Ultra-Thin ZrO_2 as an Alternative Gate Dielectric

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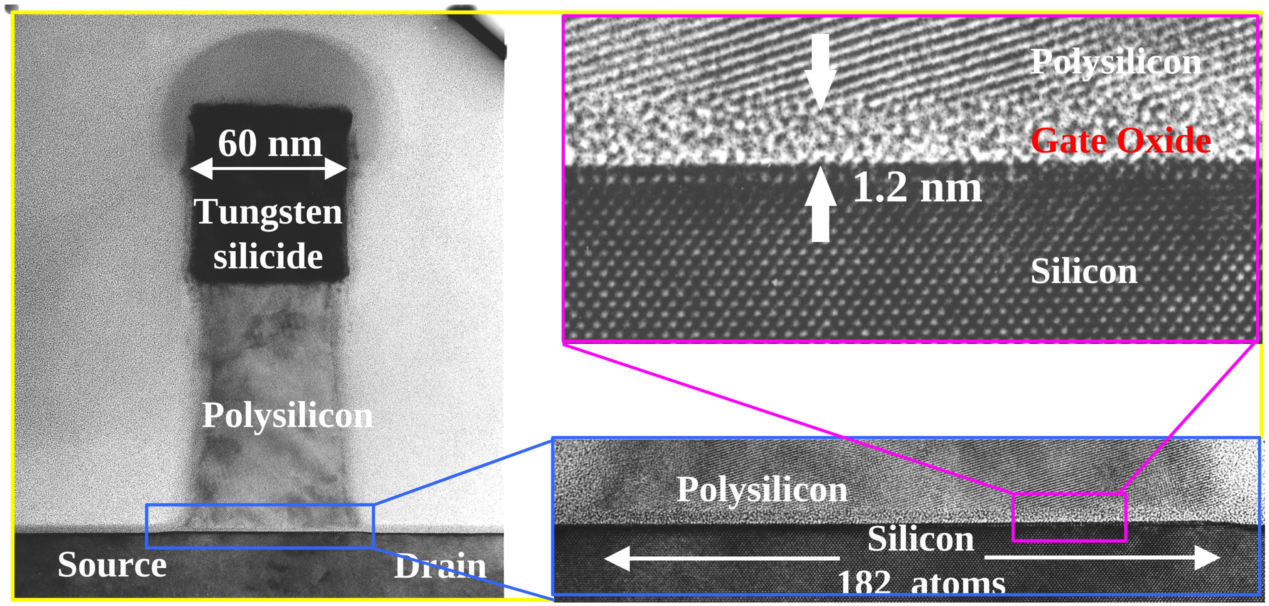
From the Dawn of Transistors

First Transistor
Bell Labs, 1947

Bardeen, Brattain & Shockley

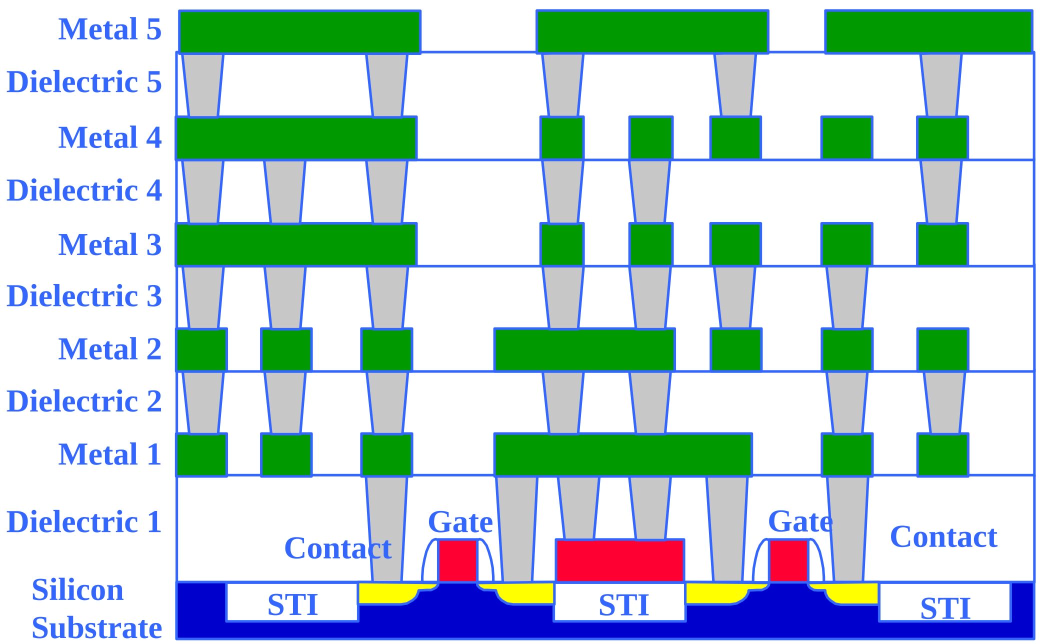
Atomic Scale Transistor
Bell Labs, Lucent Technologies, 1997

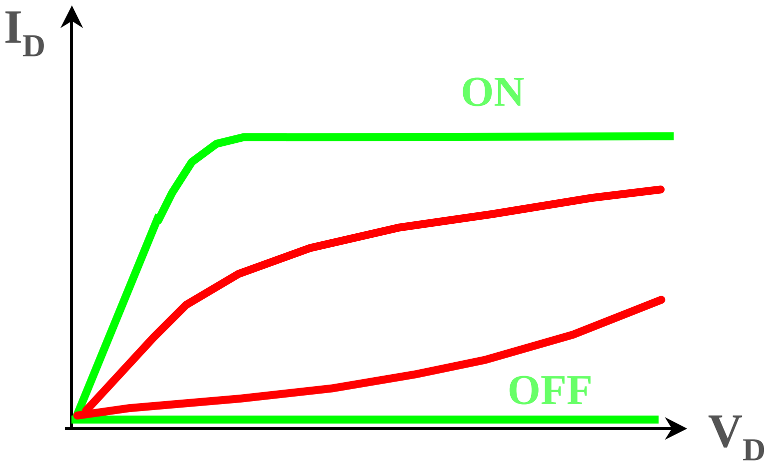


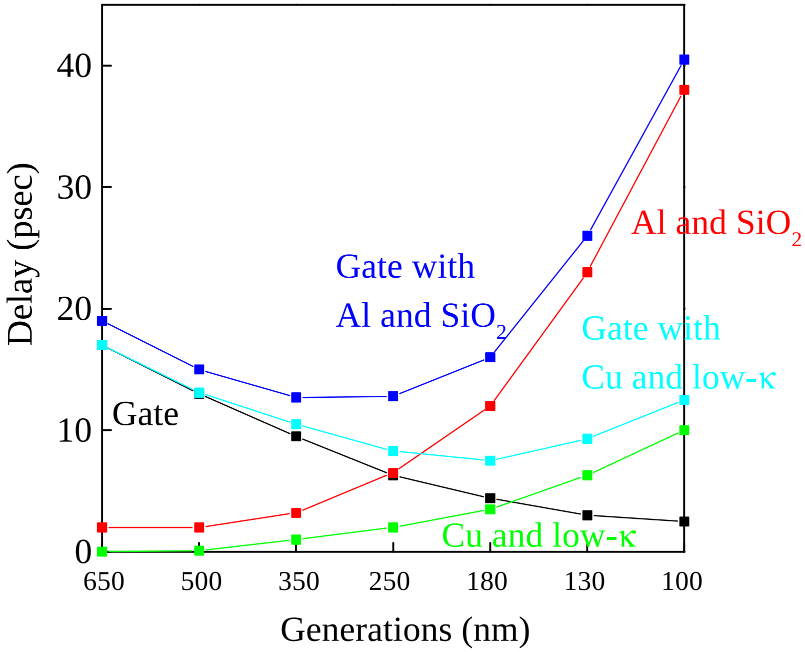
Baumann, Klemens, Kornblit, Tennant and Timp

- Near atomic scale transistor is proven to be functional
- Further scaling requires New Dielectric Materials !

Motivation and Challenge







Factors affect device performance

- Dielectric materials
- Surface cleanliness
- Thin film deposition and etching

SIA Roadmap

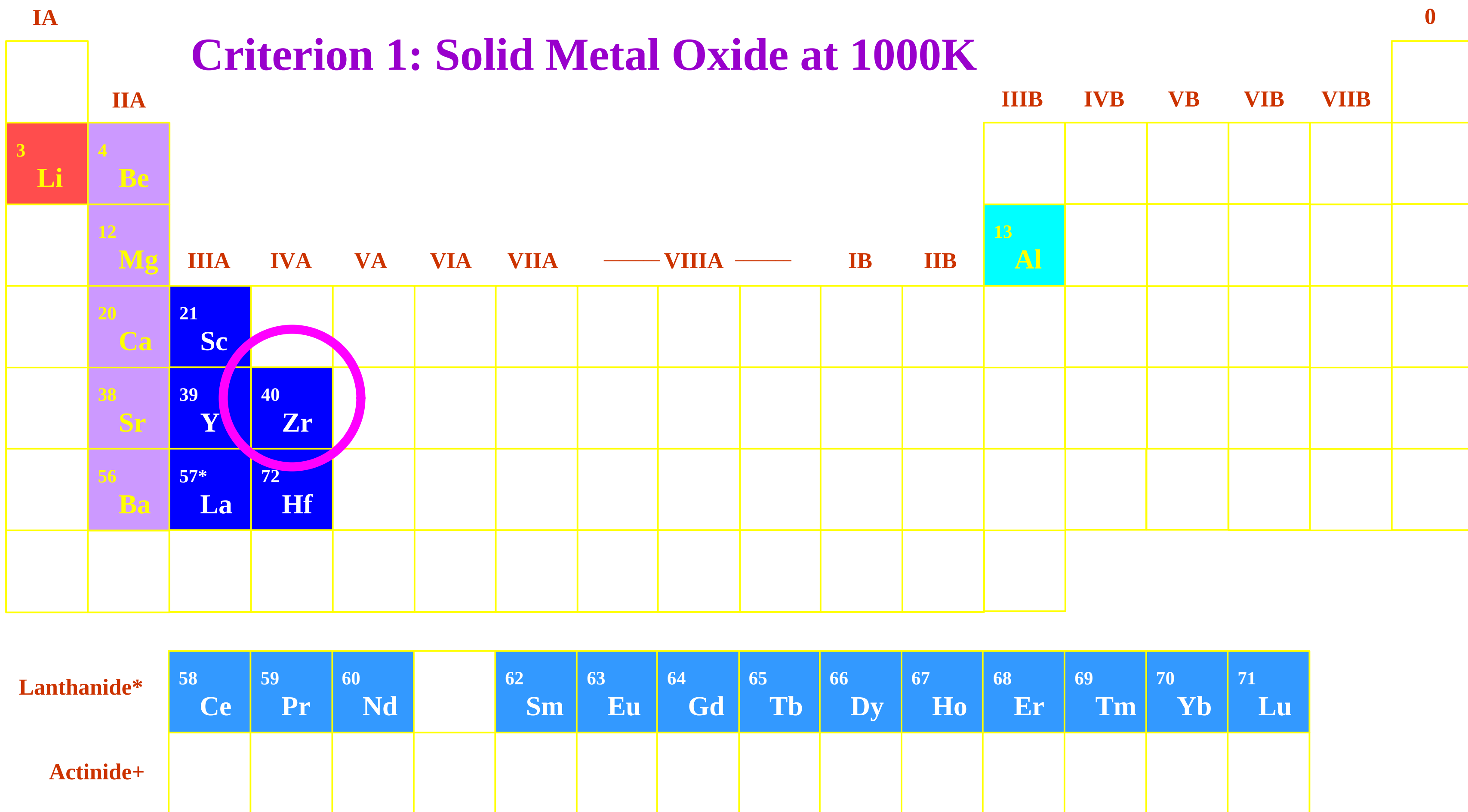
	1999	2001	2003	2006	2009	2012
Gate Length	575	475	415	320	220	160
Gate Dielectric thickness	10-16	6-10	6-10	5-6	<5	<5
Metal (atoms/cm^2)	4×10^9	3×10^9	2×10^9	1×10^9	$<10^9$	$<10^9$
ILD low-κ	2.5	2 - 2.5	1.5 - 2	1.5	≤ 1.5	≤ 1.5

Unit of length = π Angstroms ~ 1 Silicon Atom

- Reasons and challenges for high-κ dielectric materials:
  - — Reduce tunneling current through ultra-thin dielectrics
  - — Etchable
- Reasons and challenges for high-κ dielectric materials:
  - – Reduce RC delay and cross-talking

Metal Oxide Selection

Criterion 1: Solid Metal Oxide at 1000K



Criterion 2: $Si + \frac{2}{y} M_xO_y \rightarrow SiO_2 + \frac{2x}{y} M$, $\Delta G>0$ at 1000K

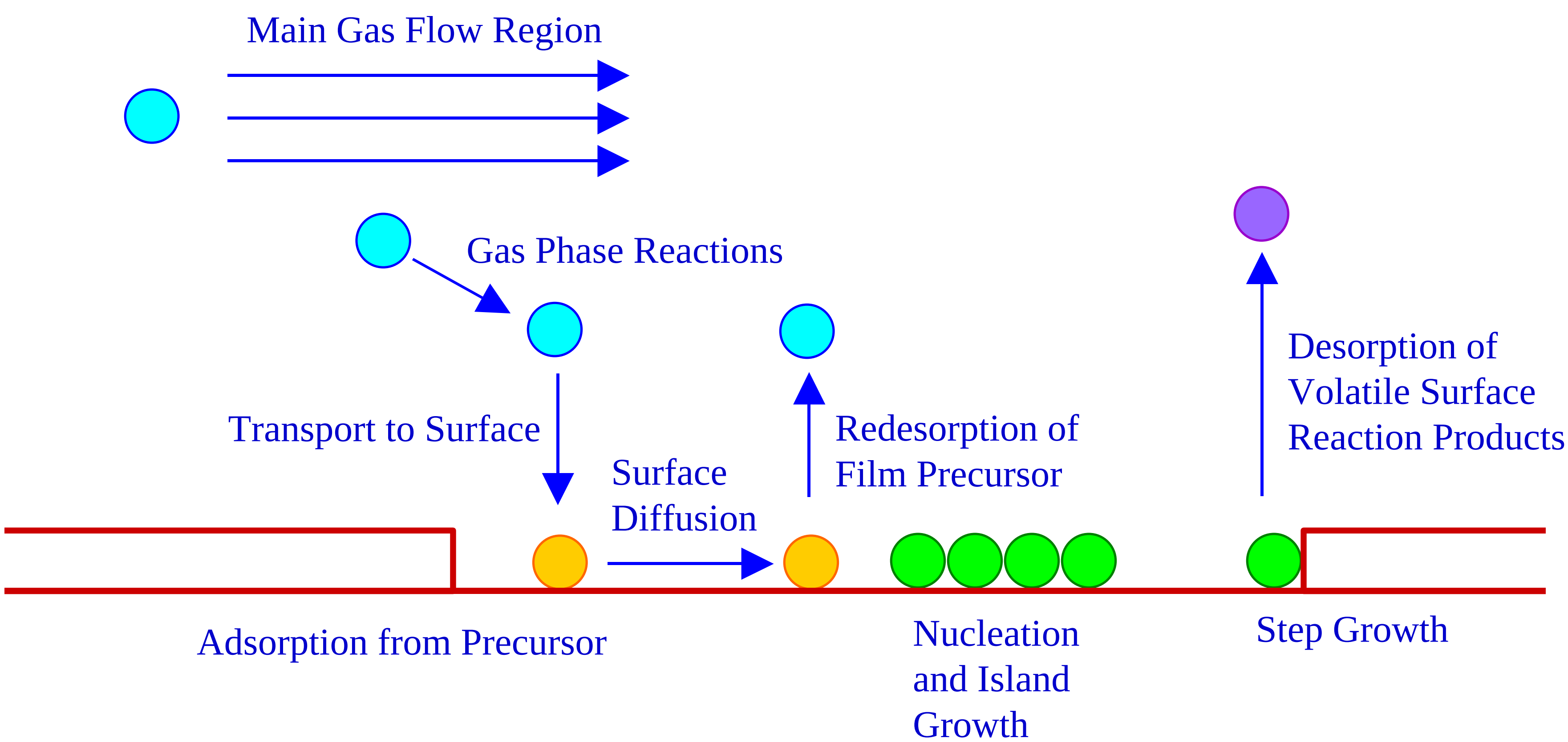
Criterion 3: $(xz + \frac{y}{2}) Si + M_xO_y \rightarrow x\, MSi_z + \frac{y}{2} SiO_2$, $\Delta G>0(1000K)$

Additional Consideration

Dielectric	ε	V_{BD} (MV/cm)	E_g (eV)
SiO_2	3.9	12-15	**8**
SiO_xN_y	~4	15-16	6
Si_3N_4	7-9	10-11	5
TiO_2	80-120	0.5	4
Ta_2O_5	20-25	3-5	3-4
ZrO_2	15-22	15-20	5-7
Y_2O_3	12-15	4-5	6
Al_2O_3	9-12	10	8
$ZrSiO_4$	13	?	?

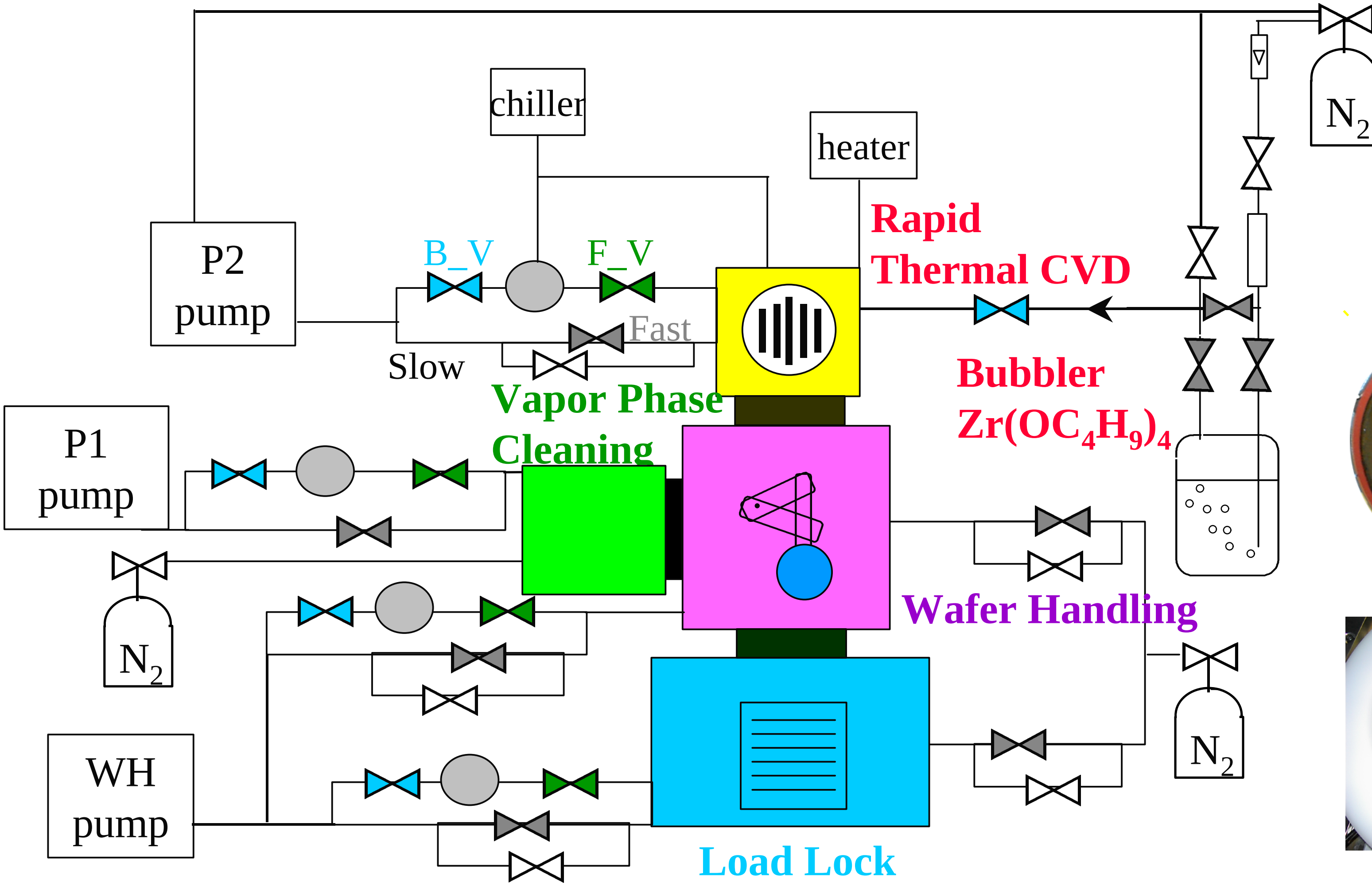
- ZrO_2 has high ε, large V_{BD}, and wide band gap

Chemical Vapor Deposition of ZrO_2

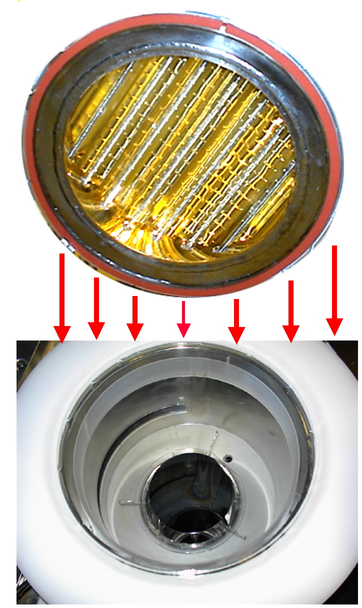


- Surface reaction: kinetically driven chemical reactions
- Gas phase reaction: lower reaction activation barrier
- **RTCVD and PECVD**

Process Schematic

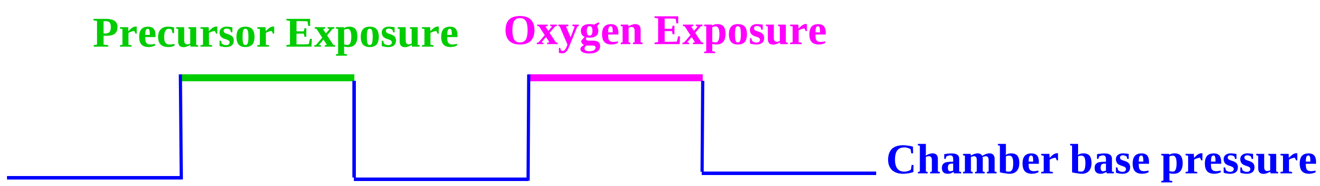


IR Radiation
in RTCVD



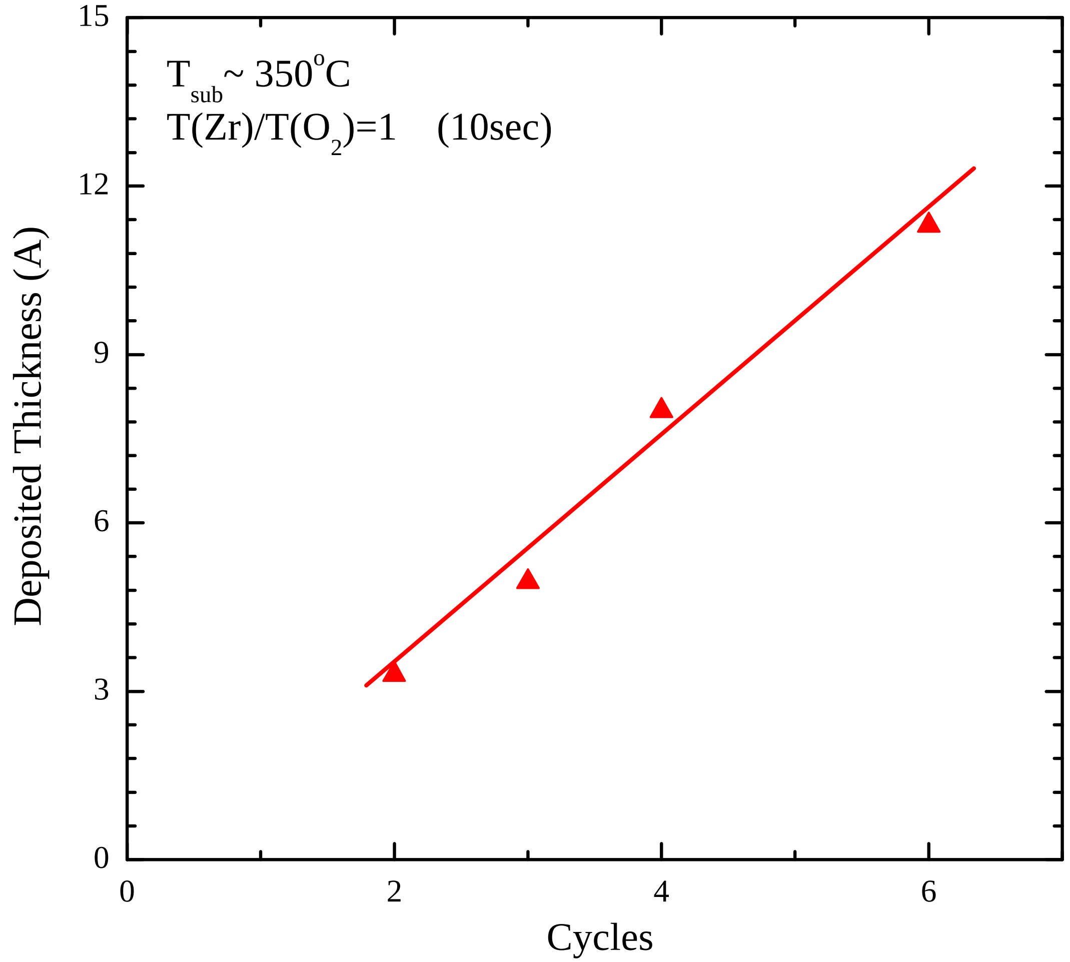
- Fully integrated in-situ chemical processing

Process Sequence



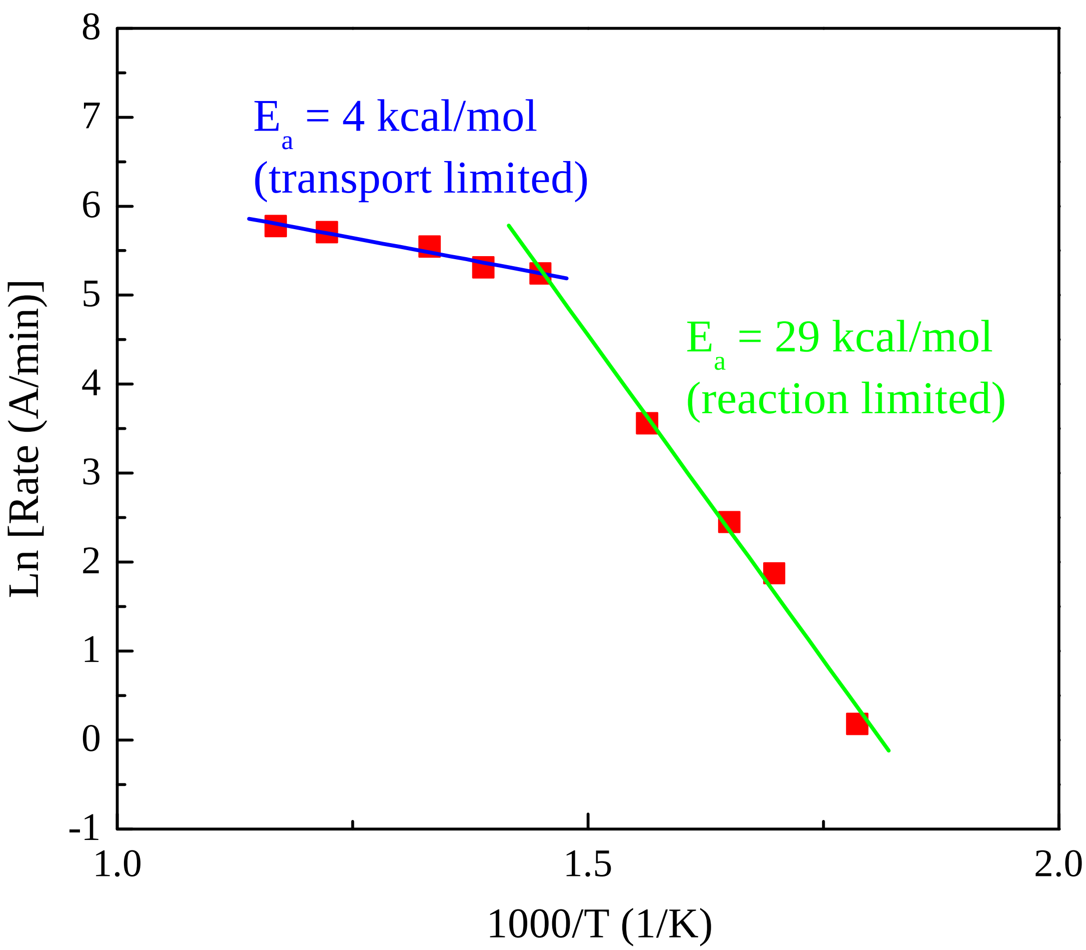
- Precursor: $Zr(OC_4H_9)_4$
  - Time
  - Bubbler temperature
  - Substrate temperature
- Oxygen
  - Time
  - Substrate temperature
- Chamber base pressure ~10^{-7} torr
- Substrate temperature < 300°C no deposition
- Substrate temperature ~ 350°C atomic layer deposition
- Substrate temperature ~ 500°C multi-layer deposition

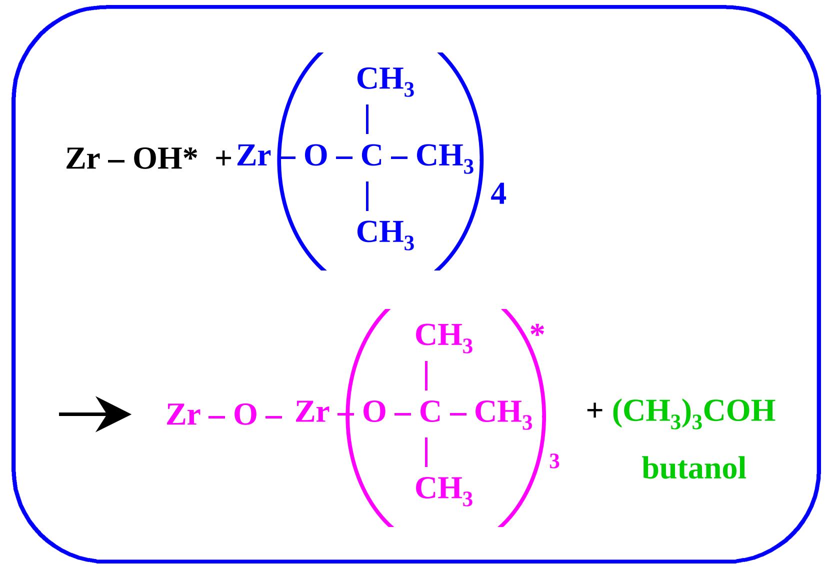
Atomic Layer Deposition

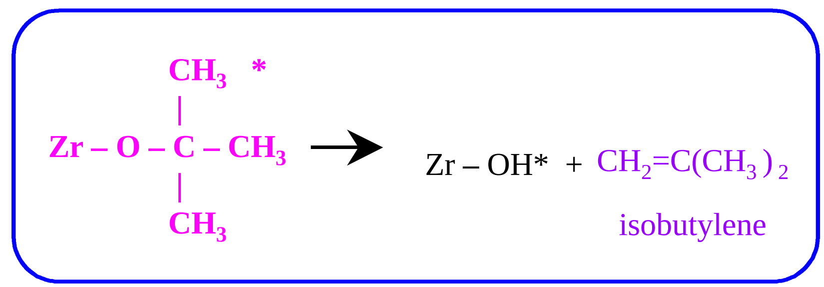


- Nearly atomic deposition at T_{sub} ~ 350°C

Plausible Reaction Mechanisms

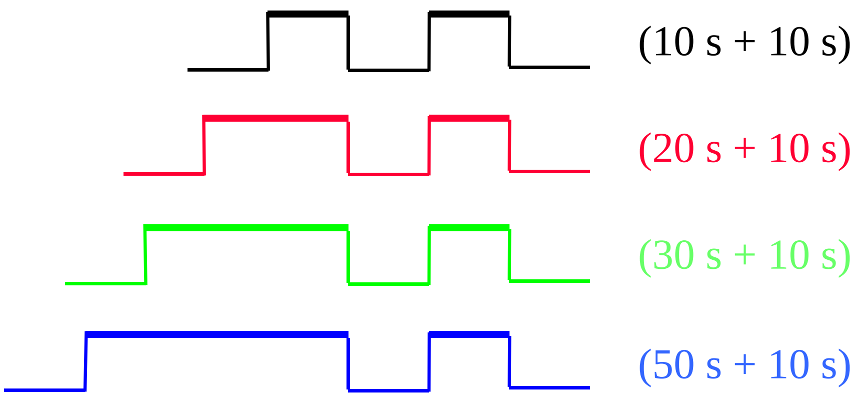


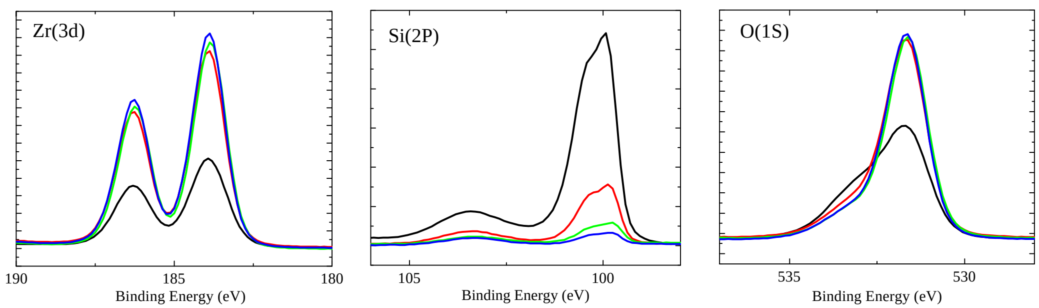


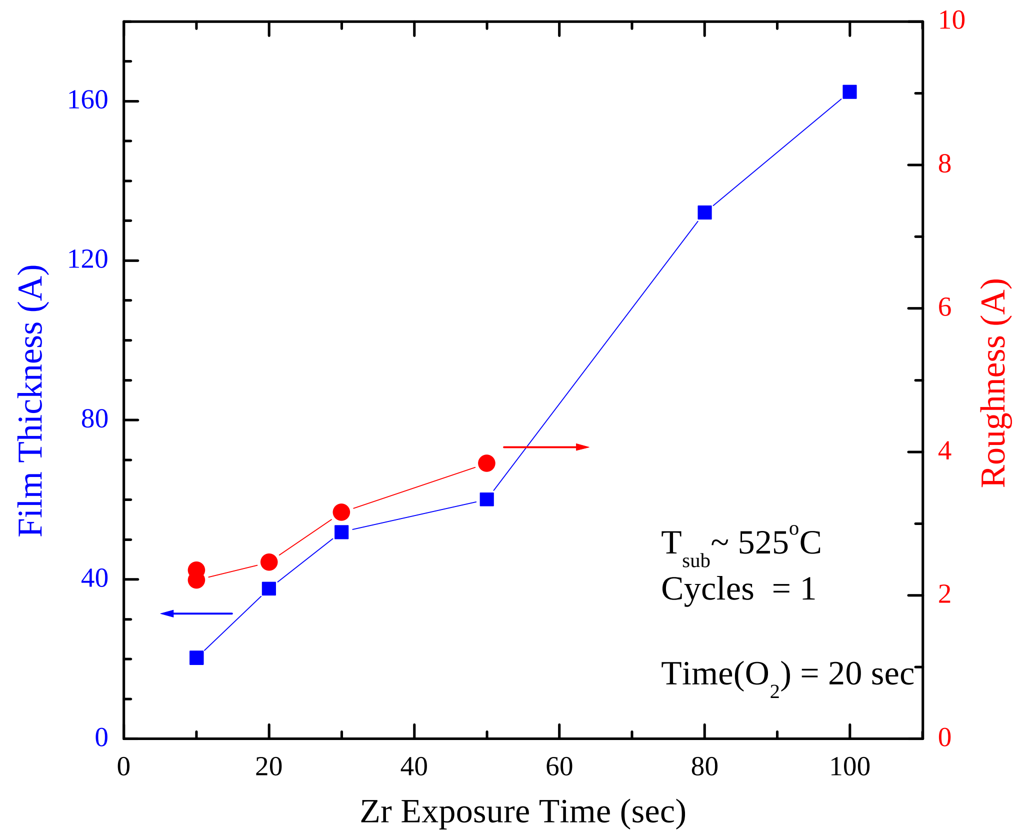


- Reaction limited to transport limited transition
- β-hydride elimination could regenerate surface hydroxyl groups

Effect of Precursor Exposure Time

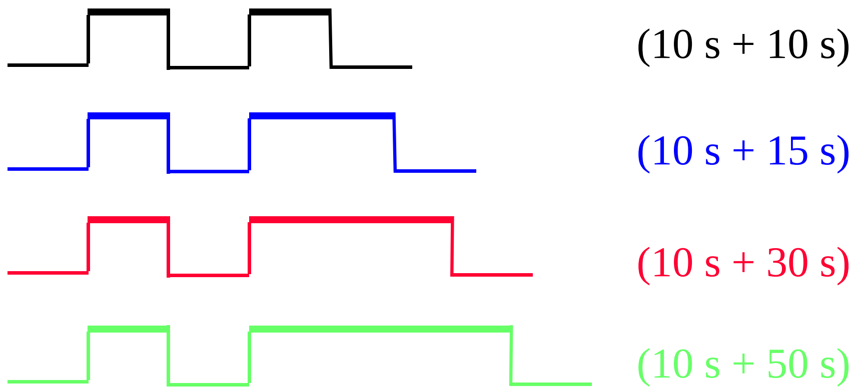


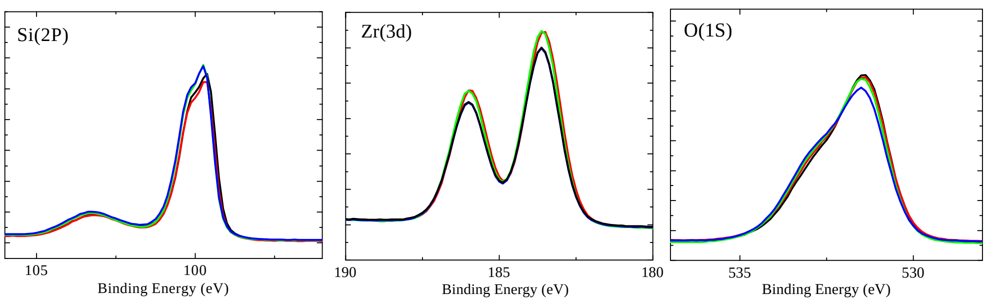


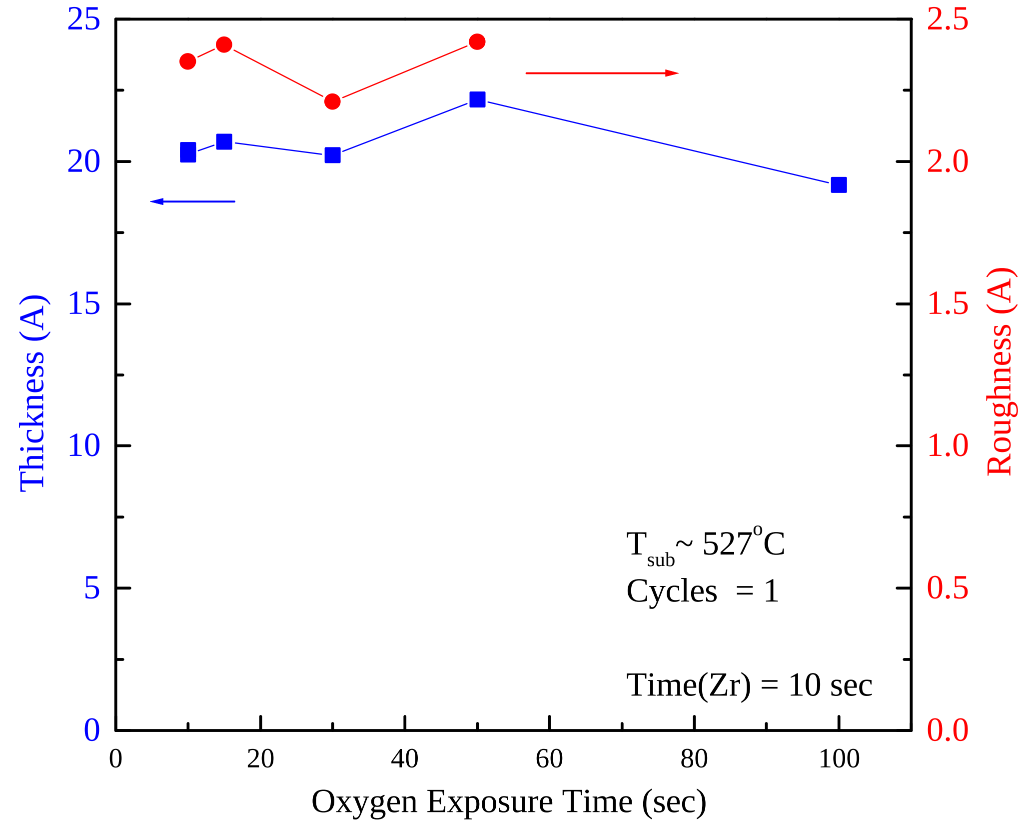


- Oxidation time is held constant at 20 seconds
- Film Thickness depends strongly on precursor exposure time.

Effect of Oxygen Exposure Time

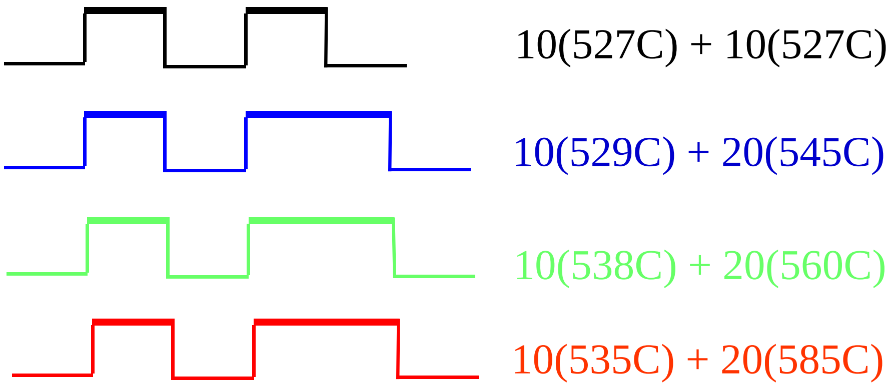


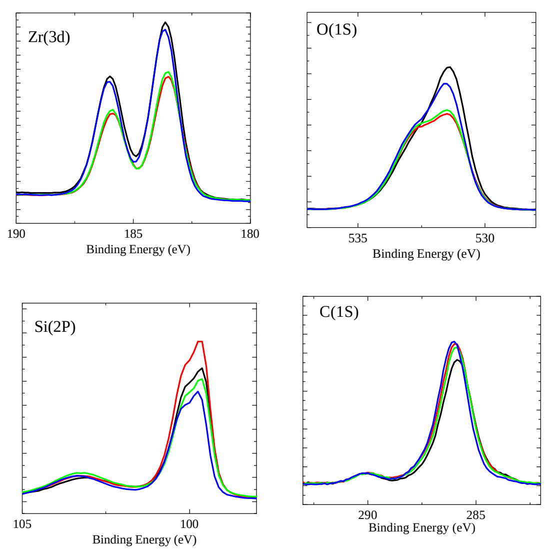


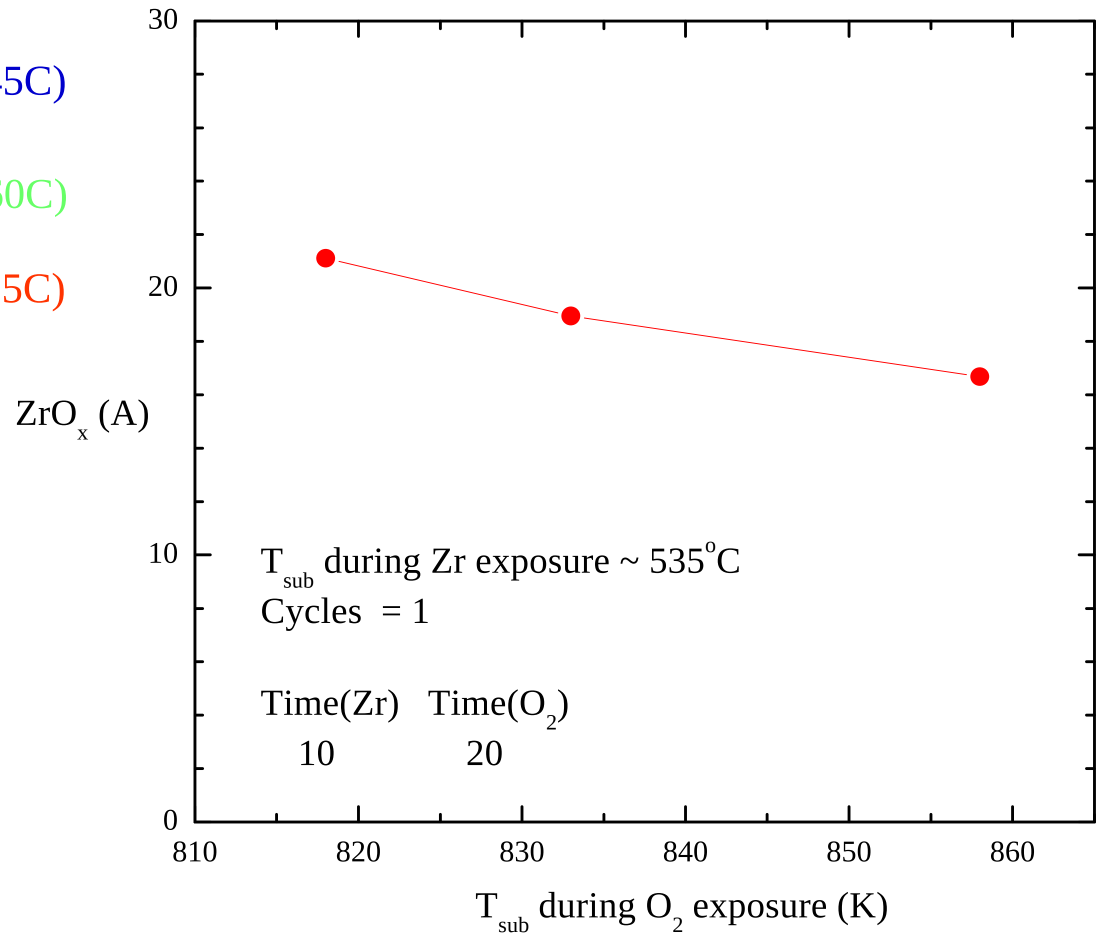


•Film thickness is nearly independent on oxygen exposure time.

Effect of Oxidation Temperature

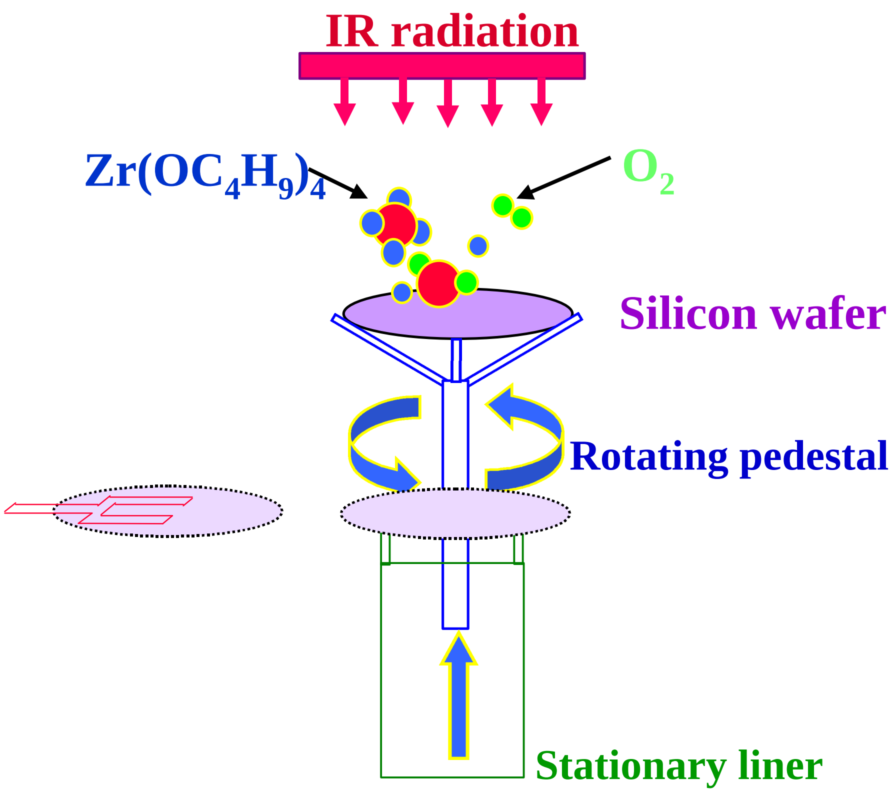


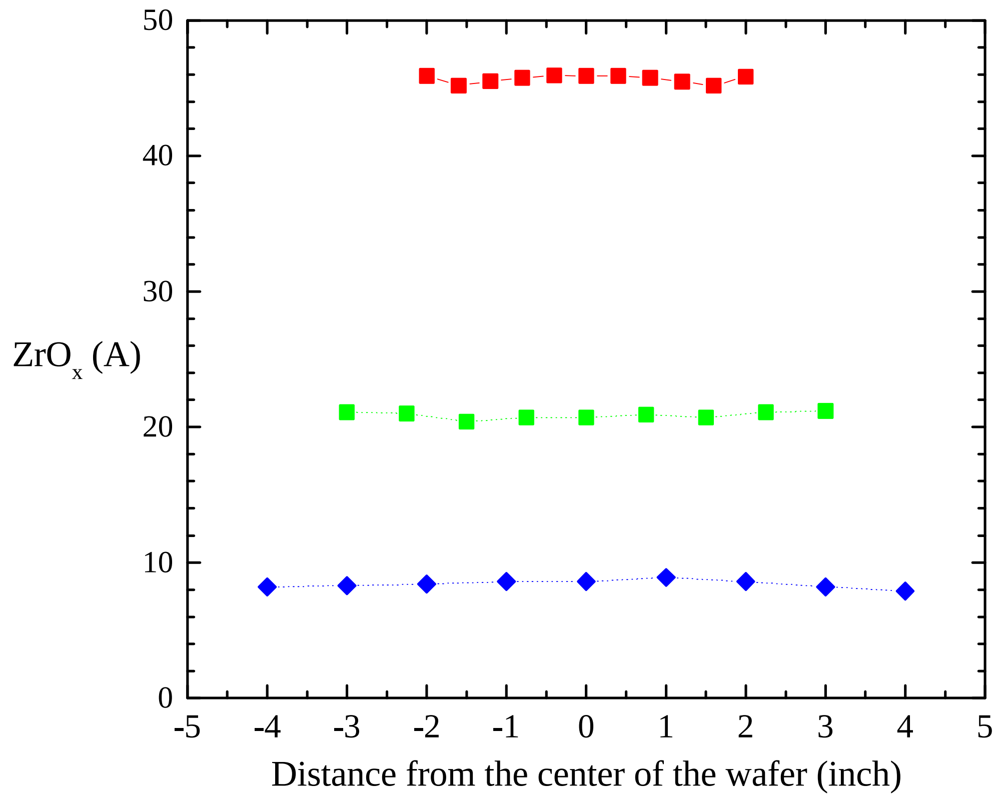




- Film thickness decreases slightly at higher oxidation temperature

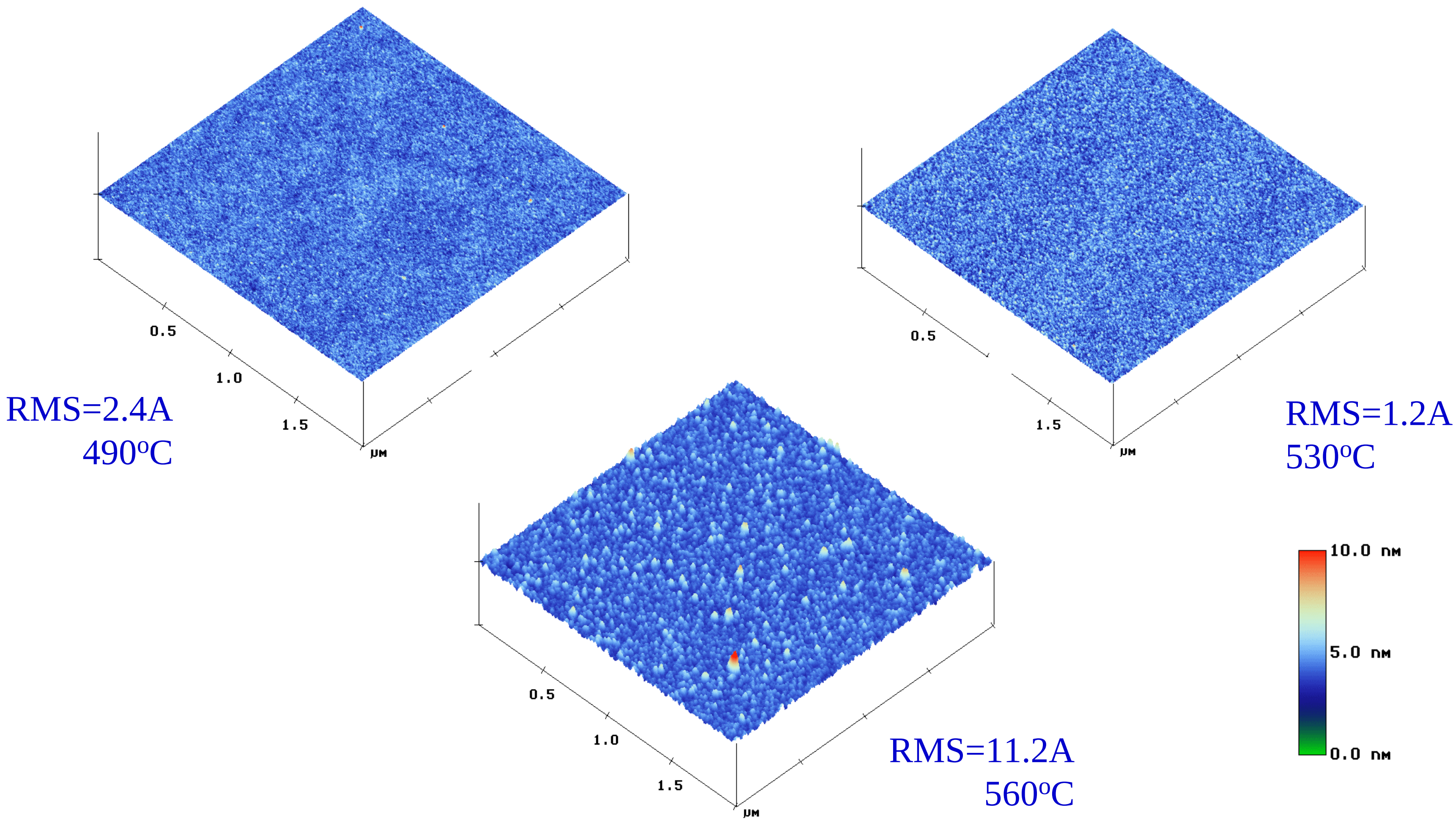
Deposition Uniformity





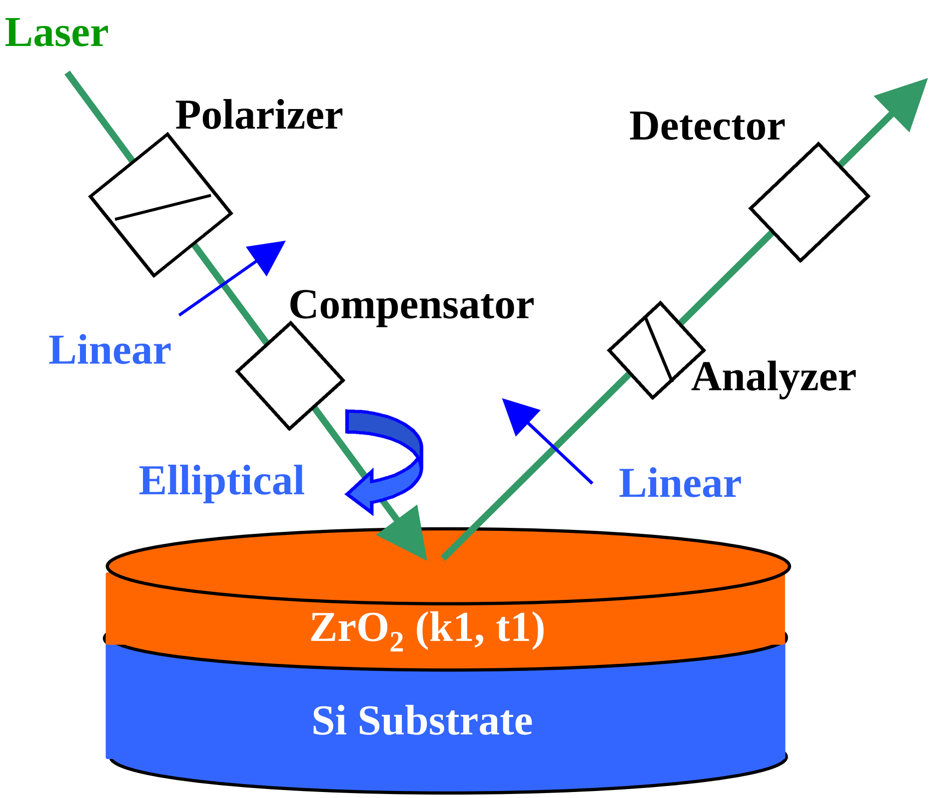
- Deposition rate and stoichiometry strongly depend on the temperature profile
- RTCVD requires **much less energy** than typical oxidation process using furnace
  (eg. Heating Time from RT to 500^0C : 15sec. by RTCVD vs. 45min in a furnace)

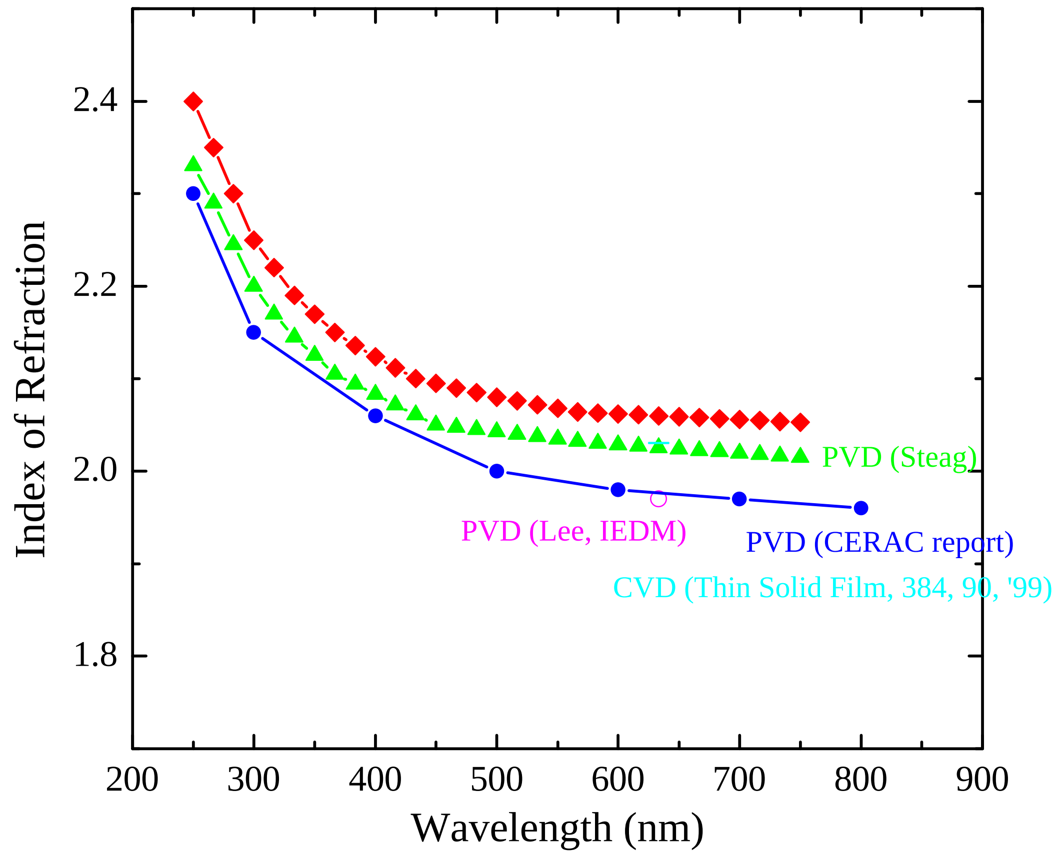
Film Morphology



- Surface roughness depends strongly on process conditions.

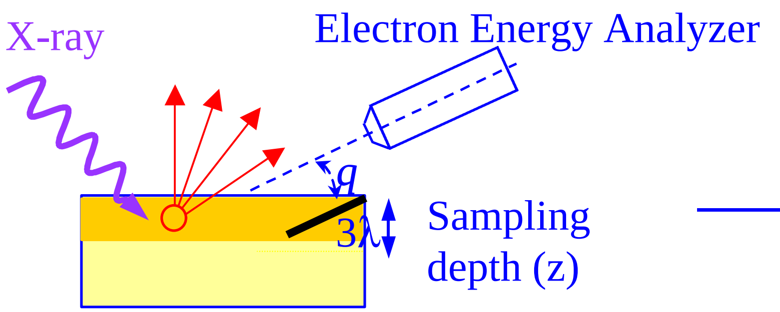
Index of Refraction

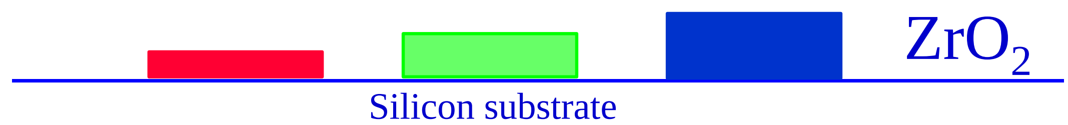


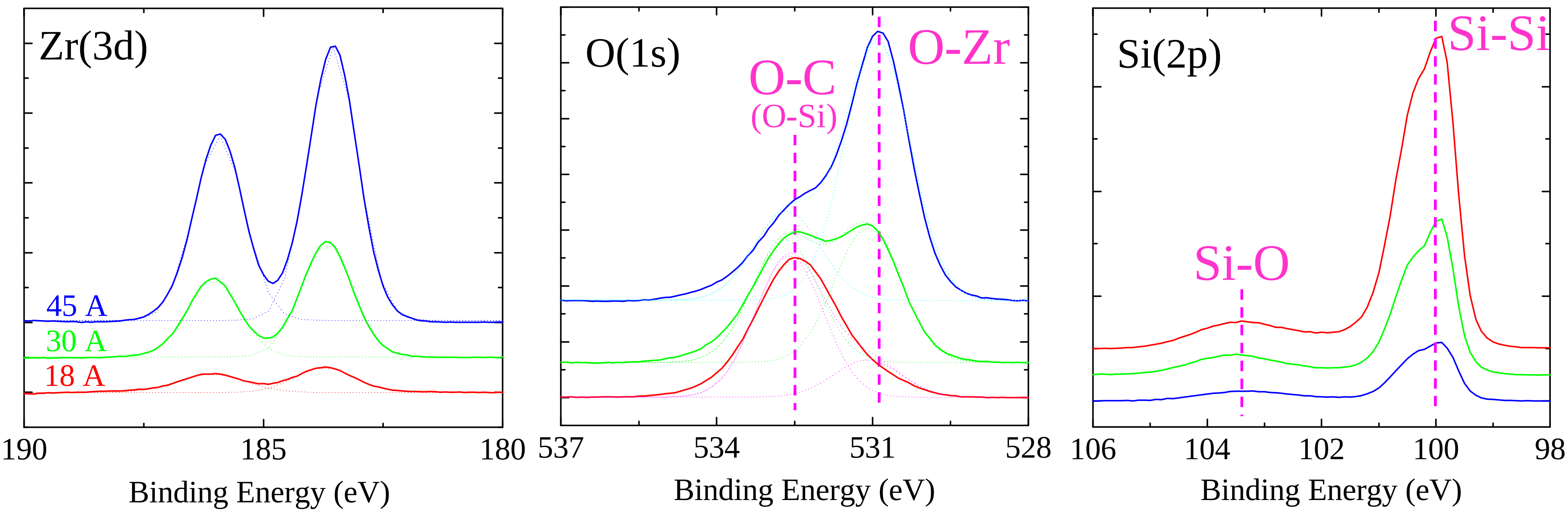


- Index of refraction ~ 2.1 (consistent with literature values)

Chemical States Analysis

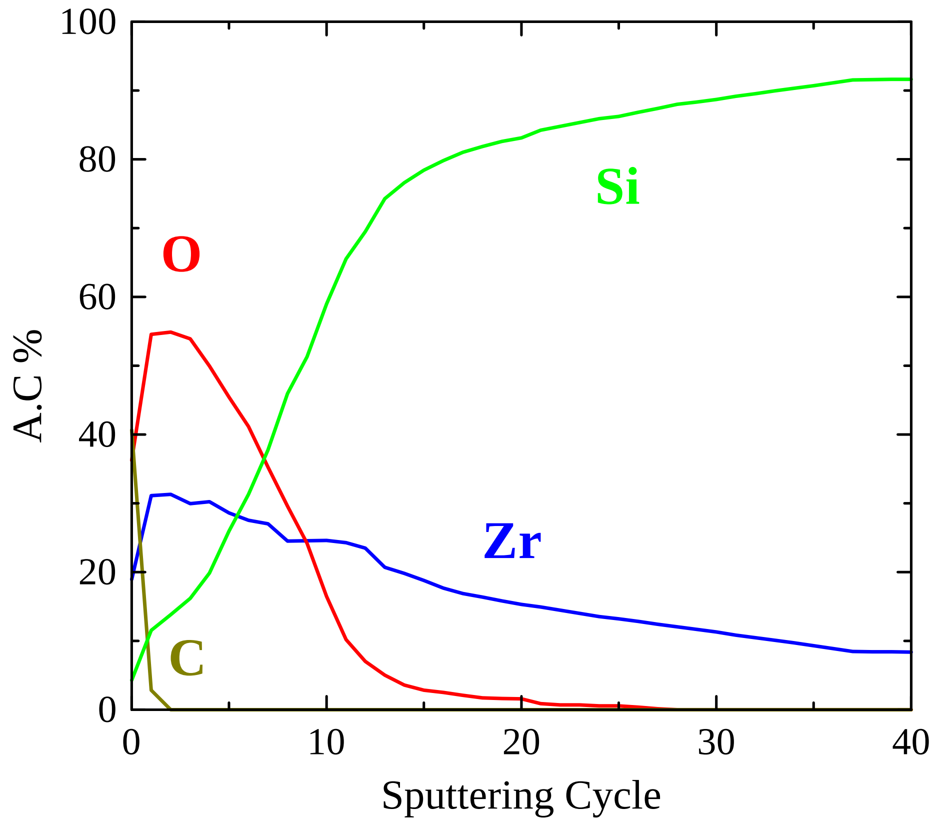


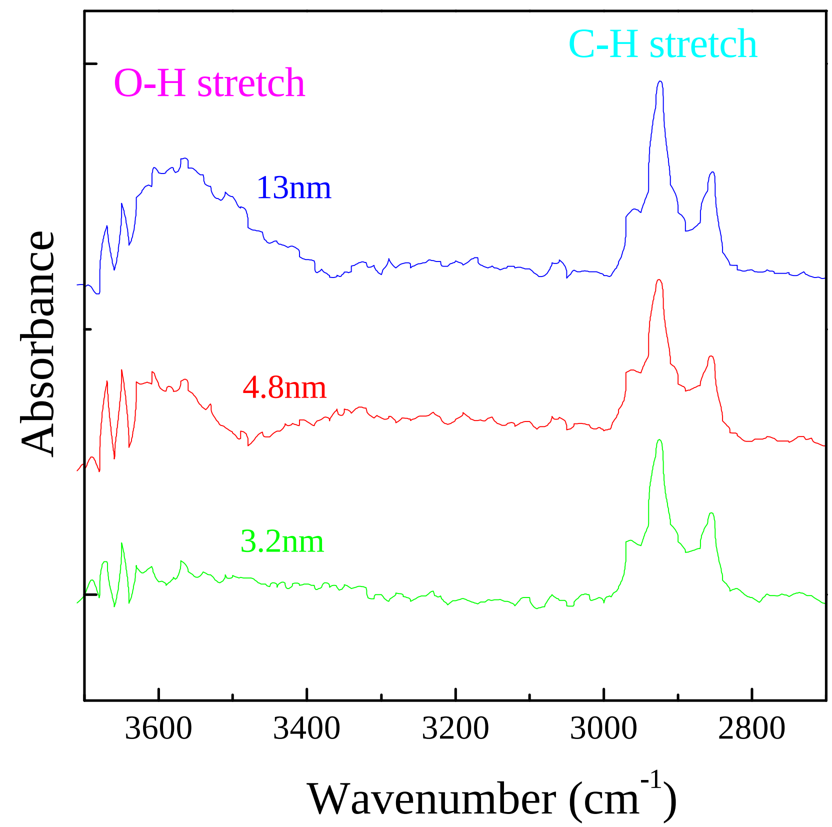




- Stoichiometric ZrO_2 deposited with some carbon incorporation

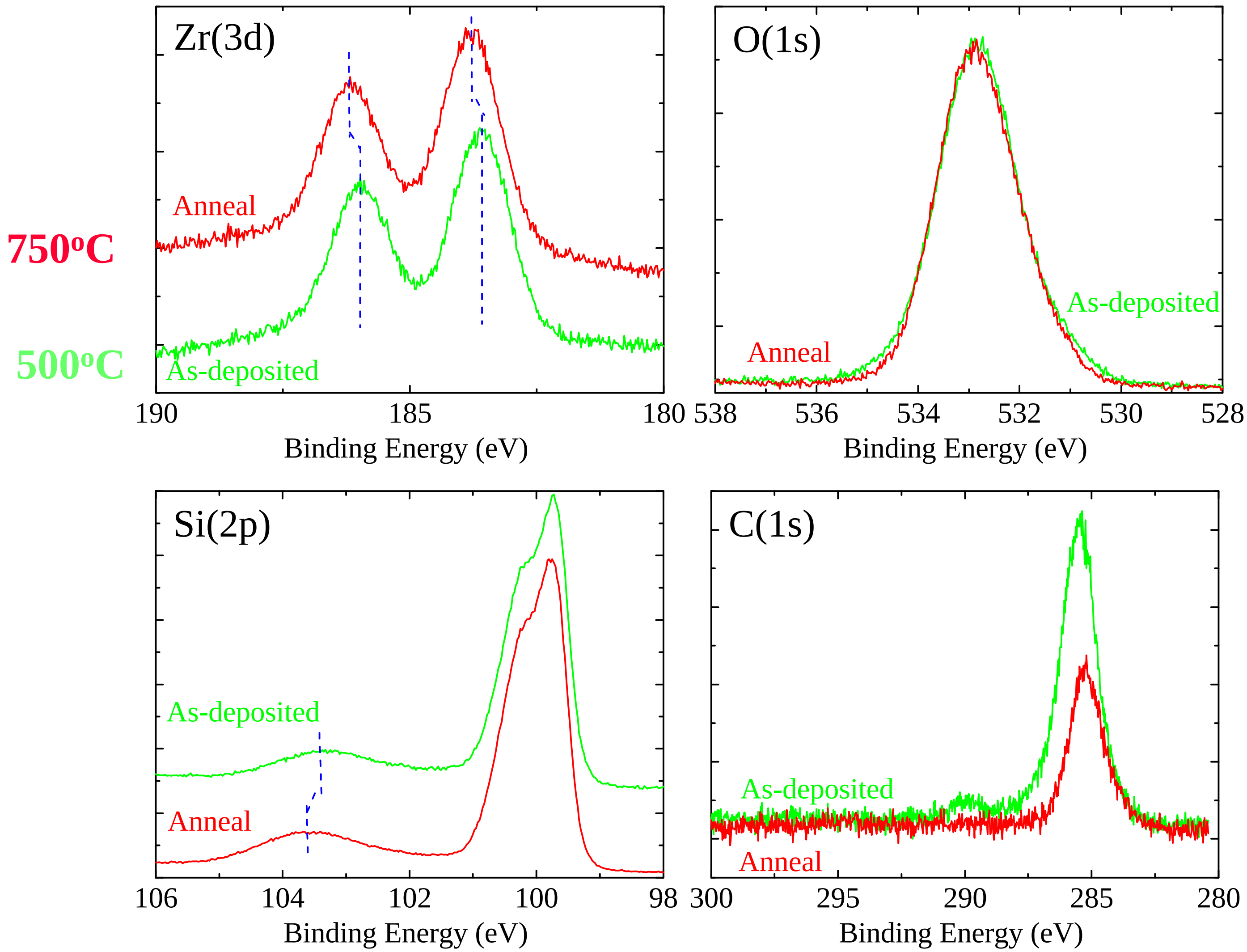
Single Transmission IR Analysis





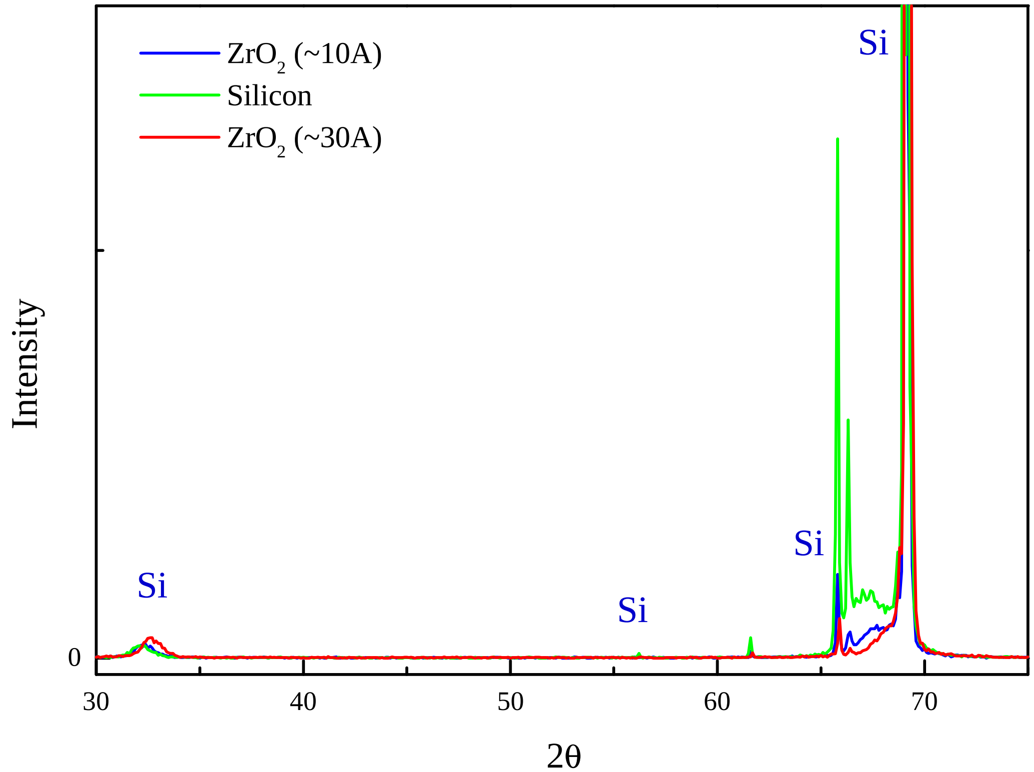
- O-H stretching vibration (3200-3700 cm^{-1}) scaled linearly with film thicknesses
- C-H stretching vibration (2920 cm^{-1}) was invariant with film thicknesses
- Most hydrocarbons were due to air exposure

Thermal Stability of ZrO_2

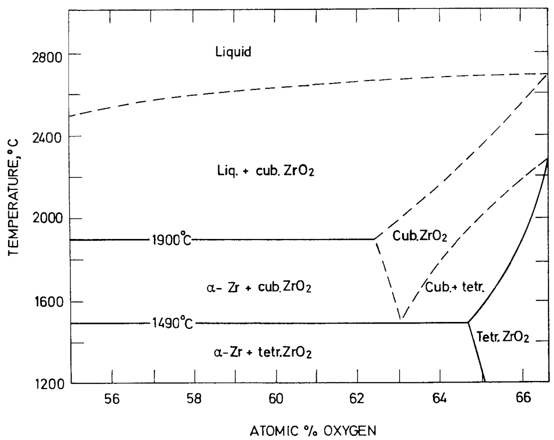


- Good thermal stability with carbon reduction at high temperatures

X-ray Diffraction

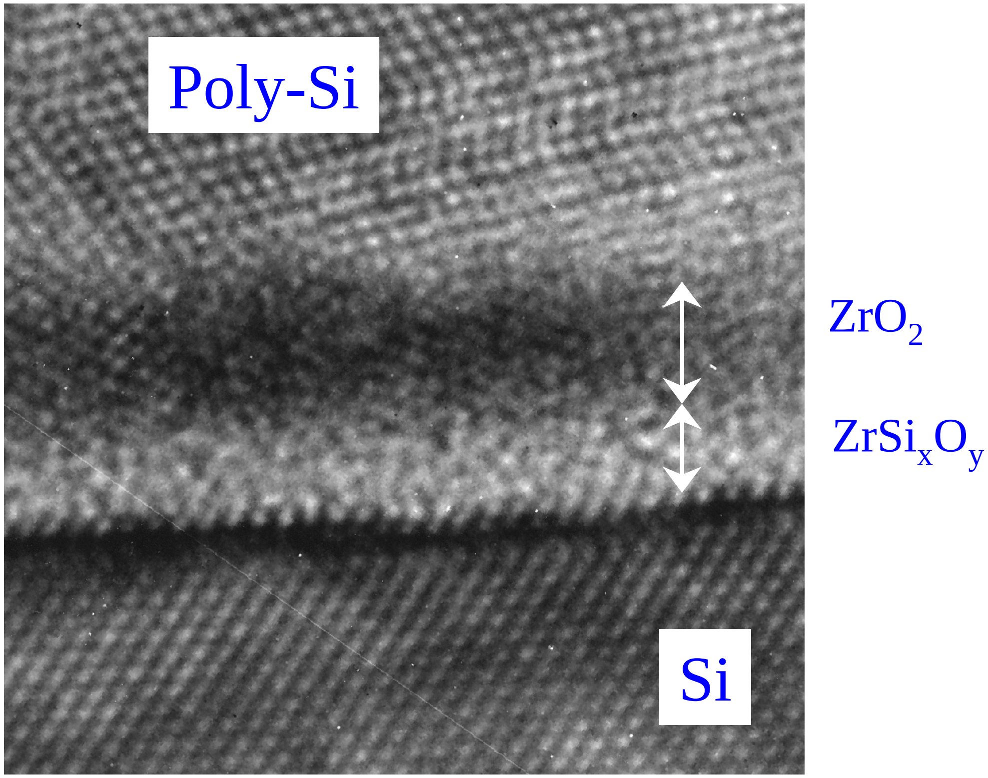


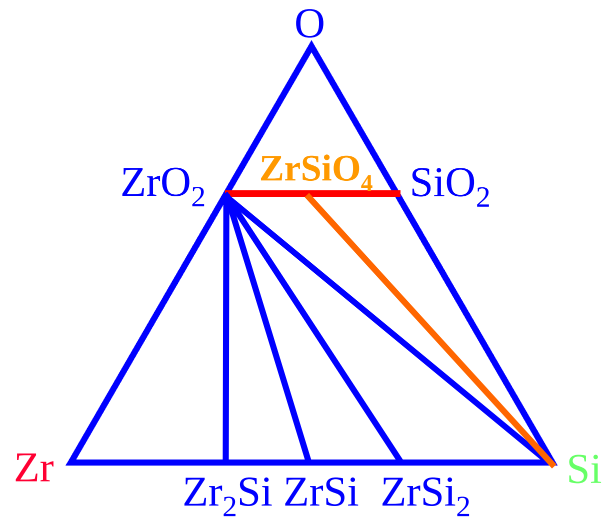
Phase	Space Group	Lattice Parameters (nm)
α Zr	Hexagonal	a=0.32312 c=0.51477
β Zr	Cubic	a=0.36090
α ZrO_2	Monoclinic	a=0.59169 b=0.5232 c=0.5341 β=99°15
β ZrO_2	Tetragonal	a=0.361 c=0.527
γ ZrO_2	Cubic	a=0.510



- Amorphous ZrO_2 films deposited
- (Crystalline ZrO_2: cubic, monoclinic, tetragonal)
- No re-crystallization observed at 750°C

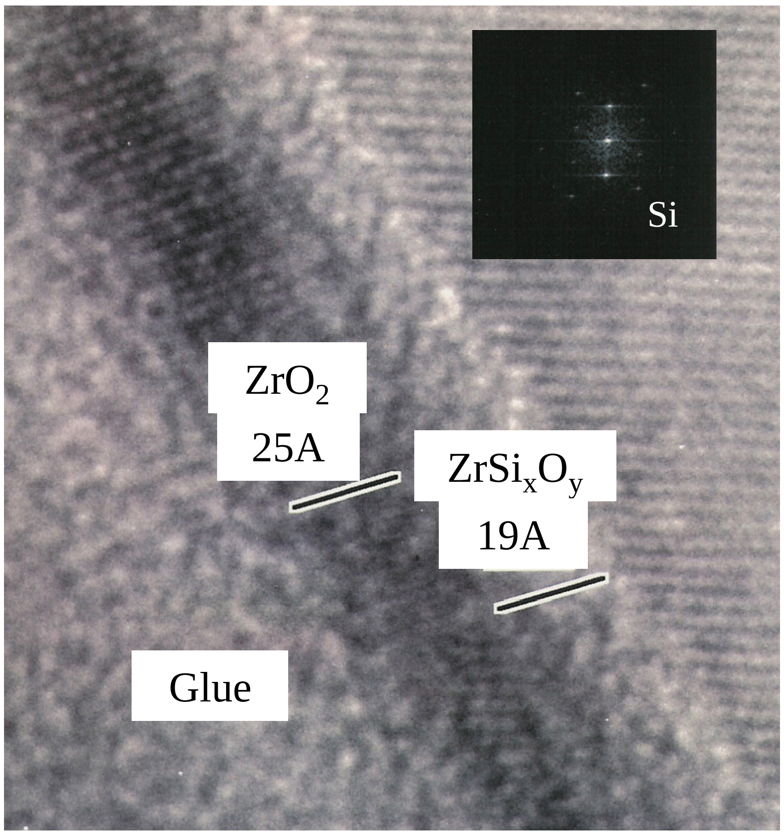
Interfacial Layer Formation

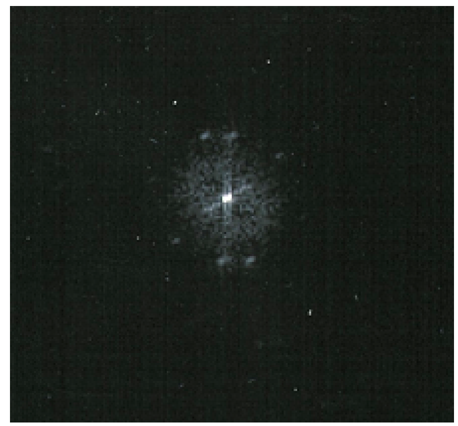


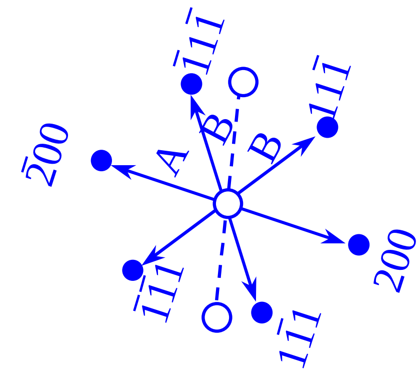


- Poly-silicon capped ZrO_2 thin film
- $ZrSiO_4$: thermally stable and chemically inert

High Resolution TEM



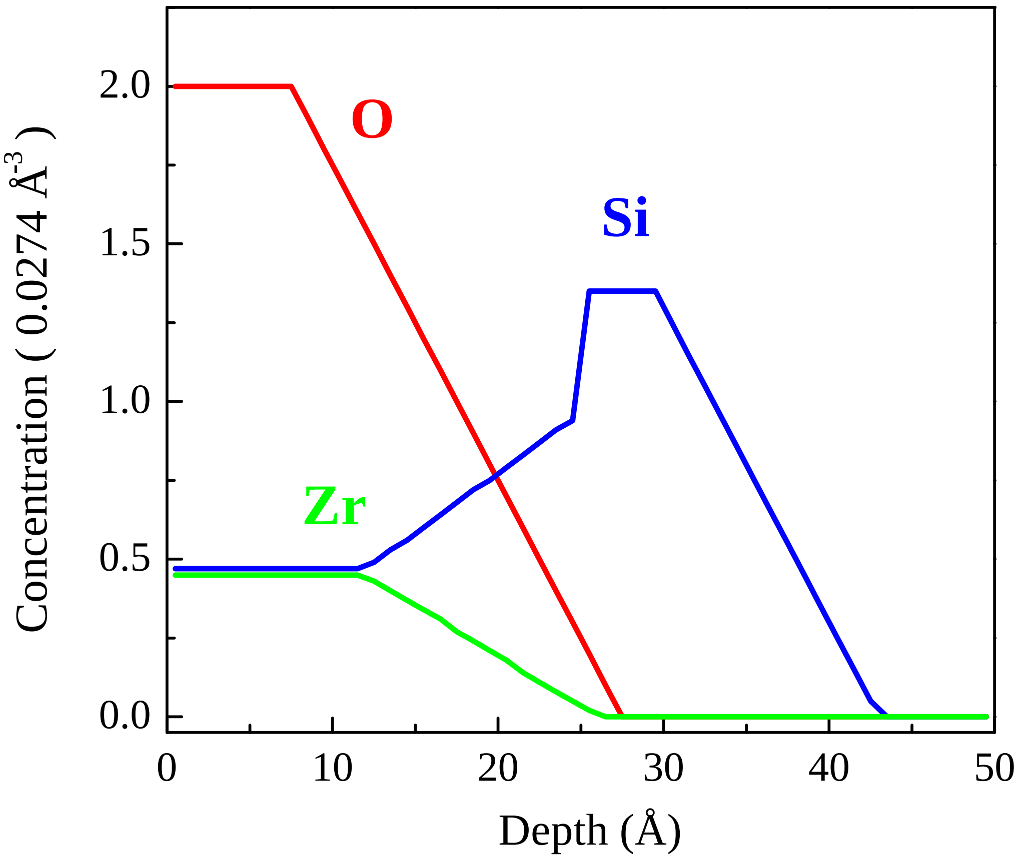


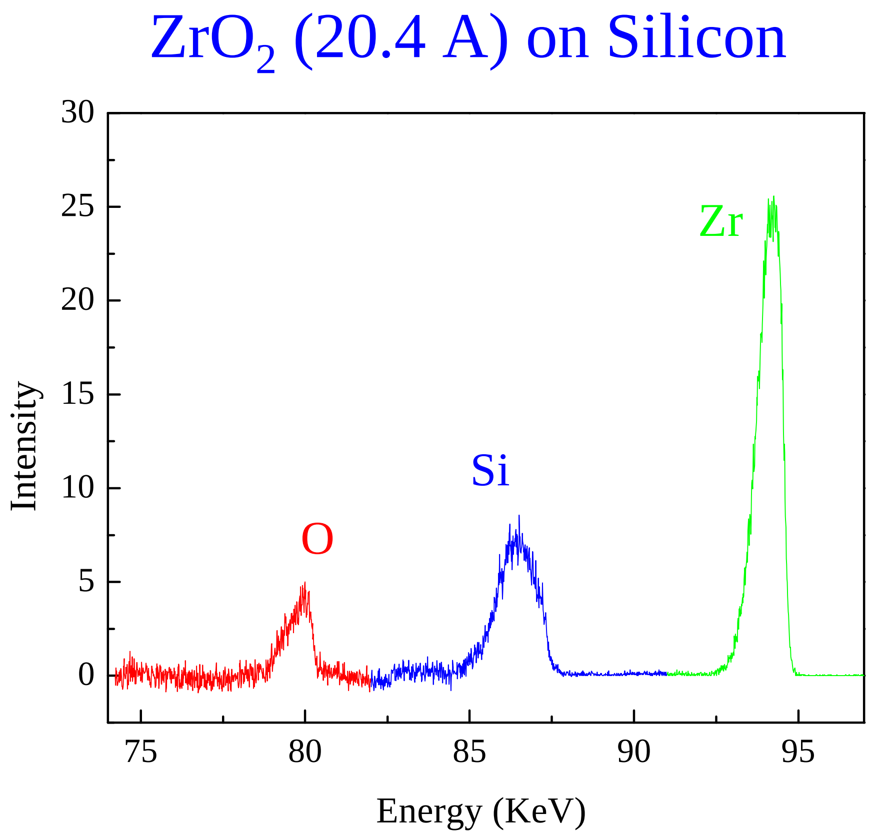


$$\frac{A}{B} = \frac{2}{\sqrt{3}} = 1.155 \qquad B = z = [011]$$

- **Interfacial layer exists between Si and ZrO_2**
- **Monoclinic ZrO_2 and amorphous $ZrSiO_4$**

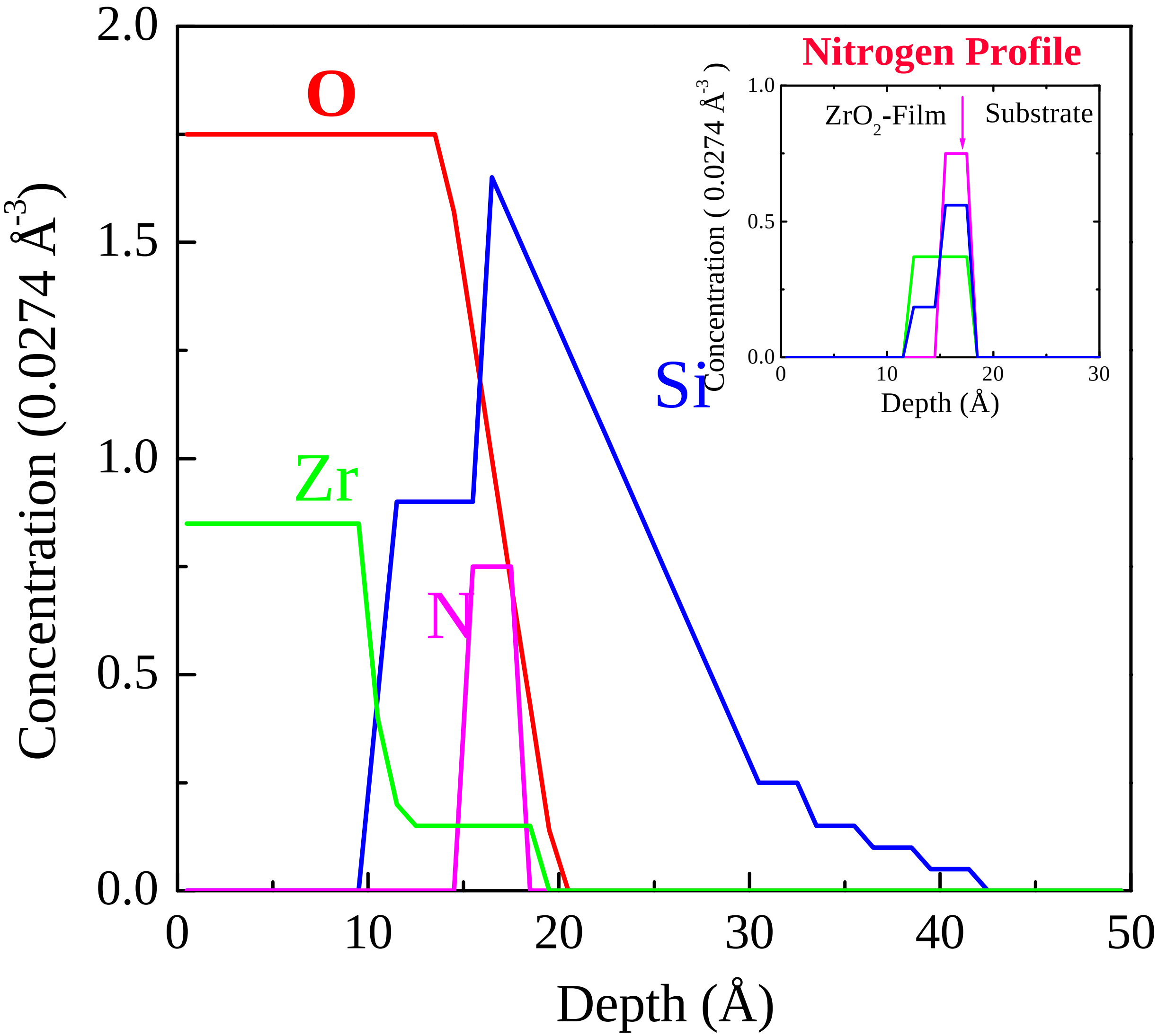
MEIS Composition Profiling



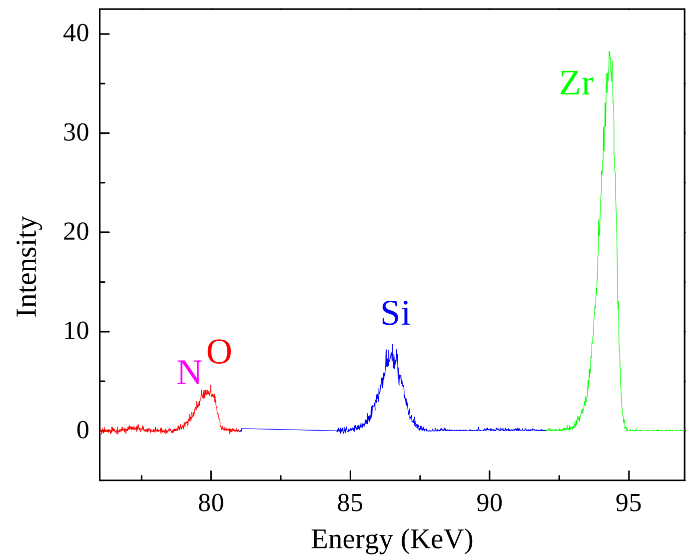


- 100keV H+ (thickness agrees with ellipsometry measurement)
- Significant mixing at the interface

SiN Interfacial Barrier



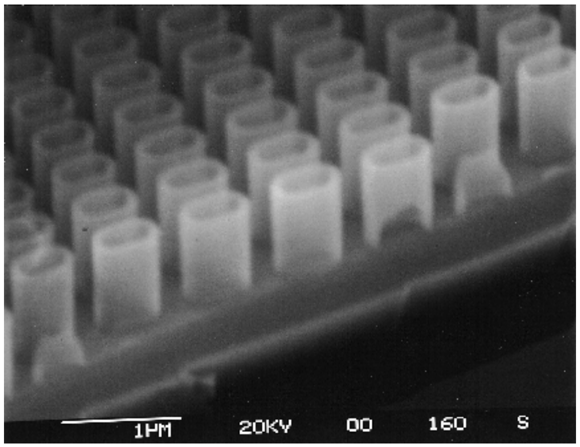
ZrO$_2$ /SiN (19 A) on Si



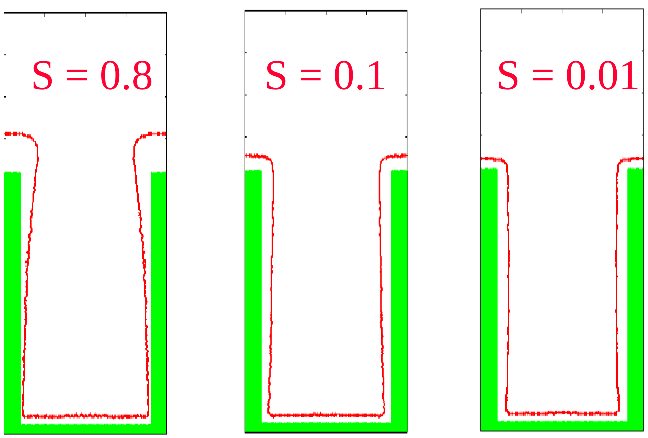
- SiN reduces interfacial reactions
- Total nitrogen content ~ 1ML

Excellent Step Coverage

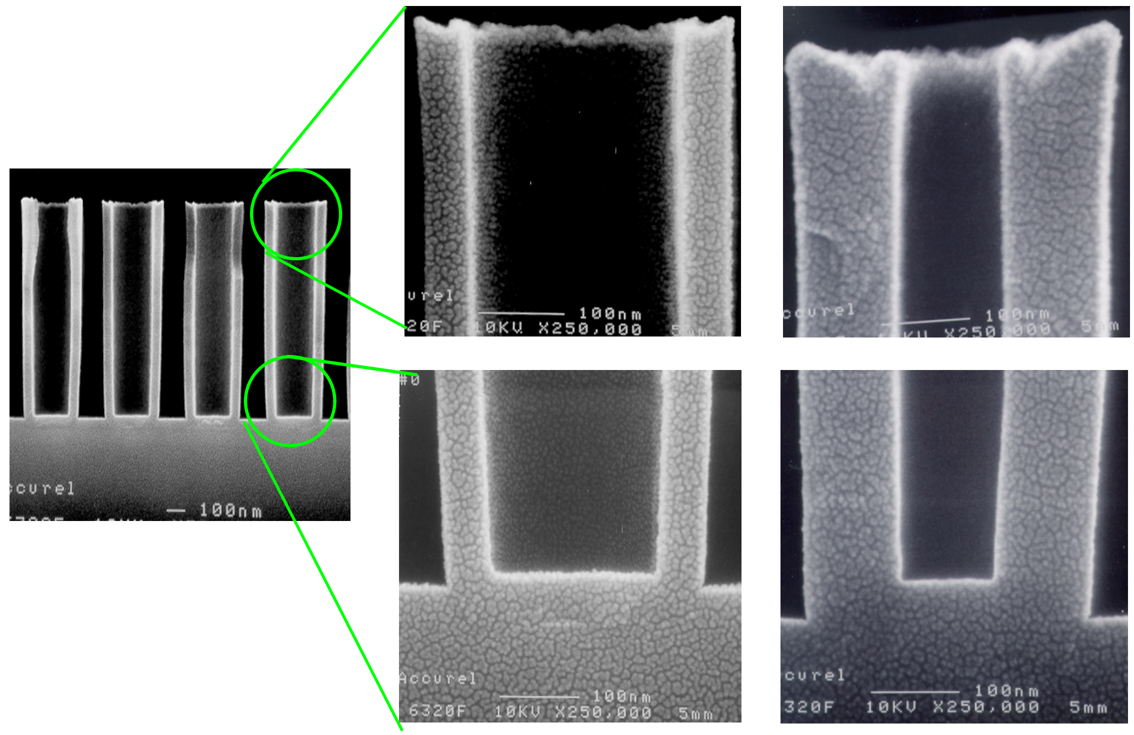
High Aspect Ratio Nano-Cylinders



Monte Carlo Simulation

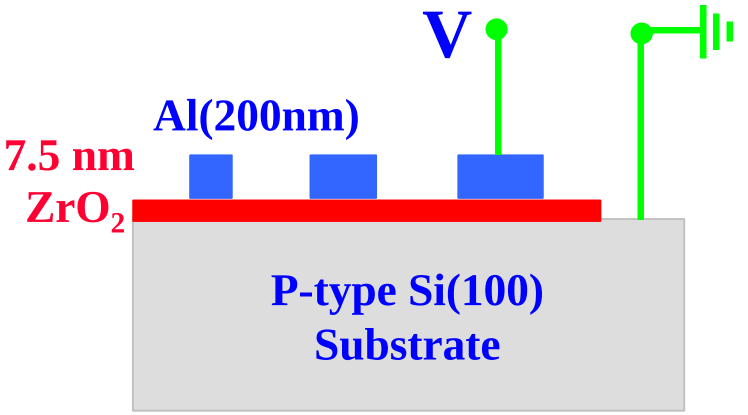


No Deposition **ZrO_2 Deposition**

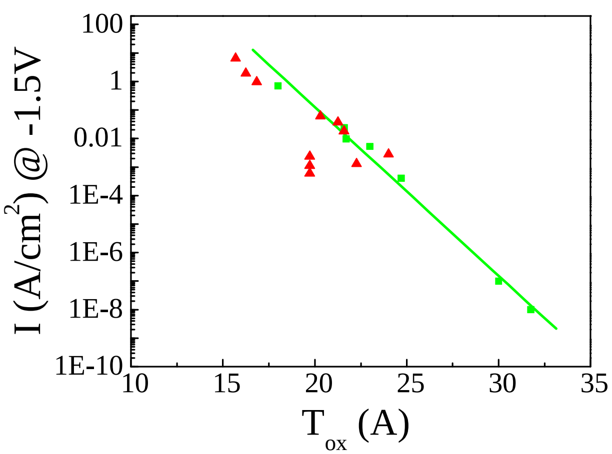


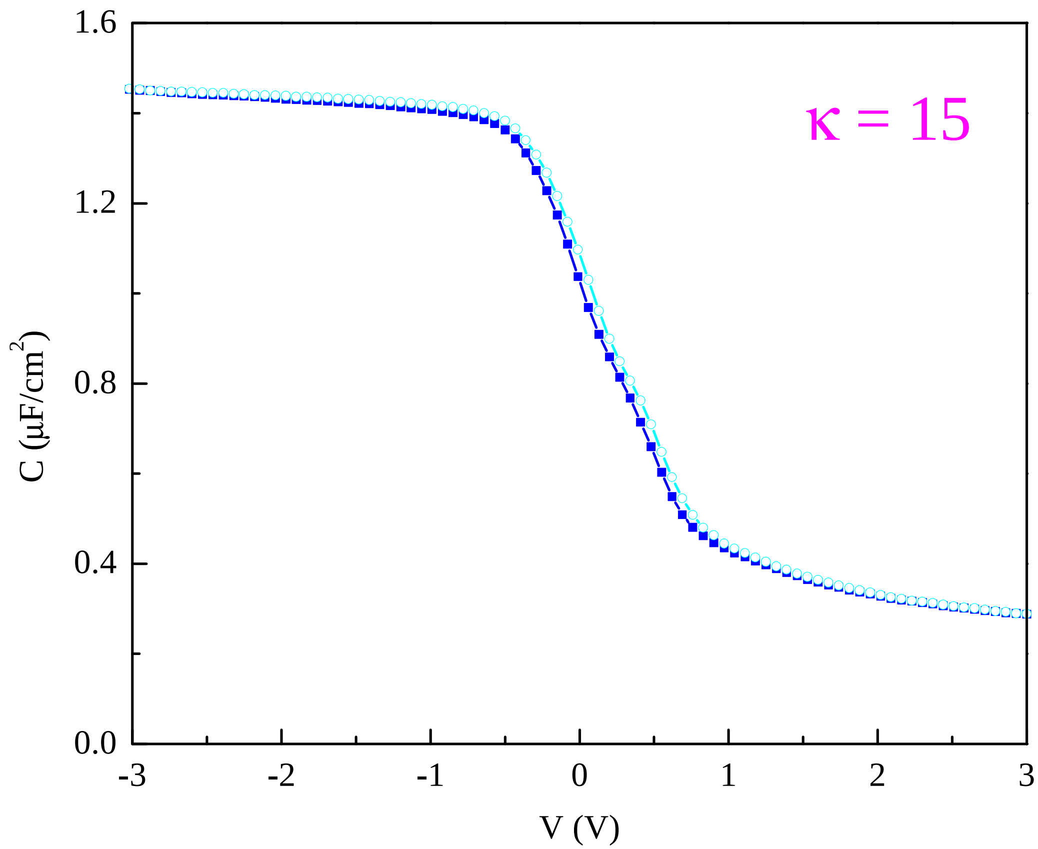
- Highly uniform thin film deposited over memory cells!
- Simulation verifies conformality vs. reactant sticking coefficients

MOS Capacitors



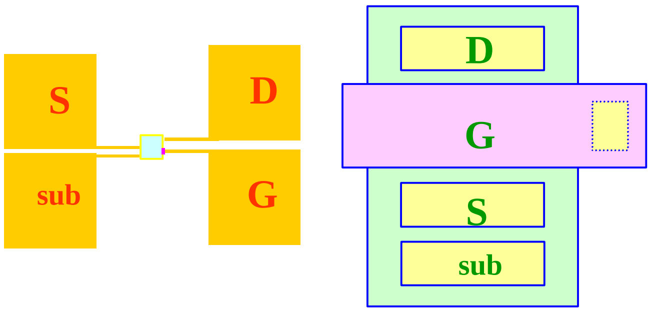
Capacitor area : $1x10^{-4}$ - $4x10^{-4}$ cm^2

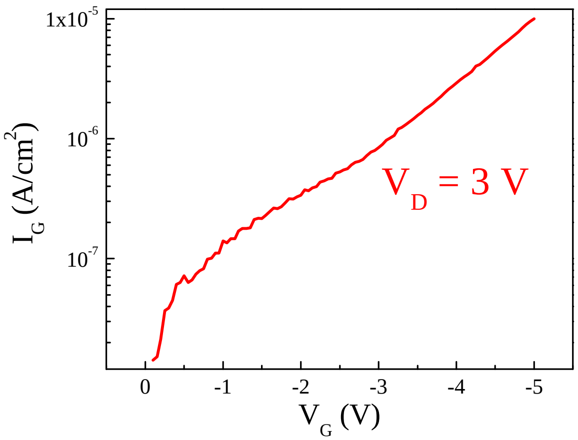


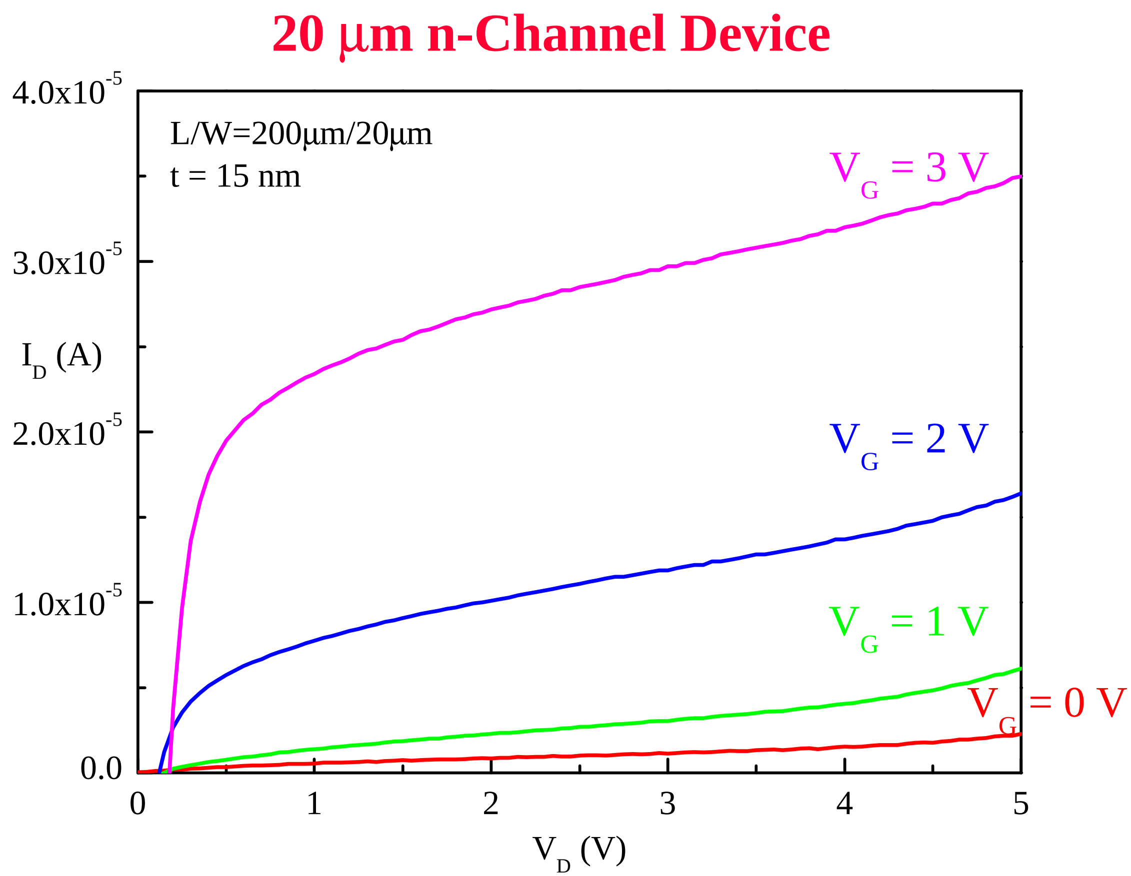


- Effective dielectric constant = 15 (1 MHz)
- Small hysteresis and low leakage current

NMOSFET Devices







- Device Dimensions: W = 100 µm; L = 1, 2, 4, 8, 12, 20, 100 µm
- No threshold adjustment
- Low leakage current obtained: 2×10^{-7} A/cm^2 @ 1.5 V
- No obvious breakdown at –5V

Summary

- Amorphous and stoichiometric ZrO_2 deposited by RTCVD
- Dielectric constant and index of refraction are 15 and 2.1, respectively
- Interfacial $ZrSiO_4$ poses challenges in device integration
- High breakdown field and low leakage current obtained for ZrO_2 based MOSCAP and NMOSFET devices
- RTCVD and etching are critical to the utilization of novel dielectric materials

Acknowledgement

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- Professor Rick Garfunkel, Rutgers University
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