



Nanoelectronics on Si

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近年奈米科技之發展

- 縮小尺度至100 nm以內的科技：
Top-down之奈米結構的雕刻細化
莫爾定律(Moore's law—每1.5年縮小30%
尺寸)
- 操控原子（分子）的科技：Bottom-up 之
奈米體系的成長組裝
費曼的主張—從底部作起，下面還有無限
寬廣的空間



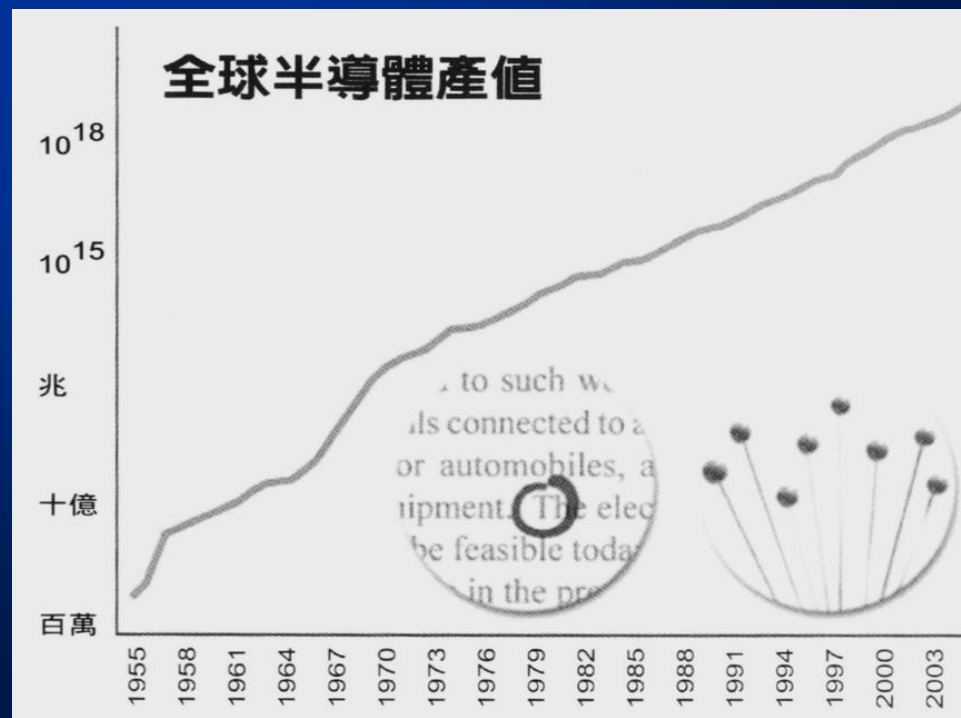
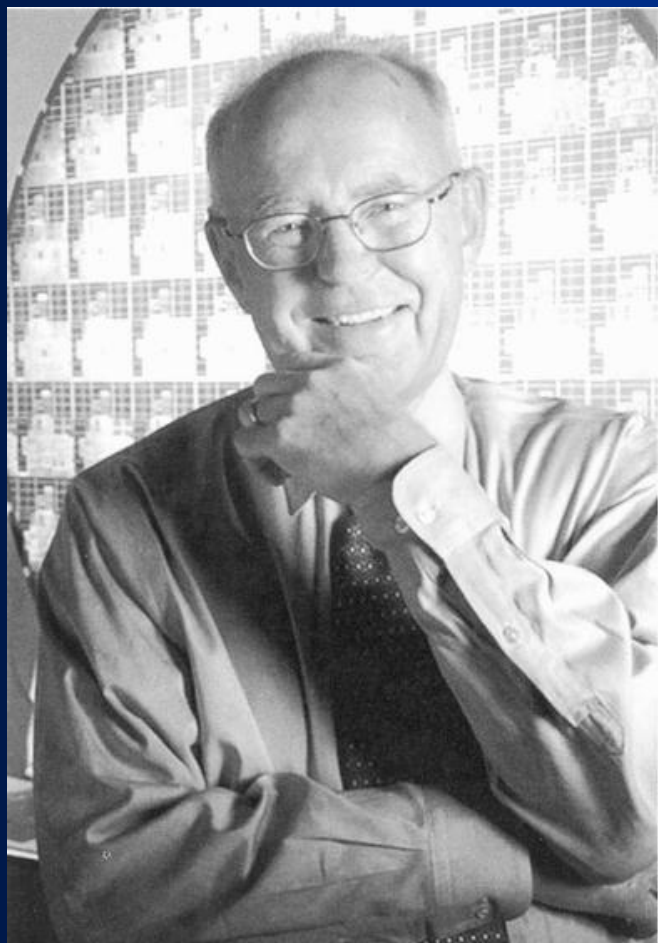
近來大力推動奈米科技的背景

來自微電子學可能遭遇瓶頸的考慮

Moore's Law : 摩爾定律

**A 30% decrease in the size of
printed dimensions every 1.5 years.**

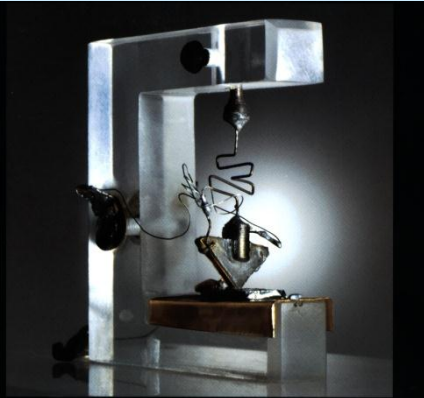
矽晶上電子原件數每1年半會增加一倍



Si CMOS Device Scaling – Beyond 22 nm node

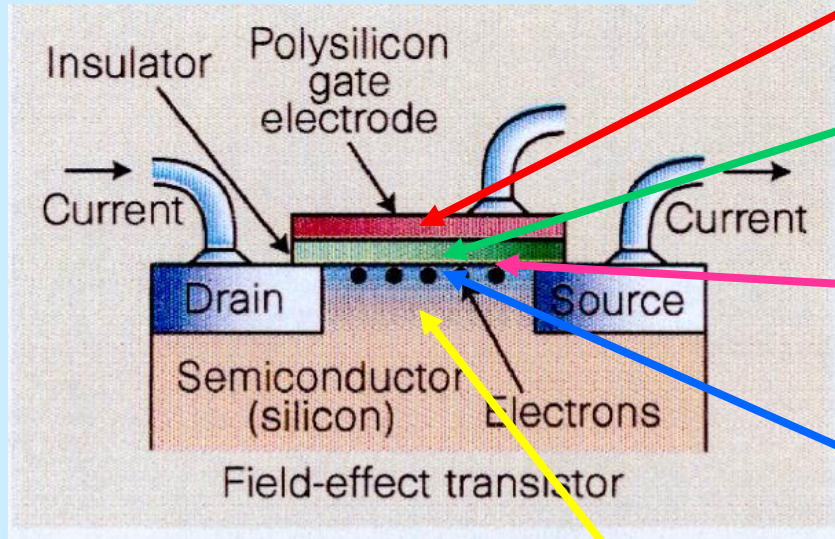
High κ , Metal gates, and High mobility channel

1947 First Transistor



The Transistor
50th Anniversary: 1947–1997

1960 First MOSFET



Metal Gate

High κ gate dielectric

Oxide/semiconductor interface

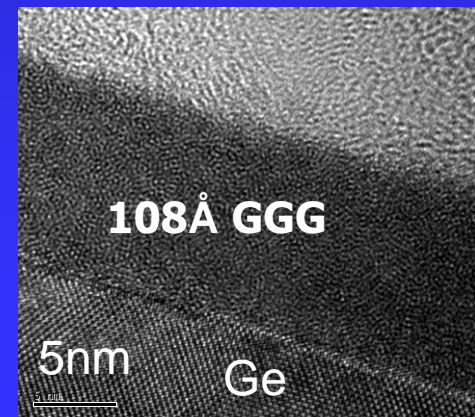
High mobility channel

Integration of Ge, III-V with Si

Moore's Law: The number of transistors per square inch doubles every 18 months

Shorter gate length L
Thinner gate dielectrics t_{ox}

Driving force :
High speed
Low power consumption
High package density



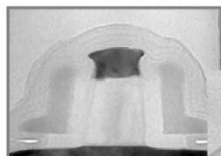


Intel Transistor Scaling and Research Roadmap

Transistor Scaling and Research Roadmap

90nm Node

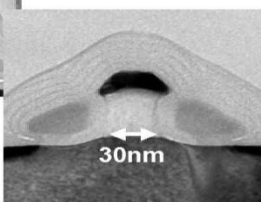
2003



50nm Length
(Production)

65nm Node

2005



30nm Length
(Development)

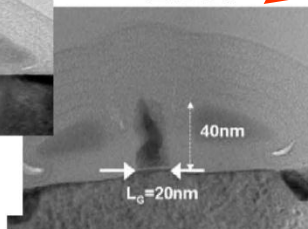
Uniaxial
Strain

SiGe S/D PMOS

1.2nm Ultra-thin SiO₂

45nm Node

2007

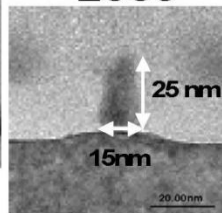


20nm Length
(Development)

High-K &
Metal-Gate
Options

32nm Node

2009

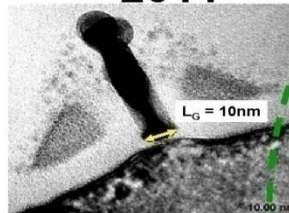


15nm Length
(Research)

Non-planar Tri-Gate
Architecture Option

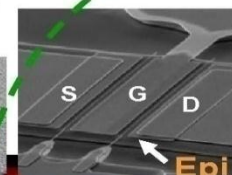
22nm Node

2011

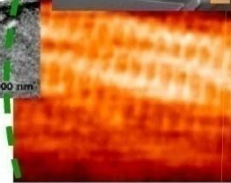


10nm Length
(Research)

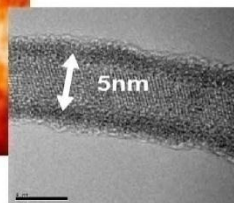
2015-2019
Research



III-V Device
Prototype
(Research)



C-nanotube
Prototype
(Research)



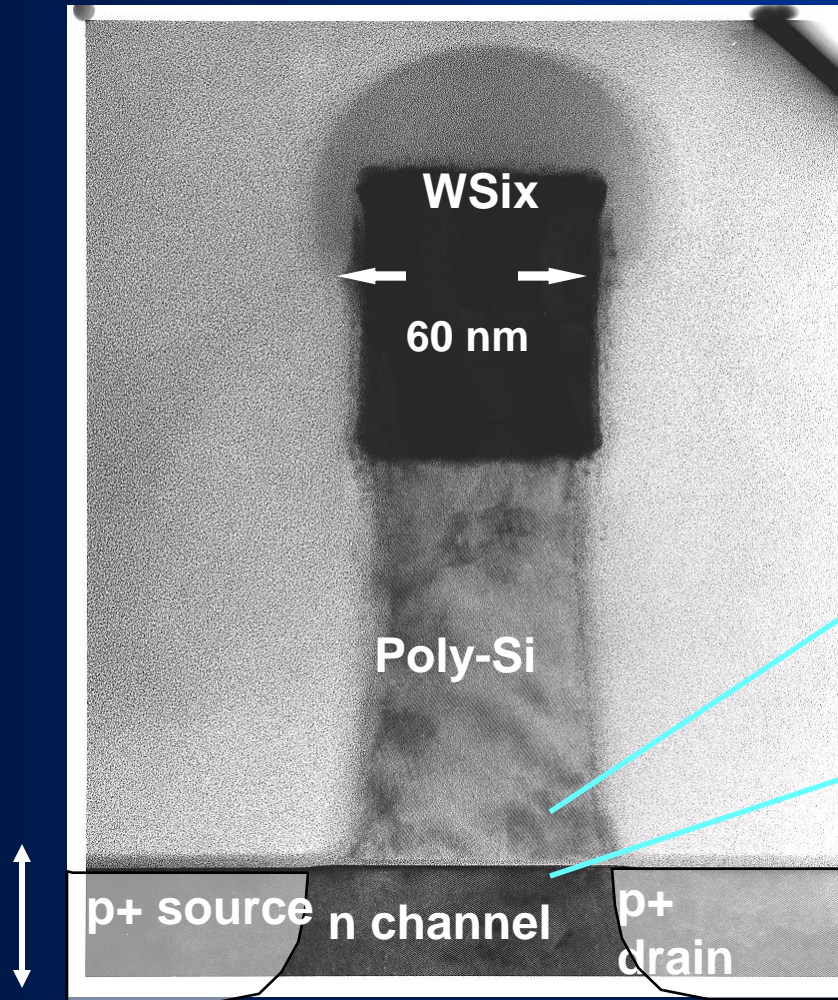
Nanowire
Prototype
(Research)

Robert Chau, Intel, ICSICT 2004

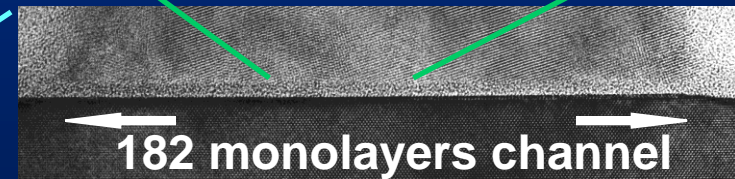
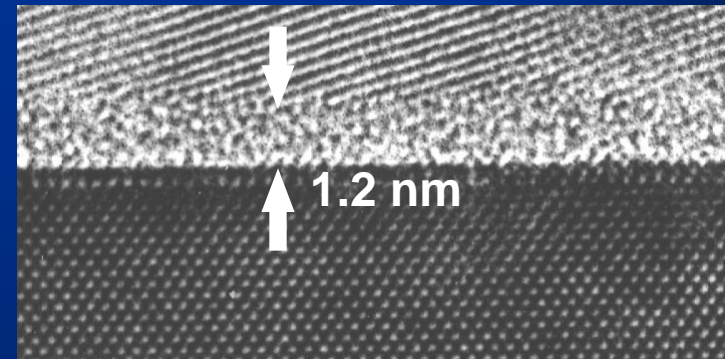
More non-silicon elements introduced



Scaling Limits to CMOS Technology



Gate Oxide ~ 5 Si Atoms thick !



Shrinking the junction depth \Rightarrow increasing the carrier concentration



CMOS scaling, When do we stop ?

Reliability: 25 ~~22~~ ~~18~~ ~~16~~ Å

processing and yield issue

Tunneling : 15 Å

Design Issue: chosen for 1 A/cm² leakage

$I_{\text{on}}/I_{\text{off}} \gg 1$ at 12 Å

Bonding:

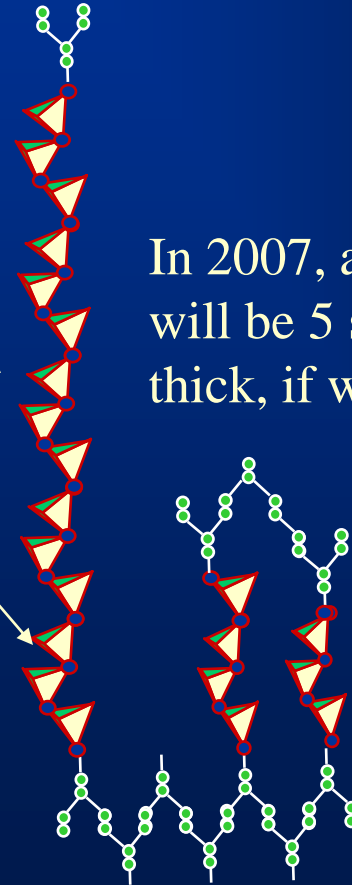
Fundamental Issues---

- how many atoms do we need to get bulk-like properties?
EELS -- Minimal 4 atomic layers !!
- Is the interface electronically abrupt?
- Can we control roughness?

In 1997, a gate oxide was 25 silicon atoms thick.

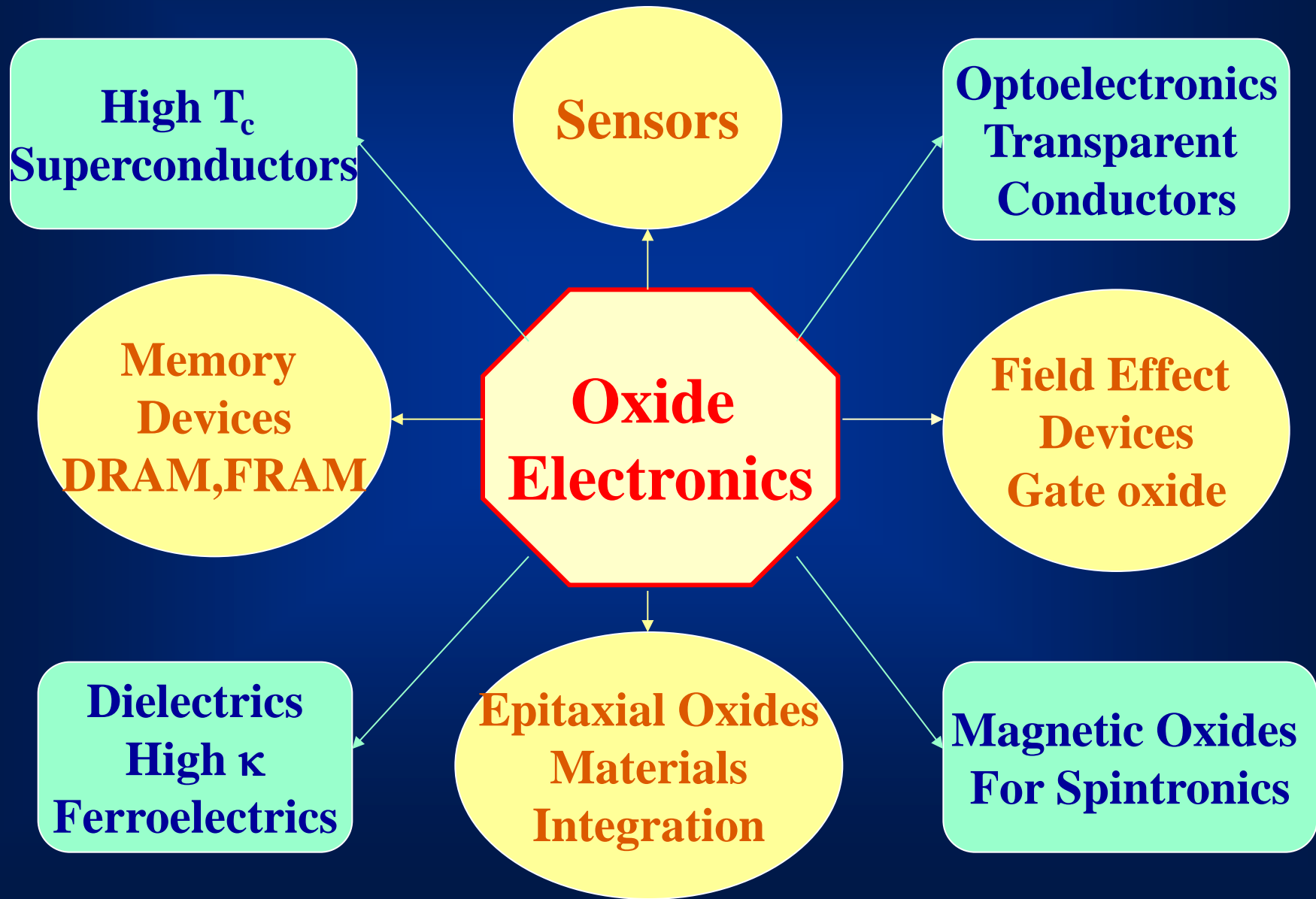
In 2007, a gate oxide will be 5 silicon atoms thick, if we still use SiO₂

and at least 2 of those 5 atoms will be at the interfaces.





The Development of Oxide Electronics in Two Decades



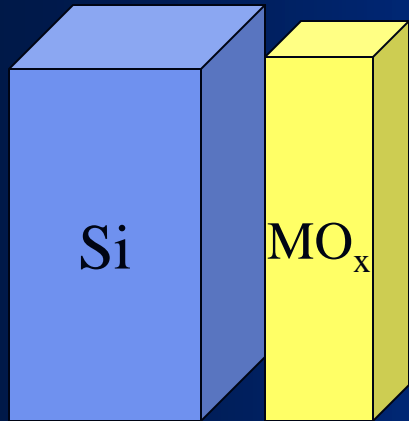


OUTLINES

- ❖ The alternative high κ gate dielectrics replacing SiO_2 for 33 nm Si CMOS by year 2009, and 22 nm for year 2011.
 - Materials requirements
 - Processing integration issues
- ❖ MBE grown HfO_2 high κ gate dielectrics
 - thermal stability studies by MEIS and TEM
 - electrical performance
- ❖ Integration of ALD + MBE template approach



Fundamental Materials Selection Guidelines



- Thermodynamic stability in contact with Si to 750°C and higher. **(Hubbard and Schlom)**
Alkaline earth oxide, IIIB, IVB oxide and rare earth oxide
- Dielectric constant, band gap, and conduction band offset
- Defect related leakage,
substantially less than SiO₂ at $t_{eq} < 1.5$ nm
- Low interfacial state density $D_{it} < 10^{11} \text{ eV}^{-1} \text{ cm}^{-2}$
- Low oxygen diffusivity
- Crystallization temperature $> 1000^\circ\text{C}$



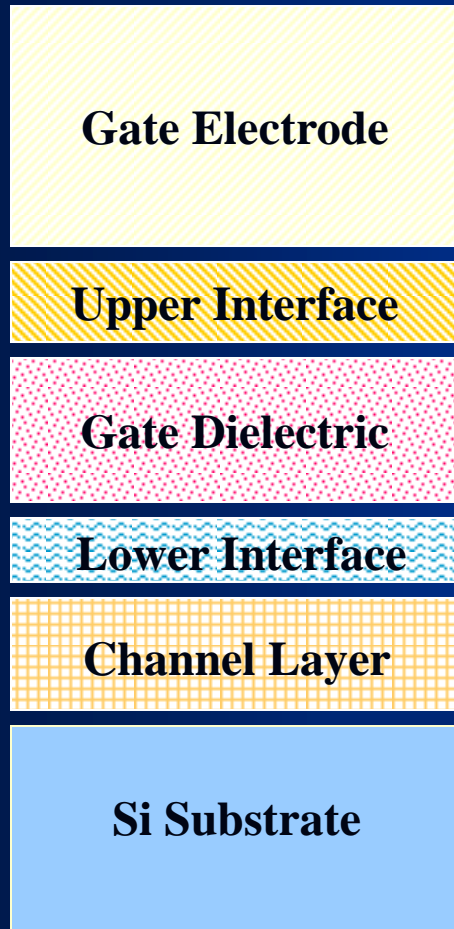
t_{eq} : **equivalent oxide thickness (EOT) to be under 1.0 nm**

$$t_{eq} = t_{ox} \kappa_{\text{SiO}_2} / \kappa_{ox}$$



Integration Issues for High κ Gate Stack

FET Gate Stack



Critical Integration Issues

- Morphology dependence of leakage
Amorphous vs crystalline films?
- Interfacial structures
- Thermal stability
- Gate electrode compatibility
- Reliability

Fundamental Limitations

- Fixed charge
- Dopant depletion in poly-Si gate
- Dopant diffusion
- Increasing field in the channel region



Basic Characteristics of Binary Oxide Dielectrics

Dielectrics	SiO ₂	Al ₂ O ₃	Y ₂ O ₃	HfO ₂	Ta ₂ O ₅	ZrO ₂	La ₂ O ₃	TiO ₂
Dielectric constant	3.9	9.0	18	20	25	27	30	80
Band gap (eV)	9.0	8.8	5.5	5.7	4.5	7.8	4.3	3.0
Band offset (eV)	3.2	2.5	2.3	1.5	1.0	1.4	2.3	1.2
Free energy of formation MO _x +Si ₂ → M+ SiO ₂ @727C, Kcal/mole of MO _x	-	63.4	116.8	47.6	-52.5	42.3	98.5	7.5
Stability of amorphous phase	High	High	High	Low	Low	Low	High	High
Silicide formation ?	-	Yes	Yes	Yes	Yes	Yes	Yes	Yes
Hydroxide formation ?	-	Some	Yes	Some	Some	Some	Yes	Some
Oxygen diffusivity @950C (cm ² /sec)	2x 10 ⁻¹⁴	5x 10 ⁻²⁵	?	?	?	10 ⁻¹²	?	10 ⁻¹³

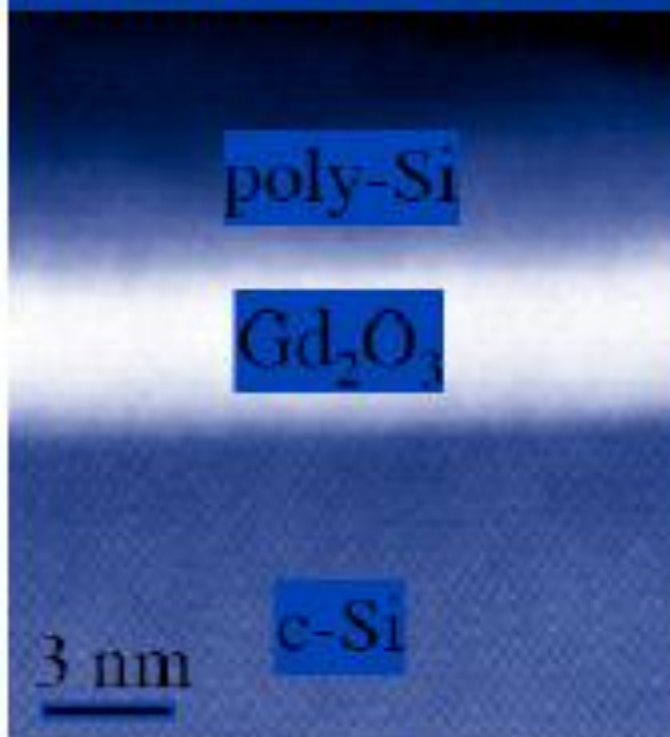
Assessing Thermodynamic Stability

Gate Dielectric
Material

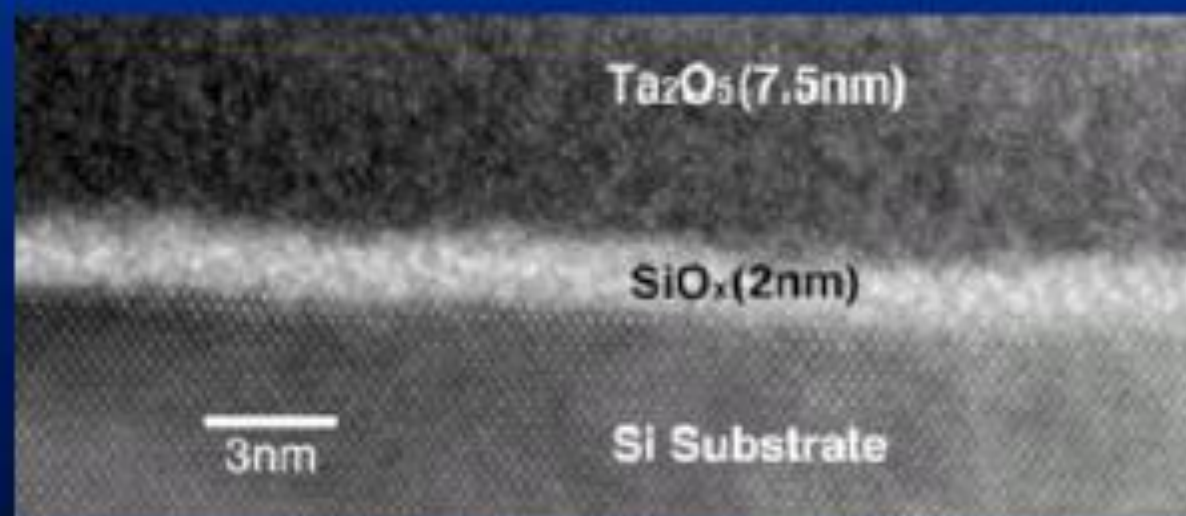
Silicon

Ideal
“Gedanken”
Interface

Stable Interface



Unstable Interface



TEM by David A. Muller

J. Kwo *et al.*, J. Appl. Phys. 89 (2001) 3920.

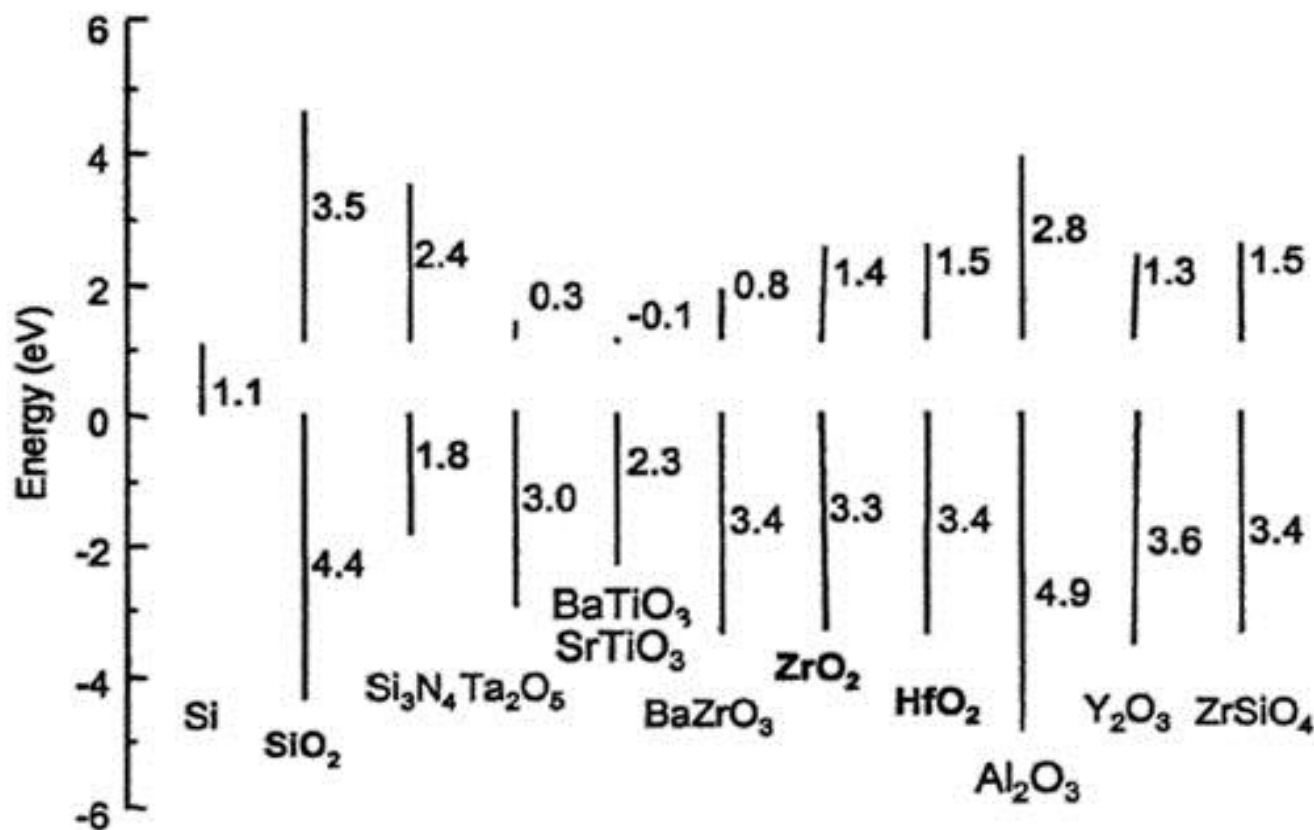
TEM by Don J. Werder

G.B. Alers *et al.*, Appl. Phys. Lett. 73 (1998) 1517.



Band Offset of High κ Dielectrics

Band Offsets of Dielectrics with Si





A Topic Well Worth Doing Research On !!!

World production in year 2003: 1×10^{19} transistors

World population: 6.4×10^9 people

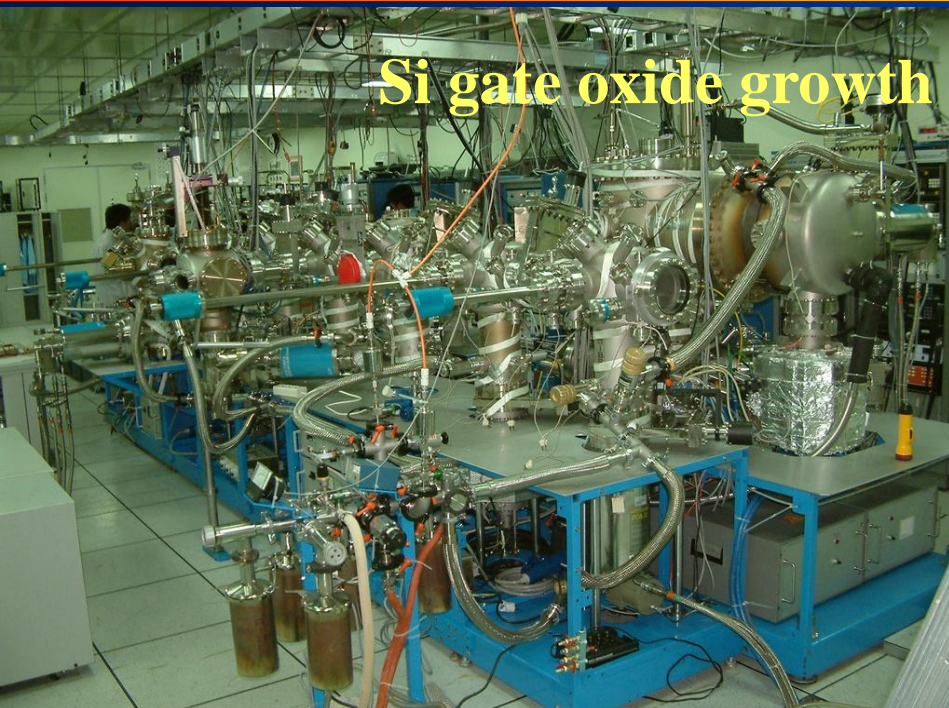
So, the world produces:

- $\sim 1.5 \times 10^9$ transistors/person each year
- $\sim 1.2 \times 10^8$ transistors/person each month
- $\sim 4\text{M}$ transistors/person each day
- $\sim 3\text{K}$ transistors/person each minute
- ~ 50 transistors/person per second

And Taiwan produces ~ 5000 transistors/person/per second



MBE Integrated Multi-chamber System For Nano Electronics

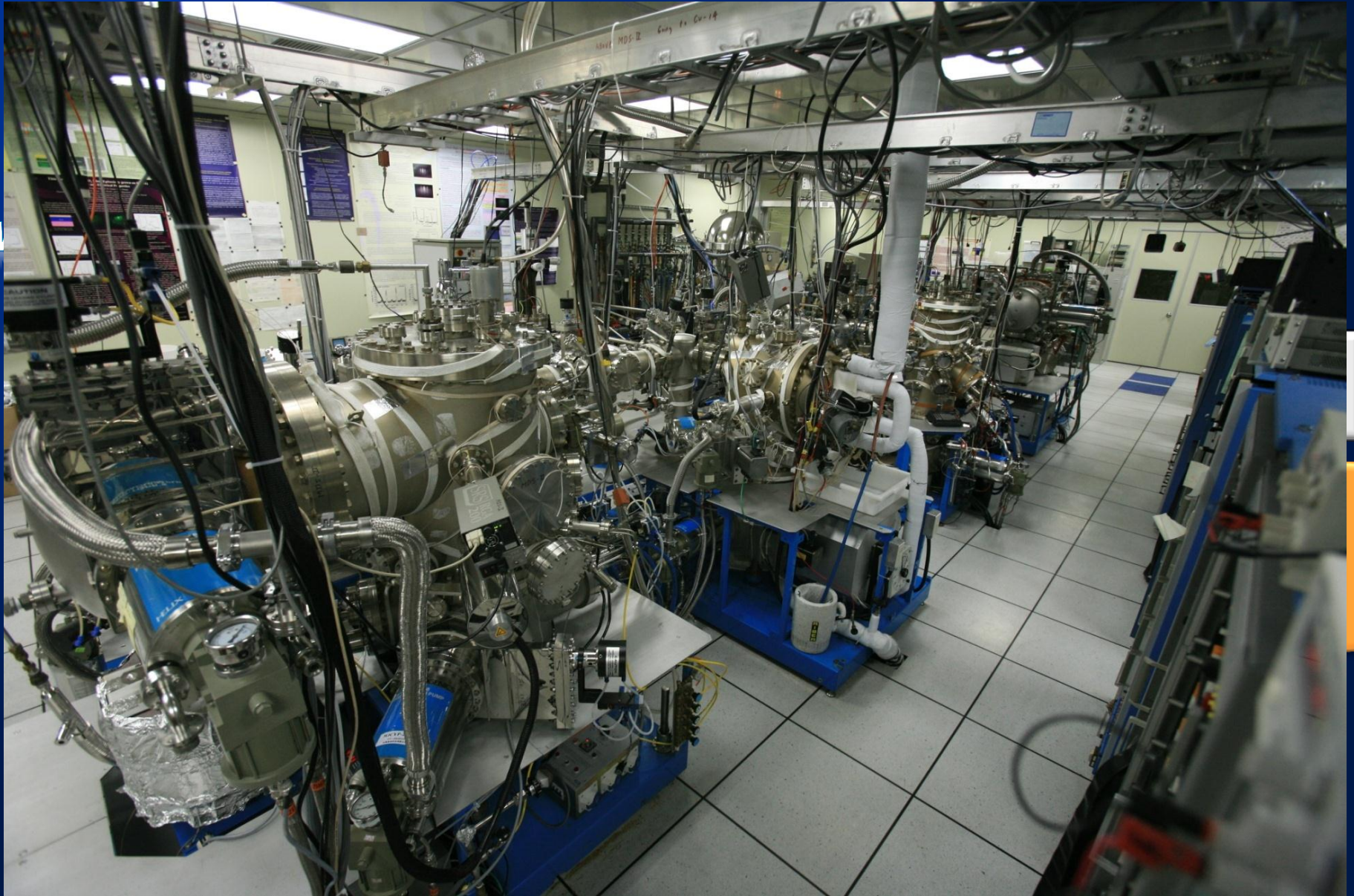


Now located in the Nano
Technology Center, ITRI,
Hsin Chu, Taiwan since
7/2003.





Multi-chamber MBE with *in-situ* ALD, XPS, SPM System





High κ Dielectrics for Si

■ Epitaxial crystalline films on Si

(A) Cubic CaF_2 structure:

(111) orientation is more common than (100)

e.g. CaF_2 (111), CeO_2 (111) on Si(111) with $\epsilon \sim 26$

YSZ (100) on Si(100) with $\epsilon \sim 25-30$

(B) Cubic Mn_2O_3 structure

~ 8 unit cells of incomplete fluorite structure

e.g. Y_2O_3 (110) on Si(100) with $\epsilon \sim 16-18$

Gd_2O_3 (110) on Si(100) with $\epsilon \sim 12-14$

(C) Ternary perovskite structure

e.g. SrTiO_3 (100) on Si(100) with $\epsilon \sim 70-80$ (Oakridge, Motorola)

using a Sr silicide $\frac{1}{4}$ monolayer for epi-growth

■ Amorphous oxide films on Si

e.g. Si_3N_4 , Al_2O_3 , Ta_2O_5 , ZrTiSnO_x , TiO_2 Interfacial layer present

- Amorphous Gd_2O_3 and Y_2O_3 films

- Amorphous SiO_2 added with Hf or Zr . (G. Wilks et al)



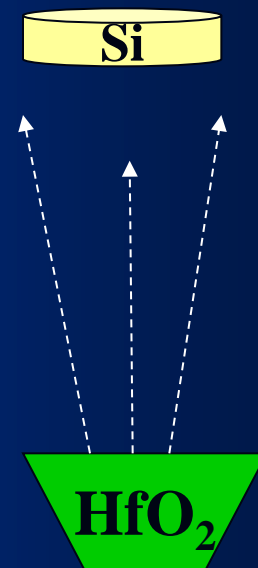
Research Programs

- Low defect high κ ultrathin films
 - Interface engineering
 - Electrical characterization and optimization
- Identify new material candidates for metal gate
 - Metal gate/high κ integration
- Integration of high κ , and metal gate with Si- Ge strained layer
 - Integration of high κ , and metal gate with strained Si
- High k dielectrics for high mobility III-V semiconductors



MBE Growth of High κ Oxides

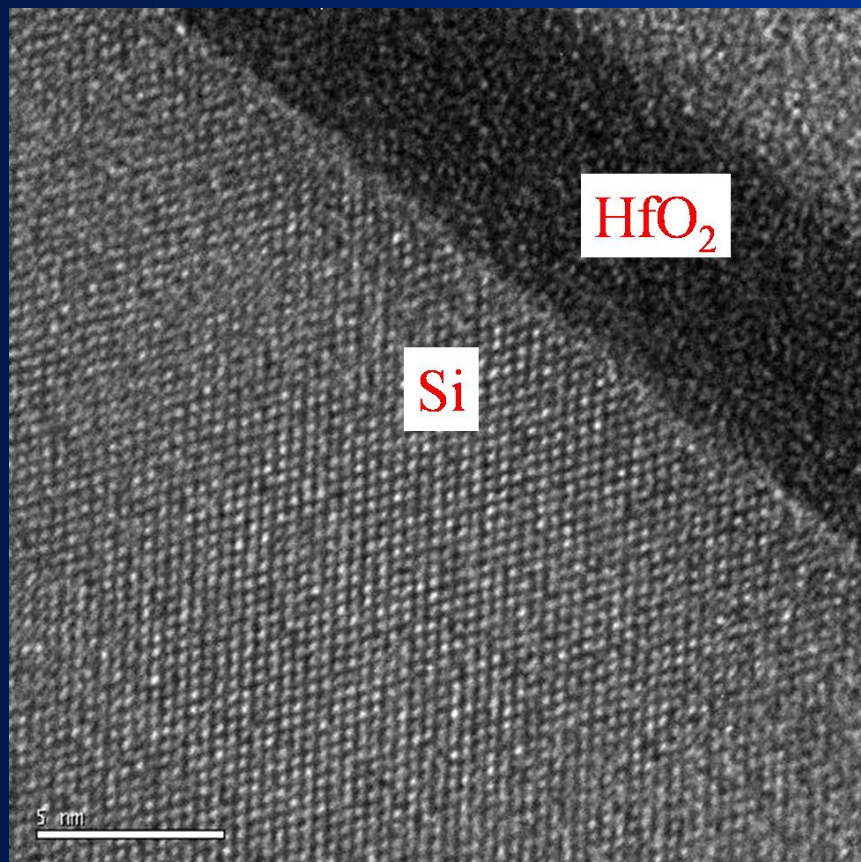
- Ultrahigh vacuum, multi-chamber MBE system.
- Electron-beam evaporation of oxide sources from pressed ceramic pellets.
- 2 inch RCA-cleaned Si wafers, hydrogen passivated, followed by prompt insertion into UHV.
- In-situ heating to 400-500C to attain a (2 x 1) reconstructed Si surface.
- Substrate temperature of 550C for **epitaxial** films.
- Room temperature deposition for **amorphous** films.
- Maintain **low pressure** during growth $< 1.0 \times 10^{-9}$ torr.





High Resolution Cross Sectional TEM and RHEED Images of HfO_2 on Si (100)

From AFM: RMS Roughness: 0.072nm

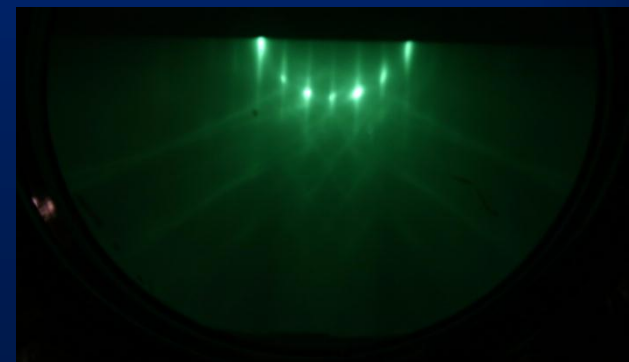


Amorphous HfO_2 film 6.0 nm
 SiO_2 and Hf silica is nearly absent !

RHEED



amorphous HfO_2 surface



atomically order Si(100) surface

The Technique of Medium Energy Ion Scattering (MEIS)

- ❑ MEIS is a refinement of the more common technique of **Rutherford backscattering spectrometry (RBS)**, but with enhanced depth and angle resolution.
- ❑ In a typical MEIS experiment, a collimated beam of mono energetic (typically **100** keV) light ions (H^+ or He^+) impinges onto a target along a known direction.
- ❑ The energy and angle of the scattered ions are analyzed simultaneously and allow MEIS to measure atomic mass, depth, and surface structure from the following physical principles;

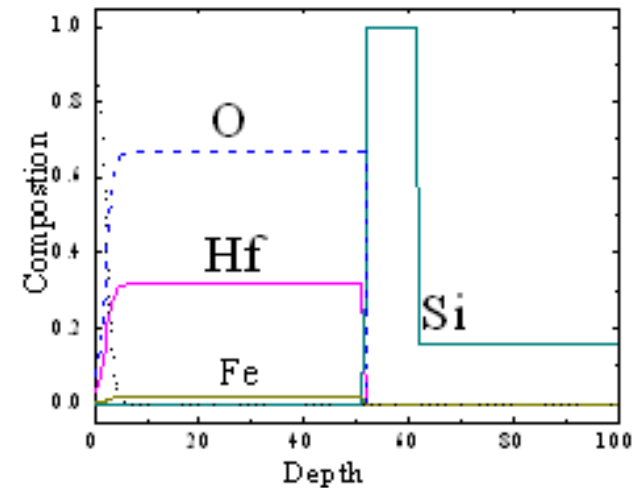
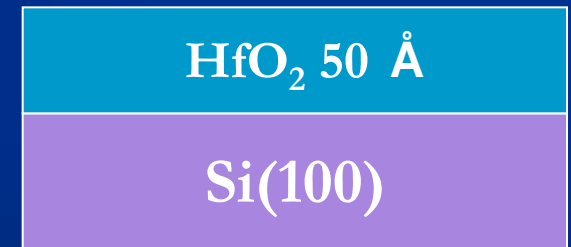
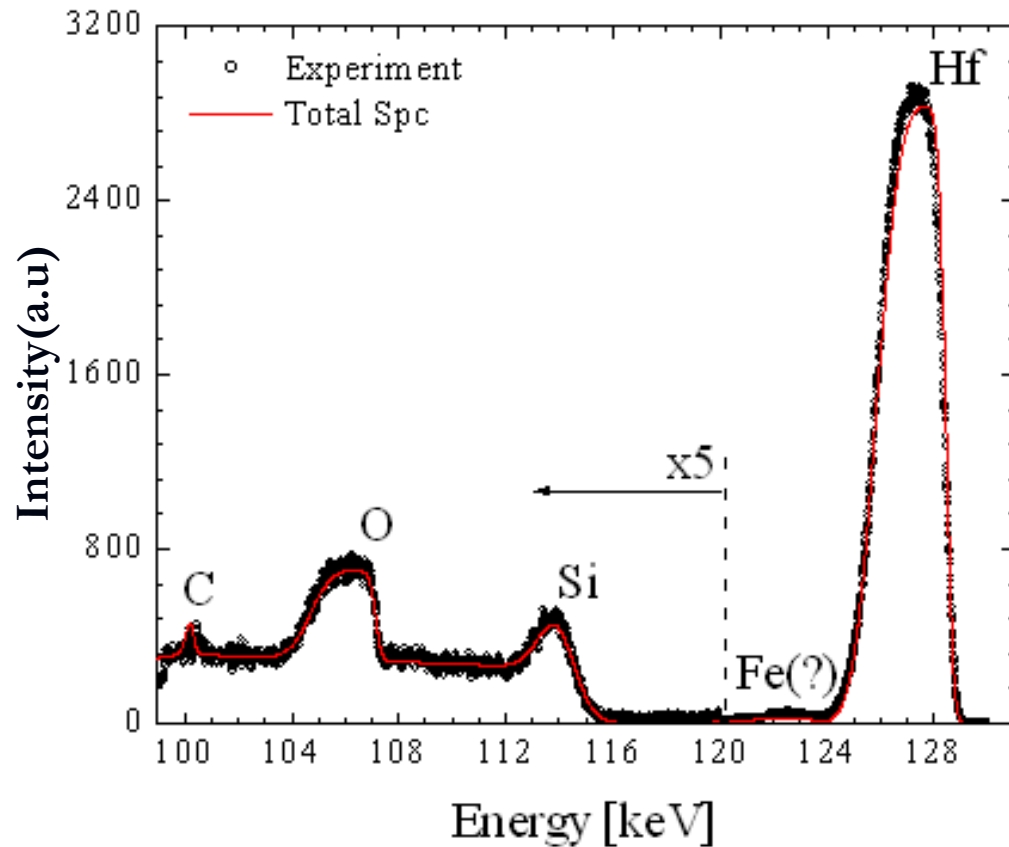
Mass - ions scattered from the surface of a material undergo energy loss by a 'billiard ball' type collision with surface atoms. The scattered ion energy thus relates directly to the mass of the scattering atom. This effect can be seen in [Figure](#) where the signal from O, Si and Ge are separated in energy

Depth - ions scattered from below the surface lose energy inelastically at a rate proportional to the ion's path length in the target. This extra energy loss thus relates directly to the depth of the scattering atom. In favorable cases MEIS can achieve a depth resolution of one atomic layer.

Surface structure - when the ion beam is aligned with a crystallographic axis the surface atoms shadow deeper atoms from the ion beam. This alignment therefore makes the technique surface specific and, for a particular crystal, certain ingoing directions can allow the ion beam to illuminate only the top one, two, or three layers according to choice. Ions scattered from the second layer will have their outward paths blocked at certain angles by first layer atoms. The variation in scattered ion intensity with angle thus relates to the geometrical arrangement of surface atoms.



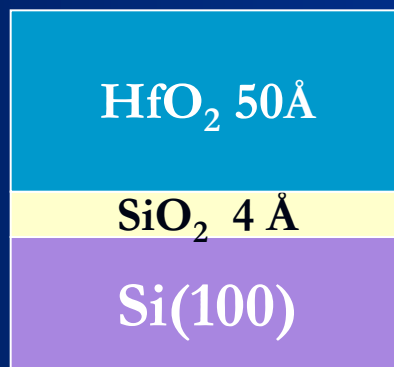
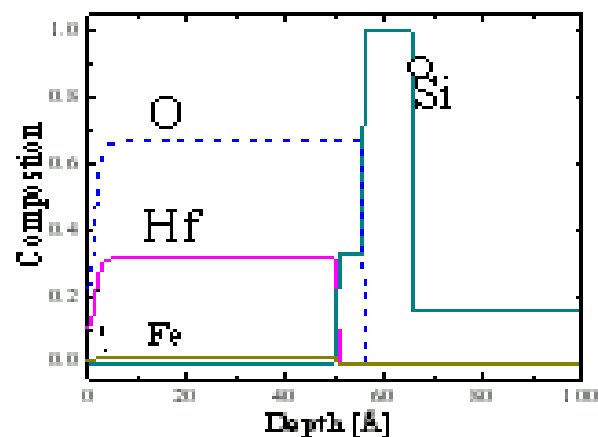
Medium Energy Ion Scattering (MEIS) Study of the High κ Dielectric / Si Interface and Stability



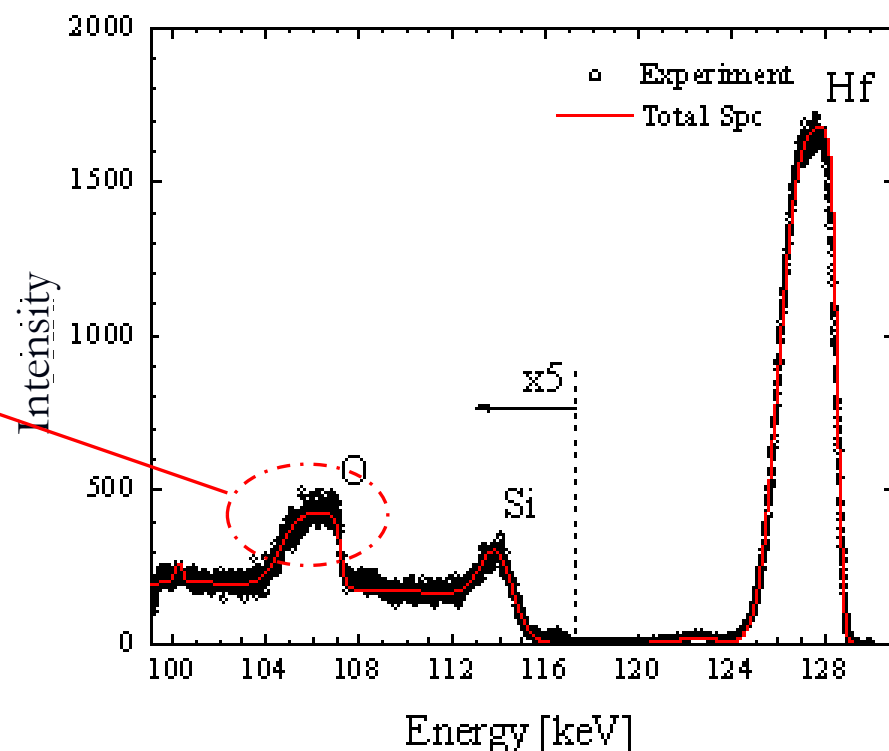
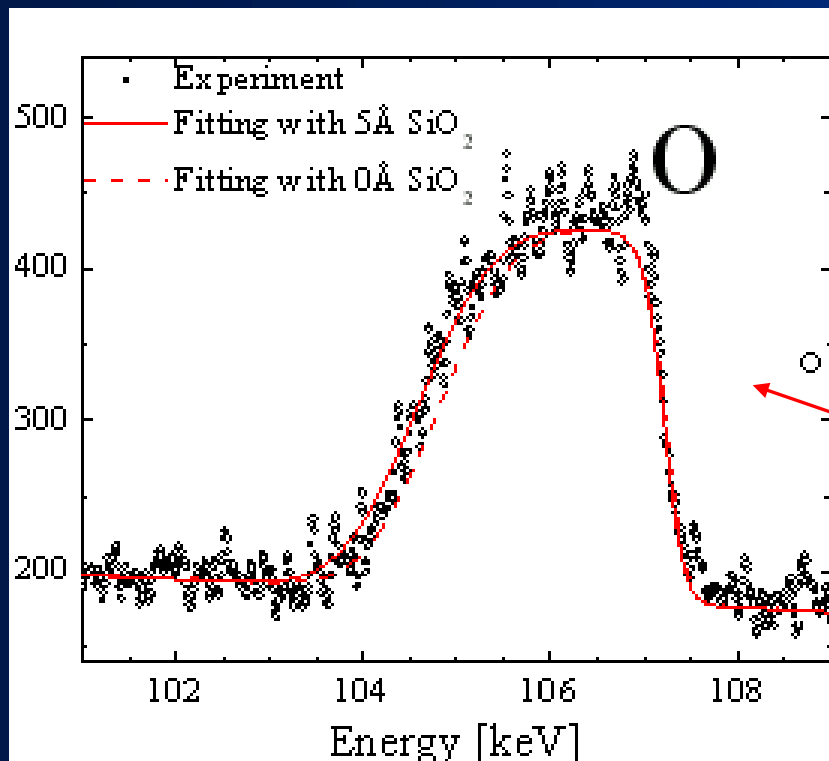
With Rutgers University using 130 keV proton beam
It shows the absence of silica near the interface.



Vacuum annealing at 630°C

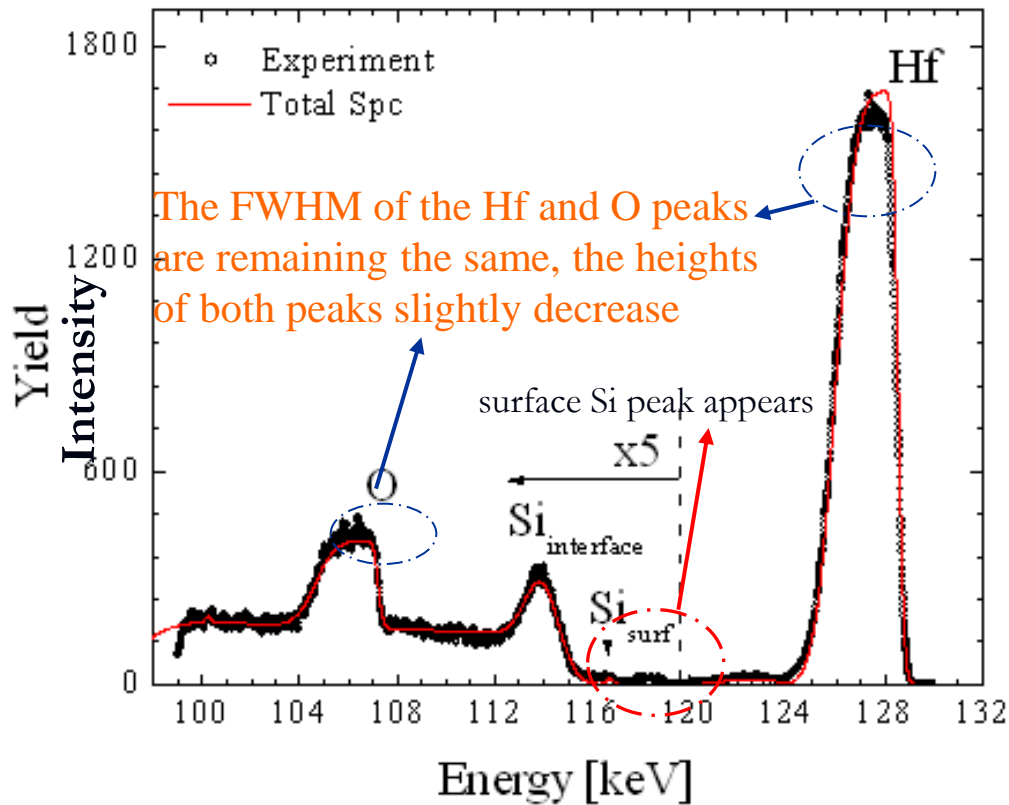


Broadening of the O peak and small increase in the Si peak indicate some interfacial SiO_2 formation about 0.4 nm.





Annealing from 630°C to 950°C



A possible structure after high temperature anneal

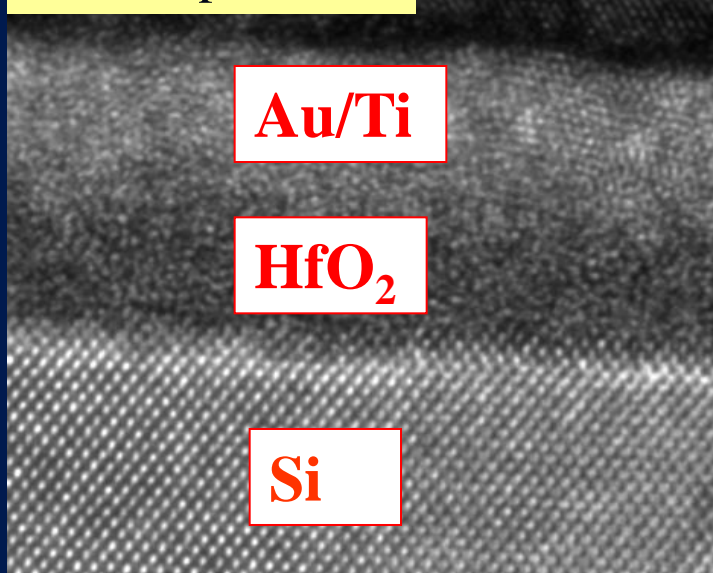


Discontinuities and islands were formed in HfO₂.

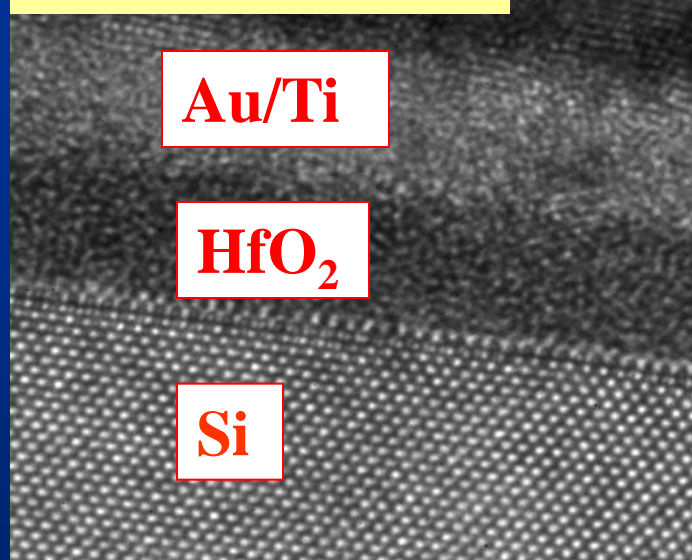


HRTEM Study of Thermal Stability of High κ HfO₂ Gate Stacks

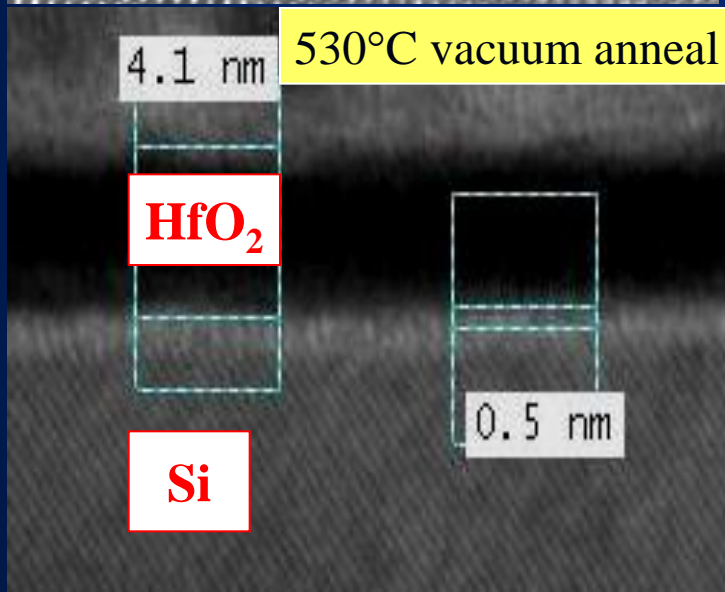
As-deposited



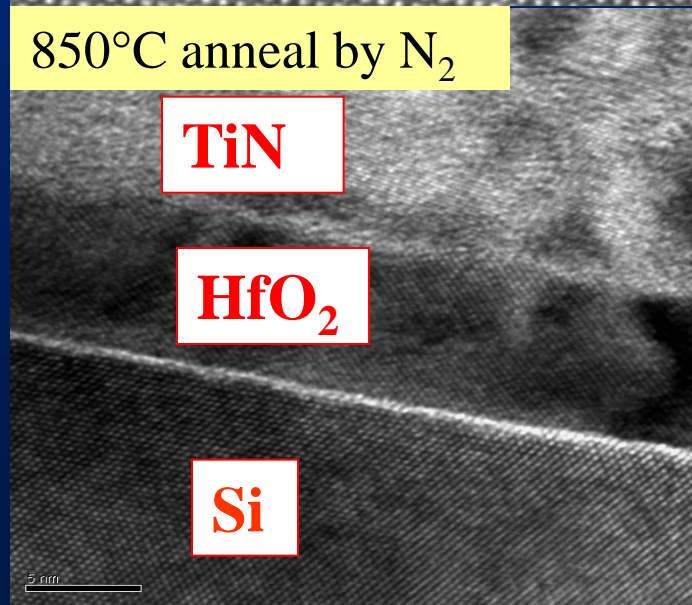
350°C anneal



530°C vacuum anneal



850°C anneal by N₂





Difficulties of High κ MOSFET Fabrications

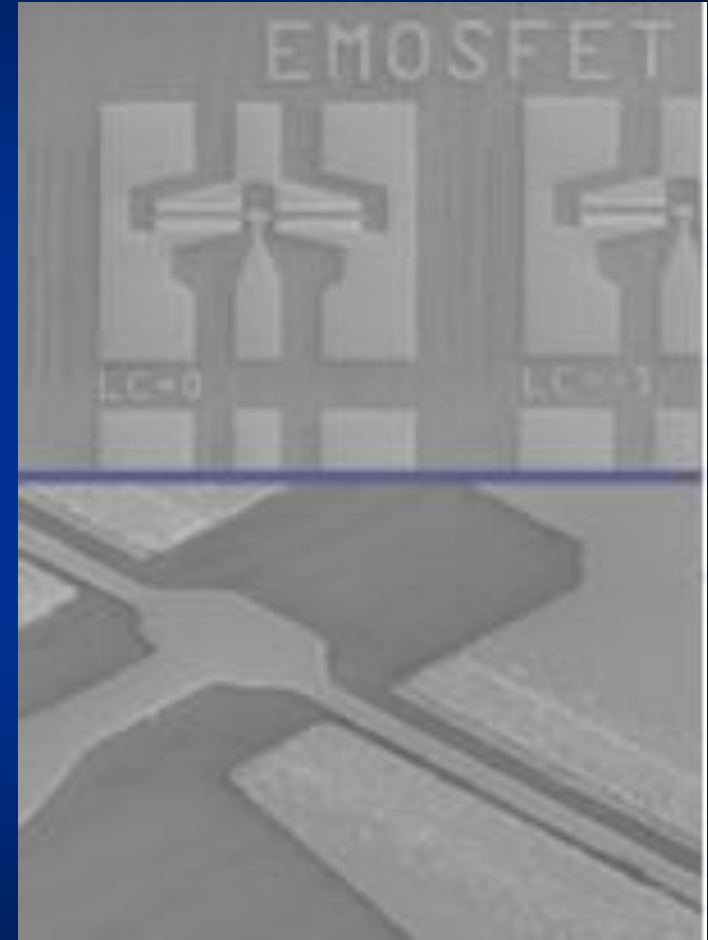
- Thermal stability of thin films
 - HfO_2 → Lowering the dopant activation temperature to 700°C
 - TiN → Using Ti/TiN bilayer structure
- Process integration
 - 4 inch Si (LOCOS) → 2 inch Si (MBE)
 - Successful integration



TiN/HfO₂/Si High κ MOSFET

- A self-aligned process
- With LOCOS isolation
- HfO₂ gate dielectrics
- TiN metal gate
- 2 inch MBE-grown high κ films
- A 4 inch Si line in ERSO for isolation
- A 6 inch Si line in NDL for processing

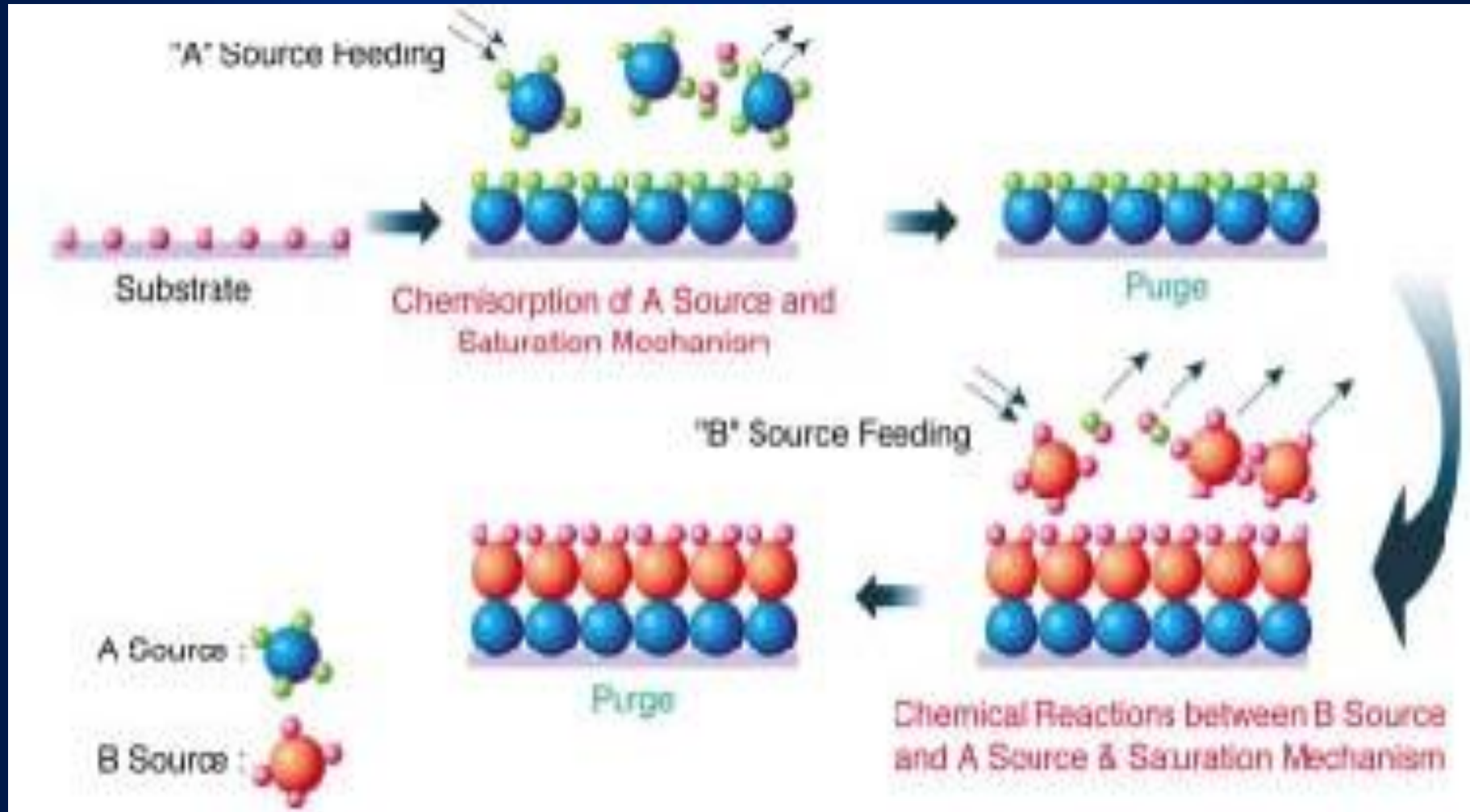
- W / L ~ 100 μm / 1.5 μm
- EOT ~ 26 Å ($t_{\text{ox}} = 10 \text{ nm}$)
- $I_d \sim 8.5 \text{ mA}$ @ $V_{\text{gs}} = 4 \text{ V}$
- $G_m = 48.5 \text{ mS/mm}$





Atomic Layer Deposition (ALD)

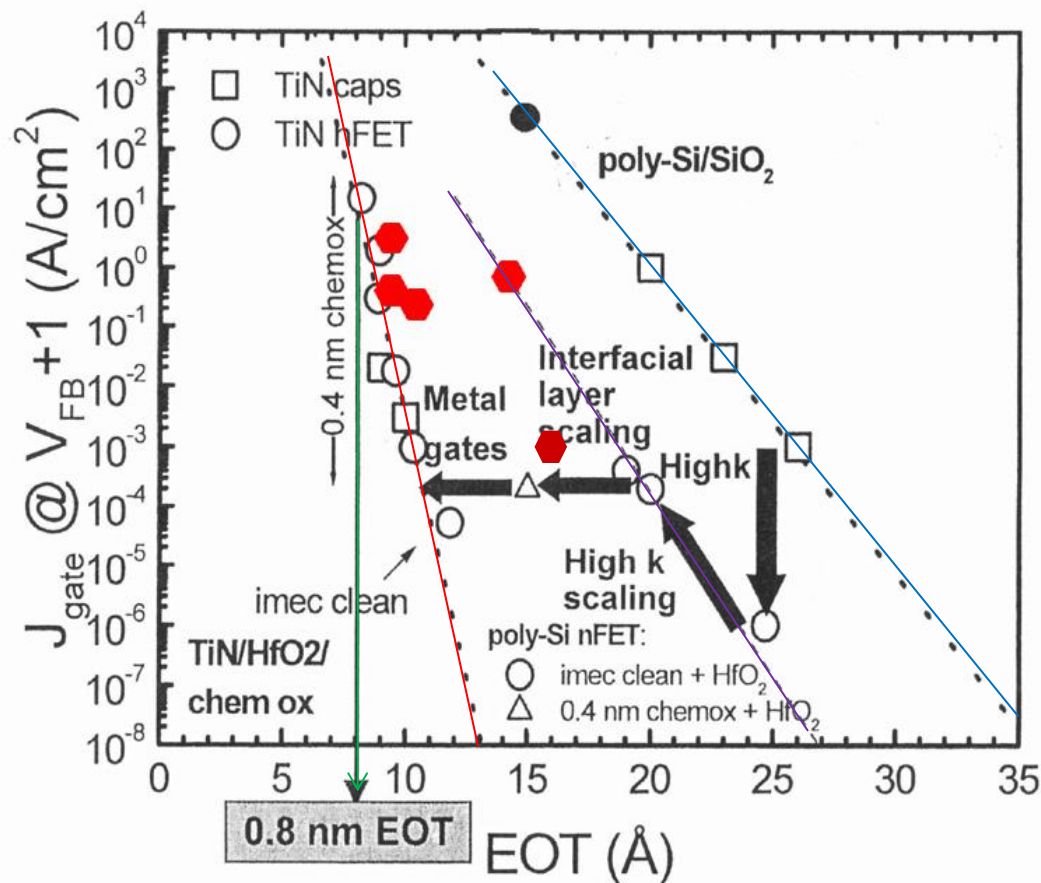
Growth Mechanism : Formation of interfacial SiO_2 is hard to avoid.





Comparison between the MBE and ALD films

MOS devices with ALD HfO_2 layers



❖ MBE-grown Au/HfO₂/Si MOS diodes are denoted in red hexagons

❖ HfO₂ film 4.4 nm thick, with $J_L \sim 10^{-3} \text{ A}/\text{cm}^2$, κ of 21, and EOT of 0.9 nm

❖ $t_{\text{eq}} = \text{EOT}$
Equivalent Oxide Thickness

$$t_{\text{eq}} = t_{\text{ox}} \kappa_{\text{SiO}_2} / \kappa_{\text{ox}}$$

M. Houssa in Symposium D,
MRS Spring Meeting, April 12-16, 2004.



Novel MBE template for ALD growth

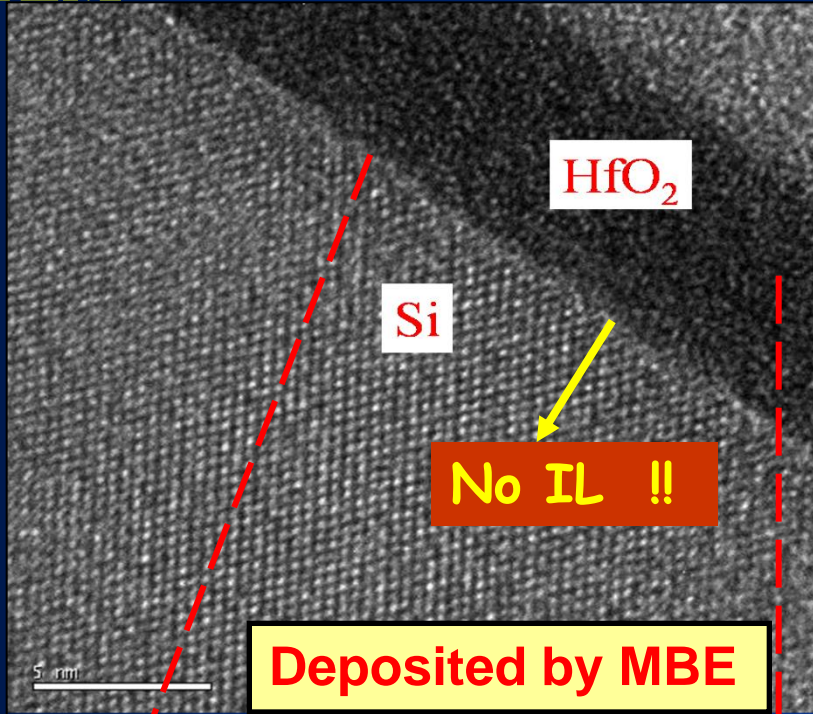
*Can you make an excellent
 HfO_2 Film with a low EOT ?*

Interface Engineering !

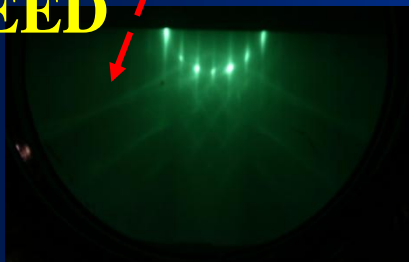


Structural properties of MBE-grown HfO_2

HRTEM



RHEED

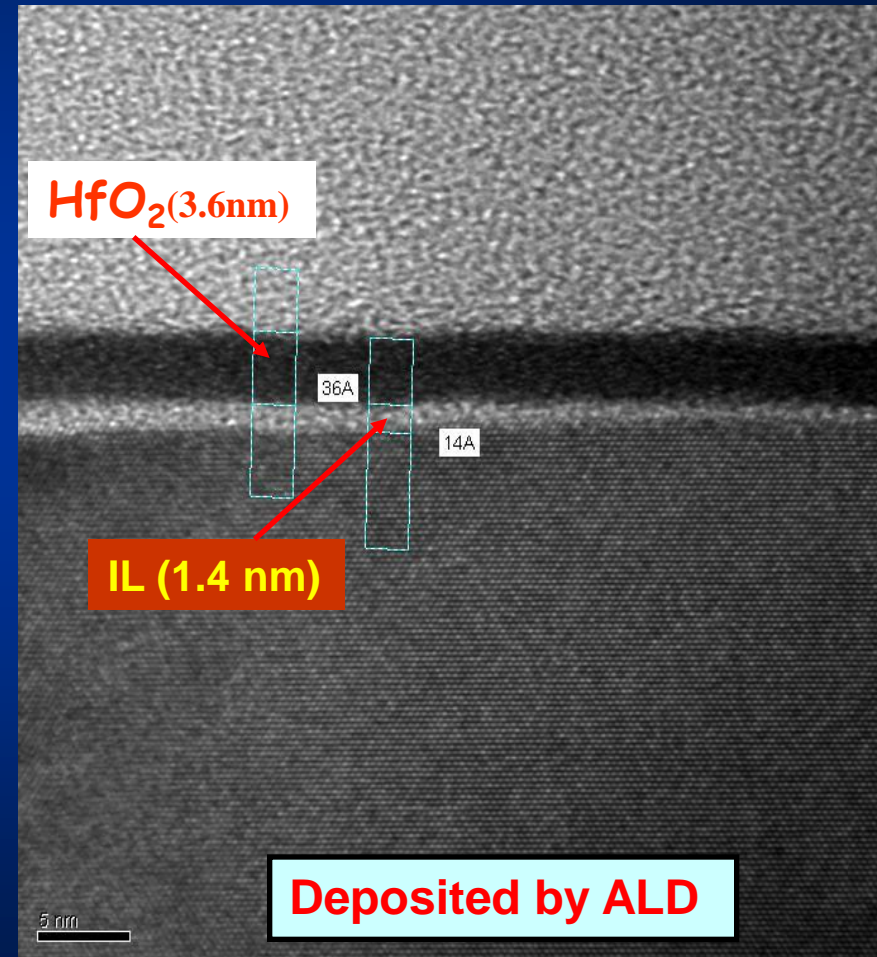


atomically order
Si(100) surface



amorphous
 HfO_2 surface

HRTEM





The MBE Template for ALD Growth

MBE and ALD composite film deposition procedure

MBE template film growth

ALD bulk film growth

MBE HfO_2

ALD HfO_2

MBE Al_2O_3

ALD Al_2O_3

Case 1

Case 2

ALD HfO_2

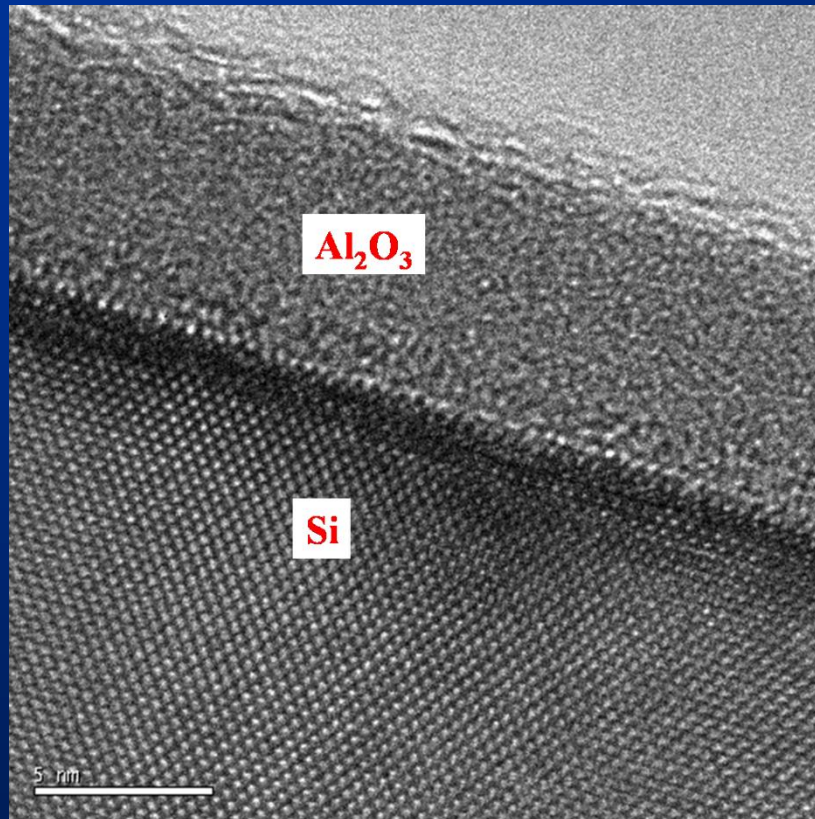
MBE HfO_2

Silicon

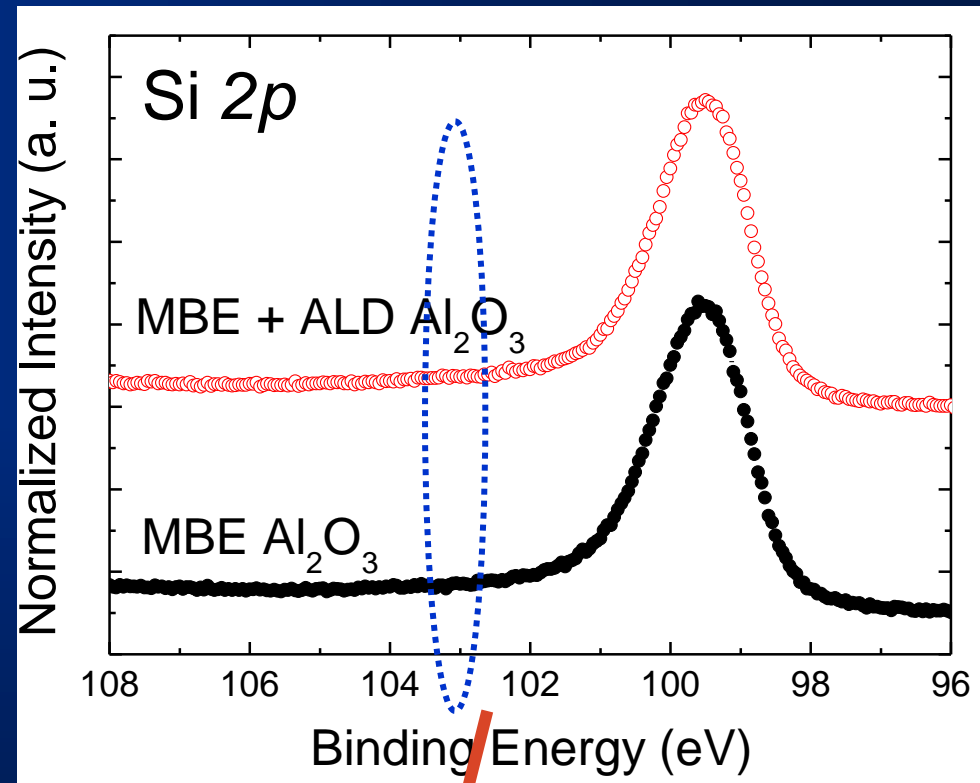
- Low pressure ($<1 \times 10^{-8}$ torr) maintained during MBE growth
- ALD precursors : TMA, H_2O , $T_{\text{substrate}} : 300^\circ\text{C}$

The structure of ALD Al_2O_3 with a MBE Al_2O_3 template

TEM



AR-XPS



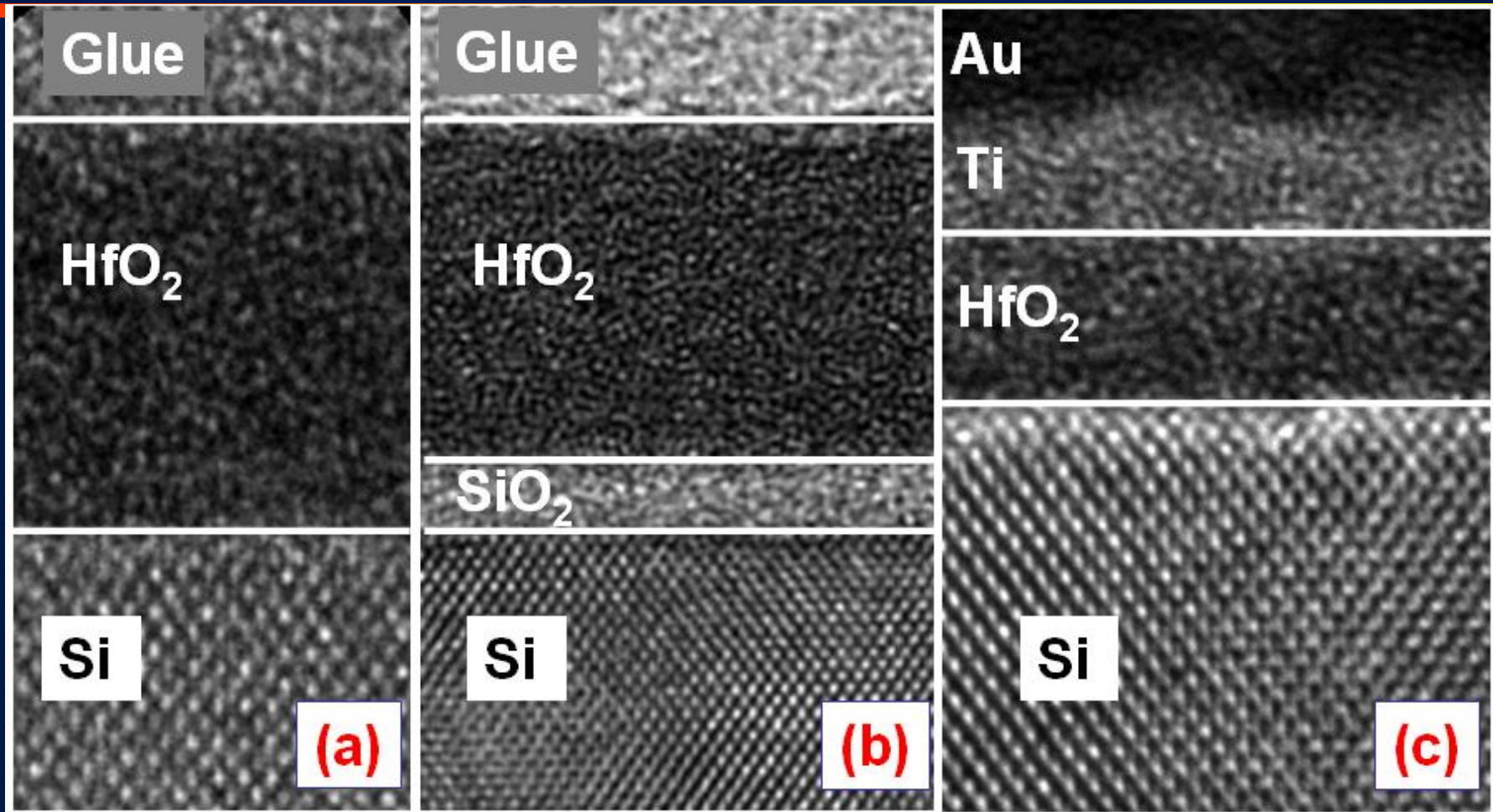
No peak formed at 103.4 eV

→ No SiO_2 formed at interface for both MBE and MBE+ALD Al_2O_3

For HfO_2 , have achieved $\text{EOT} = 0.7 \text{ nm}$



The structure of ALD HfO_2 with a MBE HfO_2 template



MBE HfO_2 (6.7nm)

Silicon

ALD HfO_2 (8.1nm)

SiO_2 (1.4nm)

Silicon

ALD HfO_2 (1.4nm)

MBE HfO_2 (1.5nm)

Silicon



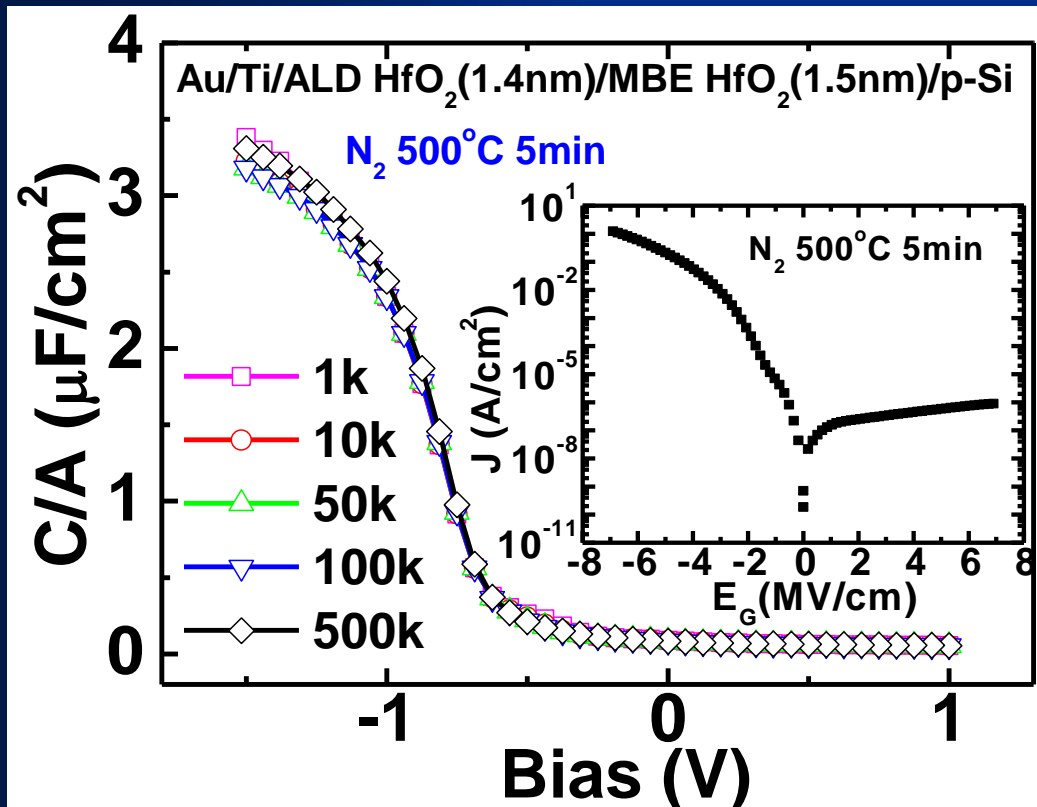
The electrical characteristics of ALD/MBE HfO_2 (2.9nm)

ALD HfO_2 (1.4nm)

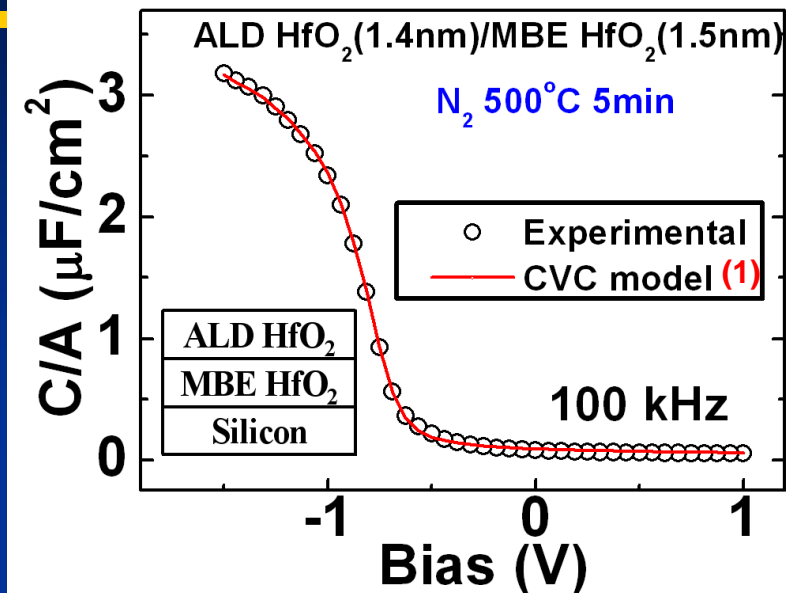
MBE HfO_2 (1.5nm)

Silicon

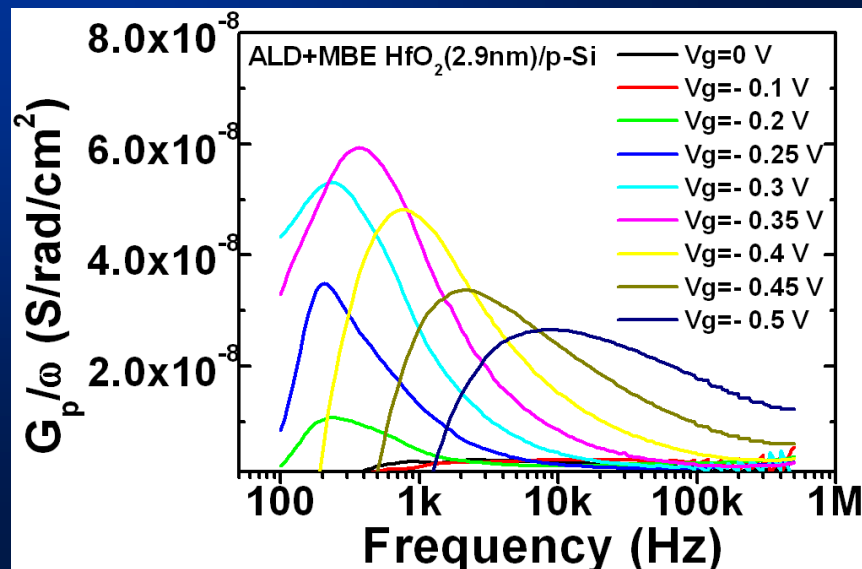
$EOT = 0.7\text{nm}$



$J_{leak} = 5.3 \times 10^{-1} \text{ A/cm}^2$ at $V_{FB} - 1\text{V}$



$D_{it} = 3.6 \times 10^{11} \text{ cm}^{-2} \text{ eV}^{-1}$ near midgap





Comparisons of MOSFET Characteristics

	Our work (TiN/..../p-Si)						<i>Intel</i> ¹
Dielectrics	MBE-HfO ₂ 10nm	ALD-HfO ₂ 10nm	YDH 10nm	ALD-HfO ₂ 8nm+ MBE-HfO ₂ 2nm	ALD-HfO ₂ 4nm+ MBE-HfO ₂ 2nm	YDH 7nm+ Y ₂ O ₃ 1nm	ALD-HfO ₂
L _g (μm)	1.5	1.5	1.5	1	1	1	0.08
EOT(nm)	2.5	3	1.5	2.5	1.5	1.6	1
G _m (mS/mm)	35	55	70	120@V _G =3.5V 100@V _G =2.5V	<u>100@V_G=2.5V</u> 1250 [#] 1875*	<u>125@V_G=2.5V</u> 1560 [#] 2500*	132 1650
I _d (mA/mm)	80	55	118	240@V _G =4V 70@V _G =2.5V	<u>155@V_G=2.5V</u> 1940 [#] 2910*	<u>195@V_G=2.5V</u> 2440 [#] 3900*	140 ¹ 1750

After normalization to gate length of 0.08 μm

* After normalization to gate length of 0.08 μm and EOT of 1 nm

¹ R. Chau, et al, IEEE Electron Device Letters **25**, No. 6, 408 (2004)



Major Research Accomplishment

- First demonstration of atomically abrupt high k HfO_2/Si interface.
- Successful integration of the 6 inch Si CMOSFET processing in NDL with our 2" MBE high κ dielectric films using a TiN metal gate to produce a gate length $1.5\text{ }\mu\text{m}$ transistor device.
- Novel ALD + MBE template approach, superior electrical performance.