

Novel Germanium Technology and Devices for High Performance MOSFETs

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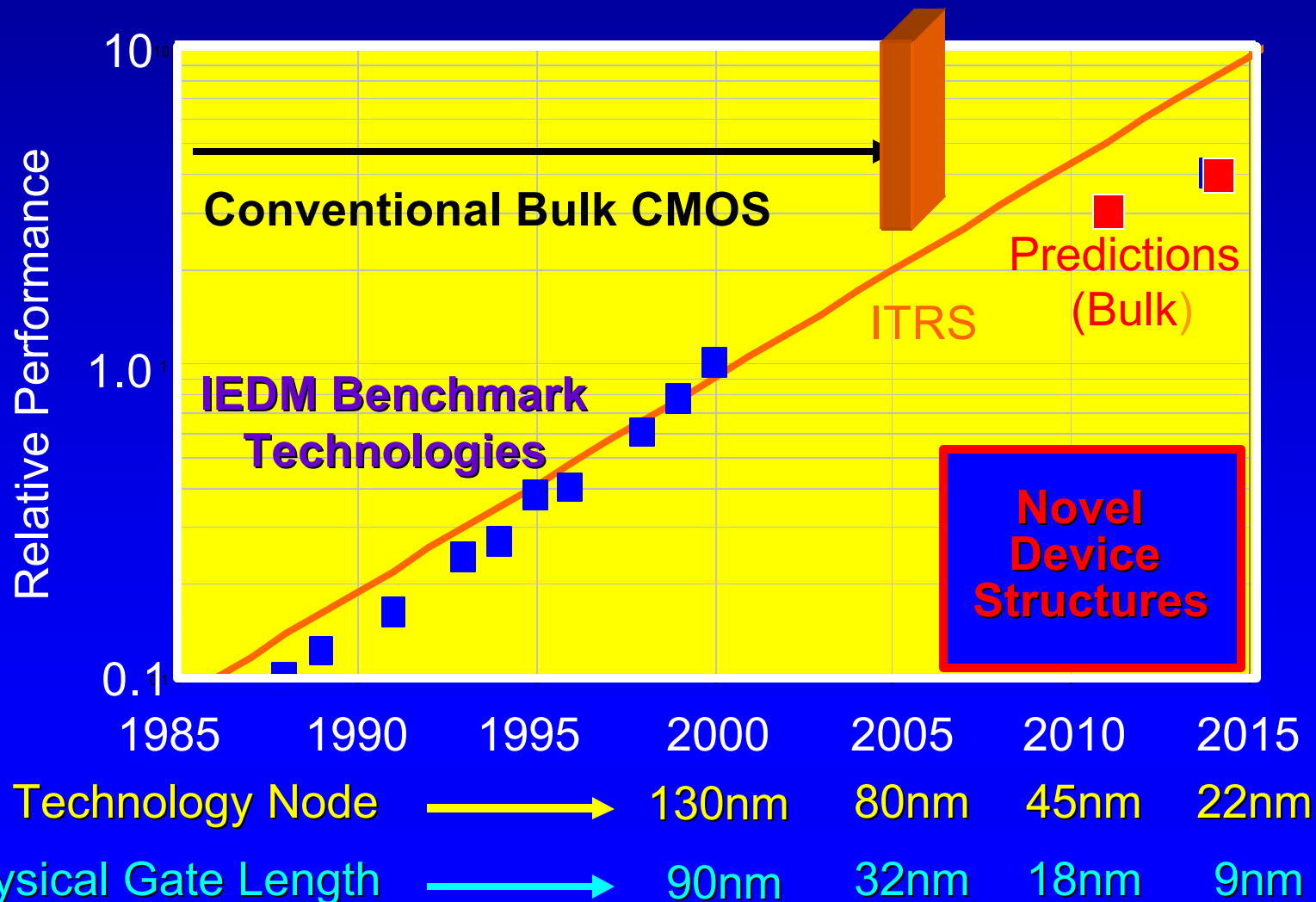
Principal Investigator: Prof. Krishna C. Saraswat
Collaborators: Profs. Paul C. McIntyre and Yoshio Nishi

Outline

- Ge CMOS Motivations
- Ge MOS Gate Dielectric Technology
 - ⇒ UVO Oxidation of Metal
 - ⇒ ALD of Metal Oxides
- Ge Dopant Incorporation Technology
- Ge MOSFETs with High- κ and Metal Gate
- Conclusions

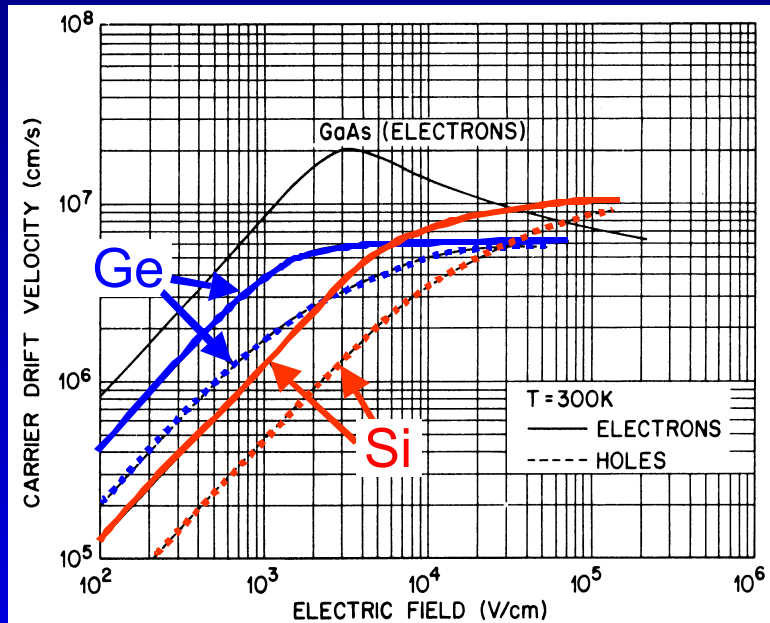
Bulk-Si Performance Trends

- Maintaining historical CMOS performance trend requires new semiconductor material and structures by 2008-2010...
- Earlier if current bulk-Si data do not improve significantly



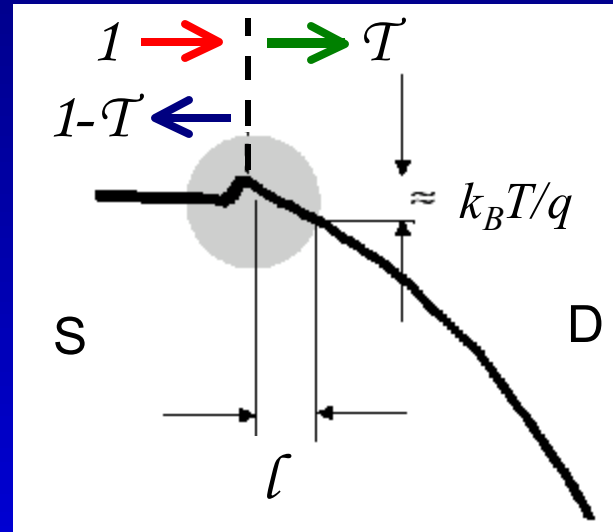
A Fundamental Scaling Limit - I_{Dsat}

I_{Dsat} no longer set by v_{sat}



(Sze, 1981)

For very short channel MOSFETs



(Lundstrom, 2001, Purdue)

$$\tau = \frac{l_0}{l + l_0}$$

$$l_0 \propto t_0$$

$$\propto m_{low-field}$$

$$\propto v_{inj}$$

Drive Current & Gate Delay

$$I_{DS} = W \times Q_{inv} \times v_{inj}$$

$$\frac{C_{LOAD} V_{DD}}{I_{DS}} = \frac{L_{gate} \times V_{DD}}{(V_{DD} - V_T) \times v_{inj}}$$

Ballisticity Comparisons

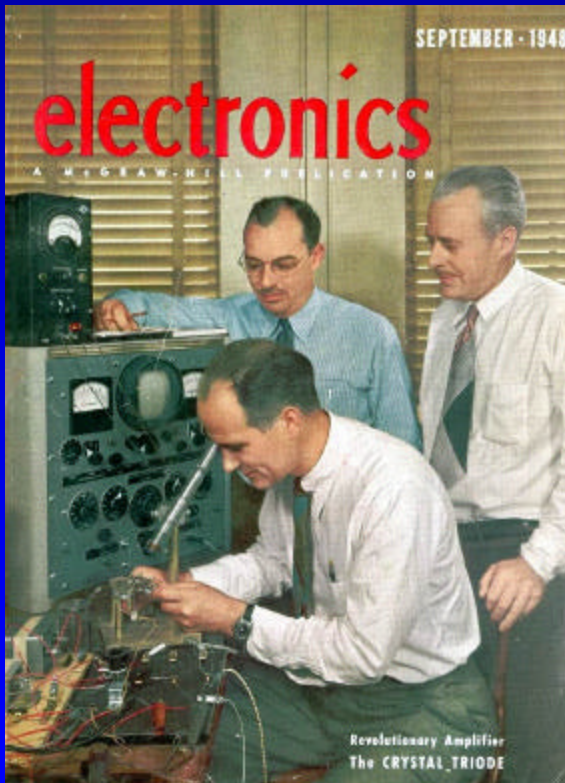
	Si <100>	Ge <100>	Ge <111>
n-MOS	0.68	0.78	0.76
p-MOS	0.48	0.70	0.56

(Chui et al., IEEE IEDM, 2003)

Germanium – A Material with History

1st Transistor is in Ge

By Bardeen, Brattain, and Shockley,
Nobel Laureates in Physics 1956



(http://www.bellsystemmemorial.com/bellabs_transistor.html)

1st Integrated Circuit is in Ge

By Kilby,
Nobel Laureates in Physics 2000



(Courtesy of TI and Huff, SEMATECH)

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Problem #1: Ge Surface Passivation

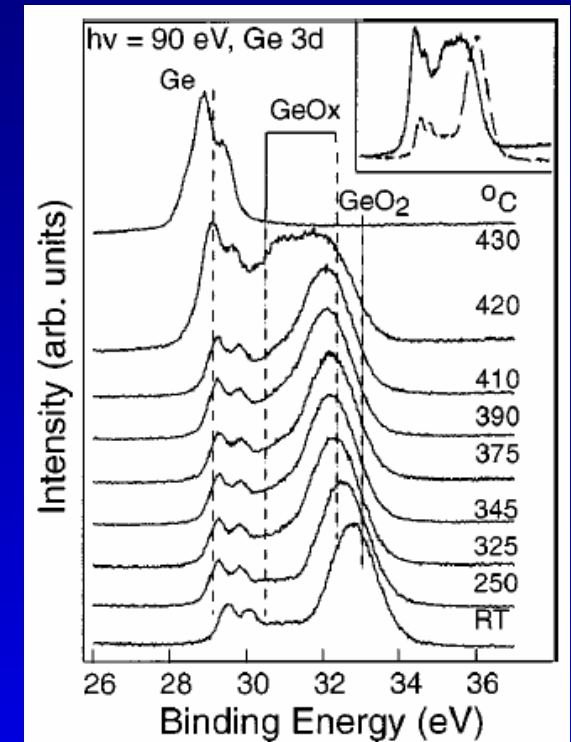
The Problems:

- The native oxide passivation on Ge surface is not stable enough either during fabrication or in the end-product
 - ⇒ GeO_2 : water soluble/hygroscopic
 - ⇒ GeO : volatile at low temperature
- Very high quality gate dielectric/Ge substrate interface is required

Prior Attempts in the Last 40 Years:

- Pyrolytic, LPCVD, RPECVD SiO_2
- Thermal, UVO GeO_x (followed by nitridation, GeO_xN_y)
- LPCVD Ge_3N_4 and Pyrolytic Al_2O_3

None of them would likely offer an EOT $\leq 10 \text{ \AA}$ to advance beyond the sub-20 nm regime



(Prabhakaran, APL, 2000)

High- κ Dielectrics on Germanium

The Surface Passivation Solution:

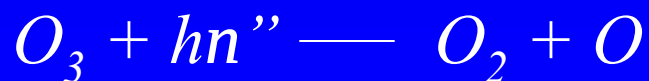
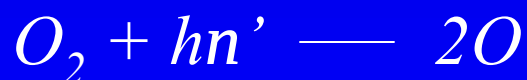
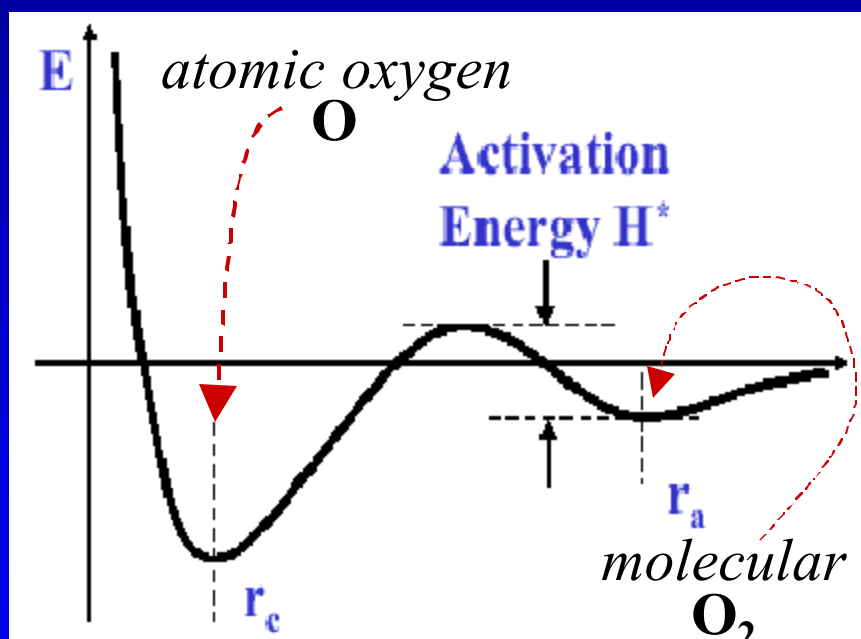
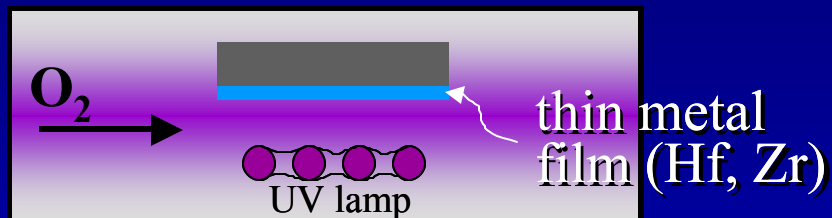
- **High- κ** (metal oxide) dielectrics are being researched to replace SiO_2 for scaled Si MOSFETs
- These dielectrics are deposited on Si, but not thermally grown, why not on Ge?
- Volatility/Instability of native oxides or sub-oxides makes surface cleaning easier for **high- κ** on Ge
- Gate dielectric stack free of the performance limiting, lower- κ , interfacial GeO_x layer could be possible
- Allows integration of metallic gate electrode to eliminate the carrier depletion problem in poly-Si gates

(Chui et al., U.S. Patent Pending (Serial No.: 10/404,876))

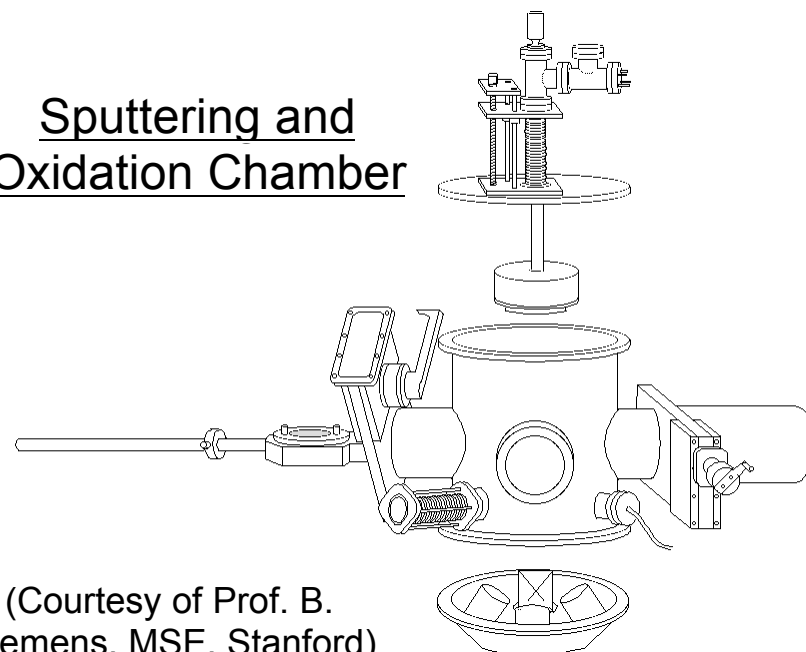
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Novel Dielectrics by UV-O₃ Oxidation



Sputtering and Oxidation Chamber



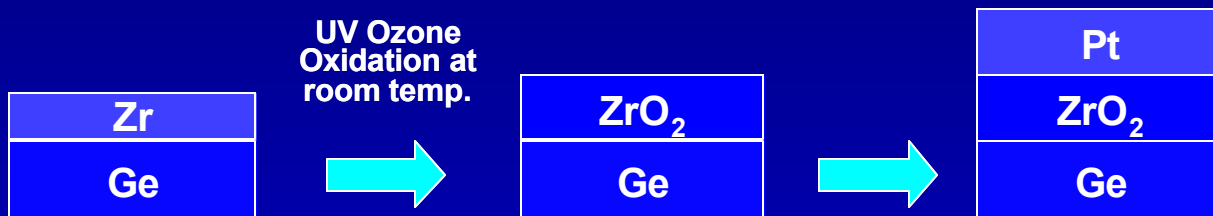
(Courtesy of Prof. B. Clemens, MSE, Stanford)

Advantages

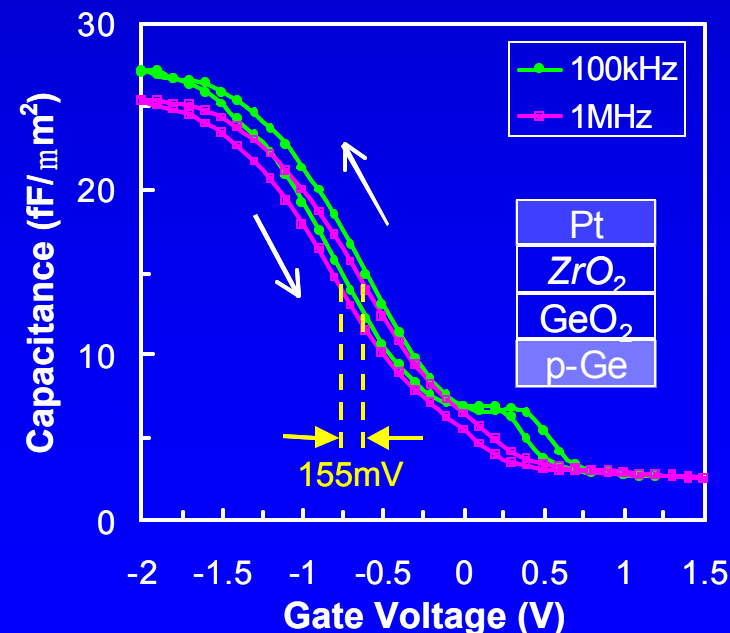
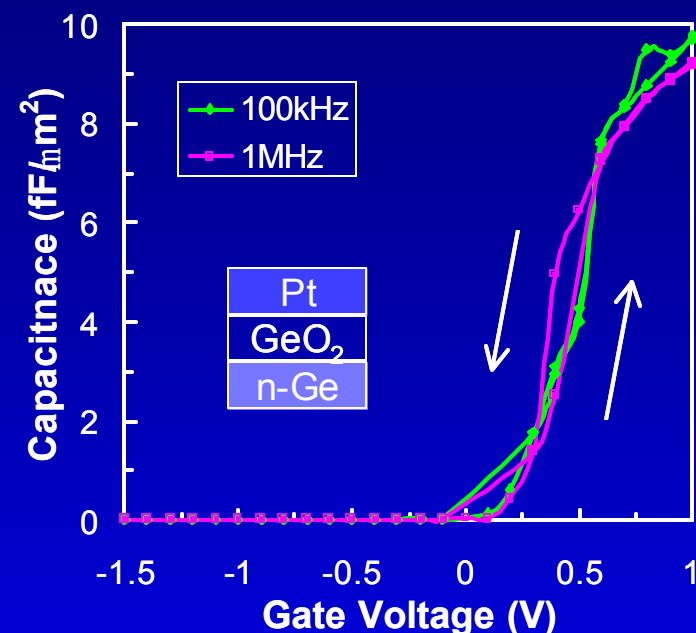
- ⇒ Low temperature
- ⇒ Low contamination
- ⇒ Process simplicity
- ⇒ *In-situ* electrode capping

(Courtesy of Prof. Paul McIntyre, MSE, Stanford)

UV-O₃ Oxidation of Zr on Ge

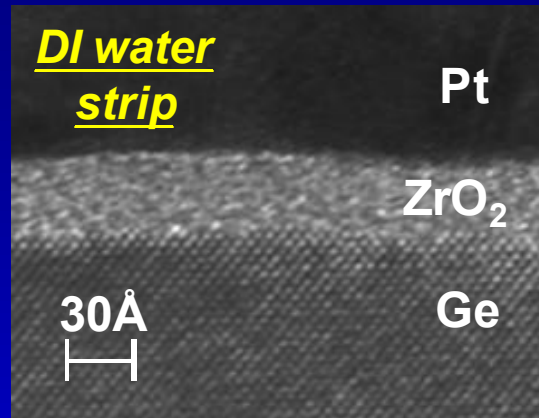
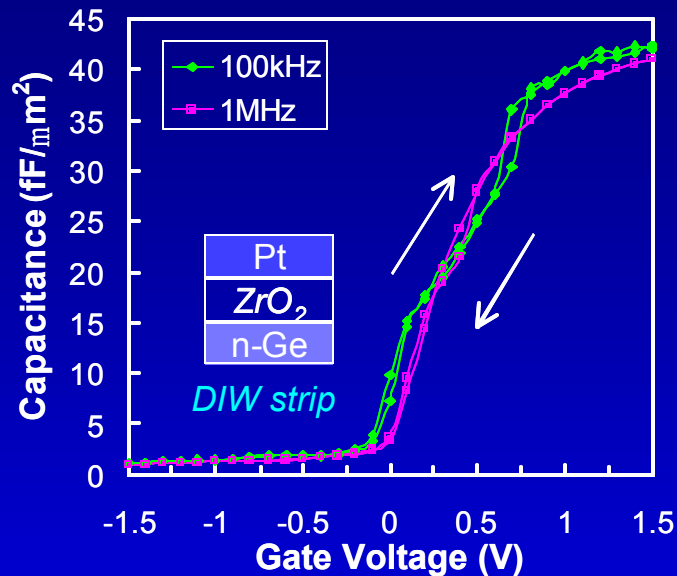


Sample	Doping	Native Oxide	Thermal Oxidation	ZrO ₂ Deposition
#1	N	Kept	500°C 2 mins	-
#2	P	Kept	-	~35 Å
#3	N	Stripped in DI Water	-	~35 Å
#4	N	Stripped in HF Vapor	-	~35 Å

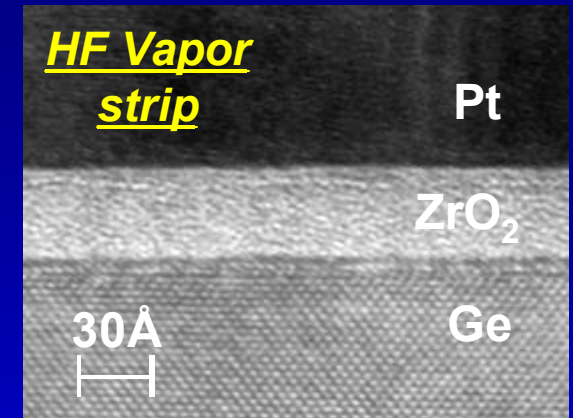


(*Best Student Paper Award: Chui *et al.*, *IEEE DRC*, 2002)

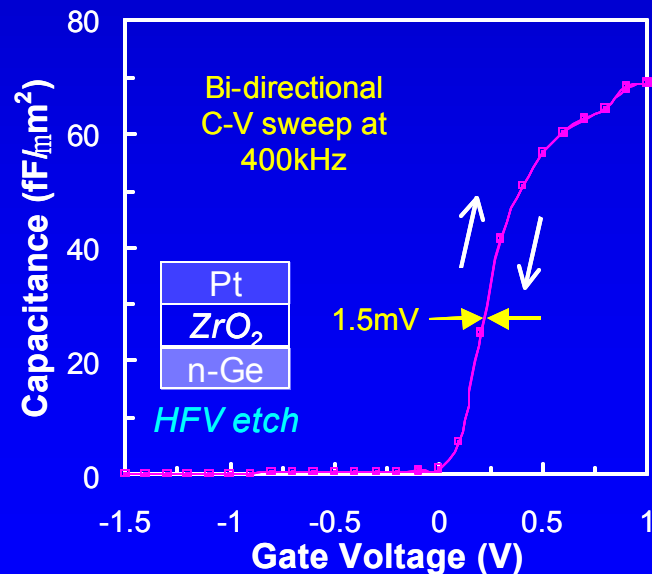
Electrical & Material Characteristics



TEM + CV $\Rightarrow$ EOT $\sim$ 8-10 Å



TEM + CV $\Rightarrow$ EOT $\sim$ 5-7 Å



- The common GeO_2 phase has poor quality
- Hysteresis become negligible in its absence
- Atomically abrupt interface
- Usually, high-quality interface layer between high- κ and Si is required
- High- κ maybe more feasible for Ge MOS applications

(Chui *et al.*, *IEEE EDL*, 2002)

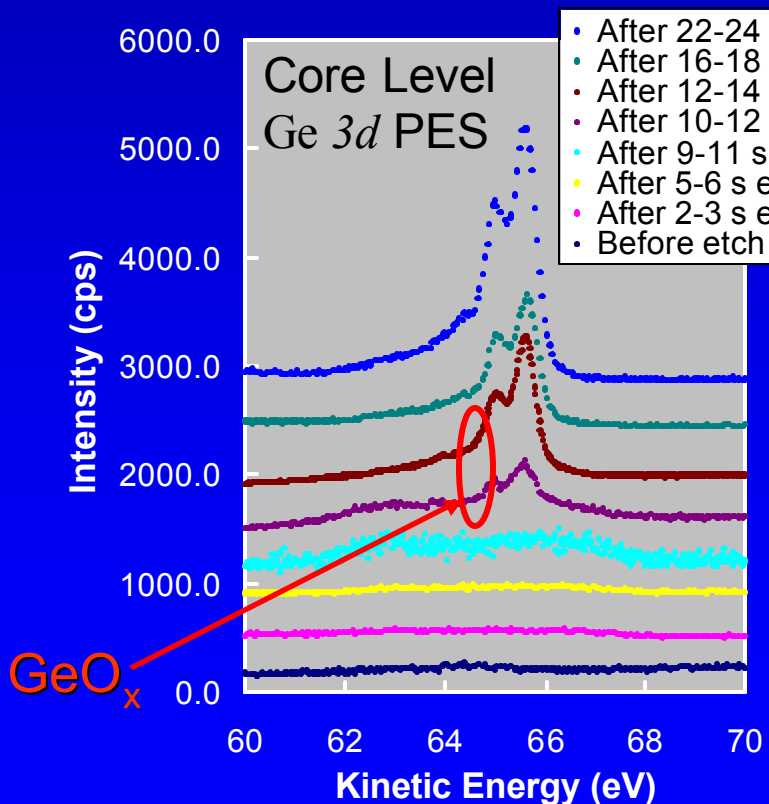
(*Best Student Paper Award: Chui *et al.*, *IEEE DRC*, 2002)

SR-PES Spectra of ZrO_2 on Ge

Stanford Synchrotron Radiation Lab

BL 8-1 $h\nu = 100 \text{ eV}$ Bias = 0 V DKE = 0.05 eV

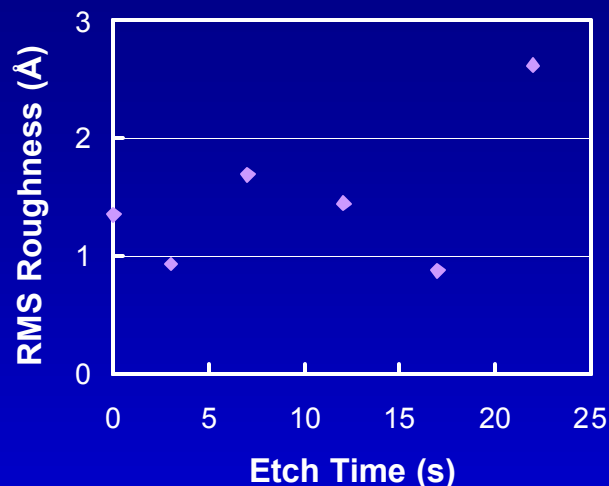
- ⇒ To identify the existence of interfacial GeO_x
- ⇒ Upon layer-by-layer wet etching of ZrO_2 , composition variation is monitored with PES
- ⇒ Little shoulder observed in lower KE side of Ge $3d$ doublet peak, i.e. interfacial GeO_x



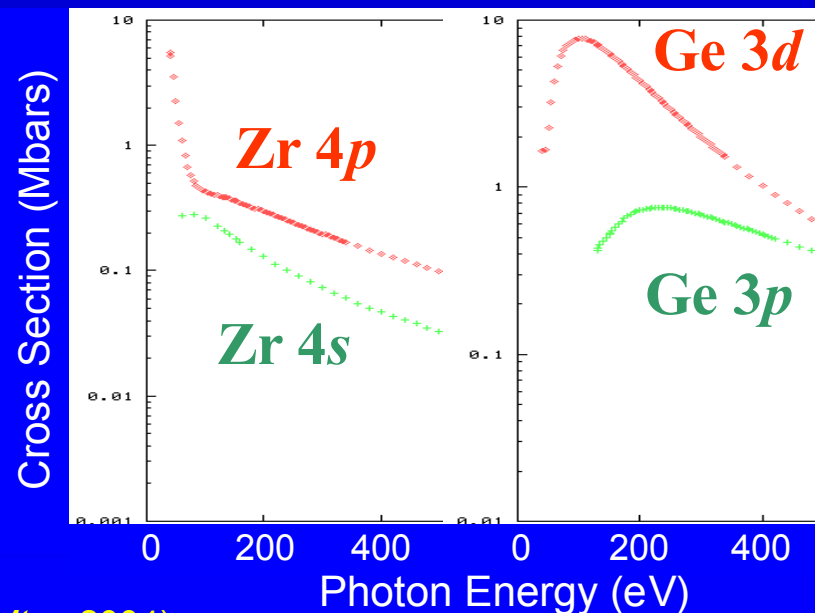
(In collaboration with Prof. Piero Pianetta, Dong-Ick Lee, and Andy Singh, SSRL, Stanford)

(Chui *et al.*, MRS Spr. Mtg., 2004)

AFM ZrO_2 Surface Roughness

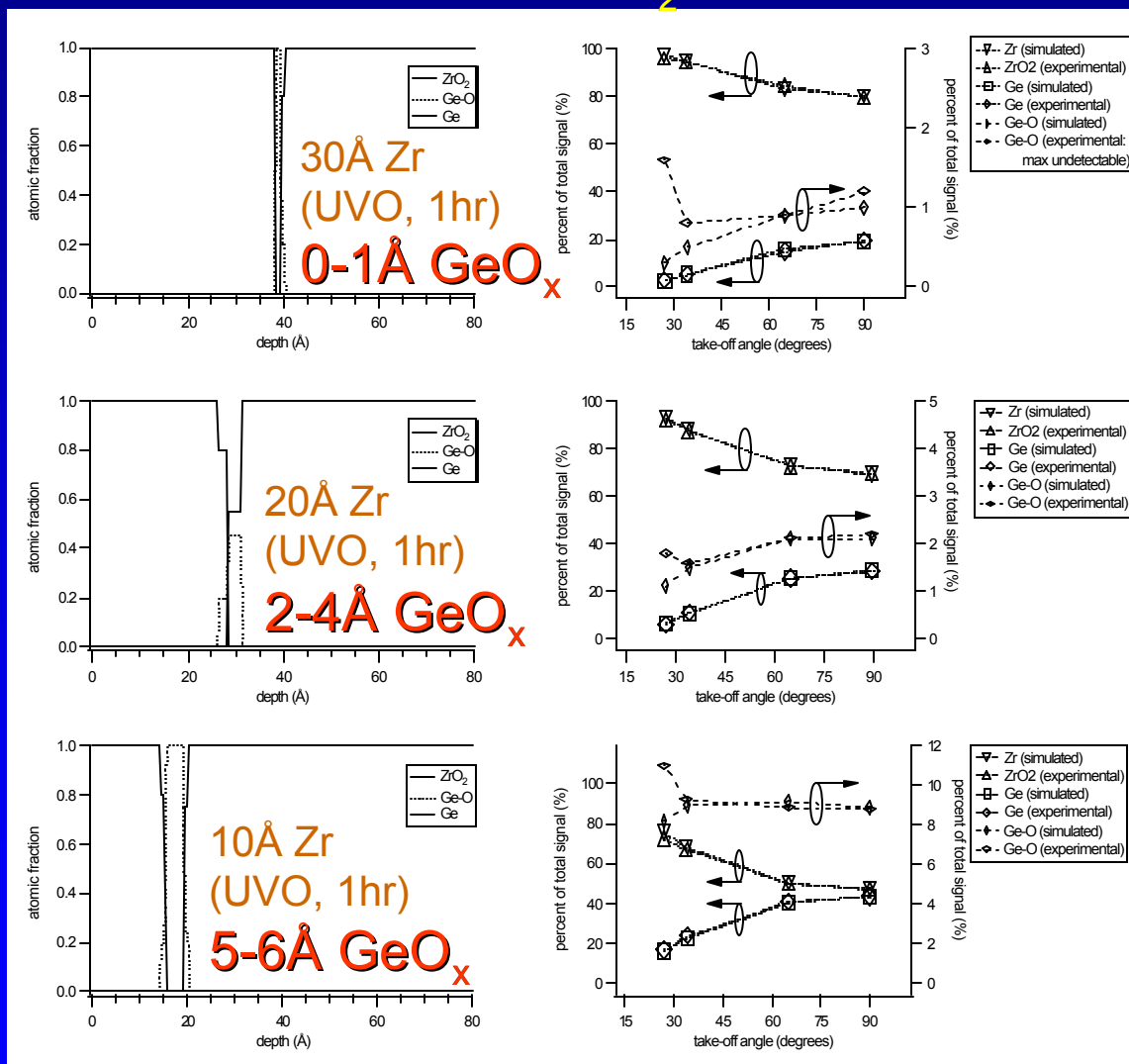


Subshell PE-XS of Zr and Ge



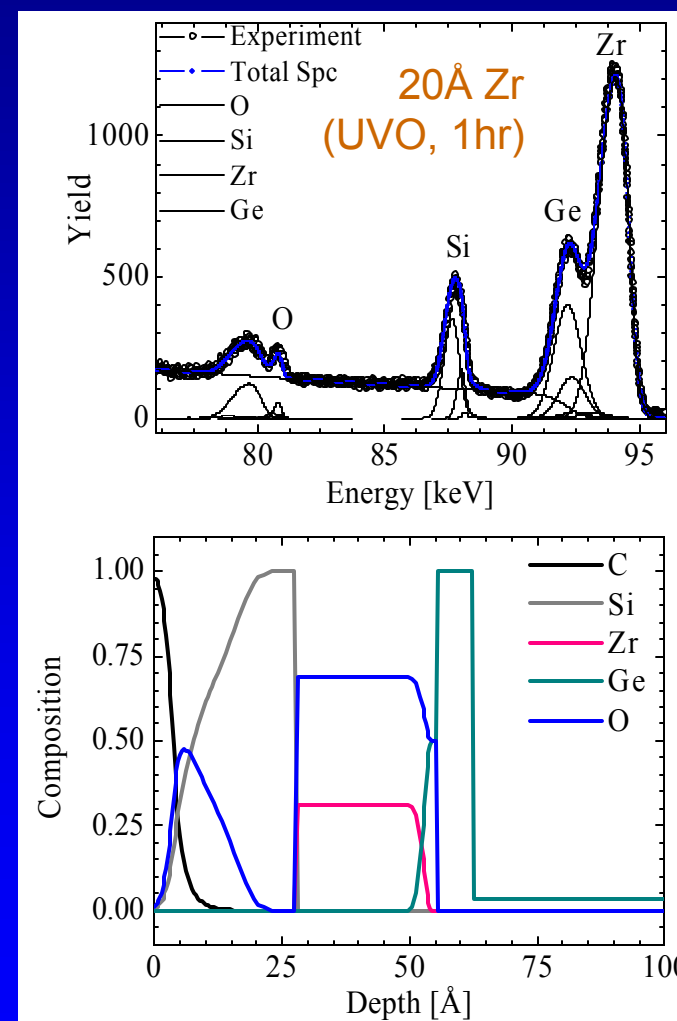
ARXPS and MEIS of ZrO_2 on Ge

Depth Profile Simulations on Experimental ARXPS for Different ZrO_2 Thickness on Ge



(Chi, Chui, Saraswat, Triplett, and McIntyre, *submitted to JAP*)

MEIS Spectrum and Depth Profile Simulation

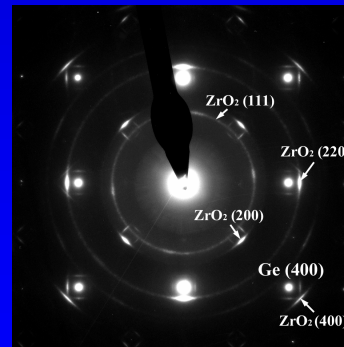
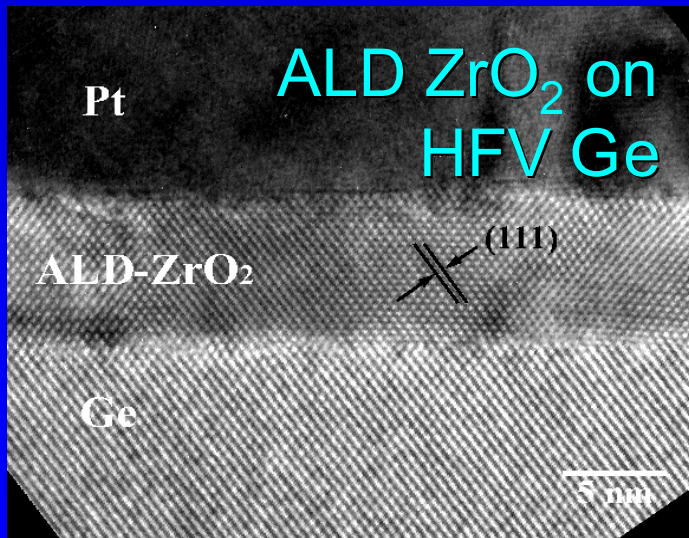
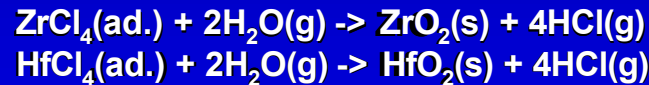
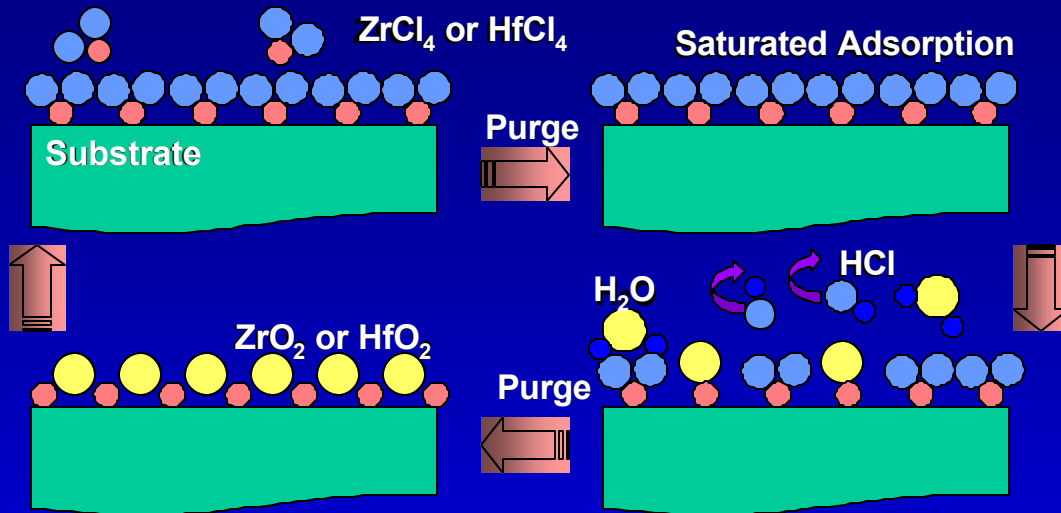


24.5Å ZrO_2 /3Å GeO /Ge(001)
(with Prof. Eric Garfunkel, Chemistry, Rutgers)

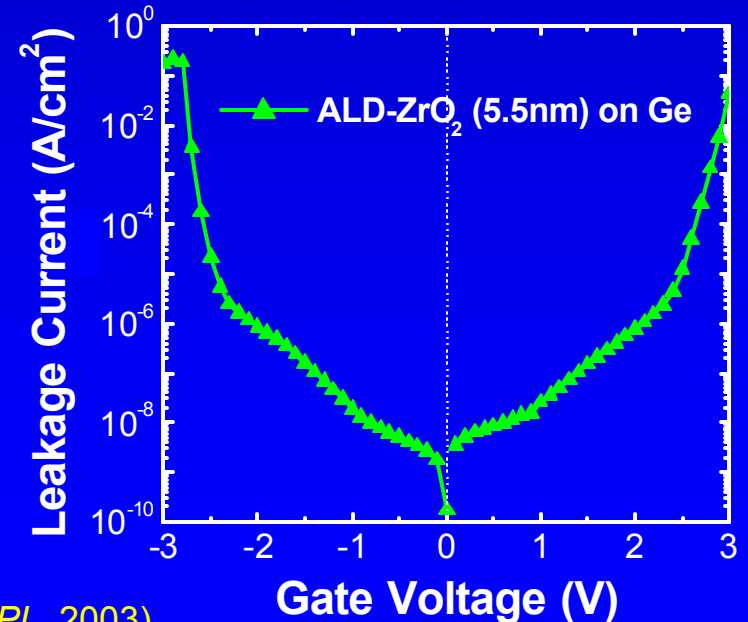
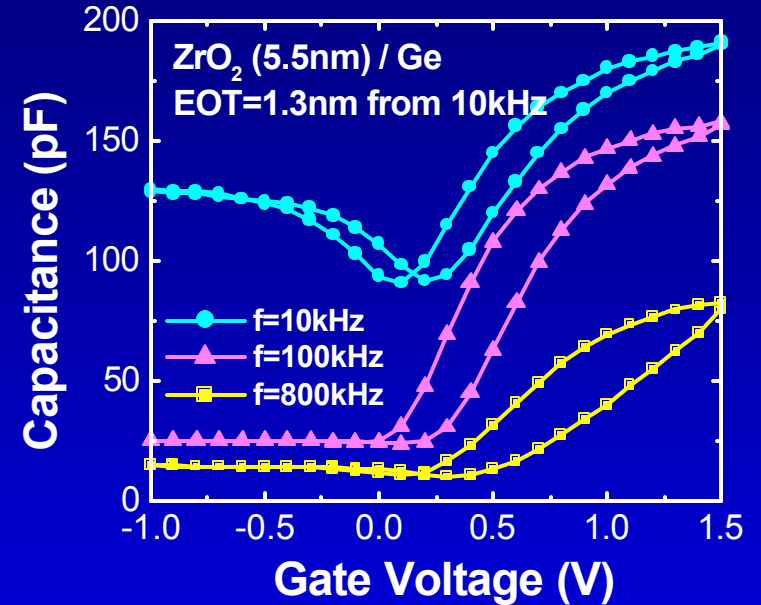
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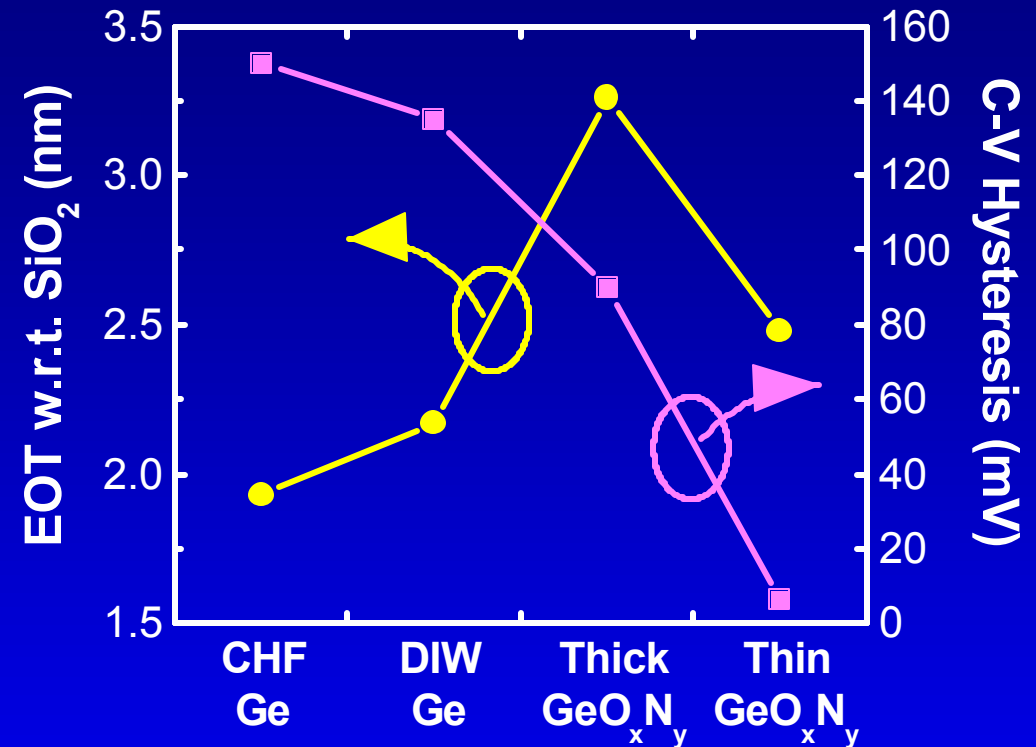
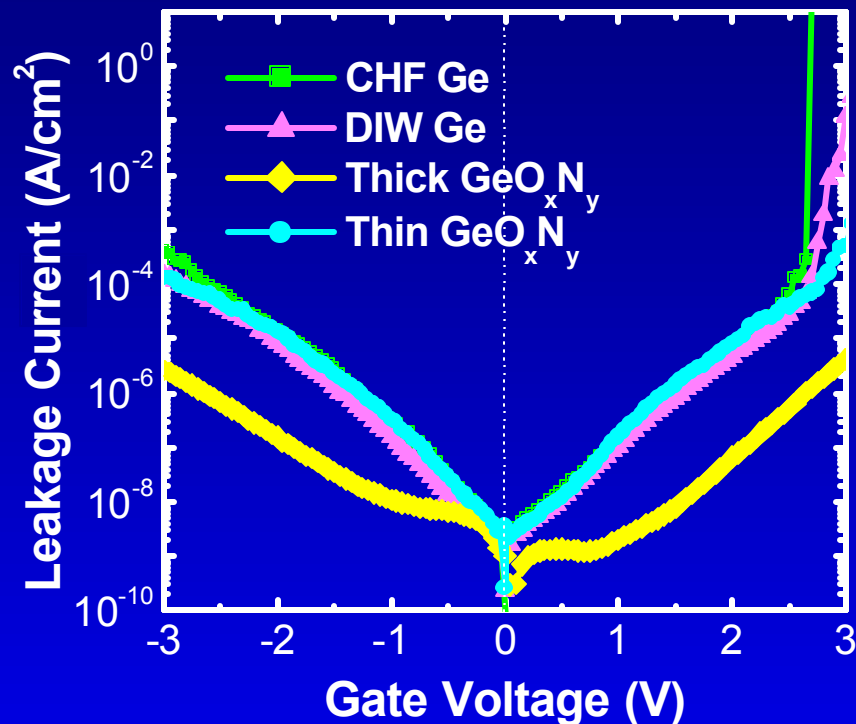
Atomic Layer CVD of High-k Dielectrics



(Kim and Chui *et al.*, APL, 2003)



Effects of Surface Preparation



- **CHF Ge:**

Cyclic rinsing between 50:1 HF and H_2O

- **DIW Ge:**

Rinsing in DI water

- **Thick GeO_xN_y :**

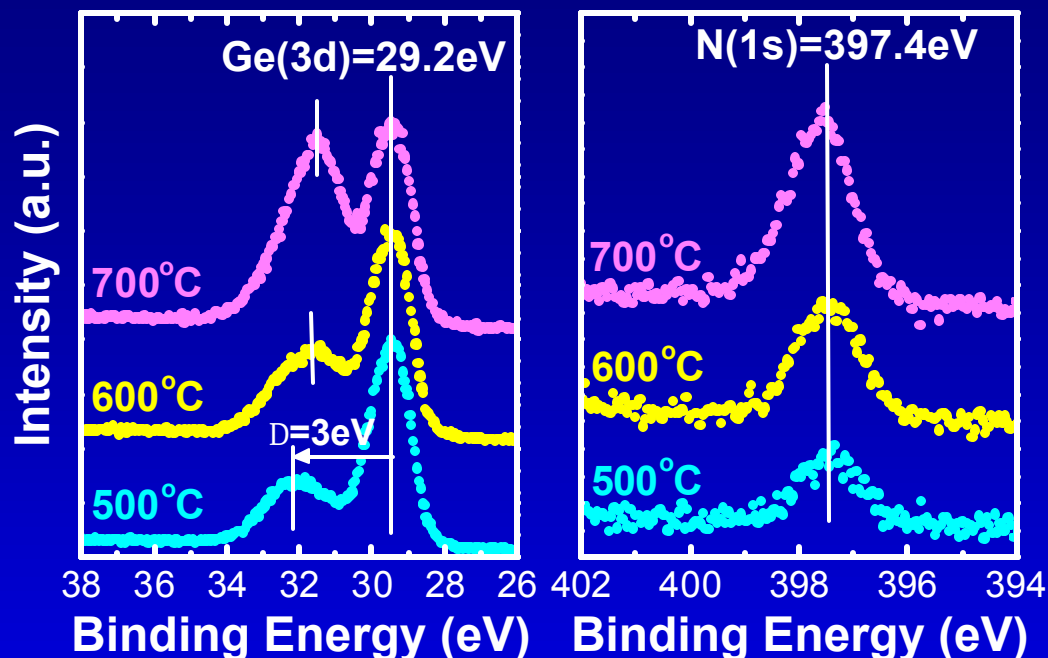
Rapid Thermal Nitridation (RTN) of thermally grown GeO_2

- **Thin GeO_xN_y :**

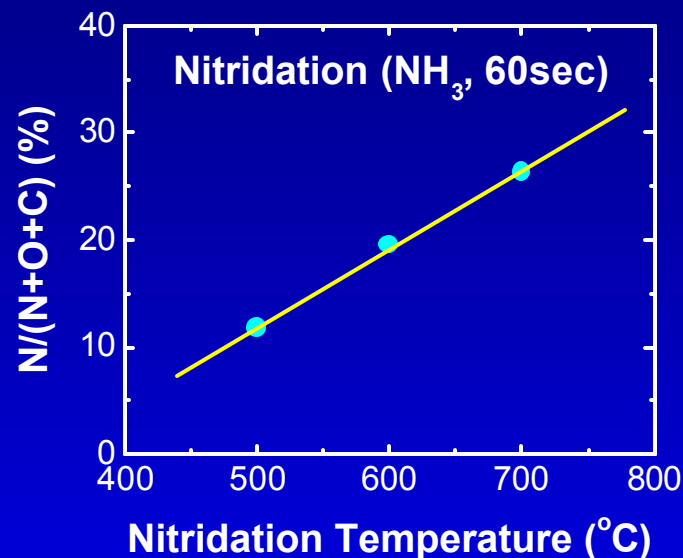
RTN of CHF Ge

(Chui et al., submitted to IEEE EDL)

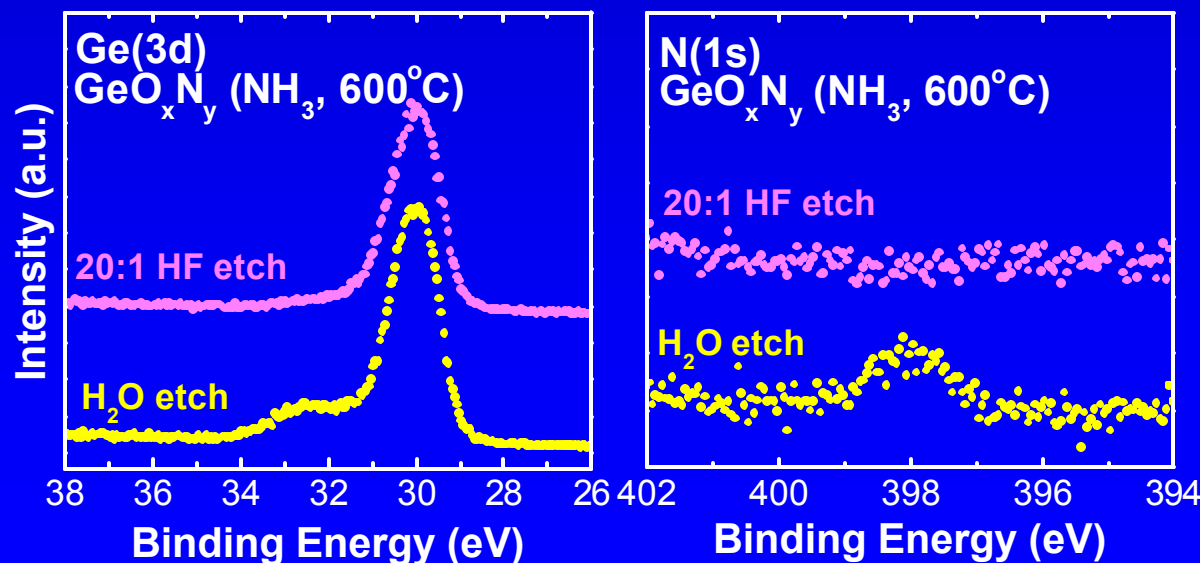
GeO_xN_y Optimization and Stability



N content vs. temperature

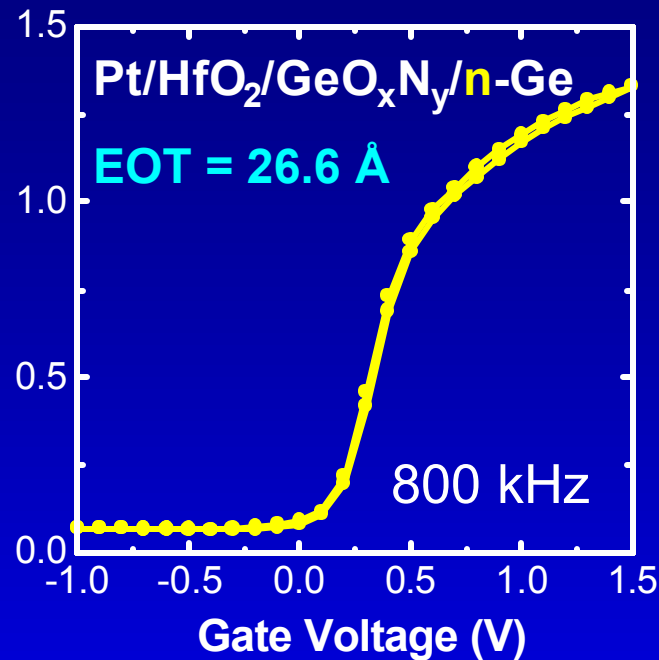
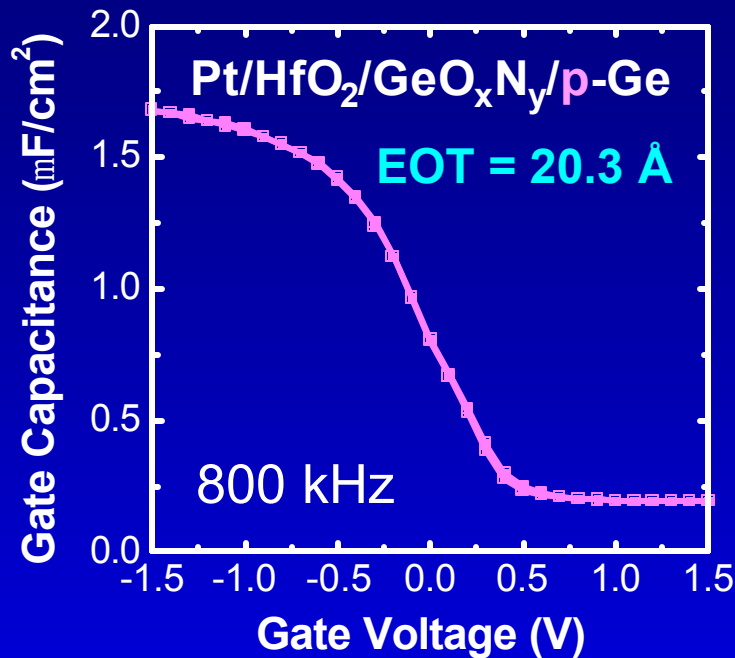


Wet etching
stability of
the optimum
GeO_xN_y

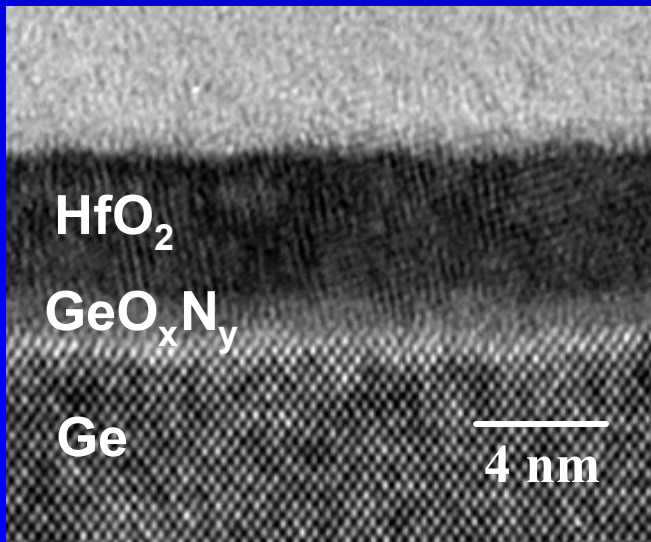


(Chui and Kim *et al.*,
in preparation)

Dielectric Stack for MOSFET



(Chui et al., submitted to IEEE EDL)



The dielectric recipe:

- 1) Ge cyclic rinsing between 50:1 HF and H₂O
- 2) RTN in NH₃ at 600°C for 1 min
- 3) ALD of high- κ films at 300°C using MCl₄ precursors

Where Do These New Materials Help?

$$I_{channel} \propto \mu \times \text{charge} \times \text{source injection velocity}$$
$$\propto \mu \times (\text{gate oxide cap} \times \text{gate overdrive}) \times v_{inj}$$
$$\propto \mu \times C_{ox} (V_{GS} - V_T) \times E_{source} \times m_{inj}$$

High- κ Gate Dielectrics

- $\Rightarrow \uparrow$ gate coupling
- $\Rightarrow \downarrow$ leakage & $\uparrow$ reliability (?)
- $\Rightarrow \downarrow$ dopant penetration

Metal Gate Electrode

- $\Rightarrow \downarrow$ gate poly depletion
- $\Rightarrow \downarrow$ remote charge scattering

High Quality Ge Channel

- $\Rightarrow \uparrow$ mobility
- $\Rightarrow \downarrow$ supply V_{DD} (V_{DD} scaling)
- $\Rightarrow \downarrow$ processing temperature

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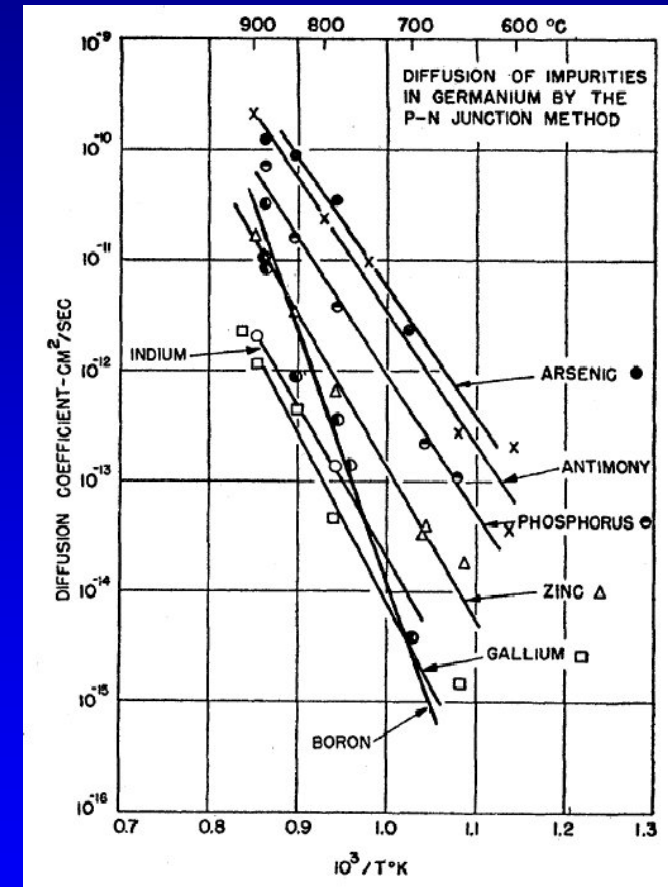
Problem # 2: Dopant Incorporation in Ge

The Problems:

- Larger n -type impurity diffusivities than Si
 - ⇒ Shallow junction in Ge NMOS difficult
 - ⇒ Unknown diffusion mechanisms
- Relatively lower Solid Solubility Limits (SSL)
 - ⇒ I_{ON} limited by source/drain resistance

Prior Attempts in the Last 30 Years:

- P -type: Furnace anneal of ion-implanted B
 - ⇒ Not suitable for shallow junction
- N -type: RTA and FA of implanted ions
 - ⇒ Mostly low dose and high energy implants achieving low level of activation

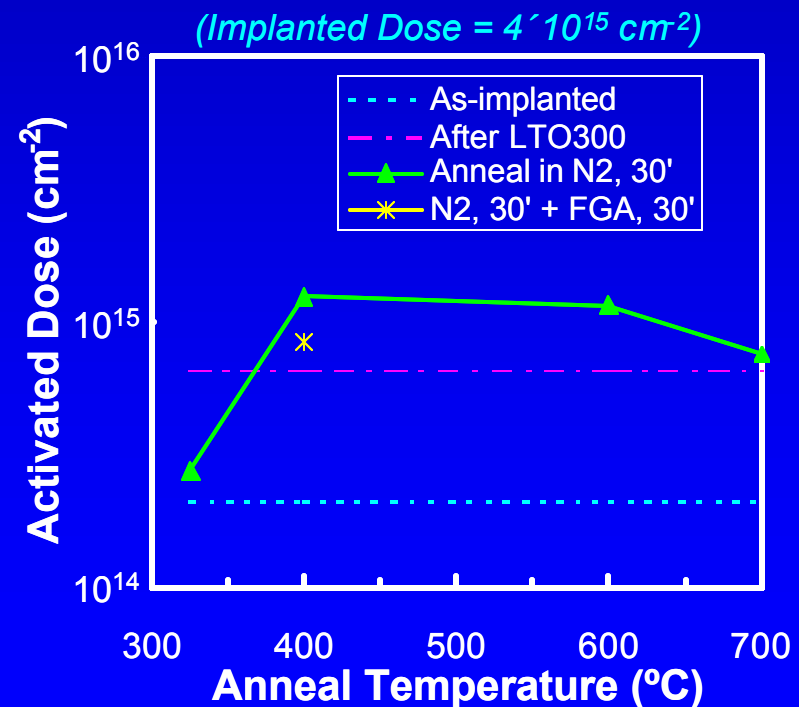
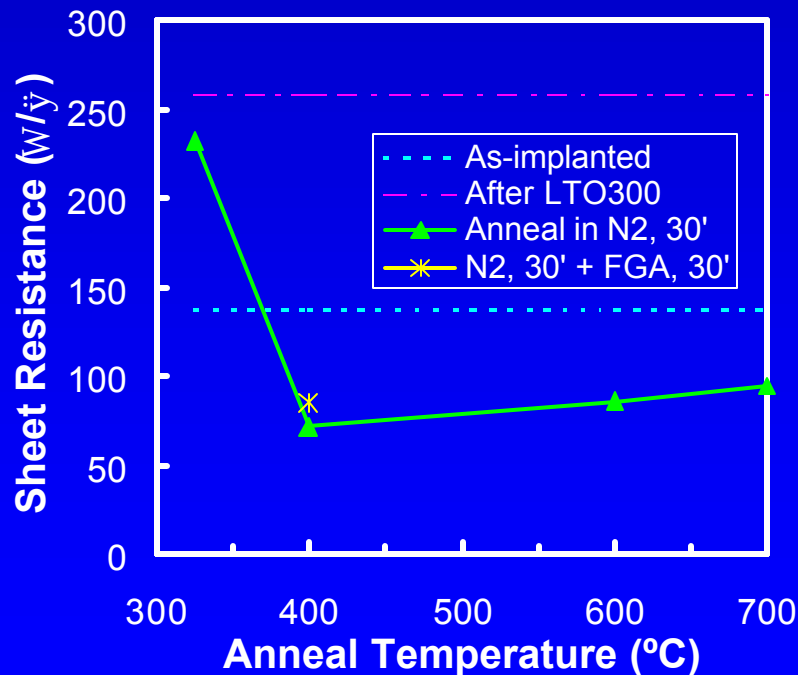
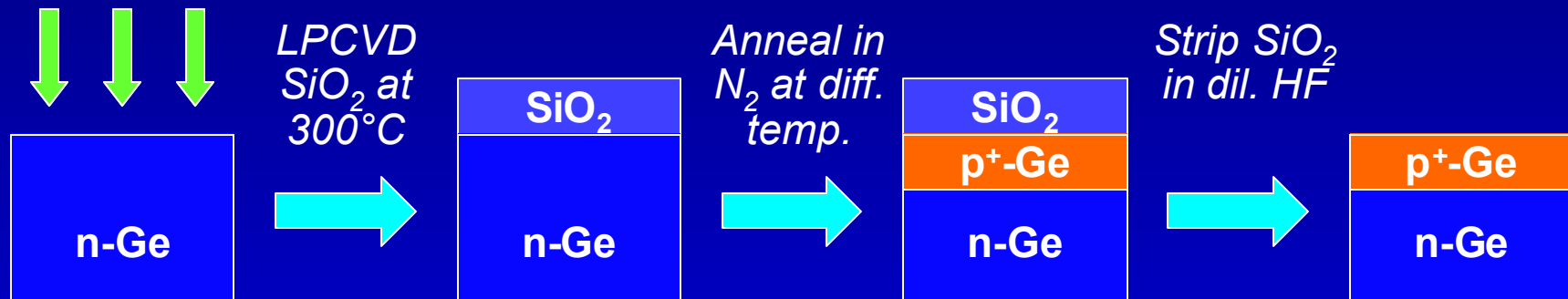


(Dunlap, *Phys. Rev.*, 1954)

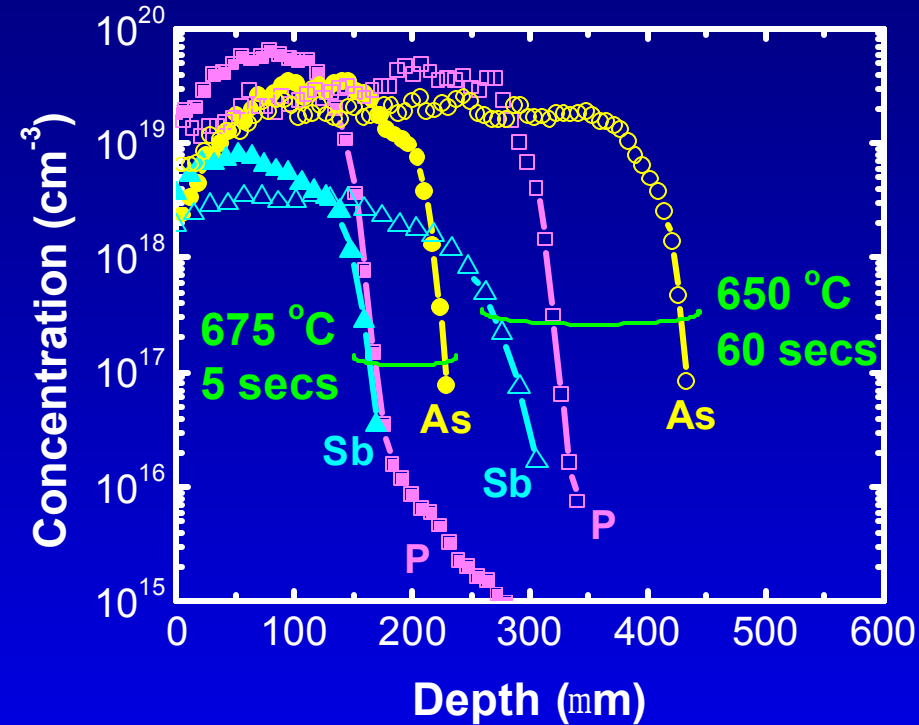
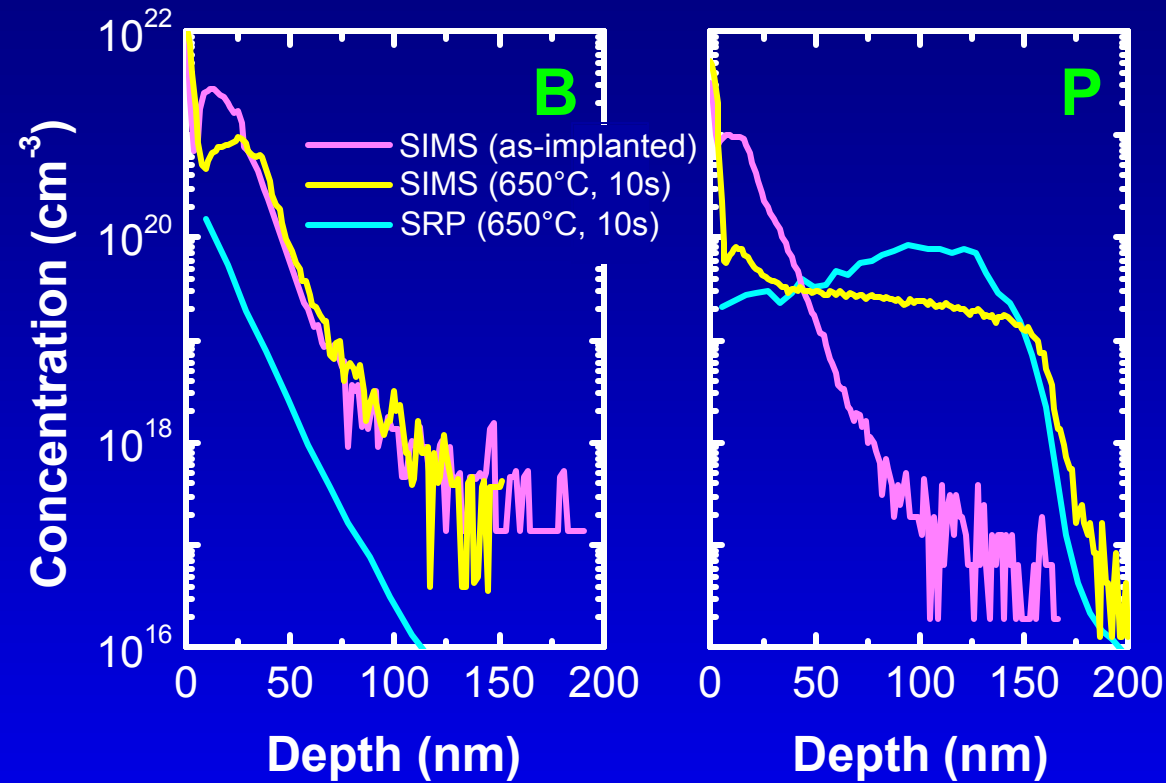
P-Type Dopant Incorporation

BF_2^+ at 35 keV
($4 \times 10^{15} \text{ cm}^{-2}$)

(Chui *et al.*, *IEEE IEDM*, 2002)



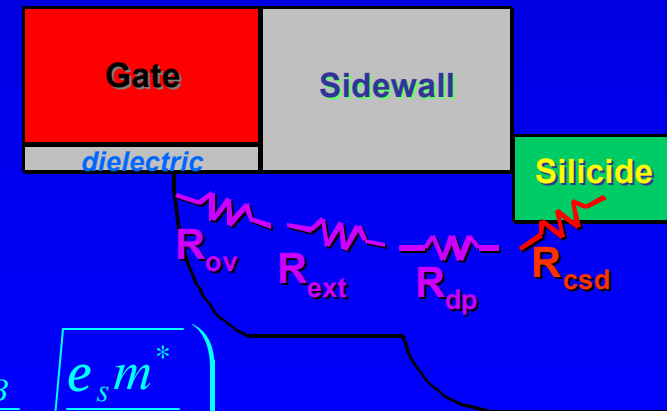
Conventional Ion Implantation Doping



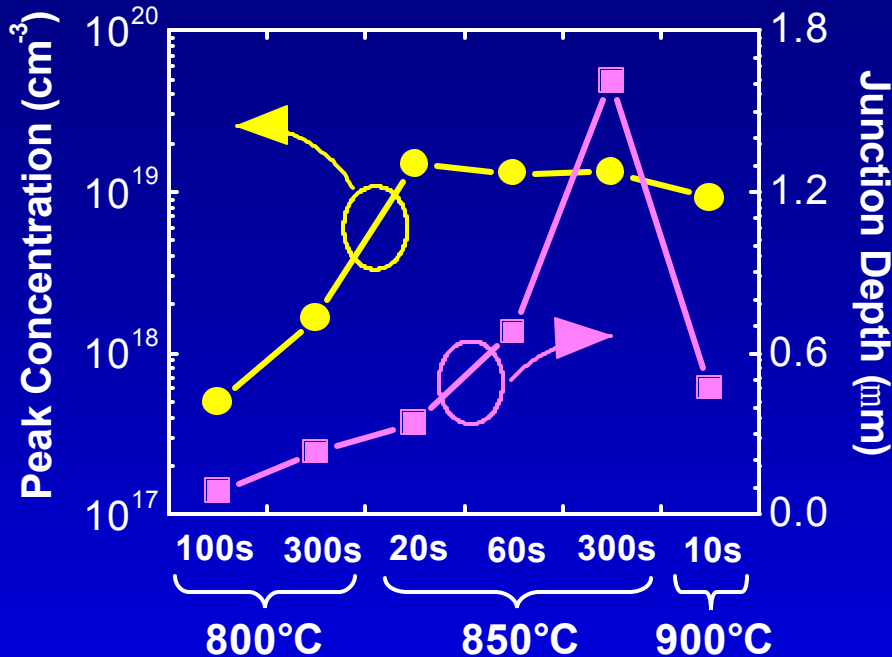
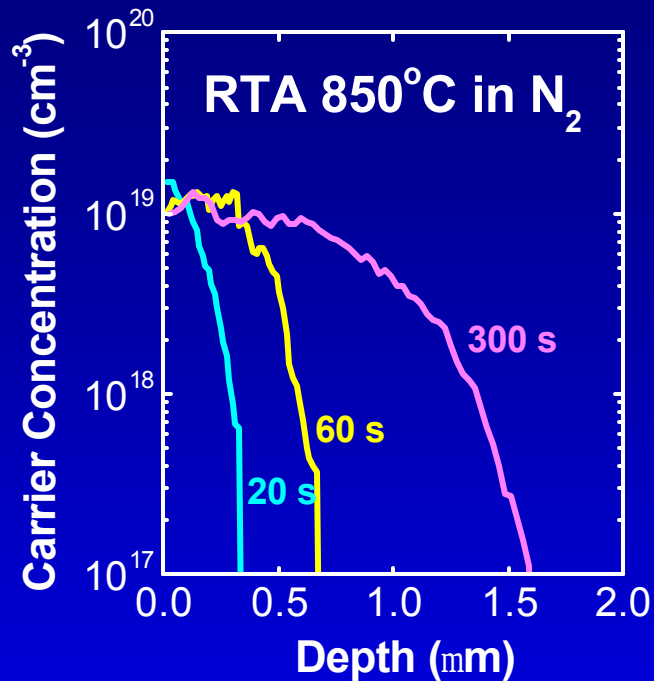
Dopants	Model	E_A (eV)	D^0 (cm ² /s)
P	$(n/n_i)^2$	2.07	4.38×10^{-2}
As	$(n/n_i)^2$	3.32	1.45×10^6
Sb	n/n_i	2.28	1.189×10^1

(Chui et al., APL, 2003)

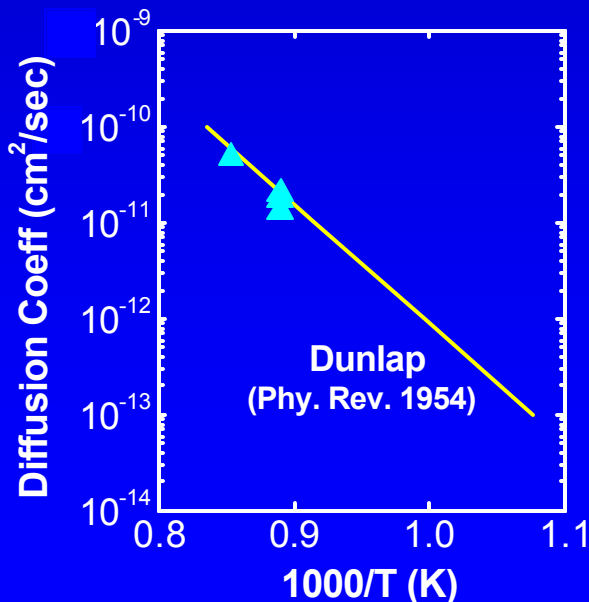
$$r_c = r_{c0} \exp\left(\frac{2f_B}{\hbar} \sqrt{\frac{e_s m^*}{N_{sub}}}\right)$$



Solid Source Diffusion from PSG



(Chui et al., IEEE IEDM, 2003)



Some advantages:

- 1) Avoid non-equilibrium effects like transient enhanced diffusion (TED) from defects
- 2) Require standard materials, e.g. phosphosilicate glass (PSG), as dopant source
- 3) Allow shallow junction with peak concentration at surface with RTA

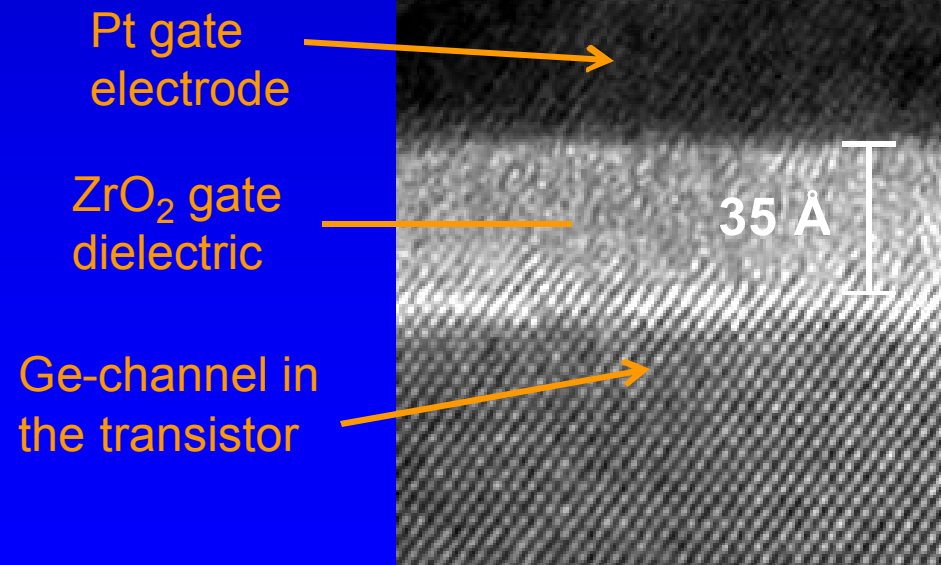
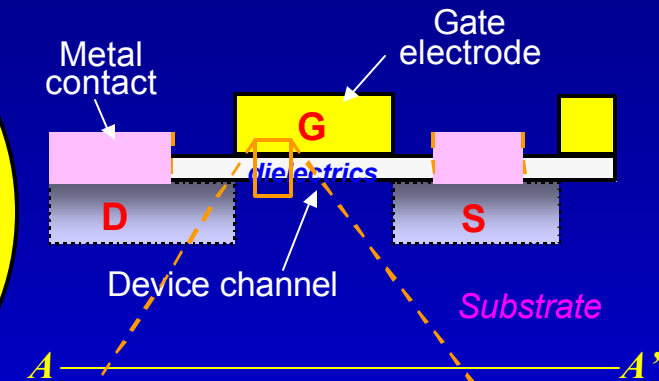
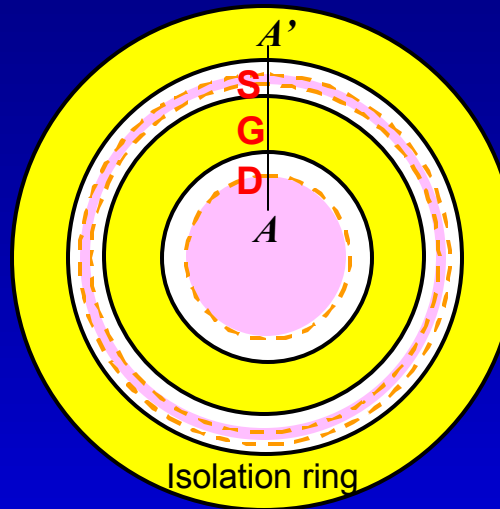
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The Stanford Sub-400°C Germanium P-MOSFET Process

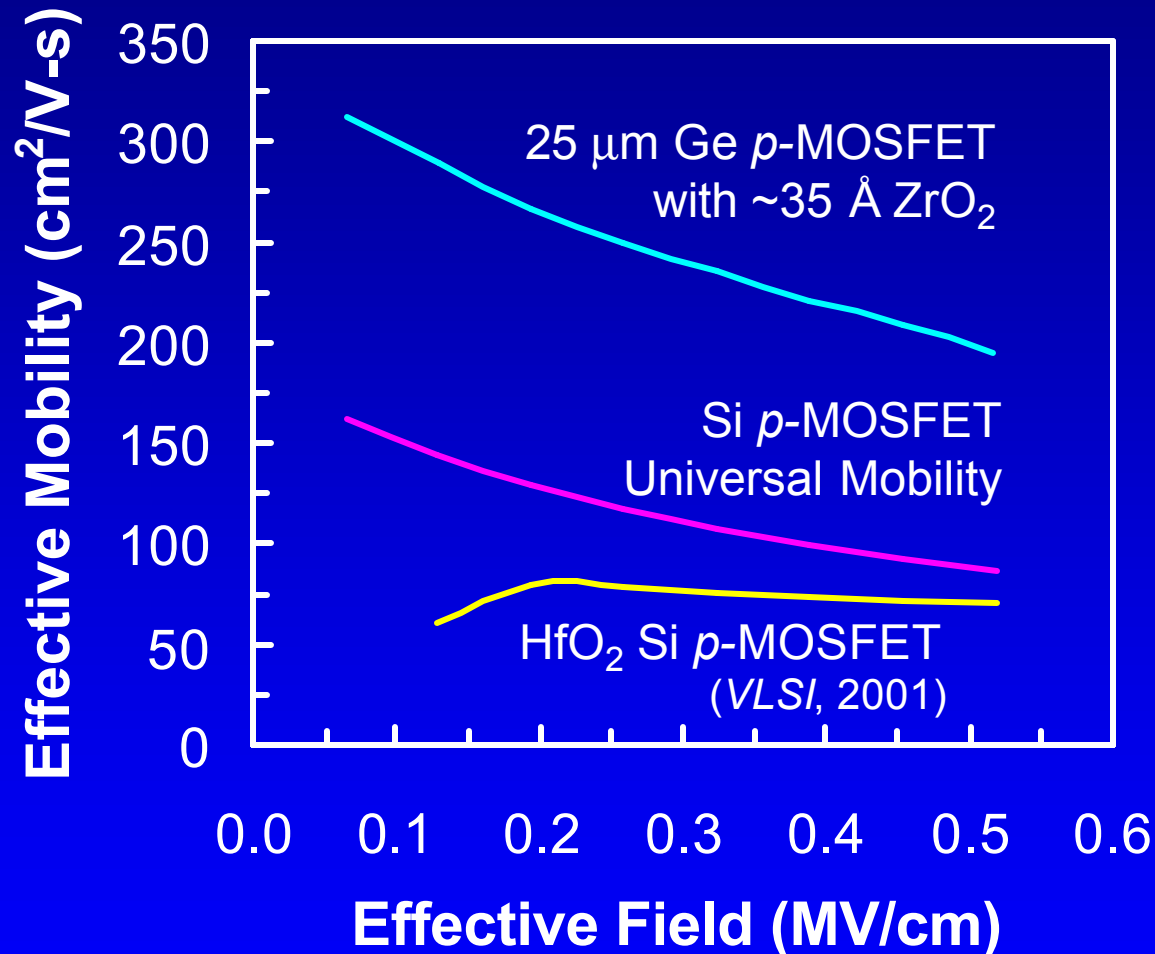
- 1) (100), $\sim 10^{16} \text{ cm}^{-3}$ n-Ge
- 2) Surface Preparations
- 3) ZrO_2 deposition at room temp*
- 4) Litho for metal gate liftoff
- 5) Pt evaporation and liftoff
- 6) Self-aligned S/D implant
- 7) Dopant activation at 400°C
- 8) Litho for contact etch and metallization
- 9) ZrO_2 contact etch**
- 10) Ti-Al evaporation and liftoff
- 11) FGA at 300°C

* Collaborations with D. Chi, B. B. Triplett, & P. C. McIntyre from MSE, Stanford
 ** with M. Liao from MSE, Stanford



(Chui et al., IEEE IEDM, 2002)

Hole Mobility Enhancement with Ge



(Chui *et al.*, *IEEE IEDM*, 2002)

- ⇒ 1st demonstration of metal gate on high- κ on Ge MOSFETs
- ⇒ 2× mobility vs. Si universal mobility
- ⇒ 3× mobility vs. Si high- κ p-MOSFETs
- ⇒ 400°C maximum temperature process
- ⇒ All the processing were done at Stanford (EE and MSE)

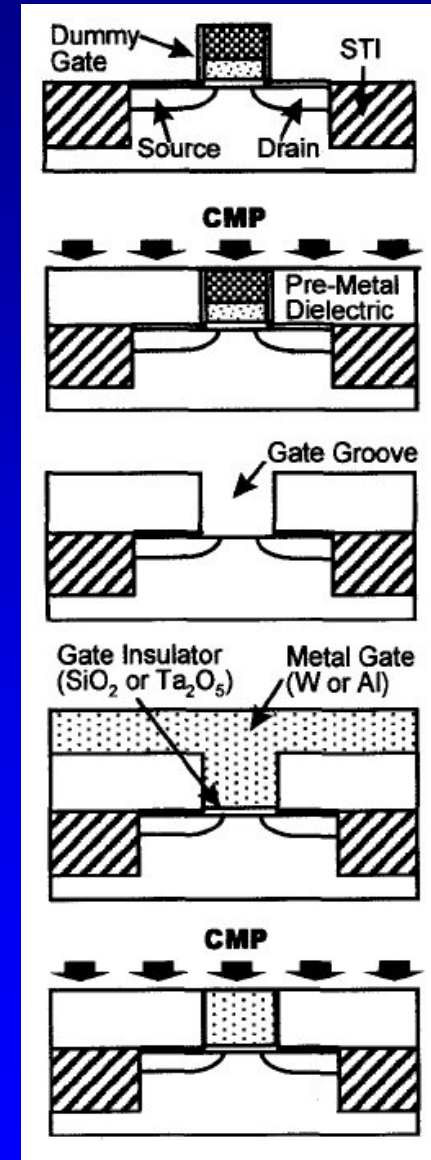
Requirements and Solutions of Metal Gate High- k MOSFET Integration

Integration Requirements:

- Thermal stability of the metal gate high- k gate stack during conventional self-aligned dopant activation
- Resemblance to the conventional VLSI device structure
- Compatibility with the Si mainline equipment set
- Inclusion of standard isolation together with planar geometry

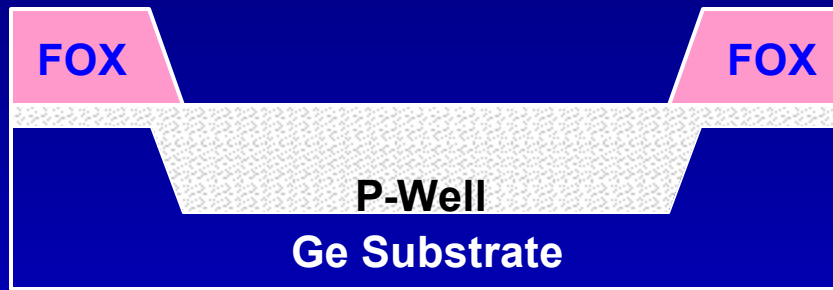
Present solutions:

- Replacement or damascene gate process

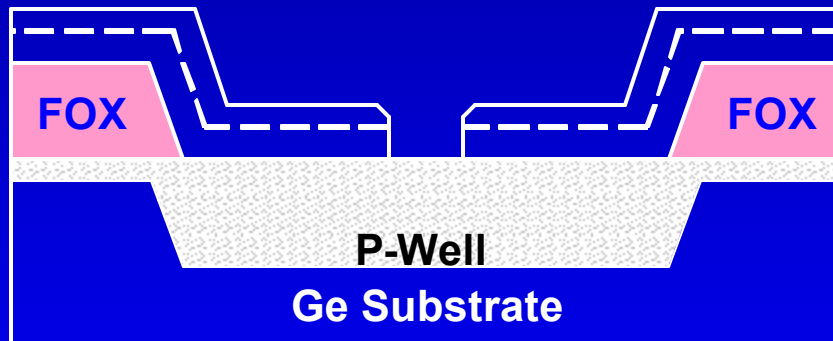


(Yagishita et al., IEEE IEDM, 1998)

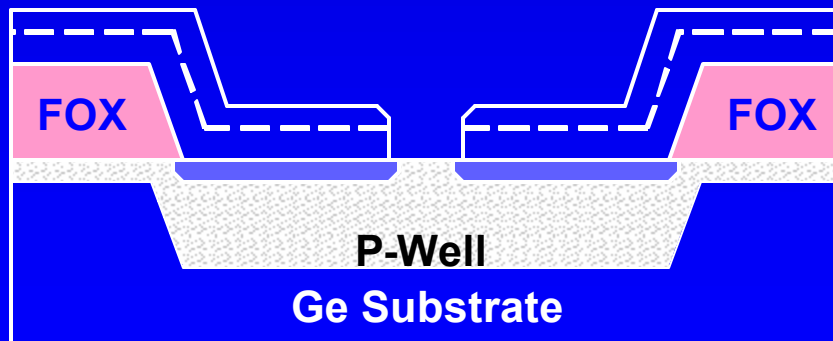
The Novel Self-Aligned Gate-Last Metal Gate High- k MOSFET Process



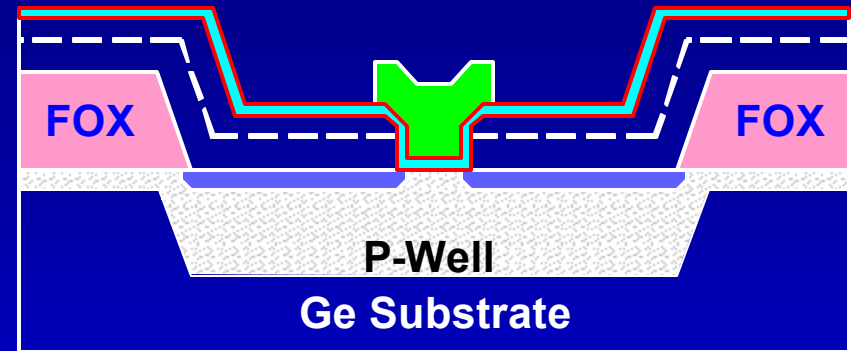
(a)



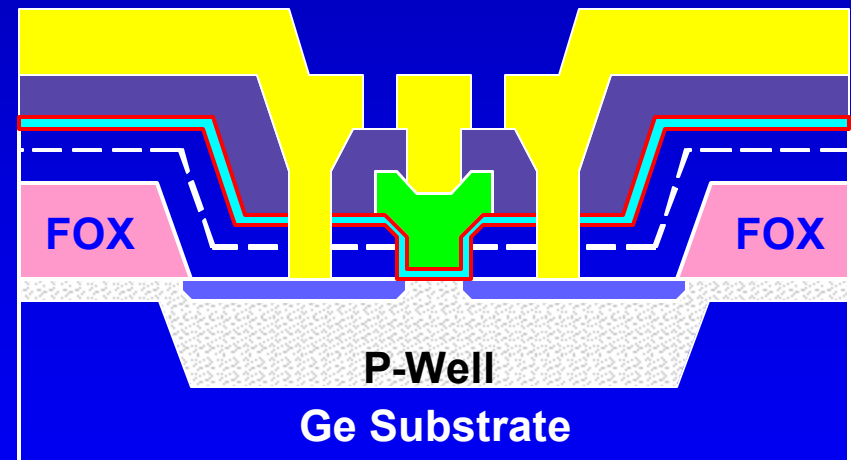
(b)



(c)



(d)

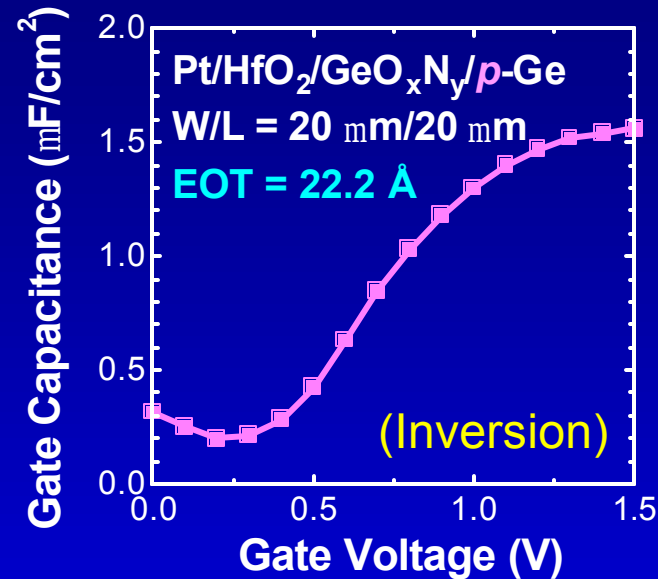
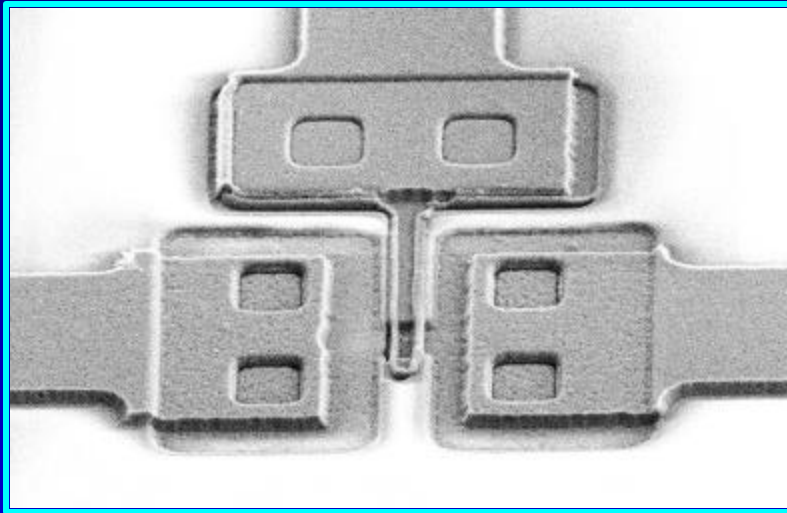


(e)

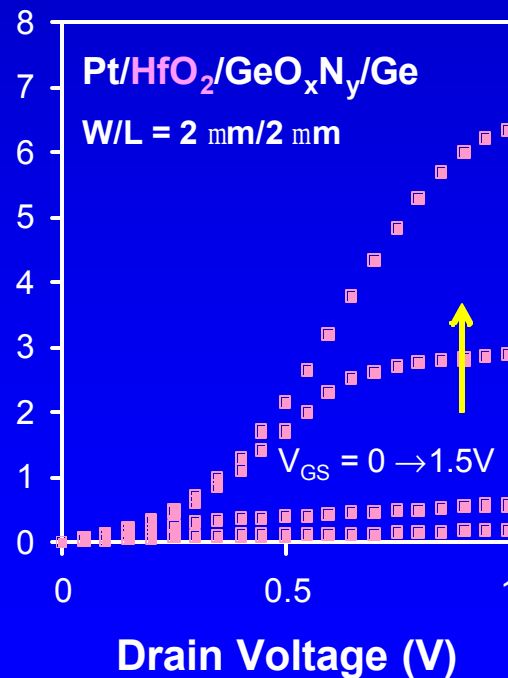
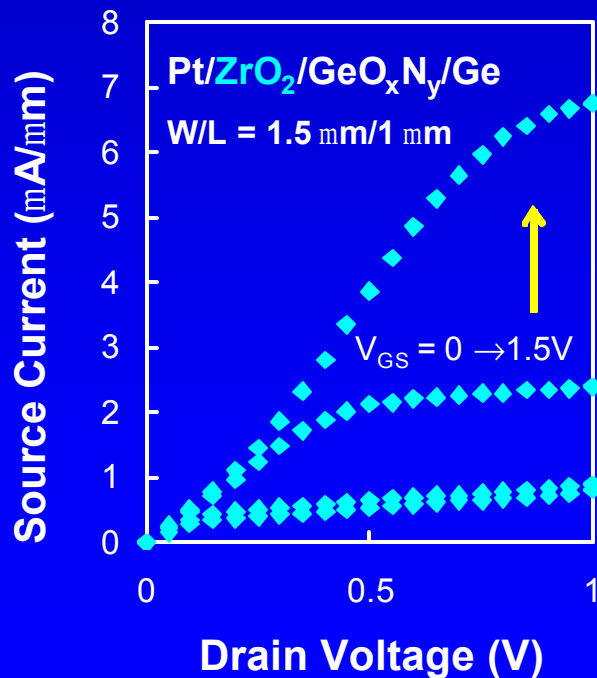
- 5-mask process compatible with the mainline Si fab

(Chui et al., IEEE IEDM, 2003; Chui et al., IEEE ISDRS, 2003)

Ge N-MOSFET Characteristics

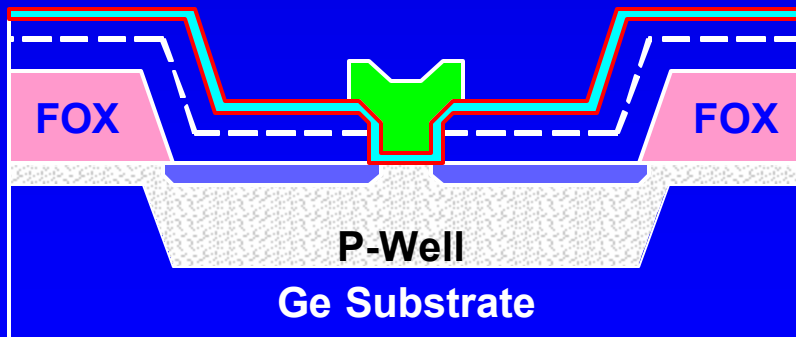
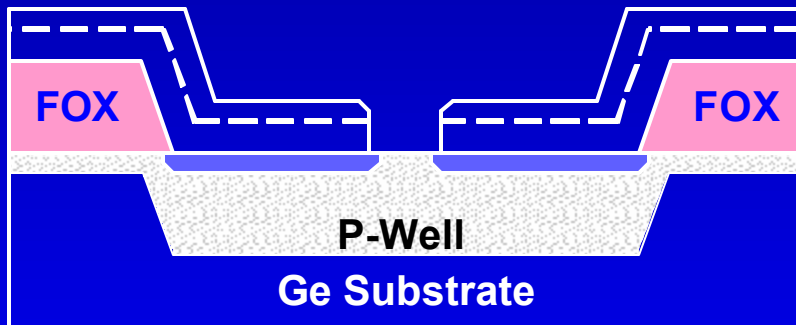
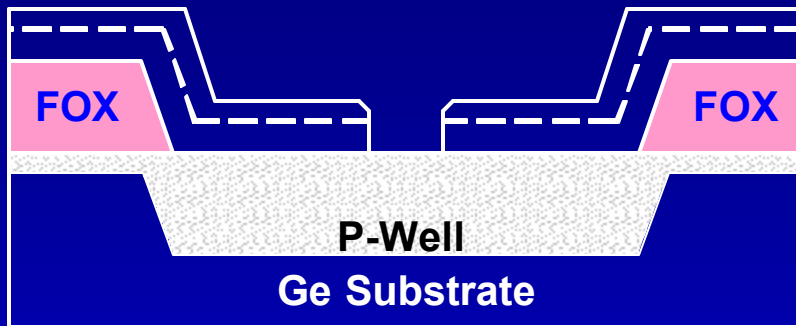


(Chui *et al.*, IEEE IEDM, 2003)



- 1st proof of concept Ge *n*-MOSFETs with both ZrO₂ & HfO₂ dielectrics and Pt gate electrode fabricated
- Functional *n*-MOSFETs with channel length down to 1-2 μm

Process Versatility



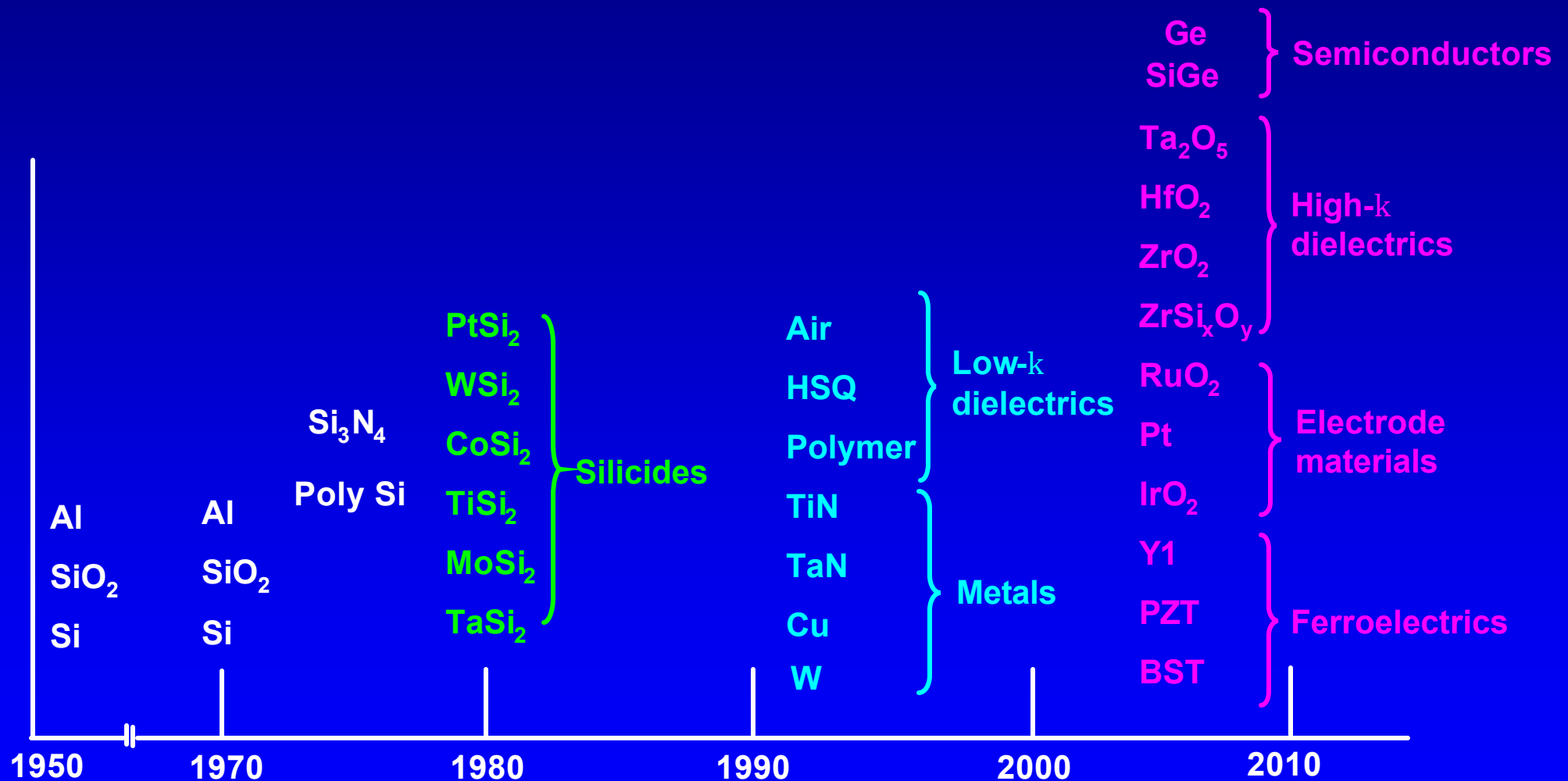
- Stringent thermal stability requirement relaxed without the need of the more-involved replacement or damascene process
- Highly selective etch of metal gate vs. high- κ , and high- κ vs. Ge not necessary on the thick LTO buffer
- Lightly-doped drains (LDD) possible with lower wt% PSG inward spacers
- CMOS formation by selective PSG removal followed by blanket BSG
- Elevated source/drains with doped-Ge instead of PSG

(Chui et al., IEEE IEDM, 2003)

Outline

- Ge CMOS Motivations
- Ge MOS Gate Dielectric Technology
 - ⇒ UVO Oxidation of Metal
 - ⇒ ALD of Metal Oxides
- Ge Dopant Incorporation Technology
- Ge MOSFETs with High- κ and Metal Gate
- Conclusions

New Materials for CMOS



Conclusions

- 1st demonstration of Ge MOS capacitors incorporating high- κ gate dielectrics (ZrO_2 & HfO_2) deposited using either UVO or ALD
- 1st demonstration of high Ge surface p - and n -type dopings by either ion implantation or solid source diffusion
- 1st demonstration of Ge p - and n -MOSFETs with high- κ gate dielectrics and metal gate down to 1-2 μm channel length
- Future work in the areas of Ge surface cleaning, passivation, and dopant activation

List of Related References

- [1] C. O. Chui, S. Ramanathan, B. B. Triplett, P. C. McIntyre, and K. C. Saraswat, "Ultrathin High-k Gate Dielectric Technology for Germanium MOS Applications," *IEEE 60th Annual Device Research Conference (DRC) Digest*, Paper VII.B-2, pp. 191-192, Santa Barbara, CA, June 24-26, 2002. **(Best Student Paper Award)**
- [2] C. O. Chui, S. Ramanathan, B. B. Triplett, P. C. McIntyre, and K. C. Saraswat, "Germanium MOS Capacitors Incorporating Ultrathin High-k Gate Dielectric," *IEEE Electron Device Lett.*, vol. 23, no. 8, pp. 473-475, 2002.
- [3] C. O. Chui, H. Kim, D. Chi, B. B. Triplett, P. C. McIntyre, and K. C. Saraswat, "A Sub-400°C Germanium MOSFET Technology with High-k Dielectric and Metal Gate," *IEEE International Electron Devices Meeting (IEDM) 2002 Technical Digest*, Paper 17.3, pp. 437-440, San Francisco, CA, December 8-11, 2002.
- [4] H. Kim, P. C. McIntyre, C. O. Chui, and K. C. Saraswat, "Atomic Layer Deposition of ZrO₂ on Si and Ge Substrate," *MRS 2003 Spring Meeting, Symposium on High-k Dielectrics*, Paper D2.11, San Francisco, CA, April 21-25, 2003.
- [5] D. Chi, B. B. Triplett, P. C. McIntyre, C. O. Chui, K. C. Saraswat, E. Garfunkel, and T. Gustafsson, "High-k Metal Oxides Dielectrics on Ge (100) Substrates," *MRS 2003 Spring Meeting, Symposium on Advanced Gate Stack Materials*, Paper D3.17, San Francisco, CA, April 21-25, 2003.
- [6] K. C. Saraswat, C. O. Chui, P. C. McIntyre, and B. B. Triplett, "Novel Ge Devices with High-k Dielectrics: High Performance MOSFETs and Optical Receivers," *The 203rd Spring Meeting of ECS*, Paper G1-0445, Paris, France, April 27-May 2, 2003. **(Invited)**
- [7] D. Chi, C. O. Chui, S. Ramanathan, B. B. Triplett, K. C. Saraswat, and P. C. McIntyre, "UV-Ozone Oxidized High-k Dielectrics on Si and Ge Substrates," *The 45th TMS Electronic Materials Conference (EMC) Digest*, Paper S5, Salt Lake City, UT, June 25-27, 2003.

References and Acknowledgements

- [8] H. Kim, C. O. Chui, K. C. Saraswat, and P. C. McIntyre, "Local Epitaxial Growth of ZrO₂ on Ge (100) Substrates by Atomic Layer Epitaxy," *Appl. Phys. Lett.*, vol. 83, no. 13, pp. 2647-2649, 2003.
- [9] C. O. Chui, K. Gopalakrishnan, P. B. Griffin, J. D. Plummer, and K. C. Saraswat, "Activation and Diffusion Studies of Ion-implanted *p* and *n* Dopants in Germanium," *Appl. Phys. Lett.*, vol. 83, no. 16, pp. 3275-3277, 2003.
- [10] C. O. Chui, H. Kim, P. C. McIntyre, and K. C. Saraswat, "A Germanium NMOSFET Process Integrating Metal Gate and Improved Hi-k Dielectrics," *IEEE International Electron Devices Meeting (IEDM) 2003 Technical Digest*, Paper 18.3, pp. 437-440, Washington, DC, December 7-10, 2003.
- [11] C. O. Chui, H. Kim, J. P. McVittie, B. B. Triplett, P. C. McIntyre, and K. C. Saraswat, "A Novel Self-aligned Gate-last MOSFET Process Comparing the High-k Candidates," *IEEE 2003 International Semiconductor Device Research Symposium (ISDRS) Proceedings*, Paper FA6-05, pp. 464-465, Washington, DC, December 10-12, 2003.

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