MURI progress report - NCSU task - May 2007- May 2008

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Ge MOS devices: alternative to Si CMOS

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research challenge

negative charge/electron trapping >5x10^{12} cm^{-2} at Ge interfaces?

nMOSCAPs and nMOSFETs for negative bias

approach: spectroscopic studies

band gaps GeO_2, Ge_3N_4 and valence band offsets wrt Ge

explanation

band alignment "mismatch" between native Ge interfacial dielectrics and high-k dielectrics

solution

eliminate native Ge interfacial layers - it works!!

native Ge interfacial dielectrics

~mid 10^{12}-10^{13} cm^{-2} - n-Ge MOSCAP, n-Ge MOSFETs;

i) Univ. Tokyo[1] and Stanford ECE[2] - GeO_x, GeON, GeN, ITRs

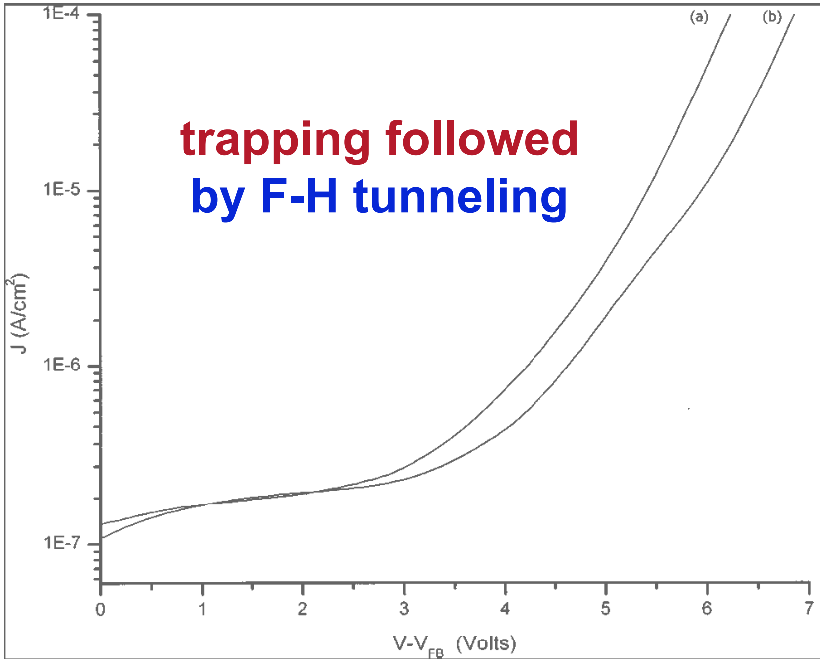
[1]S. Takagi, et al., Microelec. Eng. 84, 2314 (2007).

[2]T. Krishnamohan, et al., Microelec. Eng. 84, 2063 (2007).

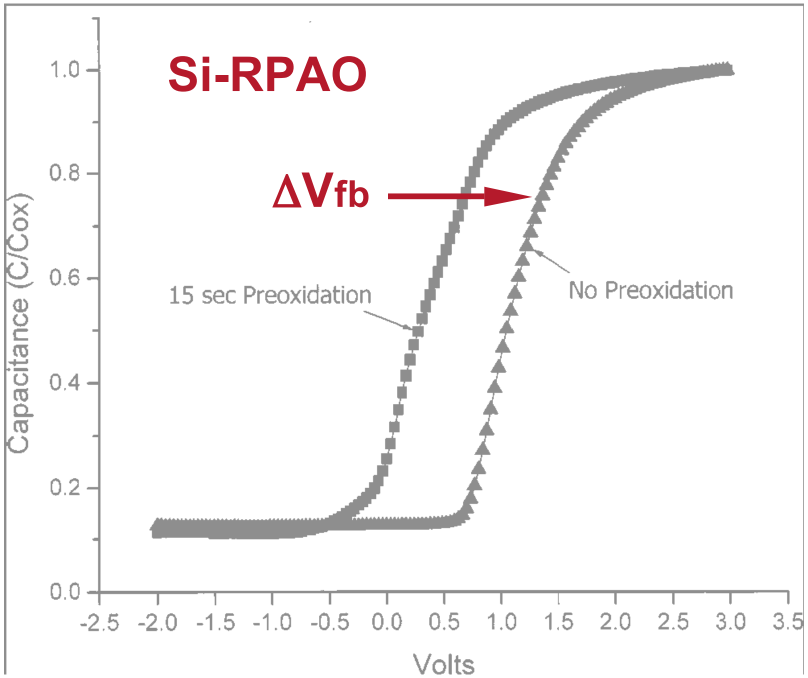
pMOSCAPs, and p-MOSFETs -- mid 10^{11} cm^{-2}

electron trapping in n-Ge-GeO_x-SiO_2

[3]R.S. Johnson, H. Niimi and G. Lucovsky, J. Vac. Sci. Technol. A,18, 1230 (2000).



trapping followed by F-H tunneling



Si-RPAO

two issues

band-gaps of GeO_2 and Ge_3N_4?

spectroscopic ellipsometry -- the *hard* way

near edge X-ray absorption spectroscopy (NEXAS)
-- the *fast and easy* way!!

conduction and valence band offset energies wrt Ge?

internal photo-emission -- the *hard* way

soft X-ray photoelectron spectroscopy (SXPS)
-- the *fast and easy* way!!

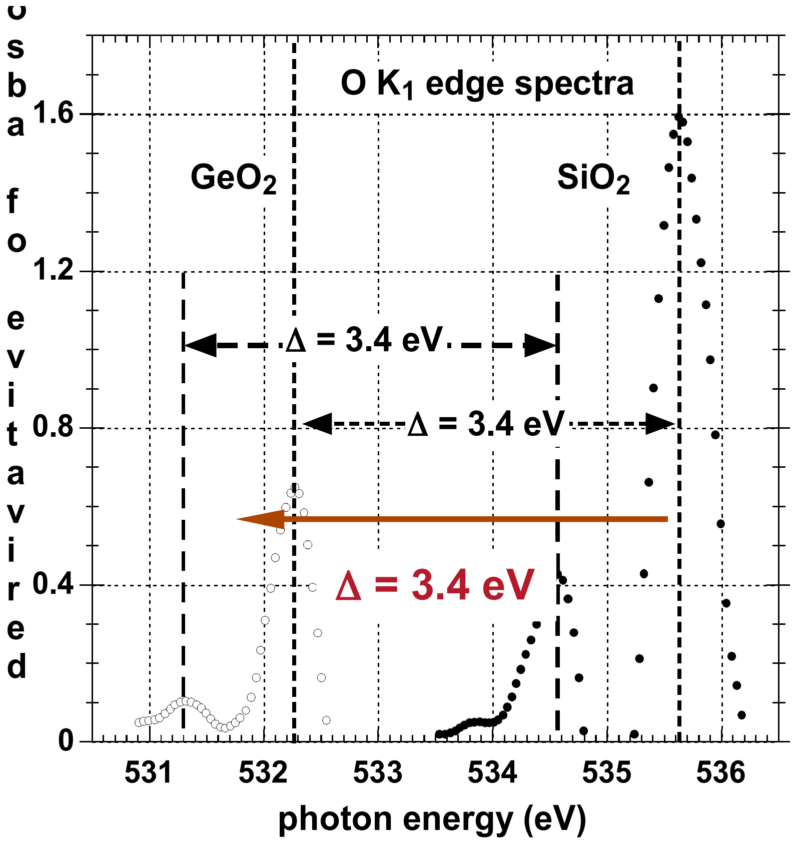
band gaps of GeO_2, Ge_3N_4,

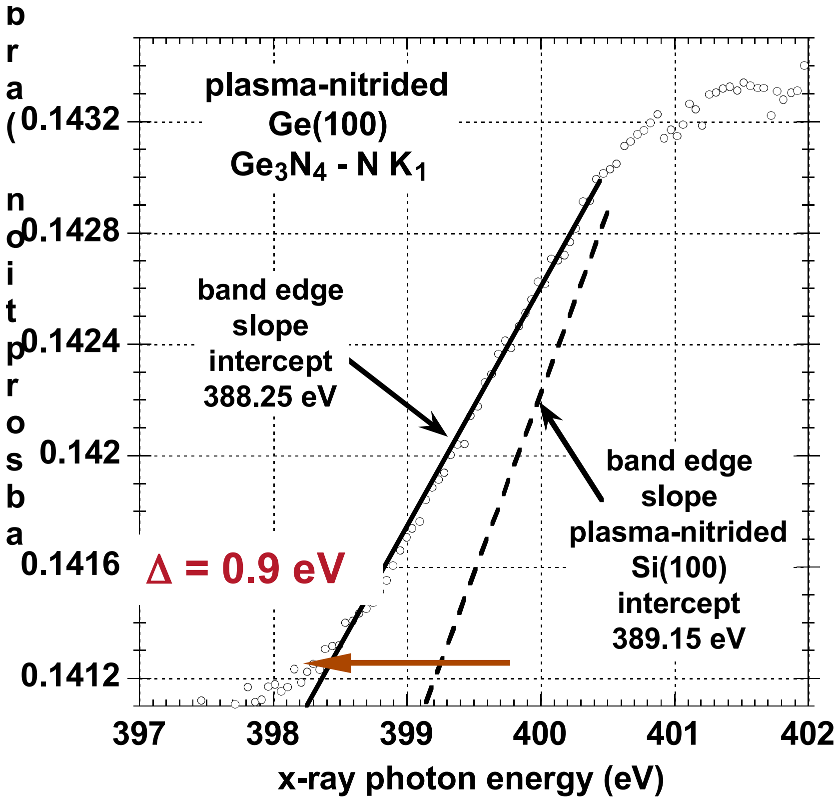
plasma oxidation /nitridation Ge → GeO_2/Ge_3N_4

Si → SiO_2/Si_3N_4 on Si: compare O K_1 and N K_1 edges

optical gaps of SiO_2/Si_3N_4 → opt. gaps of GeO_2/Ge_3N_4

Ge gaps - *red shifted* wrt to Si gaps





SiO_2 = 8.9 eV→GeO_2 = 5.5±0.15 eV

Si_3N_4 = 5.3 eV→Ge_3N_4 = 4.4±0.15 eV

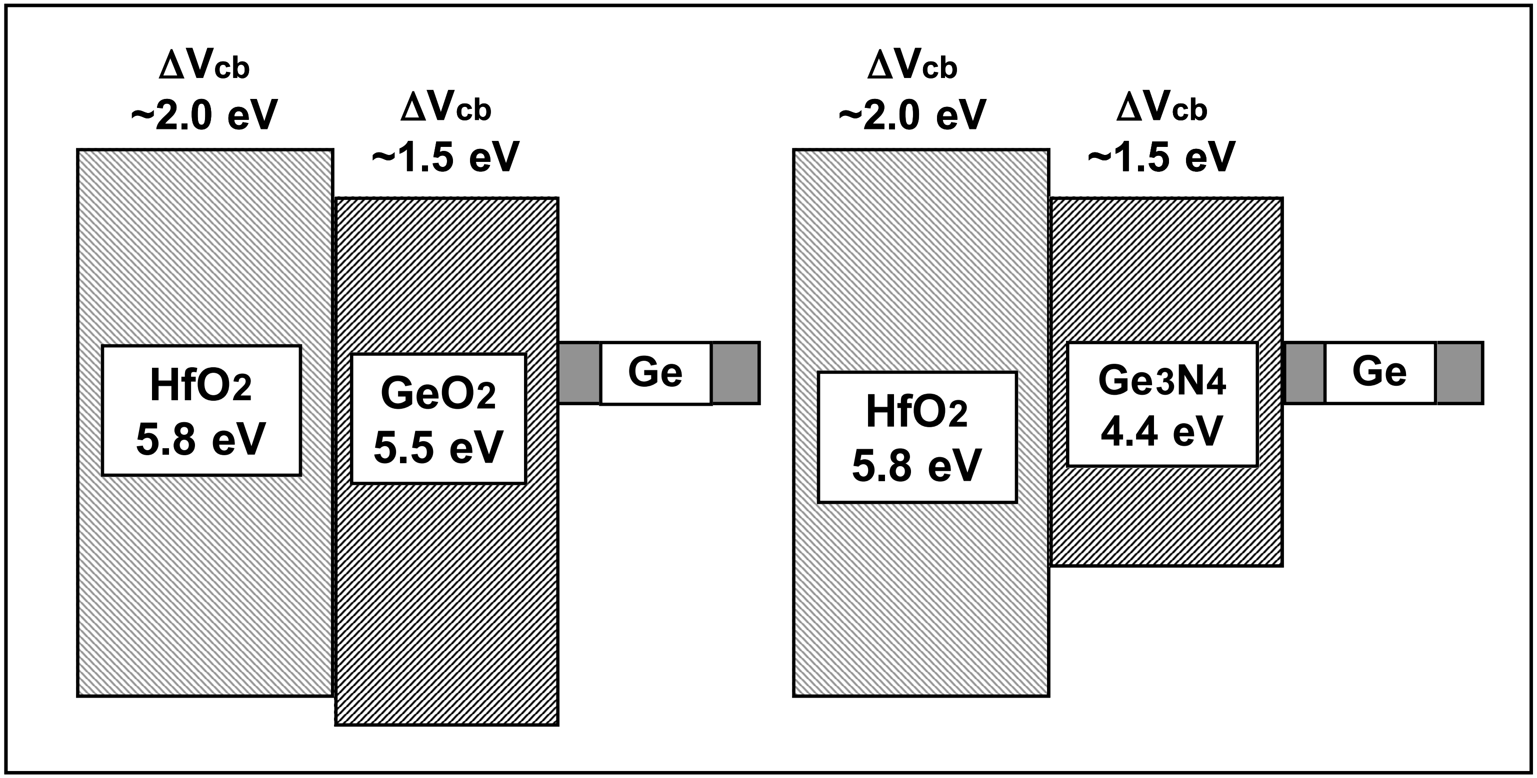
conduction band offset energies (CBOEs)

form valence band offset energies (VBOEs)

soft-x-ray photoemission (SXPS): at SSRL[4] and Spring 8[5]

[4] Y.Z. Hu, et al., Appl. Phys. Lett. 61, 1098 (1992).

[5] T. Maeda et al., J. Appl. Phys. 100, 014101 (2006).



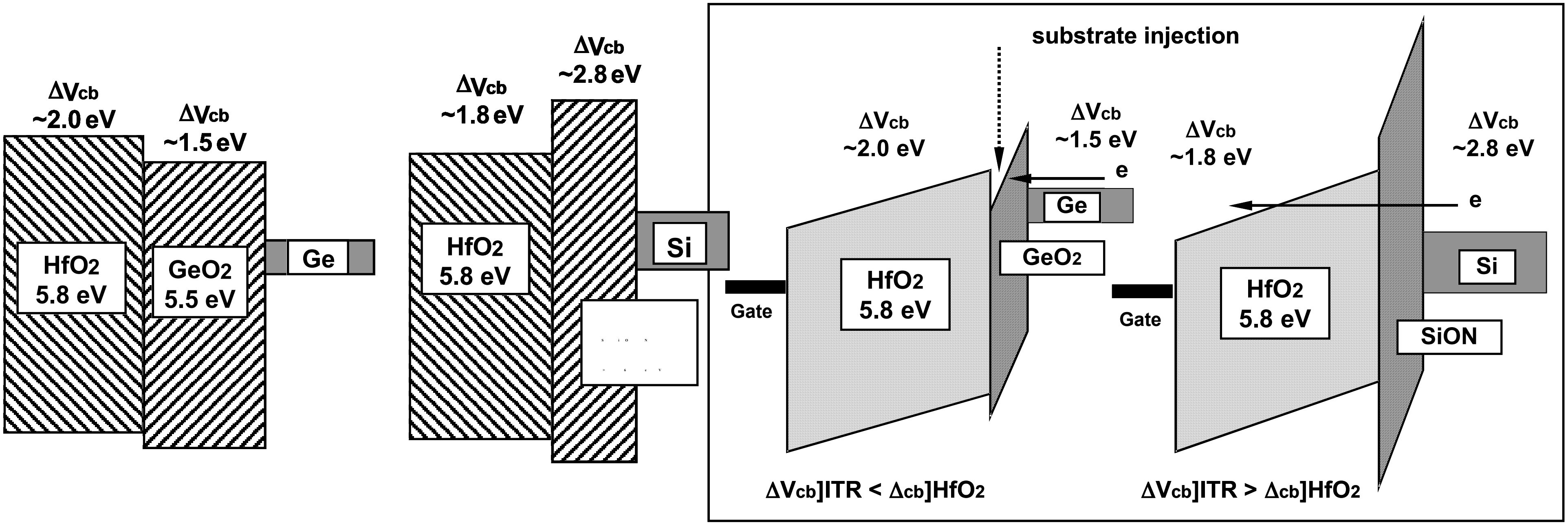
both CBOEs ~1.5±0.15 eV

< CBOEs between Ge and HfO_2

quantitative differences between CBOEs $Ge/GeO_2/HfO_2$ and $Si/SiON/HfO_2$

CBOE(SiON-Si) > CBOE(HfO_2-Si)

CBOE(GeO_2-Ge) < CBOE(HfO_2-Ge)

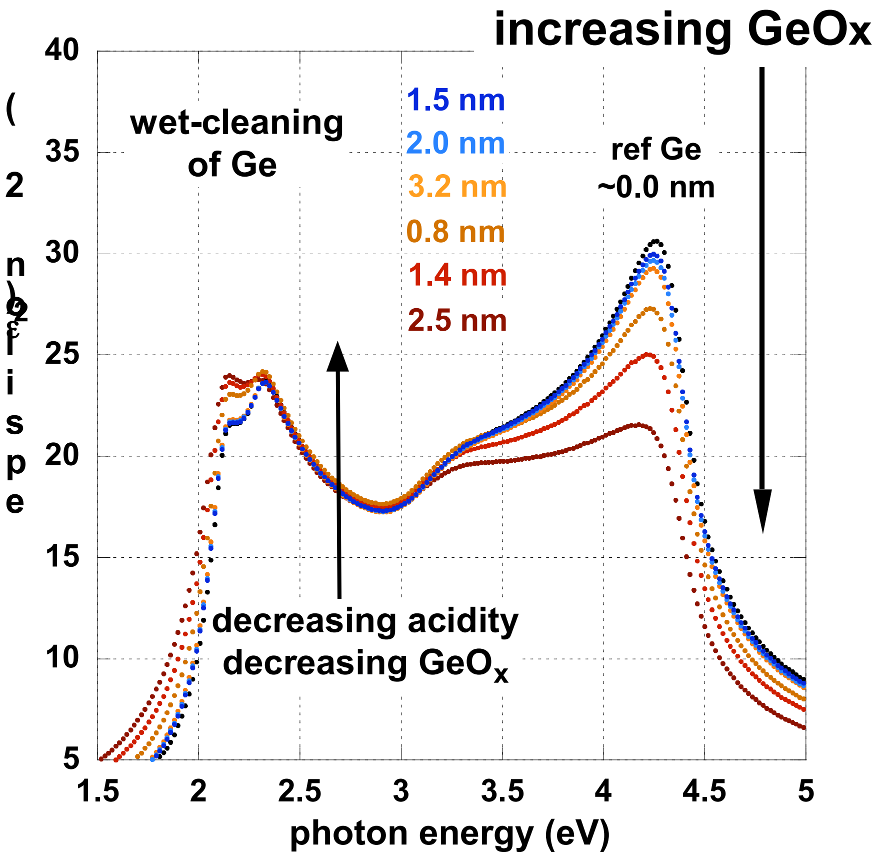


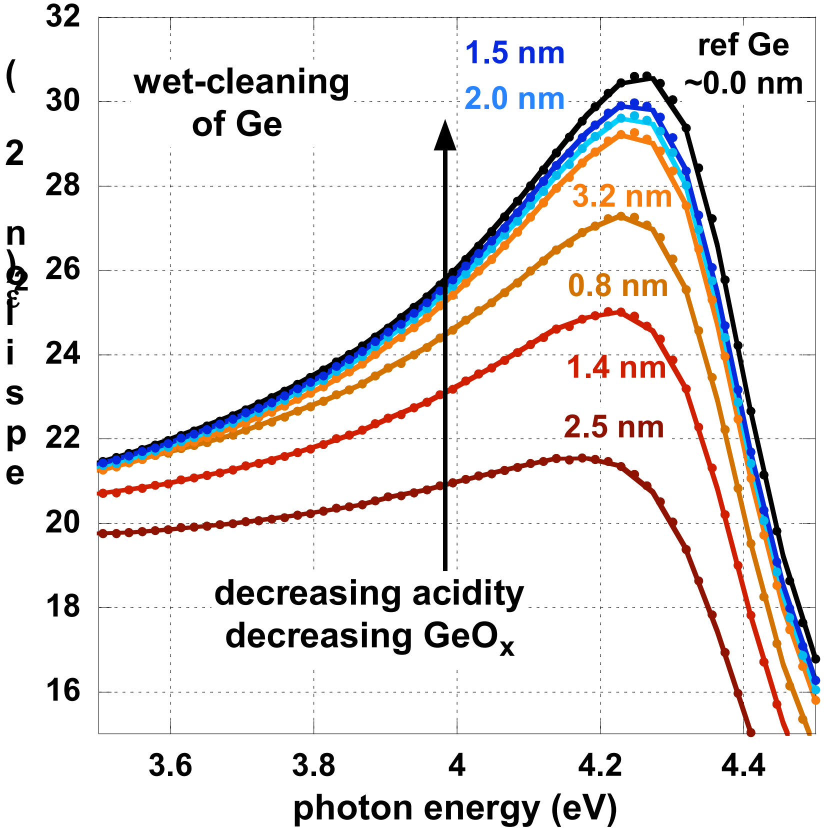
important consequences for interfacial trapping when
Ge substrate is negatively biased - nMOSCAPs or pMOSFETs

source of negative charge trapping, etc..
***potential well* f-negative substrate bias**
releases electrons for F-N tunneling at sufficiently high bias
2 step process increases F-NT wrt to 1 step

Ge wet-chemical cleaning different - what works for Si fails require low acidity for Ge -- not HF, H_2O_2

study by visible SE





T. Mori, D. E. Aspnes, Thin solid films 455 (2004) 33.

Br-methanol "pad" or dilute H_2O_2 and NH_4OH

solution to band edge interface alignment issue

no native Ge dielectric ITRs i)

prevent oxidation of Ge surface during deposition

wet cleaning - remove native oxide - (dilute H_2O_2+NH_4OH)

oxide grows in air - 7 min: >1.2 nm Ge(111); >1.7 nm Ge(100)

passivation - remote plasma assisted nitridation

ii) direct deposition of dielectrics on Ge and
elimination of native Ge ITR from N-passivation

remote plasma-enhanced chemical vapor deposition (RPECVD)
followed by post-deposition annealing

decomposition of Ge-N bonds -- 450°C

elimination of residual GeO_x

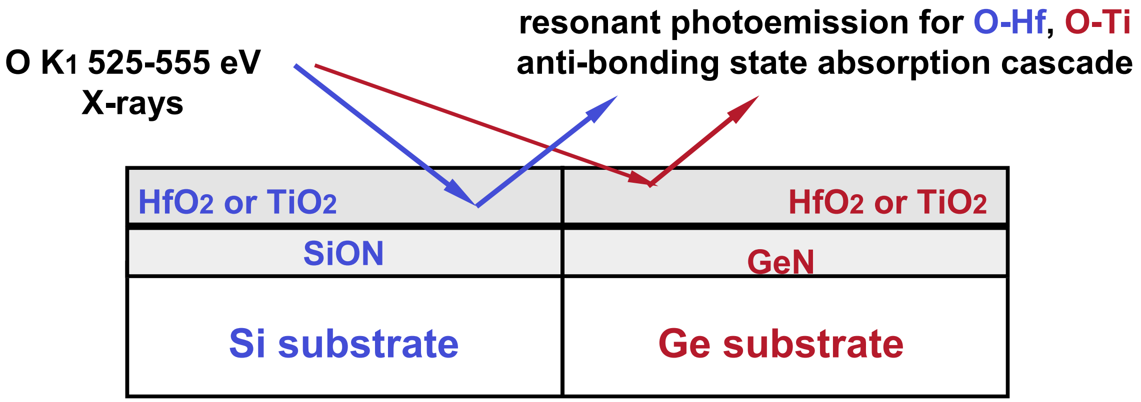
sublimation of gaseous GeO -- 710°C

off-line verification for N

resonant O K_1 and N K_1 edges - NEXAS

buried interfaces *resonant atom-specific* near edge X-ray absorption spectroscopy (NEXAS)

detects interfacial N



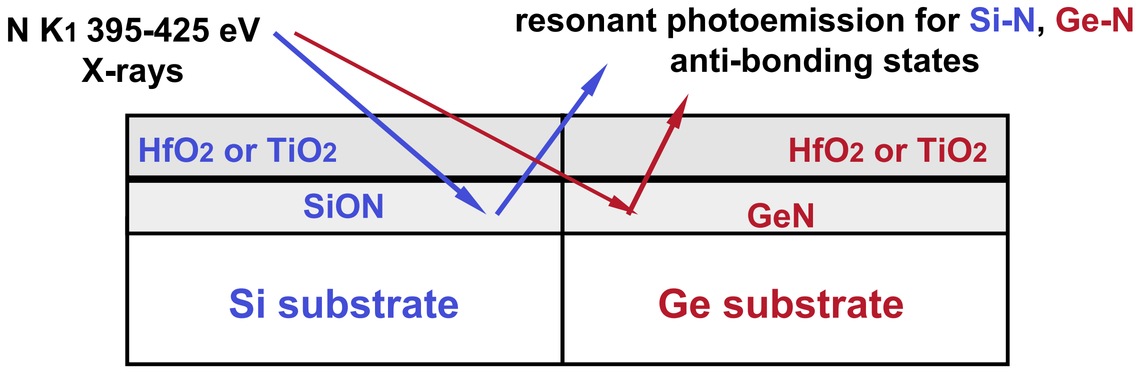
O K1 525-555 eV
X-rays

resonant photoemission for O-Hf, O-Ti
anti-bonding state absorption cascade

HfO2 or TiO2 | HfO2 or TiO2

SiON | GeN

Si substrate | Ge substrate



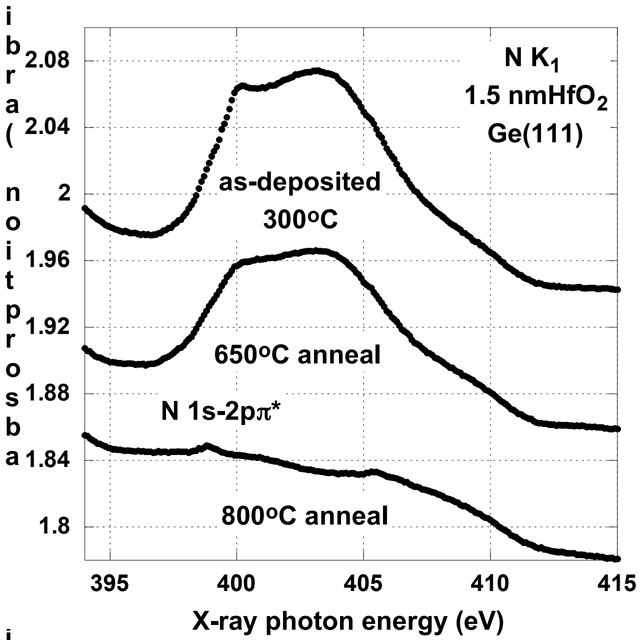
N K1 395-425 eV
X-rays

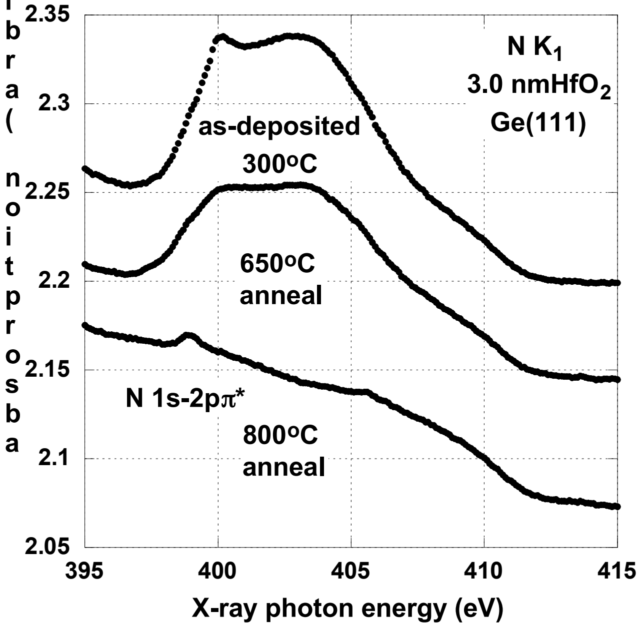
resonant photoemission for Si-N, Ge-N
anti-bonding states

HfO2 or TiO2 | HfO2 or TiO2

SiON | GeN

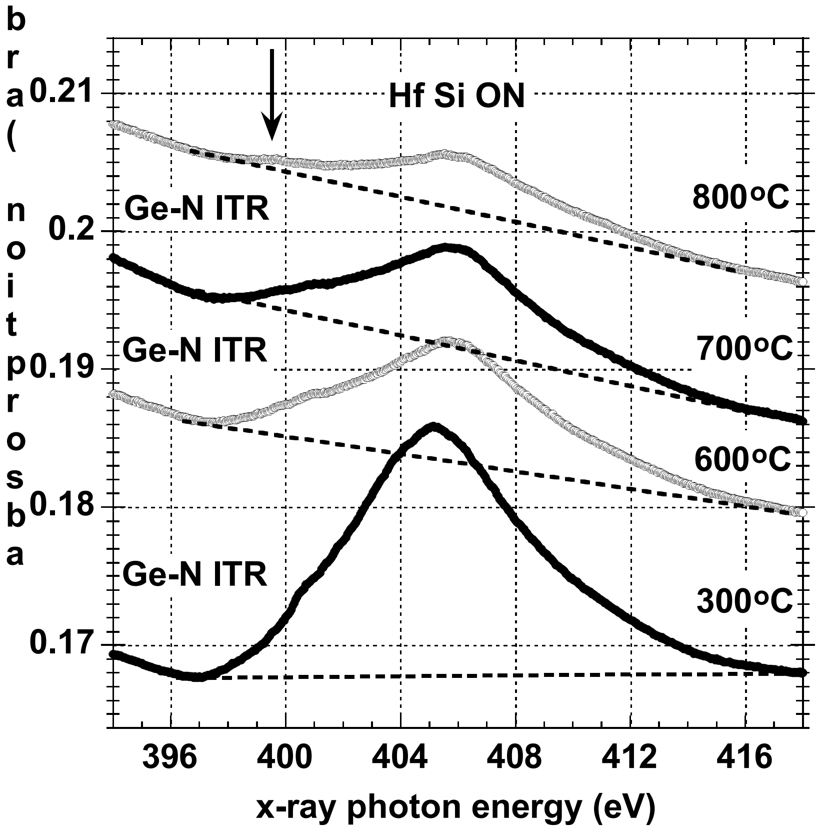
Si substrate | Ge substrate



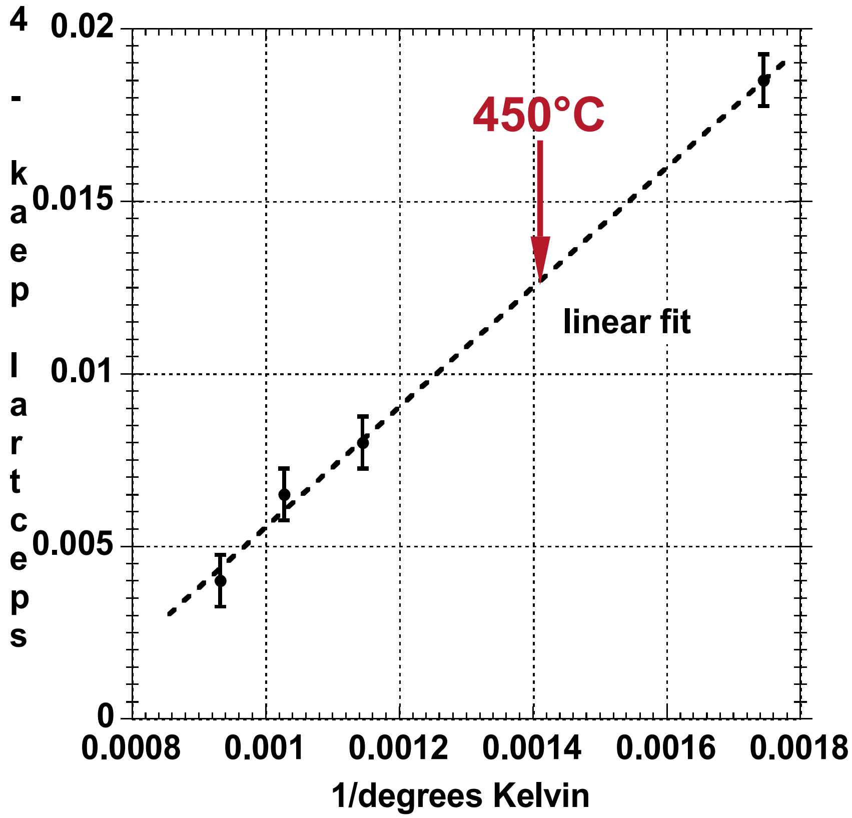


complete removal of Ge-N: except N 1s to N_{2p} π^*

loss of interfacial N as function of annealing temperature, T
high Si_3N_4 content Hf Si oxynitride alloys on Ge(100)



N K_1 edge spectra as function of T



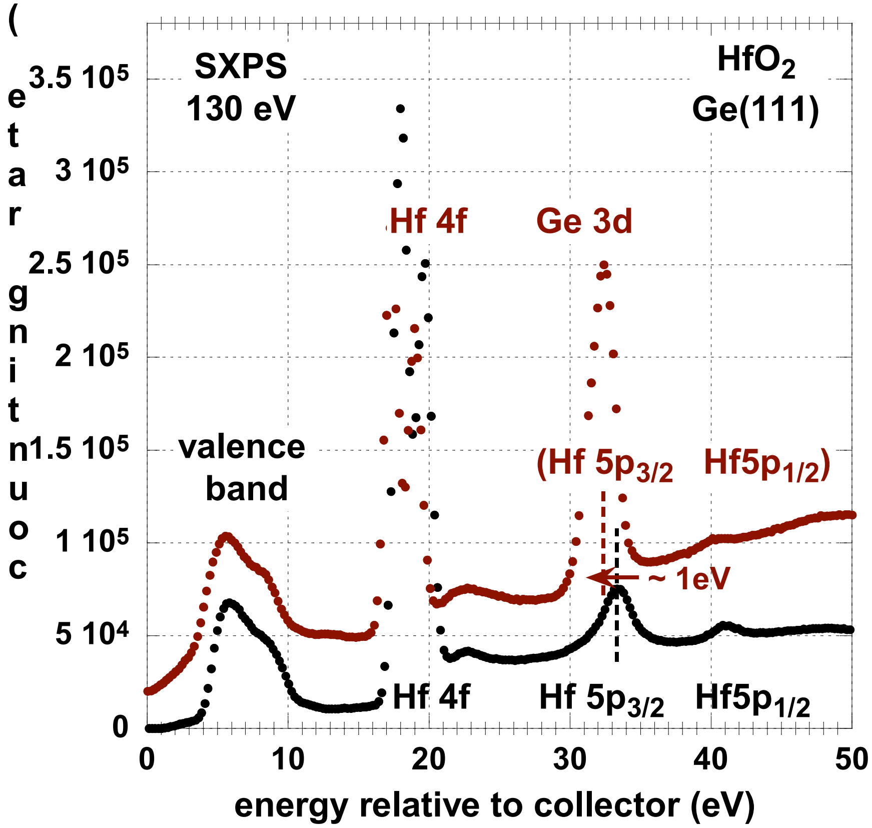
spectral peak absorption function of 1/T(degrees K)

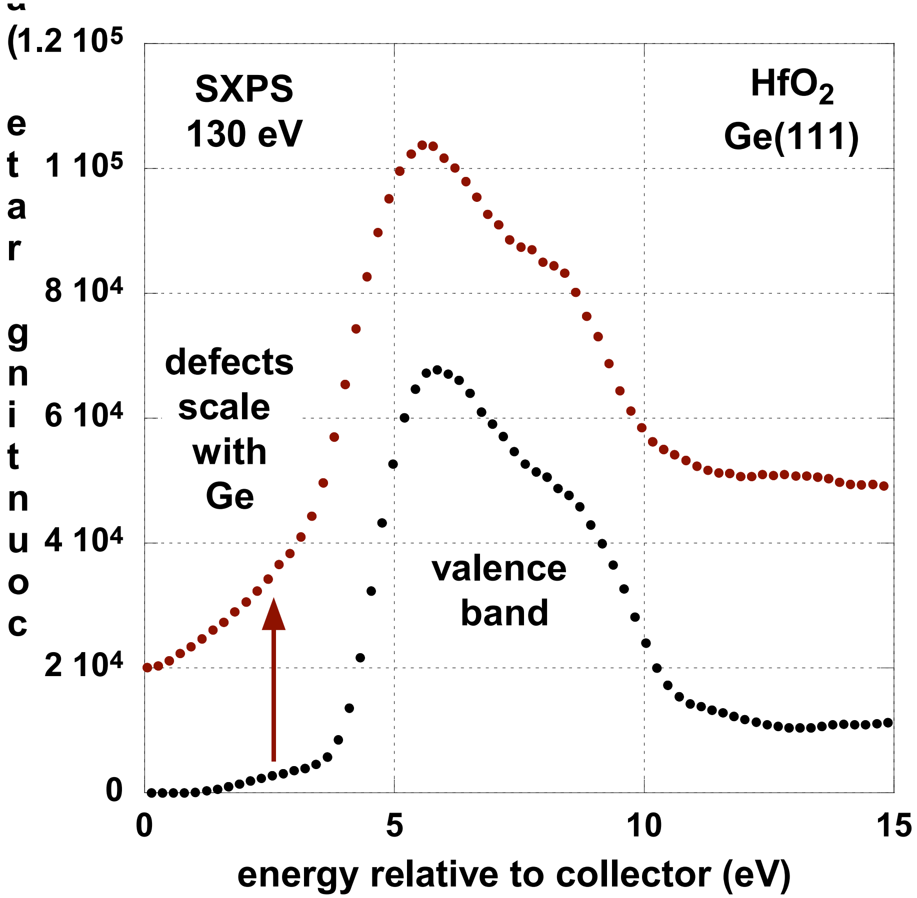
SXPS - UPS - valence band edge defects in HfO_2

annealing to 800°C - removal Ge-N at interface

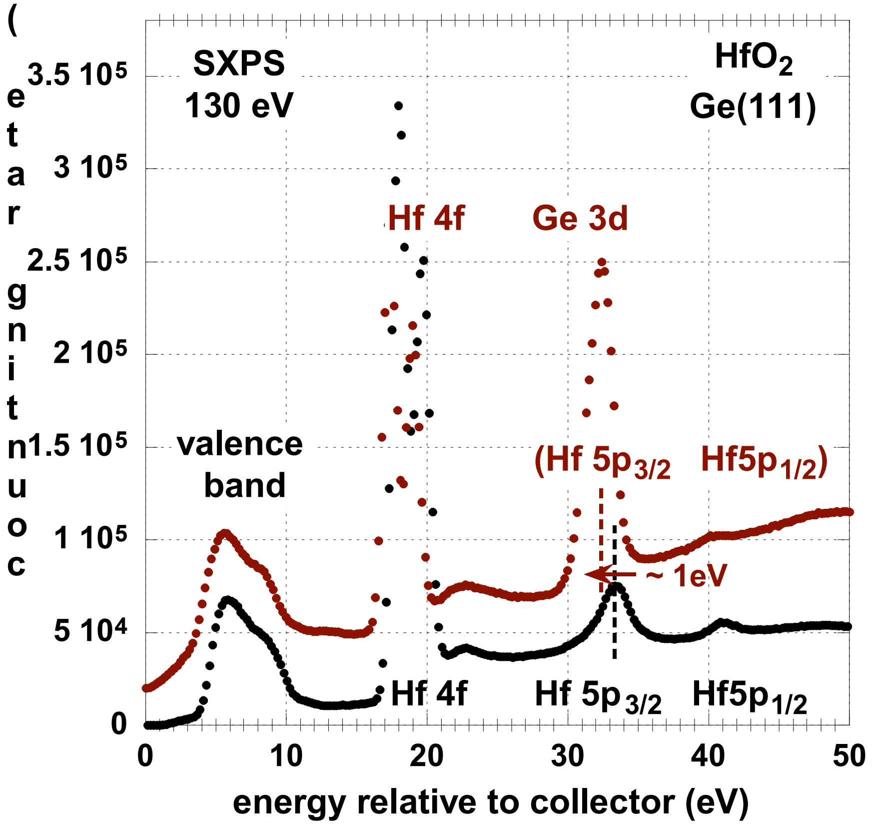
i) increase in grain size; ii) incorporation of Ge-O bonds

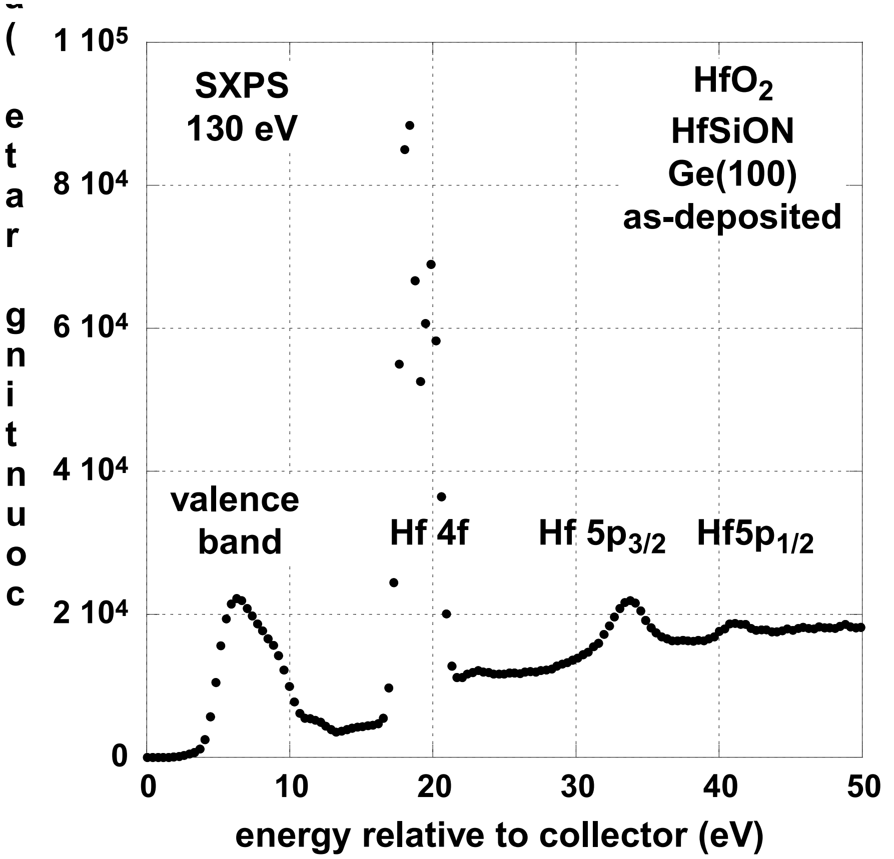
***each* contributes to increase in band edge defects**





Ge-N passivation works equally well for HfO2 and HfSiON depositions - Hf 4f, 5p’s - but, no Ge 3d



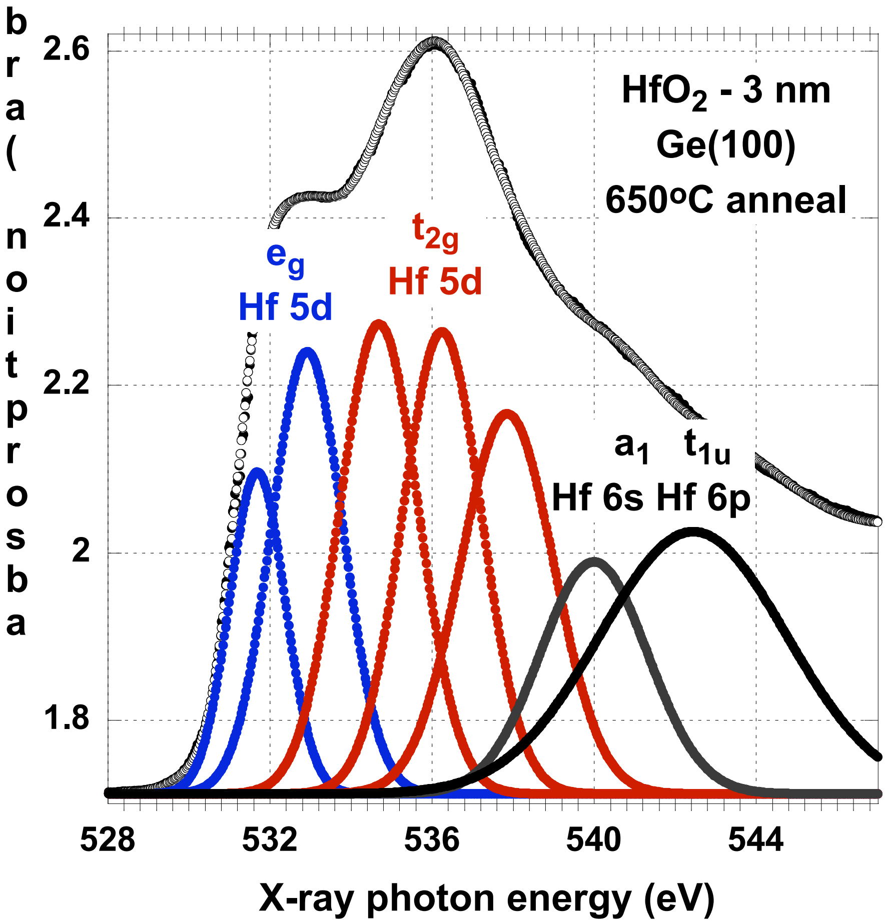


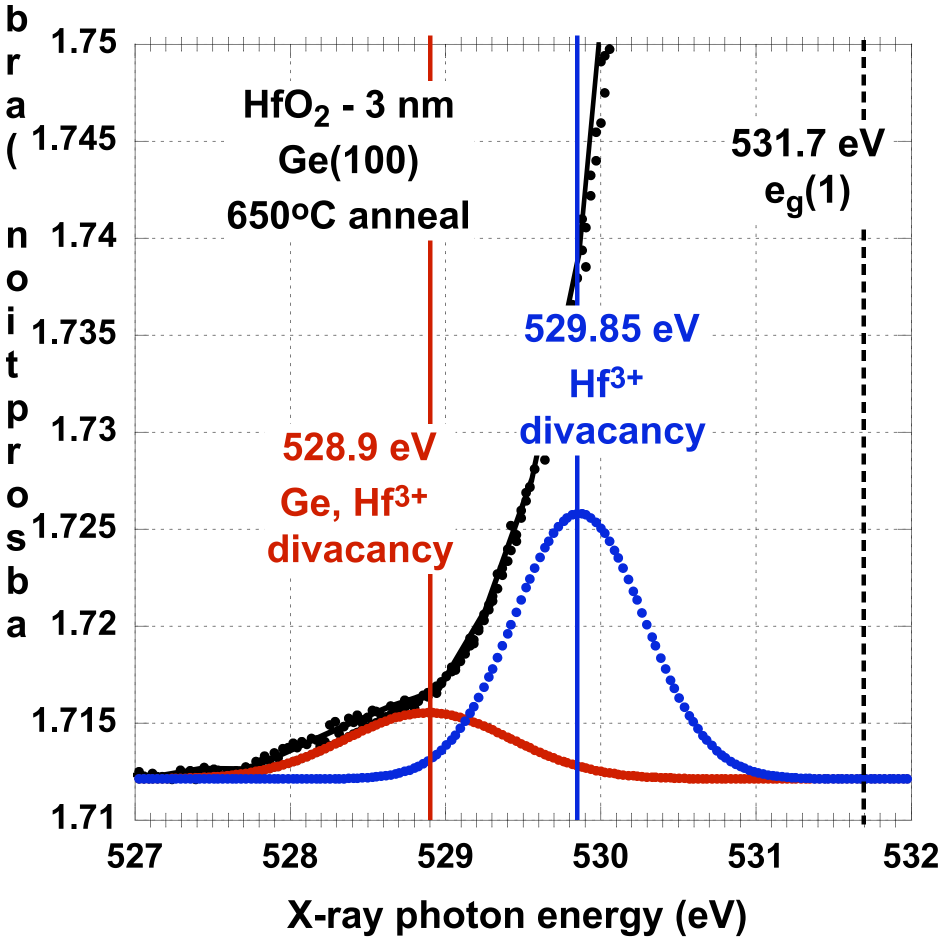
prevents Ge from being transported into HfO2 and HfSiON thin films during film deposition by RPECVD

however, both are *impregnated* with Ge after 800°C anneal

left: Gaussian fit - intrinsic Hf contributions to OK_1 spectrum

band edge π-states Hf 5d e_g, and higher-lying σ-states
Hf 5d t_{2g}, and Hf 6s and 6 p (7 MO states -- $5d^36s6p^3$)

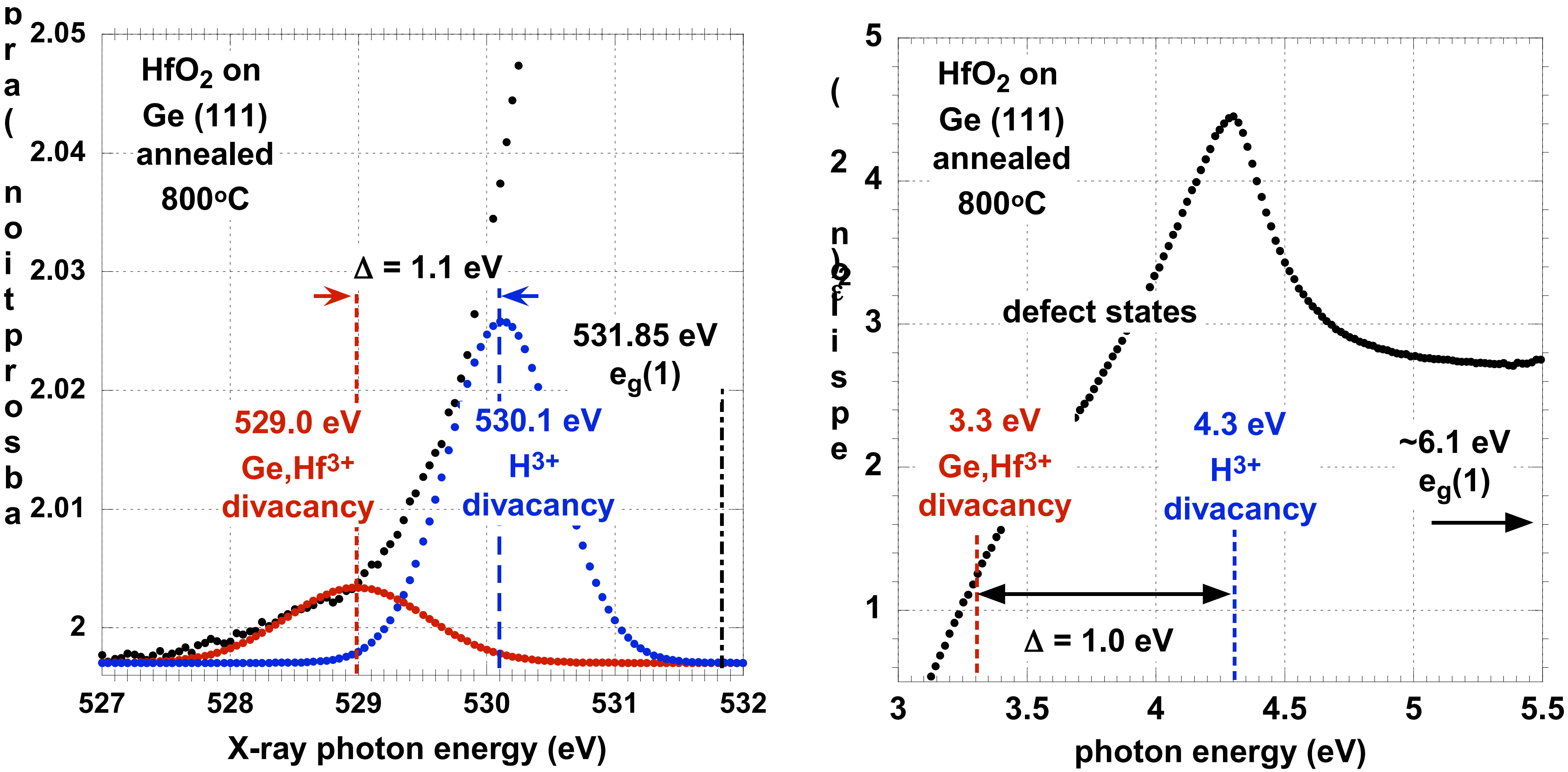




right: Gaussian fit - band edge defects in OK_1 spectrum

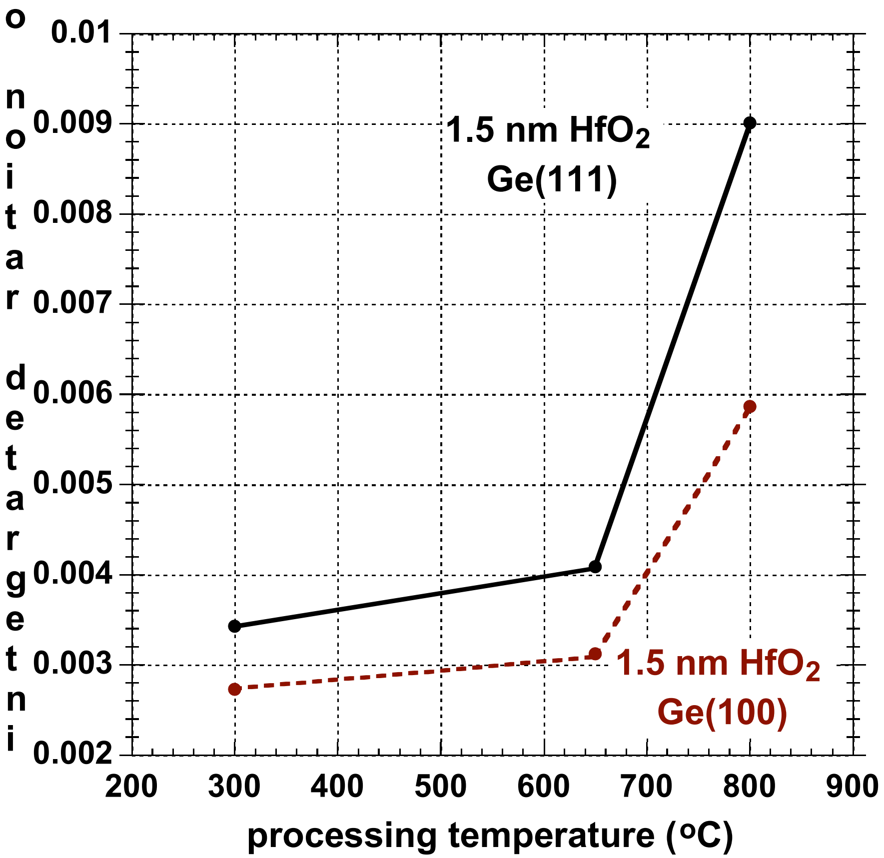
O-atom divacancies clustered at grain boundaries with a contribution of G-O trapped in film during deposition/annealing

same defect level spacing in NEXAS O K1 edge and ε2 2nd derivative - vis-VUV spectroscopic ellipsometry



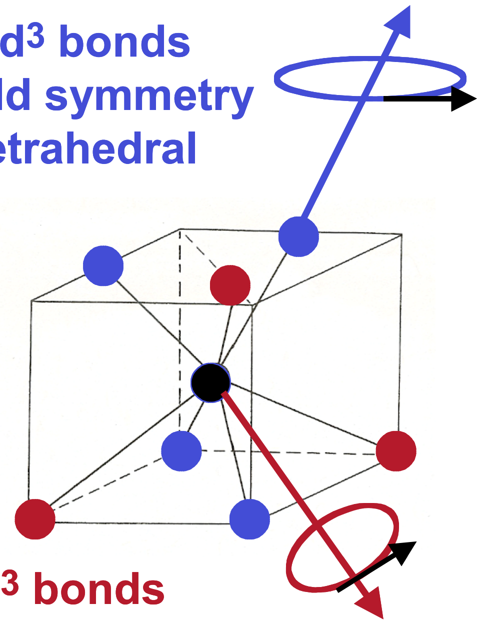
also same energy level difference with respect to lowest Jahn-Teller e$_g$(1) state above band edge

defect concentration increases after all Ge-N is eliminated & HfO2 is in direct contact with Ge substrates



next SSRL run - 6-10 June will fill in anneal temps between 600 & 750°C

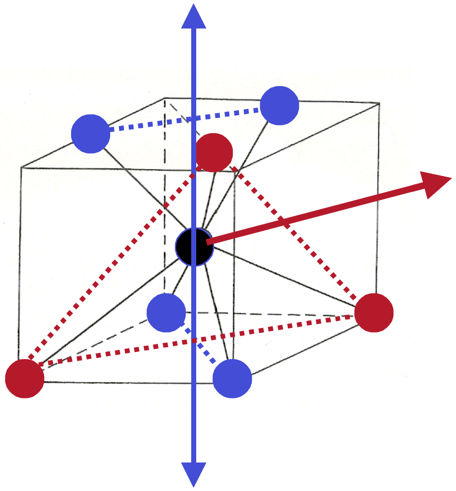
7 σ-bonds - $6s5d^3 + 6p^3$



Ge(111) columnar

3-fold O
7-fold Hf
4-fold O

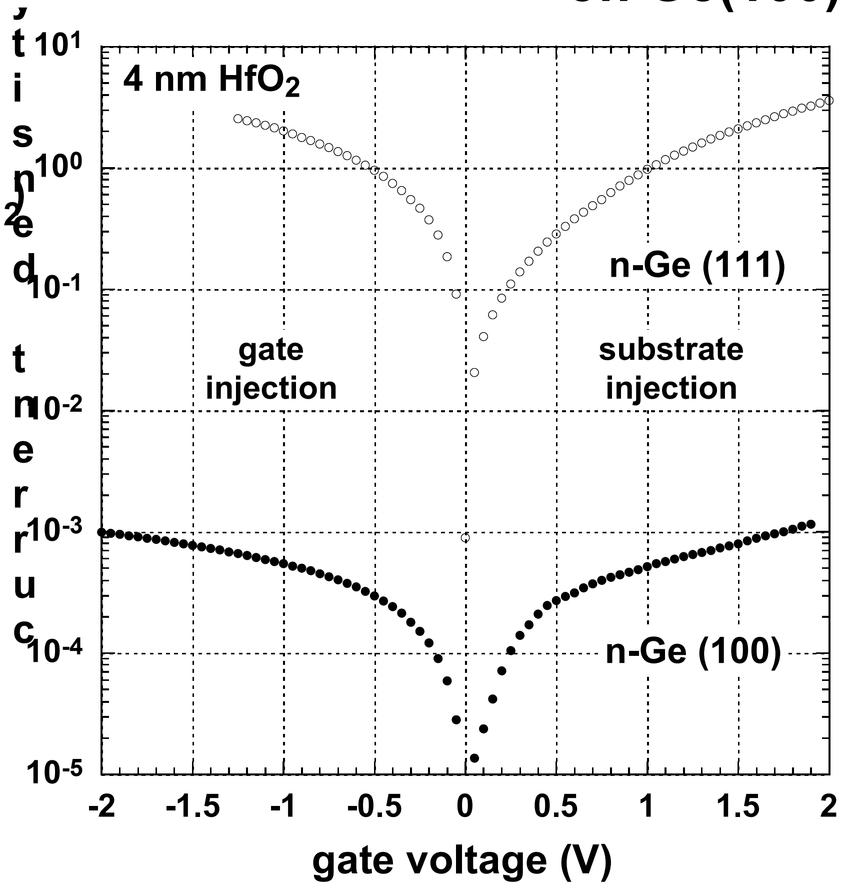
5 possible orientations

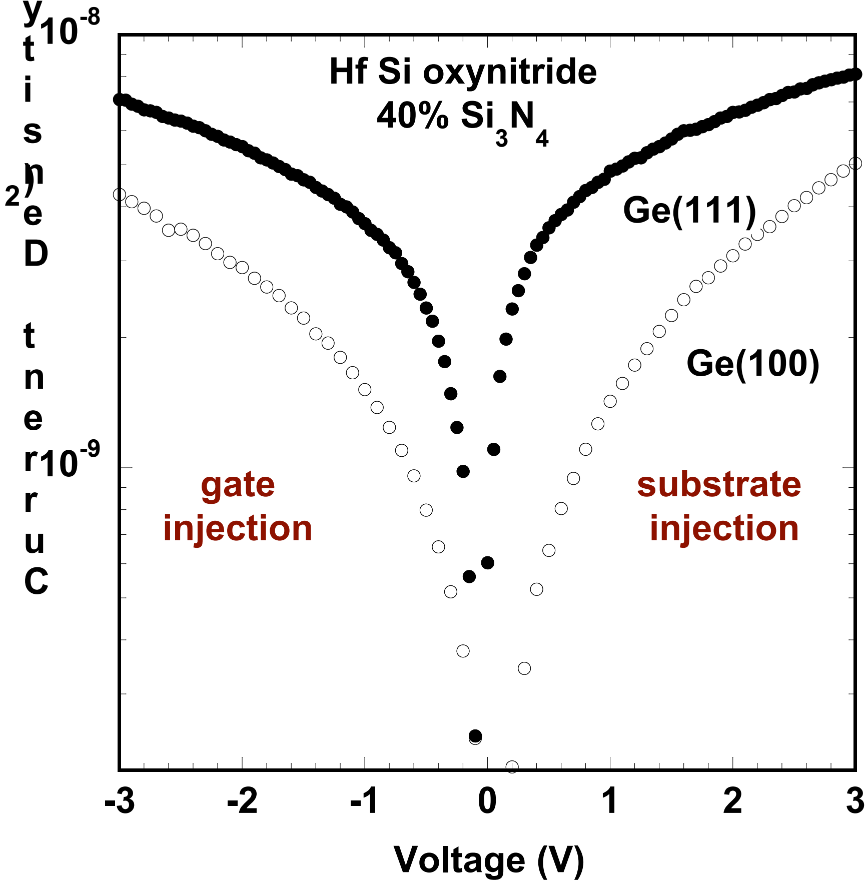


Ge(100) *less* columnar

electrical results after 800°C anneal

nano-crystalline HfO_2 - non-crystalline 40% Si_3N_4 Hf Si oxynitride on Ge(100) and Ge(111)





for HfO_2 - higher tunneling current Ge(111) correlates with larger increases in defect density after annealing

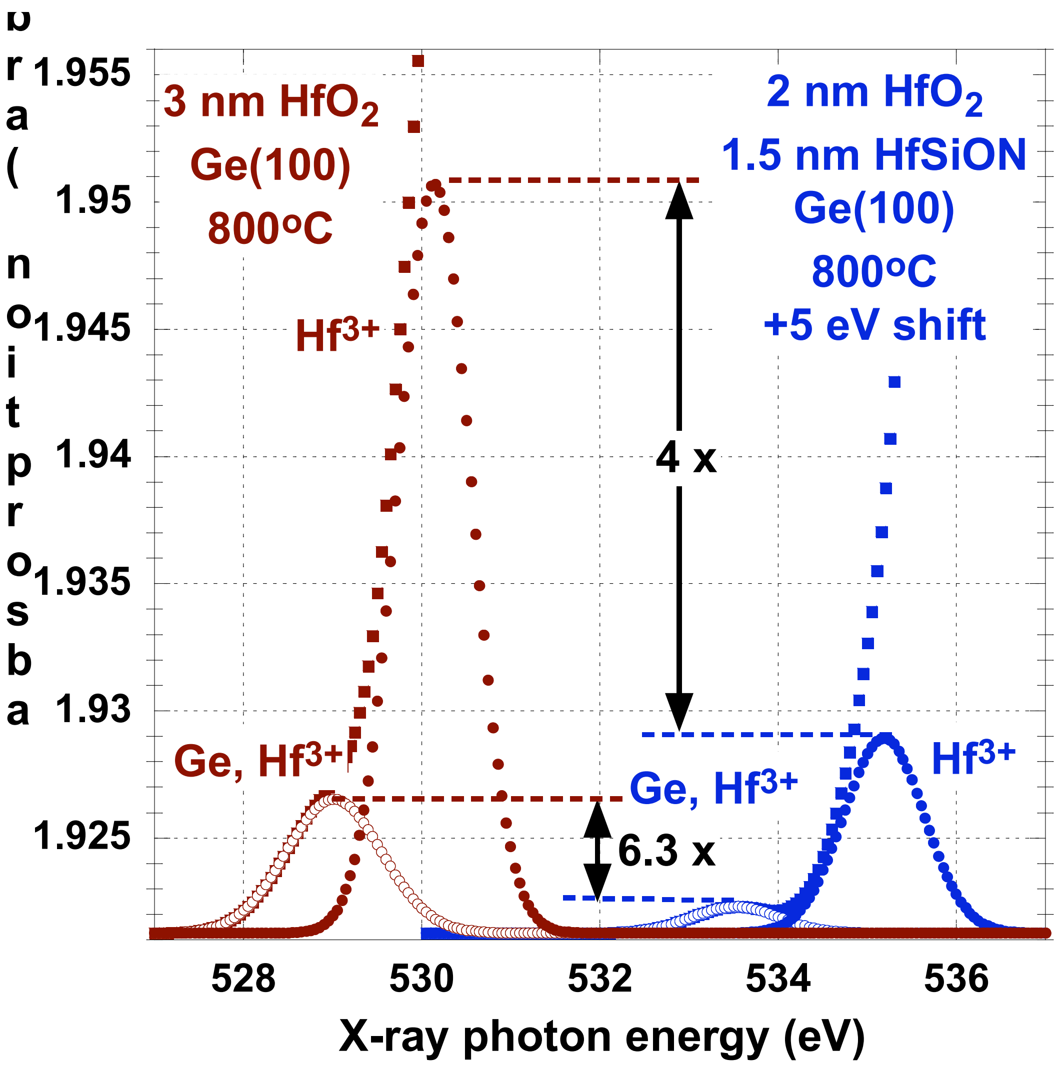
significantly lower tunneling current non-crystalline homogeneous 40% Si_3N_4 Hf Si oxynitride alloy

HfSiON works as ITR

defect reductions: 4x & 6.3x wrt HfO2

anneal temperature study, 600-750°C

June:SSRL-NEXAS/NSLS-SXPS (XPS)



germane line operative

GeN passivation on Si being evaluated

processing options for future device studies correlated with advanced spectroscopies

dielectrics

i) HfO_2 ~ 2 nm

ii) HfO_2-HfSiON stack ~1.5 nm/1 nm

substrates

i) Ge(111),(100),(110)

ii) pseudo-morphic Ge on Si(100),(111)

additional dielectric options

phase separated Hf silicates with SiO_2 = or > percolation limit of 16% (or 84% HfO_2)

where we might consider going in 2011

‘Functional Diversification‘ a novel approach for integration of non-CMOS devices into traditional CMOS platforms

SRC is going this route with ARO

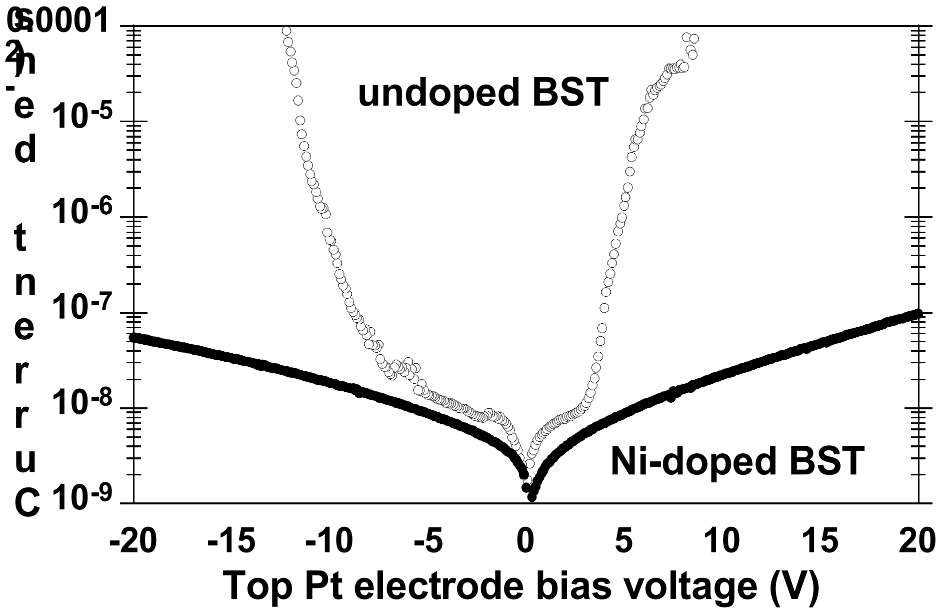


Fig. 1. J-V Characteristic of Ni-doped and undoped BST MIM cells at room temperature. Traces are included for both positive and negative gate bias in a spectral range from –20 V to + 20 V.

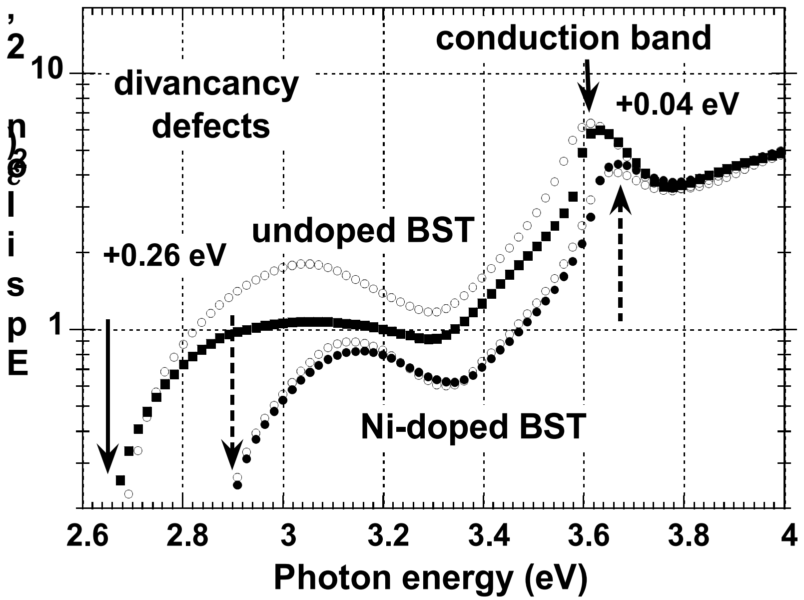


Fig. 2. Epsilon 2 (ε2) extracted from SE measurements of undoped and Ni-doped BST. The solid circle points are as-deposited films (~30C), and the open circles films annealed in Ar at 800°C

defect control functionality -- $SrTiO_3$:Nb(1%) - being prepared:

superconductivity transition easily explained by divacancy defect model and occupancy changes with ad-atom valence

summary plans for next two years

focus on (a) HfO_2: and (b) HfO_2-Hf SiON on Ge(100)/(111)/(110)*
morphology vs thickness/annealing temperature and elimination of ITRs
for Si -- e.g., HfSiON/Ge(3 atomic layers)/Si - being done as I speak!!

emphasis on 600°C to 750°C anneals

i) High resolution TEM Gerd Duscher, NCSU

ii) spectroscopic studies: SXPS/UPS at BNL/NSLS (Marc Ulrich, ARO);
NEXAS at SSRL/Stanford (G Lucovsky, students, Post Docs; vis-VUV
spectroscopic ellipsometry (GL Students and Dave Aspnes)

iii) test device measurements: I-V, C-V (NCSU,Vanderbilt)
radiation stress testing (Vanderbilt)
symmetry in I-V - effectiveness of GeO_x removal by annealing

iv) MEIS - new Post Doc Leonardo Miotti - collaboration with
Isreal Baumvol and Christiano Krug -- Porto-Allegre, Brazil

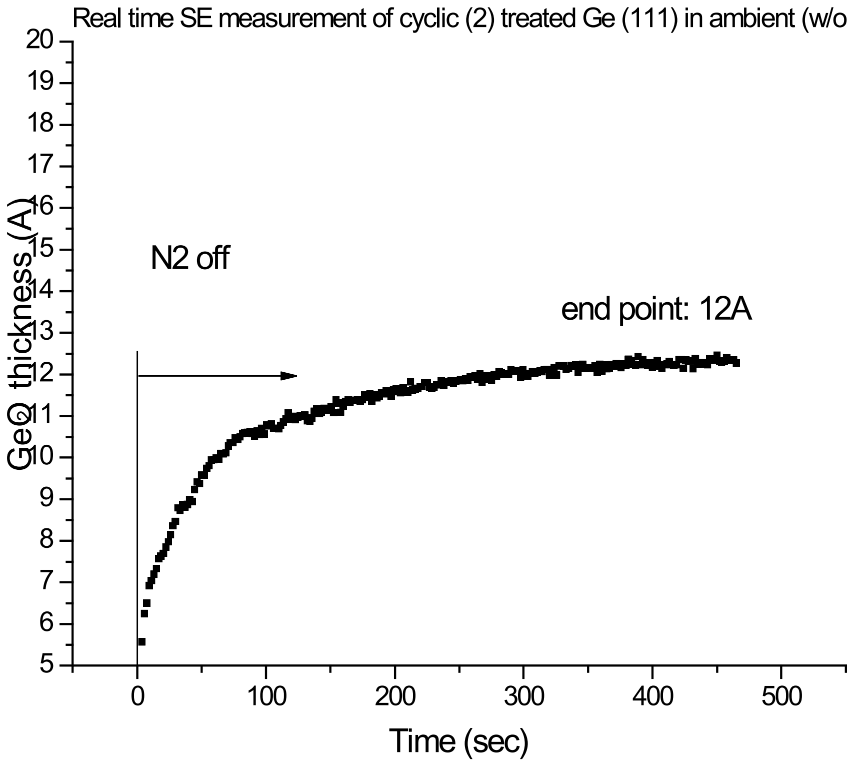
*if substrates are *donated by* AMD/Sematech

additional supporting foils

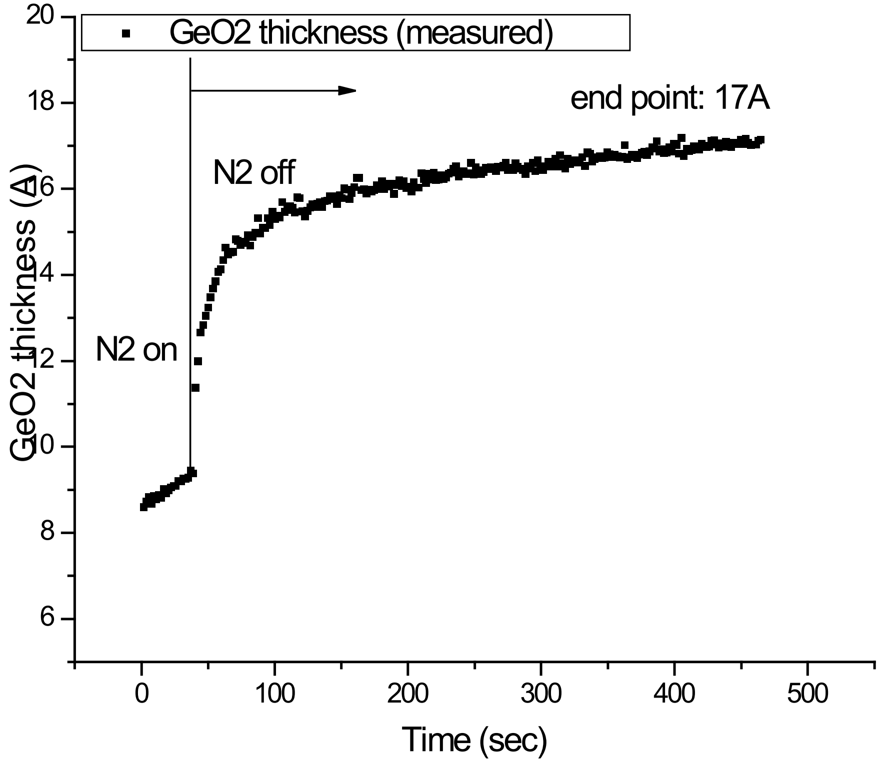
real-time SE measurements for Ge(111) and Ge(100) substrate surface - issue for processing Ge

self-limiting GeO_2 growth after optimized Ge surface cleans

Ge(111)

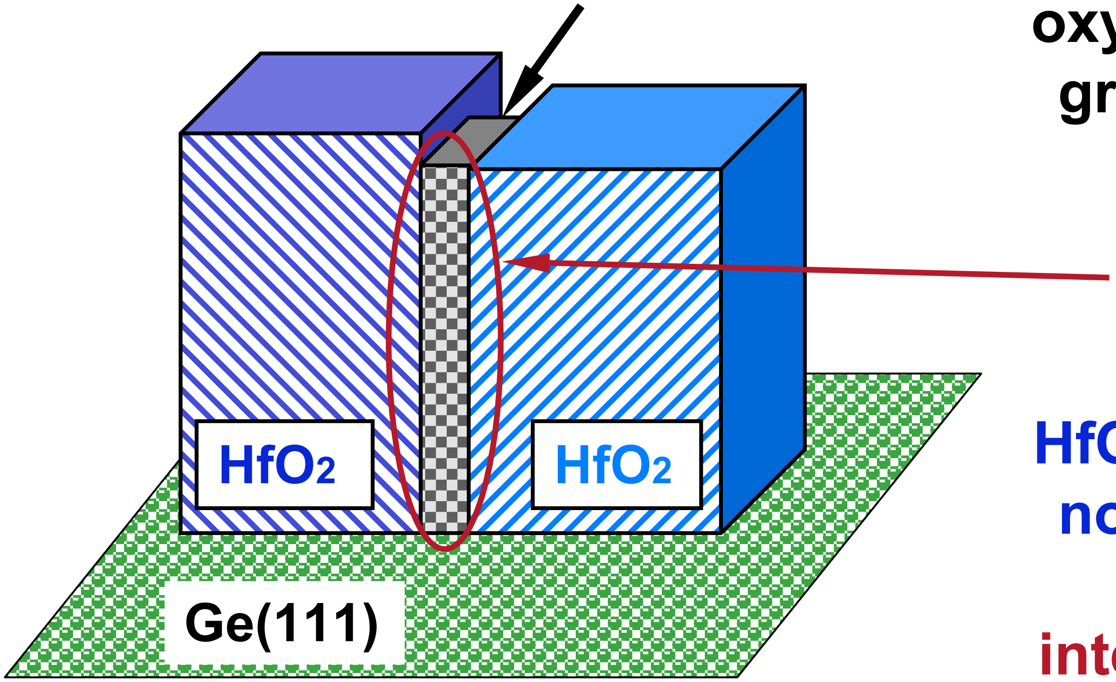


Ge(100)



schematic representation of "mosaic" in-plane epi-growth and columnar morphology - HfO_2/Ge(111) substrate

O-vacancies/transported Ge pinned on grain boundaries



oxygen vacancies cluster at grain boundaries between columns

HfO_2 nano-grains are mis-aligned

Ge has a 3-fold axis

HfO_2 (Hf 7-fold coordinated) no symmetry element that matches Ge (111)

interfacial misalignment for random surface nucleation of HfO_2 on Ge during 800°C anneal

values of ε_2 in defect regime

~50x more for HfO_2:Ge(111) columnar aligned than for

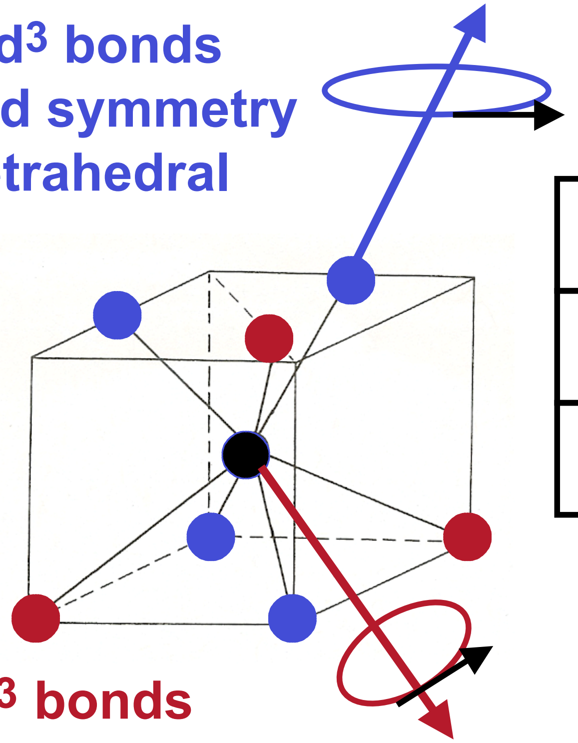
bulk nano-grains "inside" HfO_2 films in HfO_2/SiON/Si stacks

in plane mosaic alignment between HfO_2 and Ge(111)/(100)

symmetry of 7 σ-bonds (6s5d3 + 6p3) in unit cell relative to symmetry elements of Ge surface

Ge(111) alignment with dangling bonds perpendicular to Ge surface

sd^3 bonds
3-fold symmetry
tetrahedral



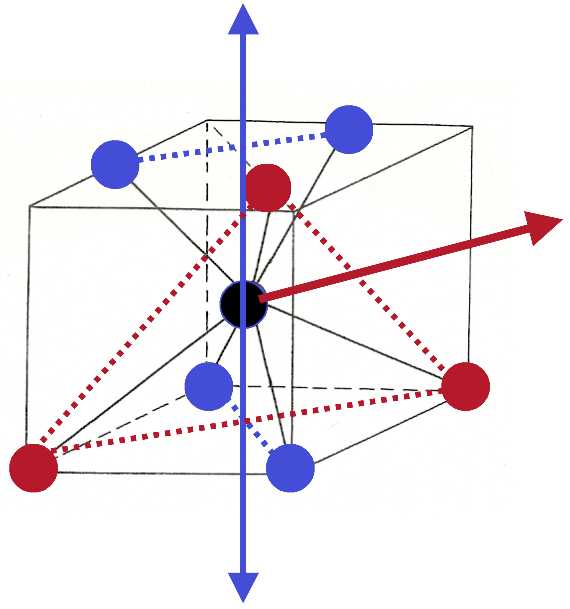
p^3 bonds
3-fold symmetry

strong driving force for columnar structure

3-fold O
7-fold Hf
4-fold O

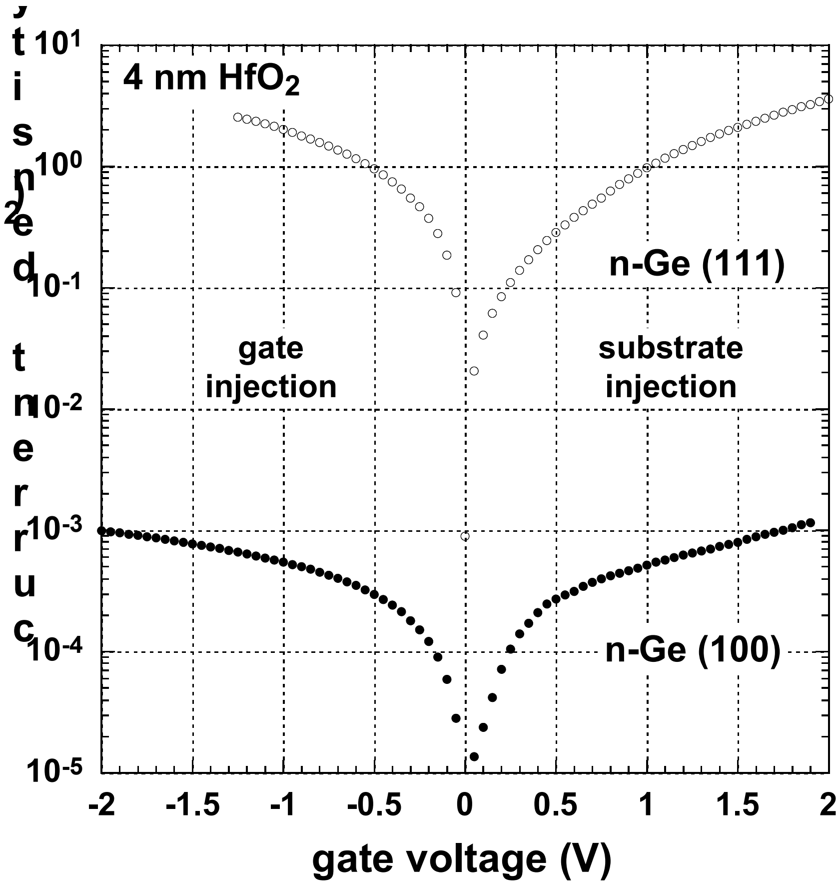
Ge(100) alignment with dangling along dimer chains

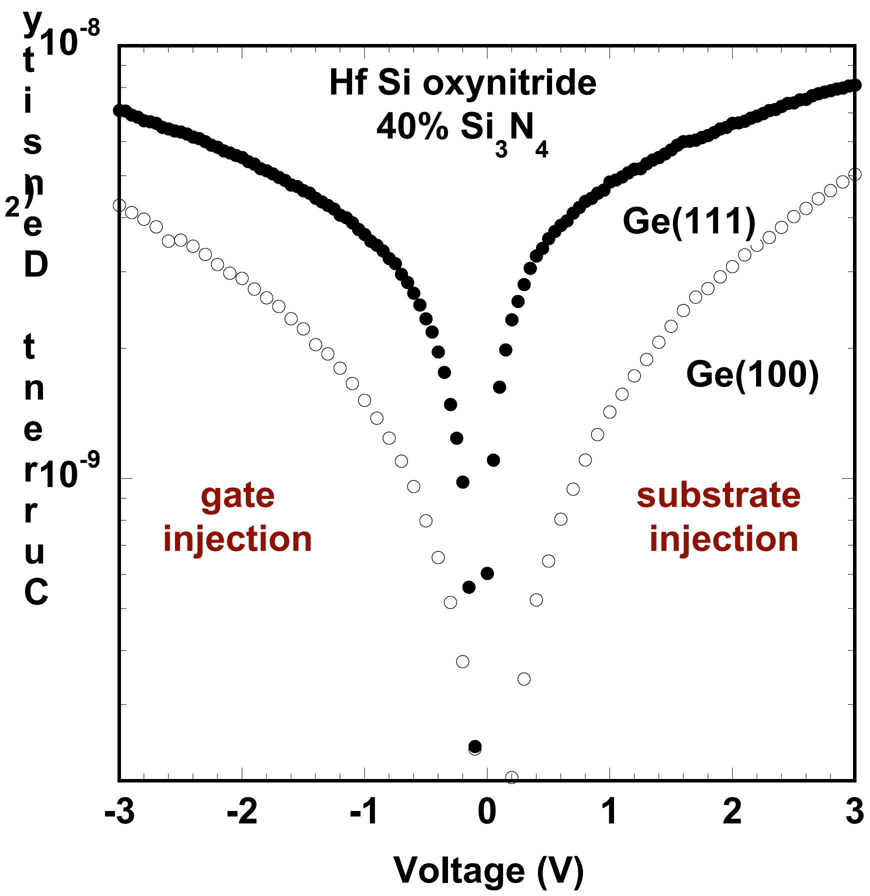
5 possible orientations



weaker driving forces for columnar structure

spectroscopic studies explain J-V





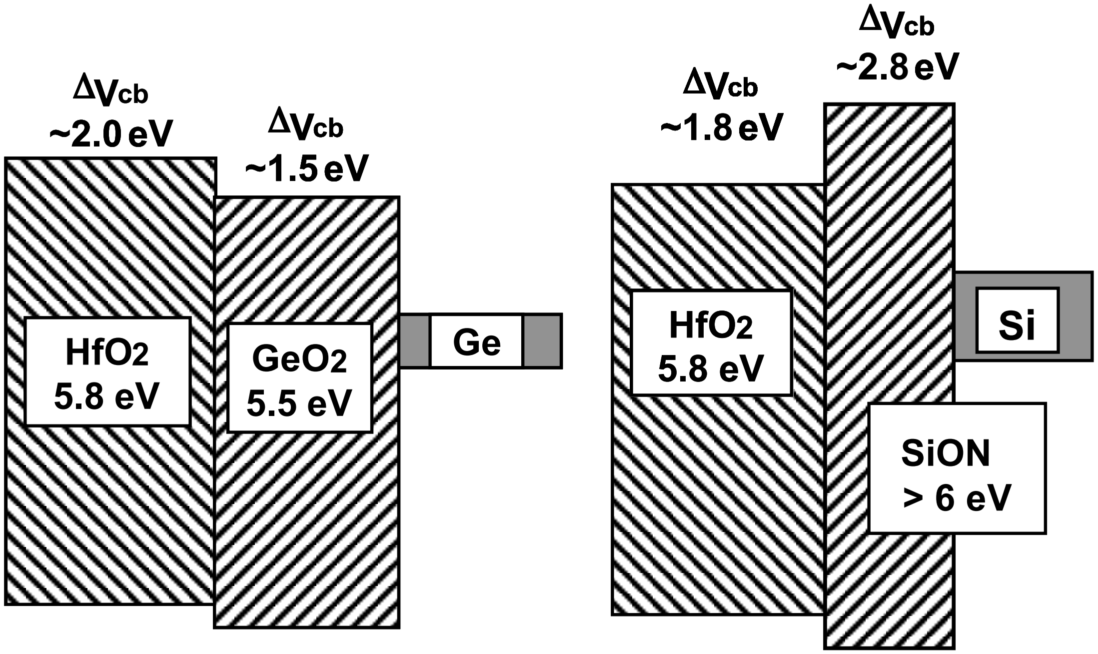
e.g., higher tunneling current for Ge(111) correlates with larger increases in defect density after annealing

and a more columnar structure based on symmetry effects

quantitative differences between CBOEs Ge/GeO_2/HfO_2 and Si/SiON/HfO_2

CBOE(SiON-Si) > CBOE(HfO_2-Si)

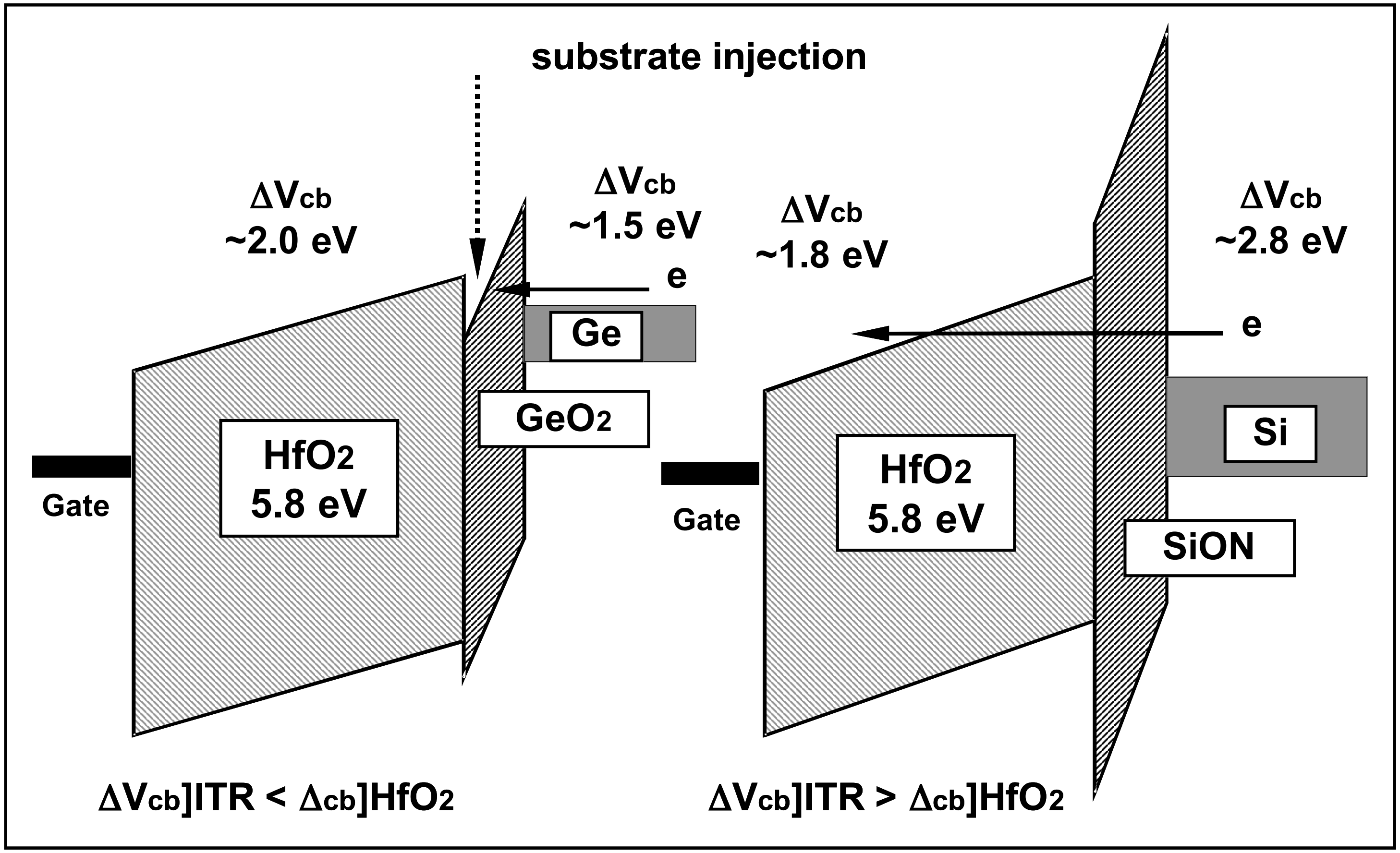
CBOE(GeO_2-Ge) < CBOE(HfO_2-Ge)



important consequences for interfacial trapping when
Ge substrate is negatively biased - nMOSCAPs or pMOSFETs

negative substrate bias

n-MOSCAPs, and p-MOSFETs



source of negative charge trapping, etc..

potential well formed under negative substrate bias

releases electrons for F-N tunneling at sufficiently high bias

2 step process increases F-NT wrt to 1 step