R(max)=49.83% at ~6.656nm

Champion data is 49.8% @ 6.66 nm

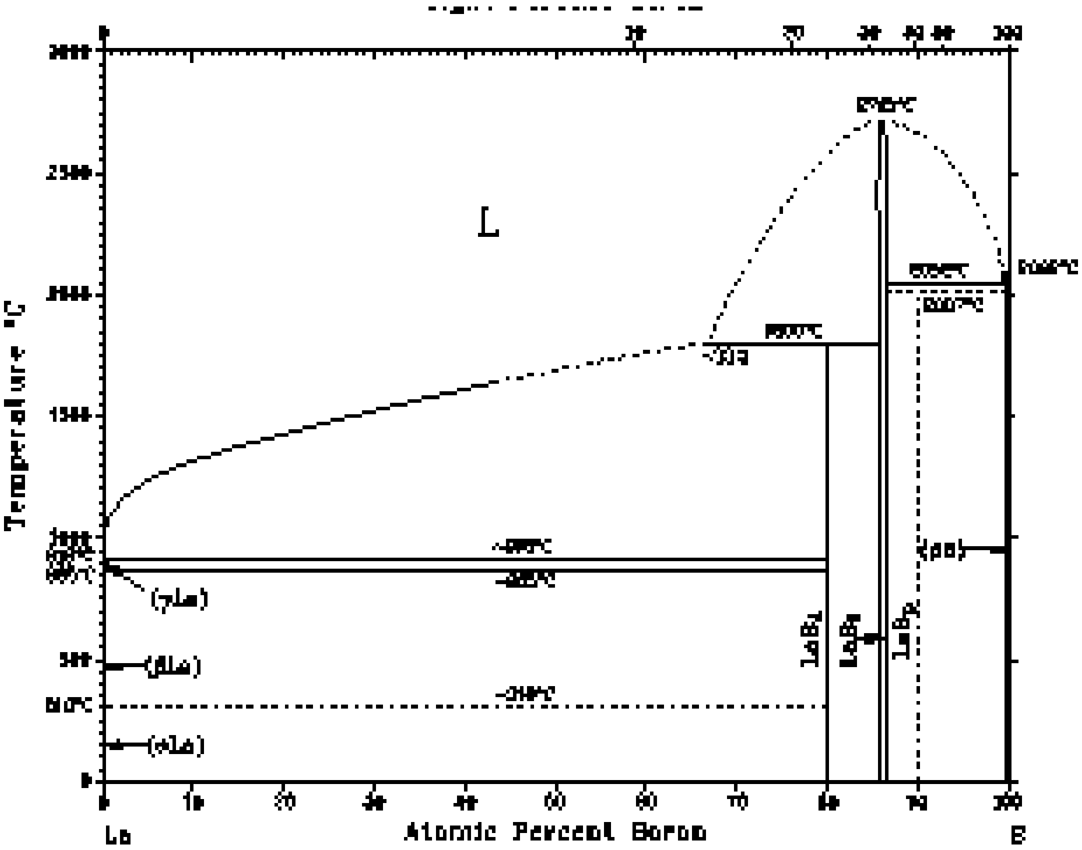
(Rigaku, Japan)

Reflectivity level > 45 % was shown

by few other multilayer suppliers

Y. Platonov et al: *Status of multilayer coatings for EUVL*: EUVL Workshop 2011, Maui, Hawaii.

La and B are not the best materials for multilayer mirrors



1) Polymorphismus in La:
   - α- La ρ = 2.46 g/cm^3
   - β- La ρ = 2.35 g/cm^3
   - γ- La ρ = 2.52 g/cm^3

La-layer is not stable

2) Three lanthanum boride:
   - LaB$_4$,
   - LaB$_6$
   - LaB$_9$

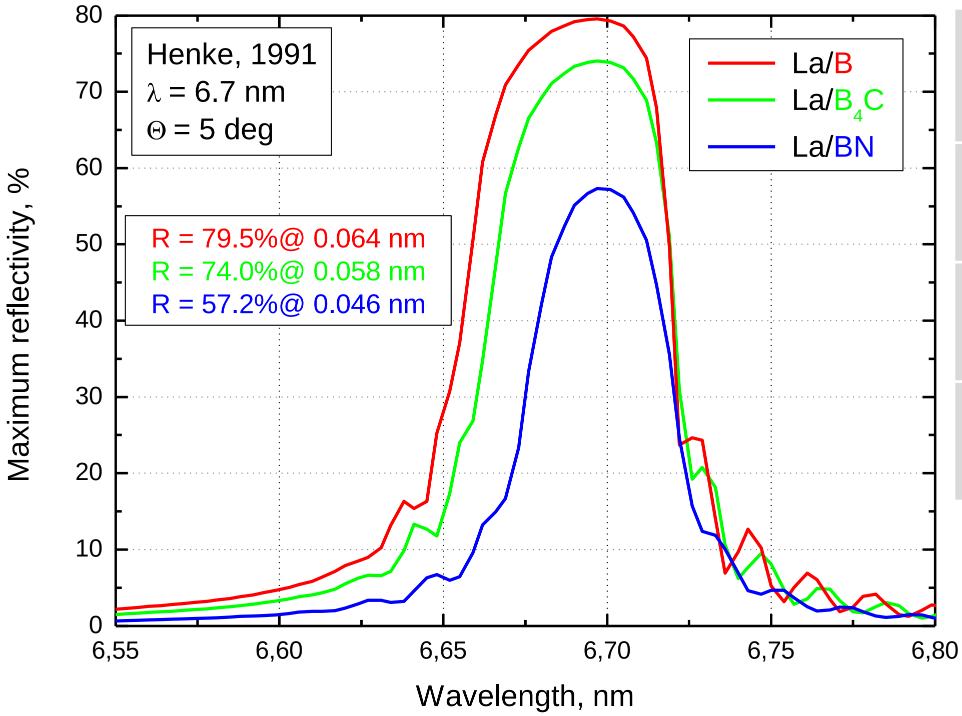
Considerable diffuse intermixing

3) La and B have extreme oxidation

Considerable surface oxidation

Currently only Mo/B$_4$C (not La/B) are commercially used for XRF !!!

Replacement of boron by boron carbide (B_4C)

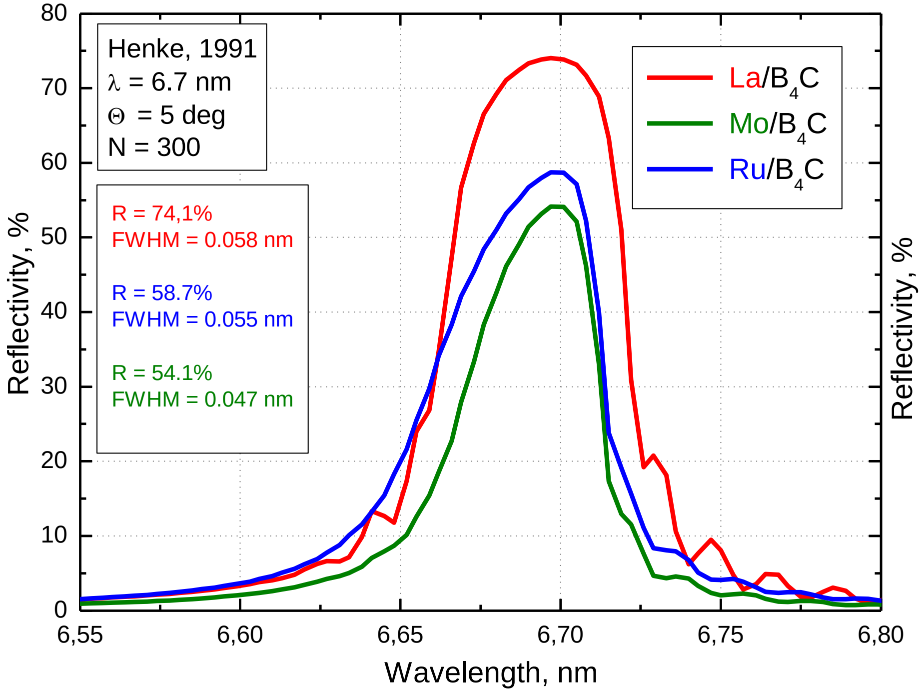


System	R, %	FWHM, nm
La/B	79.5	0.064
La/B_4C	74.1	0.058
La/BN	57.2	0.046

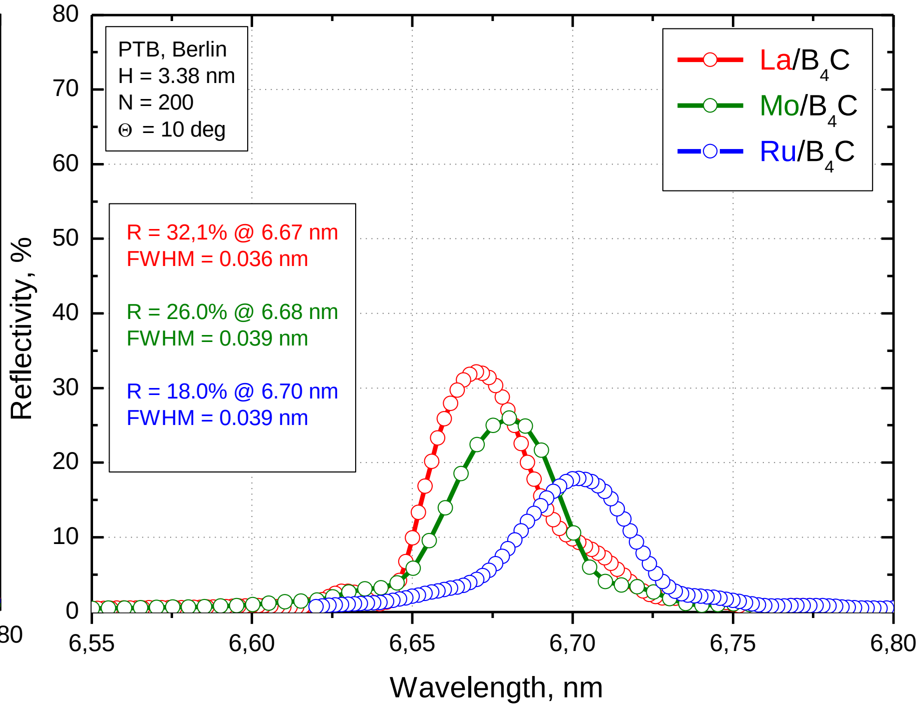
Transition from La/B to La/B_4C results in reflectivity loss of 5.4 % @ 6.7 nm.

B_4C-based multilayers with La-, Ru- and Mo-absorber layers

Theory



Experiment



Target of this study:

- interface performance
- temporal stability
- thermal stability

La/B_4C: R = 32.1% @ 6.67 nm

$R_{exp}/R_{th.}$ ~ 0.42…0.44 (σ ~ 0.8 nm)

S. Yulin et al. Reflective optics for next generation lithography, EUVL Symposium, Miami (2011)

Summary and outlook

- Remarkable progress has been made in the field of Mo/Si multilayer mirrors for EUVL application
- Interface engineering (barriers, capping layers…) was successfully used for:

improvement of optical properties:

Mo/Si/C: R = 69.6% @ 13.5 nm
Mo/Si/SiC: R = 69.1% @ 13.4 nm

enhanced thermal stability:

Mo/C/Si/C R = 60.0% & T ≤ 400 °C

Mo/X/Si/X R = 60.0% & T ≤ 600 °C

enhanced radiation stability:

$Mo/Si/B_4C + TiO_2$ R = 68.5% @ 13.5 nm

$Mo/Si/B_4C + Nb_2O_5$ R = 68.5% @ 13.5 nm

- Lifetime of EUVL optics is still actual issue for multilayer community

Acknowledgements

Support: Cymer Inc. and Intel Cor.

EUV: Ch. Laubis, Ch. Buchholz, J. Puls, A. Barboutis,
Ch. Stadelhoff, M. Biel, B. Dubrau and F. Scholze (*PTB Berlin)*

TEM: U. Kaiser (*University, Ulm*)

IOF: M. Scheler, T. Müller, St. Schulze *(IOF)*

Thanks for your attention !