Resonant photo-ionization of point defects in HfO$_2$ thin films observed by second-harmonic generation.

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High-\(k\) materials are now used in today’s leading edge transistors

<table>
<thead>
<tr>
<th><strong>SiO(_2)</strong></th>
<th><strong>Vs.</strong></th>
<th><strong>Hf-based oxides</strong></th>
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<tbody>
<tr>
<td>• Low density of defects</td>
<td>• High density of intrinsic defects</td>
<td></td>
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<tr>
<td>• Amorphous</td>
<td>• Susceptible to crystallization</td>
<td></td>
</tr>
<tr>
<td>• minimum dangling bonds</td>
<td>• Low quality SiO(_2) interface</td>
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<td>• Stable w/ poly Si gate.</td>
<td>• Elemental diffusion w/ metal gate</td>
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</table>

• Several obstacles were overcome before Hf-based oxides became a manufacturable solution for today’s chip industry.

• Further “scalability” can only be achieved by identifying and characterizing both intrinsic and process-induced 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
We use internal photoemission & time dependent EFISH to investigate charge trapping dynamics

Electric Field induced Second Harmonic (EFISH) generation:
1. fs-induced internal photoemission of charge carriers
2. Electrons transport to surface and trap O₂
3. Resultant charge separation creates electrostatic field

\[ I_{2\omega}(t) \propto \left| \chi^{(2)} + \chi^{(3)} E_{DC}(t) \right|^2 I_\omega^2 \]

*J. Bloch, et al., PRL 77 (1996)*
A spectroscopic investigation of charge trapping dynamics in HfO$_2$ film stacks

- For incident photon energies < 1.57 eV, characteristic behavior associated with electron transport and trapping at the surface is observed.

- At larger incident energies, there is a resonantly enhanced EFISH decay.
Time dependent SHG phase measurements of HfO$_2$

\[ I_{2\omega}(t) \propto \left| \chi^{(2)} + \chi^{(3)} E_{DC}(t) \right|^2 I_\omega \]

- \( \chi^{(2)} \) and \( \chi^{(3)} \) could differ in phase, thus causing decrease in EFISH.

- Frequency domain interferometric second harmonic (FDISH) generation measures the total SH phase contribution.

- No change in second harmonic phase during time evolution of EFISH.
- Resonant EFISH decay must therefore arise from decrease in \( E_{DC}(t) \).
Resonant EFISH decay is also power dependent.

Resonant EFISH decay is associated with a 2-photon absorption process.

\[ \Delta, \tau \propto (I_\omega)^n \]

\( h\nu = 1.61 \text{ eV} \)

\( n = 2.1 \)

\( Z. \ Marka, \ et \ al., \ PRB \ 67 \ (2003) \)
Understanding the lifetime of these trapped charges & where they reside in the HfO\textsubscript{2} film stacks

The photo-excited charge carriers contributing to the EFISH decay:

- a) Are long lived ($t \sim 10^3$)
- b) Discharging eliminates decreasing contribution
EFISH decay mechanism does not originate at the surface of HfO$_2$ or at the Si/SiO$_2$ interface.

Spectroscopic EFISH decay mechanism originates in the bulk of HfO$_2$. 
EFISH decay is not observed in other Hf-based silicate film stacks

- No EFISH decay for Hf-based silicate films.
- No hysteresis effects associated with charging/discharging cycles.
EFISH decay is not observed for annealed high-$k$ film stacks

- High temperature anneal eliminates EFISH decay/hysteresis mechanism.
A summary of the experimental observables

We observe a time-dependent EFISH decay that:

• Is resonantly enhanced near a two-photon energy of 3.24 eV
• Has a long lifetime and does not relax when the laser is blocked
• Demonstrates hysteresis upon successive charging/discharging cycles
• Is not present for Hf-based silicate or SiO$_2$ films (as-deposited/annealed)
• Does not originate at the surface of the HfO$_2$ film or its bottom interface
EFISH decay associated with resonant photo-ionization of negatively charge defects in HfO$_2$

Resonant photo-ionization of the 3.24 eV defect expels negative charge out of the system, thus decreasing the net electrostatic field.
Ab-initio calculations identify an oxygen vacancy defect in m-HfO$_2$ with an optical transition energy of \( \sim 3.2 \) eV.

- Type IV defect: excited state is localized above CB (resonant transition)
- $V^0$, $V^+$ most stable defects (and highest oscillator strength)
- m-HfO$_2$ exists as small polymorphs in as-grown HfO$_2$, but absent in HfSiO

**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.

<table>
<thead>
<tr>
<th>Charge</th>
<th>Type III</th>
<th>Type IV</th>
<th>Type V</th>
<th>Type VI</th>
</tr>
</thead>
<tbody>
<tr>
<td>$V^{2+}$</td>
<td>4.94</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>$V^+$</td>
<td>4.67</td>
<td>3.27</td>
<td>2.67</td>
<td></td>
</tr>
<tr>
<td>$V^0$</td>
<td></td>
<td>3.41</td>
<td>2.45</td>
<td></td>
</tr>
<tr>
<td>$V^-$</td>
<td>3.20</td>
<td>3.20</td>
<td>2.35</td>
<td>0.78</td>
</tr>
<tr>
<td>$V^{2-}$</td>
<td>3.25</td>
<td>3.25</td>
<td>2.35</td>
<td>0.92</td>
</tr>
</tbody>
</table>

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

- We use non-invasive, time-dependent SHG to measure charge trapping dynamics in Si/HfO₂ film stacks.

- We identify a unique decay in the electric field-induced SHG associated with resonant excitation of a unique point defect in as-grown HfO₂ film.

- See also, J. Price, et al., APL 95, 052906 (2009).

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Hole injection can not explain empirical observations of resonant EFISH decay

1. 3.24 eV does not span the Si CB – HfO$_2$ VB energy offset (3.85 eV).

2. Hole injection would exhibit a step function spectral response, and not a resonance.

3. Holes injected into HfO$_2$ VB would quickly tunnel back to Si, contrary to the observed long hysteresis time.