Robust ARXPS data analysis

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The University of Texas at Dallas

M. Quevedo
Texas Instruments
Content

Robust ARXPS data analysis

• Motivation
  • The structure of Hf-based high-k dielectric stacks
  • Characterization of Hf-based high-k MOS stacks (SIMS and LEIS)

• Angle Resolved XPS
  • Brief description
  • The removal of the upper layers: the need of longer attenuation lengths
  • Applying ARXPS and deconvolving the O 1s peak (HfO2 and SiO2)

• The importance of noise in XPS data peak fitting
  • Standard method (sequential fitting)
  • Robust method (simultaneous fitting)
  • Simultaneous vs Sequential fitting

• Application: Thermal stability of La in Hf-based high-k MOS stacks
  • Finding the binding energy of O 1s in HfO2 and SiO2
  • The constituting layers
  • The depth profile of La

• Conclusions
The structure of Hf-based high-k dielectric stacks

Thermal stability of dielectric stacks
(Samples grown at Texas Instruments)

- Metal
- layer to correct the Work Function
- High-k dielectric
- unavoidable silicon oxide layer

Motivation

High-k dielectric

SiO₂

Poly Si

TaN

La₂O₃

Hf N O

Si N O

Si substrate

what happen to these layers upon RTA?
Robust ARXPS data analysis

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Previous Studies of Thermal Stability

FIG. 9: Backside SIMS showing no La penetration into the Si substrate after high T (1000°C) process

Both La$_2$O$_3$ and La-Silicate were used in experiments

$^{1}$IBM VLSI 2006, V. Narayanan et. al.
Diffusion of Ta, La, or Hf into Si bulk
Backside Secondary Ion Mass Spectroscopy: All Samples

No diffusion of La, Hf, nor Ta, from any of the samples into the substrate.

Anneal recipe: 1000ºC in N₂ for 5 seconds.

Data collected at: North Carolina State – F. Stevie
Sample 1

Vertical magnification x18

Surface O

- Unannealed
- Annealed

Composition

Depth [Å]

1ch 165.00KeV
128ch 234.59KeV
256ch 304.73KeV
384ch 373.86KeV
512ch 445.00KeV

100%
80%
60%
40%
20%

100K
200K
300K
400K

1ch 128ch 256ch 384ch 512ch

165.00KeV 234.59KeV 304.73KeV 373.86KeV 445.00KeV

Ta
La
Hf
isoSi
O
N

- Unannealed
- Annealed

Surface O
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- Si N O
- Hf N O
- La$_2$O$_3$
- TaN
- Poly Si
- SiO$_2$

ARXPS

Motivation

What happens to these layers upon RTA?
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Brief description of ARXPS

Angle Resolved XPS:

Data acquisition

Electron Energy Analyzer

X-Ray Source

Sample

Si-Bulk

1nm SiO₂

Si(001)

SiO₂

25 to 75°

Binding energy (eV)

Intensity (c.p.s.)
Take-Off Angle vs. Peak Area

- Lower dependence on angle
- Atom closer to the surface
- Atom buried deep
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The removal of the upper layers: need longer EAL

Thermal stability of dielectric stacks

Layer to correct the Work Function

High-k dielectric

unavoidable silicon oxide layer

Metal

SiO₂

Poly Si

TaN

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Hf N O

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Si substrate

Angle Resolved XPS

Cinvestav
The removal of the upper layers: need longer EAL

Thermal stability of dielectric stacks

- Metal
- Layer to correct the Work Function
- High-k dielectric
- Unavoidable silicon oxide layer

Diagram:

- Poly Si
- TaN
- La$_2$O$_3$
- Hf N O
- Si N O
- Si substrate
The removal of the upper layers: need longer EAL

Thermal stability of dielectric stacks

- Metal layer to correct the Work Function
- High-k dielectric
- Unavoidable silicon oxide layer

Diagram:
- TaN
- La$_2$O$_3$
- Hf N O
- Si N O
- Si substrate
The removal of the upper layers: need longer EAL

Thermal stability of dielectric stacks

Layer to correct the Work Function
High-k dielectric
Unavoidable silicon oxide layer

Si substrate
Si N O
Hf N O
La$_2$O$_3$
The removal of the upper layers: need longer EAL

Thermal stability of dielectric stacks

Metal

Layer to correct the Work Function

High-k dielectric

Unavoidable silicon oxide layer

Si substrate

Si N O

Si N O

Hf N O

La$_2$O$_3$

TaN

Poly Si

SiO$_2$

4 nm
Thermal stability of dielectric stacks

- Metal
- Layer to correct the Work Function
- High-k dielectric
- Unavoidable silicon oxide layer

- Si substrate
- Si N O
- Hf N O
- La$_2$O$_3$
- TaN

4 nm

The removal of the upper layers: need longer EAL
The removal of the upper layers: need longer EAL

Thermal stability of dielectric stacks

- Higher intensity
- Higher energy
- Higher resolution

than regular ESCA sources

4 nm

Metal

layer to correct the Work Function

High-k dielectric

unavoidable silicon oxide layer

TaN

La$_2$O$_3$

Hf N O

Si N O

Si substrate
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XPS Data

Si 2p

La 3d

Si 2p in Si-Si

Si 2p in SiO₂

La 4d

La₄⁺ 3d₃/₂

La₄⁺ 3d₅/₂

La₃⁺ 3d₅/₂

plasmon

O 1s

Hf 4f

N 1s

532.5 eV

531.3 eV

531.3 eV
Applying ARXPS and deconvolving the O 1s peak

Anions

- Hf 4f in HfO₂
- Si 2p in bulk
- Si 2p in SiO₂
- La 3d
- Ta 4f
- O 1s in SiO₂
- O 1s in HfO₂
- N 1s in SiO₂
- C 1s (adventitious)

Cations

- Si substrate

MS4+RTA

Spurious carbon (0.5 ML)

Oxidized Ta (? ML)

Oxidized La (? ML)

Si O₂ N₂
Is it possible to robustly and uniquely get the two peaks?

HfO$_2$/SiO$_2$/Si nanofilm

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Is it possible to robustly and uniquely get the two peaks?
Is it possible to robustly and uniquely get the two peaks?

HfO$_2$/SiO$_2$/Si nanofilm

Applying ARXPS and deconvolving the O 1s peak

Is it possible to robustly and uniquely get the two peaks?
Applying ARXPS and deconvolving the O 1s peak

Thick HfO$_2$

Thick SiO$_2$


<table>
<thead>
<tr>
<th></th>
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• Conclusions
The importance of noise in XPS data fitting

Simulated data mimicking O 1s from HfO$_2$ (peak 1) and SiO$_2$ (peak 2)
The importance of noise in XPS data fitting

Standard fitting method: Sequential
Standard fitting method: Sequential

The importance of noise in XPS data fitting

Kinetic Energy (eV)

Gaussian Width (eV)

File Number
Standard fitting method: Sequential

The importance of noise in XPS data fitting

![Graph showing kinetic energy (eV) and Gaussian width (eV) against file number.](image)
The importance of noise in XPS data fitting

Standard fitting method: Sequential

![Graph showing area (a.u.) vs. file number](chart.png)
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Robust fitting method: Simultaneous

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Simultaneous vs Sequential

The importance of noise in XPS data fitting

Graphs showing the comparison between simultaneous and sequential fitting methods.
The importance of noise in XPS data fitting

Simultaneous vs Sequential

What happens with slightly larger noise?

![Graph showing kinetic energy vs eV with simultaneous vs sequential fitting examples.]

The importance of noise in XPS data fitting
The importance of noise in XPS data fitting

Simultaneous vs Sequential

Kinetic Energy (eV)
Simultaneous vs Sequential

The importance of noise in XPS data fitting

File Number

Area (a.u.)

0 1 2 3 4 5

0 800 900 1000 1100 1200 1300 1400 1500
Simultaneous vs Sequential

The importance of noise in XPS data fitting

Noise 1

Area slope

Trial Number
The importance of noise in XPS data fitting

Simultaneous vs Sequential

Noise 1

Kinetic Energy (eV)
Simultaneous vs Sequential

Slopes of Peaks 1 and 2

- Peak 1 Sequential fitting
- Peak 2 Sequential fitting
- Peak 1 and 2 Simultaneous fitting
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Thermal stability of La in Hf-based MOS stacks

Metal

unavoidable silicon oxide layer

layer to correct the Work Function

High-k dielectric

Si substrate

Poly Si

SiO$_2$

ARXPS

Thermal stability of dielectric stacks

what happens to these layers upon RTA?

Application

ARXPS

Thermal stability of dielectric stacks

Hf N O

La$_2$O$_3$

TaN

Si N O
Thermal stability of dielectric stacks

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layer to correct the Work Function

High-k dielectric

unavoidable silicon oxide layer

what happen to these layers upon RTA?

Poly Si

TaN

La$_2$O$_3$

Hf N O

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Si substrate
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- Layer to correct the Work Function
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Thermal stability of dielectric stacks

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What happens to these layers upon RTA?
Application

XPS Data

Thermal stability of La in Hf-based MOS stacks

Si 2p

La 3d

O1s

Hf 4f

N1s
Robust ARXPS data analysis

- **Motivation**
  - The structure of Hf-based high-k dielectric stacks
  - Characterization of Hf-based high-k MOS stacks (SIMS and LEIS)

- **Angle Resolved XPS**
  - Brief description
  - The removal of the upper layers: the need of longer attenuation lengths
  - Applying ARXPS and deconvolving the O 1s peak (HfO2 and SiO2)

- **The importance of noise in XPS data peak fitting**
  - Standard method (sequential fitting)
  - Robust method (simultaneous fitting)
  - Simultaneous vs Sequential fitting

- **Application: Thermal stability of La in Hf-based high-k MOS stacks**
  - Finding the binding energy of O 1s in HfO2 and SiO2
  - The constituting layers
  - The depth profile of La

- **Conclusions**
Finding the binding energy of O 1s in HfO$_2$ and SiO$_2$

**Part a)**

- Binding Energy (eV) for O 1s in HfO$_2$:
  - 532.5 eV
  - 531.3 eV

**Part b)**

- Resulting composition: SiO$_{1.98}$ and HfO$_{1.61}$
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Dealing with straight or ratio data

so far we have been dealing with the peak areas directly
ARXPS Data

The take-off angle dependence of the peak areas (ARXPS Data)

Anions

- Hf4f in HfO₂
- La3d
- Si2p in bulk
- Si2p in SiO₂
- Ta4f

Cations

- O 1s at 531.3eV
- O 1s at 532.5eV
- N 1s
- C 1s (adventitious)
Estabilidad térmica de multicapas

Algunos ejemplos de aplicación de ARXPS

Anions

Hf4f in HfO₂

Si₂p in bulk

Si₂p in SiO₂

Take Off Angle

Peak Area

 Thickness assuming bulk density

MS4+RTA

Spurious carbon (0.5ML)

Hf O₂

8.4 Å ± ?

Si O₂ N₂

15.3 Å ± ?

Si substrate

Si substrate
Composition found from the cation data

- **Si substrate**
  - Thickness: 15.3 Å
- **Si O\(_{1.7\pm0.13}\) N\(_{0.5}\)**
  - Thickness: 8.4 Å
- **Hf O\(_{1.9\pm0.11}\)**
  - Thickness: 8.4 Å

Spurious carbon (0.5 ML)

**Cations**

- **O 1s in HfO\(_2\)**
- **O 1s in SiO\(_2\)**
- **N 1s in SiO\(_2\)**
- **C 1s (adventitious)**

Graph showing peak area vs. take off angle.
Going around ill-conditioning

Extra information from TEM images

TiN
HfON
SiON
Si
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Conclusions
A “difficult problem”: the position of La

At the HfO₂/SiO₂ interface
At the surface
Throughout HfO₂ layer
Throughout SiO₂ layer

Si O₁.₇ N₀.₅
Si substrate

Oxidized Ta (0.1 ML)
Oxidized La (0.3 ML)

Spurious carbon (0.5 ML)

8.4 Å
15.3 Å

La amount and position

Experimental data
At the HfO₂/SiO₂ interface
At the surface
Throughout HfO₂ layer
Throughout SiO₂ layer
Robust ARXPS data analysis

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Conclusions

- The characterization of the La depth profile, is a challenging problem. ARXPS is the ideal technique because it provides both chemical and depth profile information.
- The noise could be a killing factor in ARXPS analysis.
- For XPS data peak fitting, simultaneous analysis is (much) more robust than sequential analysis.
- For the recovery of the depth profile from the angle dependence of the peak areas, the parametric methods (such as the Multilayer Model) is more robust and less dependent on noise than the back transform or regularization methods (such as Maximum Entropy).
- By employing robust methods for both XPS data analysis and depth profile analysis, it is possible to recover the structure of the films.
- La diffuses into the HfO2/SiO2 interface
Thank you!