Status and Prospects for VUV Ellipsometry

(applied to high-k and low-k materials)

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- Requires invention/ potential showstopper
- Development required
- Solution known

Outline

1. **Quick Introduction to Ellipsometry**
   - Why do we need the VUV?
2. **VUV SE: Initial Challenges**
   - Instrumentation and analysis
3. **Applications and Advantages of VUV SE**
   - Increased sensitivity to film thickness
   - Increased access to unique spectral features
4. **VUV SE of High- k Materials**
   - Thickness, bandgap, interface layer
5. **VUV SE of Low -k Materials**
   - Porosity, low index inclusions
6. **Conclusion**

1

Introduction: What is ellipsometry?

- Traditional SE can be static or dynamic, 1770 to 190 nm
  - In-line metrology (thickness, index)
  - Material diagnostics (band gap, alloy composition, strain)
  - Optical constants (index of refraction, dielectric constant)
  - Control/ monitoring of, e.g,
    - **Semiconductor growth**
    - **Etching**
    - **Deposition of proteins on semiconductors**

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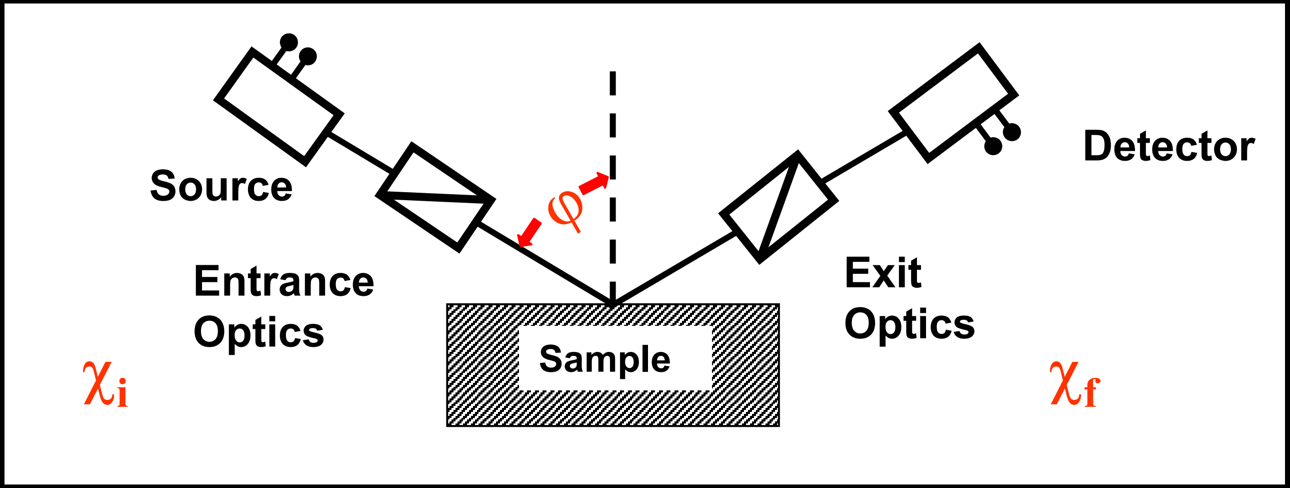
VUV: <190 nm or > 6.5 eV

1 Introduction: What is ellipsometry?

- Why do we need VUV?
  - Lithography
    - **157 nm**
    - **EUV**
  - Front end processing
    - **Thin high k films**
  - Back end processing
    - **Porous low –k interlayer dielectrics**

Potential applications for analyzing any "transparent" dielectric and wideband gap semiconductor

1 Introduction: What is ellipsometry?

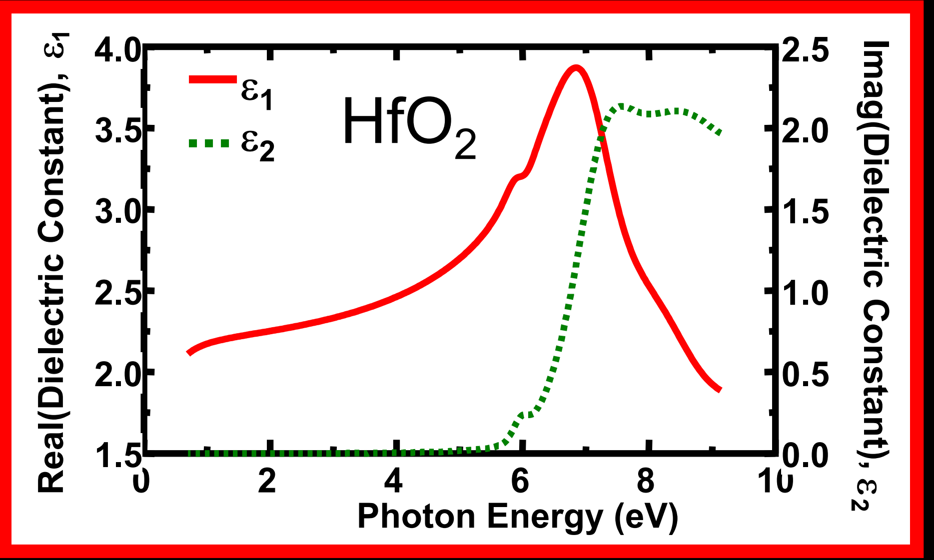


$$\chi_f / \chi_i \rightarrow \rho$$

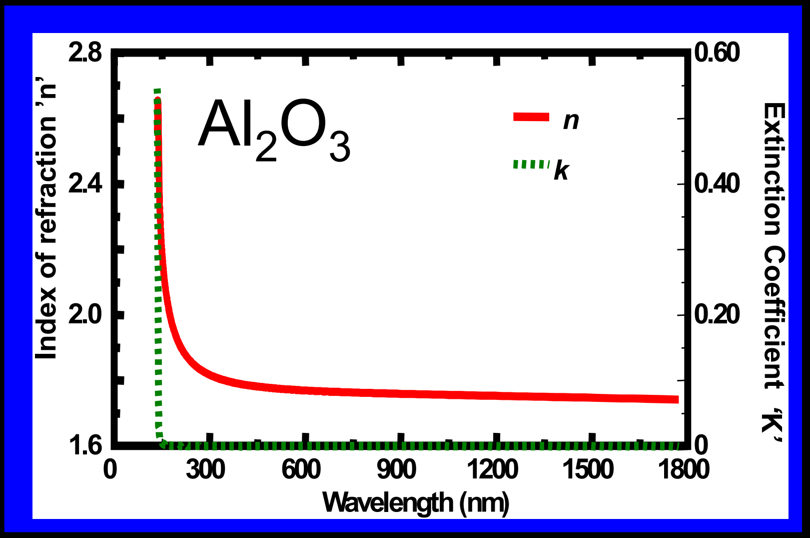
1 Introduction

ρ ⇒ Optical Constants ⇒

Real and imaginary part of dielectric function, $\varepsilon = \varepsilon_1 + i\,\varepsilon_2$



Index of refraction n,
Extinction coefficient k,
$n = n + i\,k$

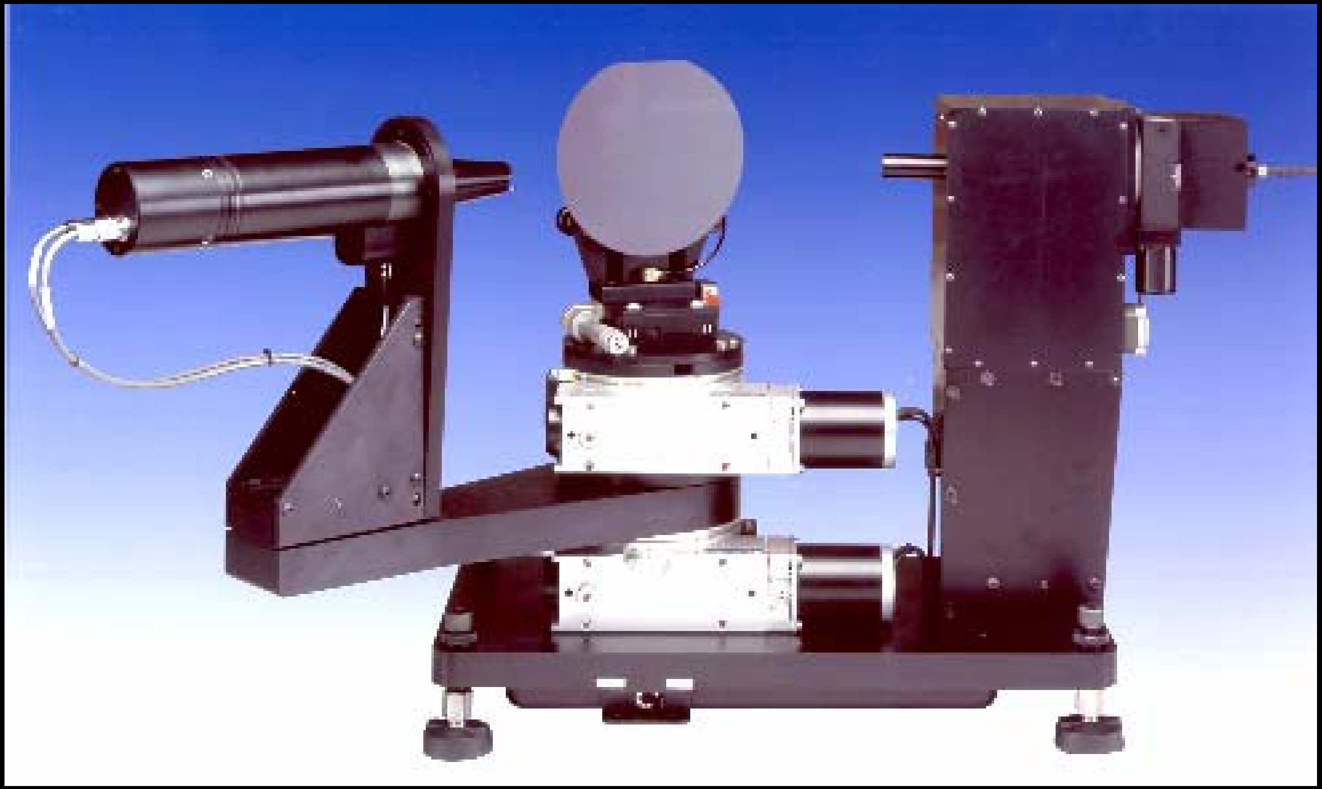


$$n^2 = \frac{1}{2}\varepsilon\left\{\left[1+\left(\frac{2\sigma}{\nu\varepsilon}\right)^2\right]^{1/2}+1\right\}$$

$$k^2 = \frac{1}{2}\varepsilon\left\{\left[1+\left(\frac{2\sigma}{\nu\varepsilon}\right)^2\right]^{1/2}-1\right\}$$

2

Challenges: Instrumentation

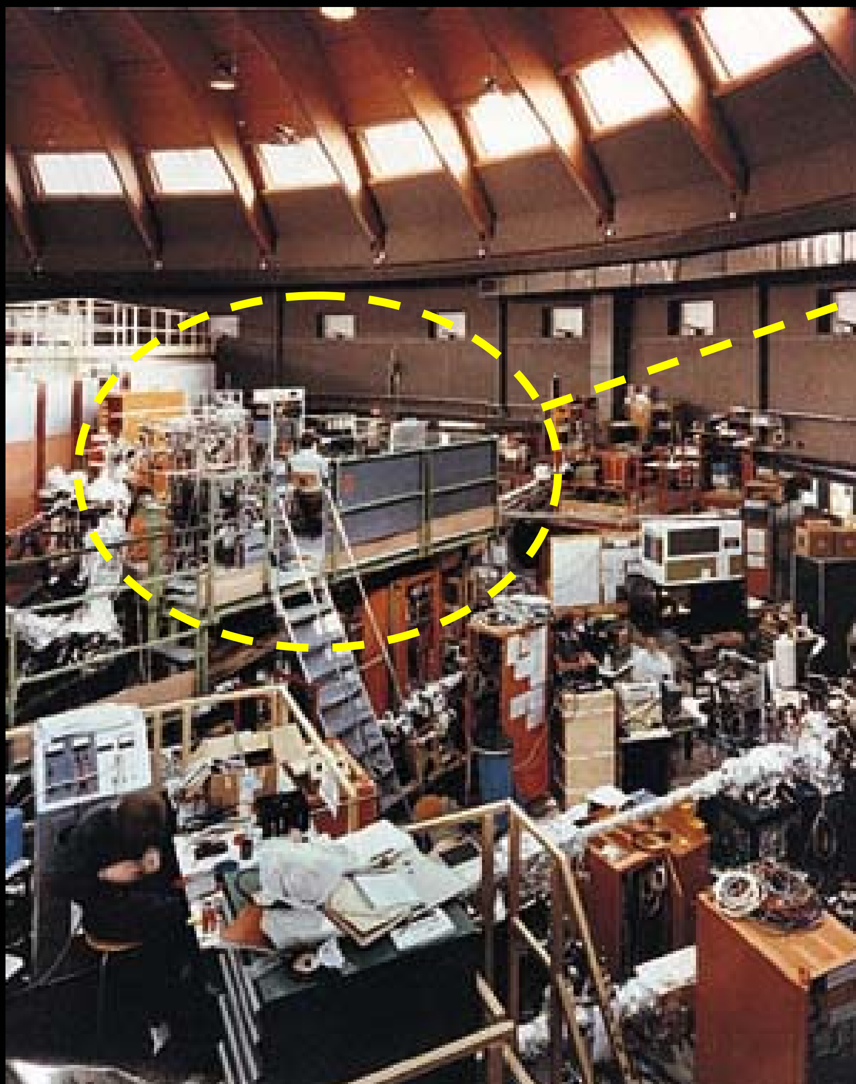


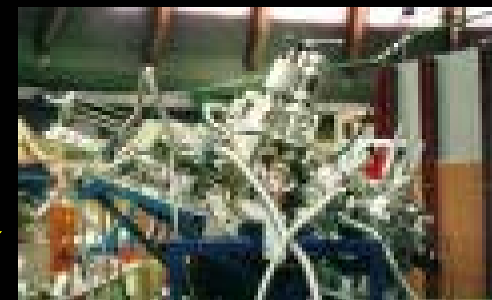
Measurements made:

- in air (any transparent medium will do)
- with quartz optical elements

Quartz and air absorb below 190nm

2 Challenges: Instrumentation





The world's first VUV ellipsometer at the BESSY-I synchrotron source

but not quite appropriate for industrial use……..

2

Challenges: Instrumentation

Xenon→ Deuterium
quartz → MgF_2

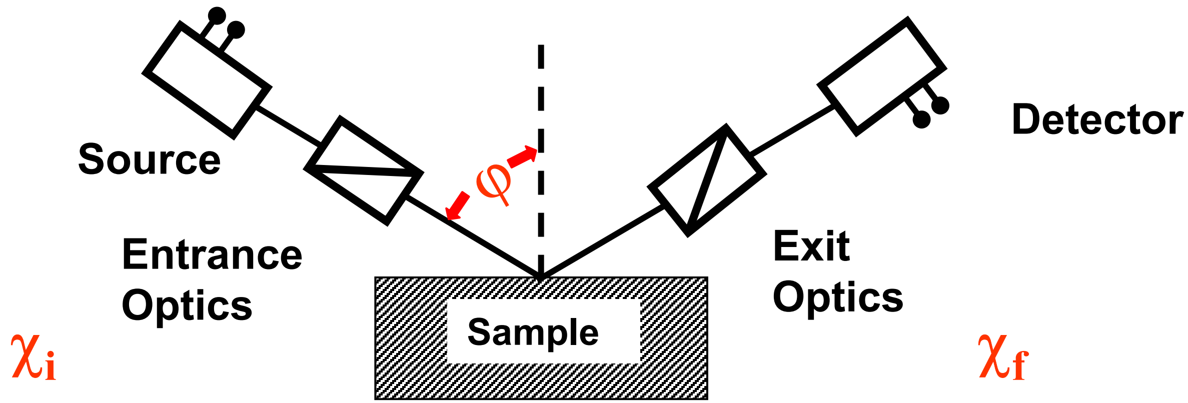
Spectral Range:
131 to 1770nm
or
0.7 to 9.5 eV

Available A.O.I. = 20° to 80°

Compensator for high accuracy measurements of transparent region

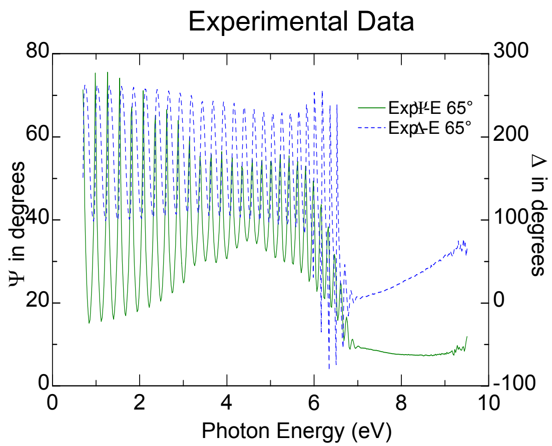
However, reducing data to optical constants still was not routine

2 Challenges: Data Reduction for VUV SE



$\chi \rightarrow \rho \rightarrow \varepsilon$

← 131 to 1770 nm →

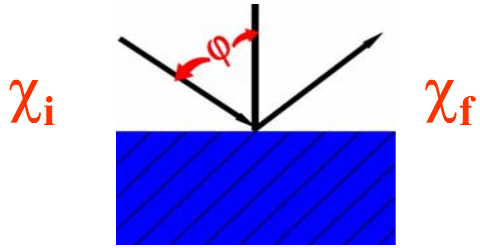


Model

Sample Properties:
***d*, n, k, ε**
composition
roughness
bandgap
porosity

2 Challenges: Data Reduction

2-phase model:



ambient ε_a

substrate ε_s

$$\varepsilon_s = \sin^2\varphi + \sin^2\varphi \tan^2\varphi \left(\frac{1-\rho}{1+\rho}\right)^2$$

3-phase model:

ambient ε_a

overlayer ε_o

substrate ε_s

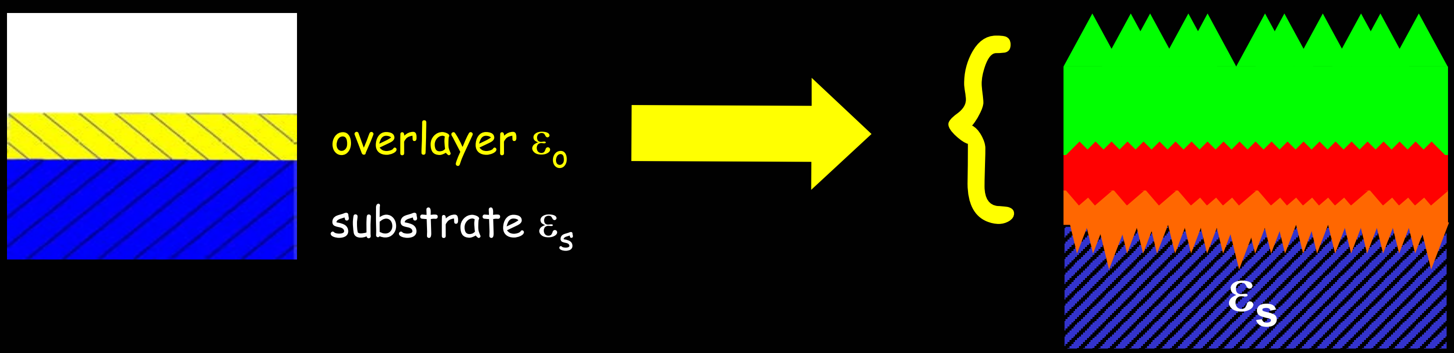
} $\langle\varepsilon\rangle$ *

$$\langle\varepsilon\rangle = \varepsilon_s + \frac{4\pi i d\, n_a}{\lambda} \frac{\varepsilon_s(\varepsilon_s-\varepsilon_o)(\varepsilon_o-\varepsilon_a)}{\varepsilon_o(\varepsilon_s-\varepsilon_a)} \left(\frac{\varepsilon_s}{\varepsilon_a} - \sin^2\varphi\right)$$

2 Challenges : Data Reduction

* Model assumes mathematically sharp interfaces

* Information is returned over the penetration depth of light in the heterostructure (penetration depth is a function of λ)



* Must account for:

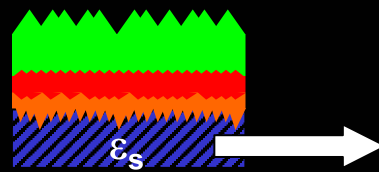
- Inorganic/ organic contamination
- Roughness
- Interface layers

} Significant for VUV SE of high and low k films

Challenges : Data Reduction

2

ε_s :



Substrate is foundational;
Substrate = Si

Fitting up to DUV is routine; Si optical constants are well known:

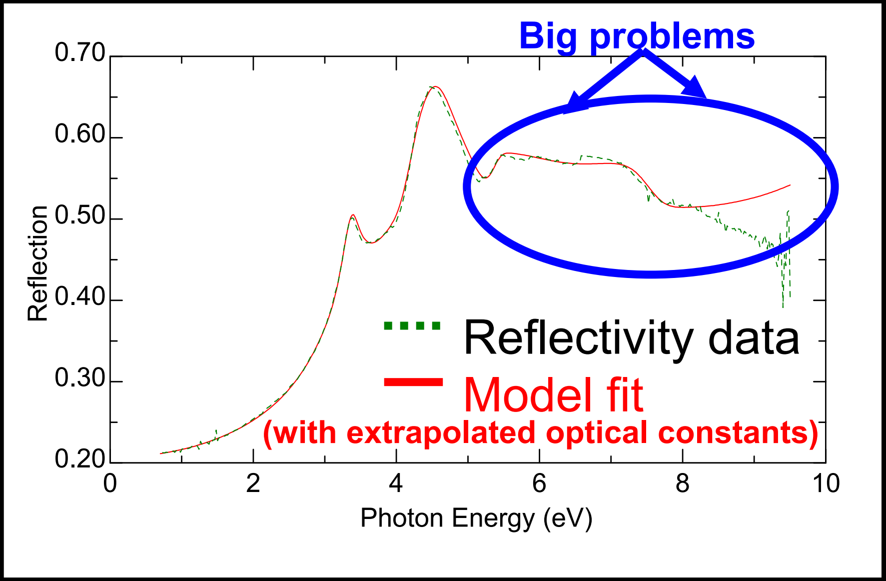
Aspnes, Herzinger
Jellison, Yasuda

No optical constants for Si in VUV

2

Challenges: Data Reduction

Can't we just extrapolate optical constants?



No! Need to determine VUV optical constants for Si.

Approach:

- **9 thermal oxide samples grown on Si, from ~8 Å to 2200 Å thick**
- **multiple angle of incidence (45 to 75°)**
- **multi-sample analysis**

2

Challenges: Data Reduction

- interface layer of 9.4 Å for all samples
- fit parameters coupled in interface and SiO_2 layers, except for Amp, E1 offset
- could NOT fit data without interface layer

SiO_2: Tauc-Lorentz oscillator

Amp= 40.024, En= 10.643, C= 0.72608, Eg= 7.5258
Pole 1: Pos= 13.167, Mag= 94.386
Pole 2: Pos= 0.135, Mag= 0.0127
E1 offset= 1.263

Interface Layer

Si: Parameterized Semiconductor Layer

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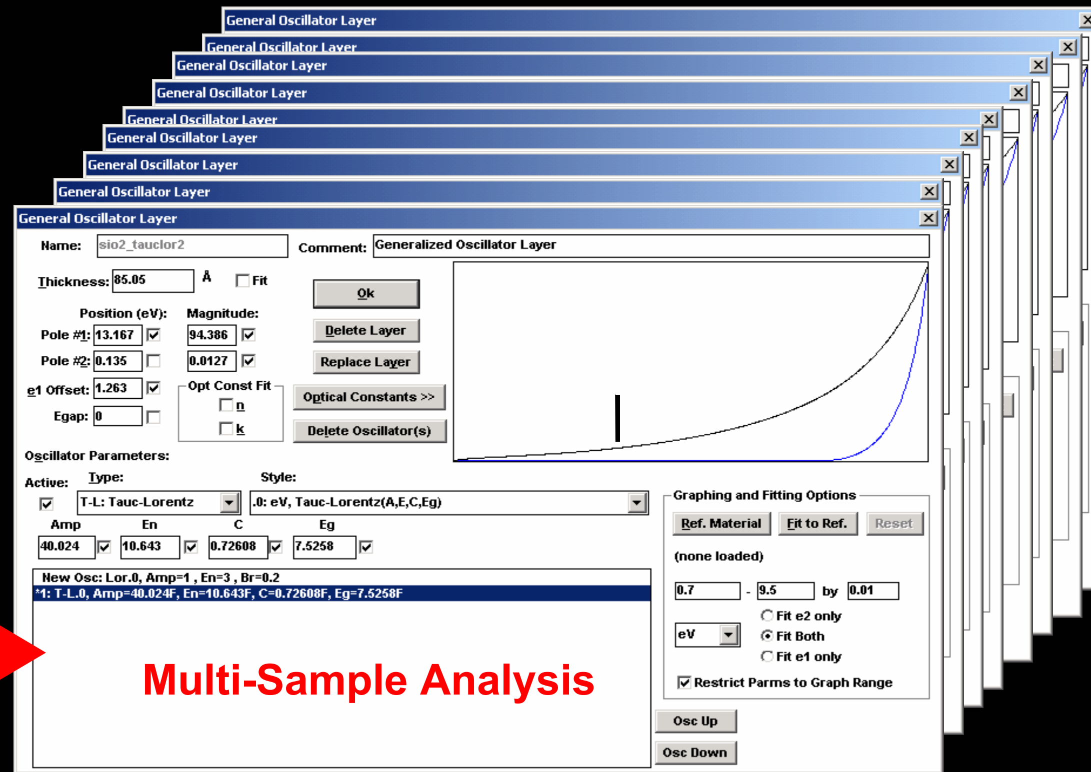

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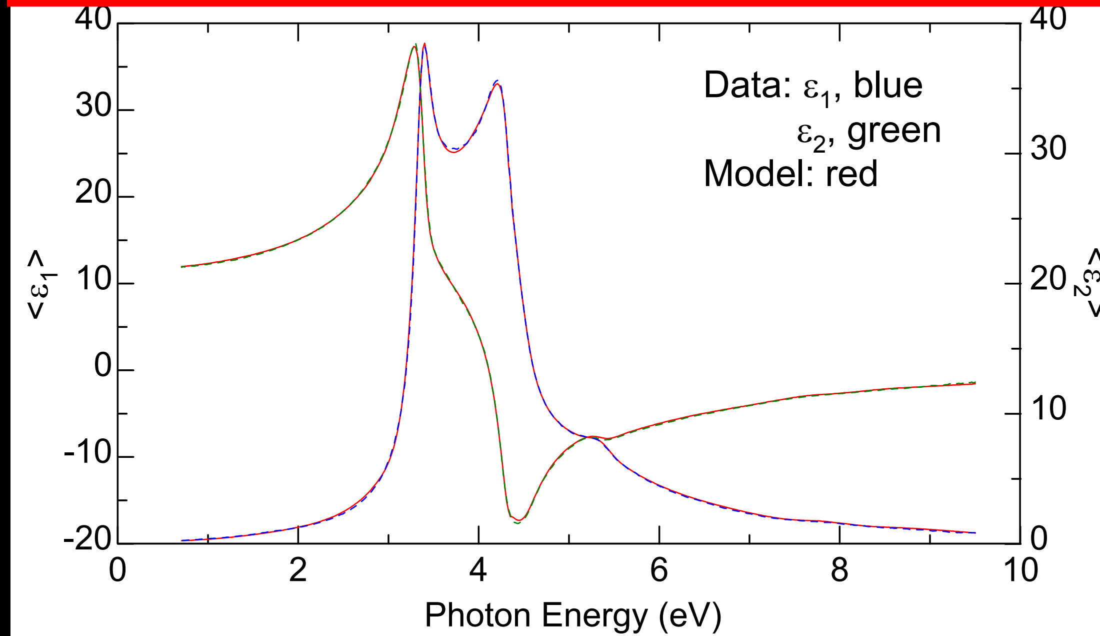
2 Challenges: Data Reduction

SiO_2/Si: Selected Fits from Multi-Sample Analysis

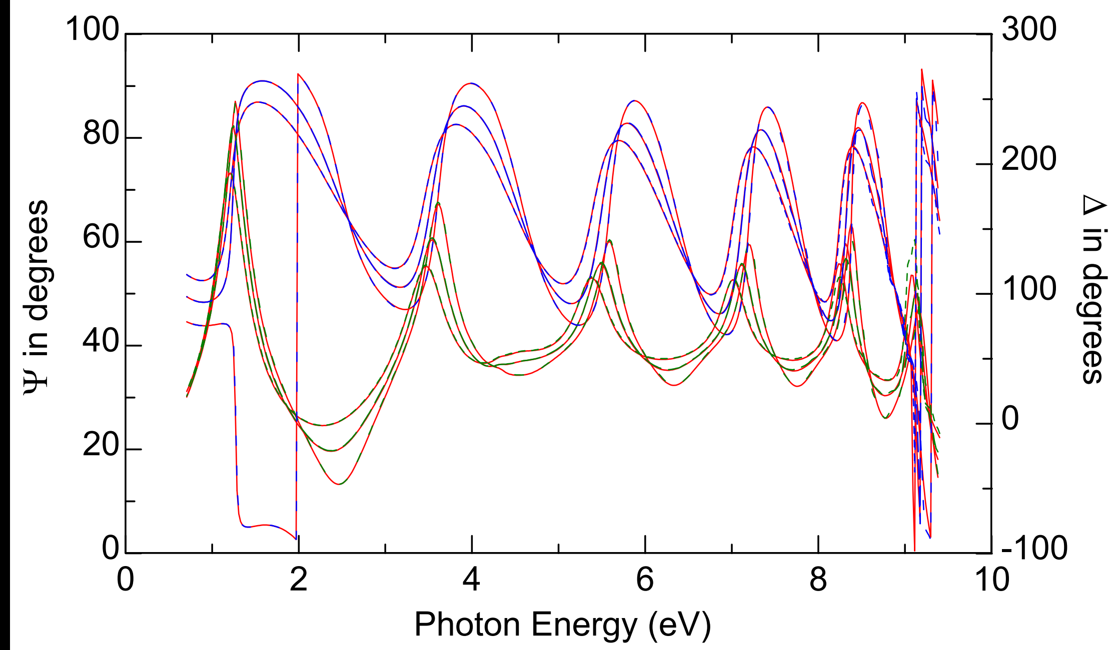
Thinnest Sample:

SiO2 7.5 Å
Int. Layer 9.4 Å
Si Substrate



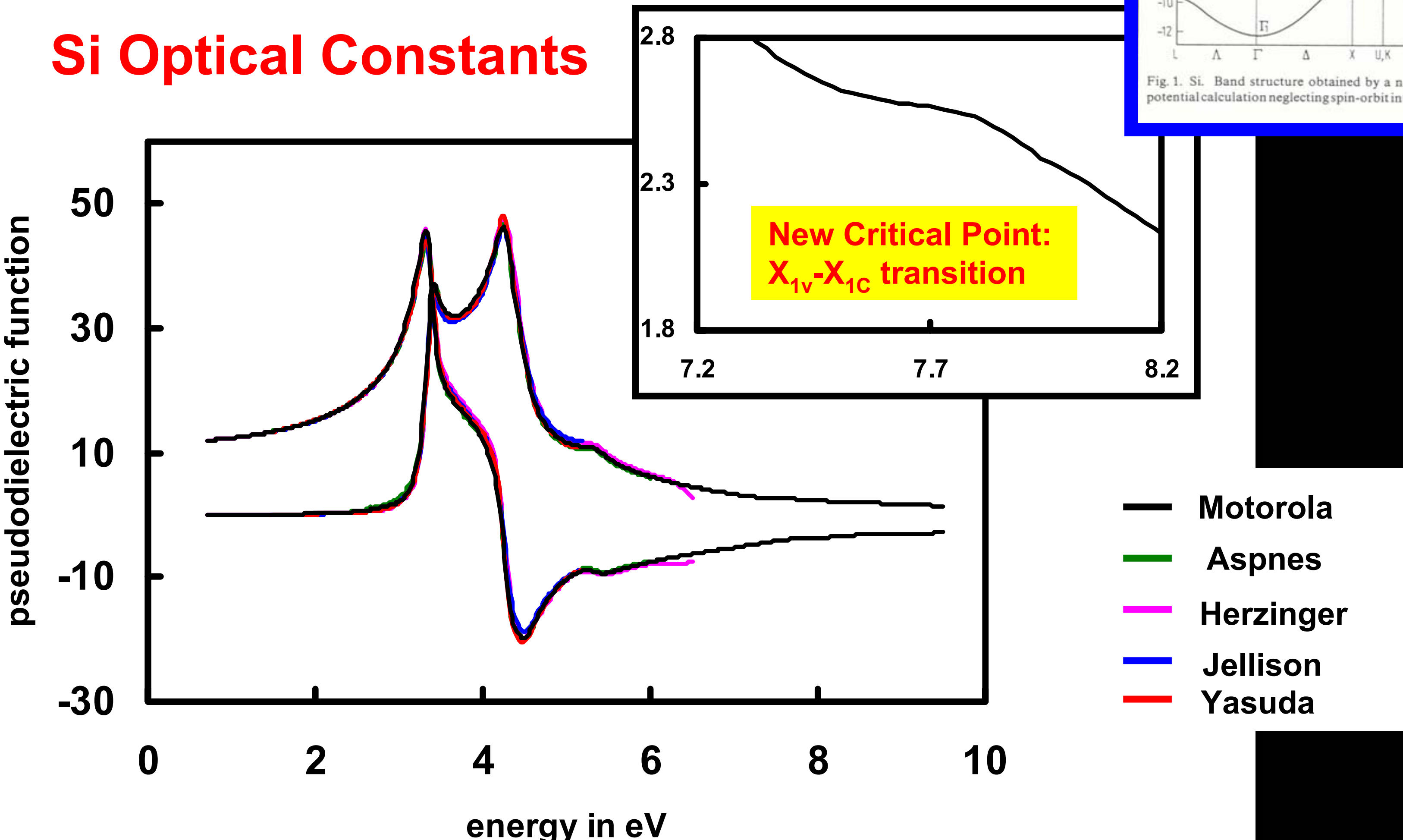
Thickest Sample:

SiO2 2189.3 Å
Int. Layer 9.4 Å
Si Substrate



2 Challenges: Data Reduction

Si Optical Constants



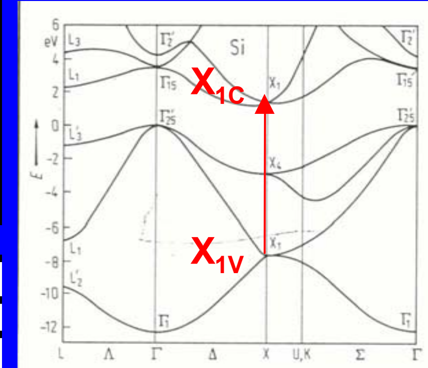
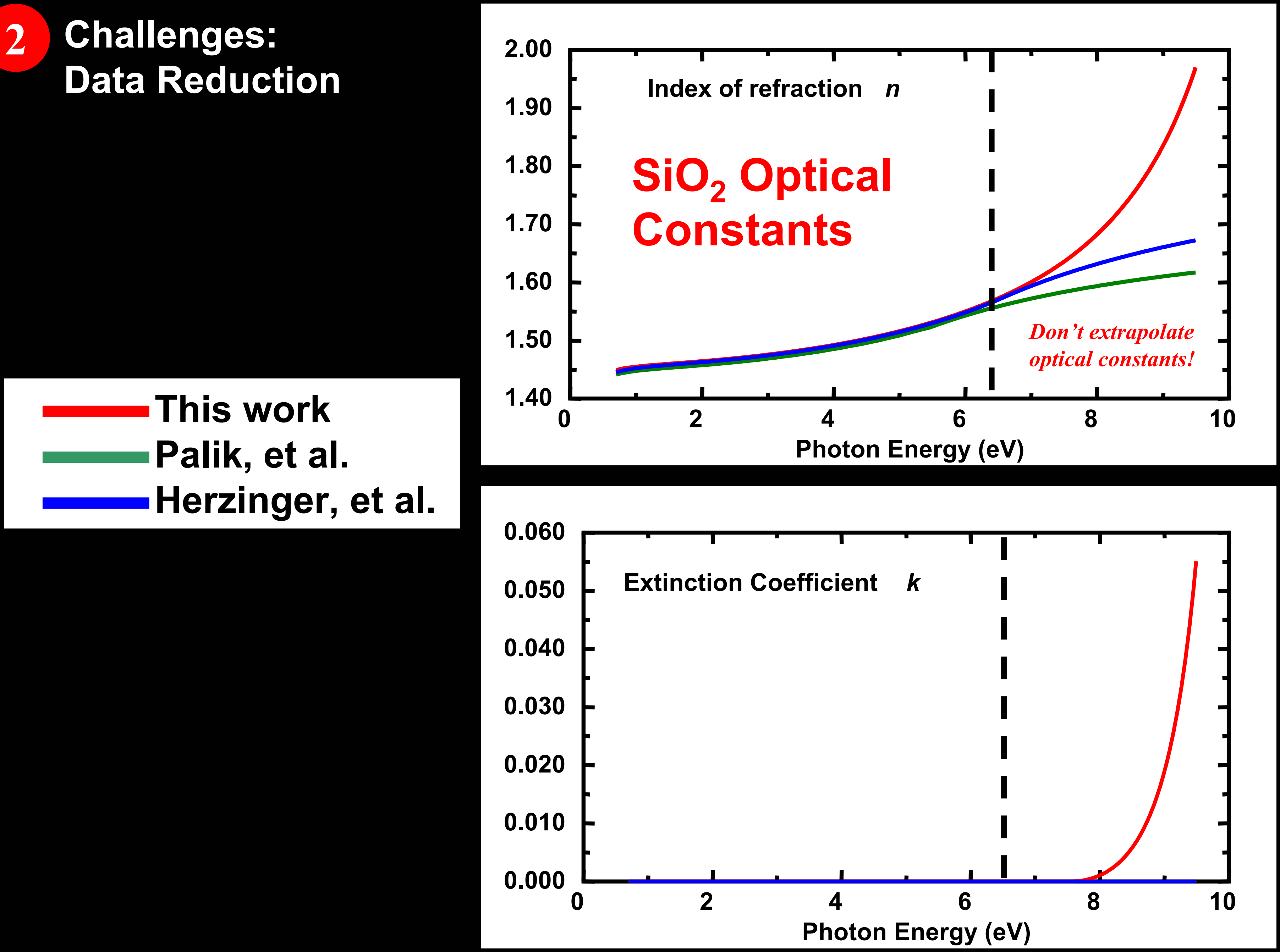
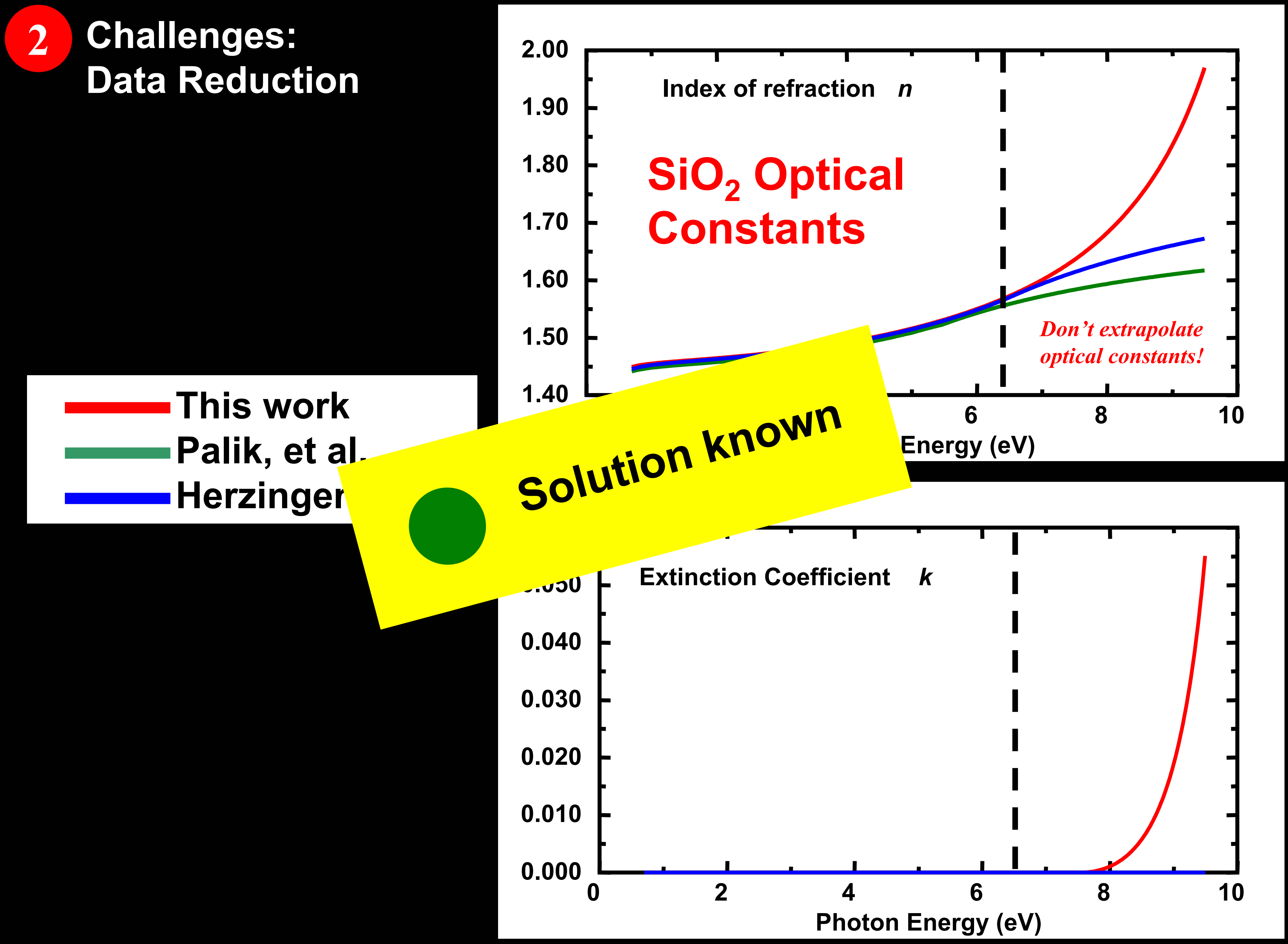


Fig. 1. Si. Band structure obtained by a non-local pseudopotential calculation neglecting spin-orbit interaction [76C2].

2 Challenges: Data Reduction

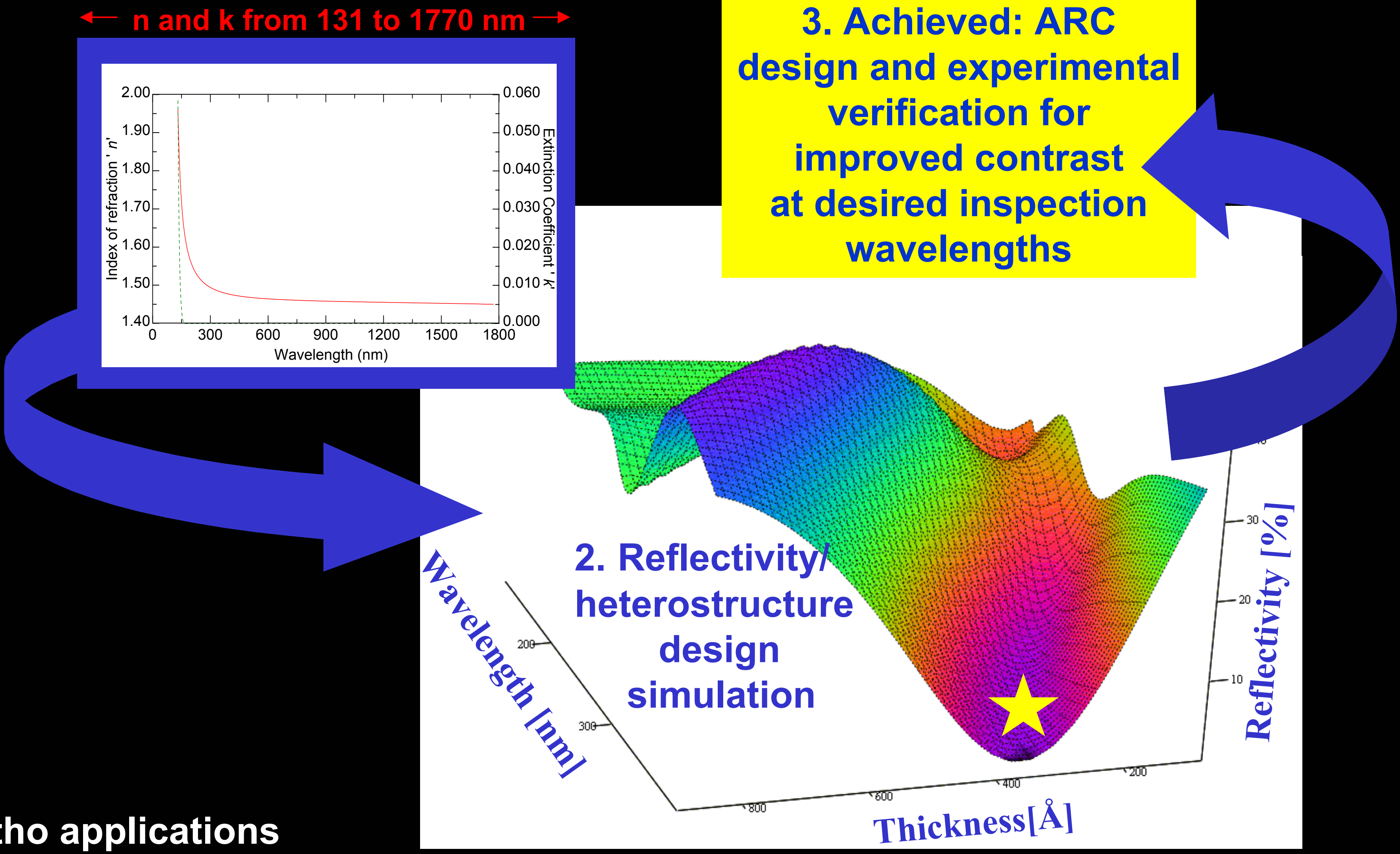


Challenges: Data Reduction



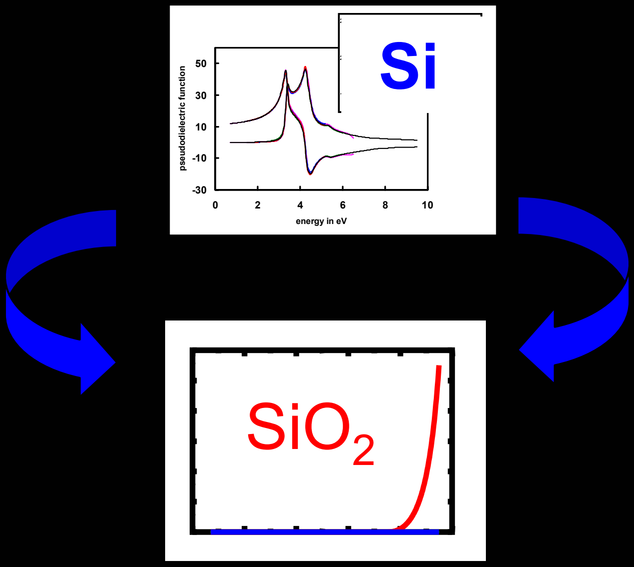
Applications and Advantages of VUV SE

1. Optical Constants from VUV SE

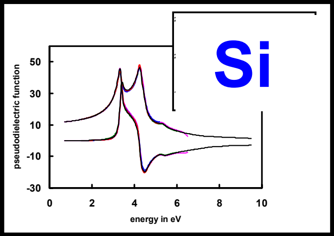


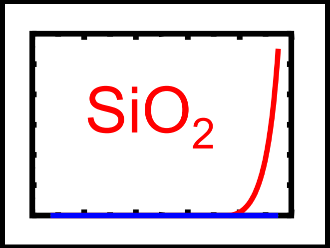
Litho applications are numerous and obvious….

3 Applications and Advantages of VUV SE



3 Applications and Advantages of VUV SE





High- k Gates

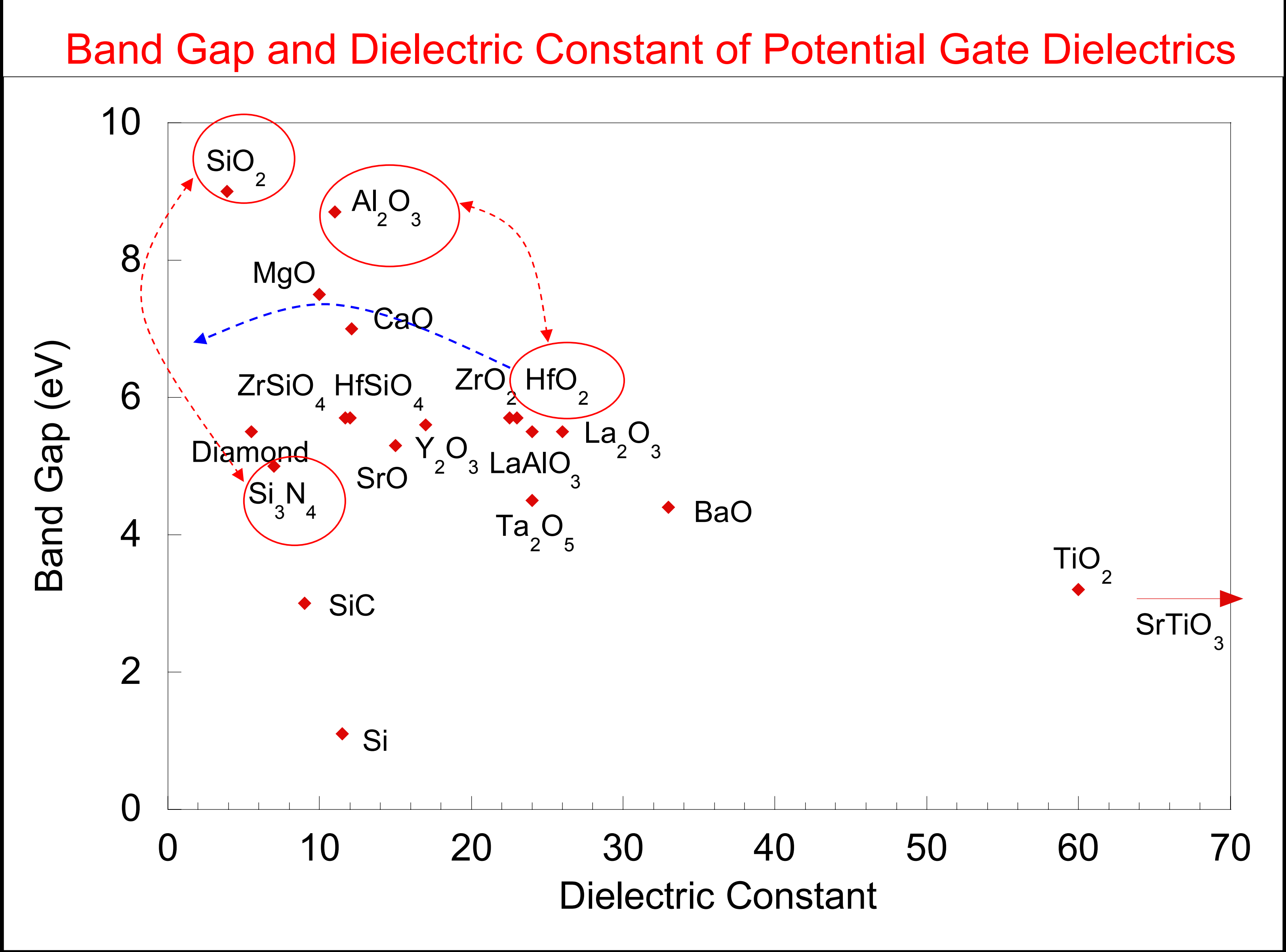
SiO_2
SiON
Metal oxides

Low-k ILDs

SiO_2
TEOS
OSGs

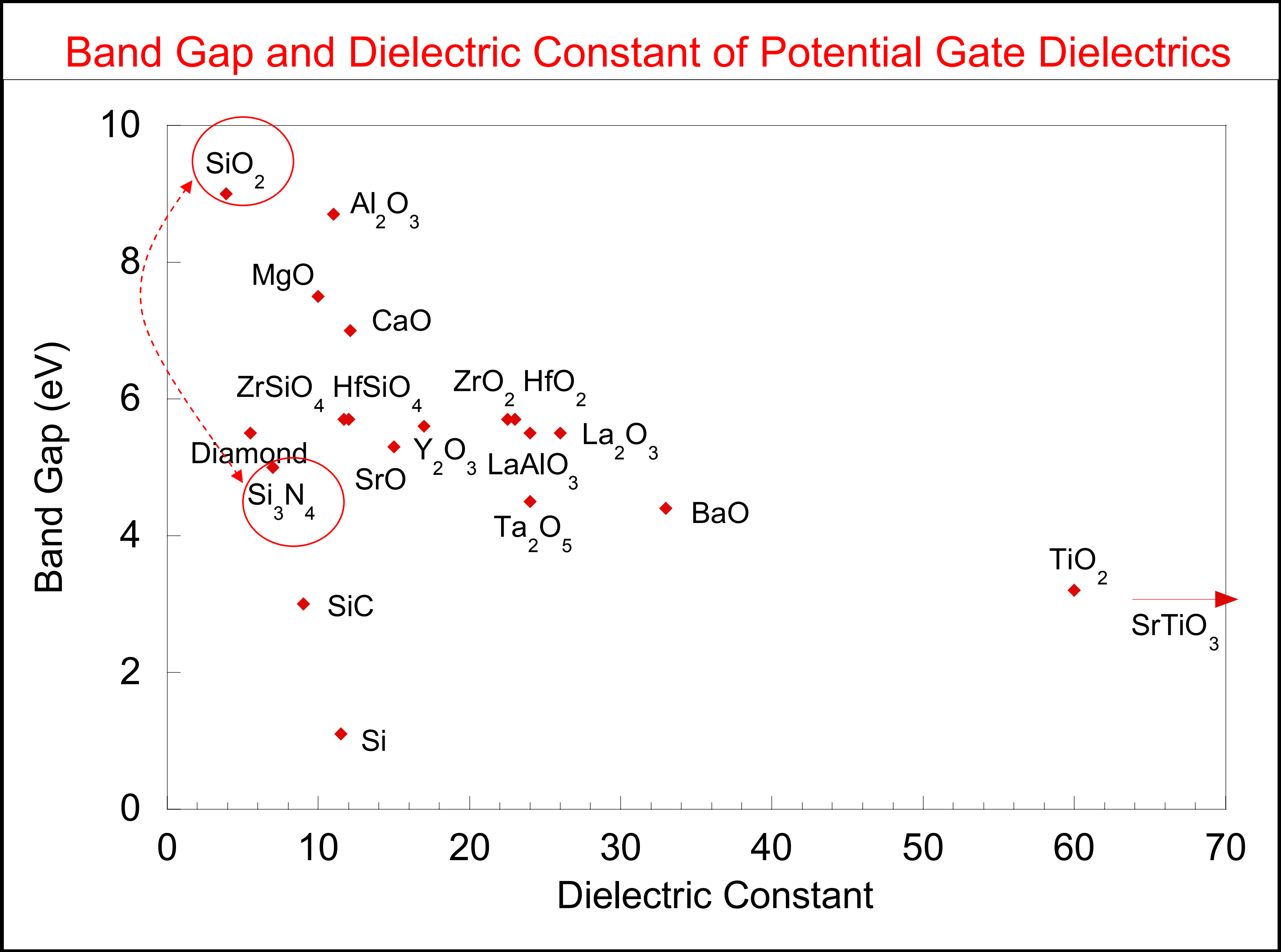
- **Increased sensitivity to film thickness**
- **Increased access to unique spectral features**

VUV SE of High k Materials



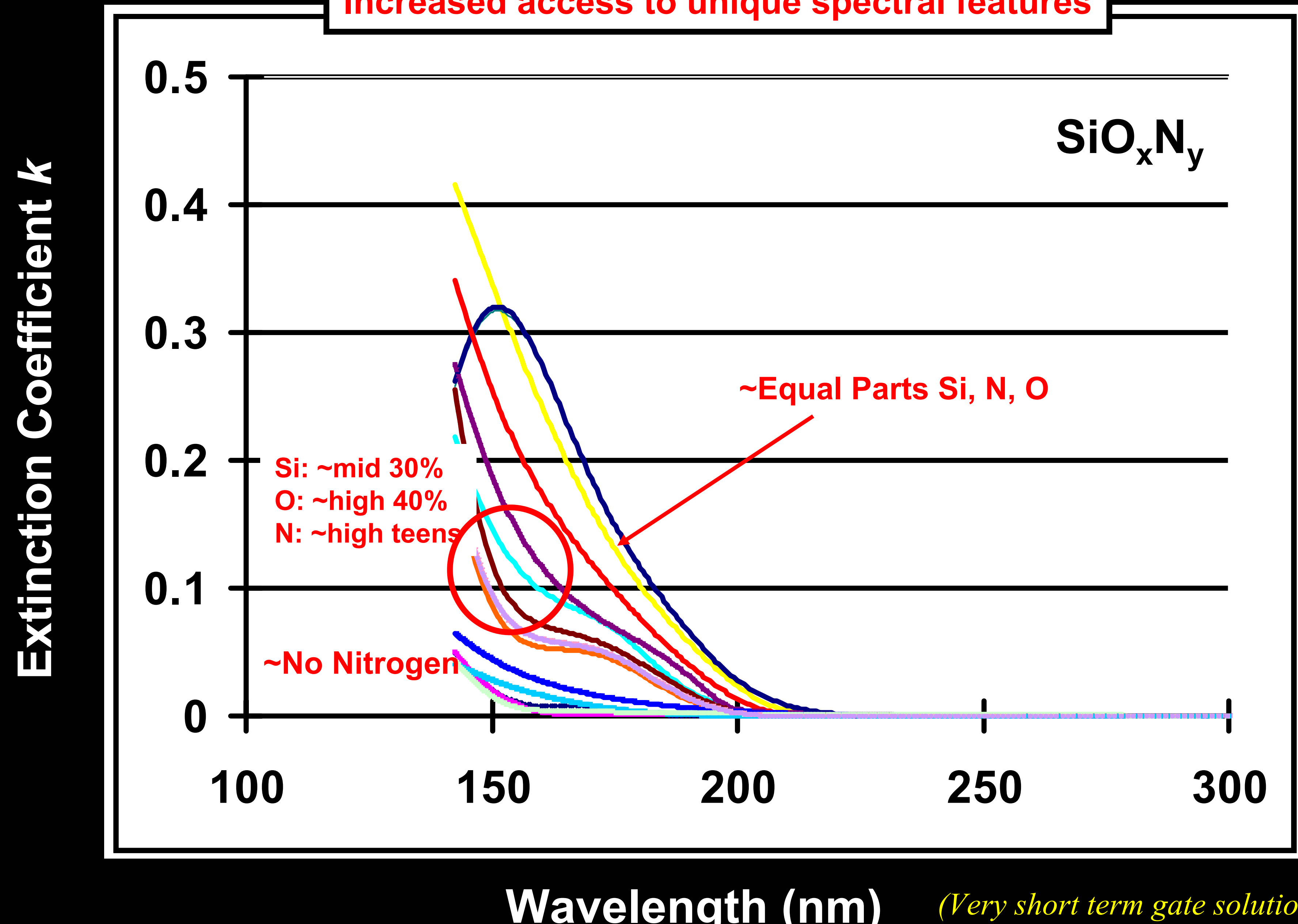
4

VUV SE of High k Materials



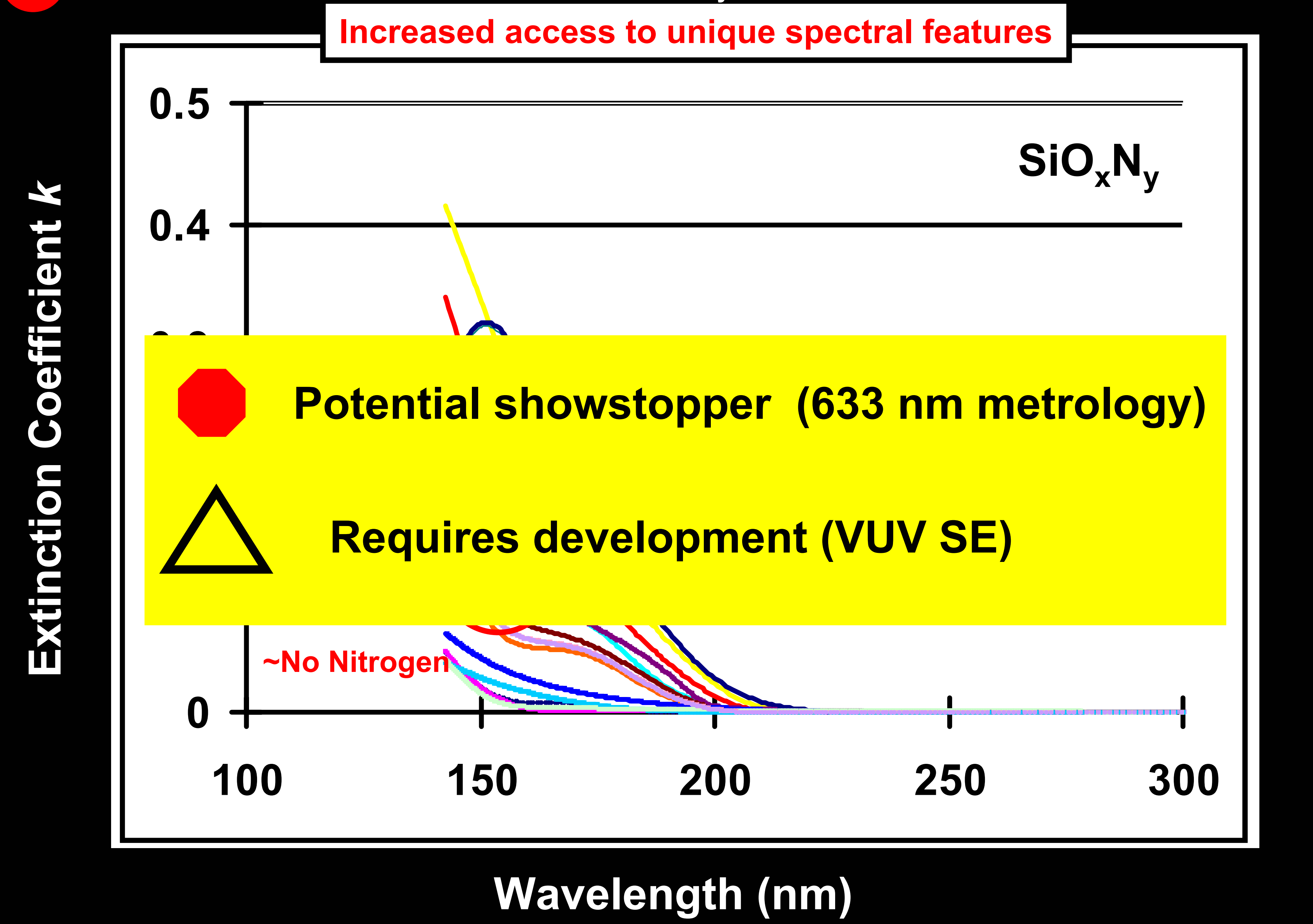
4 VUV SE of High k Materials: SiO_xN_y

Increased access to unique spectral features



(Very short term gate solution)

VUV SE of High k Materials: SiO_xN_y



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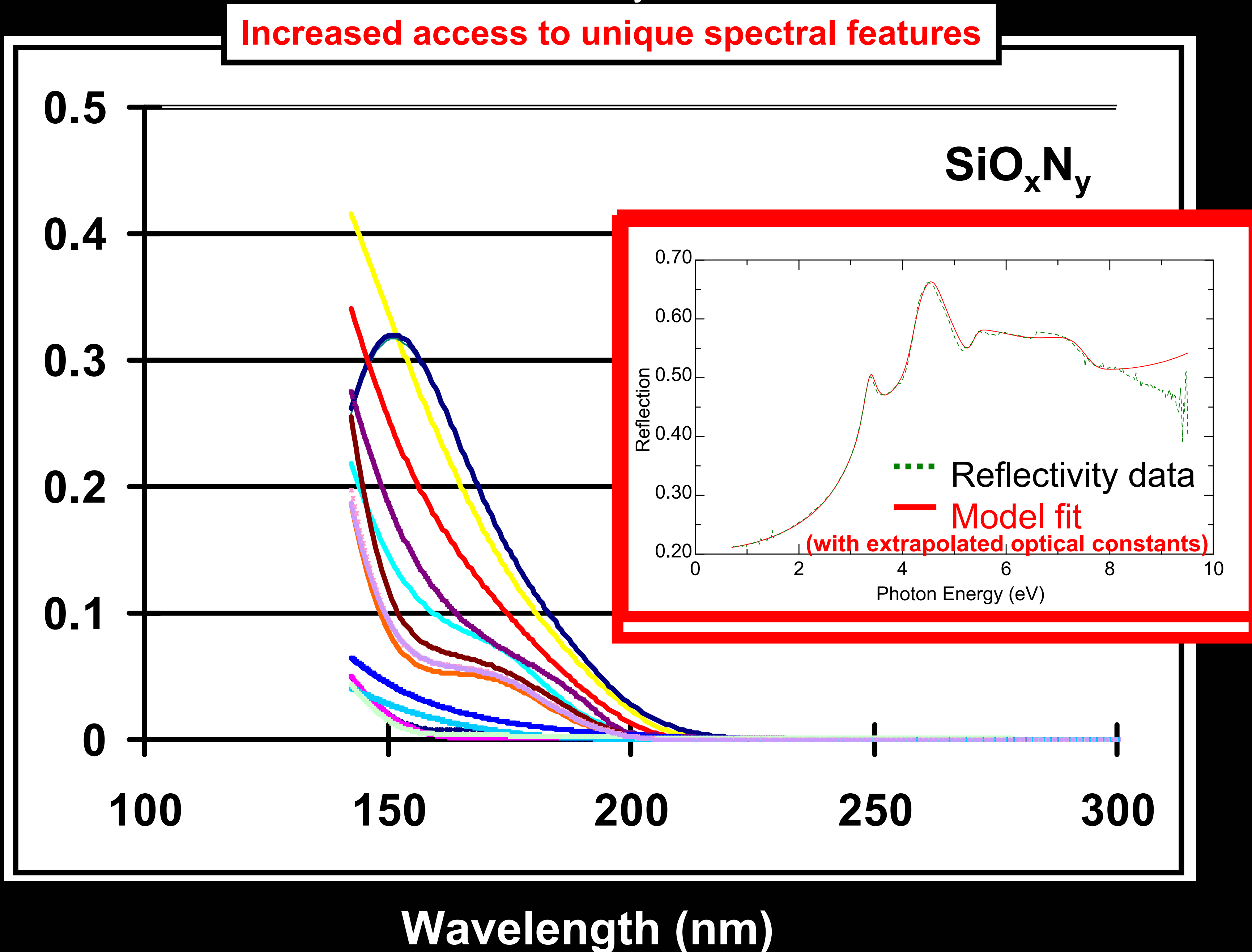
VUV SE of High k Materials: SiO_xN_y



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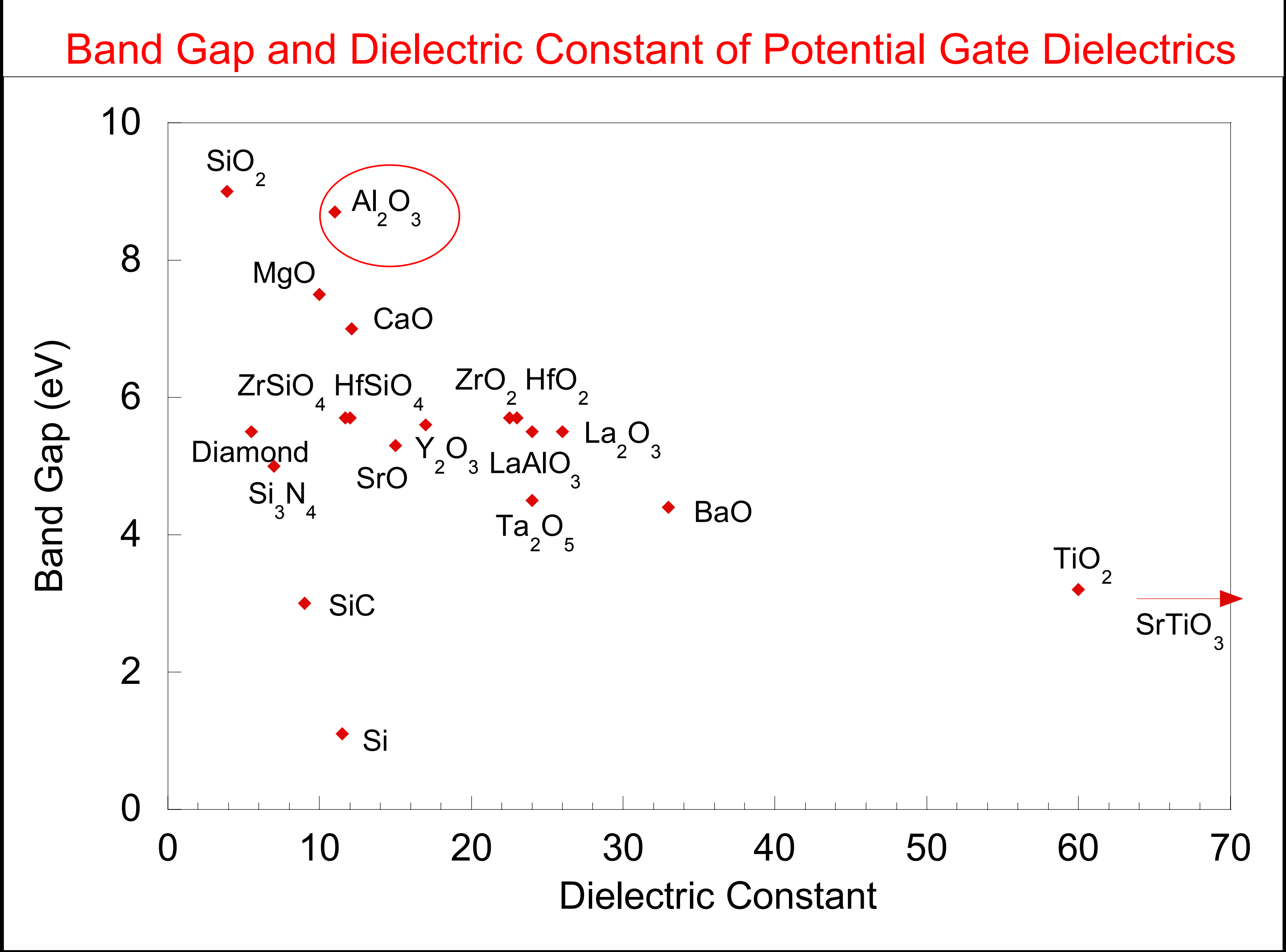
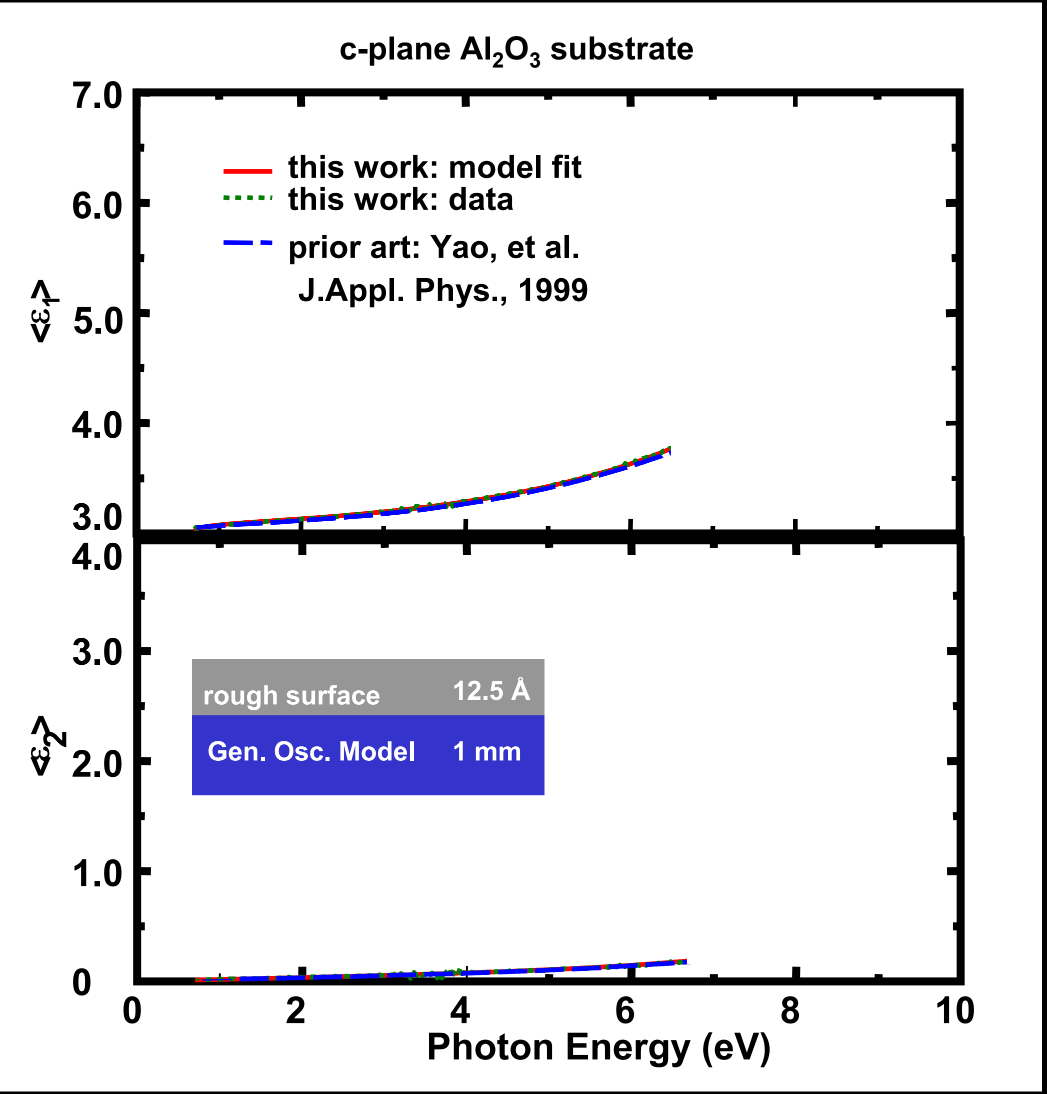
VUV SE of High k Materials



4 VUV SE of High k Materials: bulk Al_2O_3



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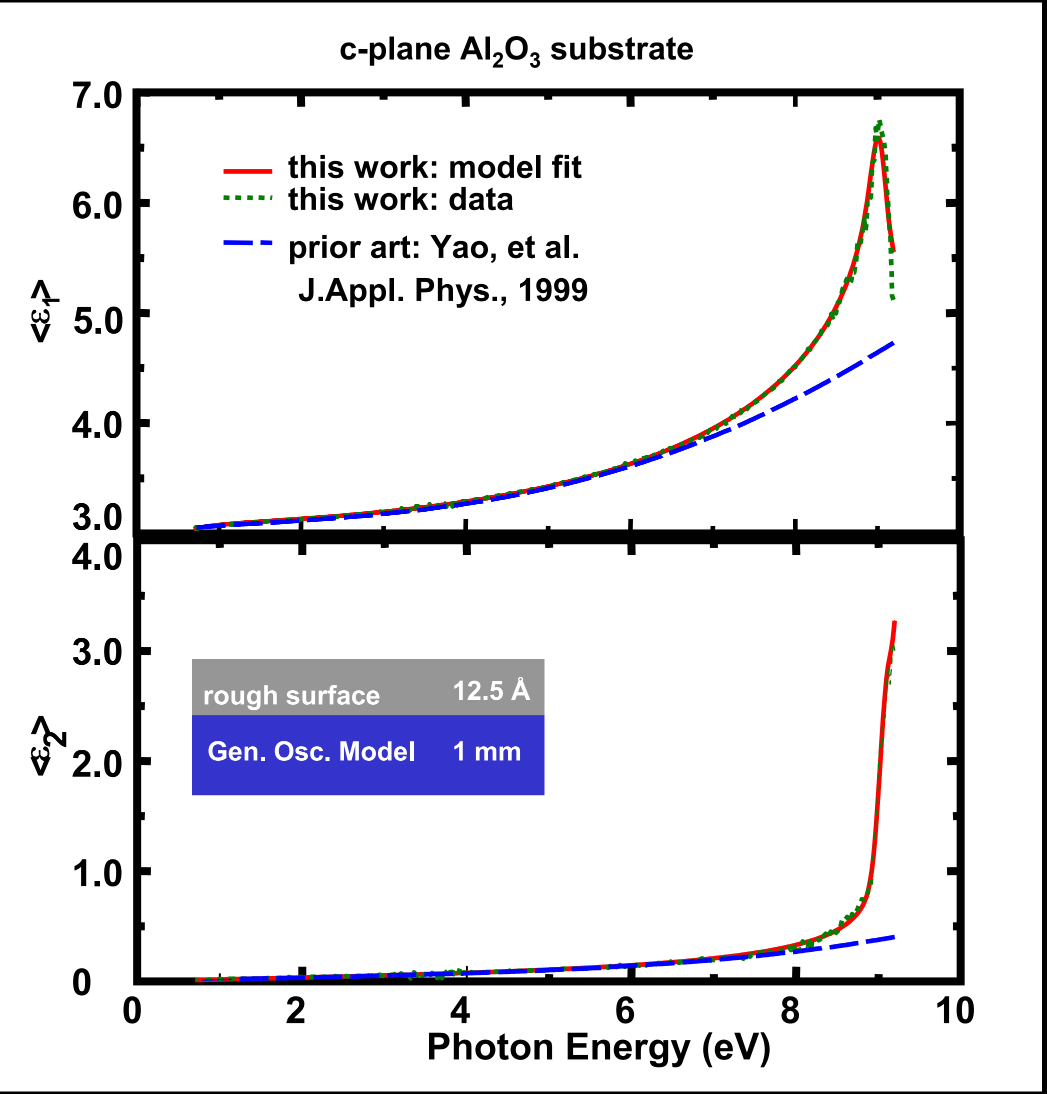
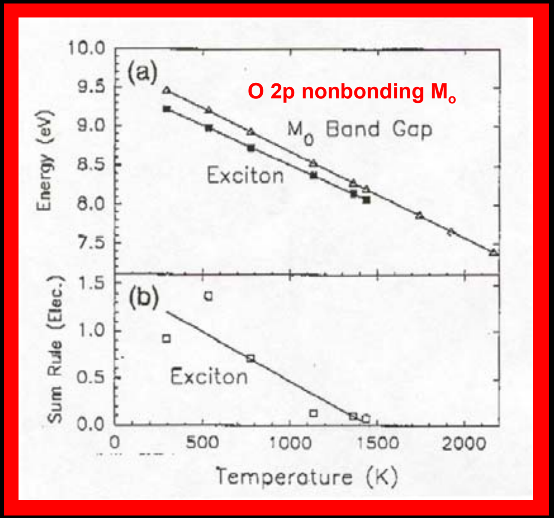
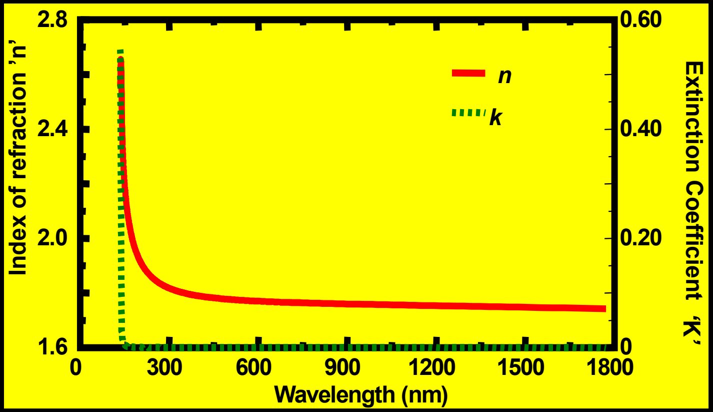




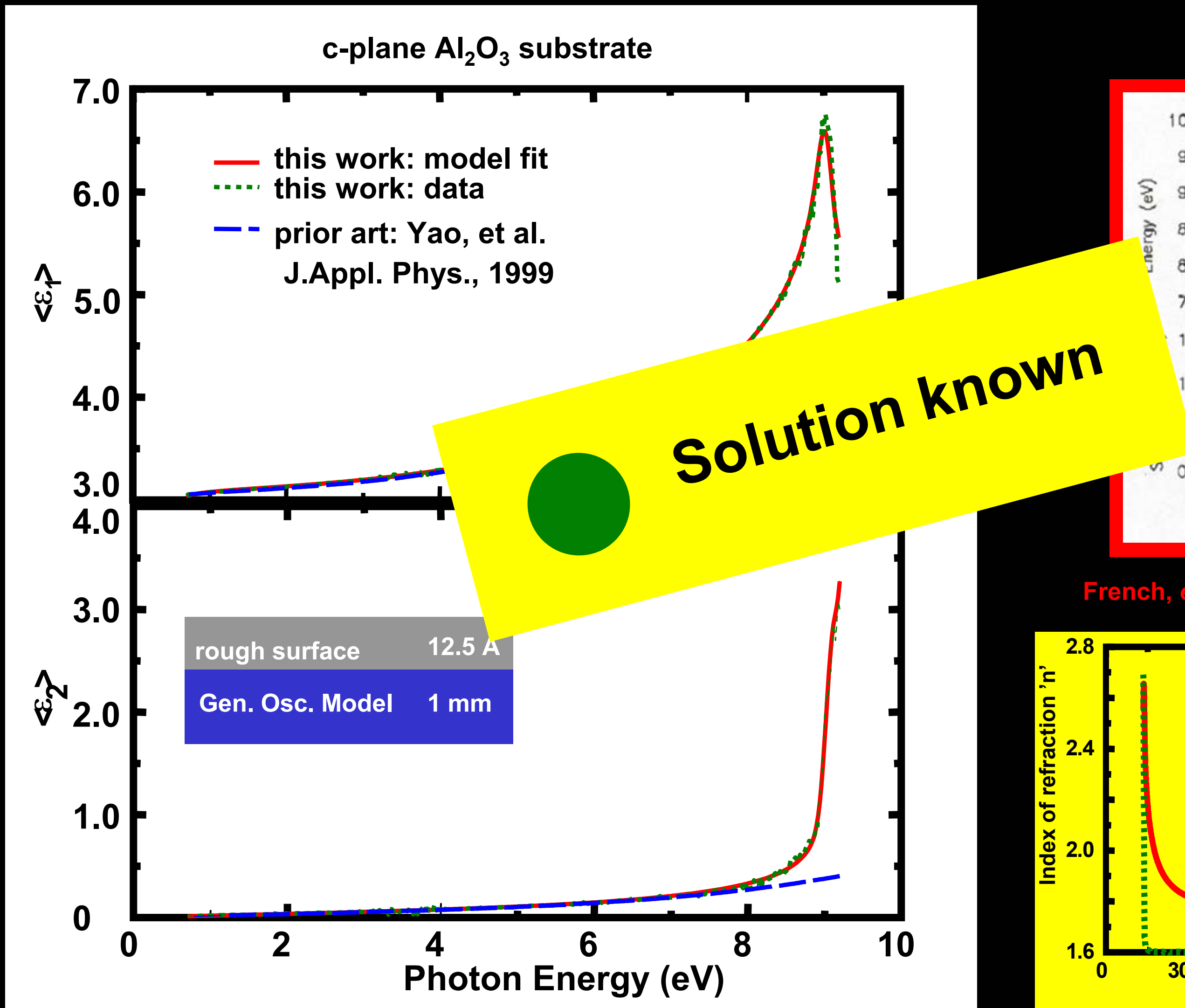
French, *et al.*, J.Am. Ceram. Soc. 77[2] 412 (1994)

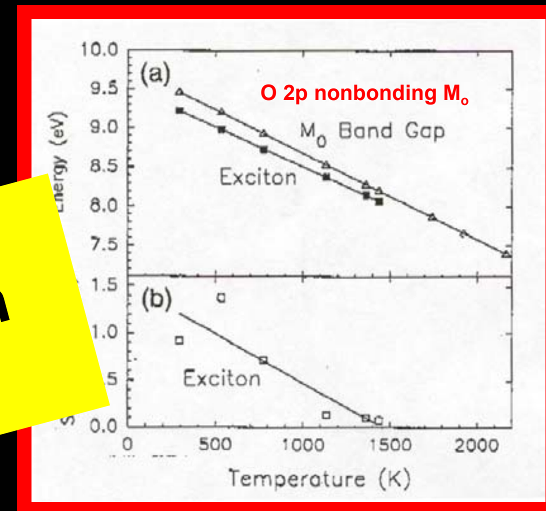


Calculated from our model

4

VUV SE of High k Materials: bulk Al_2O_3





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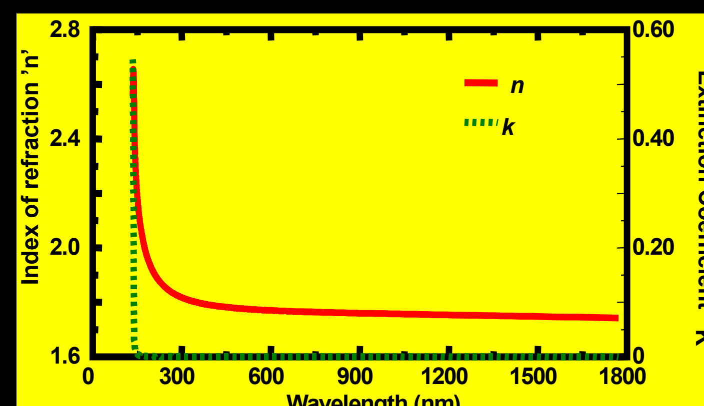

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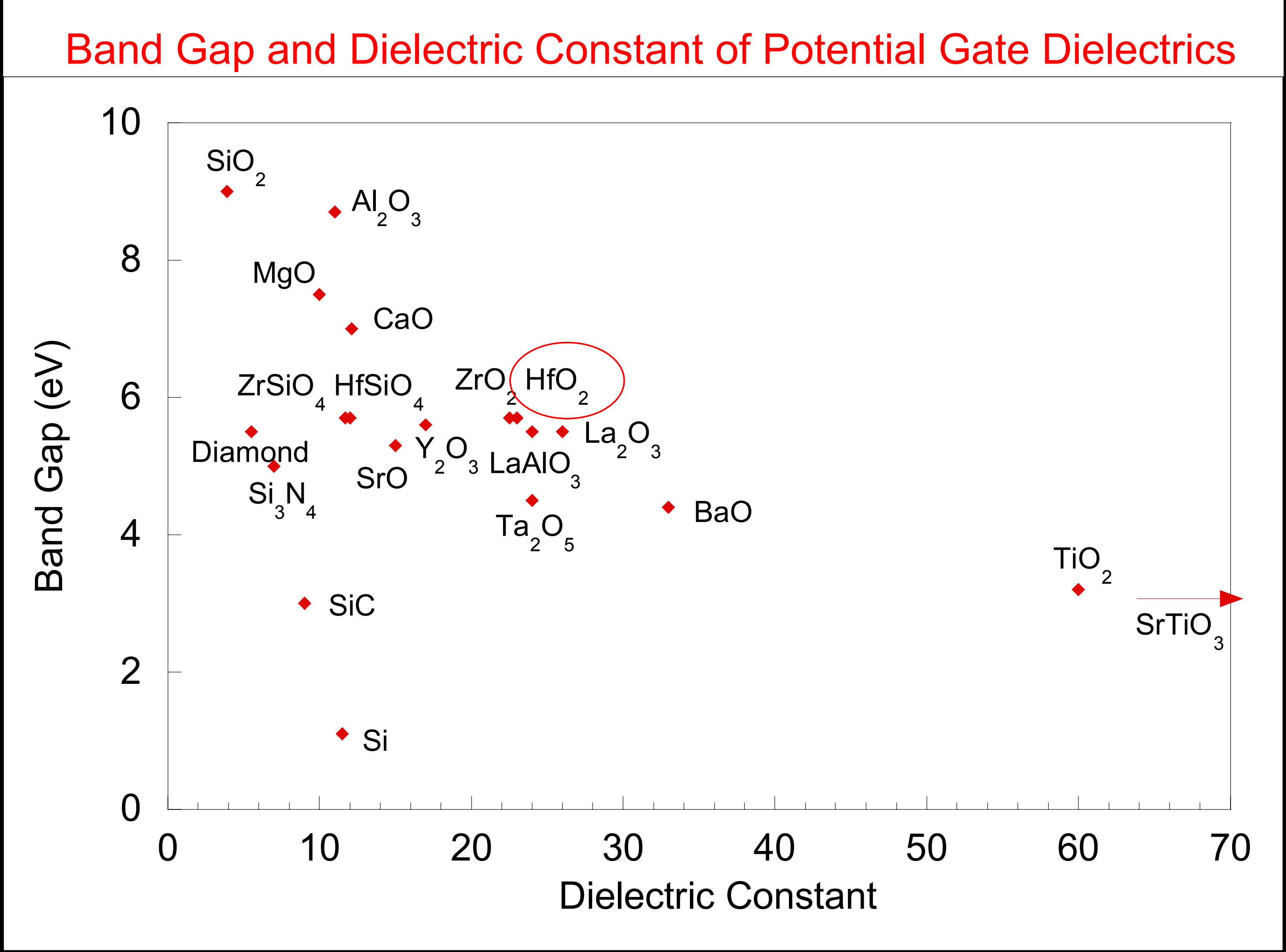
VUV SE of High k Materials



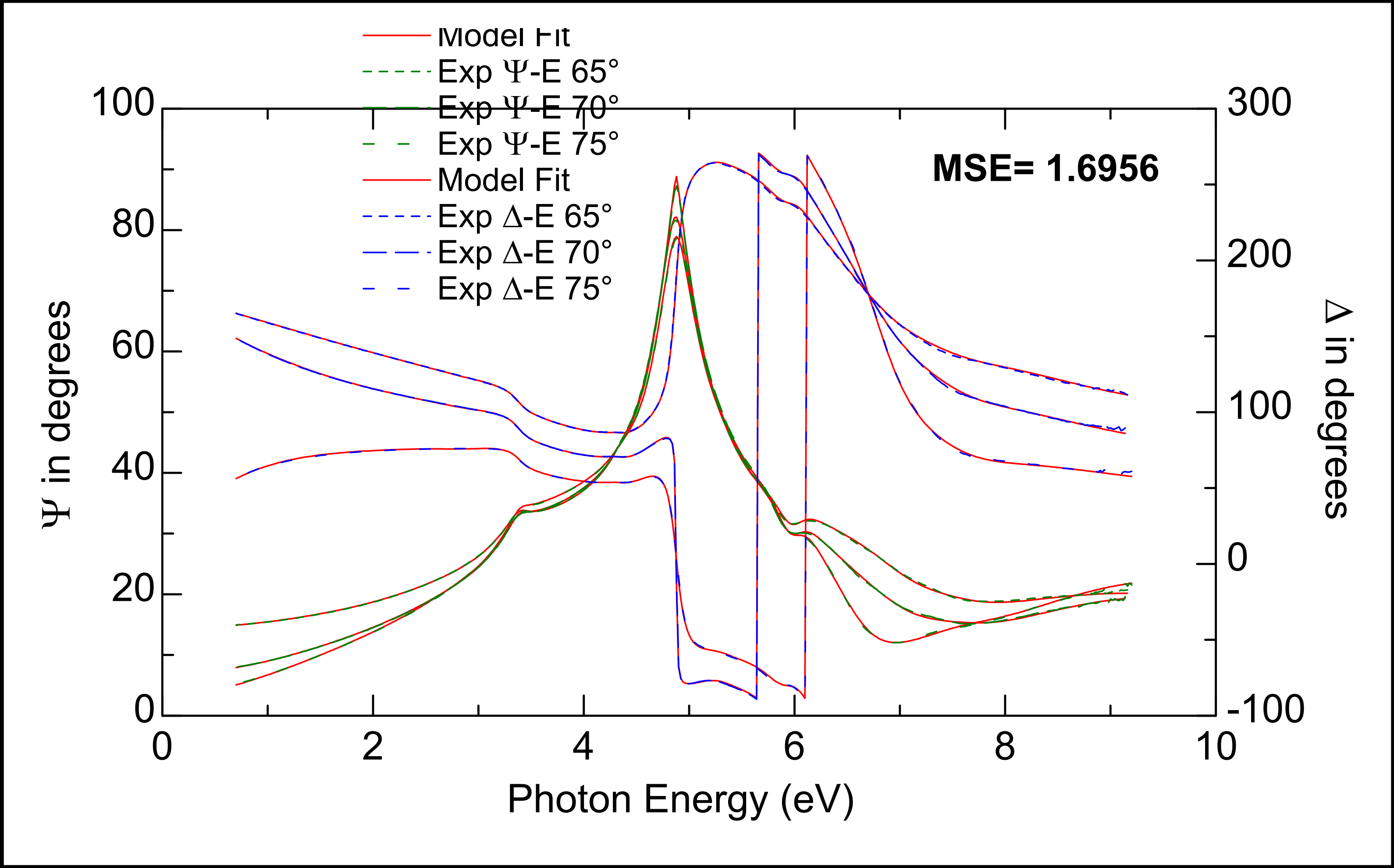
4

VUV SE of High k Materials: 'thin' hafnia films on Si

Surface Roughness	9 Å
Hafnia	207 Å
Interface Layer	2 Å
Si Substrate	1 mm

Phase: monoclinic

Confirmed with XRD analysis, (Rich Gregory, PMCL)



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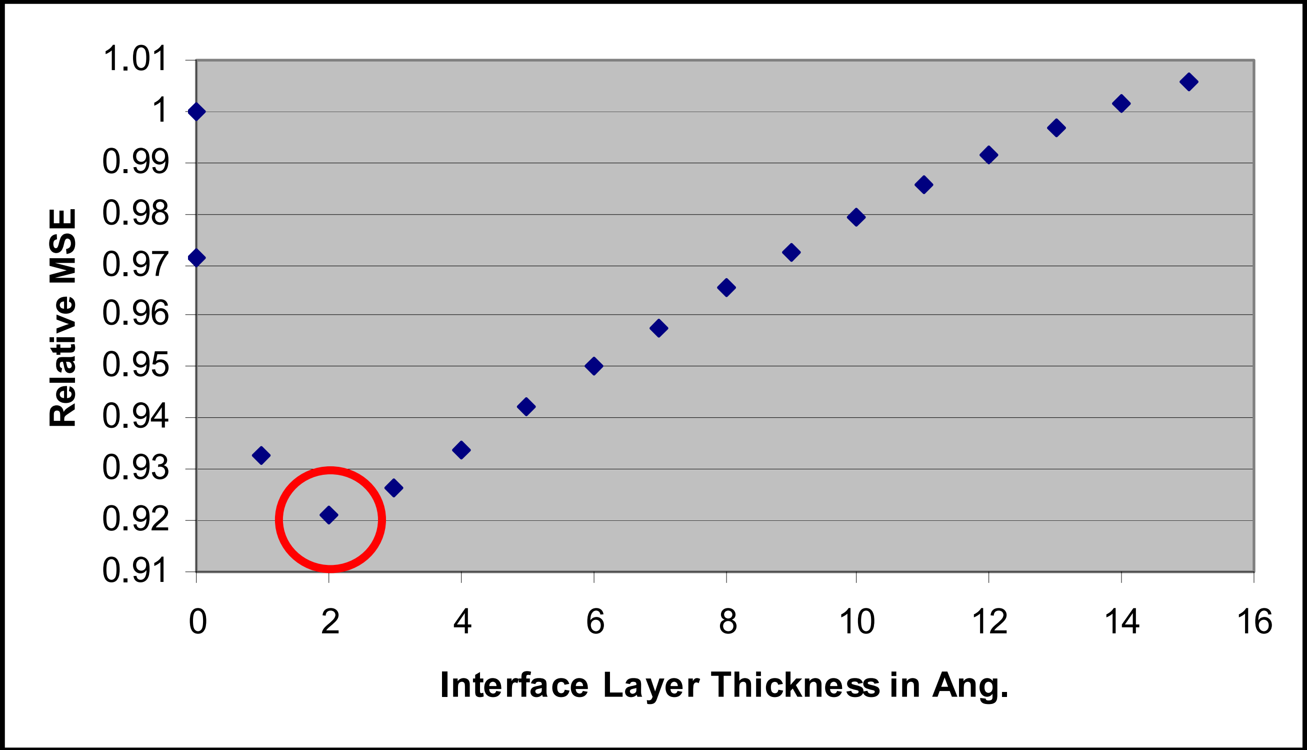
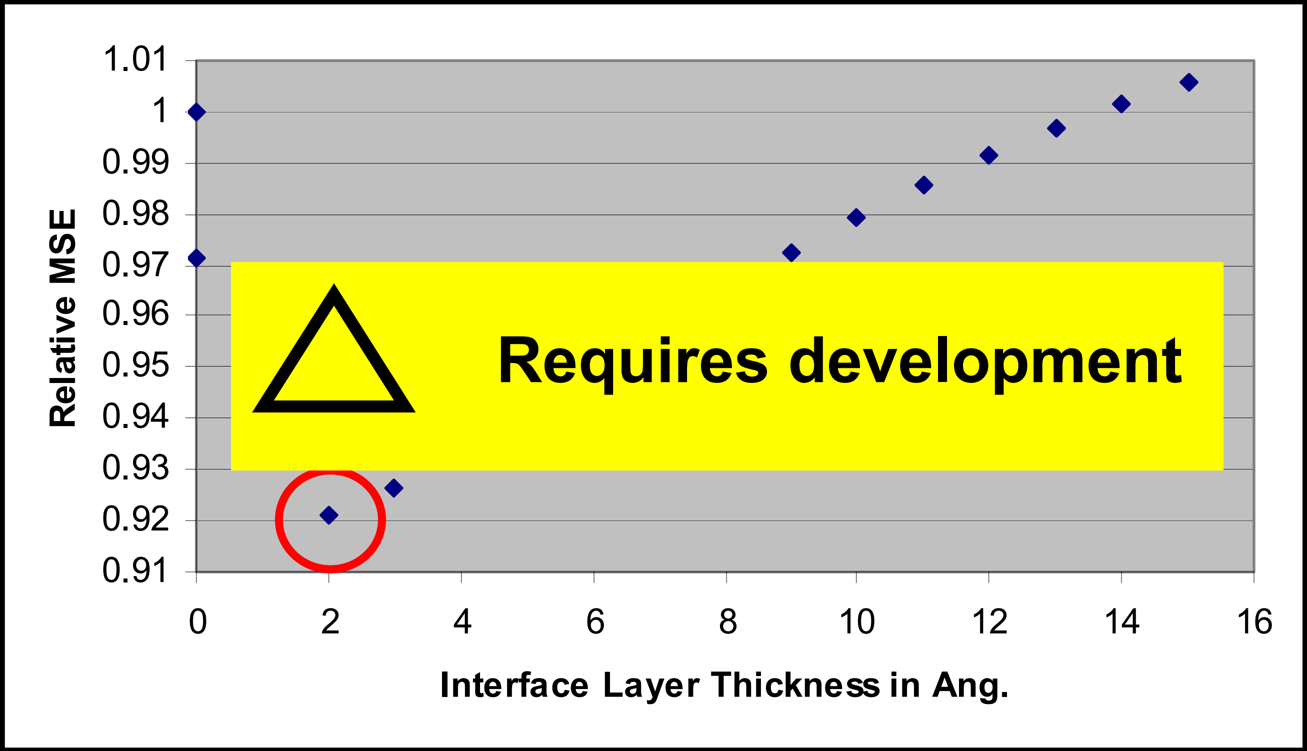


- fix parameter to be evaluated
- allow other parameters to vary
- calculate relative MSE
- repeat for next iteration

Surface Roughness	9 Å
Hafnia	207 Å
Interface Layer	2 Å
Si Substrate	1 mm

4

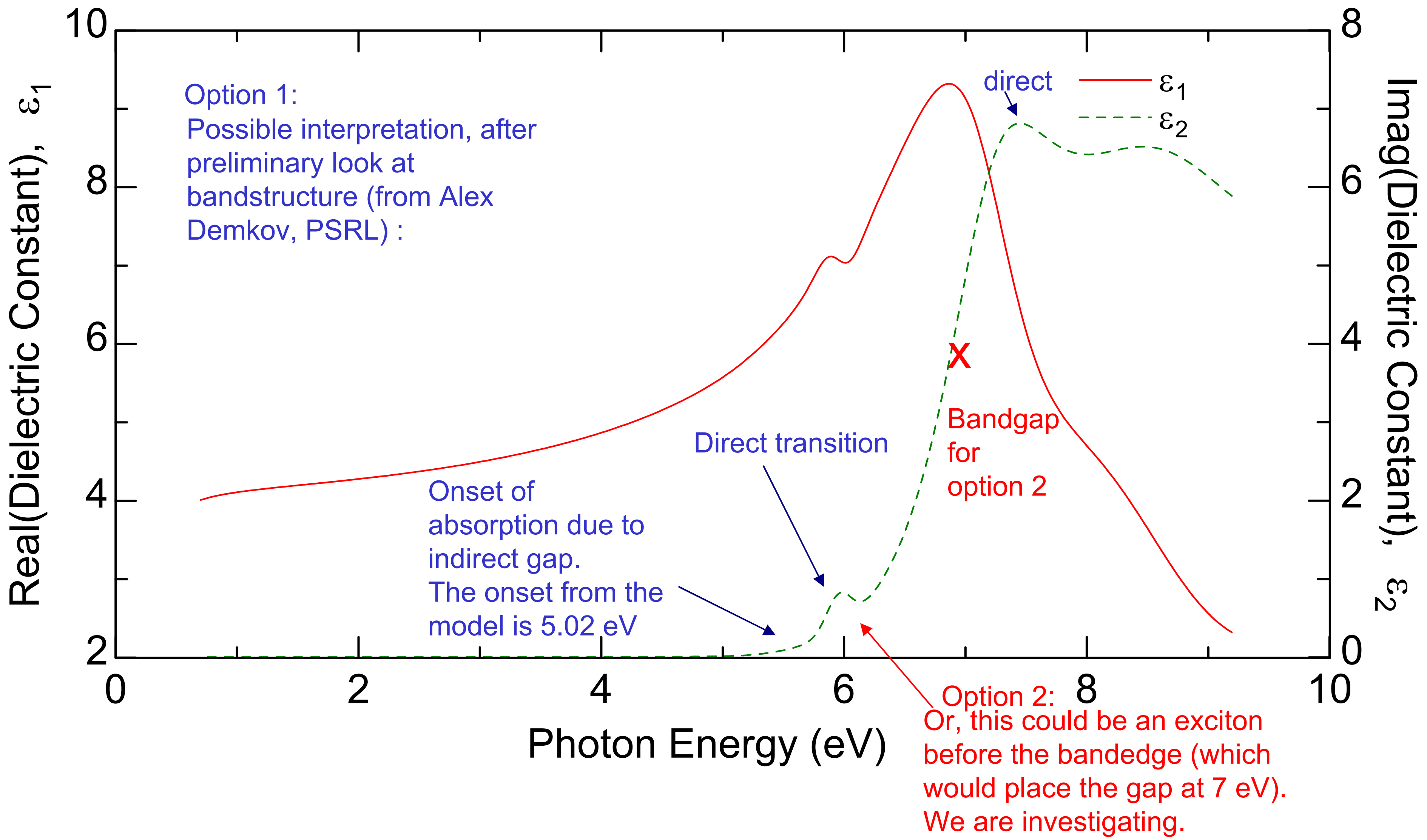
VUV SE of High k Materials: 'thin' hafnia films on Si



- fix parameter to be evaluated
- allow other parameters to vary
- calculate relative MSE
- repeat for next iteration

Surface Roughness	9 Å
Hafnia	206.6 Å
Interface Layer	2 Å
Si Substrate	1 mm

VUV SE of High k Materials: 'thin' hafnia films on Si



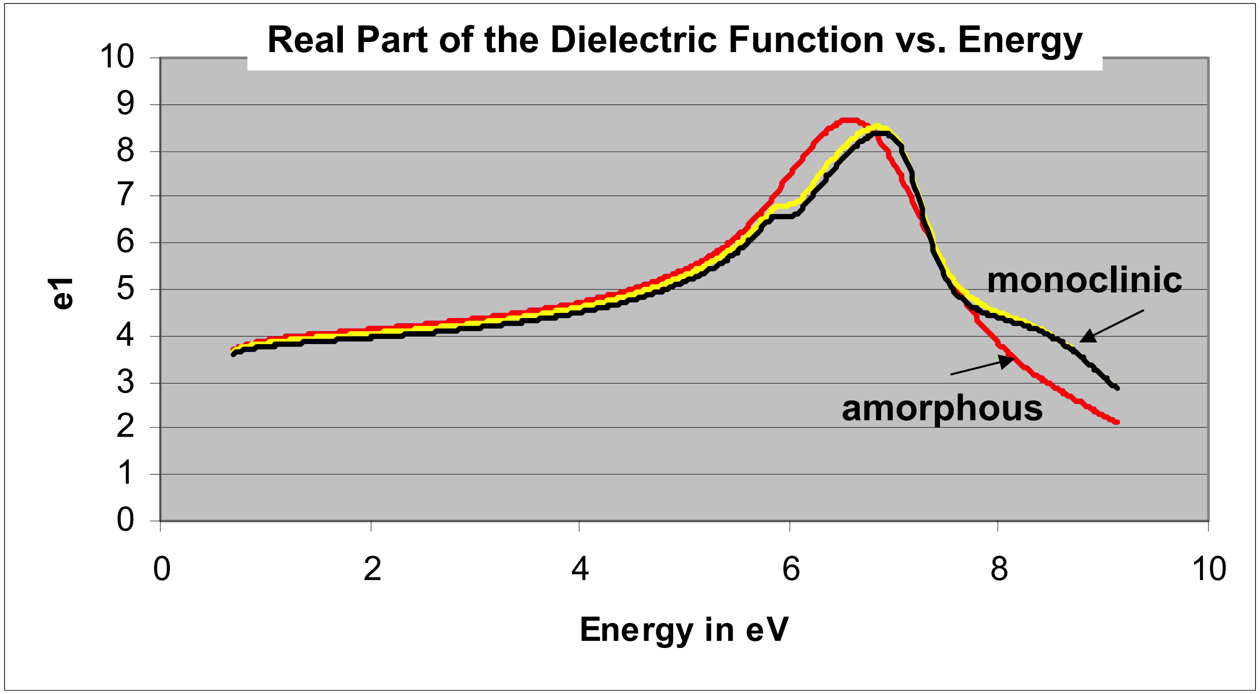
4

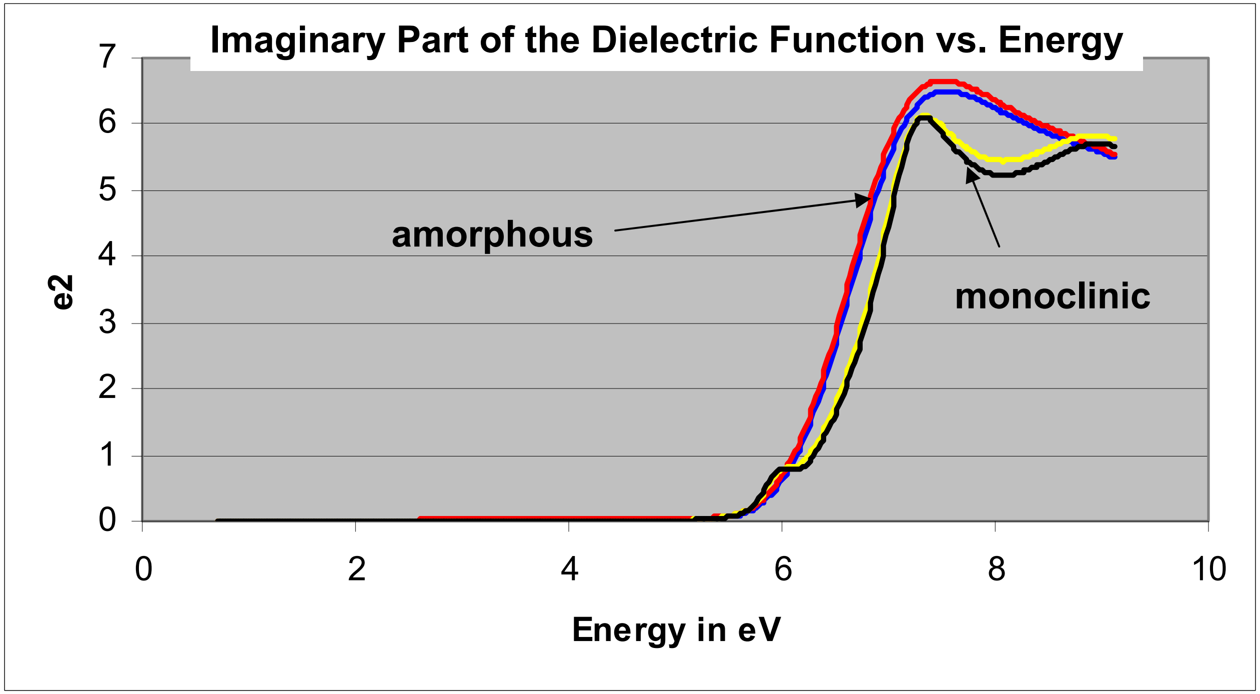
VUV SE of High k Materials: 'thin' hafnia films on Si

T1

No anneal

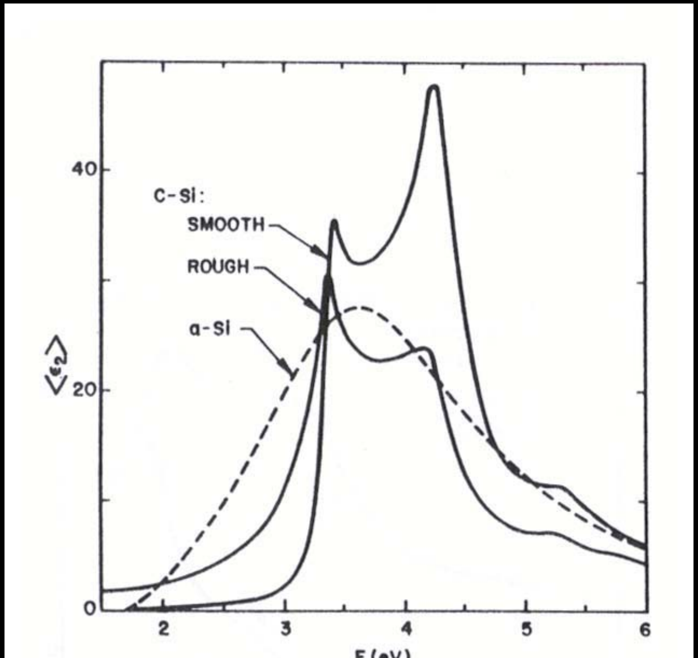
Increasing anneal temp





VUV SE of High k Materials: 'thin' hafnia films on Si

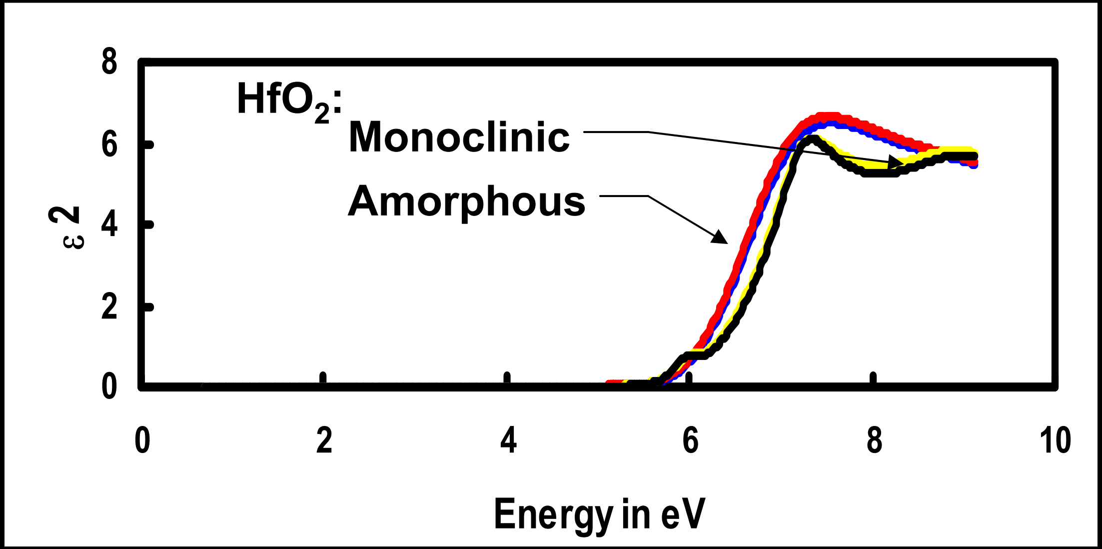
4



D. E. Aspnes, SPIE Vol. 452 (1983), p. 60.

- ellipsometric critical points will broaden & shift in energy with changes in crystal structure
- sensitivity due to dependence of electronic polarizabilities on the presence (or absence) of long-range order on the scale of 10 to 100Å
- $\varepsilon = \varepsilon_1 + i\varepsilon_2$ →→ dipole moment per unit volume

→→ ellipsometry is a nondestructive means of determining densities of amorphous, poly, or microscopically inhomogeneous materials



Direct gap of Si shown, top. Higher lying optical transitions of wide bandgap materials are similar, but at higher energies (VUV).

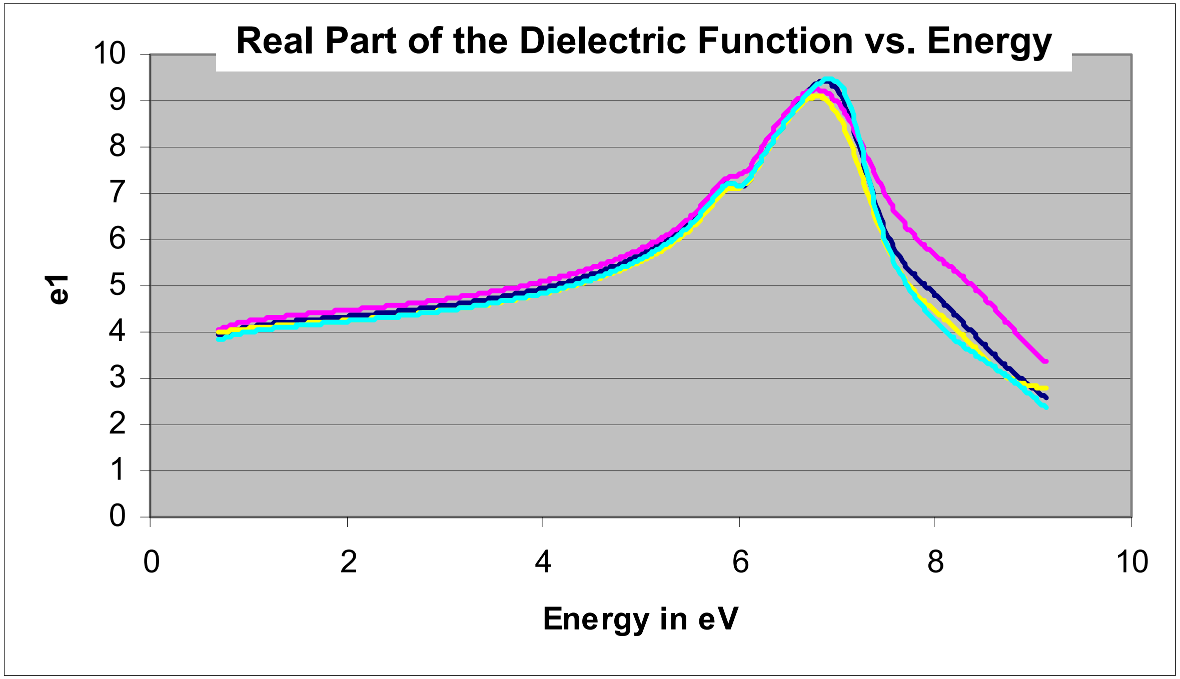
VUV SE of High k Materials: 'thin' hafnia films on Si

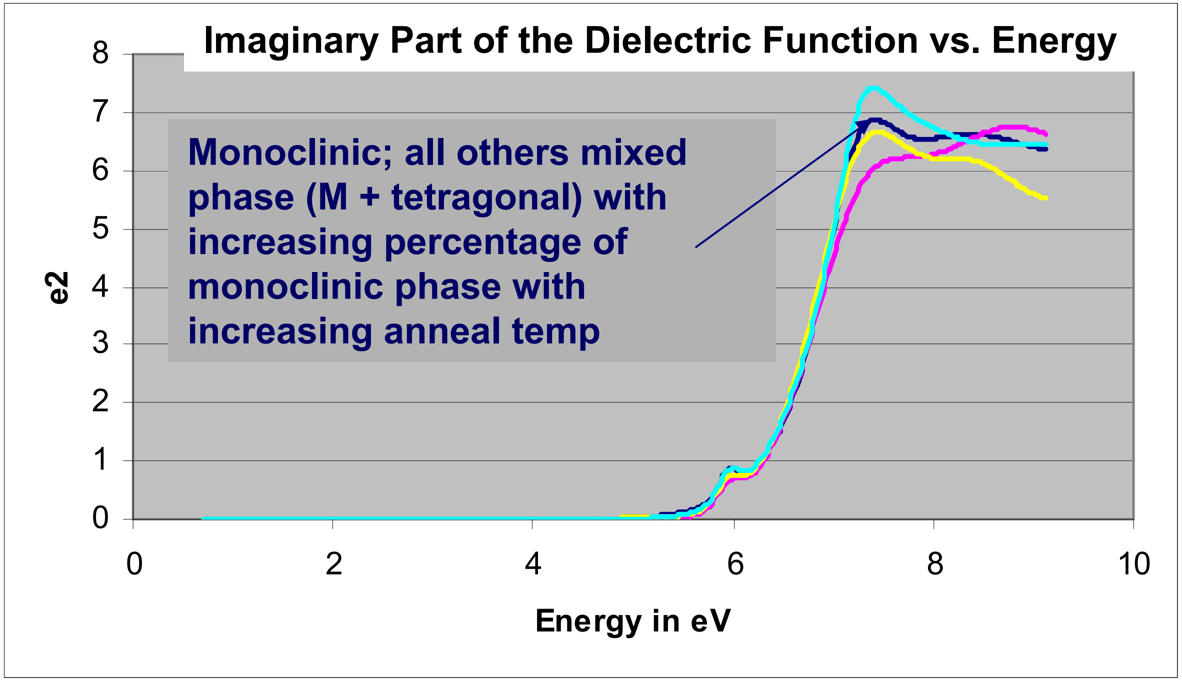
4

T2

No anneal

Increasing anneal temp





4

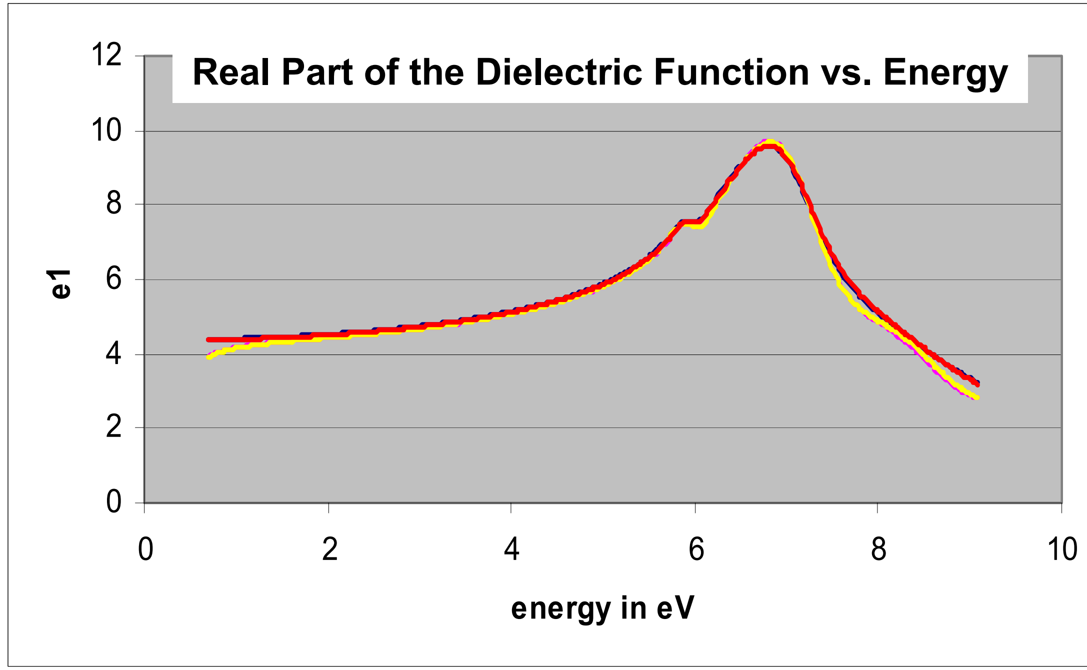
VUV SE of High k Materials: ‘thin’ hafnia films on Si

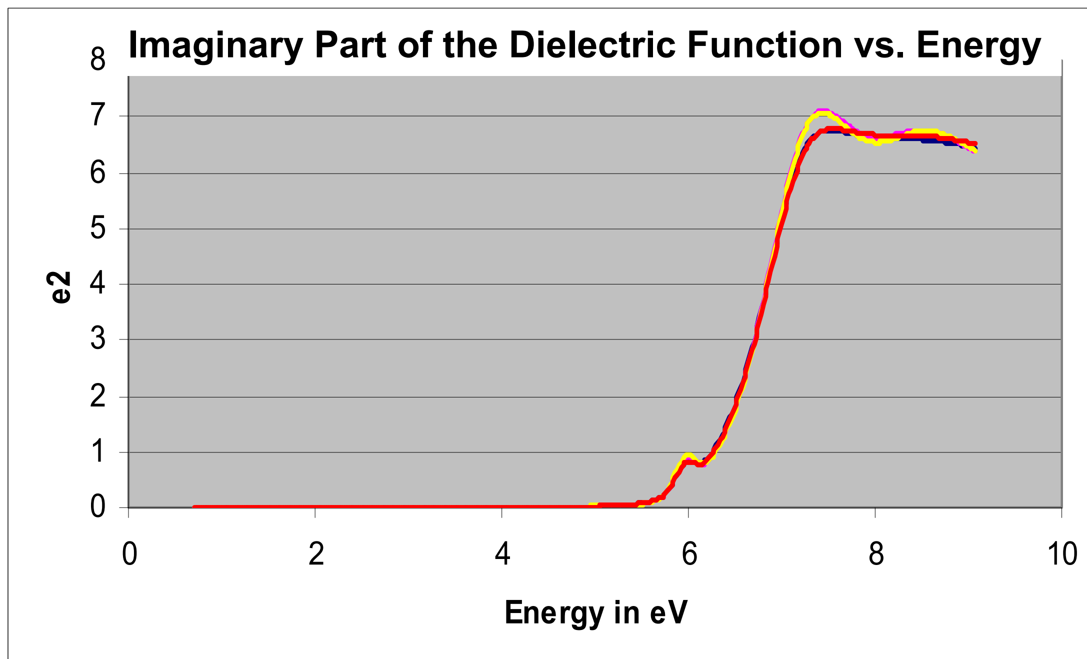
T3

No anneal

Increasing anneal temp

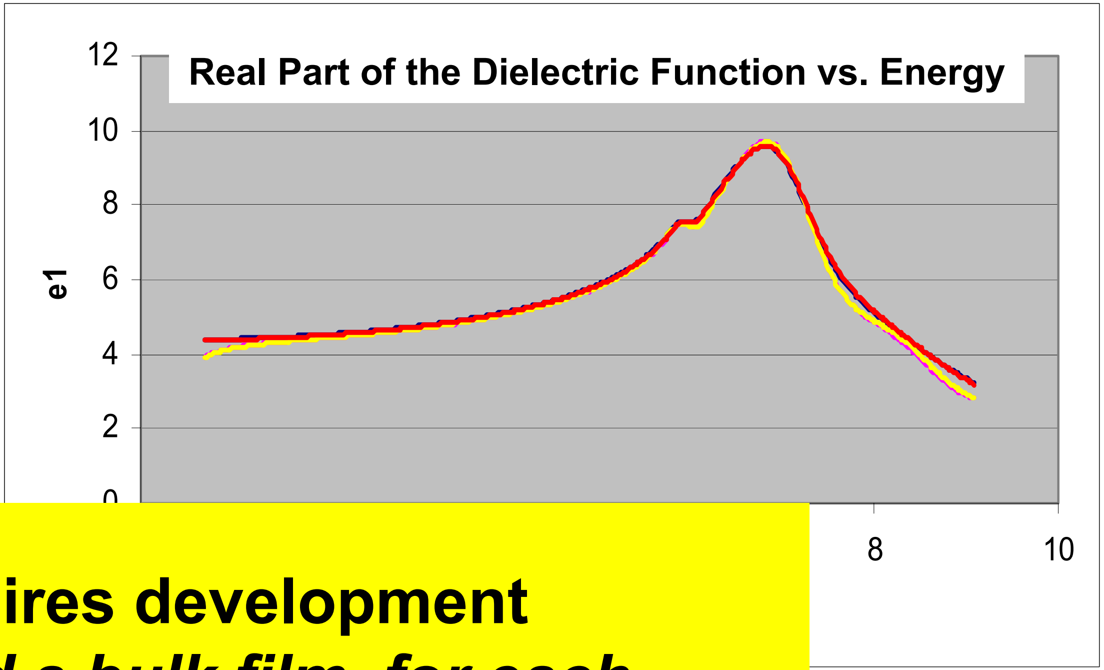
Samples were mixed phase (T +M) as deposited and under all of the annealing conditions, except for the highest anneal temp, which was single phase monoclinic.





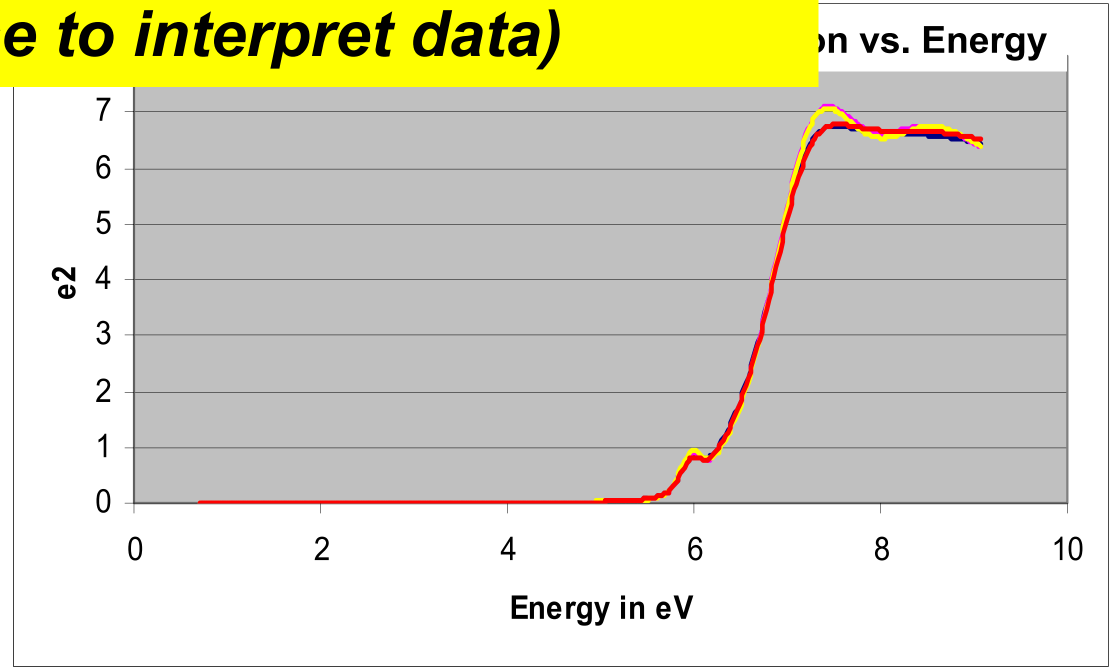
4

VUV SE of High k Materials: 'thin' hafnia films on Si



T3

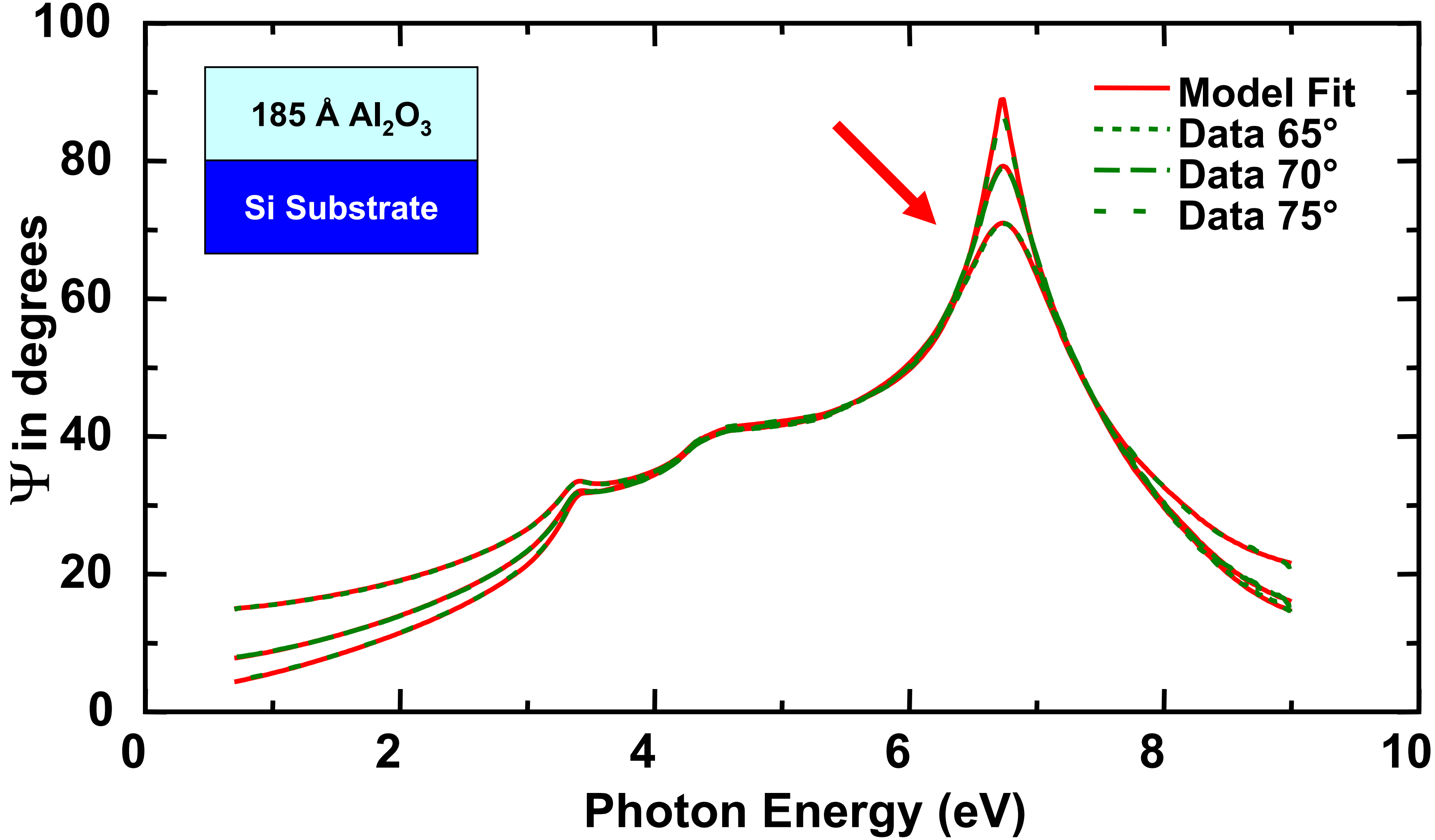
N



Requires development
(need a bulk film, for each phase to interpret data)

Samples were mixed phase (T +M) as deposited and under all of the annealing conditions, except for the highest anneal temp, which was single phase monoclinic.

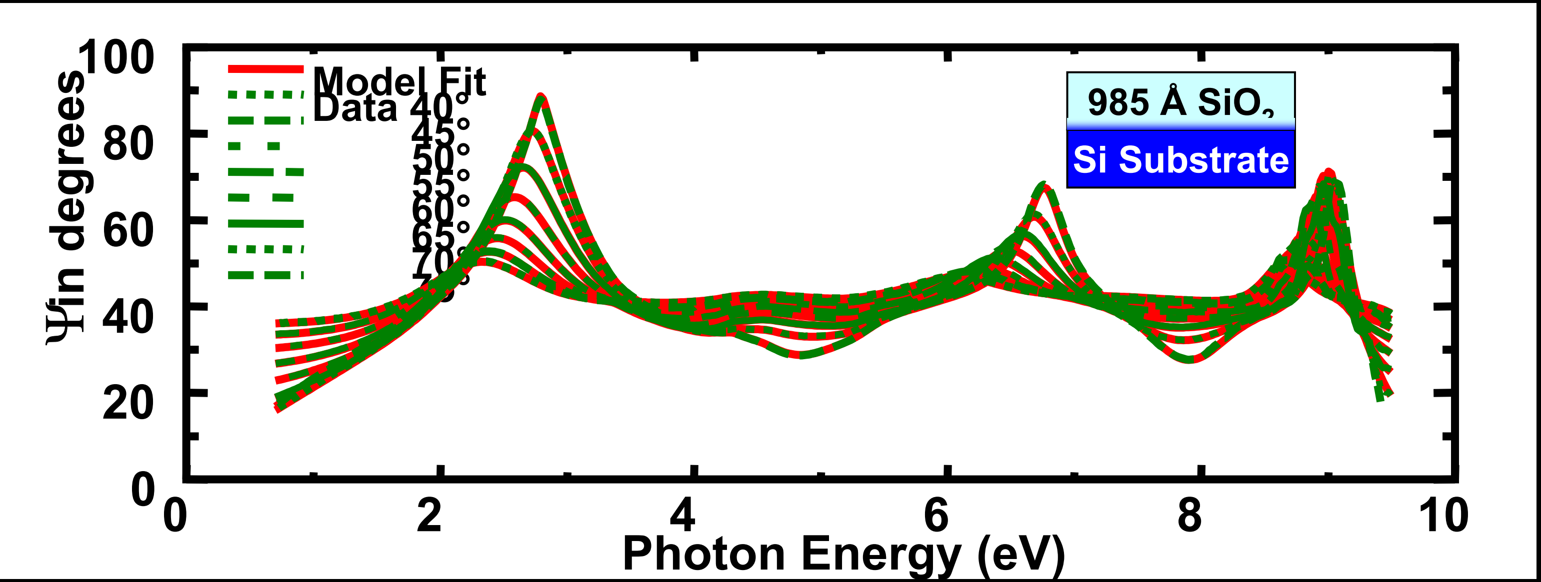
4 VUV SE of High k Materials: sensitivity to thickness



4 VUV SE of High k Materials: sensitivity to thickness

1) Why do we have increased sensitivity for measuring thin films in the VUV?

2) Ellipsometry gives optical thickness nd. How do we separately determine n and d?



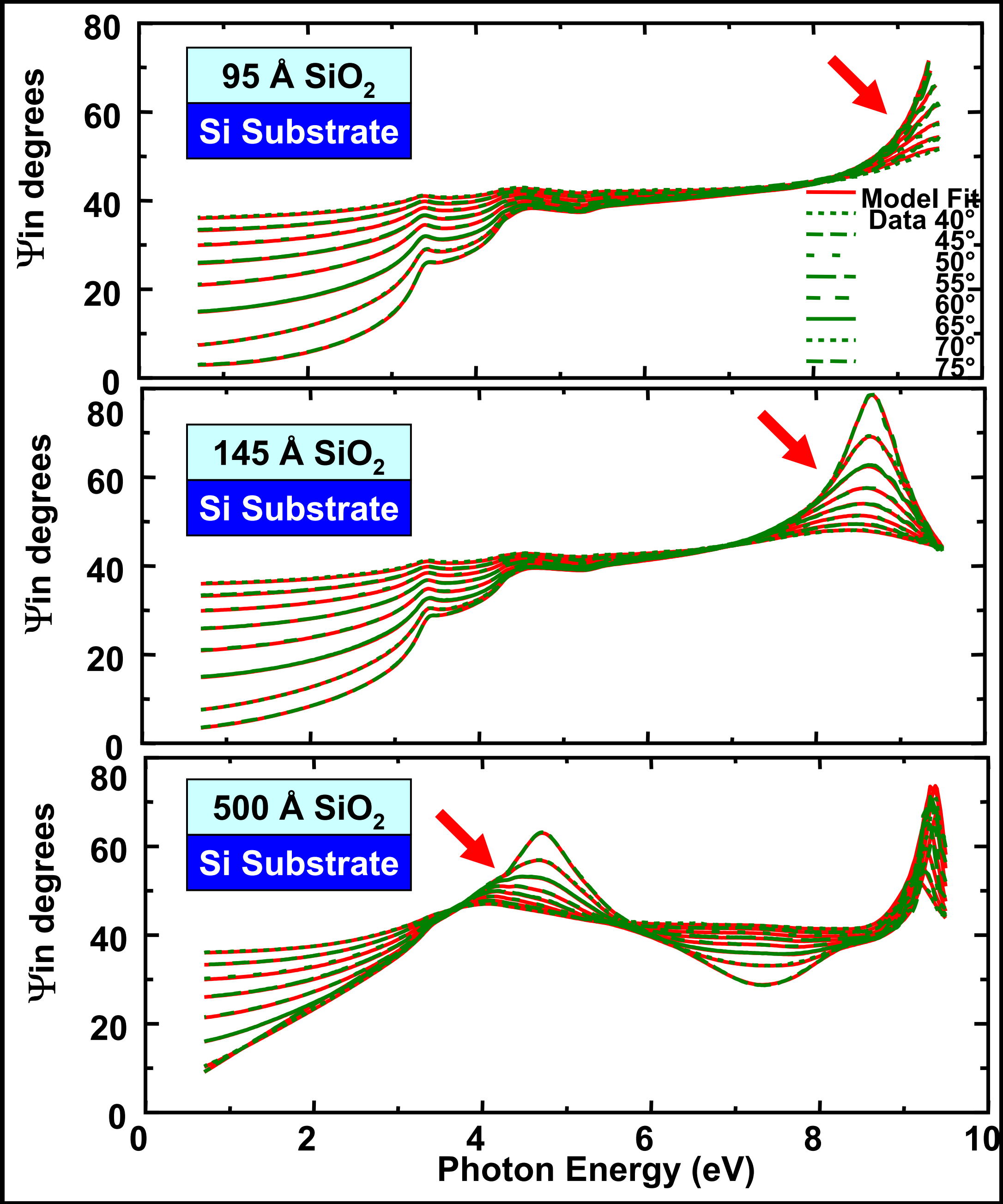
for 1 interference cycle:

$$2\pi = \Delta\theta = \frac{4\pi nd}{hc}\Delta E$$

$$\frac{\lambda^2}{\Delta\lambda} = -2nd$$

Small values of d will occur for small values of λ

4 VUV SE of High k Materials: sensitivity to thickness



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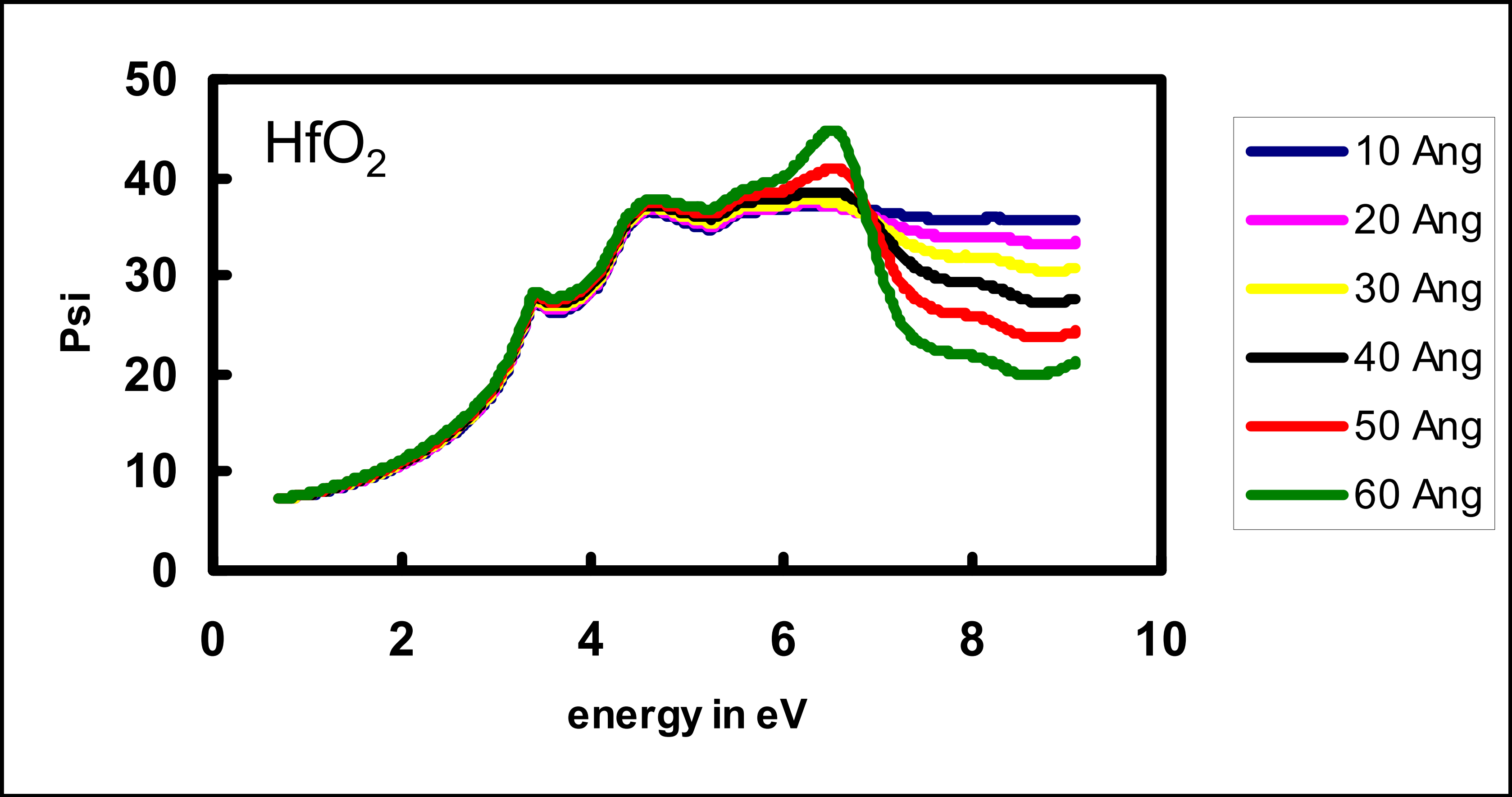
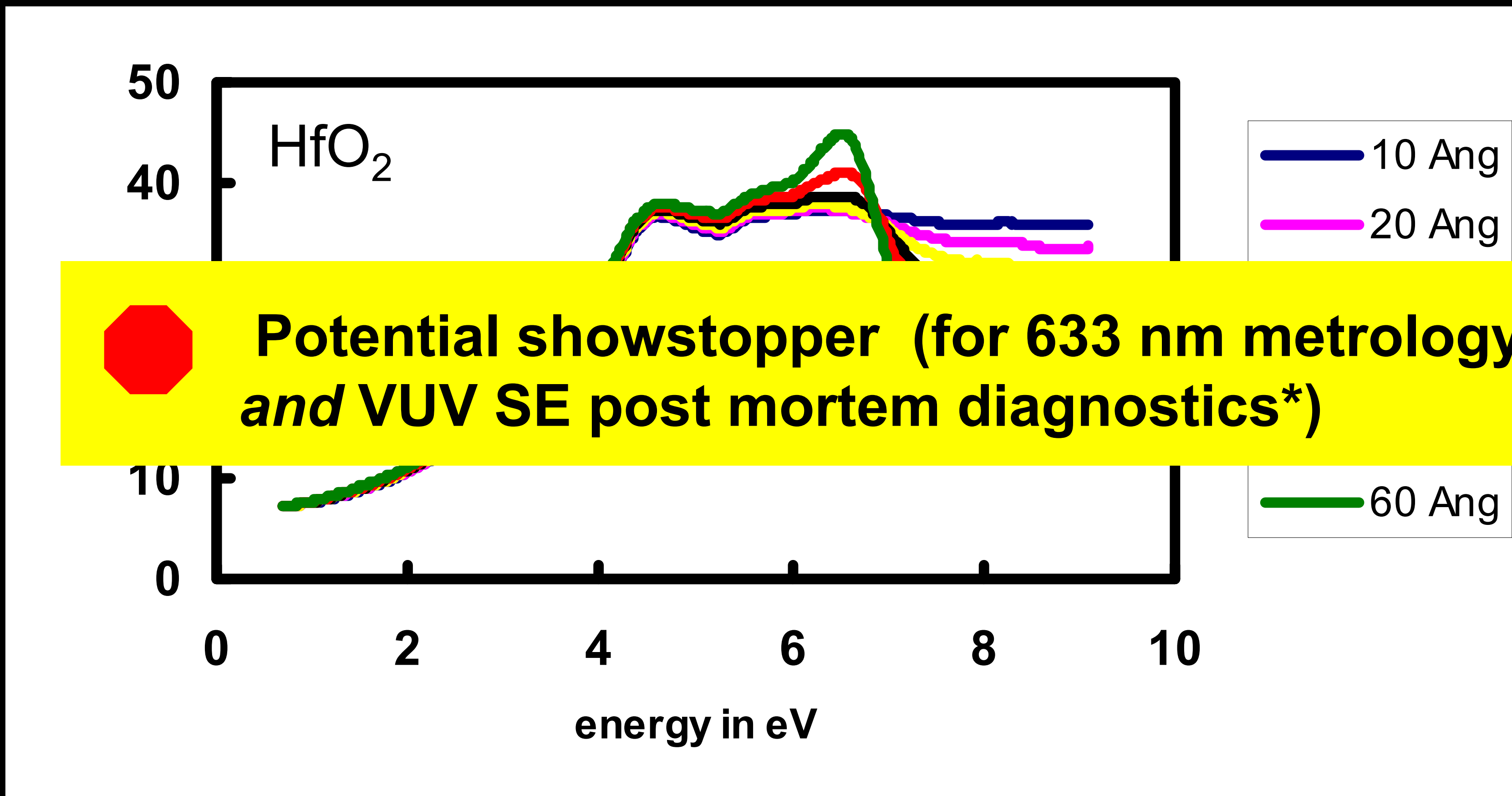
VUV SE of High k Materials: sensitivity to thickness



Projected gate thickness 40-50Å

4 VUV SE of High k Materials: sensitivity to thickness

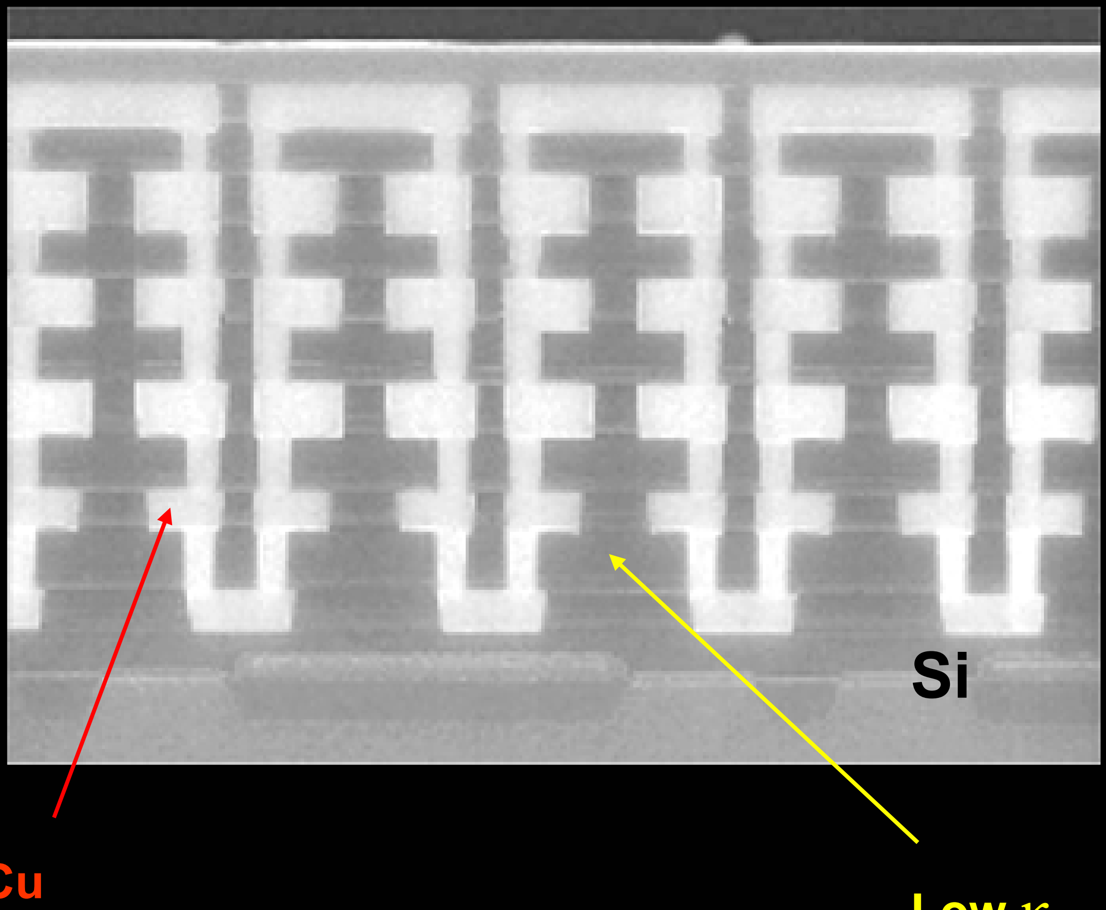


Potential showstopper (for 633 nm metrology *and* VUV SE post mortem diagnostics*)

**Aspnes group is working on a solution*

5

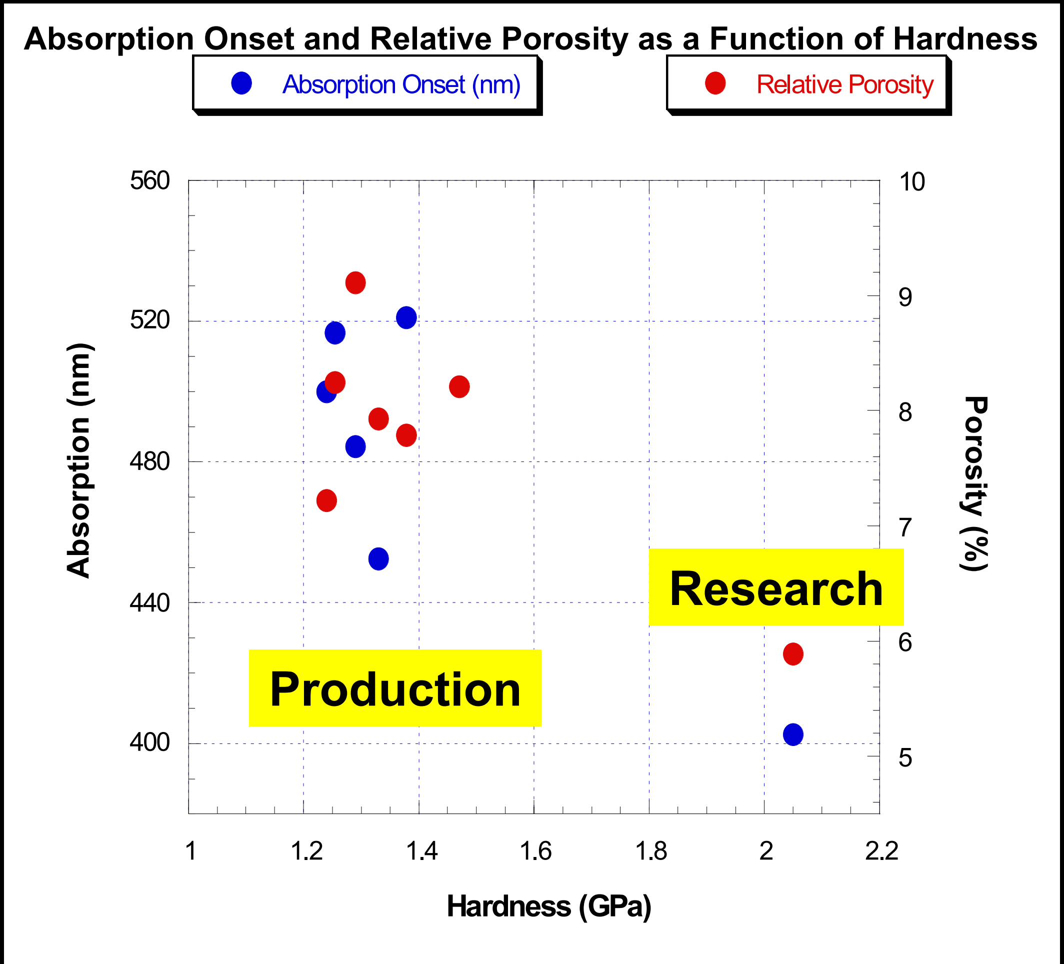
Low k Primer



Thicknesses are greater, other problems exist

5

Low k Primer

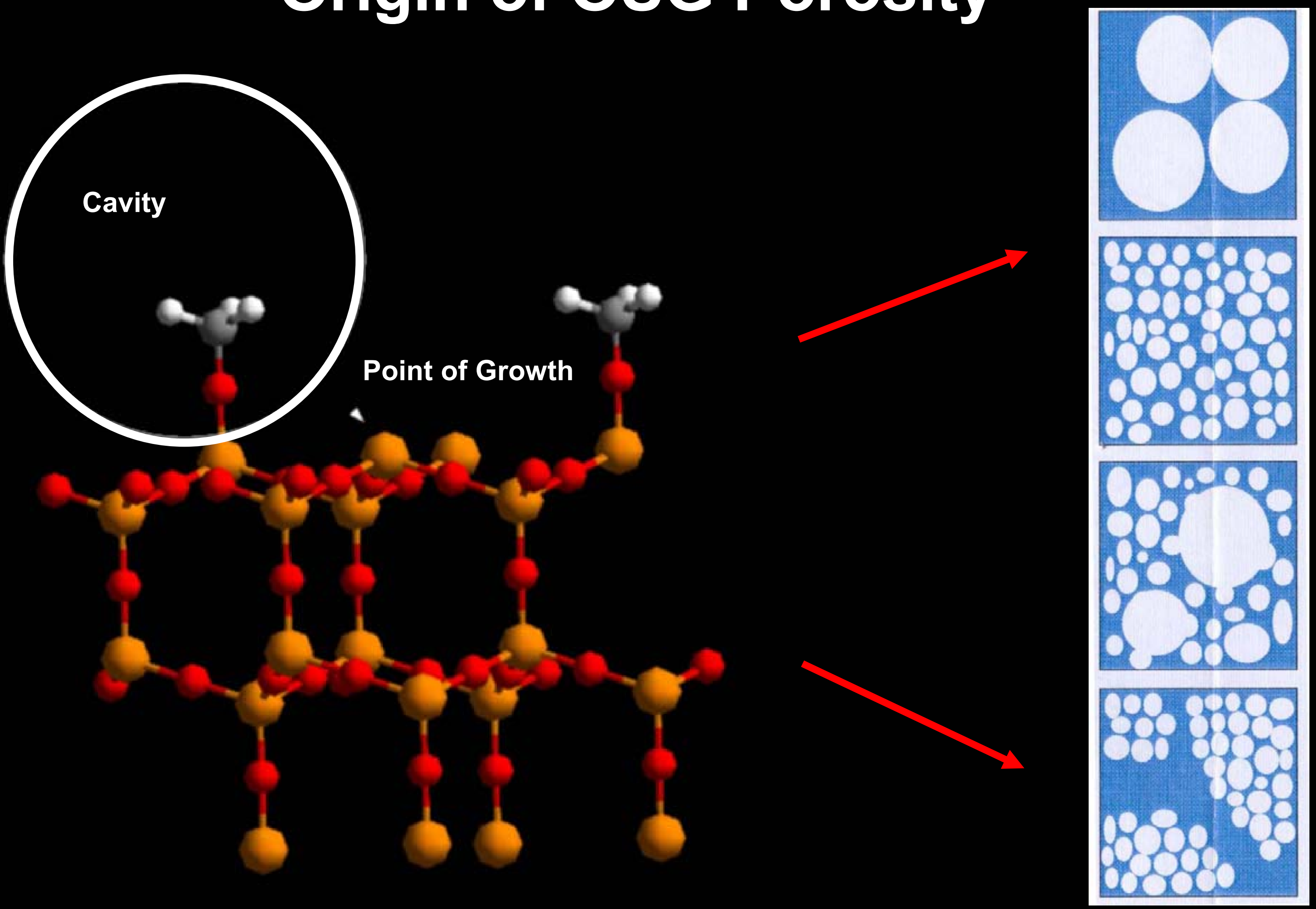


- Institution to institution
- Reactor to reactor
- For slight adjustments to process parameters…

nominally similar OSGs can be dramatically different

Why?

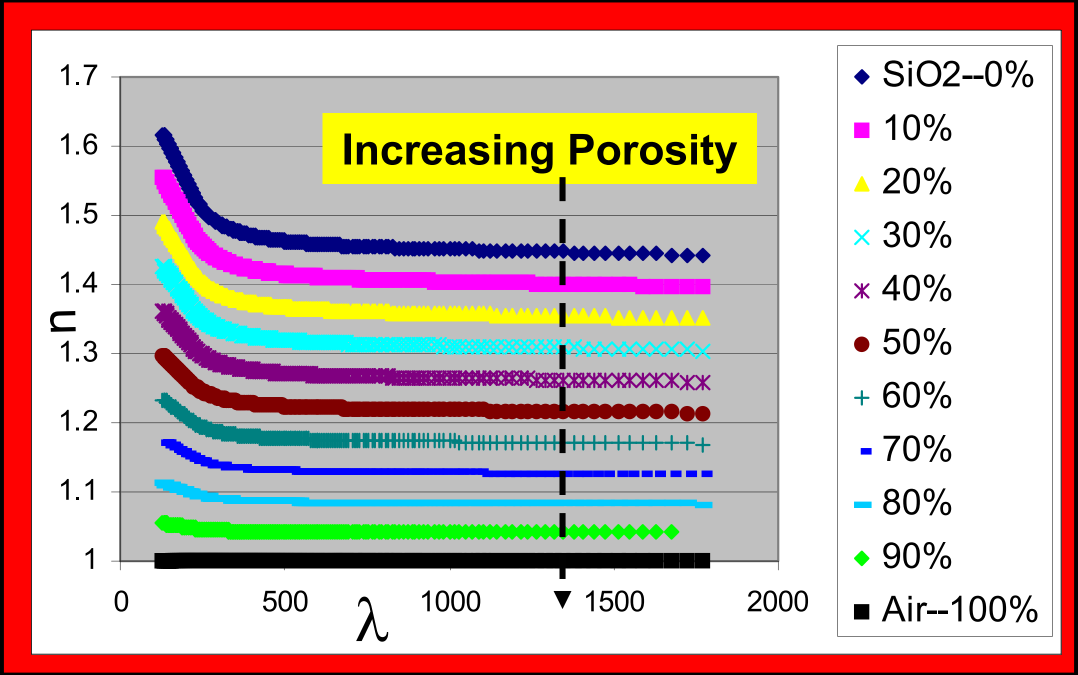
Origin of OSG Porosity



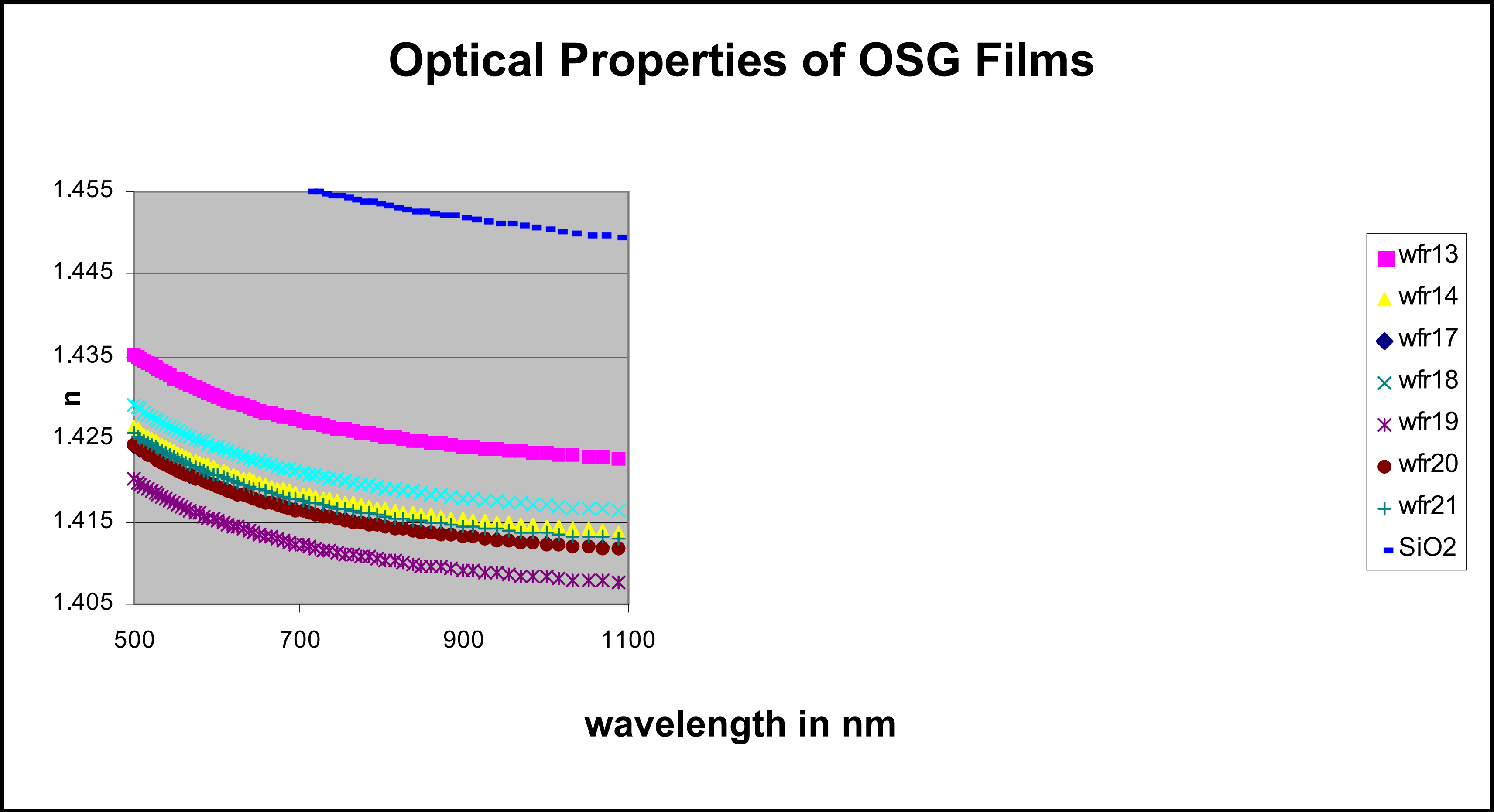
5 VUV SE of Low k Materials: sensitivity to density

Recall that SE is sensitive to long range order on the scale of 10 to 100Å…

EMA Calculation of SiO_2 *n* with increasing void fraction

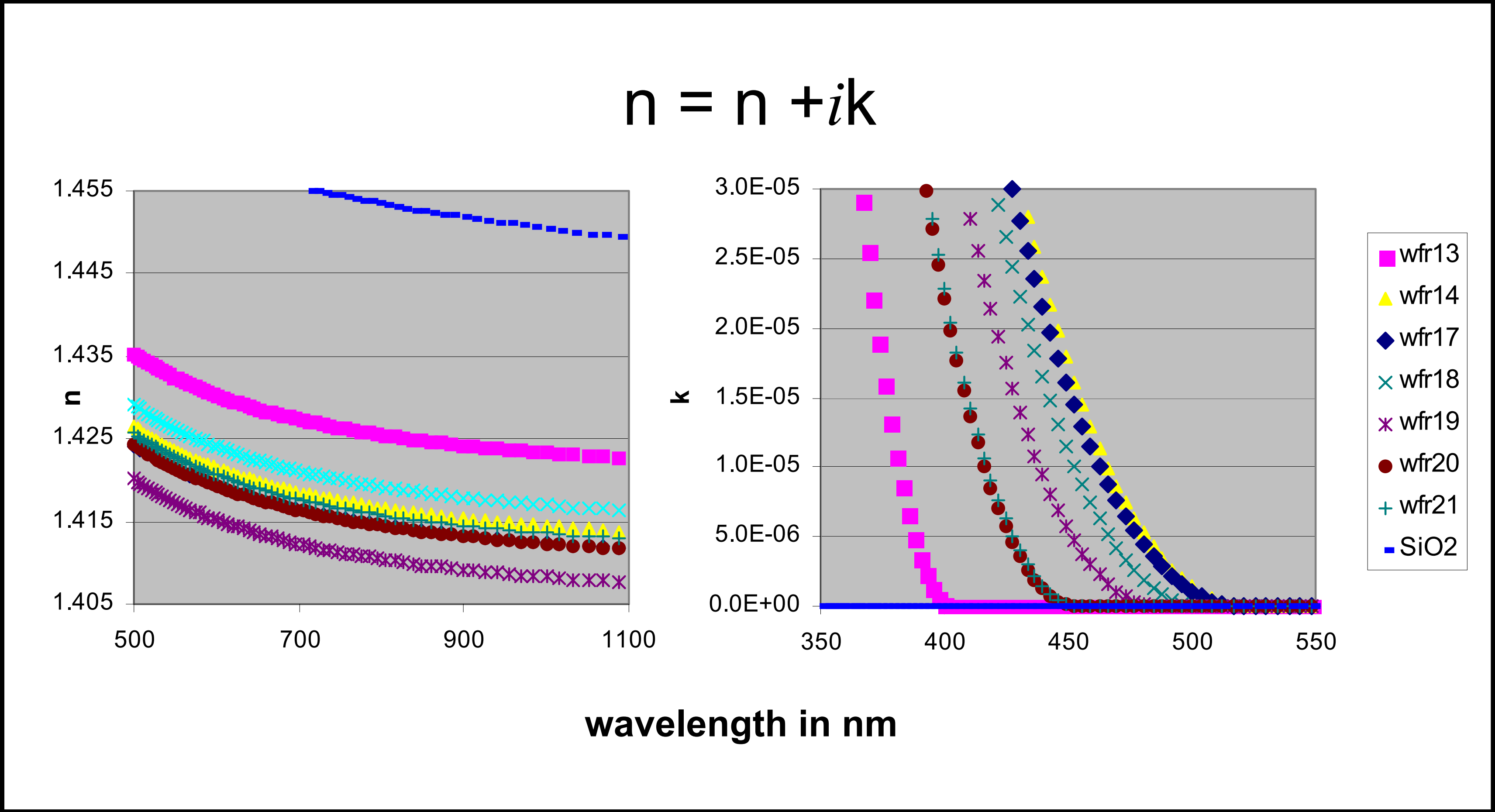


VUV SE of Low k Materials: sensitivity to density



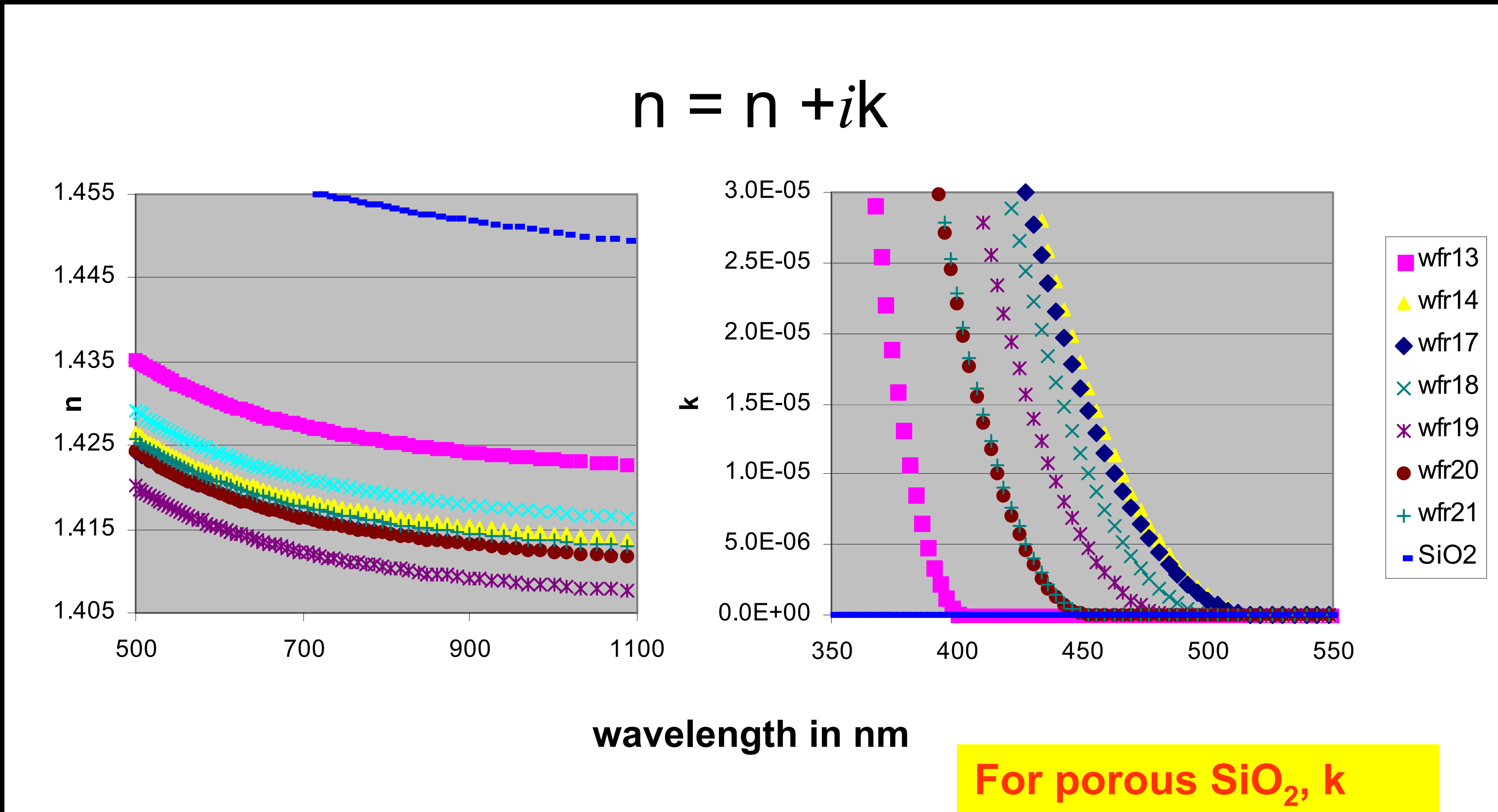
5 VUV SE of Low k Materials: sensitivity to density

Optical Properties of OSG Films



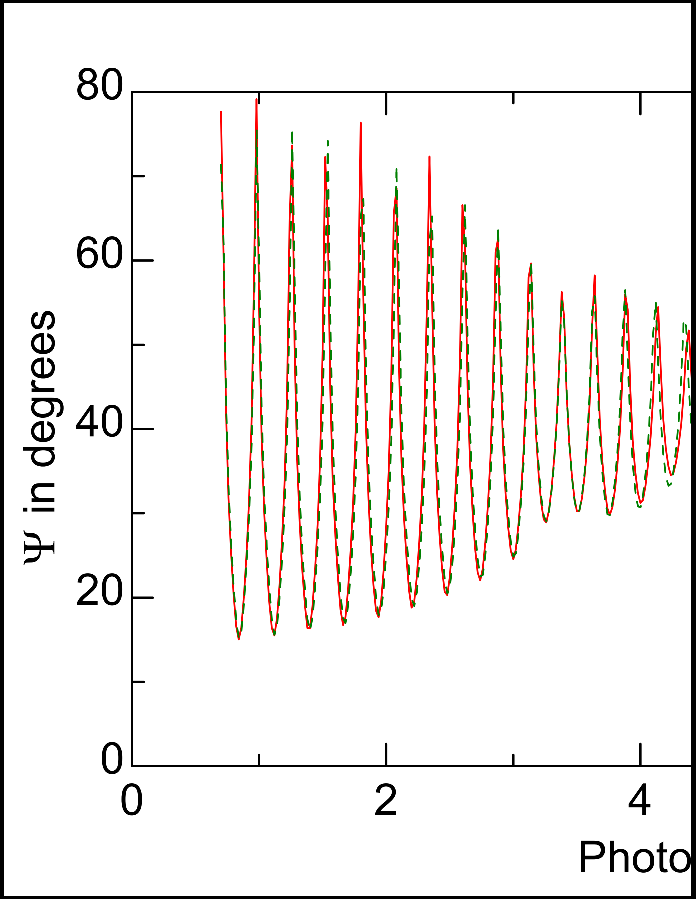
5 VUV SE of Low k Materials: sensitivity to density

Optical Properties of OSG Films

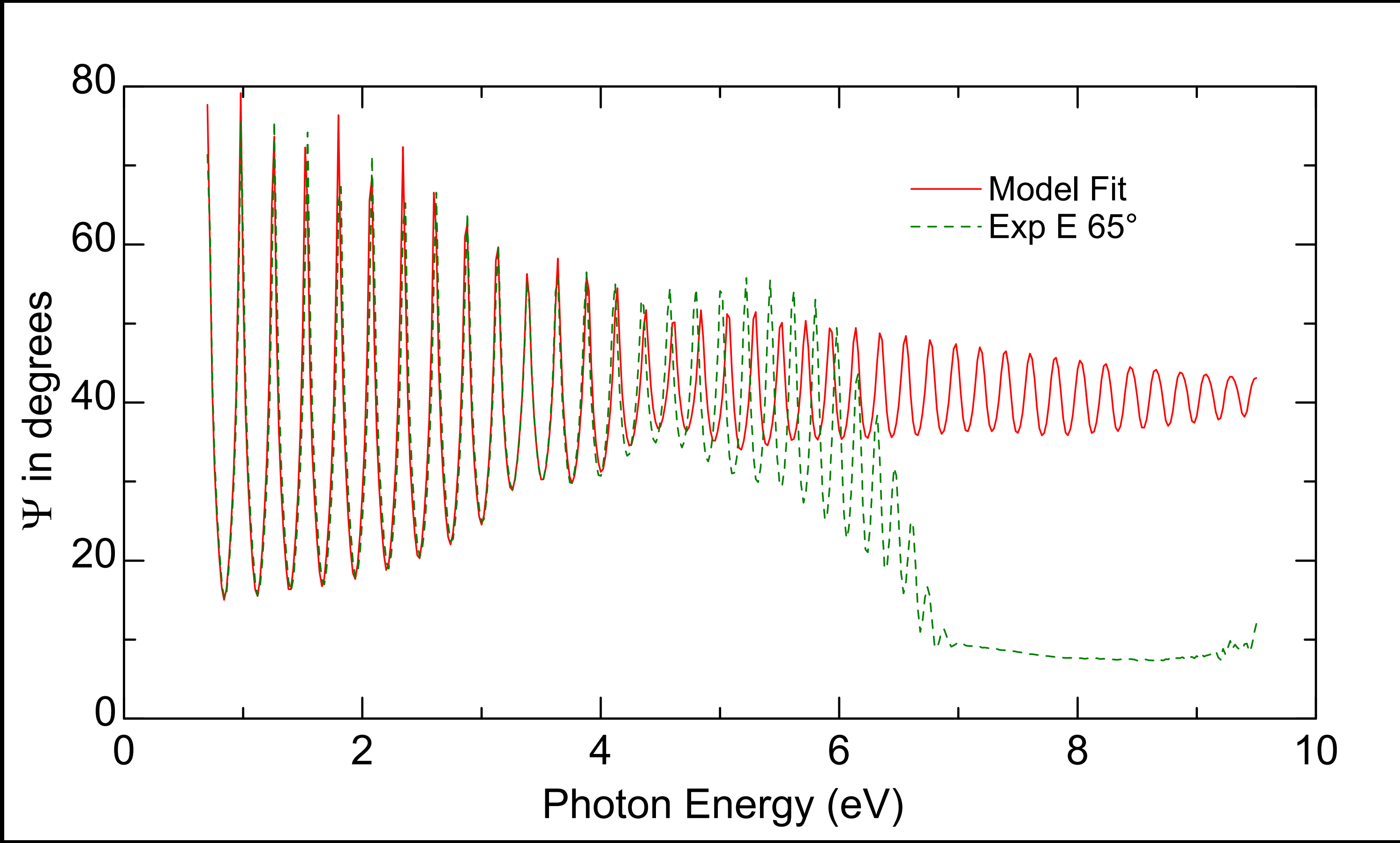


For porous SiO_2, k should be 0 for whole spectral range….what is going on?

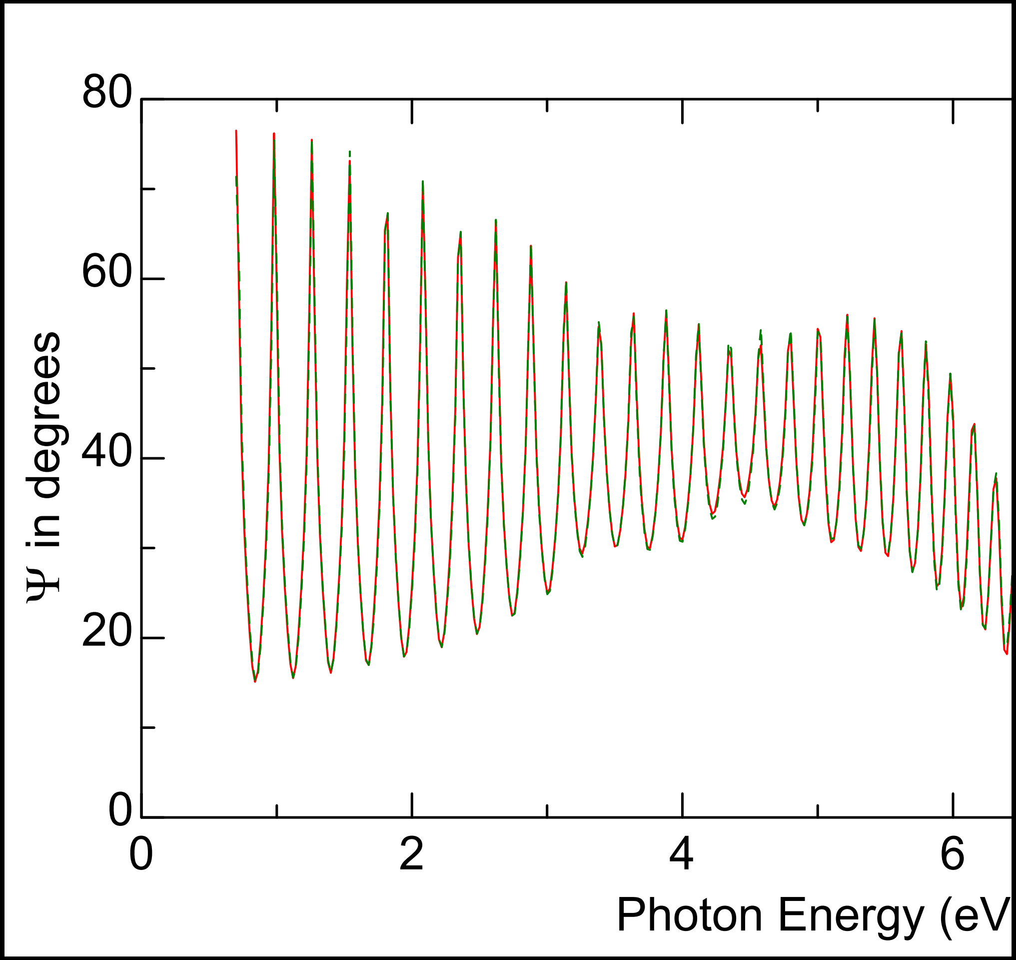
Why can't OSG be treated like an oxide?..............................



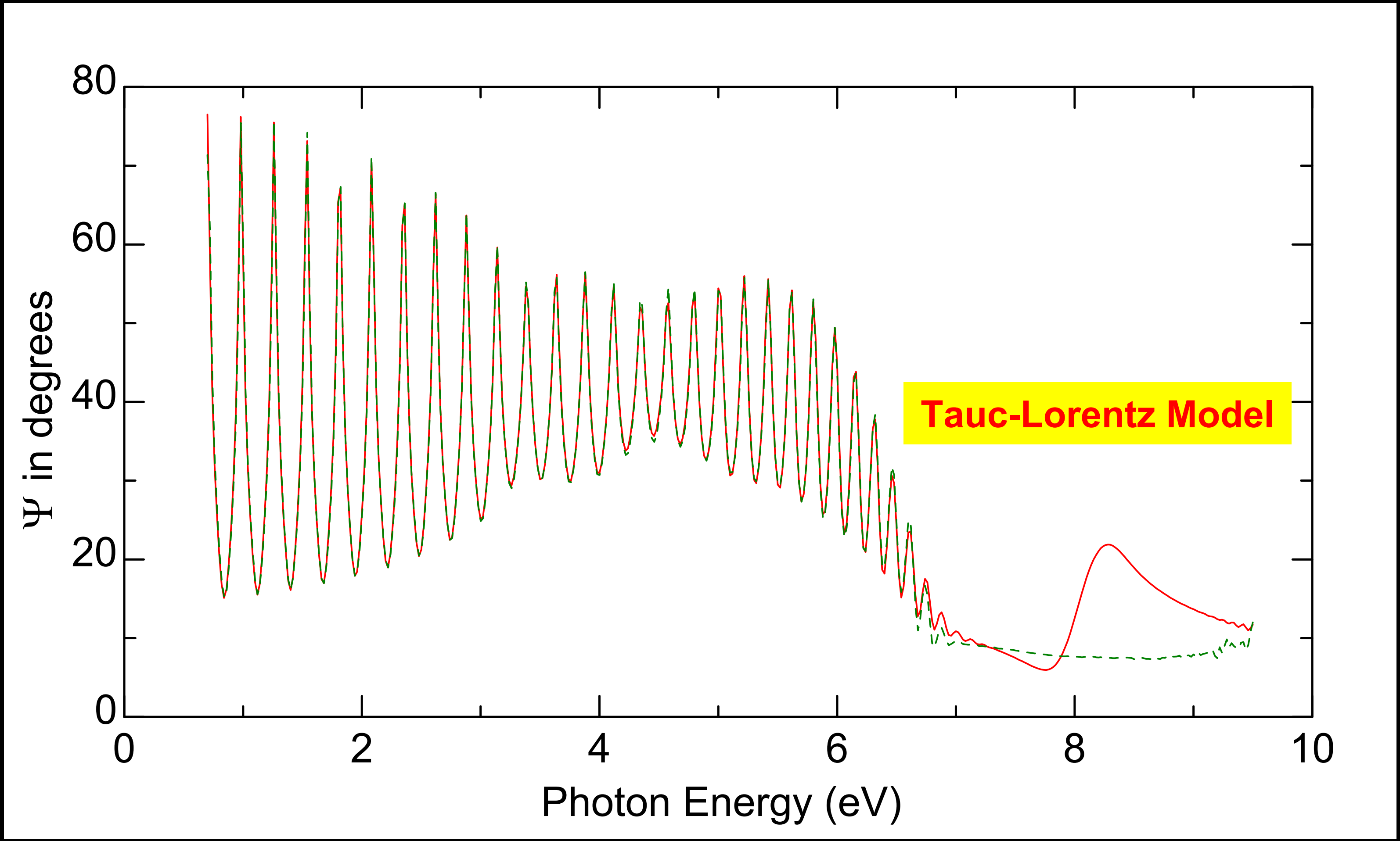
Why can't OSG be treated like an oxide?..................................(or like a porous oxide?)



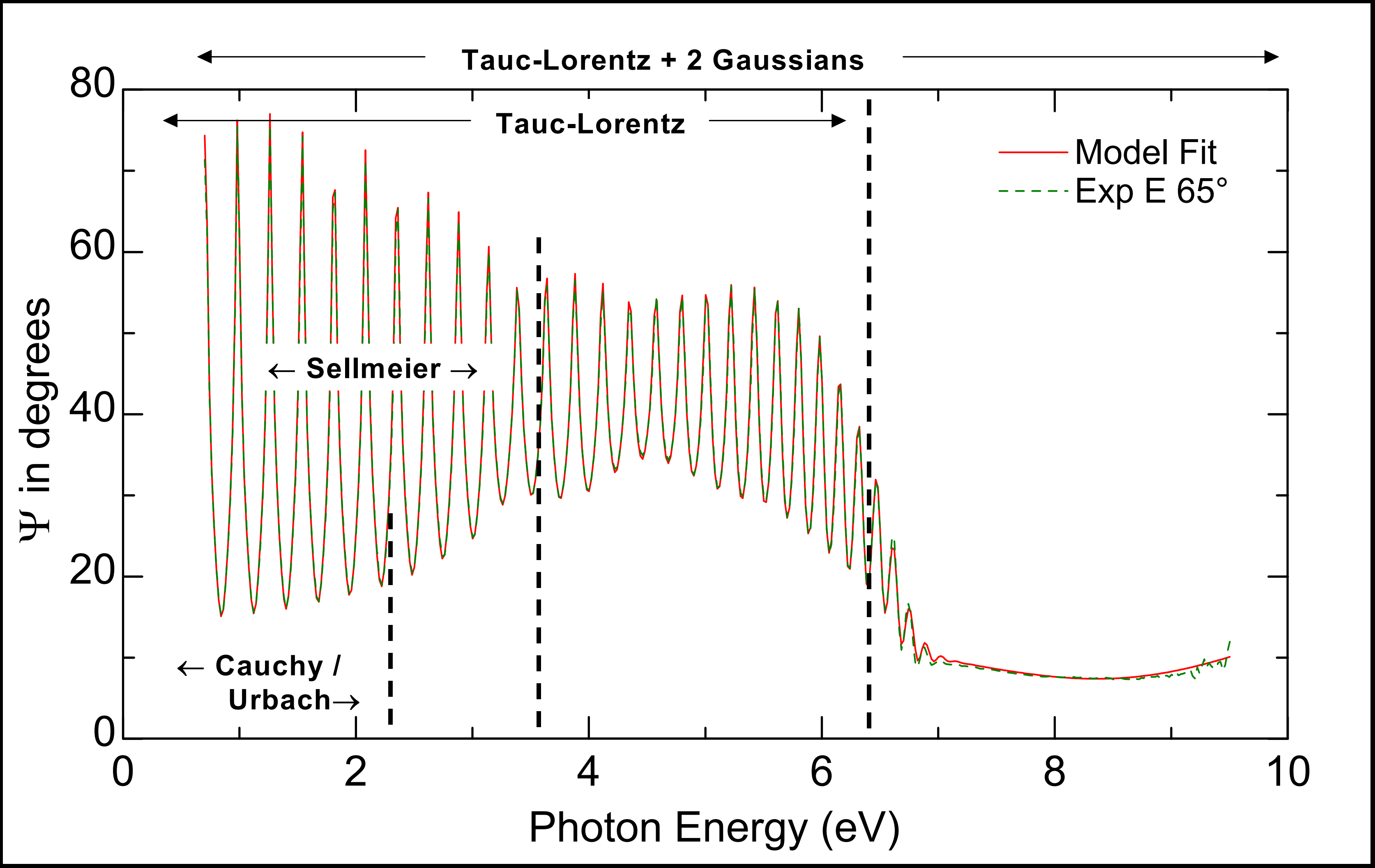
5 VUV SE of Low k Materials



5 **VUV SE of Low k Materials**



5 VUV SE of Low k Materials



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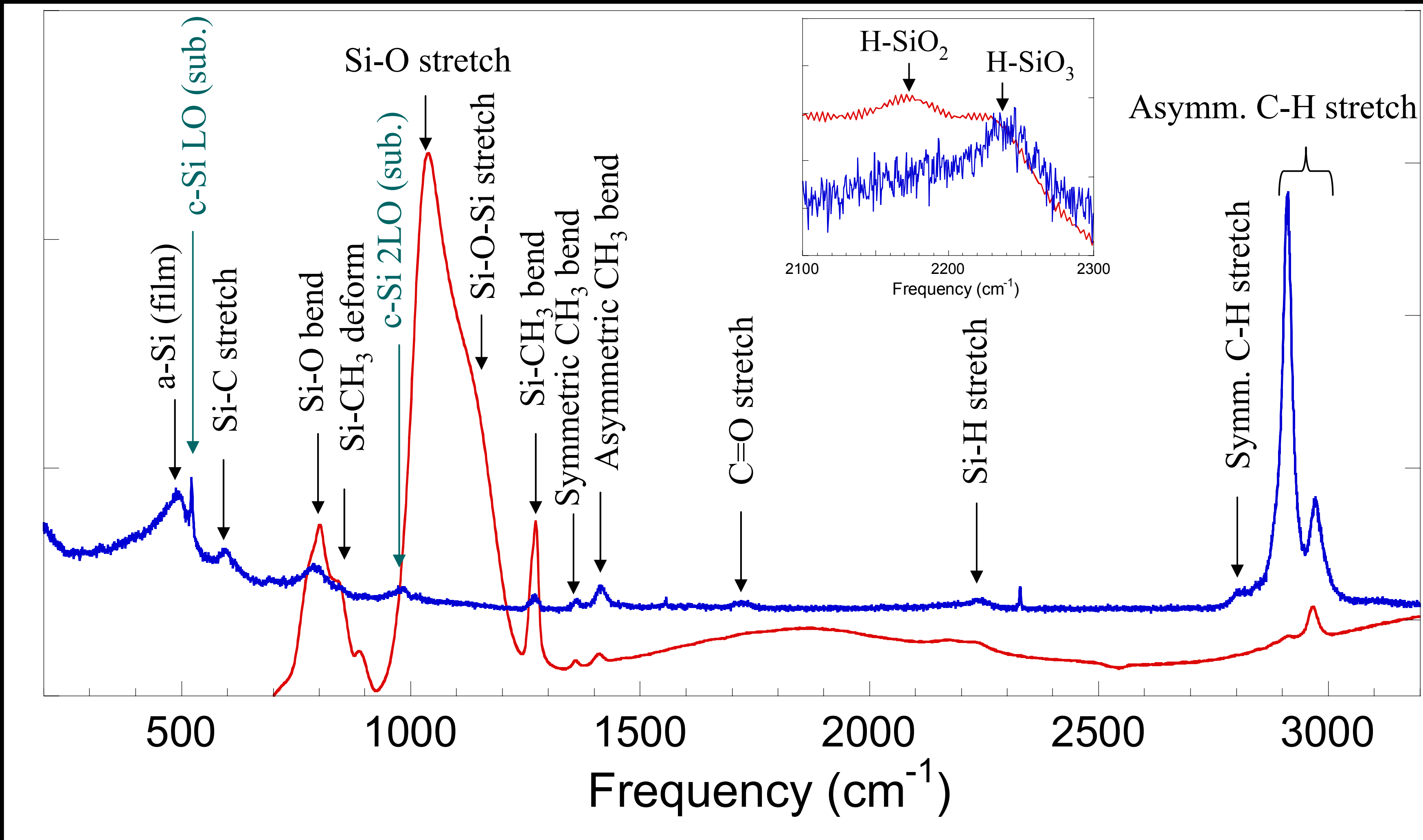
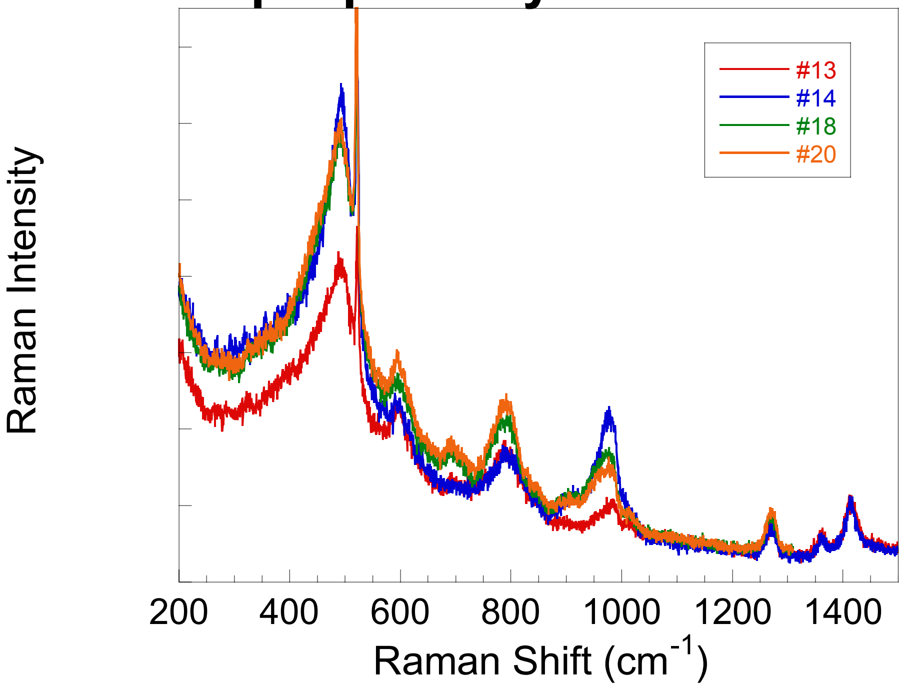
VUV SE of Low k Materials: low index inclusions complicate simple porosity measurements



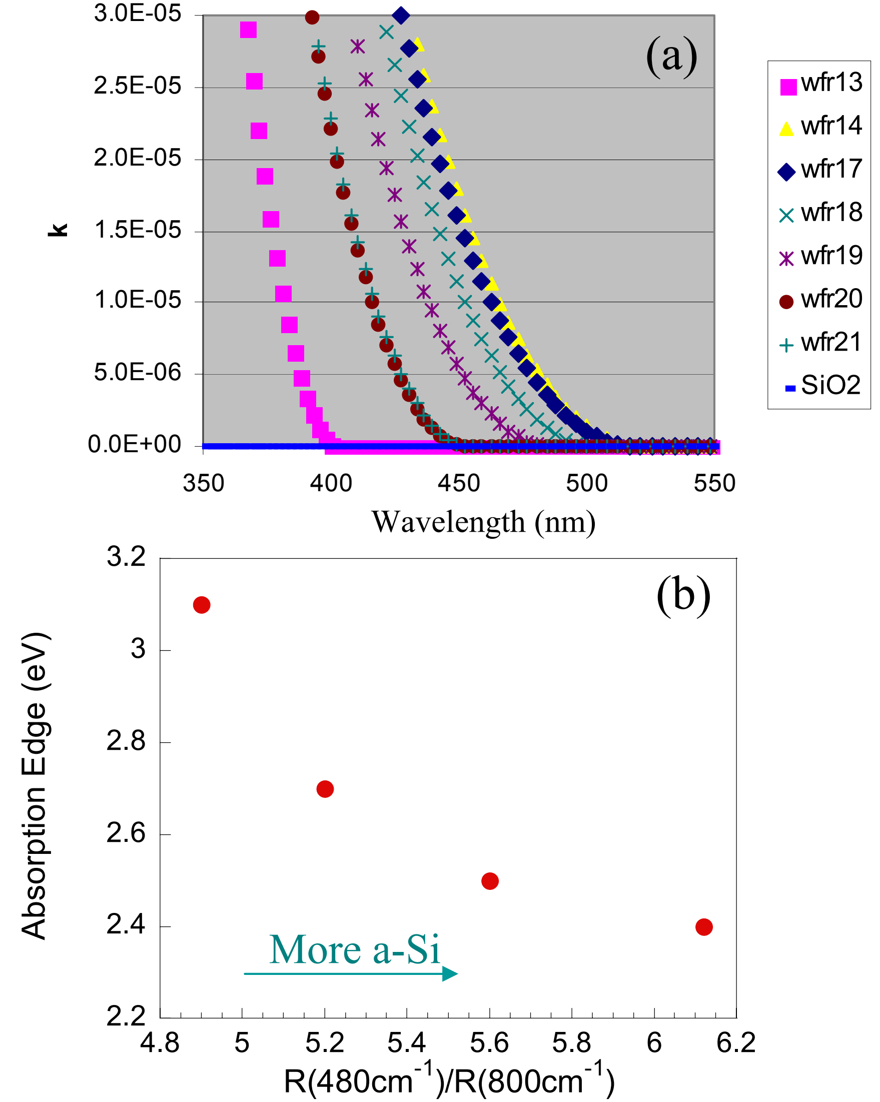
Raman (blue) and absorbance (red) spectra of a SiCOH film (#13) on Si.

Ran Liu, PMCL

simple porosity measurements



Comparison of the Raman spectra of several SiCOH films.



Absorption edges of the SiCOH films from SE (b) and correlation between the absorption edge and the a-Si cluster concentration.

Conclusions

- Samples with dramatically higher hardness had high RI values
  - » and thus higher electron densities/ lower relative porosities
- Films did not have the same optical properties as porous SiO_2 across the spectral range measured
  - » the change in structure introduced by interstitial CH_x is causing something more than a mere increase in porosity

Raman, FTIR, XRR, EELS

VUV SE of Low k Materials

Some Advice…..

- DO NOT treat these films as oxides in in-line metrology recipes without first confirming that they are not absorbing.

- DO NOT apply optical models outside of their range of applicability, for either in-line or spectroscopic instruments.

The dramatic difference between the onset of absorption and onset of opacity in OSG films makes this very dangerous for those hoping to extract film thickness or porosity from their optical measurements.

VUV SE: status and prospects….

High k

- Extract n and d independently for thickness required for process
- Sensitive to interface layer and surface roughness in ‘thick’, single layer films
- Sensitive to interface layer and surface roughness for multilayers

Low k

- Extract n and d independently for thickness required for process
- Sensitive to density and surface roughness in ‘thick’, single layer films
- Sensitive to pore size and distribution

Comparison to in-line metrology (633nm)…..

High k

- Extract n and d independently for thickness required for process
- Sensitive to interface layer and surface roughness in ‘thick’, single layer films
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- Sensitive to pore size and distribution

Comparison to in-line metrology (633nm)…..

High k

- Extract n and d independently for thickness required for process

Low k

- …dently
- Sensitive to pore size and distribution

Propose dynamic SE measurements as the solution to shortcomings of VUV SE and traditional in-line metrology

(it's like a multi-sample analysis measurement, in time)

Acknowledgements:

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