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Can the entire gate stack layers be investigated without sample manipulation?

**Outline:**

- High-k/Metal gate: Entire film stack physical characterization (thickness, composition, depth profile and chemical state).

- Soft x-ray XPS fails to provide depth profile and chemical state information of the entire film stack.

- Hard-X ray XPS using a synchrotron beam at Sping8 provides non-destructive depth profile and chemical state.
Metal Oxide Silicon (MOS) Transistor

- **Gate**
  - Provides control for on/off state
  - Poly-Si

- **Oxide**
  - Insulating gate electrode from channel
  - TiN, HfOx/SiO2

- **Source**
  - Provides carriers for channel conduction

- **Drain**
  - Drains away channel current
  - Allows S/D connection

- **Base**
  - Provides substrate bias

- **Channel**
  - 20Å
  - 100Å
  - T>500Å
  - Provides substrate bias
Experiment: Sample description

- Si wafer: substrate
- SiO2
- HfO2
- TiN
- Cap layer: poly-Si

- ~100 Å
- ~50 Å
- ~20 Å
- ~8 Å

TiN/highK interface influences the Vt shift

Highk/SiO2 interface influences the mobility & leakage current

This sample was annealed at T=1000°C
Soft X-ray XPS depth profile: Ar sputtering

Problems:
1) Is Ar sputtering changing the material chemical state?
2) Is Ar sputtering increasing the surface roughness?

Is this Hf⁰ HfN, or an artifacts??
Soft X-ray: AR-XPS after Ar sputtering

- TiN about 30-40Å
- HfO₂
- SiO₂
- Si wafer sub.

Qualitative depth atom distribution

High Roughness

SiO₂ Film thickness
1st Conclusion:

The combination of Ar sputtering and AR-XPS analysis fails to provide a chemical characterization of the entire stack layer of about 150 Å.

The use of Ar sputtering introduces artifacts such as ion mixing and differential sputtering.

The surface after partial Ar sputtering is so rough (roughness by AFM data increases of more than 1 order of magnitude) that AR-XPS is compromised.

So.....
Feasibility Study of HK-MG stack by

Hard X-ray photoemission

AR-XPS Data at \( \sim 6 \) keV were collected at SPring8
Hard X-ray (X-ray Energy=6000eV): survey spectrum

Hf is detected without any sample manipulation or sample sputtering
Angle Resolved Hard X-ray data

\[ \Theta = 10^\circ \text{(top film surface)} \]
\[ \Theta = 88^\circ \text{(bulk film)} \]
Sample: 1 Si sub/8Å SiO2/20Å HfO2/100Å/TiN/50Å/ poly-Si

SESSA

Si wafer: substrate
SiO2
HfO2
TiN
Cap layer: poly-Si

Legend:
- Silicon - Si
- Titanium - Ti
- Nitrogen - N
- Hafnium - Hf
- Oxide - O
- Silicon - SiO2

Concentration [Atomic fraction]

0.0 0.5 1.0
Depth [Ångstrom]

0 14.0 23.0 32.0
Concentration [Atomic fraction]
Experimental data of angle resolved XPS hard-X-ray are fitted by Sessa Simulation

- Experimental data: Area of Hf4f and Ti2s
- Sessa simulation: Area of Hf4f and Ti2s of the simulated spectra
Conclusions:
(from previous presentation at LBNL October workshop on Hard X-ray)

• Hard X-ray AR-XPS shows the following advantages in comparison with traditional AR-XPS and Ar sputtering XPS:
  
  • Surface and bulk information are obtained without sample manipulation
  
  • The interface at TiN/HfO2 layer is observed and the dielectric layer consists of HfOx.
Recent data analysis
Chemical State Information as a function of depth

\[ \frac{I(x)^{30\degree}}{I(x)^{88\degree}} \]

where
\[ x \equiv Si; O; C; N; Ti; Hf \]

The intensity of SiO2 and Si° at the bottom of the film stack are too weak to be discriminated from the top Si layer.
X-ray = 6KeV
Data analysis : Si2p
Si2p spin/orbit splitting.

Spectral resolution \( \sim 0.47\text{eV} \) for all the take-off angles.
Experimental data: O1s

- BE (eV) vs. counts/sec graph showing O-Si and O-Me peaks.
- Relative % O-Me graph with data points at various angles.
- Graphs showing %O-Me, Top surface, Si-O, TiN O, HfOx.
- Kinetic Energy (eV) vs. Counts/s (Resid. x 2) for different angles (29, 39, 49, 59, 69, 79, 89).
Experimental data: Ti2p and N1s

Ti2p

N1s

N1s BE is constant for all the angle.
Ti2p comparison with reference samples:
1) TiN; TiOx

XPS International data base
Experimental data: Hf4f

Comparison: references: HfO2 and HfON
Hf4f peak fitting

Counts / s (Resid. × 1)

Kinetic Energy (eV)

angle=88

Hf4f7N

Hf4fNO

Hf4f7O

Hf4f5O

Hf4f5N

$\frac{I(x)_{30}}{I(x)_{88}}$ = $\ln(I(x))$

TiN interface

Substrate

HfN

HfNO

HfO2
Standing wave: 100Å TiN/ native SiO2/ MoSix mirror

TiN:
- without cap layer
- not annealed

Christian Papp et al.; See poster
Summary

Suggested stack layer structure by H-AR-XPS and by standing wave analysis

SiO₂ 16 Å
Poly-Si ~30Å

TiNO 80Å

HfON 19Å
HfO₂

Si substrate

Film stack was annealed at T=1000°C for mimicking Gate First device
Conclusions:

• The chemical characterization of Si, O, Ti and Hf shows that our film does not have sharp interfaces between each layer.

• The presence of O in the TiN layer could explain the higher than expected resistivity.

• The intermixing of TiN with HfO2 explains the large leakage current of this sample.

• For the first time the diffusion of N into the HfO2 layer has been demonstrated.

• The intermixing layer of N-Hf-O is about 19Å

• This work shows that HAXPES, including standing wave excitation, is a powerful technique providing useful information for advanced semiconductor film development.

• Collaborations between industry and universities may greatly help in developing advanced devices.
Outlook: HAXPES applications

1. Metal gate characterization: New films under investigations.
2. High K dielectric with K > HfO2 and EOT < HfO2.
3. Ultra shallow junction As and B dopants distribution and chemical state

Si based- Photovoltaic cells:
1. AZO characterization: Zn-O atomic distribution. Where is Al?