Electronic Structure of Ge:GeO_2 interfaces for future CMOS

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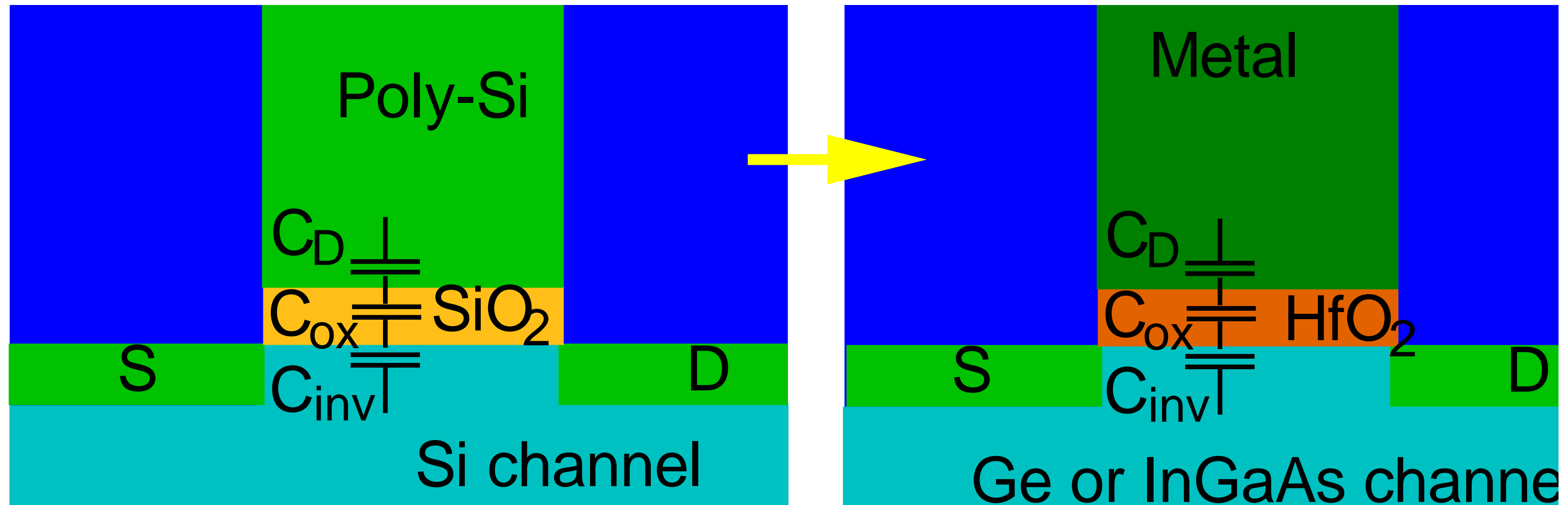
- Need for Ge
- Problems of Ge
- Defects in GeO_2
- Hydrogen in GeO_2

Future CMOS



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

- Change geometry

Need for Ge

- Ge has higher carrier mobilities than Si, particularly holes
- Ge pFET, GaAs nFET
- But Ge nFET, pFET also 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

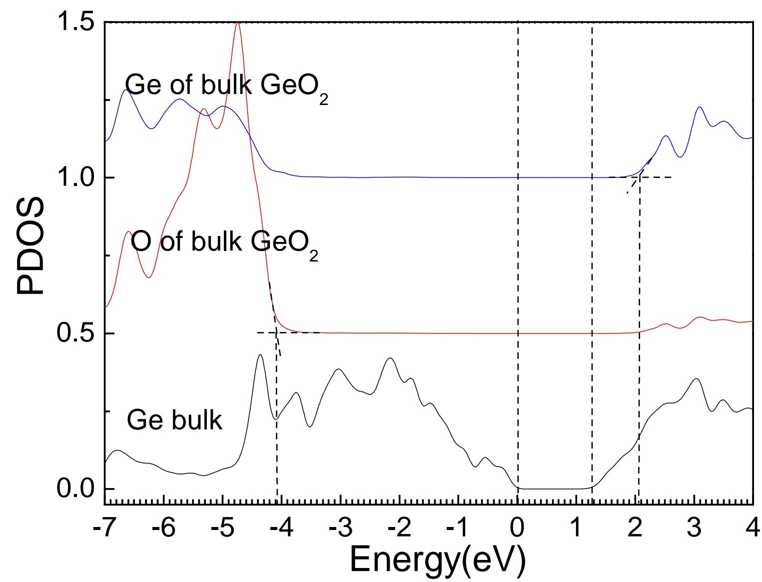
Thermodynamics etc

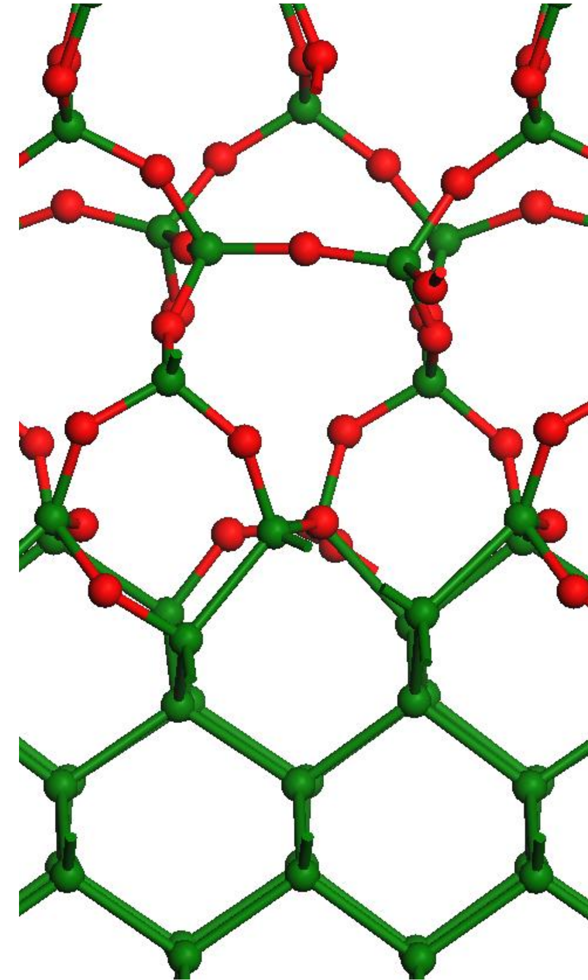
- GeO_2 is considerably less stable than SiO_2
- Ge^{2+} more stable
- Band gap much less
- Ge-H bond strength not much less

	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 4.3 eV VB offset



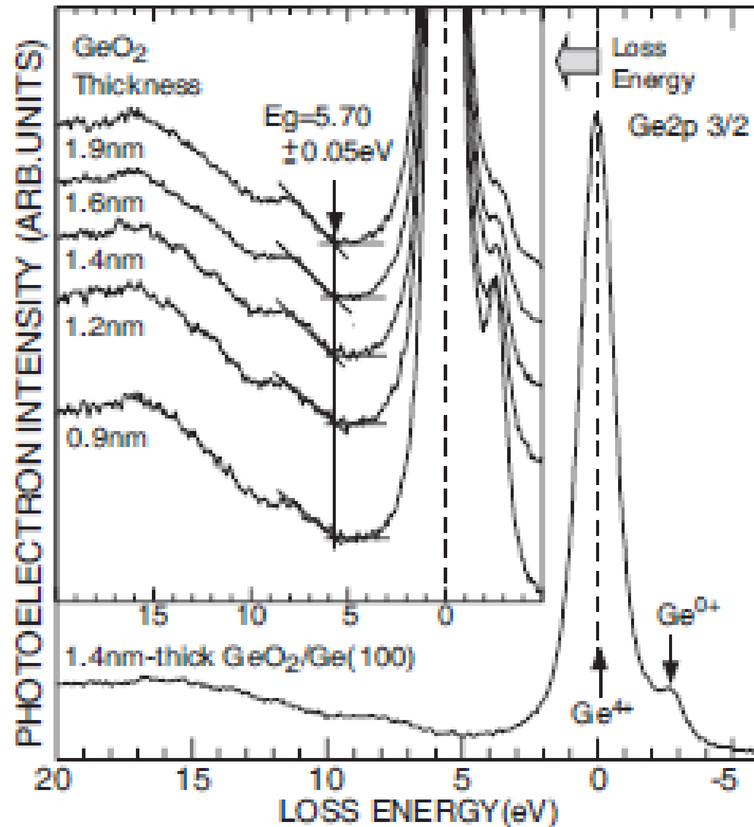


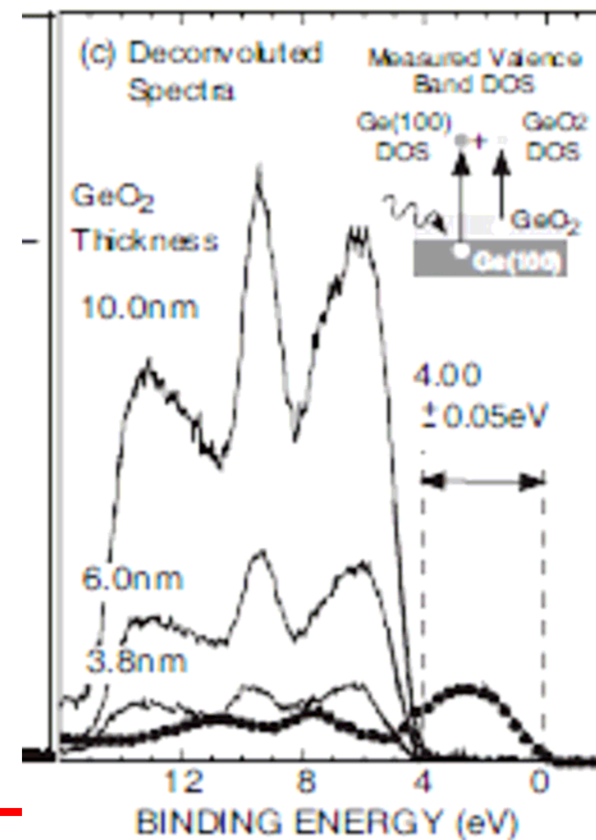
GeO_2 Band Gap, Band Offsets from Photoemission

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

- Band gap

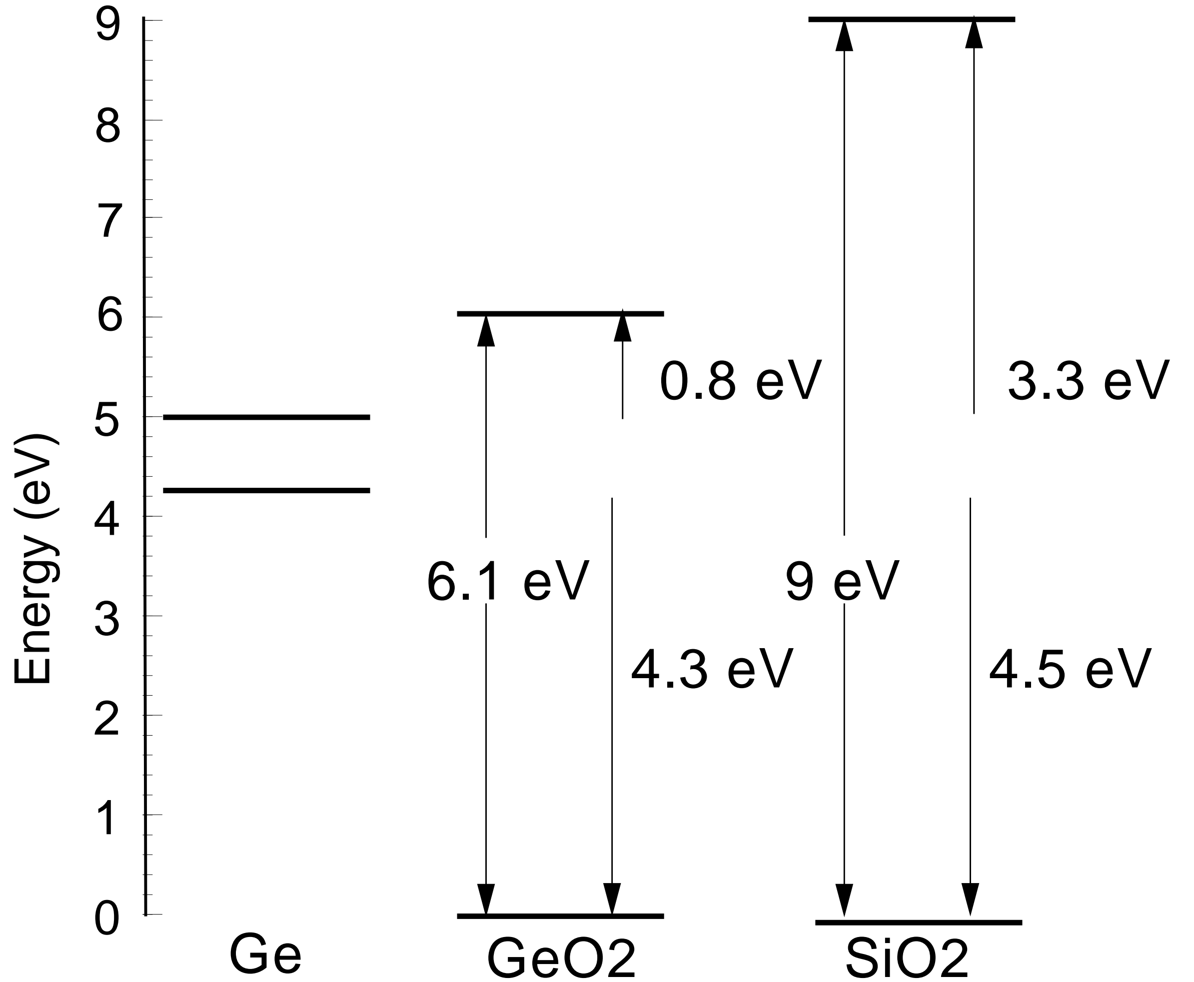
VB offset





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)
- Calculation using Screened Exchange



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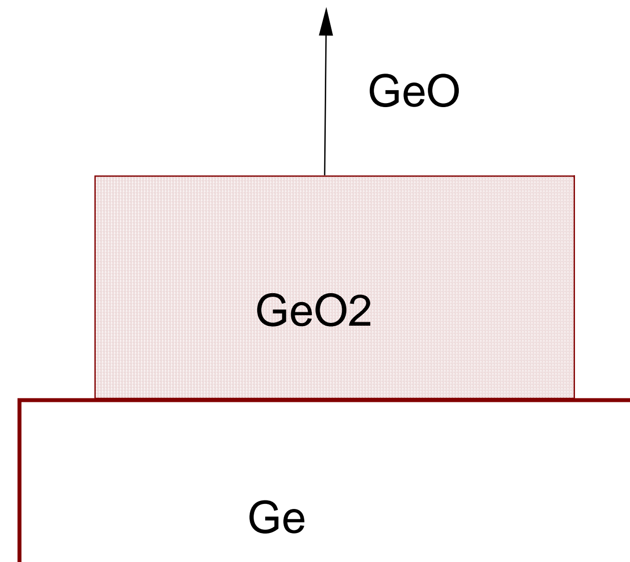
GeO_2 as gate oxide

- Small CBO explains use of relatively thick GeO2 layer in Ge FETs with GeO2 gate oxide (Toriumi, IEDM 2009)

GeO volatilisation

- GeO evolution causes defects and worse electrical behavior
- Needs supply of Ge to occur –
  - not for GeO_2 on Si
- GeO desorbs from surface
- O vac diffusion through GeO_2
- Toriumi (JJAP 2008), Kita (IEDM 2009, JAP 2010)

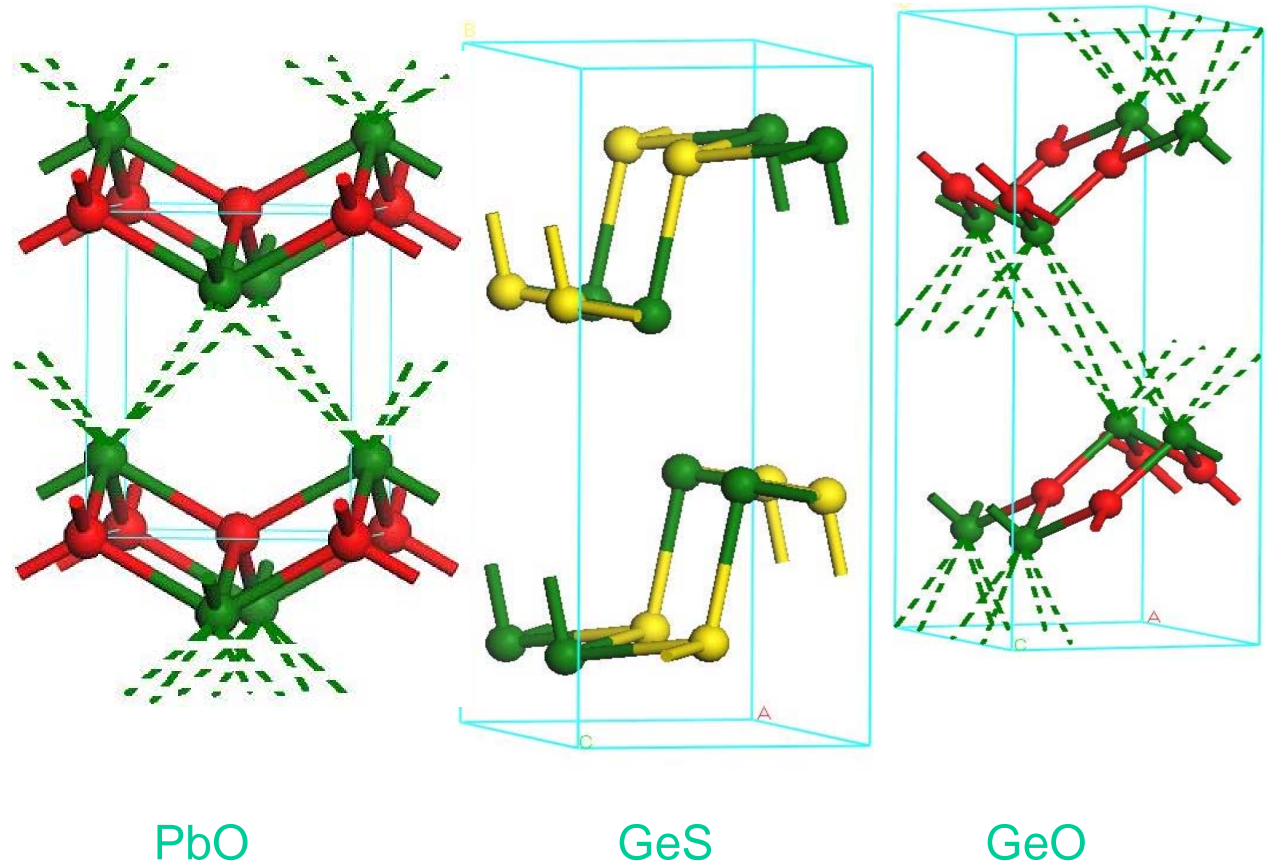


Si oxidation

- During initial stages of Si oxidation (< 5nm) reactive layer model
- Deal-Grove model based on O2 diffusion (interstitial)
- O^{17} isotope tracer analysis suggests not O_2 diffusion (Rochet, Adv Phys 35 237 1986)
- But Baumvol, PRB 60 1492 (1999) shows no mobility of Si^{29}.
- Hence O diffusion

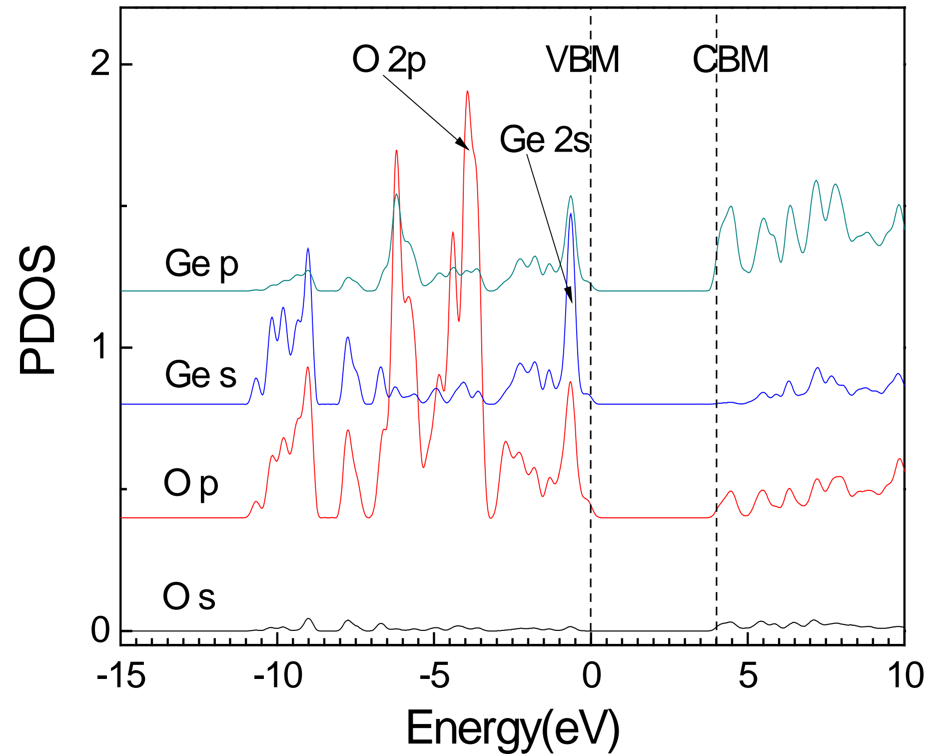
Solid GeO structure

- GeO molecule
- Geo solid, at interfaces
- What is its structure?
- Iso-electronic to PbO
- But has structure of GeS, but with planar O site (as in Si3N4)
- Lin, Robertson, APL (2010)



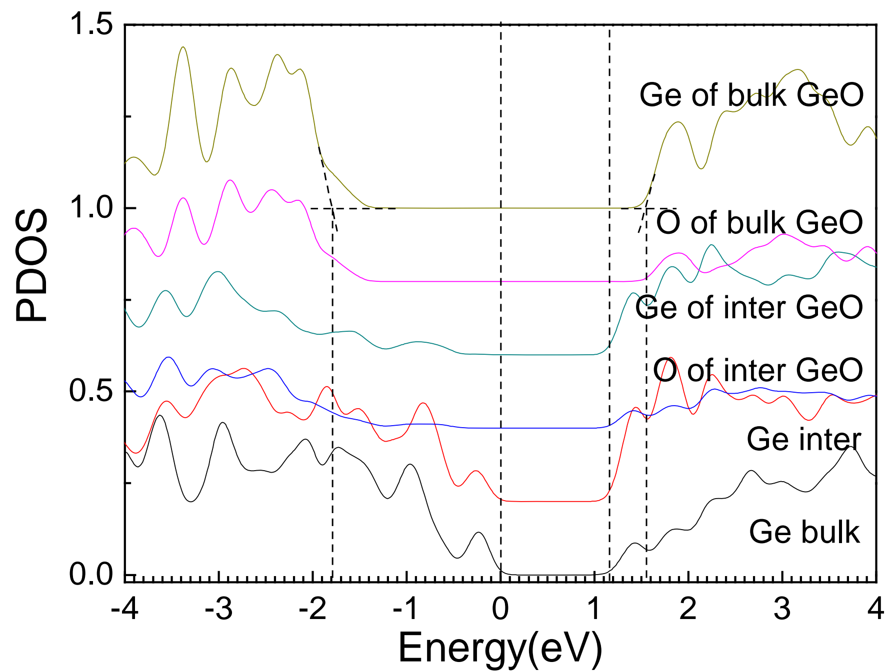
GeO states

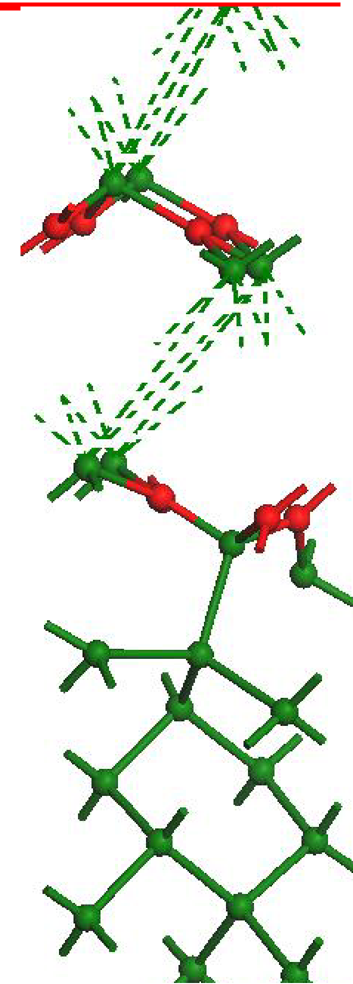
- GeO has filled Ge s states,
- VB of Ge s, O 2p.
- CB of Ge p states



Ge:GeO interface

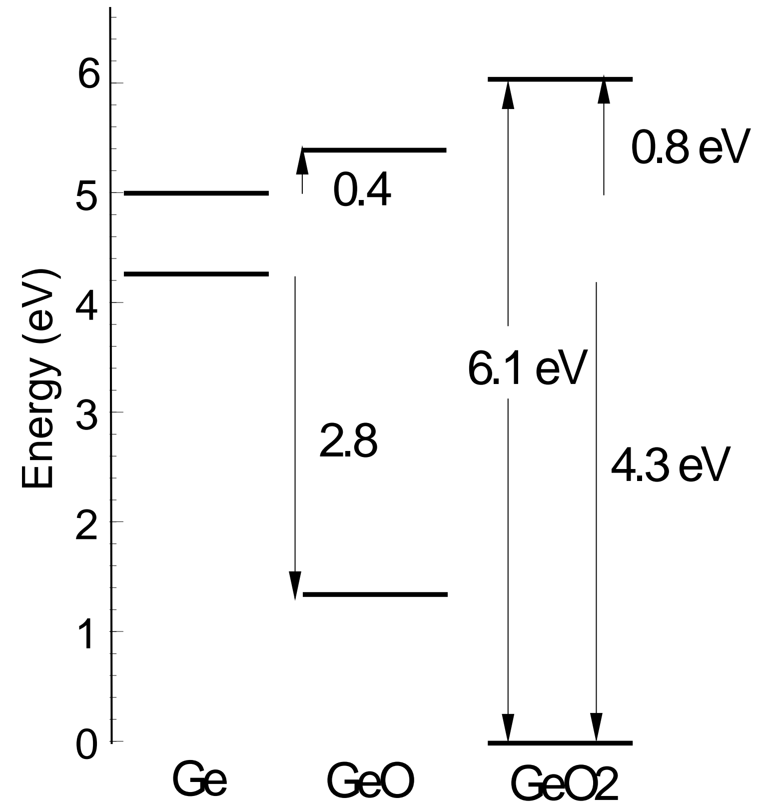
- Ge:GeO epitaxial model used to calculate band offsets





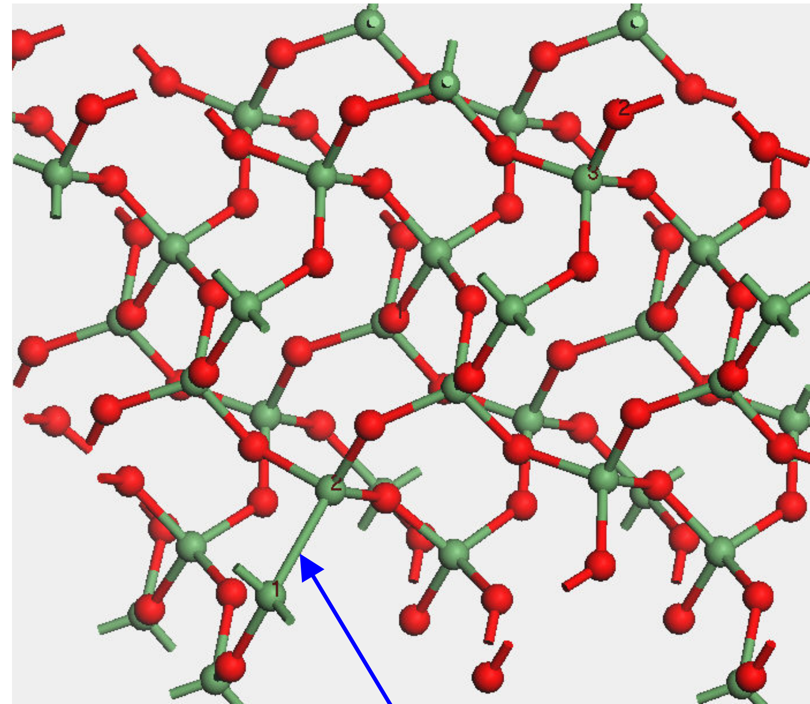
Ge:GeO_2 interface

- Presence of GeO_2 and GeO at interface with small CBO is a trap
- means that GeO_2 should be avoided
- But GeO_2 needed to stop mobility degradation
- To stop poor reliability



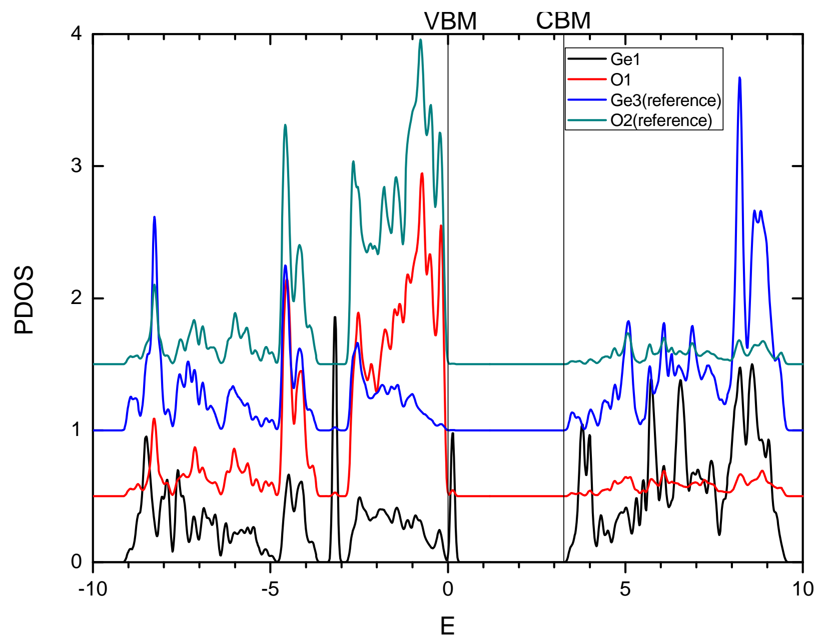
Defects in SiO_2

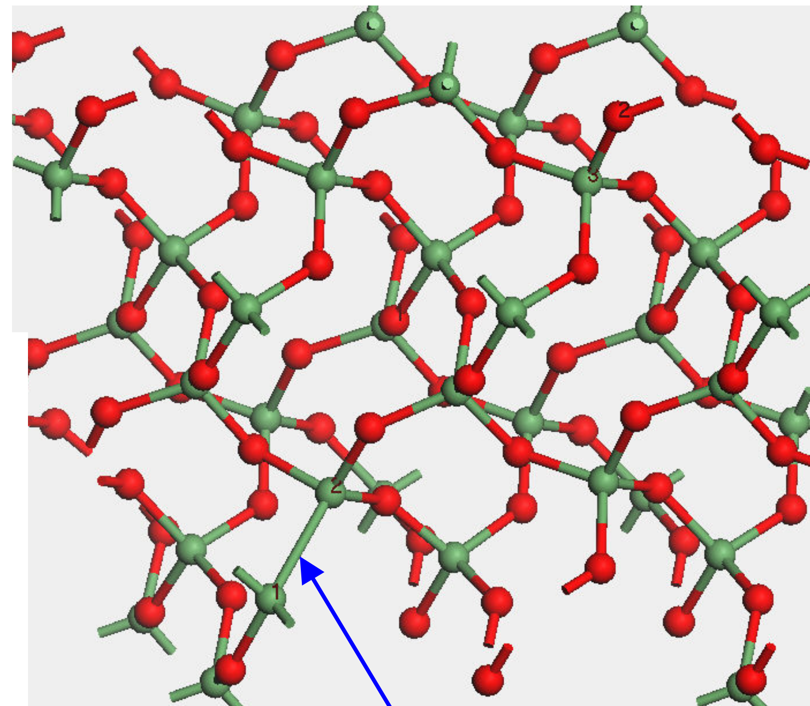
- E' centers
- Neutral Oxygen vacancy in SiO_2 relaxes to a Si-Si bond



Defects in GeO_2

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





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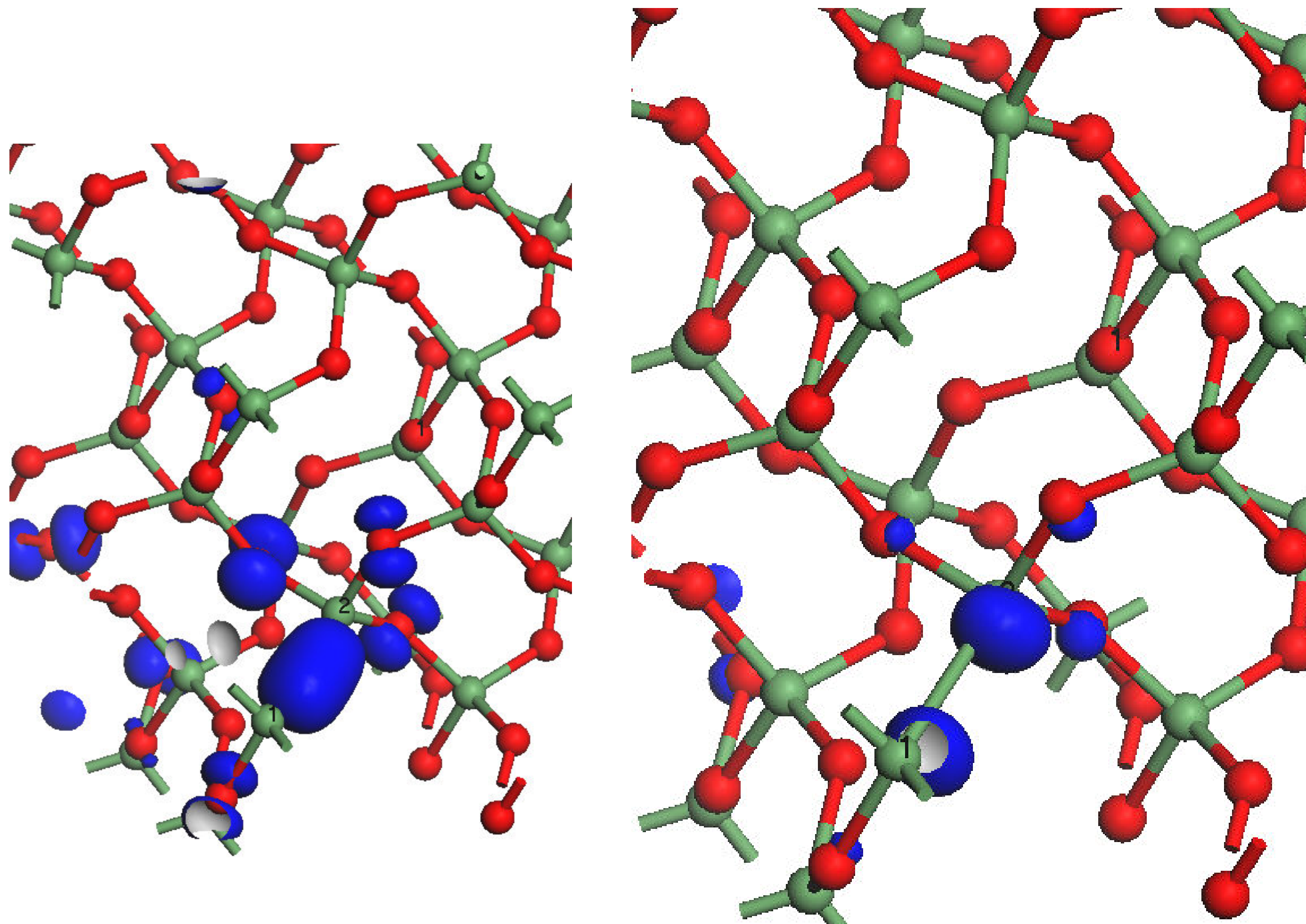
Wavefunctions



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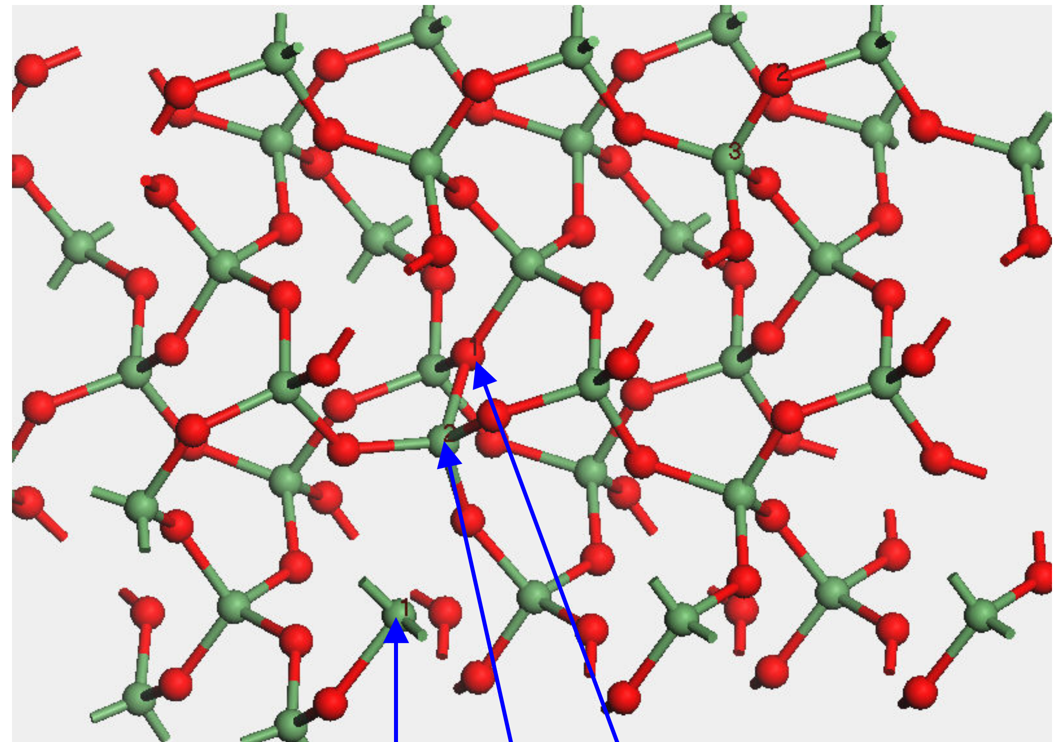
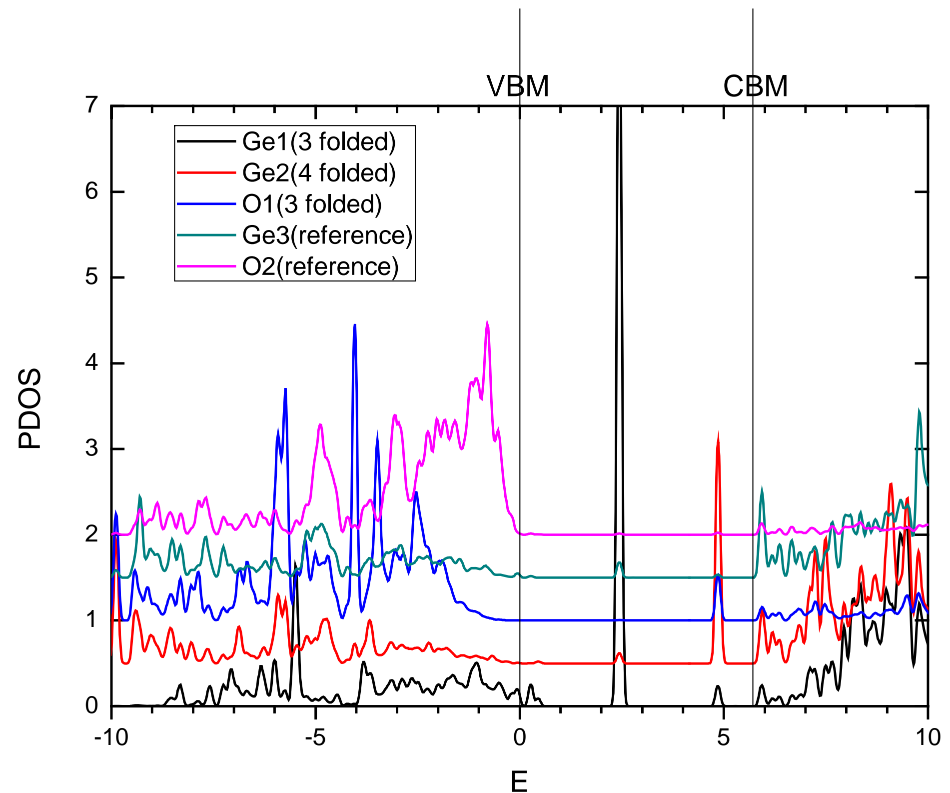
Novel defects in GeO_2

- 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

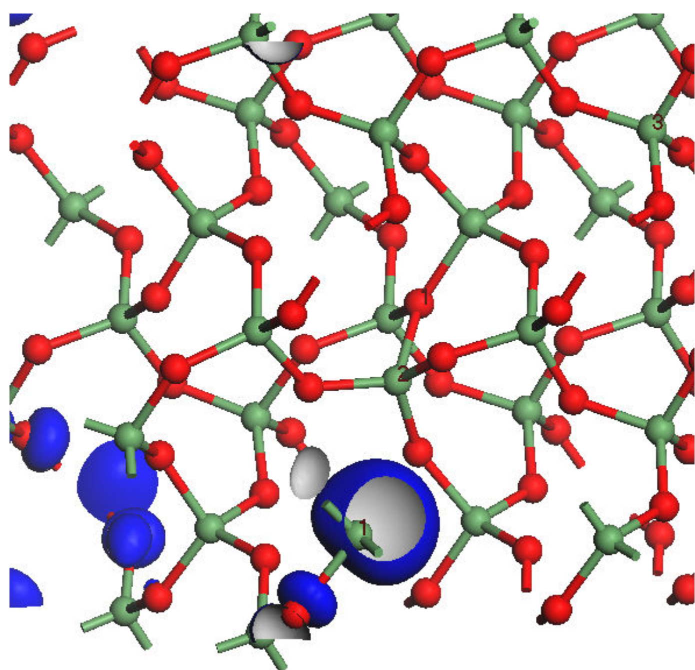


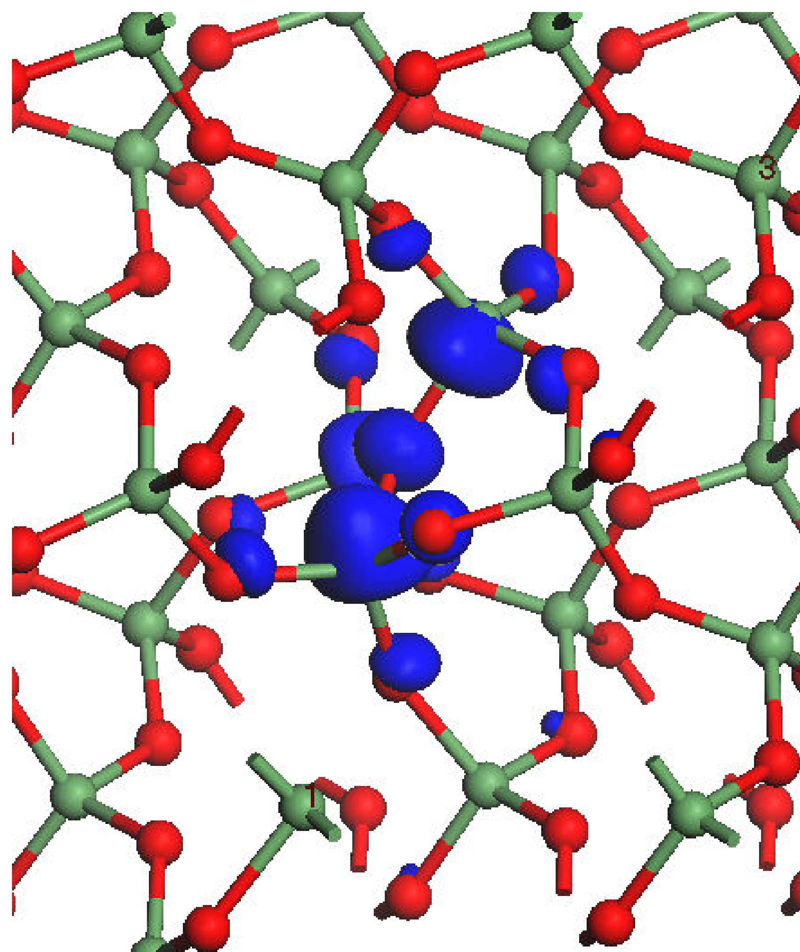
Novel defects in GeO_2

- 3-fold G gives gap state (sX)
- 3-fold O gives state at CB edge, localised on adjacent Ge sites
- Similar to 'Valence alternation pairs in GeO_2' by Pasquarello et al, APL (2010)



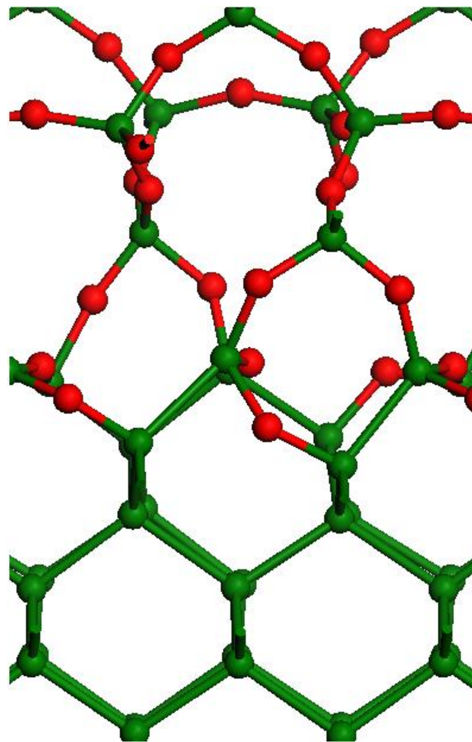
wavefunctions

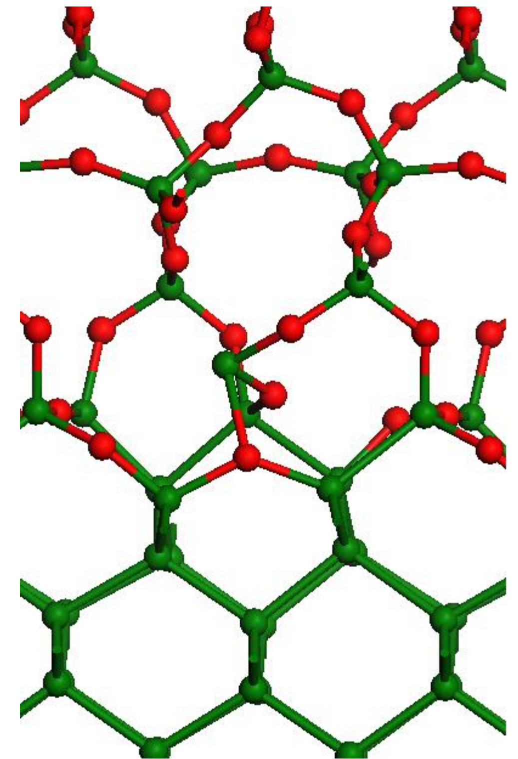




Poor interface

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



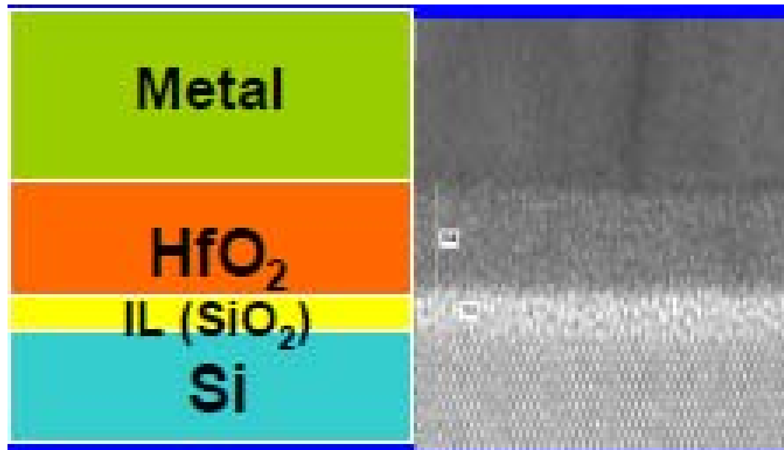


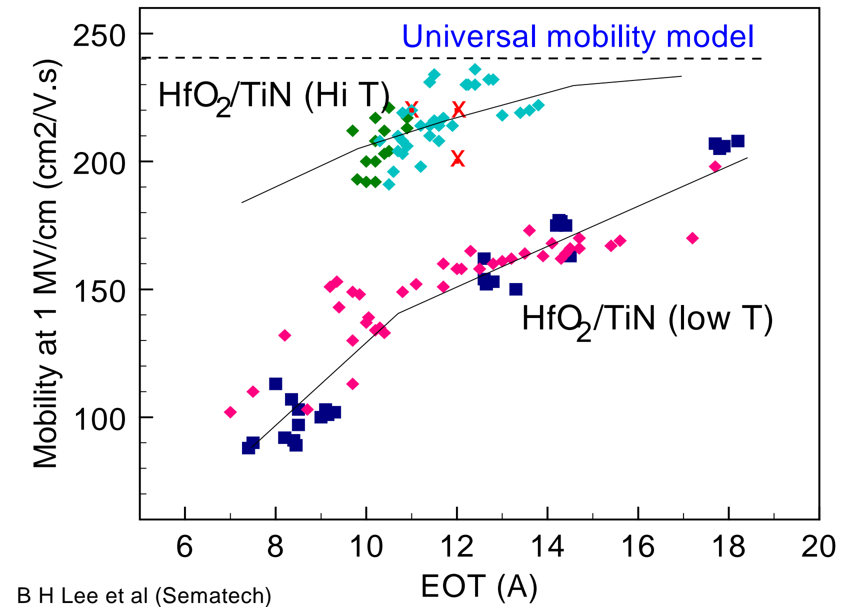
solutions

- Remove GeO_2 layers
- $LaGeO_x$ (Dimoulas etc)
- GeSr, etc (Kamata)

Improving mobility in HK-MG

- Separate HfO_2 from channel by 1 nm of SiO_2 improves mobility by screening remote scattering
- K Maitra,..IBM, JAP (2007)

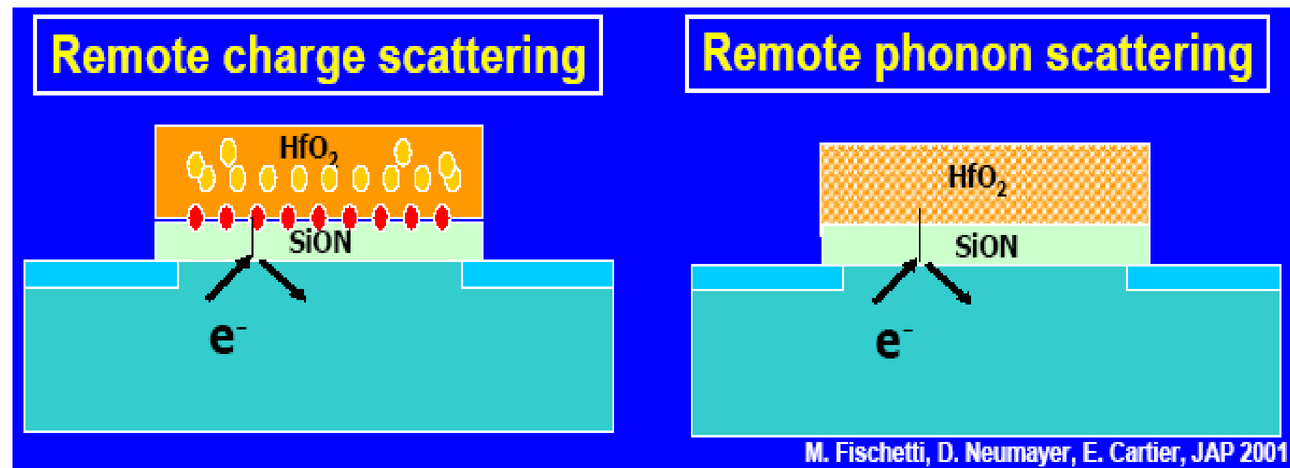




Role of SiO_2 interfacial layer

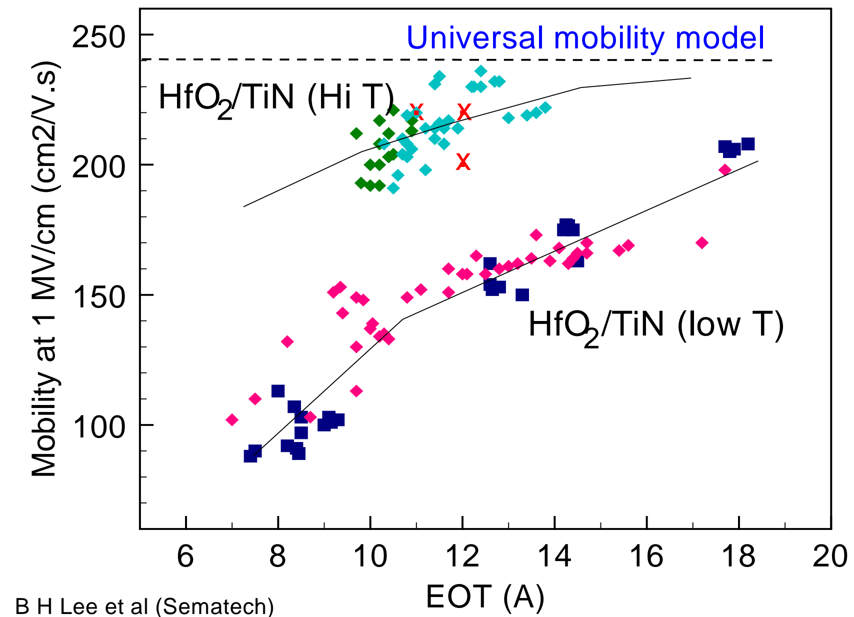
- SiO_2 interfacial layer is retained,
- To limit mobility degradation due to remote phonon scattering, remote Coulomb scattering

- To limit interfacial defects/ reliability problems



Mobility degradation

- GeO_2 interlayer may also be needed to lessen degradation

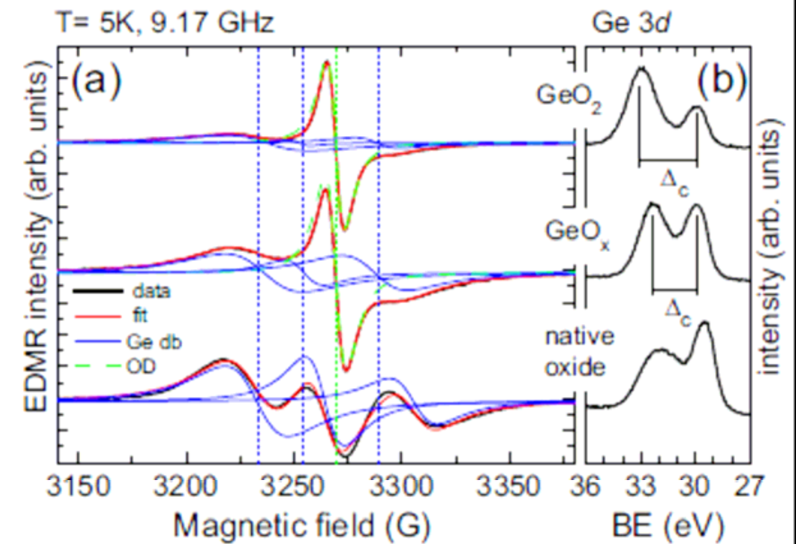


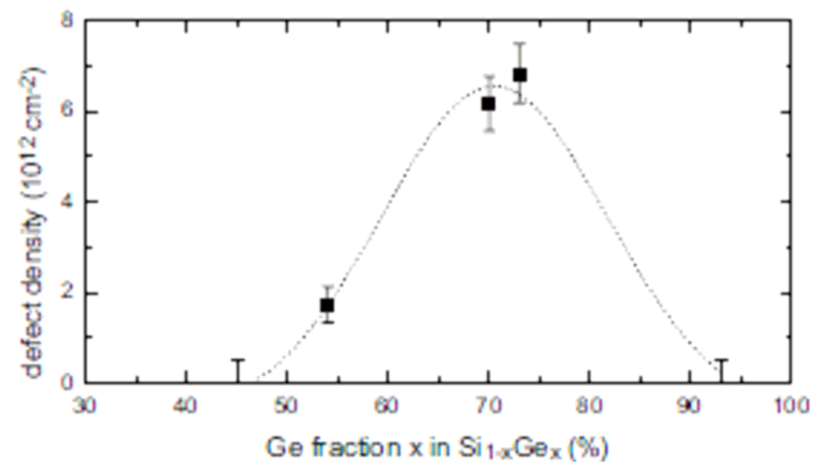
Defect passivation

- Interface defects such as P_b centre (Ge dangling bond)
- Why is defect density D_{it} high?
- Why does not Hydrogen passivate them?

Ge dangling bonds

- Baldovino, APL 93 242105 (2008) does find Ge DB by electrically detected ESR
- Stesmans finds no ESR for 100% Ge (PRB 2009)





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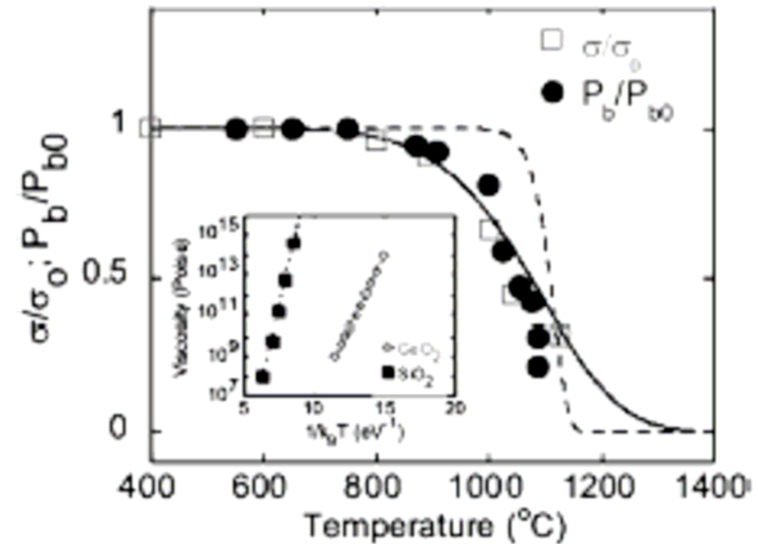
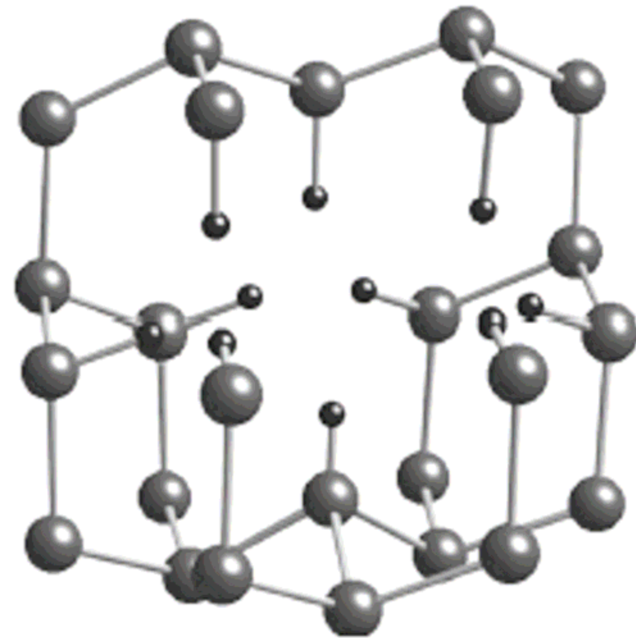
Ge dangling bonds

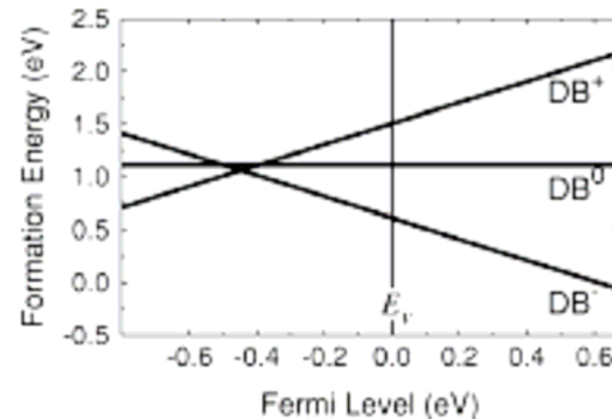
- Houssa says GeO_2 relaxation removes DBs
- Does not explain why so many Dit's !



Ge dangling bond + Hydrogen

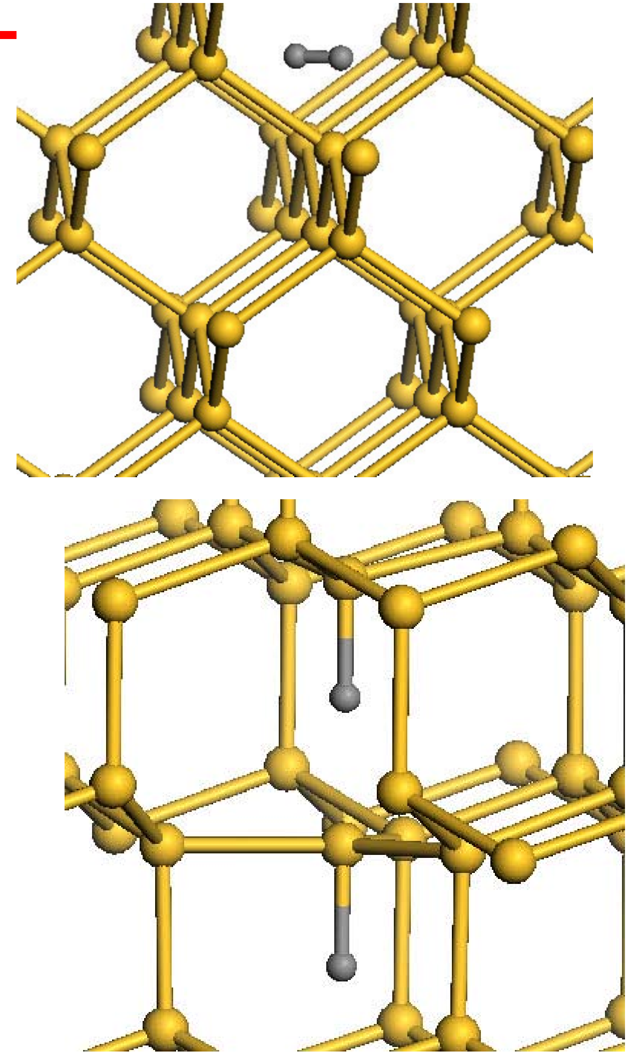
- Poor passivation of Ge P_b centres attributed to
- Ge dangling bond lying below VB edge (Janotti + van de Walle, APL 2007)
- Pasquarello found it ok
- That is Ge^- and H^- repel





Hydrogen in Ge

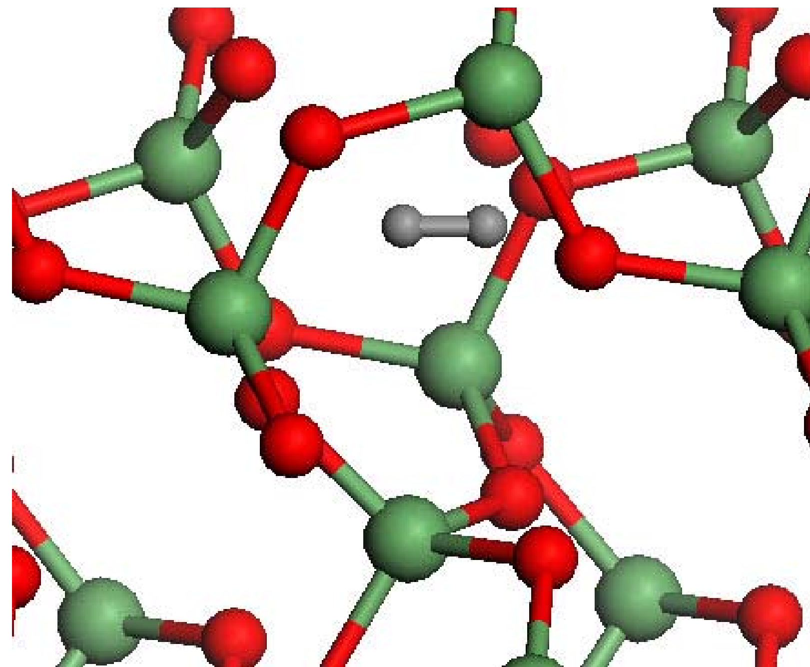
- H c\an diffuse through Ge



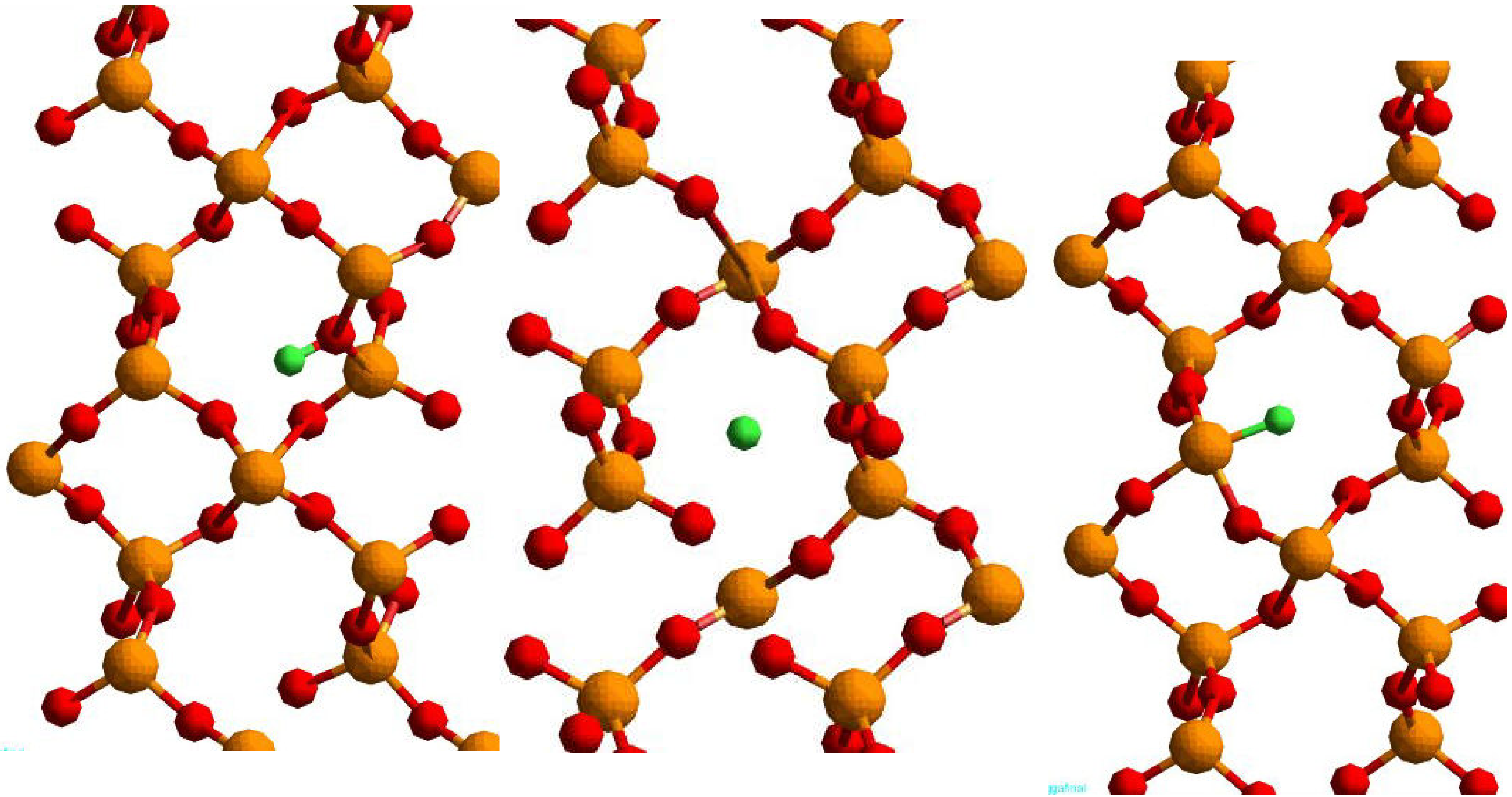
H in GeO2

- H2 can diffuse through GeO2 as H2 interstitial

- And react with Ge dangling bond



Interstitial H atom



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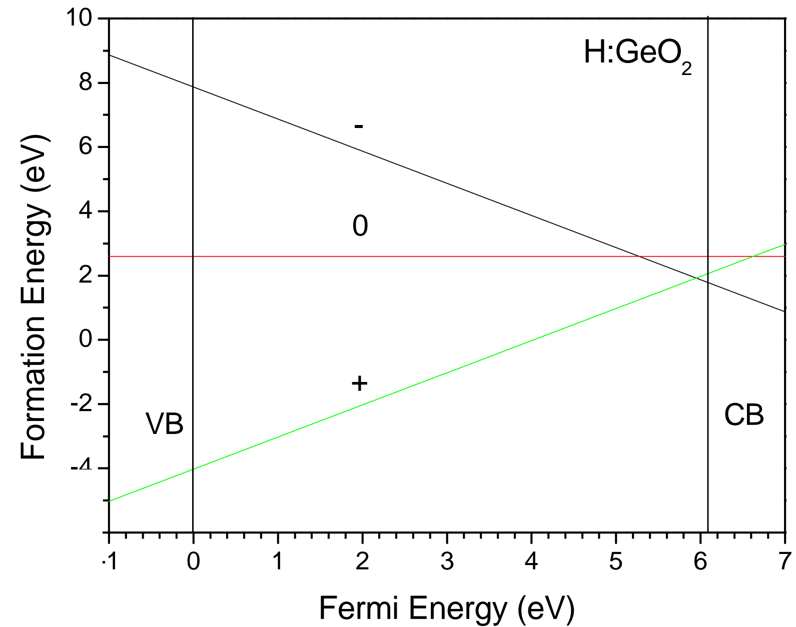
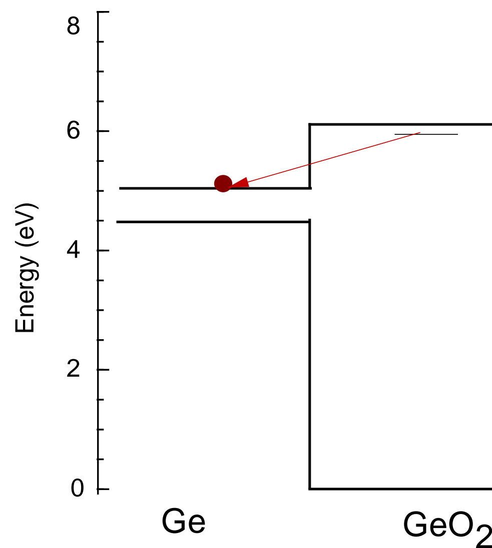
H in GeO_2

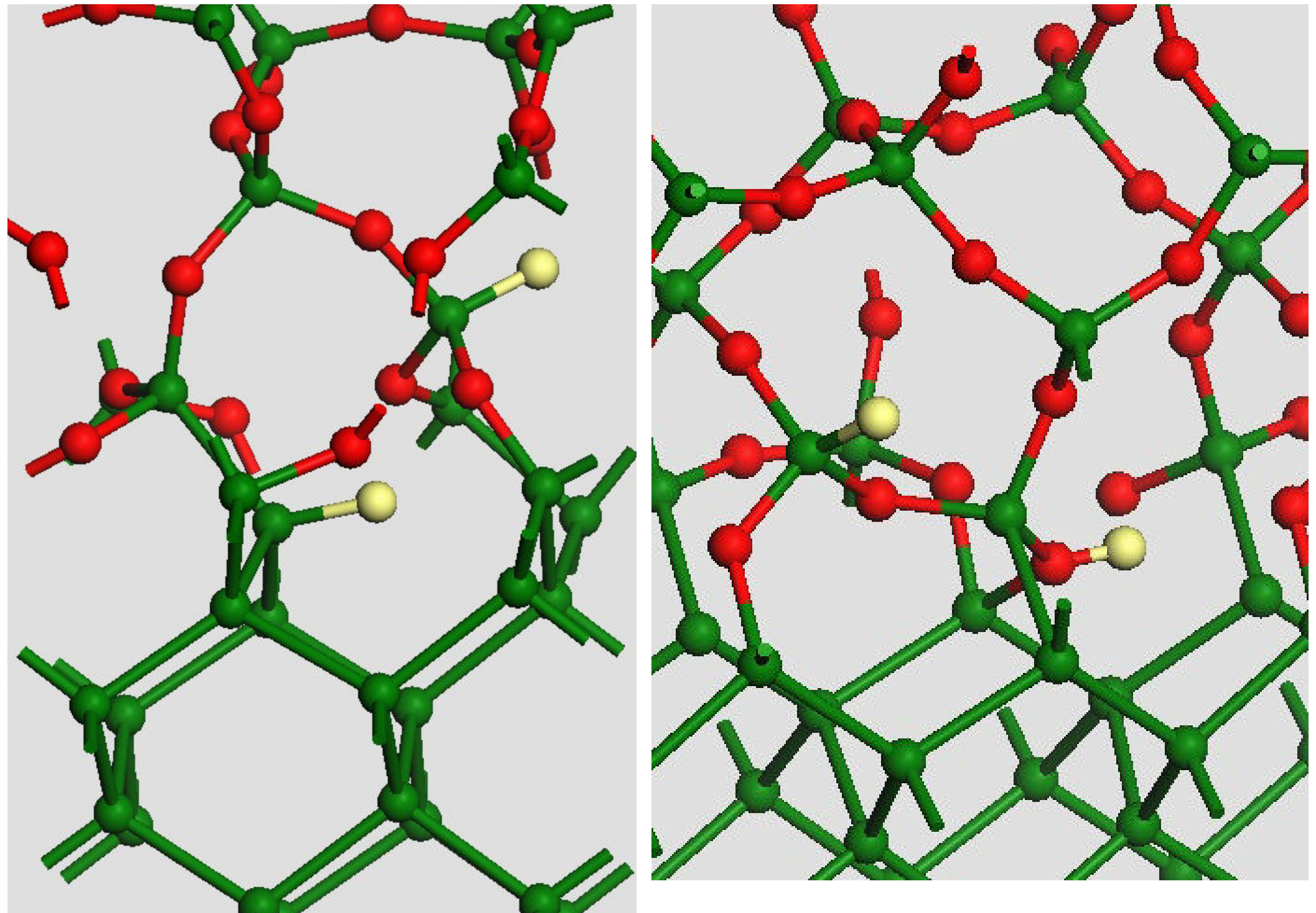
- Unlike in SiO2, H in GeO2 is a donor, level likes just at CB edge
- Donates electron
- Donates electron to Ge





H moves from Ge-H to O site

- H may go to O bond, not to Ge DB
- Tsertis and Pantelides, APL (2010)



Conclusions

- Ge is not so like Si
- Poor band offset – avoid GeO_2 interfacial layer
- Non-stoichiometry
- Role of hydrogen