Multilayer X-Ray Mirrors & The Extraordinary Swelling of Yttria Thin Films in VUV light.

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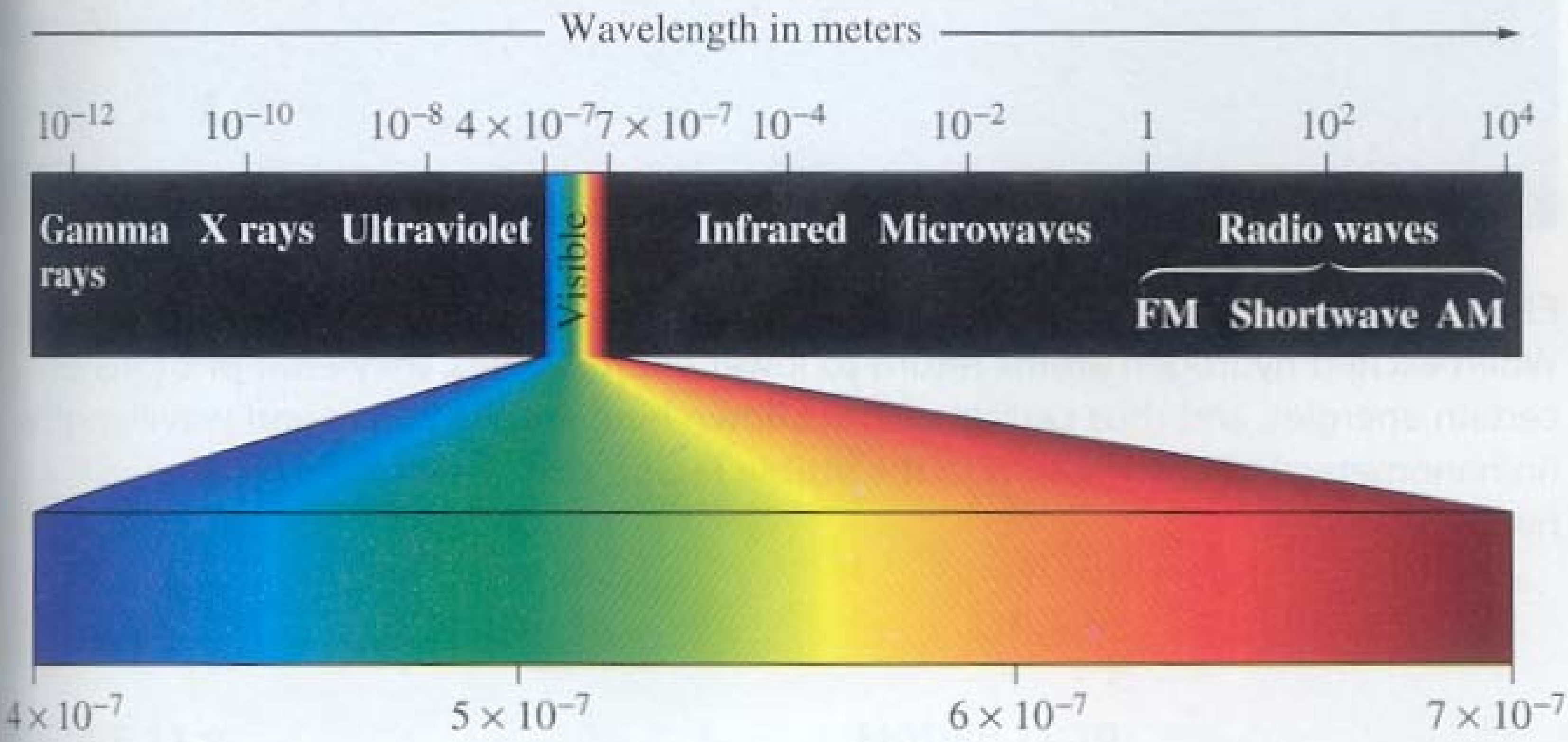
1895 Roentgen discovers x rays

This achievement that earned him the first Nobel Prize in Physics in 1901.

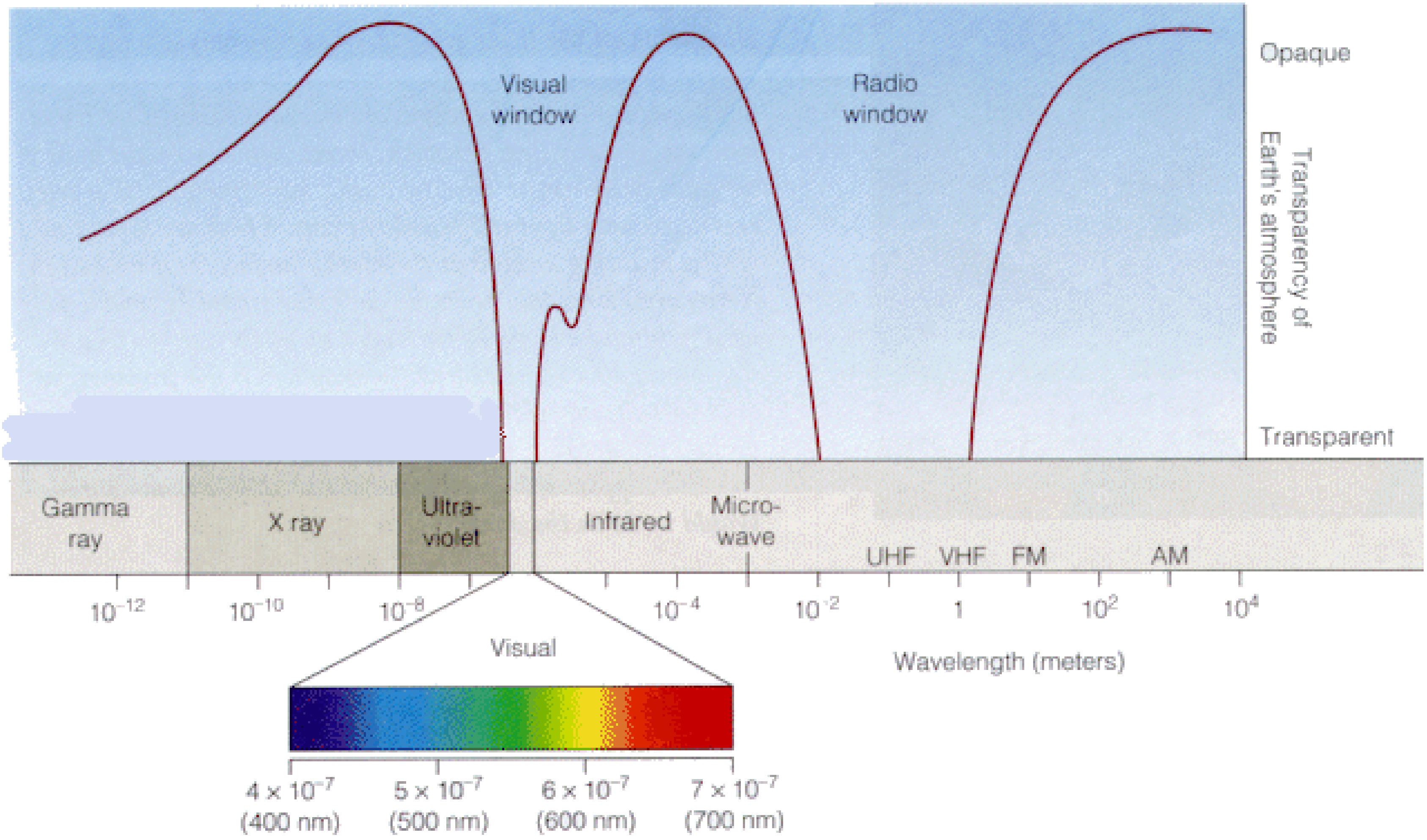
http://library.tedankara.k12.tr/chemistry/vol1/period/trans43.jpg



Why weren’t EUV and Soft X-rays studied early?

- Characteristics:
- interact strongly with all matter
  - Human hair is about 100 micron
  - Absorption length of 40 eV light (30.4 nm) is about 100 nm.
- Index is not high.
- Consequences?
  - Vacuum
  - How do we manipulate light in visible?

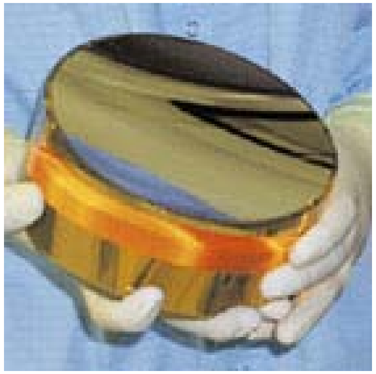
http://users.zoominternet.net/~matto/M.C.A.S/electromagnetic_spectrum.gif



Where do the EUV and Soft X-rays fit?

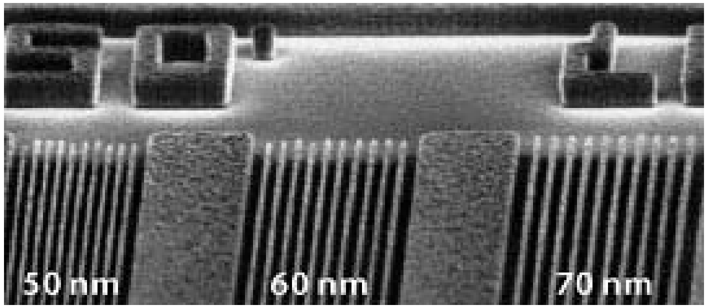
Why Extreme Ultraviolet (EUV) and Soft X-Rays?

Thin Film or Multilayer Mirrors

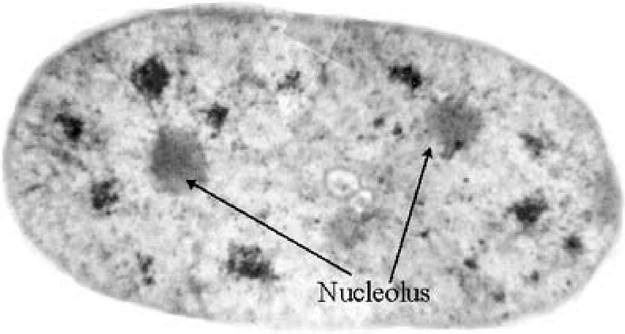


EUV Lithography

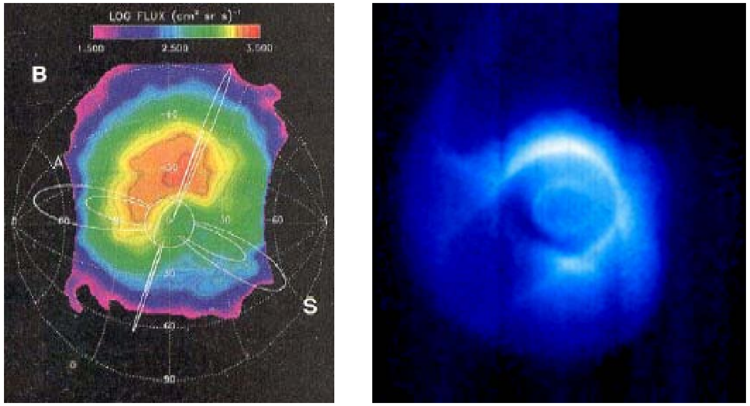
(making *really* small computer chips)



Soft X-Ray Microscopes



EUV Astronomy



The Earth's magnetosphere in the EUV

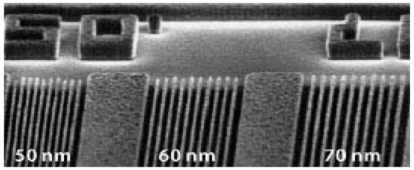
Images from www.schott.com/magazine/english/info99/ and www.lbl.gov/Science-Articles/Archive/xray-inside-cells.html.

Our Goal – EUV Applications

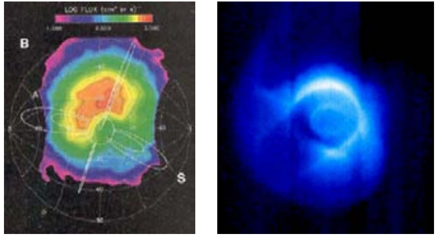
- Extreme Ultraviolet Optics has many applications.
- These Include:
  - EUV Lithography
  - EUV Astronomy= image mission
  - Soft X-ray Microscopes
- **A Better Understanding of EUV <u>Optics & Materials</u> for EUV applications is needed.**
  - Materials compatible with
  - Cleaning and storage methods compatible with

Traveling, Modest budgets & Undergraduate researchers

EUV Lithography

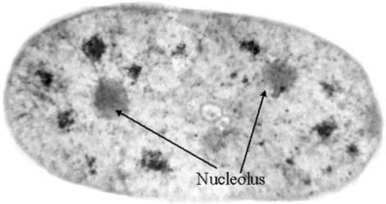


EUV Astronomy

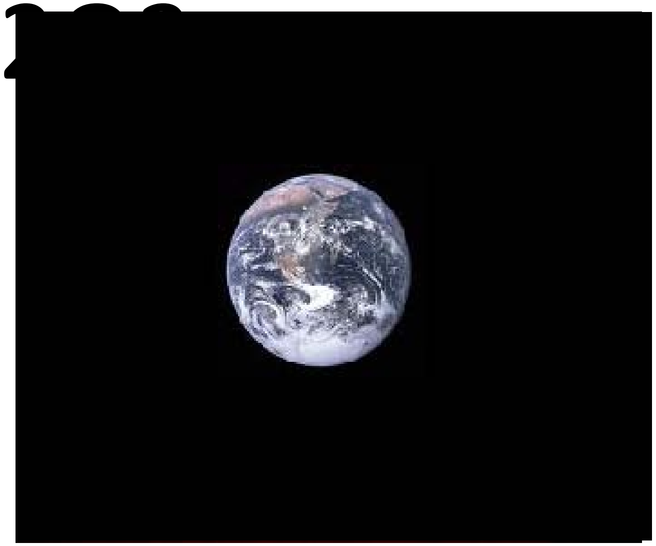


The Earth's magnetosphere in the EUV

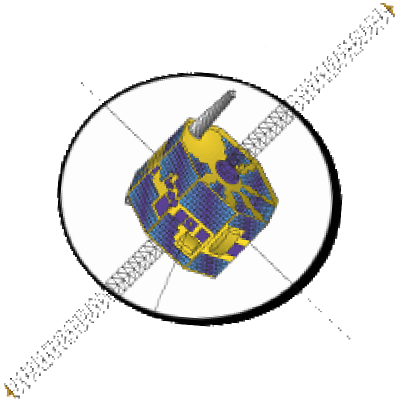
Soft X-ray Microscopes



Uses of Y



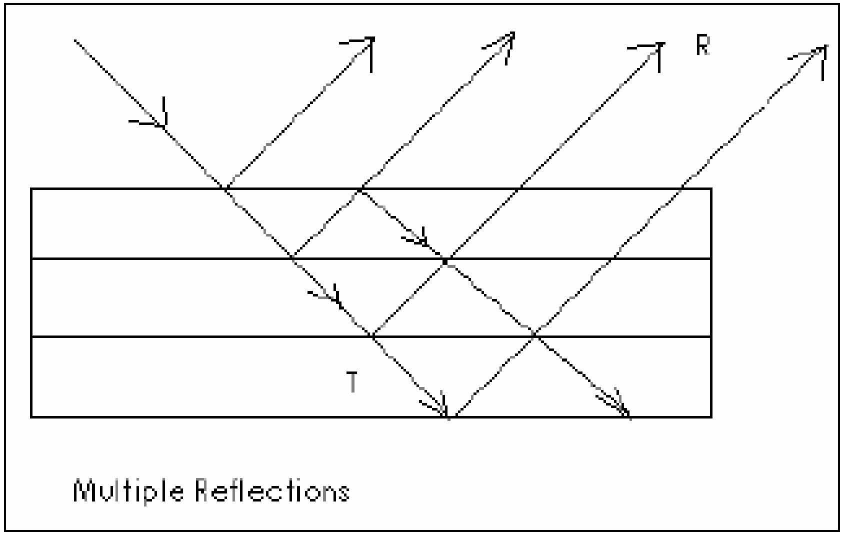
- Multilayer Mirrors



  - Imager for Magnetopause to Aurora Global Exploration (IMAGE) – “It’s a weather satellite for space storms”
    -Dr. James L. Burch

- Lithography and High-Resolution Microscopy

Multilayer Mirrors



- Problems
  - Need constructive interference
  - Absorption in layers

EUV Multilayer Optics 101

High reflectivity multilayer coatings require:

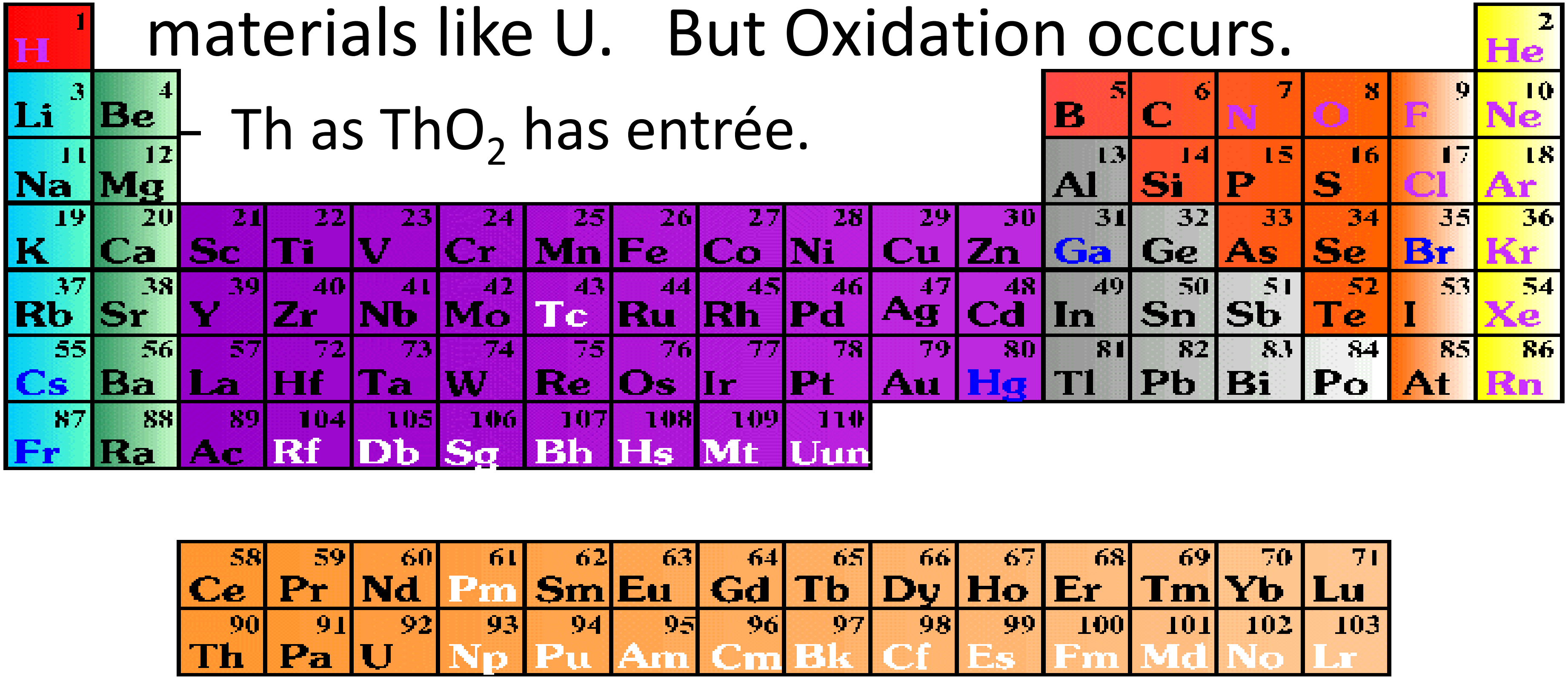
- Refractive index ($n = 1-\delta+i\beta$) contrast at the interfaces: for most materials, these optical constants are not well known in this region.
- Minimal absorption in the low-Z material
- Interfaces which are chemically stable with time
- Minimal interdiffusion at the interfaces
- Thermal stability during illumination
- Chemically stable vacuum interface

Even with the very best designs, multilayer mirrors have only achieved a reflectivity of around 70% in the EUV.

- *n=1-δ+iβ*

Solutions

- Find materials with big *δ* and small *β*
- Good candidates: High Density, High -Z materials like U. But Oxidation occurs.
  - Th as ThO_2 has entrée.



1 H																	2 He
3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
55 Cs	56 Ba	57 La	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
87 Fr	88 Ra	89 Ac	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Uun								

58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu
90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr

The solution? Research of new materials with these properties

Uranium:

- Highly reflective in the region from 124-248 eV [1]
- **Not** chemically stable with time

Uranium Oxide:

- Highly reflective in the region from 124-248 eV [1]
- **Not** chemically stable with time

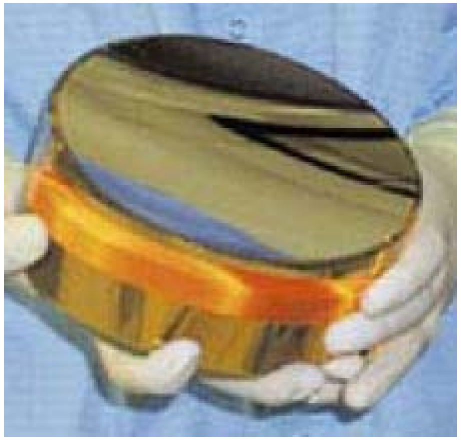
Thorium:

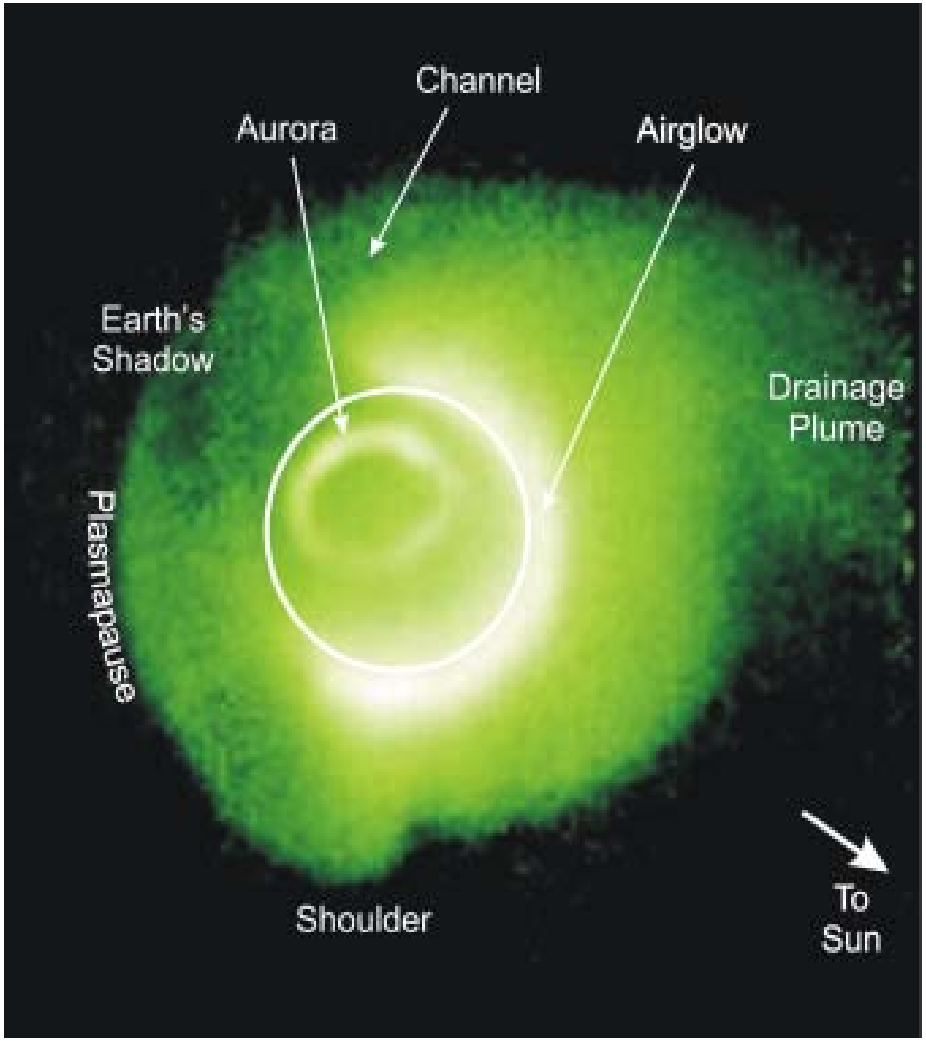
- Highly reflective in the region from 138-177 eV [2]
- **Not** chemically stable with time, tho better than U.

[1] RL Sandberg, DD Allred, JE Johnson, RS Turley, " A Comparison of Uranium Oxide and Nickel as Single-layer Reflectors", Proceedings of the SPIE, Volume 5193, pp. 191-203 (2004).

[2] J. Johnson, D. Allred, R.S. Turley, W. Evans, R. Sandburg, “Thorium-based thin films as highly reflective mirrors in the EUV”, Materials Research Society Symposium Proceedings **893**, 207-213, 2006.

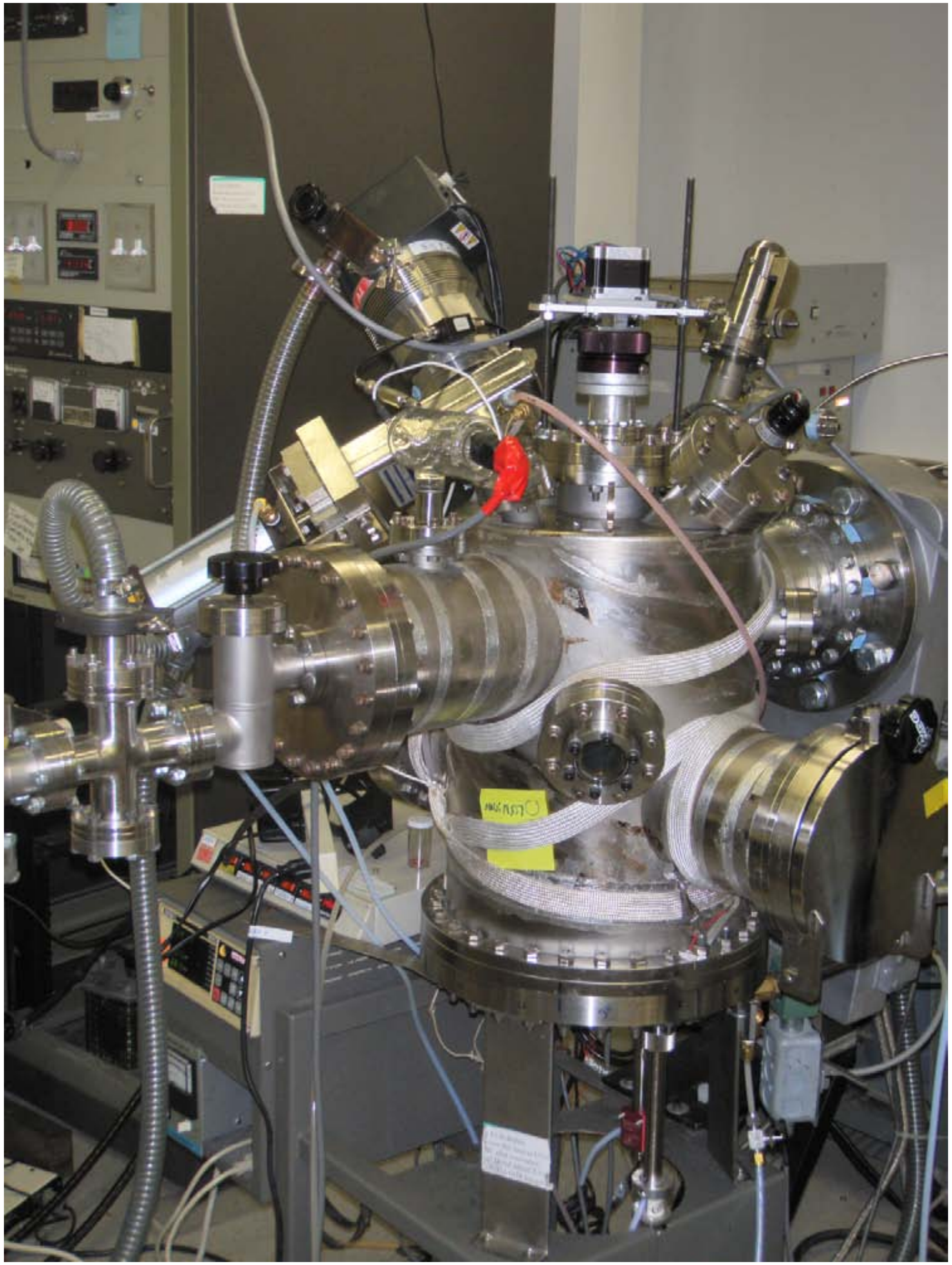
Image Mirror





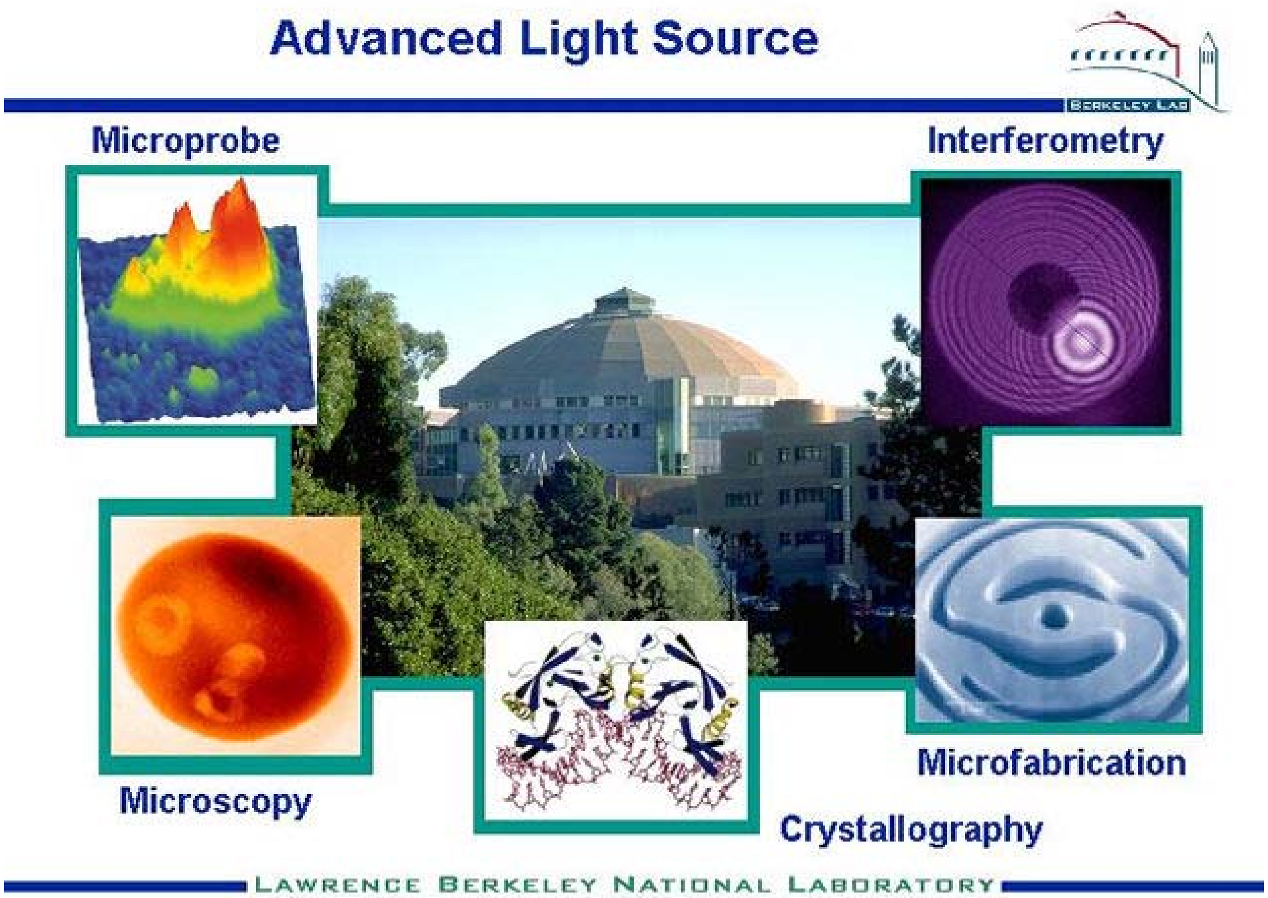
U/Si ML coating for EUV instrument

- Picture (41 eV) is from EUV imager on the IMAGE Spacecraft. He (II) in magnetosphere
- This was student powered project 1997-98
- Designed: needed 7 degree width off normal, 7.5 layer U/Si ML with U Oxide cap- peak R 25%
- Coated &
- Tested
- Launched 2000 March 25
- Returned more data than any NASA satellite by time it fell silent in 2005.



We have several sputterers, evaporators etc.

Optics like n-IR, visible, & n-UV? First you need a light.



Measurements.

Other Participants

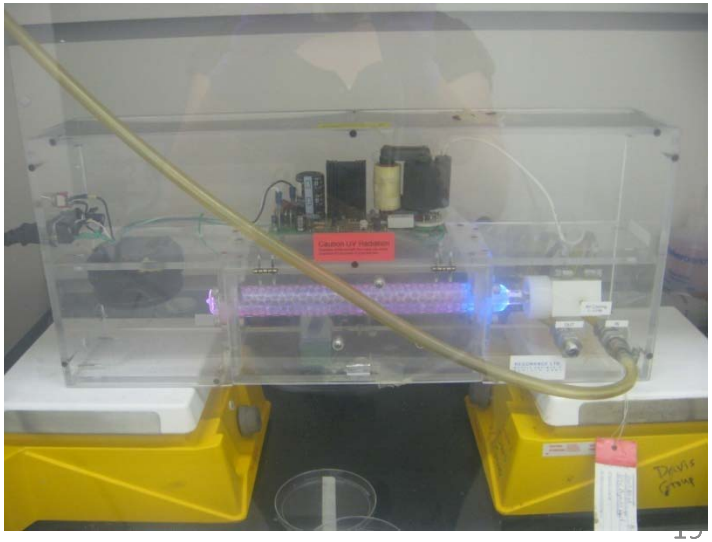
- Those who made samples and studied the strangely expanding film: Alison Wells, Kristal Chamberlain *(Wellesley) , Devon Mortensen*, now U of Washington) Thomas McConkie, Liz Strein (now U of Washington), Brett Bostrom,*
- and The BYU EUV Thin Film Optics Group, past and present who went to ALS : Jacque Jackson, Elise Martin, Lis Strein, Joseph Muhlestein, Megan McGranagain*,
- And made measurements heres Jordan Bell, Heidi Dumais, Greg Hart, Keith Jackson Samuel O. Keller*, Zephne Larsen Vaterlaus*, Victoria Lee, Quintin Nethercott, James Vaterlaus
- R. Steven Turley & David Allred
- XPS: Amy B. Grigg
  *supported by NSF REU grant PHY0852074.

Summary to this point.

The Extraordinary Swelling of Yttria Thin Films in VUV light.

- XUV Optics
  - Applications -Production
- Review of Optics for EUV/ x-rays (E>15 eV)
- Why Actinides and column-3 metals in EUV?
  - Why Oxides?
  - besides ML there are low-angle front surface mirrors
- Optical constants from R and T
  - Cleaning surfaces
  - And what became of it.

This xenon lamp excimer (VUV) lamp generates photons at 7.2eV. so energetic that they only go about 1 cm in air before they are absorbed producing atomic O and ozone.

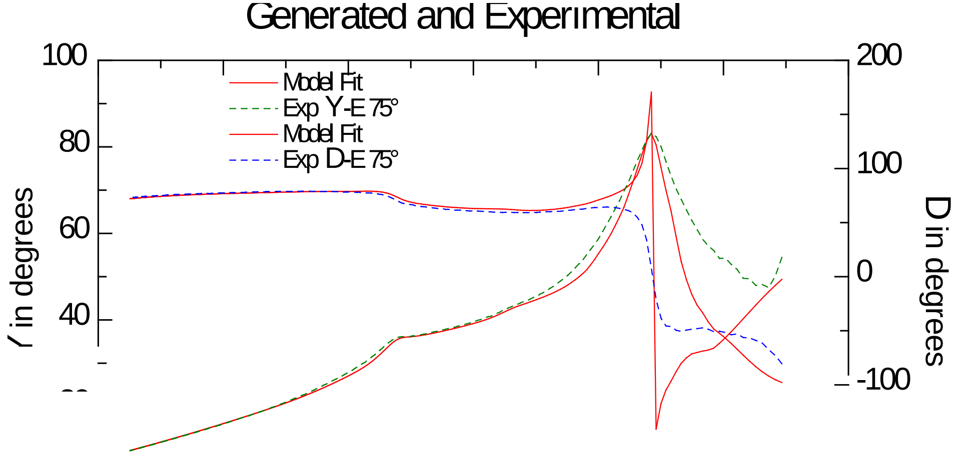


The Setup

- We took some samples to Berkeley for measurements using the Advanced Light Source.
- While there we needed to clean the sample.
  - Why? Because there is a sort of “gunk” composed mainly of hydrocarbons that permeates all space and likes to deposit itself on samples.
- Problem: the plasma cleaner was not available to take.
- Solution: Let’s use the excimer (VUV) lamp instead. We had taken it with us.
  - This lamp generates photons at 7.2eV, which produce O atoms in air and cleans hydrocarbons from Si wafers.

Enter the Mystery

- After approximately 5 minutes under the VUV lamp, the sample became visibly thicker.
- Use ellipsometry measurements to determine if this is true.
  - Before cleaning: 24.94 nm

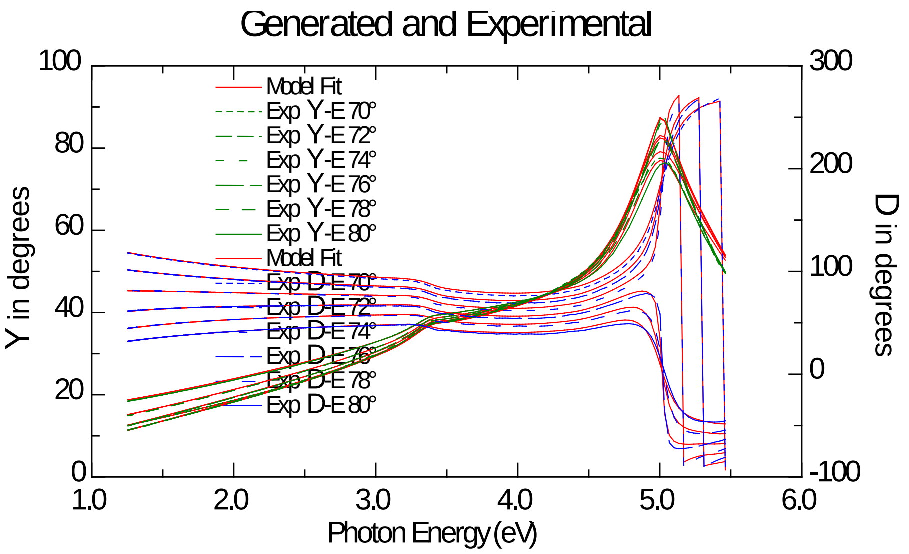


4	srough	0.500 nm
3	polycarb	0.000 nm
2	ema y2o3/30% void	24.733 nm
1	sio2_jaw	2.000 nm
0	si_jaw	1 mm

Thick.2 =24.733±0.139 nm

Ellipsometry Measurements

– After 5 min VUV: 31.061 nm



3	srough	0.500 nm
2	y2o3 constants based on 091130b on si	31.061 nm
1	sio2_jaw	1.800 nm
0	si_jaw	1 mm

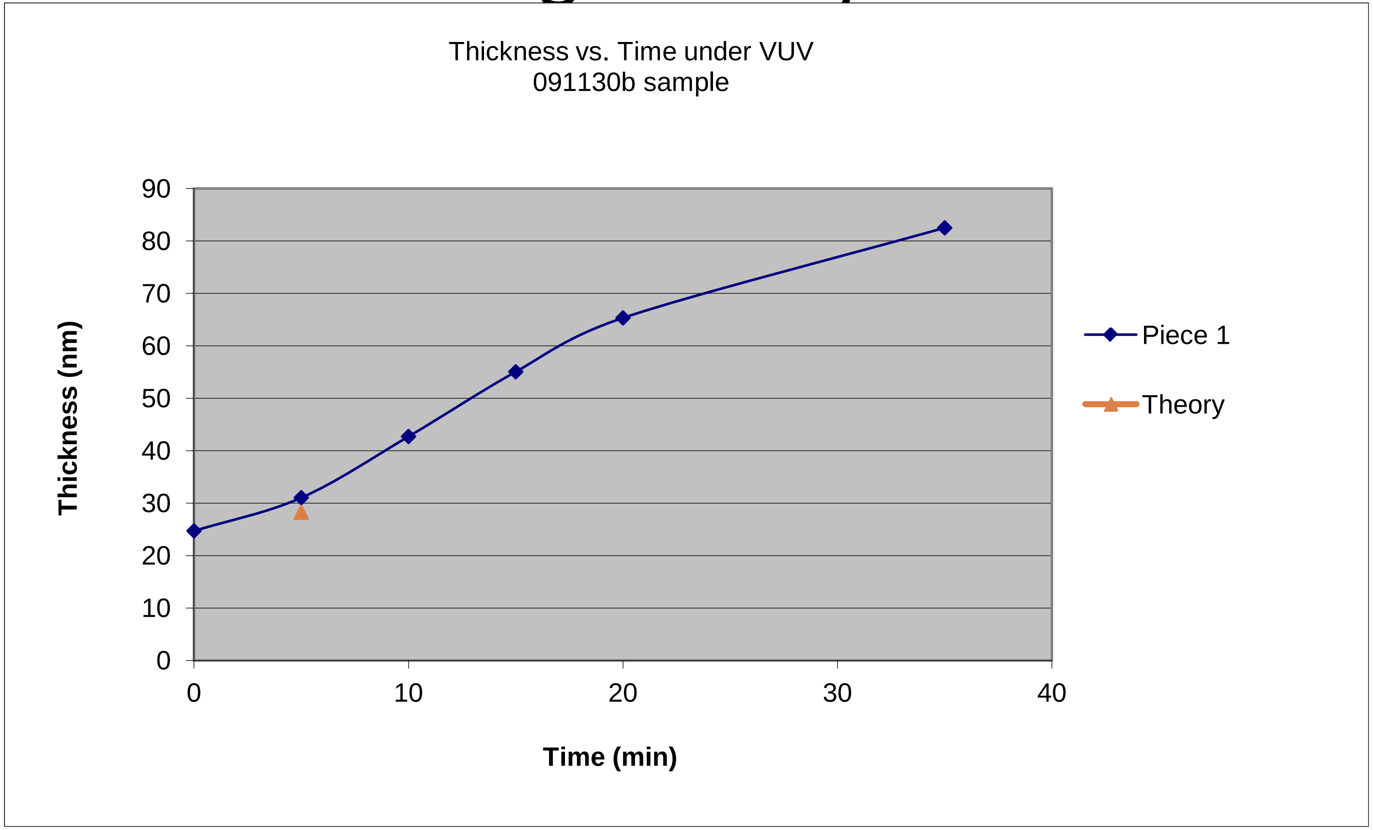
Thick.2 =31.061±0.0717 nm

- As you can see this is quite a significant change.

24.94 nm → **31.06 nm**

Search for the Answer

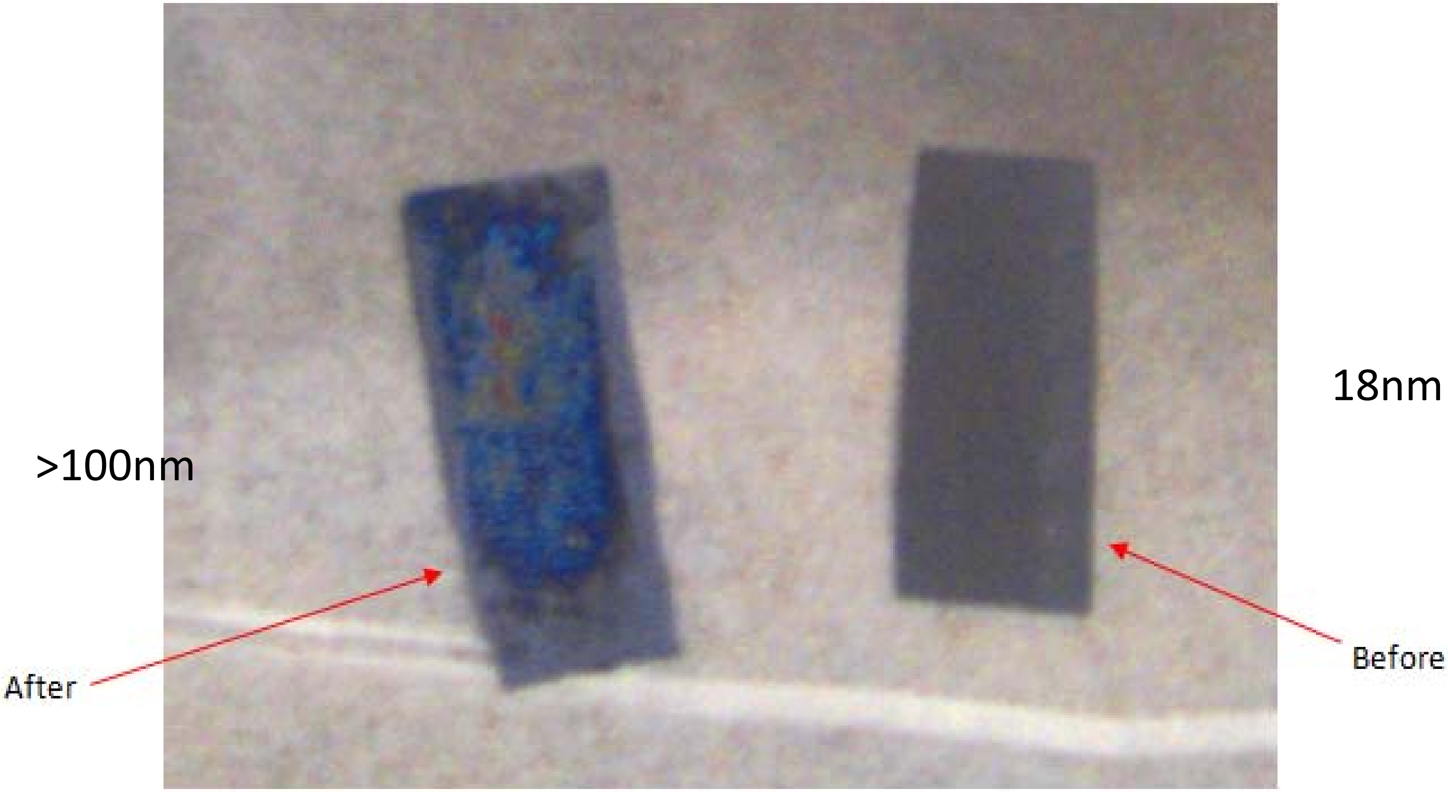
- Big question is: What's going on here?
- First thought: the yttrium is not fully oxidized.



If the yttrium were complete unoxidized expected film growth would be **3.34 nm**

Actually film growth was **6.12 nm**

We discovered that when yttrium oxide thin films (prepared by reactively sputtering Y in O_2) are exposed to VUV photons they can grow MUCH, MUCH thicker.



How can this be?

Could it be Weird Chemistry?

- **A Few Theories Tested up front:**
  1. **Film oxidation**? Reactively sputtered films may not be fully oxidized.
- *But no: **too** much growth*
  2. **New Deposition?** A dirty environment might contribute something to UV polymerize. (We had moved the lamp from a physics to a chemistry lab.)

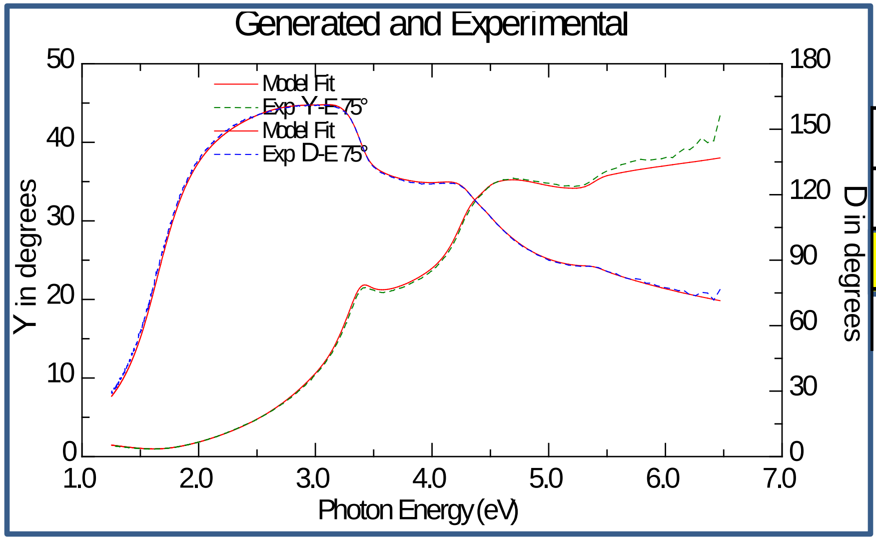
  3. **Oxidation of Silicon Substrate?** Perhaps catalyzed by Yttria?

Second Theory

- Is it possible that the VUV lamp is actually depositing material onto the sample?
  - Not possible that more Y_2O_3 is being added to film.
  - Perhaps it is knocking molecules off of the support base and these molecules are finding their way to the sample.
- Subject a blank silicon substrate to same VUV treatment and look for film deposition.

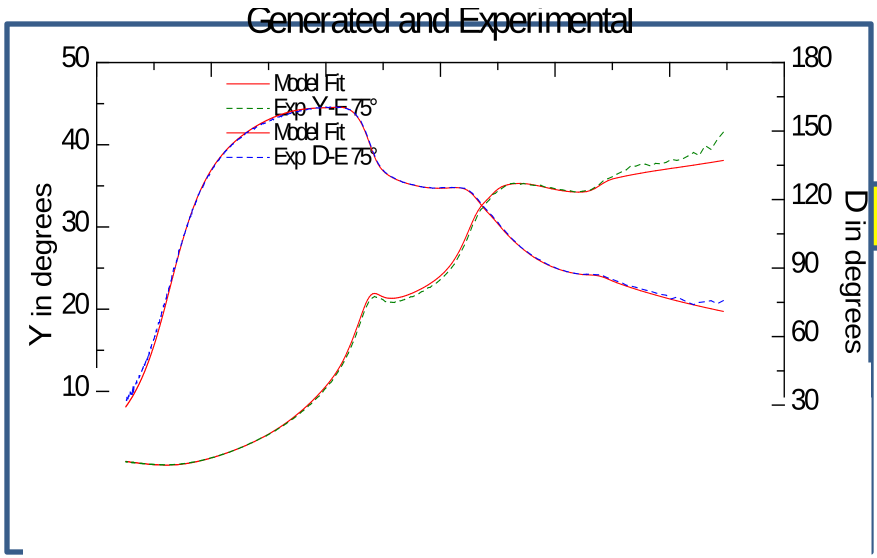
Blank Silicon Wafer

- Before VUV:



3	srough	0.000 nm
2	y2o3 constants based on 091130b on si after 5min uv	0.500 nm
1	**sio2_jaw**	**2.074 nm**
0	si_jaw	1 mm

MSE=5.786 Thick.1 =2.074±0.0081 nm

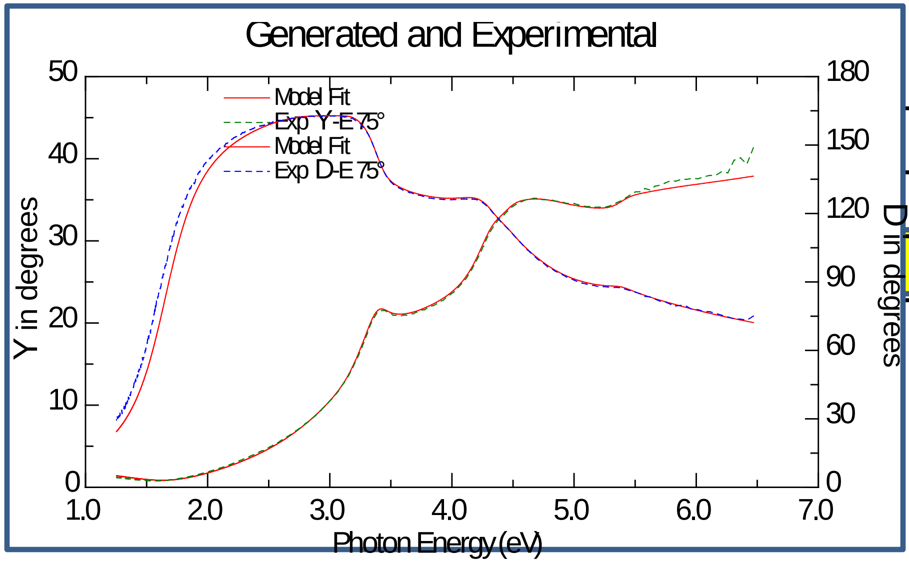


3	srough	0.000 nm
2	y2o3 constants based on 091130b on si after 5min uv	0.500 nm
1	**sio2_jaw**	**2.221 nm**
0	si_jaw	1 mm

MSE=6.713 Thick.1 =2.221±0.00942 nm

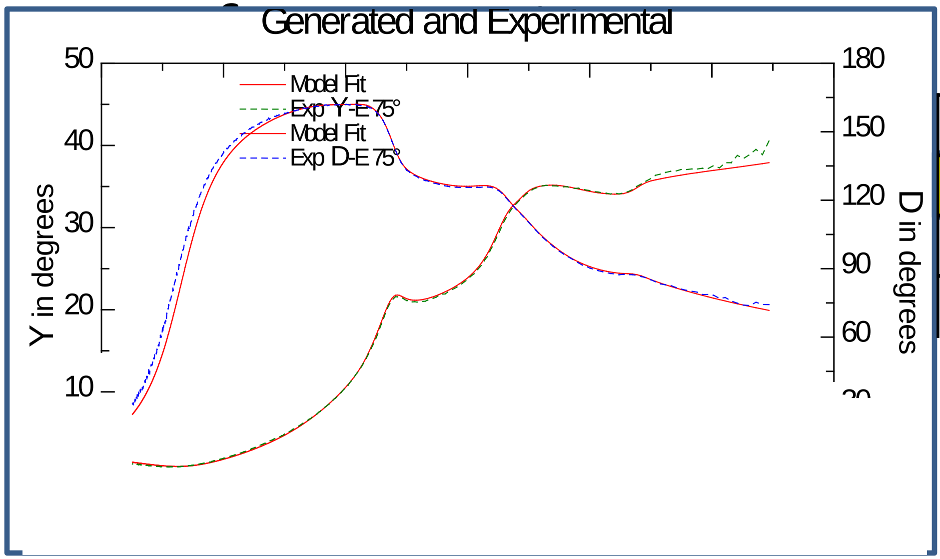
Blank Silicon Wafer

- After 10 min VUV:



3	srough	0.000 nm
2	y2o3 constants based on 091130b on si	0.000 nm
1	sio2_jaw	1.797 nm
0	si_jaw	1 mm

MSE=9.096 Thick.1 =1.797±0.012nm



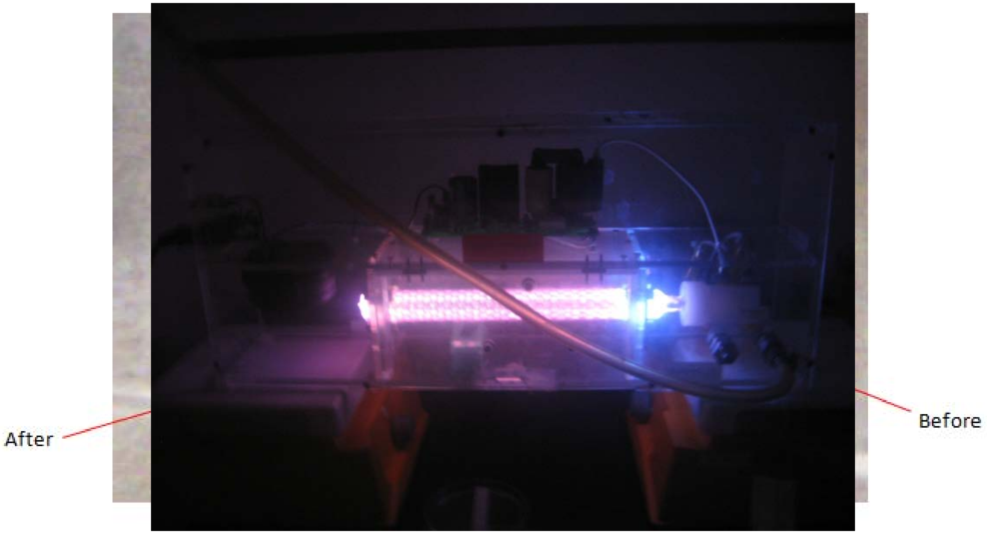
3	srough	0.100 nm
2	ema y2o3 constants based on 091130b on si after 10 mi	0.000 nm
1	sio2_jaw	1.863 nm
0	si_jaw	1 mm

MSE=8.125 Thick.1=1.863±0.0112nm

First Set of Conclusions

- No apparent change in thickness of the silicon witness.
- It doesn’t seem likely that the VUV lamp is depositing material onto our film.
- Only other option is that what is already on the film is somehow being altered.
- It is possible that the Y_2O_3 is catalyzing the oxidation of the silicon wafer underneath.

Y2O3 Film growth: How can this be? Could it be Weird Chemistry?



- Theories Tested
  - Film oxidation
    - Too thick
  - New Deposition
    - Blank Silicon Wafer- no growth
  - Oxidation of Silicon Substrate
    - *But no, Thickness of VUV exposed film decreased back to ~20 nm after furnace air treatment.*

Other data & questions:

1. Are there other techniques which will also produce the increase in thickness?

Not that we found.

Samples which were plasma cleaned or furnace cleaned did not grow thicker and in some cases if they had been plasma cleaned the sample did not increase in thickness when subsequently exposed to VUV light.

2. Do other oxides show the same effect?

We tried reactively sputtered scandium (Sc_2O_3) which is right above Y in the periodic table. At first nothing. And later with newly prepared samples found that it did.

3. Also yttrium oxide prepared by RF sputtering of Y_2O_3 was not observed to expand when exposed to VUV.

Other observations:

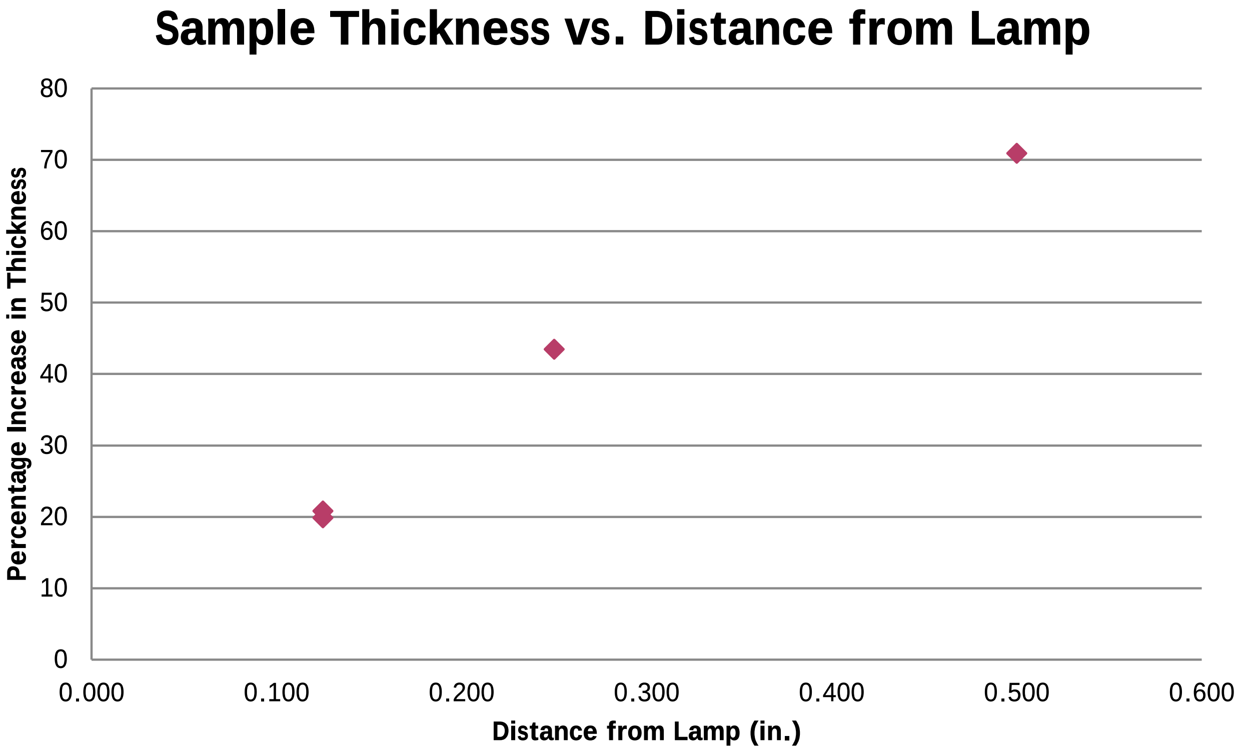
As the thickness goes up the index of refraction (as measured via ellipsometry) goes down. It starts at about 1.6 and goes down to less than SiO_2 which has one of the lowest indices of any oxide.

The films become increasingly delicate as they get thicker. They are easily scratched and flaky. The thickness increase is less around the edges of the substrate. See **the arrow** on the figure and note the blotchiness.

New Theories and Tests

Effect is stronger when the film is Farther from the VUV lamp. Why?
Maybe the VUV photons need to be absorbed in air in the air first.

- Importance of Distance from VUV Lamp



What do 7.27 eV photons do? They will produce atomic oxygen in air, which can also produce ozone. These are the species that are thought to remove contamination. Could O or O_3 be making some new compound which is much thicker than the original oxide?

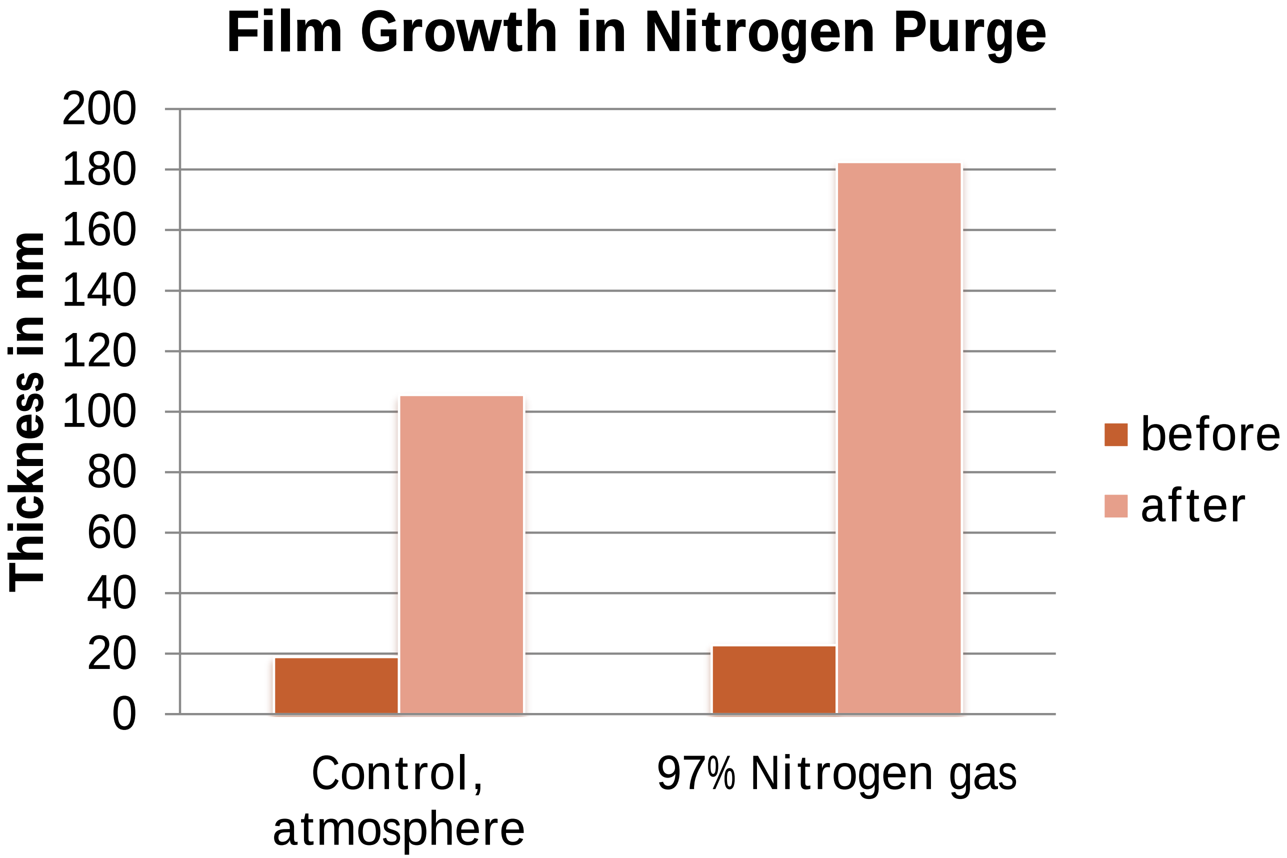
Ozonides are known for alkali metals & recently reported for some alkali earth metals. Could they occur for group III metals? That is $Y(O_3)_3$. It would have 6 times as much O as Y_2O_3. Still, that is a lot of expansion!

New Theories and Tests (Cont.)

Oxygen is needed to make an ozonides.

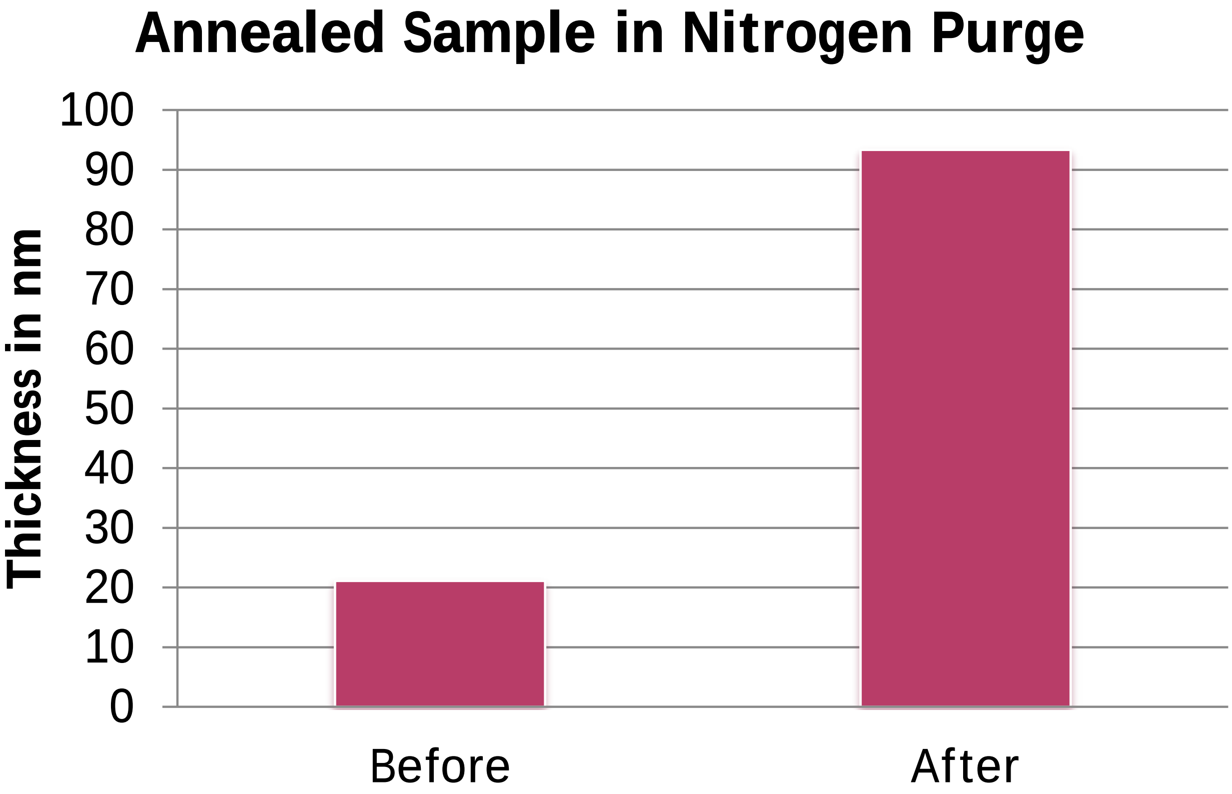
What if there is no oxygen in the atmosphere when the lamp is on? We expected no expansion.

- Formation of an Ozonide



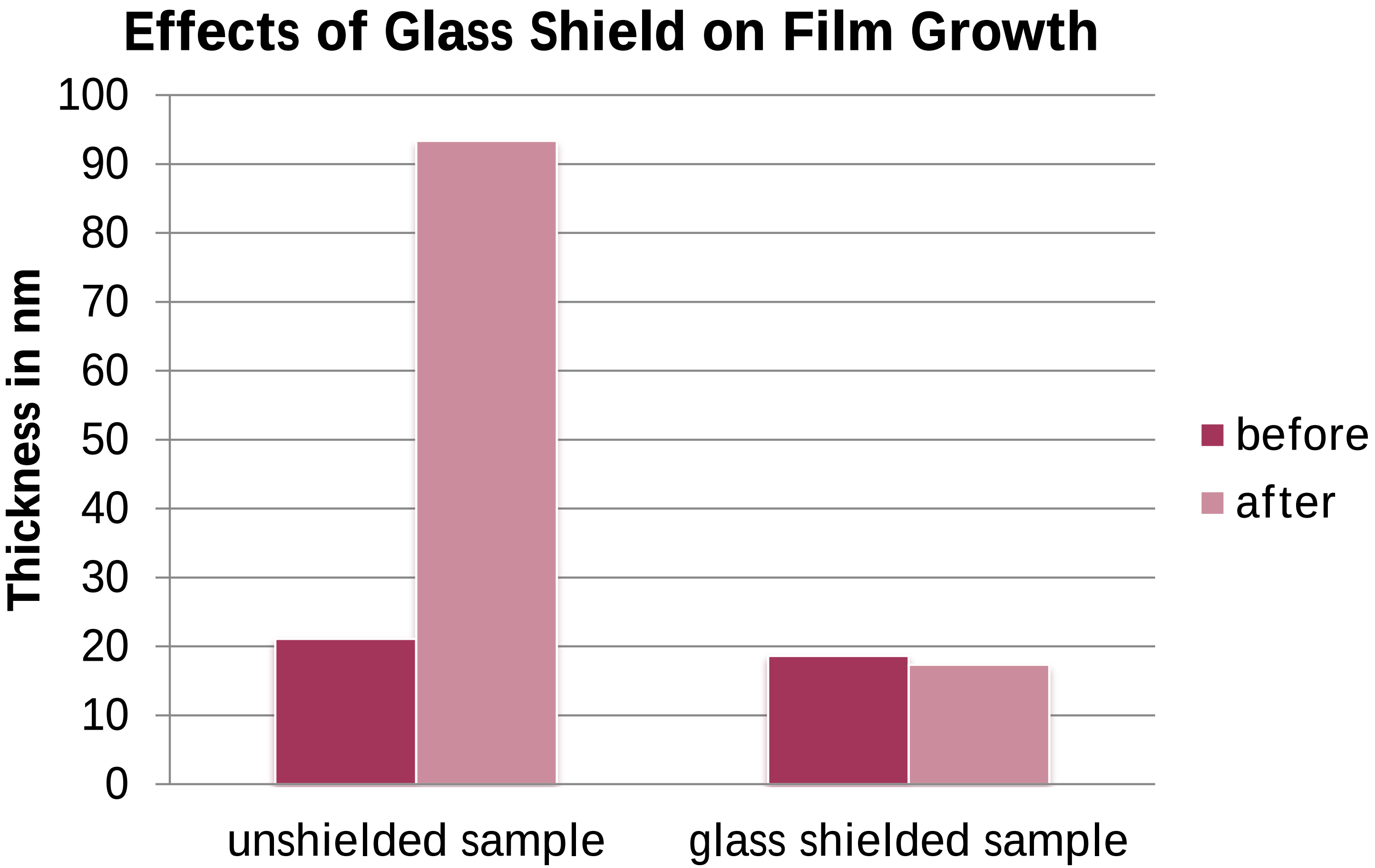
New theories and Tests (cont.)

- Water Expansion During Lamp Exposure



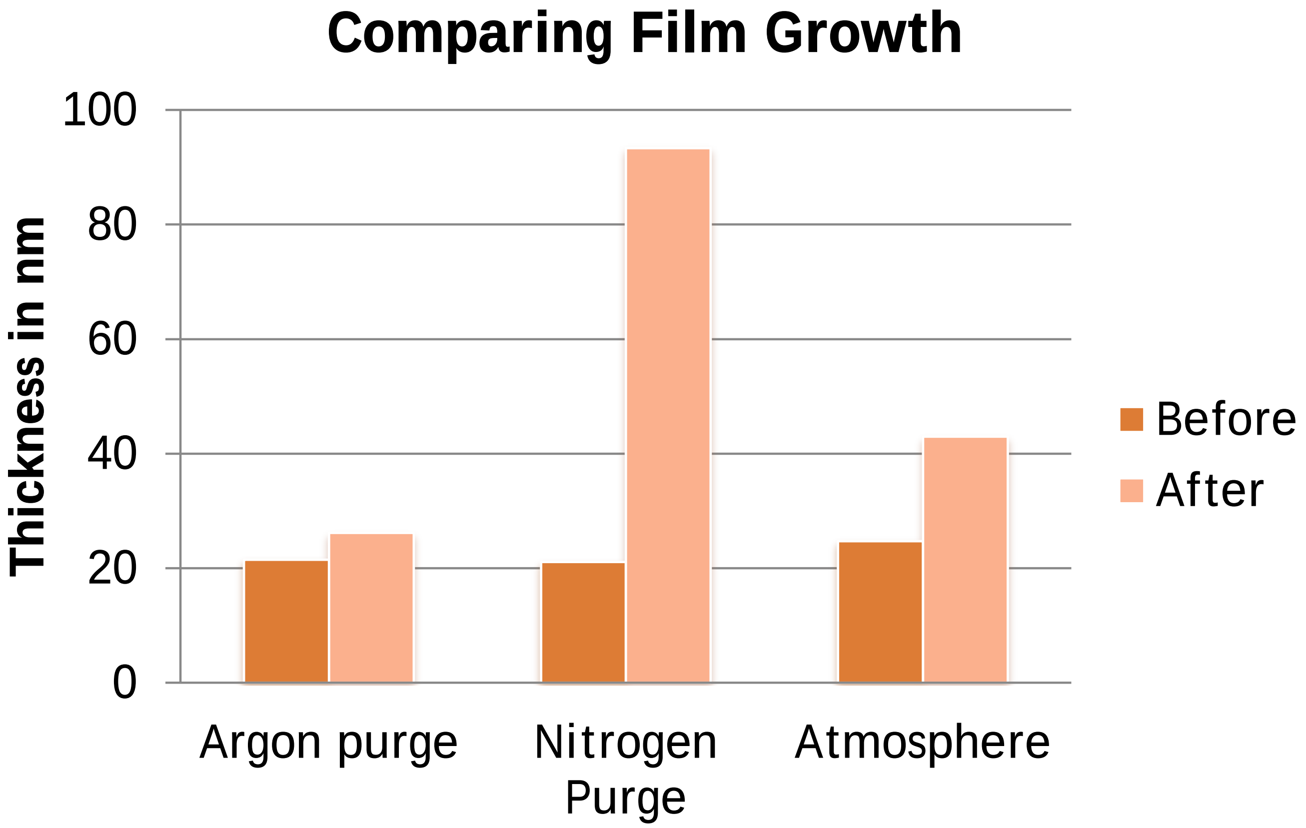
New Theories and Tests (cont.)

- Necessity of VUV Interaction with Sample



New Theories and Tests (cont.)

- Formation of Nitrogen Containing Product



Could it be Weird Physics?*

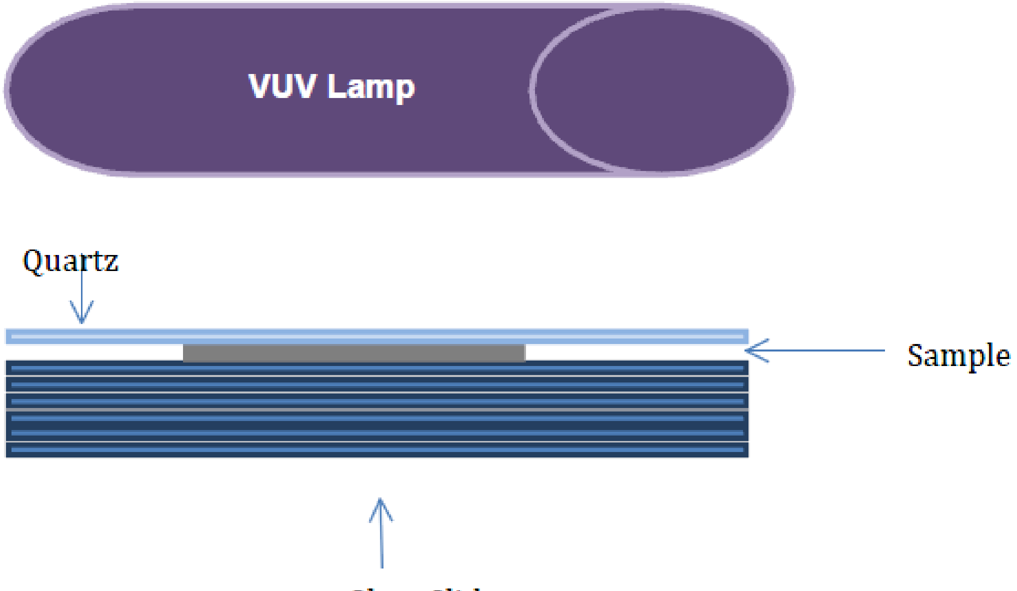
Could the photons themselves be delivering energy directly to the lattice?

For example. Popcorn theory: Something is causing the yttrium oxide to fluff up. But,

1. What would the mechanism be? Could the photons be delivering energy to yttria and making it change as near UV light does to TiO_2? Band gap of Y_2O_3 ~ 7.0 eV.
2. Yttria is hygroscopic and can take CO_2 out of air.
3. What evidence do we have of this? It is time for TEM analysis.

2.5.1 The Photon Effect

We next conducted another shielding experiment that would only allow the photons to interact with the sample surface. The set-up for this experiment is shown in Figure 2.5. A fuzed quartz window that was transparent to UV light was placed directly on top of the scandium sample. The quartz



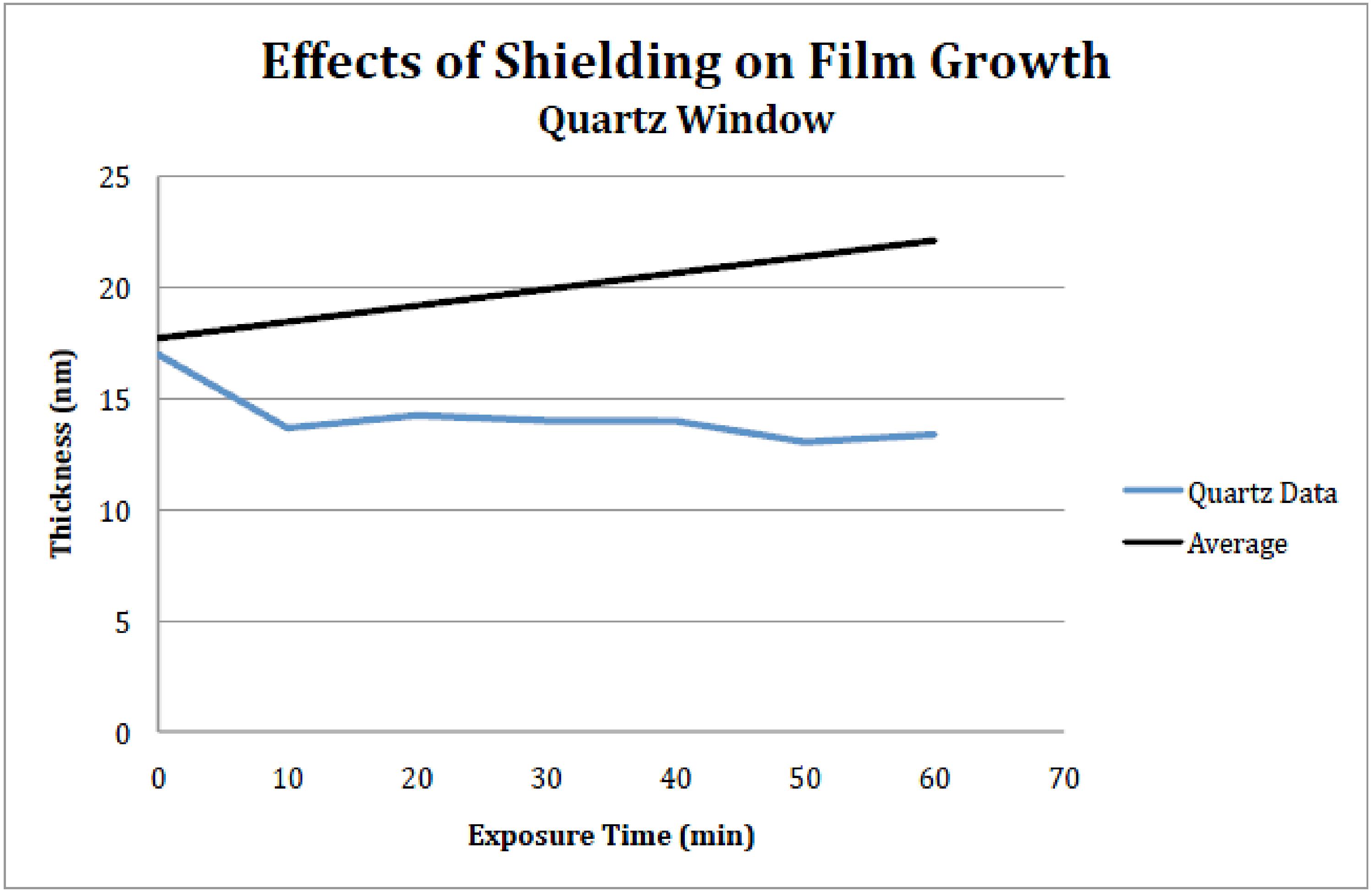
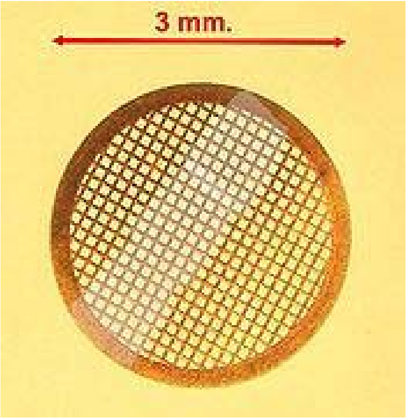


Figure 2.6 Thickness of the film vs. the exposure time when subjected to photons. Average growth observed in the absence of the quartz (the heavy black line) is graphed along side the data collected.

Further Theories and tests

- Use TEM (Transmission Electron Microscope) to characterize new material being formed
  - Figure out how to transfer the new material onto the delicate TEM grid
    - Sputtering destroys grids
    - VUV process destroys grids



Take home message: Films expand from about 20 nm to almost 200nm and we still don’t know why. Unprecedented!

We have looked at a lot of mechanisms. Yttria is thermodynamically very stable. If a VUV lamp can do this maybe the behavior of hafnia (now being used in the gate oxide of silicon devices) should be examined.
Help us figure this out. What mechanism do you suggest and what experiments should we use to sort this out?