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Atomic Layer Deposition of High-k Dielectric and Metal Gate Stacks for MOS Devices

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Outline

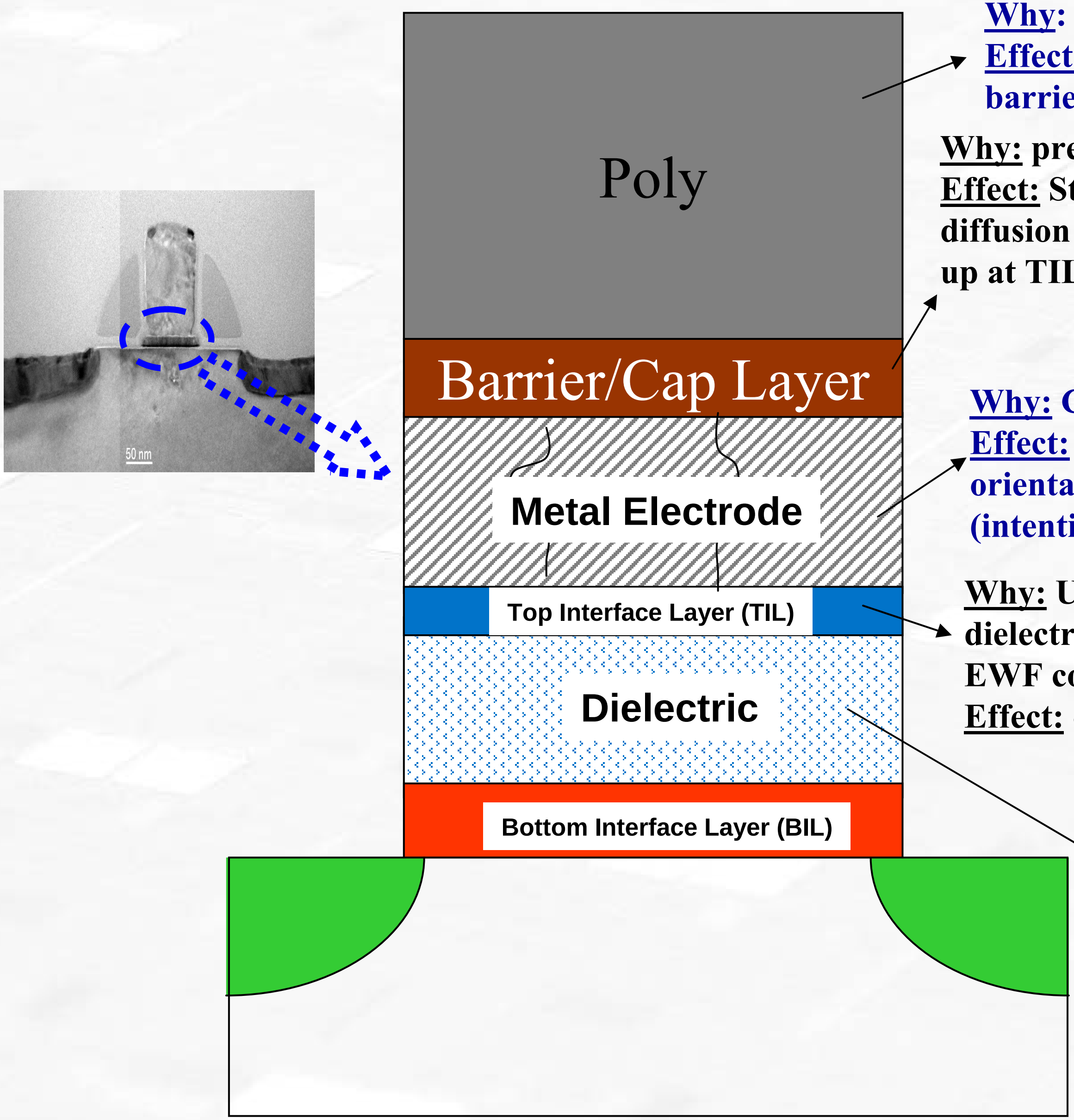
1. Introduction
2. ALD of High-k Dielectric
   - High-k dielectric ALD processes
   - Electrical properties of MOS devices
   - Scaling the Hf-based dielectric
3. ALD of Metal Gate
   - ALD Metal Nitrides - TiN, HfN, HfSiN, TaN
   - Work function evaluation

MOSFET Device Goals for 45 nm node and beyond

Application	EOT (nm)	CET (nm)	Jg (A/cm^2)
High Performance (HP)	</= 0.8	</= 1.2	</= 100
Low Standby Power (LSTP)	</= 1.6	</= 2.4	</= 2.2×10^{-3}

- Density of interface traps (D_{it}) </= 5×10^{10} # / cm^2·eV
- High frequency (100kHz) CV hysteresis </= 10 mV
- $V_t \pm 0.2V$ of control SiO_2 with same EOT
- V_t stability ± 10mV of unstressed film
- Mobility >/= 90% of SiO_2 at EOT 0.8nm
- Defect Density </= 0.14 defects / cm^2
- Thermal stability (physical and electrical) at 1000ºC, 5 sec
- Thickness uniformity (3 sigma) </= 4%
- Reliability comparable to SiO_2

Factors That Influence Metal Electrode Properties



Why: Ease of integration
Effect: Stress ?, Reaction with electrode if no barrier layer ?

Why: prevent interaction between Electrode and Poly;
Effect: Stress ?, Reaction with metal electrode? Metal diffusion through electrode grain boundary and pile up at TIL ? Overlay effect if electrode very thin ?

Why: Control WF, EOT scaling (no poly depln)
Effect: main contributor to WF , Crystallinity, grain orientation, thickness effect? Overlay effect if TIL (intentional) very thin ?

Why: Unintentional (due to reaction of metal with dielectric); Intentional (dual metal integration and EWF control via overlay effect)
Effect: controls EWF if TIL forms

Why: High-k for scaling
Effect: reaction with metal to form TIL + Fermi level pinning, fixed charges shift Vfb shift.

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Introduction: Why Metal ALD ?

- Why metal electrodes?
  - ✓ **poly electrode depletion** limits device scaling
  - ✓ poly electrode can interact with high-k materials

- Why ALD metal electrodes?
  - ✓ **Excellent thin film thickness uniformity control**
  - ✓ **Excellent composition control**
  - ✓ **Little damage to gate oxide (compared to PVD)**
  - ✓ **Low temperature deposition with low impurity**
  - ✓ **Conformality at nanoscale structures and potentially 3-D devices**

- Multiple potential applications for ALD metal films
  - ✓ **Metal gate electrode: TaN, TiN, W, Ru..**
  - ✓ **Cu diffusion barrier/adhesion promoter: TaN, Ta, TaSiN, TiN, WN..**
  - ✓ **Cu seed layer: Cu**
  - ✓ **Plug for via hole: W, WN_x**
  - ✓ **Barrier: TiN, Ti**

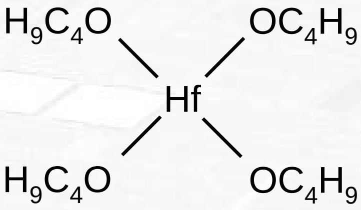
Gate "ELECTRODE" Specifications

Application	EWF (n metal)	EWF (p metal)
CMOS on bulk Si	**4.1 +/-0.05**	**5.2 +/-0.05**
CMOS on FDSOI, FINFET	4.4 +/-0.05	4.9 +/-0.05

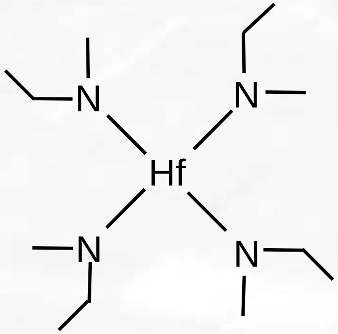
- **Gate stack subjected to S/D dopant activation anneal (1000 C, 5 sec)**
- **$V_t \pm$ 0.1 V of control SiO_2 with same EOT**
- **V_t stability ± 10mV of unstressed film**
- **Mobility >/= 95% of SiO_2**
- **Density of interface traps (D_{it}) </= 5×10^{10} # / $cm^2 \cdot eV$**
- **High frequency (100kHz) CV hysteresis </= 10 mV**
- **Reliability comparable to Poly/SiO_2**
- **Defect Density </= 0.14 defects / cm^2**
- **Thickness uniformity (3 sigma) </= 4%**

ALD Processes:
Metal-Organic Liquid Precursors for HfO_2

Hf-t-Butoxide **$Hf(C_4H_9O)_4$**
Dep. Rate: 0.24Å/cycle



TEMAHf (Tetrakisethylmethyl amino hafnium) **$Hf(NMeEt)_4$**

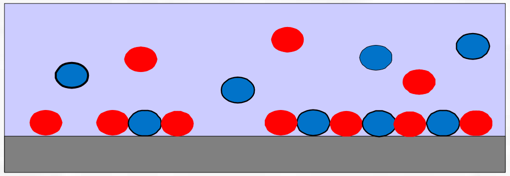


Dep. Rate: 0.89Å/cycle
Less impurities in the HfO_2 films
Lower leakage current of HfO_2

--> Precursor of choice

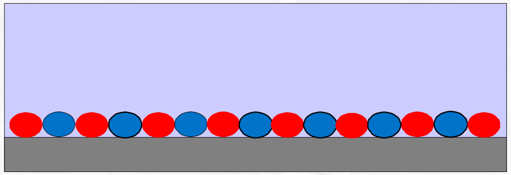
ECS Proceedings, 2003

Precursor Co-injection ALD Concept for HfSiOx



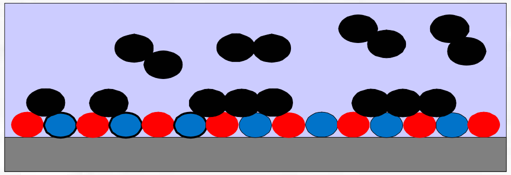
●A+B(g)

●Introduction of A+B(g) onto the substrate surface



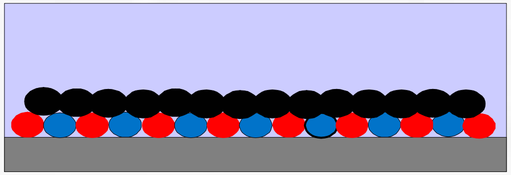
●A+B(S)

●Formation of an A+B(s) monolayer surface



●C(g)

●Introduction of C(g) onto A+B(s) surface

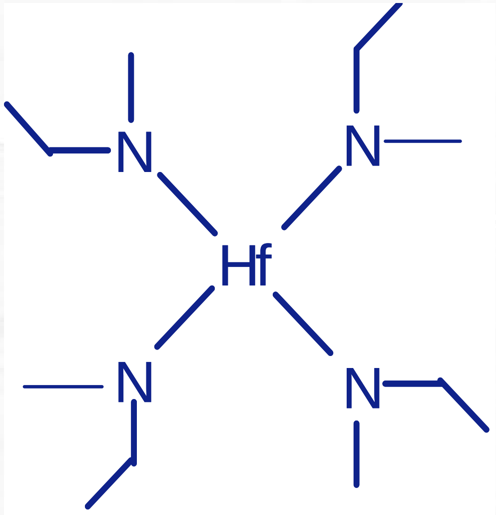


●C(S)

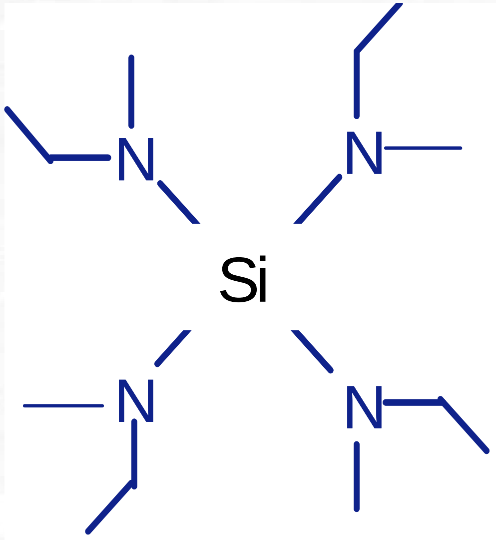
●Formation of C(s) monolayer surface

- **Introduction of A(g) + B(g) onto the substrate surface**
- **Formation of an A+B(s) monolayer surface**
- **Introduction of C(g) onto A+B(s) surface**
- **Formation of C(s) monolayer surface**

HfSiOx ALD Precursors



TEMAHf



TEMASi

Chemical compatibility

-> suppresses gas phase reaction

J. Vac. Sci. Technol. (A), vol. 22, p.1175 (2004).

$HfSiO_x$ ALD Coinjection vs Nano-laminate

Precursor coinjection

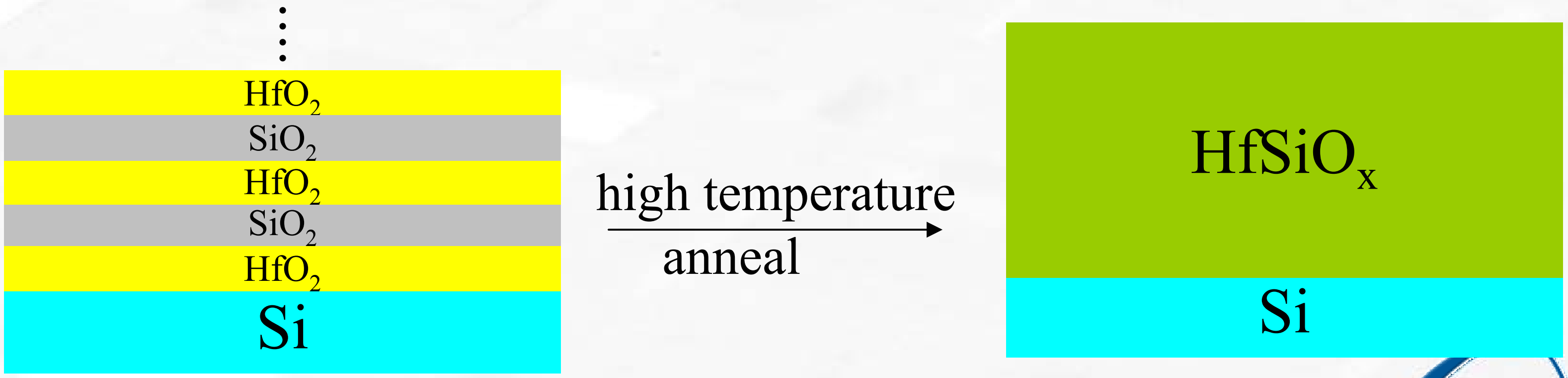
Hf/Si pulse/purge

+ Oxidizer pulse/purge

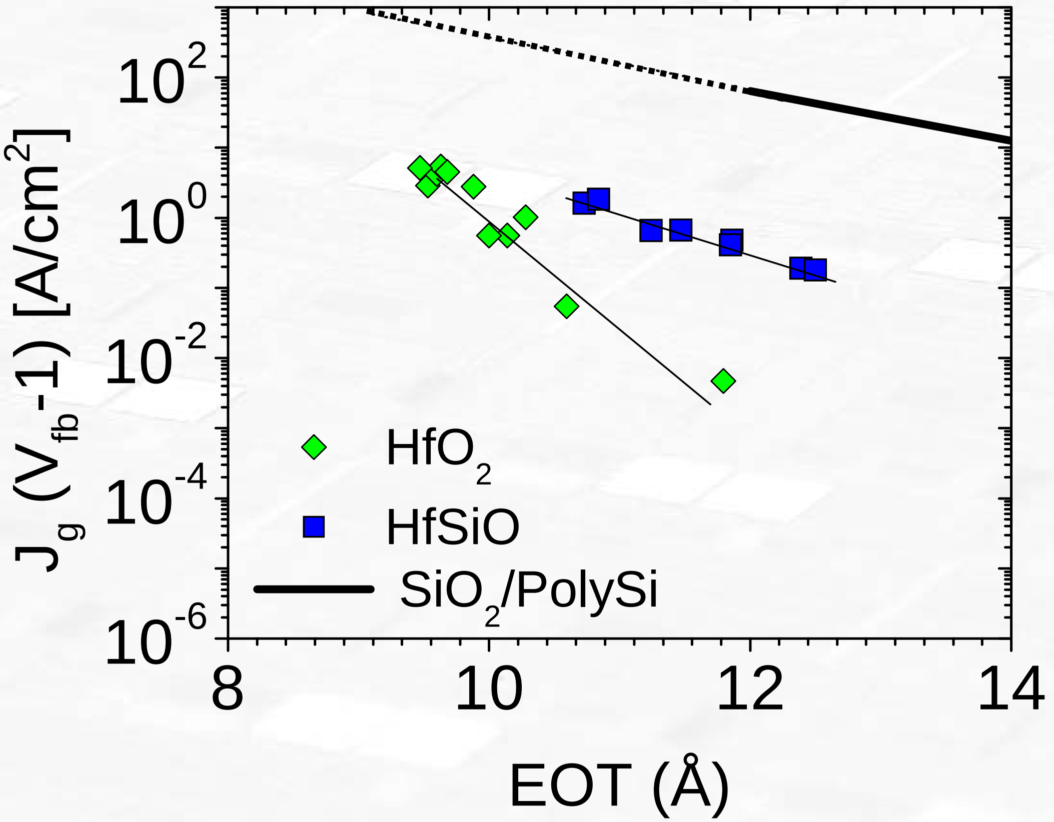
Nano-laminate

Hf pulse/purge + Ox pulse/purge

+ Si pulse/purge + Ox pulse/purge → → →



Leakage Current (J_g) Reduction of Hf(Si)O



J_g reduction: 10^2 –10^3x vs. SiO$_2$/PloySi

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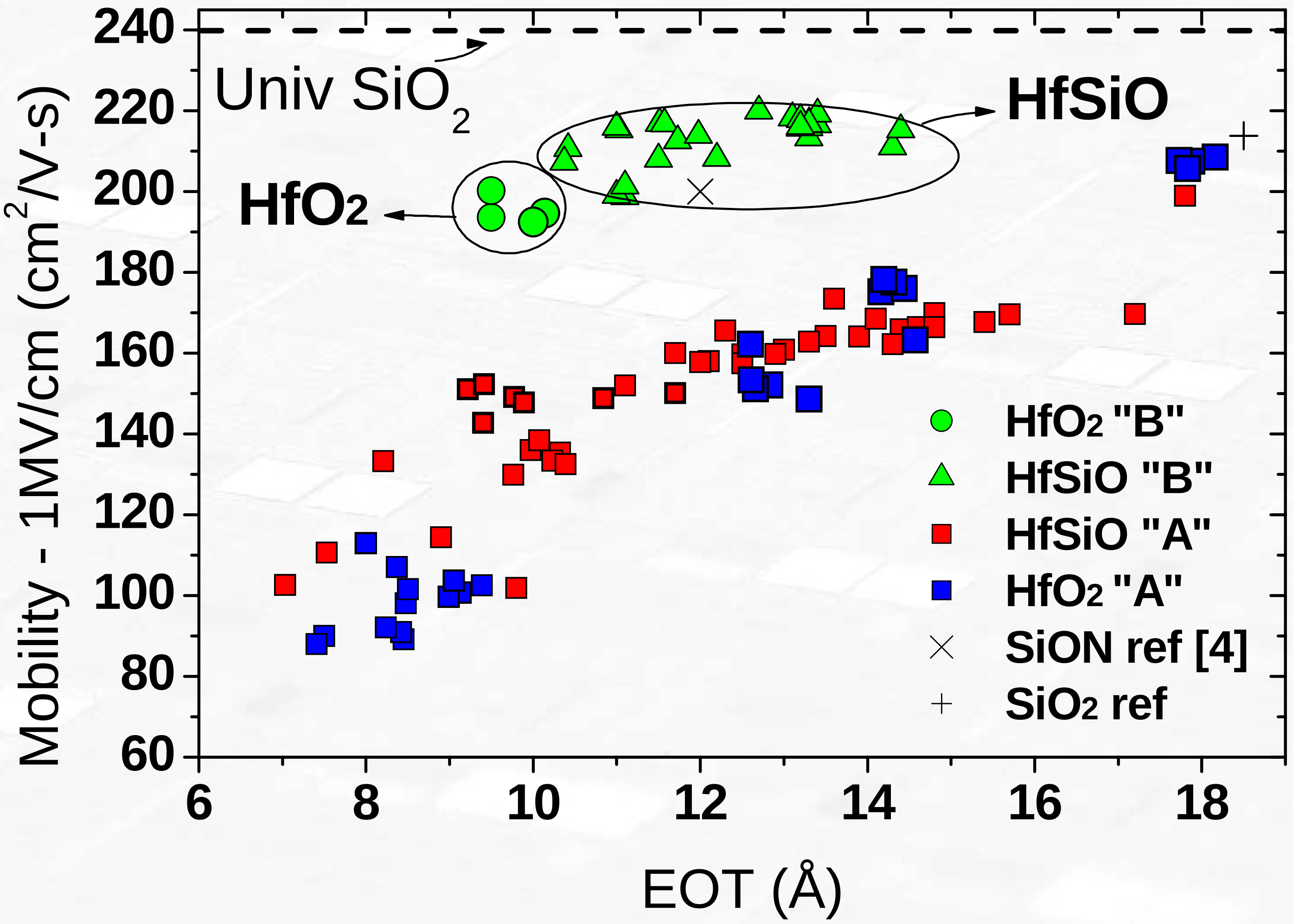
Mobility Progress with HfO_2 and HfSiO



- HfO_2 and HfSiO show mobility results similar to nitrided oxide
- Significant improvement relative to historical dataset

[4] P.A. Kraus *et al.*, Semiconductor Fabtech v. 23, p. 73 (2004).

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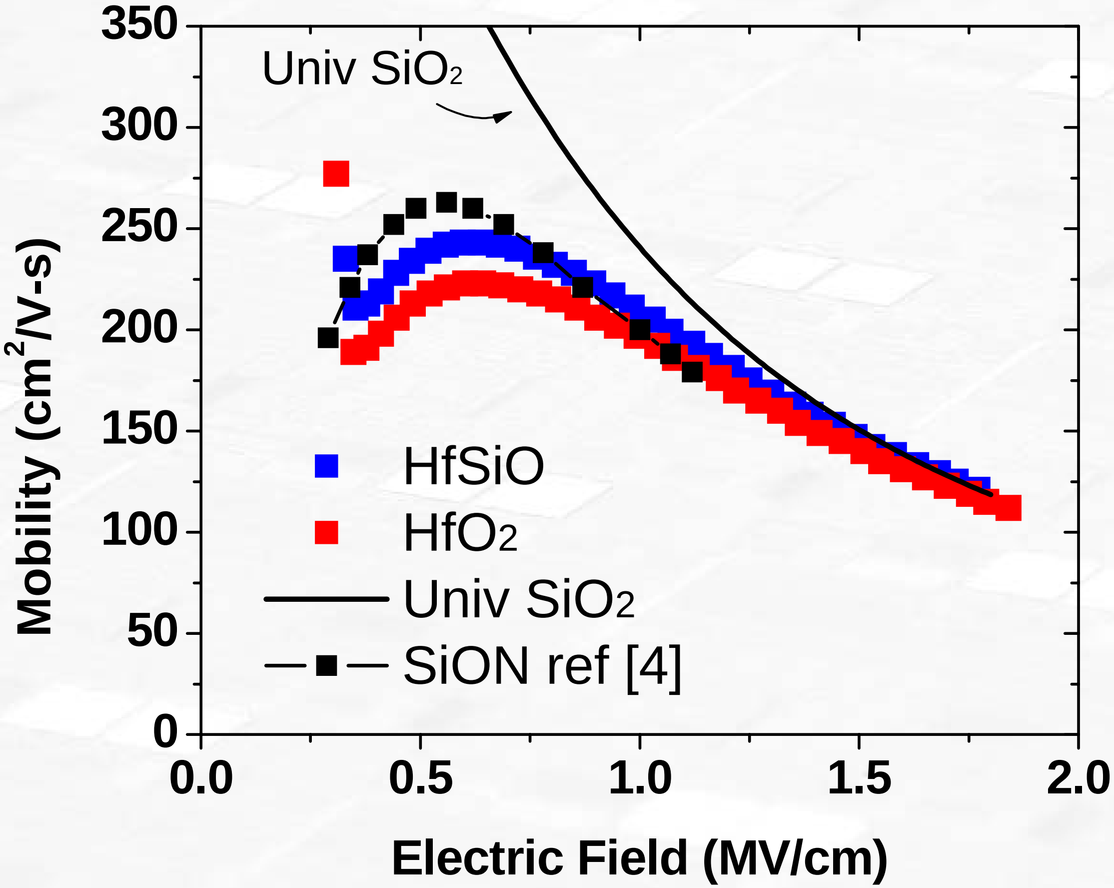
Mobility Progress at Peak and High Field

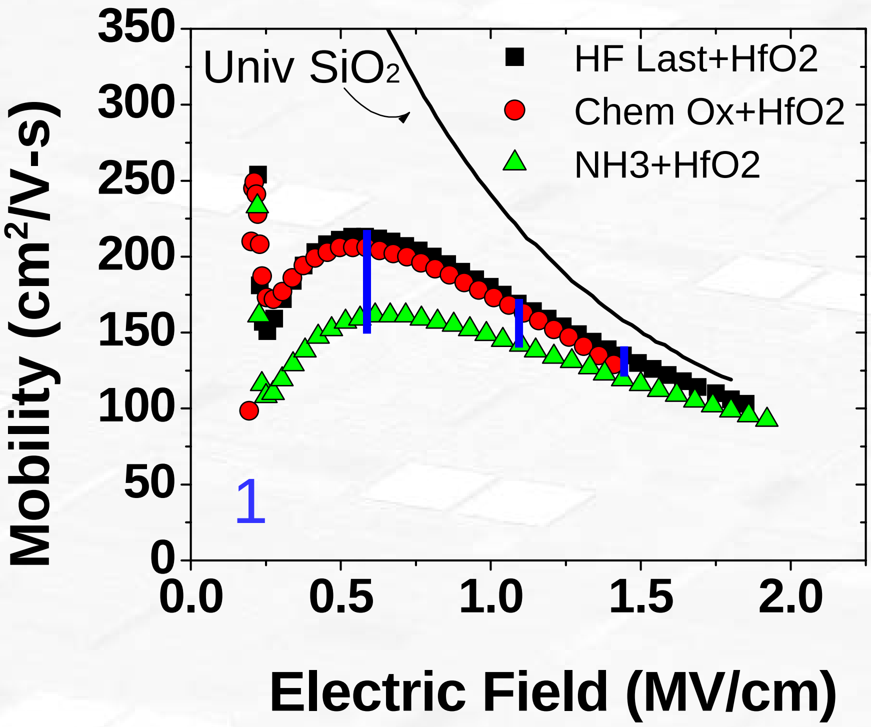


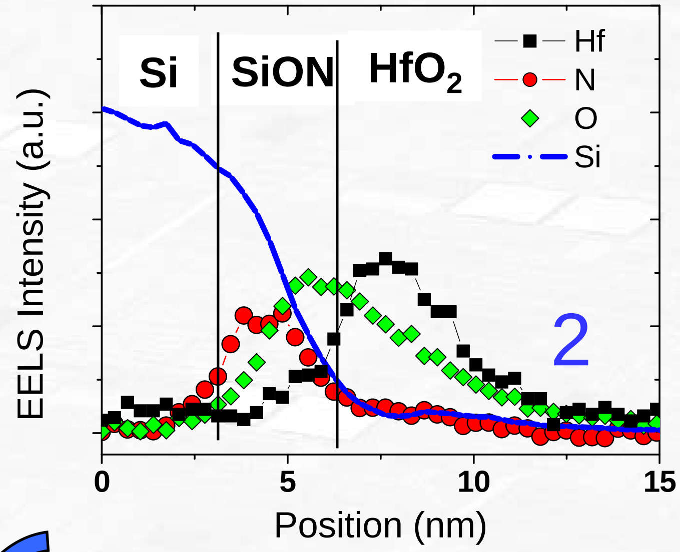
	SiON *	**HfSiO**
EOT (nm)	**1.2**	**1.07**
μ_{pk} (cm^2/V-s)	**260**	**245**
μ(1MV/cm) (cm^2/V-s)	**200**	**210**
J_g (A/cm^2) (V_t+1V) or (V_{fb}-1V)	**150**	**1**

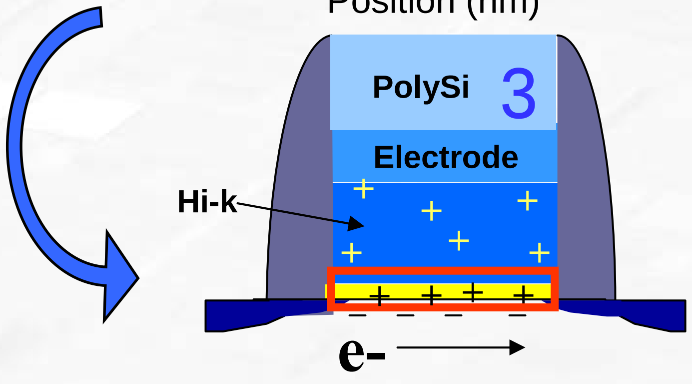
- HfSiO performs similarly to SiON but with scaling benefit

* P.A. Kraus *et al.*, Semiconductor Fabtech v. 23, p. 73 (2004).

N Content in Interfacial SiON Layer

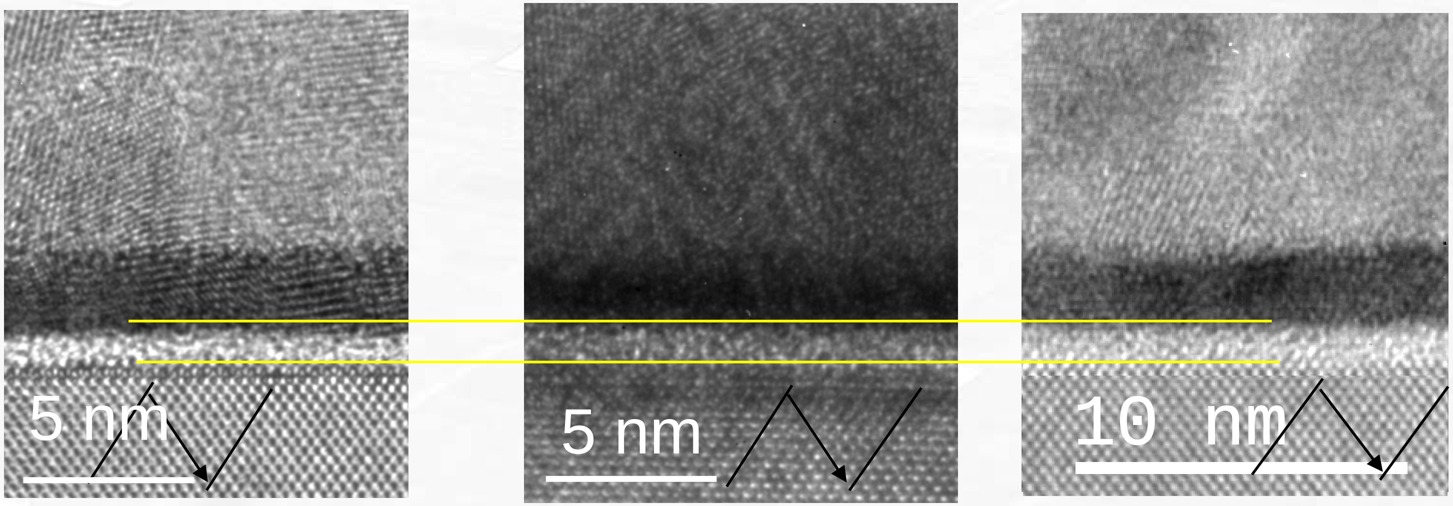






1. Mobility: NH_3 N in interfacial layer degrades mobility.
2. EELS: High N content near Si substrate (inversion layer).
3. -25% (peak μ) -15% (1MV/cm μ).

Similar Physical Thickness in SiO$_x$ and SiON



HF Last\HfO$_2$\TiN **O$_3$\HfO$_2$\TiN** **NH$_3$\HfO$_2$\TiN**

- After processing (1000C-5s), SiO(N) T_{phy} is similar (TEM is ±2Å)
- Suggests fixed charge from N [rather than physical thickness screening effect] degrades mobility
- Consistent with peak / high field mobility results

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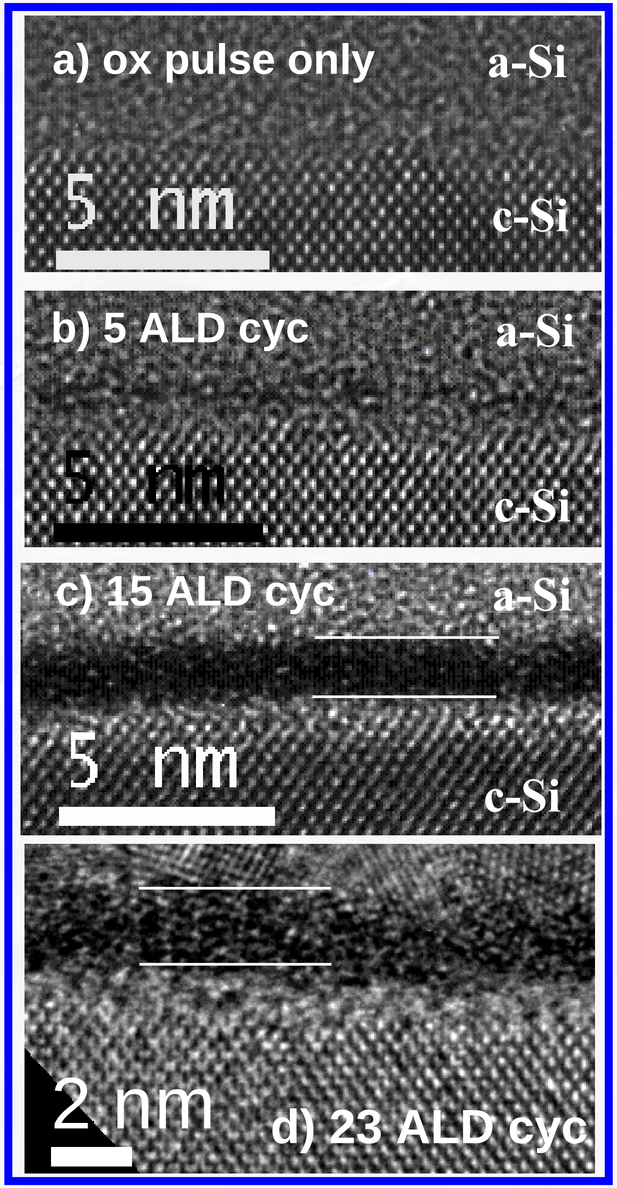
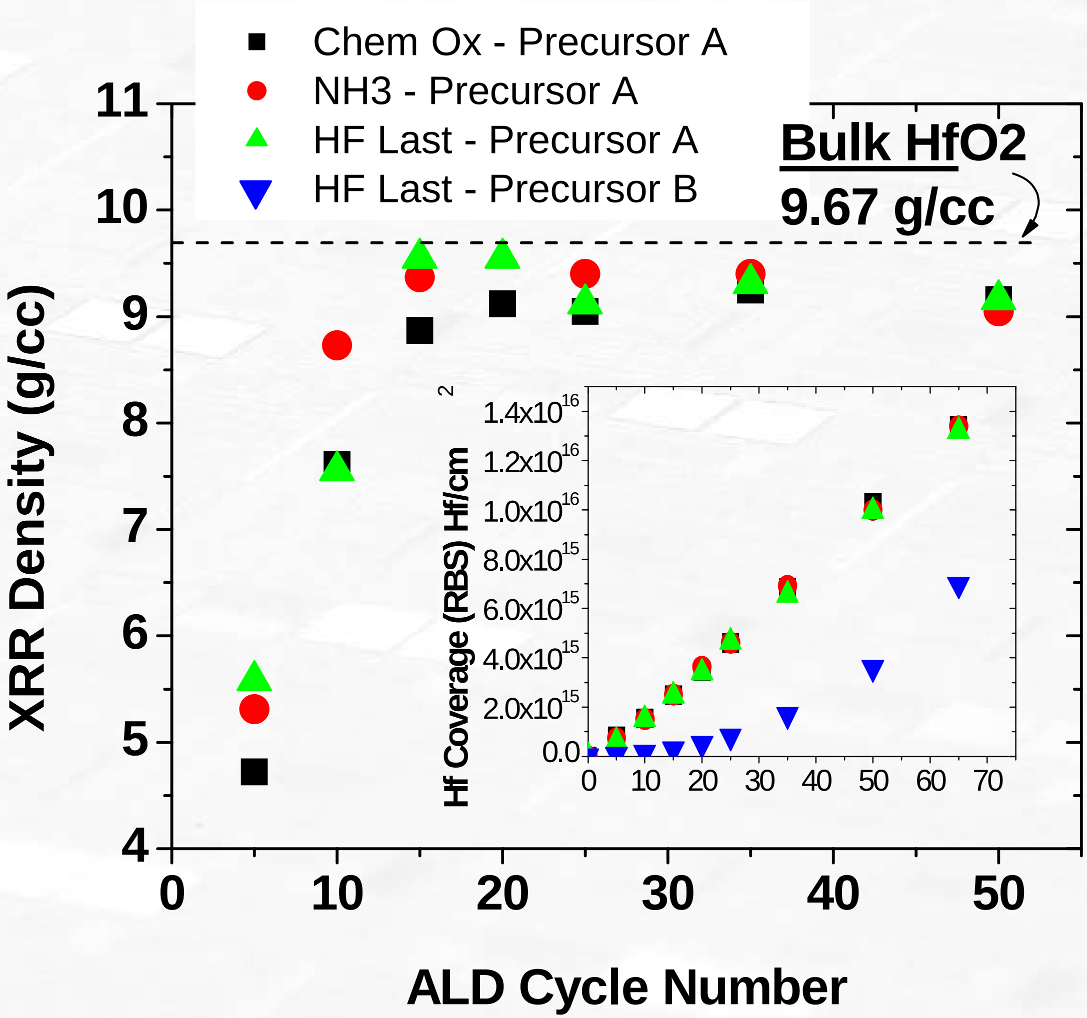
Scaling the Hf-based dielectric

Blanket





Scaling to below 2.0 nm feasible

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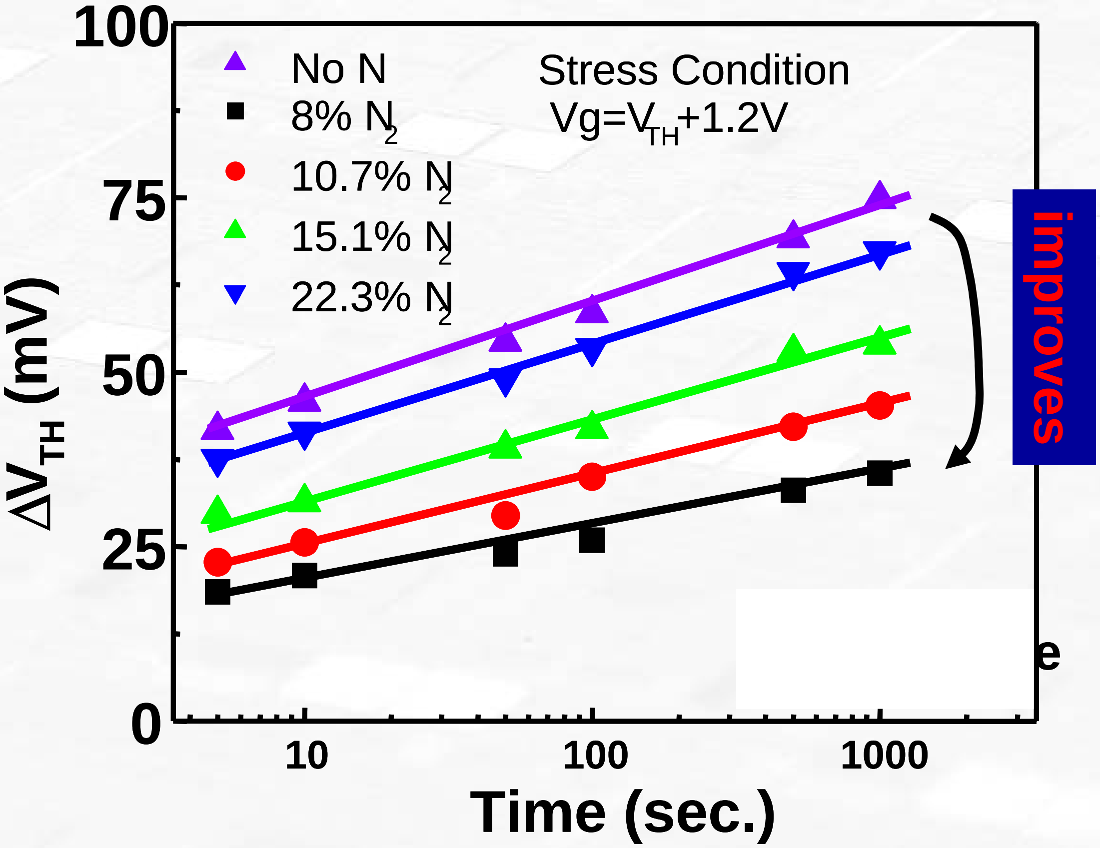
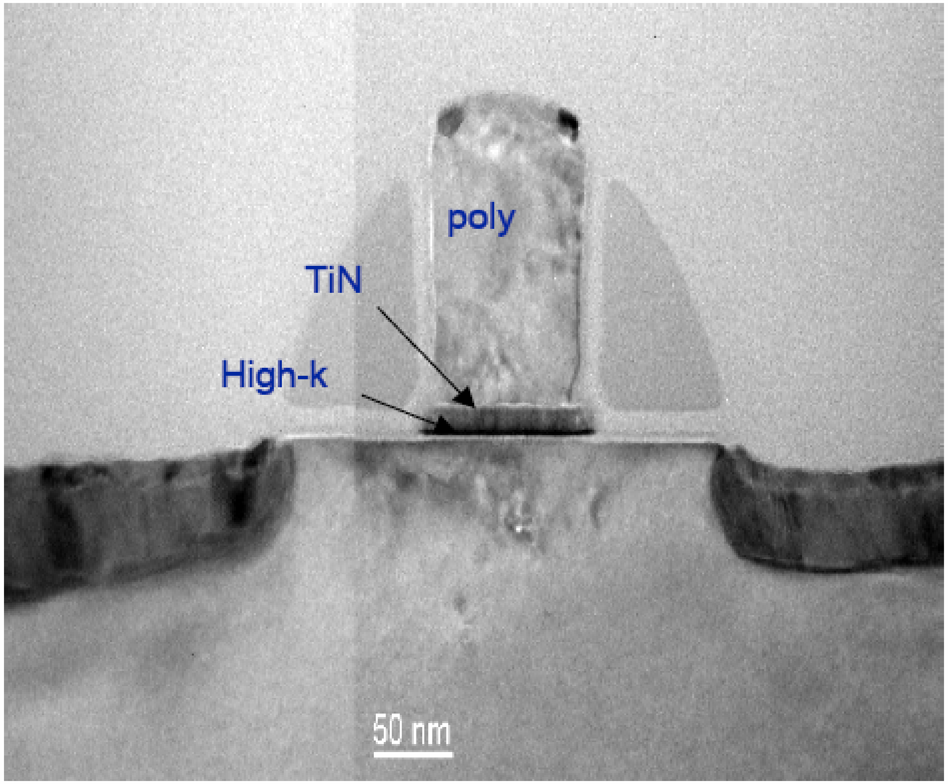
HfSiO Nitridation Improves V_t Stability



Metal Electrode: Test Structures

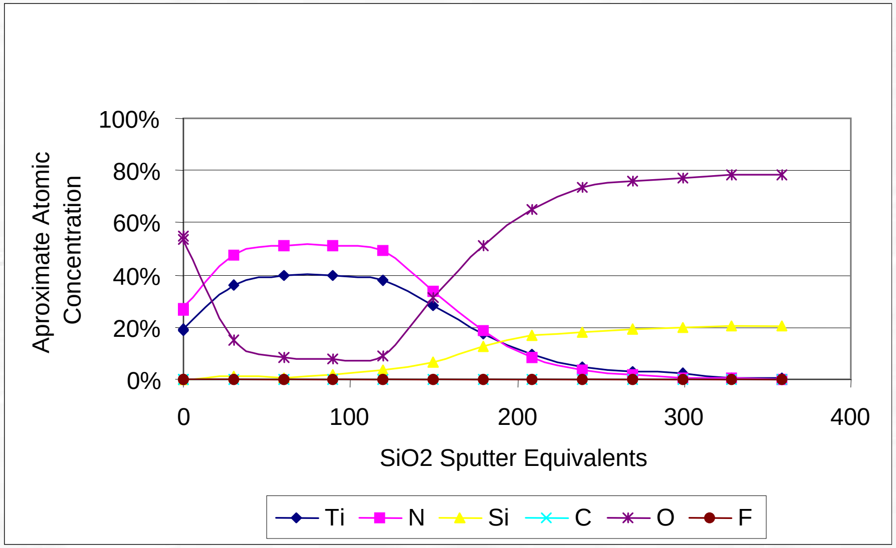


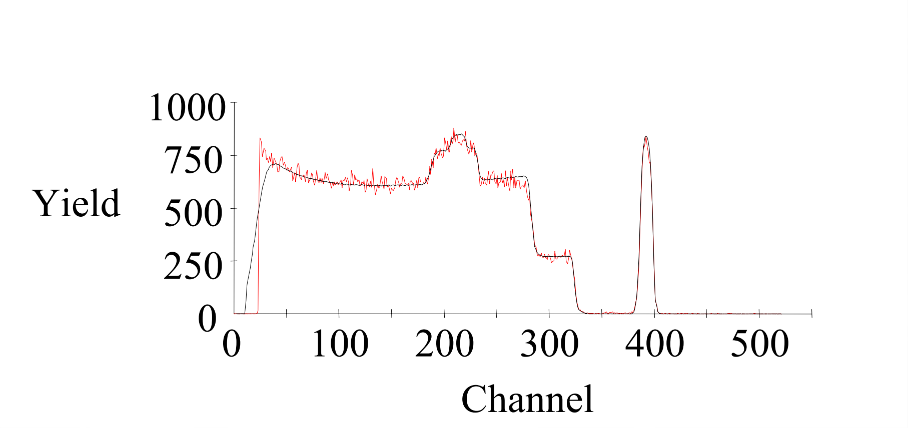
Process route/flow in place for PFET and NFET with various metal gates

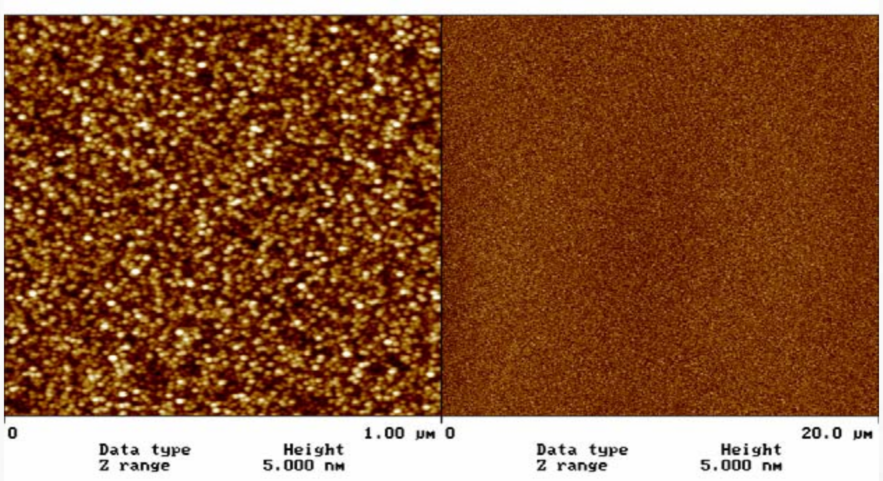
- **Capacitors:**
  Primary vehicle for initial work-function evaluation
- **Transistors:**
  thin (~10 nm) metal layer under poly electrode
- **Concentrating on dual work function (band edge) metal gate stacks in conjunction with Hf-based high-k films**
- **Also assessing near mid-gap metals for FD-SOI applications**

TiN Film Characterization

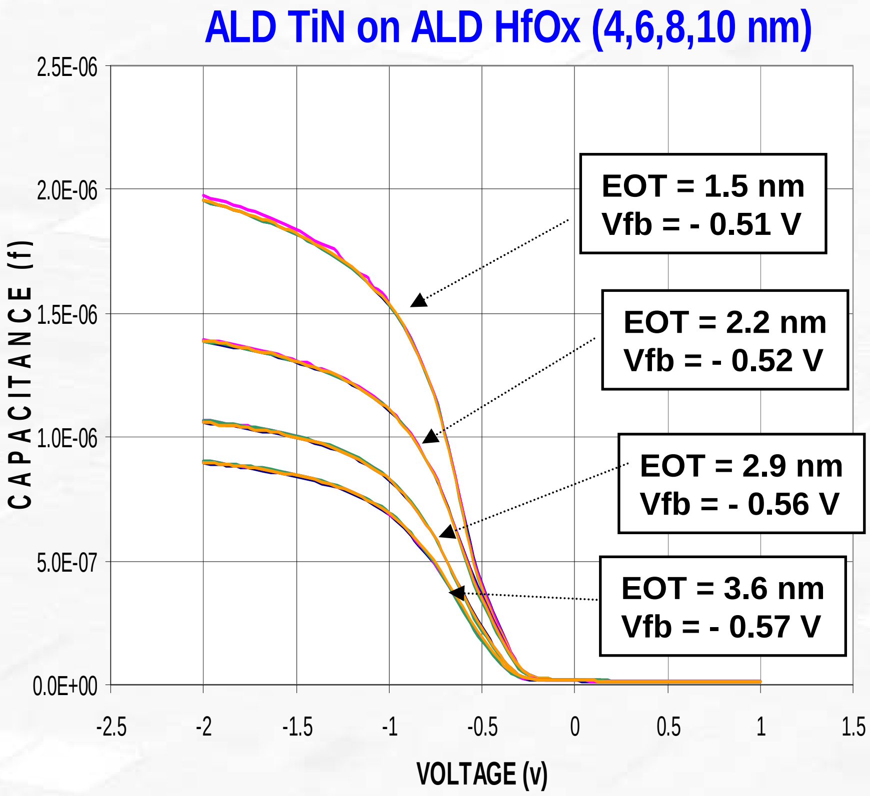
- **Surface oxide that drops to 5-8% in the bulk**
- **RMS roughness ~0.8 nm**
- **Ti/N ~1.0-1.2 depending on technique**







ALD-TiN MOSCAP Data



$$V_{fb} = \Phi_{ms} - Q_f/\varepsilon_{ox} \cdot EOT$$

V_{fb} : flat band voltage

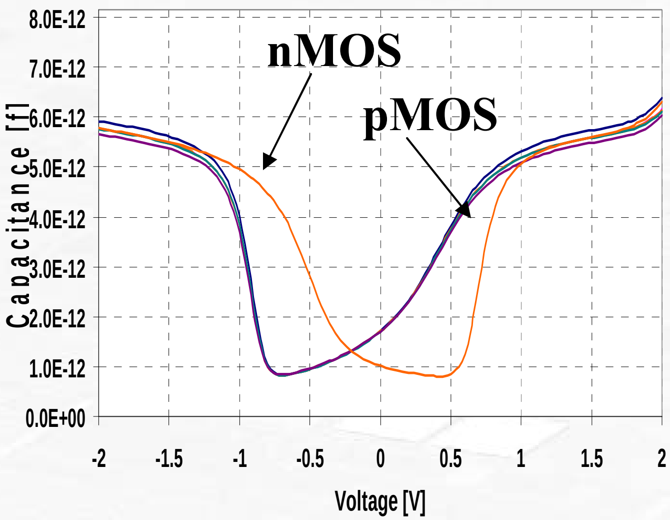
Φ_{ms}: gate work function

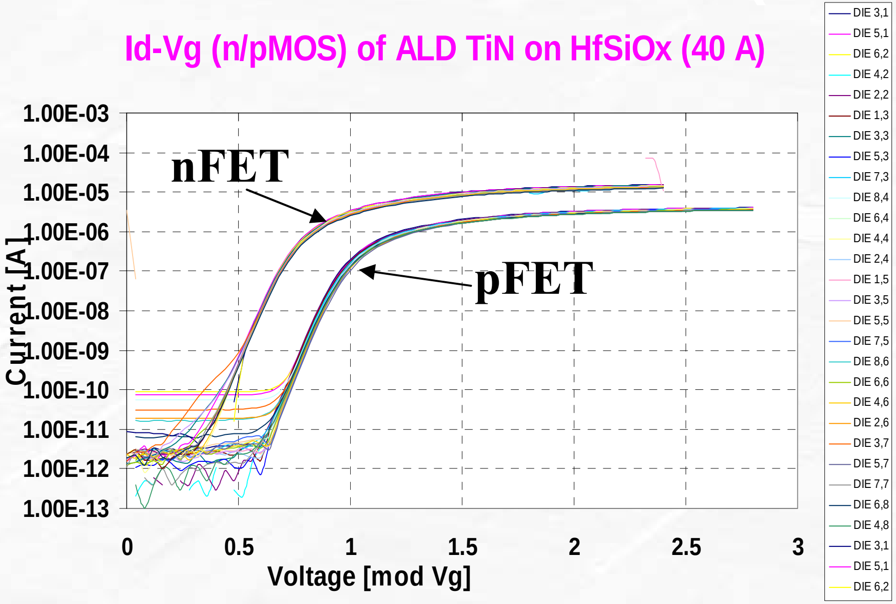
Q_f: interface charge density

Electrode	Gate Dielectric	Φ_{ms}' [V]	Nf [chg/cm^2]	Work Function Φ_m [eV]
100 A ALD-TiN	ISSG	-0.52	1.1x10e11	4.5
100 A ALD-TiN	ALD-HfOx	-0.46	7x10e11	4.5
100 A ALD-TiN	MOCVD-HfOx	-0.37	1x10e12	4.6

Marginal dependence of Work function and N_f on the gate dielectric material

Transistor Characteristics of ALD TiN on ALD HfSiOx (40 A)


C-V (n/pMOS) of ALD TiN on HfSiOx (40 A)

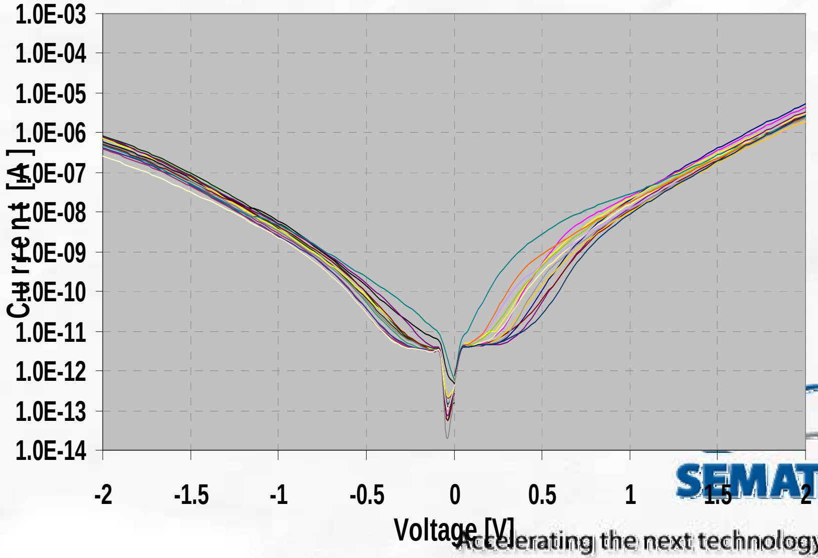

Id-Vg (n/pMOS) of ALD TiN on HfSiOx (40 A)

EOT = 2.0 nm

$V_{fb}(n)$ = -0.55 V

$V_{fb}(p)$ = 0.45 V

$Jg_{(n)\ ([Vfb-1])} = 5\ e\text{-}3\ [A/cm^2]$


Ig-Vg (n/pMOS) of ALD TiN on HfSiOx (40 A)

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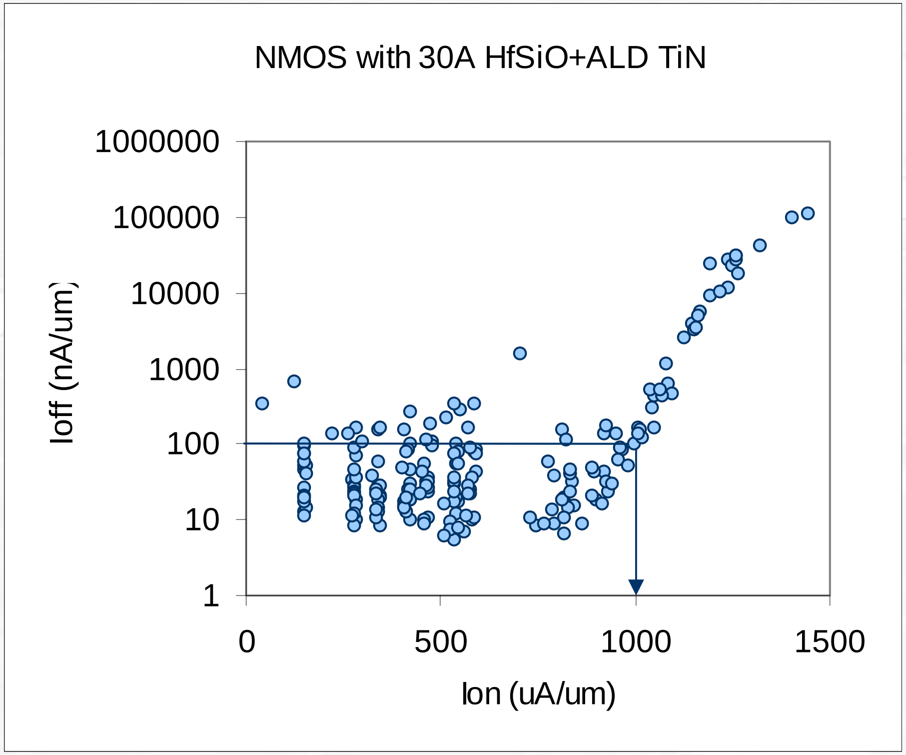
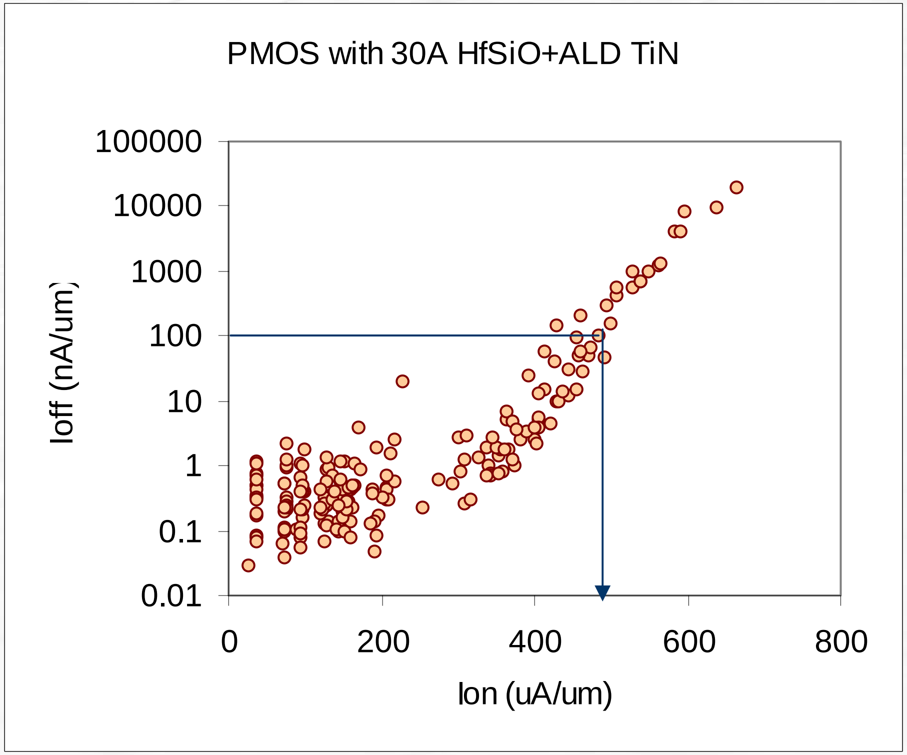
Demonstration of High Performance with High-k and TiN (Mid-Gap) Gate





- 85 nm baseline exhibits high performance
- Mobility (e/h) NOT a showstopper
- NEED band-edge metals

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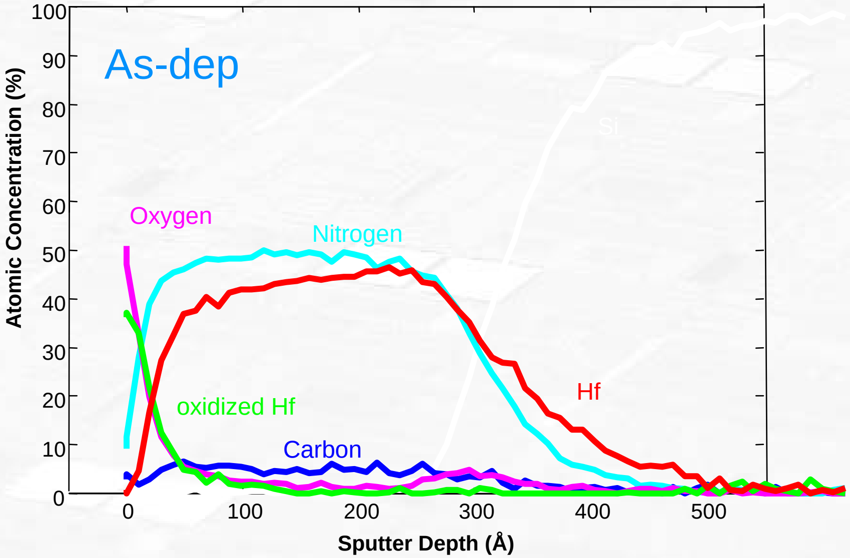
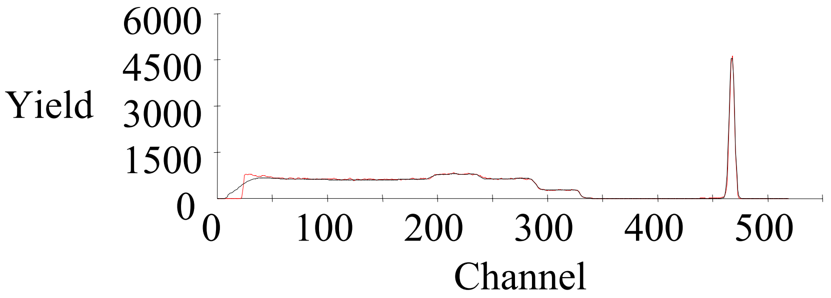
HfN Film Analysis

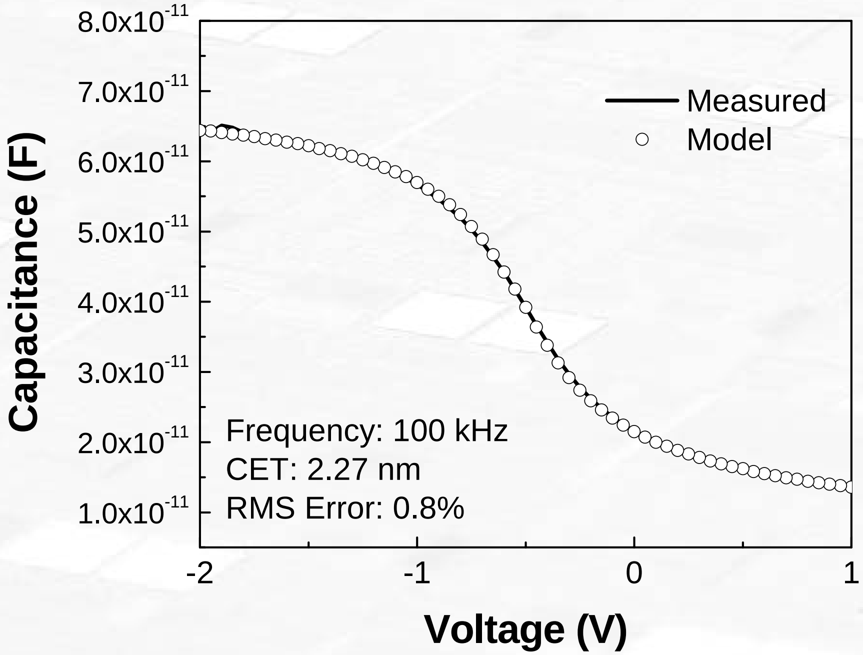
- < 5% Carbon in the film

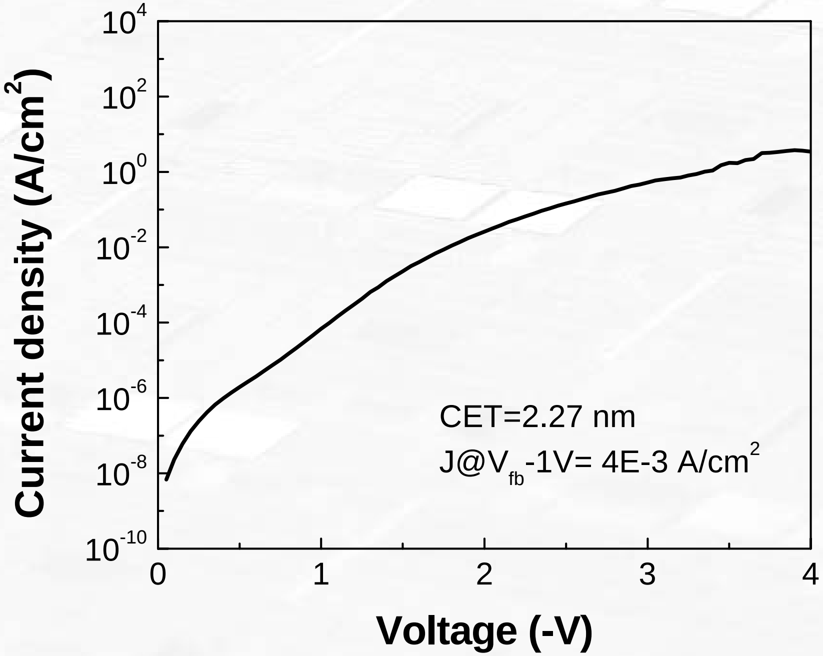
- High concentration of surface oxide that quickly drops to ~2%





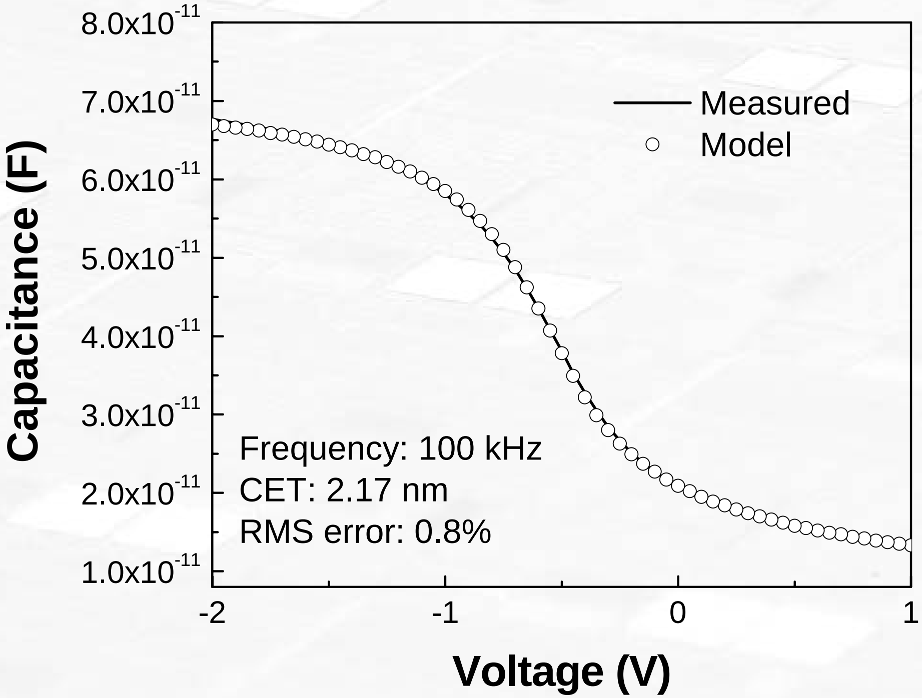
C-V and I-V curves of HfN/HfSiO/SiO$_2$ stack

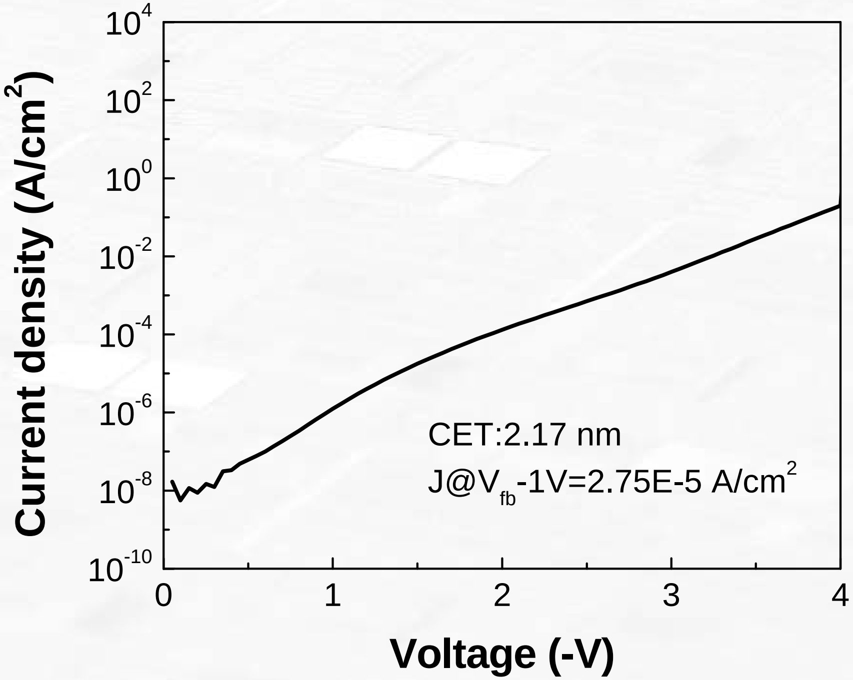




HfN 15nm /HfSiOx 3nm/SiO$_2$ 2nm
dot size: 5e^{-5} cm^2

C-V and I-V curves of HfSiN/HfSiO/SiO_2





HfSiN 15nm /HfSiOx 3nm/SiO_2 2nm
dot size: $5e^{-5}$ cm^2

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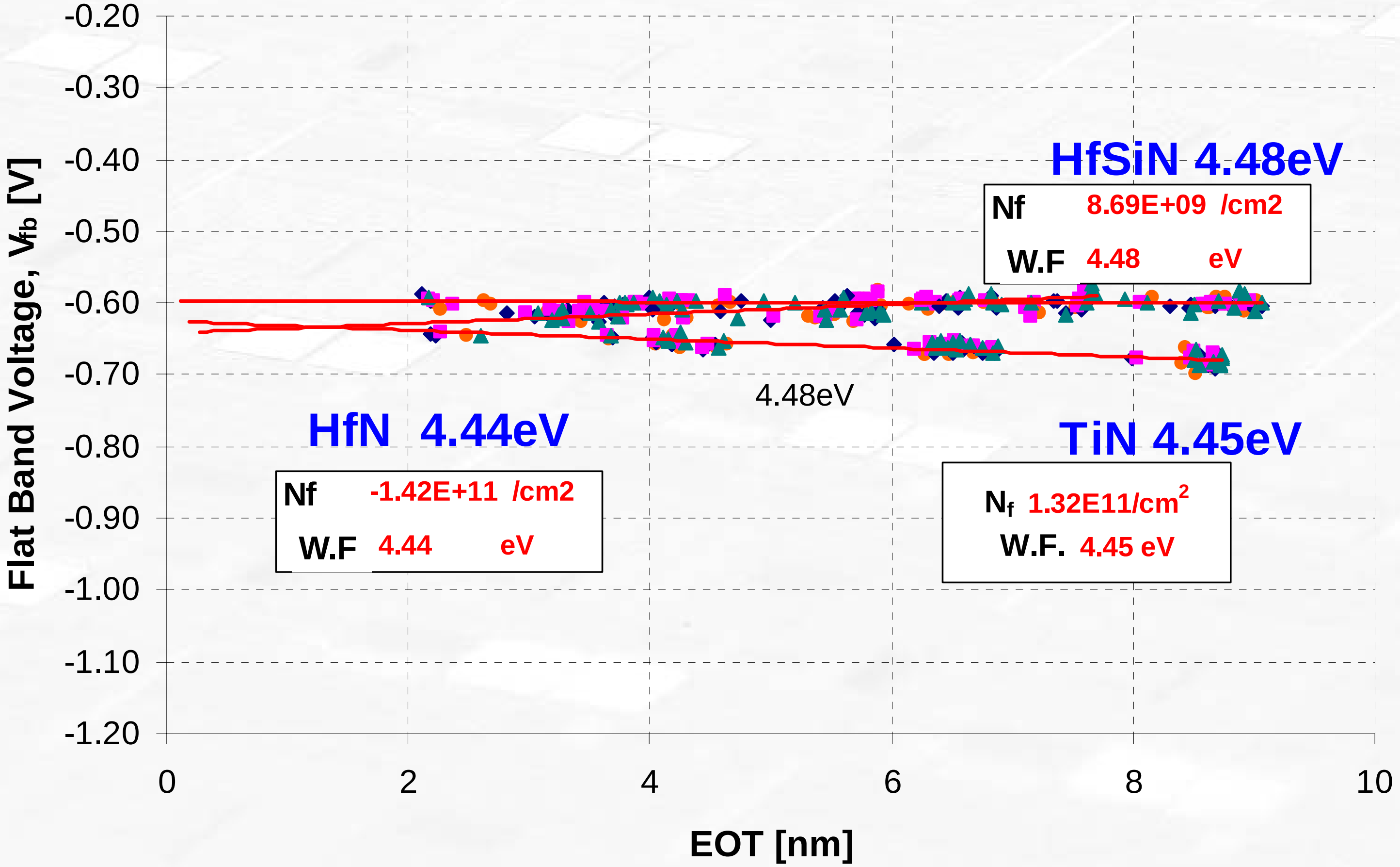
Work Function of ALD Metal Nitrides



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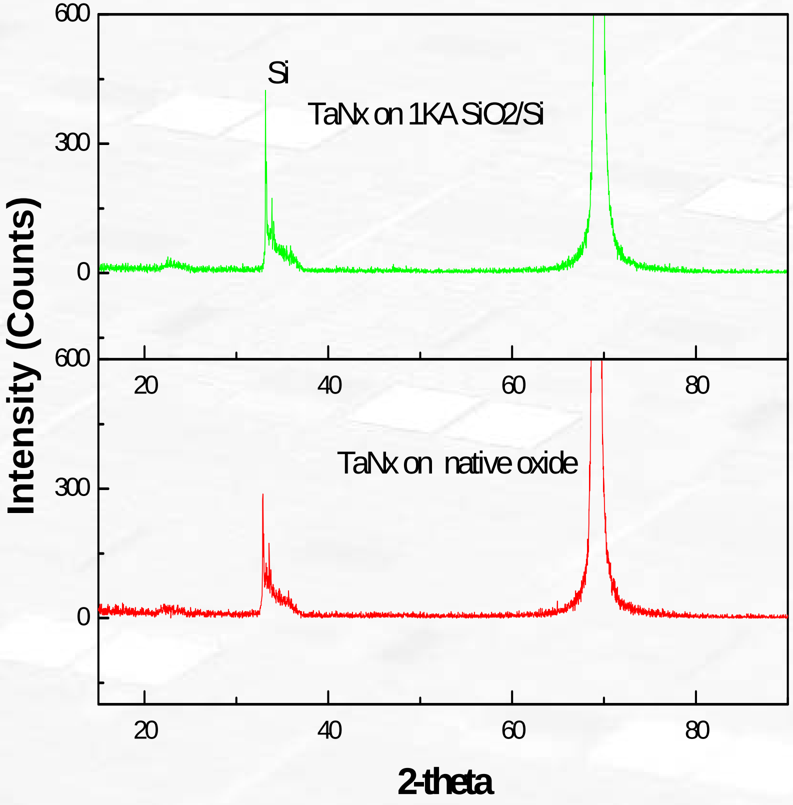
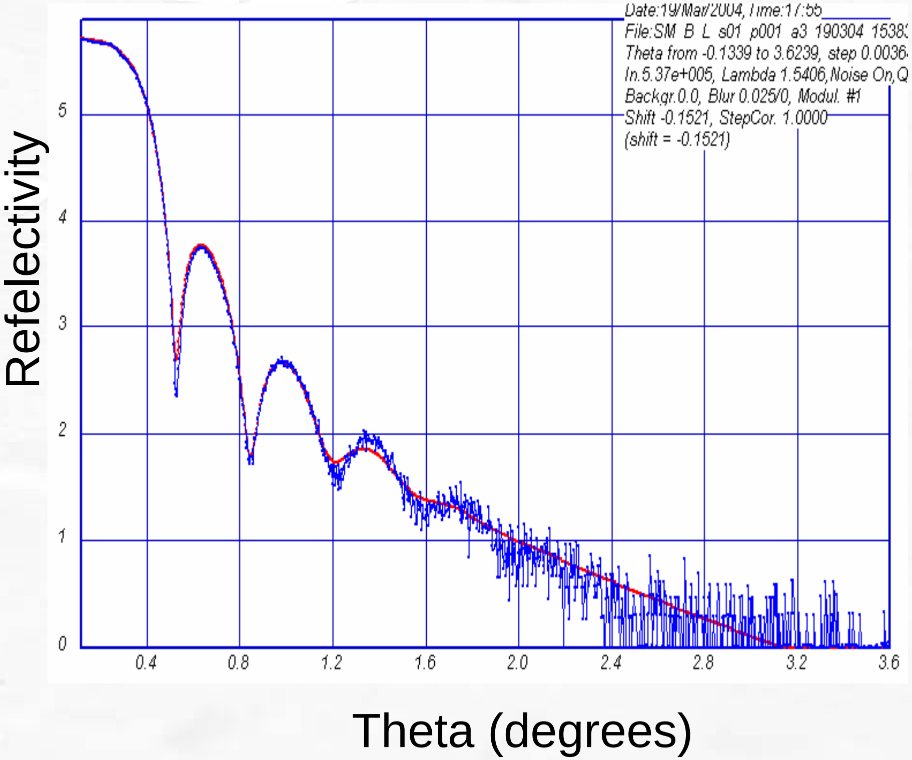
XRD and XRR of ALD TaN$_x$





-XRD confirmed amorphous nature of films (even after annealing up to 900°C)

- XRR density ~ 8g/cc; half of bulk value

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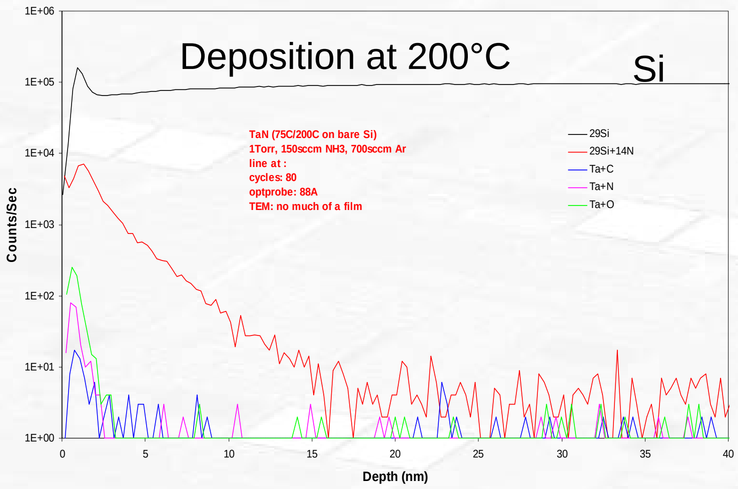
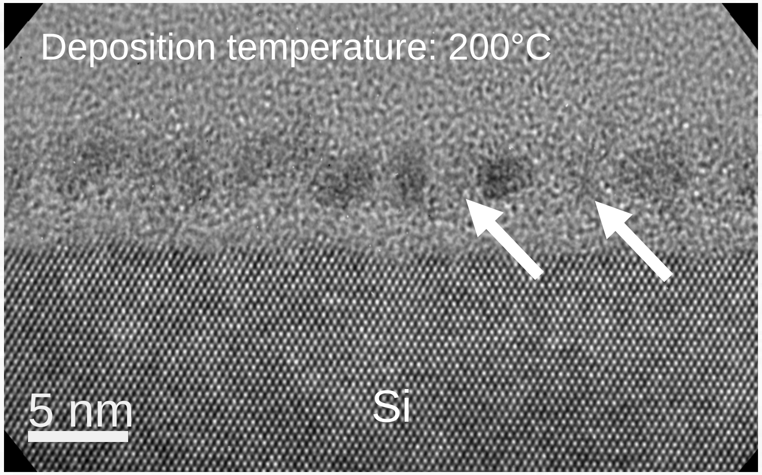
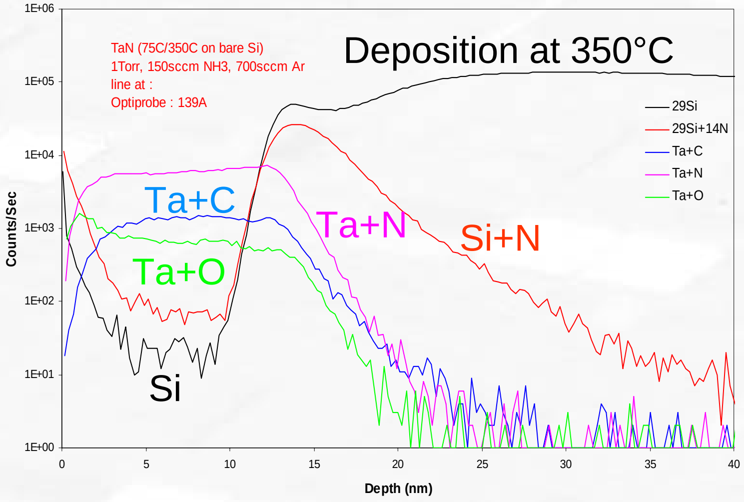
ALD TaN Deposition Temperature Effect







- **Dep rate is strongly dependent on temp. (~1.5 Å/cycle at 350°C and ~ 0.25 Å/cycle at 200°C)**
- **TaN film deposited at 200°C resulted in discontinuous film**
- **SIMS data with high silicon count at the surface confirms TEM data**

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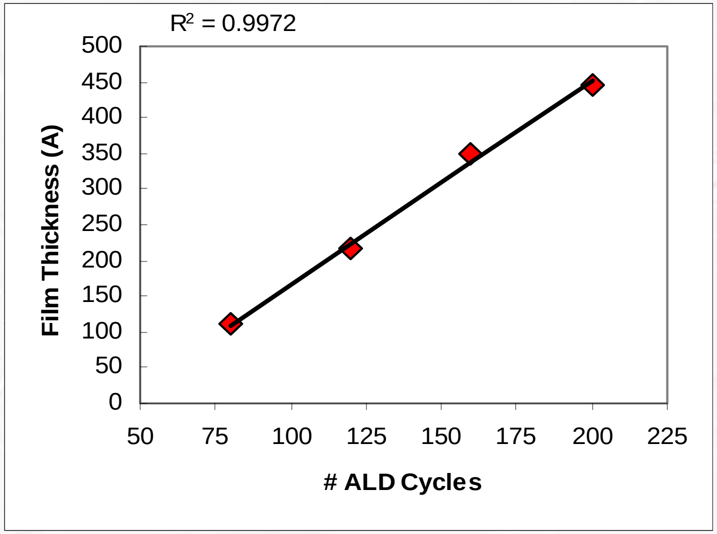
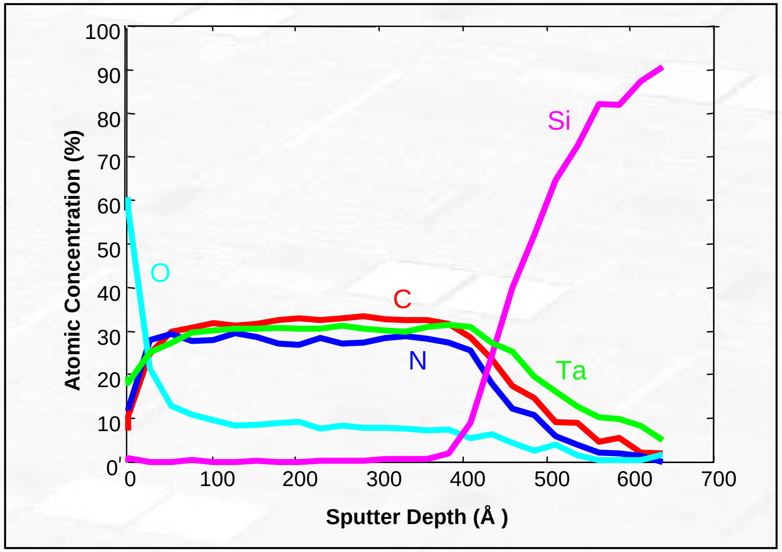
350°C ALD TaN Properties of ALD-TaN

Linear growth of TaN Film on bare Si at 350°C



AES data: carbon content in TaN film is high

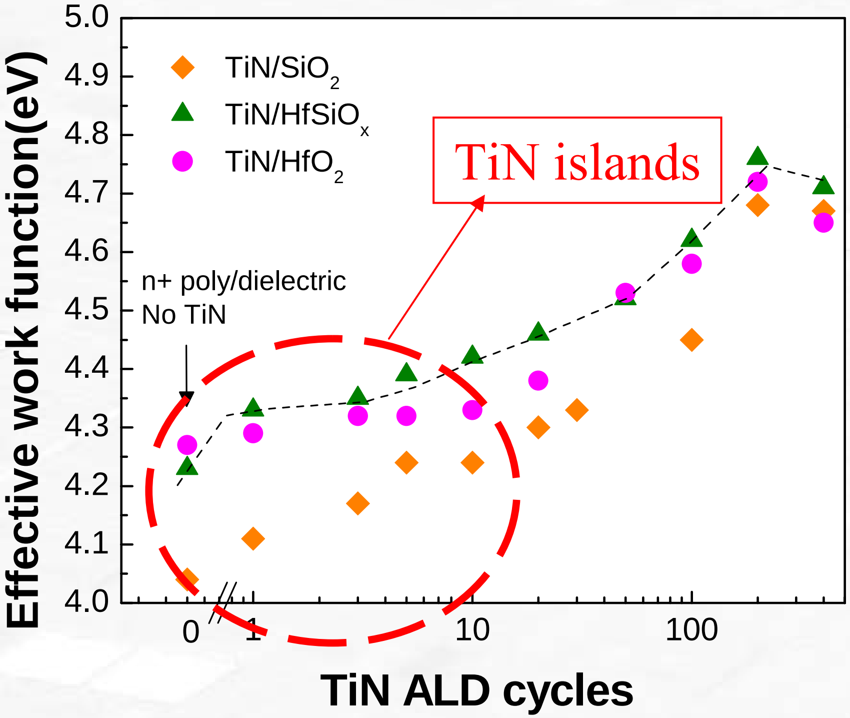


- Linear increase of thickness with # of ALD cycles.
  Dep rate > 0.1nm/cycle

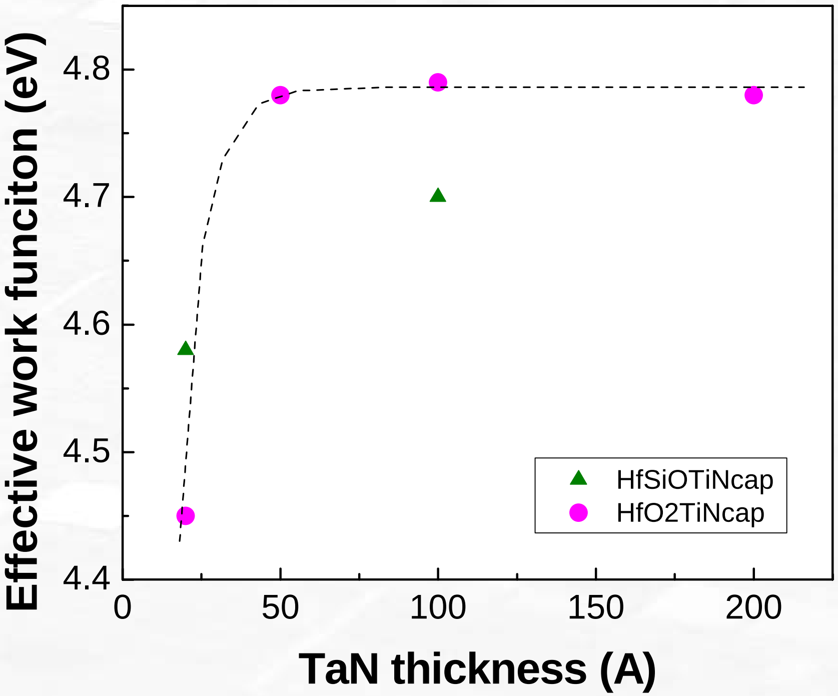
- The TaN film has a surface oxide and ~10% O in the bulk
- The N : Ta in the bulk is nearly 1 : 1
- C present at a similar % ~ 1:1:1 C:N:Ta

METAL ELECTRODE: Thickness Effect

ALD TiN



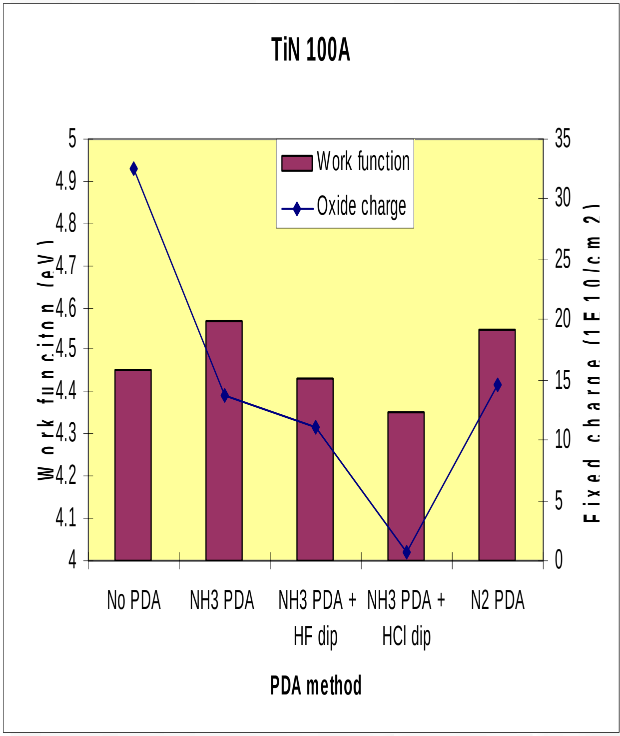
ALD TaN

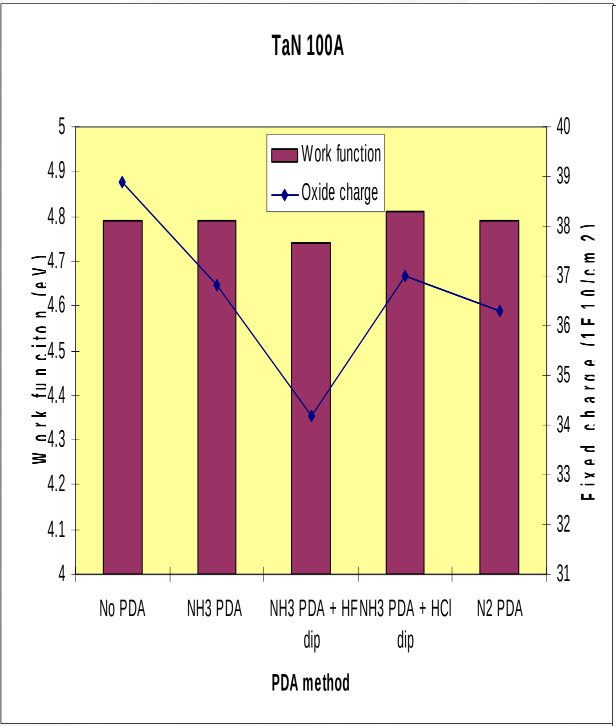


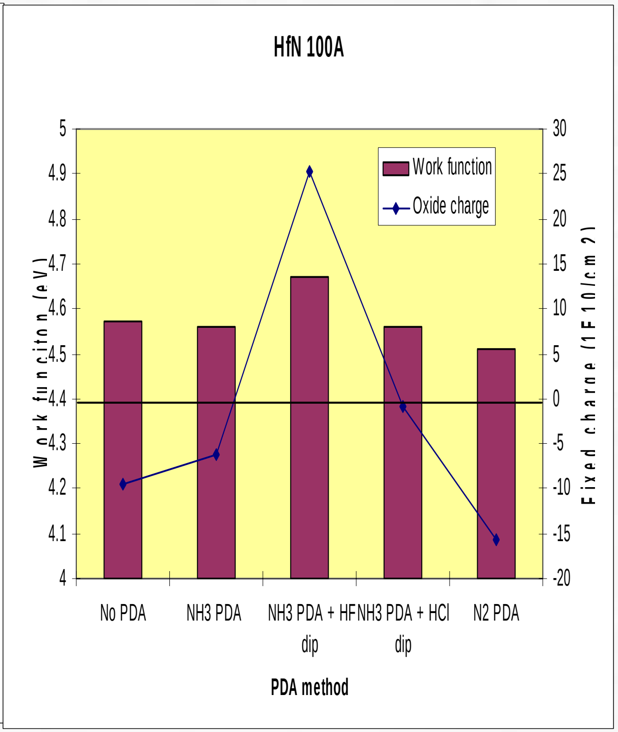
Work Function of ALD TiN saturates around 200 cycles at ~4.7 eV

Work Function of ALD TaN saturates < 50 Å at ~4.8 eV

High-k (HfSiOx) Surface Treatment Effects on Work Function of Metal Electrodes



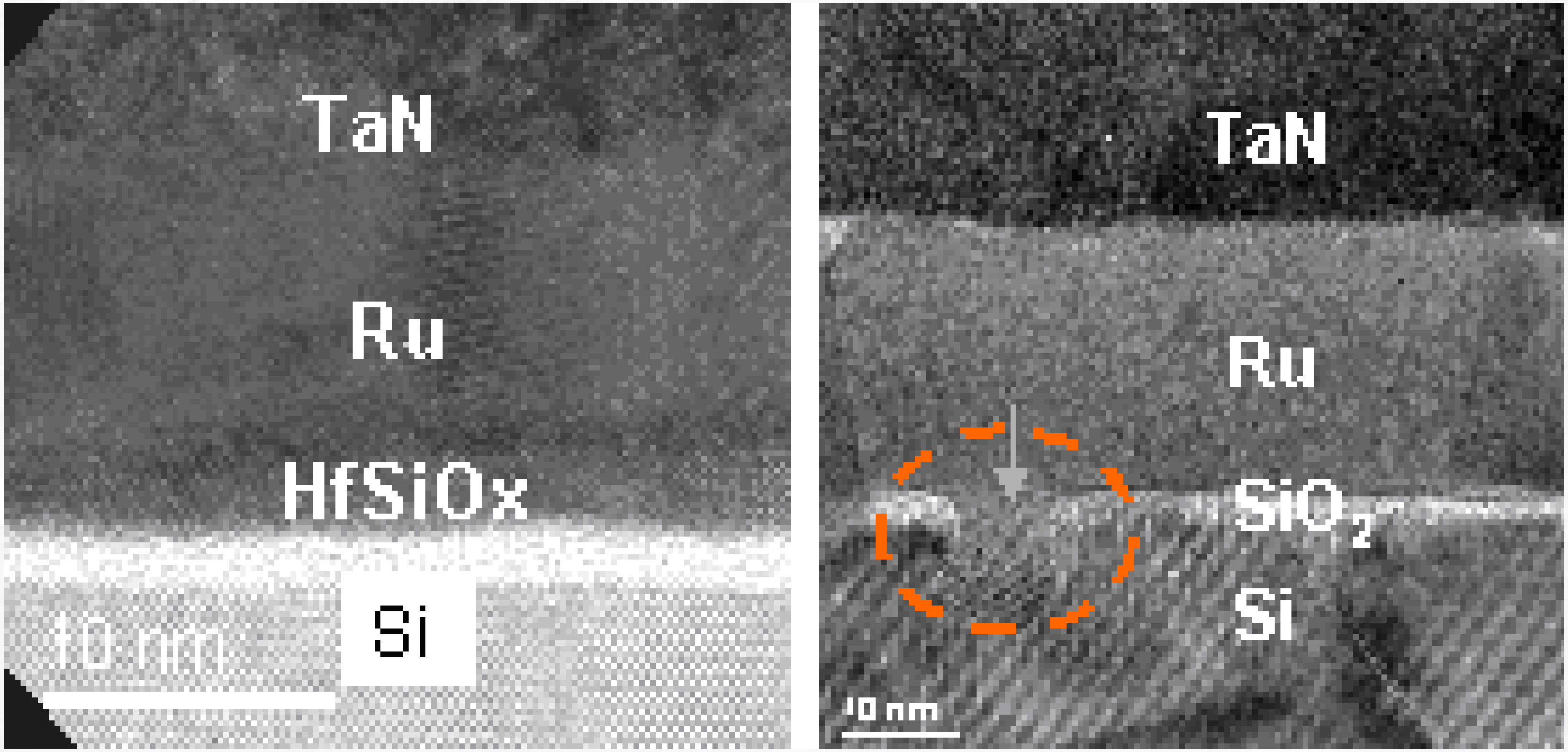




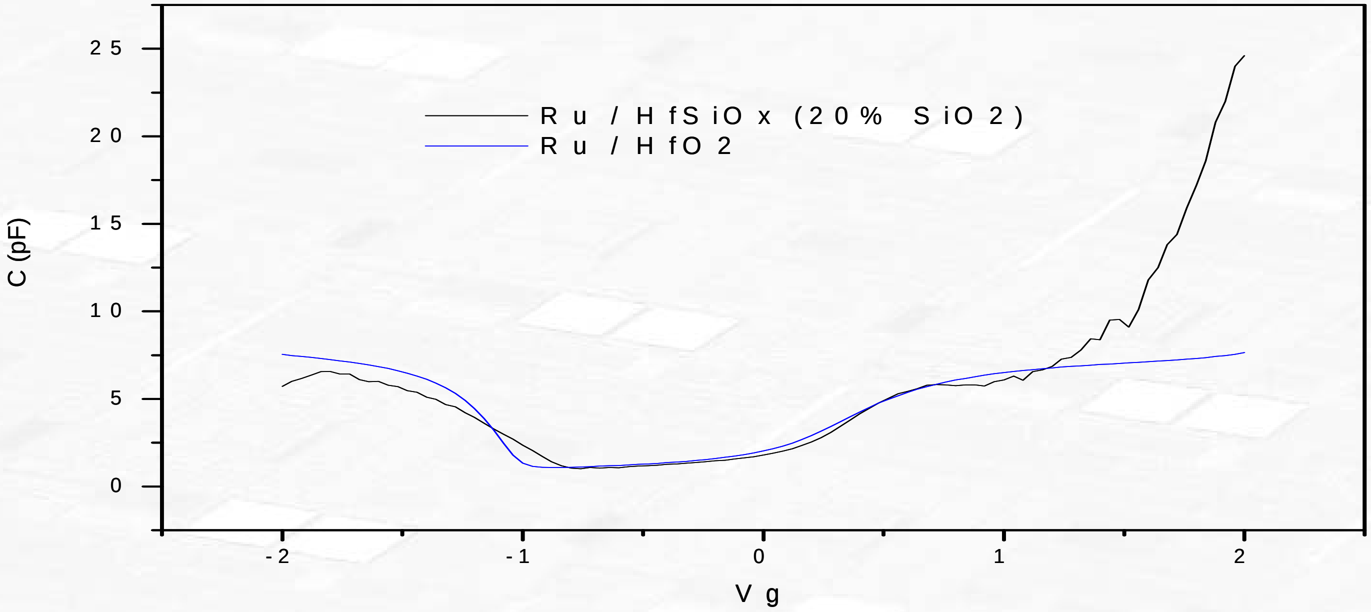
- **HCl treatment helps reduce TiN Work Function by more than 0.2eV**
- **TaN is relatively independent on dielectric modification**

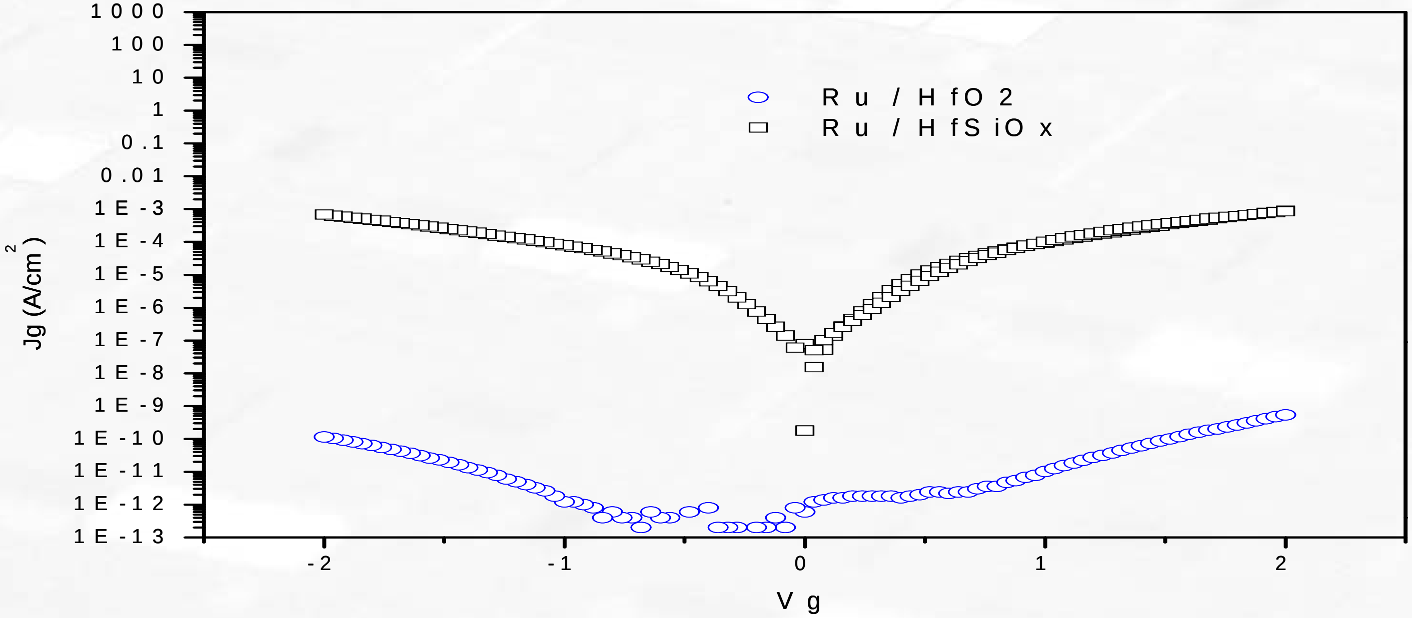
Thermal Stability of Ru on HfSiOx and SiO$_2$

HRTEM cross section analysis



C-V and I-V curves for Ru/HfO_2 vs Ru/HfSiOx





Accelerating the next technology revolution.

Conclusions

1) HfO_2 and $Hf_xSi_{1-x}O_2$ ALD processes scale physical thickness below ~2nm utilizing metal-amide precursors and ozone.

2) ALD chemistry proceeds similarly on multiple surface preparations including HF last without growth incubation.

3) Promising high field mobility more than 85% of universal SiO_2 mobility has been achieved at EOT ~1nm with 100-1000x Jg reduction.

Conclusions (cont'd)

5) ALD metal gate electrodes such as TiN, HfN, HfSiN deposited on HfO_2 and HfSiOx showed mid gap characteristics.

6) Thickness dependency of Work Function of metal electrode was observed for ALD TiN.

7) PVD Ru is thermally more stable on HfO_2 as compared with SiO_2 and $HfSiO_x$.