Passivation principles for Ge MOSFETs

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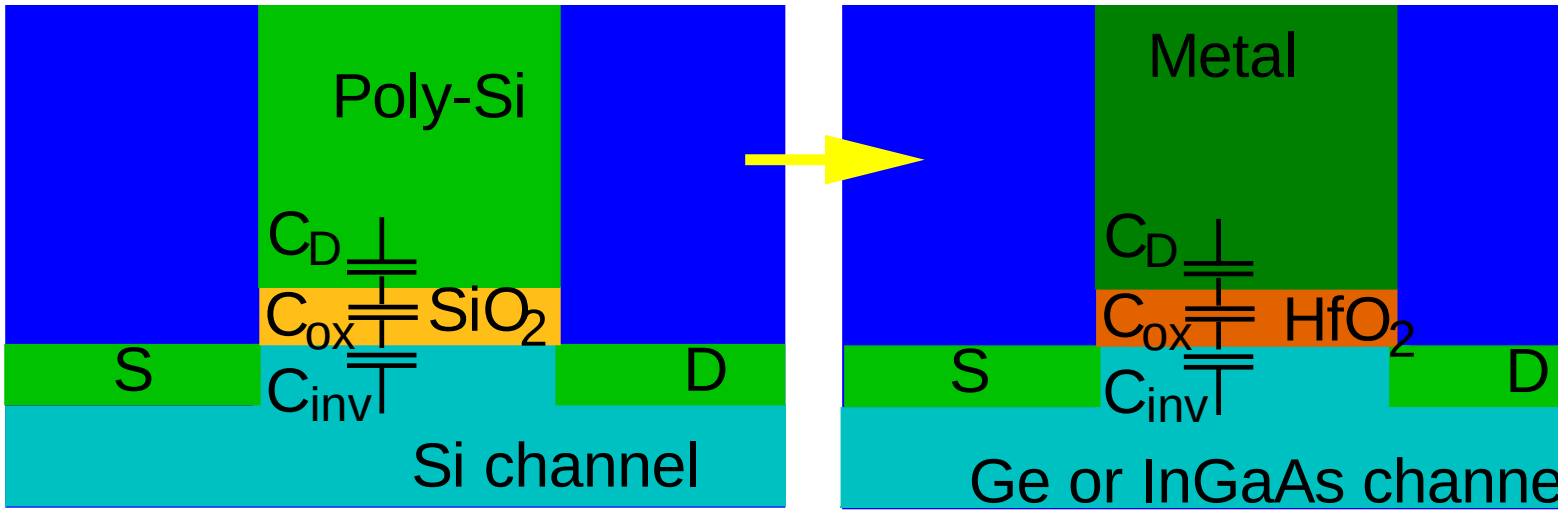
- Need for Ge
- Defects in GeO_2
- Various oxides on Ge
- Diffusion barriers

Future CMOS



- Replace SiO2 with high K oxide, HfO2
- Replace poly-Si gate with metal gate
- Replace Si channel with high mobility channel

Need for Ge

- Ge has higher carrier mobilities than Si, particularly holes
- Ge pFET, GaAs nFET
- Ge nFET, pFET both possible

	Si	Ge	GaAs
Band Gap (eV)	1.1	0.66	1.42
Electron mobility ($cm^2/V.s$)	1500	3900	8500
Hole mobility ($cm^2/V.s$)	450	1900	400

Problems

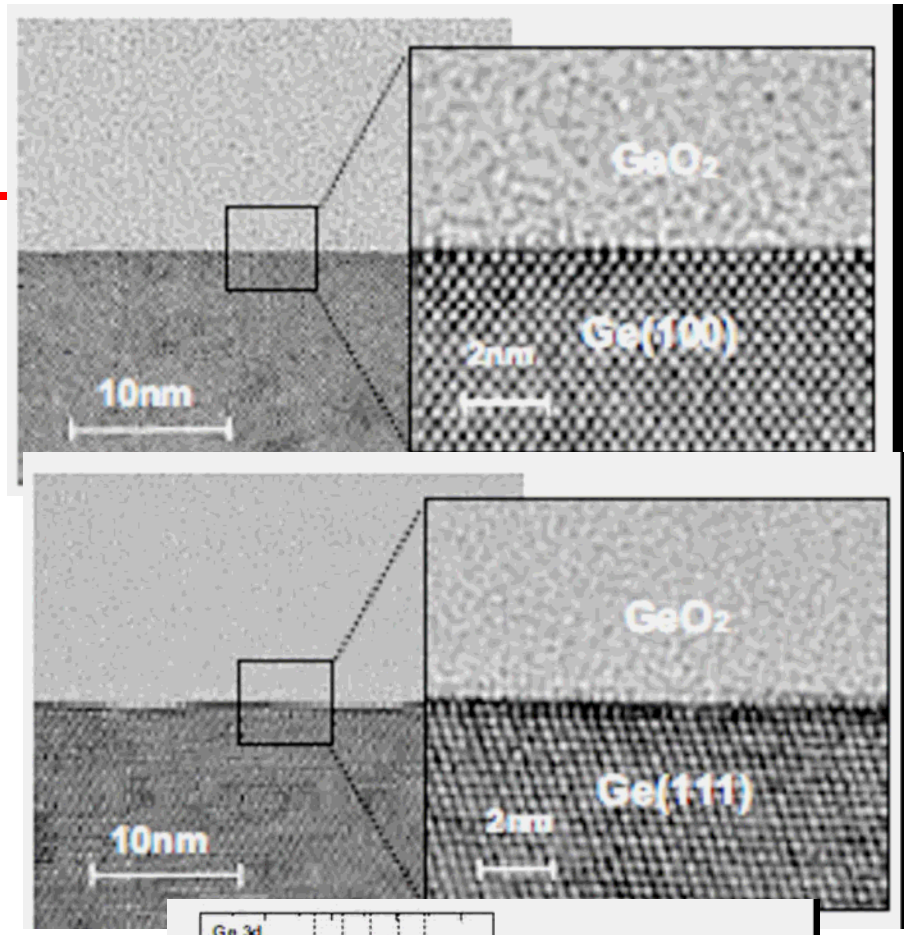
- GeO_2 - Lack of insulating properties
- GeO_2 poor passivation
- GeO volatilisation

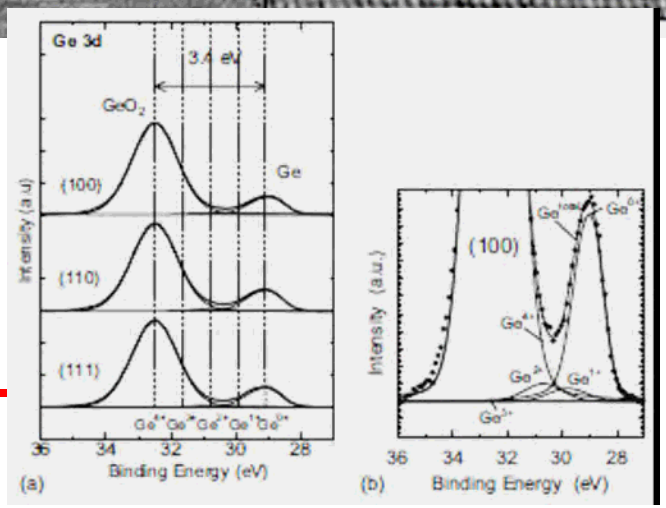
- Fermi level pinning near VB for nFET

Ge:GeO_2 interfaces

- Ge:GeO_2 interface is smooth, and abrupt
- Sasada, Takagi, JAP 106 073716 (2009);
- Zhang, Takagi VLSI (2011)

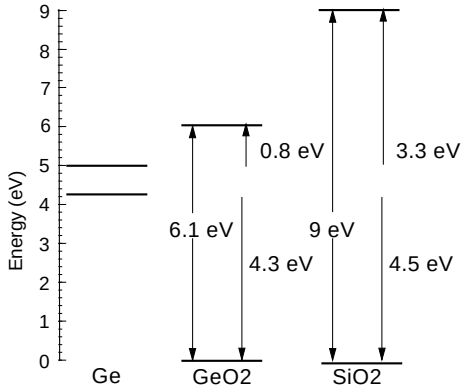
- GeO_2 on Si is electrically good. Kita, Toriumi, Jpn J App Phys 47 2349 (2008)

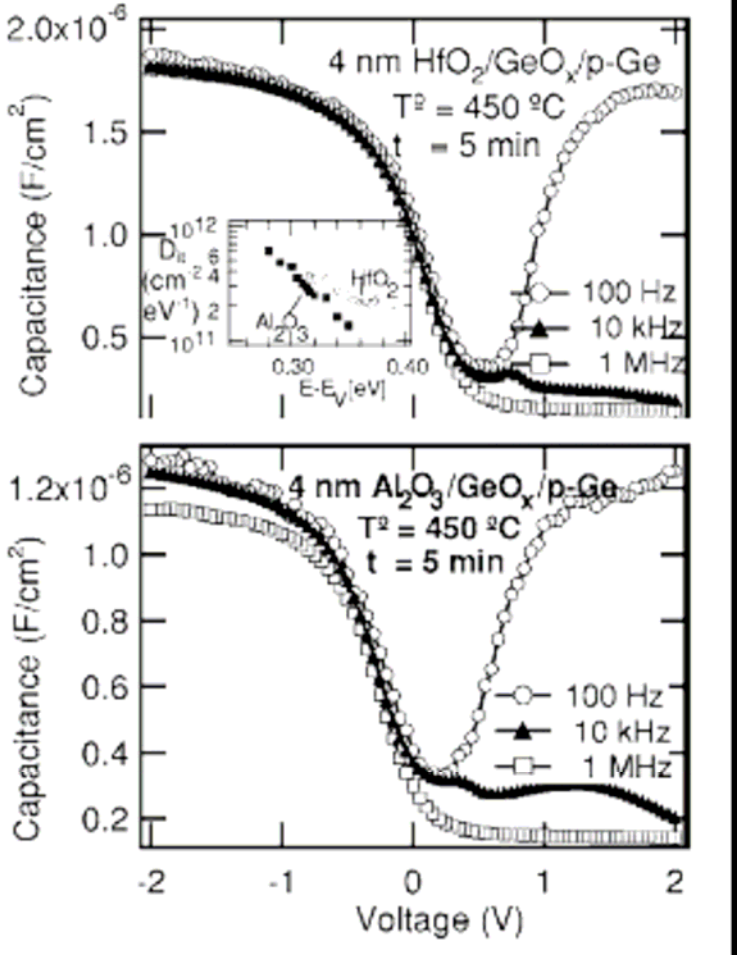




Ge:GeO_2 interfaces

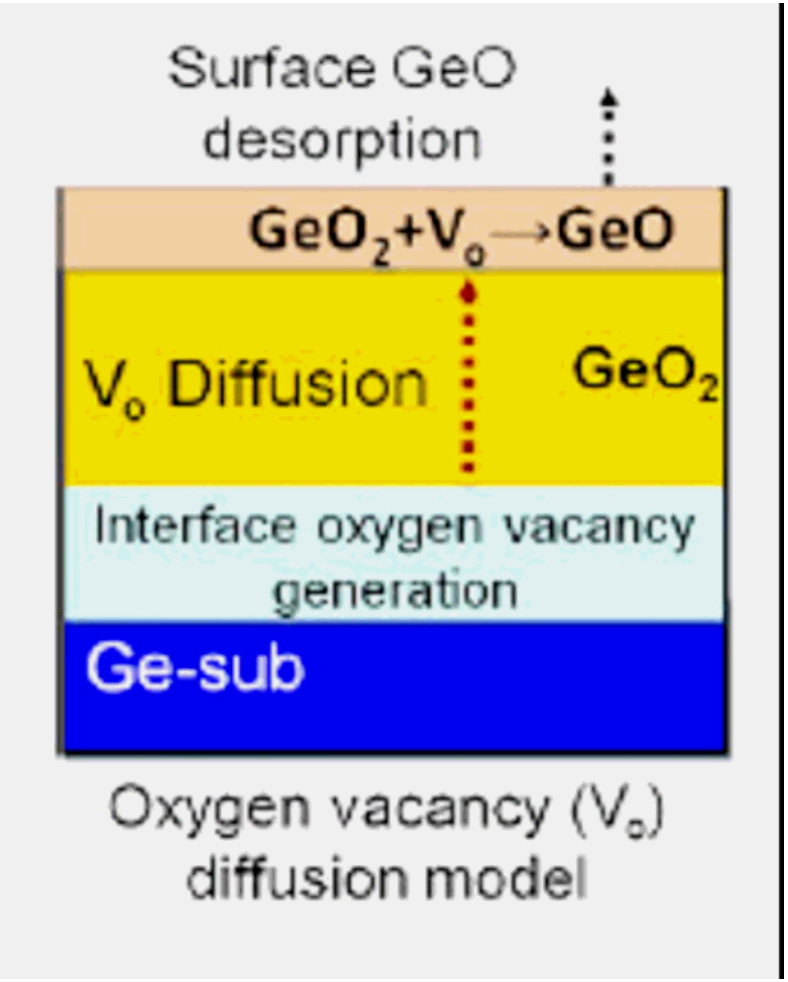
- GeO_2 as good passivant for Ge, Delabie (IMEC), APL 91 082904 (2007)
- But CBO of GeO_2 is too small, and GeO_2 has too high leakage; by itself does not scale





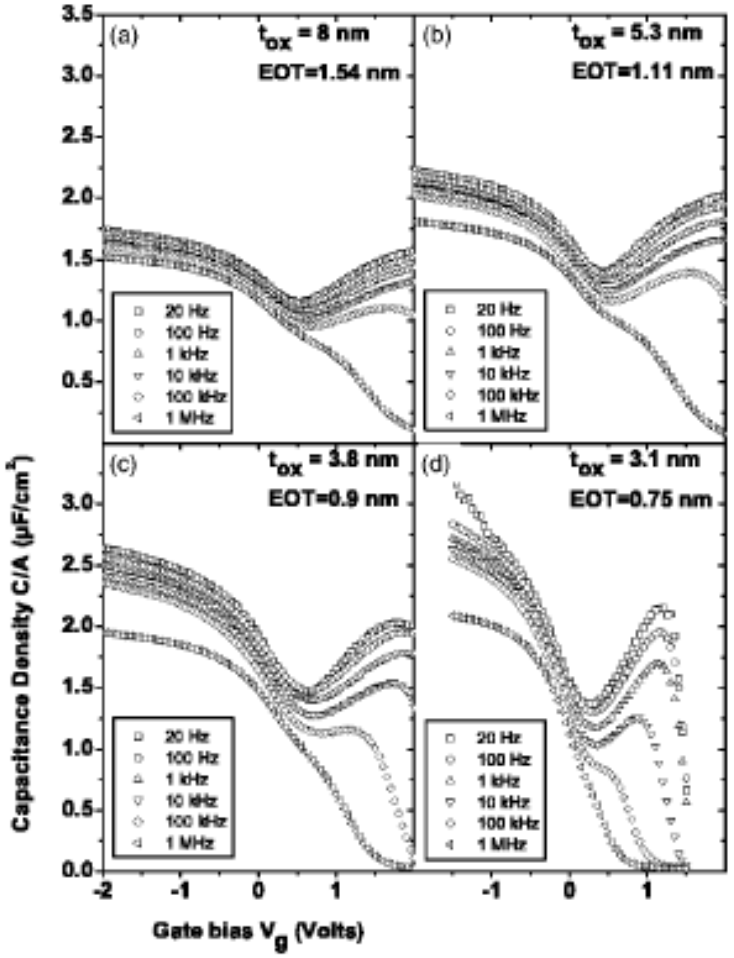
GeO volatilisation

- GeO evolution causes defects and poor electrical behavior
- Needs supply of Ge to occur –
  - not for GeO_2 on Si
- GeO desorbs from surface
- O vac diffusion through GeO_2
- Kita, Toriumi, IEDM 2009, JJAP 50 04DA01 (2011)



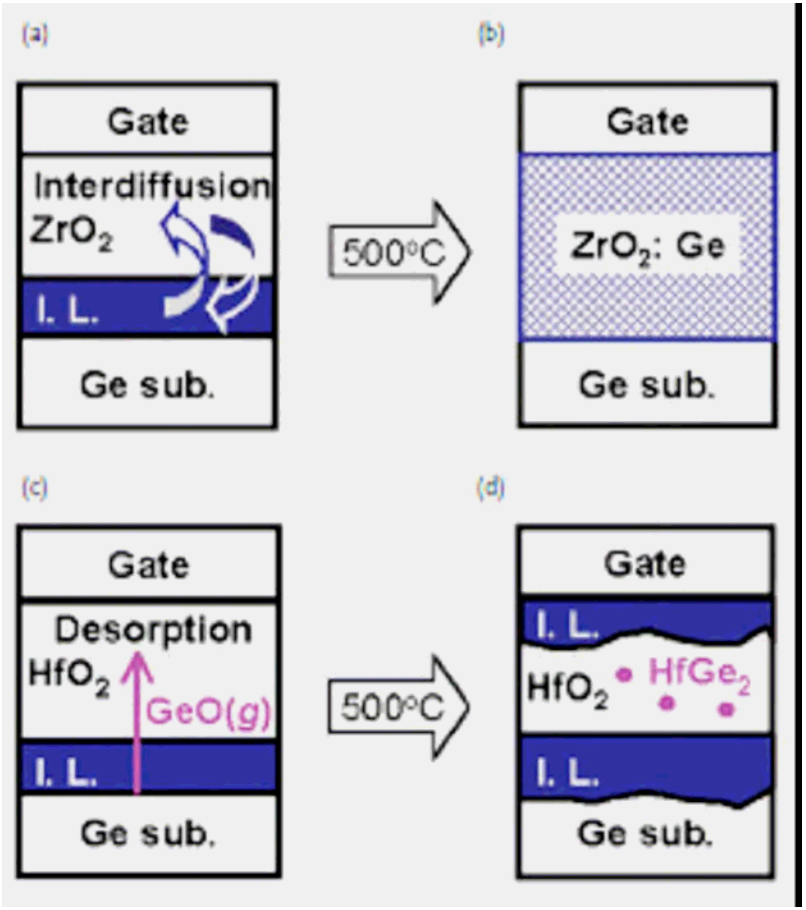
Ge:HfO_2

- CV of HfO_2 on Ge can be poor. (Dimoulas, APL (2005)
- Partly because of small Ge band gap
- Partly poor interface or reaction



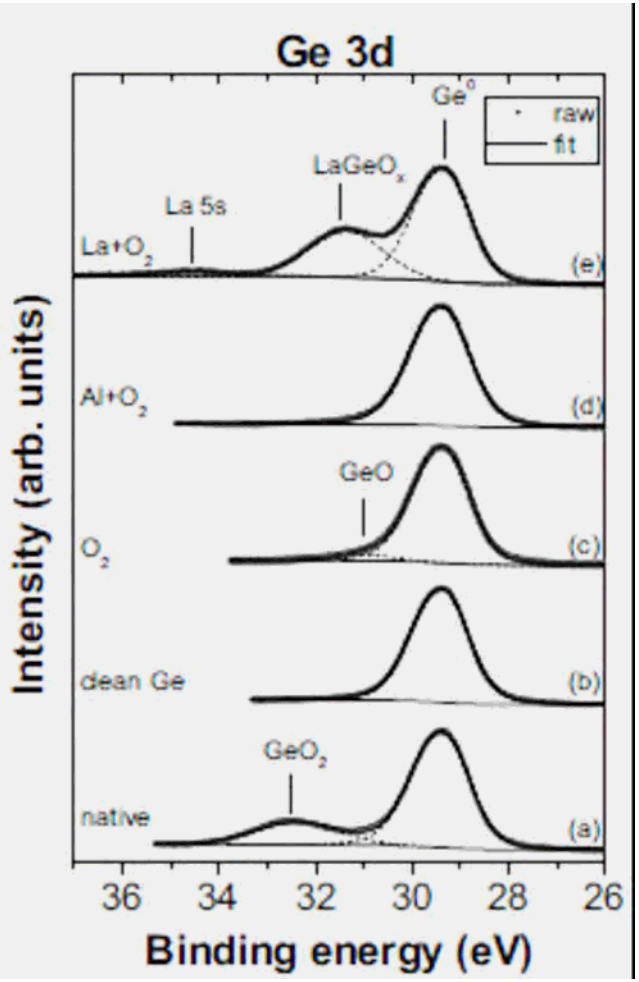
Ge:HfO_2

- Reaction of GeO with HfO_2 (Kamata, Materials Today 2008)
- avoid



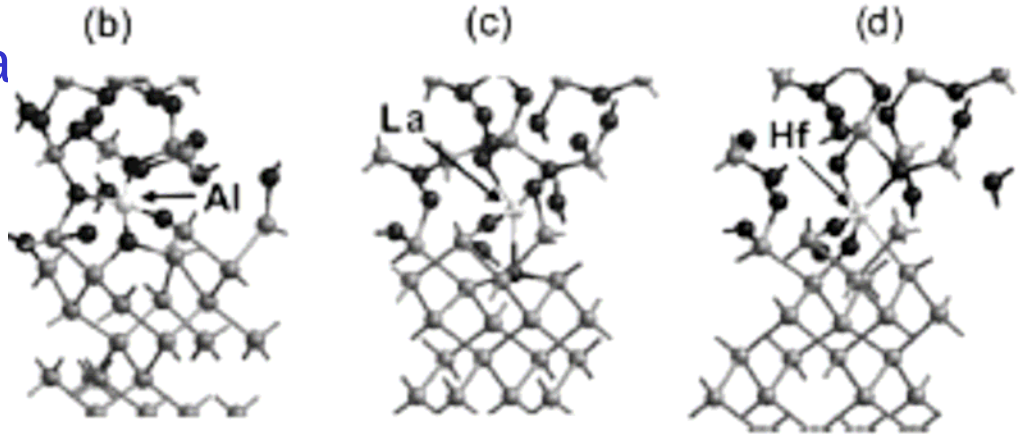
Proposals

- Remove GeO_2 (Kamata, Materials Today 2008)
- Don't use HfO_2, use LaO_x
- LaO_x has strong reaction with Ge
- Dimoulas, APL 96 012902 (2010);
- Afanasev, APL 93 102115 (2008);
- Houssa APL 92 242101 (2008)



Proposals

- LaO_x has strong reaction with Ge
- Different reasoning but simila conclusion
- Dimoulas, APL 96 012902 (2010); Afanasev, APL 93 102115 (2008);
- Houssa APL 92 242101 (2008)
  - Hf makes Hf-O and Hf-M bonds, La makes only La-O bonds



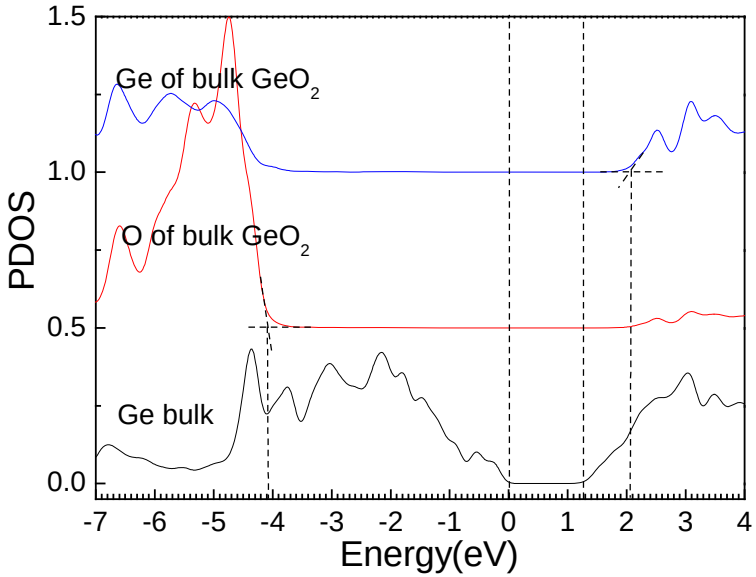
Thermodynamics etc

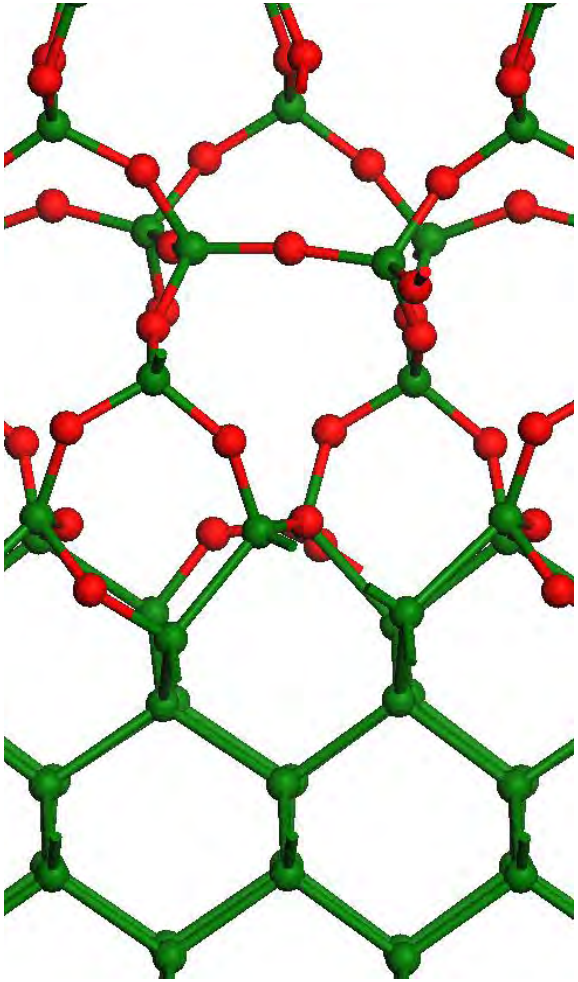
- GeO_2 is considerably less stable than SiO_2
- Ge^{2+} more stable
- Band gap much less
- Ge-H bond strength similar to Si-H

	SiO_2	GeO_2
ΔH_f (eV)	-4.80	-3.27
Band gap (eV)	9.0	6.0
Si-H bond (eV)	3.3	3.1
CNL (of semiconductor) (eV)	0.3	0

Ge:GeO_2 interface

- Calculated VB offset = 4.3 eV, CBO = 0.8 eV

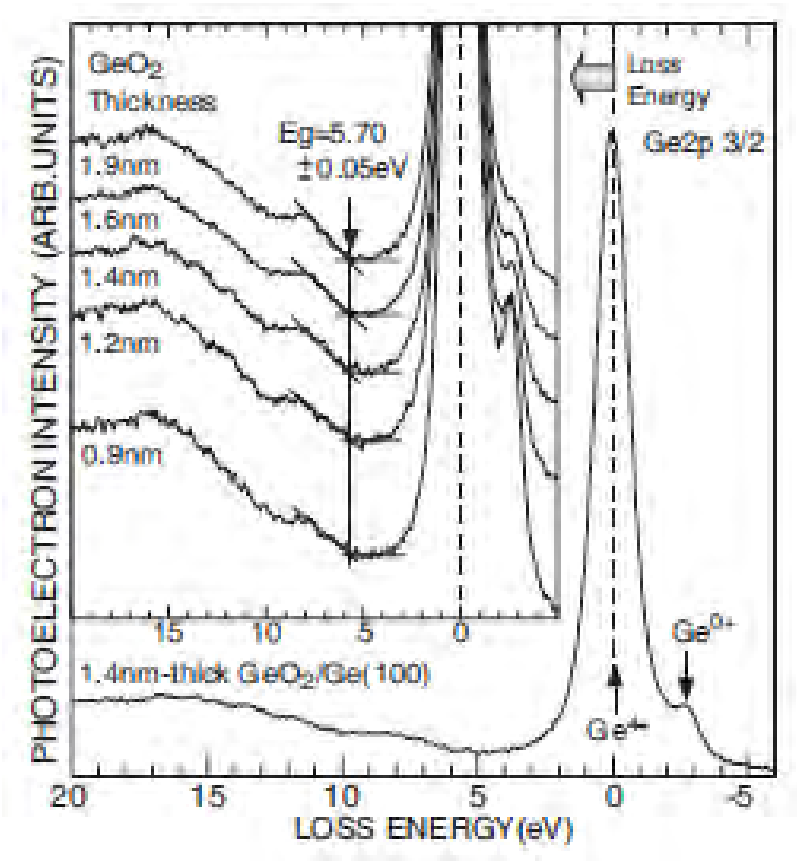




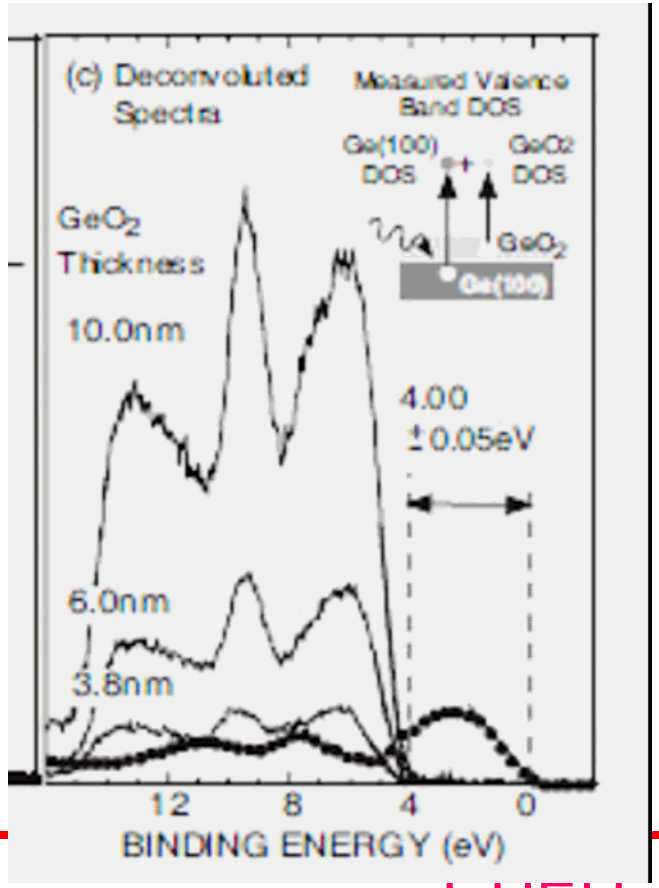
GeO_2 Band Gap, Band Offsets from Photoemission

- A Ohta, S Miyazaki et al, eJ Surf Sci Nanotech 4 174 (2006)

- Band gap

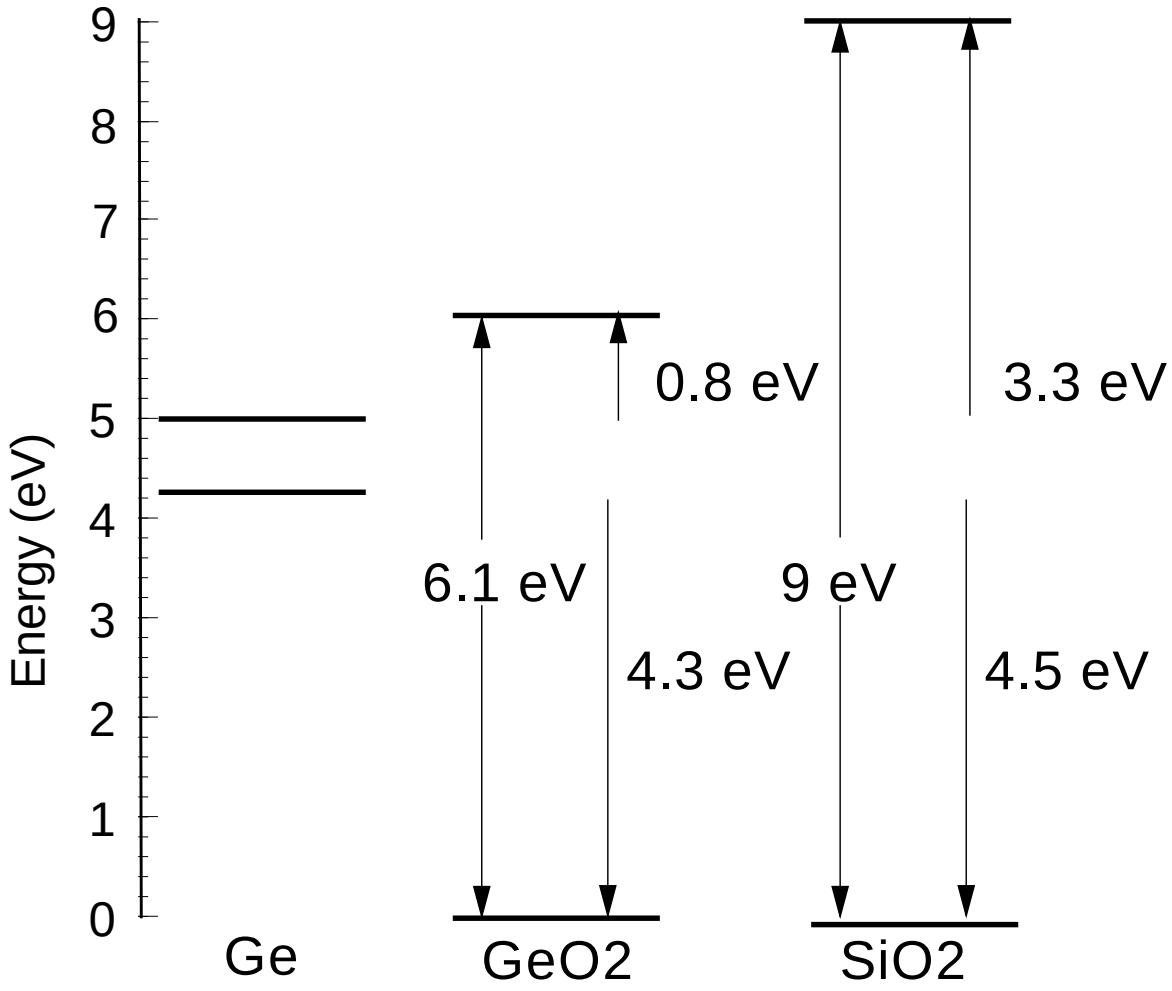


VB offset



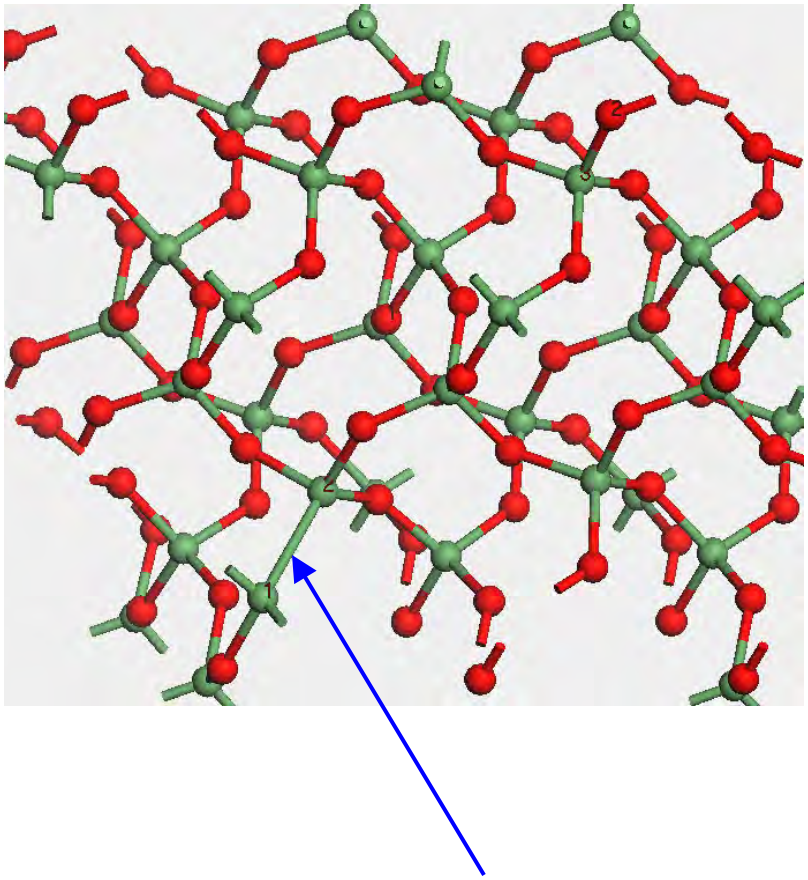
Band gap, band offsets

- Band gap is much lower for GeO_2 due to smaller CB offset
- VB offset almost unchanged (O-like character of VB top)



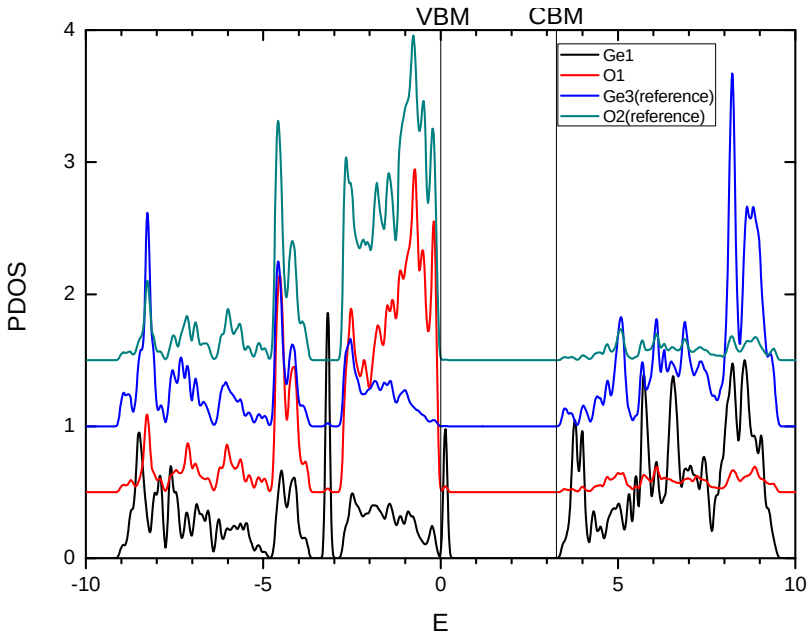
Oxygen Vacancy Defects in SiO_2

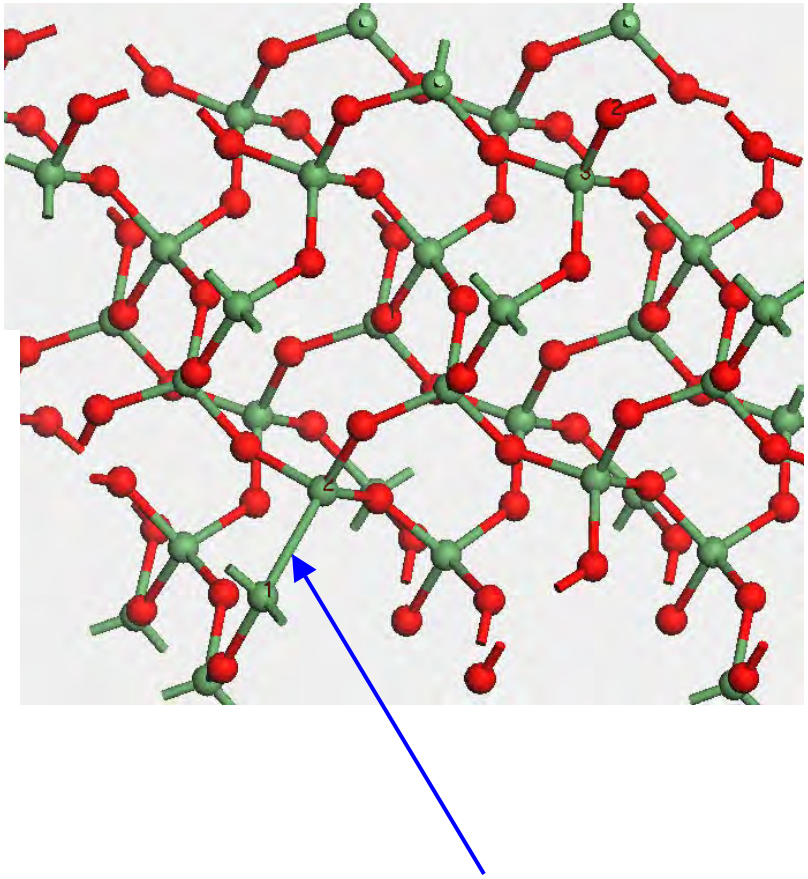
- E’ centers
- Neutral Oxygen vacancy in SiO_2 relaxes to a Si-Si bond



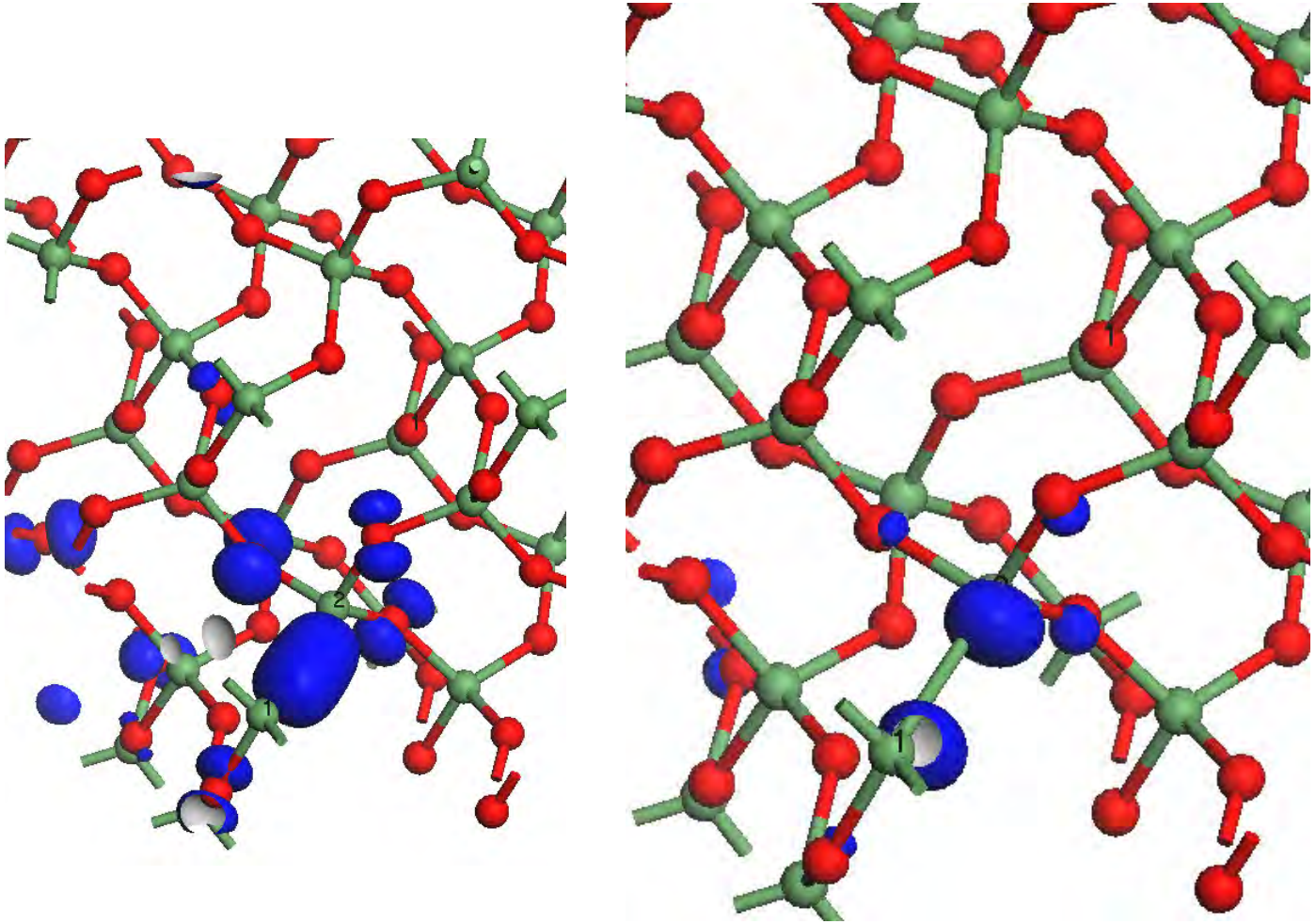
Oxygen Vacancy Defects in GeO_2

- E’ centers
- Neutral Oxygen vacancy in GeO_2 relaxes to a Ge-Ge bond
- No states in gap (GGA)



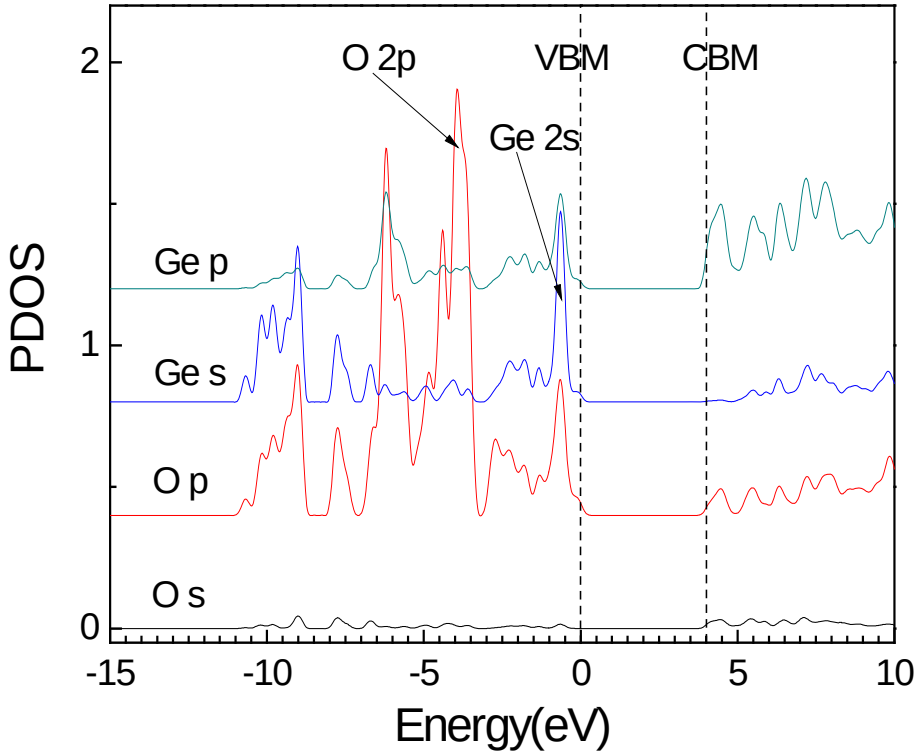


Defect Wavefunctions



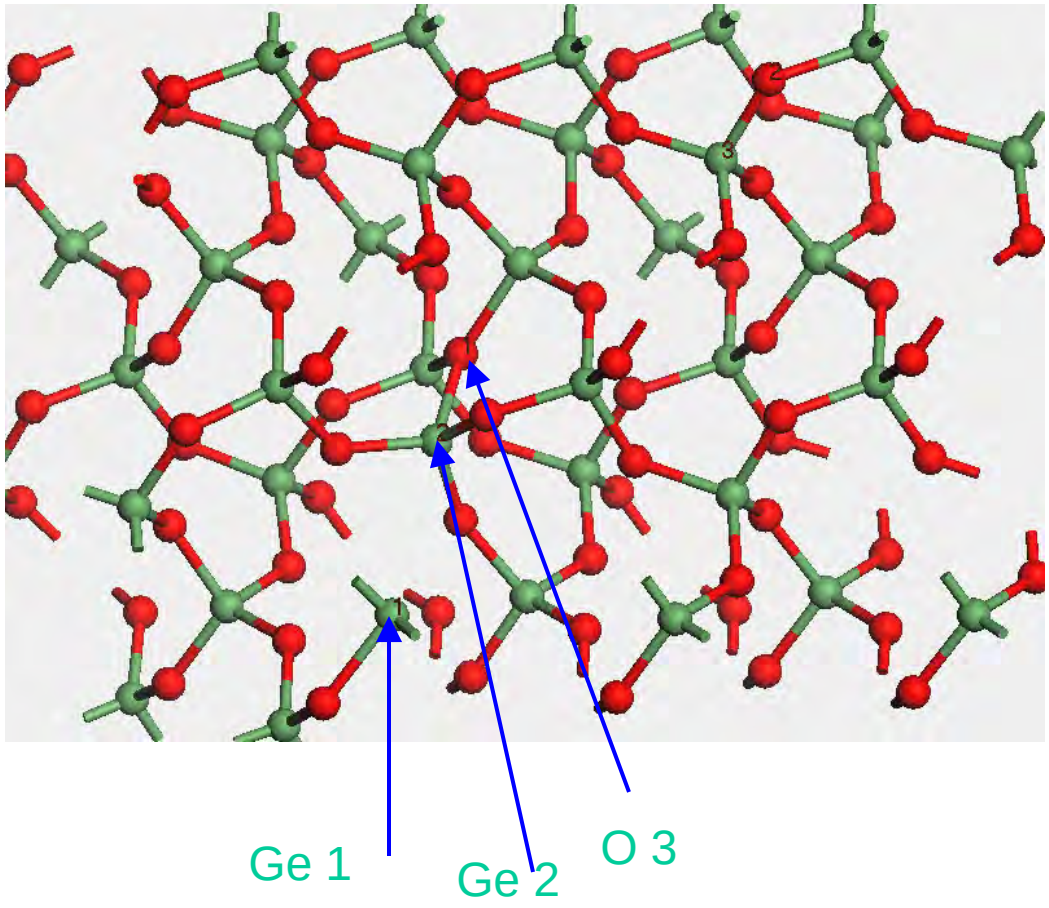
GeO states

- GeO has filled Ge s states,
- VB of Ge s, O 2p.
- CB of Ge p states



Novel defects in GeO_2

- Ge-Ge bond breaks
- One 3-fold Ge atom flips through Ge-O, to bond to back Oxygen
- Makes 3-fold Ge +3-fold O



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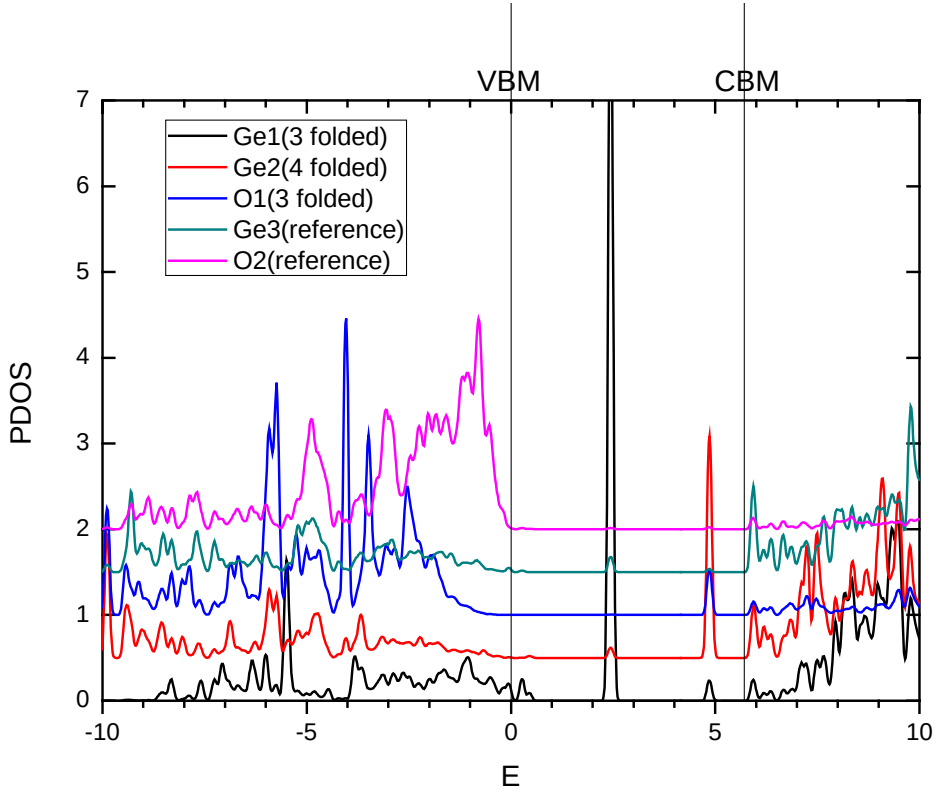
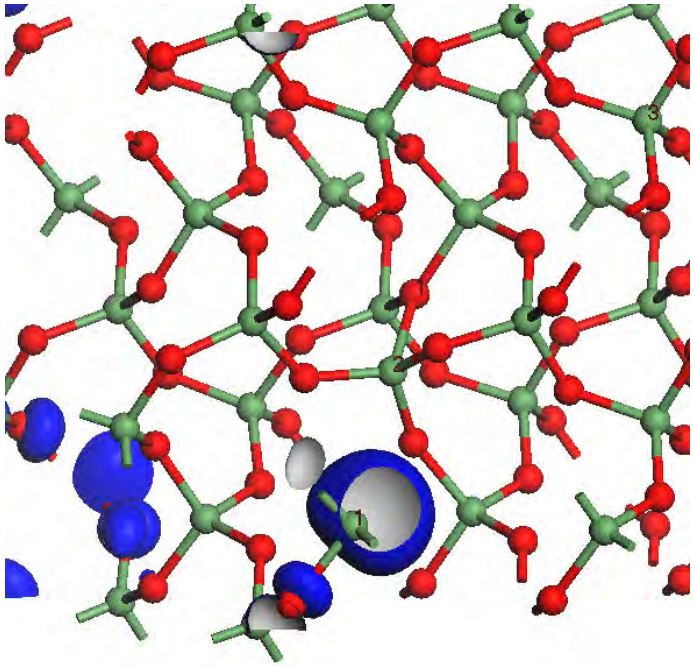
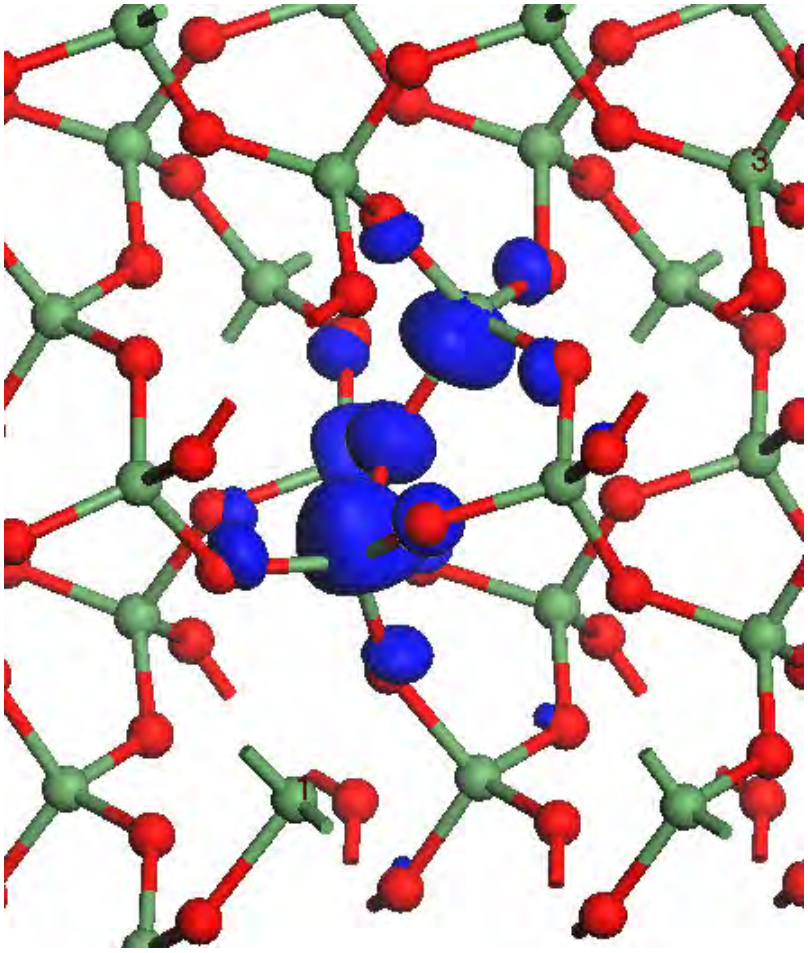
Novel defects in GeO_2

- 3-fold G gives gap state (sX)
- 3-fold O gives state at CB edge, localised on adjacent Ge sites
- Will create defects at Ge:GeOx interface, as GeO volatilisation



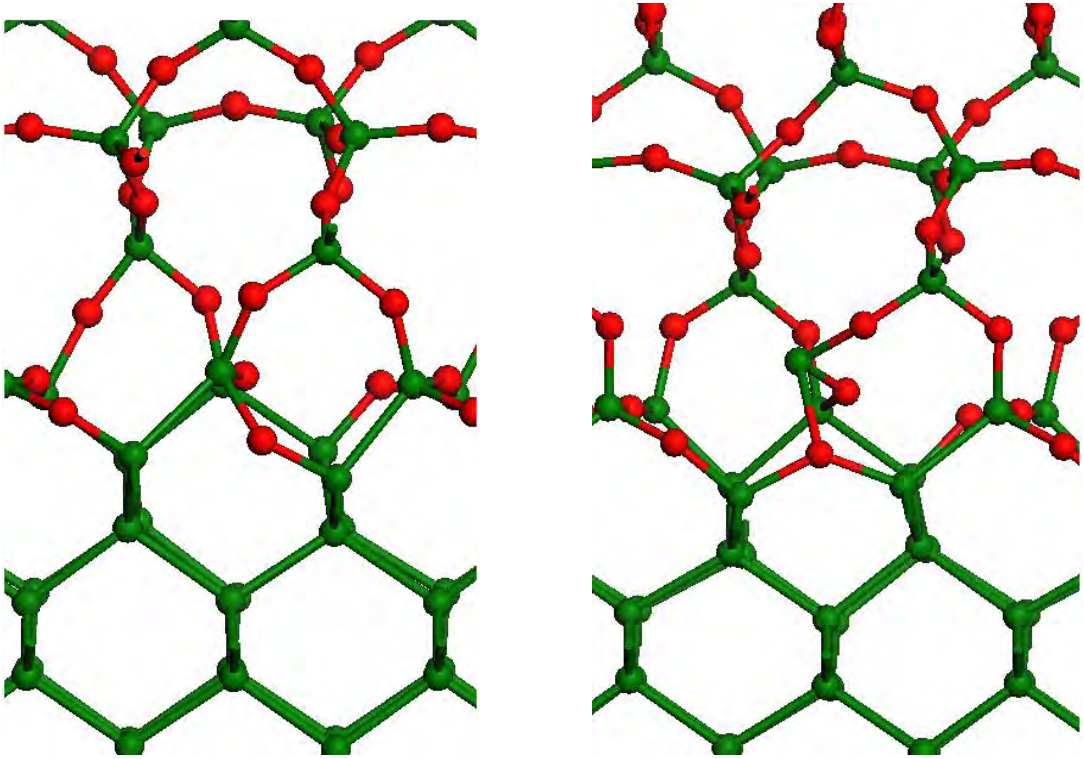
wavefunctions





Poor interface

- Si:SiO_2 interface is abrupt and smooth for T<1100C.
- SiO_x dissociates into Si and SiO_2 (Lucovsky, JNCS 227 1 (1998)
- GeO_x would not do same



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Possible solutions

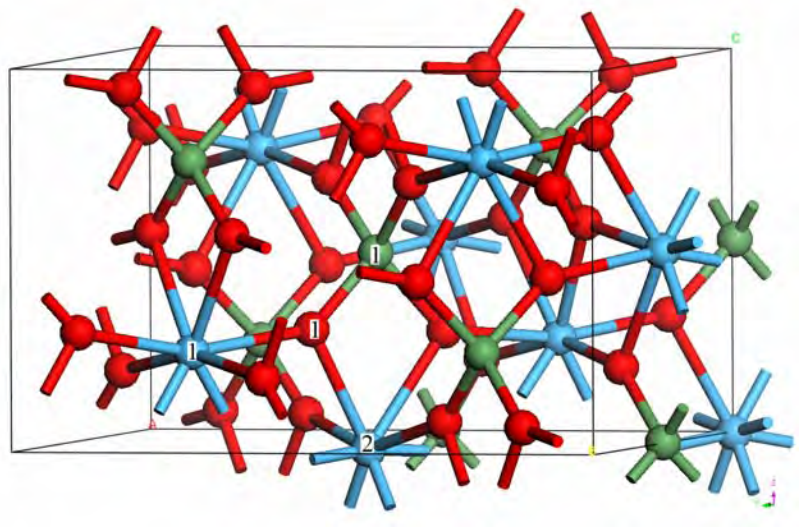
- Remove GeO_2 layers (but only good interface?)
- $LaGeO_x$ (Dimoulas etc)
- GeSr, etc (Kamata)
- GeN_x
- Check nature of these interfaces and bulk structures

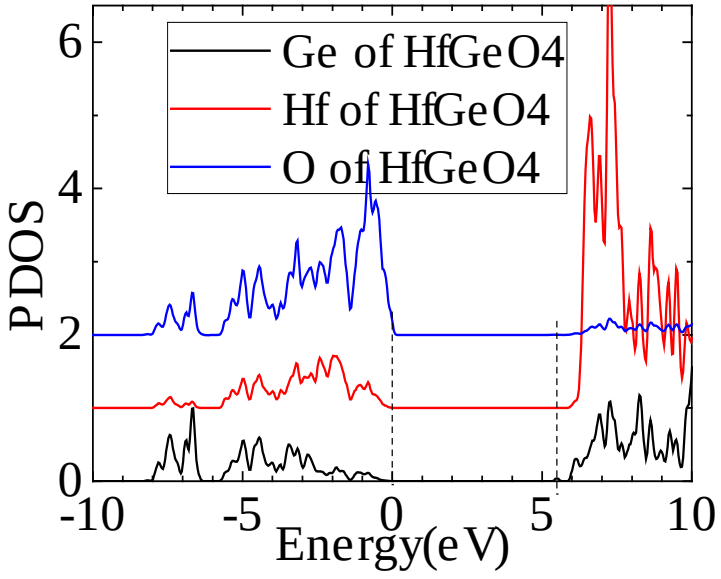
$HfGeO_4$ interfaces

- $HfGeO_4$ has $ZrSiO_4$ structure,
- 3-fold O,
- 4-fold Ge,
- 8-fold Hf

- Gap = 5.2 eV

- CB min = Ge s,p





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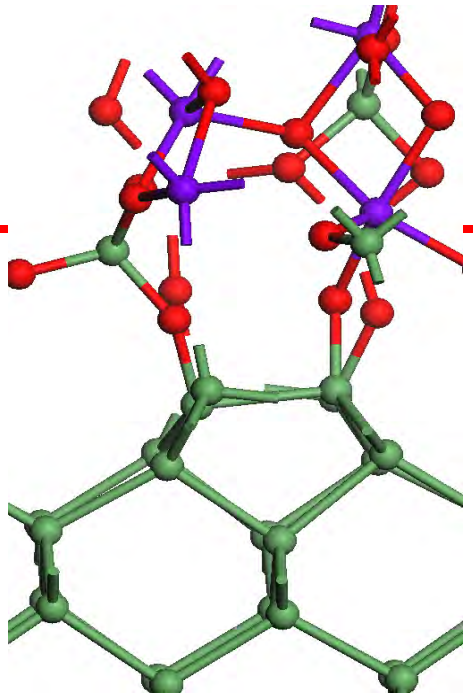
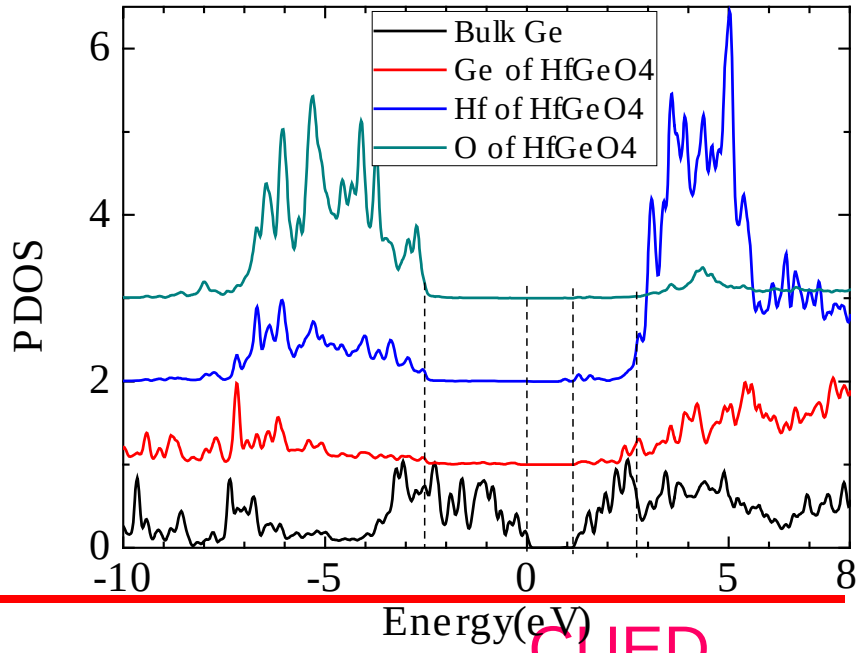
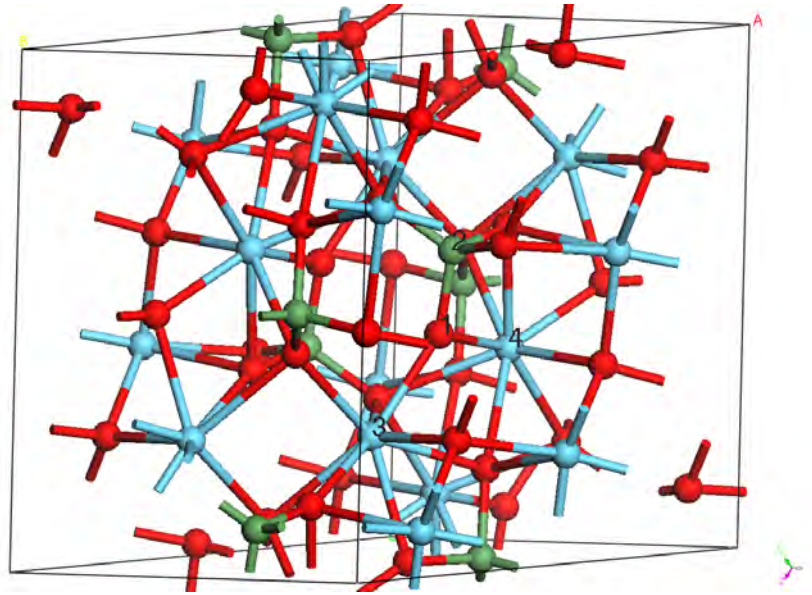
$HfGeO_4$ interfaces



- Ge(100): $HfGeO_4$ interface is well bonded
- gap = 5.2 eV
- VBO = 2.8 eV,
- CBO = 1.5 eV (SX not LDA)

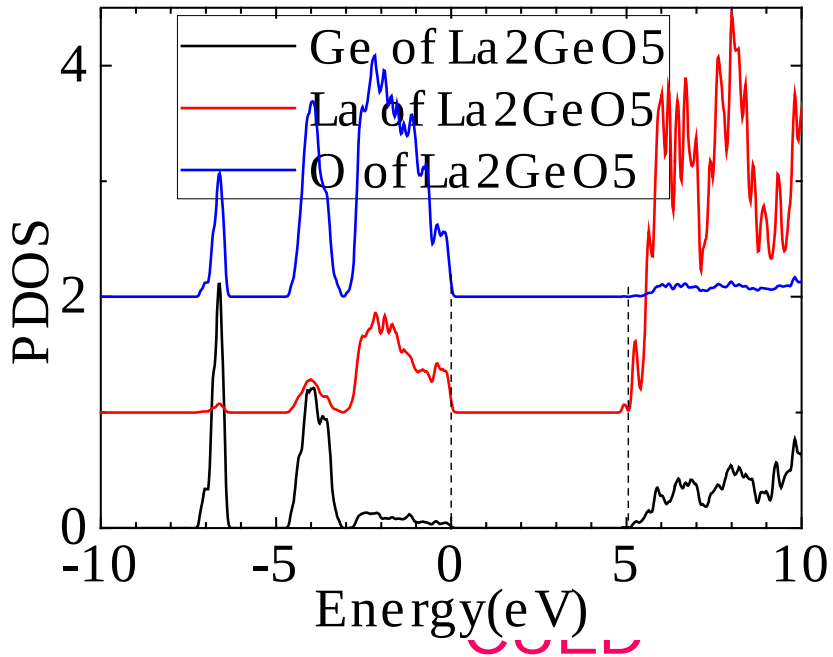


Structure of La_2GeO_5



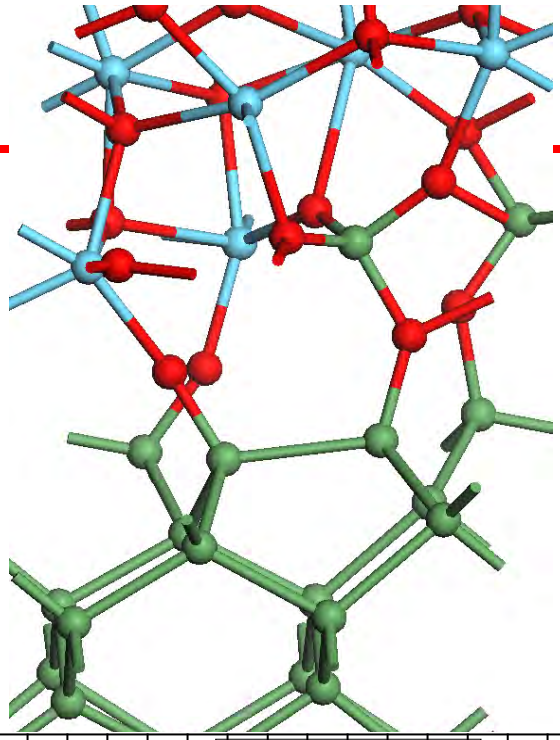
- La2GeO5 has low symmetry
- Ge =4-fold
- O = 3,4,5-fold

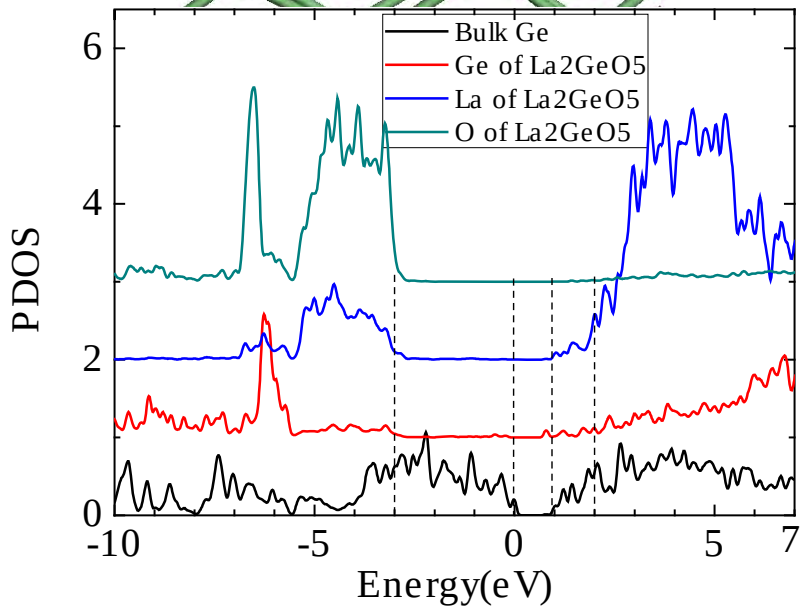
- Band gap = 5.0 eV,
- CB min = La d states



La_2GeO_5 interfaces

- (100)Ge: La2GeO5 interface
- VBO = 3.0 eV

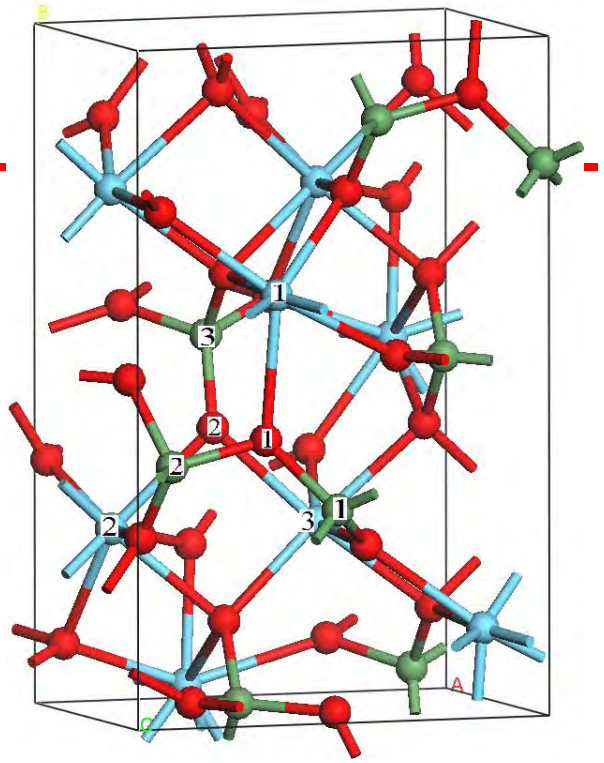


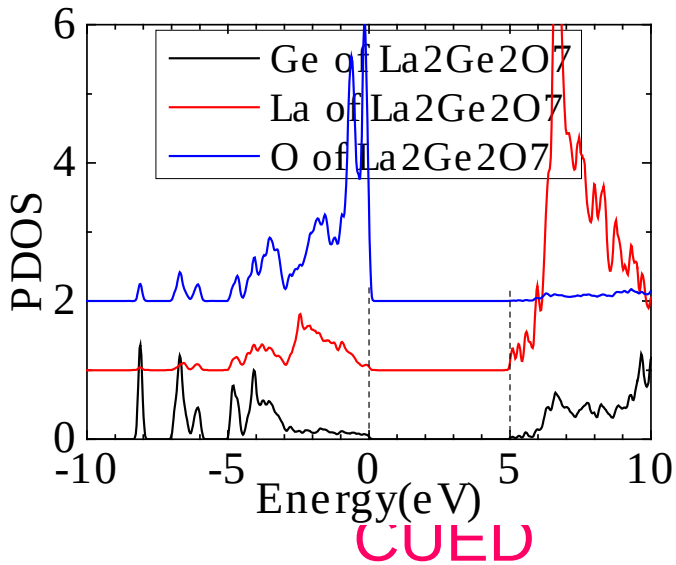


$La_2Ge_2O_7$

- Triclinic (P1) crystal structure
- O = 3, 4-fold
- Ge= 4-fold

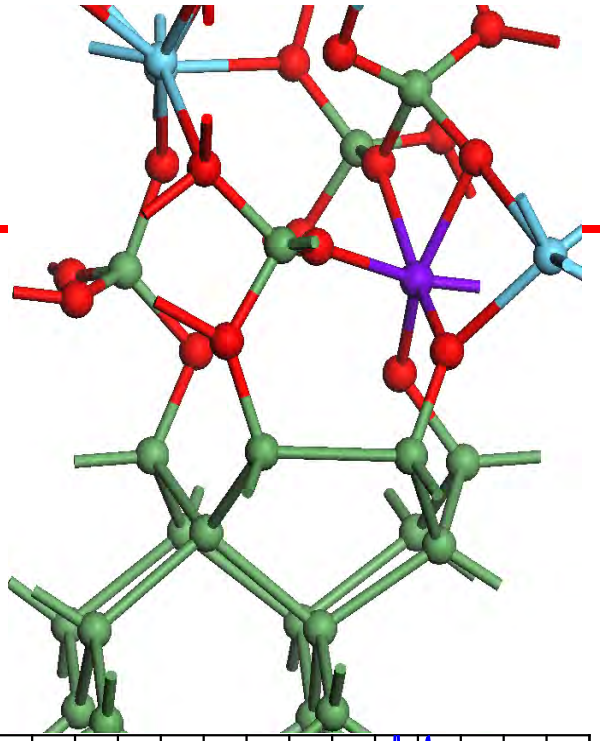
- Calculate band structure in SX, which gives correct band gap
- Band gap = 5.1 eV
- VB max = O 2p
- CB min = La d

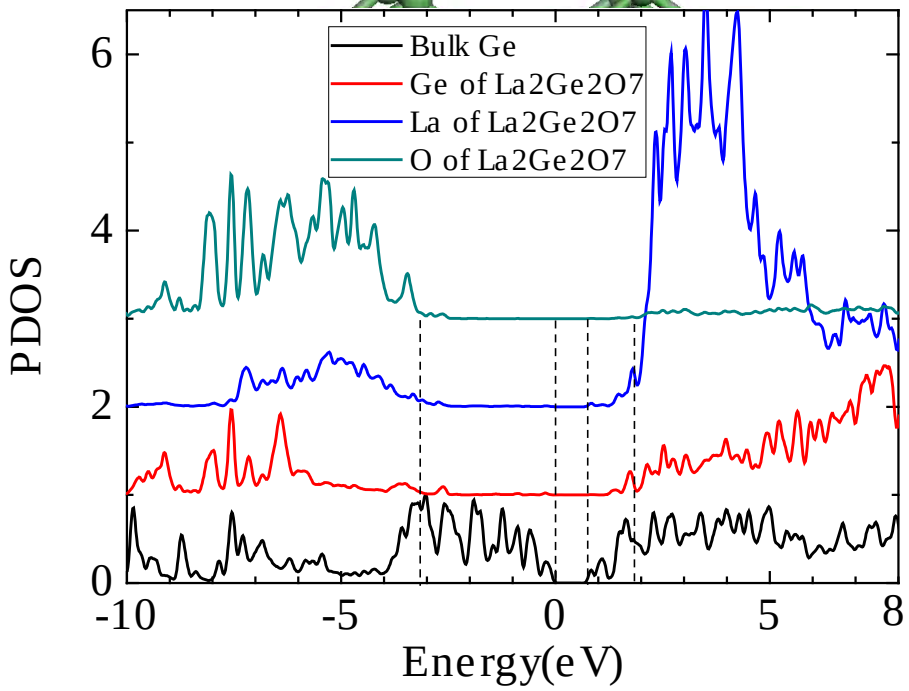




$La_2Ge_2O_7$ interfaces

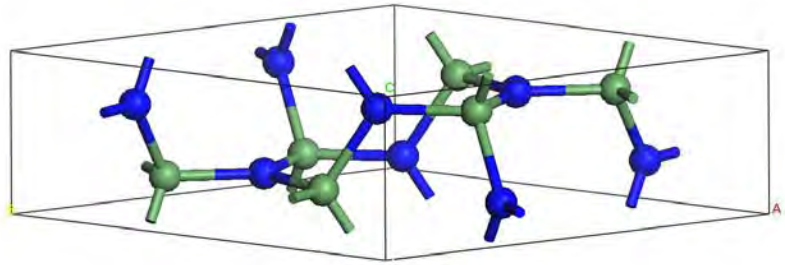
- Create (100)Ge:oxide interface
- Use La atoms to balance valences – no gap states
- Calculate band offsets for interface model
- VBO = 3.0 eV



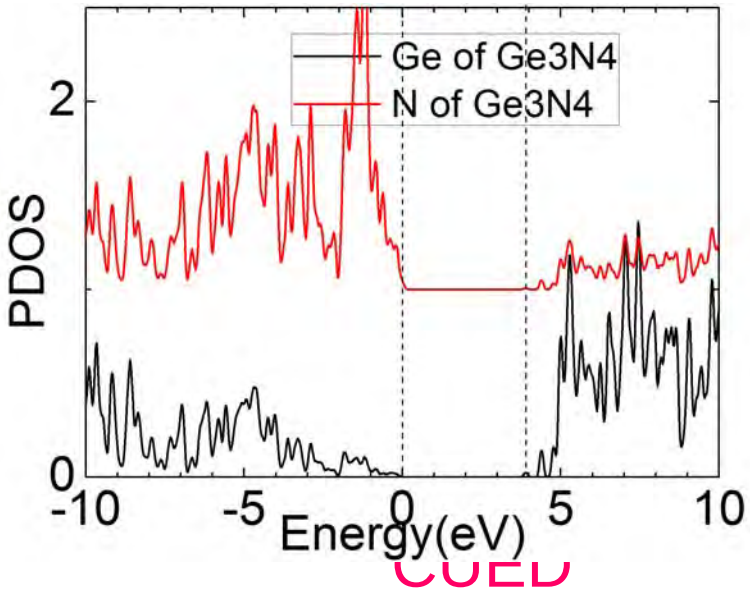


Ge_3N_4

- Try Nitridation – McIntyre, APL 85 2902 (2004)



- Ge3N4 band gap = 4.0 eV
- VBO = 1.1 eV



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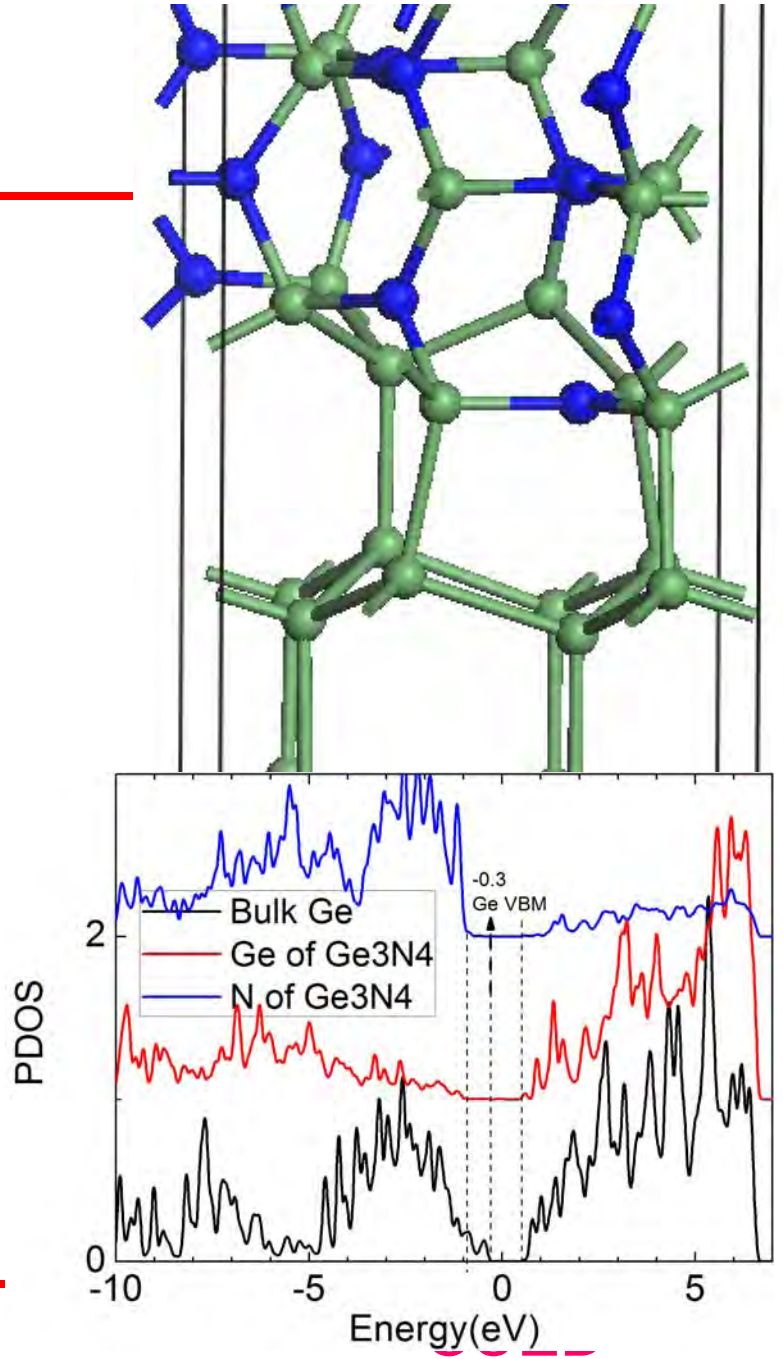
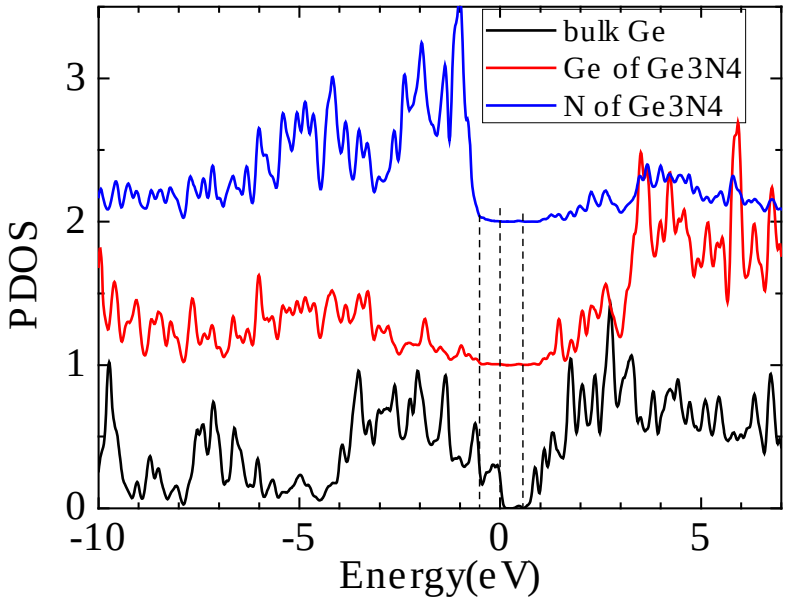
Ge(111):Ge_3N_4

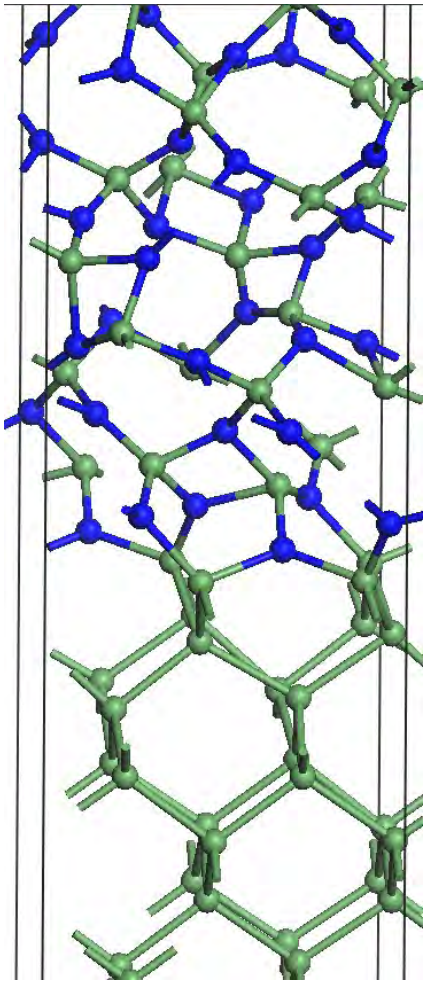
- Try Nitridation – McIntyre, APL 85 2902 (2004)
- Ge(111) is lattice matched to hexagonal Ge3N4 (S J Wang, APL 93 222907 (2009)
- Ge3N4 band gap = 4.0 eV
- VBO = 1.1 eV



Ge(100): Ge_3N_4

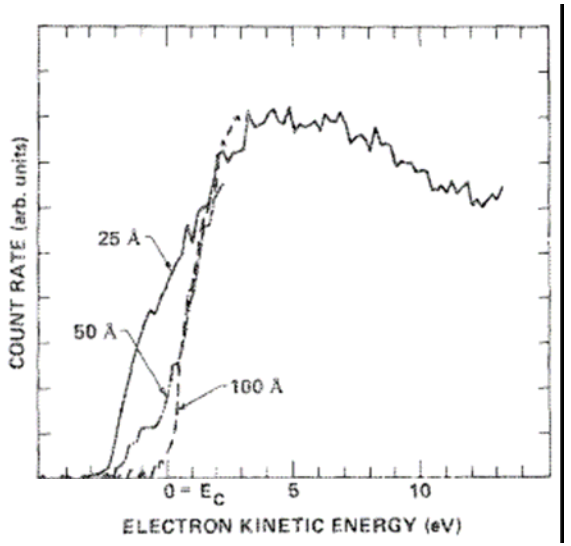
- Ge(100) can interface with Ge3N4
- Ge3N4 band gap = 4.0 eV
- VBO = 1.1 eV

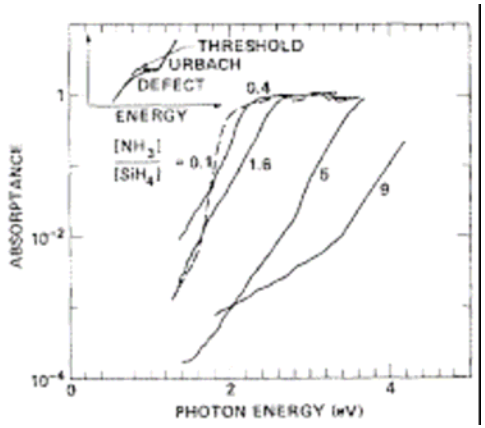




Nitrides

- Ge:Ge3N4 interface has too small VBO (Yang, APL 93 222907 (2009)
- Si:Si3N4 interface VBO = 1.8 eV (Iqbal, JAP 61 2947 1987)
- Si:HfO_xN VBO = 2.5 eV
- GeNx, SiNx have valence band tail, causes hole trapping





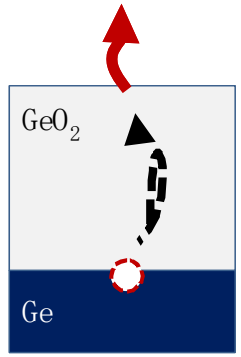
Summary of MO_x

- Ge:$GeHfO_4$ interface is ok
- Ge:$GeLaO_x$ interface is ok
- Ge:Ge_3N_4 interface has too small VBO and has VB tail of hole traps

Is Ge:GeO_2 or HfO_2 poor?

- Large D_{it}
- GeO_2 on Si is good oxide
- GeO_2 only bad on Ge

- Ge:HfO_2 is poor but why ?

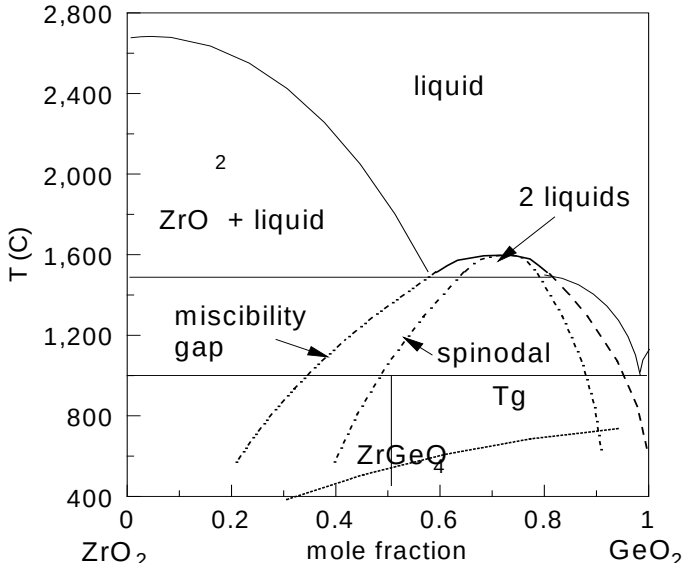


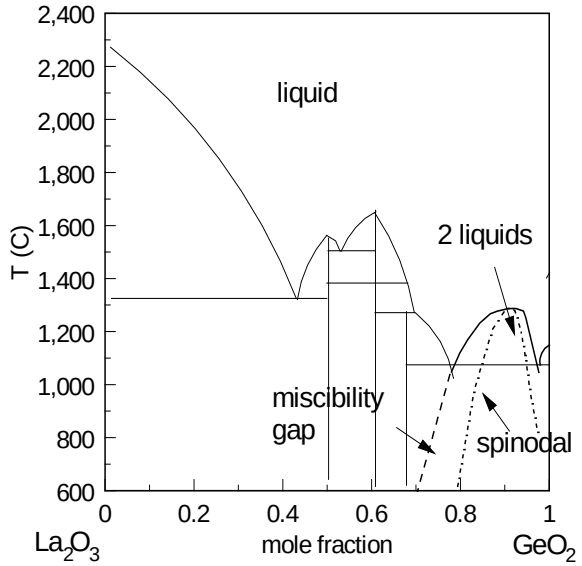
Vo diffusion
(3)

$MGeO_x$ phase diagrams

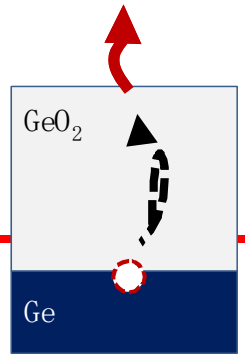
- Phase diagrams scaled from those of $MSiO_x$
- Ordering calculated from $MO_x + GeO_2$ stability by LDA

- Hf-GeO_x shows spinodal decomposition
- $LaGeO_x$ does not



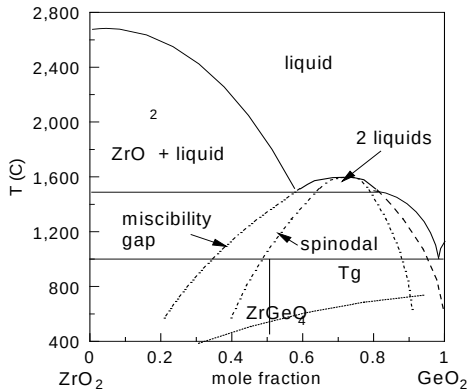


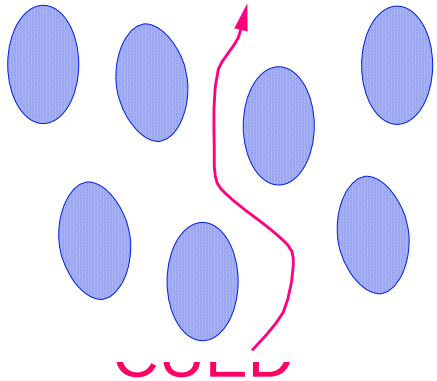
$Ge:GeO_2:HfO_2$



Vo diffusion
(3)

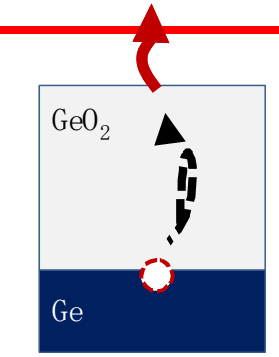
- $GeHfO_x$ will phase separate (spinodal decomposition)
- V_O will diffuse through HfO_2 minority phase, allowing GeO volatisation / GeO defect formation
- avoid $GeHfO_x$

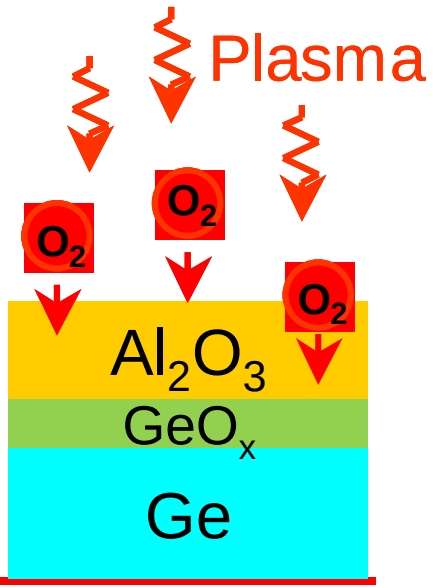




$Ge:GeO_2:Al_2O_3$

- Need diffusion barrier
- GeHfOx will phase separate
- LaGeOx will not phase separate.
- But LaOx has n-type Vfb shifts, not suitable for pFET
- GeNx is diffusion barrier; but too small VBO and hole traps
- Al2O3 is diffusion barrier but low K
- D_{it} $<10^{11}$ with Ge:GeO2:AlOx - best
  - Zhang..Takagi, APL 98 112902 (2011)
- Al2O3:HfO2 bilayer, cf Al2O3:TiO2 bilayer of McIntyre, APL 96 082904 (2010)





Conclusions

- $Ge:GeO_2$ interface can be good, like $Si:SiO_2$, but avoid GeO volatilisation

- GeO_2 has low CBO, needs another oxide on top
- $Ge:HfO_2$ is not good combination by itself

- La, Sr appear useful, but n-FET

- $GeHfO_x$ is bad due to spinodal decomposition, leaves diffusion path

- Use Al_2O_3 barrier, $Ge:GeO_2$ interface; then HfO_2 on top if necessary