2007 International Conference on Frontiers of Characterization & Metrology for Nanoelectronics

Optical Characterization Methods for Identifying Charge Trapping States in Thin Dielectric Films

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Accelerating the next technology revolution.

Outline:

- Introduction
- Dielectric defects and device performance
- Sub-E_g absorption measurements (SE)
- Second Harmonic Generation (SHG)
- Electric field-induced changes in E_g (SE)
- Conclusions & acknowledgements

What drives Characterization & Metrology?

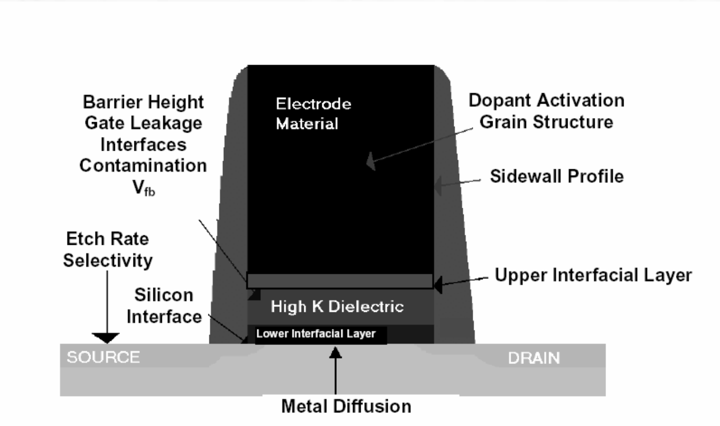
In the past (CMOS & microelectronics):

- R & D
- Typical process needs (thickness, composition, etc.)

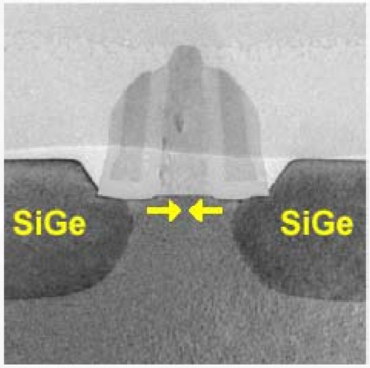
In the Future (advanced CMOS & nanoelectronics):

- New metrology metrics (New gate stacks, strain, 3D, etc)

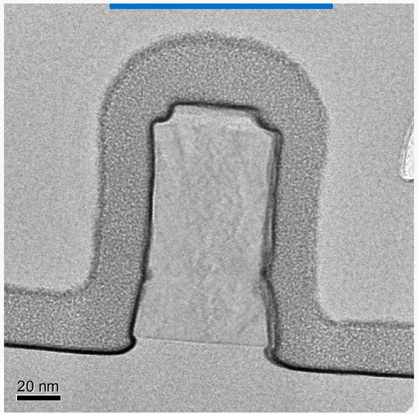
Advanced gate stacks



Strained channels



FINFETS



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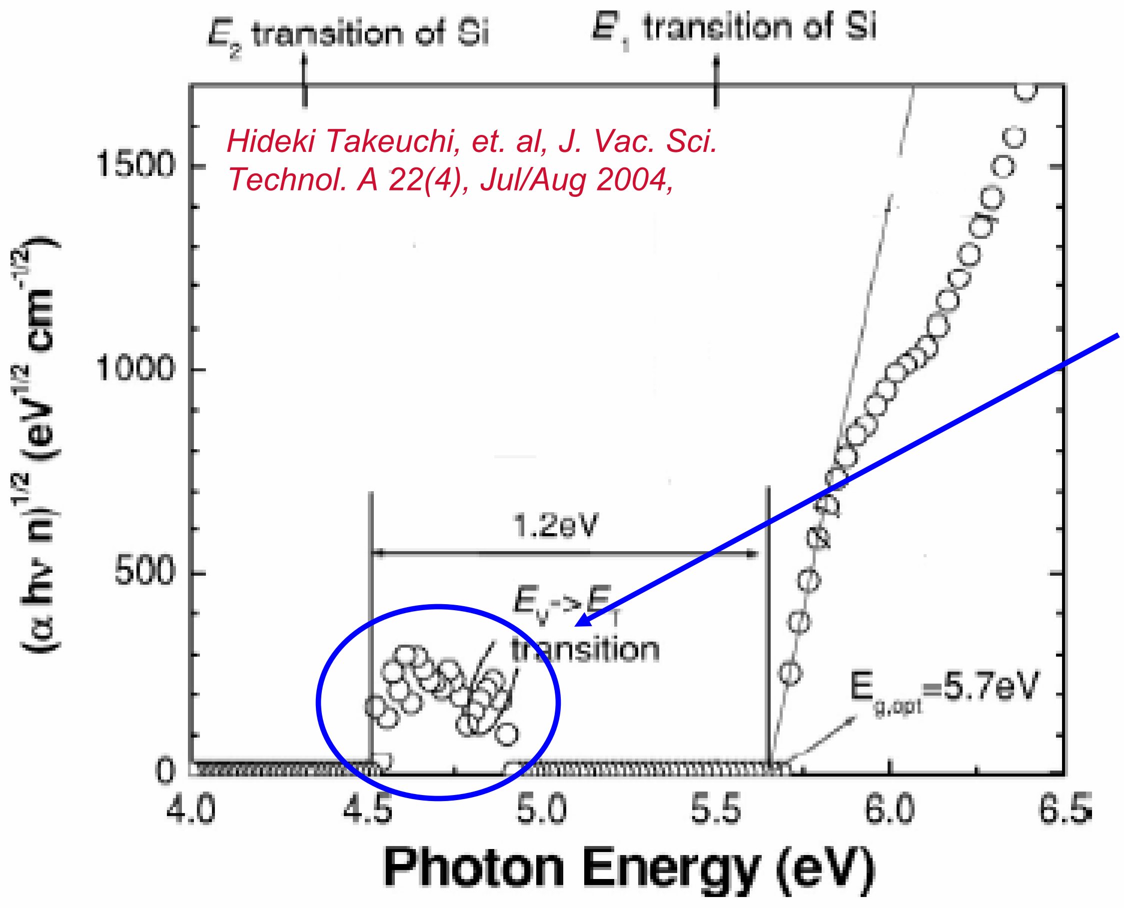
- “Do more for less”, and “The all inclusive package”

1st Observations of O_2 vacancies using SE:

An example of extending existing metrology platforms with new applications.



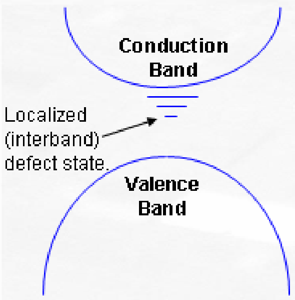
Hideki Takeuchi, et. al, J. Vac. Sci. Technol. A 22(4), Jul/Aug 2004,

Sub-bandgap absorption region indicative of defect states for HfO_2.

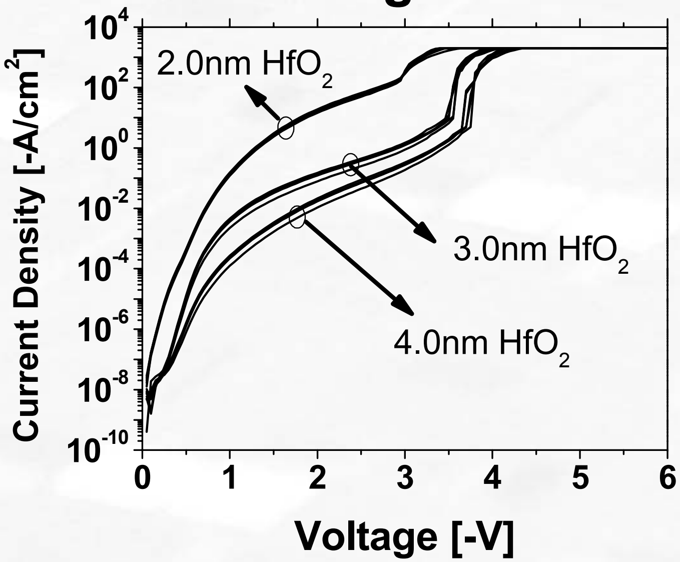
Potential to extend SE beyond physical characterization and towards electrical characterization!

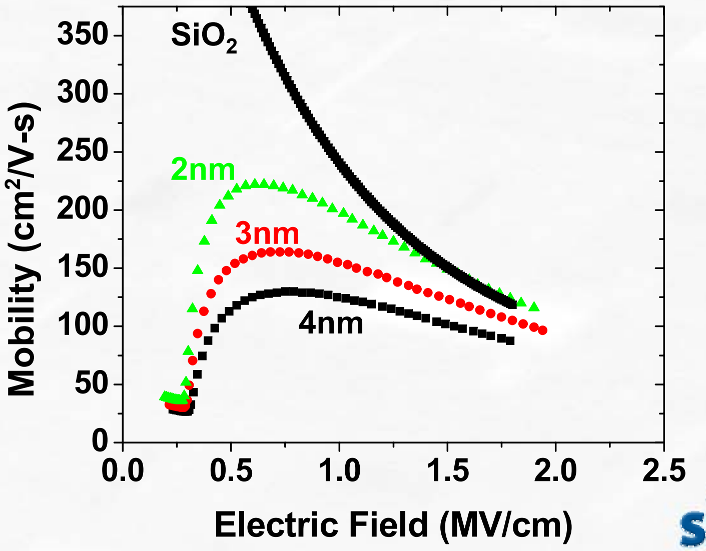
Dielectric defects and device performance:

- **What are they? Anything that can trap electrons.**
  - 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?**
  - Degradation of carrier mobility.
  - Charge trapping.
  - increase in leakage current.





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

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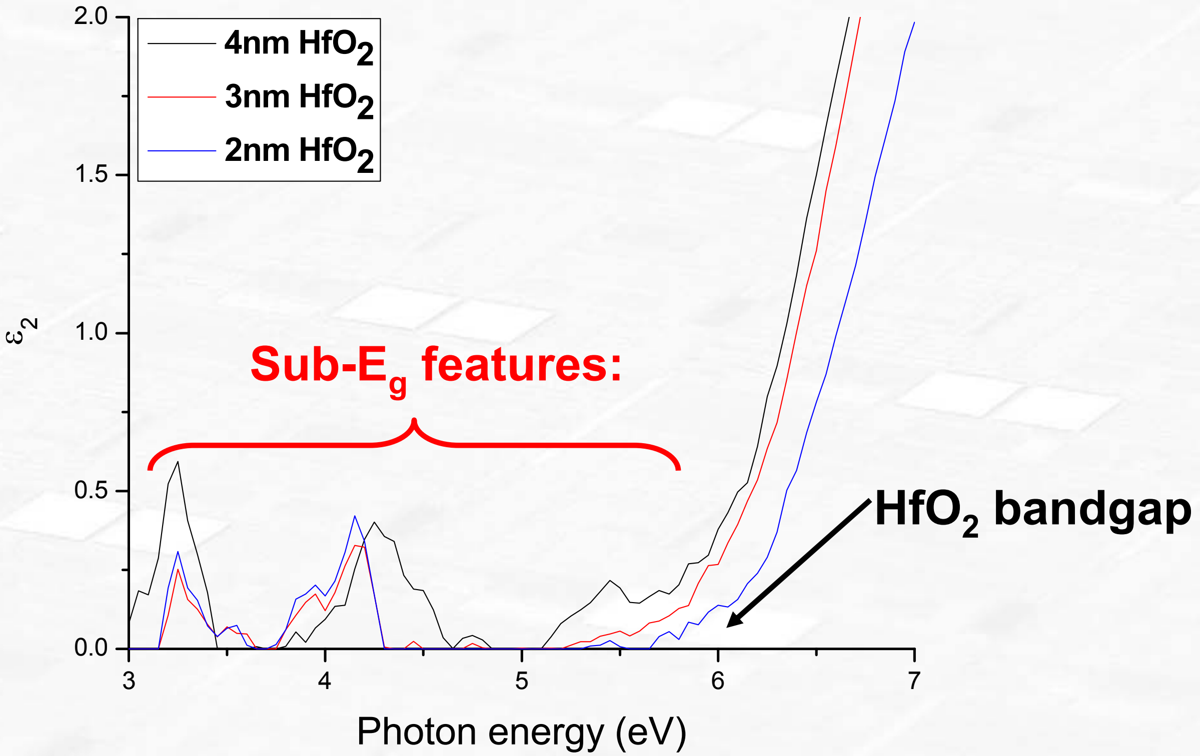
Sub-E_g absorption measurements:



- Agrees with electrical results (i.e. less defects for thinner films)
- Agrees with theory (i.e. energy location of defects calculated by DFT)
- Also verified for other material systems (HfSiON, HfTaTiO, etc.)
- But…

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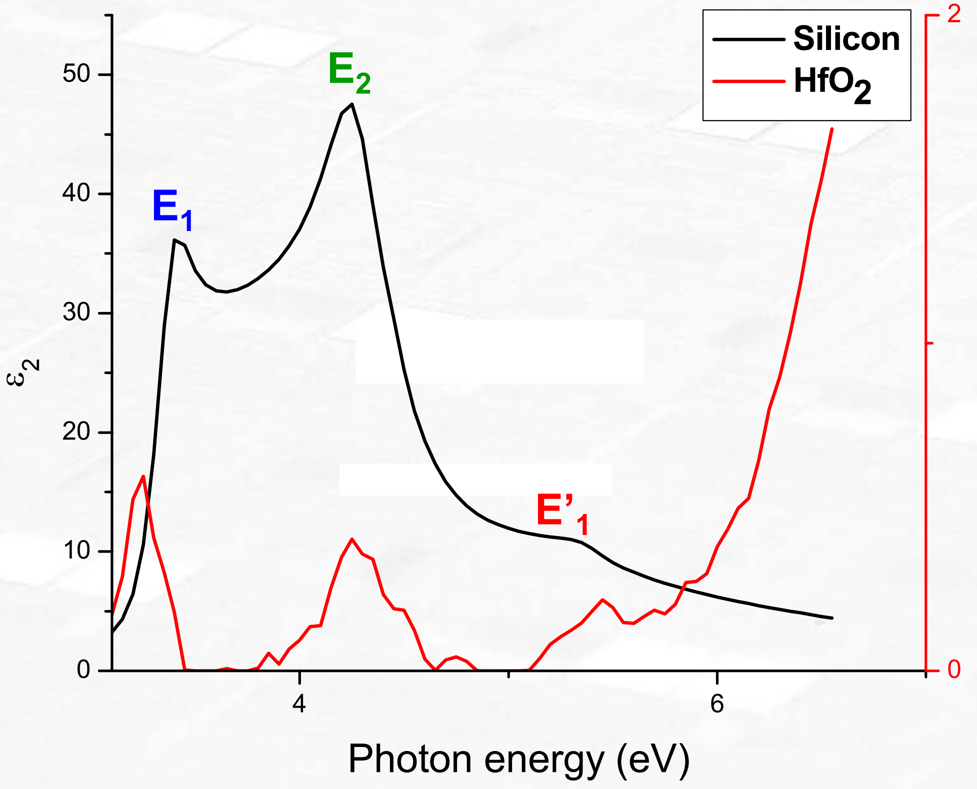
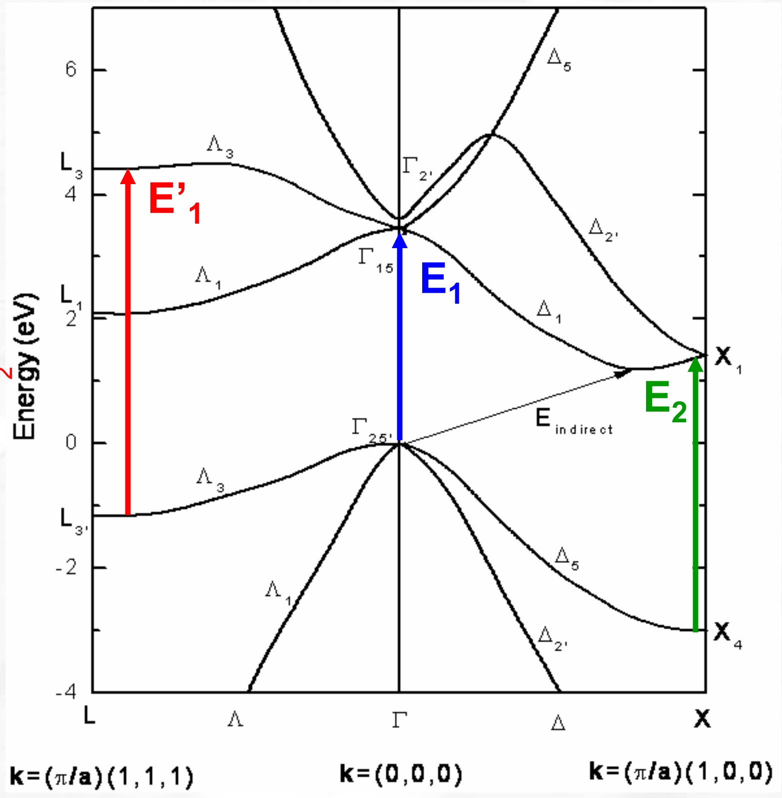
Sub-E_g absorption measurements:

Sub-E_g absorption features coincidentally appear at same energy as silicon critical points!

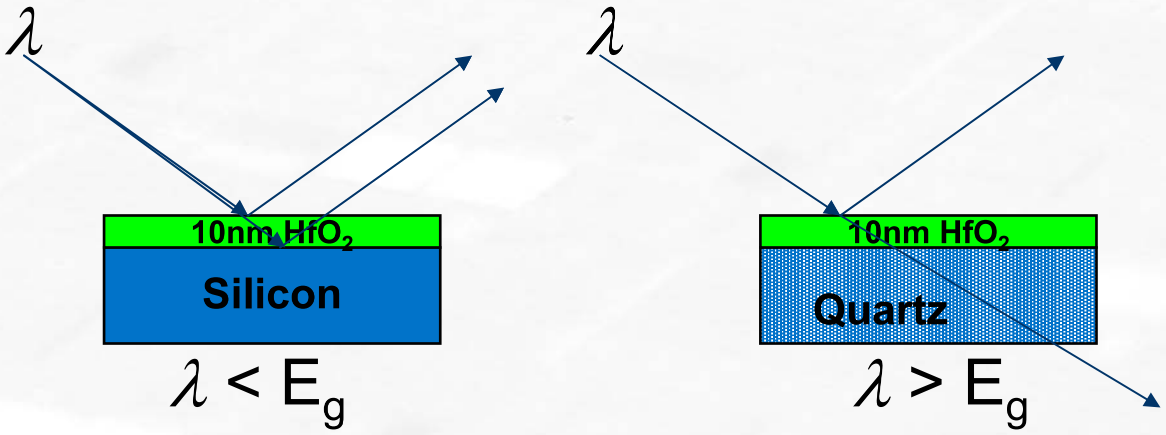




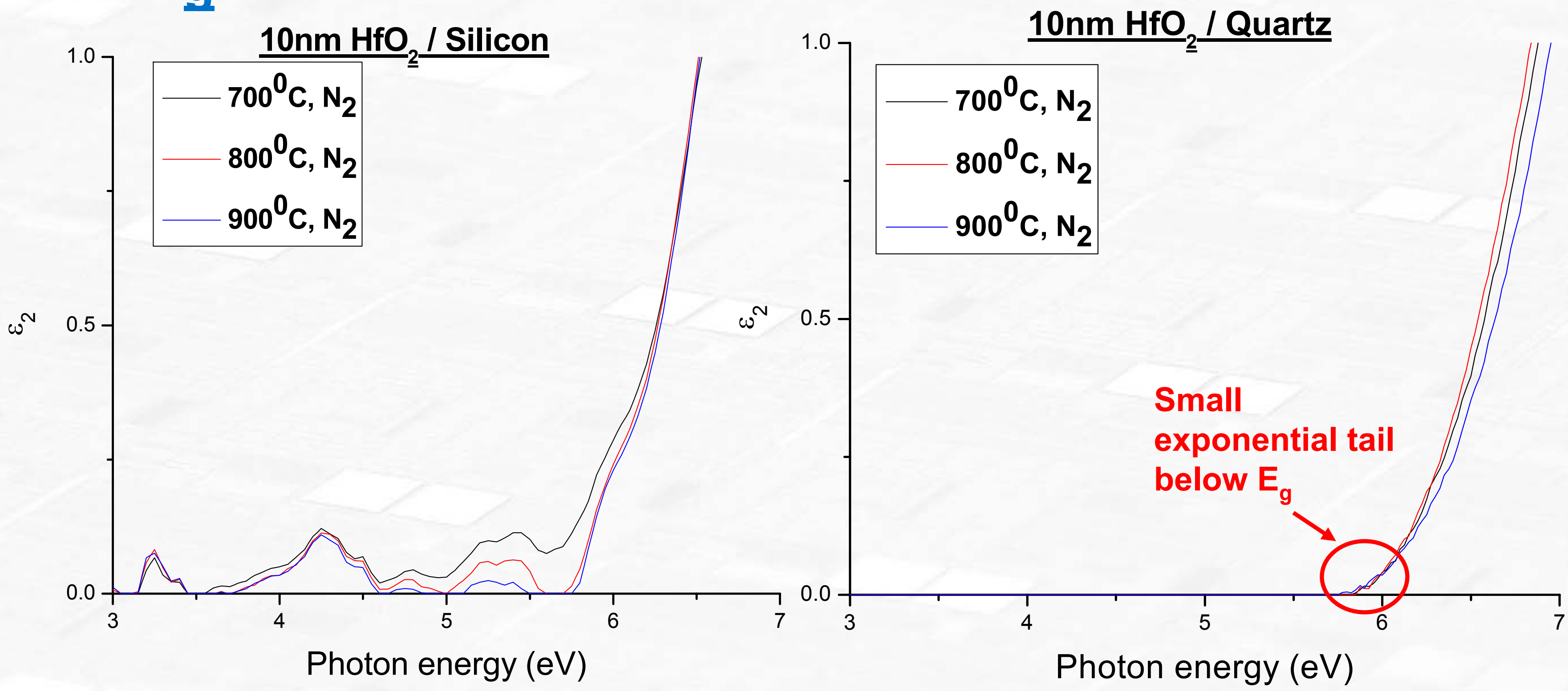
Are we mistakenly identifying substrate effects instead of dielectric defects?

Sub-E_g absorption measurements:

- If we suspect the silicon substrate is contributing to our data, what happens if we deposit the HfO_2 on a quartz substrate:
    - » No critical points
    - » No absorption (Band gap ~ 9.0eV)
    - » Easy to characterize optically
- Therefore, any absorption observed would be solely attributed to the HfO_2 film.
- Deposited three 10nm HfO_2 films on each substrate and annealed at 700^0C, 800^0C, and 900^0C.



Sub-E_g absorption measurements:


10nm HfO_2 / Silicon

10nm HfO_2 / Quartz

Small exponential tail below E_g

- **Below band gap absorption tail still present for quartz samples!**
- **But, Silicon absorption peaks are now absent!**

Why are silicon critical point features appearing in the optical spectra of the dielectric?

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- **Second Harmonic Generation (SHG)**
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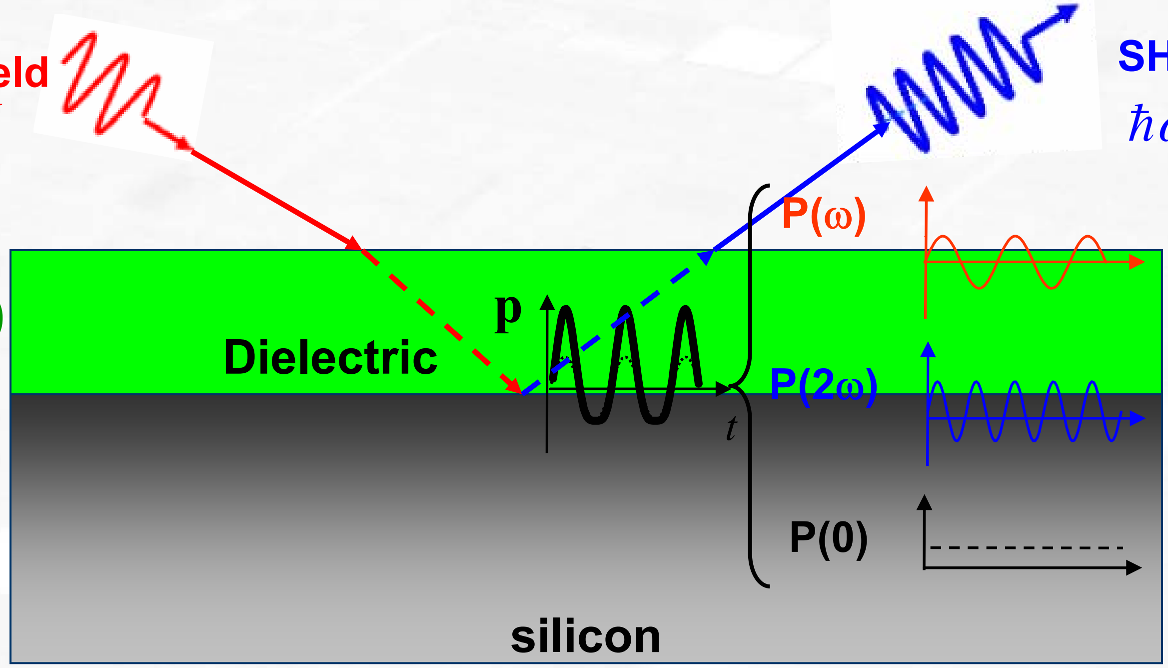
Second Harmonic Generation:

Second Harmonic Generation (SHG) is a non-invasive optical probe that is sensitive to surfaces, interfaces, and electrostatic fields in centrosymmetric materials.

When using a high intensity laser, a perturbative approach must be used to understand the electric dipole response and induced polarization in the medium:

$$\vec{P}(\omega)=\chi^{(1)}\vec{E}(\omega)+\chi^{(2)}\vec{E}^{2}(\omega)+\chi^{(3)}\vec{E}^{3}(\omega)+\dots$$
$$=\vec{P}^{(1)}(\omega)+\vec{P}^{(2)}(2\omega)+\vec{P}^{(3)}(3\omega)+\dots$$

Symmetry arguments restrict $\chi^{(2)}$ to be zero. But may be non-zero where symmetry is broken or E-fields are present.



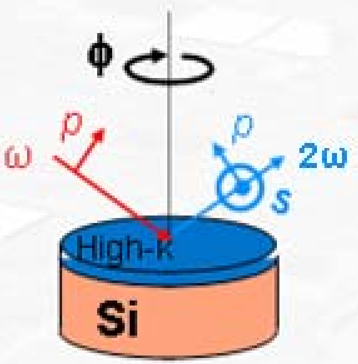
Incident EM field
$\hbar\omega=1.65eV$

SH radiation
$\hbar\omega=3.3eV$

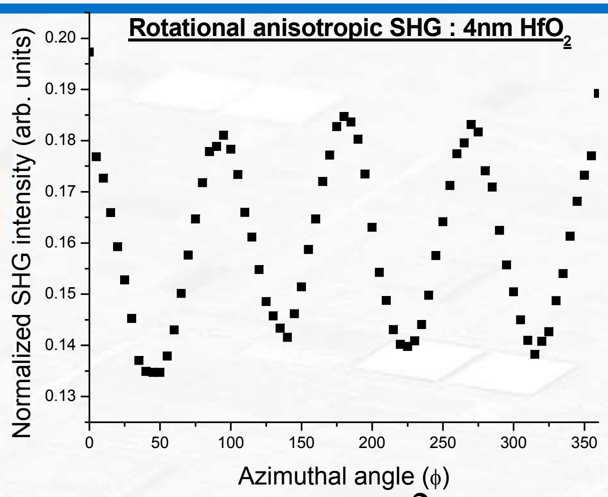
$$\chi^{(2)}_{dielectric}=0$$

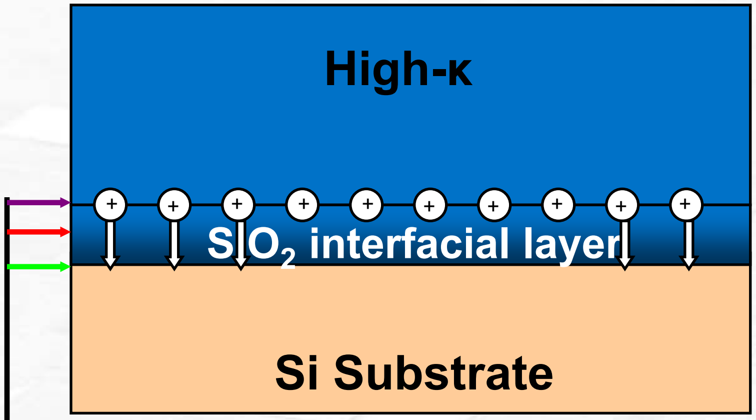
$$\chi^{(2)}_{silicon}=0$$

Second Harmonic Generation (SHG):



Rotational anisotropic SHG : 4nm HfO_2





$$I_{PP}^{(2\omega)} = \left| a_0^{PP} + a_4^{PP} Cos(4\varphi) \right|^2$$

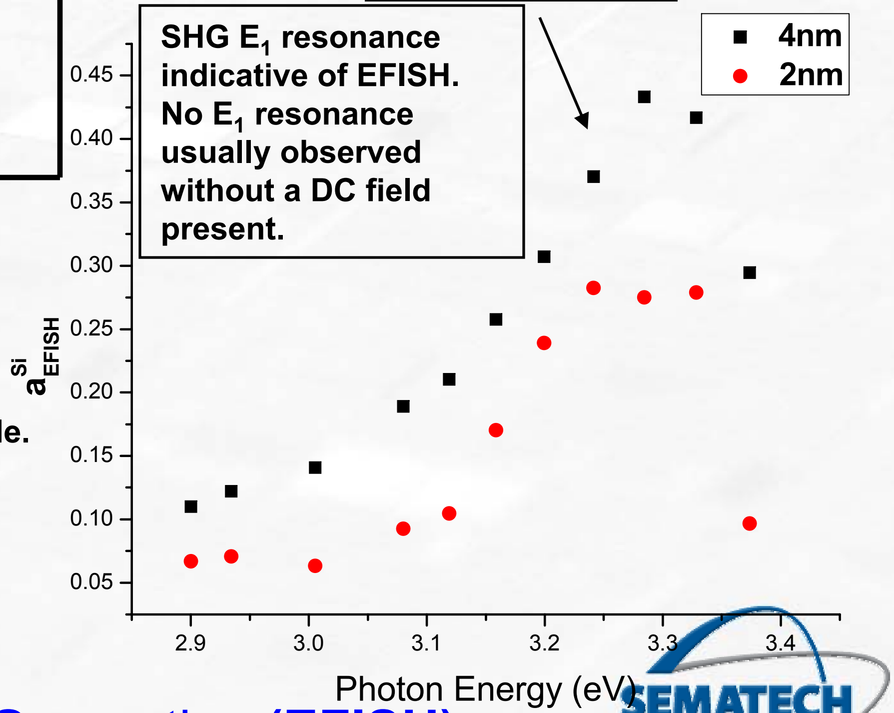
- a_4^{PP} is from silicon, but very weak

$$a_0^{PP} = \underbrace{\cancelto{0}{a_0^{Si/SiO_2}} + \cancelto{0}{a_0^{SiO_2/High-k}}} + a_{EFISH}^{Si}$$

Previous work demonstrated these two coefficients are negligible.

- $\therefore a_{EFISH}^{Si} \neq 0$ **(Dominant contribution)**

Spectroscopic SHG



SHG E_1 resonance indicative of EFISH. No E_1 resonance usually observed without a DC field present.

Electric **F**ield **I**nduced **S**econd **H**armonic **G**eneration **(EFISH).**

Second Harmonic Generation (SHG):

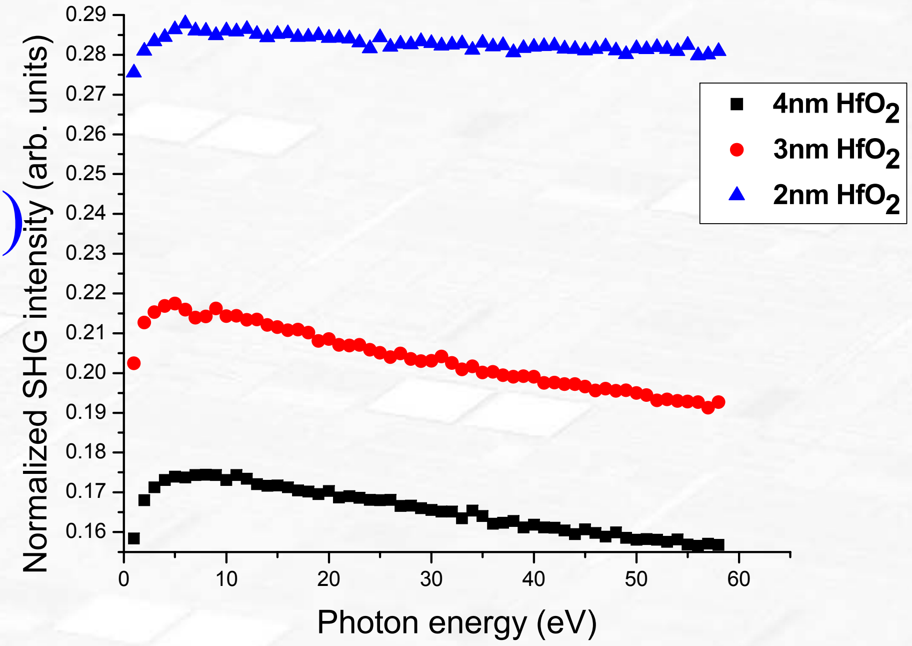
Time Dependent SHG (TD-SHG):

Lack of inversion symmetry can be created by electric fields:

$$I^{2\omega}(t) \propto \left|\chi^{(2)} + \chi^{(3)} E_{DC}(t)\right|^2 I^2(\omega)$$

TD-SHG provides information on:

- **Trap Densities and Lifetime**
- **multiphoton electron-hole injection and dynamics.**



What's SHG telling us?

- ➢ Interfacial electrostatic fields are primary contribution to SHG response.
- ➢ These interfacial fields are modified by subtle film growth conditions (thickness, composition, and anneal temperature).
- ➢ Thermal assisted electrons from the substrate, trapped in the dielectric defect centers, are the source of these DC field.

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E-field induced changes in ε:

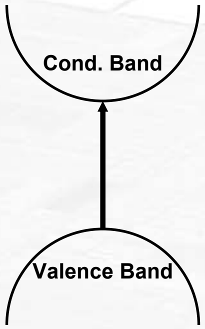
- **Does this explain the Sub-E_g SE anomalies?**
  - ➢ SE data analysis uses an “un-perturbed” silicon dielectric function.
  - ➢ Perhaps these interfacial electrostatic fields are affecting the silicon dielectric function, and subsequently, the SE data analysis.

Instead of measuring the direct effect of these defect states on the high-κ optical properties, how about trying to measuring the indirect effects imposed on the underlying silicon substrate?

E-field induced changes in ε:

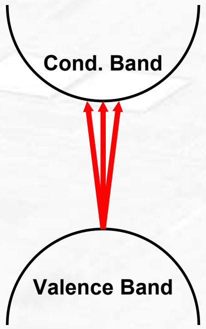
Crystalline silicon dielectric function:

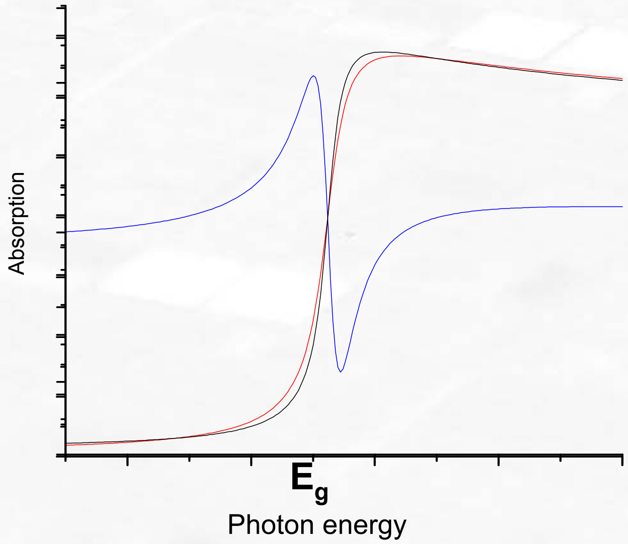
$$\varepsilon \propto \delta(E_g - \hbar\omega)$$



DC field-induced effect on the dielectric function:

$$\varepsilon \propto Ai(E_g - \hbar\omega)$$





Change in the dielectric function:

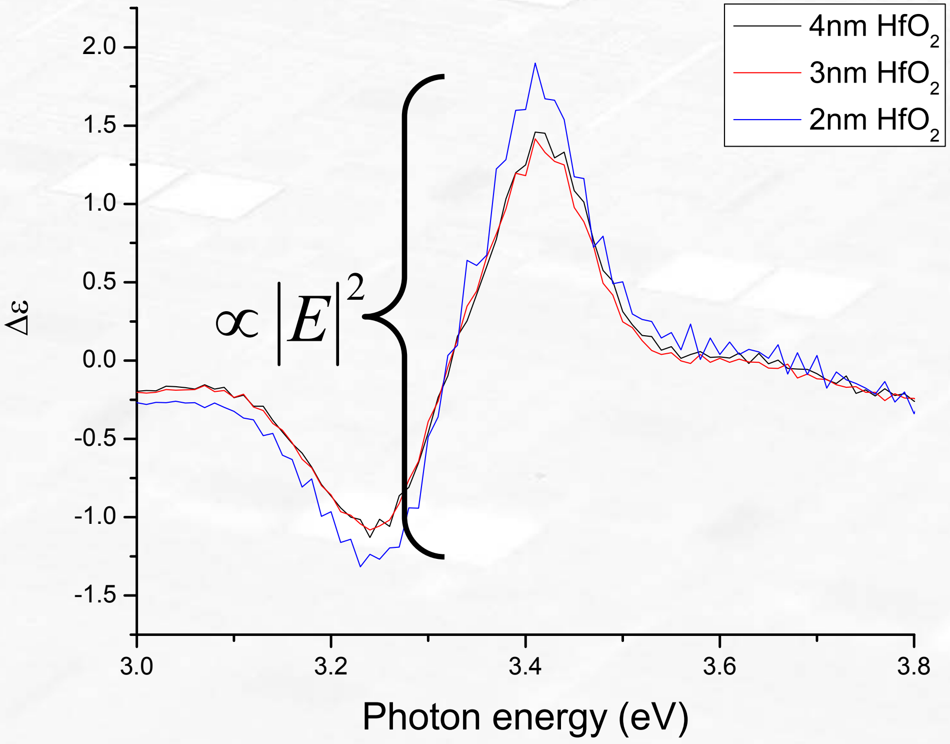
$$\Delta\varepsilon \propto |E|^2 \frac{\partial^3(\varepsilon_0)}{\partial(\hbar\omega)^3}$$

1. **Amplitude scales quadratically with field.**
2. **Band gap does not change.**

Foundation of optical modulation techniques which use an externally applied electric field to induce a change in the band structure.

E-field induced changes in ε:

- **Looked at the same samples previously measured with Sub-E_g SE, SHG, and verified with electrical data.**
- **For each sample, measured the silicon dielectric function before and after HfO_2 deposition, and then subtracted the two.**



Note, if strain were responsible for the change in the silicon dielectric function, we would observe a shift in E_g. In this case, all three spectra have an inversion origin at 3.375 eV (i.e. the silicon direct band gap).

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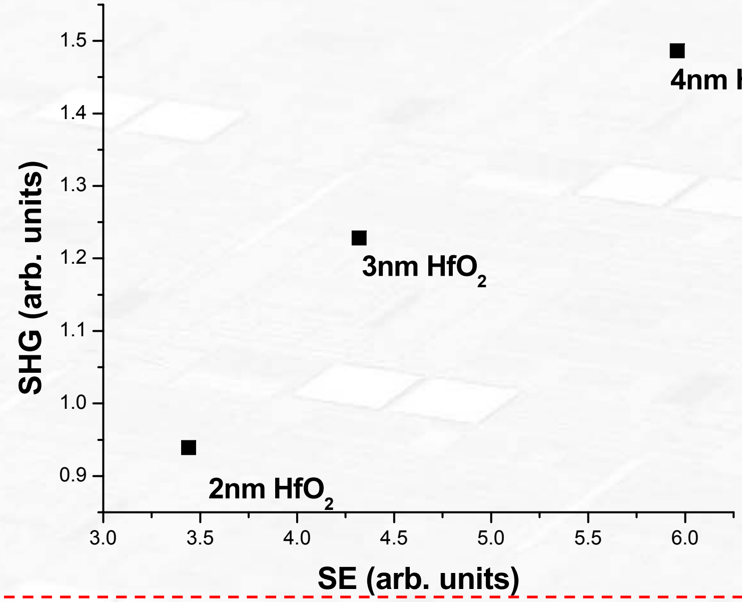
E-field induced changes in ε:

If the electric field is due to the oxygen vacancy defects, then to estimate the charge trap density, σ:

$$\sigma \propto thickness \times \sqrt{amplitude}$$

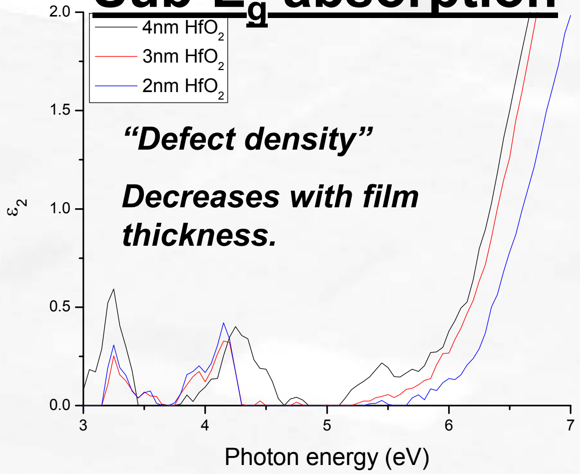
- **Thickness determined independently by SE.**
- **Peak amplitude extracted from Δε by curve fitting.**

Comparison of SE & SHG extracted potential



Field induced change method also correlates with sub-E$_g$ absorption and FTIR!

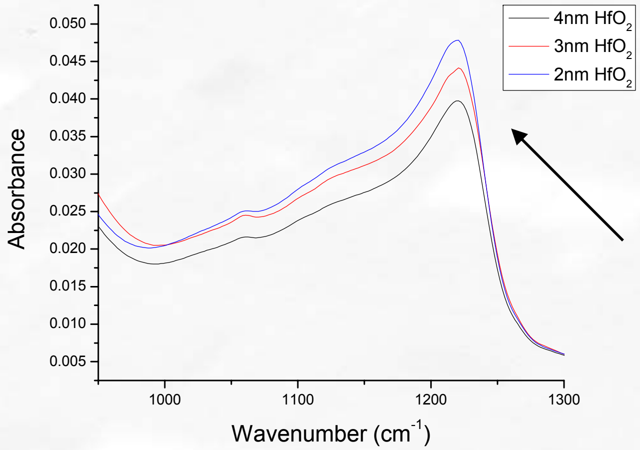
Sub-E$_g$ absorption



"Defect density"

Decreases with film thickness.

Grazing angle FTIR



Si-O LO phonon mode @ ~1250cm^{-1} increases with decreasing thickness.

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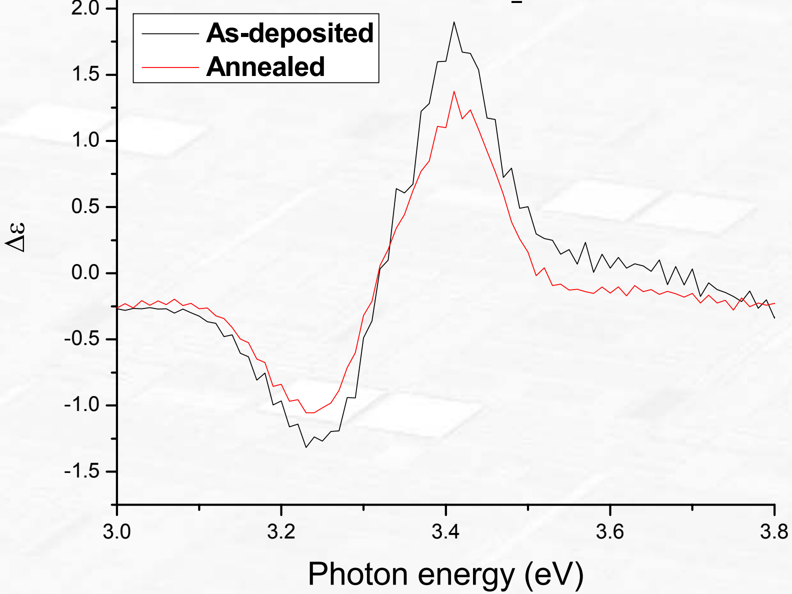
E-field induced changes in ε:

Example #2 : Annealing effects.

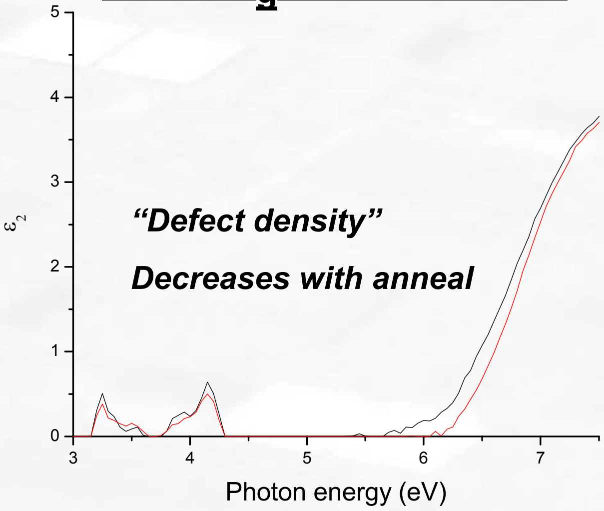
- 1000^0C NH_3 anneal expected to passivate Oxygen vacancies.
- Extracted peak amplitude decreases by ~ ½ after anneal.

2nm HfO_2



Field induced change method correlates with sub-E_g absorption, SHG, and FTIR!

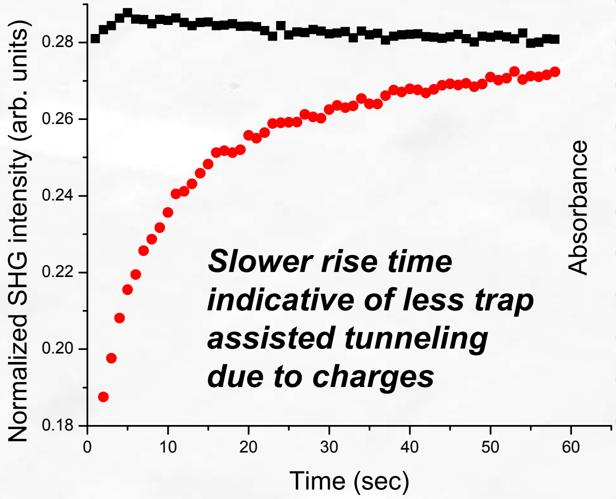
Sub-E_g absorption



"Defect density"

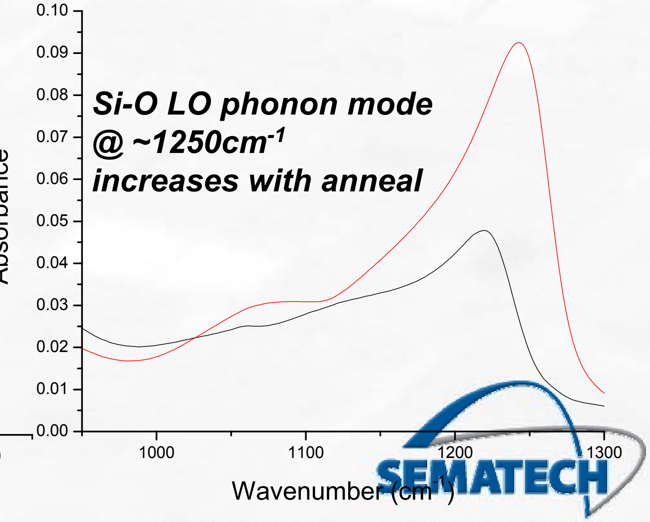
Decreases with anneal

Time dependent SHG



Slower rise time indicative of less trap assisted tunneling due to charges

Grazing angle FTIR

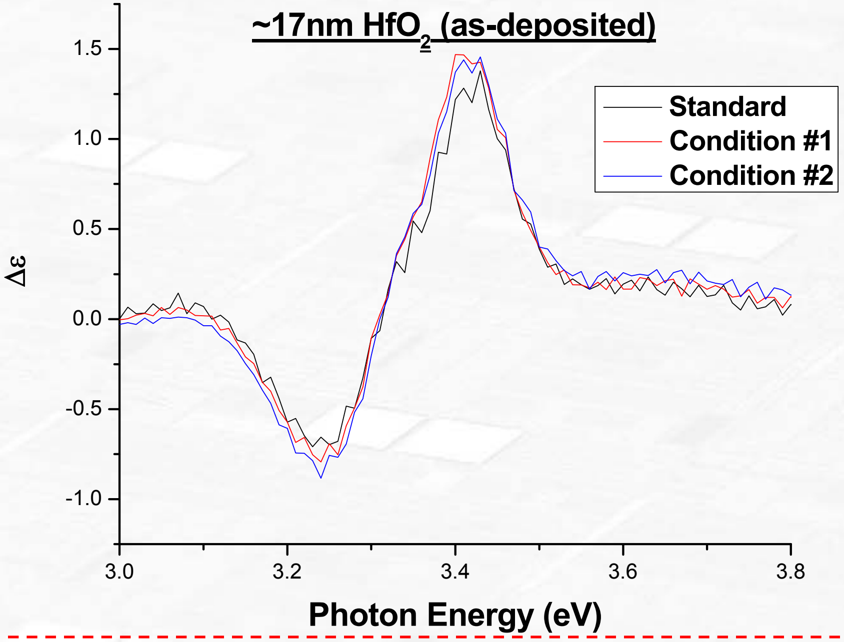


Si-O LO phonon mode @ ~1250cm^{-1} increases with anneal

E-field induced changes in ε:

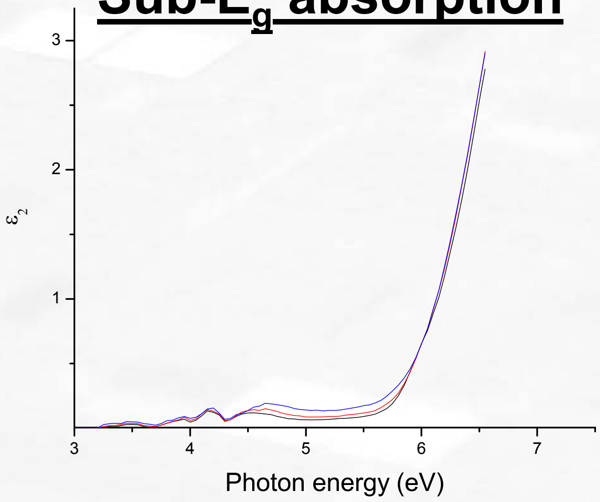
Example #3:

- **Isolate the oxygen vacancy defects by intentionally "choking-off" the available O_2 during deposition.**
- **Standard = SMT best know ALD method for HfO_2 deposition.**
- **Condition #1 = Decreased the available flow (amount) of ozone during ALD deposition.**
- **Condition #2 = Decreased the ozone pulse time during ALD deposition.**

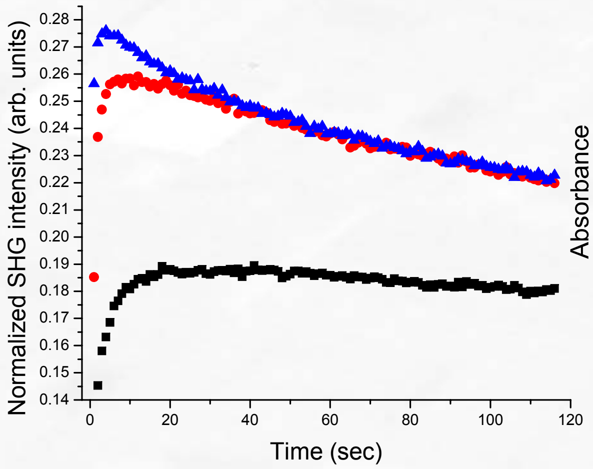


~17nm HfO_2 (as-deposited)

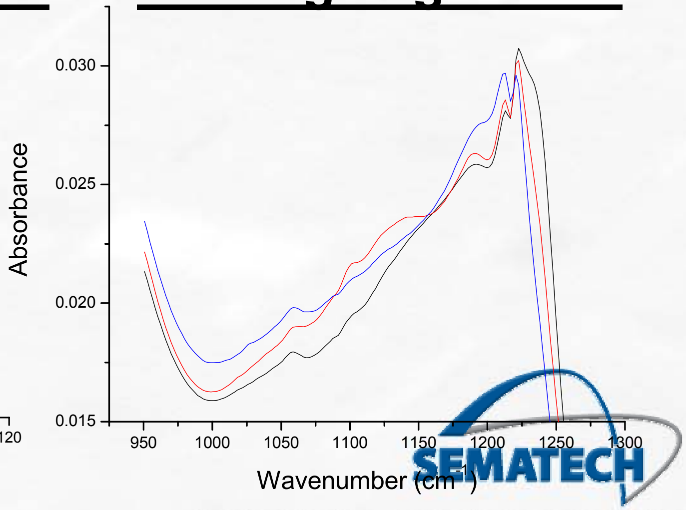
Field induced change method correlates with sub-E_g absorption, SHG, and FTIR!



Sub-E_g absorption

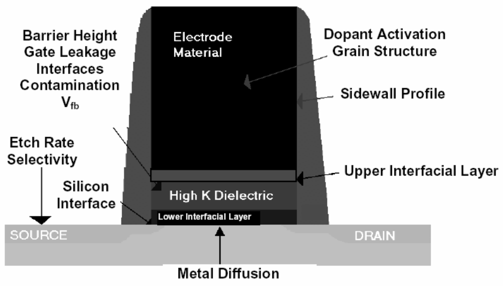


Time dependent SHG

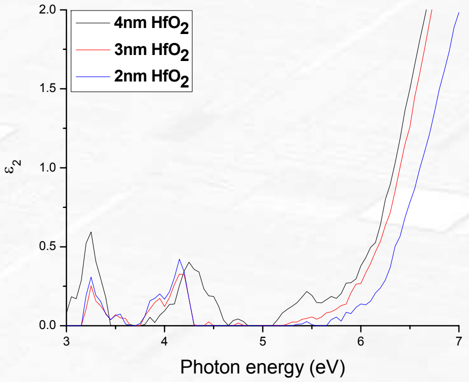


Grazing angle FTIR

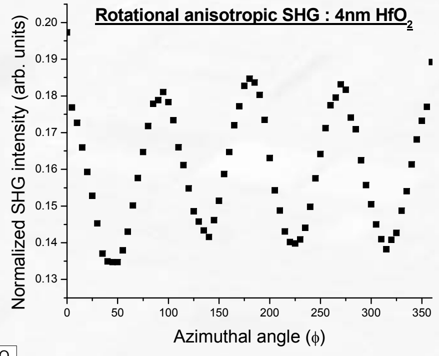
Conclusions:



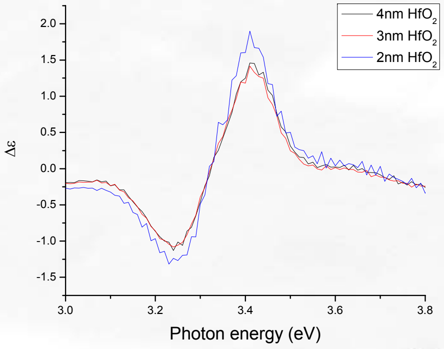
- Exciting time for metrology! New materials, new structures, and new physics & characterization needed.



- Sub-E_g absorption measurements "see" more than just defects.



- Second Harmonic Generation "sees" only the interface, but with exceptional sensitivity. Nano-technology is a made-for SHG problem.



- "Someone's trash is another's treasure". Interfacial electrostatic fields responsible for changes in silicon features. Identifying these changes is a potential way to extend SE applications.

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Acknowledgements:

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