Working towards High Reflectivity in the Extreme Ultraviolet & Soft X-ray

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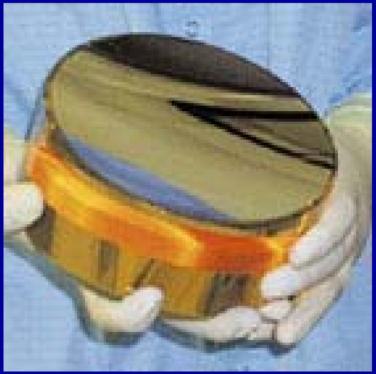
A tale of two materials & understanding very thin layers

- Scandium- the promise
  - Needs a partner and/or barrier
  - Vanadium ?
- Klaprothium and variations
- Understanding ultrathin layers
  - The role of oxides
  - The role of cleaning

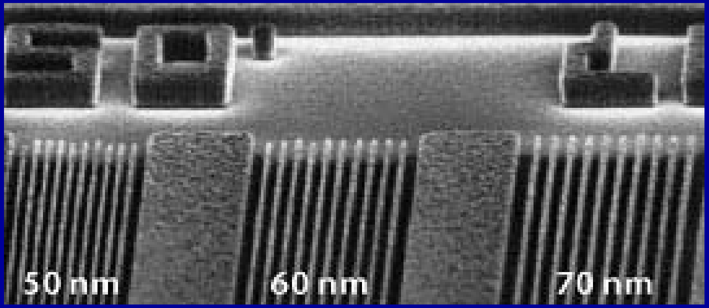
Why Extreme Ultraviolet & Soft X-rays?

Thin Film or Multilayer Mirrors

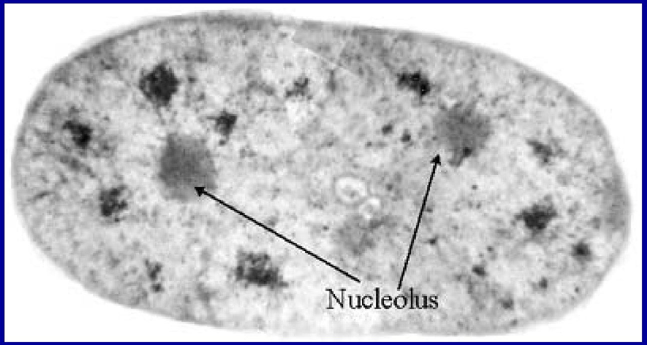


EUV Lithography

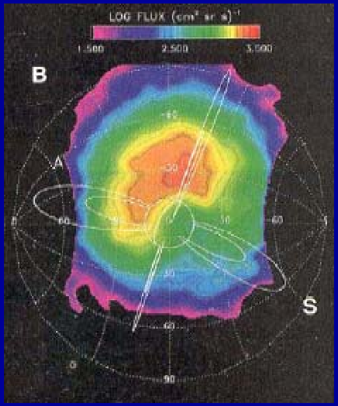
(making *really* small computer chip features)

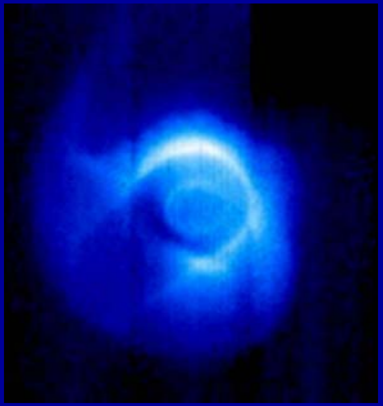


Soft X-ray Microscopes



EUV Astronomy





The Earth's magnetosphere in the EUV

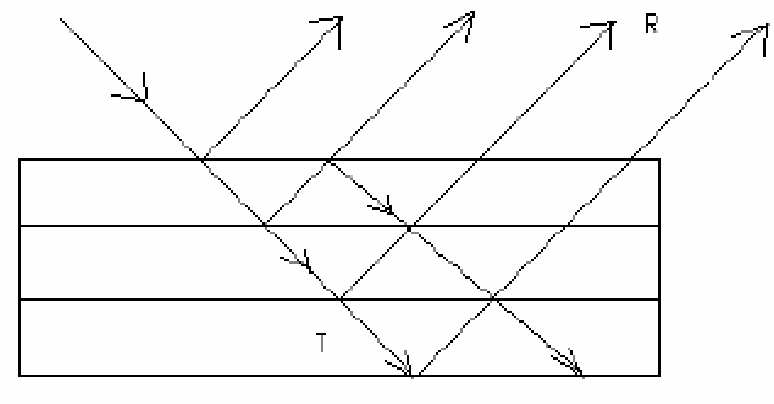
Images from www.schott.com/magazine/english/info99/ and www.lbl.gov/Science-Articles/Archive/xray-inside-cells.html.

EUV & soft x-rays

- Visible is ~400 to ~700 nm (1.7 to 3 eV)
- UV down to about 170 nm (~7 eV)
- VUV- Vacuum UV (starts where N_2 is absorbing) then there is FUV & EUV
- EUV/soft x-ray
  - 47 nm is the λ for the Ne-like-Ar X-ray Laser, (Capillary Discharge- CSU, Jorge Rocca) But
- (projection) EUV lithography at ~13.5 (92 eV).
- X-rays first understood came from electrons being knocked out of K shell and electron falling in.
- I put the division at about 11 nm (110 eV)- Be K edge.

Why Ultrathin Films Reflectors?

- Goal: To maximize delivery of light in the EUV
- Problem: EUV is absorbed quickly by most materials; a beam of EUV light is absorbed in 100 nm of H_2O. Even worse, conventional optical devices will not reflect EUV light.
- Solution: Use thin films or multiple layers to optimize reflectance
  - Most of the light that passes through the top layer will be reflected from a subsequent layer.
  - H/L stacks If the thicknesses and compositions of all films are carefully controlled the reflected light will constructively interfere resulting in the brightest possible reflection.



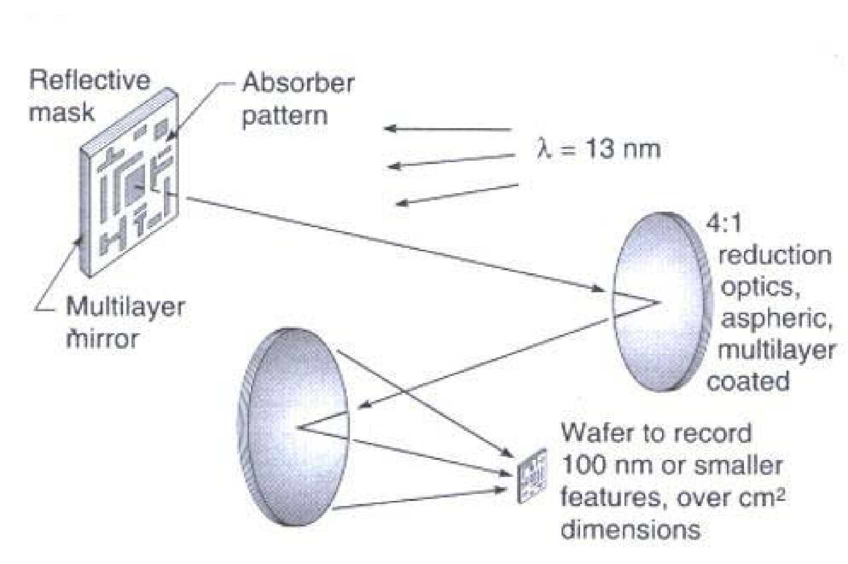
Multiple Reflections

Why Projects in the EUV ~ 45 nm?

1. We have experience (Image Space craft)
2. Laser.
3. Consider planned 13.5-nm lithography

Projection EUV lithographic

- Big jump from 157 to ~13 nm. Before this has about ¼ increase in energy. Now 10x.
- Mo/Si ~40 layer pairs ~68% reflectance Where Mo and Si are most transparent.
- Mo/Be is higher but narrower.

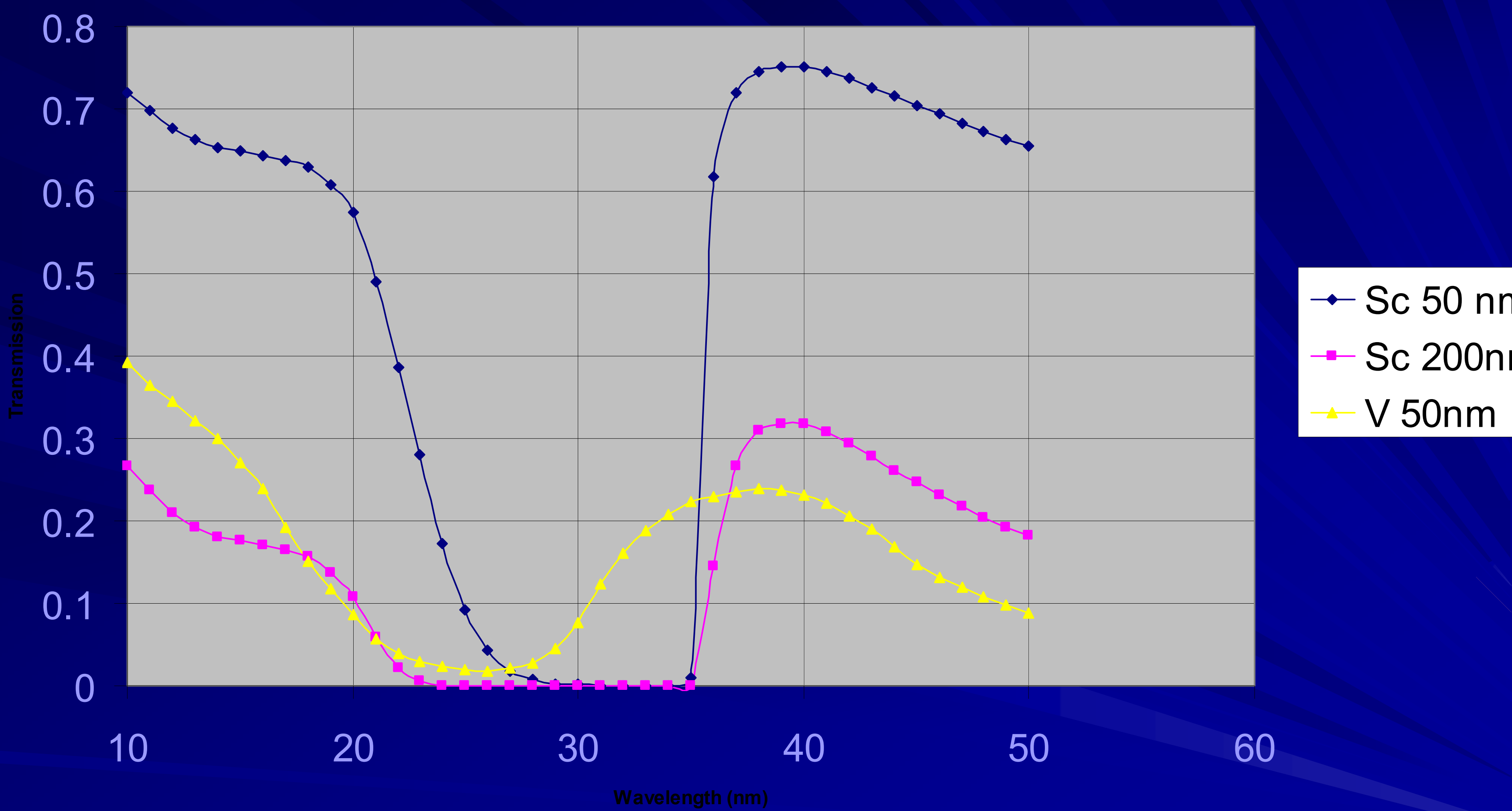


Why not a stop at ~46 nm?

- Hard to get high reflectances
- Materials and thicknesses
- A Russian group suggested scandium/ silicon MLs. Scandium was "calculated" to have exceptional transparency above ~ 35 nm. Computed normal incidence R of ~70%.
- Highest seen is in the 40%'s- evidence of substantial interdiffusion.(~2 nm/interface)

Scandium

- We tried Sc/Al ML
- No evidence of layering
- We examined binary phase diagrams and literature optical data.
  - Sc & V


0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
Transmission
10
20
30
40
50
60
Wavelength (nm)
Sc 50 nm
Sc 200nm
V 50nm

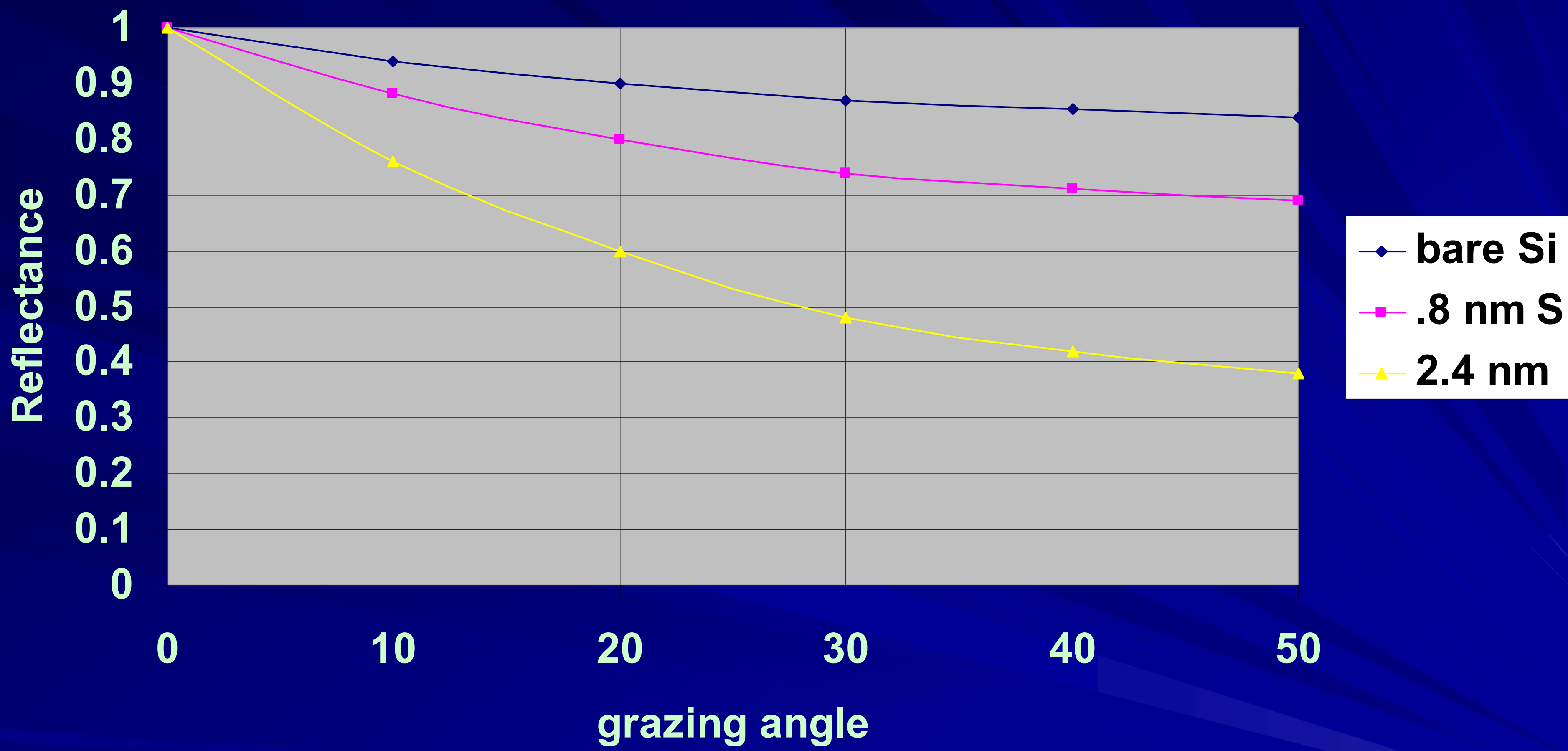
How to use it

- Sc as spacer. V as Absorber
- Scandium / Si or Al with V as barrier

Intermediate Steps

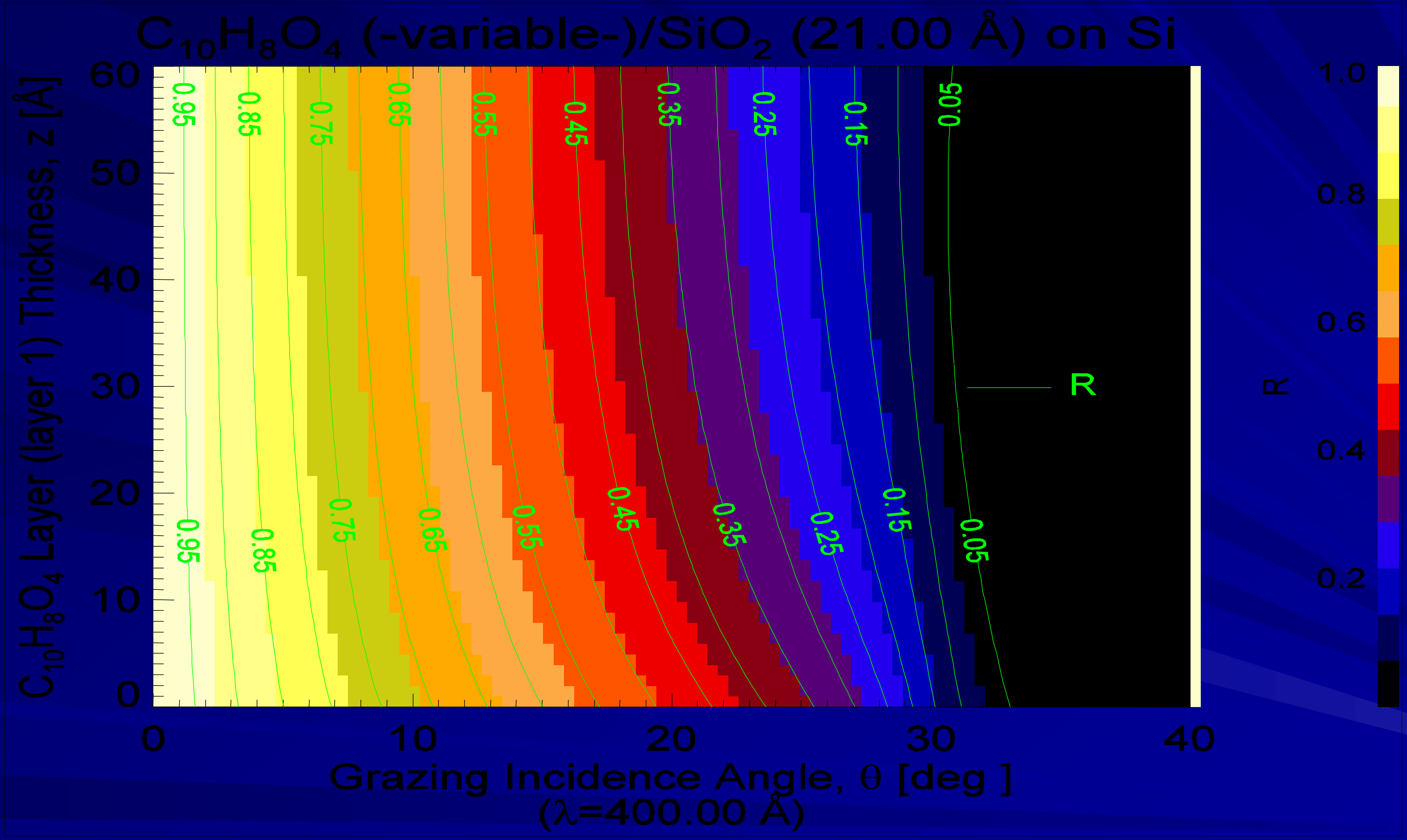
- Optical constants
- Optical constants and thicknesses of oxides
- Getting clean surfaces

10.2 eV



1
0.9
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
Reflectance
0
10
20
30
40
50
grazing angle
bare Si
.8 nm Si
2.4 nm

Hydrocarbon Buildups Lower Reflectance

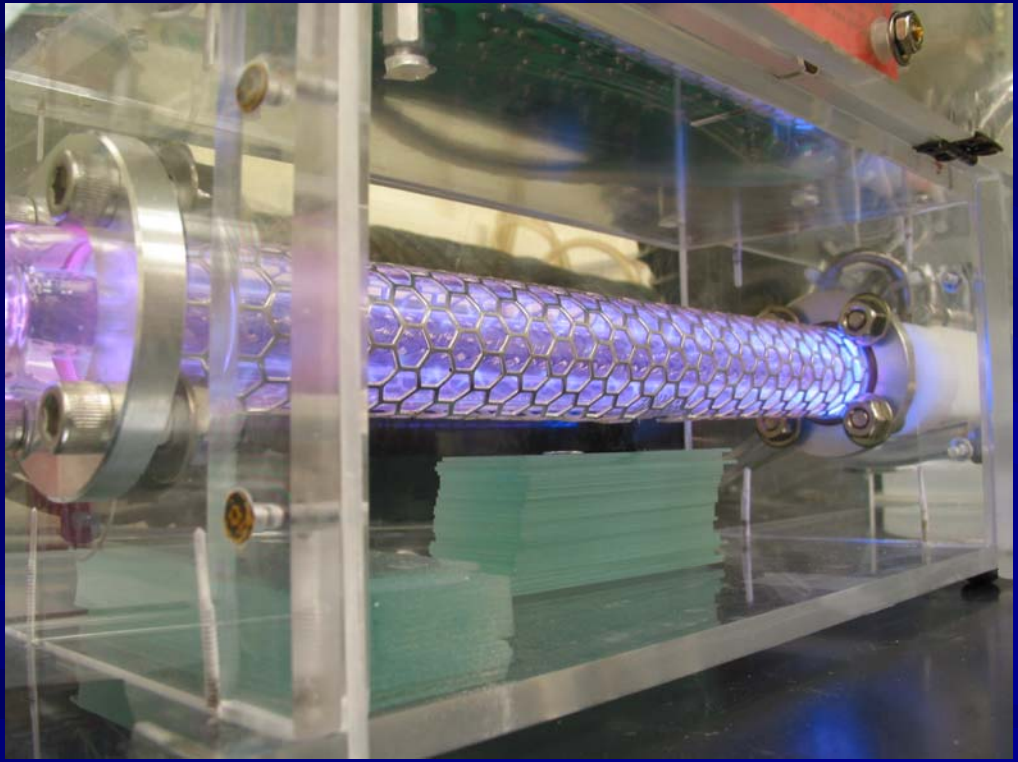


Reduced Reflectance with Hydrocarbon Thickness. Theoretical change in reflectance vs. grazing angle and organic thickness. (at λ=40.0 nm)

Four Methods of Cleaning Tested

- Opticlean®
- Oxygen Plasma
- Excimer UV Lamp
- Opticlean® + Oxygen Plasma

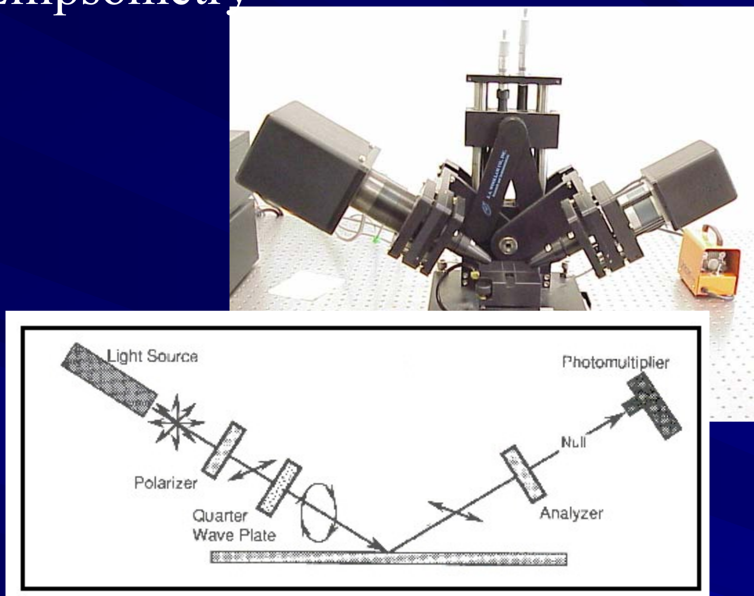
UV Lamp Theory



- High energy photons break up hydrocarbon bonds. Volatile fragments leave the surface.
- UV produces oxygen radicals which react with oxygen gas to form ozone. The reactive ozone & UV oxidize contaminants and they evaporate.

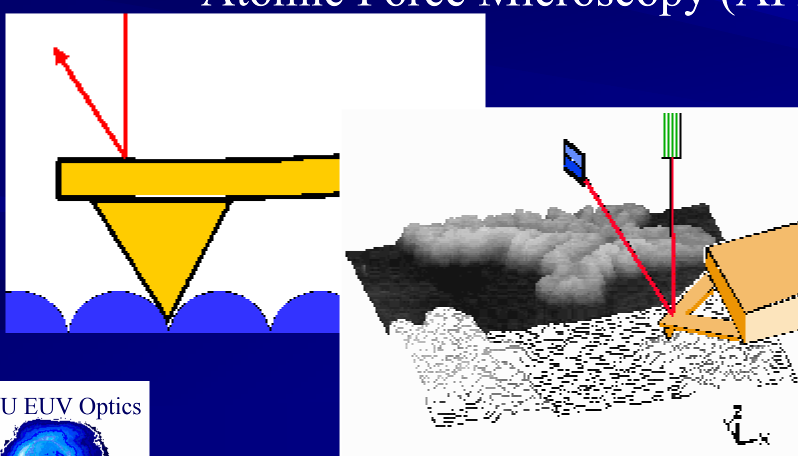
Studying Our Samples

Ellipsometry

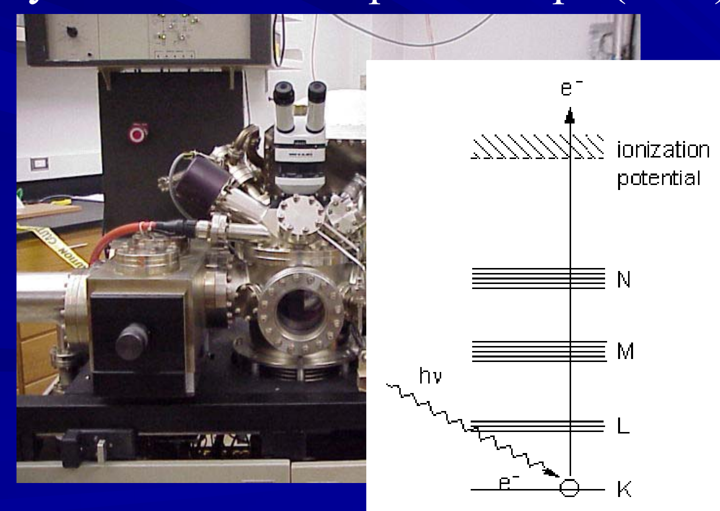


Scanning/Tunneling Electron Microscopes (SEM/TEM)

Atomic Force Microscopy (AFM)



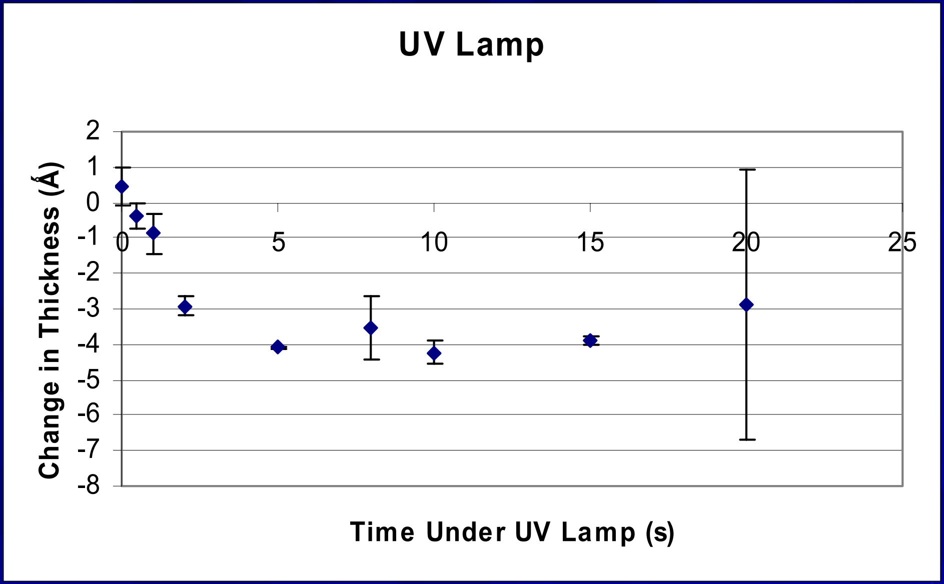
X-ray Photoelectron Spectroscope (XPS)

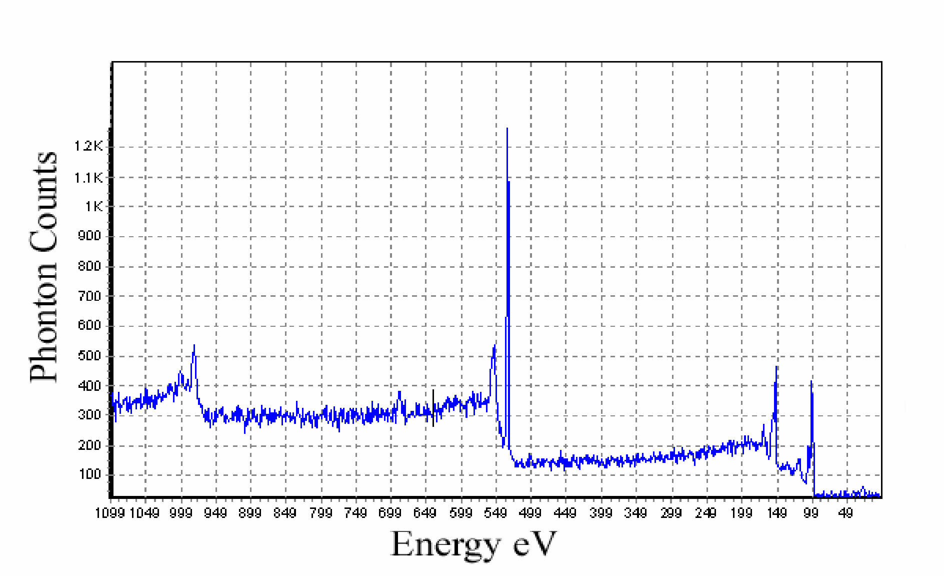


Images courtesy of http://www.weizmann.ac.il/surflab/peter/afmworks/, http://www.mos.org/sln/SEM/works/, http://www.swt.edu/~wg06/manuals/Gaertner117/ellipsometerHome.htm and http://volta.byu.edu/adamson03.pdf.

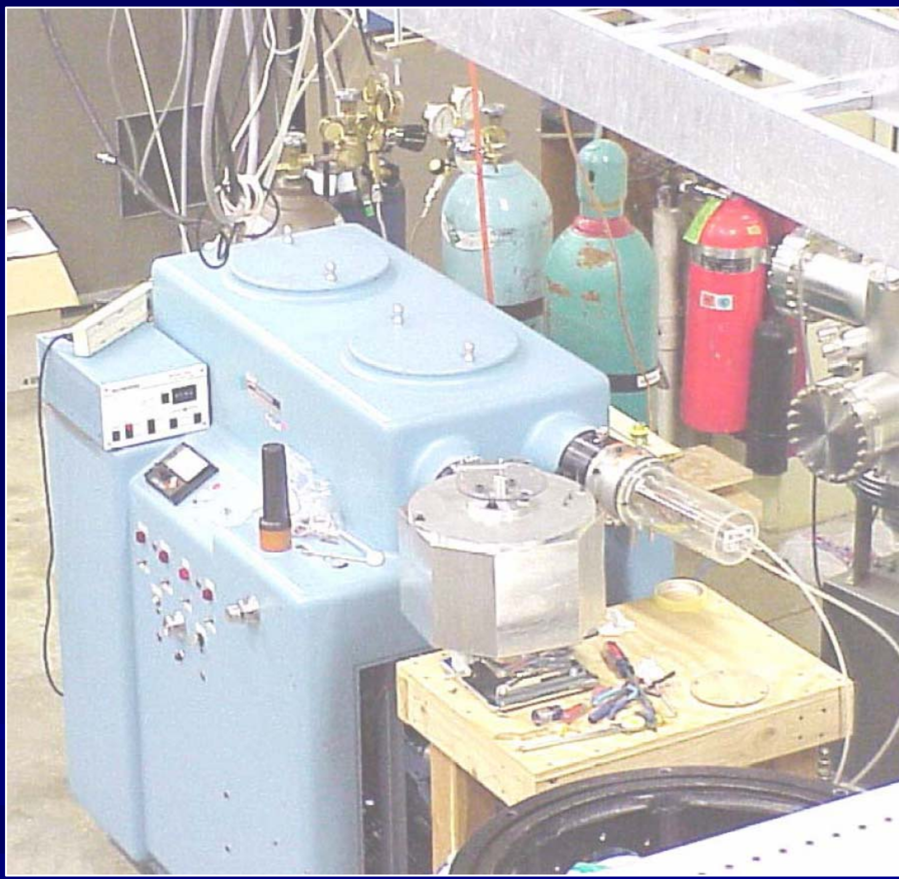
UV Results

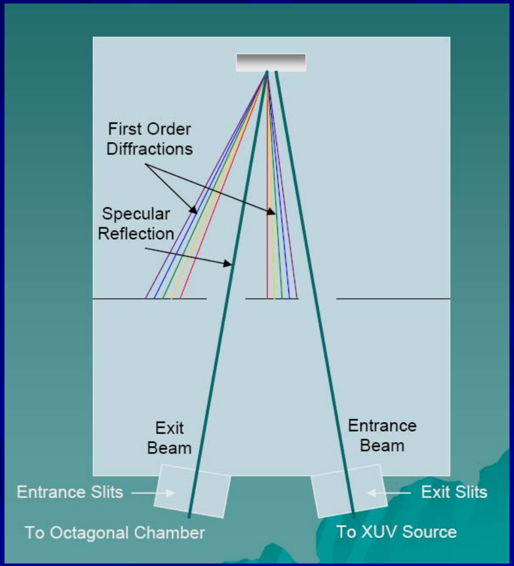
- 4.5 Å DADMAC layer eliminated rapidly, followed by slow oxidation.
- XPS shows no carbon peak.
- Concern: silicon doesn't appear to oxidize, but mirror coatings such as U and Ni do.

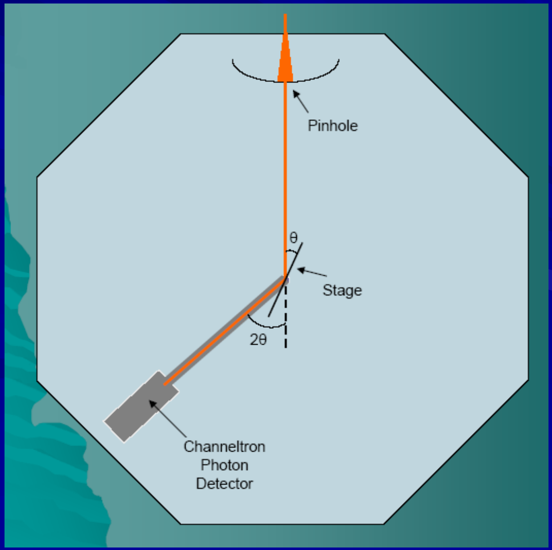




Taking Reflectance Measurements with the Monochromator







40 nm results to date

- We have learned how to clean up some substrates and samples
- protocols to study oxides
- Spend too much time of preparation
- Will use facts learned soon to prepare ML

Klaprothium

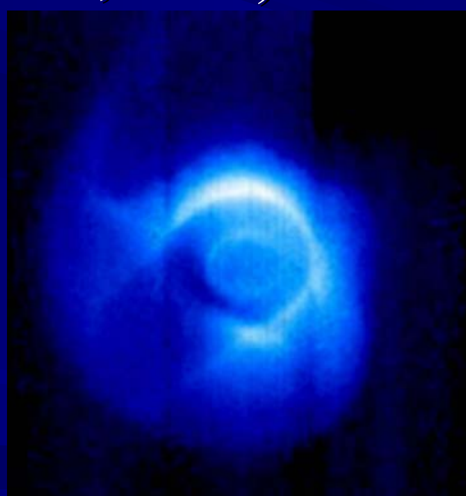
- In late 18th Century German Chemist, Klaproth discovered a new element which some suggested be called after him.

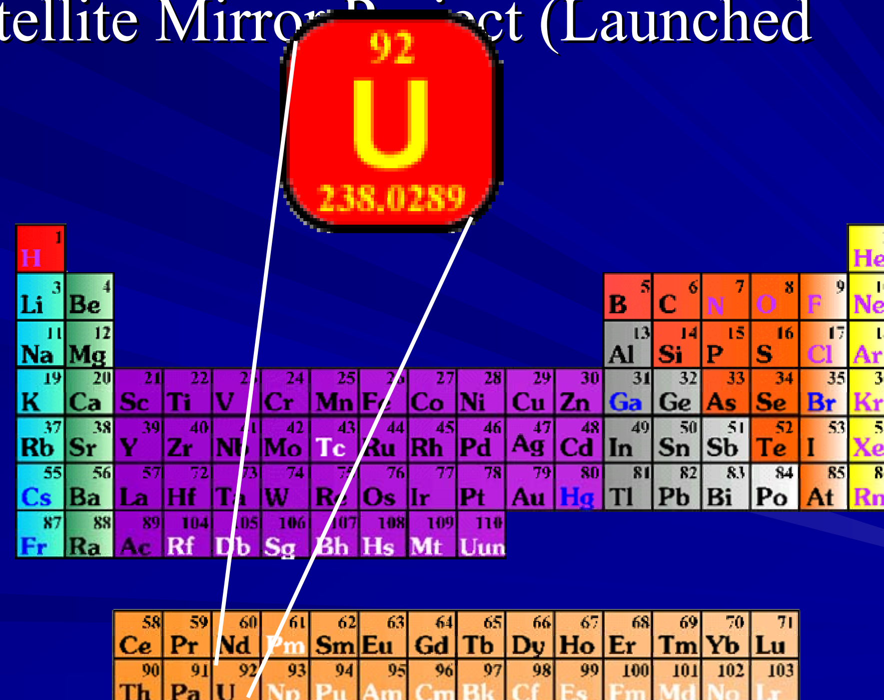
- He called it Uranium. I will call it Kp

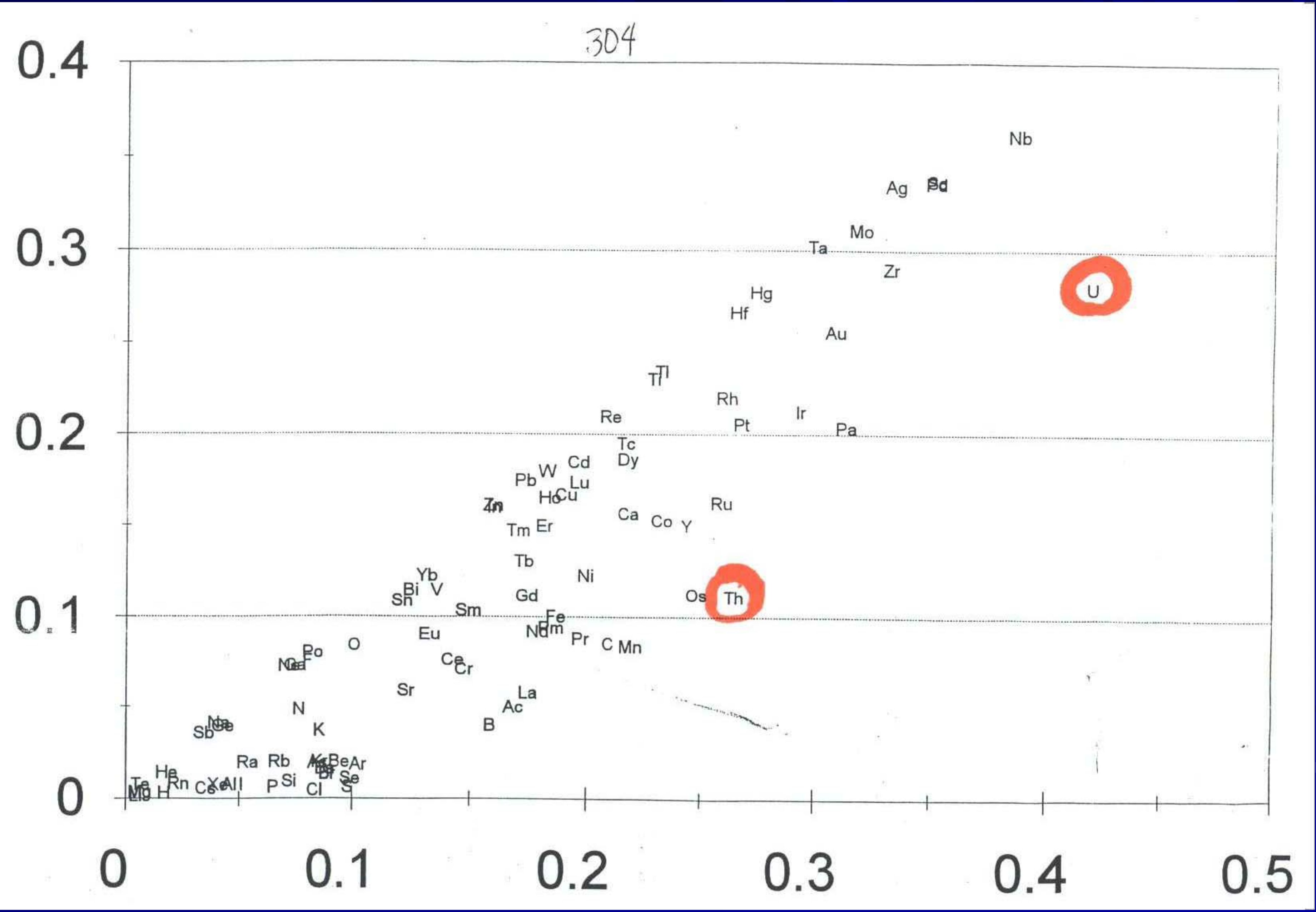
- He died in early decades of 19th Century, thinking he had isolated the element Uranium
- About two decades later however
  - This reaction was use $Kp + 2C + 2Cl_2 \rightarrow 2CO + UCl_4$.
  - This established kp was actually and oxide
  - Now known to be UO_2

Why Uranium?

- Uranium has many electrons to interact with photons (light) and is more dense than many materials, causing them to interact with high energy EUV photons.
- High Theoretical Reflectivity: Low absorption, β and high δ
- Previous Success: IMAGE Satellite Mirror Project (Launched March 25, 2000)

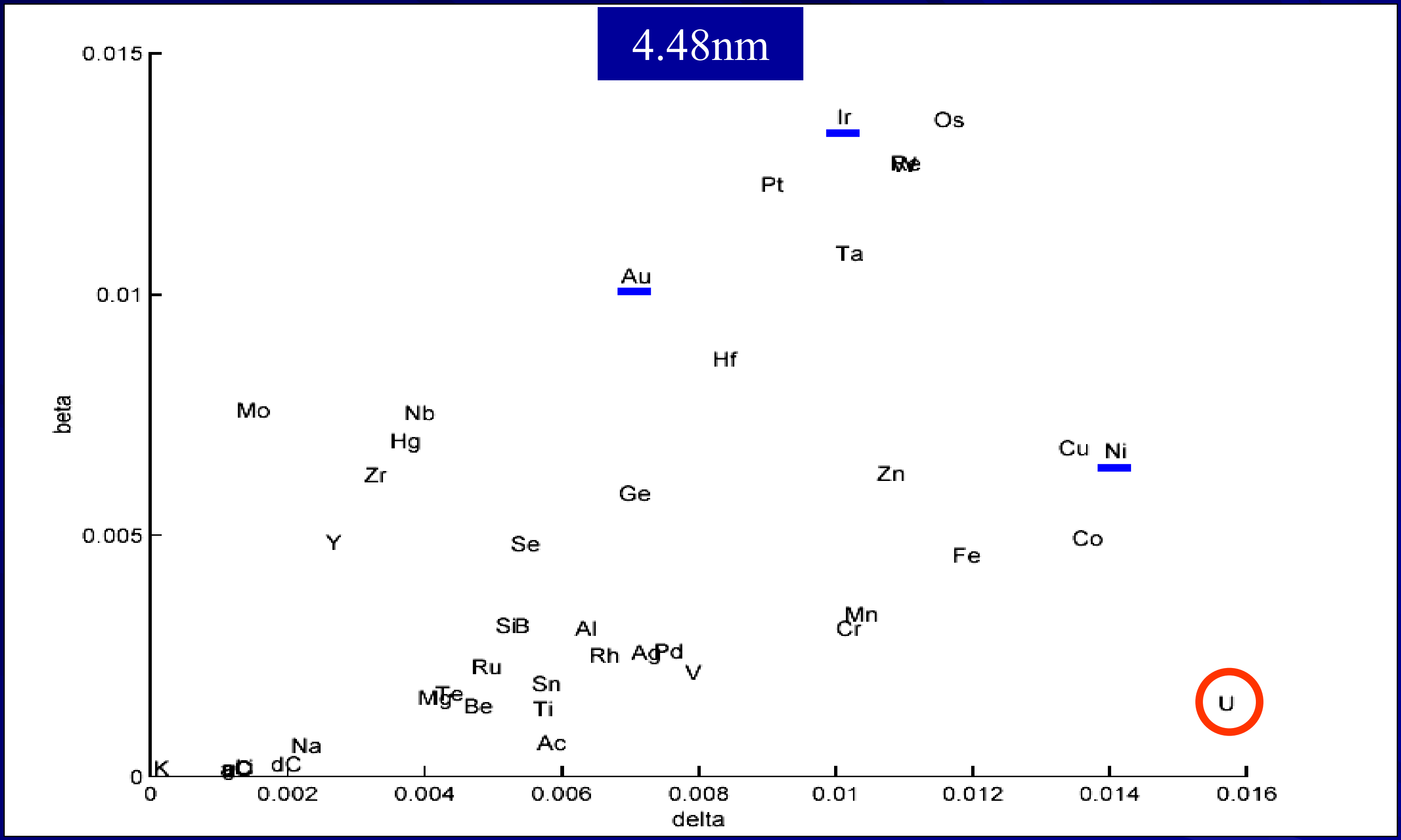






304
0.4
0.3
0.2
0.1
0
0
0.1
0.2
0.3
0.4
0.5
Nb
Ag
Mo
Ta
Zr
U
Hg
Hf
Au
Tl
Rh
Ir
Re
Pt
Pa
Tc
Dy
Cd
W
Pb
Lu
Cu
Ru
Ca
Co
Y
Tm
Er
Tb
Ni
Yb
Bi
V
Gd
Os
Th
Sm
Fe
Eu
Pr
C
Mn
O
Po
Sr
La
Ac
N
B
K
Ra
Rb
Ar
Si
P
Cl
Se
S
H

Delta vs. beta plot for several elements at 4.48 nm

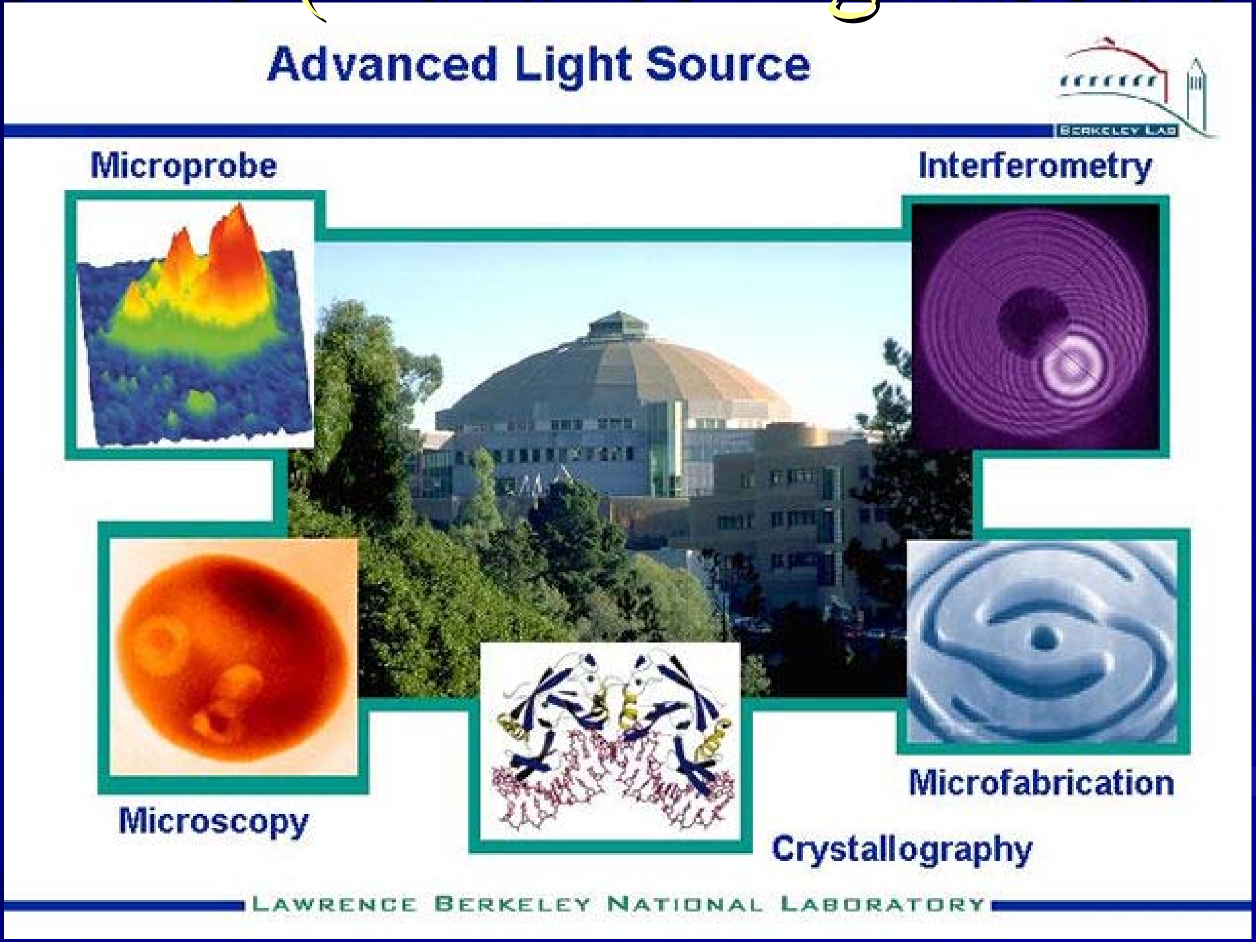


Note: Nickel and its neighboring 3d elements are the nearest to uranium in this area.

$$\tilde{n}_r = n + ik = 1 - \delta + i\beta$$

$$\delta = 1 - n, \quad \beta = k$$

Taking Reflectance Measurements at the ALS (Advance Light Source)

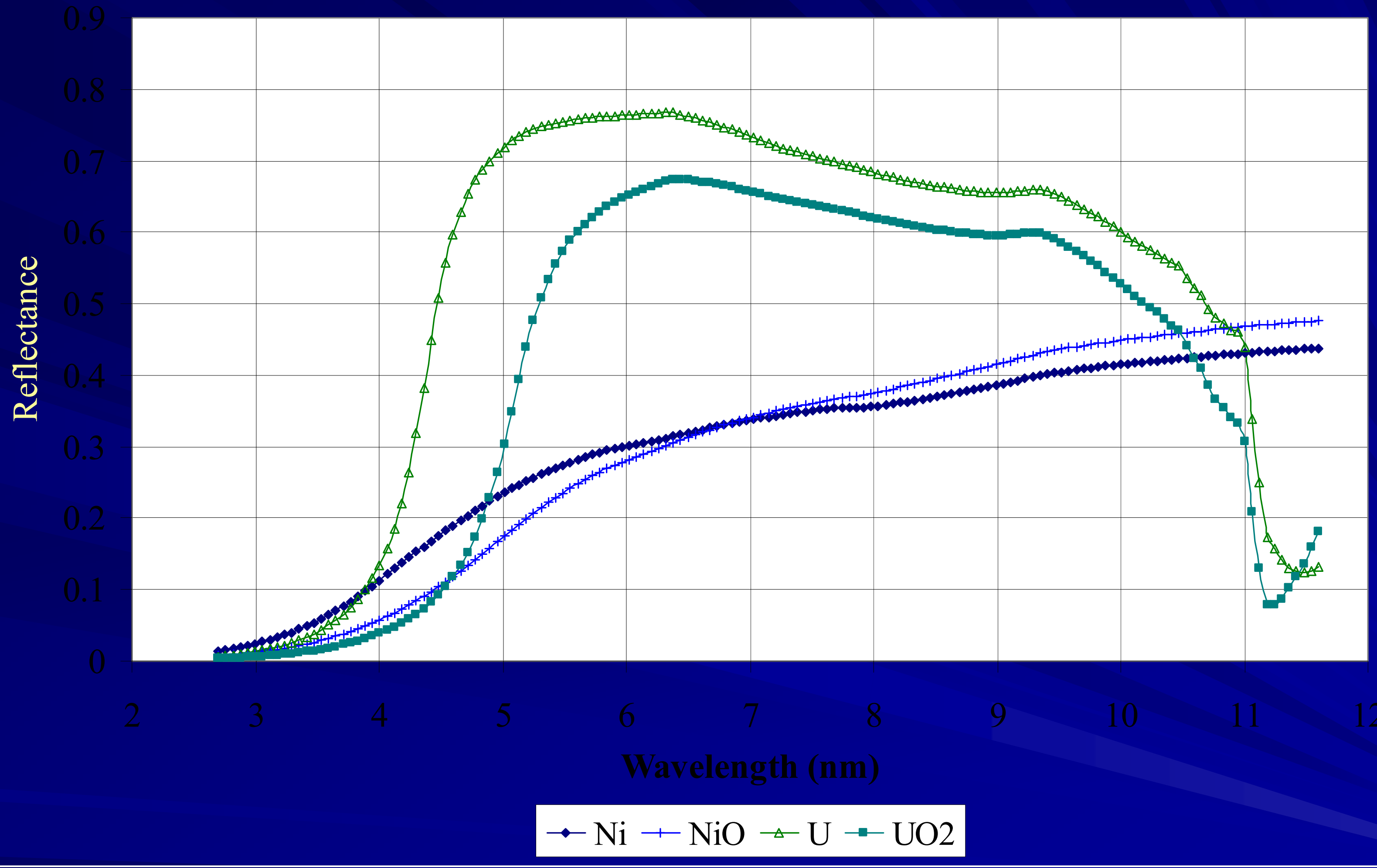


Inage courtesy of http://www.lbl.gov/

Uranium Oxide as a Highly Reflective Coating from 2.7 to 11.6 Nanometers-

- **specific application low-angle of incidence.**

Computed Reflectance, ASF model, CXRO



Reflectances for Ni, NiO, U, and UO2 predicted by the atomic scattering factor model from the Center for X-Ray Optics (CXRO) website (www-cxro.lbl.gov).

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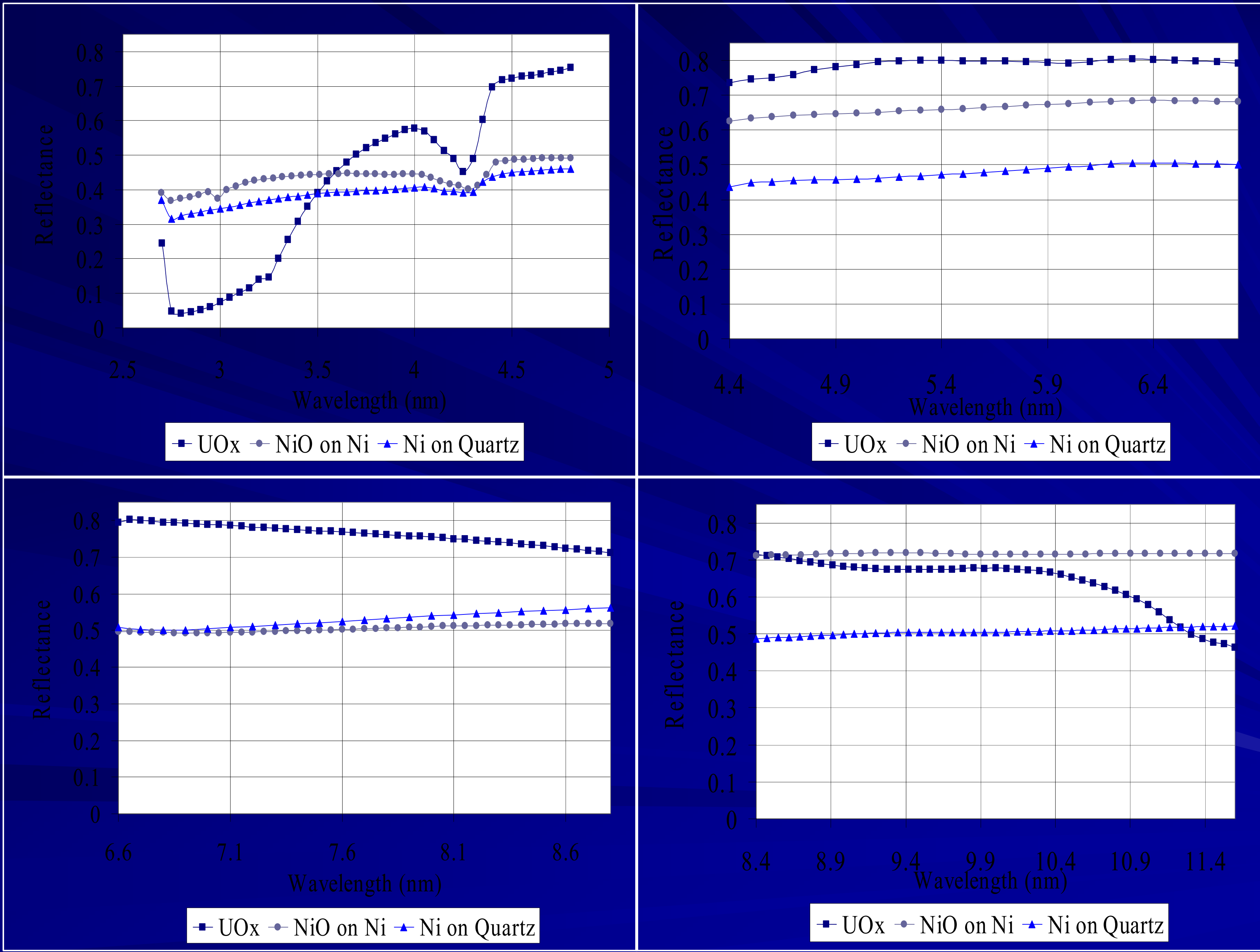
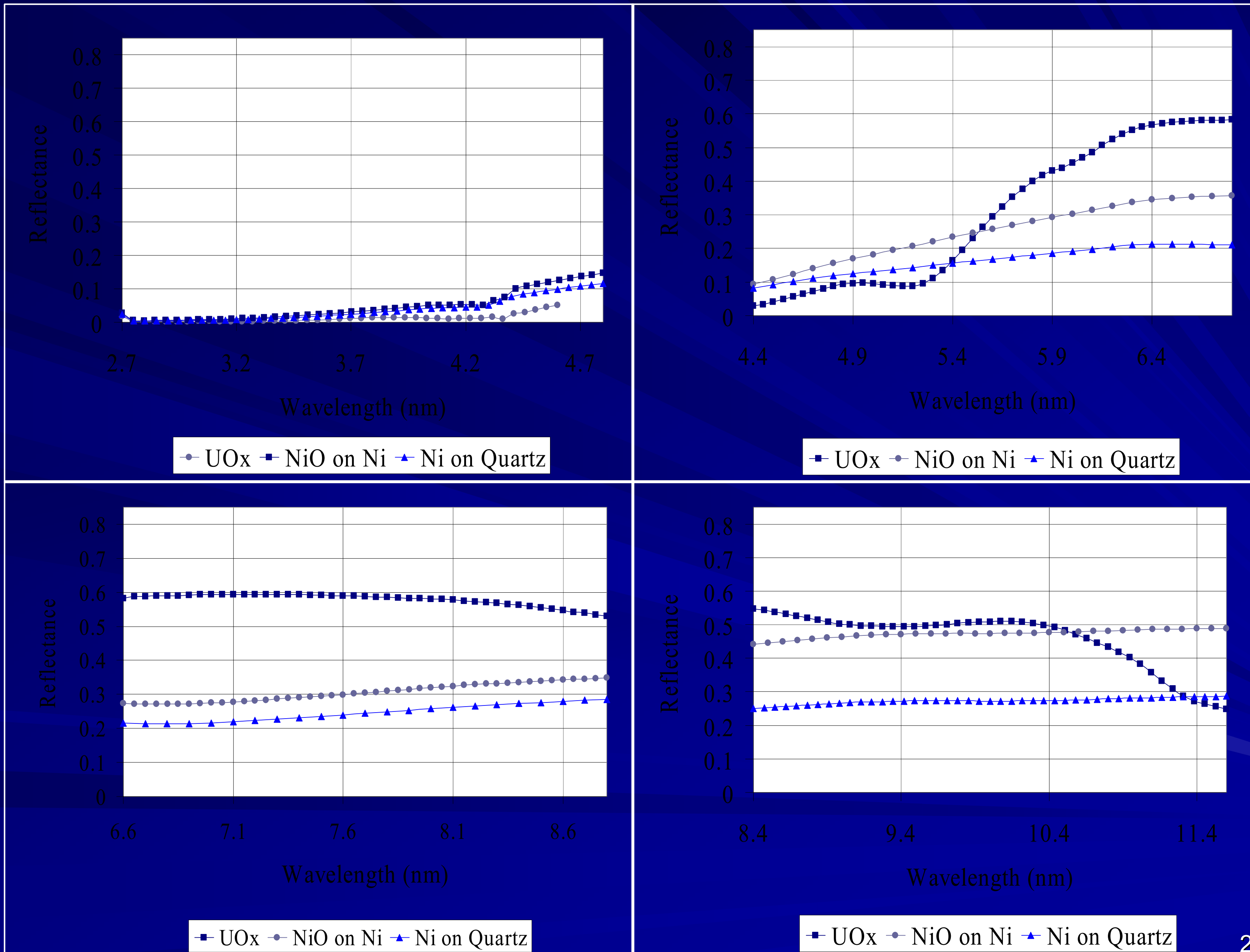
October 25, 2003

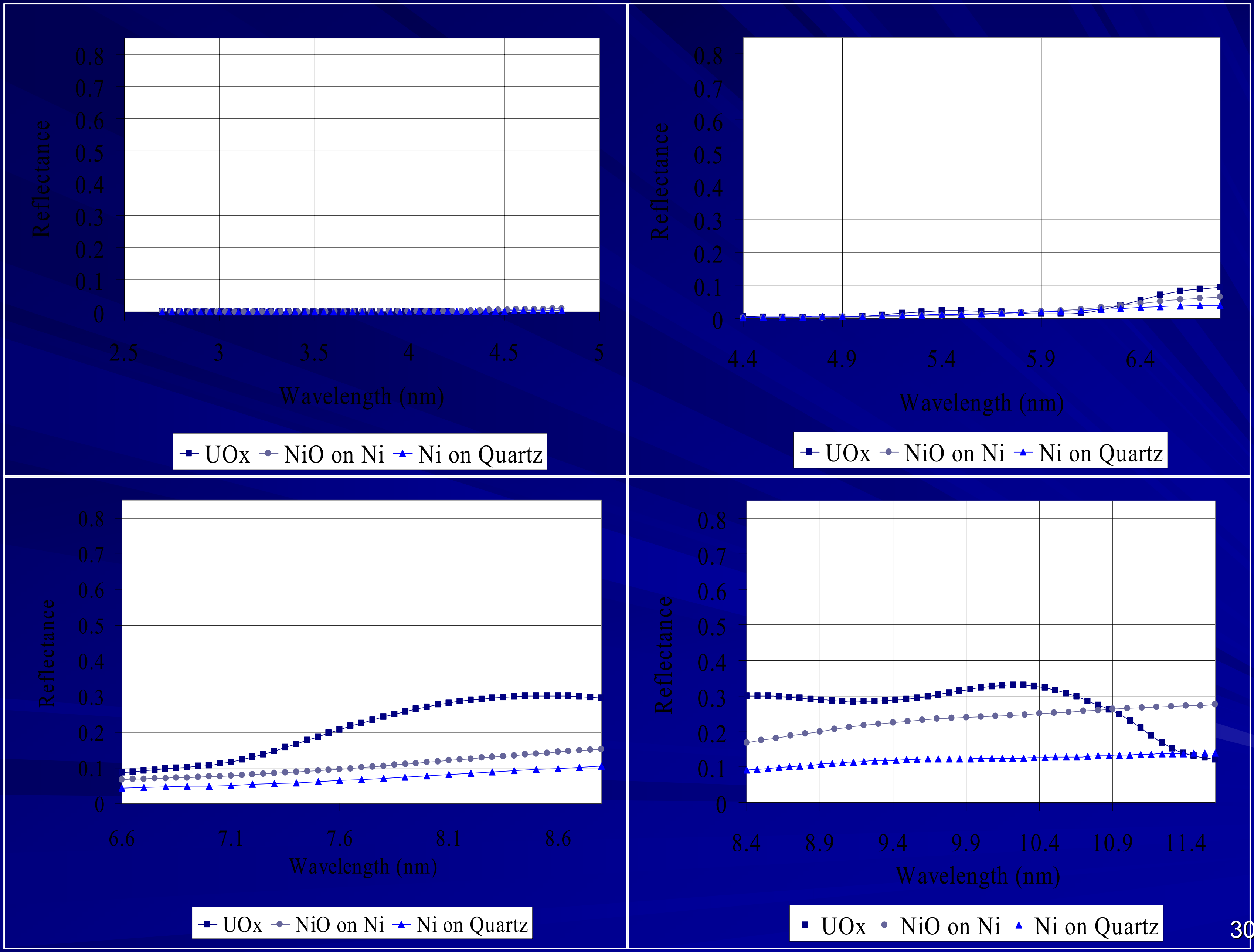
Measured reflectances of UOx, NiO on Ni, and Ni on quartz at 5 degrees from 2.7-11.6 nm

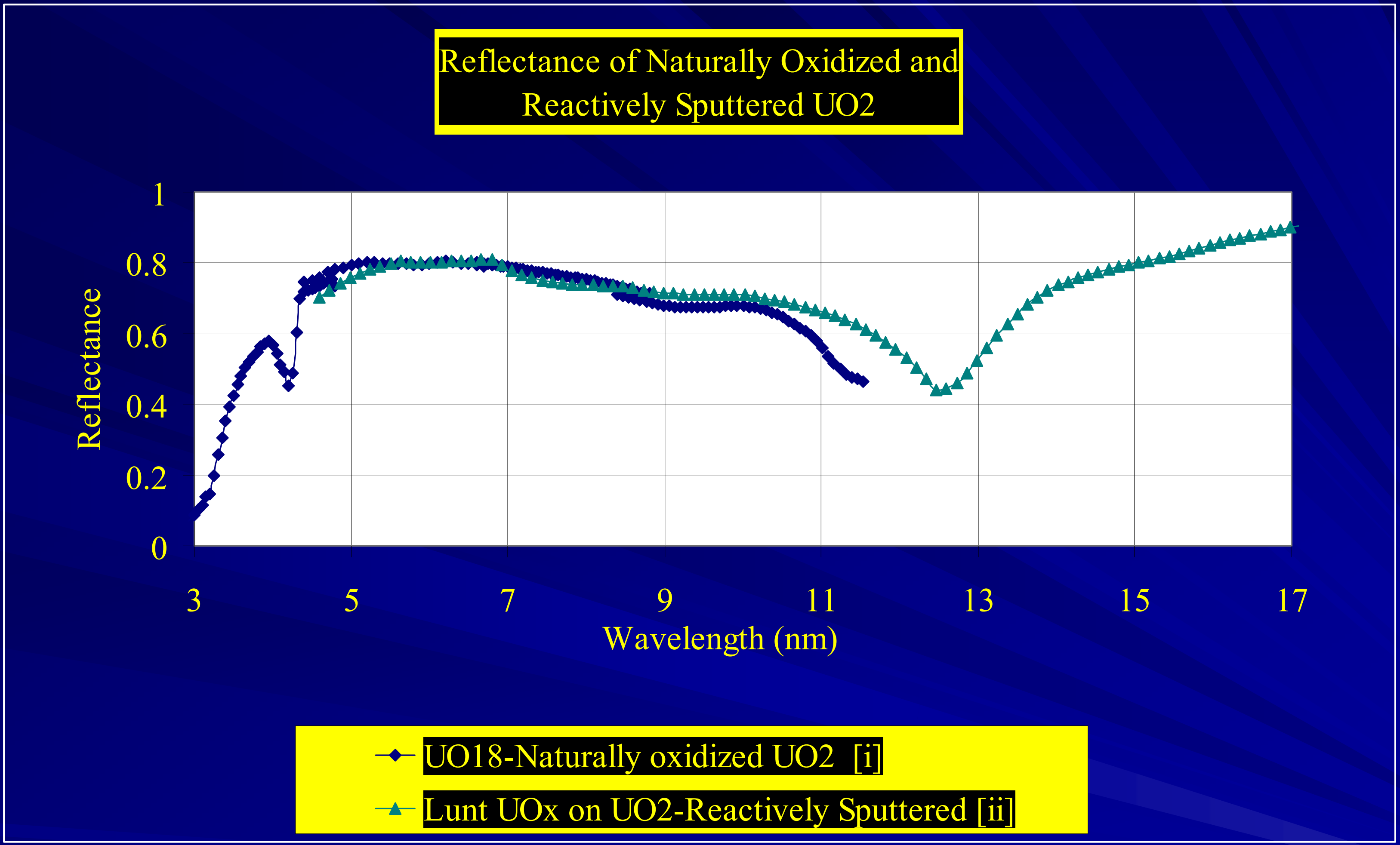


Measured reflectance at 10 degrees of UO2, NiO on Ni, Ni on Quartz from 2.7-11.6 nm



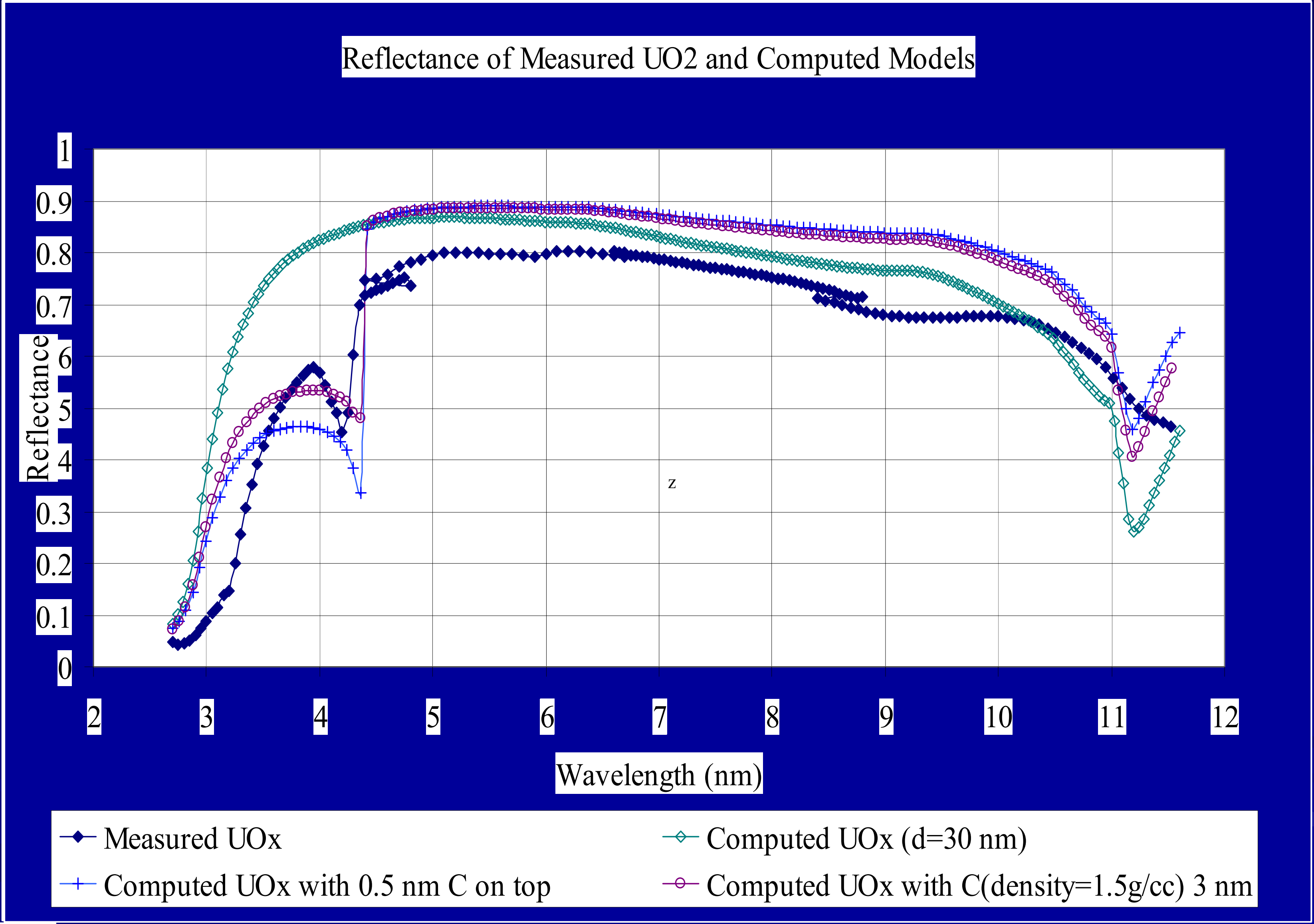
Measured reflectance at 15 degrees of UO2, NiO on Ni, and Ni on Quartz from 2.7-11.6 nm.



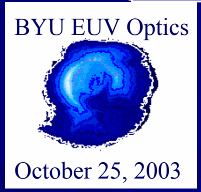


[i] Sandberg et a., *Advances in Mirror Technology for X-Ray, EUV Lithography, Laser, and Other Applications*, Ali M. Khounsary, Udo Dinger, Kazuya Ota, Editors, Proc. SPIE 5193, SPIE, Bellingham, WA, 2003.

[ii] Shannon Lunt, *Determining the Indices of Refraction of Reactively Sputtered Uranium Dioxide Thing Films from 46 to 584 Angstroms*, Masters Thesis, Dept. of Physics and Astronomy, BYU, Provo, UT 2002.



Reflectance of Measured UO2 and Computed Models
Reflectance
1
0.9
0.8
0.7
6
5
4
0.3
0.2
0.1
0
z
2
3
4
5
6
7
8
9
10
11
12
Wavelength (nm)
Measured UOx
Computed UOx (d=30 nm)
Computed UOx with 0.5 nm C on top
Computed UOx with C(density=1.5g/cc) 3 nm



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October 25, 2003

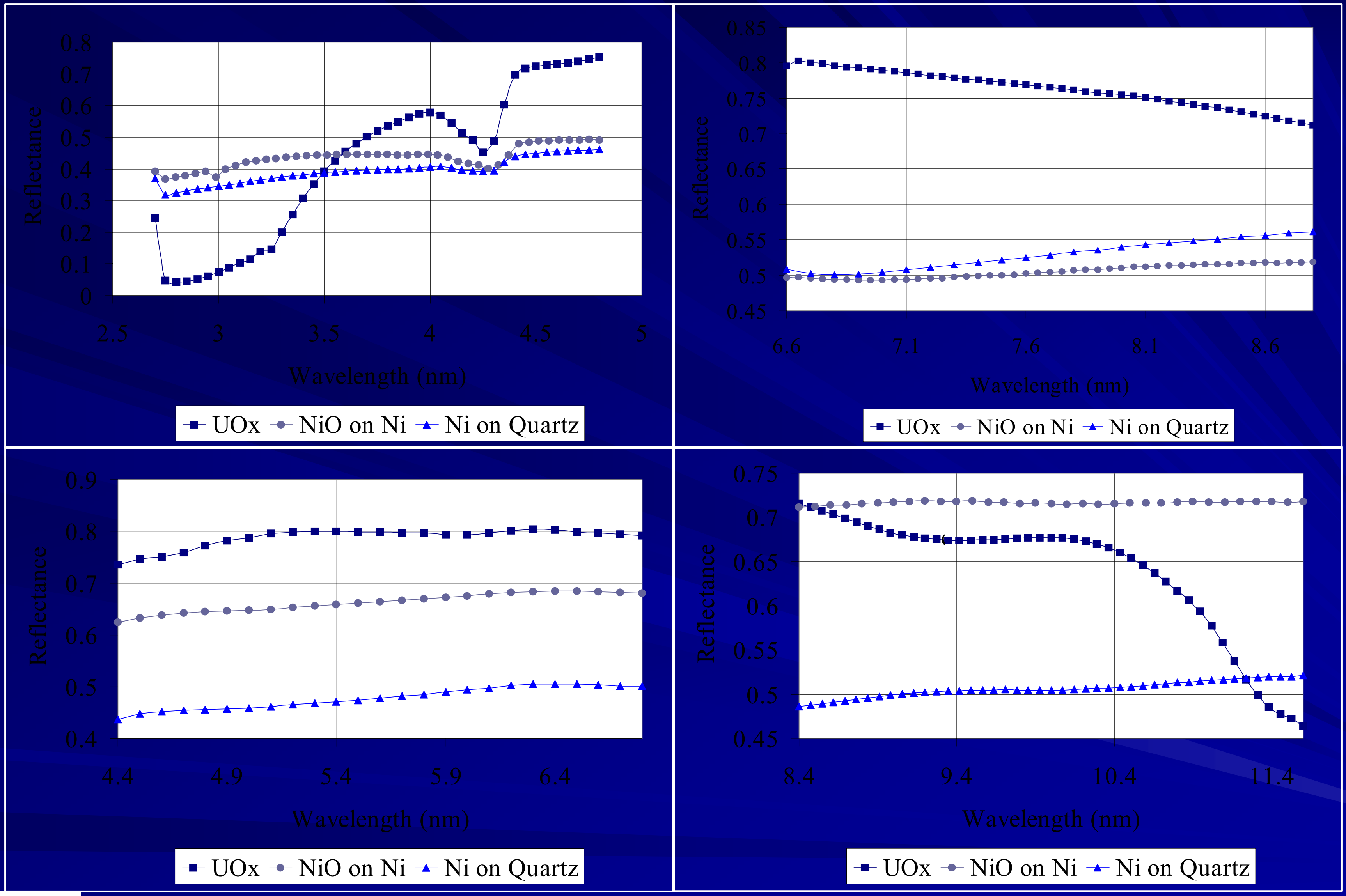
Conclusions- 1

1. In an UG student environment, We know how to
    1. Clean Si surfaces
    2. Study oxidation
2. We are making Sc based mirrors and want collaborations

Conclusions 2

1. Uranium oxide reflects significantly better than nickel, the current material with highest reflectance, between 4 and 11 nm.
2. Uranium oxide reflectance differs from the reflectance predicted by the atomic scattering factor model (ASF).
3. Reflectances of naturally oxidized uranium (UO_2) matches reactively sputtered UO_2 –Thus the material (Klaprothium) can be made in a number of different ways and is stable enough for practical use.

Measured reflectance of UOx, NiO on Ni, and Ni on quartz at 5° Conducted at the ALS



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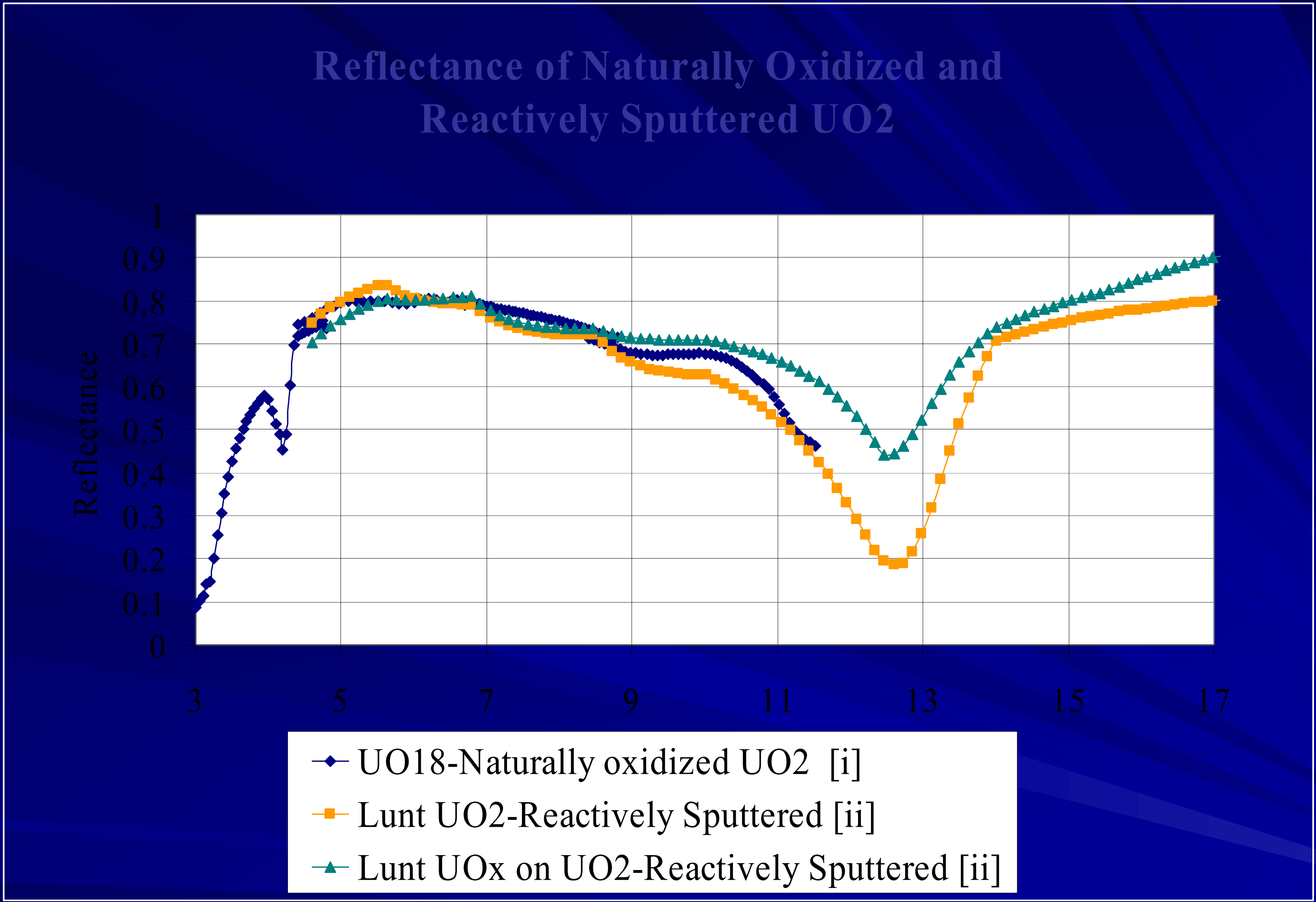
October 10, 2003

From Richard L. Sandberg, David D. Allred, Jed E. Johnson, R. Steven Turley "A Comparison of Uranium Oxide and Nickel as Single-layer Reflectors from 2.7 to 11.6 Nanometers," in *Advances in Mirror Technology for X-Ray, EUV Lithography, Laser, and Other Applications*, Ali M. Khounsary, Udo Dinger, Kazuya Ota, Editors, Proc. SPIE 5193, SPIE, Bellingham, WA, 2003.



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[ii] Shannon Lunt, *Determining the Indices of Refraction of Reactively Sputtered Uranium Dioxide Thing Films from 46 to 584 Angstroms*, Masters Thesis, Dept. of Physics and Astronomy, BYU, Provo, UT 2002.

Recent BYU EUV Group Successes

- Produce the Neutral Particle Detector mirror for the Mars Express Mission funded by the European Space Agency (Launched on June 2, 2003).
- Produced the EUV Mirrors for the IMAGE satellite funded by NASA and the Southwestern Research Institute (Launched on March 25, 2002).
- 6 Trips to the Advanced Light Source (ALS) at Lawrence Berkeley National Laboratory
- Selected Awards/Scholarships:
  – Outstanding Manuscript/Presentation in Physics at Utah Academy 2003—Kristi R. Adamson
  – Best Student Presentations at 2002 APS Four Corners Conference—Kristi R. Adamson, Richard L. Sandberg
  – 2003 Goldwater Scholarship—Kristi R. Adamson
  – 2003 BYU ORCA Scholarships—Luke J. Bissell, Ross Robinson
  – 2003 SPIE Scholarship—Richard L. Sandberg
  – 2003 John Hale Gardner Scholarship—Richard L. Sandberg
  – 2002 SPIE Scholarships—Luke J. Bissell, Guillermo A. Acosta
- Selected Publications:
  – David D. Allred, Matthew B. Squires, R. Steven Turley, Webster Cash, and Ann Shipley, "Highly Reflective Uranium Mirrors for Astrophysics Applications," in *X-ray Mirrors, Crystals and Multilayers*, Andreas K. Freund, Albert T. Macrander, Tetsuya Ishikawa, and James. T. Wood, Editors, Proc. SPIE 4782, pp. 212-223, SPIE, Bellingham, WA, 2002.
  – Kristi R. Adamson, R. Steven Turley, David D. Allred, "Determining Composition through X-Ray Photoelectron Spectroscopy," in *Journal of the Utah Academy* (Accepted for publishing, official reference forthcoming, originally presented April 11, 2003).
  – Richard L. Sandberg, David D. Allred, Jed E. Johnson, R. Steven Turley, "A Comparison of Uranium Oxide and Nickel as Single-layer Reflectors from 2.7 to 11.6 Nanometers," in *Advances in Mirror Technology for X-Ray, EUV Lithography, Laser, and Other Applications*, Ali M. Khounsary, Udo Dinger, Kazuya Ota, Editors, Proc. SPIE 5193, SPIE, Bellingham, WA, 2003.
  – Richard L. Sandberg, David D. Allred, Luke J. Bissell, Jed E. Johnson, R. Steven Turley, "Uranium Oxide as a Highly Reflective Coating from 100-400 eV," in *Proceedings of the Eighth International Conference on Synchrotron Radiation Instrumentation, San Francisco, 2003*, American Institute of Physics. (To be published, official reference forthcoming).

For more information…

BYU EUV WebPages:

http://xuv.byu.edu/

http://volta.byu.edu/xray.html

Or contact Dr. Allred or Dr. Turley:

allred@byu.edu, 801-422-3489, Office is N265 ESC

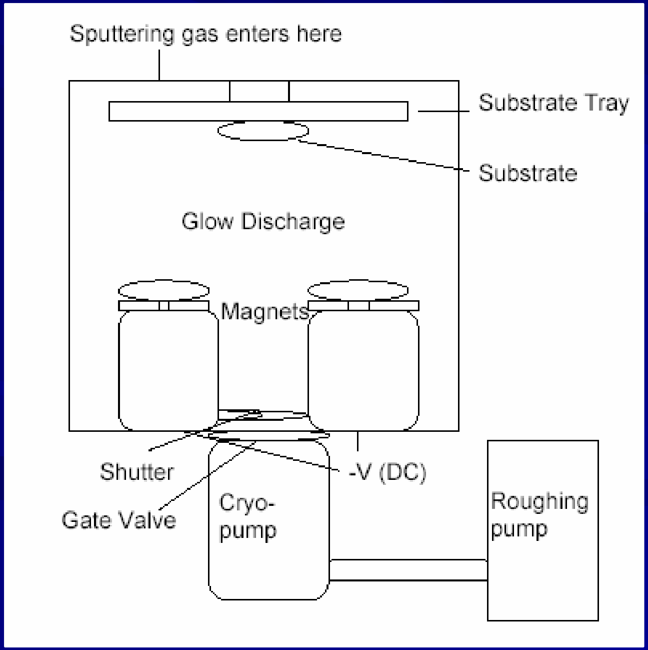
turley@physics.byu.edu, 801-422-3095, Office is N308 ESC

Group Meetings:

3:00 pm on Tuesdays, C247 in the Eyring Science Center (ESC)

Making Thin Films

- Films are made using a process called sputtering or through thermal evaporation. These processes are conducted in high vacuum systems.
- For sputtering, a target or piece of the material we want deposited as a film, is bombarded with ions from the RF argon plasma causing particles to be released from the target which then deposit to the silicon or quartz substrate.
- For thermal evaporation, a wire or boat is resistively heated by passing a large current through it. The heated metal (ie. aluminum, nickel, gold) evaporates and is deposited on the silicon or quartz substrate.



Taking Reflectance Measurements

- Our Very Own Reflectometer
  - Monochromator
    - *Mono: one. Chromatic: color.*
    - A grating, like a prism, diffracts the light into a rainbow.
    - The rainbow falls on a pinhole so that only one wavelength passes through.
  - Octagonal Chamber
    - Light enters the chamber and is reflected from the surface being studied.
    - The reflected light is measured as a function of angle.
- The Advanced Light Source
  - Fieldtrips to the Lawrence Berkeley National Laboratory in Berkeley, CA to use their Advanced Light Source (Synchrotron—accelerated beam of electrons produces bright EUV/X-ray light).

Calculating Optical Constants and Reflectance

(A quote from the Center for X-ray Optics)

The primary interaction of low-energy x rays within matter, viz. photoabsorption and coherent scattering, have been described for photon energies outside the absorption threshold regions by using atomic scattering factors, f_1 and f_2. The atomic *photoabsorption cross section*, μ_a, may be readily obtained from the values of using the relation:

$$\mu_a = 2 \cdot r_0 \cdot \lambda \cdot f_2$$

where *r0* is the classical electron radius, and λ is the wavelength. The transmission of x rays through a slab of thickness *d* is then given by:

$$T = \exp(-n \cdot \mu_a \cdot d)$$

where *n* is the number of atoms per unit volume in the slab. The *index of refraction* for a material is calculated by:

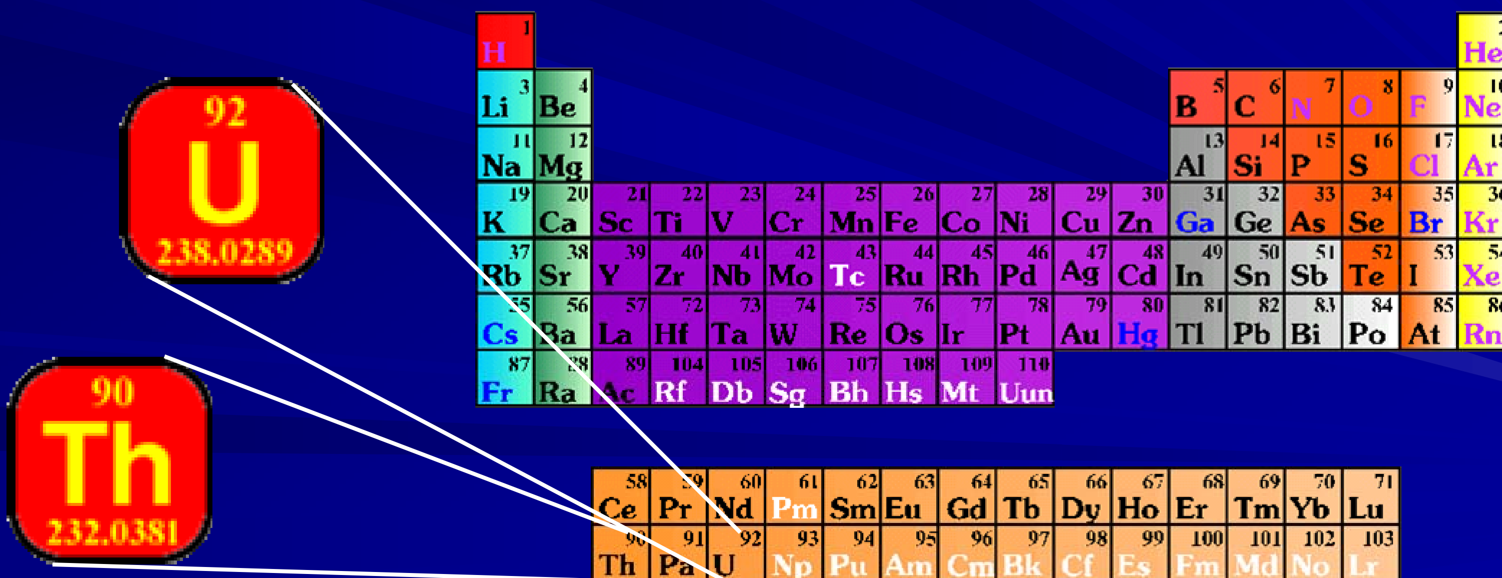
$$\tilde{n}_r = \frac{1 - n \cdot r_0 \cdot \lambda \cdot \left(f_1 + i f_2\right)}{2\pi}$$

These (semi-empirical) atomic scattering factors are based upon photoabsorption measurements of elements in their elemental state. The basic assumption is that condensed matter may be modeled as a collection of non-interacting atoms. This assumption is in general a good one for energies sufficiently far from absorption thresholds. In the threshold regions, the specific chemical state is important and direct experimental measurements must be made.[i],[ii]

[i] CXRO webpage (July, 2003). http://www-cxro.lbl.gov/optical_constants/intro.html.
[ii] B.L. Henke, E.M. Gullikson, and J.C. Davis, *X-ray interactions: photoabsorption, scattering, transmission, and reflection at E=50-30000 eV, Z=1-92*, Atomic Data and Nuclear Data Tables **54** no.2, 181-342 (July 1993).

Why Uranium and Thorium?

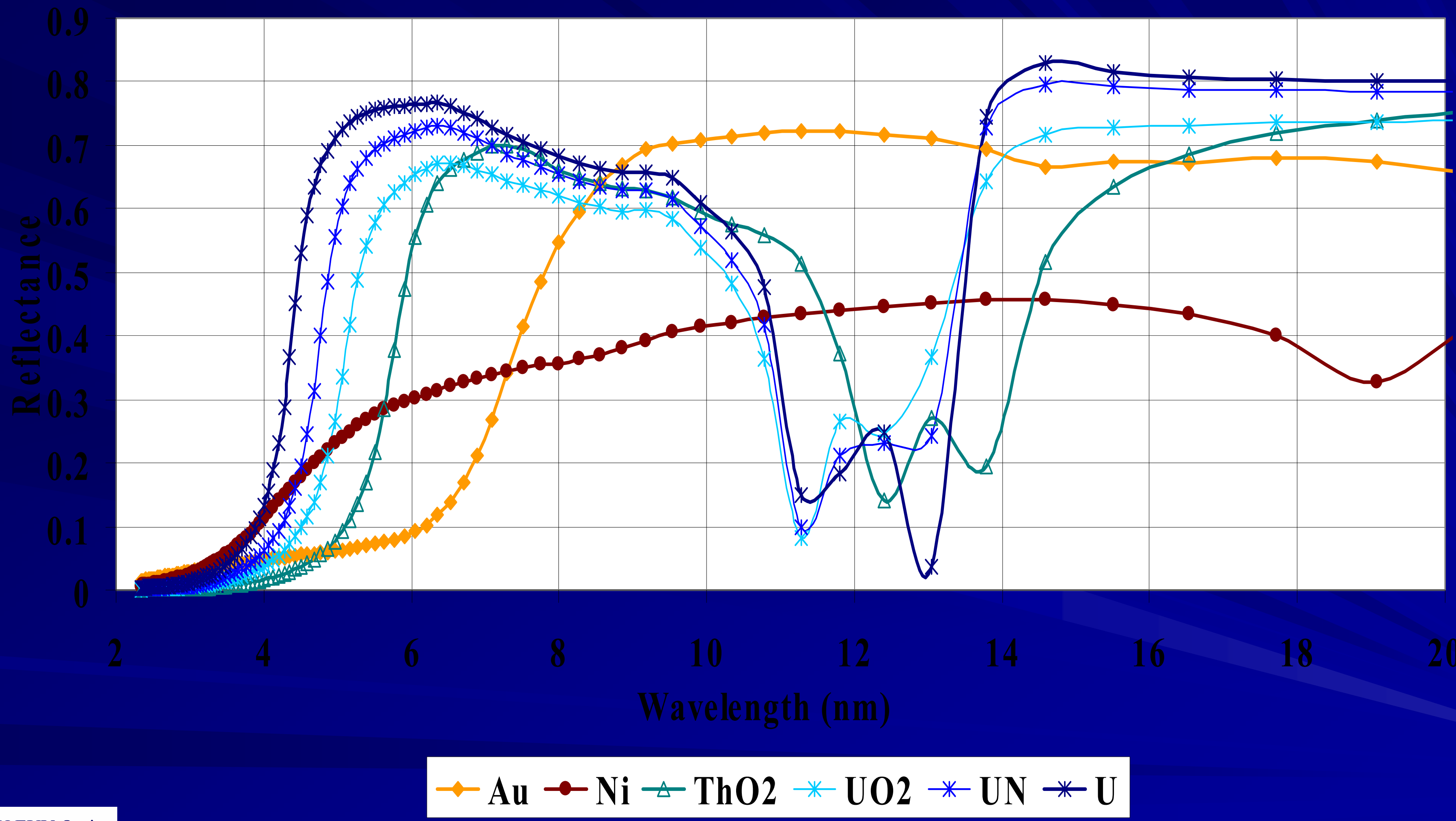
- In the EUV, uranium and thorium have many electrons to interact with photons (light) and is more dense than many materials, causing them to interact with high energy EUV photons.
- We study different compounds of uranium and thorium, such as uranium-oxide (UO_2), uranium-nitride (UN), and thorium-oxide (ThO_2) in search of compounds with the best optical constants and that do not react with air.



BYU EUV Optics

October 10, 2003

Computed Reflectance at 10 degrees of various materials



Reflectance computed using the CXRO Website: http://www-cxro.lbl.gov/optical_constants/mirror2.html

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