ELECTRICAL AND PHYSICAL CHARACTERIZATION OF GATE STACKS AND INTERFACES

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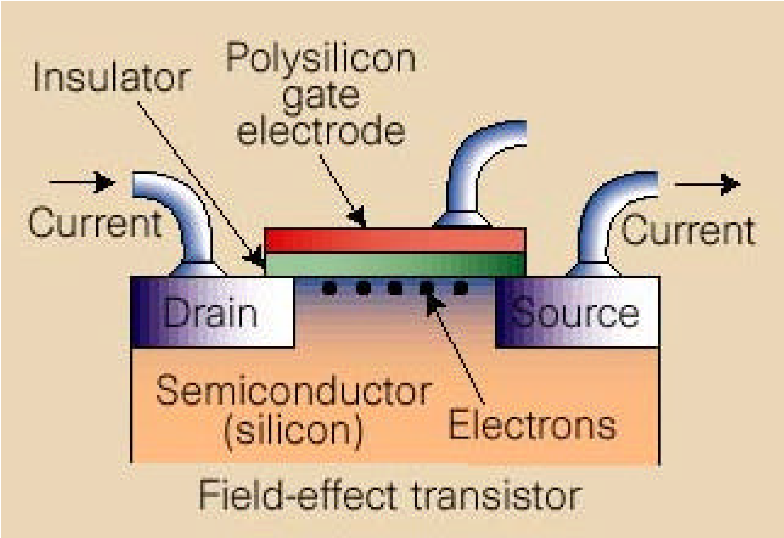
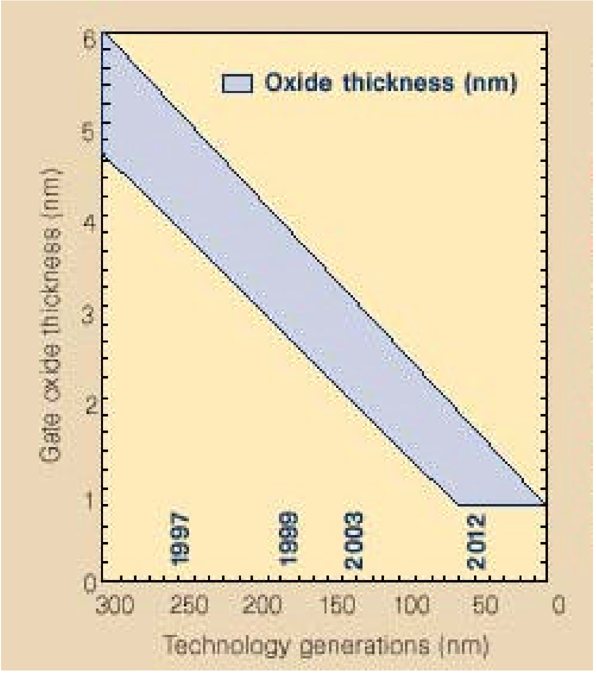
OUTLINE

- Introduction to *alternate* gate dielectrics
- Growth of ultra-thin dielectric films by UV-ozone oxidation
- Physical and Electrical Characterization of dielectric stacks
- Structure-Property Relations
- Summary

ALTERNATE GATE DIELECTRICS FOR CMOS DEVICES



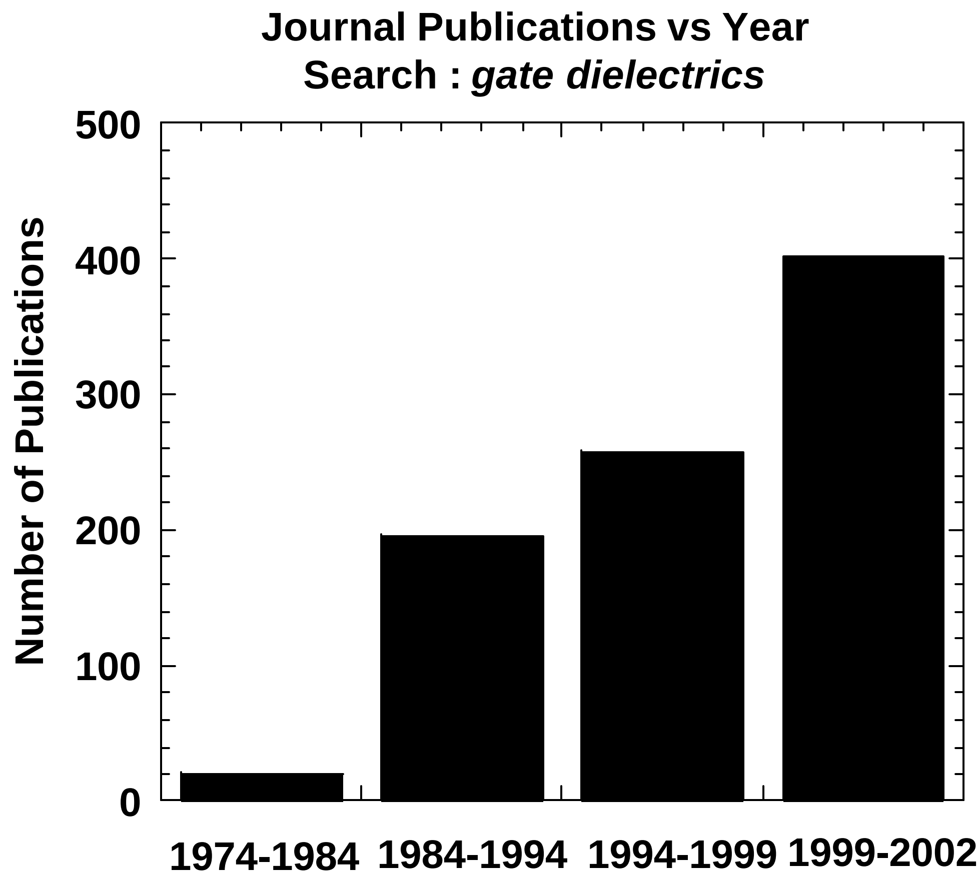


Schulz, *Nature*, 1999

Need to scale gate dielectric thickness for future CMOS devices

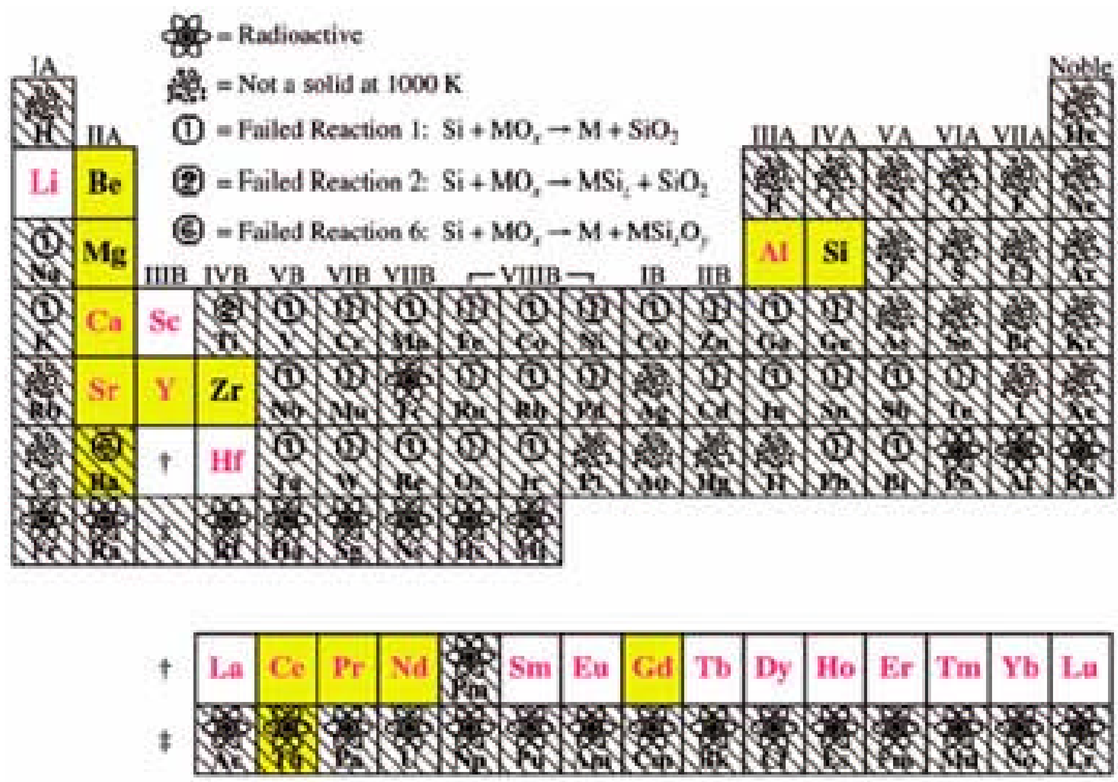
Some issues with SiO_2: high leakage current, boron penetration, etc.

Hence, replace SiO_2 with higher-k dielectric to get similar electrical thickness, (EOT) $t_{eq} = (t_{high\text{-}k} / k_{high\text{-}k}) k_{SiO2}$



Shriram Ramanathan, Stanford University, *2002*

Stability of oxides on Si



• Oxides of **Zr**, Hf, Gd etc. are predicted to be stable directly on Si (R. Beyers, *PhD thesis*, Stanford, 1989, Schlom et al. *MRS Bull*. 2002)

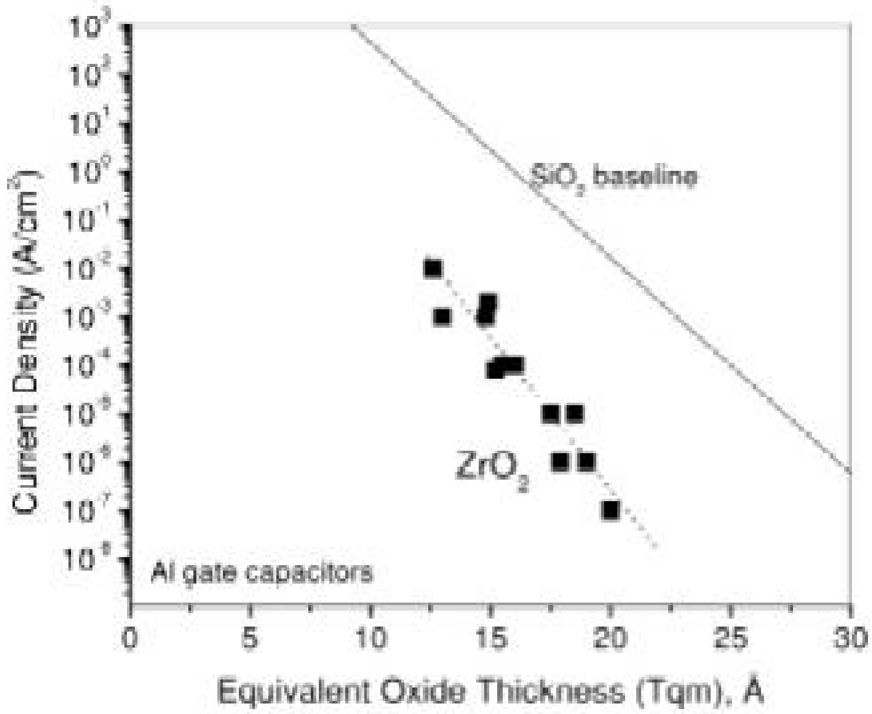
• Necessary to avoid interfacial layer formation, silicidation etc.

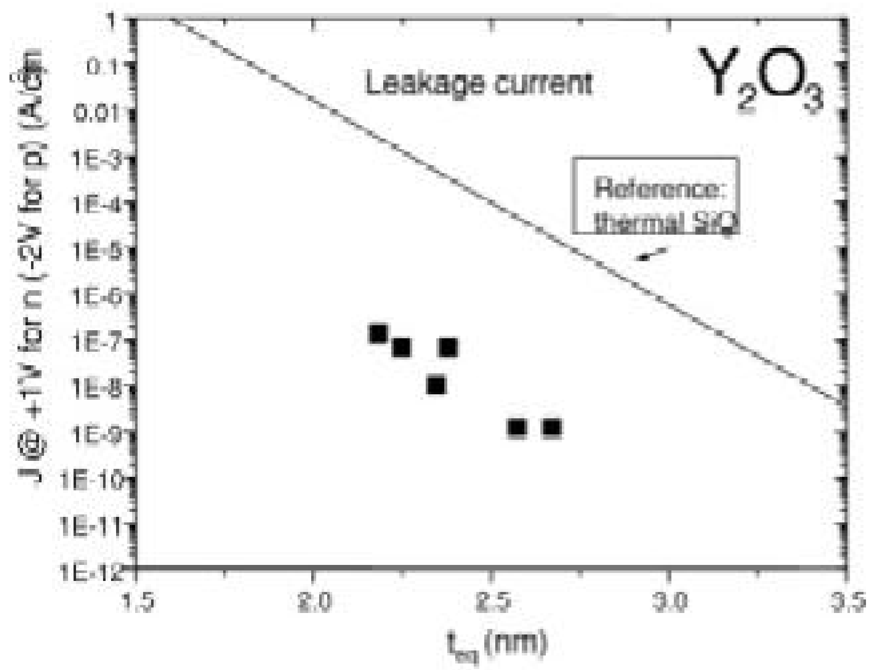
KEY ISSUES IN GATE DIELECTRICS RESEARCH

- Desire alternate gate dielectric with high *e* on Si with low EOT (~ 1 - 1.5 nm)
- Choice of gate dielectric material : ZrO_2, HfO_2, Gd_2O_3, $ZrSiO_x$, $HfSiO_x$, etc.
- Deposition methods : ALD, Sputtering, Oxidation, etc.
- Interfacial layers between high-k and Si
- High temperature stability of dielectric stacks

- Characterizaton methods !

EOT versus leakage current: SiO_2 versus high-k





Gusev et al. *Microelec*. *Eng*. 2001

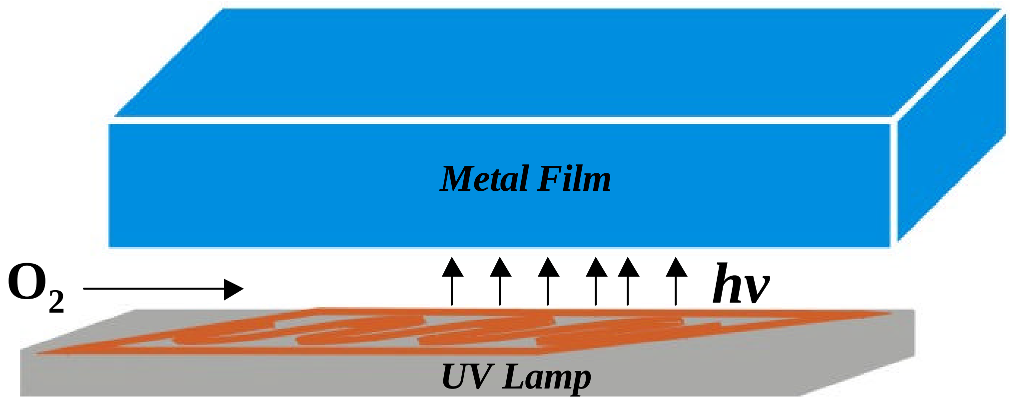
These are crystalline oxides !

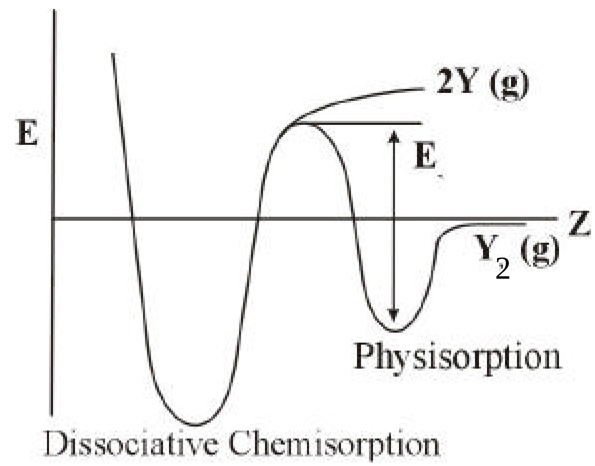
GOALS

- Develop the method of UV-ozone oxidation to grow ultra-thin metal-oxide films
- Structural and chemical characterization of dielectric stacks and interfaces at the atomic scale
- Study the relation between oxidation kinetics and electrical performance

GROWTH OF THIN METAL-OXIDE FILMS BY UV - OZONE OXIDATION

- Sputter metal film on suitable underlayer at R.T.
- Oxidation performed by *in-situ* exposure of metal film to O_2 in presence of UV light





- UV light interacts with oxygen and leads to the following reactions:

$O_2 + h\nu \longrightarrow 2O$ **(l = 185 nm)**

$O + O_2 \longrightarrow O_3$

$O_3 + O \longrightarrow 2O_2$

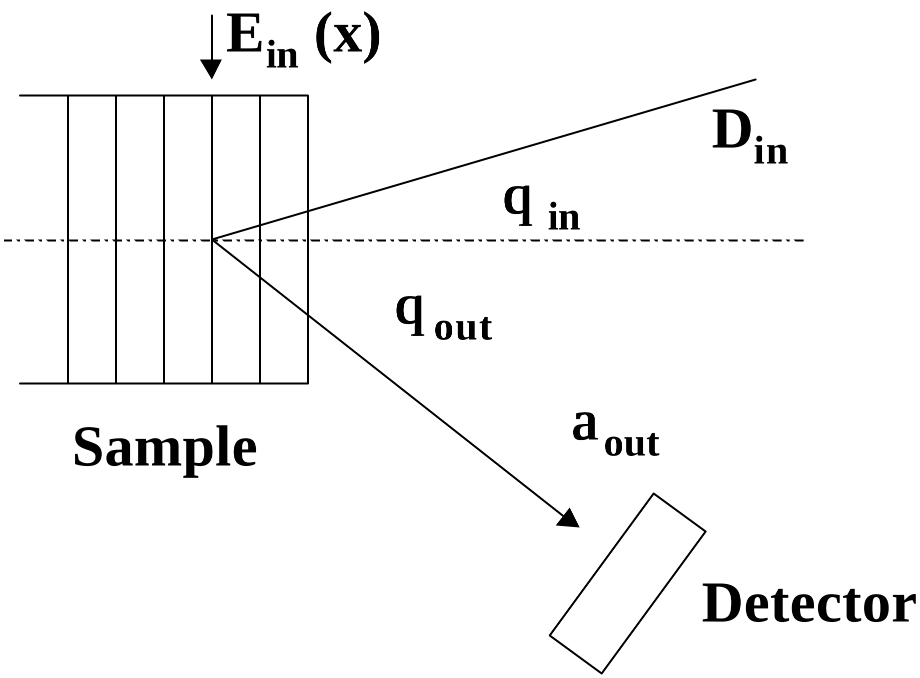
$O_3 + h\nu \longrightarrow O_2 + O$ **(l = 254 nm)**

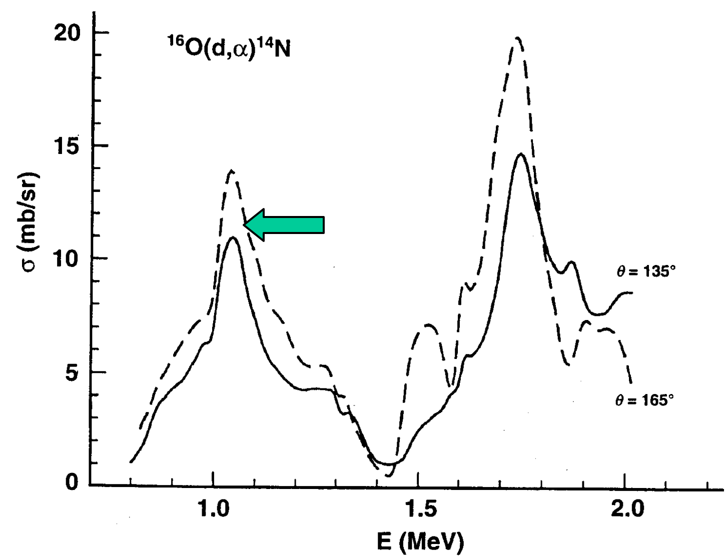
- No activation energy need for creation of atomic oxygen (Adamson, *Physical Chemistry of Surfaces*)

Shriram Ramanathan, Stanford University, *2002*

STUDYING THE OXIDATION KINETICS

- Use ^{16}**O (d,a)** ^{14}**N** nuclear reaction to investigate oxygen concentration in the sample
- Sensitive to sub-monolayer of oxygen, can calculate oxide thickness with high accuracy[1]





Tesmer and Nastasi, *Handbook of Ion Beam Analysis*

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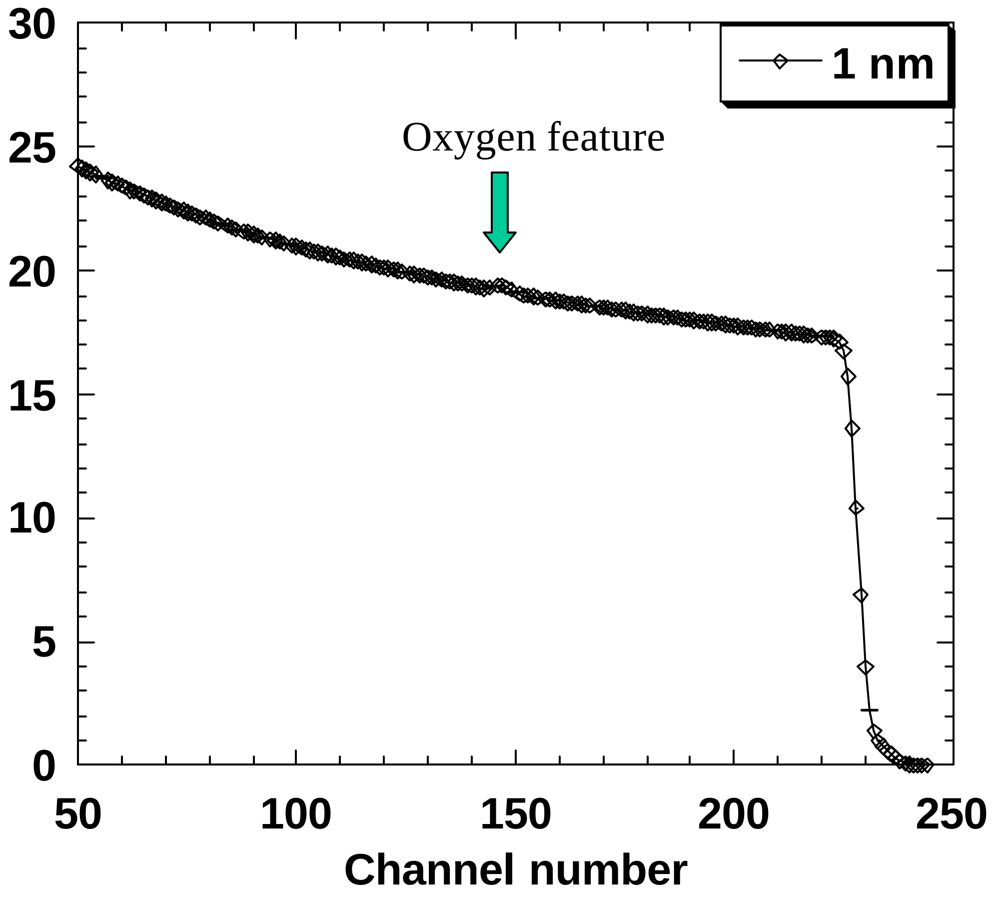
1. Turos et al., *NIM B*, **111** (1973), 605

Simulated RBS spectrum from 1 nm SiO_2 film on Si

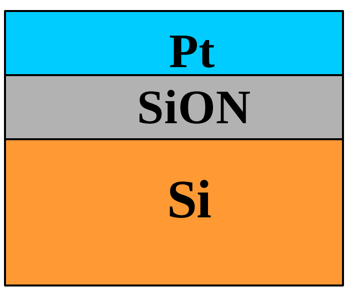


Quantitative analysis of oxygen concentration difficult !

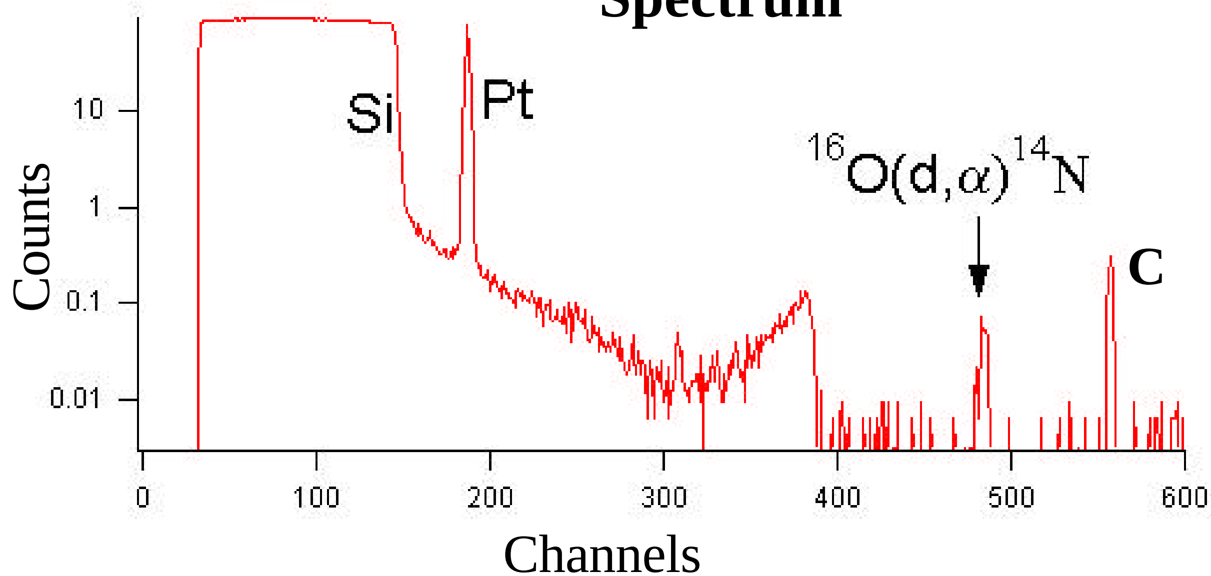
BACKSCATTERED SPECTRUM

- Oxygen peak well separated from Rutherford backscattered peaks
- Oxygen concentration (in *at/cm^2*) can be calculated from the integrated peak area for **^{16}O (d,a) ^{14}N** reaction

Film Structure



Spectrum



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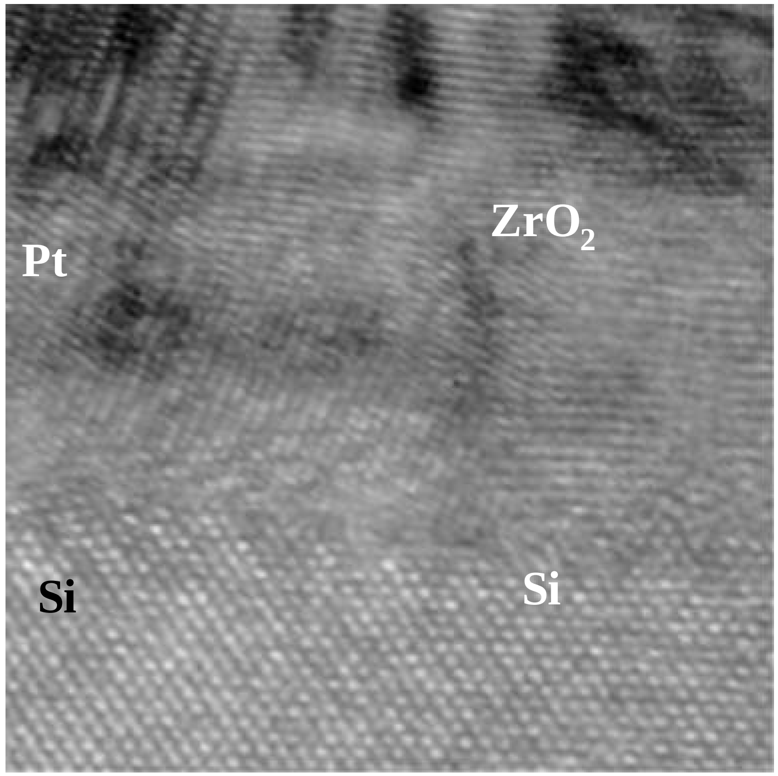
NRA Oxide Thickness Measurements *contd.*

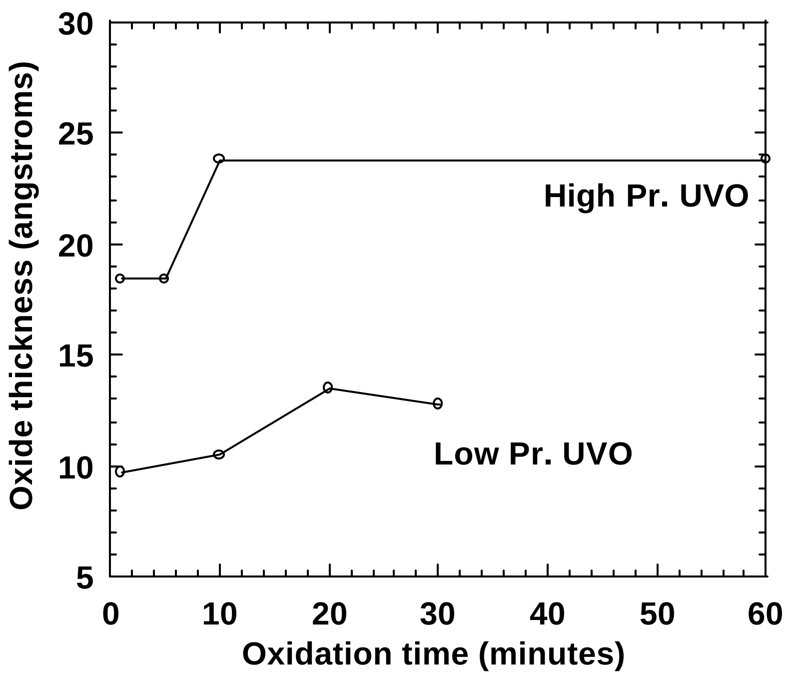
HF-last Si



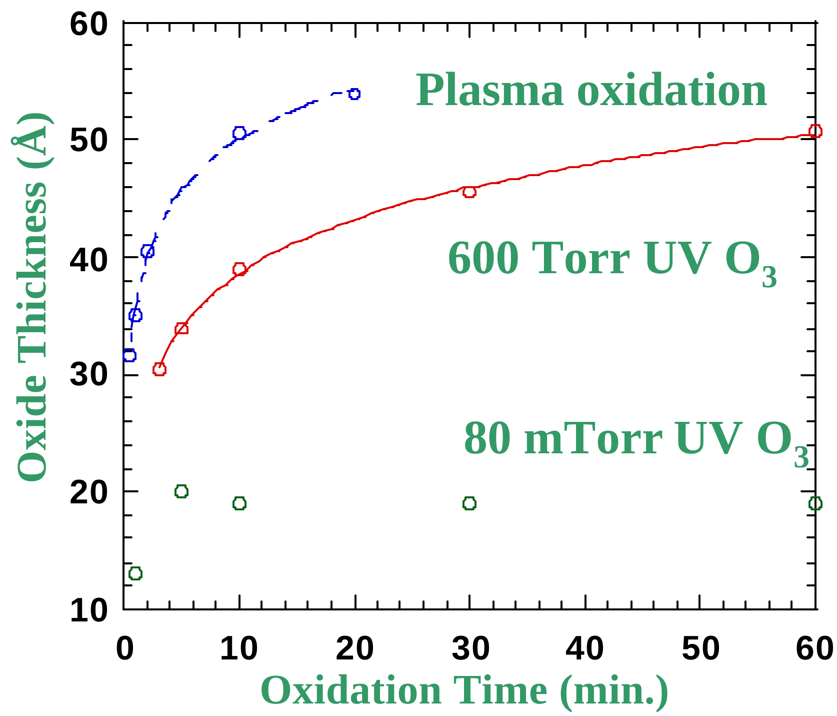
$(Nt)_{SiO2}$ = 9.8 x 10^{14} at./cm^2
Calc. physical thickness ~ 2 Å

OXIDATION KINETICS OF Al and Zr FILMS

- Oxidation rate significantly higher compared to natural oxidation for both Zr and Al films
- Self-limiting oxide growth for ozone oxidation at low pressures
- Room temperature oxidation leads to crystalline ZrO_2



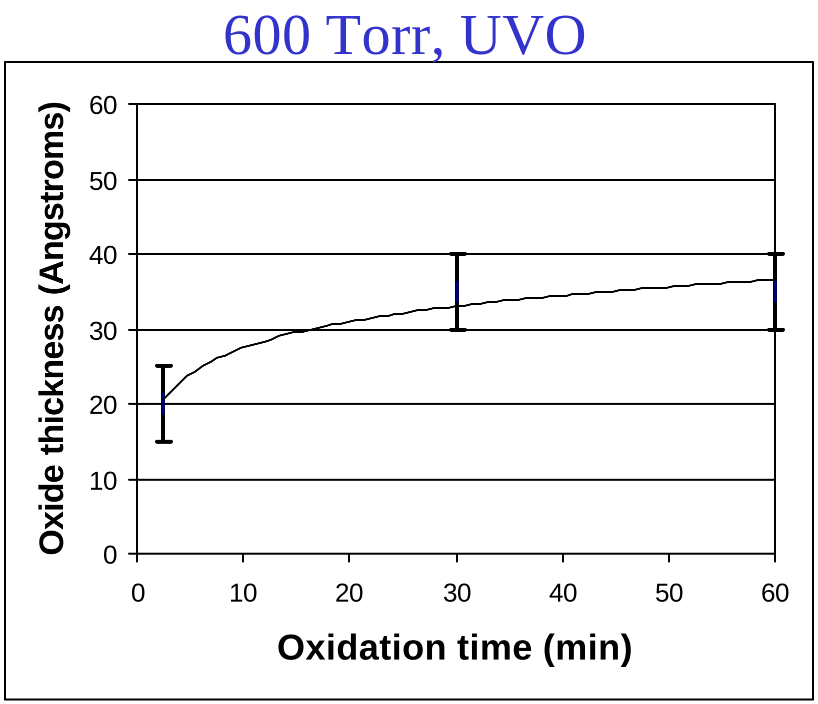
Oxidation of Al films at R.T.

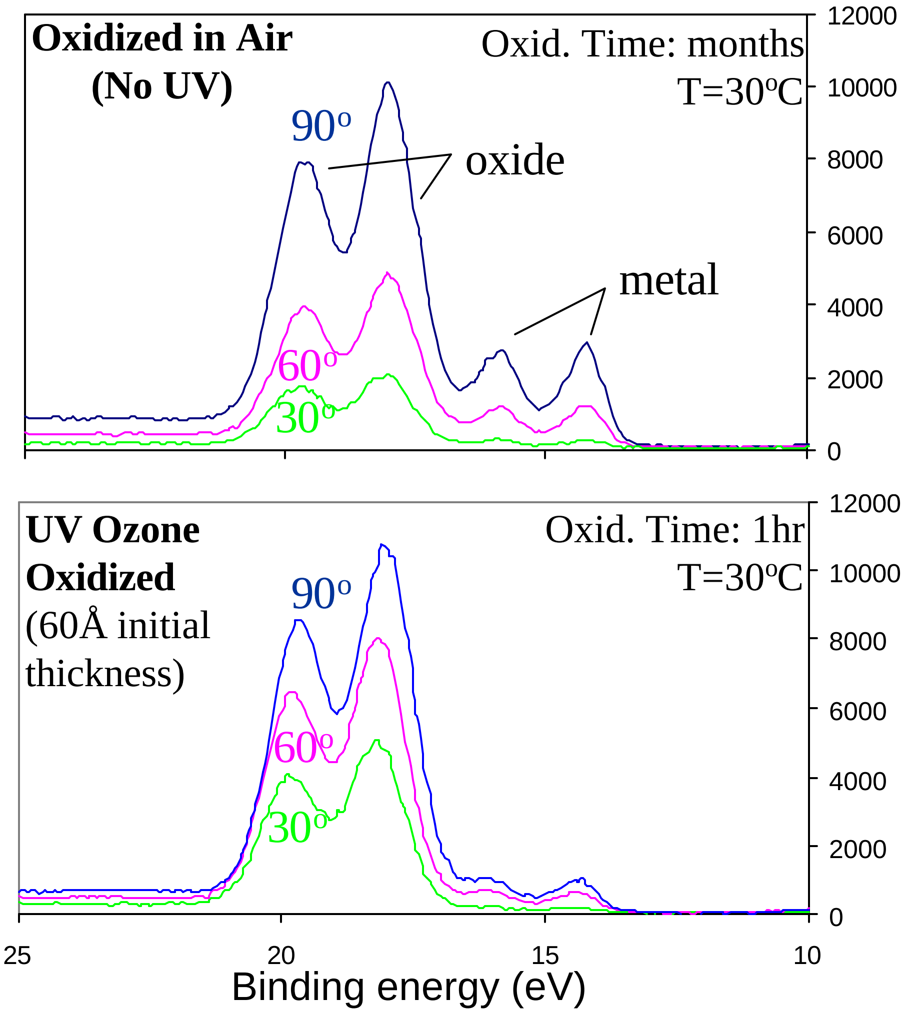


Oxidation of Zr films at R.T.

Shriram Ramanathan, Stanford University, *2002*

Oxidation kinetics of thin film Hf
(Results from David Chi, unpublished)





Lower than Zr UVO oxidation rate !

Shriram Ramanathan, Stanford University, *2002*

Interfacial Roughness: **an important consideration !**

F.H. Baumann, D.A. Muller et al., MRS, 2000)

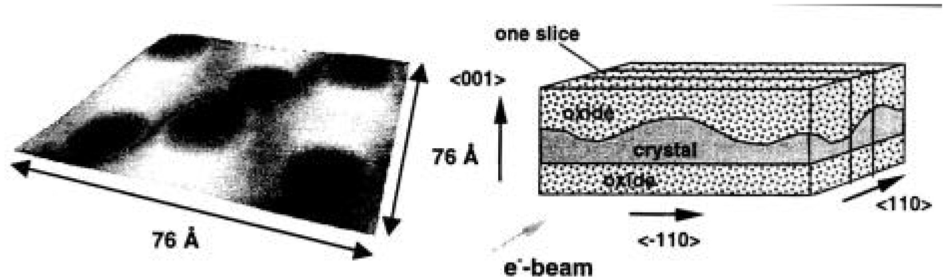
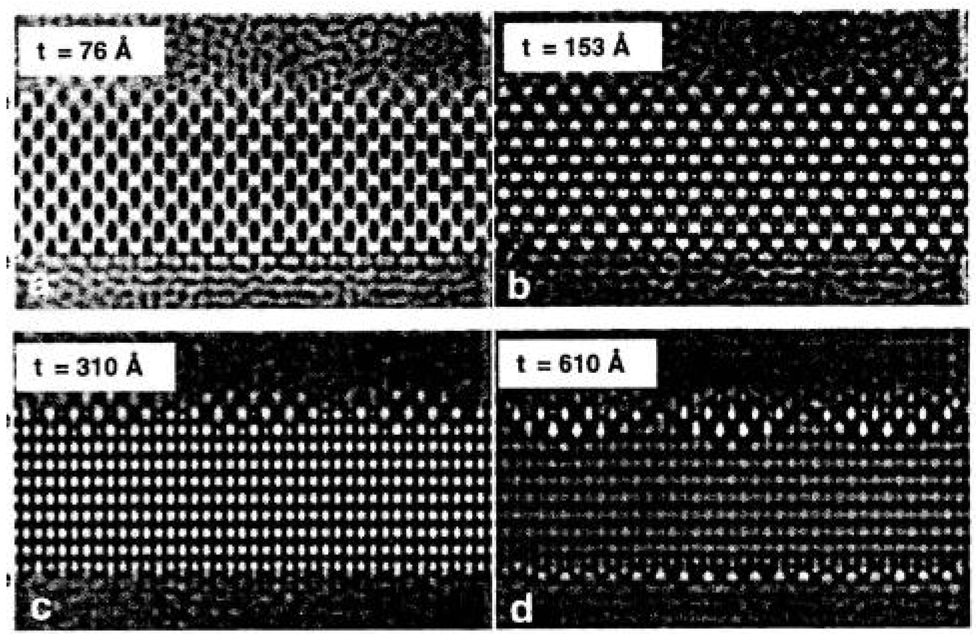
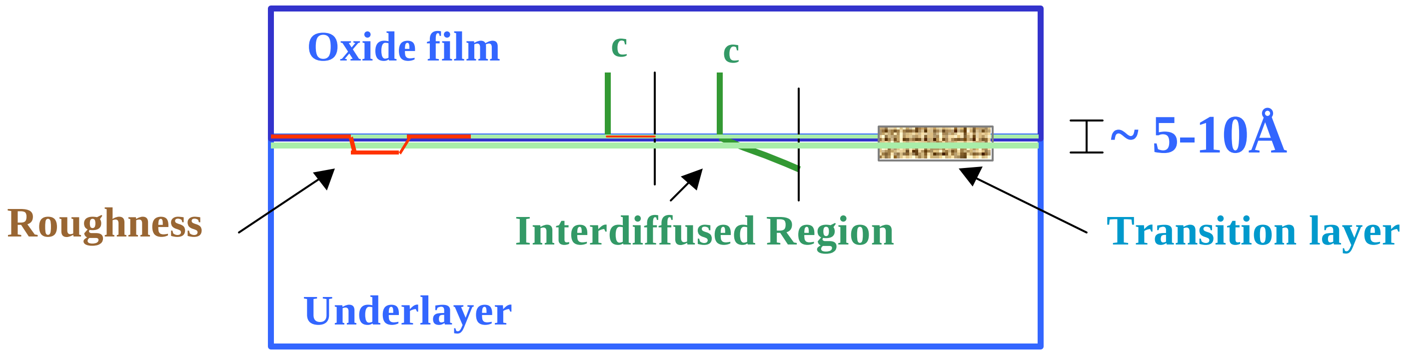


Figure 9. *Final geometry of virtual specimen for image simulation. The sinusoidally rough Si surface builds the top part of a Si slab, which is sandwiched between two 50 Å thick SiO_2 layers. The lower interface is atomically sharp.*

Image simulations



MICROSTRUCTURAL STUDIES



Need to characterize:

- Atomic scale roughness (~ 5-10Å)
- Sub-stoichiometric / Reaction layers (~ 5 - 10Å)

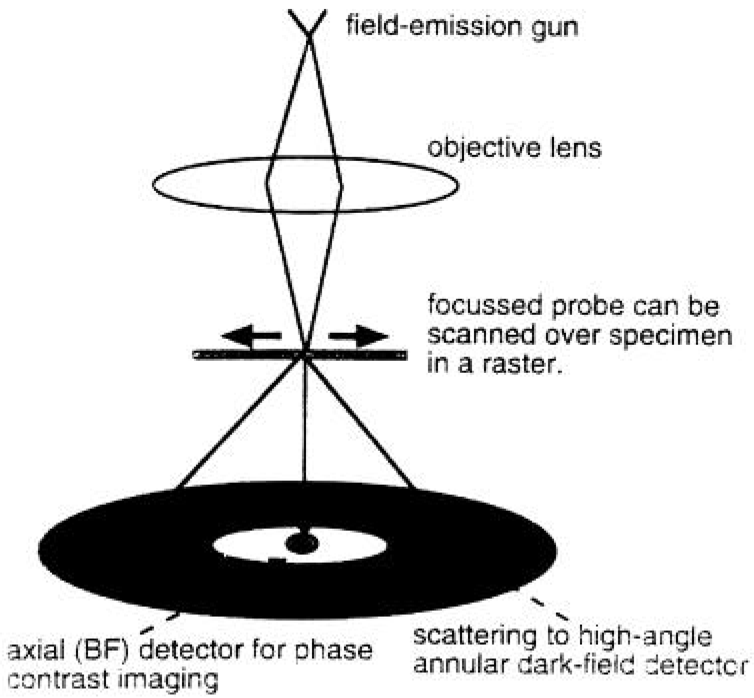
High-Resolution TEM: Phase Contrast

Scanning Transmission Electron Microscopy: Z-Contrast

Electron Energy Loss Spectroscopy: Chemical and Electronic Structure Information (at high spatial resolution)

X-ray Absorption Spectroscopy: Chemical and Electronic Structure Information (at high energy resolution)

SCANNING TRANSMISSION ELECTRON MICROSCOPY (STEM)



- Convergent beam of electrons incident on sample

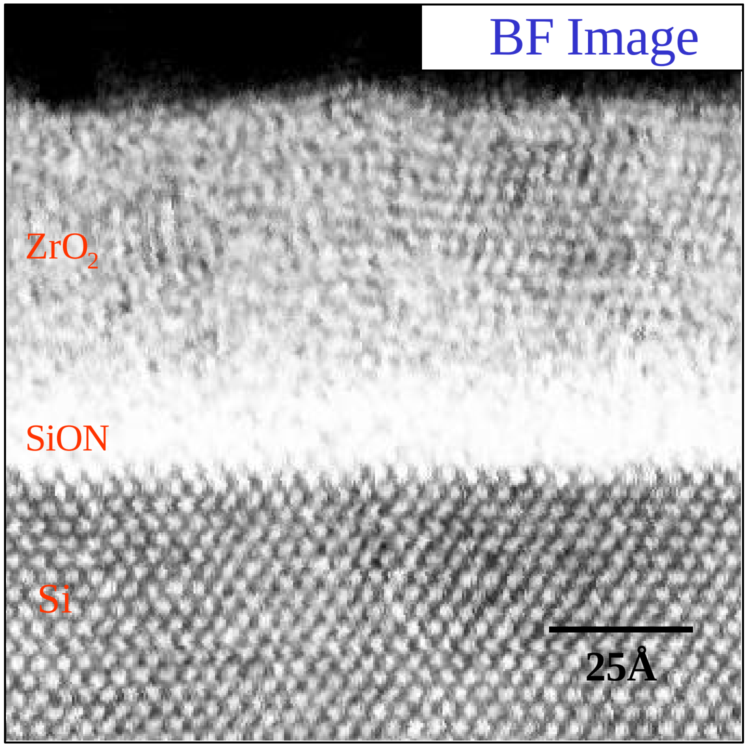
- Probe size is of the order of ***2-3Å*** (in JEOL 2010F, Lucent)

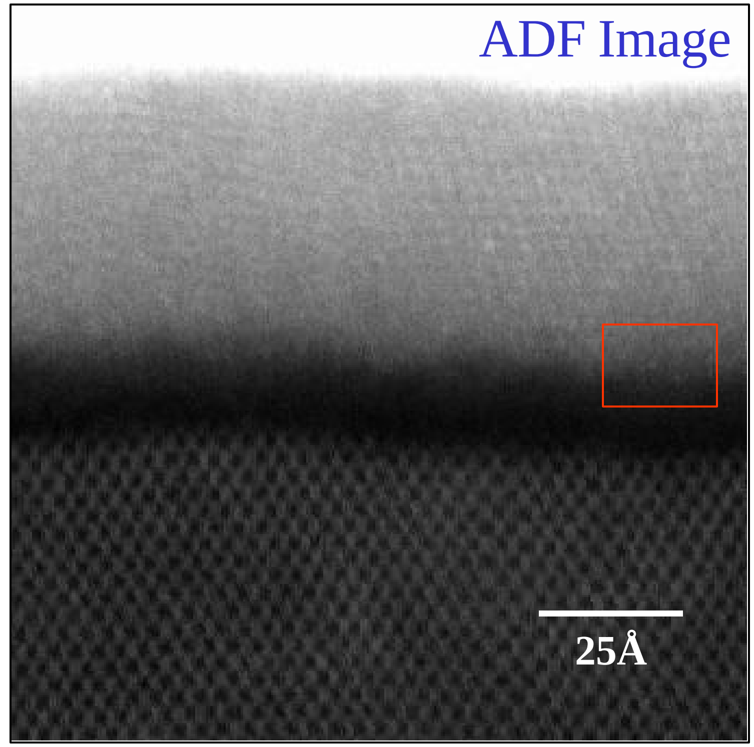
- Beam is rastered across sample to form image

- Annular dark field (ADF) imaging conditions lead to ***Z-contrast***

- Structural information can be obtained from local **(< 2 nm)** regions using nano-diffraction

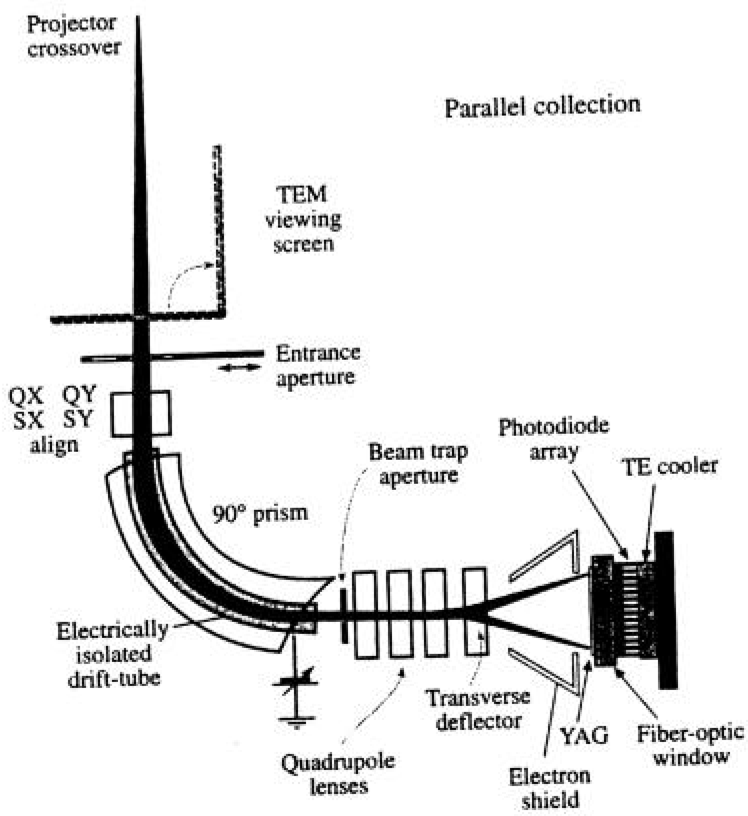
MICROSTRUCTURE OF AS-DEPOSITED ZrO_2 FILMS





- BF and ADF STEM images showing polycrystalline ZrO_2 grown on SiON by ozone oxidation at room temperature
- The interface between the Si and SiO_xN_y is atomically sharp
- The interface between the SiO_xN_y and ZrO_2 is however slightly diffuse

ELECTRON ENERGY LOSS SPECTROSCOPY (EELS)

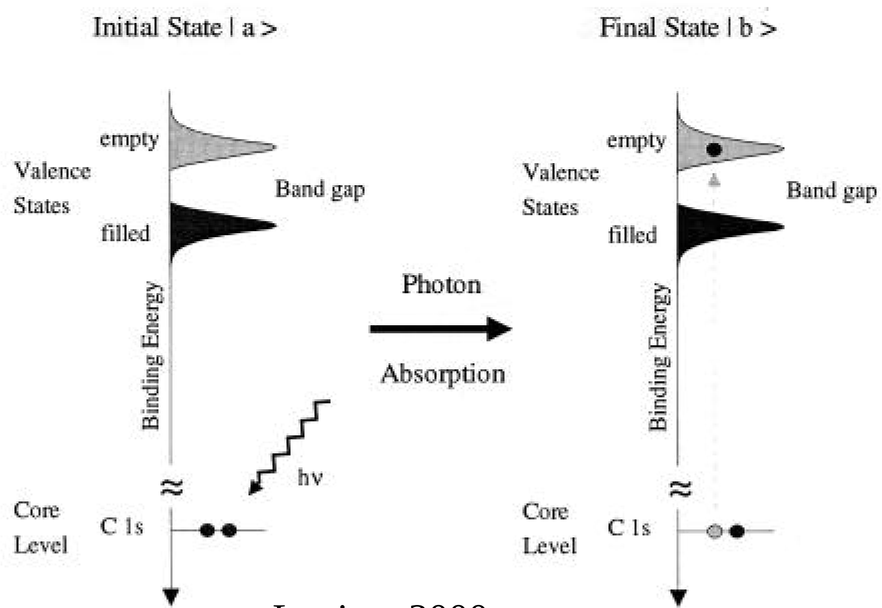


• Analysis of energy distribution of electrons that have undergone inelastic collisions in the sample

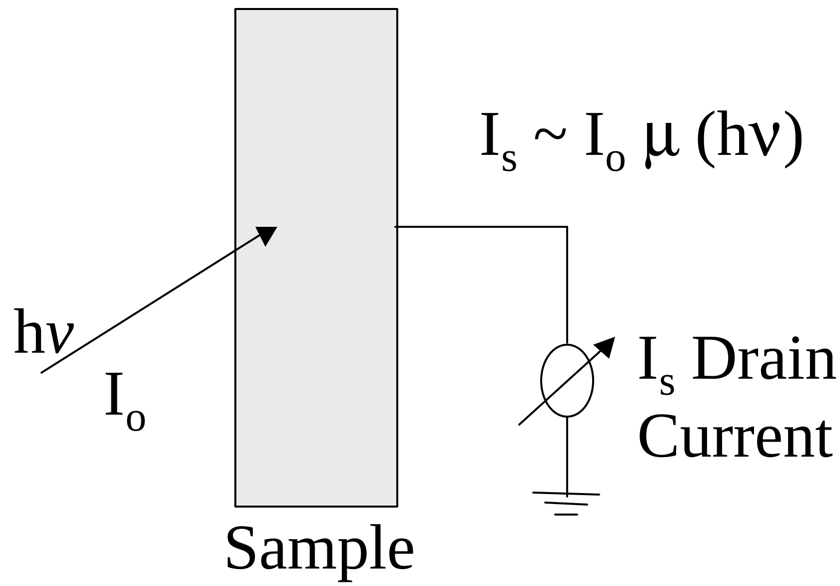
• Chemical mapping across an interface possible with sub-nanometer resolution

• Can probe electronic structure of the material locally (Muller et al., *Nature*, 1999)

X-RAY ABSORPTION SPECTROSCOPY (XAS)

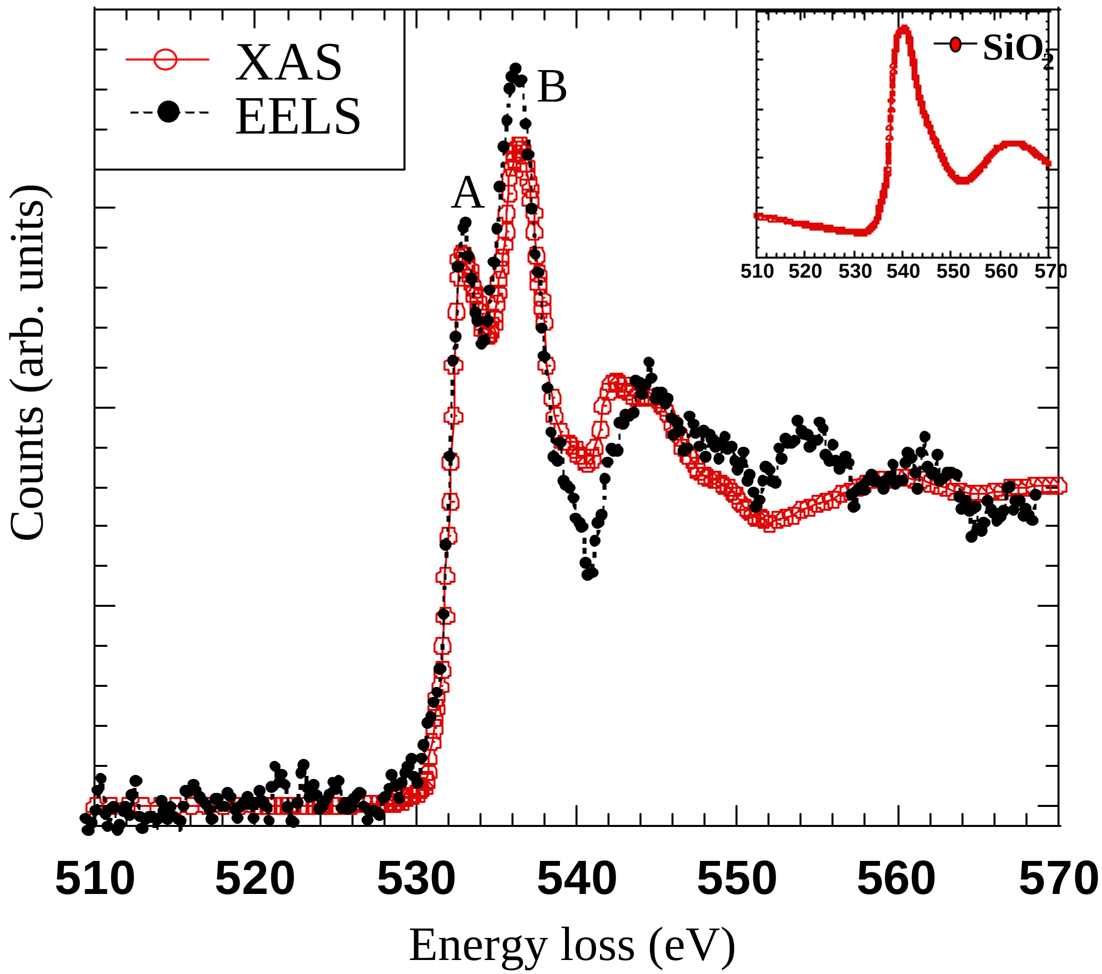


Luning ,2000



- Monochromatic photon beam incident on sample in an UHV chamber (BL 10-1, SSRL)
- Absorption is measured as a function of photon energy (TEY mode)
- Shape of absorption peak reflects the unoccupied density of states ***similar to EELS***
- Higher energy resolution than EELS, however spatial resolution is less

XAS AND EELS OF UVO ZRO_2



• EELS and XAS spectra match well with measured spectrum for bulk tetragonal ZrO_2 (McComb, *Phy. Rev. B*, 1996, Chen, *Surf. Sci*. 1997)

Shriram Ramanathan, Stanford University, *2002*

EECTRICAL STUDIES ON ZrO_2 FILMS

• Discuss C-V characteristics of ZrO_2 films grown by ozone oxidation

- Effect of annealing ambient
- Effect of underlayer :
    1. Chemical oxide
    2. UV-Ozone grown SiO_2
- Effect of oxygen partial pressure
- Hysteresis and frequency dispersion
- Effect of oxidation time
- Effect of UV light

THICKNESS EXTRACTION FROM C-V CURVES MEASURED FROM ULTRA-THIN DIELECTRICS

Effect of series resistance

- can decrease the accumulation capacitance

Quantum mechanical corrections

- up to 30% discrepancy in the various QM simulators available (Richter *et al. Elec. Dev. Lett.* 2001)

EOT measured at a certain voltage in accumulation

(at -2 V in our work presented below)

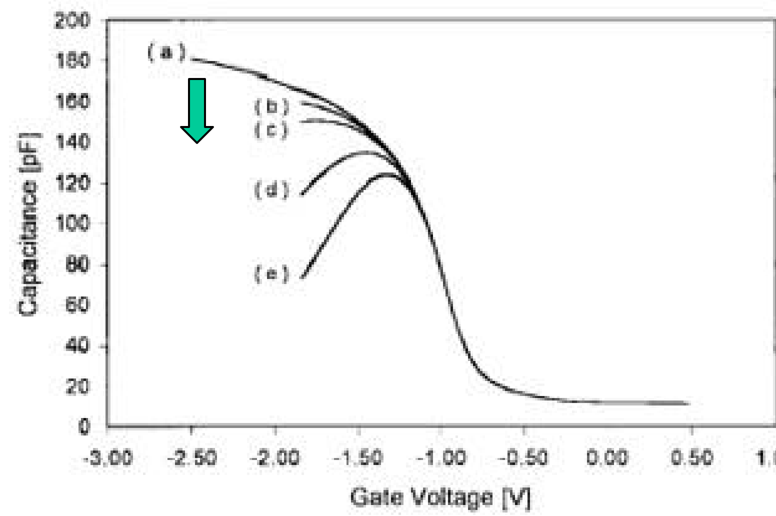
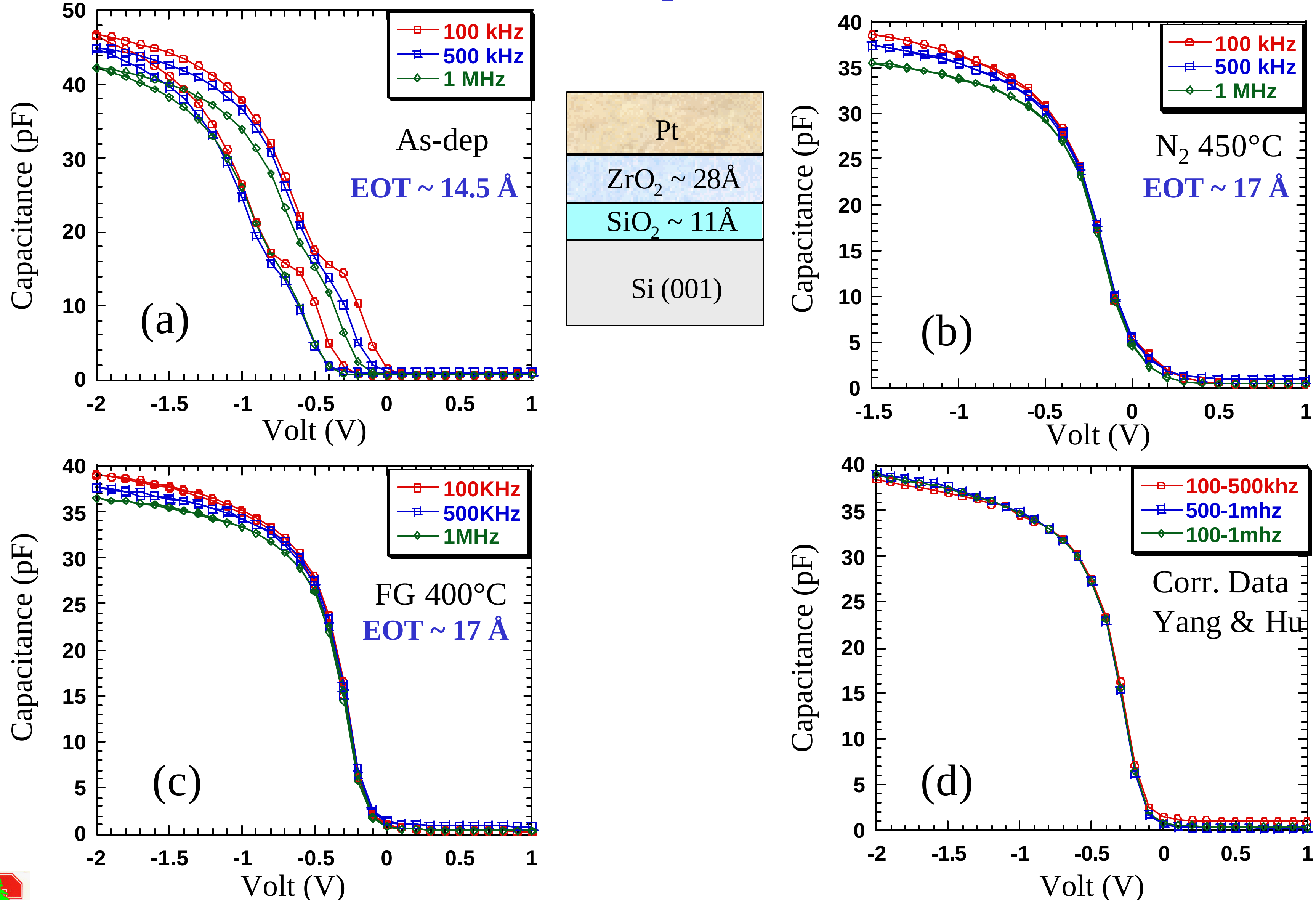


Fig. 3. Simulations of C_{m} from a theoretical C_c and measured G_T for a 1.4-nm tunnel oxide. Curve (a) is the theoretical curve C_c ($R_s = 0\ \Omega$). Curve (b) represents C_m with a series resistance of 10 Ω. Curve (c) represents C_m with a series resistance of 25 Ω. Curve (d) represents C_m with $10 * G_T$ and a series resistance of 10 Ω. Curve (e) represents C_m with $10 * G_T$ and a series resistance of 25 Ω. Area of capacitor is $1 \times 10^{-}$ cm^{-}.

Henson *et al*. *Elec*. *Dev*. *Lett*. 1999

UVO ZrO_2 on chemical oxide



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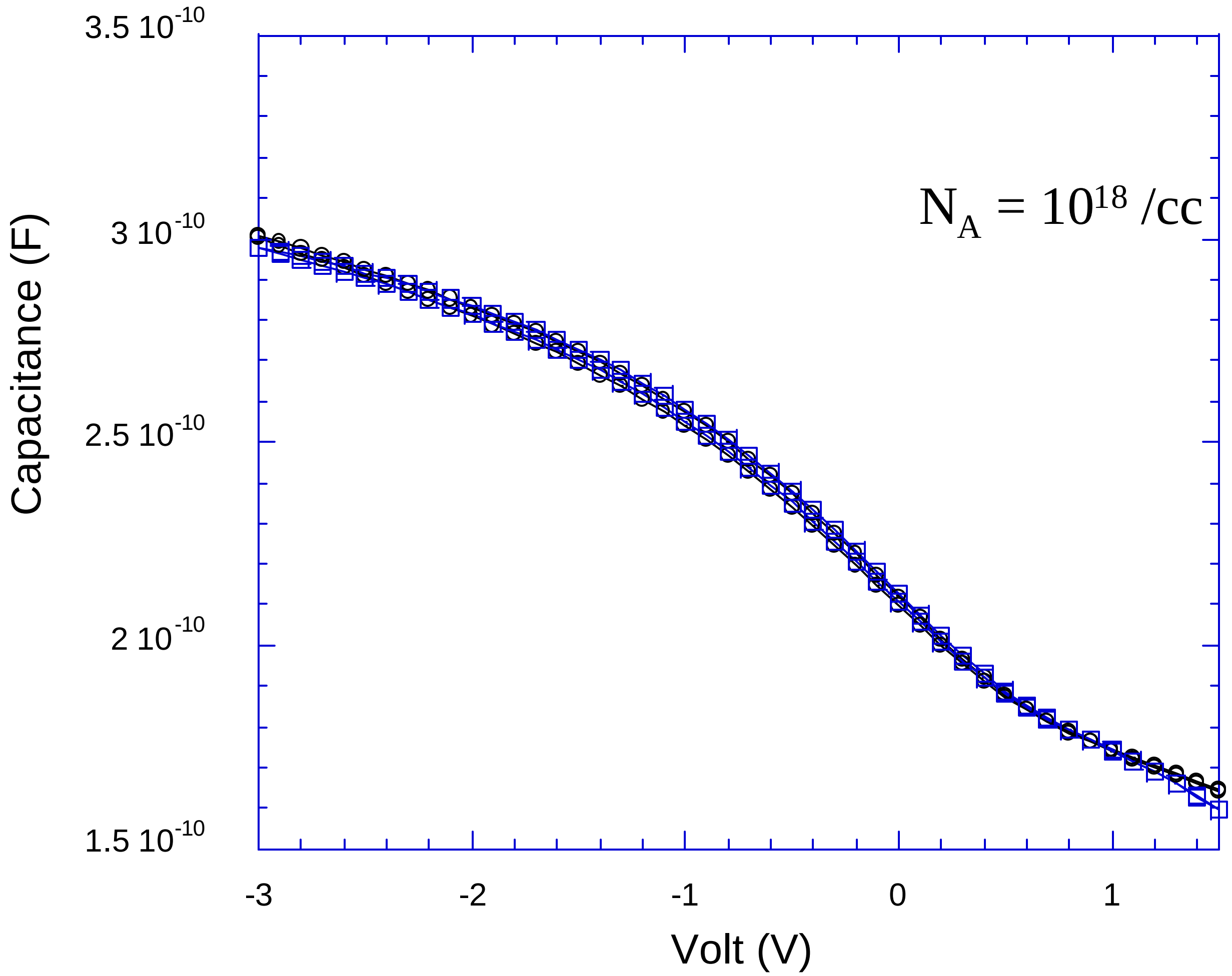
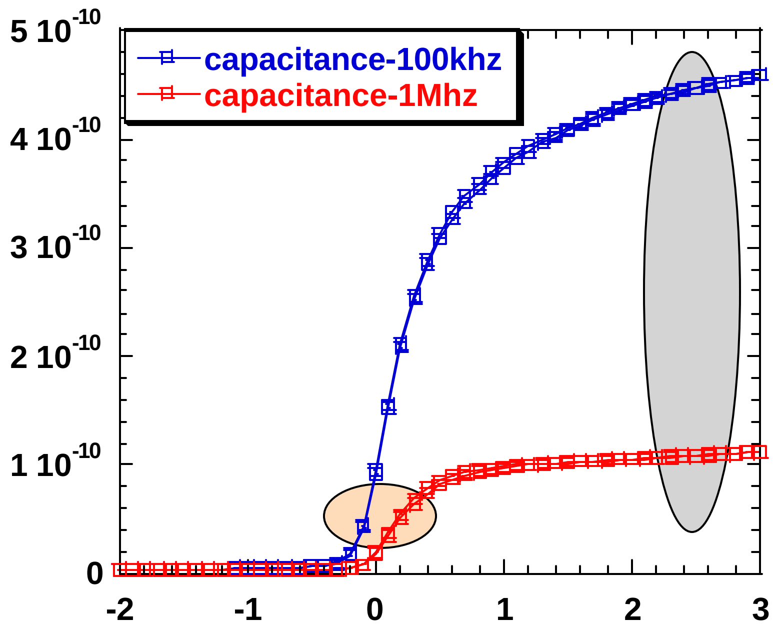
Overlay CV data measured at 100 KHz and 1 MHz

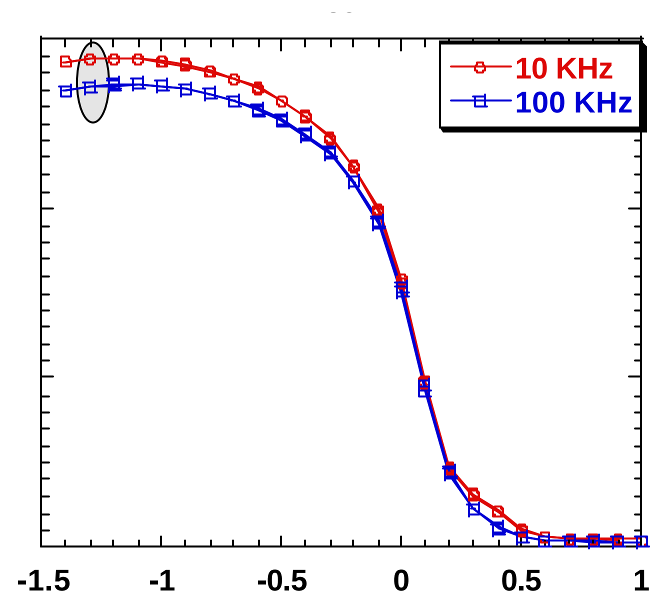


Related references: Depas et al., *Sol. St. Elec.* 1994, Nicollian and Brews, *MOS textbook*, 1982

Effect of Oxidation time : Low Pressure UV oxidation

Zr metal precursor thickness : 13 Å





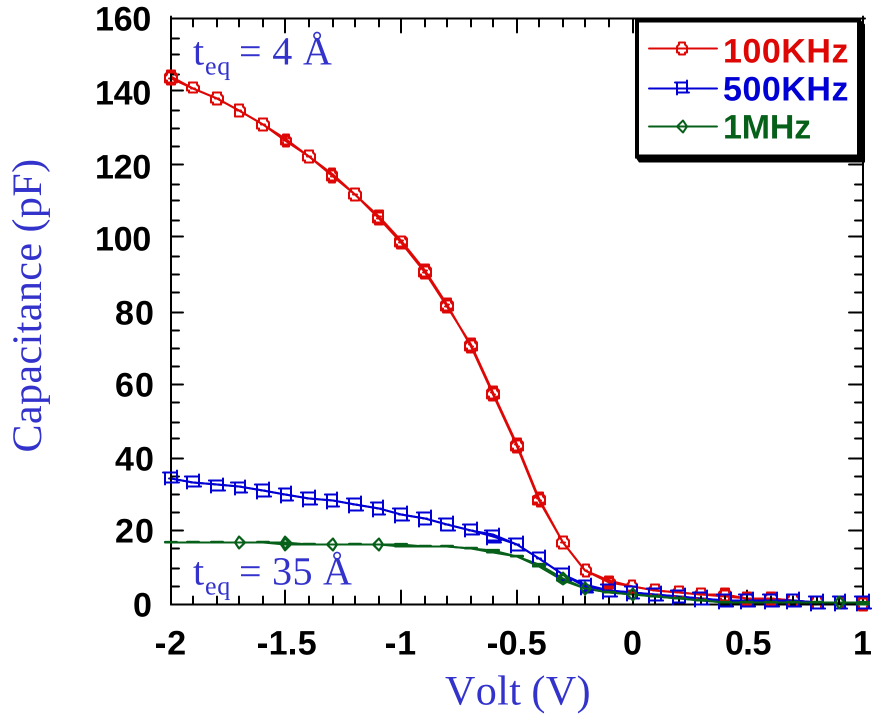
1. P_{O2} = 80 mTorr, 5 min.

2. P_{O2} = 80 mTorr, 20 min.

Note huge frequency dispersion in *both* depletion and accumulation region in **1**

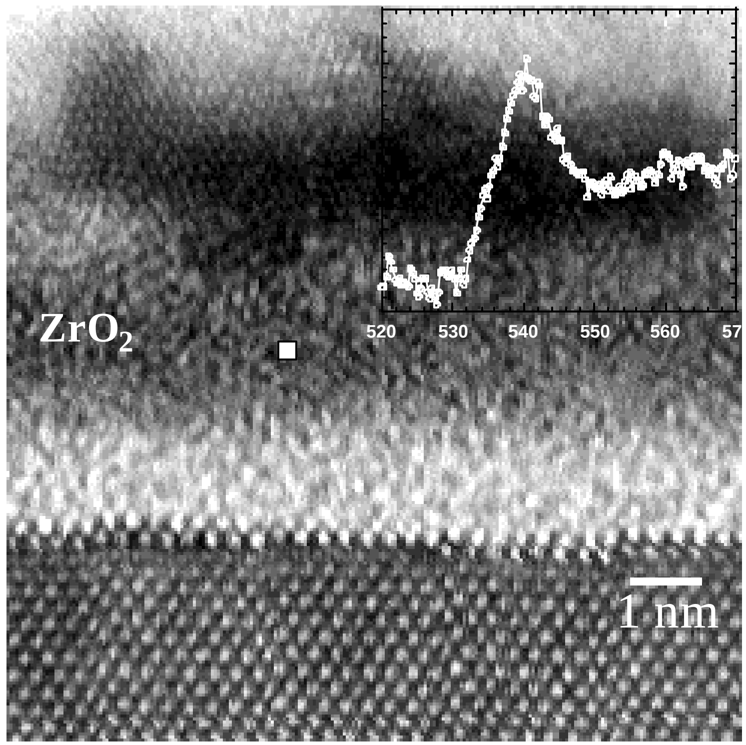
Shriram Ramanathan, Stanford University, *2002*

ZrO_x grown by Natural Oxidation : No UV light



EOT = 4 Å at 100 KHZ

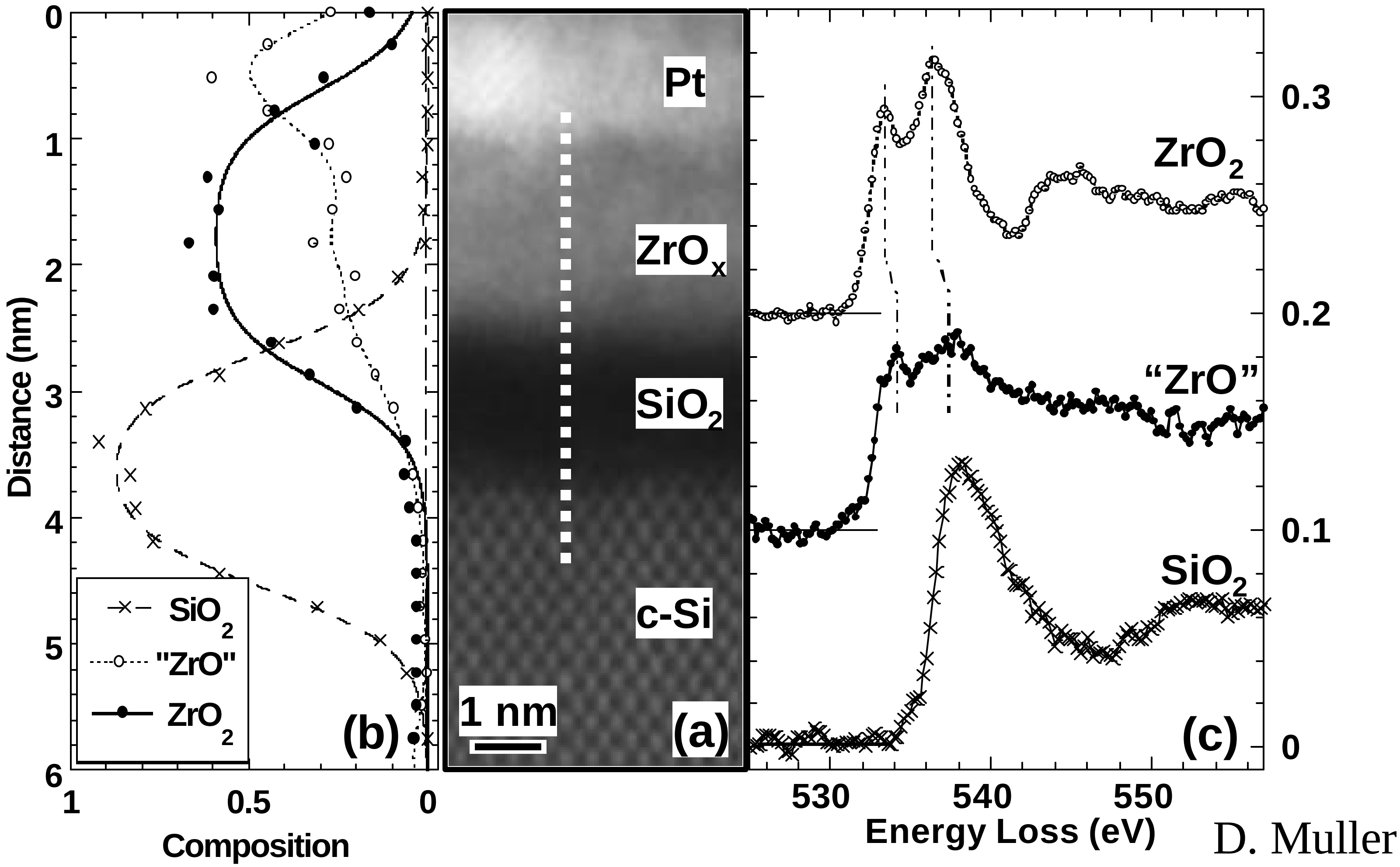
EOT = 35 Å at 1 MHz !



Intentionally grew sub-stoichiometric zirconia to study CV behavior

Shriram Ramanathan, Stanford University, *2002*

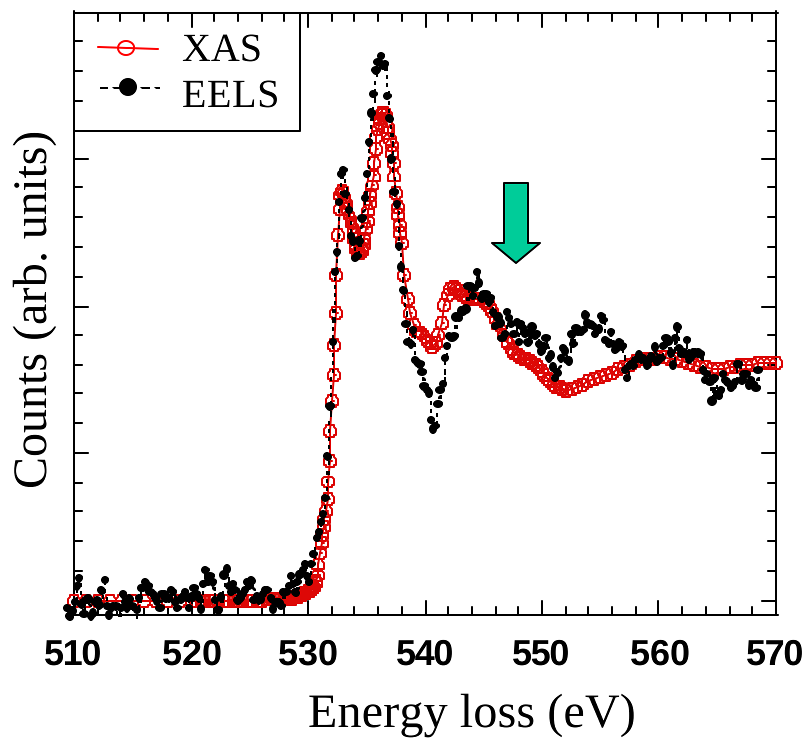
QUANTITATIVE EELS ANALYSIS



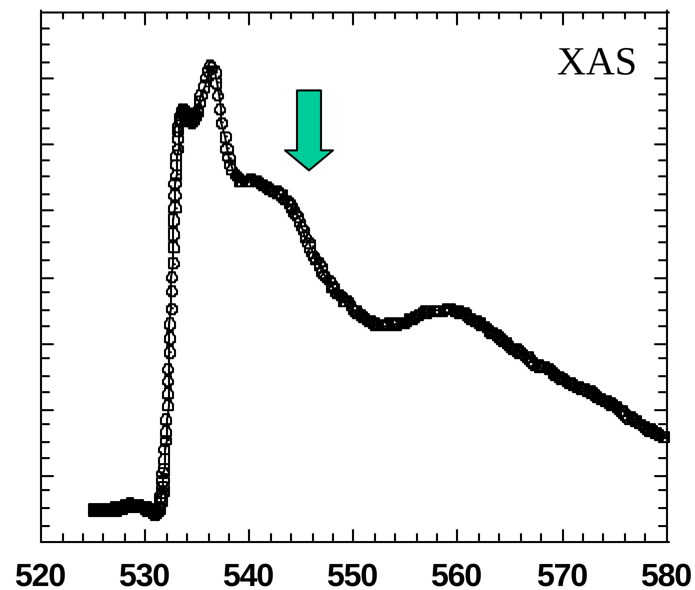
• Quantitative analysis of EELS O-K fine structure detects ***additional*** sub-stoichiometric ZrO phase (Ramanathan et al. *Philos*. *Mag*. *Lett*. accepted, April 2002)

XAS studies on zirconia

UVO ZrO_2



ZrO_x: No UV light

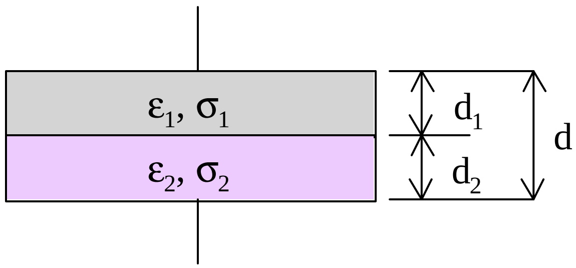


Ramanathan et al. Philosophical Magazine Letters, 2002

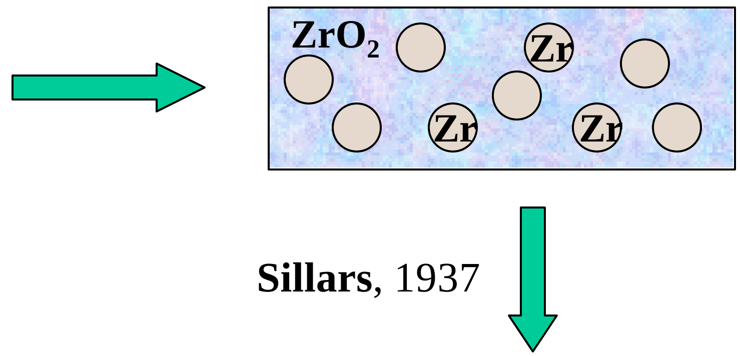
• Note absence of fine structure in the ZrO_x case: due to *reduced* number of oxygen nearest neighbors (D. Wallis, PhD Thesis, Cambridge, 1996)

Acknowledgement: Jan Luning, Prof. Pianetta, SSRL

Maxwell-Wagner-Sillars Interfacial Polarization



Maxwell, 1892
Wagner, 1924



Sillars, 1937

Model for ZrO_2 / Zr system,
q is volume fraction of
Zr metal inclusions

Ramanathan et al. JAP, 91, 4521,2002

Well-studied in ceramics, has been observed in several studies on layered ceramics

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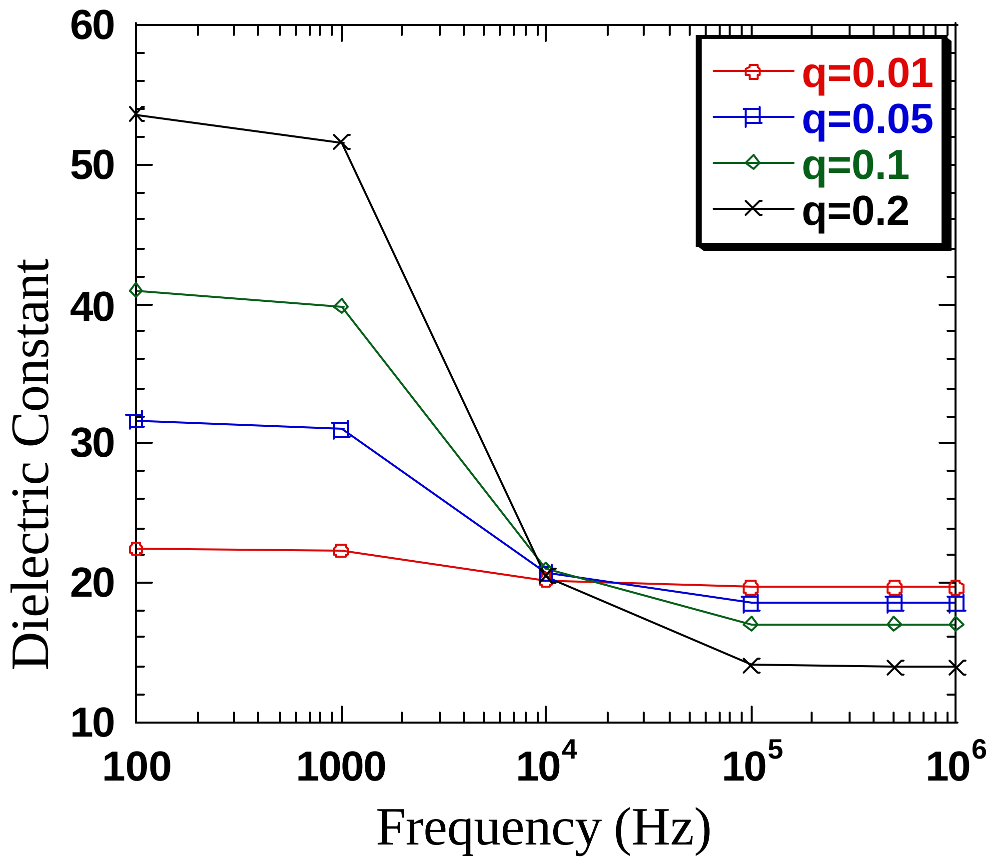
References: Von Hippel, *Dielectrics and Waves*, 1954

Dielectric Constant vs Measurement Frequency dependence for under-oxidized ZrO_x films

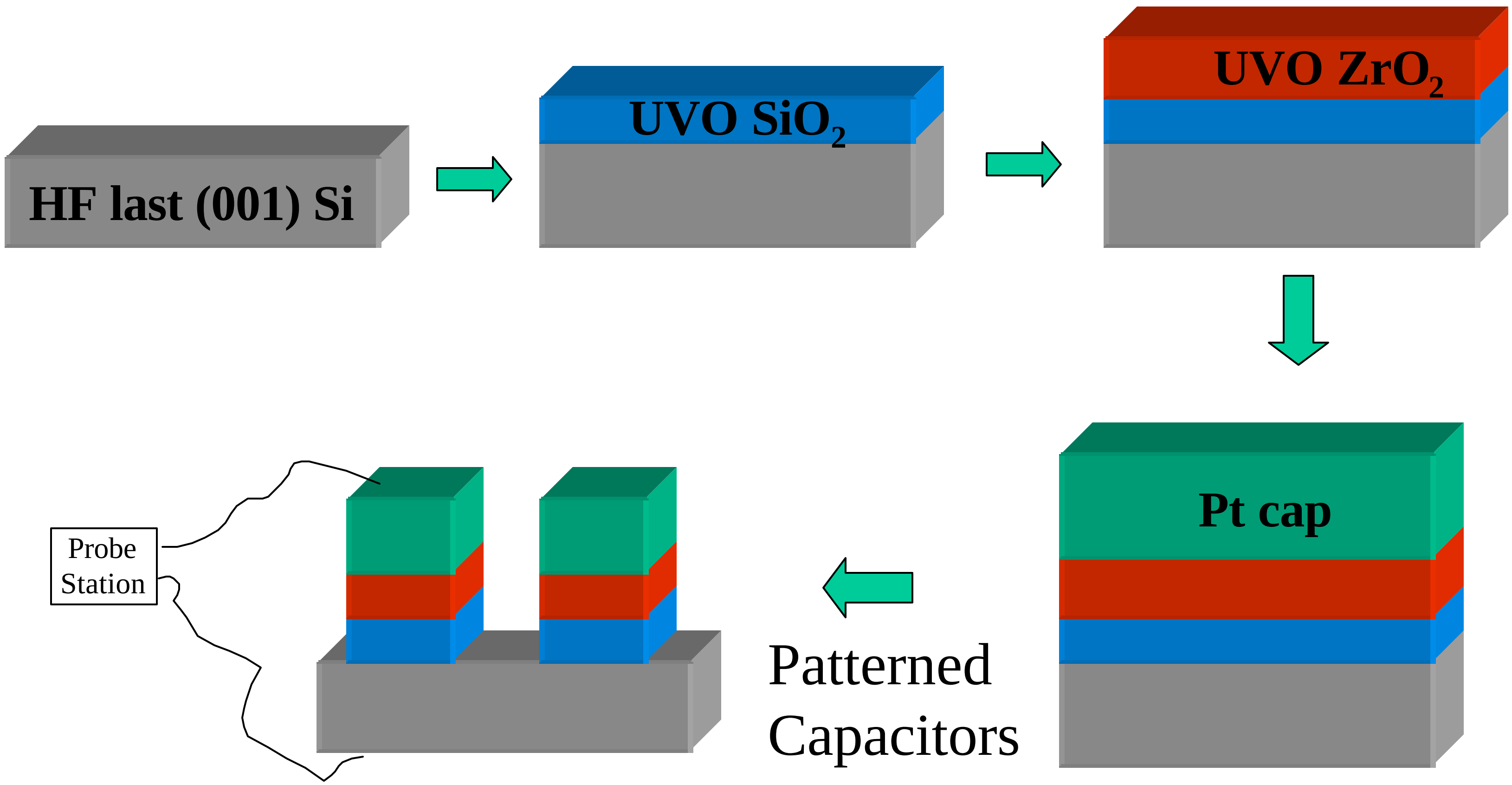


q = volume fraction of Zr metal

- As measurement frequency decreases, the measured dielectric constant increases due to polarization effects
- Similar frequency dependence has been observed in under-oxidized ZrO_x (Jeon and Hwang, *JECS*, 2002, Stemmer, JAP, 2002)

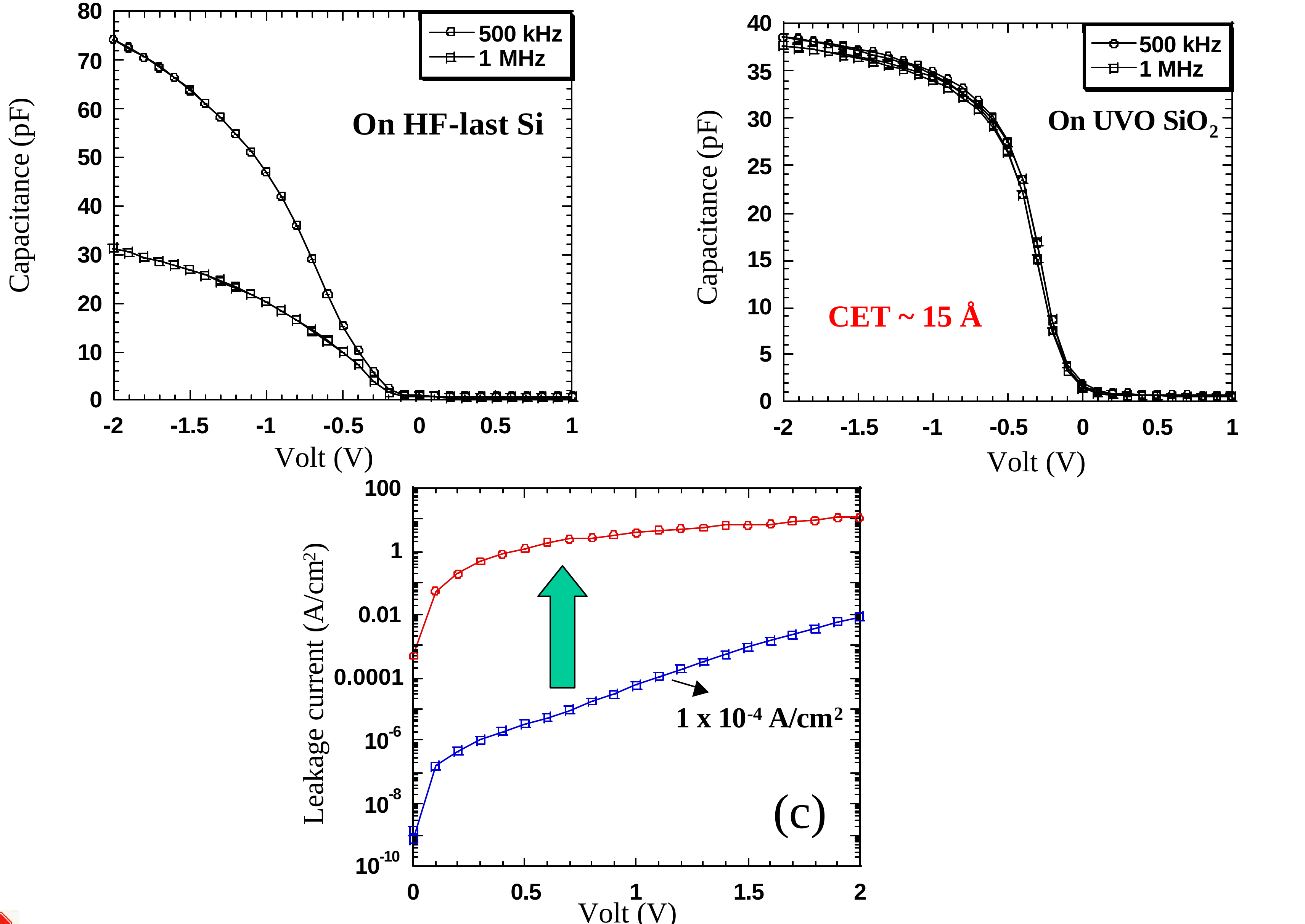
ZrO_2 / SiO_2 GATE STACK GROWN *in-situ* BY UV-OZONE OXIDATION at 300 ºK

Experiment



Acknowledgement: Dr. Chang Man Park

Shriram Ramanathan, Stanford University, *2002*



Dispersion due to under-oxidized silicide ?

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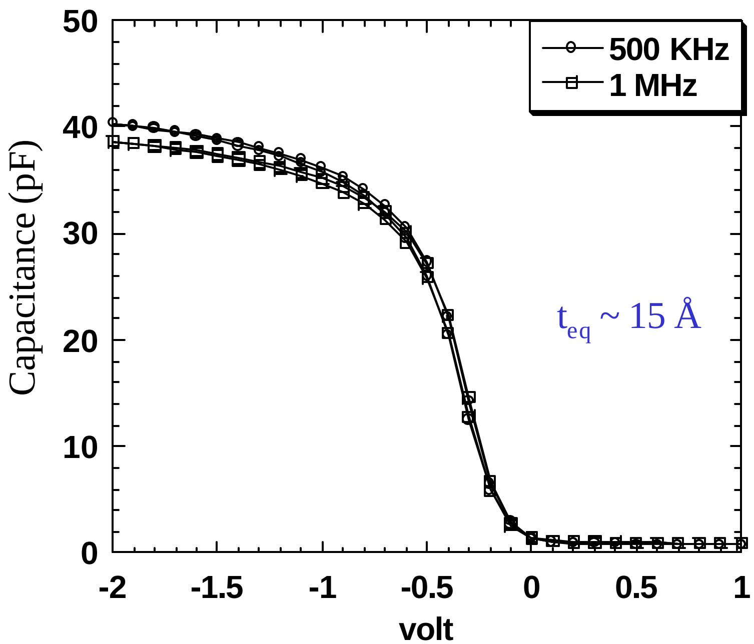
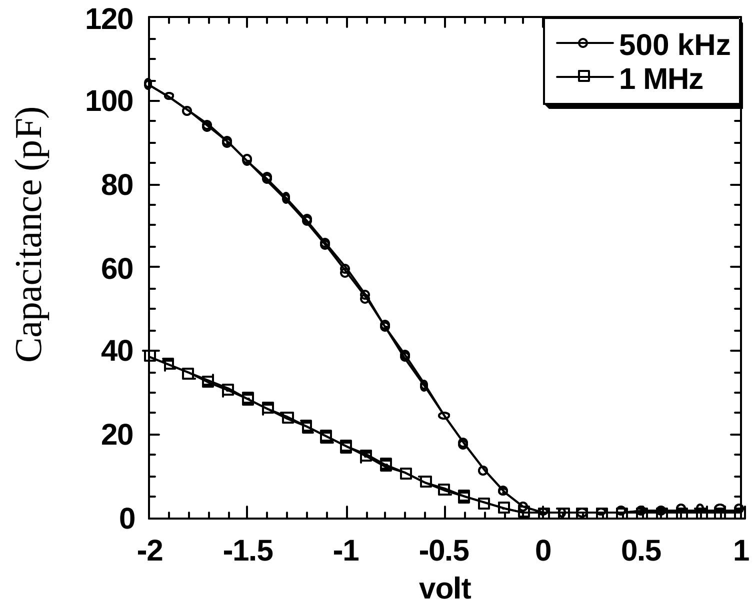
Effect of oxygen partial pressure on Zr oxidation



600 Torr, 60 minutes



80 mTorr, 60 minutes

- Oxygen partial pressure crucial to growing stoichiometric zirconia films
- Electrical results in good agreement with oxidation kinetics data

SUMMARY

• Systematic studies of UVO grown zirconia has been performed

• Dielectric stacks with 1.5 nm EOT (QM corrected EOT ~ 1.1 nm), low leakage current, low hysteresis and dispersion have been fabricated

•Scanning transmission electron microscopy coupled with EELS and XAS has been used to understand the correlation between the electrical and structural properties

• UVO SiO_2 films have been found to be promising templates to grow high-k dielectrics