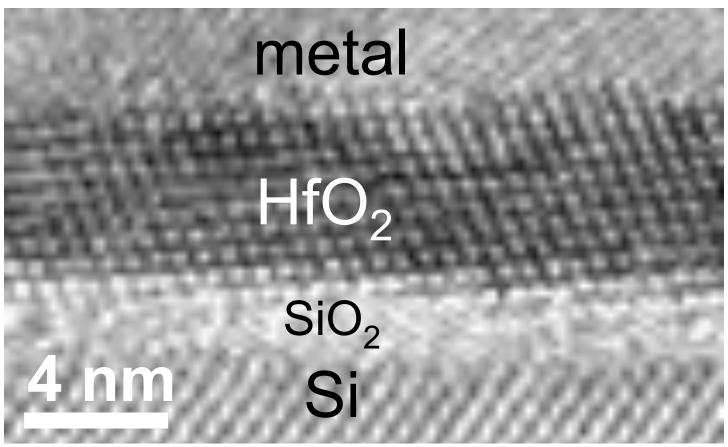
EPI-OPTICS 11
Erice, Italy
July 21, 2010

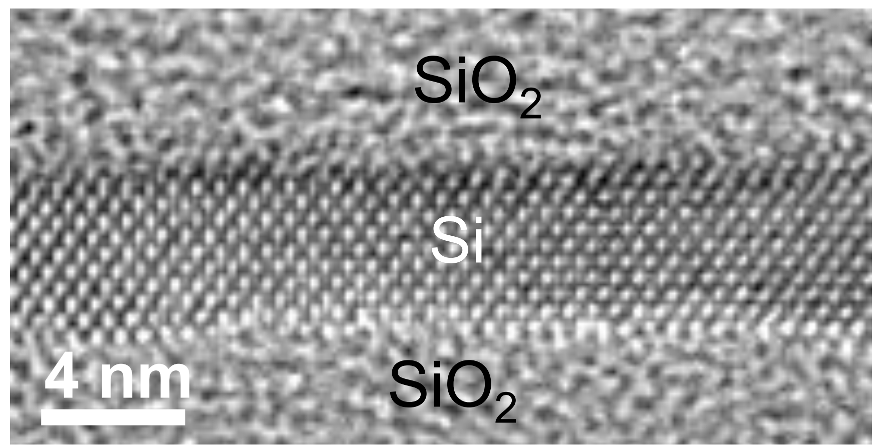
Optical spectroscopy of defects in nm-scale high-*k* dielectric and silicon-on-insulator (SOI) films

Mike Downer

University of Texas at Austin

Nanometer-scale high-k dielectric and SOI films have enabled devices to continue operating with high-speed and low power consumption...





... but are susceptible to formation of defects

"Faster, non-destructive ways of detecting these defects are needed." ITRS 2009

Co-workers

Accelerating the next technology revolution.

$Si/SiO_2/Hf_{1-x}Si_xO_2$	SOI	Sematech

Jimmy Price
PhD 2009

Ming Lei

Gennadi Bersuker

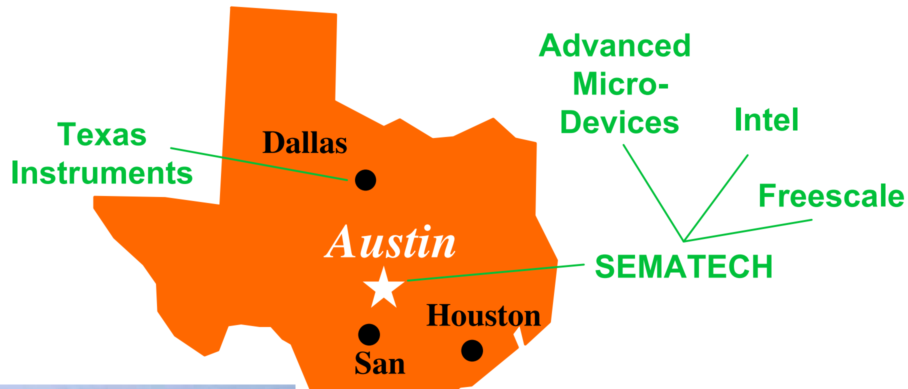
Pat Lysaght

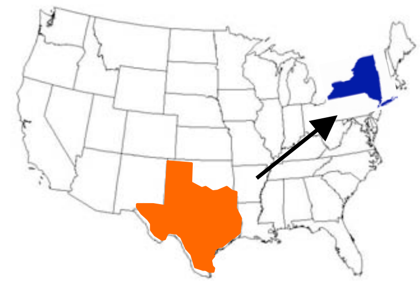
Financial Support:

- Robert Welch Foundation
- U.S. National Science Foundation
- Sematech (support of J. Price)

A University-Industry Collaboration

Accelerating the next technology revolution.





The University of Texas at Austin

Founded 1886

www.utexas.edu

Sematech's Albany, NY facility

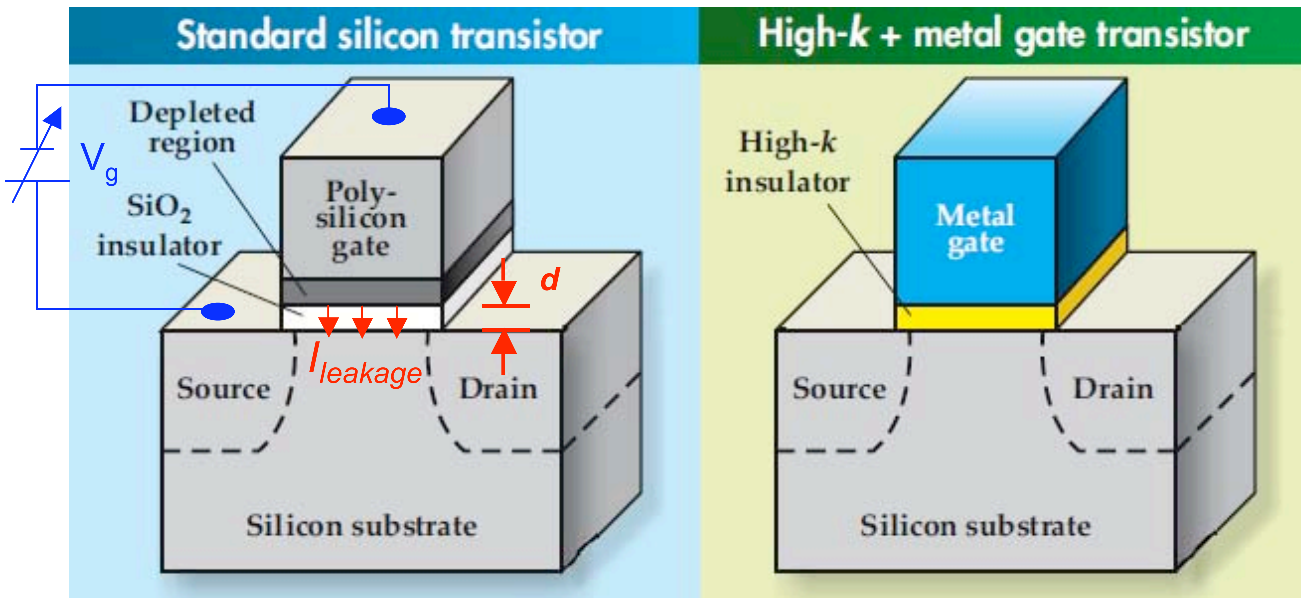
Founded 2008

www.sematech.org

February 2008 Physics Today 25

Semiconductor industry switches to hafnium-based transistors

Plagued by quantum tunneling of charge carriers through gate insulators, chip manufacturers are shifting to high-dielectric-constant materials that maintain sufficient capacitance and reduce power leaks.



The new standard for smaller transistors will be high-dielectric-constant hafnium-based materials and metal-gate electrodes that will replace the silicon oxide–based insulator and the polysilicon gate. In the figure, *k* represents the dielectric constant.

A decade of intensive materials research preceded the commercial introduction of Hf-based dielectrics

PROBLEM:

As $d \rightarrow 1$ nm,

$I_{leakage} \rightarrow 100$ A/cm^2

because of quantum tunneling

⇓

power loss & **heating**, *esp.* in cell phones, laptops

SOLUTION:

Maintain high $C = k\varepsilon_0 A/d$, for high device performance by replacing

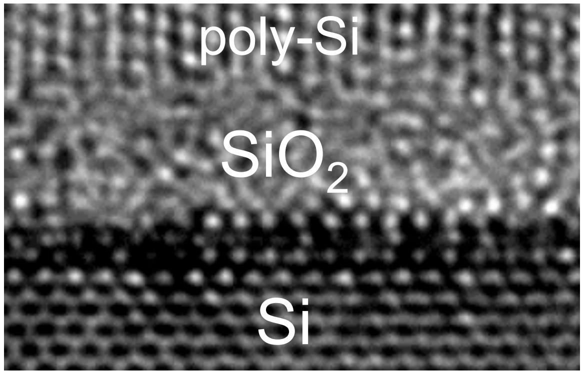
$k_{SiO2} = 3.9$

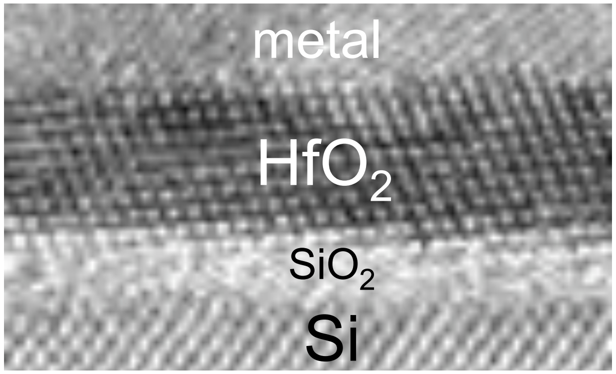
with

$18 < k_{Hf\text{-}silicate} < 30$

Numerous obstacles were overcome before Hf-based oxides became a manufacturable solution for today's chip industry.

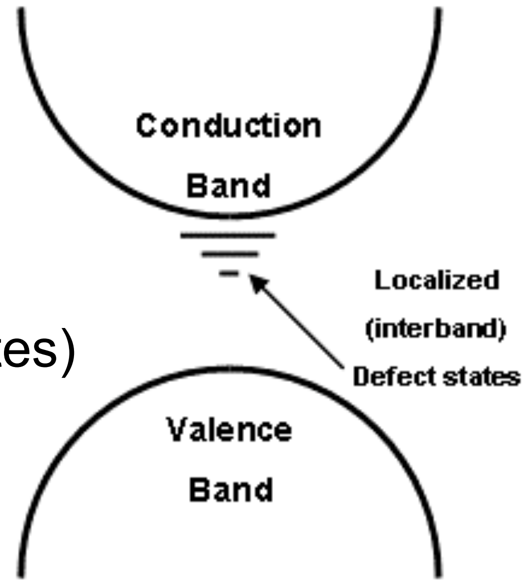
<u>**SiO_2**</u> vs.	<u>**Hf-based oxides**</u>
• Low density of defects	• High density of intrinsic defects
• Amorphous	• Susceptible to crystallization
• minimum dangling bonds	• Low quality SiO_2 interface
• Stable w/ poly Si gate.	• Elemental diffusion w/ metal gate





Further scalability depends on developing **non-invasive** methods for characterizing <u>**intrinsic**</u> & <u>**process-induced**</u> defects.

What are dielectric defects and how do they affect device performance

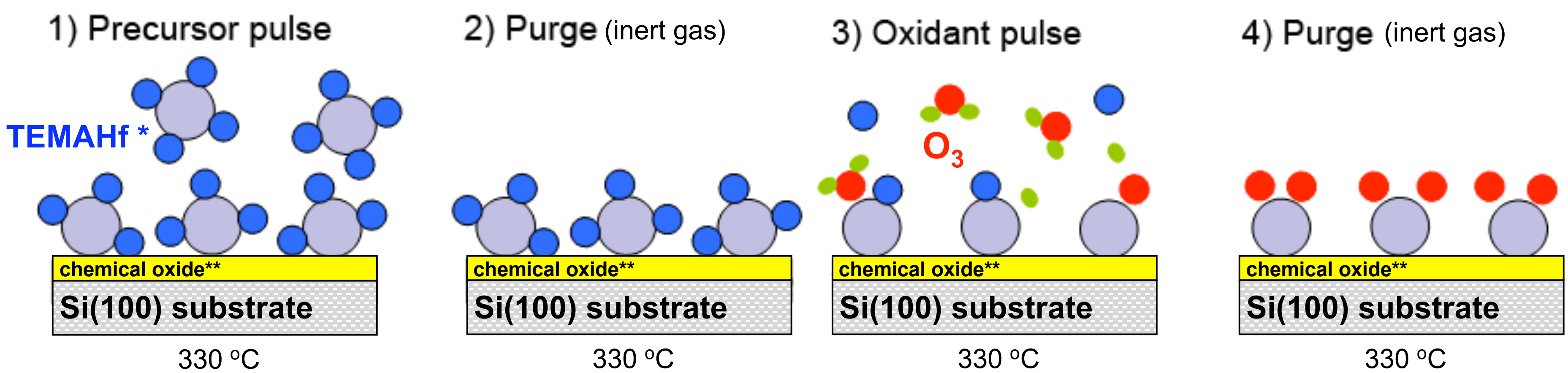


- Defects: anything that can trap an electron.
  - O_2, N_2, vacancies and / or interstitials
  - Impurities (C, B, etc.)
  - Crystal imperfections (grain boundaries, surface states)
  - All are discrete localized states within the band gap

- How does this affect device performance?
  - Charge trapping and V_t instability
  - Increase in leakage current
  - Degradation of carrier mobility

Atomic Layer Deposition (ALD) was critical to integrating high-*k* dielectric layers into commercial devices

Kirsch *et al*., J. Appl. Phys. **99**, 023508 (2006)



* tetrakis(ethylmethylamino)hafnium

** aqueous ozone treatment in commercial wet bench

Benefits of ALD:

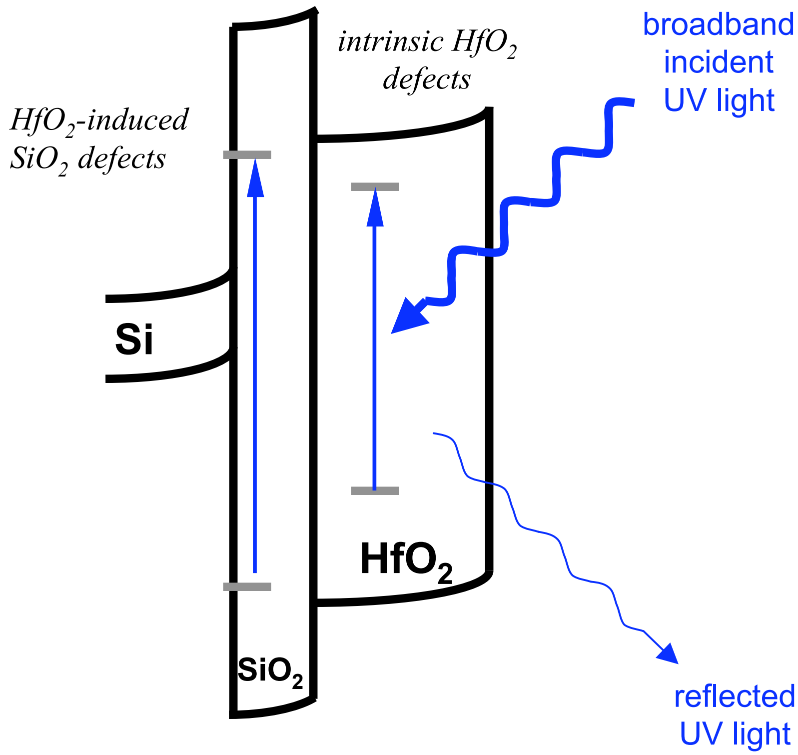
- Atomic level control of film composition
- Uniform thickness over large areas
- Very smooth surfaces
- High density, minimal defects
- Low deposition temperature.

www-rpl.stanford.edu/.../sofc/electrode/ald/

We have employed two complementary optical methods for identifying defects in $Si/SiO_2/Hf_{1-x}Si_xO_2$ structures

Spectroscopic Ellipsometry

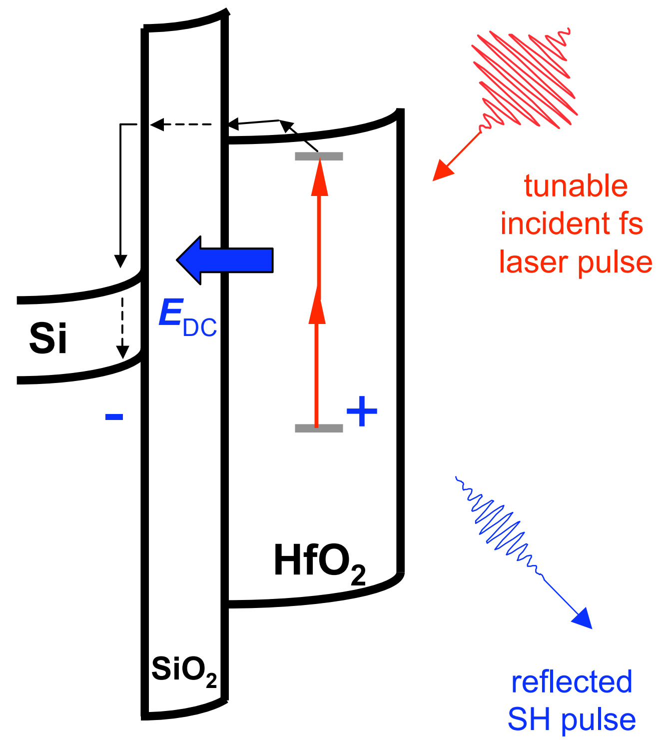
(*i.e.* absorption)



Price *et al.*, Appl. Phys. Lett. **91**, 061925 (2007)
J. Vac. Sci. Tech. B **27**, 310 (2009)

Internal PE + EFI-SHG

(EFI = Electrostatic-Field-Induced)



Price *et al.*, Appl. Phys. Lett. **95**, 053906 (2009)

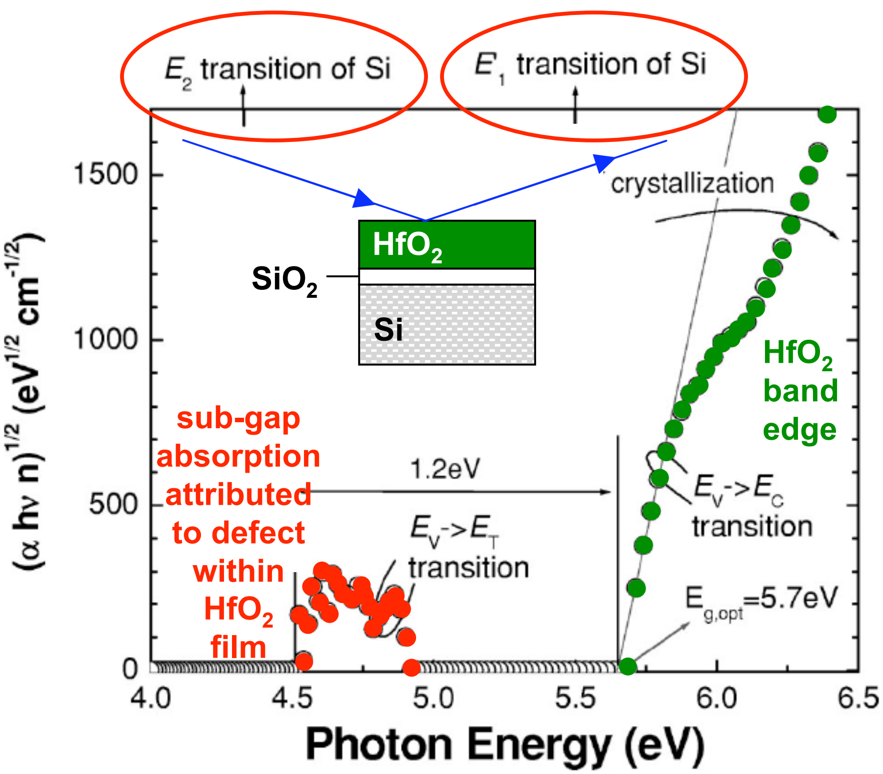
Both methods are fast, non-invasive, defect-specific & compatible with in-line metrology; neither requires device fabrication

The need for non-invasive high-*k* defect metrology has driven an extension of SE methodology & application...

... from traditional role: characterizing thickness & broad-band $\varepsilon(\omega)$ of ultra-thin films

...to new role: identifying **weak**, **discrete**, **sub-high-*k*-gap** absorption features relevant to electrical performance of high-*k* devices

Takeuchi *et al*., JVST-A **22**, 1337 (2004)
Li *et al*., Appl. Phys. Lett. **89**, 103523 (2006)
Sancho-Parramon *et al*., TSF **516**, 7990 (2008)



...but the extension has pitfalls:

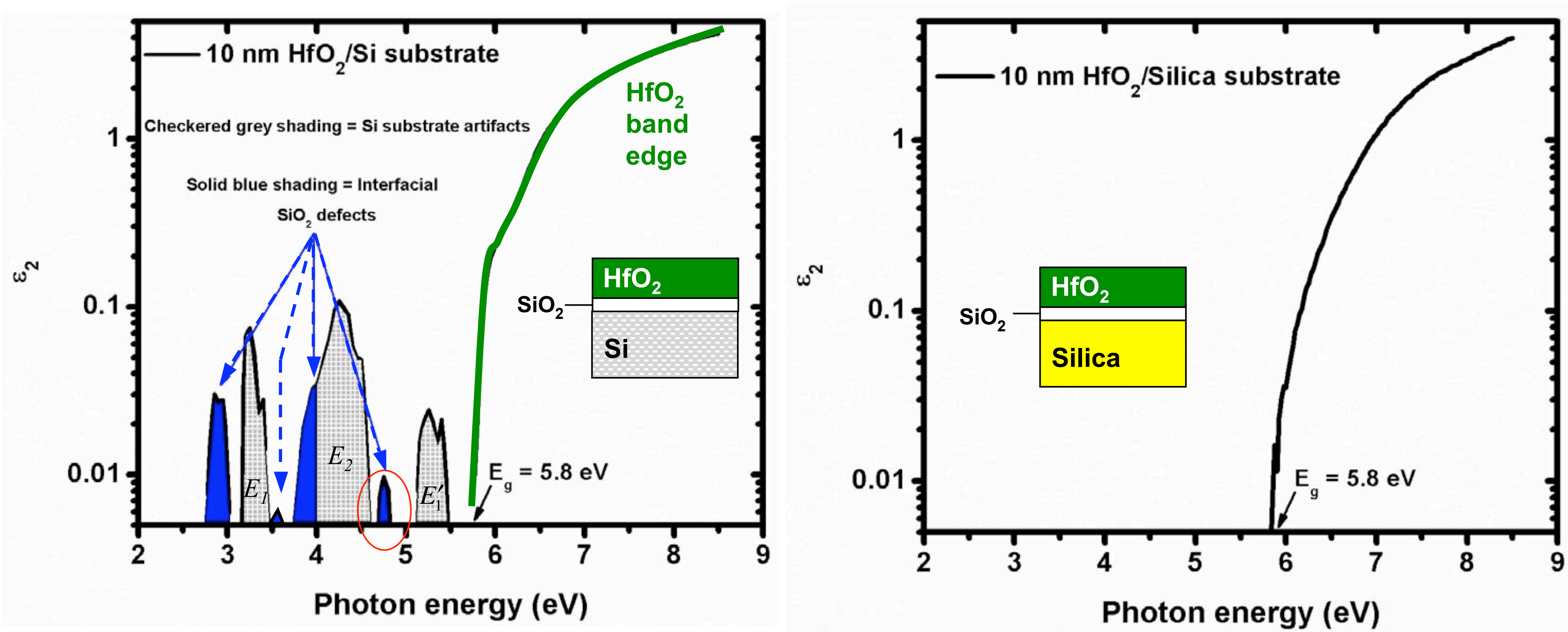
- relies on traditional parametrized $\varepsilon(\omega)$ models for Si substrate & bulk of SiO_2, HfO_2 layers
- absorption coefficient near discrete feature must be extracted using point-by-point data inversion methods
- artifacts from Si substrate CPs can appear if parametrized $\varepsilon(\omega)$ models are incorrect

e.g. because of strain, electrostatic fields, etc.

We also observe Takeuchi's 4.75 eV absorption peak

+ "ghosts" of Si E_1, E_2 and E_1' critical points ...

+ additional peaks at 2.9, 3.6 and 3.9 eV



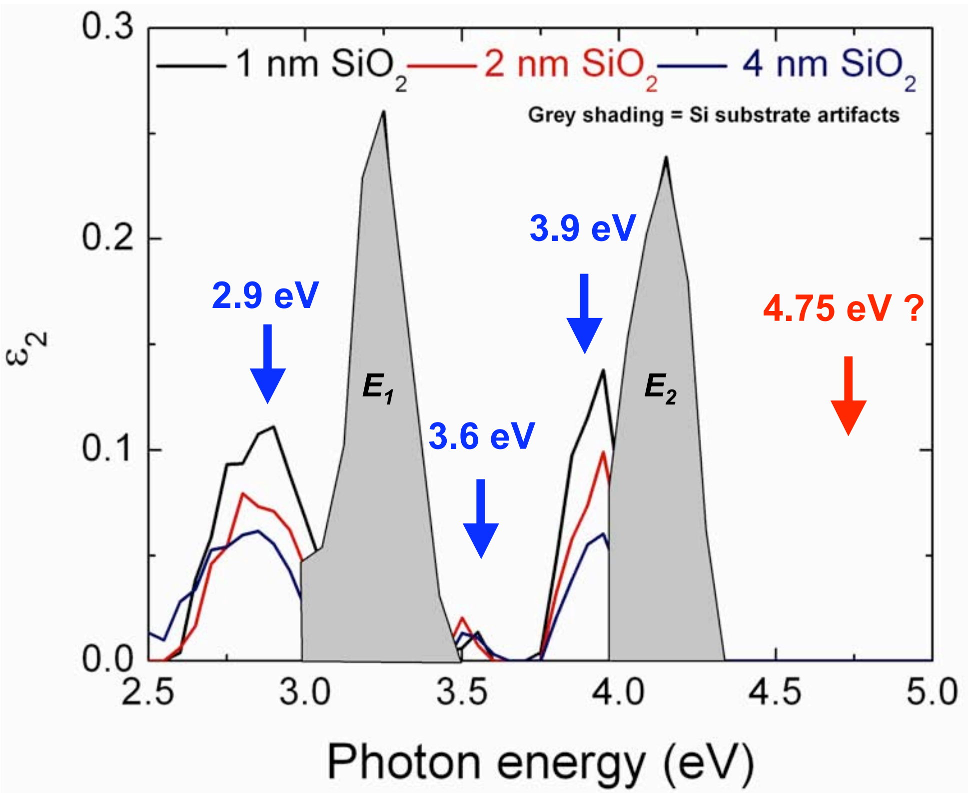
... but they all vanish when Si substrate replaced with SiO_2

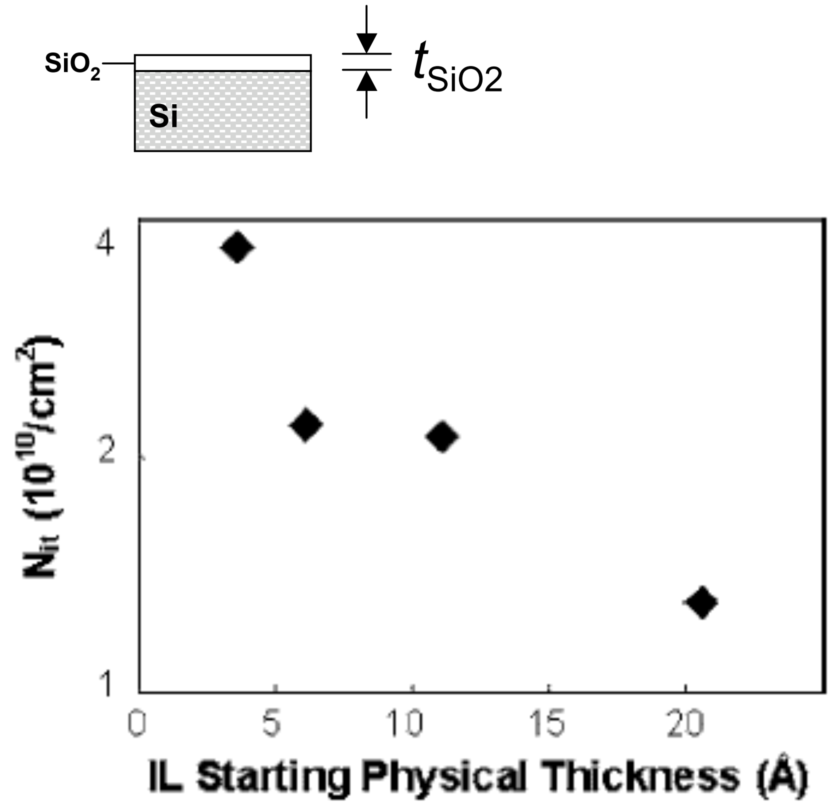
⇒ the optically active defects cannot be in bulk HfO_2

Are they Si/SiO_2 defects? ⇒ remove the HfO_2 layer to find out

3 of 4 absorption peaks persist in absence of HfO_2

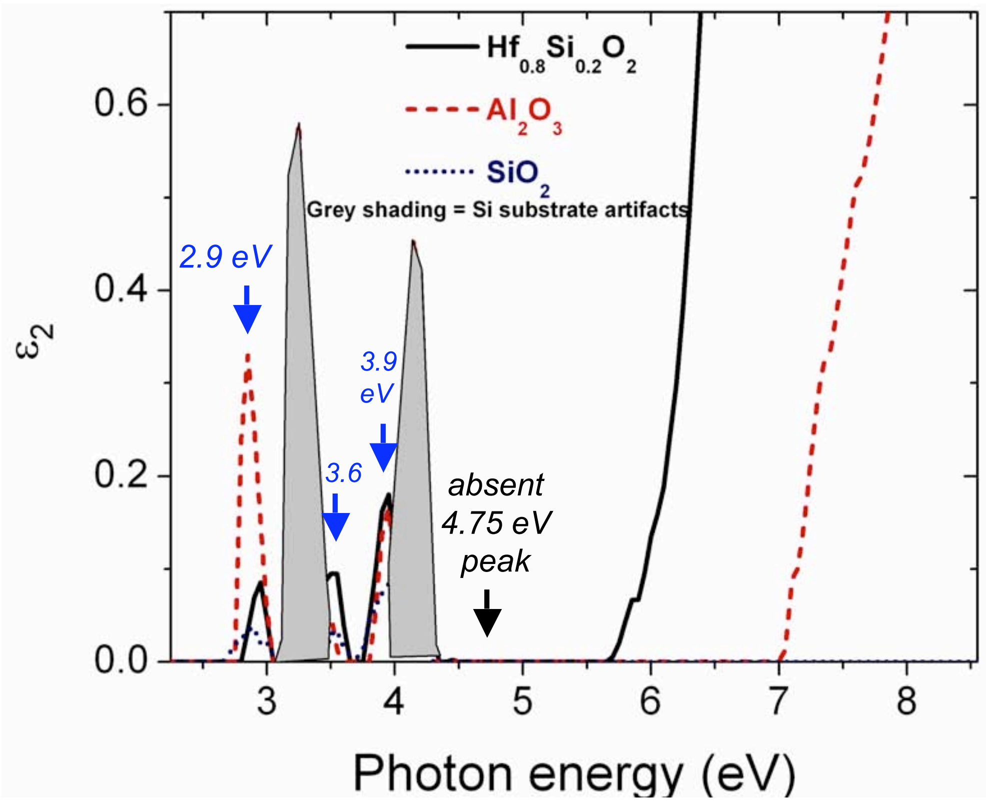
Peak height dependence on t_{SiO2} tracks N_{it} derived from electrical data





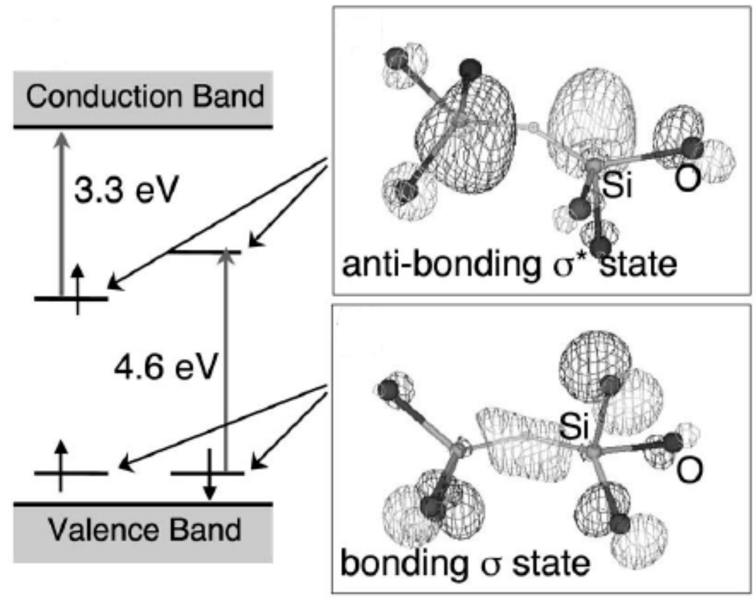
- **1st spectroscopic identification of sub-gap defects in Si/SiO_2**
- **4.75 eV peak:**
  - noticeably absent, suggesting it's HfO_2-induced.
  - also absent with $Hf_{1-x}Si_xO_2$ and Al_2O_3 overlayers, showing it's HfO_2-specific

Peak amplitudes (but not energies) are sensitive to the high-*k* dielectric overlayer



Ab-initio calculations:

Sushko, *Microelectronics Eng*. **80**, 292 (2005)



Ab initio calculations predict that **oxygen vacancies** possess sub-SiO_2-gap optical transitions at energies close to the observed peaks

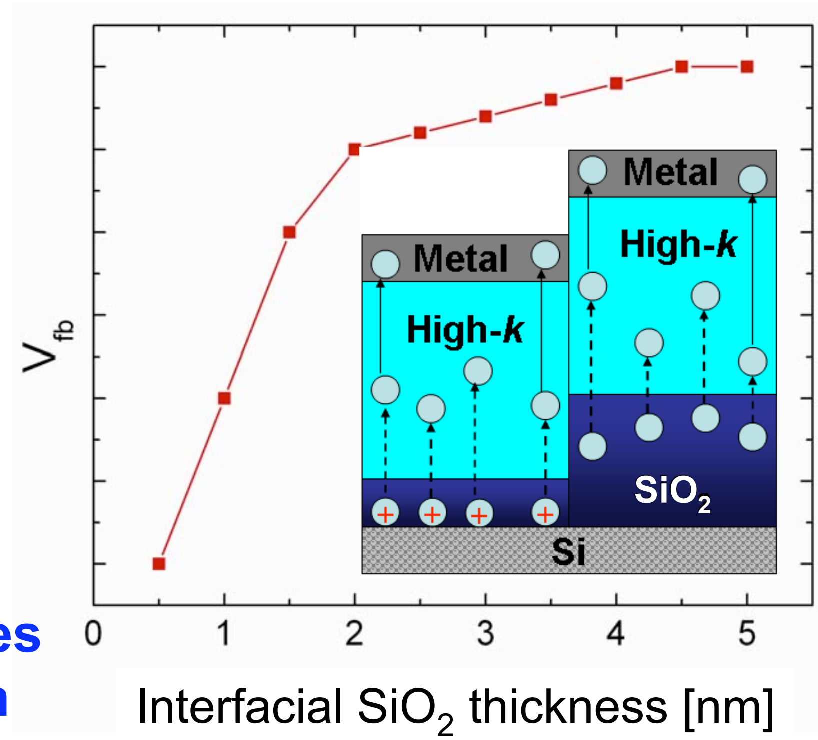
Identification of sub-gap absorption peaks with O vacancies suggests a connection with "$V_{flatband}$ roll-off" in high-*k* devices

- V_{fb} in Si/SiO_2/high-*k* devices is observed to "roll off" quickly for $t_{SiO2} < 3$ nm →

  [V_{fb} also varies in well-documented ways with ***anneal treatment***, ***electrode work function***, ***high-k material***, etc.]

- V_{fb} variability leads to irreproducibility in device performance.

- A widely-accepted model* attributes V_{fb} variations to creation of **oxygen vacancies** in the SiO_2 interfacial layer due to **oxygen gettering by the high-*k* overlayer**.

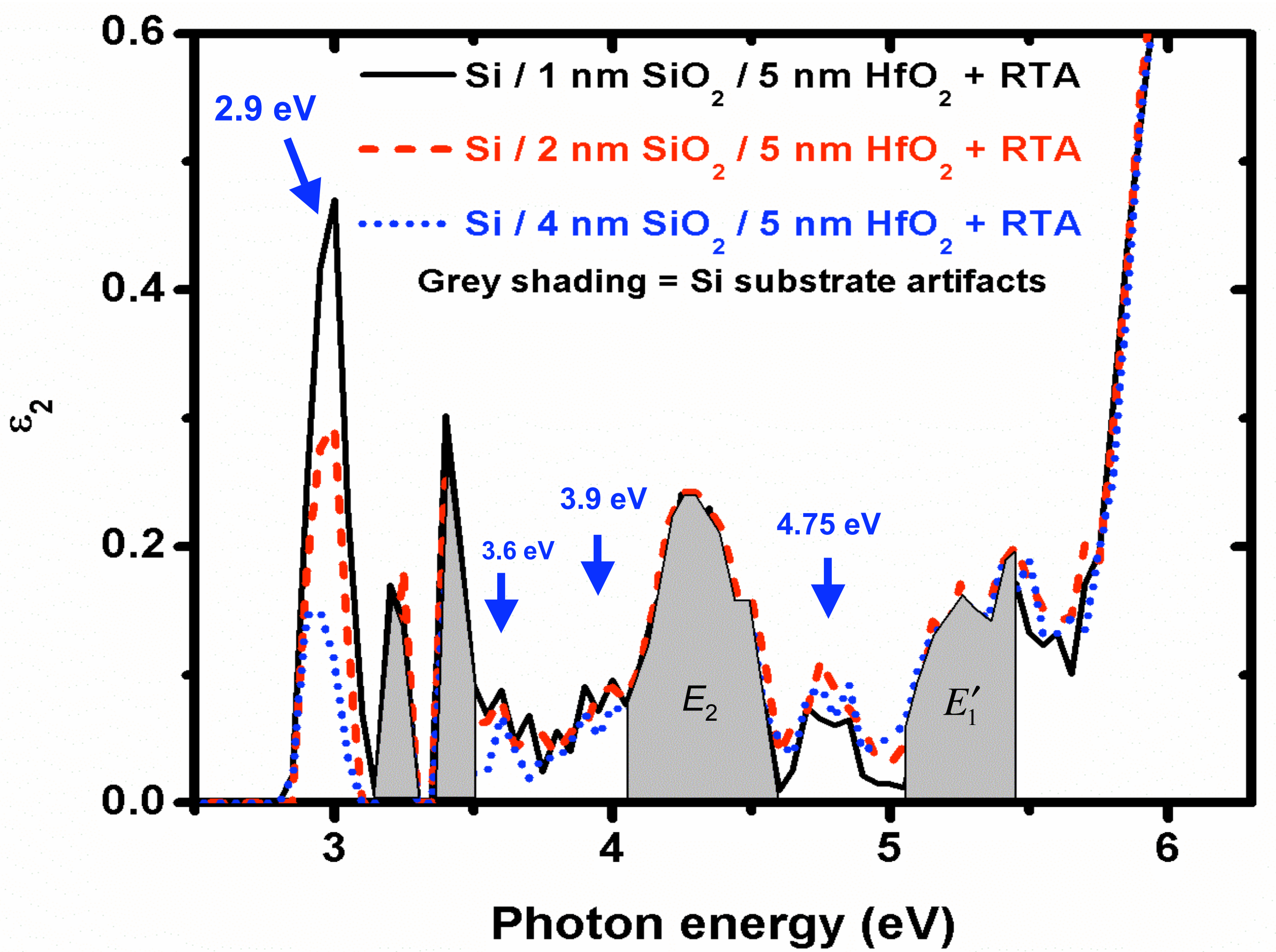


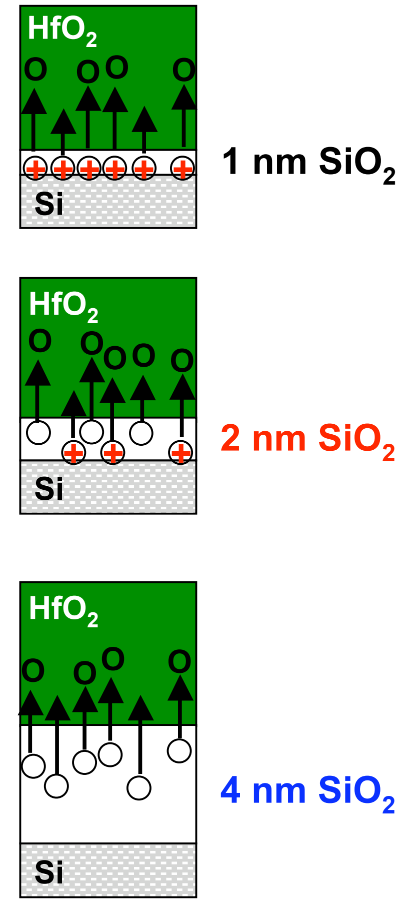
- O vacancies created in the thinnest SiO_2 layers, where strained SiO_x dominates, are preferentially **positively charged**.

*G. Bersuker *et al.*, J. Appl. Phys. **100,** 094108 (2006); **ibid.,** Proc. 38th Eur. Sol. St. Dev. Res. Conf., p. 134 (2008).

2.9 eV peak closely tracks V_{fb} dependence on t_{SiO2}

3.6, 3.9, and 4.75 eV peaks are less sensitive to t_{SiO2}

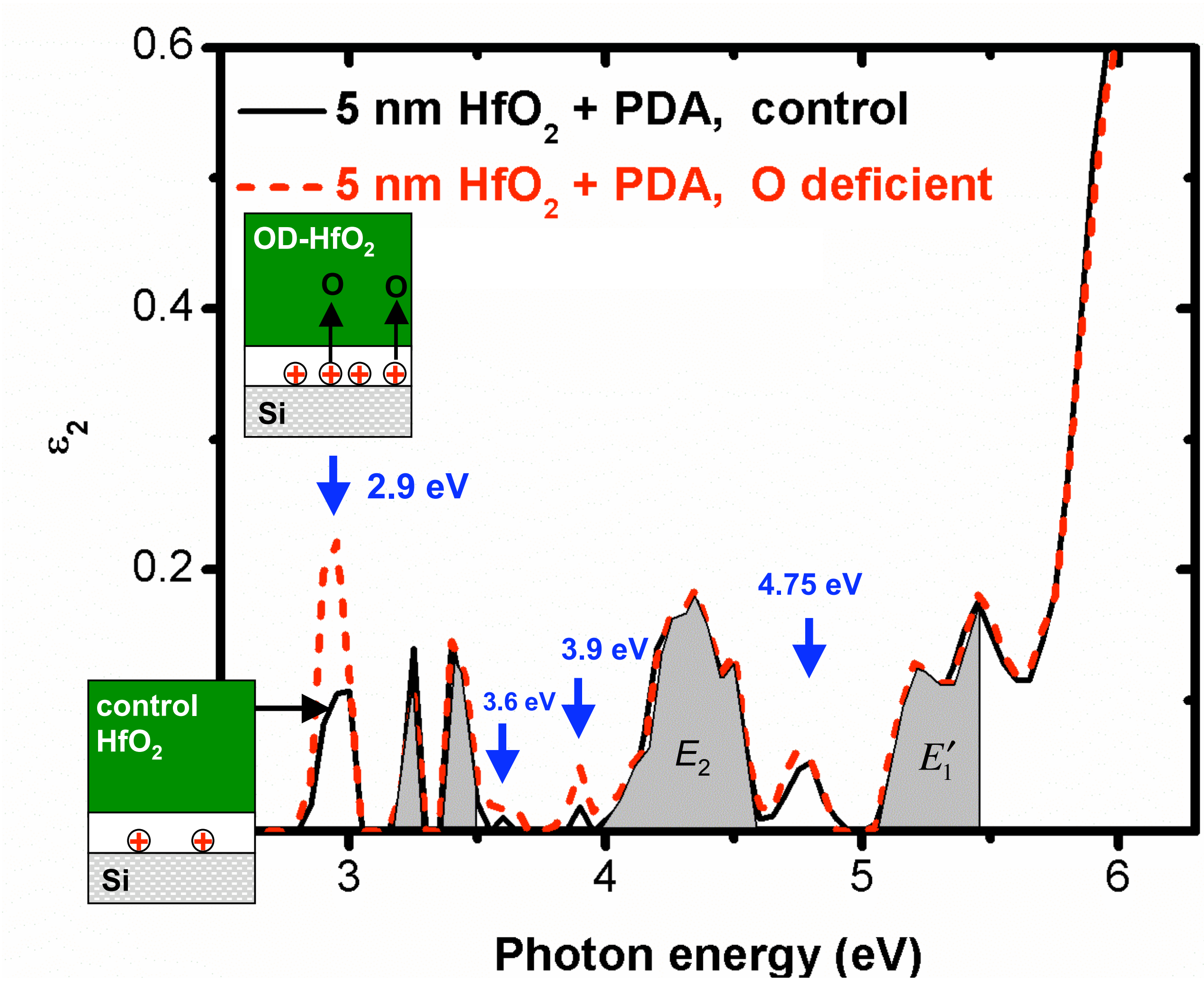




Results suggest 2.9 eV peak originates from positively-charged O-vacancies at the Si/SiO_2 interface that are responsible for V_{fb} roll-off

Intentional deposition of O-deficient HfO_2 film* simultaneously strengthens O-gettering & sub-gap absorption

* *by reducing duration of O_3 pulse during ALD*



- 2.9 eV peak doubles in strength in OD-HfO_2 sample because of enhanced O-gettering.
- 3.6, 3.9, 4.75 eV peaks strengthen by smaller fractions.
- Corresponding variations in V_{fb} and ESR spectra are observed.

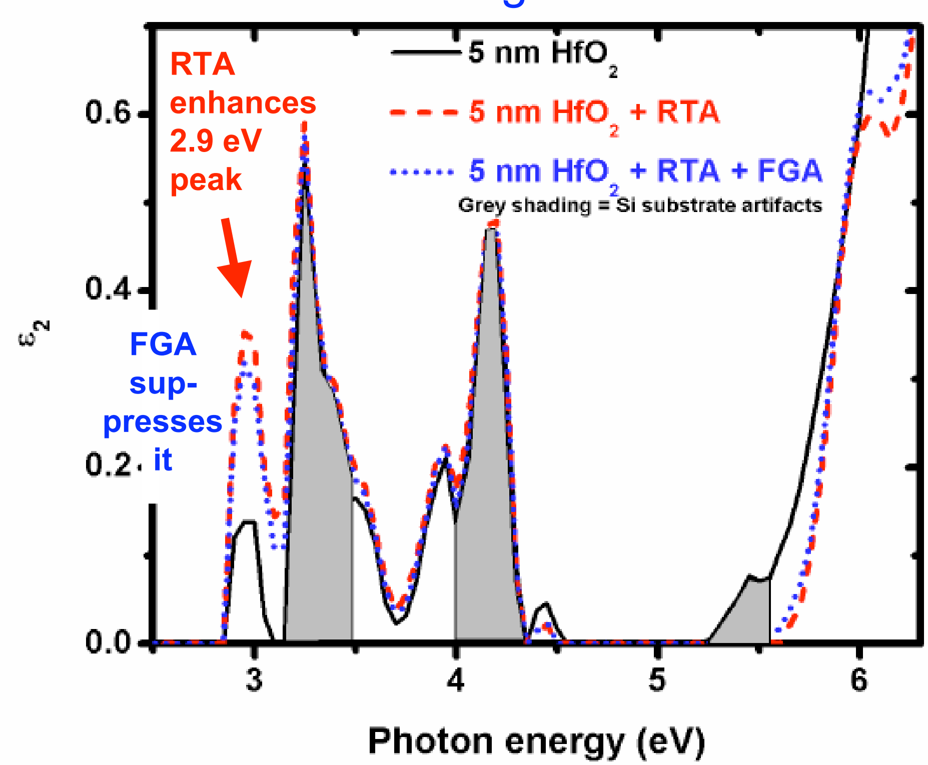
Sub-gap absorption gives <u>immediate feedback</u> on on influence of processing steps on electrical properties, and correlates with known dependencies of V_{fb} roll-off

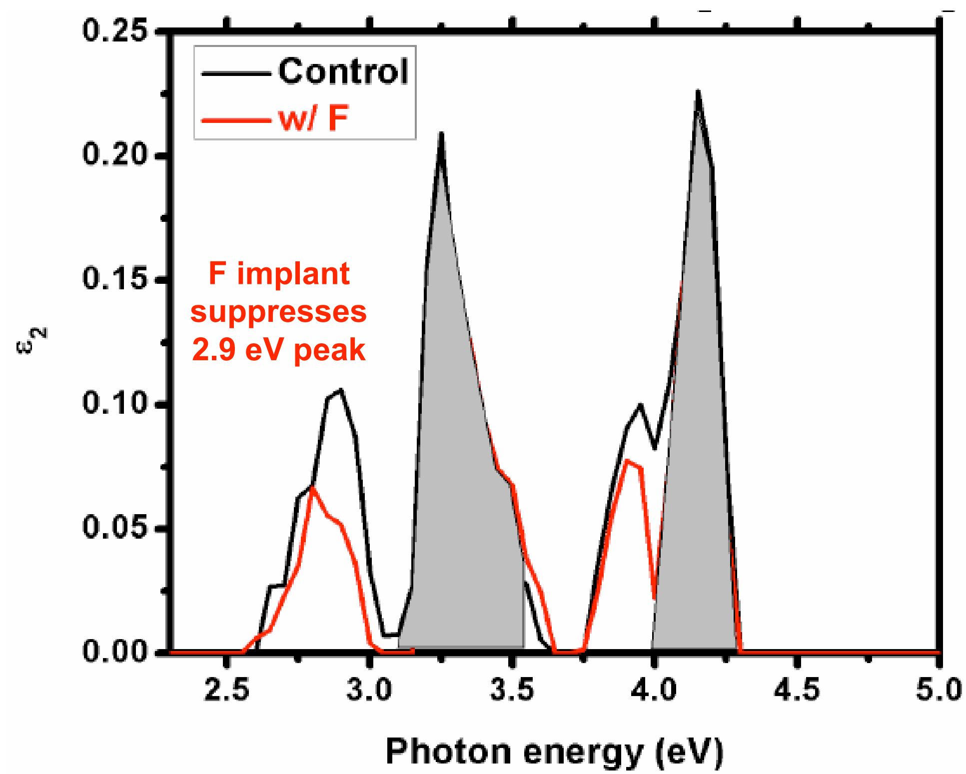
J. Price, PhD dissertation (2009)

RTA = Rapid Thermal Anneal*

FGA = Forming Gas Anneal**

F implant into Si/SiO_2 interface before high-*k* deposition***





* RTA contributes to V_{fb} roll-off

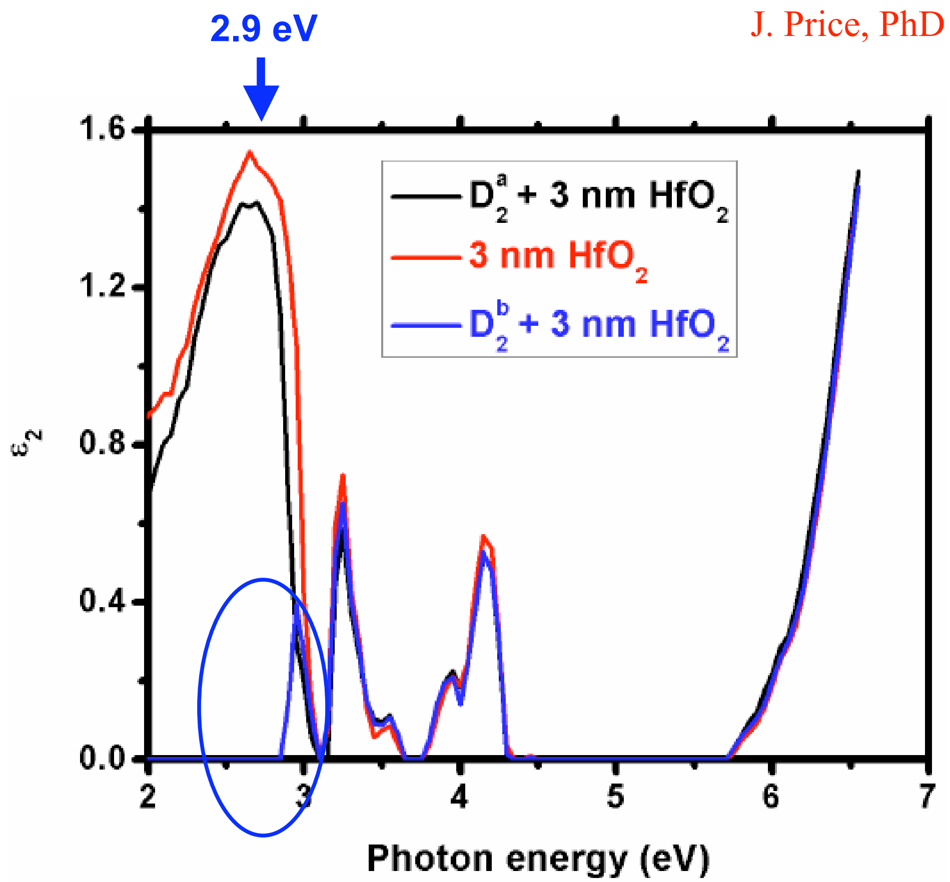
** FGA helps passivate Si/SiO_2 interface defects

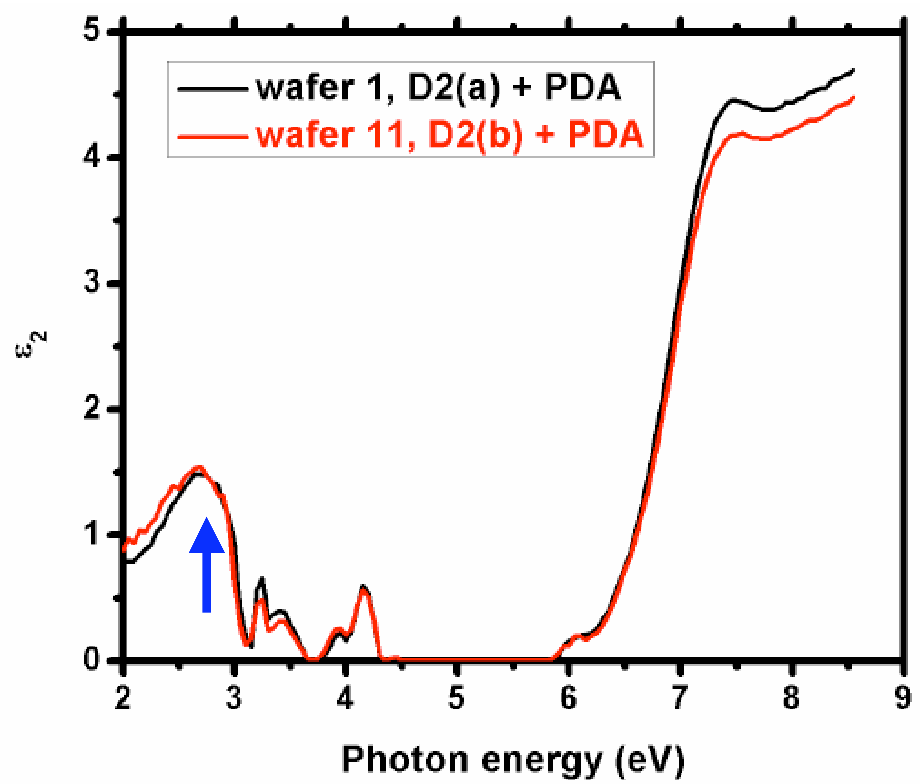
** F-implant suppresses V_{fb} roll-off

Choi *et al.*, IRPS 2007

In-situ feedback from optical monitor can help find process sequences that improve device performance

J. Price, PhD dissertation (2009)





D_2(a): low temp/pressure deuterium anneal

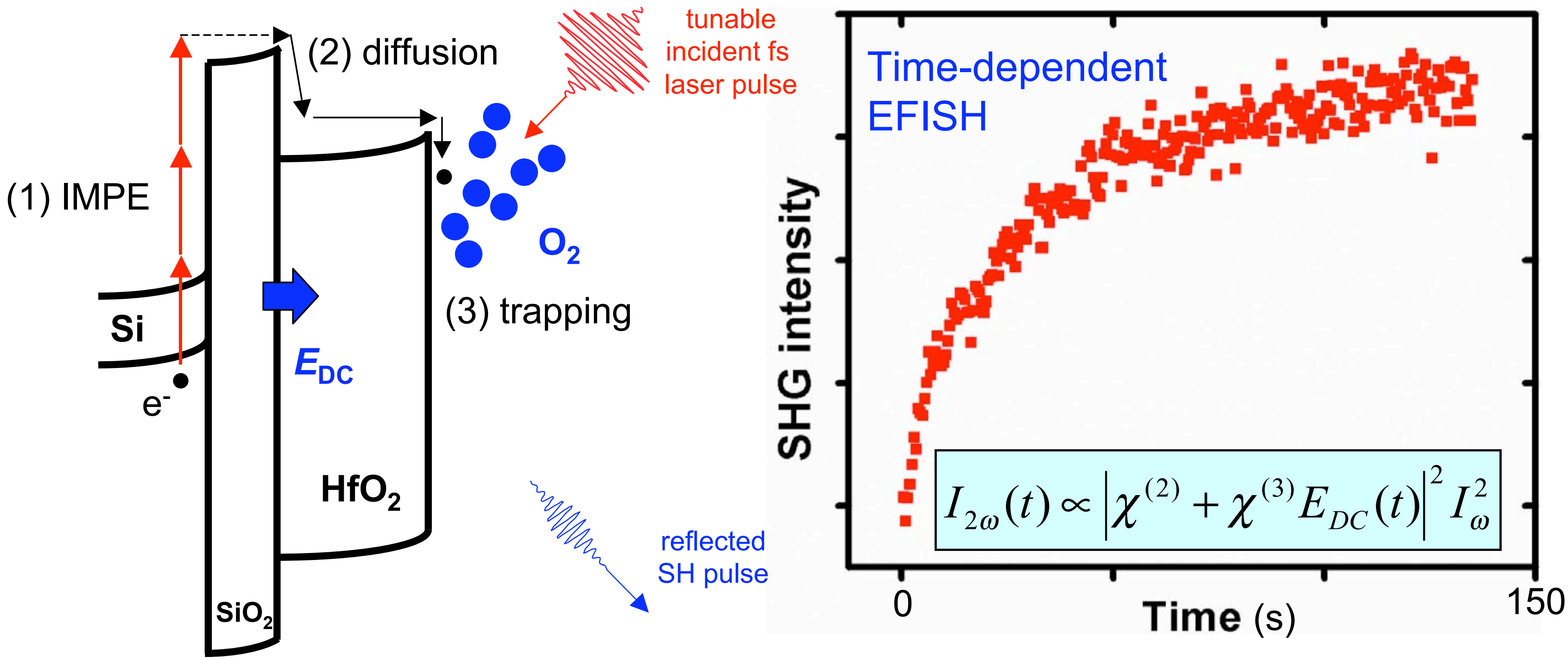
D_2(b): high temp/pressure deuterium anneal

D_2(b) + **ALD of 3 nm HfO_2** almost completely suppresses 2.9 eV peak !

Unfortunately, the 2.9 eV recovers after a post-deposition anneal (PDA)

Internal multi-photon photoemission & time-dependent EFISH* are widely used to investigate charge trapping at oxide surfaces

previous TD-SHG studies of high-*k* dielectrics: Marka *et al.*, Phys. Rev. B **67**, 045302 (2003)



***Electrostatic-Field-Induced Second Harmonic (EFISH) generation:**

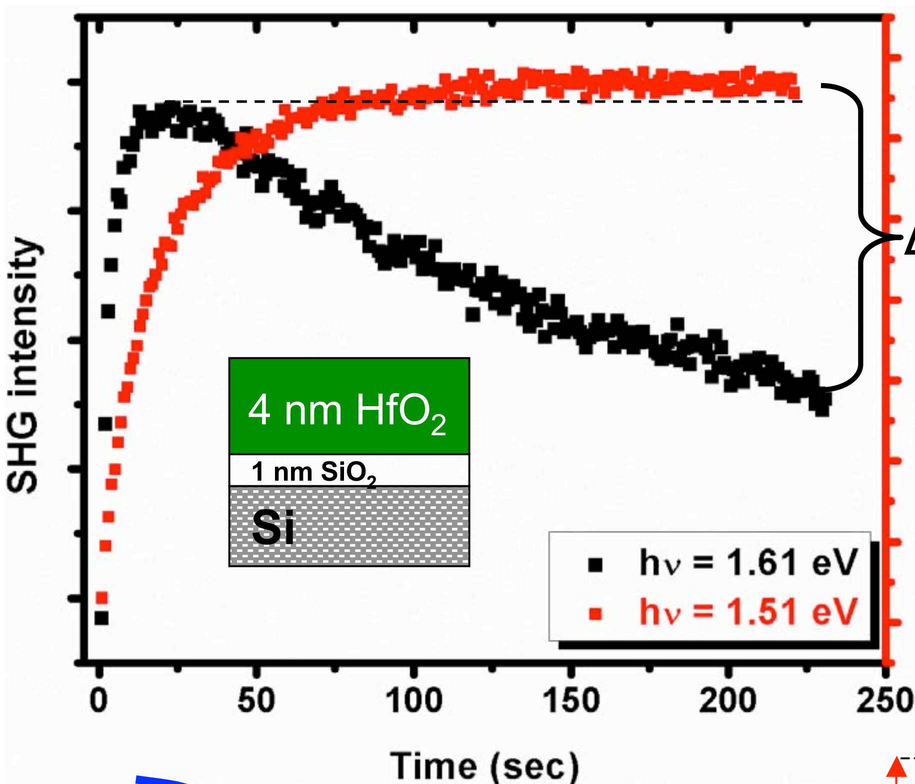
(1) Incident fs pulse 3-photon-excites electrons above SiO_2 CB barrier

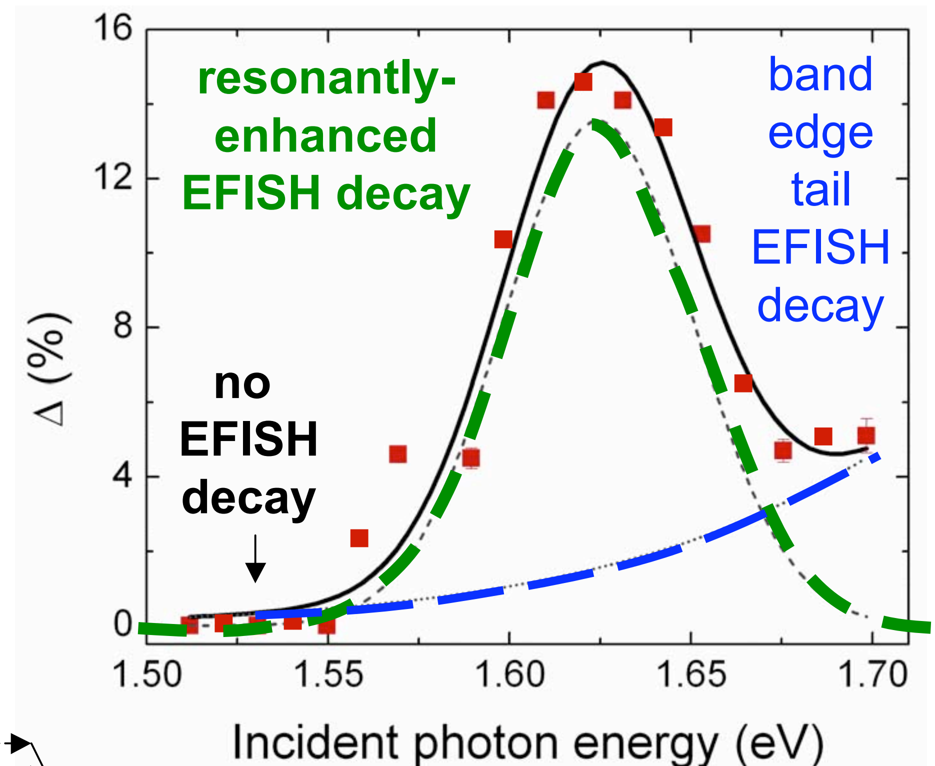
(2) Electrons drift to oxide surface

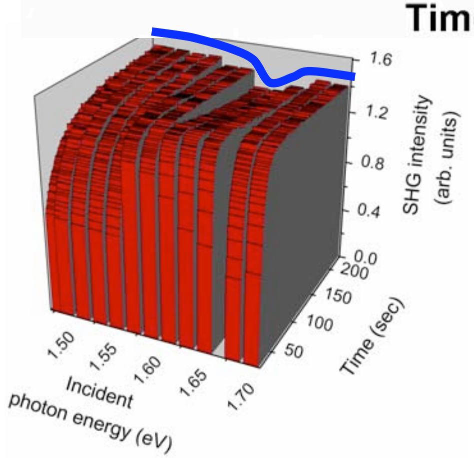
(3) Electron trapping, catalyzed by ambient O_2, creates electrostatic field

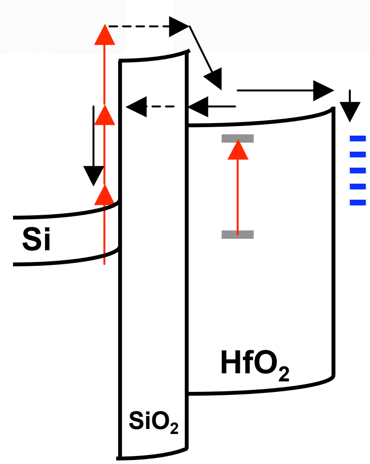
*J. Bloch, et al., PRL **77** (1996)*

For a narrow band of incident photon energies, we observe delayed EFISH decay in samples with as-grown HfO_2 films



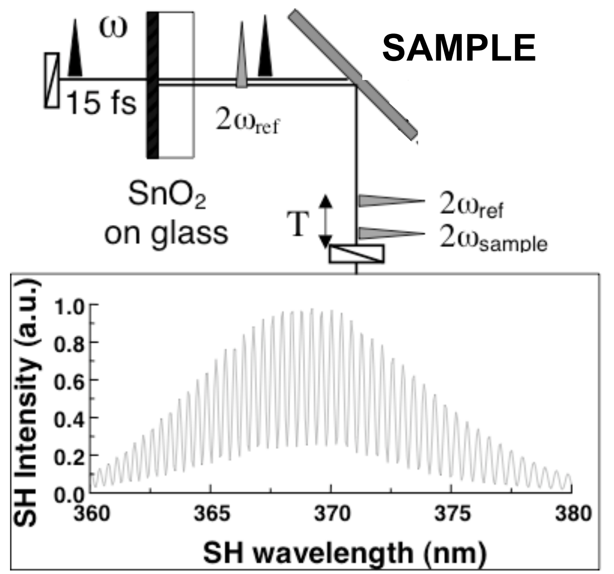






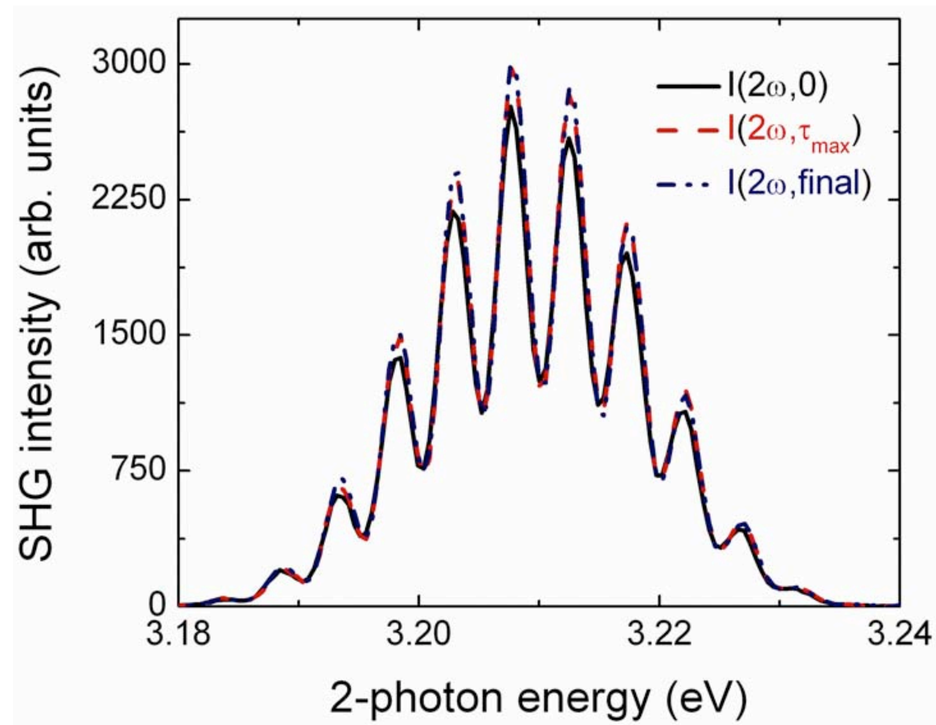
Time-dependent FDISH* measurements show no variation in SHG phase during scan

$$I_{2\omega}(t) \propto \Big|\,\big|\chi^{(2)}\big| + \big|\chi^{(3)}\big|\, e^{i\Phi(t)} E_{DC}(t)\Big|^2 I_{\omega}^2$$



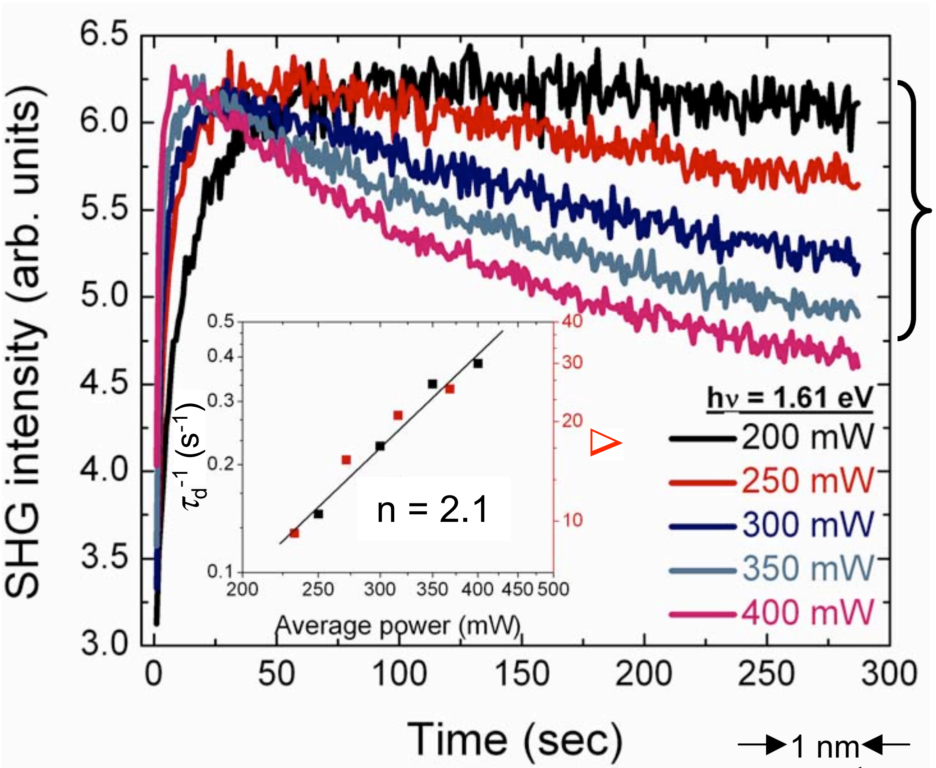
*Frequency-Domain Interferometric Second-Harmonic (FDISH)

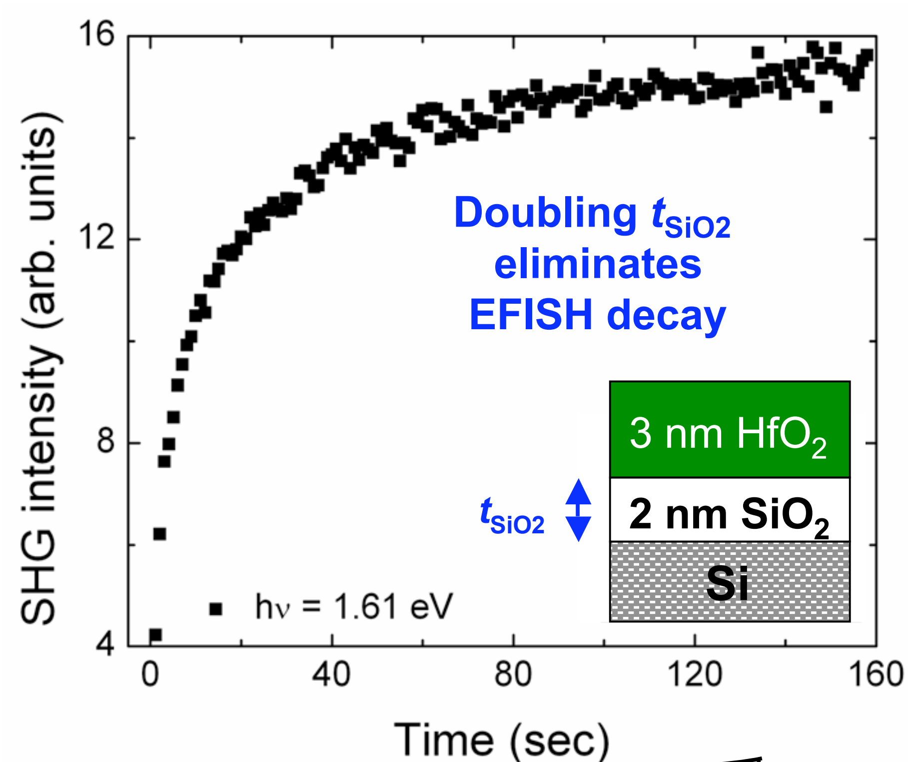
Wilson *et al*., Opt. Lett. **24**, 496 (1999)



This rules out the possibility that EFISH decay is destructive interference between $\chi^{(2)}$ and monotonically growing $\chi^{(3)}E_{DC}(t)$ $e^{i\Phi(t)}$

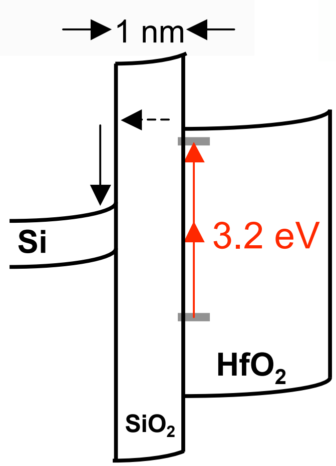
Resonant EFISH decay depends quadratically on incident power ...





... indicating it is induced by 2-photon excitation of transition with $2h\nu_{laser}$ = 3.2 eV

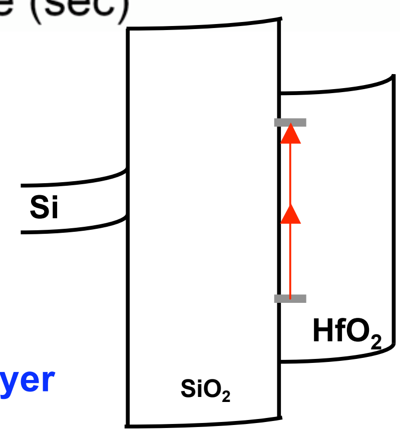
... placing the ground state below the Si VB maximum



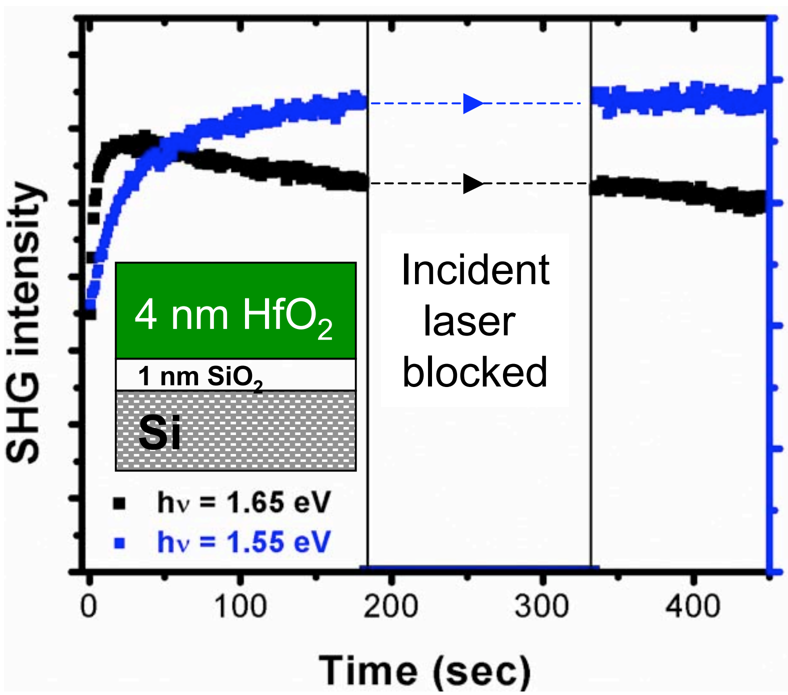
t_{SiO2}: 1 → 2 nm

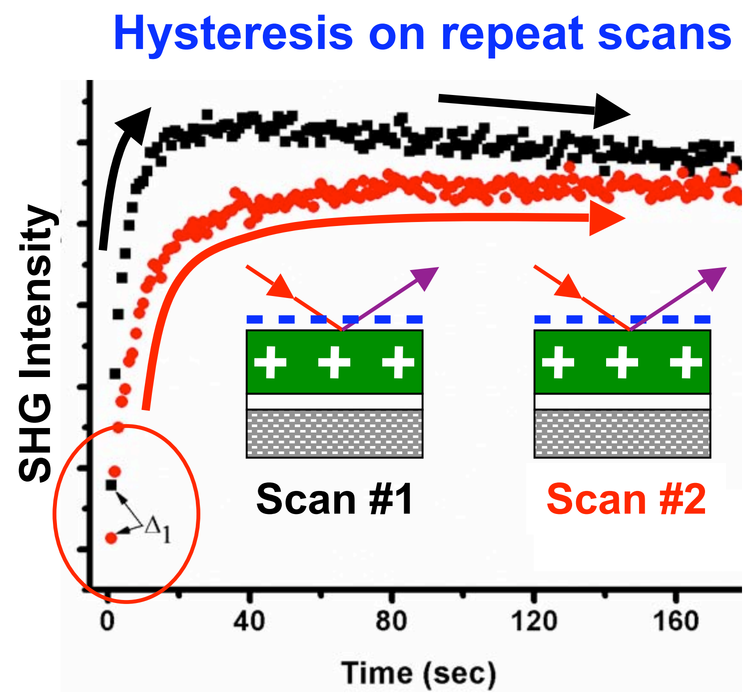
τ_{tunnel}: $10^{-6} \rightarrow 10^{4}$ s

locates defect in HfO_2 layer

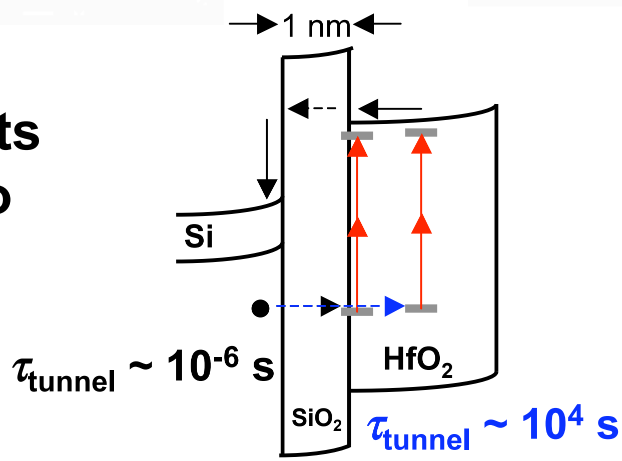


The photo-ionized defect ground state takes several hours to refill from the Si VB ...

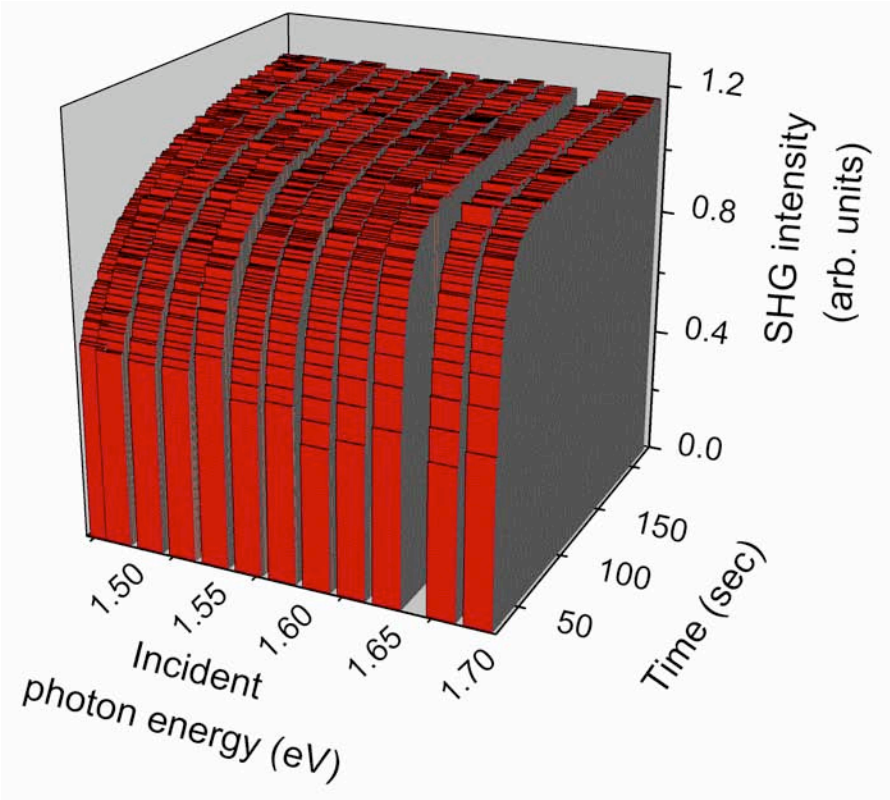


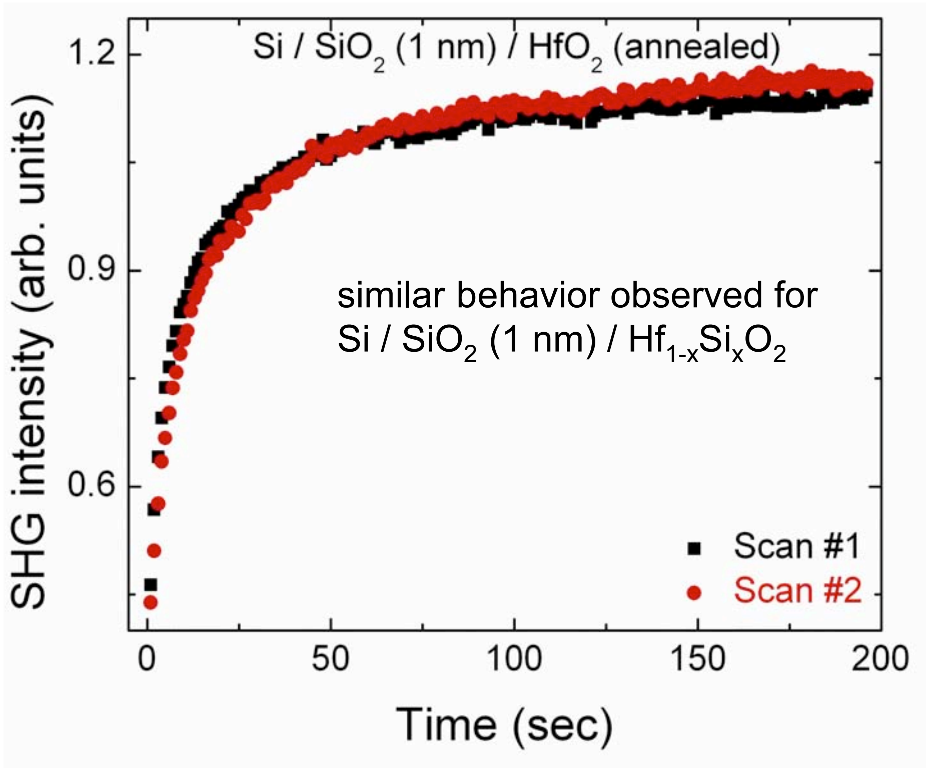


... indicating the defects are located ≥ 1 nm into the HfO_2 bulk



EFISH decay is not observed for $Si/SiO_2/Hf_{1-x}Si_xO_2$ nor annealed $Si/SiO_2/HfO_2$ film stacks





Optical methods enable detection of defects prior to processing (*e.g.* annealing, device fabrication)

Ab-initio calculations identify an oxygen vacancy defect in m-HfO_2 with an optical transition energy of ~ 3.27 eV

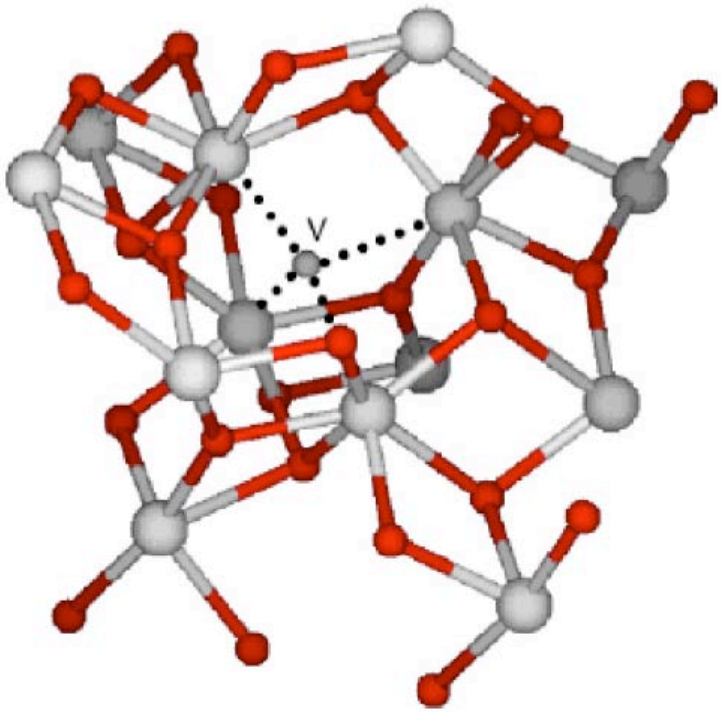


TABLE I. The optical transition energies (in eV) with the largest oscillator strength for oxygen vacancies in *m*-HfO_2 involving defect gap states. The nature of each type of transition is explained in Fig. 5.

Charge	Type III	Type IV	Type V	Type VI
V^{2+}	4.94			
V^{+}	4.67	3.27	2.67	
V^{0}		3.41	2.45	
V^{-}		3.20	2.35	0.78
V^{2-}		3.25		0.92

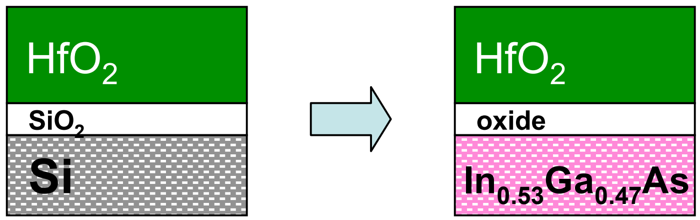
MUÑOZ RAMO *et al.* PHYSICAL REVIEW B **75**, 205336 (2007)

- V^{o}, V^{+} most stable defects (and highest oscillator strength)
- m-HfO_2 exists as small polymorphs in as-grown HfO_2, but absent in HfSiO

Summary of defects identified optically in $Si/SiO_2/HfO_2$ for the first time

Defect Energy [eV]	Location	Nature	Method
2.9	**Si/SiO_2 interface**	Oxygen vacancy; responsible for V_{fb} roll-off	**SE**
3.2	**HfO_2 bulk**	Oxygen vacancy; HfO_2-specific; removed by annealing	**SHG**
3.6	**SiO_2**	Intrinsic to Si/SiO_2	**SE**
3.9	**SiO_2**	Intrinsic to Si/SiO_2	**SE**
4.75	**SiO_2**	Oxygen vacancy; HfO_2-induced HfO_2-specifi c	**SE**

Current work: with high-k, who needs silicon?



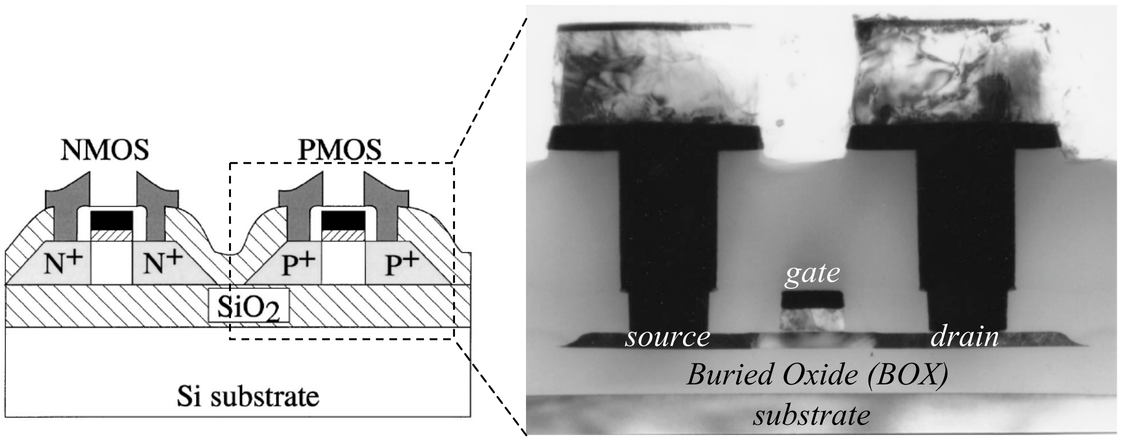
μ_n = 1350 cm²/V

μ_n = 12000 cm²/V

Since IBM introduced it in 1998,* SOI has entered the mainstream of high-performance electronics & photonics ...

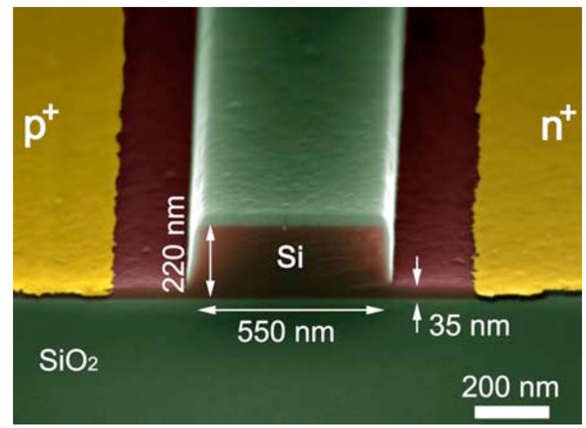
*www-03.ibm.com/press/us/en/pressrelease/2521.wss

SOI MOSFETS



Celler, Cristoloveanu, "Frontiers of SOI," J. Appl. Phys. **93**, 4955 (2003)

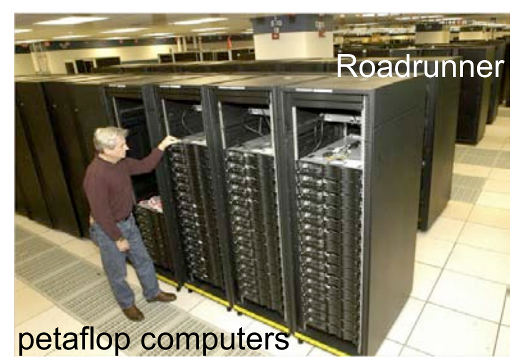
SOI waveguides & MEMS



Reed, Knights, *Silicon photonics: an introduction* (Wiley 2004)

... everyday life

... and high-end computing



SOI provides advantages over conventional ICs at 2 levels...

Celler, Cristoloveanu, "Frontiers of SOI," J. Appl. Phys. **93**, 4955 (2003)

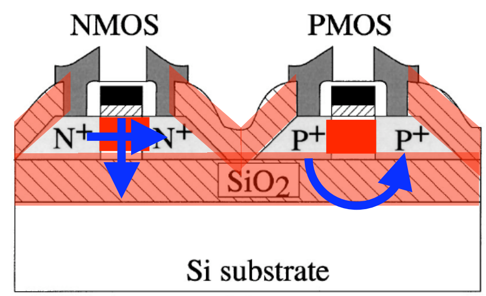
<u>IC level</u>: superior transistor isolation

conventional ICs: **p-n junction isolation*** ⇒ parasitic capacitance, limited transistor density

* J. S. Kilby, "Invention of the Integrated Circuit," Nobel Prize lecture (2000).

SOI: **dielectric isolation**

Each transistor is isolated from the Si substrate and from every other transistor by the BOX below, and by oxides above & on the sides



<u>Device level</u>: alleviate "short channel" effects

conventional ICs: $\vec{E}_{gate}$ competes with $\vec{E}_{source-drain}$ ⇒ $V_{threshold}$ roll-off, reduced reliability

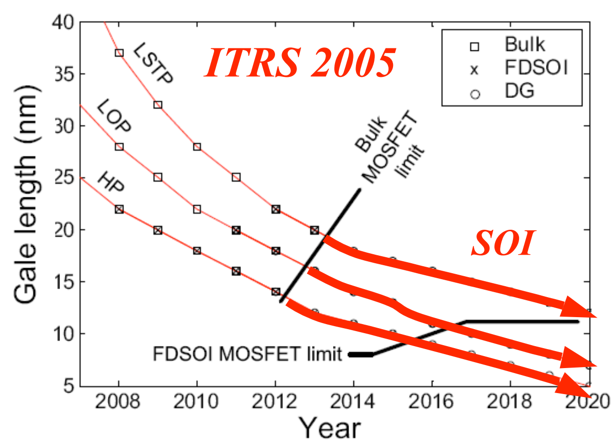
Source-Drain leakage grows ⇒ high power consumption

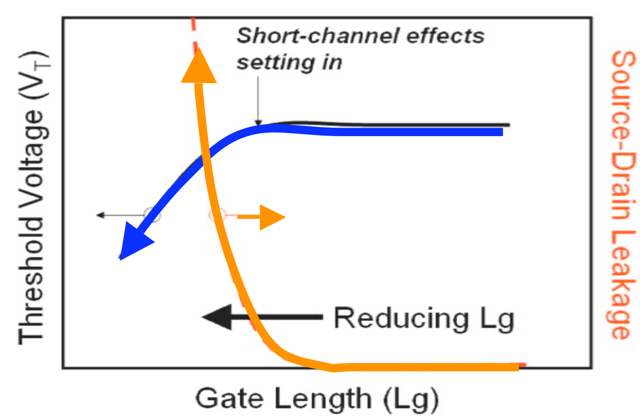
SOI: thin fully-depleted (FD) Si channel on insulator alleviates both problems

LSTP = Low Stand-by Power

LOP = Low Operating Power

HP = High Performance

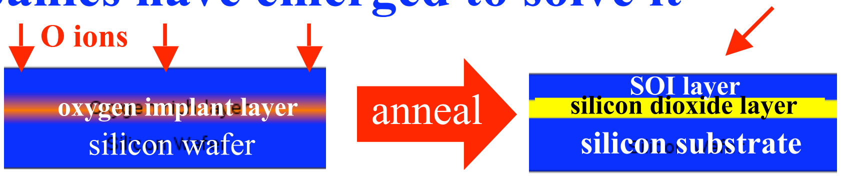




Preparing an ultrathin single-crystal Si film on an amorphous insulator is a challenging problem:

Several competing technologies & companies have emerged to solve it

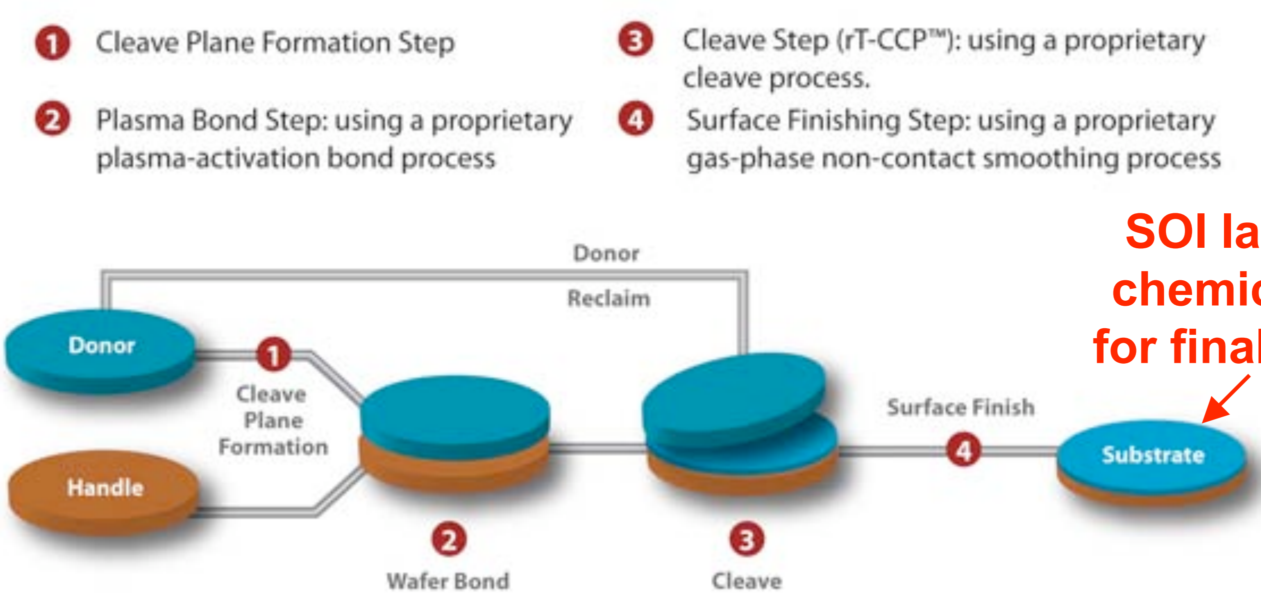
SIMOX: Separation by IMplantation of OXygen



Wafer Bonding:
Smart Cut(R) from Soitec
Layer Transfer from SiGen
ELTRAN from Canon (Yamagata *et al., Mat. Res. Soc. Symp. Proc.* **681E** (2001))

Seed Methods: Si layer grown directly on chemically-treated or crystalline insulator

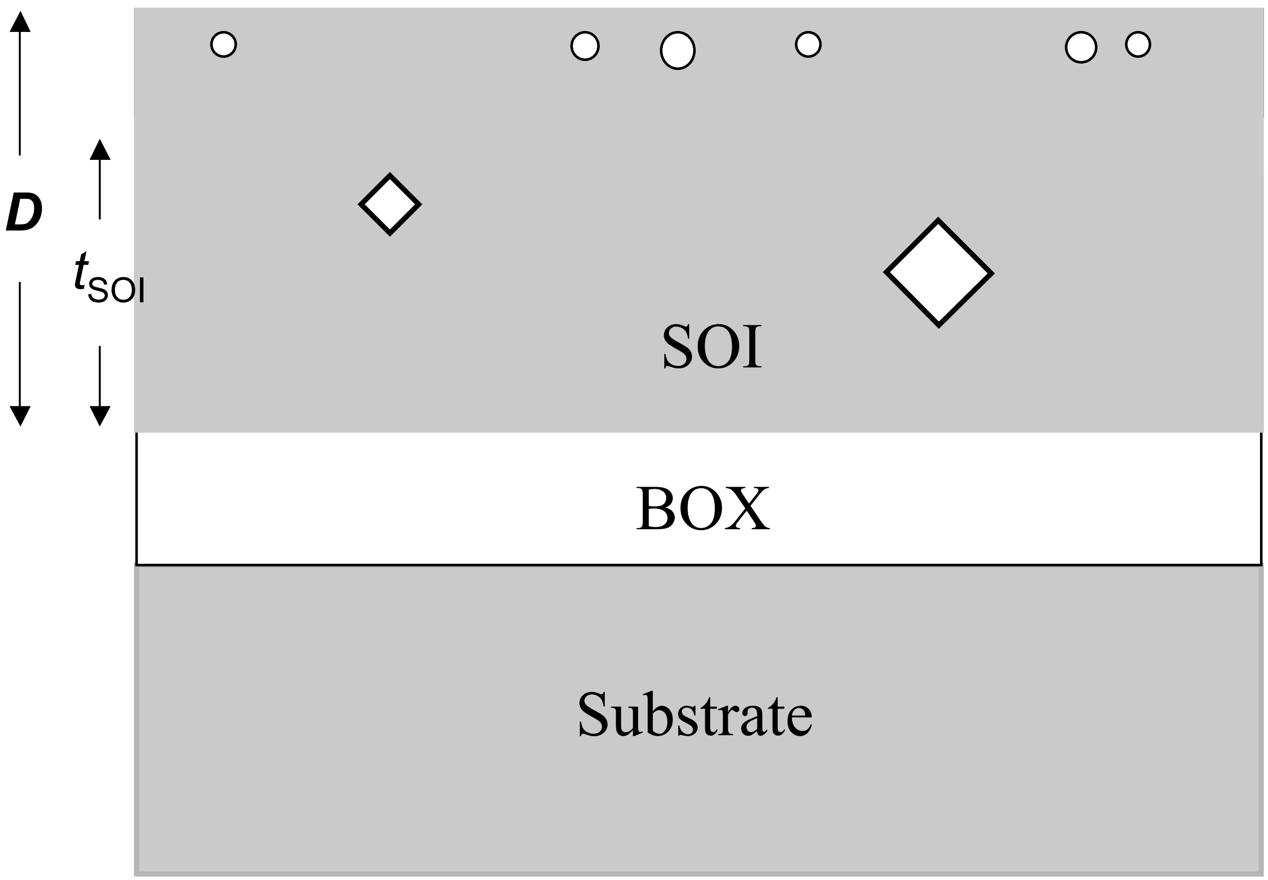
Our samples were prepared by Plasma-Activated Wafer Bonding



SOI layer must be chemically thinned for final device prep.

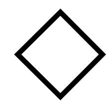
During thermal oxidation thinning, defects created at the external surface migrate to the SOI/BOX interface ...

O. Naumova *et al*, Mater. Sci. Eng., B **135**, 238 (2006)

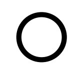


Defect density *N* increases as t_{SOI} thins, but how?

Linearly?
Super-linearly?



Crystal-Oriented-particles (COPs) formed during CZ growth

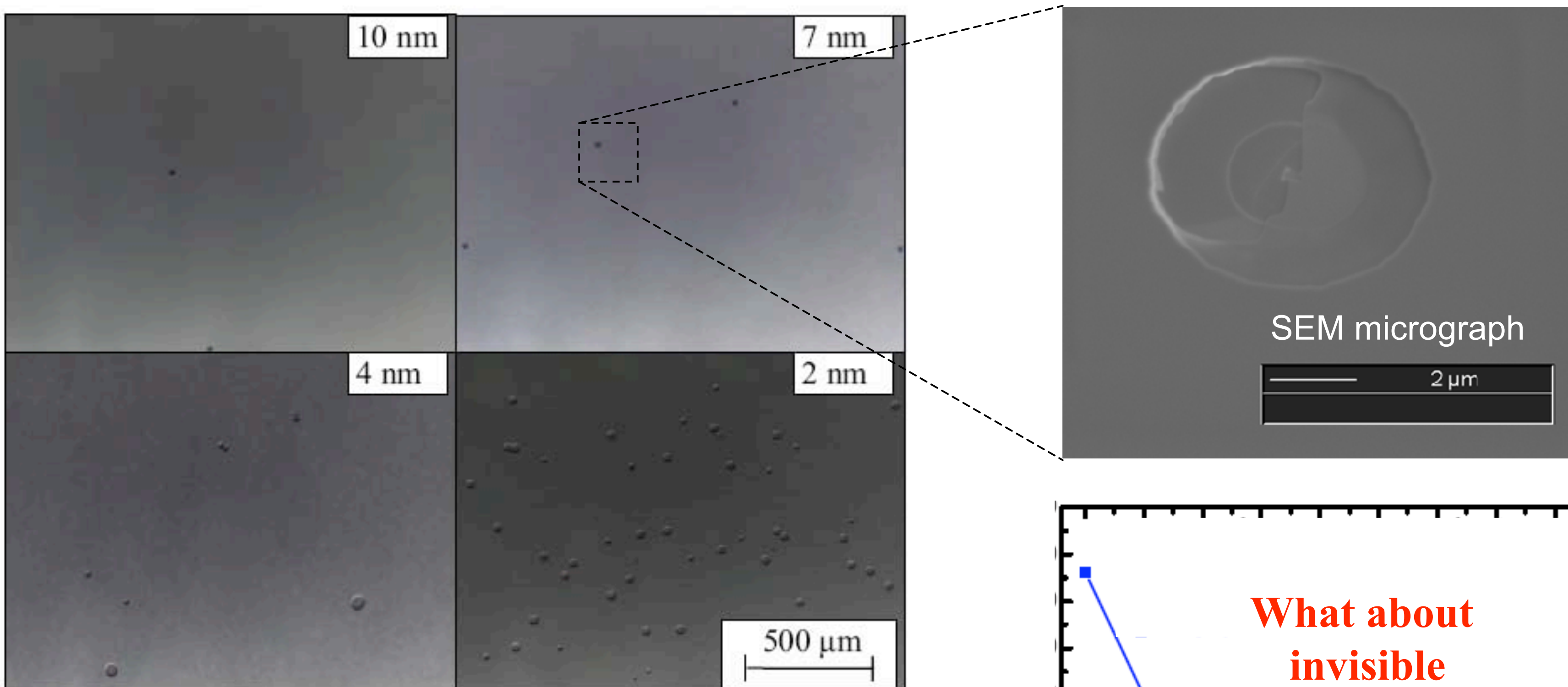


Si vacancy or O precipitate formed during SOI thinning

... where they become performance-limiting charge traps

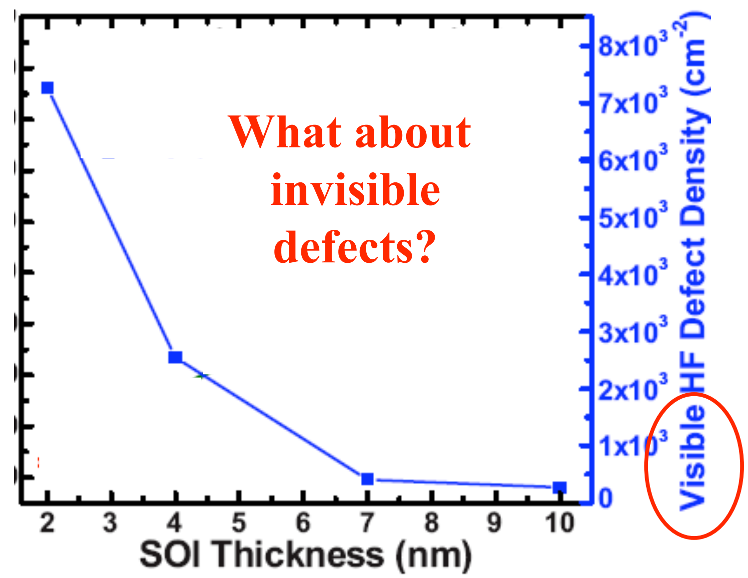
We reveal some SOI/BOX interface defects (destructively) by HF dipping (the standard diagnostic)

O. Naumova *et al*, Mater. Sci. Eng., B **135**, 238 (2006)



Optical micrographs of "punch-through" defects in 10, 7, 4 and 2 nm SOI films after HF soaking

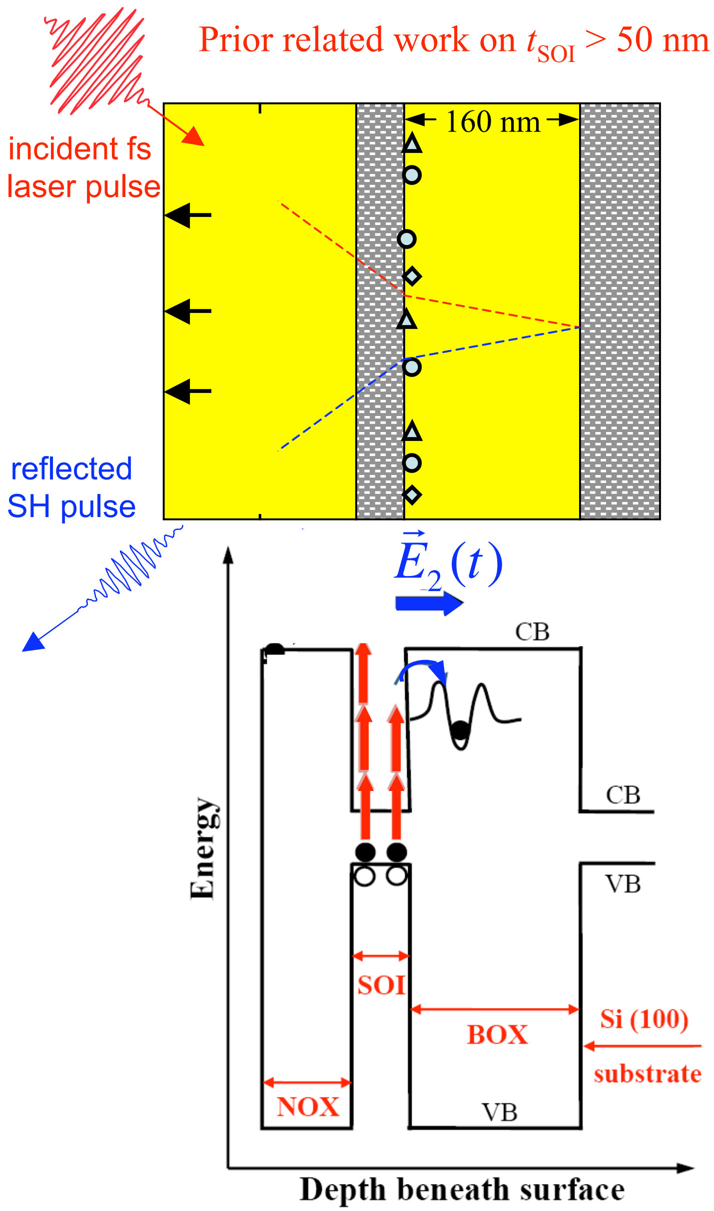
"Faster, non-destructive ways of detecting these defects are needed." ITRS 2009



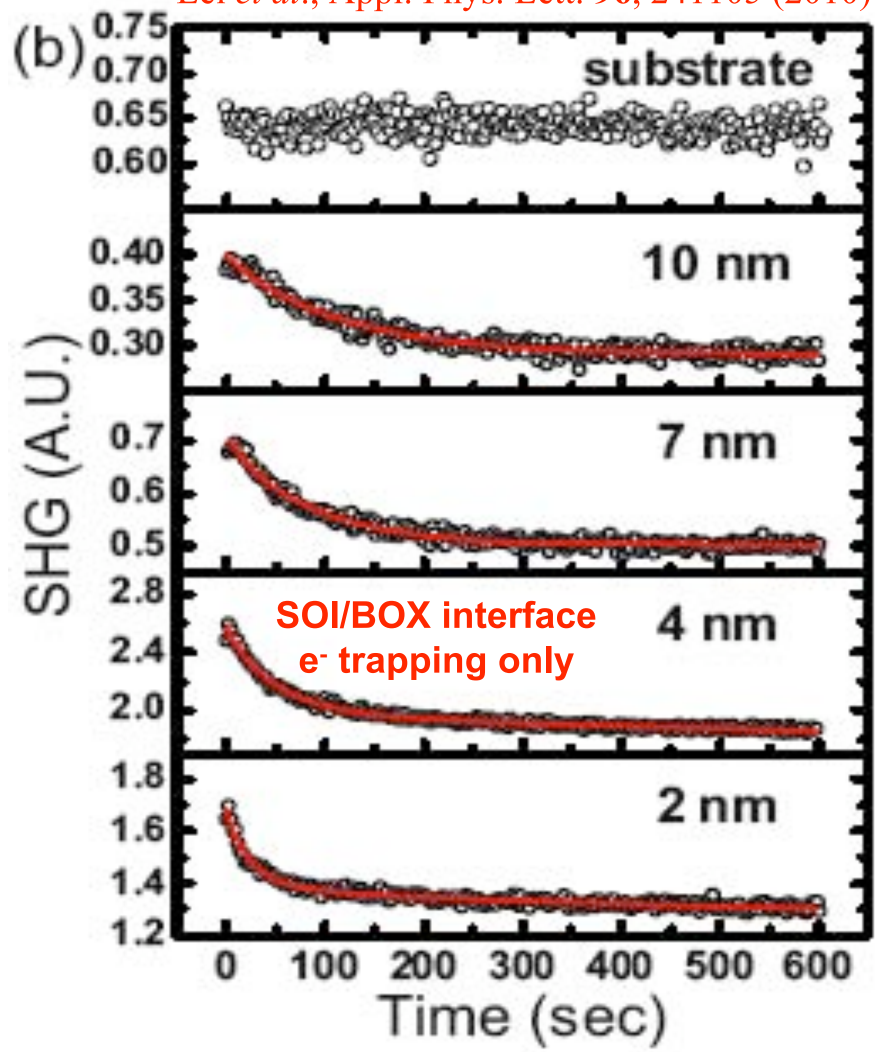
We use internal PE + SHG to detect trapping of hot carriers in <u>ultrathin</u> (t_{SOI} < 10 nm) films

Prior related work on t_{SOI} > 50 nm films: Alles *et al*., IEEE Trans. Semicond. Manuf. **20**, 107 (2007)

Jun *et al*., Appl. Phys. Lett. **85**, 3095 (2004)

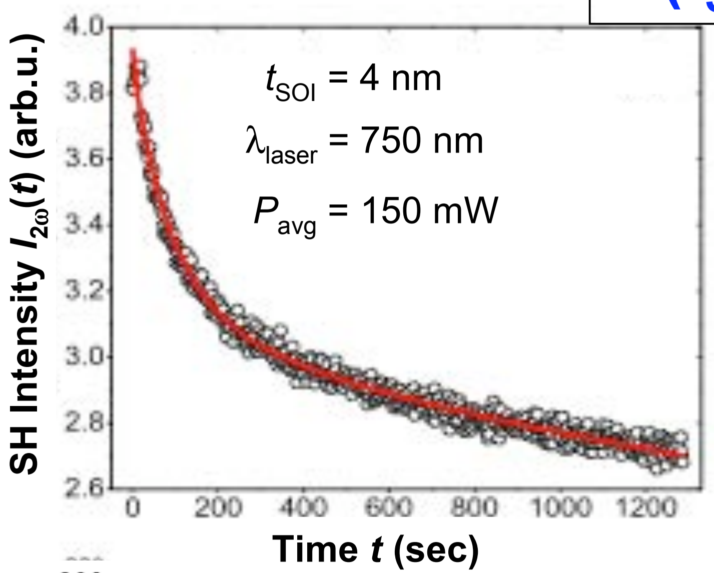


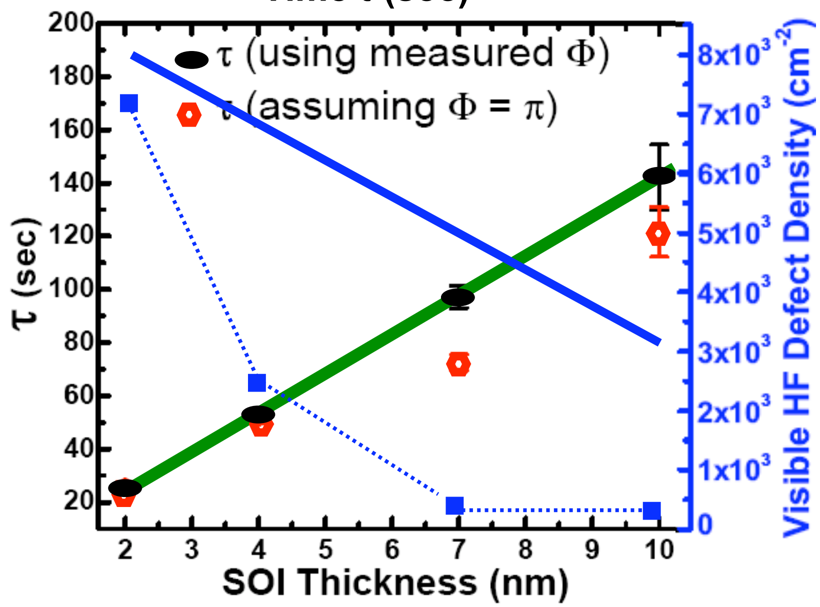
Lei *et al*., Appl. Phys. Lett. **96**, 241105 (2010)



Quantitative analysis of TD-EFISH reveals defect density at SOI/BOX interface increases linearly as t_{SOI} thins

$$N(t_{SOI}) = \eta(D - t_{SOI}) + N_0$$





$E_2(t) \propto q_{trapped}(t) \propto 1 - e^{-t/\tau}$ + small correction

$$I_{2\omega}(t) \propto |\chi^{(2)} + \chi^{(3)} E_2(t)|^2$$

$$\propto |p_0 + (1 - e^{-t/\tau})\, e^{i\Phi}|^2$$

measured by FDISH*

t_{SOI} [nm]	Φ [rad]
2	2.82 ± 0.22
4	3.03 ± 0.18
7	2.06 ± 0.13
10	2.35 ± 0.34

$$\tau^{-1} \propto N(t_{SOI})$$

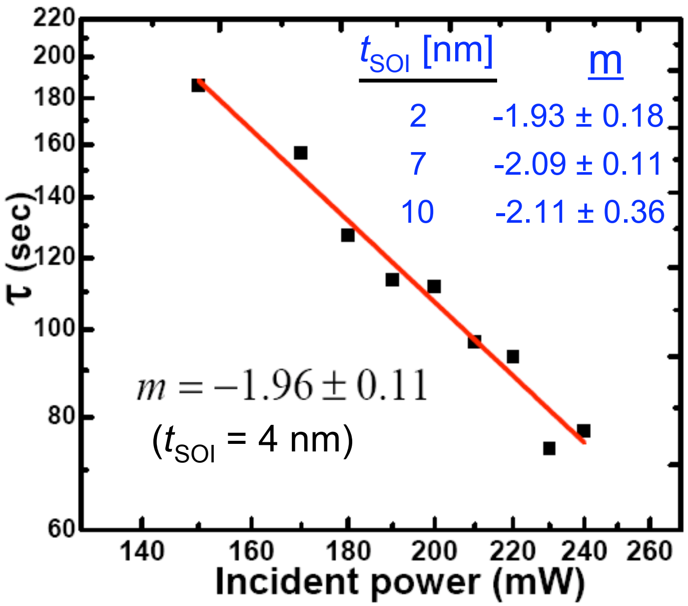
$$\Rightarrow \tau \propto N^{-1}(t_{SOI})$$

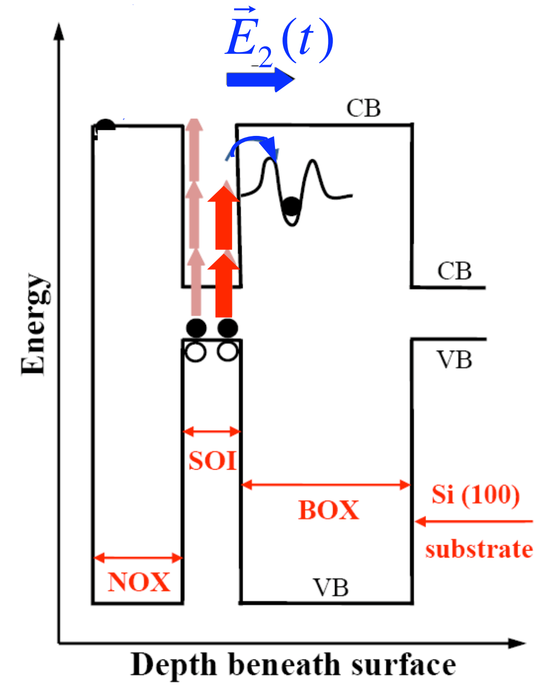
$$\propto \frac{1}{N_o + \eta D}\left[1 + \frac{\eta t_{SOI}}{N_o + \eta D} + \ldots\right]$$

for $\eta t_{SOI} << N_0 + \eta D$

(valid for ultrathin SOI)

Power-dependence shows SOI/BOX interface defect levels are excited by a two-photon process ...





... and thus lie ≥ 1 eV below SiO_2 CB edge

But spectral dependence is weak for $1.5 \leq h\nu_{laser} \leq 1.7$ eV; no sharp resonant features observed.

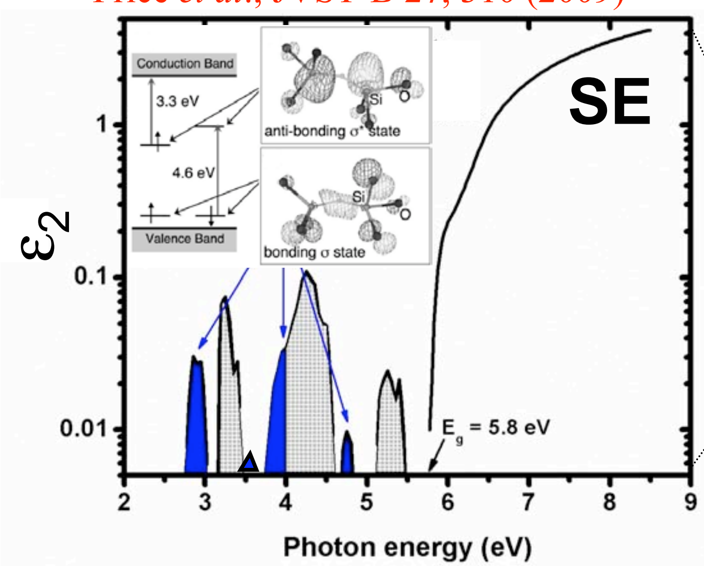
SUMMARY

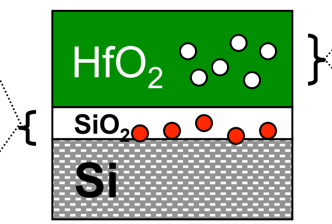
Epi-optics provides one answer to the clarion call of ITRS 2009:

"Faster, non-destructive ways of detecting these defects are needed."

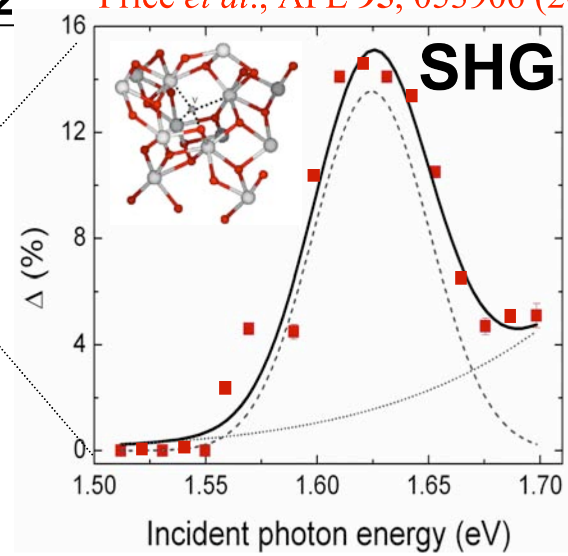
$Si/SiO_2/Hf_{1-x}Si_xO_2$

Price *et al.*, JVST-B **27**, 310 (2009)

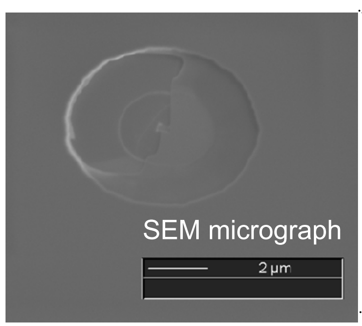


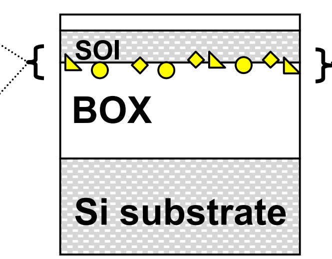


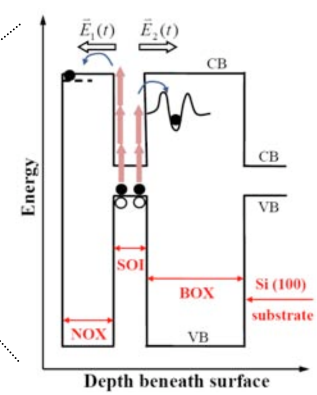
Price *et al.*, APL **95**, 053906 (2009)



Ultrathin SOI







Lei *et al.*, APL **96**, 241105 (2010)

END