The Abdus Salam
International Centre for Theoretical Physics

SMR/1758-10

**"Workshop on Ion Beam Studies of Nanomaterials:
Synthesis, Modification and Characterization"**

26 June - 1 July 2006

Semiconductor-Dielectric Interfaces in the Nano Age

L.C. Feldman
Department of Physics and Astronomy
Vanderbilt University
Nashville, USA

Trieste

July, 2006

Semiconductor-Dielectric Interfaces

In the Nano Age

L. C. Feldman

Department of Physics and Astronomy

Vanderbilt University

Themes of Solid-State Science

Nanostructures-matter at 1 to 100 nm scale

Dynamics-excited state physics and chemistry

New materials -Hi T_c, magnetic, heterostructures, interfaces

Quantum control- spintronics,

Biological materials- organic/inorganic interface

Interfaces-new functionality, surface control

Silicon MOSFET

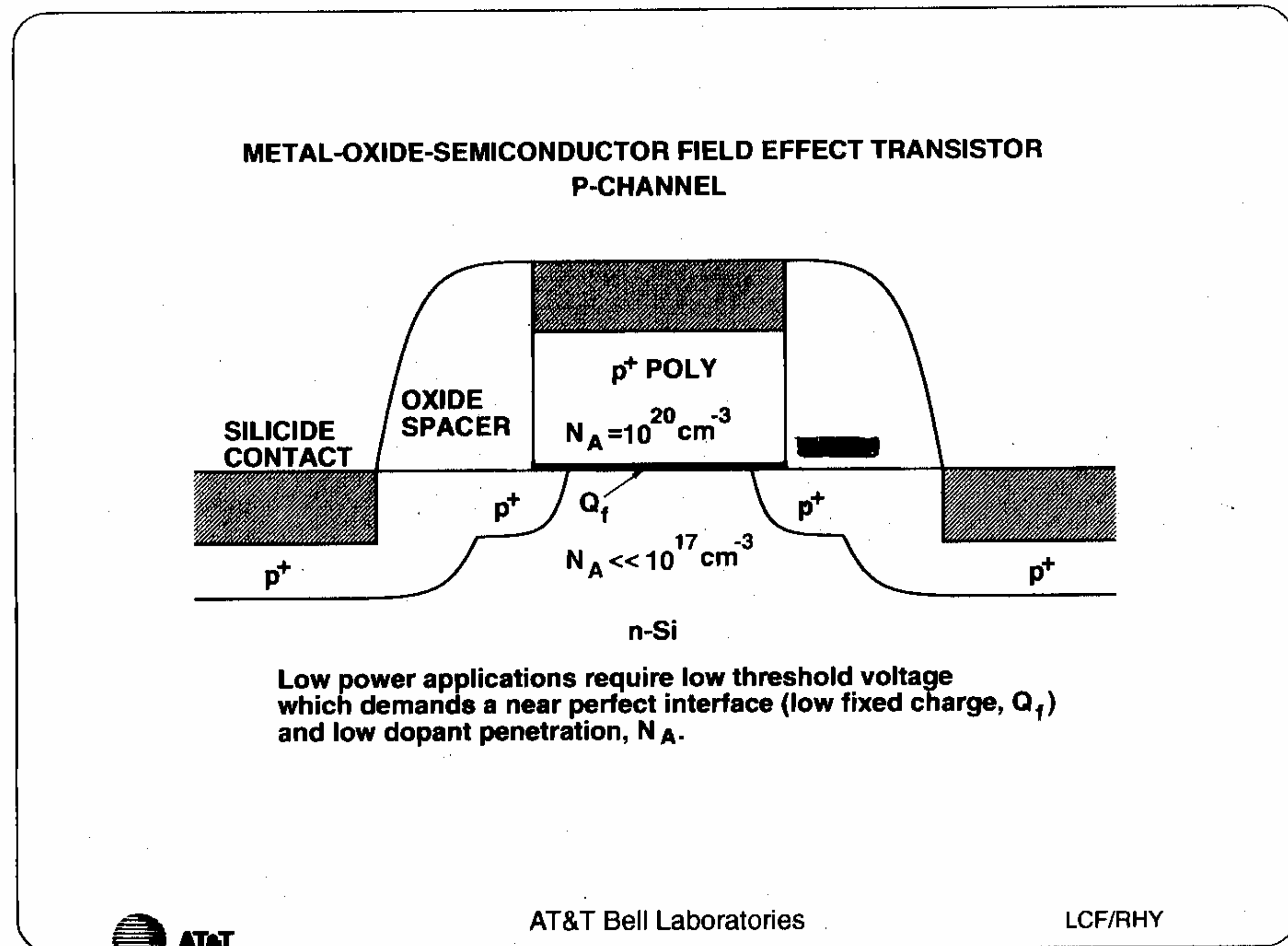
Limits:

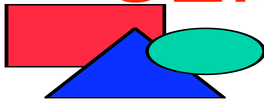
Temp

~ 300K

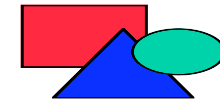
Voltage

~500V.



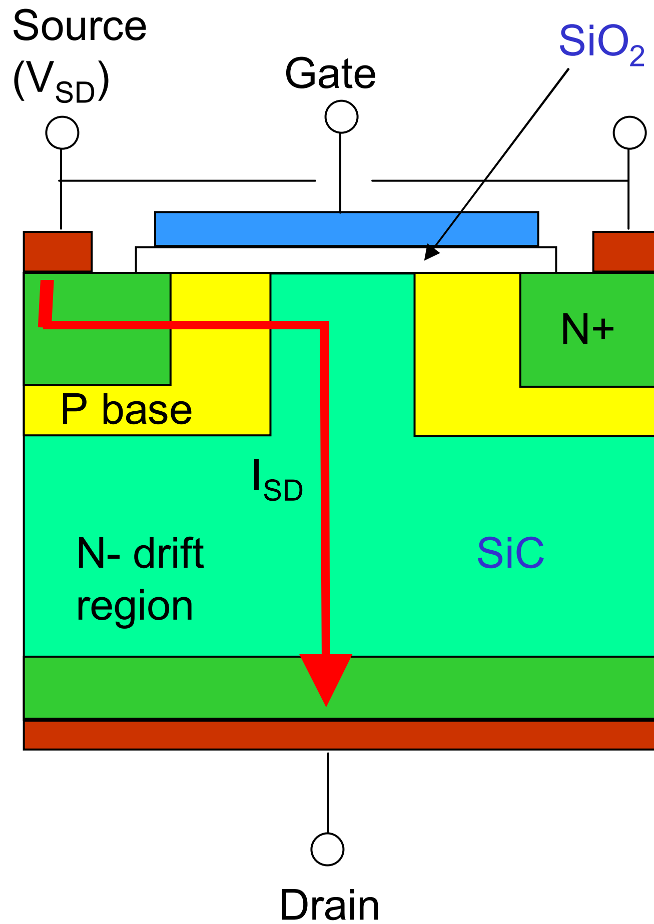


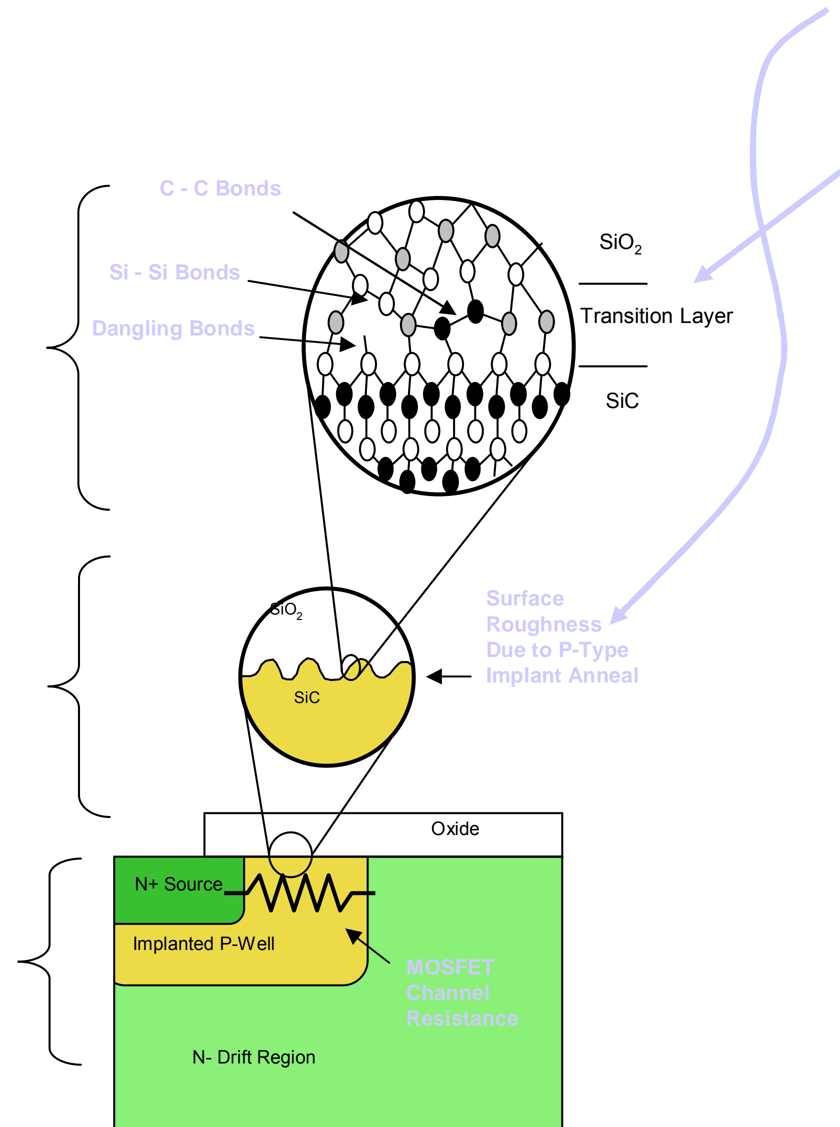
SEMICONDUCTOR GLAMOUR INDEX



Silicon	The class of the field, the grand dame, if you can do it with Si do it, ageing slightly	9
GaN	Emits light, young and mysterious, not quite predictable	10
GaAs	Emits light, always trying, quantum effects, never quite lives up to promise	6
C nanotubes	Nano and pretty – that's all it takes	10
Ge	Role in life is to make Si look good	4
Diamond	Always good for a few jokes	2
SiC	It's a ceramic, used for coating, full of defects	0

SiC Power MOSFET





$$R = R_{chan} + R_{intrinsic}$$

$$R_{chan} \sim (\text{mobility})^{-1}$$

ACKNOWLEDGEMENTS

Collaborators:

Vanderbilt: **Sarit Dhar**, S.T. Pantelides

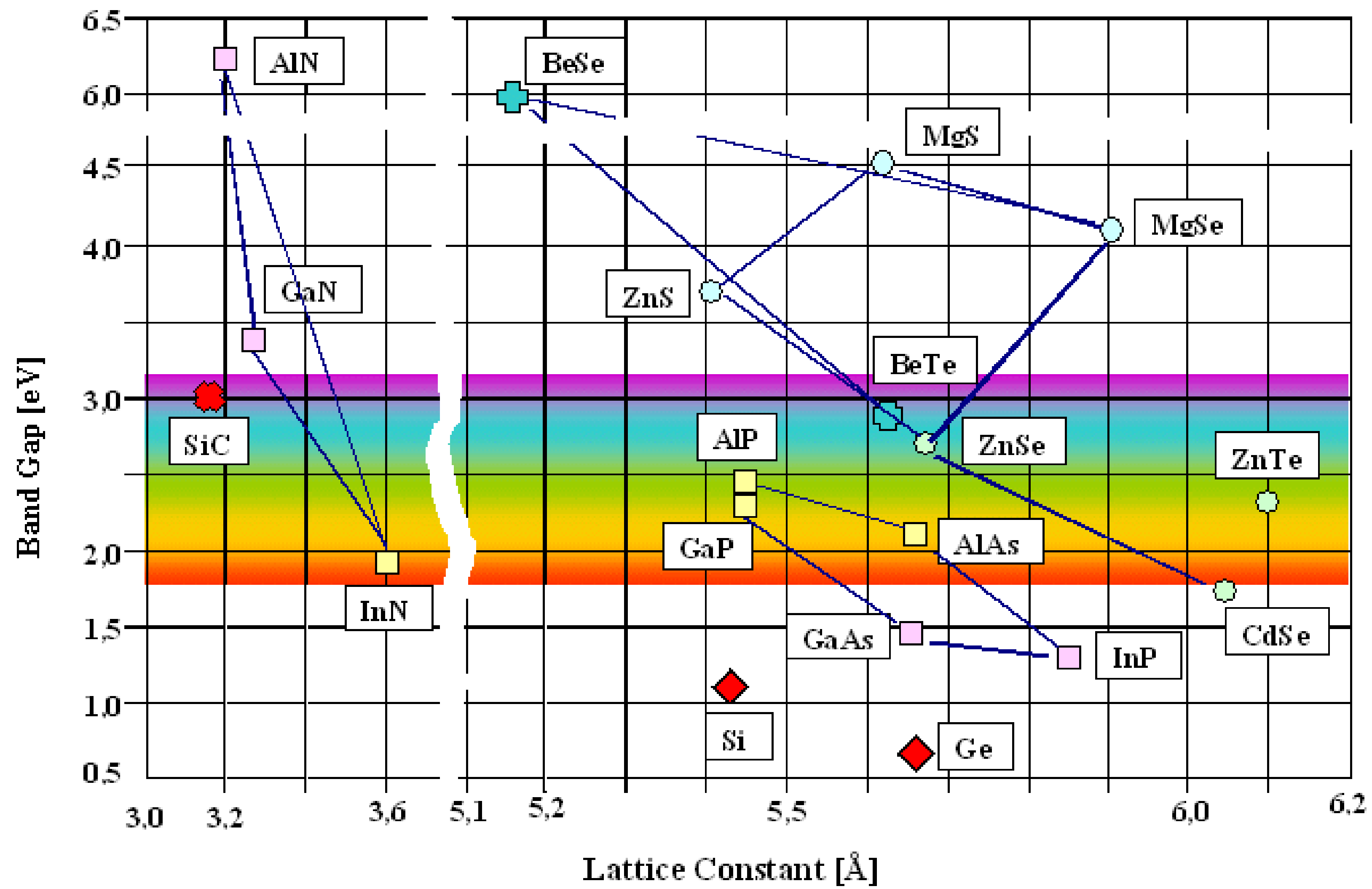
Auburn: J. Williams and group

Purdue: J. Cooper and group

Carnegie-Mellon: L. Porter, K.C. Chang, Y. Cao

ORNL: J. Bentley

Funding: DARPA and ONR-J.Zolper


AlN
BeSe
MgS
MgSe
GaN
ZnS
BeTe
SiC
AlP
ZnSe
ZnTe
GaP
AlAs
InN
GaAs
InP
CdSe
Si
Ge
6,5
6,0
4.5
4,0
3,0
2,0
1,5
1.0
0.5
Band Gap [eV]
3,0
3,2
3,6
5,1
5,2
5,5
6,0
6,2
Lattice Constant [Å]
IV - IV
III - V
II - VI

Why SiC vs. all other wide band-gaps ?

Simply-it is the most “processable” at this time!

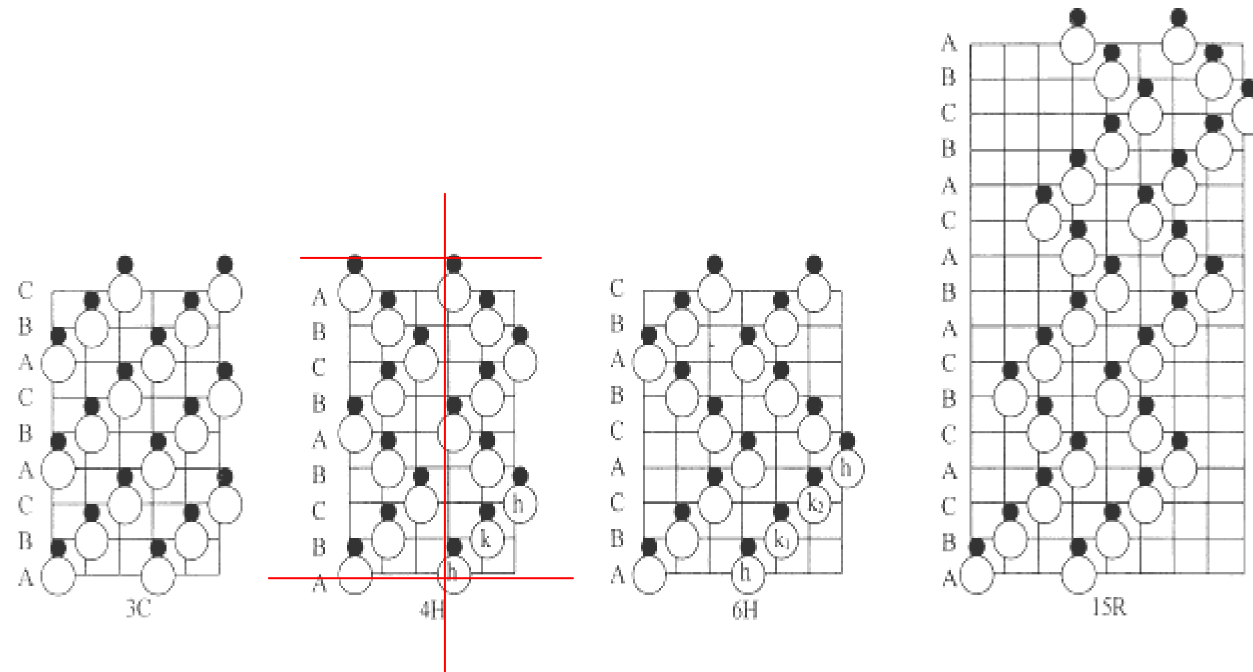
Implant—p,n

Contacts/metallization—

Wafer availability-

Oxidation- this talk!

Polytypes of Silicon Carbide



	3C	4H	6H	15R
E_g	2.2	3.3	2.9	3.0

with the valence bands ~ aligned.

SURFACE STATES

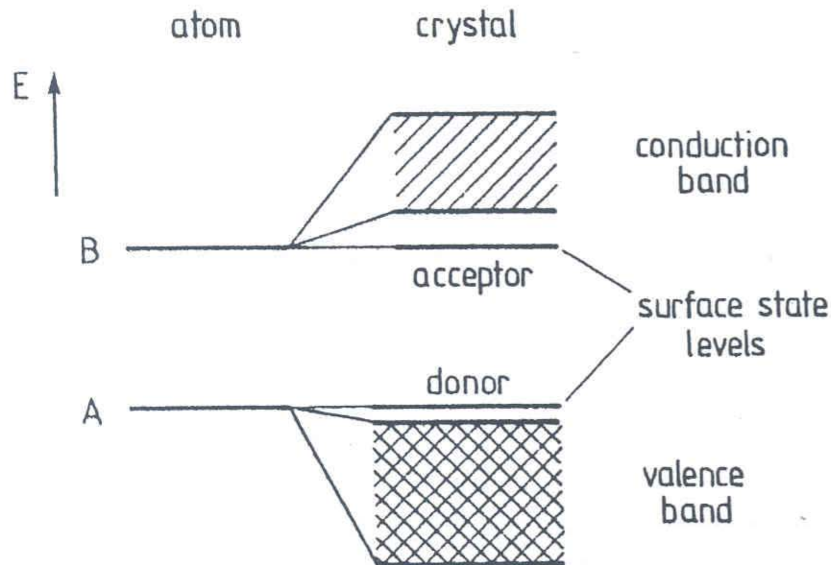
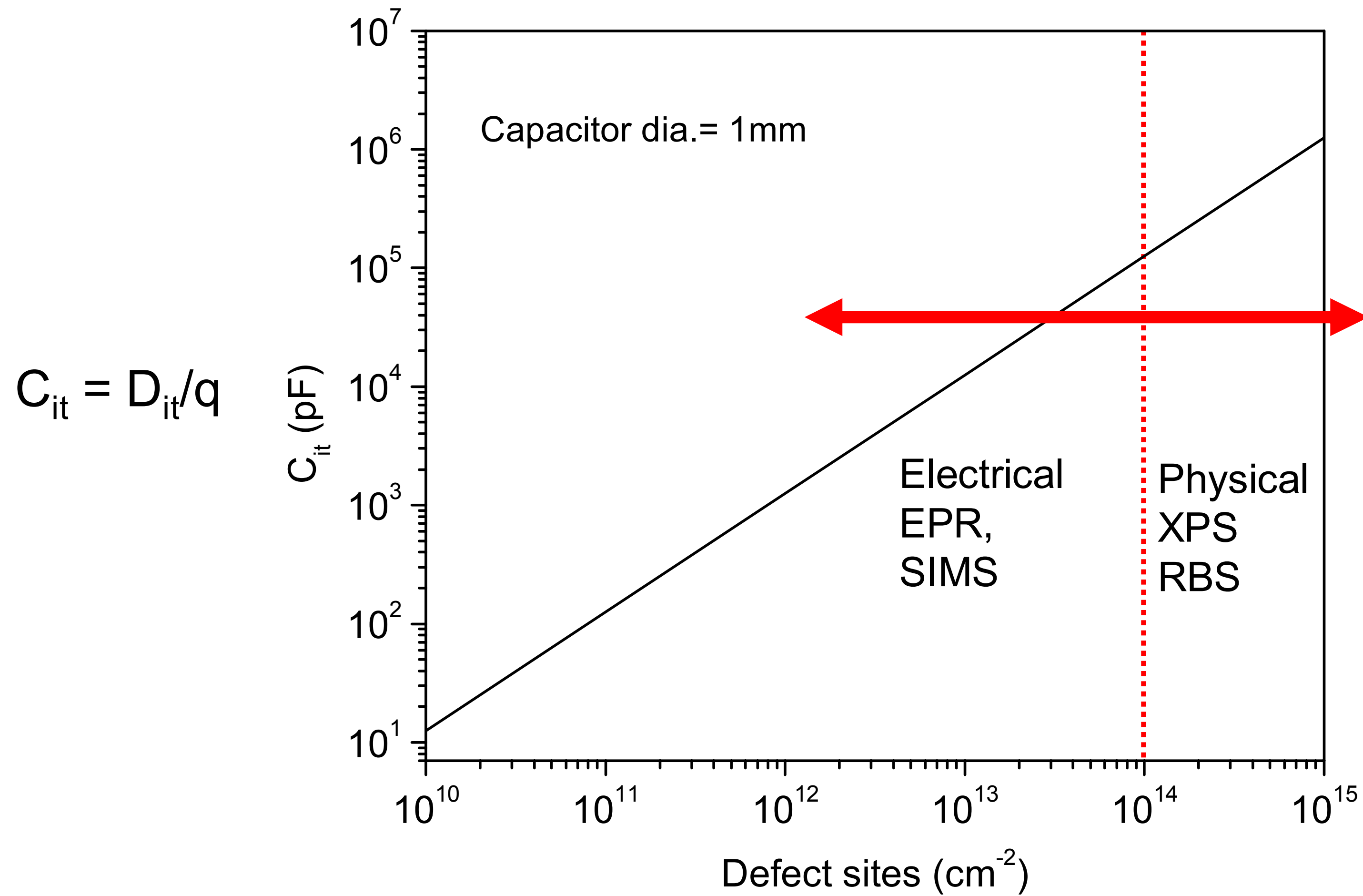


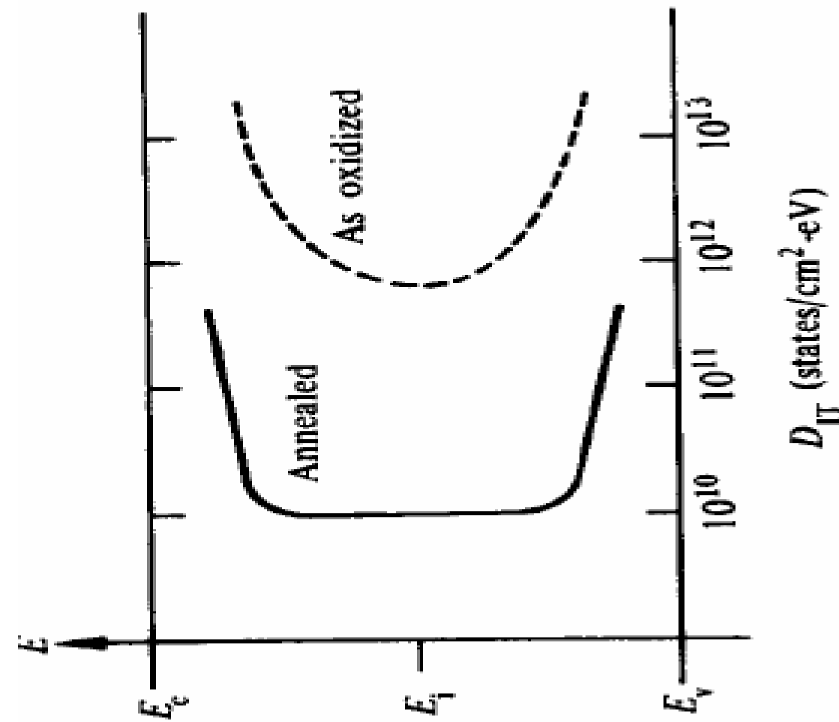
Fig.6.5. Qualitative explanation of the origin of surface states in the tight-binding picture. Two atomic levels A and B form the bulk valence and conduction bands, respectively. Surface atoms have fewer bonding partners than bulk atoms and thus give rise to electronic energy levels that are closer to those of the free atoms, i.e. surface state levels are split off from the bulk bands. Depending on their origin, these states have acceptor- or donor-like charging character

Sensitivity of electrical measurements



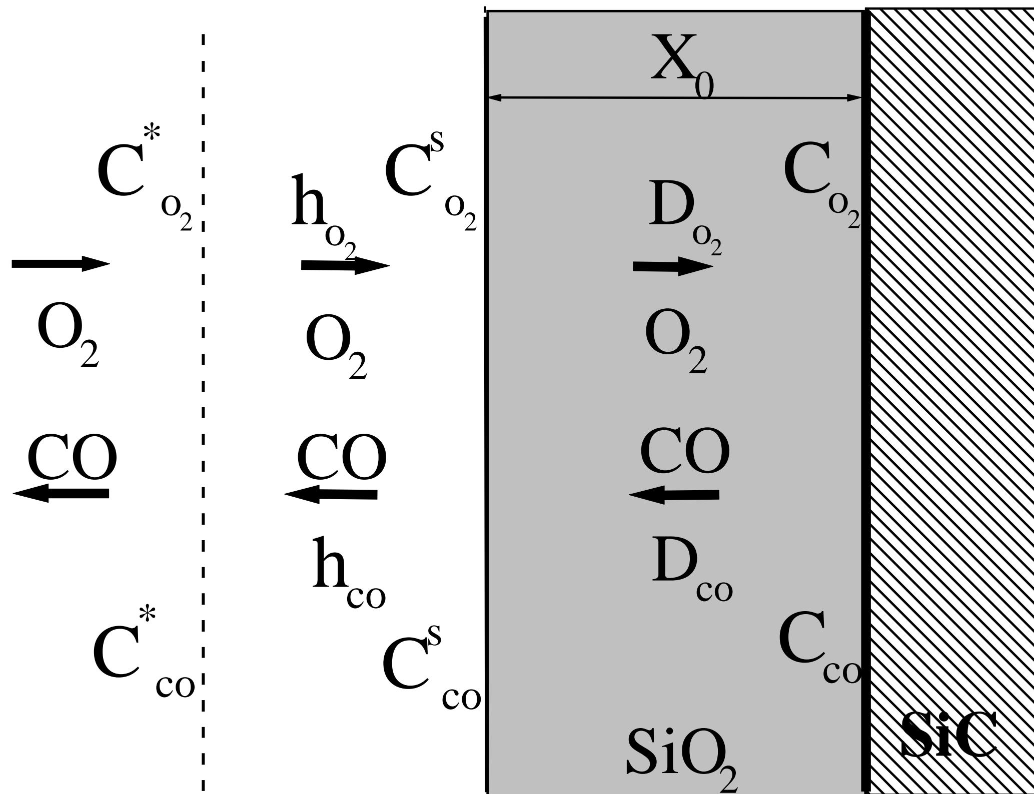
Sensitivity of Capacitance

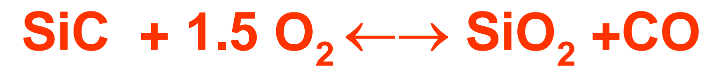
Si/SiO$_2$ Interface State Density



Interface trap density is reduced by post-oxidation annealing in H_2 ambient

SiC Oxidation – Modified Deal Grove model





I. Transport of molecular oxygen gas to the oxide surface.

II. In-diffusion of oxygen through the oxide film.

III. Reaction with SiC at the oxide/SiC interface.

IV. Out-diffusion of product gases (*e.g.* CO) through the oxide film.

V. Removal of product gases away from the oxide surface.

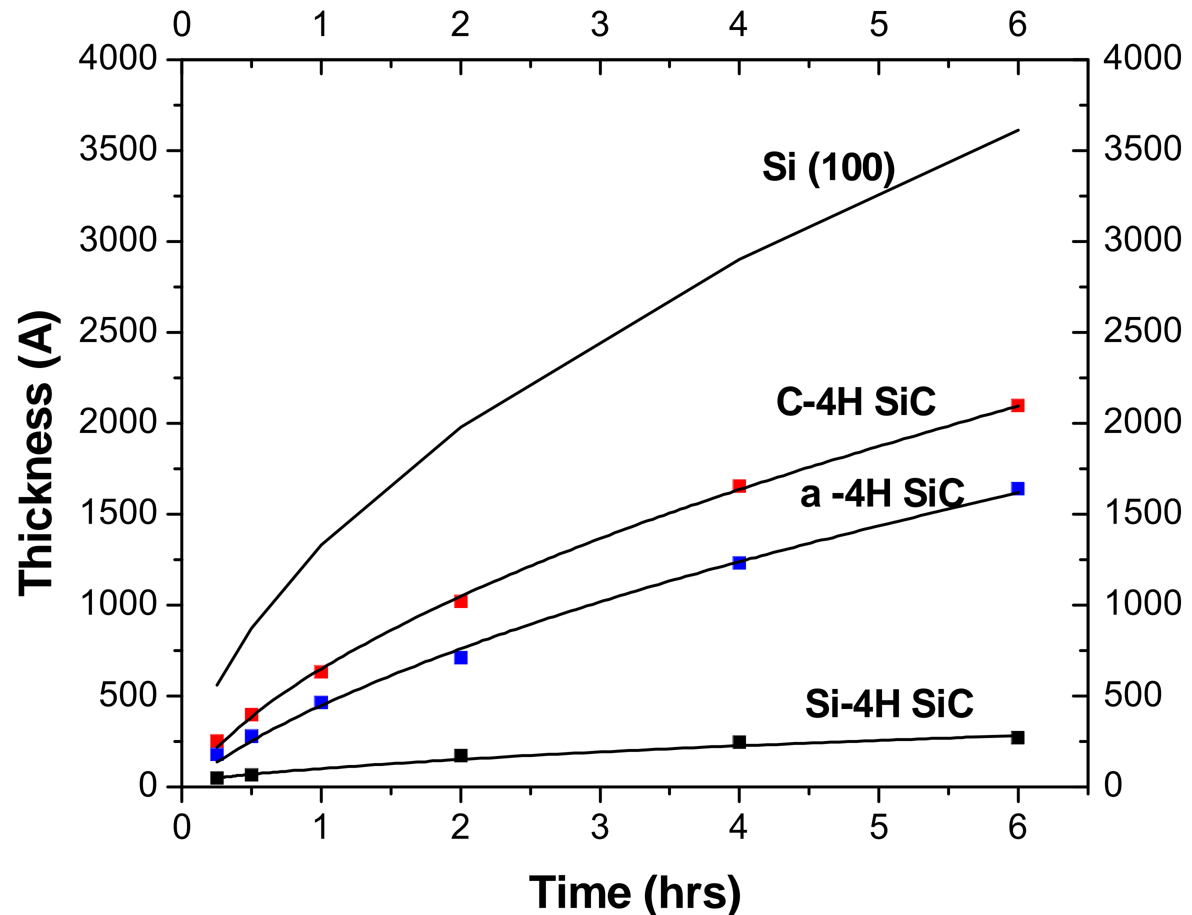
Oxidation anisotropy in 4H-SiC

- Large variation in oxidation rate among different crystal faces

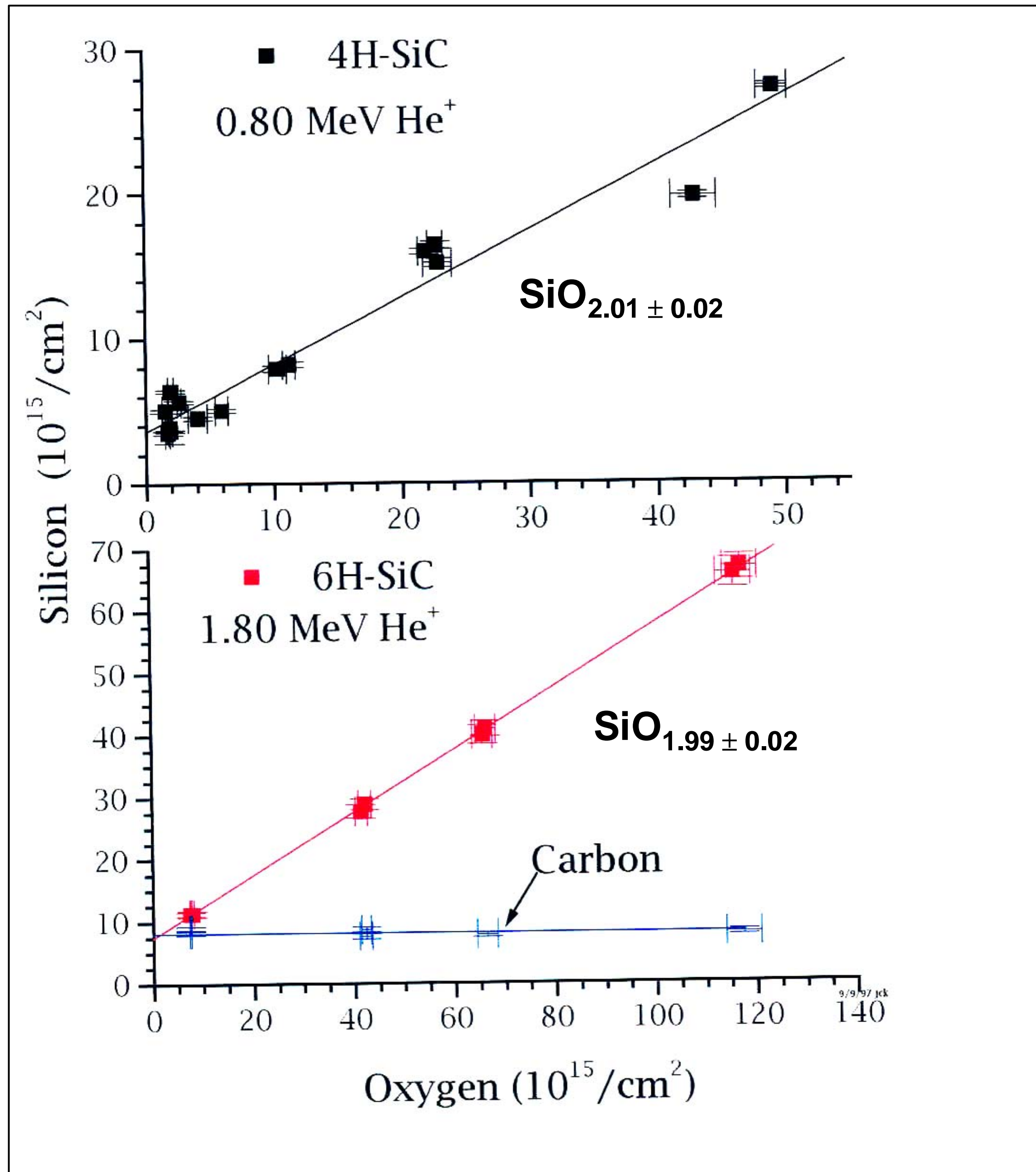
- Oxide growth rate : $\overline{R}_{Si} < \overline{R}_{a} < \overline{R}_{C}$

- Direct application of Deal Grove model cannot explain oxidation anisotropy.

- Different crystal faces could have very different interface properties .



Dry oxidation at 1100ºC, compared to the growth kinetics of Si (100)



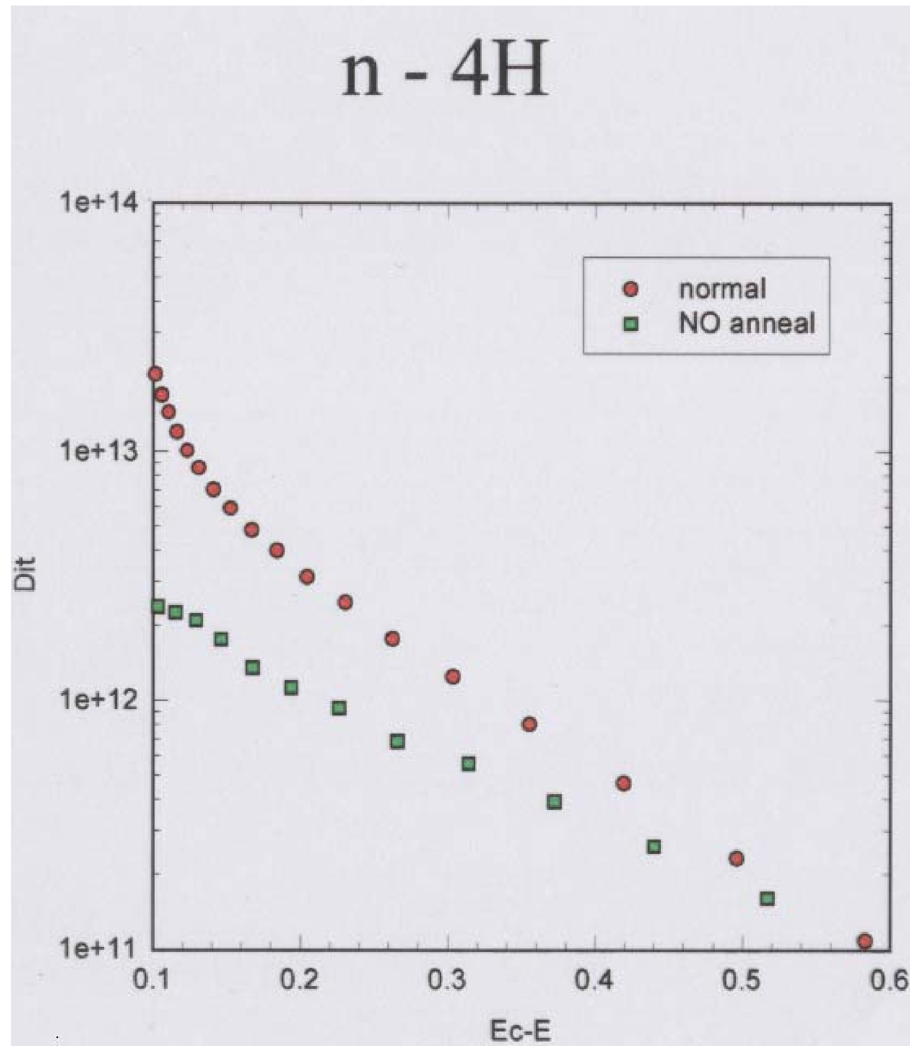
SiO_2/SiC

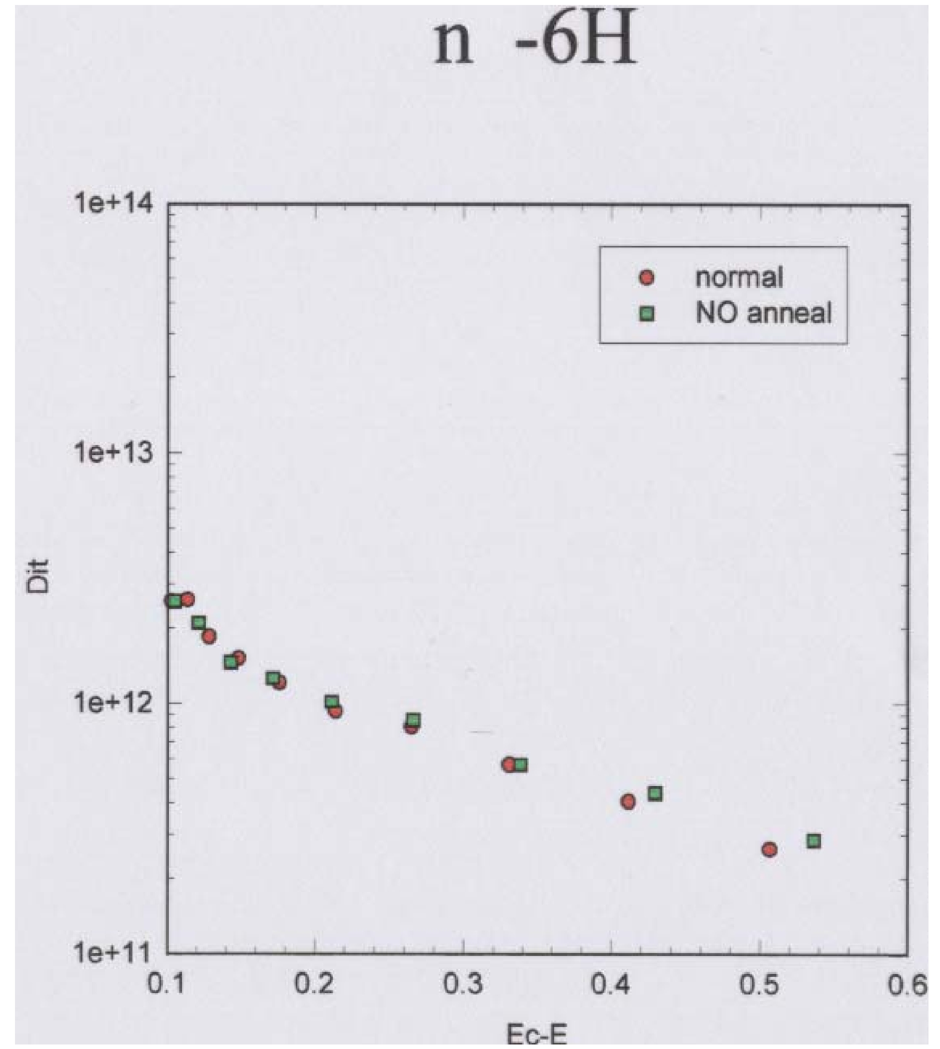
RBS/CH

SiO_2

"No" carbon

Interface State Density-----6H-4H Polytypes





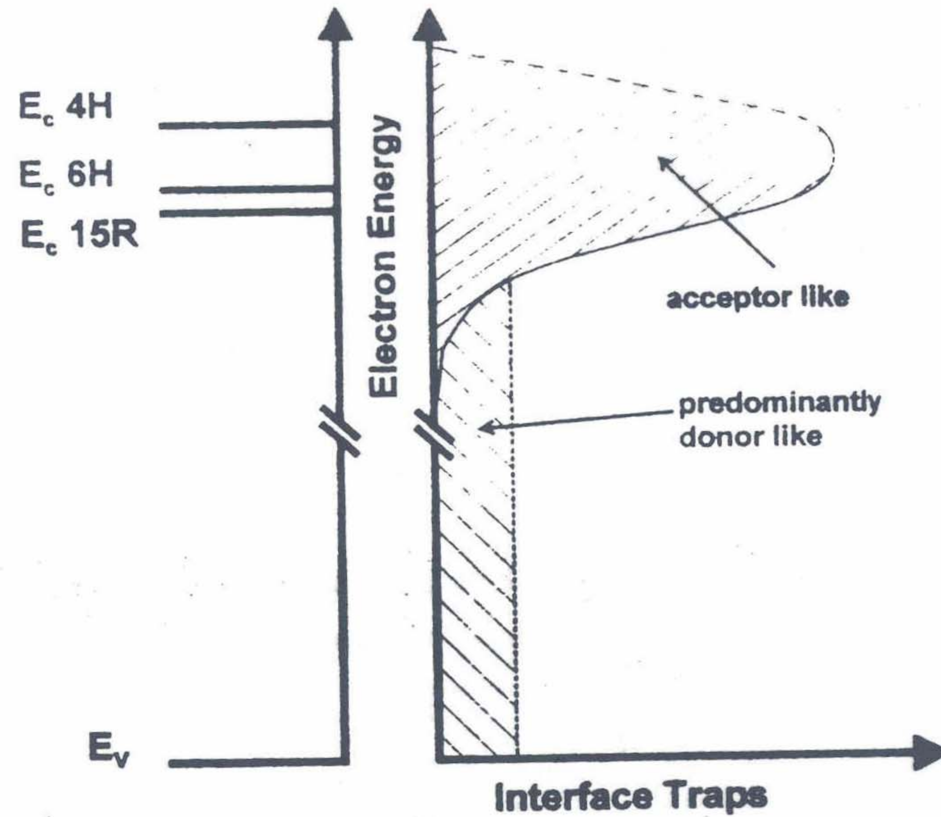
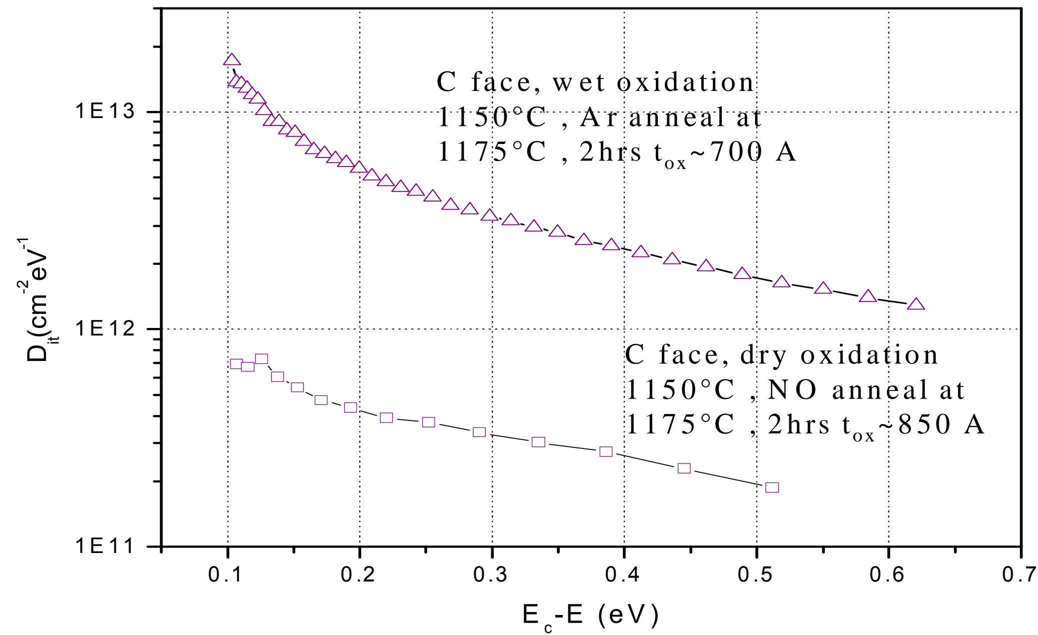


Fig. 3. Scheme of the postulated distribution of interface defects at the SiO_2–SiC interface for 4H-SiC, 6H-SiC, and 15R-SiC.

Schorner etal IEEE Elec. Dev. Let. 20 341, (1999).

Effect of NO on the (0001) C face



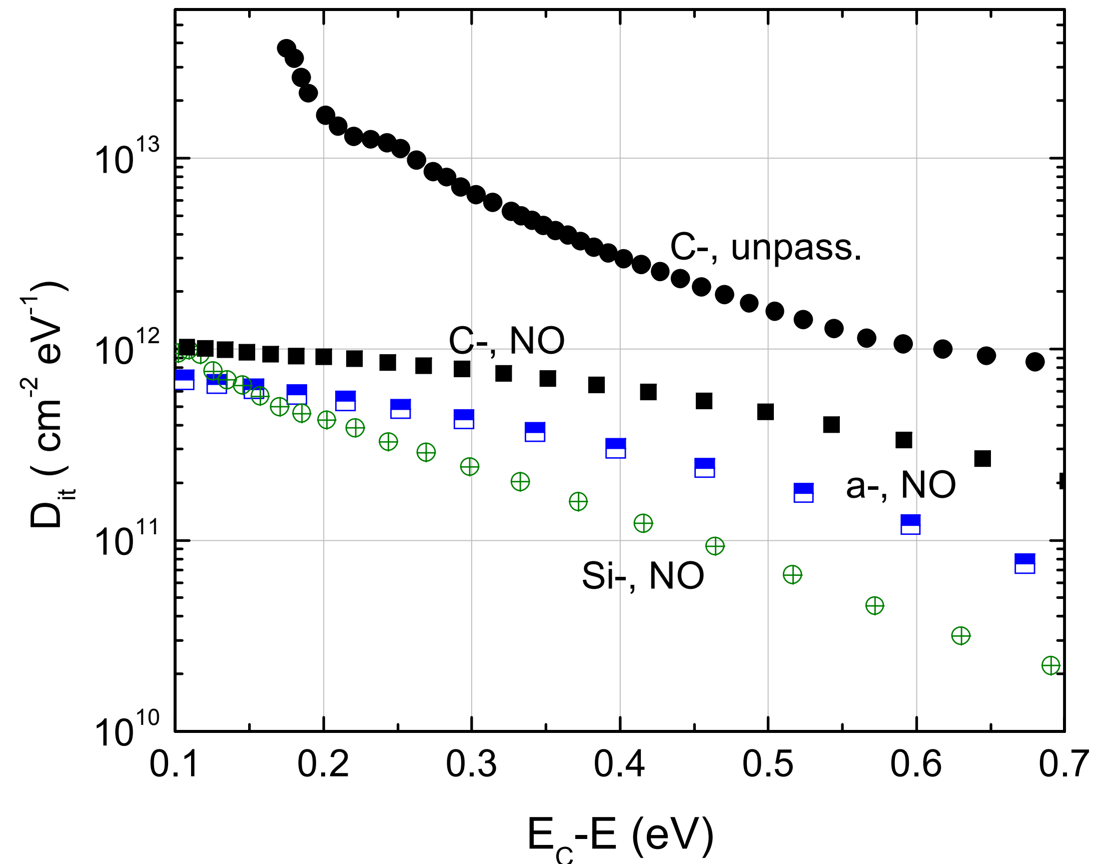
First demonstration of reduction if D_{IT} on carbon face

Effect of NO post-oxidation anneal

- 1175°C, 2h NO (0.5 l/min flowing gas)

(t_{ox}: Si~57 nm, a~28 nm, C~40 nm)

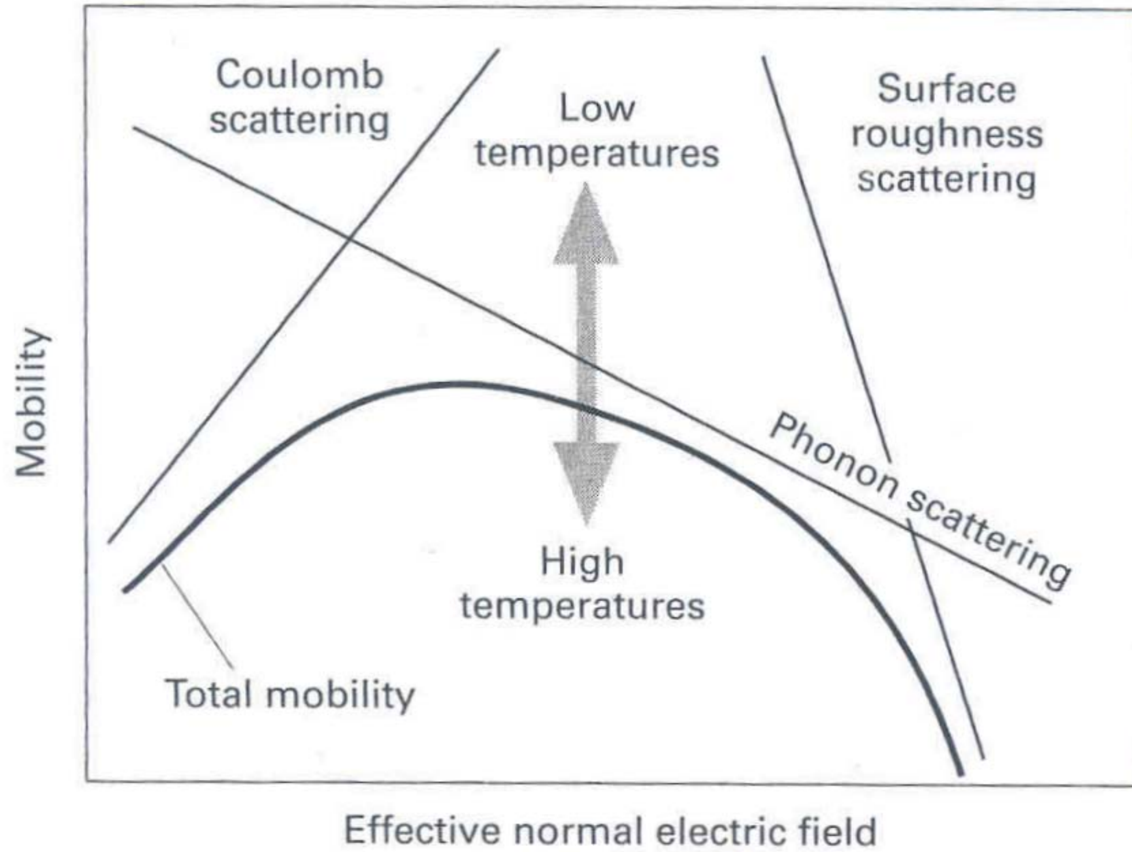
- hi-lo C-V at room temperature



- **NO anneal results in significant reduction of D_{it} on all three faces.**

•D_{it} of nitridated C-face is higher than the other faces.

S.Dhar et. al., accepted for publication in J. Appl. Physics (January 2005)

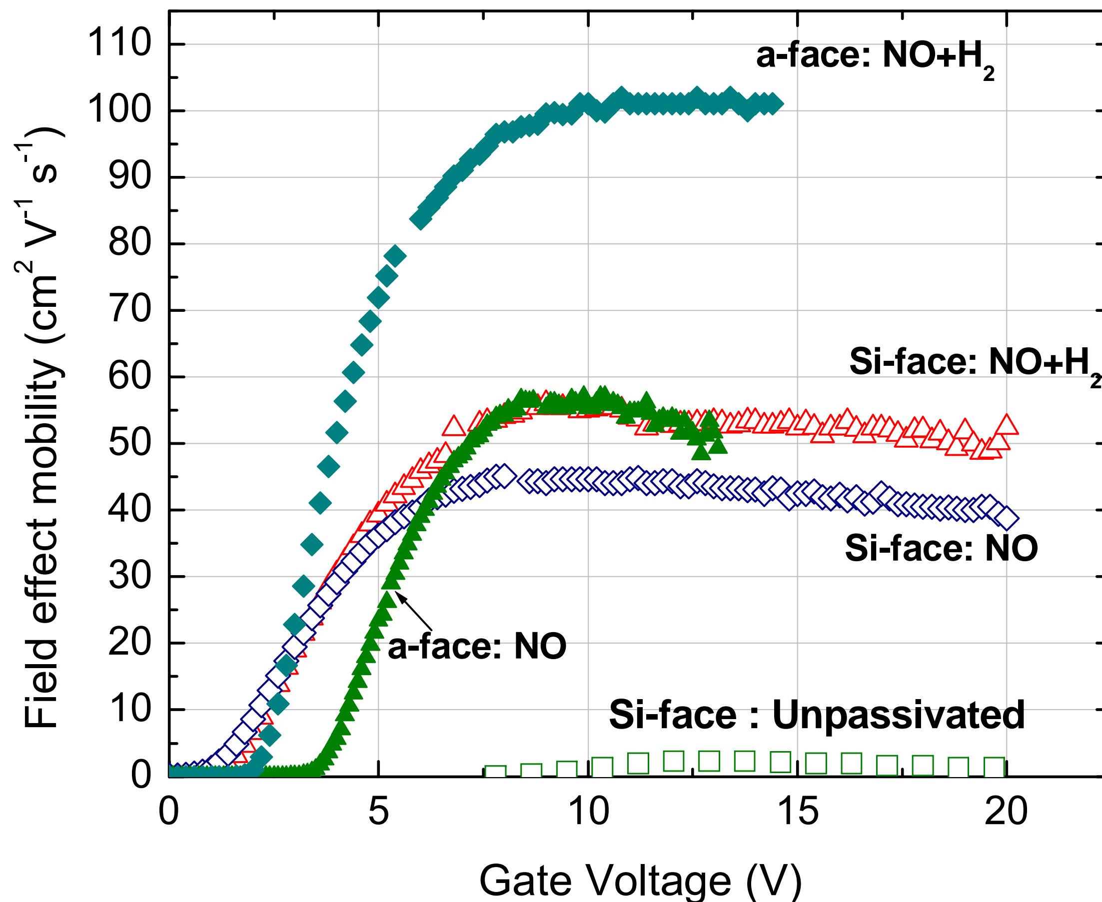

Coulomb scattering
Low temperatures
Surface roughness scattering
Mobility
Phonon scattering
High temperatures
Total mobility
Effective normal electric field

MOSFET Mobility: Si-face and a-face

- **Record high mobility for (NO+H_2) a-face MOSFETs**

$\mu_{max} \approx 100$ cm^2 V^{-1} s^{-1}

S.Dhar, L. C. Feldman, S. Wang and J. R. Williams, to be published in MRS bulletin (April 2005).



- Highest field effect mobility inspite of having similar D_{it} as Si-face
  - Traps E_C- E < 0.1 eV?
  - Interface roughness?
  - Other reasons?

The Analysis Problem

What is the role of the nitrogen?

How much is present?

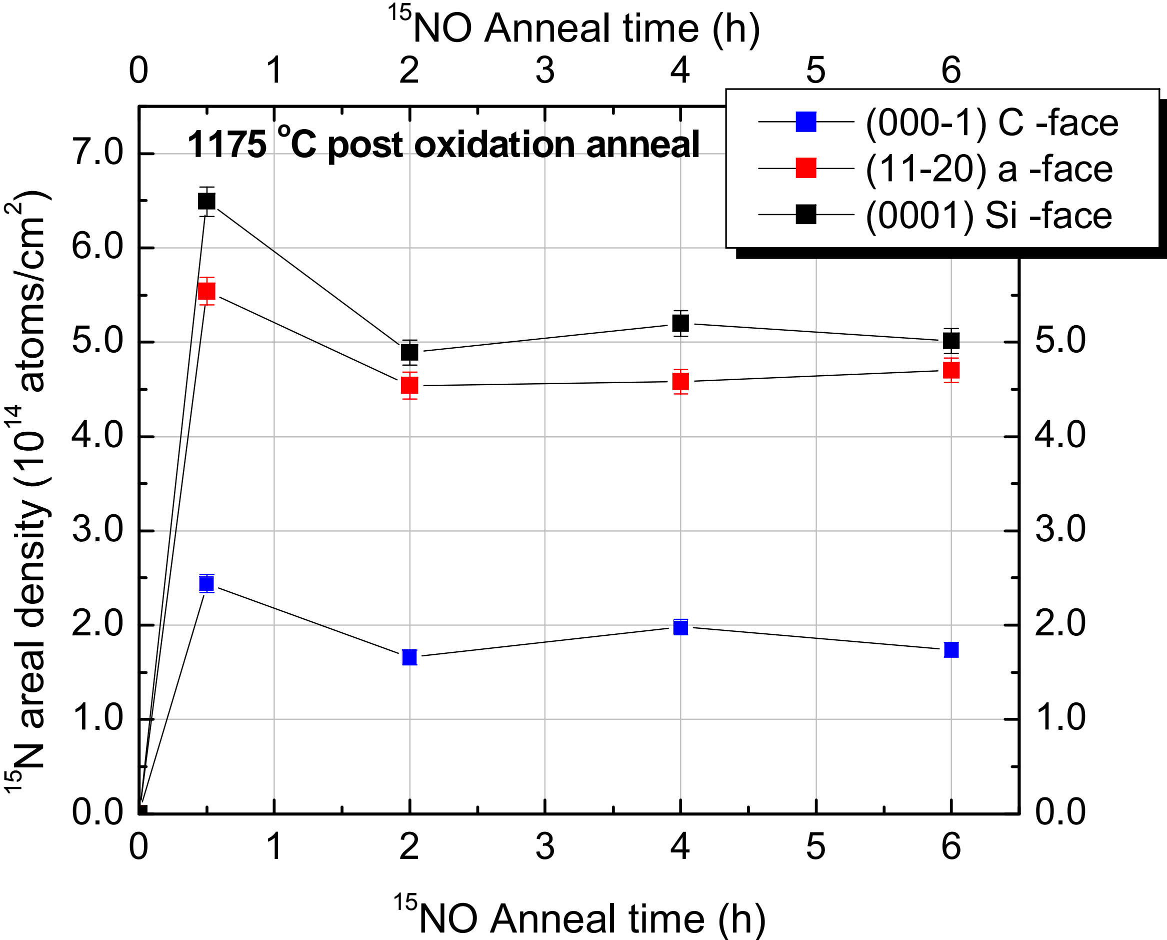
What is the depth profile?

Comparison of techniques.

Nitridation anisotropy among crystal faces

^{15}N (p,^{4}He) ^{12}C

Nitrogen uptake on the (0001) C-face and (1120) a-face greater than the (0001) Si-face by a factor of ~3



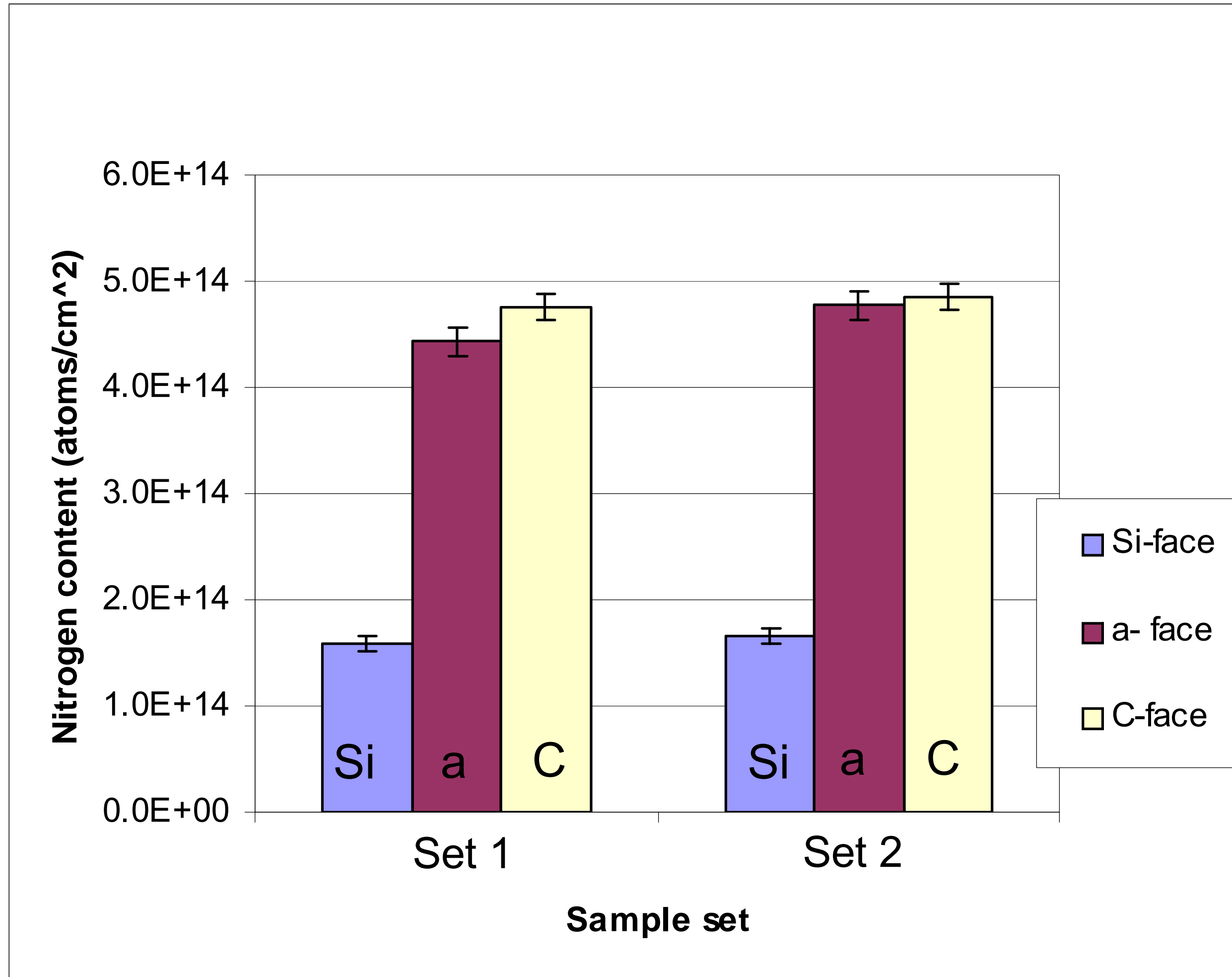
^{15}NO anneal , 1175 °C , 100 Torr

Initial oxide thickness ~30 nm on all faces,

Nitridation anisotropy among crystal faces

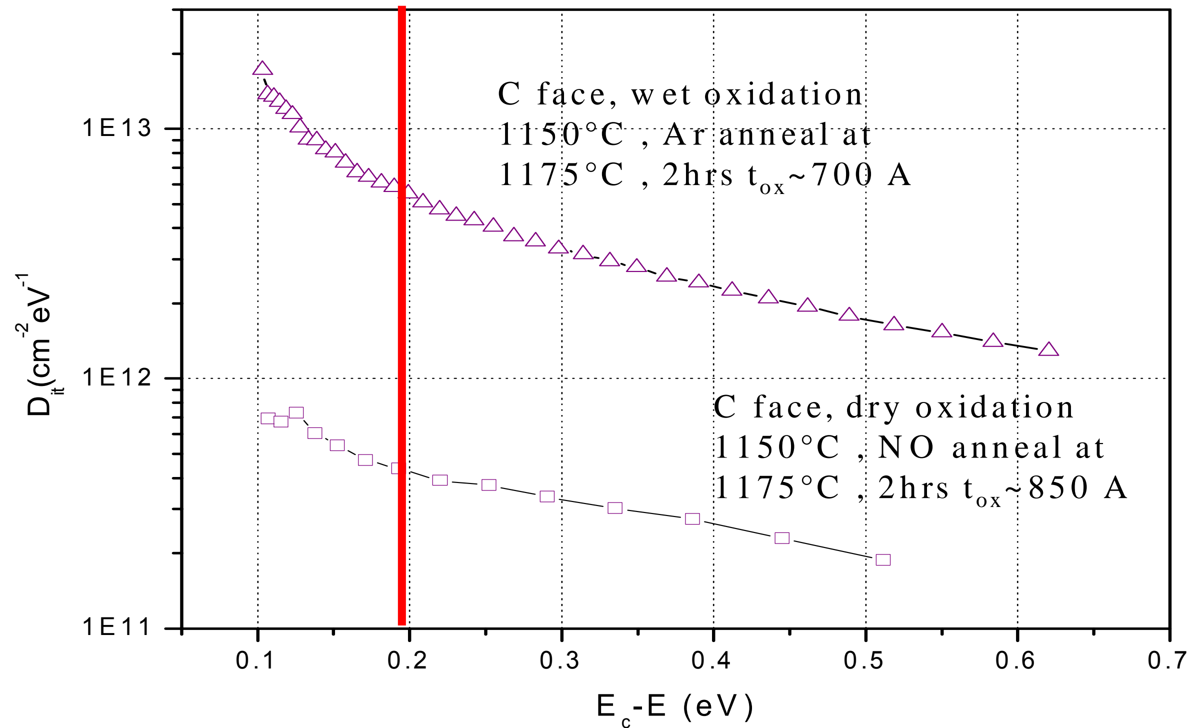
^{15}NO anneal , 1175 °C , 120 Torr, 2 h

Initial oxide thickness ~30 nm on all faces, **^{15}N (p,^{4}He) ^{12}C**



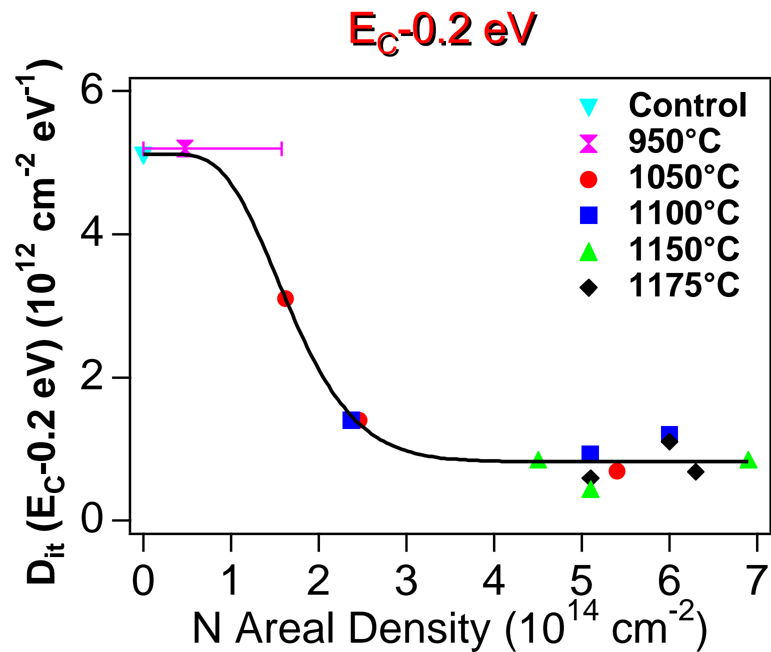
Nitrogen uptake on the $(000\bar{1})$ C-face and $(11\bar{2}0)$ a-face greater than the (0001) Si-face by a factor of ~3

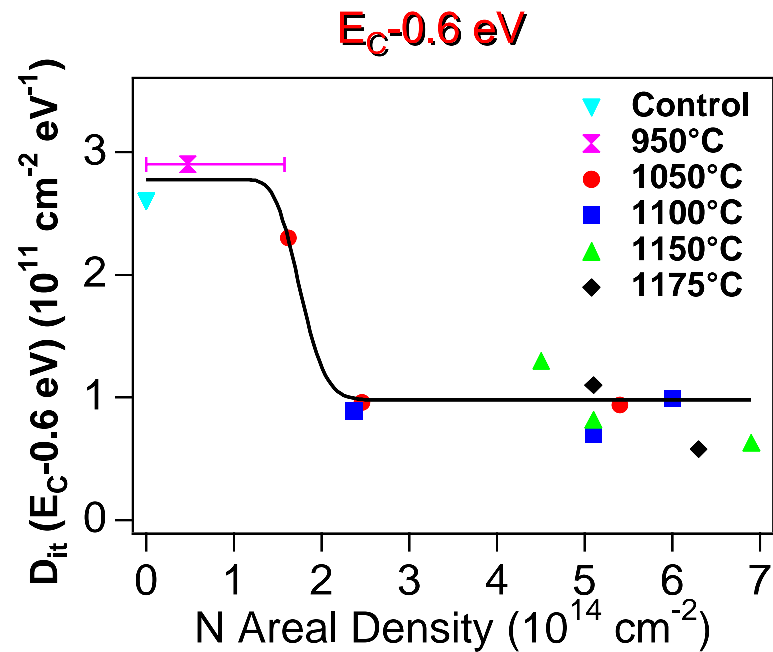
Effect of NO on the (0001) C face



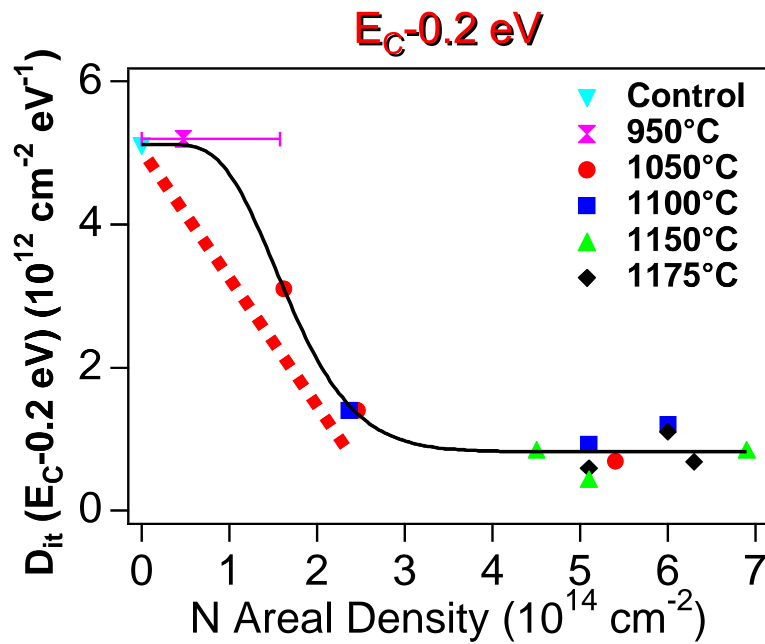
Defect density at a specific energy level in the band-gap.

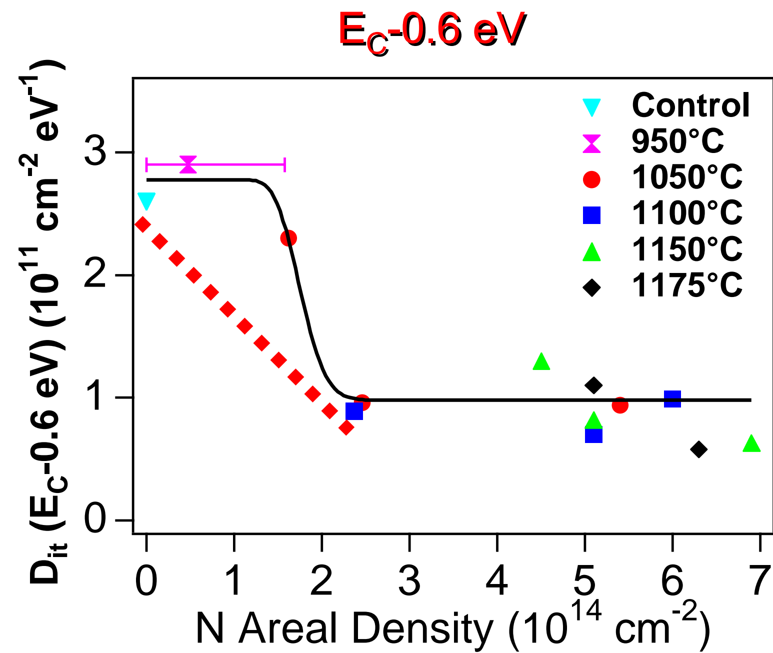
Fits to the D_{it} vs N Data



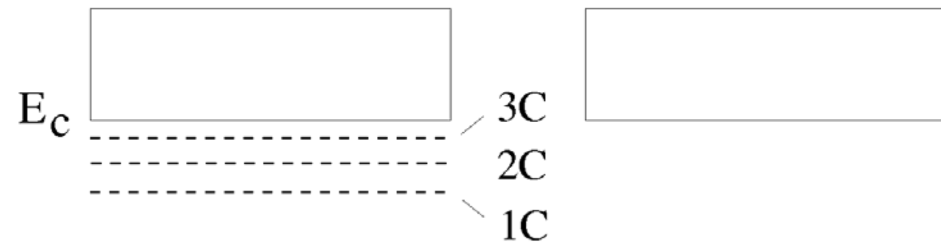


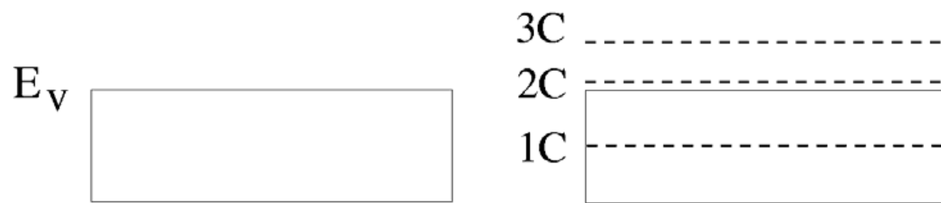
Fits to the D_{it} vs N Data





C/SiO States in SiC Bandgap

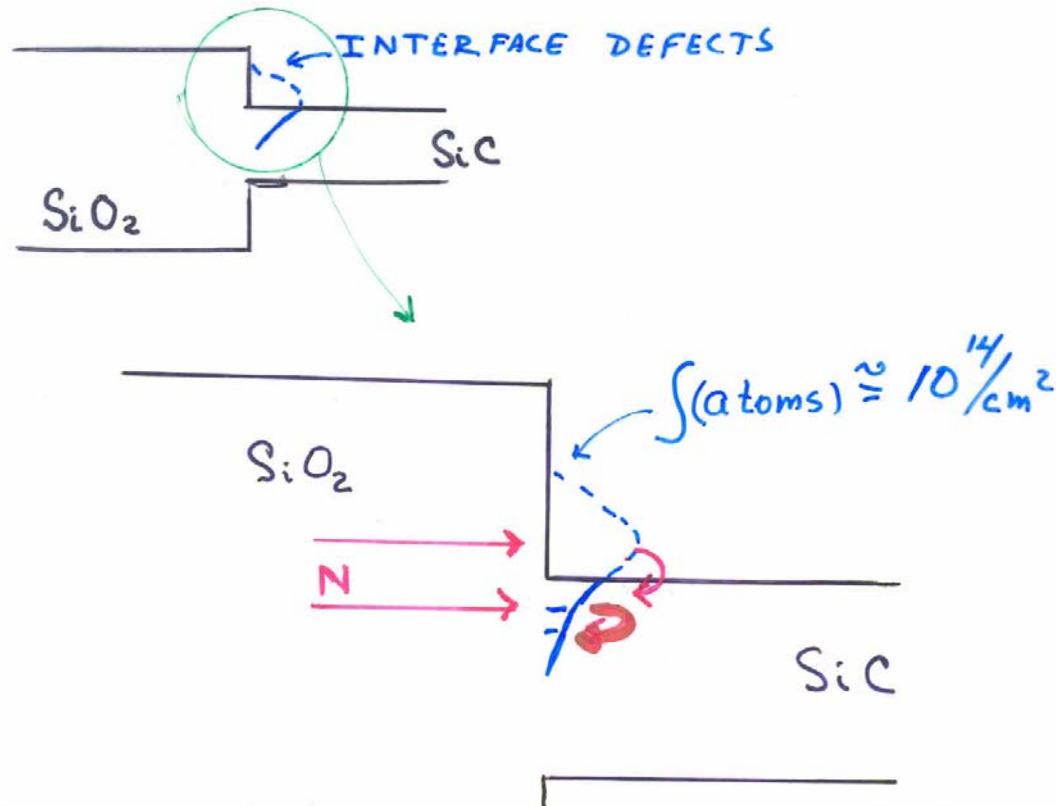




(a) Without N

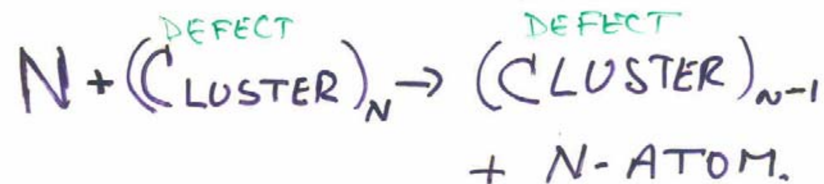
(b) With N

Passivation Dynamics

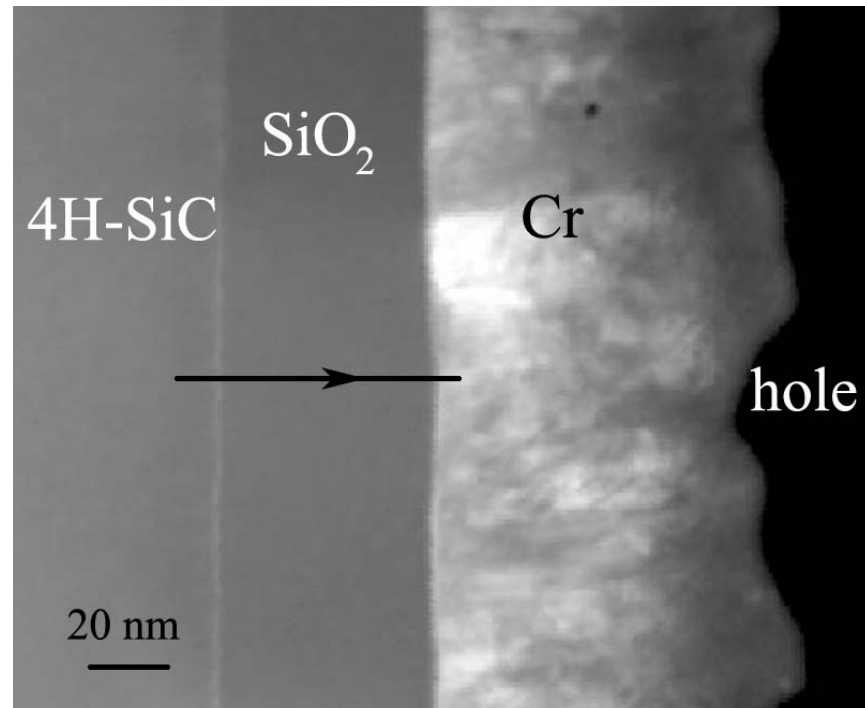


Explains why $10^{14}/cm^2$ nitrogen is required to passivate $10^{12}/cm^2$ defects.

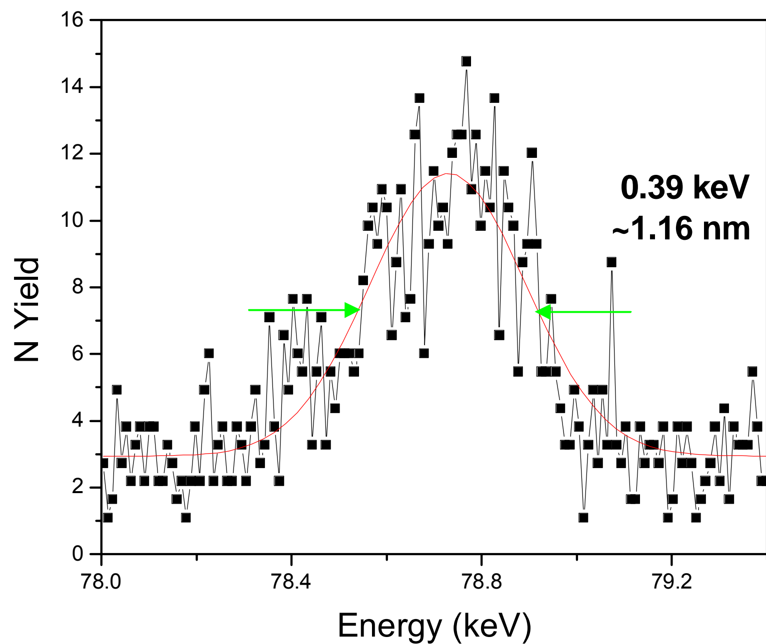
1) V.V. Afanasev, M. Bassler, G. Pensl, and m. Sculz, Phys. Stat. Sol.(A) 162, 321 (1997).



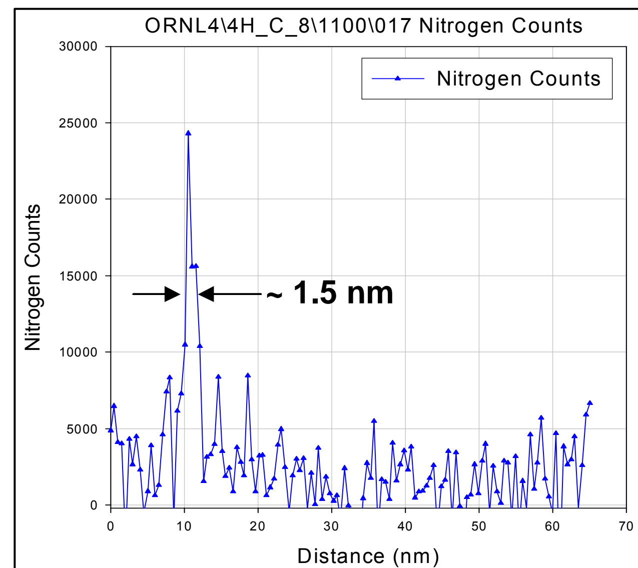
NITROGEN DEPTH PROFILES



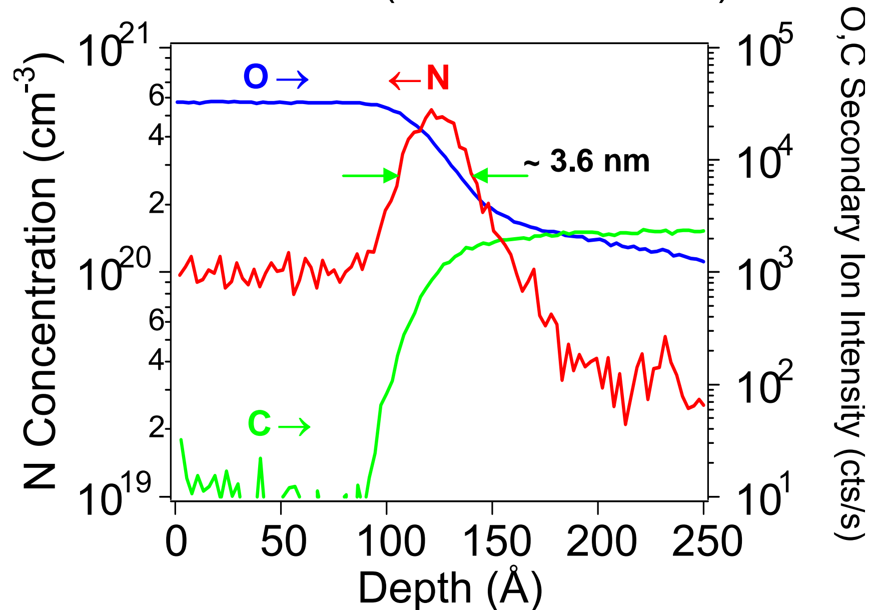
MEIS ~1.16 nm (Song et. al.)



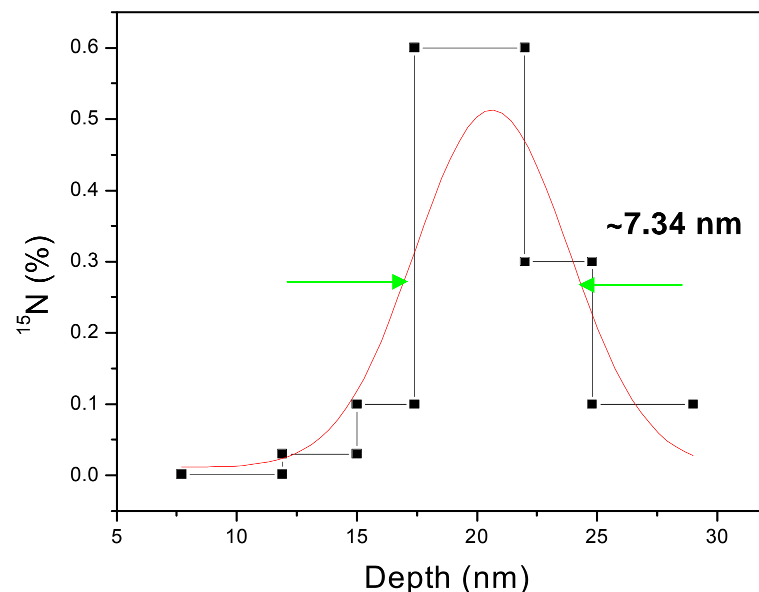
EELS ~1.5 nm (Chang et. al.)



SIMS ~3.6 nm (Mc Donald et. al.)

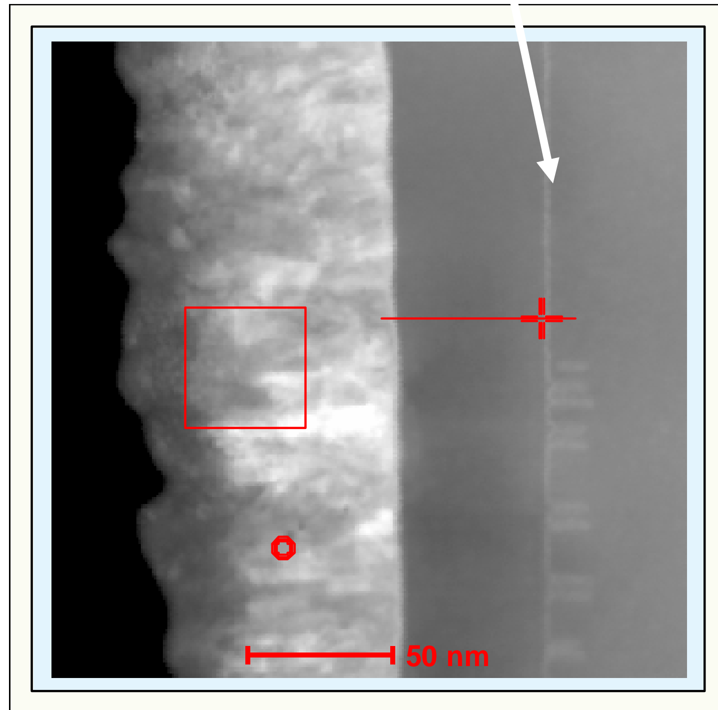


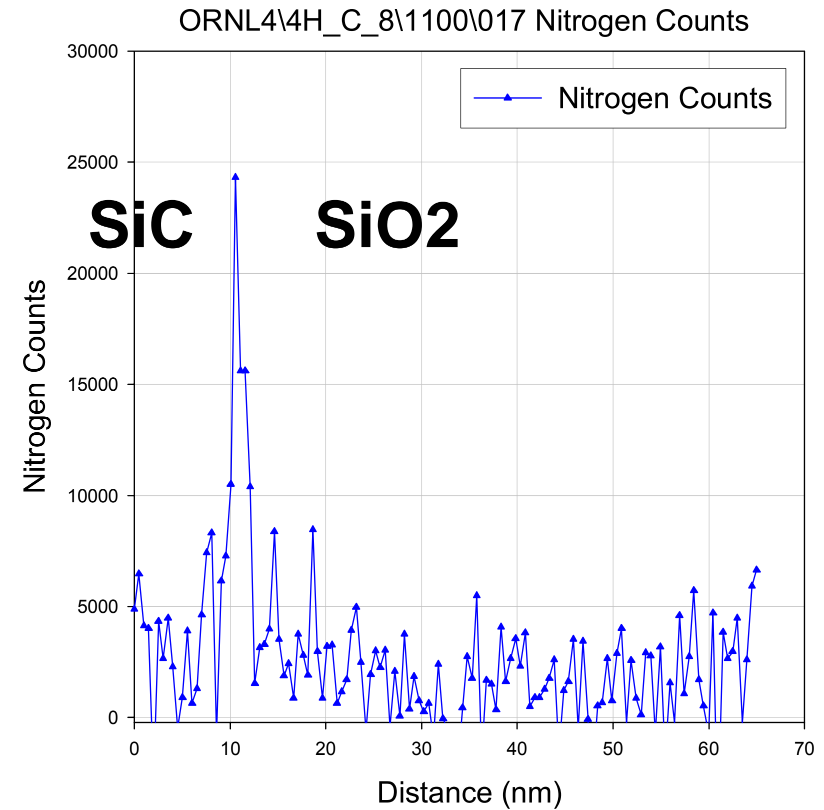
NRA ~ 7.34 nm (Mc Donald et. al.)



EELS results – scanning TEM (STEM)

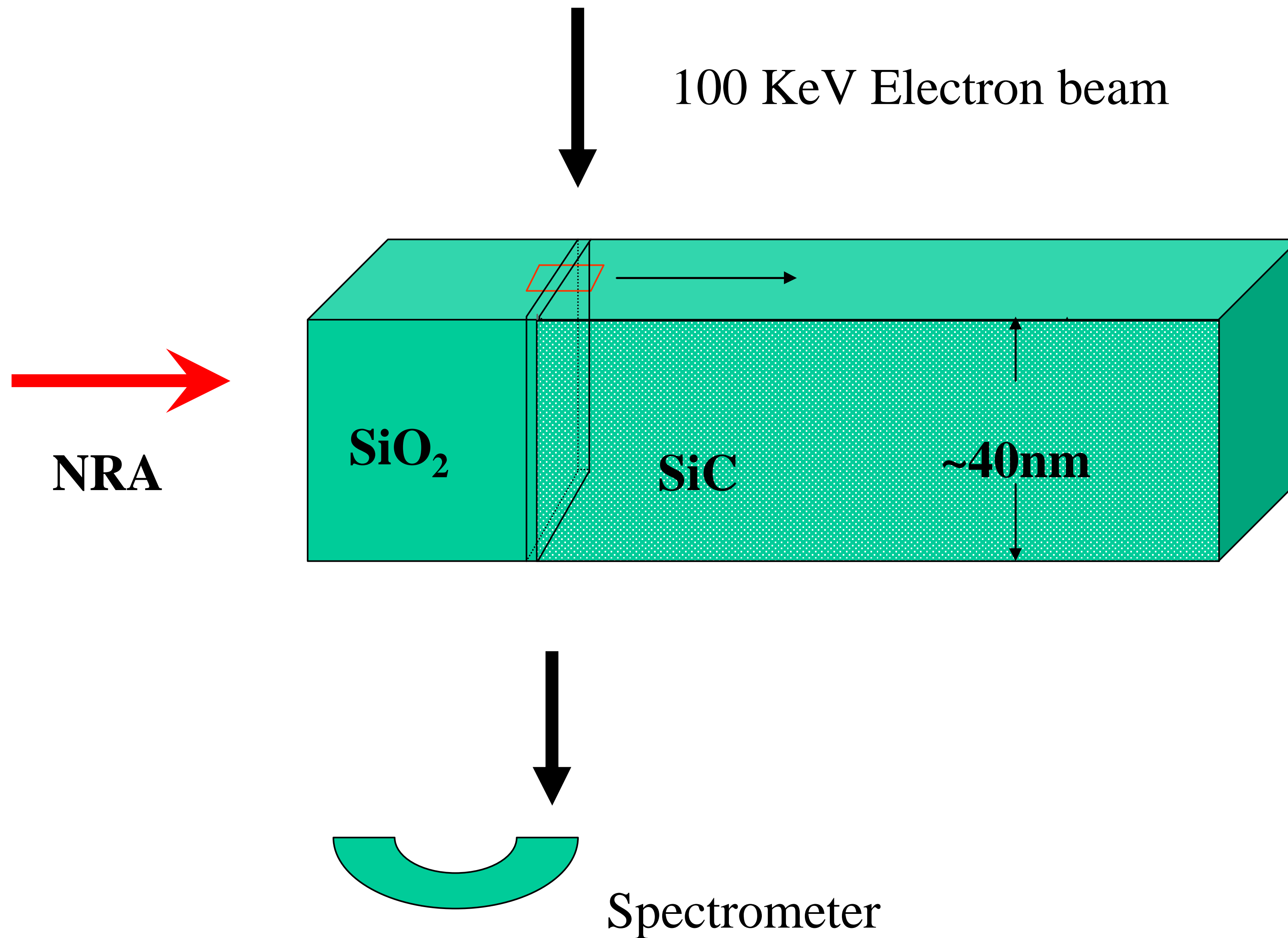
Electron beam at the interface



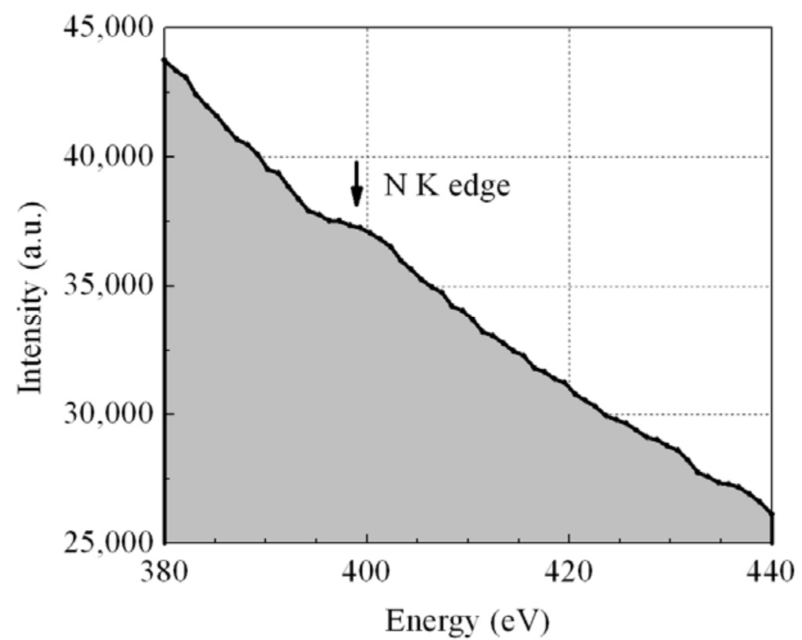


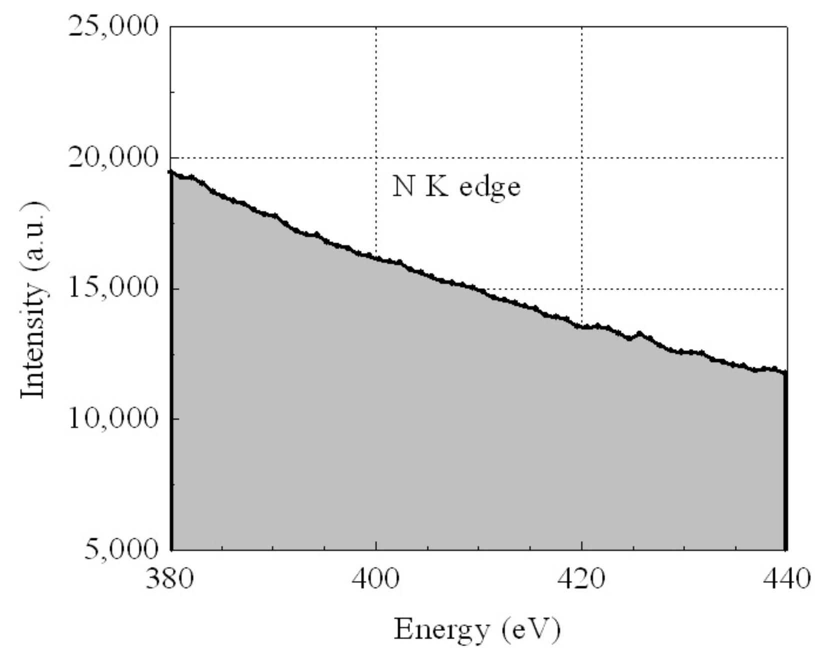
Nitrogen Profile At the SiC/SiO2 Interface

EELS PROFILE and NUCLEAR REACTION ANALYSIS

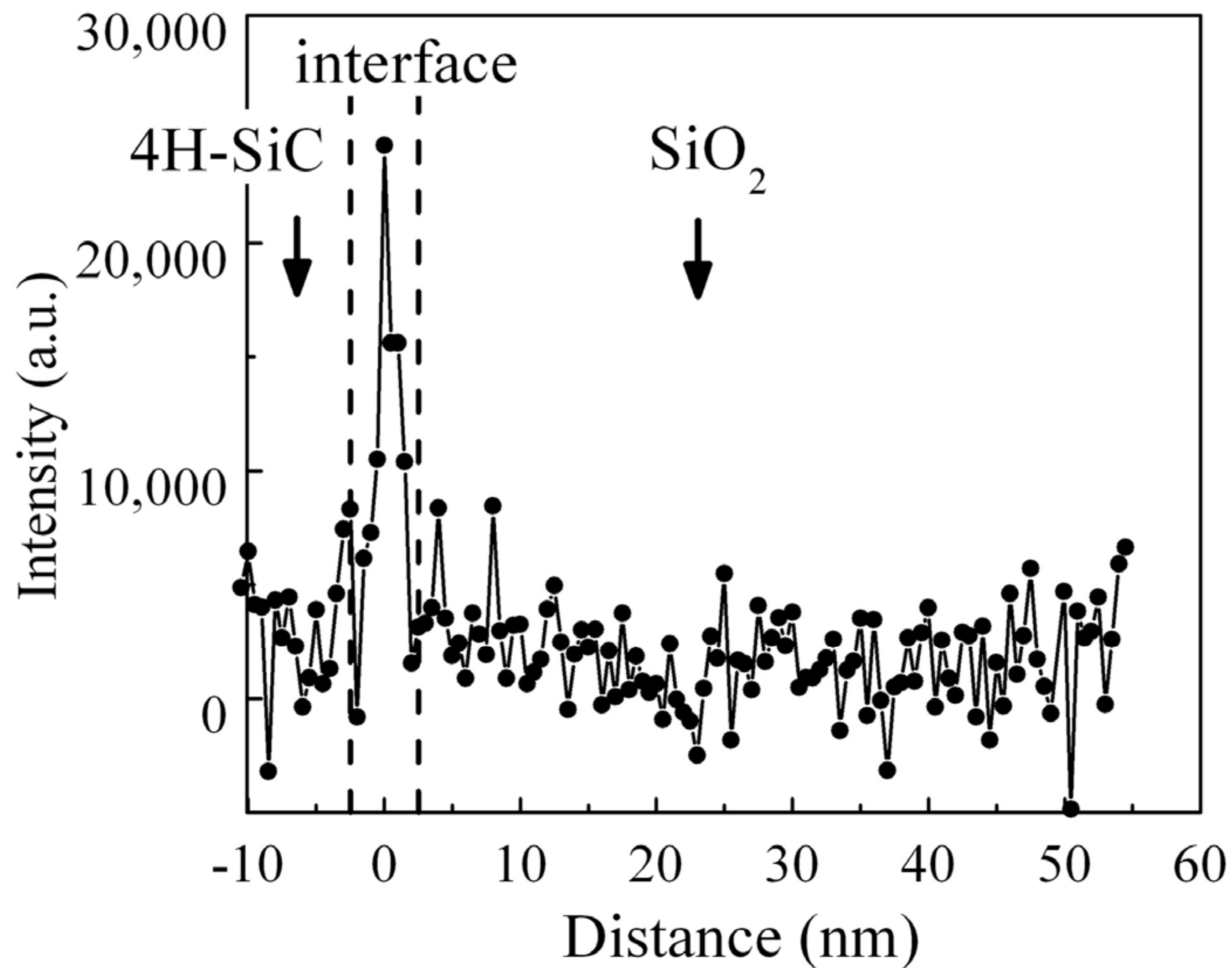


EELS SPECTRA W/WO NITROGEN

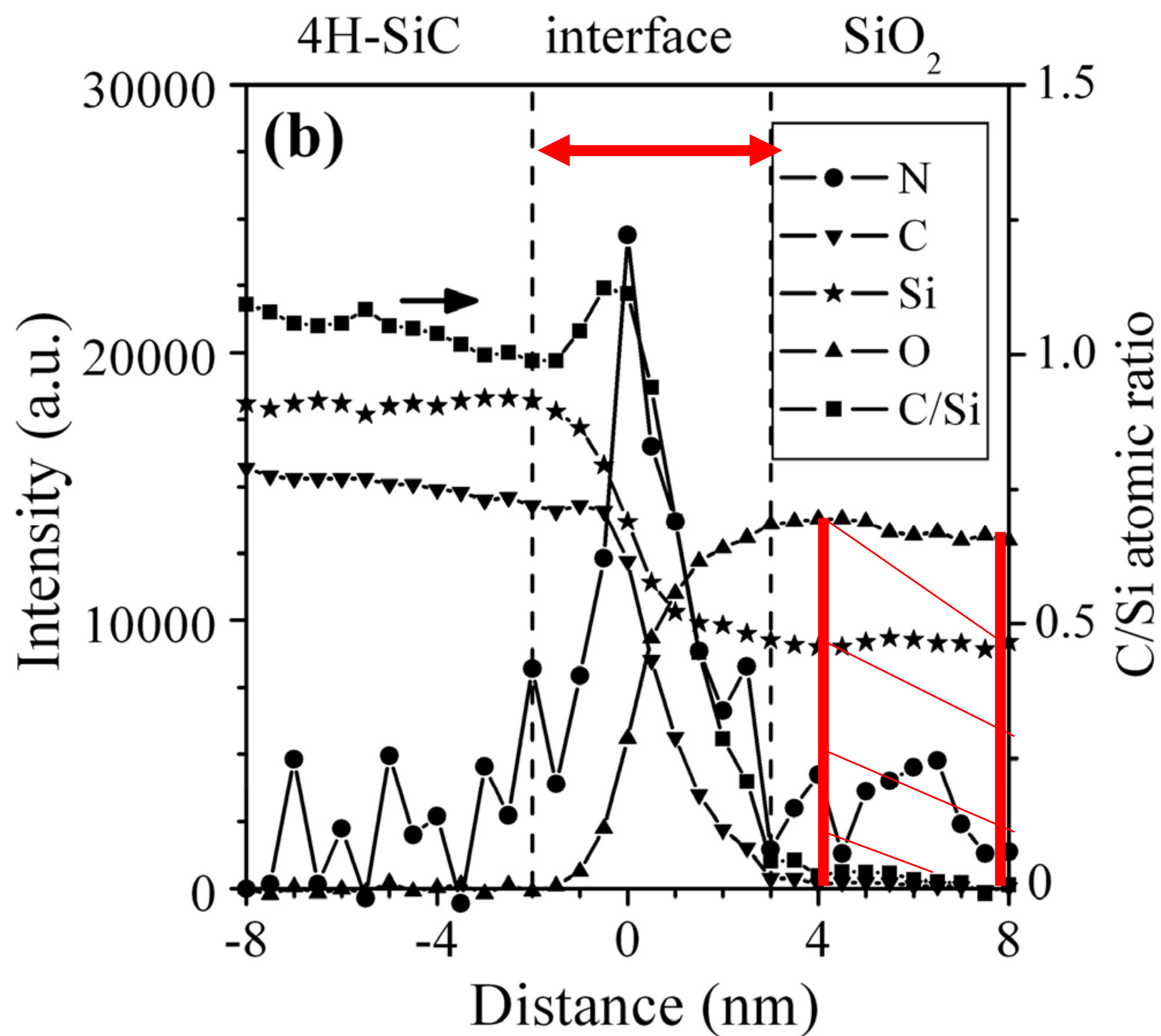




"BURIED" NITROGEN PROFILE



WINDOWS FOR C and N SUMS



QUANTITATIVE ANALYSIS

$$\frac{N_A}{N_B} = \frac{I_A}{I_B} * \frac{\sigma_B}{\sigma_A}$$

$$\frac{N_N}{N_C} = \frac{\Sigma I_N}{\Sigma I_C} * \frac{\sigma_C}{\sigma_N} = \frac{A_N \cdot w \cdot t_N}{A_C \cdot w \cdot t_C}$$

$$A_N = \frac{\Sigma I_N}{\Sigma I_C} \cdot \frac{\sigma_C}{\sigma_N} \cdot \frac{t_C}{t_N} \cdot A_C$$

Calculated Partial Ionization Cross Sections

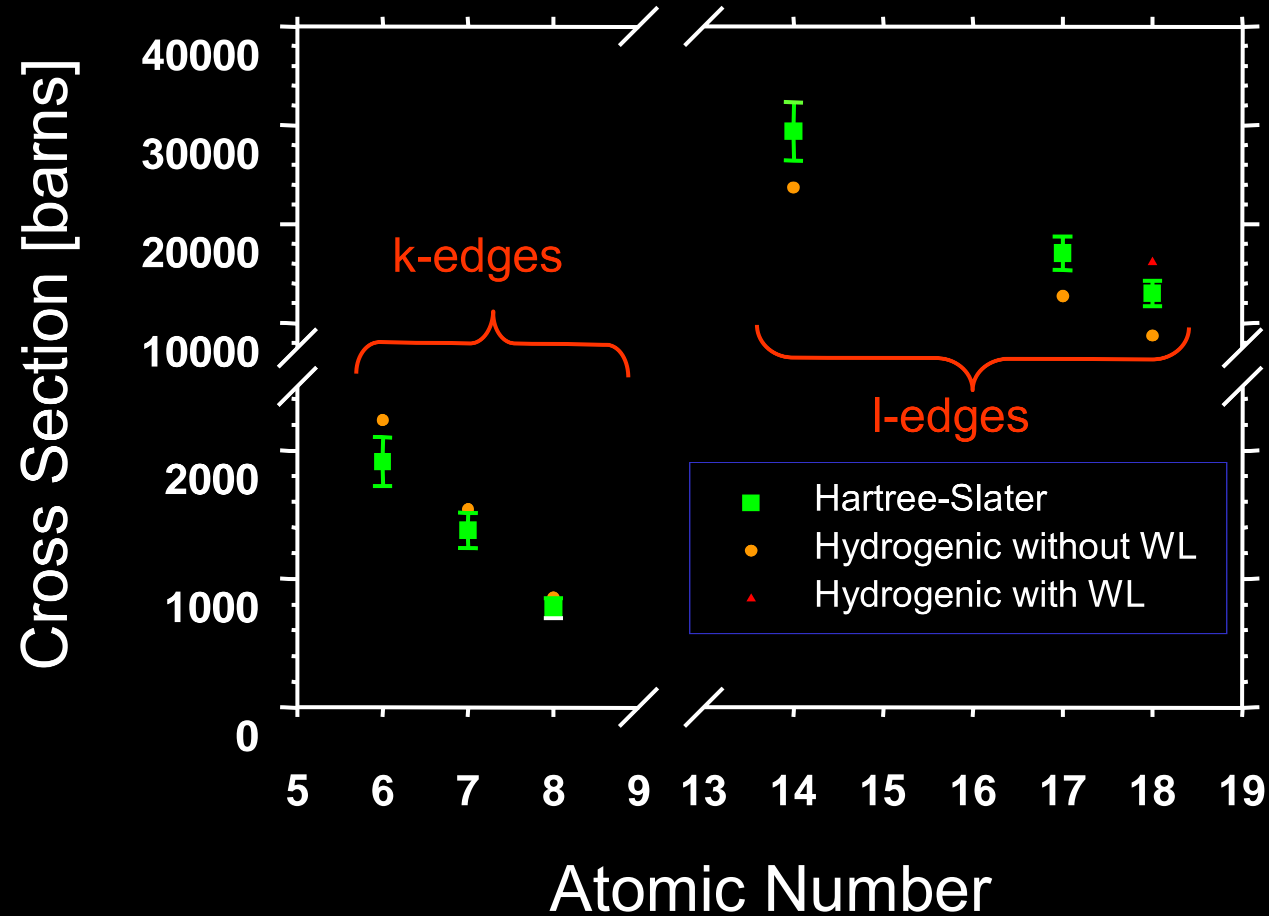
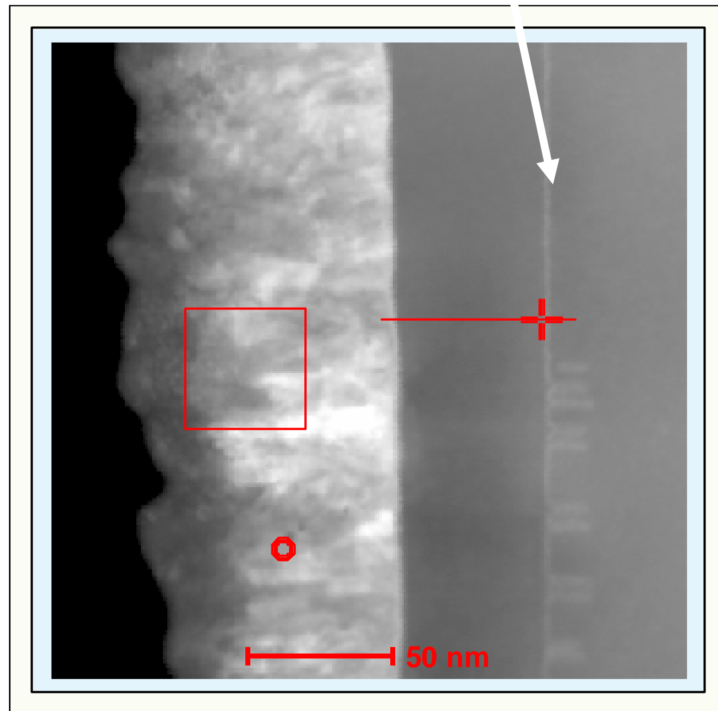


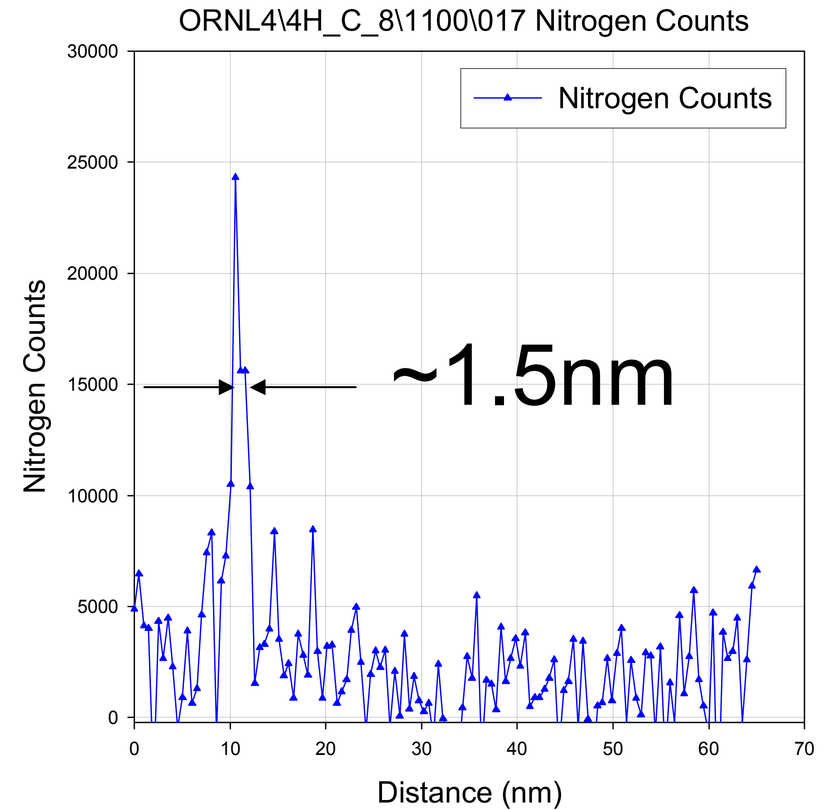
Table II. Comparison of N areal densities by EELS and NRA

SiC substrates	EELS	NRA
C-face	$(1.0 \pm 0.2) \times 10^{15}$ cm^{-2}	$(1.05 \pm 0.03) \times 10^{15}$ cm^{-2}
Si-face	$(0.35 \pm 0.13) \times 10^{15}$ cm^{-2}	$(0.35 \pm 0.02) \times 10^{15}$ cm^{-2}

EELS results – scanning TEM (STEM)

Electron beam at the interface





Nitrogen Profile At the SiC/SiO2 Interface

SPATIAL RESOLUTION

1. Fundamental interaction-

adiabatic distance ~hv/E_b = 0.05nm

K shell radius~a_o/Z ~.01nm

2. Beam spot size ~1.2 nm

3. Beam convergence~0.5nm

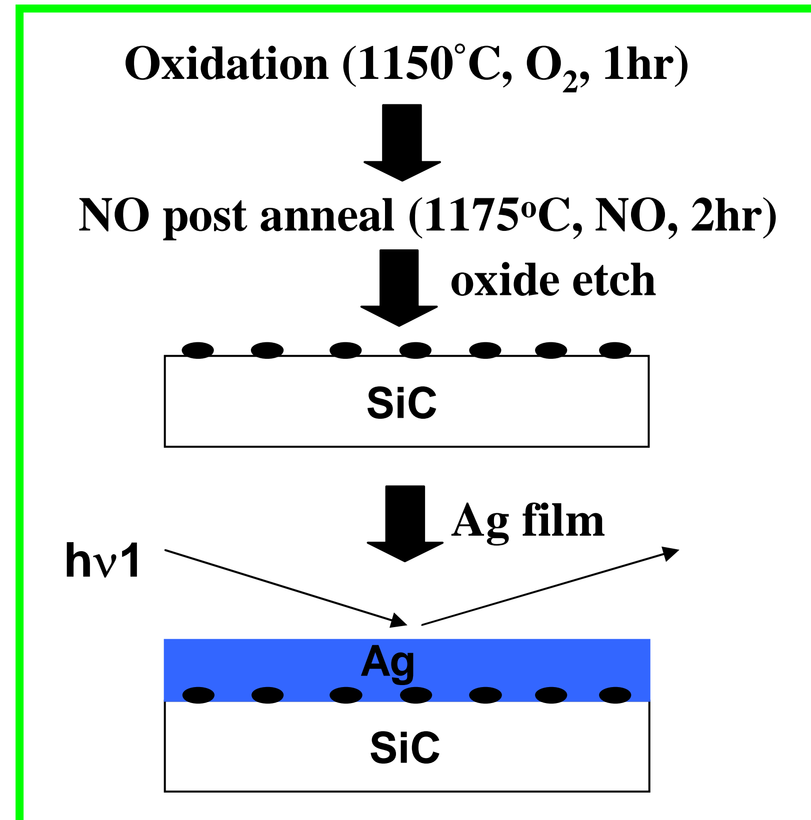
4. Multiple scattering~<1.0nm

5. Interface alignment~<0.6nm

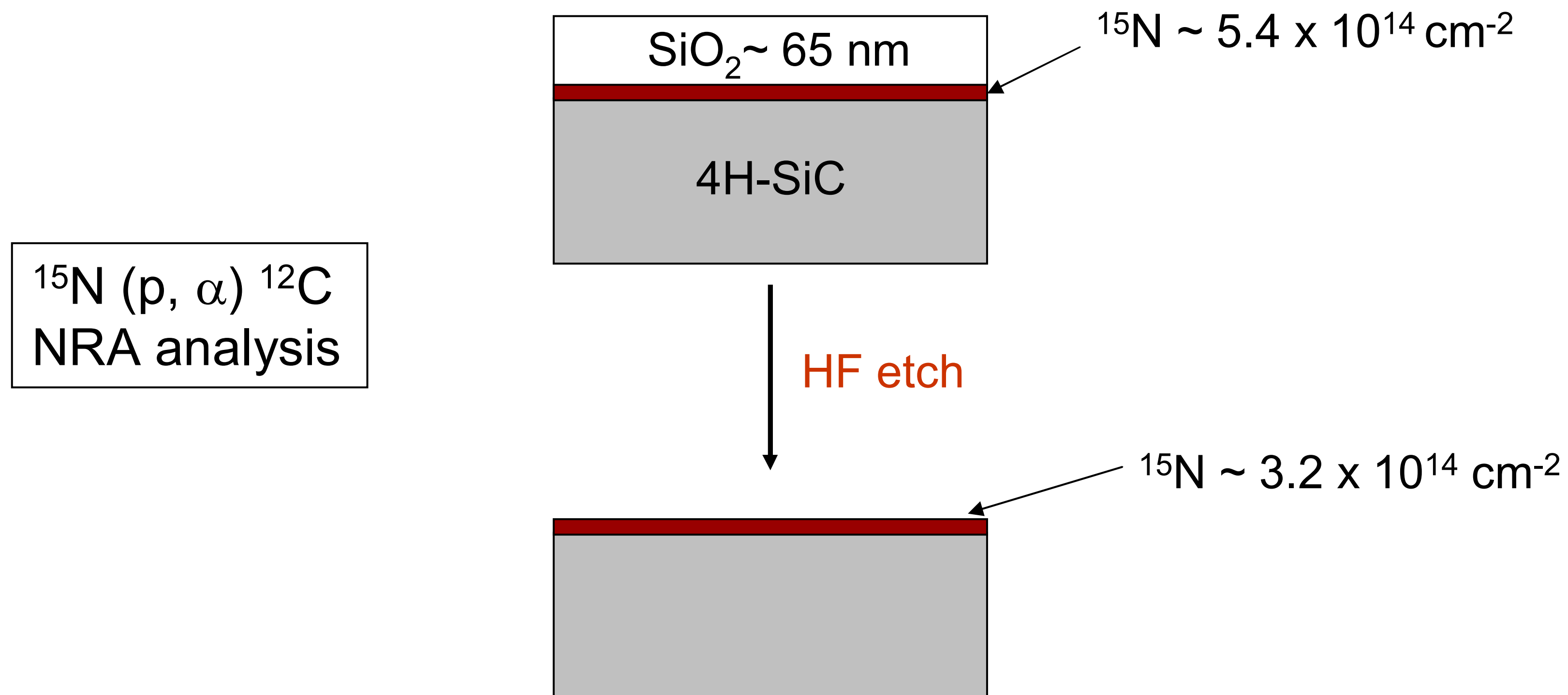
SiO_2/SiC interface: Physical analysis

Surface enhanced Raman spectroscopy (SERS)

▪ <u>Goal & sample preparation</u>
To investigate carbon clusters at the SiO_2 /SiC interface

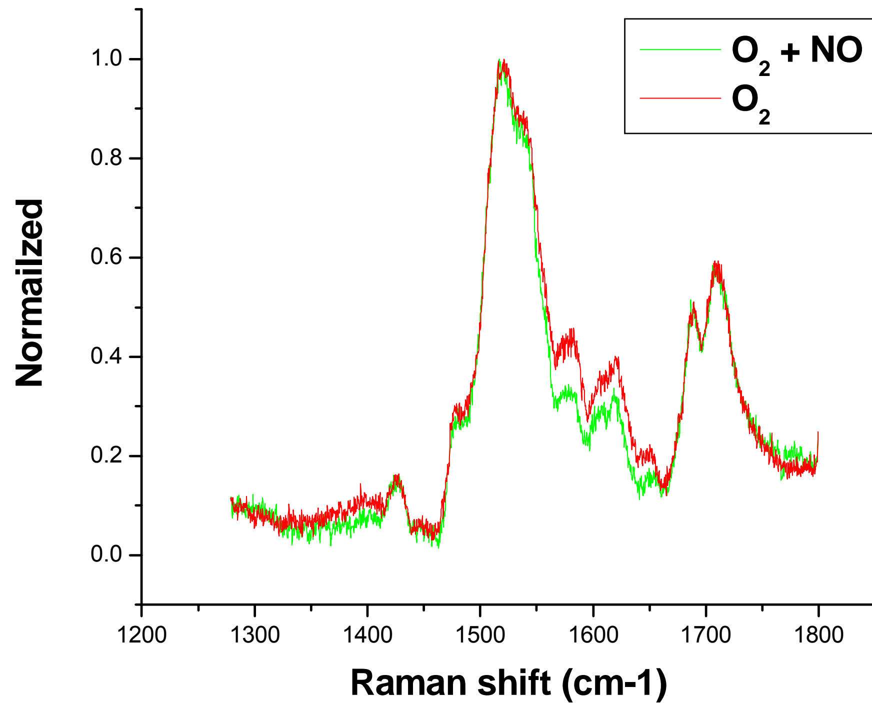


Effect of HF etching on NO annealed SiO_2/SiC

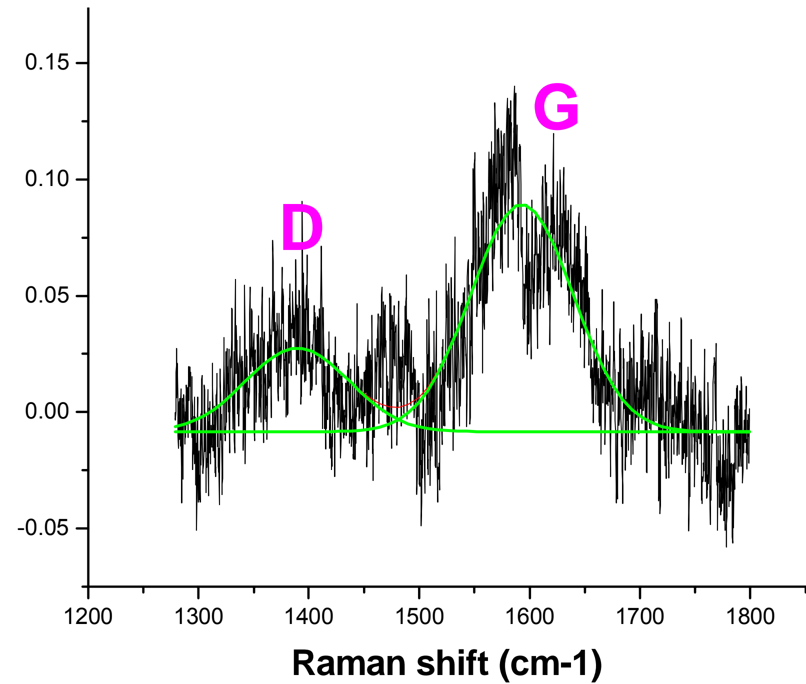


- **Nitrogen compound has higher HF etch resistance than SiO_2 or Si_3N_4**

Surface enhanced Raman spectroscopy (SERS) analysis



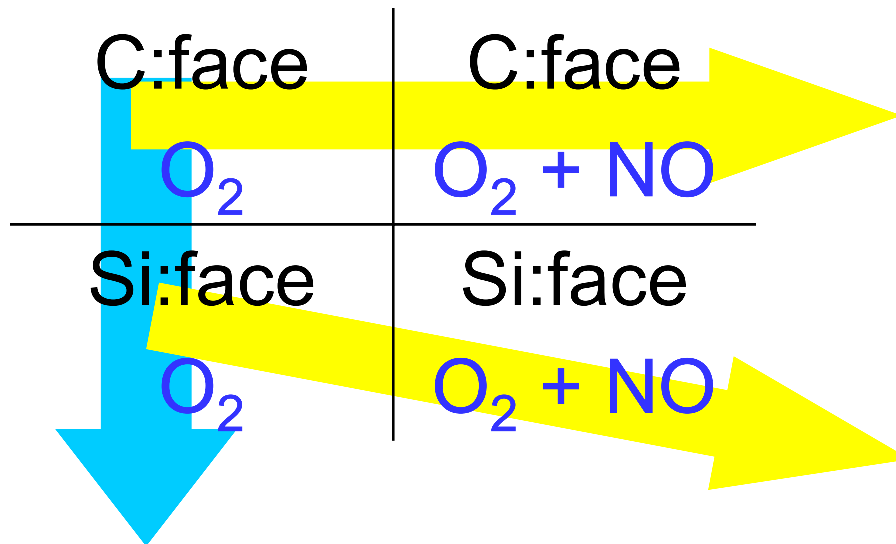
SERS spectra of oxidized C-face SiC

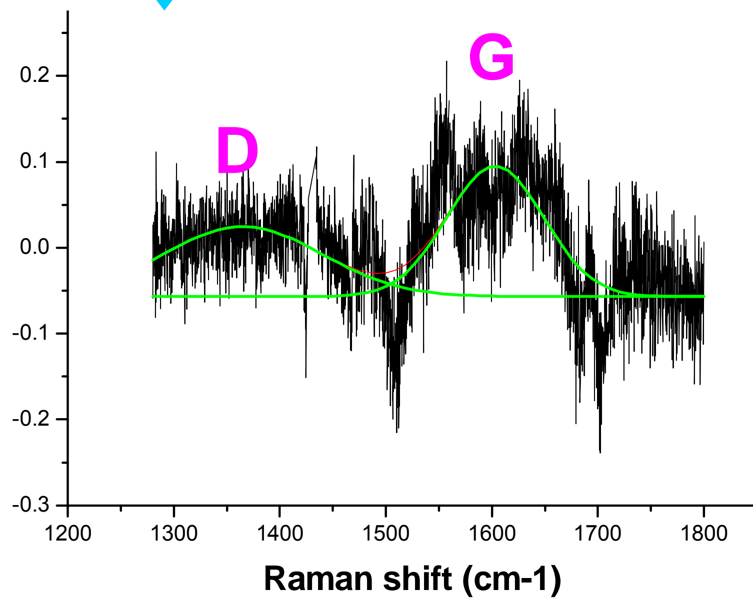


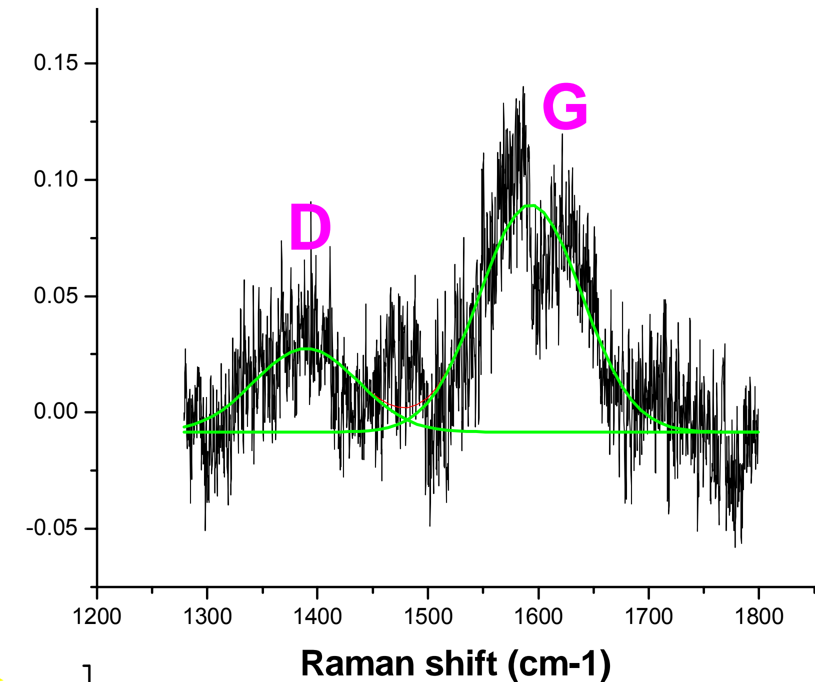
Carbon related peaks after subtracting (O_2 + NO) spectrum from (O_2) spectrum

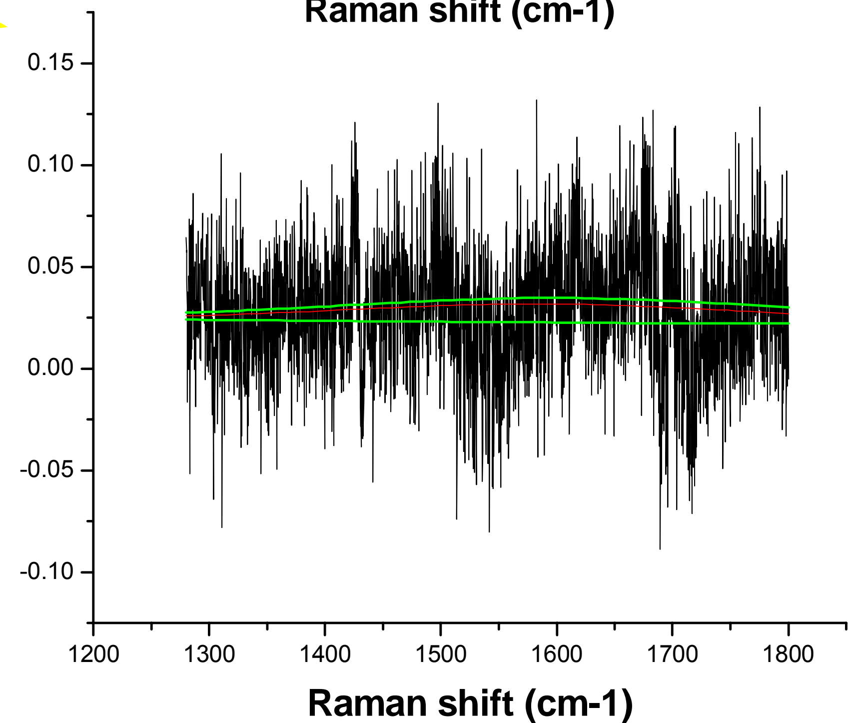
D(1390 cm^{-1}) and G(1580 cm^{-1}) band intensity decreases after NO anneal.

D & G bands as a function of face and processing









Materials science of hydrogenation process

- Effect of metal layer on H uptake
- Hydrogen incorporation at the SiO_2/4H-SiC
- Kinetics of H uptake and desorption

Sequential anneals in NO and H_2

Dry oxidation 1150 °C, 1-4 h

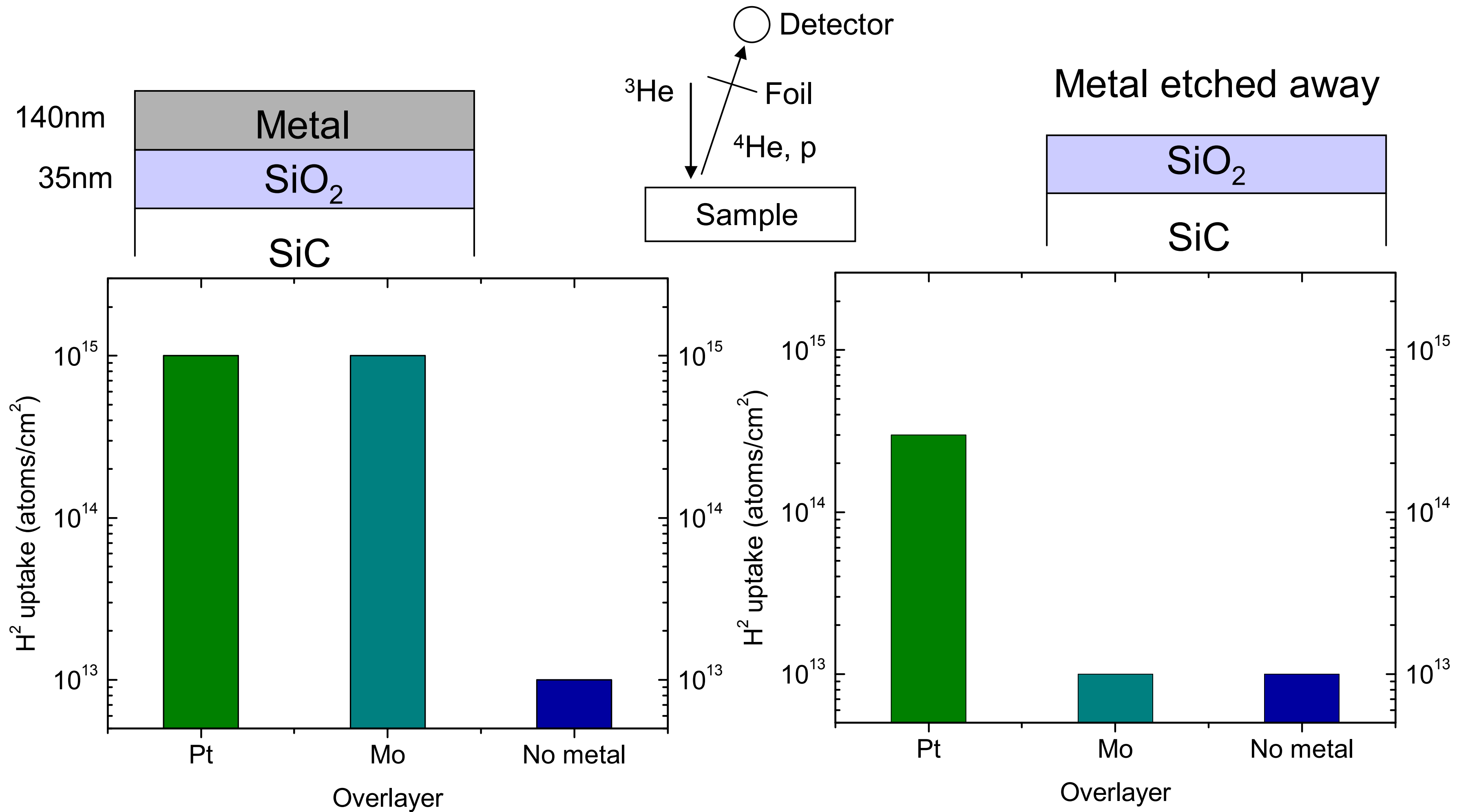
Post-oxidation anneal in NO, 1175 °C, 2 h

Gate metal Pt

Post- metallization anneal in H_2, 500 °C, 1 h

Effect of metal over-layer

Substitute ^2H for ^1H NRA : ^2H (^3He,p) ^4He Sensitivity ~ 10^{13} atoms cm^{-2}

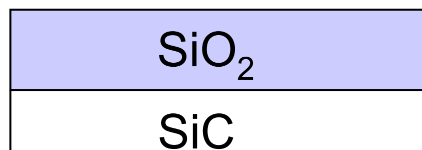


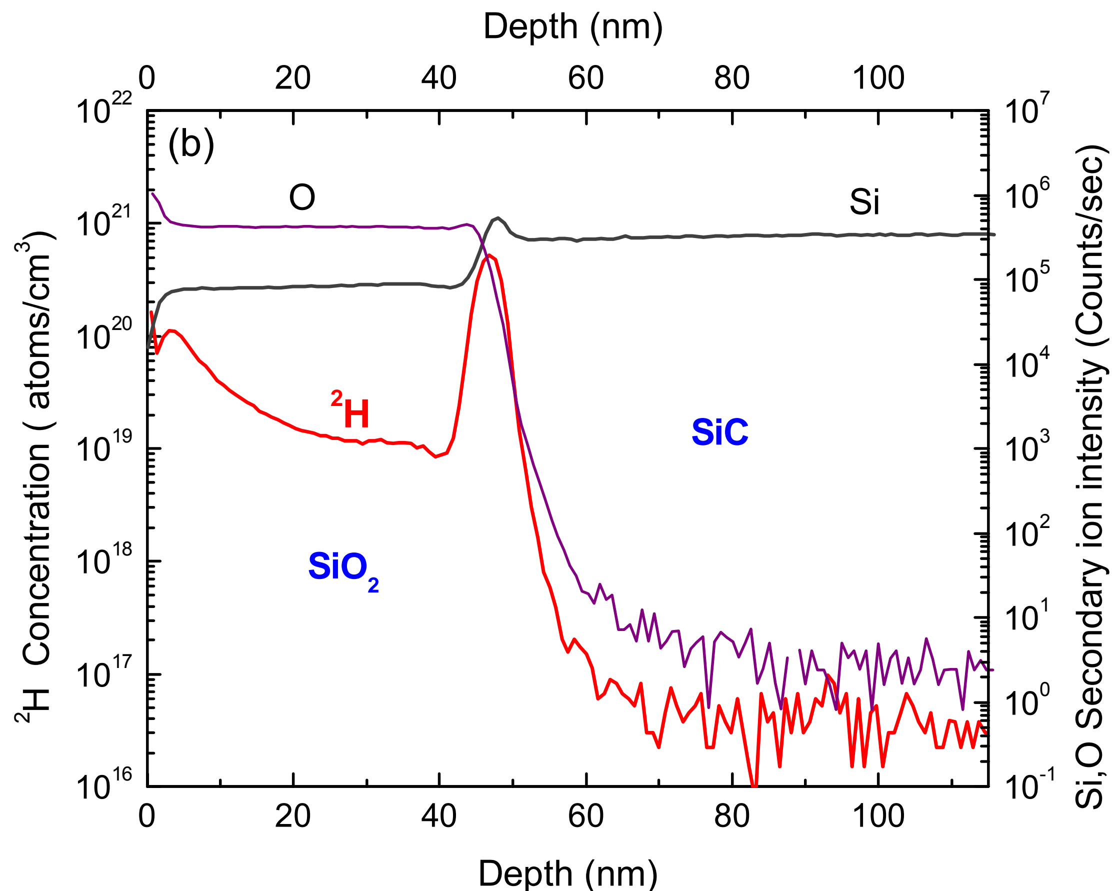
Presence of Pt leads to at least two orders of higher H incorporation in the oxide and at the interface

Hydrogen (deuterium) depth profile: SIMS

500°C, 1h ^2H anneal

Pt etched

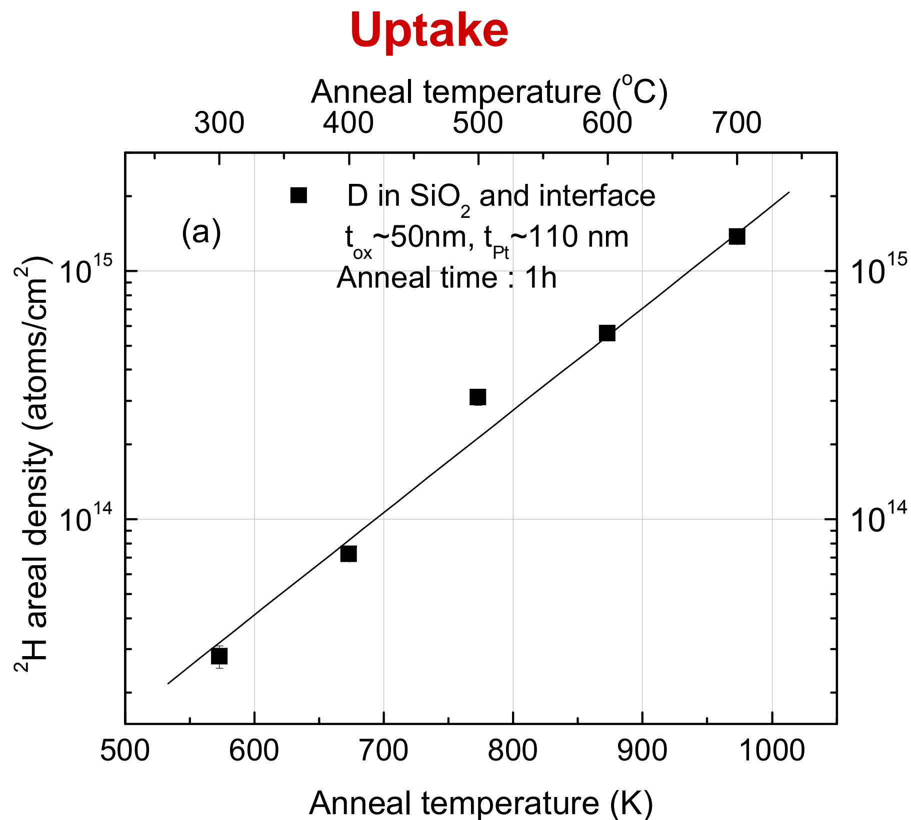




- **Near interfacial D concentration (using Pt over-layer) ~ 2.5 x 10^{14} cm^{-2} FWHM ~ 3.5 nm (within the depth resolution of SIMS)**
- **~80% of D in the oxide is at the interface.**

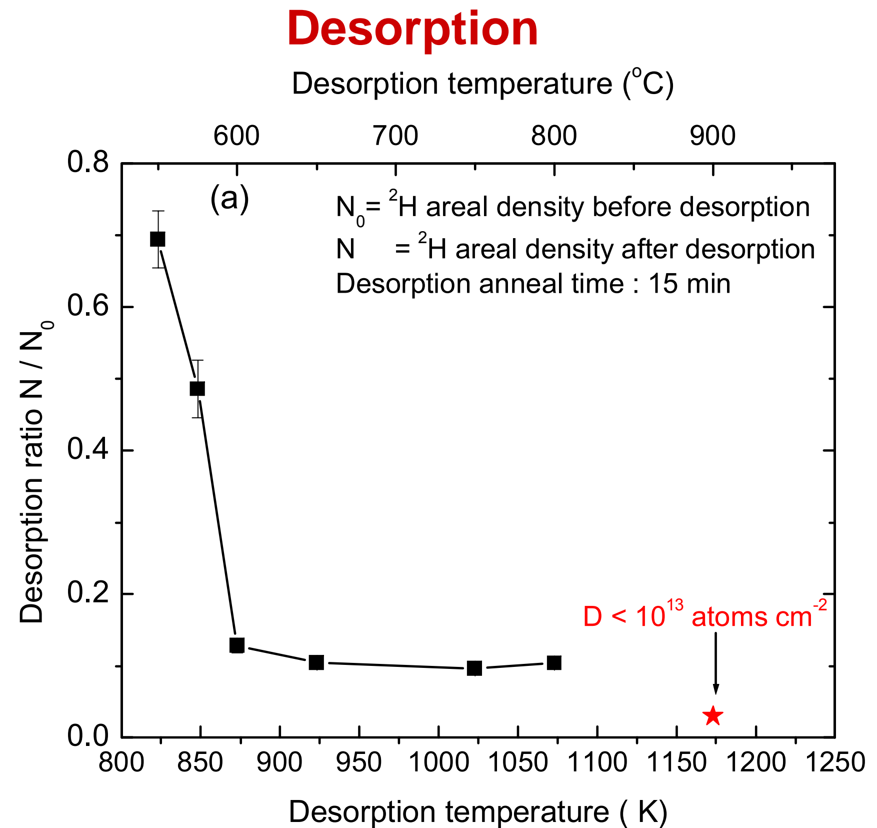
H uptake and desorption kinetics

Uptake



Apparent activation energy of H uptake into oxide : 0.47 eV

Desorption



Apparent activation energy of H desorption from oxide in the temp. range 550°C-600 °C: 2.1 eV

Hydrogenation at 500°C in the presence of Pt is a kinetically favorable process for H uptake.

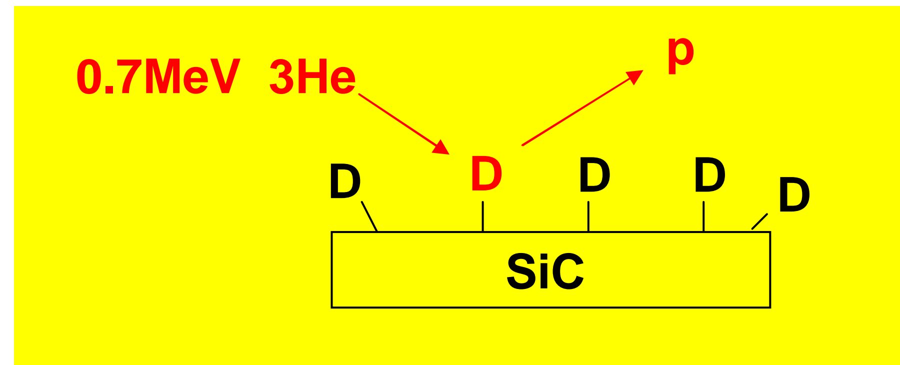
Deuterium detection using NRA

- **Motivation**

  Hydrogen passivation after HF wet etching in SiC faces

- **NRA condition**

  - D(3He, p)4He



- **Sample**

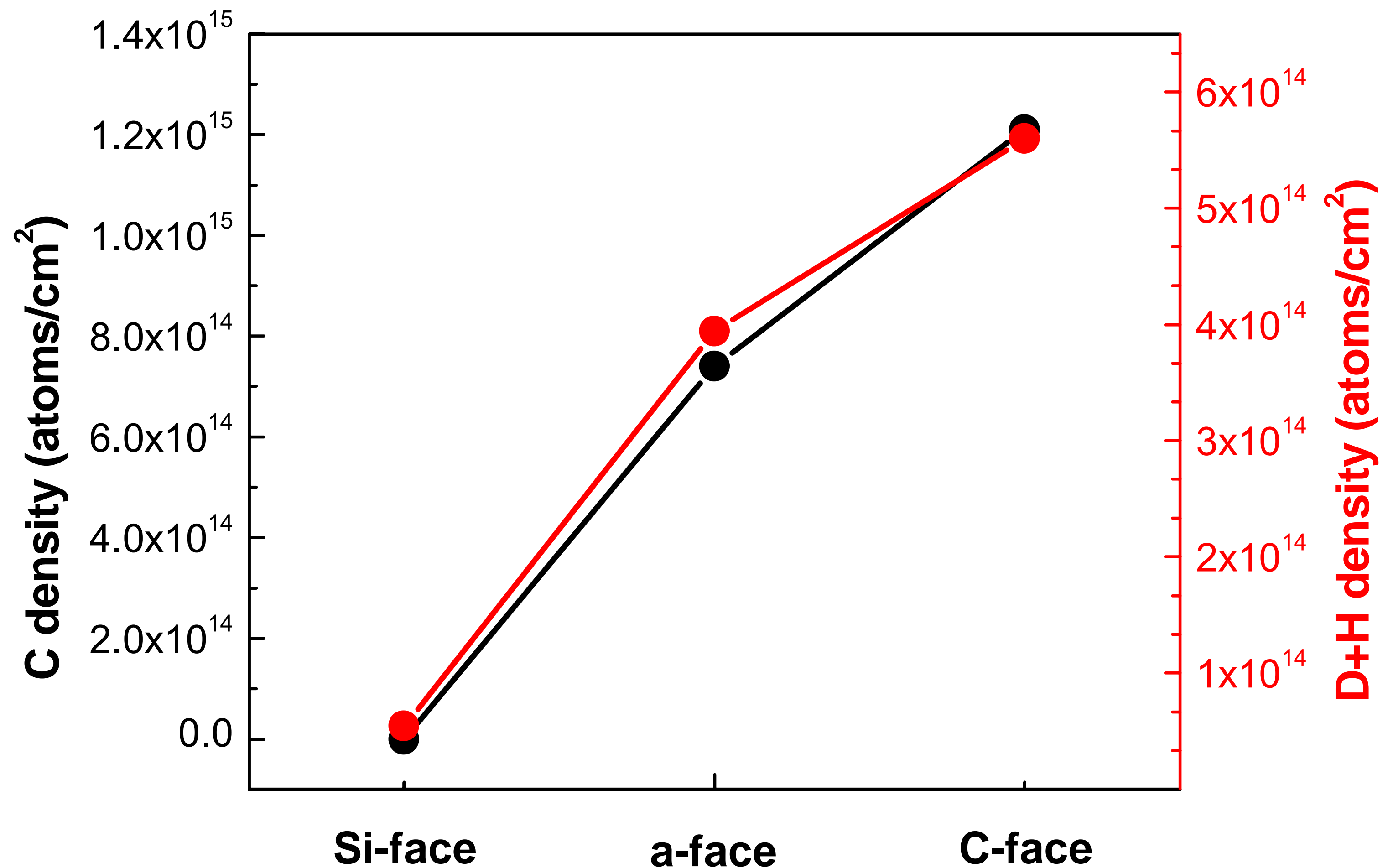
- 99.9% D_2O 10ml+50% HF 10ml

- Dipping → drying in air

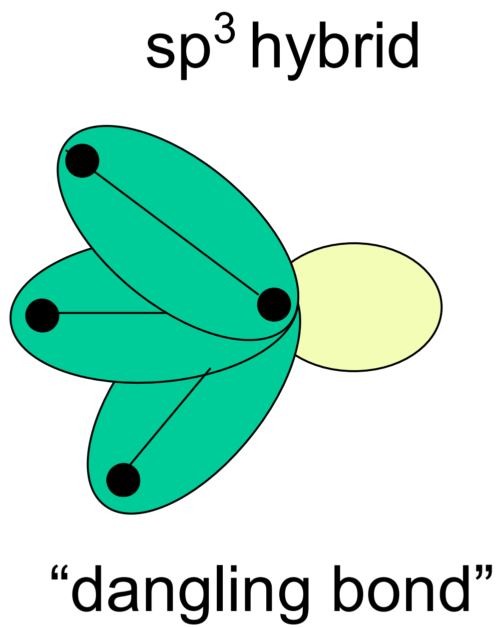
1) Virgin : Si-face, c-face, a-face SiC & Si (111)

2) Oxidized : Si-face, c-face, a-face SiC & Si (111)

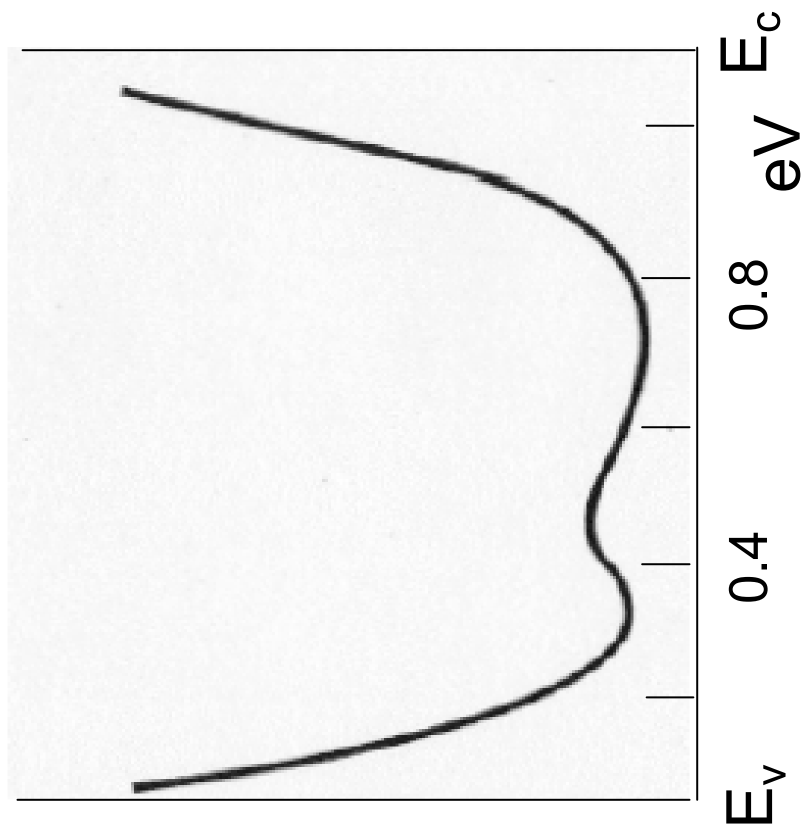
HYDROGEN COVERAGE ON SiC FOLLOWING HF OXIDE ETCHING



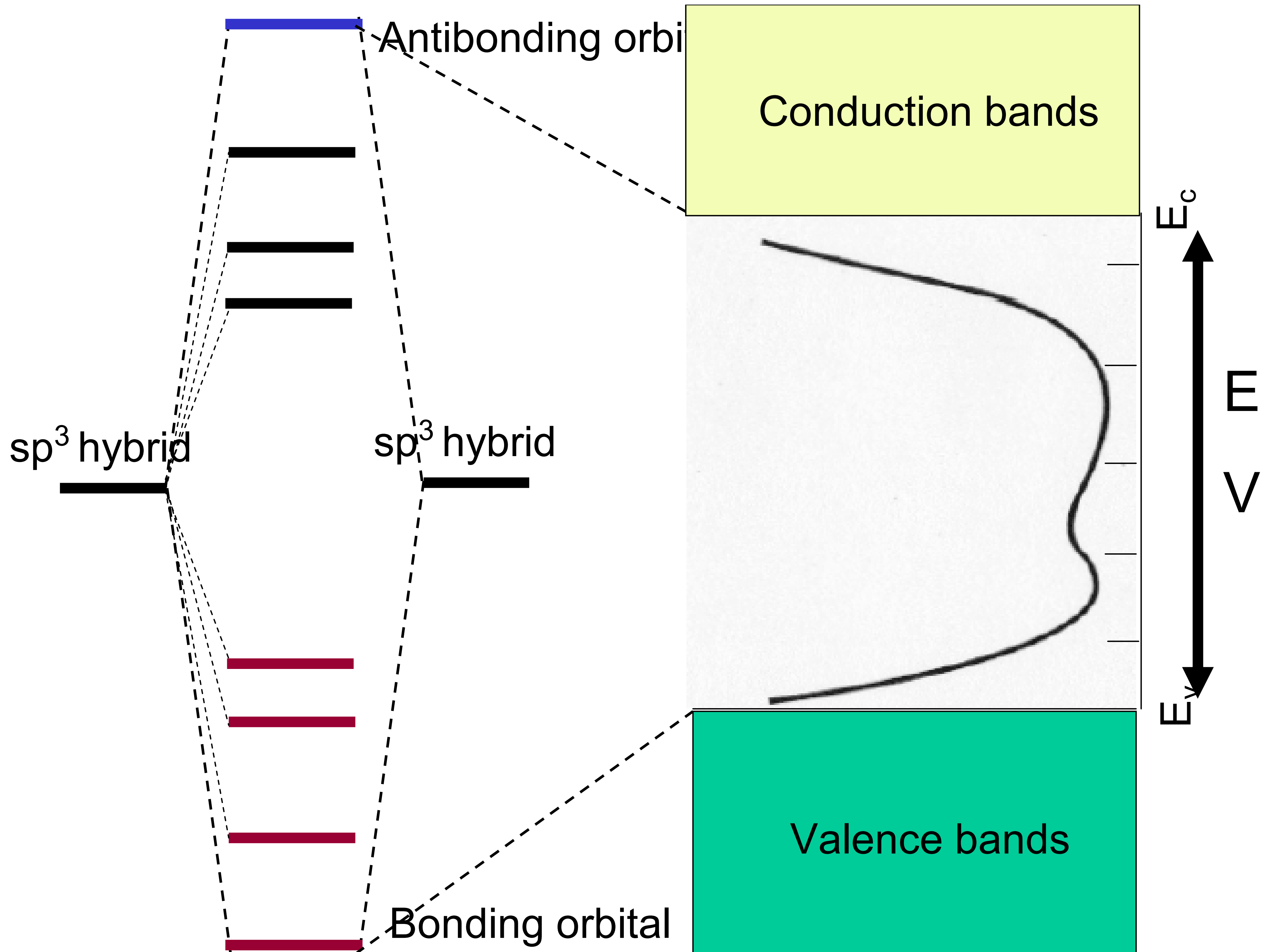
S. Choi et al., Vanderbilt University



sp3 hybrid
“dangling bond”

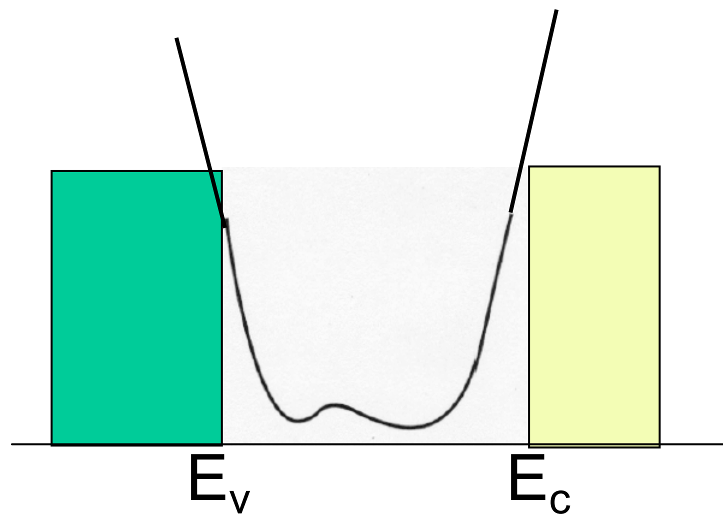


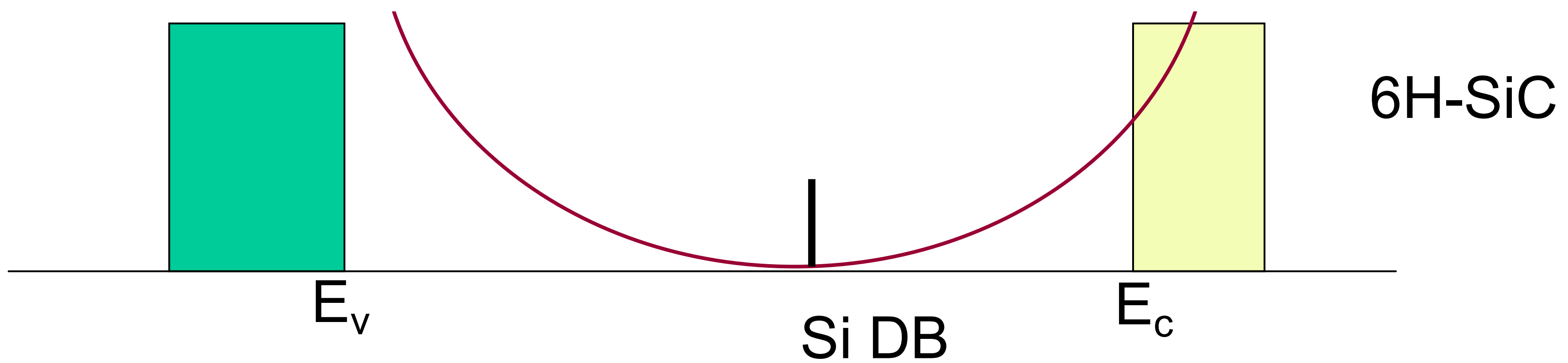
Ec
eV
0.8
0.4
Ev



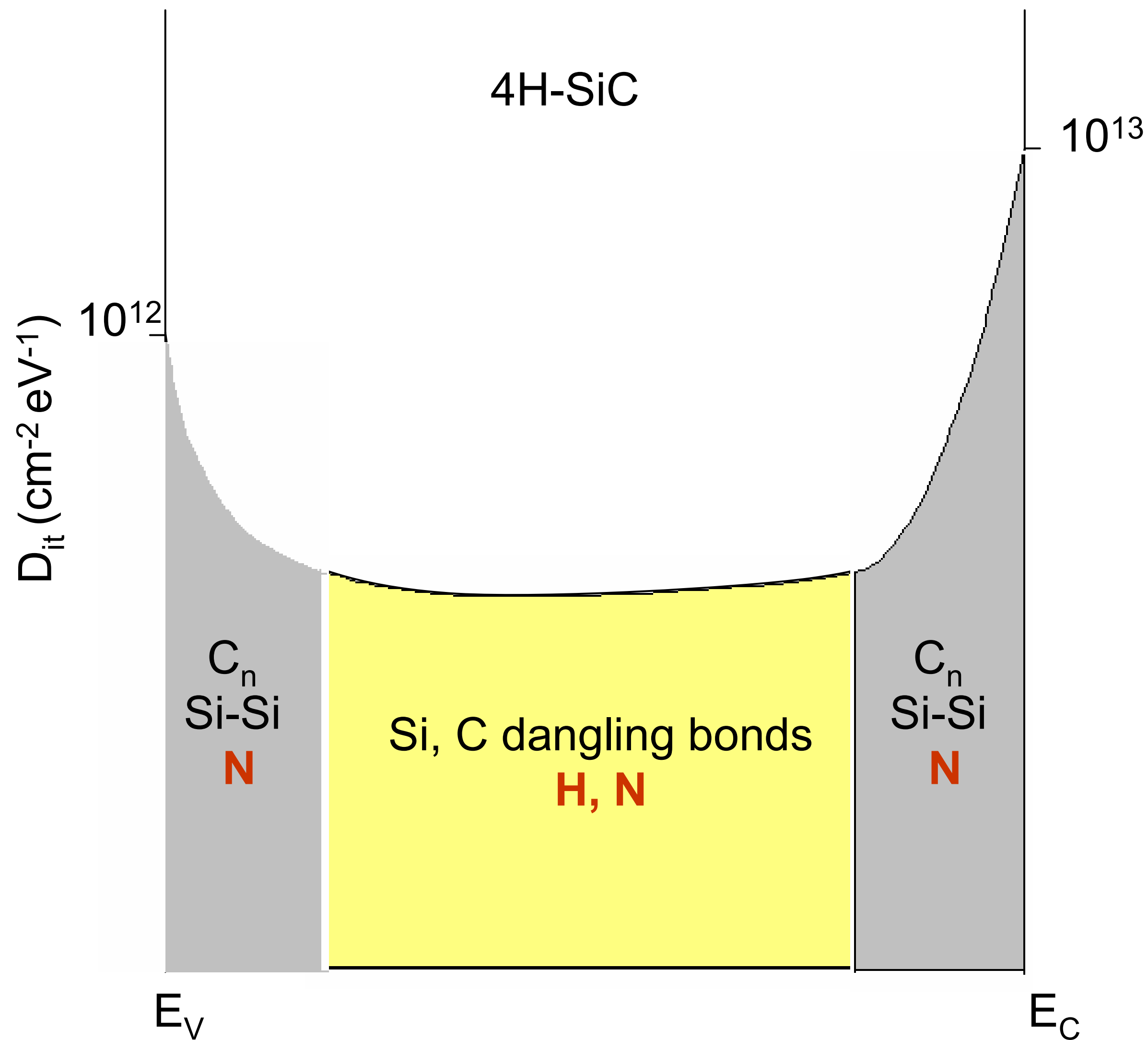
Antibonding orbi
Conduction bands
sp3 hybrid
sp3 hybrid
E
V
Valence bands
Bonding orbital

Si-Si bonds





Phenomenological picture of the SiO_2/SiC interface passivation



Sequential anneals in NO and H_2

Dry oxidation 1150 °C, 1-4 h

Post-oxidation anneal in NO, 1175 °C, 2 h

Gate metal Pt

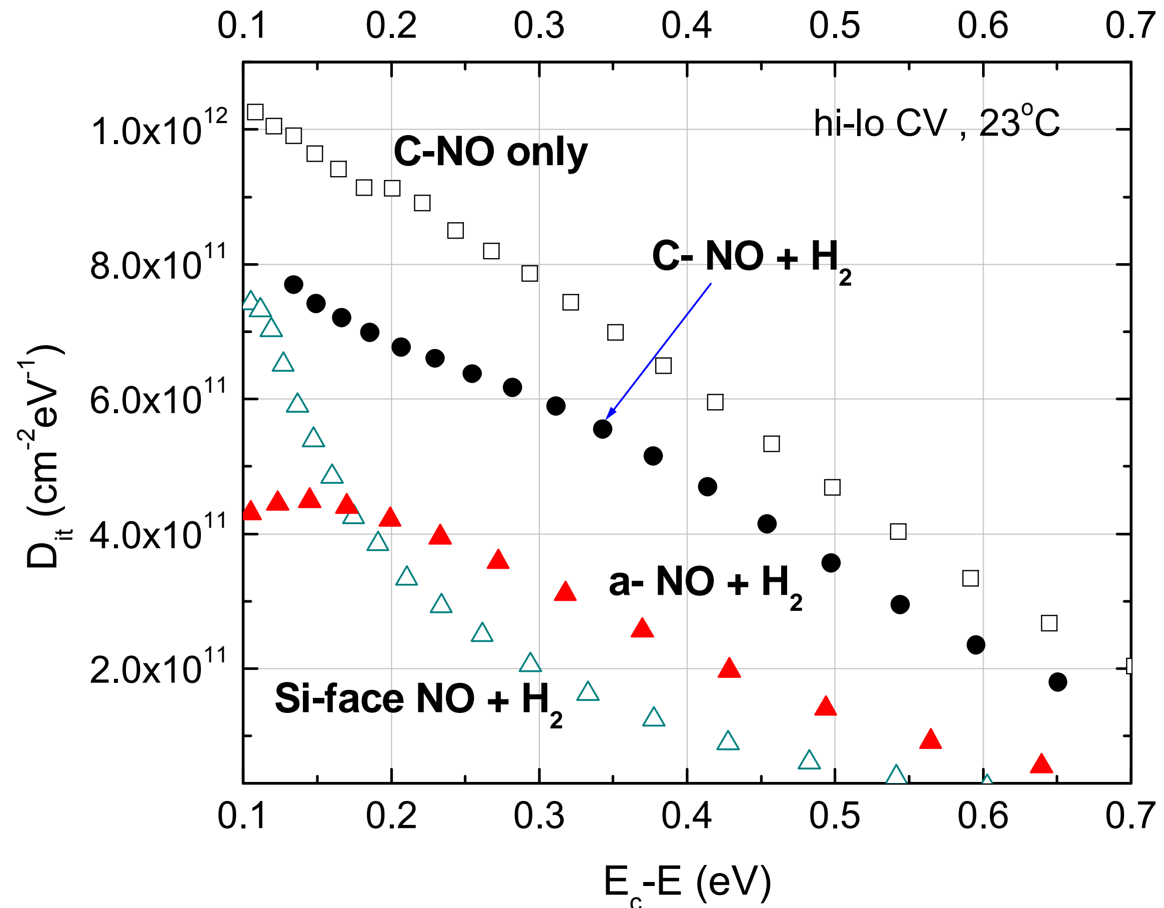
Post- metallization anneal in H_2, 500 °C, 1 h

Sequential anneals in NO and H_2- all faces

- 1175°C, 2h NO (0.5 l min^{-1} flowing gas)

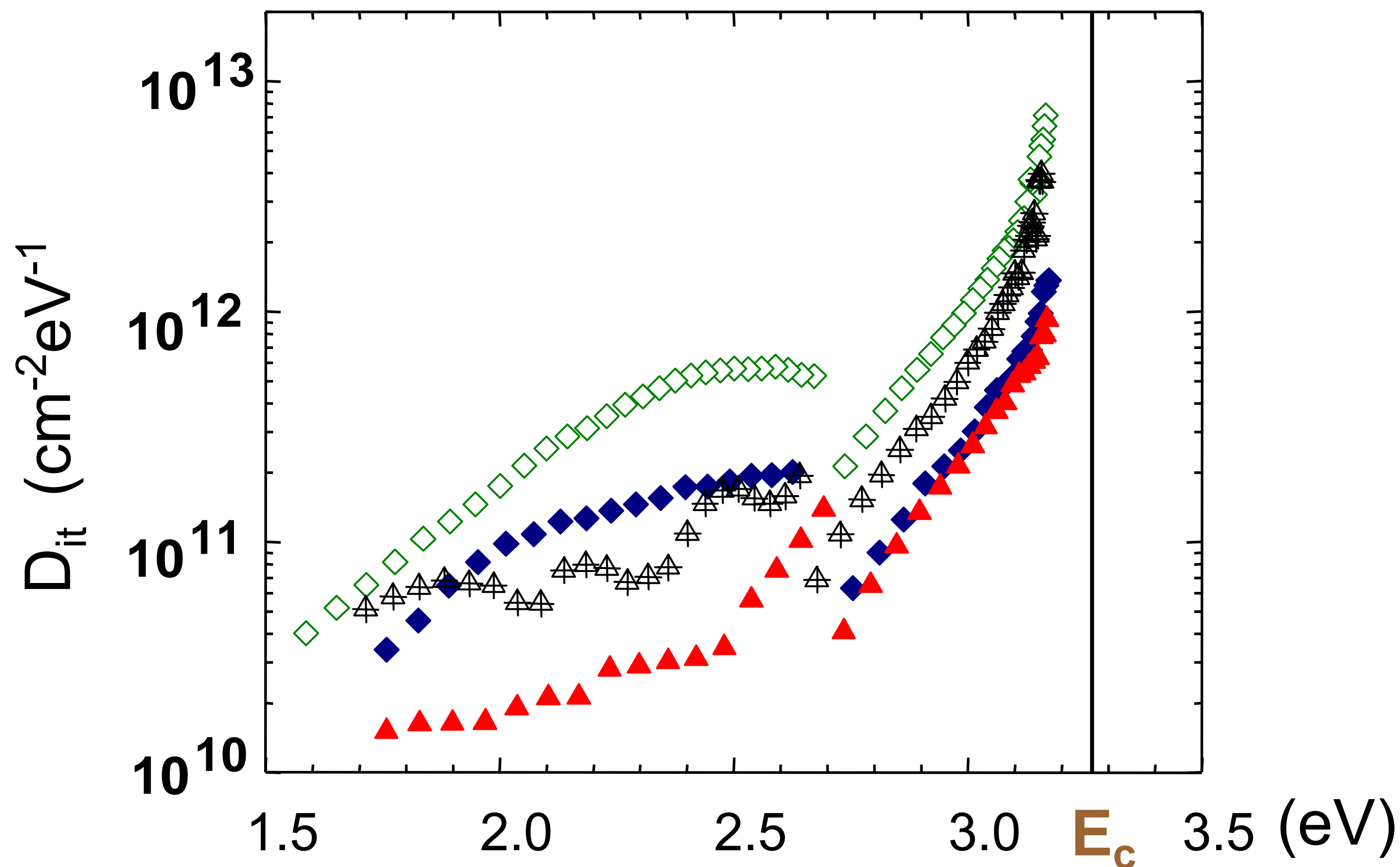
(t_{ox}: Si-~53 nm, a~28 nm, C~40 nm)

- Pt used as gate metal
- 500 °C, 1h H_2 (1 l min^{-1})



- **Lowest D_{it} on all faces obtained by (NO + H_2) process**
- **$D_{it} < 10^{12}$ cm^{-2} eV^{-1} at E_c- E ≈ 0.1 eV on all faces**

4H-SiC/SiO_2 (0001) Si-face



◇ AS-OXIDIZED

PASSIVATED – **H** ONLY

PASSIVATED – **NO** ONLY

PASSIVATED – **NO** FOLLOWED BY **H**

MAXIMUM INVERSION LAYER MOBILITYAND INTERFACE STATE DENSITY

i) Scattering

$$\mu = e\tau/m^* = e\lambda/m^*v$$

	μ	"λ"
Bulk Mobility	**800cm²/V-s**	**0.050u**
Elec. field	**400cm²/V-s**	**0.025u**
Oxide Penetration	**300cm²/V-s**	**0.018u**
		(0.025u)
N_{it}	$10^{12}/cm^2$	**0.01u**
N_{it}	$10^{10}/cm^2$	**0.10u**

ii) Trapping: n_{free} is of order $10^{13}/cm^2$ so significant trapping is expected.

Electron Wavefunction Penetration into Gate Dielectric and Interface Scattering - An Alternative to Surface Roughness Scattering Model

Igor Polishchuk and Chenming Hu

2001 Symposium on VLSI Technology Digest of Technical Papers

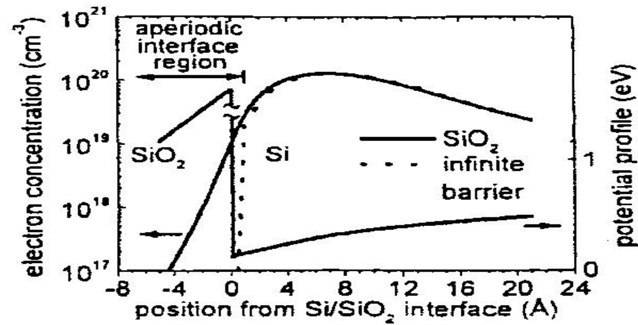


Fig 1. Electron wavefunction penetration into gate dielectric.

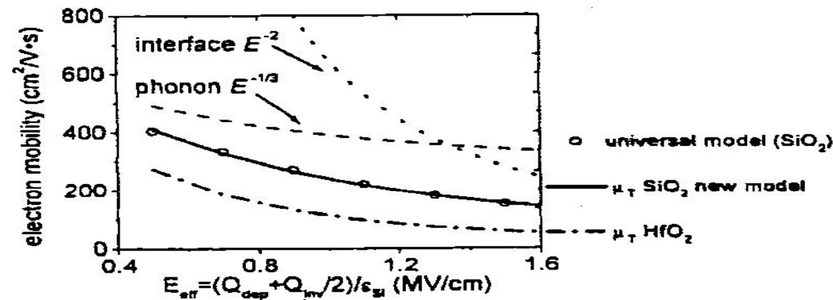


Fig. 5. Proposed interface scattering mechanism matches the universal mobility model.

CONCLUSIONS

The nitrogen/hydrogen process has enabled the possibility of a SiC MOSFET technology!

Themes of Solid-State Science

Nanostructures-matter at 1 to 100 nm scale

Dynamics-excited state physics and chemistry

New materials -Hi T_c, magnetic, heterostructures,..

Quantum control- spintronics,

Biological materials- organic/inorganic interface

Atomic Level Characterization of CdSe Nanocrystals-TEM and RBS

Collaborators

James McBride, S. J. Rosenthal, L.C. Feldman

Vanderbilt University

S.J. Pennycook

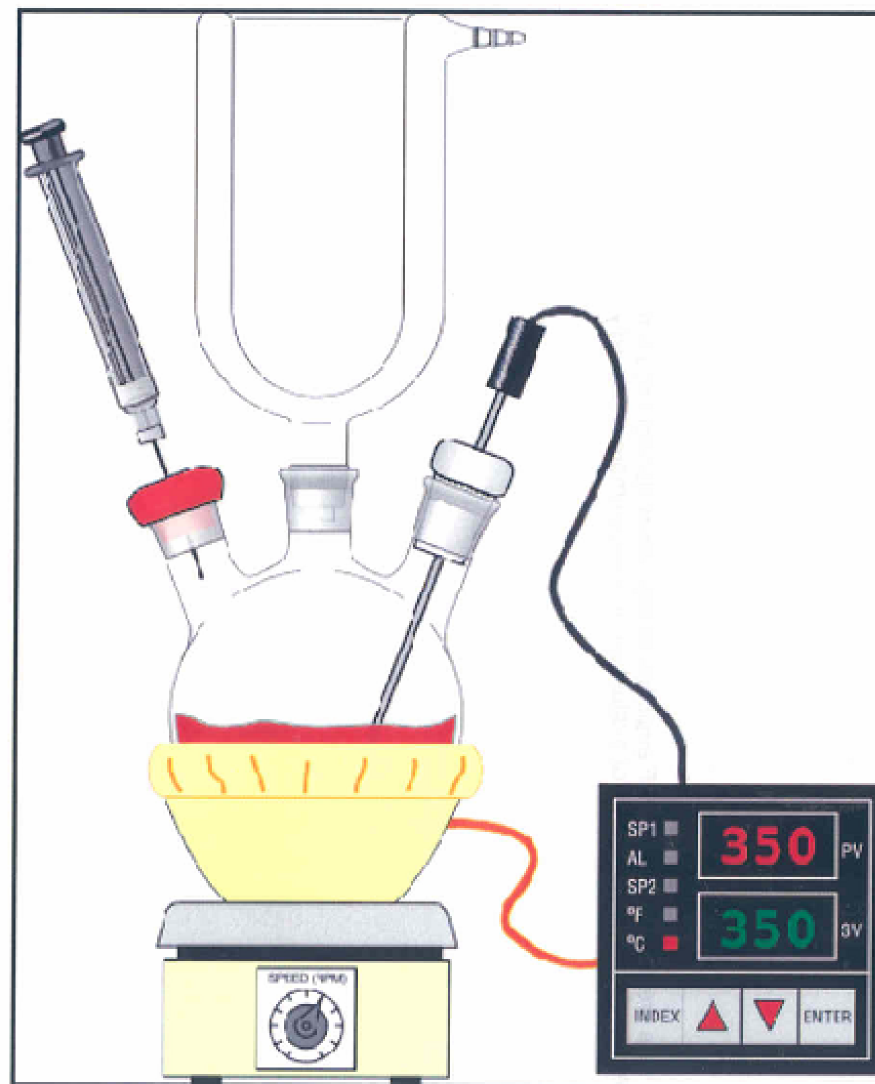
Oak Ridge National Labs

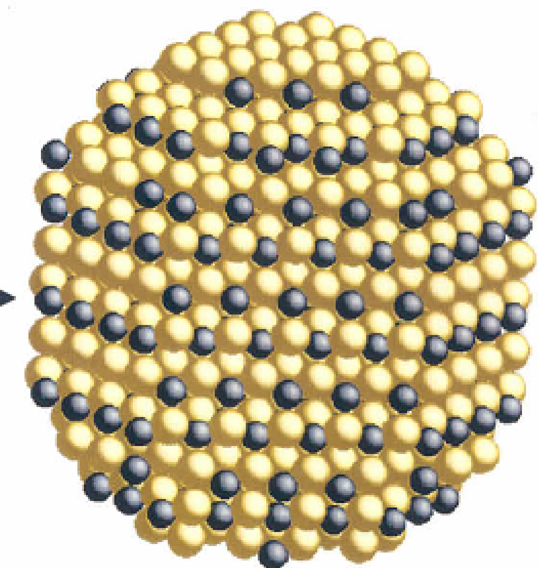
$(CH_3)_2Cd$ + Se:TBP

isolate CdSe

$(CH_3CH_2)Zn$ + $(TMS)_2S$

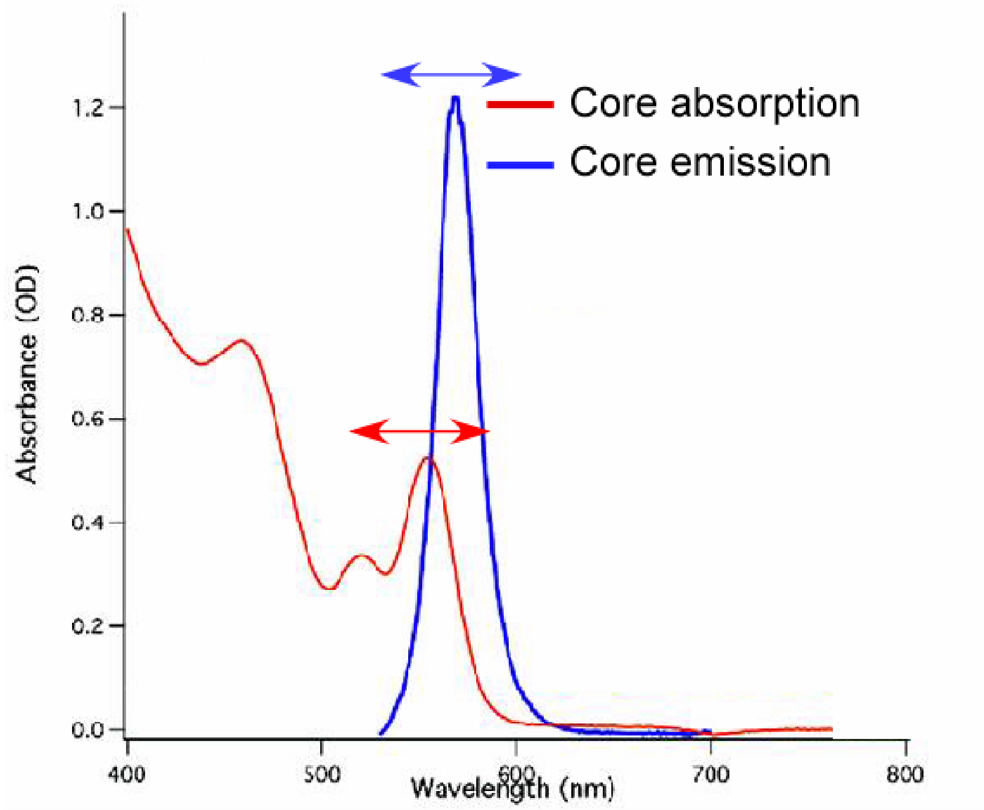
isolate CdSe/ZnS



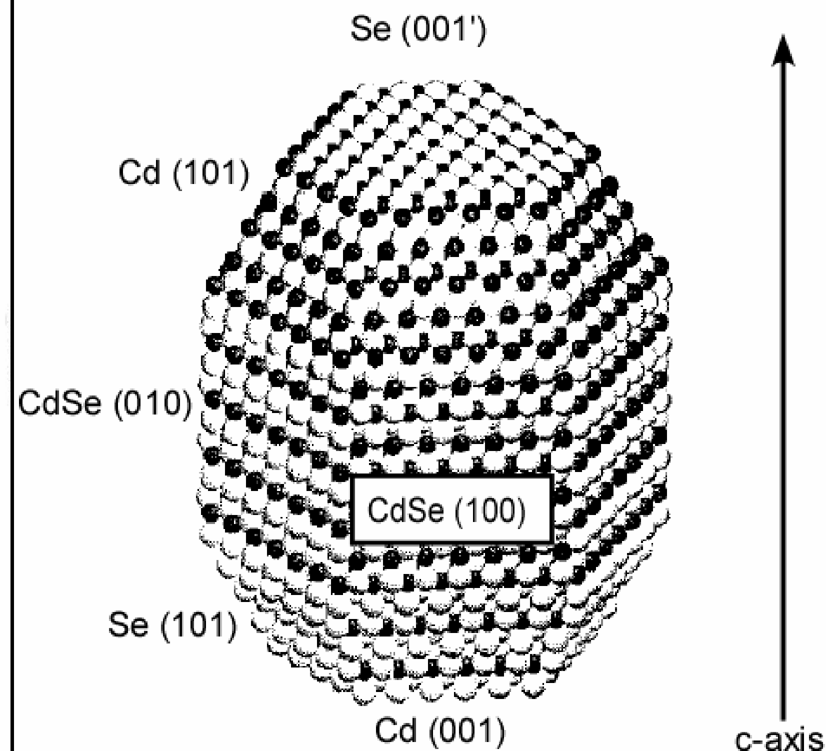


CdSe Nanocrystals

Absorption and Emission of CdSe Nanocrystals



CdSe Nanocrystal Model



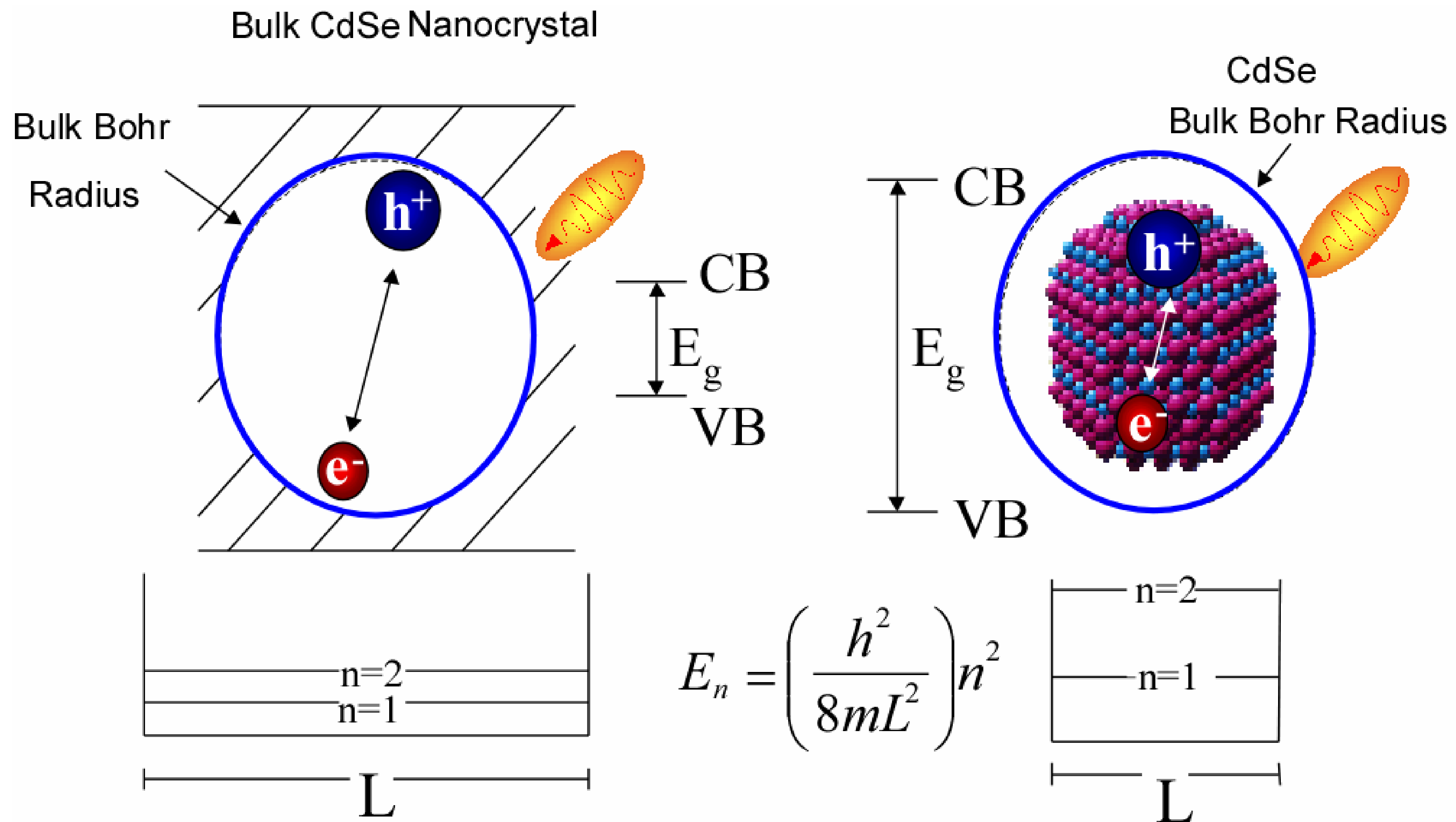
Hexagonal prism

Polar surfaces

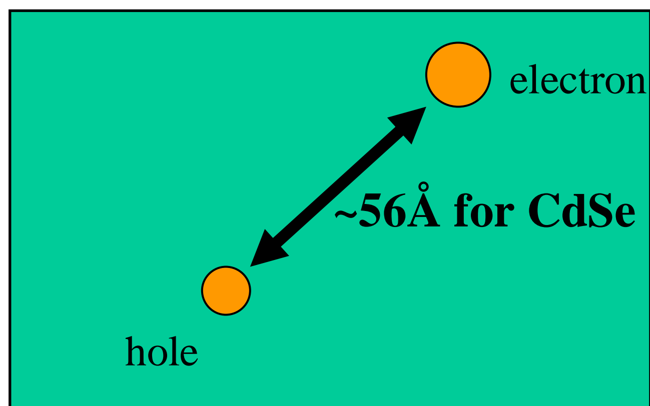
C_{3v} symmetry

Tunable absorption and emission

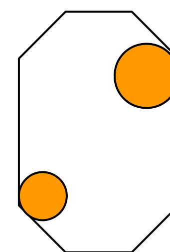
Tunable Absorption and Emission: Quantum Confinement



Origin of size-dependent optical properties: Quantum Confinement



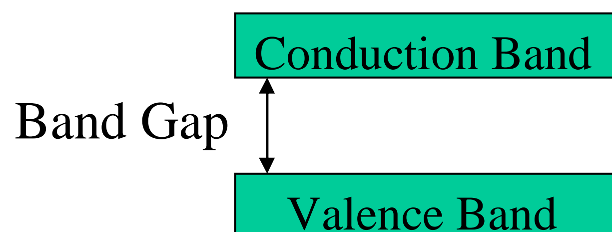
Bulk semiconductor

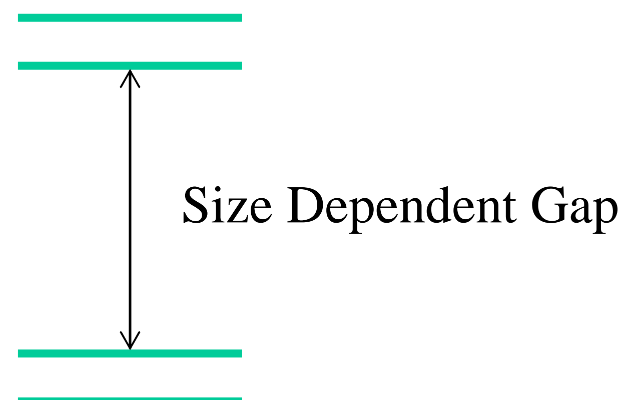


nanocrystal

Electron and hole are "confined" to the nanocrystal!

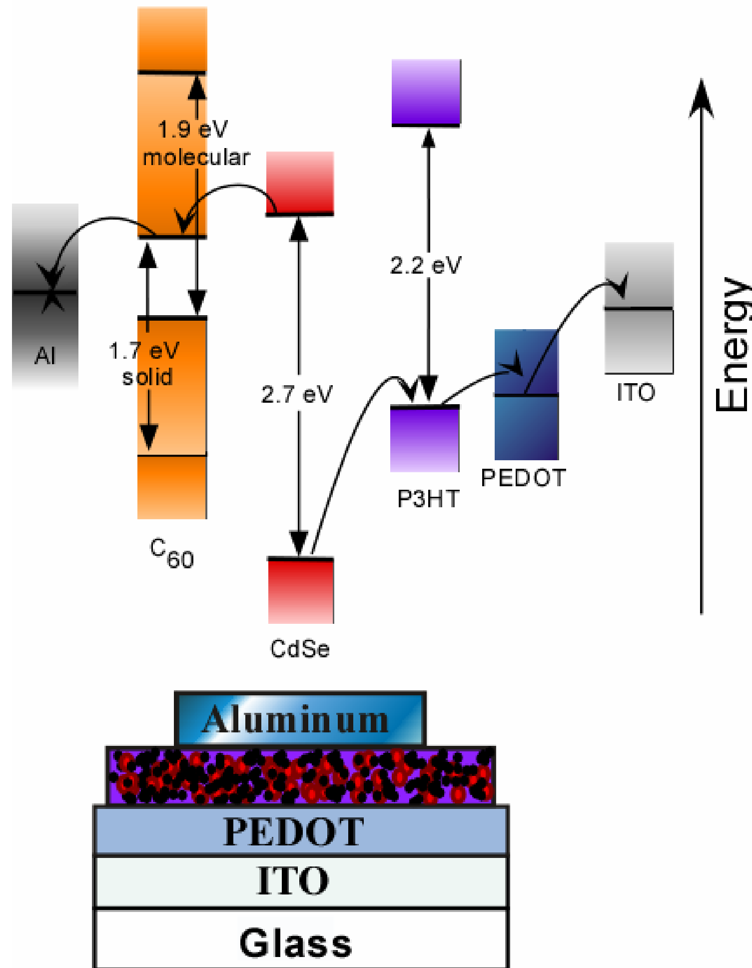
The smaller the crystal, the higher the energy of confinement





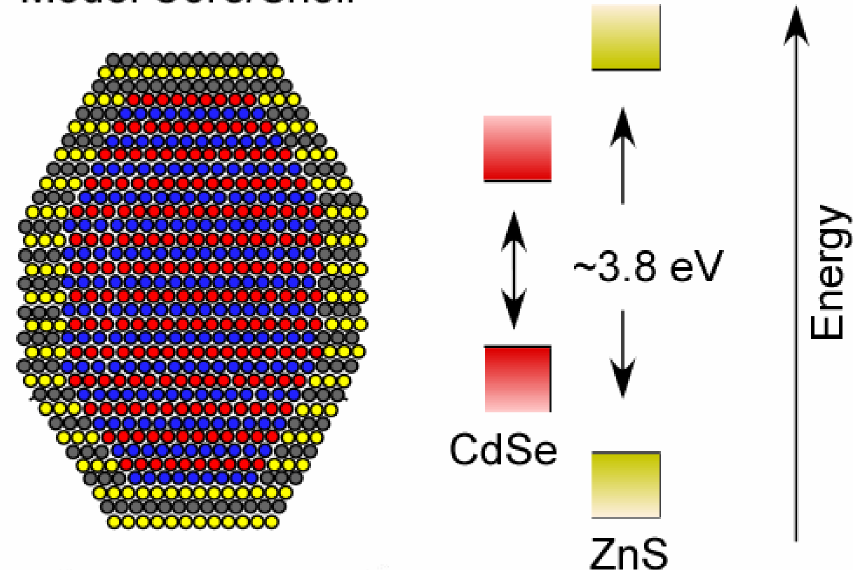
The Function of Nanocrystals is Highly Dependant on the Surface

Photovoltaics



Efficient transfer of charges from nanocrystal to device

Fluorescence Imaging



Efficient recombination of charges for maximum fluorescence

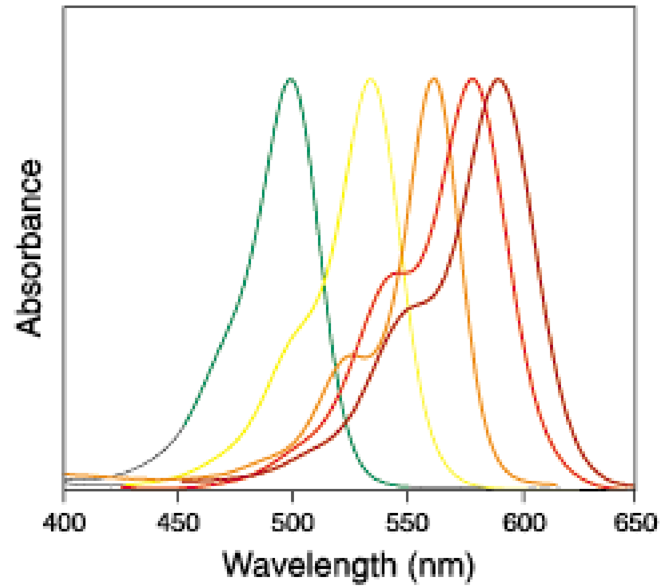
Quantum dots are useful in biology because:

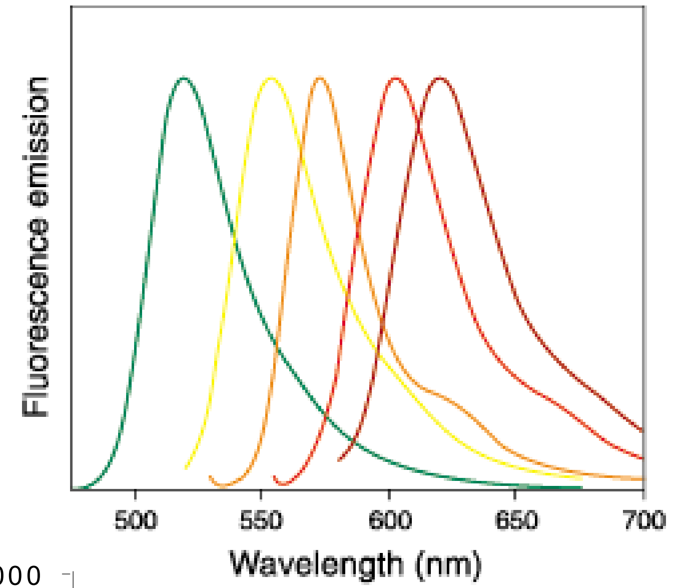
- Small size (=> image cellular components)
- Incredibly bright (= enhanced sensitivity, early detection)
- Multiplexed detection (=> multiple simultaneous signals)
- Photostability (= dynamic imaging, sample archive)
- Multivalent Surface (=> enhanced recognition and targetting)

All of these properties originate from the nanometer size of the dots.

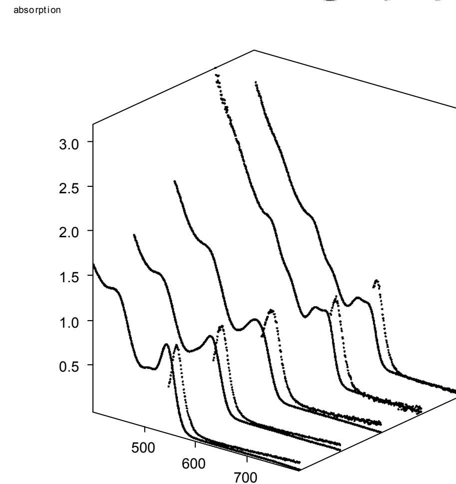
Dye vs. Nanocrystal Spectral Characteristics

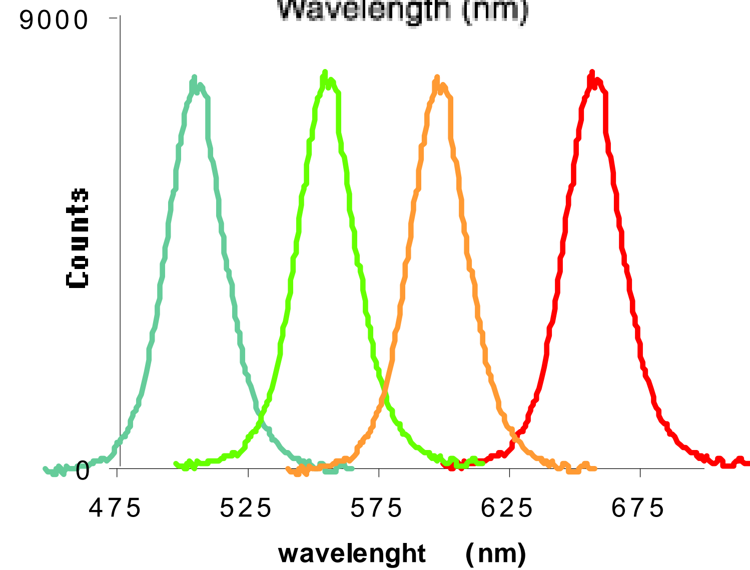
Dye Molecules (Alexa)

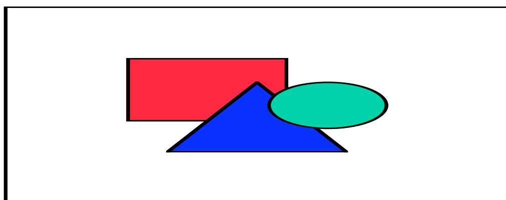


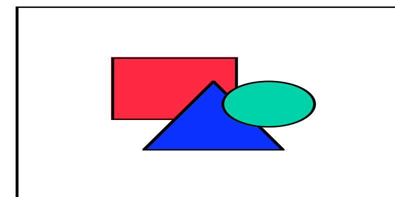


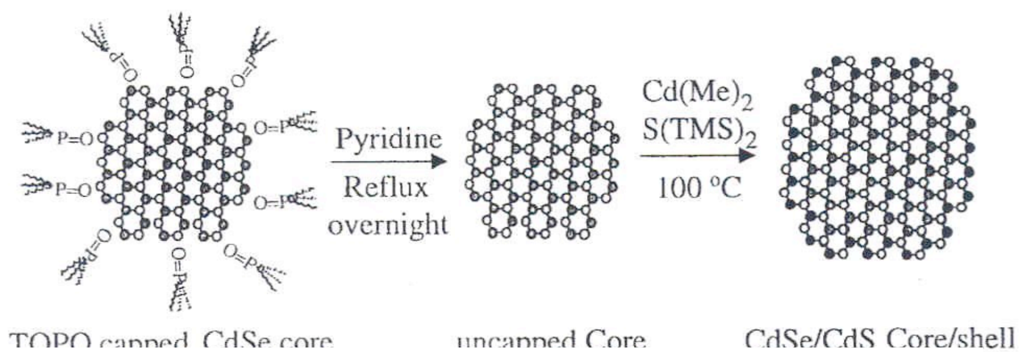
Nanocrystals



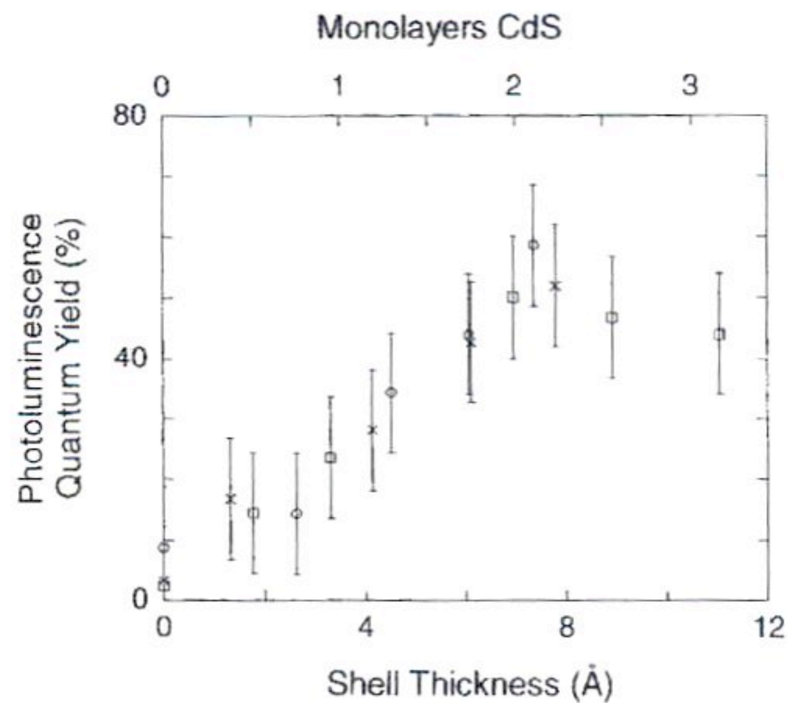




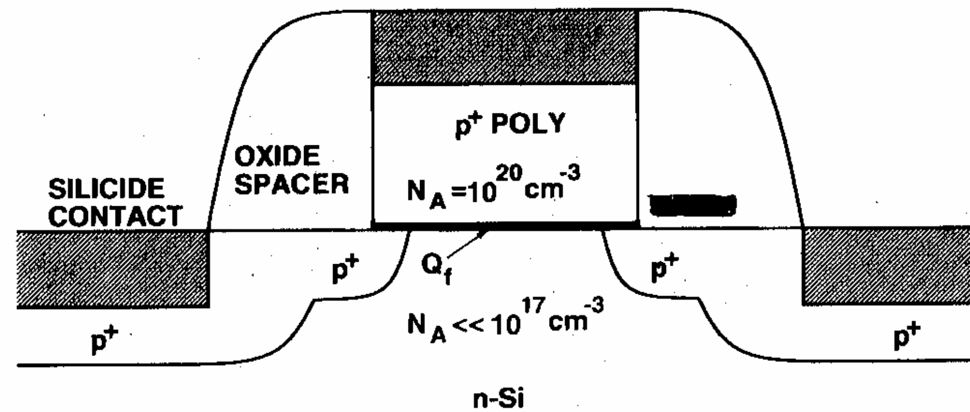




Peng et al, JACS, **119, 7019 (1997).**



METAL-OXIDE-SEMICONDUCTOR FIELD EFFECT TRANSISTOR
P-CHANNEL



Low power applications require low threshold voltage which demands a near perfect interface (low fixed charge, Q_f) and low dopant penetration, N_A.

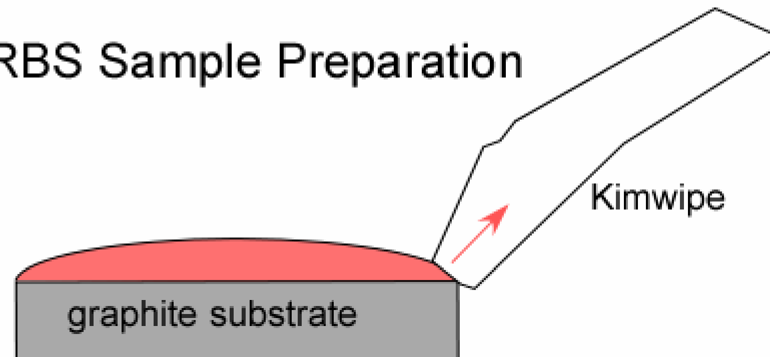
AT&T Bell Laboratories LCF/RHY

TEM Sample Preparation

A drop of dilute nanocrystal solution is allowed to dry on an ultra-thin carbon-coated TEM Grid (Ted Pella Inc.)

anti-capillary tweezers

RBS Sample Preparation

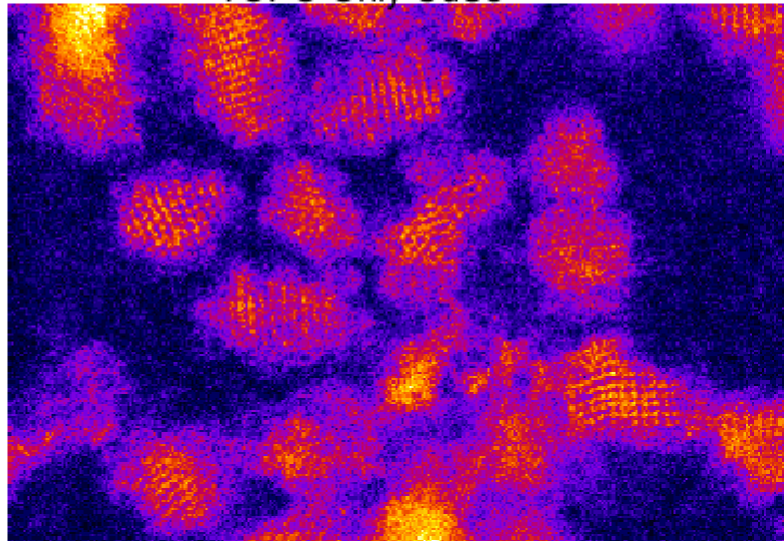


The surface of the graphite substrate is coated with the nanocrystal solution. The excess solvent is then wicked off.

Comparison of TOPO vs TOPO/Hexadecylamine

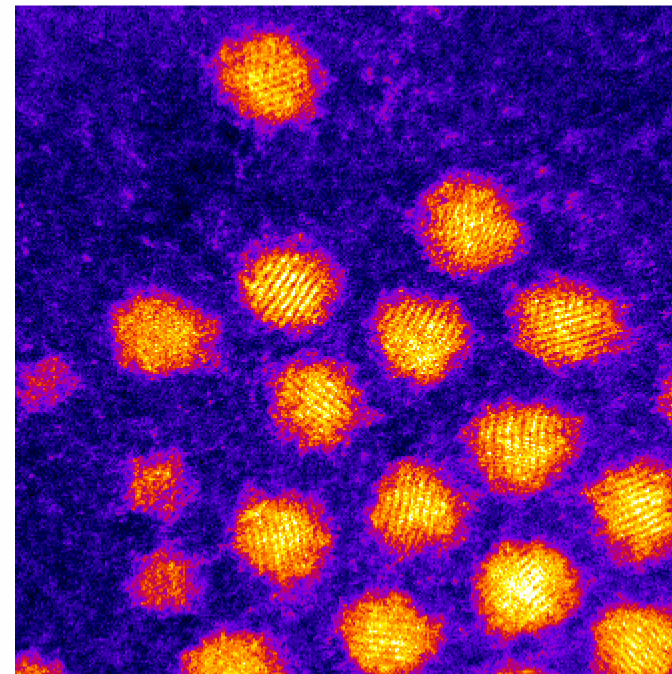
The addition of hexadecylamine (HDA) to the surfactant mixture has been known to improve size dispersion in the preparation of CdSe nanocrystals

TOPO Only CdSe



3 nm

TOPO/HDA CdSe

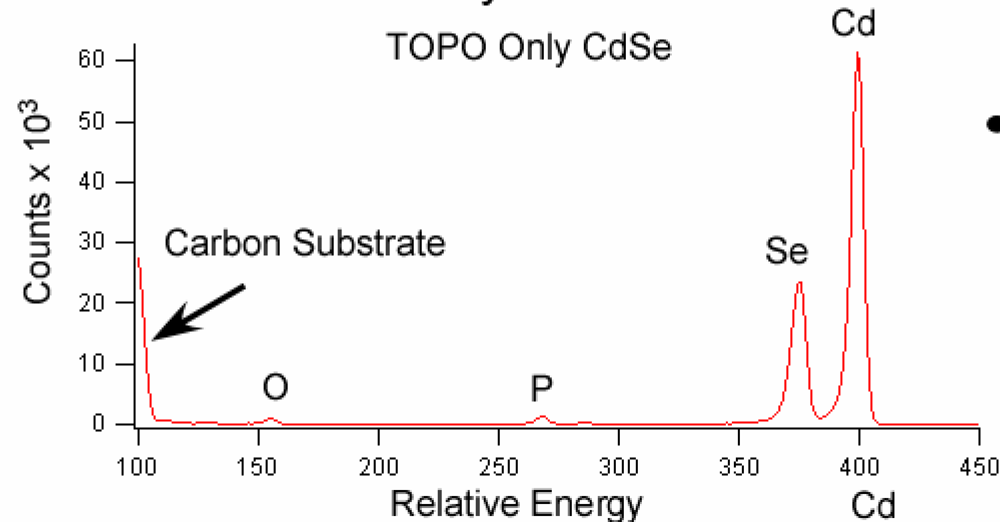


3 nm

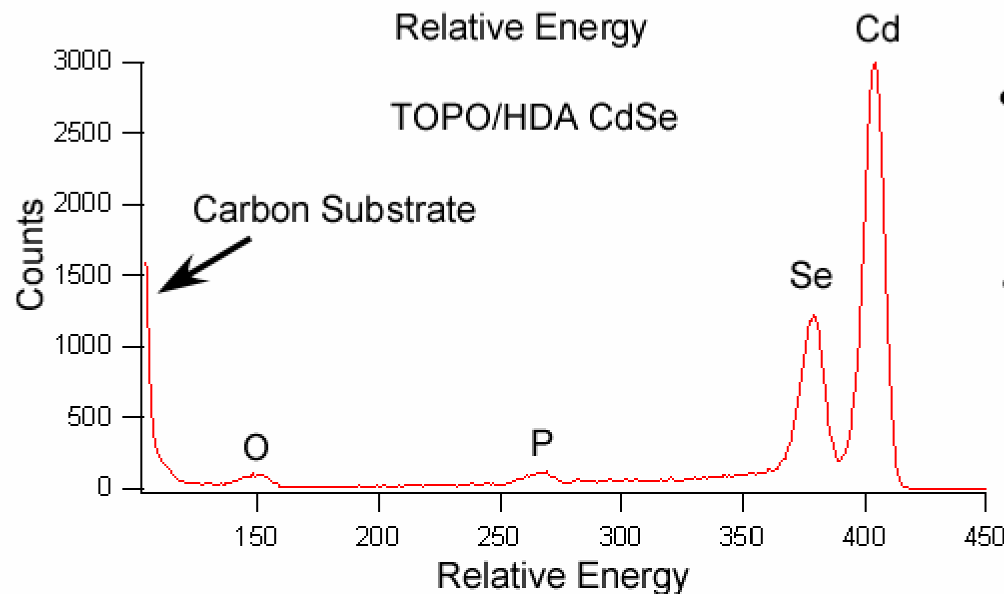
- Z-STEM images show elongated growth along c axis in the TOPO only sample
- The addition of hexadecylamine (HDA) slows growth along C axis creating near-perfect spherical nanocrystals

* All Z-STEM images have been smoothed to reduce noise

Rutherford Backscattering Spectroscopy (RBS): Comparison of TOPO only CdSe vs TOPO/HDA CdSe

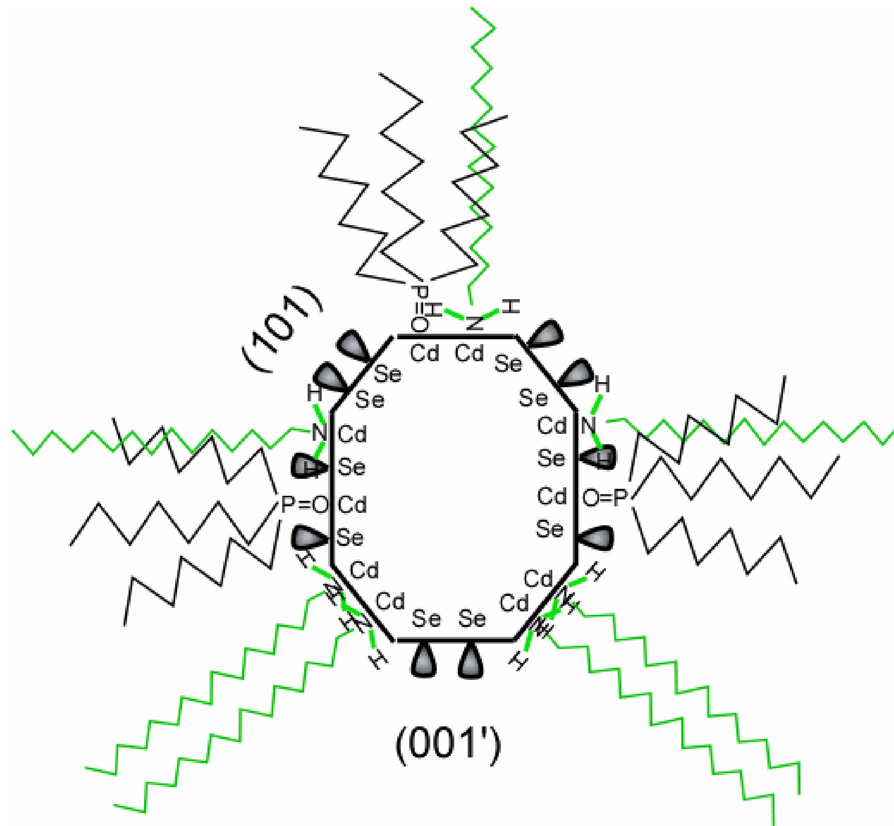


- RBS of TOPO only cores shows the existence of excess Cd with a Cd:Se Ratio of 1.2:1



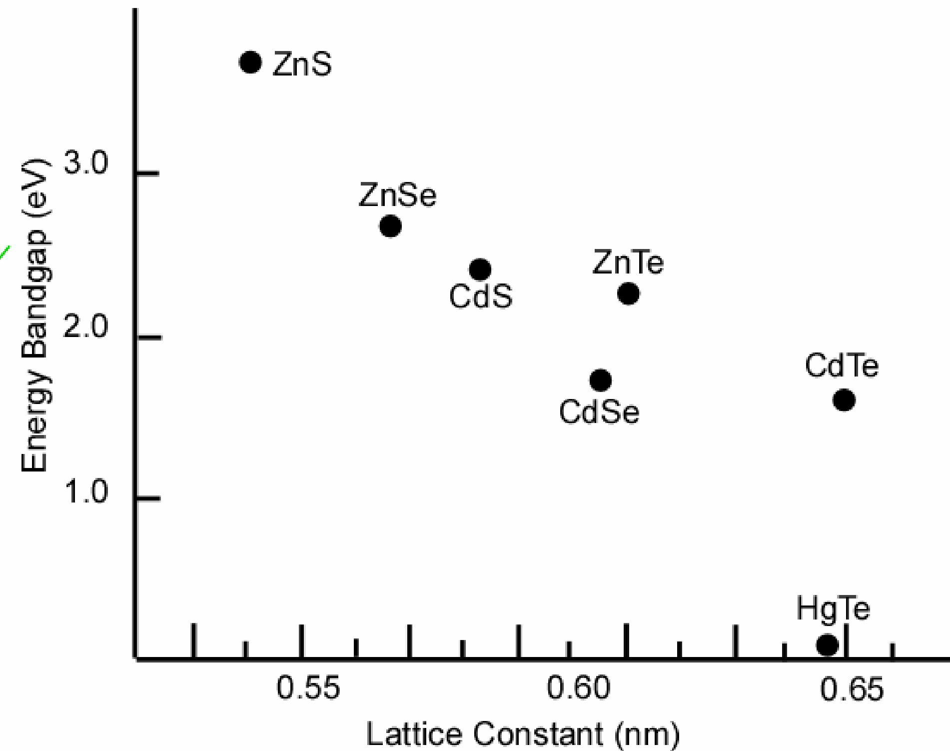
- The addition of HDA to the reaction mixture has changed the Cd:Se ratio to 1:1
- The RBS data combined with Z-STEM data indicates that the excess cadmium existed in the elongated facets not found in the spherical, TOPO/HDA nanocrystals

Why Asymmetric Growth



(001) Surface most reactive face

Se face is 'bare'

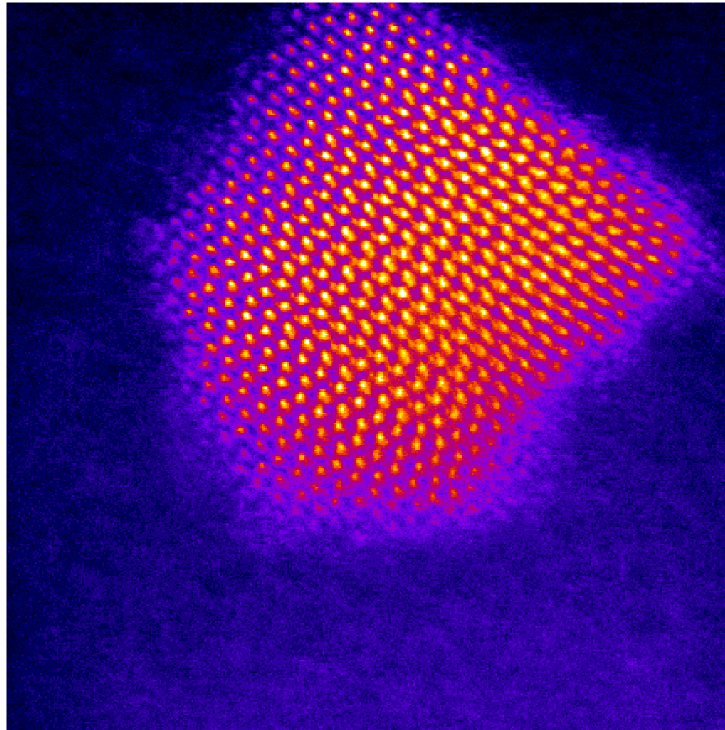


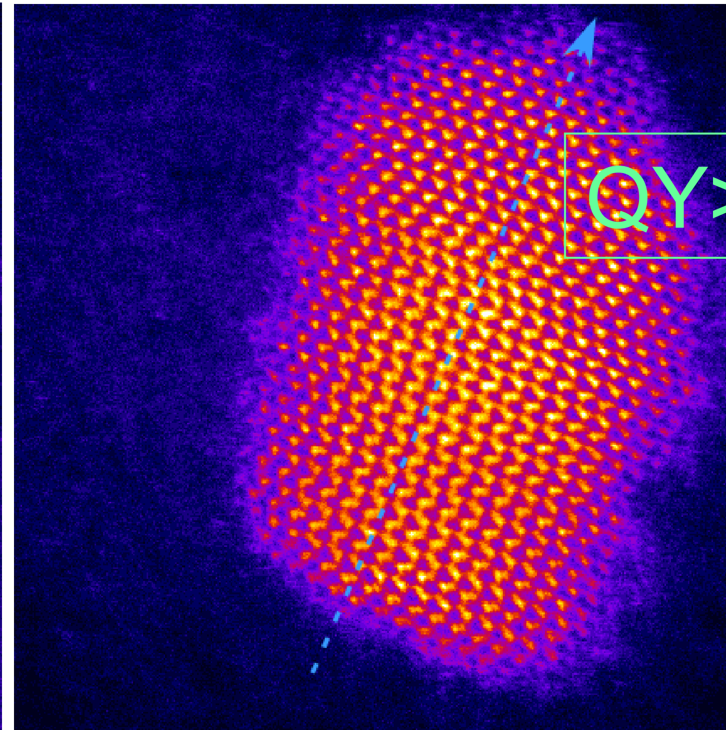
~12 % lattice mismatch between CdSe and ZnS

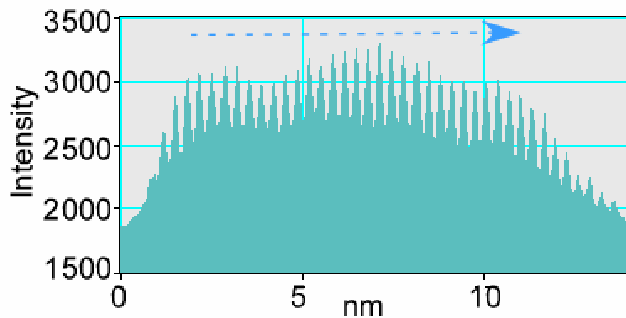
Once the critical thickness is reached, dislocations likely form reducing the lattice strain

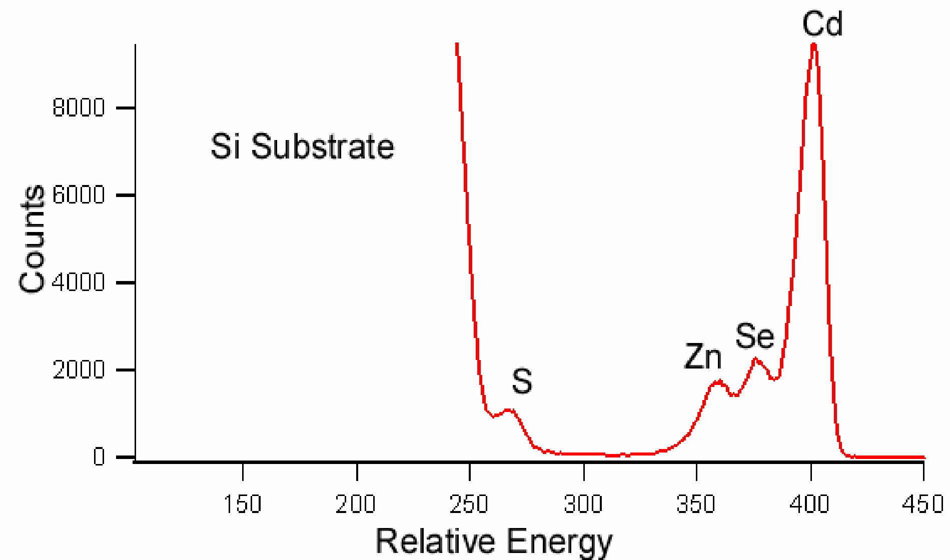
The 'relaxed' ZnS surface then becomes the optimal surface for growth

Z-STEM of ‘655 Qdot’ Quantum Dot Core/Shell Rods



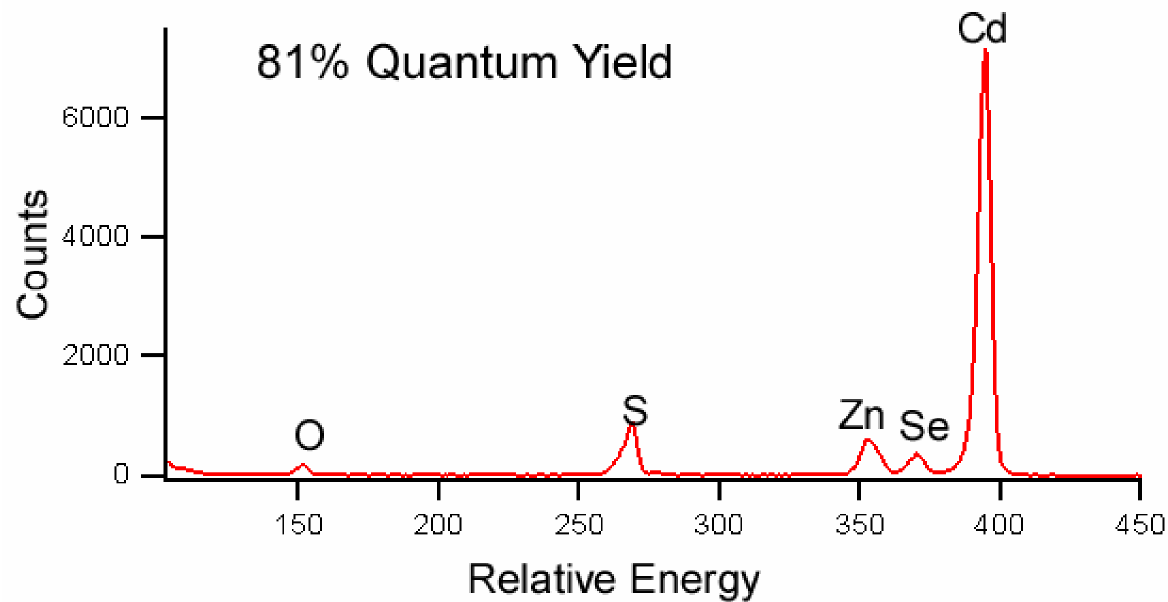




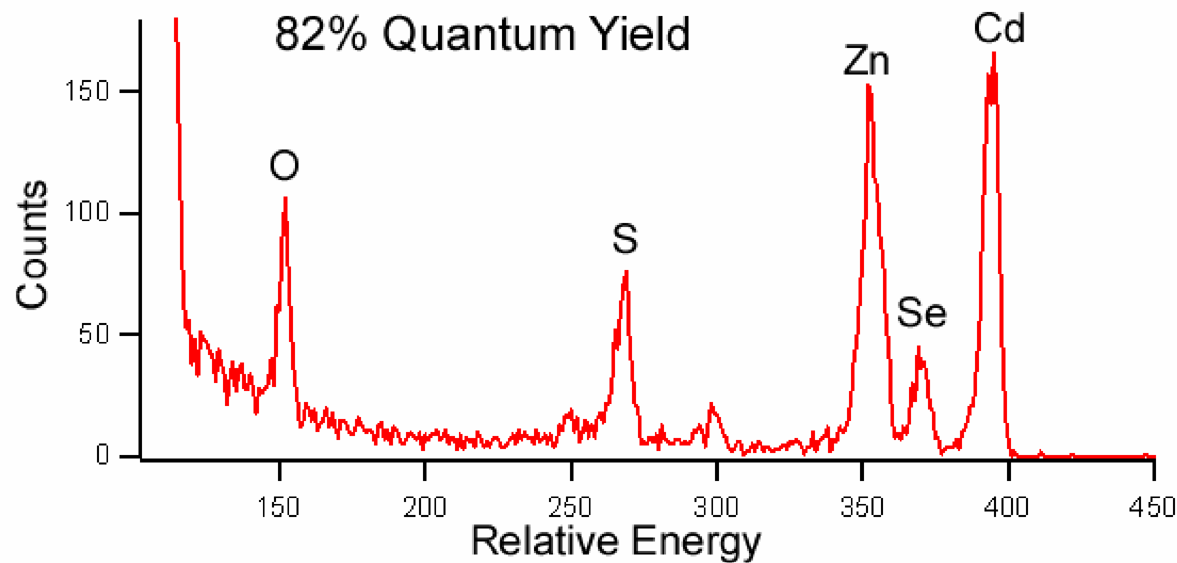


Quantum yield near unity
Water solubilized by AMP coating
Loss of anion-dumbbell intensity signifies transition for CdSe to CdS
ZnS on the surface?

RBS of ‘Cd-Doped’ CdSe/ZnS Core/Shells



Additional Cd content confirmed



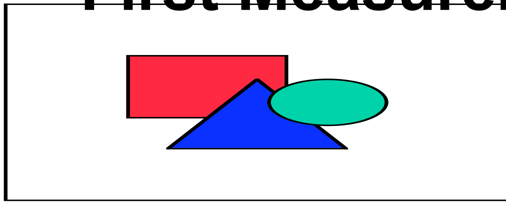
Quantum yield unaffected by the amount of Cd added

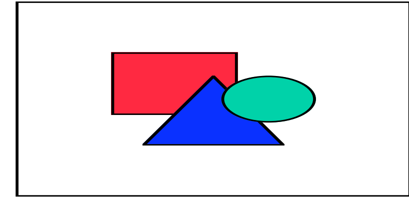
CONCLUSION

Surface control is critical for all electronic and optical devices.

Nanostructures provide a great challenge-large surface component, extremely difficult to probe.

First Measurement of Ionoluminescence from CdSe/ZnS nanocrystals





Inset

Detector

H^+ beam

CdSe nanocrystals on SiO_2/Si substrate

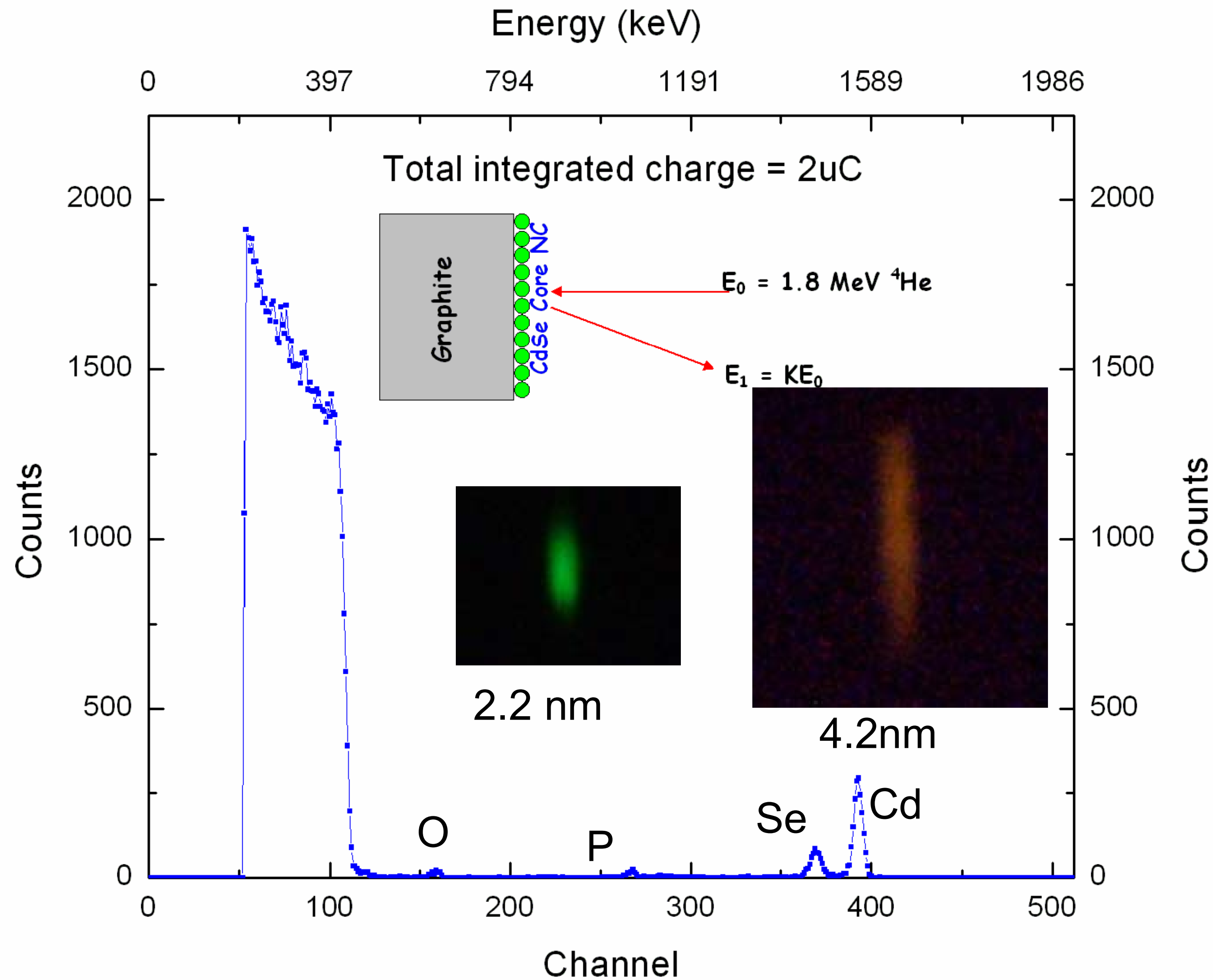
Beam Line

2" Lens

Optical Table

Optic Fiber connected to the Spectrometer

He Rutherford Scattering and Proton Luminescence



CONCLUSIONS

Ion beams analysis---

not only useful but great fun!