HR(A)TEN for Nano-electronic Materials Research

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Session 7: Microscopy

- 10:00 AM  STEM w/ Monochromator
- 10:30 AM  HR(A)TEM for Materials Research
- 11:00 AM  Aberration corrected SEM
- 11:30 AM  Aberration corrected STEM

I have a theory!
Things Natural

- Ant ~ 5 mm
- Dust mite ~ 200 µm
- Human hair ~ 10-50 µm wide
- Red blood cells with white cells ~ 2-5 µm
- AT&T synthase ~ 10 nm diameter
- DNA ~ 2-1.2 nm diameter
- Atomic columns of silicon spacing ~ tenths of nm

Things Manmade

- Head of a pin 1-2 mm
- MicroElectroMechanical Devices 10-100 µm wide
- Red blood cells Pollen grain ~ 10-20 µm
- Nanotube electrode
- Nanotube transistor
- Quantum corral of 48 iron atoms on copper surface positioned one at a time with an STM tip Corral diameter ~ 14 nm
- Carbon nanotube ~ 2 nm diameter

21st Century Challenge

Combine nanoscale building blocks to make functional devices, e.g., a photosynthetic reaction center with integral semiconductor storage.

The Scale of Things -- Nanometers and More

http://www.nano.gov/
Why HR(A)TEM?

**High Resolution (Analytical) Transmission Electron Microscopy**
- essential tool for investigators in **nanoscale science and engineering**
- nanostructure and chemistry of materials down to an atomic scale
- (3D information).

**Image Resolution**
- Atomic resolution structure imaging (coherent)
- Atomic resolution Z-contrast STEM imaging (incoherent)

**Atomic Column-by-Column Spectroscopy**
- Probe size
- Probe current
- Detection sensitivity

\[
\delta = 0.66 C_s^{1/4} \lambda^{3/4}
\]
\[
\delta = 0.43 C_s^{1/4} \lambda^{3/4}
\]

\[
d_{\text{min}} = 1.1 \left( \frac{4i_p}{\pi^2 \beta} + 0.37 \lambda^2 \right)^{3/8} C_s^{1/4}
\]
\[
i_p = \frac{\pi^2}{4} \beta d_{\text{source}}^2 \alpha^2
\]

<table>
<thead>
<tr>
<th>Element</th>
<th>$\sigma_k \text{ (cm}^2 \times 10^{-22})$</th>
<th>$\sigma_{b} \text{ (cm}^2 \times 10^{-22})$</th>
<th>MMF (at. %)</th>
<th>MDN (atoms)</th>
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<tr>
<td>B</td>
<td>111</td>
<td>38</td>
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<tr>
<td>N</td>
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Minimum Mass Fraction (MMF) and Minimum Detectable Number of Atoms (MDN) within a 10-nm thick carbon matrix. MDN values are for an incident-beam diameter of 0.2 nm.

Advanced EM Facility

**Instrumentation**
- Dual column FIB (FEI Nova NanoLab 200) with Zywex nanomanipulator
- High resolution Imaging FEG TEM (JEOL 2100F)
- High resolution Analytical FEG TEM/STEM with remote microscopy
- Comprehensive Sample Preparation Lab.
- Computing/Visualization Lab.
- Cryo, STM-TEM nanofactory, 3D tomography
New NSM Research Facility

- Dedicated EM facility
  - Vibration
  - EM field
  - Temperature
  - Air flow & pressure
  - Acoustic
Under the Microscope?

That's not what I had in mind when I said examine the specimen under the microscope.
TEM Techniques – Now and Then

- Monochromator
- Cs corrector - STEM
- Cs corrector - HREM

MSA Bulletin

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The Erik Jonsson School of Engineering and Computer Science
HR(A)TEM: Application to Nano-X Materials

✓ Thermal stability of high-k gate dielectric films
  – Current SiO$_2$ gate oxide
  – ALCVD ZrO$_2$-based
  – HfSiO$_4$-based
  – Hf$\text{Si}_x\text{O}_y\text{N}_z$-based

• Ultra low-k dielectric films
  – Nanoscale structural damage by plasma ash/etch

• Ni-silicides
  – Thin film morphology and phase identification

• Nanoscale lattice strain in Si CMOS Devices
  – New method of measuring local nanoscale strains
Cross-sectional high resolution TEM images of poly-Si/SiO$_2$/Si interfaces: (a) as-deposited and (b) after rapid thermal annealing (RTA) at 1050$^\circ$C for 60 sec. (c) Thick gate oxide after RTA at 1050$^\circ$C for 60 sec. The observed amorphous SiO$_2$ gate oxides are thermally stable, as expected at this temperature.

“Only problem with SiO$_2$ ... low-k.”
High Resolution EELS for Si-O

- Si-L edge of various silicon oxygen compounds. Marked differences exist in the near edge fine structure, showing changes in bonding from covalent bonding in Si to nearly complete ionic bonding in SiO₂. The onset of the Si-L edge from SiOₓ is also reduced relative to SiO₂. [Catalano, Kim, Carpenter, Das Chowdhury and Wong, J. Mater. Res. 8, 2893-2901 (1993)].

Crystalline vs. Amorphous Gate Dielectric

- Robust, thermal SiO$_2$ the benchmark
- Avoids orientation/grain size dependence of polarizibility
- Avoids enhanced leakage or diffusion through grain boundaries
- New single crystal dielectrics require Epitaxial approach
ZrO$_2$-based: as-deposited

(a) High Resolution TEM, (b) high resolution annular dark field (ADF) images of as-deposited ALCVD Zr-O/SiO$_x$/Si stack. (c) A series of nanoprobe high spatial resolution electron energy loss spectra (EELS) of as-deposited Zr-O/SiO$_x$/Si stack shown in (a). The spectra are displaced vertically for easy shape comparison. Note nanocrystalline nature of the as-deposited film.

ZrO$_2$-based: as-deposited

- Nanostructure and nanochemistry of the as-deposited ALCVD Zr-O/SiO$_x$/Si stack. The Zr-O layer is a compositionally graded ZrO$_2$-rich Zr silicate glass with nanocrystalline precipitates, and the interlayer (IL) is an amorphous bilayer of SiO$_x$ and compositionally graded SiO$_2$-rich Zr silicate.
ZrO$_2$-based: annealed

(a) HRTEM image of annealed Zr-O/SiO$_x$/Si stack. (b) A series of nanoprobe EELS spectra of annealed Zr-O/SiO$_x$/Si stack shown in (a). (c) EELS spectra of standard single crystalline (stoichiometric) specimens. The spectra are displaced vertically for easy shape comparison.
ZrO$_2$/SiO$_2$/Si

- Wafer Bonded $\rightarrow$ single crystal ZrO$_2$ on SiO$_2$/Si(100)

- HREM image of the bonded ZrO$_2$/SiO$_2$ interface (center), together with high spatial resolution EELS spectra from the amorphous (left) and crystalline (right) regions adjacent to the interface. The interface is sharp structurally and chemically down to atomic scale.

**ZrO$_2$-based: annealed**

- Nanostructure and nanochemistry of the annealed ALCVD Zr-O/SiO$_x$/Si stack. The Zr-O layer is a **heterogeneous** glass nanoceramic. The thick interlayer (IL) is partitioned into an upper SiO$_2$-rich Zr silicate and the lower SiO$_x$. The latter is substoichiometric and the average oxidation state increased from $\text{Si}^{0.86+}$ in SiO$_{0.43}$ (as-deposited) to $\text{Si}^{1.32+}$ in SiO$_{0.66}$ (annealed). This high oxygen deficiency in SiO$_x$ is indicative of the low mobility of oxidizing specie in the Zr-O layer.
HfSi$_x$O$_y$ : as-deposited

- As-deposited Hf-silicate film is amorphous.
- Silicate composition:
  - (HfO$_2$)$_{0.48}$(SiO$_2$)$_{0.52}$
- The ~5 nm dielectric film consists of:
  - ~1 nm SiO$_x$ and ~4 nm HfSi$_x$O$_y$

B-doped HfSi$_x$O$_y$ : 1050°C / 60s RTA

- Nanocrystalline regions observed after 1s RTA anneal
- Crystalline regions appears to be tetragonal HfO$_2$
- Consistent with Hf composition
  - (HfO$_2$)$_{0.48}$(SiO$_2$)$_{0.52}$
- Longer annealing times
  - more crystallization
  - higher B penetration

Both films show crystallization after annealing, consistent with the B doped films results.

No effect of the dopant on crystallization the HfSi$_x$O$_y$ films.

No evident growth of the SiO$_x$ interfacial layer after annealing.

Nitrogen Incorporation in HfSi$_x$O$_y$

- Brown found that $k$ increases as $N$ in the SiO$_2$ film.
  - However, a major drawback in increasing the N content: decreases the band gap, decreasing the barrier height for electron and hole tunneling.*

- Si-O-N film acts like the diffusion barrier to impurities (such as B, P and As) from the poly-Si gate. Lesser diffusion in HfSi$_x$O$_y$N$_z$ as compared to HfSi$_x$O$_y$ has been observed.

- Better thermal stability.

- Only small amount of N incorporation is needed.

Hf$_{x}$Si$_{y}$O$_{z}$N$_{w}$ : with ~5-6 at.% Hf and ~18 at.% N

- Cross-sectional TEM images of the poly-Si capped Hf$_{x}$Si$_{y}$O$_{z}$N$_{w}$ thin films on Si(100): (a) as-deposited (HREM), (b) as-deposited (ADF STEM), and (c) 60 sec RTA at 1050ºC. The total physical thickness is ~ 2.5 nm with an intentional interfacial (SiO$_{x}$) layer of ~ 1.1 nm.
- No detectible crystalline regions are observed.

[Quevedo-Lopez, Cl-Bouanani, Kim, Gnade, Wallace, Visokay, LiFatou, Chambers and Colombo, Appl. Phys. Lett. 82, 4669 (2003)]
HfSi$_{x}$O$_{y}$N$_{z}$ : with higher Hf content

- Cross-sectional HRTEM images of the poly-Si capped HfSi$_{x}$O$_{y}$N$_{z}$ thin films with higher Hf content on Si(100), compared with the previous ones: (a) as-deposited, (b) 1 sec and (c) 60 sec RTA at 1050ºC.
- HfSi$_{x}$O$_{y}$N$_{z}$ films with high Hf content are thermally stable after a “spike” anneal for 1 sec, but crystallization was observed after 60 sec.
- A slight thickening of the HfSi$_{x}$O$_{y}$N$_{z}$ layer is also noticed, indicating a volume change associated with the crystallization as well as inter-diffusion of Hf and Si upon extended annealing.
HfSi$_x$O$_y$N$_z$ : with thicker HfSi$_x$O$_y$N$_z$ layer

- Cross-sectional HRTEM images of the poly-Si capped thick HfSi$_x$O$_y$N$_z$ thin films on Si(100): (a) as-deposited, (b) 60 sec RTA at 1050ºC and (c) N and O concentration profiles across the interface shown in (a). The profiles are displaced vertically for easy comparison.

- Note nanocrystals and diffuse interfaces in the annealed.
HR(A)TEM: Application to Nano-X Materials

- **Thermal stability of high-k gate dielectric films**
  - Current SiO₂ gate oxide
  - ALCVD ZrO₂-based
  - HfSiO₄-based
  - HfSiₓOᵧNₜ-based

✓ **Ultra low-k dielectric films**
  - Nanoscale structural damage by plasma ash/etch

- **Ni-silicides**
  - Thin film morphology and phase identification

- **Nanoscale lattice strain in Si CMOS Devices**
  - New method of measuring local nanoscale strains
Ultra Low-K: Pore structure & Plasma damage

Xerogel spin-on films

Less solvent

Aerogels

Less solvent

O$_2$ ash

H$_2$ ash

Fresnel imaging

C1s intensity

sputtering depth (nm)

- virgin (A)
- 30secO2 ash

damaged region

HR(A)TEM: Application to Nano-X Materials

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  - HfSi$_x$O$_y$N$_z$-based
- **Ultra low-k dielectric films**
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- ✔ **Ni-silicides**
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Nano- Ni-Silicides
HR(A)TEM: Application to Nano-X Materials

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• Ultra low-k dielectric films
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✓ Nano-scale lattice strain in Si CMOS Devices
  – New method of measuring local nanoscale strains
Convergent Beam Electron Diffraction (CBED)

- Changes in the lattice parameter → shifts in the HOLZ lines
  \[ \frac{\Delta \theta}{\theta} = \frac{\Delta a}{a} \]

- Limit to the accuracy
  \[ \frac{\Delta a}{a} = \frac{\Delta E}{2E} = \frac{40 \text{ eV}}{2 \cdot 100 \text{ keV}} = \frac{1}{5000} \]

- Change of lattice parameter of an alloy or compound → directly related to its chemical composition → deduced from shifts in the HOLZ line positions

- Strains → measured in an exactly equivalent fashion to the chemical changes

- Spatial resolution → depends on the probe size and its broadening by the specimen
Lattice parameter increase of ~0.09 nm ± 0.01nm (~0.15%)
→ excess phosphorus content of about 3% (Vegard’s law)

Experimental

Simulation

Top of the LT layer

Bottom of the LT layer

[Rajesh, Kim, Bow, Carpenter and Maracas, Proc. 51st MSA, pp. 810-811 (1993).]
True (‘effective’) Electron Beam Energy

Silicon, unstrained, <230>, 200kV

- Simulated HOLZ line patterns in the central CBED disc taken in the <230> zone axis based on the kinematical approximation, illustrating the effect of electron beam energy on the HOLZ line position.
Effect of Strains

Silicon, <230>, 200kV

- Simulated HOLZ line patterns in the central CBED disc taken in the <230> zone axis, showing the HOLZ line shifts due to changes in lattice parameter.
Site-specific TEM Sample Preparation by FIB

T = ~50 µm
W = ~2.5 mm

Area of interest

Grid

FIB etching

Area of interest

TEM observation

0.50 µm
Nanoscale Strain in Advanced CMOS

Local uni-axial strain approach with SiGe at the drain extension

Nanoscale Strain in Advanced CMOS

Cross-sectional TEM image (left) of 37 nm gate with SiGe layer in the DE region.

Convergent Electron Beam Diffraciton (CBED) patterns taken from the indicated area shown as insets. Lattice spacing measurements show ~0.3% peak compressive strain on silicon channel under the gate, and ~0.3% peak tensile strain below the drain.

Energy-filtering
Nanoscale Strain in Advanced CMOS

Experimental <230> CBED patterns, superimposed by the simulated ones, showing a compressive strain gradient that decays from the center channel region.
Nanoscale Strain in Advanced CMOS

<560> CBED

<560> convergent beam shadow images.

<110> Z.A.
Conclusions

★ Resolution limits
  – Aberration-corrected TEM/STEM
    → < 0.1 nm spatial resolution
    → < 0.1 eV energy resolution
  – Practical
    → Radiation effects
      ❖ Mass loss
      ❖ Displacement damage
    → Quality of TEM samples
      ❖ Preparation methods
      ❖ Contamination, Preferential milling
    → Probe/Specimen stability
      ❖ Environment

★ Future
  – Remote operation, in-situ
  – Nano and Beyond 🚴
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P. Sivasubramani
VNB Modification in TEM

As-received, unstained VNB with 5 nm Au particles attached.

After 2 min e-beam exposure. Note contact between Au particles.

After 4 min e-beam exposure, increased Au “melting”
Direct Wafer Bonded Ge/Si

- HREM (a) image of the bonded Ge/Si interface. Their 4% lattice mismatch accommodated by misfit dislocations along the interface (b). (Left) Z-contrast image shows the chemical width of the interface to be about 2 monolayers. (Right) Low voltage I-V curve of the bonded p-Si/n-Ge heterojunction.