Wet etching of TiN in 1-D and 2-D confined nano-spaces of FinFET transistors

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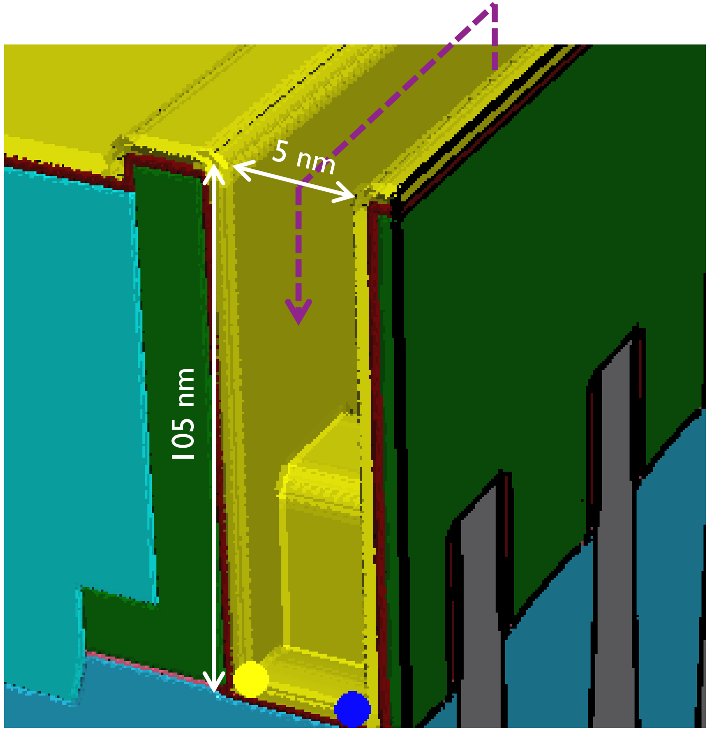
SPCC 2017, March 28-29, Austin, TX, USA

Outline

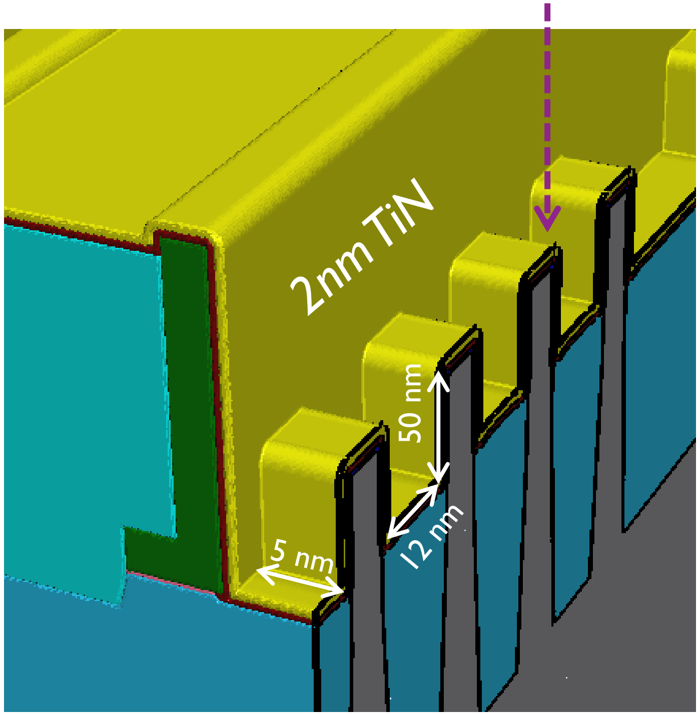
1. Motivation
2. Study of TiN etching
   - in nanotrenches
   - in nanoholes
   - etch mechanism
3. Conclusions

RMG wet etching of WF metal in multi-Vt FinFET at N7

Nanotrench with 1-D confinement



Nanohole with 2-D confinement



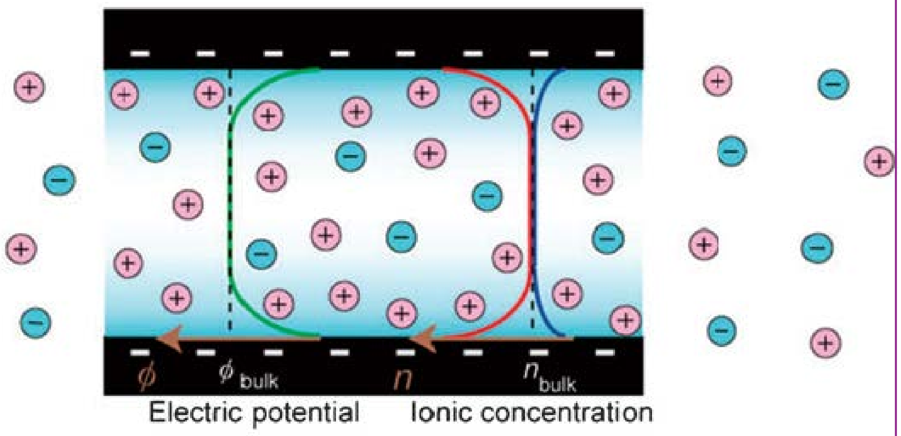
Feature	nm
Fin pitch	24
Fin width	4
Fin Height	50-70
Gate Pitch	42
Gate CD	14-18
Final Gate Height on Fin	25
Gate Height at RMG	105

Coventor view (not to scale)

→ Wet etching still feasible ?

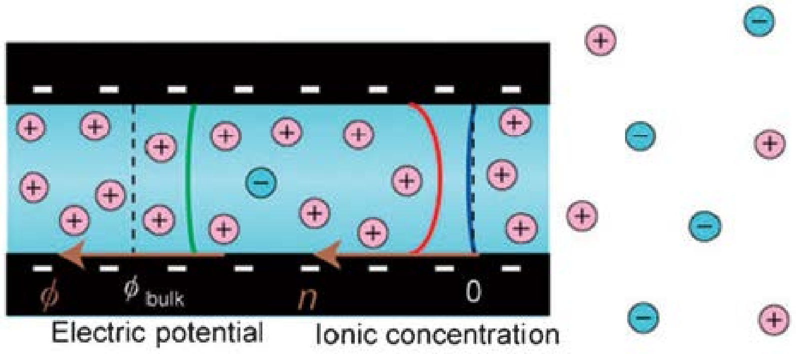
Overlap of electrical double layers in nanospaces

- Microchannel



- Neutral solution in channel as in bulk
- Excess of charged ions only in diffuse part of EDL to neutralize surface charge

- Nanochannel

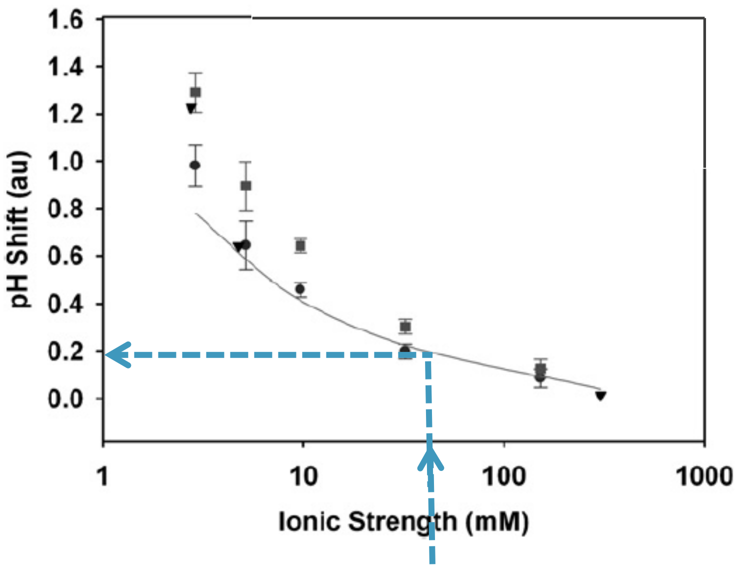


- Overlap of EDLs in channel
- Depletion of ions with same charge as surface in channel → no electroneutrality

H. Daiguji, *Chem. Soc. Rev.*, 2010, **39**, 901.

Impact of EDL overlap on chemical reactions

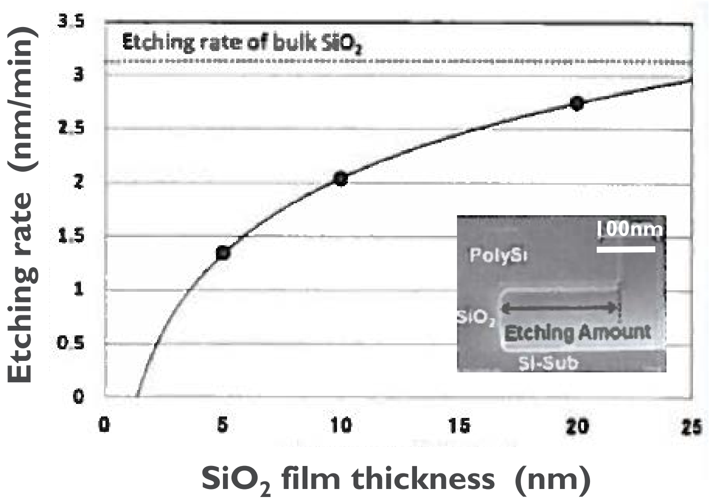
- pH shift in 100nm-wide SiO_2 channels



APM 1:4:20 used in etching of TiN

- Larger shifts expected in smaller FinFETs

- Etching of SiO_2 film in filled nano-slit by dHF



- Decreasing etch rate explained by increasing depletion of HF_2^-

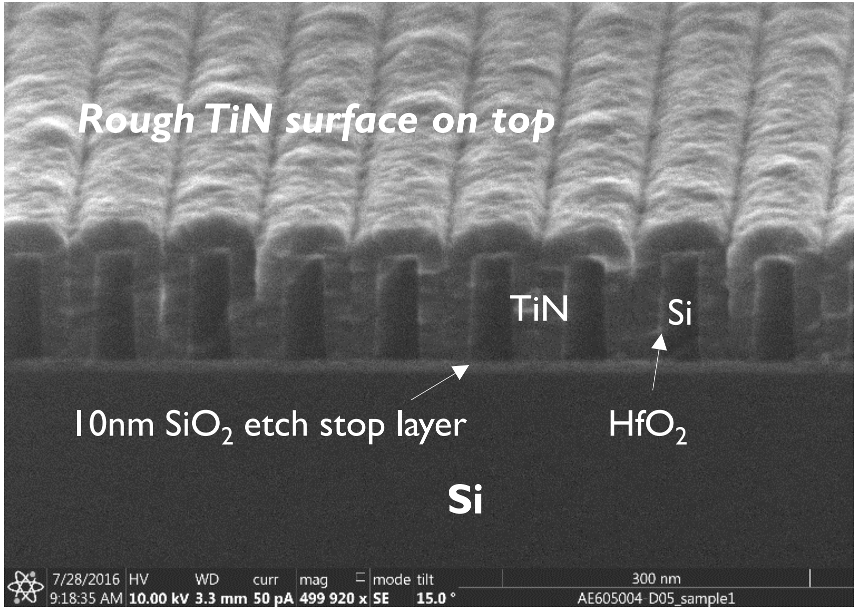
D.Bottenus et al., *Lab on Chip*, 2009, **9**, 219.

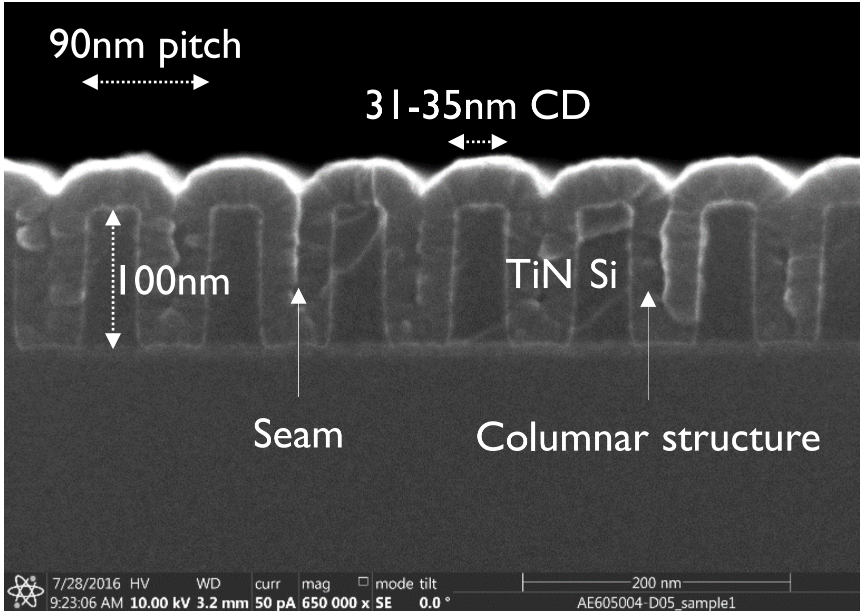
A. Okuyama et al., *Solid State Phenom.* 2015, **219**, 115.

TiN etching in filled nanotrenches

Test structure with filled nanotrenches

Nanotrenches covered with 1.5nm ALD HfO2 + 25nm ALD TiN

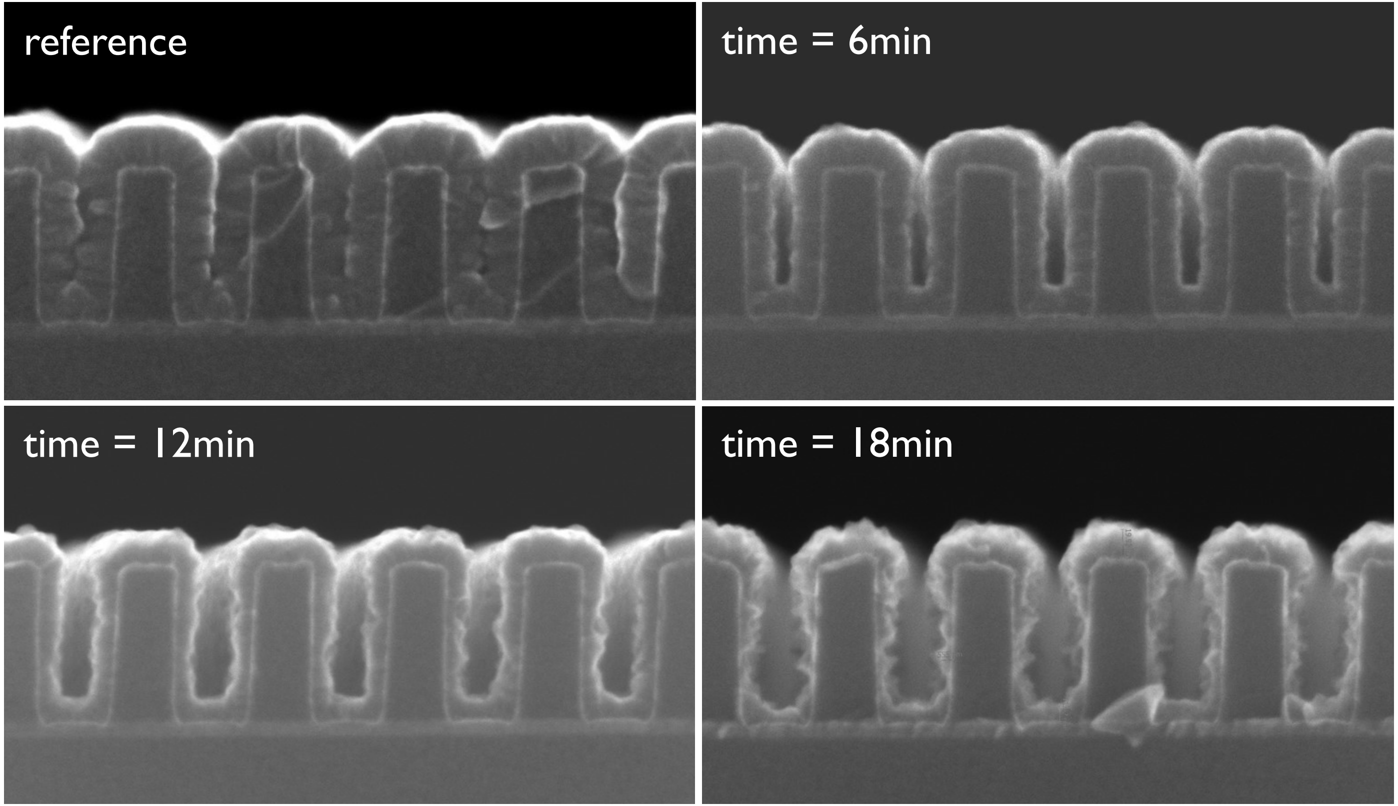




Structures after dHF clean (TiOx etched away) → ~1nm seam

TiN etch in nanolines

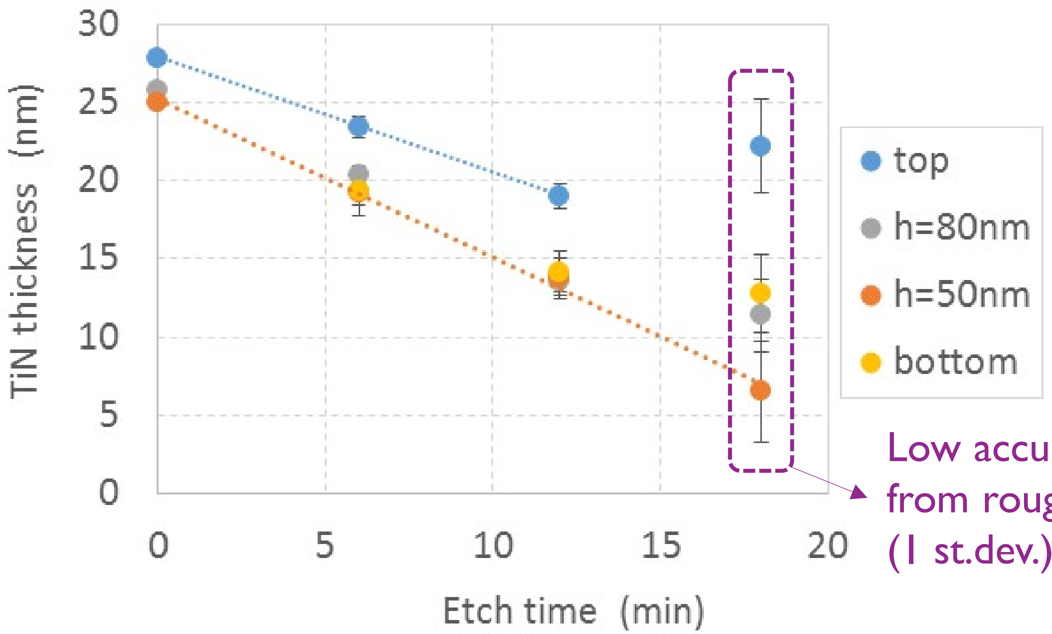
Pre-clean: 2min HF 0.5% & etch: APM 1:4:20 at RT



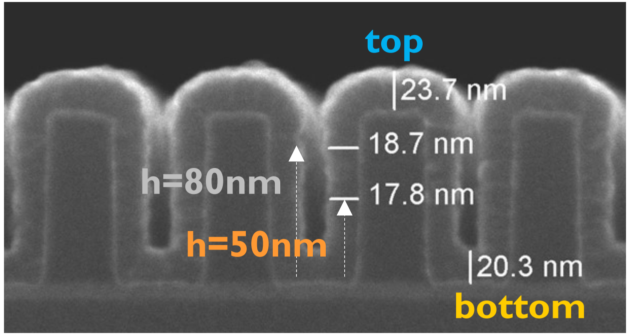
- Uniform etching along the seam → fast capillary wetting of seam
- Faster etching in the formed trench vs. top of lines
- Very rough TiN surface at end from columnar structure of TiN (non-uniform etching)

TiN etch kinetics

Pre-clean: 2min HF 0.5% & etch: APM 1:4:20 at RT



Low accuracy from roughness (1 st.dev.)



- TiN etch rate on top = 0.73±0.01nm/min
- TiN etch rate in trench (h=50nm) = 1.02±0.05nm/min

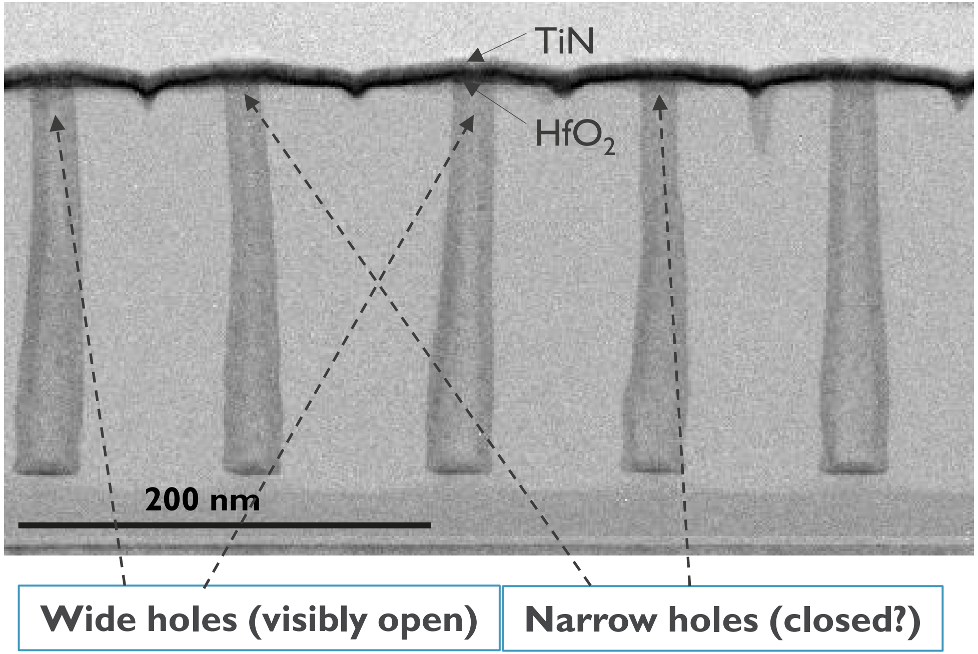
- Faster etch rate in trench vs. top of lines (38%)
- No wetting issue

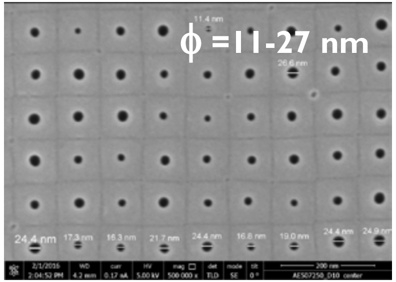
TiN etching in nanoholes

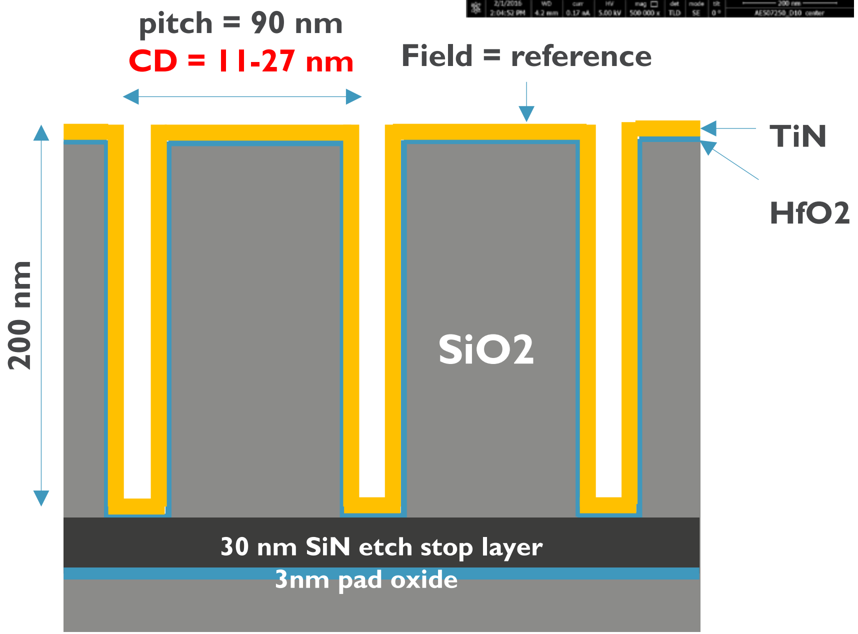
Nanoholes test structure

Nanoholes covered with 1.5nm ALD HfO2 + 5nm ALD TiN

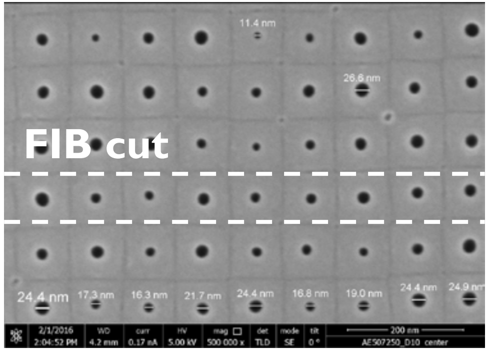
- FIB-TEM inspection: Uniform TiN deposition from top to bottom

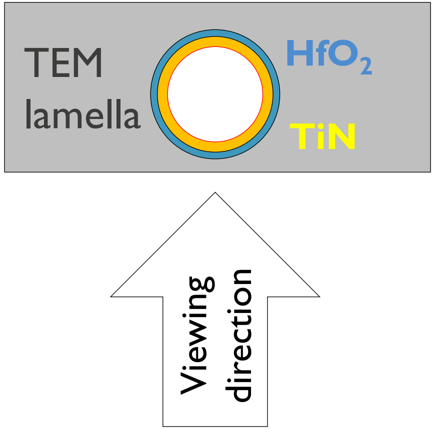


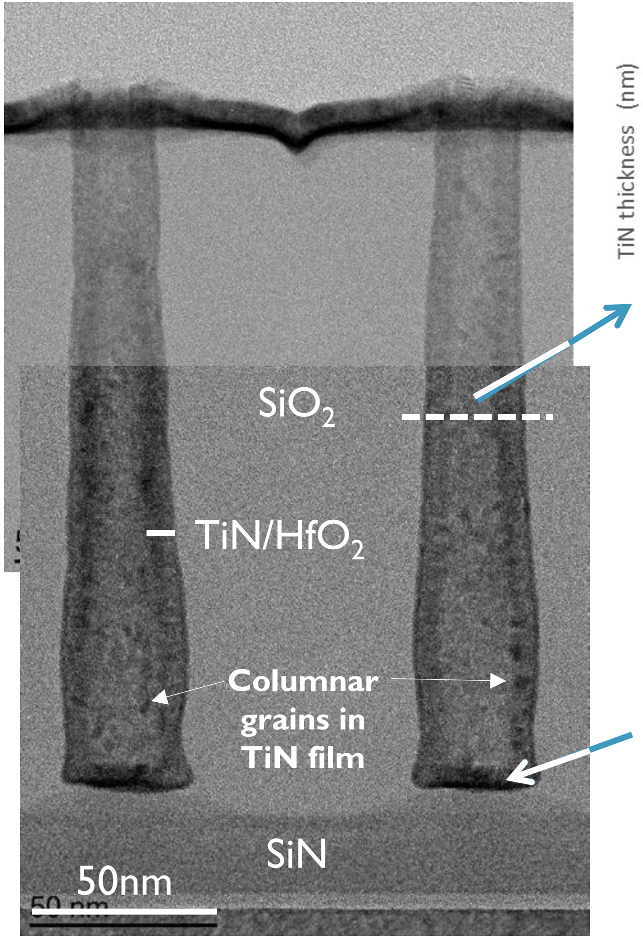


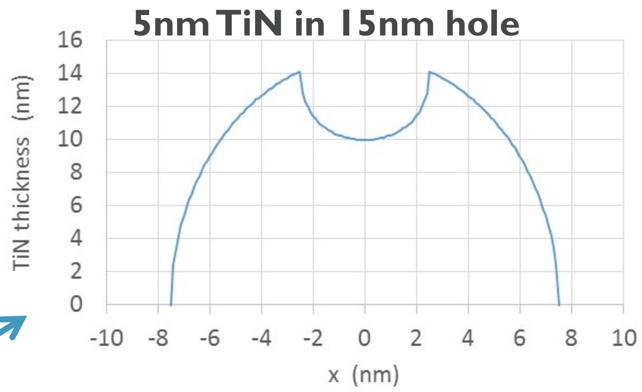


FIB-TEM nanoholes







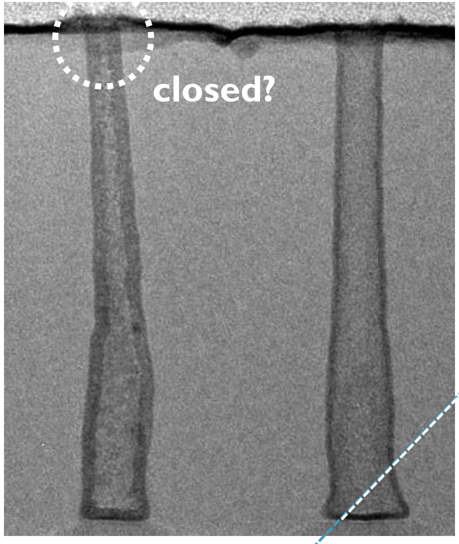


- In projection the layers on front/backside of the hole are seen as well, decreasing the contrast
- At the bottom the HfO_2 & TiN are seen in projection over the full diameter of the holes → higher contrast

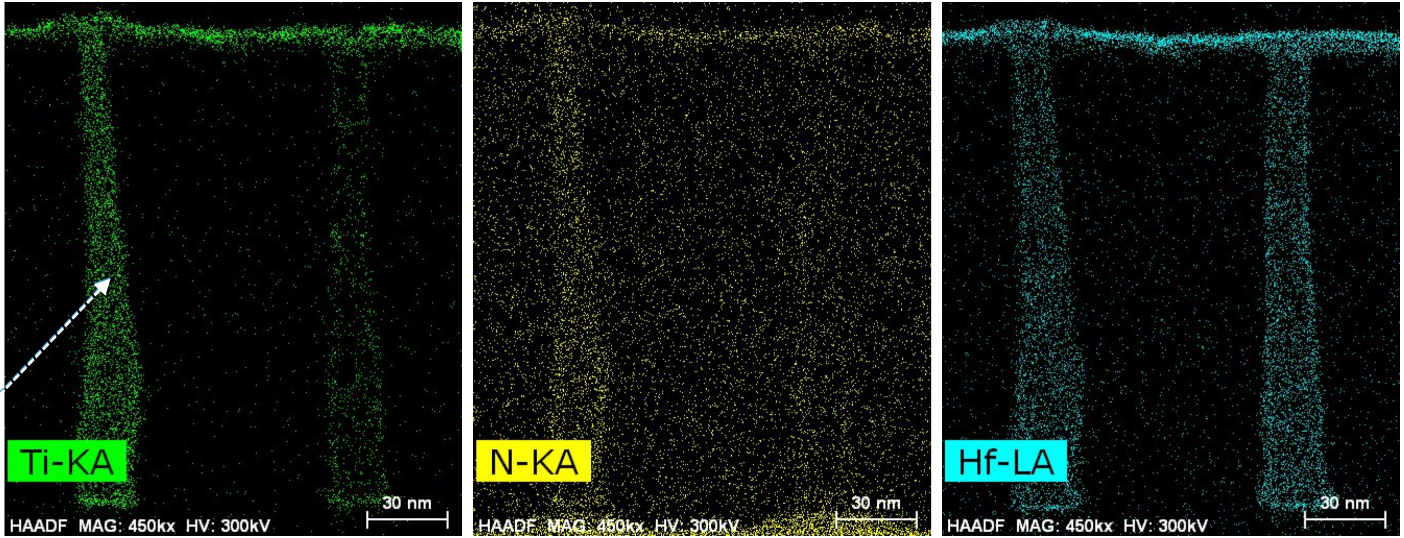
TiN etching at RT

Similar results with 9min etch

2min HF 0.5% + 3min APM 1:4:20 at RT



EDS maps



A little of Ti & N left in wide hole

No etching of HfO_2

No etching in narrow (closed?) hole

- Wide holes: >> 50% TiN removed
- Etch rate in wide hole (>0.9nm/min) > planar film (0.73nm/min)

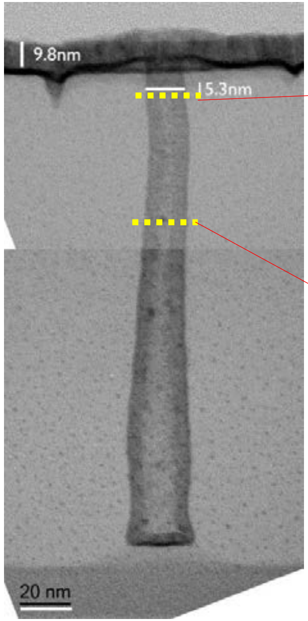
umec

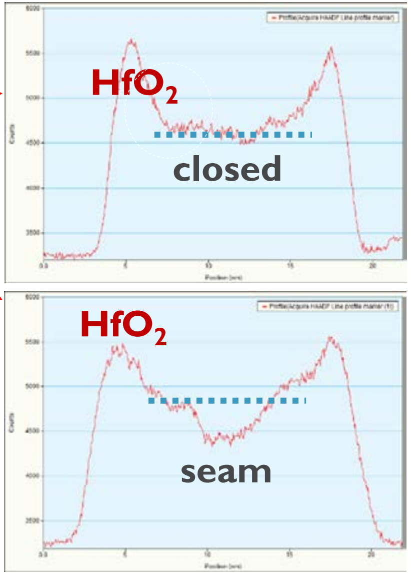
TiN etching at T = 65°C

2min HF 0.5% + 3min APM 1:4:20 at 65°C

etch rate of planar TiN = 26nm/min at 65°C

Nanoholes with 1.5nm HfO_2 + 10nm TiN

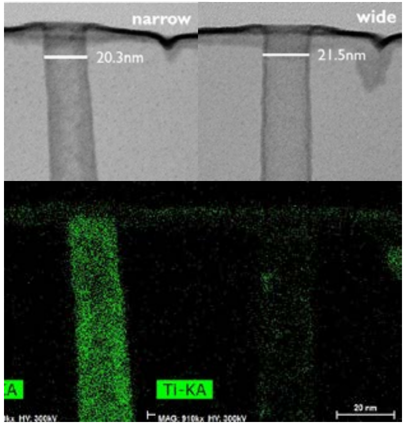




HAADF-STEM profiles

0.5min etch: partial removal

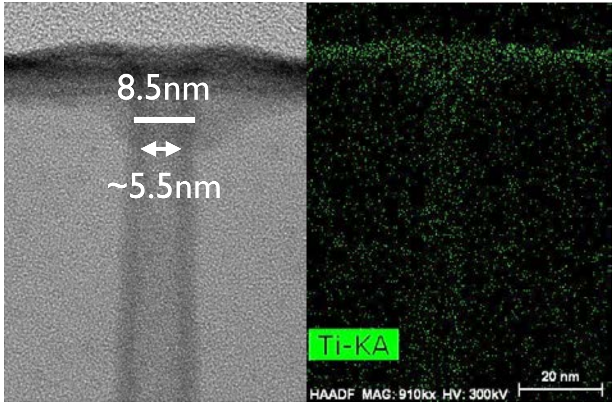
narrow wide



- No etching in narrow hole
- Ti mostly gone in wide hole & in the field

1.5min etch: TiN completely removed

Narrow hole



- Ti mostly removed in the field
- Ti not clearly detected above noise level in the holes

Etching mechanism

Etch mechanisms proposed in literature

Rate determining step vary depending on authors (marked with *)

1. Oxidation of TiN to TiO_x

   * S. O'Brien et al., *Proc. UCPSS*, 1996, 205.
   * A. Philipossian et al., *Proc. UCPSS*, 1994, 275

   1. by $HO^{\cdot}$ radicals generated in-situ by Ti-catalyzed H_2O_2 decomposition
   2. by HOO^- anions from H_2O_2 ionization

2. Dissolution of TiO_x by complexation

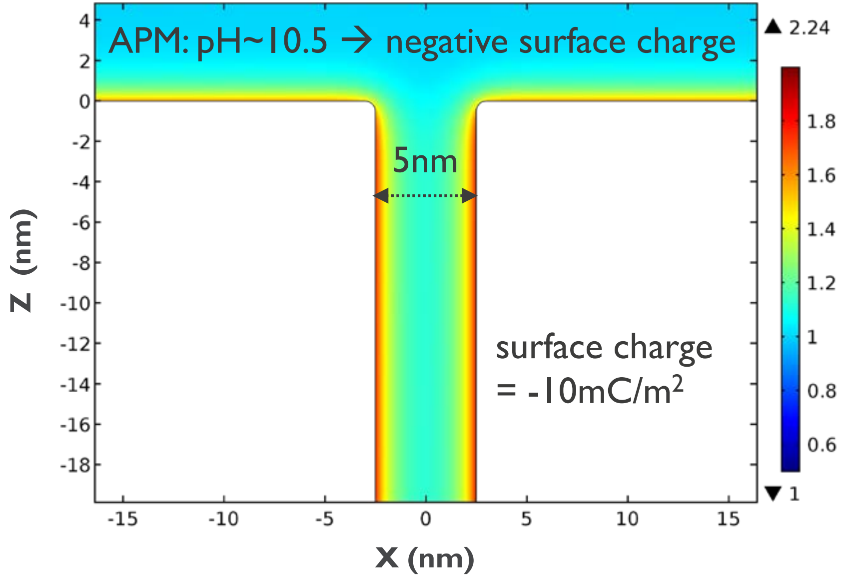
   1. Complexation by HOO^- anion
      in analogy with an established titration method for Ti
      * S. Verhaverbeke et al., *Mat. Res. Soc. Symp. Proc.* 1997, **477**, 447.
   2. Complexation by NH_4^+ cation
      in analogy with the cleaning of metallic impurities by APM
      * this work

Numerical simulations: Concentration of ions in TiN nanoholes

Solution of Poisson-Boltzmann and Poisson-Nernst-Planck equations for APM 1:4:20 at RT

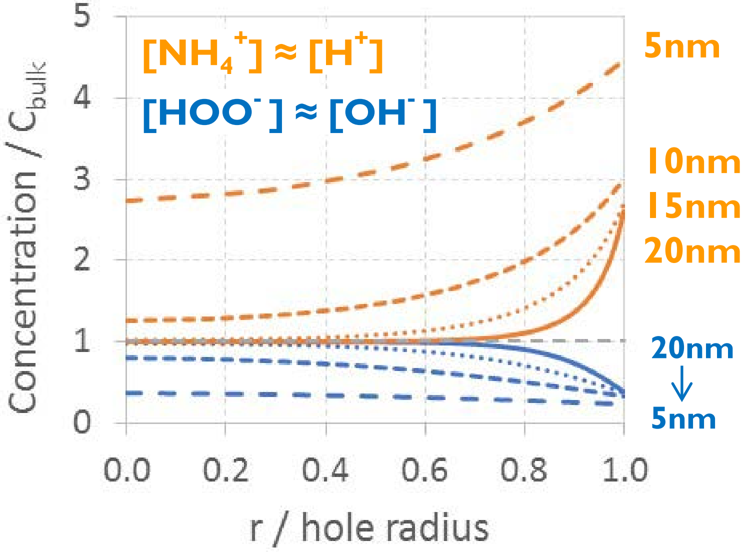
B.Lu et al., *Phys. Rev. E* 2012, **86**, 011921. Implementation in Comsol.

Relative concentration map of [NH4$^+$] ≈ [H$^+$]



Relative concentration profiles

surface charge = -20mC/m^2



- Negative surface charge → cations enrichment and anions depletion
- Loss of electroneutrality in confined solution for CD < 10-15nm

Rate determining step in nanospaces

Considering impact of EDL overlap on kinetics

1. Oxidation of TiN to TiO_x
   1. by $HO^{\cdot}$ radicals generated in-situ by Ti-catalyzed H_2O_2 decomposition
   2. by HOO^- anions from H_2O_2 ionization
2. Dissolution of TiO_x by complexation
   1. Complexation by HOO^- anion
      in analogy with an established titration method for Ti
   2. Complexation by NH_4^+ cation
      in analogy with the cleaning of metallic impurities by APM

- Faster etch rate in nanolines vs. planar films suggests that complexation by $NH4^+$ is dominant

- Constant etch rate in nanolines a.f.o. time, i.e. at increasing opening, implies that reactions with HOO^- would also play a role

Conclusions

Conclusions

- No issue found for APM etching of TiN in advanced FinFET's RMG module, at the contrary
  - No wetting issue in narrow openings (~1nm seam after dHF)
  - Faster etch rate in narrow trenches vs. top of structures (~40%)
  - Faster etch rate in open nanoholes vs. top of structures (only qualitative)
  - Closed nanoholes with 10nm TiN cleared by APM@65°C in 0.5-1.5min
- Learnings on etching mechanism
  - Faster etch rate in nanospaces suggest kinetics dominated by TiOx complexation-dissolution by NH_4^+
  - No dependency of etch rate on opening size in nanotrenches
    → kinetics cannot be described by a single ionic reaction

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