

Ultra-thin ALD HfO₂ Growth Mechanism Studied By Atomic Force Microscope (AFM)

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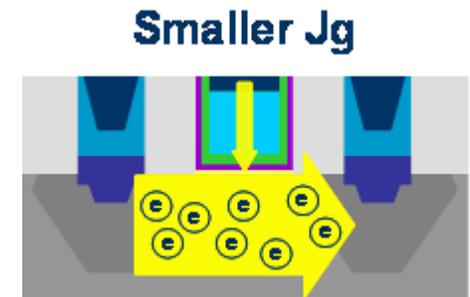
Outline

- **Introduction**
- **Description of analytical techniques used in this study**
- **Influence of silicon oxide interface layer (IL) surface chemistry on the HfO₂ growth**
 - **Growth rate, surface coverage and morphology**
- **HfO₂ growth mechanism**
- **Correlation of HfO₂ morphology with leakage current performance**
- **Conclusions**

Introduction

▪ Incentives of high-k HfO_2 gate dielectric

- Tradition SiO_2 and SiON dielectrics cannot sustain low gate leakage current (J_g) for EOT below 10 Å
- Higher k dielectrics can afford large physical thickness to reduce J_g



▪ Why SiO_2 and SiON based dielectrics are hard to replace?

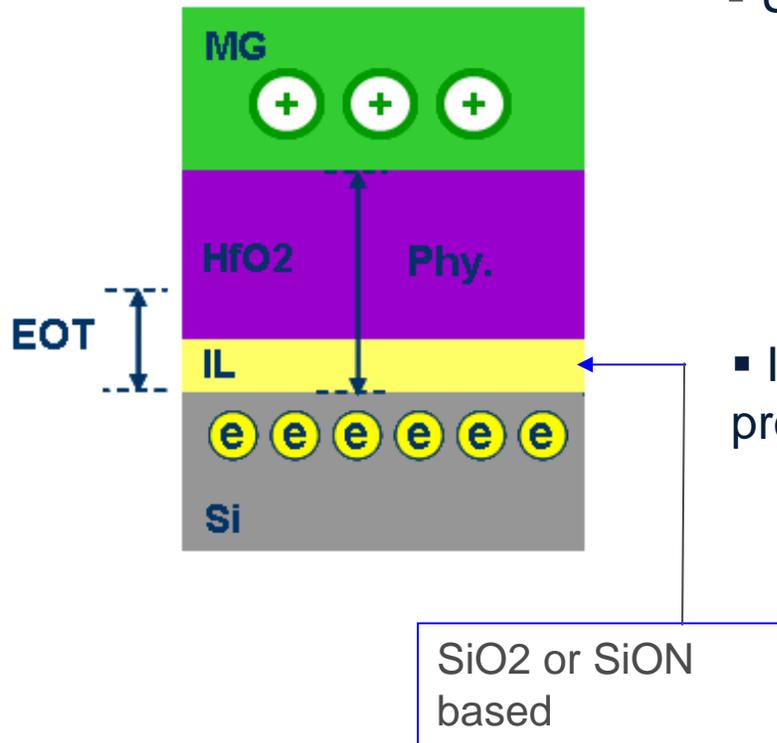
- Natively grown, high purity, conformal, dense and stable!
- Good electrical properties: low defect density and good interface property

▪ Challenges of HfO_2 deposition processes

- ALD process for conformal deposition
- Control of composition, impurity content, phase and crystallinity
- ***Density and uniformity – affecting current leakage property***
- Interface with Si channel – interface roughness induced carrier scattering

Introduction

Interface engineering is important in high-k/metal gate processing

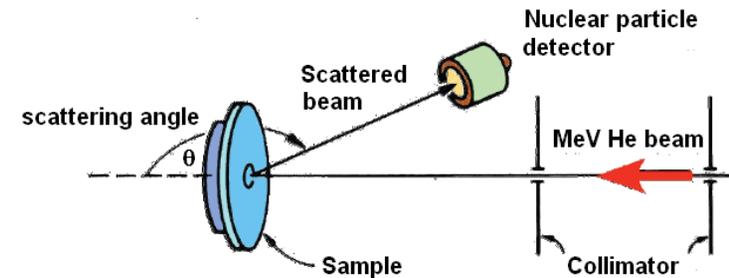


- Unintentionally formed IL (interface layer)
 - unstable
 - poor interface with Si channel
 - poor electrical properties
- IL engineering to grow good IL with good properties
 - low roughness interface to decrease carrier scattering
 - chemically stable to reduce interface states and traps
 - as thin as possible, not to consume EOT budget
 - **good surface properties for easy high-k oxide nucleation!**

Descriptions of analytical techniques

▪ RBS – Measures surface dose of Hf

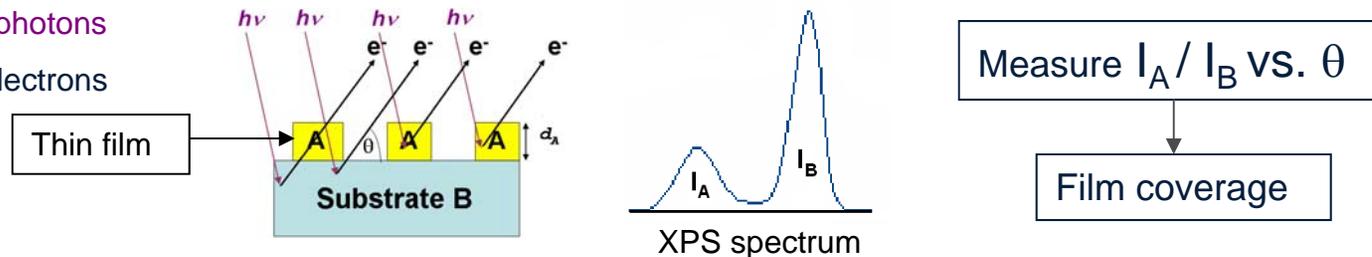
- Energy of scattered He depends on the atomic # of the atoms on surface
- 10^{11} atoms/cm² detection limits for Hf
- **For determination of HfO₂ growth rate**



▪ AR-XPS - Measures thin hafnium oxide composition and coverage

$h\nu$ - X-ray photons

e^- - photoelectrons

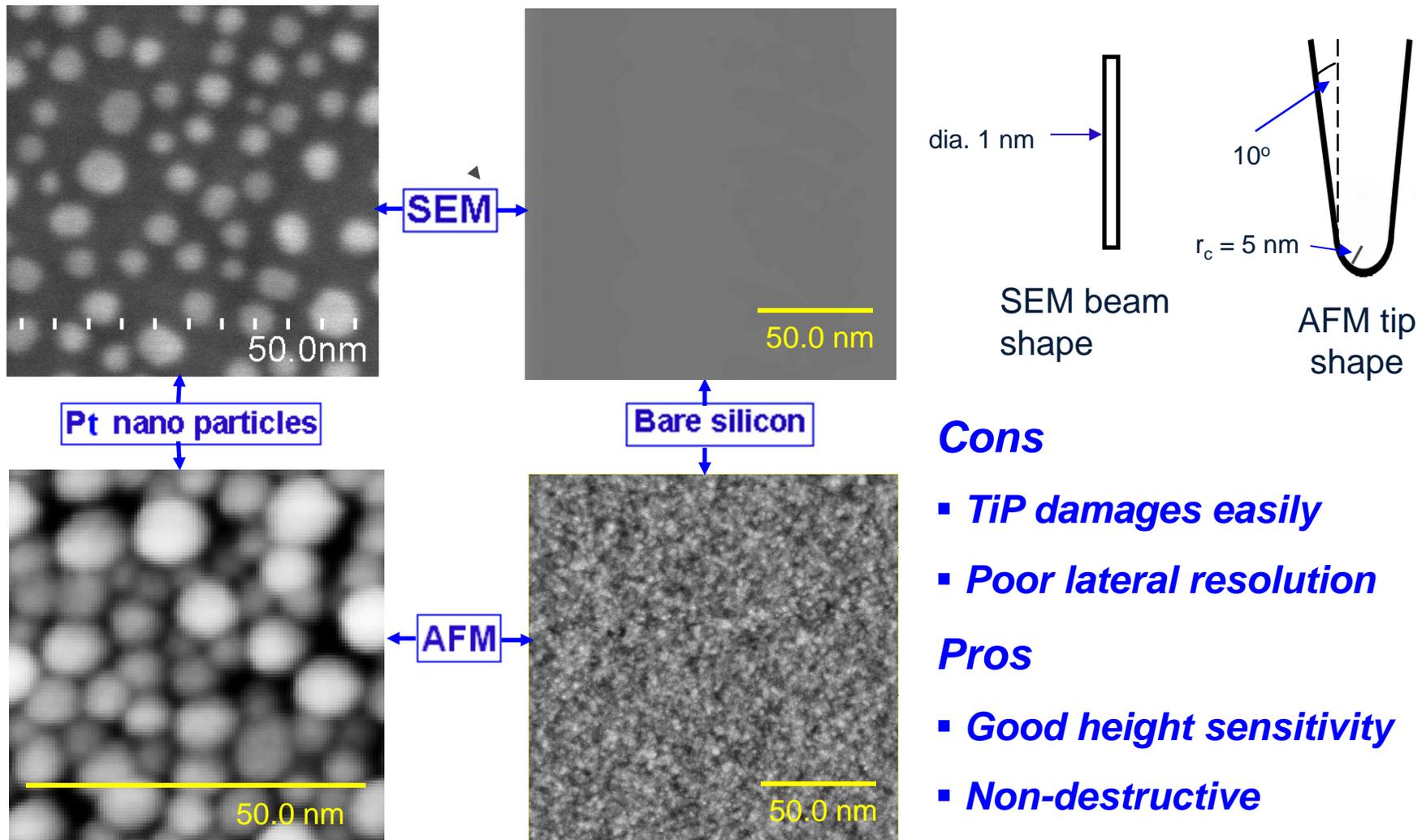


▪ Atomic force microscope (AFM, non-destructive)

- **Imaging of film morphology at different stages of film growth, best for providing direct film growth mechanism information**
- Not successfully applied before due to easy tip damage and low image resolution

Pros and cons of AFM for high resolution imaging

Comparison with secondary electron microscope



Cons

- *TiP damages easily*
- *Poor lateral resolution*

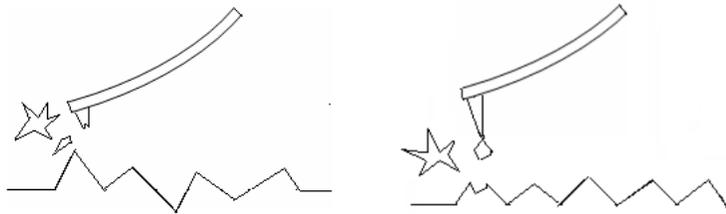
Pros

- *Good height sensitivity*
- *Non-destructive*

Low tip damage technique development

Non-contact AFM

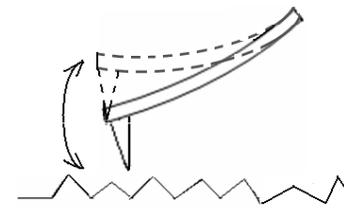
Traditional tapping mode



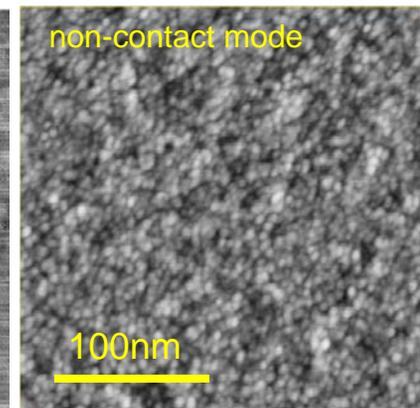
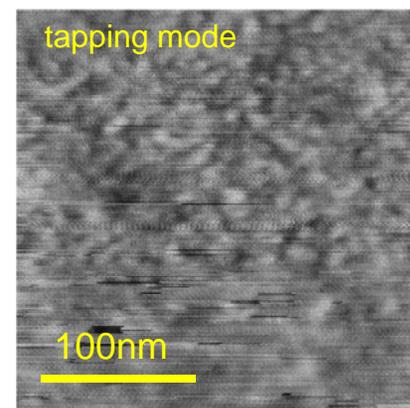
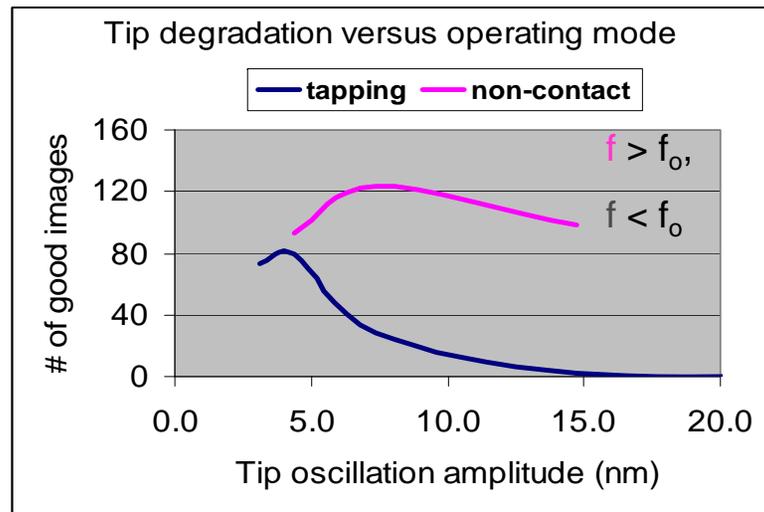
Broken tip

Contaminated tip

New non-contact mode



Intact tip



AFM images of bare Si

Non-contact AFM technique considerably prolongs tip life and improves image quality

C. C. Wang, Y. Pu, L. Fu, Y. Ma and Y. S. Uritsky, *AIP Conference Proceedings* **788**, 194-199 (2005)

B. Liu, C. C. Wang, P. Huang and Y. S. Uritsky, *Proc. of SPIE* **7729**, 77290O-1-77290O-11 (2010)

High resolution AFM tip development

Proprietary AFM tip sharpening technique to improve resolution $\geq 1.5X$

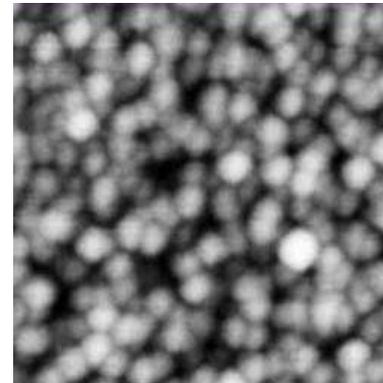
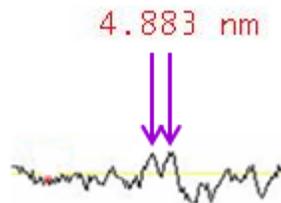
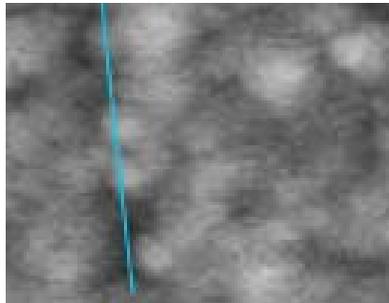


Bare silicon surface

Silicon nano crystals

Not sharpened tip

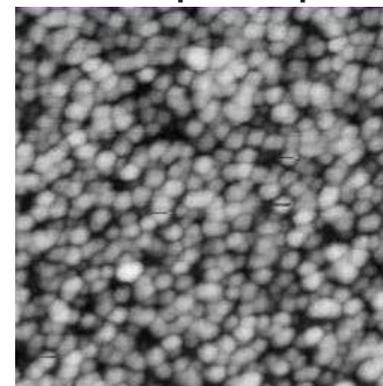
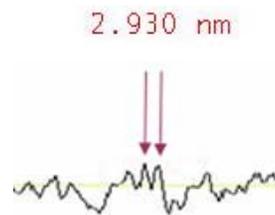
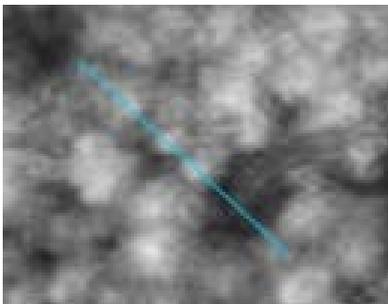
Not sharpened tip



- **Considerable improvement in lateral resolution.**

Sharpened tip

Sharpened tip



- **In-house tip sharpening avoids shipping, handling and aging damage to AFM tip.**

HfO₂ growth study – descriptions of ALD HfO₂ samples

TABLE 1. Descriptions of the Six IL sample groups, on which ALD HfO₂ films[@] were deposited

Group No.	Group 1	Group 2	Group 3	Group 4	Group 5	Group 6
IL type/thickness [^]	IL1/10 Å	IL2/15 Å	IL3/15 Å	IL4/15 Å	IL5/15 Å	IL6/12 Å
Oxide process [*]	T1	T1	T2	T3	T1	ChemOx [#]
Surface treatment	none	none	none	none	SC1(25°C) ⁺	none

[@] 0, 5, 11, 17 and 23 cycles of ALD HfO₂ films were deposited on the different IL layers to study the HfO₂ growth mechanism.

[^] Thicknesses of the IL layers were verified by XPS measurements.

^{*} “T” stands for thermally grown oxide.

[#] ChemOx is the oxide formed on Si surface by SC1 clean (NH₄OH + H₂O₂ in DI water at 87°C) . It is abundant in OH-terminated sites on surface.

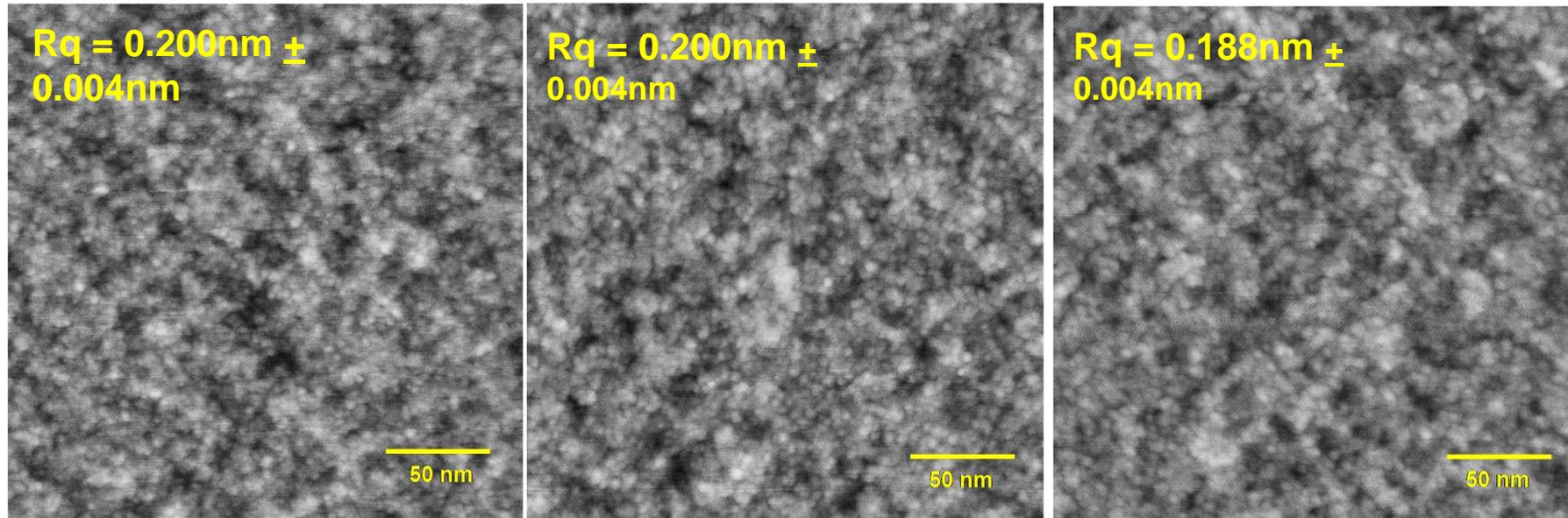
⁺ IL5 was IL1 dipped in SC1 (25°C) solution for a few seconds then rinsed clean with DI water.

HfO₂ growth study – AFM images of IL with no HfO₂ film

IL1 10Å

IL2 15Å

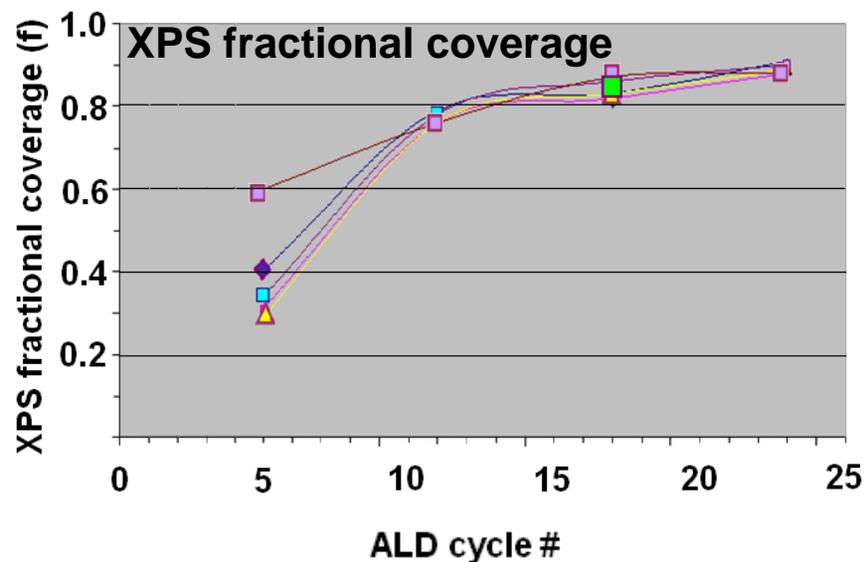
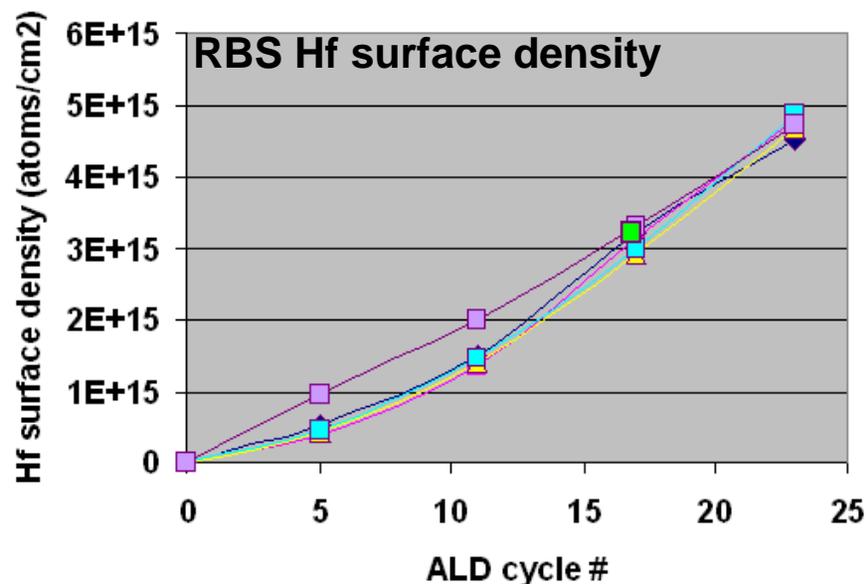
IL5 15Å



- *Both IL1 and IL2 surfaces have more tiny protruding features.*
- *IL5 surface is slightly smoother than both IL1 and IL2 surfaces and is without the tiny protruding features.*
- *All the surfaces are not atomically flat (rms roughness > 0.5nm).*

HfO₂ growth study – RBS and XPS results

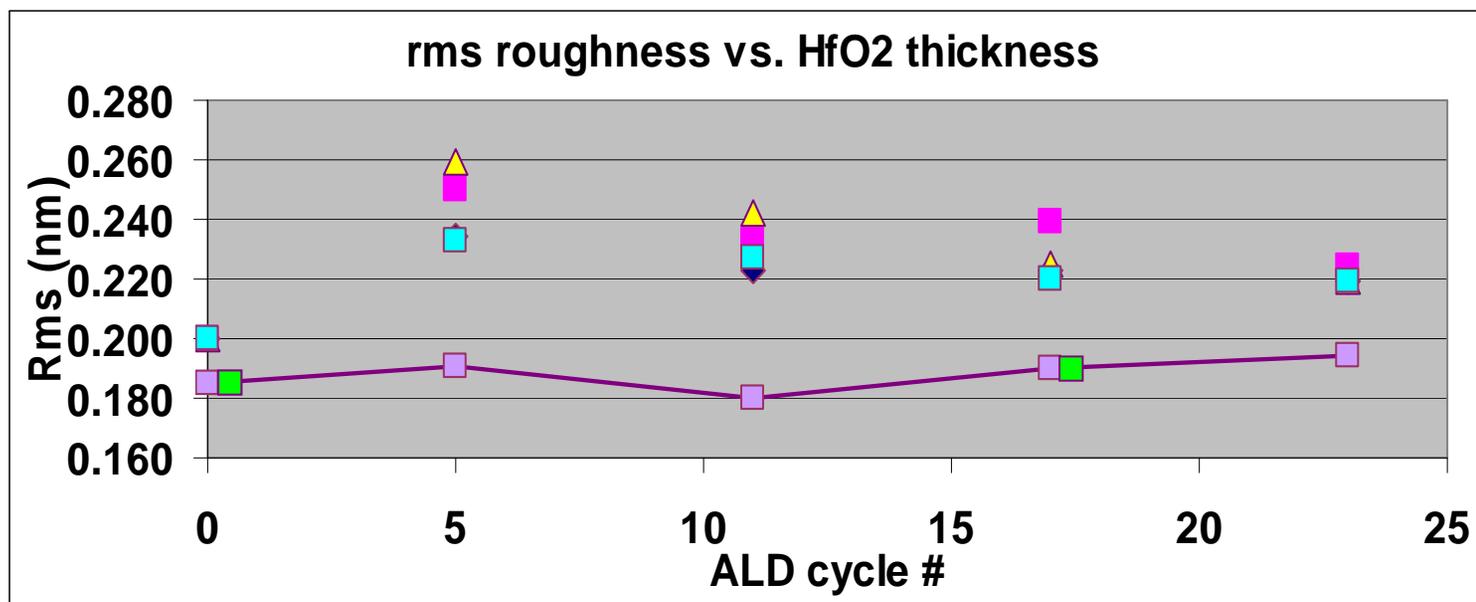
- ◆ IL1 10A
- ▲ IL3 15A
- IL5 (Tox surface treated with SC1 solution)
- IL2 15A
- IL4 15A
- IL6 (ChemOx)



- **Linear growth rate of HfO₂ film on IL5 is observed.**
- **Similar growth rates are observed on all the other four thermally grown IL types.**
- **Initial Growth rate on thermally grown ILs = ½ initial growth rate on IL5 (thermally grown IL with ChemOx treatment).**
- **XPS coverage study showed that HfO₂ has higher initial coverage on IL5 than on the other four IL types. At higher coverages, XPS coverage failed to distinguish the difference of HfO₂ films on the different types of ILs.**

HfO₂ growth study – AFM roughness results

- ◆ IL1 10A
- ▲ IL3 15A
- IL5 (Tox surface treated with SC1 solution)
- IL2 15A
- IL4 15A
- IL6 (ChemOx)

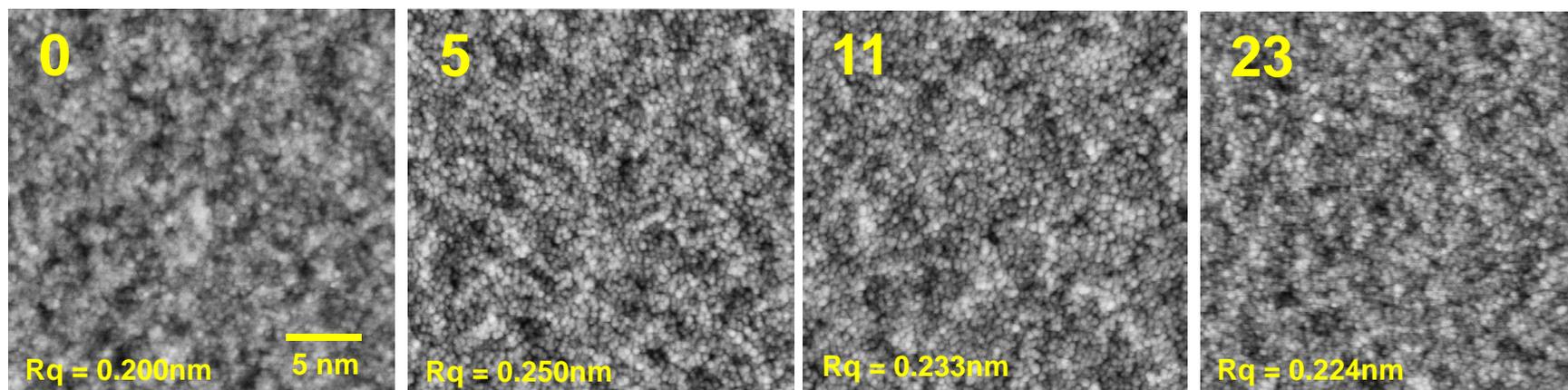


- HfO₂ films deposited on IL5 shows no increase in roughness with increasing ALD cycle #.
- HfO₂ films deposited on all other four types of thermally grown ILs show large increase in roughness at 5 ALD cycles then gradual decrease in roughness with increasing ALD cycle #.

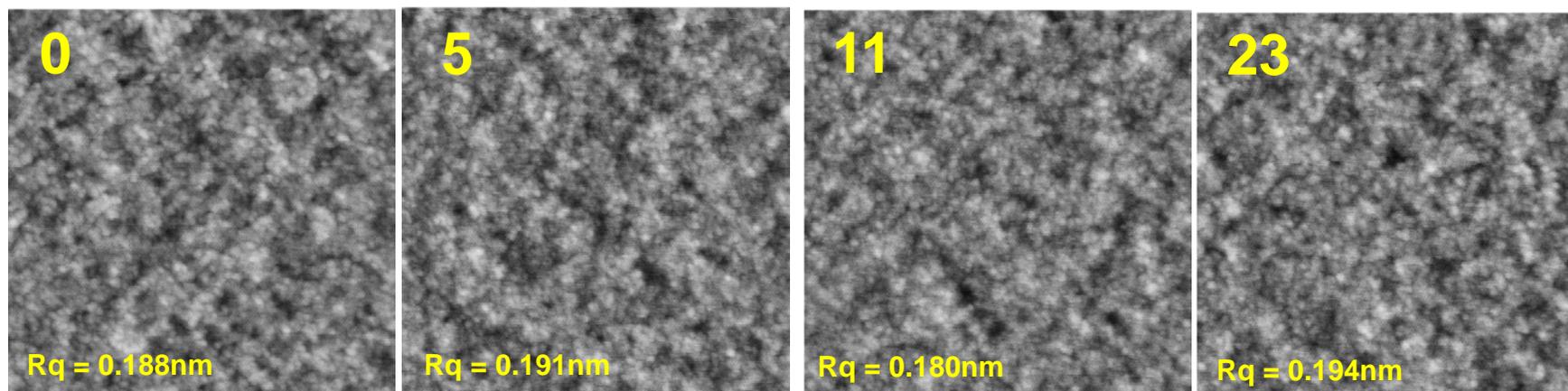
HfO₂ growth study – HfO₂ AFM images

ALD HfO₂ on 15 Å IL1

Yellow # indicates ALD cycle #



ALD HfO₂ on 15 Å IL5

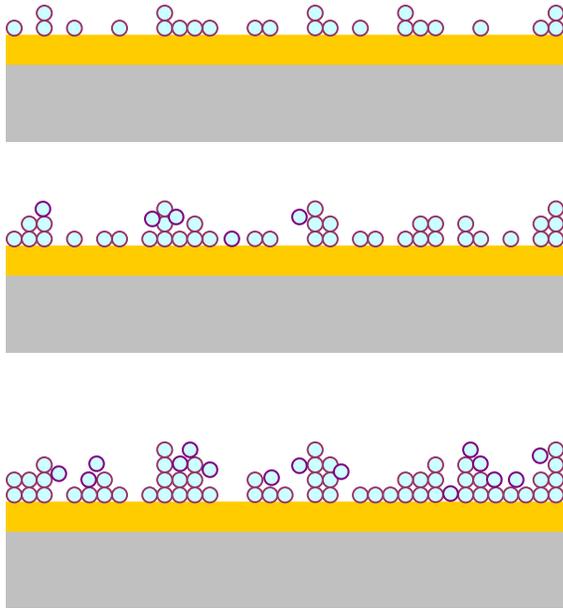


- Numerous tiny nodules can be seen on 15 Å IL1 after 5 cycles of HfO₂ growth, indicating islands growth mechanism. Such was observed on all the other three thermally grown IL layers.
- No morphology change after 5 cycles of HfO₂ on 15 Å IL5, indicating conformal growth mechanism.

HfO₂ growth study – growth mechanism hypothesis

On all thermally grown ILs

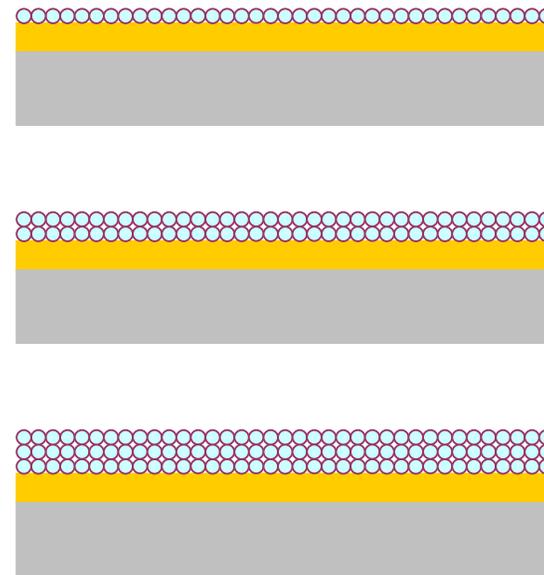
Islands (three dimensional) growth – due to scarcity of –OH terminated nucleation sites



- **Growth rate increases with the increase of surface area**
- **HfO₂ films are porous and non-uniform**

On thermally grown IL treated with SC1 (IL5)

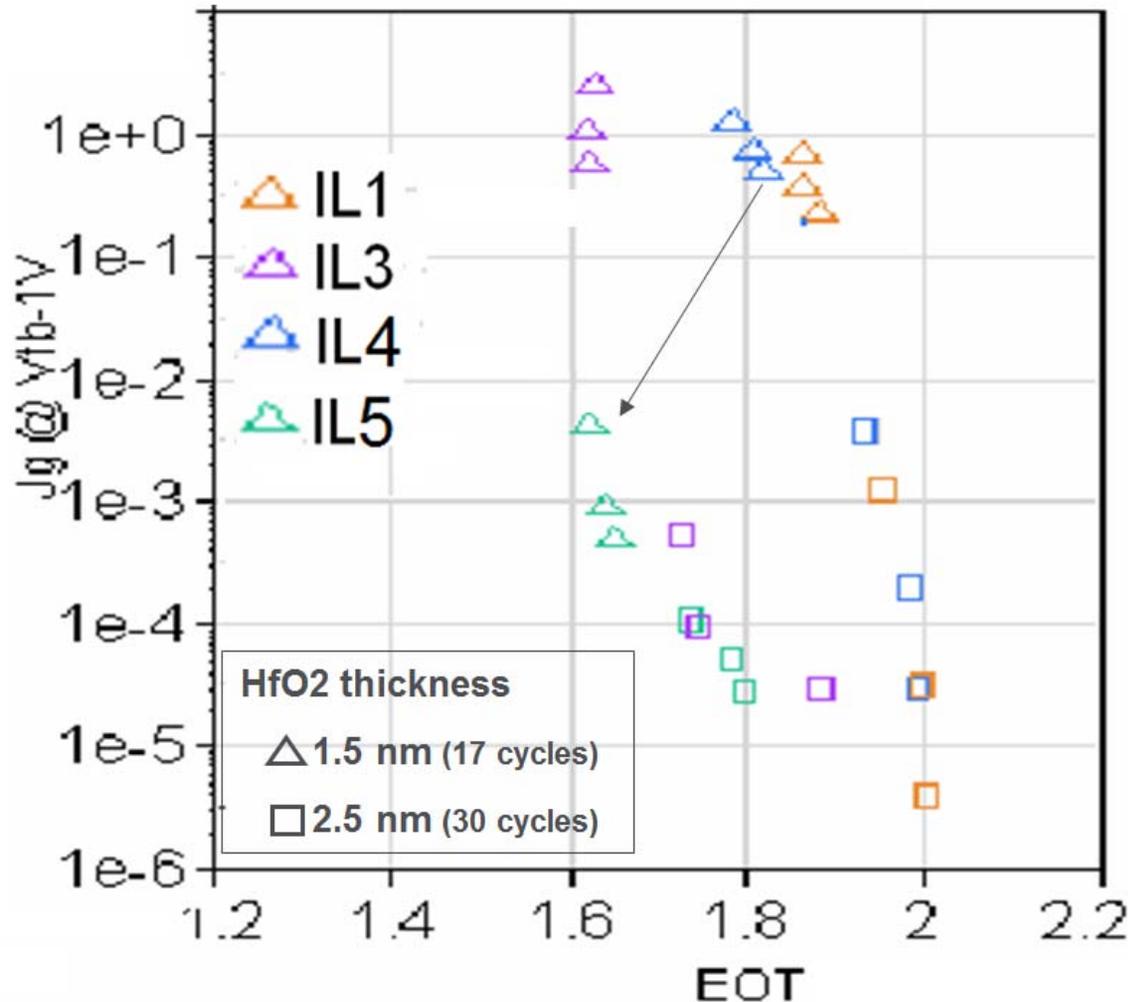
Layer by layer (two dimensional) growth – due to abundance of –OH terminated nucleation sites



- **Growth rate stays the same**
- **HfO₂ films are dense and uniform**

Justin C. Hackley, Theodosia Gougousia and J. Derek Demaree, JOURNAL OF APPLIED PHYSICS 102, 034101 (2007)

HfO₂ growth study – correlation with electrical tests



Three data points are from center, middle radius & edge of the wafer.

- The IL5 with 1.5 nm HfO₂ shows X1000 lower Jg than the other ILs with the same thickness HfO₂
- The IL5 wafer shows better within wafer uniformity in Jg test.
- **Jg data correlates with AFM morphology study results well!**

Conclusions

- ***New AFM imaging techniques were developed that enables the direct observation of the morphology of ALD films during the initial stages of film growth***
- ***The same technique can be used to study***
 - *the continuity of ultra-thin film*
 - *Morphology of nano-crystalline materials*
 - *2-dimensional materials*
- ***AFM study of the ALD HfO₂ on different ILs***
 - *reveal that Islands growth on thermally grown SiO₂ ILs results in less dense HfO₂ and its higher leakage current*
 - *validates the conformal growth of ALD HfO₂ on SC1 treated SiO₂, which is abundant with hydroxyl (-OH) groups that facilitate the uniform nucleation of the HfO₂ and growth of a dense HfO₂ film that in turn results in low leakage current.*