Materials Related Problems/Solutions of the Next Generation Computer Chips

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Outline

- Introduction-current status and issues
- Pulsed Laser Deposition method (synthesizing high-k dielectric thin films)
- X-ray absorption fine-structure spectroscopy (XAFS)
- Local structural information from XAFS
- Combining the synthesis and characterization in high-k and clustering problems of semiconductor industry
- Conclusions and future work
Building Blocks of Computer Chips: CMOS Devices

Current Technology

- Region 1: Silicodioxide gate
- Region 2: Silicon with dopants to increase conductivity

The challenge is to be able to shrink these blocks as much as possible in order to put more of them into a computer chip for faster operations and greater number of calculations per second.

Problems:

1. Dielectric region- SiO₂ must be replaced
2. Clustering and precipitation of dopants
# Continuation of Moore’s Law

<table>
<thead>
<tr>
<th>Process Name</th>
<th>P856</th>
<th>P858</th>
<th>Px60</th>
<th>P1262</th>
<th>P1264</th>
<th>P1266</th>
<th>P1268</th>
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<td>0.13(\mu)m</td>
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<td>65 nm</td>
<td>45 nm</td>
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<td>22 nm</td>
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<td>Cu</td>
<td>Cu</td>
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<tr>
<td>Channel</td>
<td>Si</td>
<td>Si</td>
<td>Si</td>
<td>Strained Si</td>
<td>Strained Si</td>
<td>Strained Si</td>
<td>Strained Si</td>
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<tr>
<td>Gate dielectric</td>
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<td>SiO(_2)</td>
<td>SiO(_2)</td>
<td>SiO(_2)</td>
<td>SiO(_2)</td>
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<td>Gate electrode</td>
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<td>Poly-silicon</td>
<td>Poly-silicon</td>
<td>Metal</td>
<td>Metal</td>
<td>Metal</td>
</tr>
</tbody>
</table>

*Introduction targeted at this time*  
Subject to change

Source: Intel
The Need for High-k Dielectrics

Basic CMOS Transistor

\[ C = \frac{A \kappa \varepsilon_0}{t_{ox}} \]

As thickness of SiO\textsubscript{2} decreases, leakage current increases exponentially due to quantum tunneling of electrons → breakdown of the device

Challenge: is to preserve capacitance, without decreasing the oxide thickness (so no tunneling). Can’t use SiO\textsubscript{2} anymore → find a replacement with higher k value

Source: Intel
With the ever decreasing size of the transistors SiO\textsubscript{2} will reach its physical limits by 2007(8)…

By 2007(8) gate-SiO\textsubscript{2} will be too thin to block the unwanted electron tunneling so new candidates, high-k dielectric materials, are needed to replace SiO\textsubscript{2}.

Our method is using pulsed laser deposition to synthesize novel materials (based on HfO\textsubscript{2}, ZrO\textsubscript{2}, Y\textsubscript{2}O\textsubscript{3}) on silicon crystals.

We determine the structure and quality of the high-k dielectric thin films by x-ray methods in our lab. and Brookhaven National Laboratory.
Problems with the High-k dielectrics

- Interface abruptness
  - SiO$_2$/Si interface has almost atomic layer sharpness

- Formation of interfacial oxide

- Thermal stability
  - The new materials should be stable at high-temp semiconductor processing conditions

- Crystallinity
  - In order to reduce leakage current films should preserve specific crystal structures

- Channel mobility
  - Carrier mobility in the channel should not be diminished by high-k dielectric replacement
Our Approach: PLD and Local Structural Probing

- Our approach is using pulsed laser deposition to synthesize novel materials (based on HfO$_2$, ZrO$_2$, Y$_2$O$_3$) on silicon crystals.

- Can we determine the local structural modifications caused by the variations by the deposition conditions by XAFS (even in amorphous films)?
  
  *If yes, then that means we have a powerful tool (PLD+ XAFS) controlling the thin film synthesis of these materials.*
PLD System at Seton Hall

- Krf Excimer Laser, $\lambda = 248$nm
- Laser frequency up to 100Hz
- Rotating substrate and target
- Heated substrate up to 850°C
Advantages of PLD

- High quality epitaxial thin films
- Control over the structural properties of the thin films by varying the deposition parameters
  - (e.g., oxygen partial pressure, substrate temperature, laser frequency, laser energy)
- Relatively cheaper than molecular beam epitaxy (MBE) → or as they say sometimes:
  “poor assistant professor’s MBE”
**Characterization: X-ray Absorption and Fluorescence**

**X-ray Absorption**

Incident x-ray ejects a core level electron. Kinetic Energy (KE) of the photo-electron is:

\[ KE_e = E_{x-ray-in} - E_0 \]

\( E_0 \): Energy of core level e.

**X-ray Fluorescence**

Higher energy core electron fills empty electron level, and ejects an x-ray of fixed energy.

\[ E_{x-ray-fl.} = E_1 - E_0 \]
X-ray Photoelectron Spectroscopy for HfO$_2$/Si(100)

**HfO$_2$: Fully oxidized**

**Shoulder: HfSi$_x$O$_y$ presence**
Backscattering and the Absorption Coefficient: Wave picture

- Outgoing photoelectrons backscatter from near-neighbor atoms B.
- Interference between the outgoing and the backscattered photoelectron waves causes modulations (oscillations) in the x-ray intensity and thus the absorption coefficient.
- Therefore, the oscillations in the absorption coefficient have all the information about the local structure:
  - The distance between A and B;
  - How many and what kind of atoms A is surrounded with.
**X-ray Absorption Spectroscopy**

**X-ray Absorption Spectroscopy**: Measures energy-dependence of the x-ray absorption coefficient $\mu(E)$.

$$I = I_0 \exp[-\mu(E)d]$$

$$\mu(E) = \frac{1}{d} \ln(I_0/I)$$

$$\mu(E) \propto I_f/I_0$$
With another atom nearby, the photo-electron can **backscatter** from a neighbour atom.

Interference between the outgoing and the backscattered photoelectron waves alters the photo-electron wave-function at the absorbing atom, modulating the absorption coefficient $\mu(E)$.

Therefore, the oscillations in the absorption coefficient have all the information about the local structure:

- The distance between A and B.
- How many and what kind of atoms A is surrounded with.
- Local structural disorder
Extracting the oscillatory part: XAFS Function

After subtracting the atomic absorption, the oscillatory XAFS part of the modulating the absorption coefficient $\chi(k)$ is extracted.

$$E - E_0 = KE = \frac{1}{2}mv^2 = \frac{p^2}{2m}$$

$p = \hbar/\lambda$; De Broglie wavelength or,

$p = \hbar k/2\pi$; where $k = 2\pi/\lambda$ is the wave number.

Then,

$$E - E_0 = \frac{(\hbar k/2\pi)^2}{2m} \Rightarrow k = \sqrt{\frac{2m(E - E_0)}{(\hbar/2\pi)^2}}$$
Structural Information From XAFS

$\chi(k)$ is a sum of sine waves with scattering amplitudes and phases.

$$\chi(k) = \sum_j \chi_j(k) = \frac{Nf(k)}{kR^2} \sin[2kR + \delta(k)]$$

- $f(k)$ is the scattering amplitude
- $\delta(k)$ is the scattering phase

A-B

N=4

R
The Effect of the Substrate Temperature During Deposition

- HfO$_2$/Si(100) PLD with different substrate temperatures
- Fourier Transformed (FT) XAFS data shows an increase with substrate temperature for the first and second shell peaks
  - *Due to increase in the coordination numbers, (higher crystallinity)*

XAFS experiments at Beamline X23A2 of NSLS of Brookhaven National Laboratory
The Effect of Compositional Variance on the Local Coordination

- $(\text{HfO}_2)_x(\text{ZrO}_2)_{1-x}/\text{Si}(100)$ films with $x = 0.50, 0.75, 0.90, 1.00$
- The second shell peak is affected more in the Fourier Transformed (FT) XAFS data.
  - $\text{Hf-Hf}$ coordination decreases with more $\text{Zr}$ introduced to the system.

M. A. Sahiner et al., Gordon Research Conference on Ceramics, Andover, NH (August 13-18, 2006)
XAFS Data and the Non-linear Least-squares Fits to the Data for All the PLD Films

- Top three: temperature variation
- Bottom four: compositional variance

XAFS fits were performed using FEFF8.2 calculations for scattering amplitudes and phases.

2 Univ. Of Washington’s multiple scattering simulation code
## XAFS Fit Results

<table>
<thead>
<tr>
<th>PLD Film</th>
<th>1st shell</th>
<th>2nd shell</th>
</tr>
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<tbody>
<tr>
<td></td>
<td>$N_{\text{Hf-O}}$</td>
<td>$R(\text{Å})$</td>
</tr>
<tr>
<td>HfO$_2$/Si(100) $T=200^\circ\text{C}$</td>
<td>5.52</td>
<td>2.01</td>
</tr>
<tr>
<td>HfO$_2$/Si(100) $T=300^\circ\text{C}$</td>
<td>5.64</td>
<td>2.02</td>
</tr>
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<td>HfO$_2$/Si(100) $T=400^\circ\text{C}$</td>
<td>6.39</td>
<td>2.02</td>
</tr>
<tr>
<td>$(\text{HfO}_2)_x(\text{ZrO}<em>2)</em>{1-x}$/Si(100) $x=0.90$ $T=400^\circ\text{C}$</td>
<td>6.09</td>
<td>2.01</td>
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<tr>
<td>$(\text{HfO}_2)_x(\text{ZrO}<em>2)</em>{1-x}$/Si(100) $x=0.75$ $T=400^\circ\text{C}$</td>
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<td>$(\text{HfO}_2)_x(\text{ZrO}<em>2)</em>{1-x}$/Si(100) $x=0.50$ $T=400^\circ\text{C}$</td>
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1.4, 1.8, and 4.0 nm HfO₂

Monoclinic phase emerges for all films post RTA, although suppressed for 1.4 and 1.8 nm as-deposited NH₃ PDA and Ht sample second order peaks due to competition between phases.

NH₃ PDA + N₂ RTA

Coordination number variation with thickness may correlate to GB fraction of sample volume.

Monoclinic phase for all films.

Thickness Effects

Second order peaks near identical for 1.4 and 1.8 nm as-dep and PDA.

Monoclinic phase for 4 nm PDA.

Hf L₃ FT Spectra of Scaled HfO₂
All films appear structurally amorphous as-deposited with evidence for incipient nanocrystallinity.

Monoclinic phase emerges for all films post RTA, although suppressed for 1.4 and 1.8 nm.
**Conclusions (high-k)**

- **XAFS local structural analysis:**
  - Substrate temperature during deposition is closely correlated with the Hf near-neighbor correlations (Hf-O and Hf-Hf), could be used as a sensitive probe for crystalline quality as higher the temperature closer to the monoclinic coordination numbers.
  - ZrO₂ incorporation does not affect the Hf-O coordination but Hf-Hf coordination in the second shell (Hf replacement by Zr).
  - A stable monoclinic phase is strongly dependent on thickness (1.8nm-4.0nm) and post deposition annealing process.
  - **Future work:** Very thin PLD films of Hf-based high-k dielectric materials will be (local) structurally analyzed by XAFS in order to probe the effects of the PLD parameters such as: temperature, laser energy, frequency, and partial oxygen pressure on the interface.

Films will be annealed and local structures of single-crystal films will be probed.
Paul A. Packan from Intel, describing the current main challenges facing the semiconductor industry:

“Although the transistors can shrink in size, the smaller devices still need to maintain the same charge. To do that, the silicon has to have a higher concentration of dopant atoms. Unfortunately, above a certain limit the dopant atoms begin to clump together, forming clusters that are not electrically active. You can’t increase the concentration of the dopant, because all the extras just go into the clusters.”

1 Science, Volume 285, Number 5436, Issue of 24 September 1999
Doping of Semiconductors

- **Si**: Intrinsic (undoped) semiconductor:
  - 4 outer shell electrons
  - Two electrons are shared between near-neighbors

- **Arsenic (As) doped Si**: *n-type* semiconductor
  - As has 5 outer shell electrons
  - One is free to move around
  - More dopant atoms $\Rightarrow$ more free charge carriers
  - **Higher Conductivity**
Region 2: Importance of High Level Doping in Transistors

- Although the transistors can shrink in size, the smaller devices still need to maintain the same charge.
- To do that, the silicon has to have a higher concentration of dopant atoms.

**Solution:** Put more dopant (arsenic) atoms into the Si crystal to increase the carrier concentration.
Region 2: Problems in High Level Doping in Transistors

- Unfortunately, above a certain limit the dopant atoms begin to clump together, forming clusters or precipitates that are not electrically active.
- One cannot increase the concentration of the dopant, because all the extras just go into the clusters.

![Diagram showing As₄V and Monoclinic-SiAs precipitate]
Energy Bands in Conductors, Insulators, and Semiconductors

- **Conductors:**
  - Energy gap ($E_g$) = 0
  - Resistivity $\sim 10^{-6}$ ohm-cm

- **Insulators:**
  - $E_g \sim 5$-10 eV
  - Resistivity $\sim 10^{11}$-10$^{17}$ ohm-cm

- **Semiconductors:**
  - $E_g \sim 1$ eV
  - Resistivity $\sim 10^3$-10$^6$ ohm-cm
Problem 2 and proposed solution: annealing

- Some of the important challenges in the semiconductor technology are:
  - Doping intrinsic semiconductors with impurities above solid solubility limits to increase carrier concentration in shallow junctions.
  - Sustaining high level carrier concentration and eliminating any inactive structures (cluster or precipitates) formed by the dopants by annealing mechanisms.

Therefore, information on the local structure around the impurity atom is of crucial importance to face with these requirements.
Using x-rays:

- What can X-ray Absorption Fine Structure Spectroscopy (XAFS) do for me in clustering problem?
Application to Problems in Semiconductor Industry

- XAFS being capable of probing
  - The short range order in crystalline and amorphous materials
  - One element at a time

- Can provide information on the number, distance and chemical identity of the neighbors of the main absorbing atom (e.g. As, Sb, B).

  This information can be used to identify the nature and amount of any dopant-related inactive structures in the material\textsuperscript{1,2,3,4}.

\textsuperscript{1}M. A. Sahiner et al., Microelectronics Journal (Elsevier), \textbf{36}, 522-526 (2005).
Arsenic in Si:
Effects of High Dose As Implantation on the Local Structure

- As ion implantation may lead to:
  - Substitutional As:
    - Nearest neighbor: Si
    - Coordination number: 4 (4 Si atoms around)
    - Nearest neighbor distance (R): ~2.40 Å
  - Precipitates in the form of monoclinic SiAs
    - Nearest neighbor: Si
    - Coordination number: 3 (3 Si atoms around)
    - Nearest neighbor distance (R): ~2.37 Å
  - $\text{As}_2V$, $\text{As}_4V$ clusters ($V$: vacancies):
- XAFS analysis provides the coordination numbers and the nearest neighbor distances around As.
- In this way, we are going to determine the structure of the As at different As doping levels after annealing
Comparison of Low and High Dose As Implants-
Secondary Ion Mass Spectroscopy

Are the concentrations for the 1E16/cm² second implants higher than critical clustering/precipitation concentration?

XAFS information is needed to investigate if there is any clustering/precipitation or not.
The first peak shows the As-Si scattering. First shell peaks are well-resolved so the coordination numbers and near neighbor distances can be extracted easily by working on this peak only.
Least Square Fits to the Back-Fourier Transforms

These results indicate high dose arsenic implants (>1E16/cm²) form As clusters and precipitates in the form of SiAs causing electrical deactivation.
Substitutional vs Precipitated Arsenic Ratio

As bulk with low As concentration is a standard for pure substitutional As.
As implanted Si at a very high dose of $1E18/cm^2$ serves as a pure precipitate standard.
Using the linear combinations of XAFS functions of these two standards, the percentages of the substitutional As can be determined at different implant doses.
Conclusion (As in Si)

- XAFS can directly probe the clustering/precipitation/substitution problem in ion-implanted Si crystals. The weight of these three mechanisms can be manipulated by modifying the annealing conditions and impurity concentrations in the light of the local structure information.

- The critical concentration values for the cluster/precipitate formation under different annealing conditions can be determined.

- Using the substitutional and precipitated forms of arsenic as standards, the ratios of the substitutional vs precipitated arsenic in a specific sample can be determined.