High resolution core level photoemission studies of high-k dielectric semiconductor interface formation

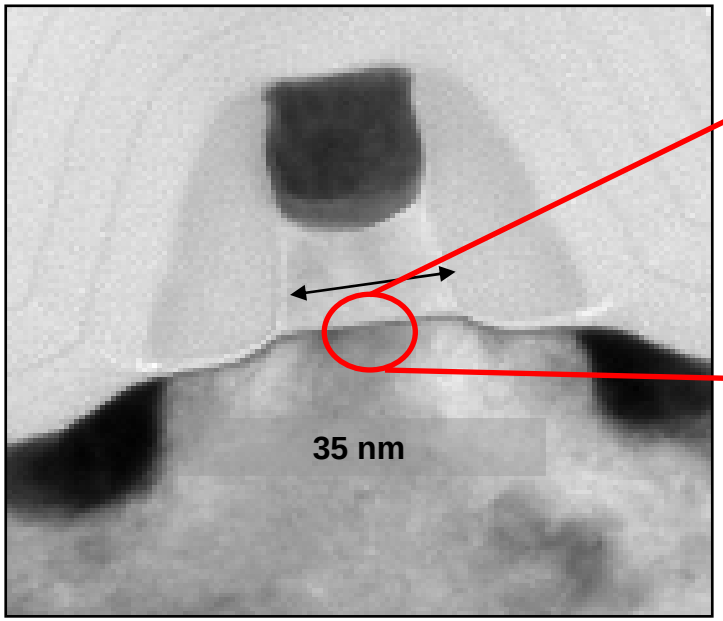
Prof Greg Hughes
School of Physical Sciences
Dublin City University
Glasnevin
Dublin 9

Outline of talk

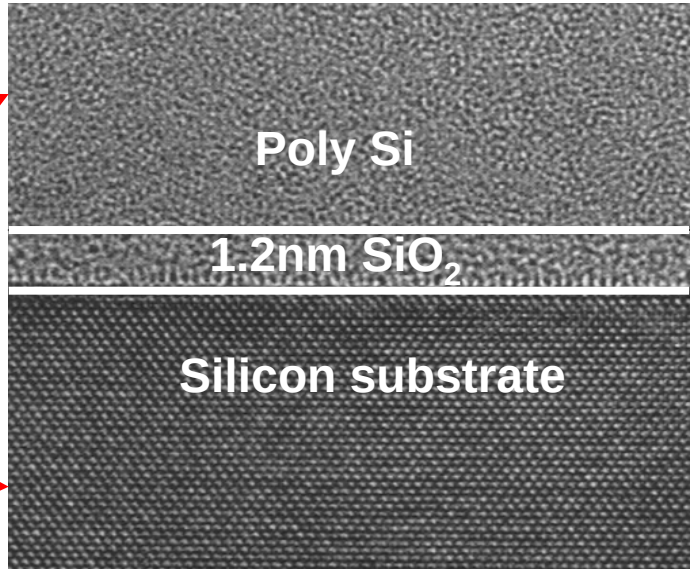
- Why high-k dielectrics?
- Issues associated with integration – control of interface layer
- High resolution photoemission study of interface formation between HfO_2 and MgO on ultrathin SiO_x interlayer.
- CV measurements on MgO based MOS structures

HIGH-K MATERIALS: MOTIVATION
MOSFET dielectric replacement

65 nm (2007) MOSFET
[Source: INTEL]



Gate Oxide



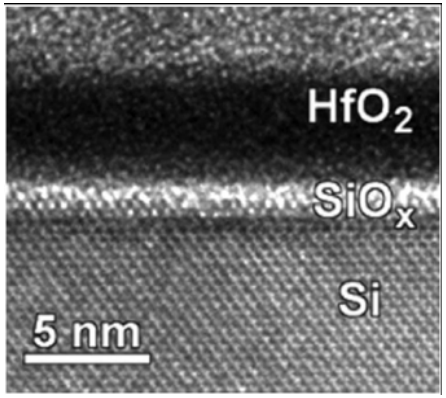
T_{ox} < ~ 2.5 nm – direct quantum mechanical tunneling

Importance of interface characterisation

Control of SiO_x interface layer is critically important to device performance

$$\mathrm{EOT} = \left(\frac{3.9}{\kappa}\right) t_{hi-\kappa} + t_{SiOx}$$

= High-k layer + Interface layer

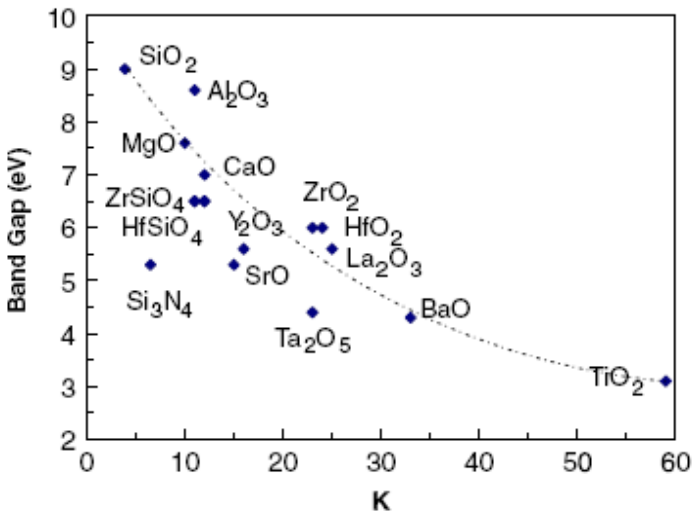


Locquet et al JAP 100 051610 (2006)

If you want to achieve EOT below 1nm, it is critical to control thickness of SiO_x interface layer

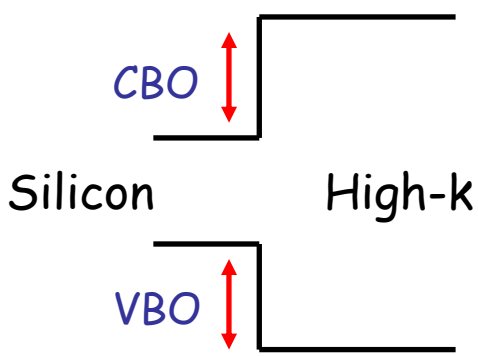
- XPS
- Synchrotron radiation based photoemission
- TEM
- HAADF-STEM

Why MgO?



High chemical stability
Wide bandgap
Thermal stability
Possibility to form abrupt interfaces

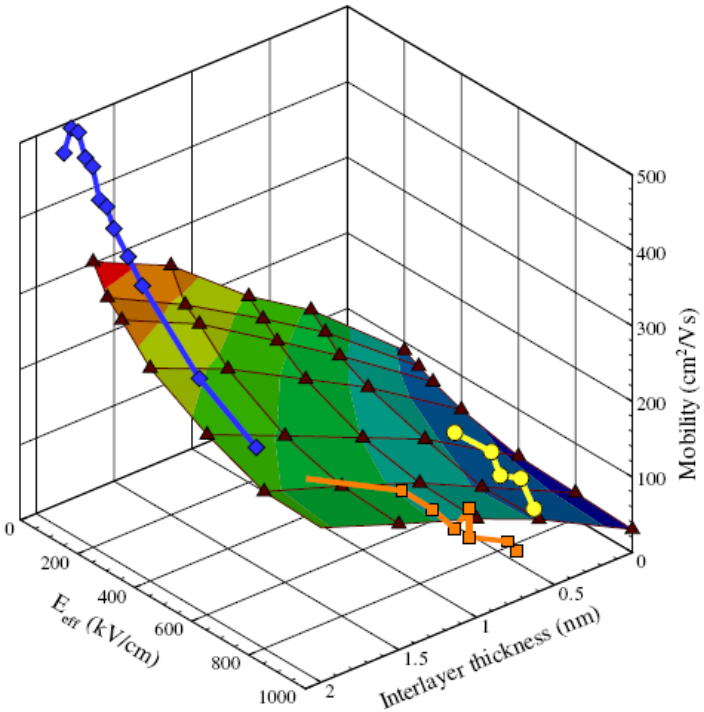
	k	Eg(eV)	CBO(eV)	VBO(eV)
SiO_2	3.9	9.0	3.2	4.7
Al_2O_3	9	8.8	2.8	4.9
MgO	10	7.8	3.4	3.3
HfO_2	25	5.8	1.4	3.3



Heats of Formation
MgO = -601.8 kJ/mol
SiO_2 = -859 kJ/mol
HfO_2= -1113kJ/mol
Al_2O_3= -1675kJ/mol

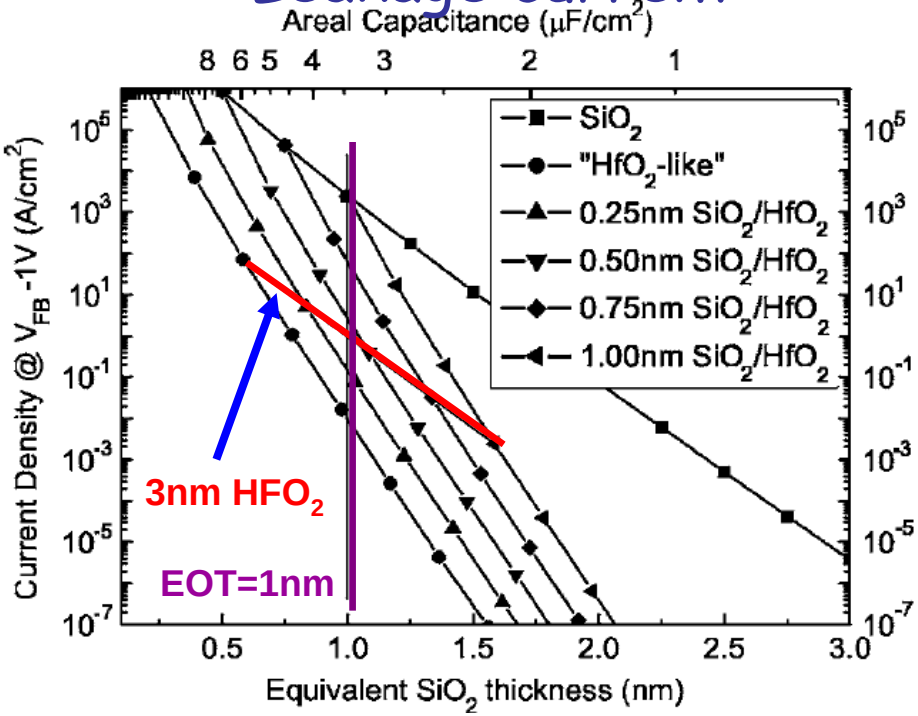
Integration issues for high-k materials

Mobility Degradation



J.Non-Cry Sol 353(2007) 630
Decreasing interlayer thickness reduces mobility in substrate

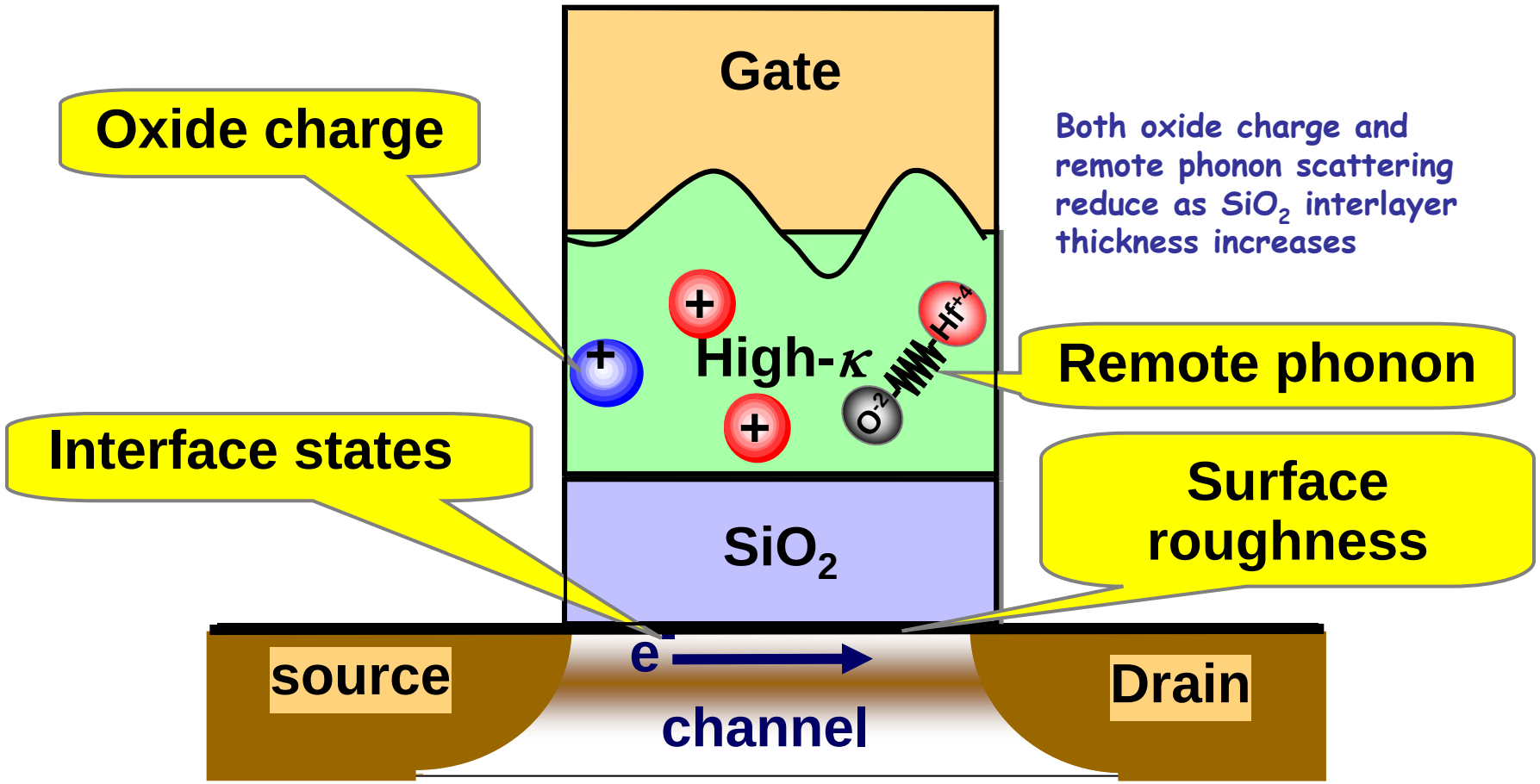
Leakage current



Locquet et al JAP 100 051610 (2006)

Leakage decreases by factor of 10 for every monolayer of SiO_2 at the interface – however EOT increases.

Mobility Degradation in High-k Gate MOSFETs

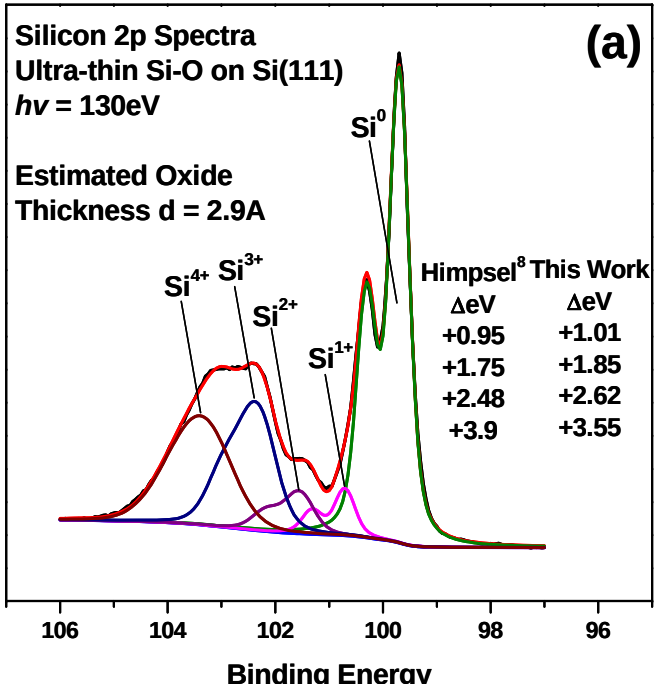


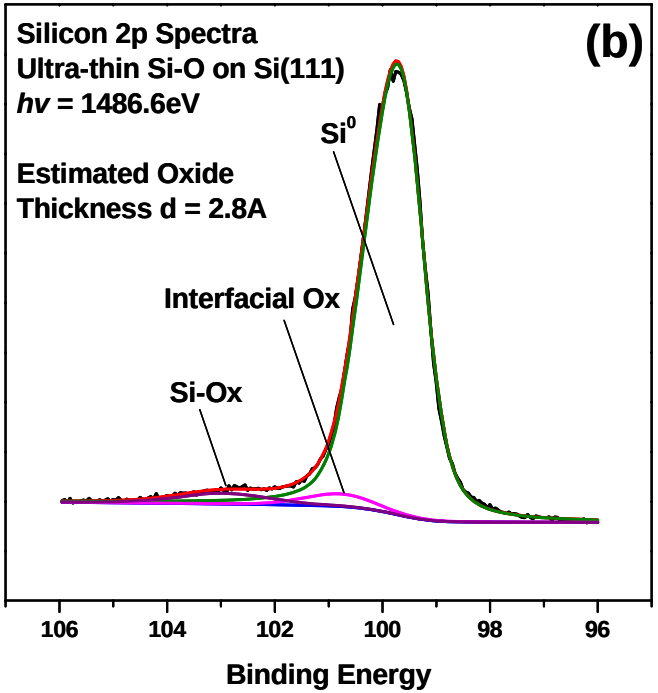
Both oxide charge and remote phonon scattering reduce as SiO_2 interlayer thickness increases

HfO_2 and MgO on silicon comparison study

- Grow ultra thin self limiting buffer oxide on silicon
- In situ deposition and characterisation of high-k layers
  - (a) HfO_2 on ultra thin buffer oxide
  - (b) MgO on ultra thin buffer oxide
- MgO on H-terminated silicon and CV characterisation on MOS structures

Interfacial buffer oxide - atomically abrupt





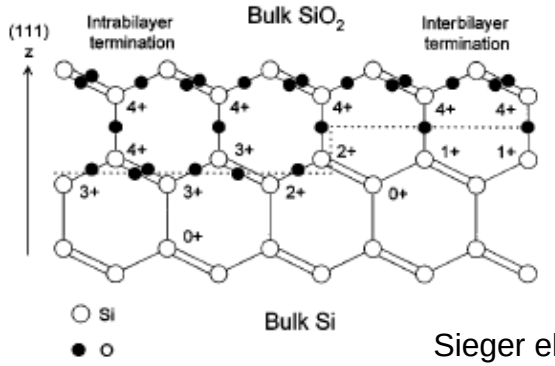


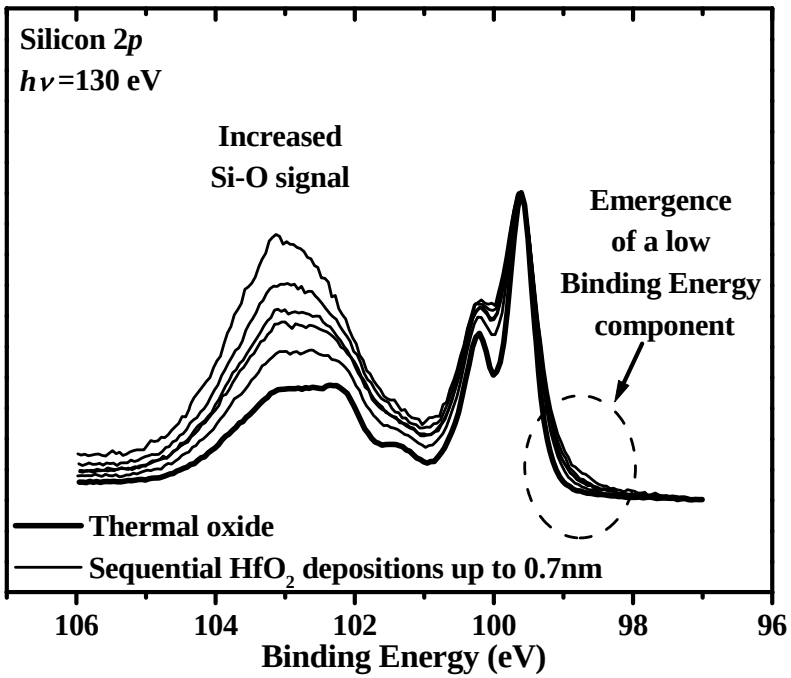
FIG. 4. An abrupt interface model for SiO_2/Si(111). There are two possible terminations, as indicated in the figure. The oxidation states for Si atoms at and near the interface boundary are labeled.

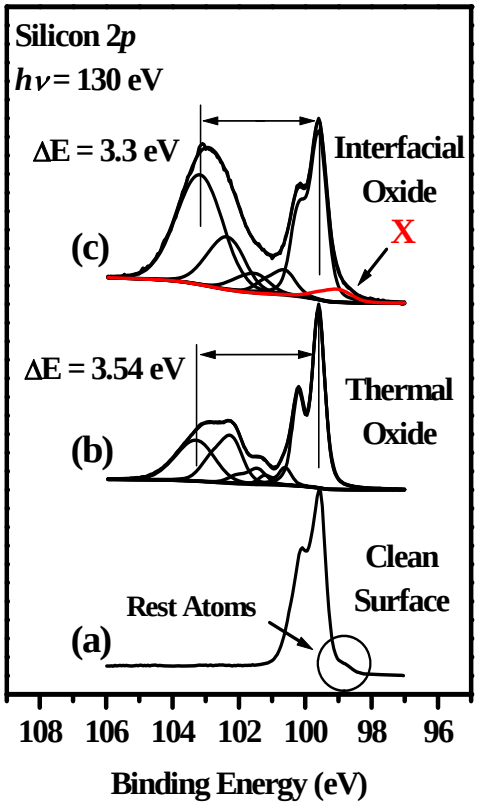
Expose atomically clean Si(111) surface to molecular oxygen at 600°C.

Thermally grown self limiting ultrathin (0.3nm) SiO_x layer

Sieger el at PRL 77 2759 (1996)

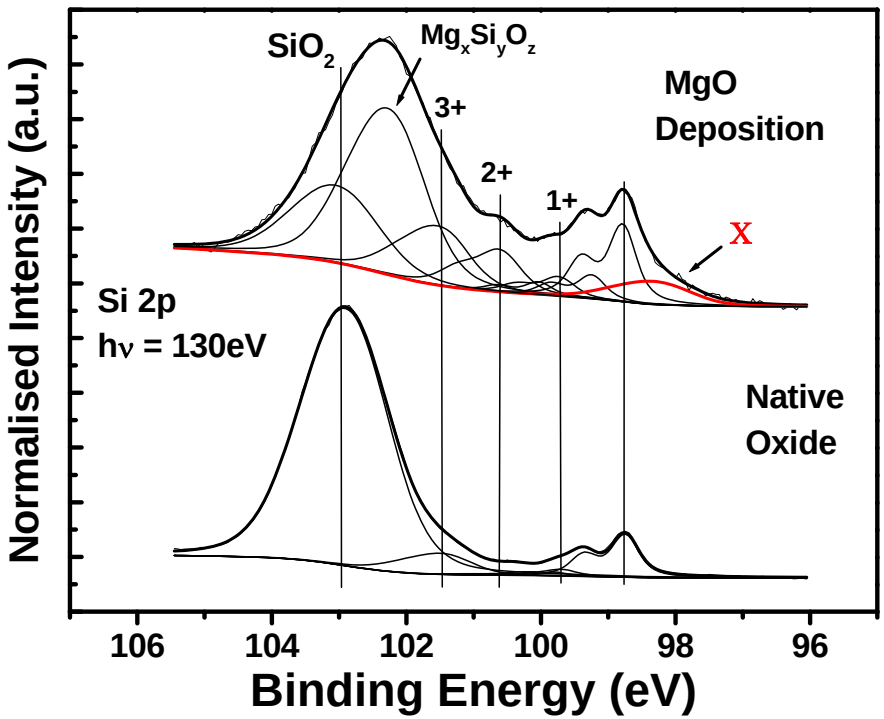
HfO_2 /SiO_x interface formation

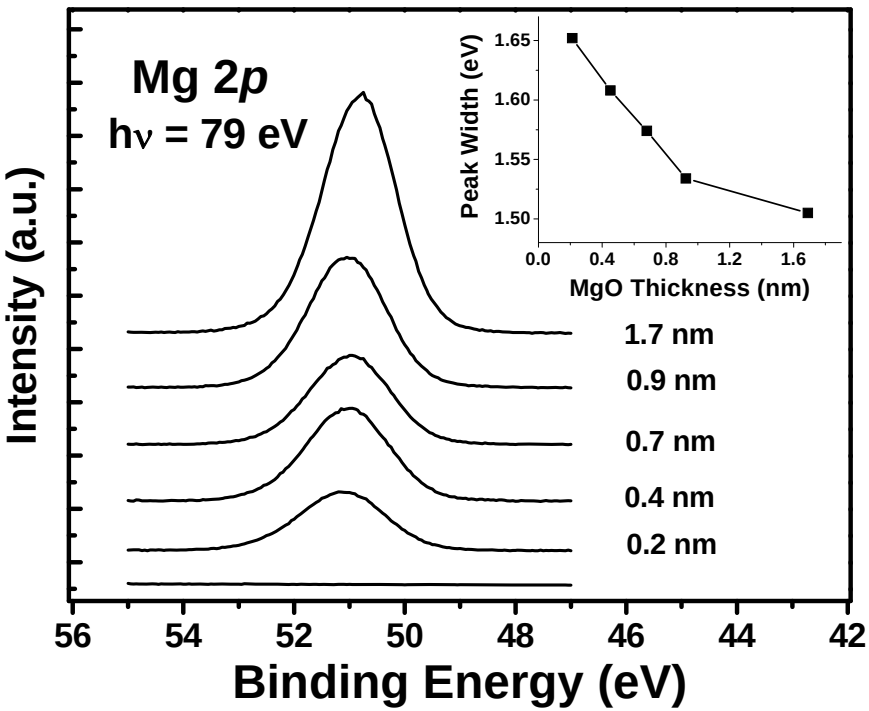




Thickness of interfacial oxide increases as HfO_2 is deposited at RT

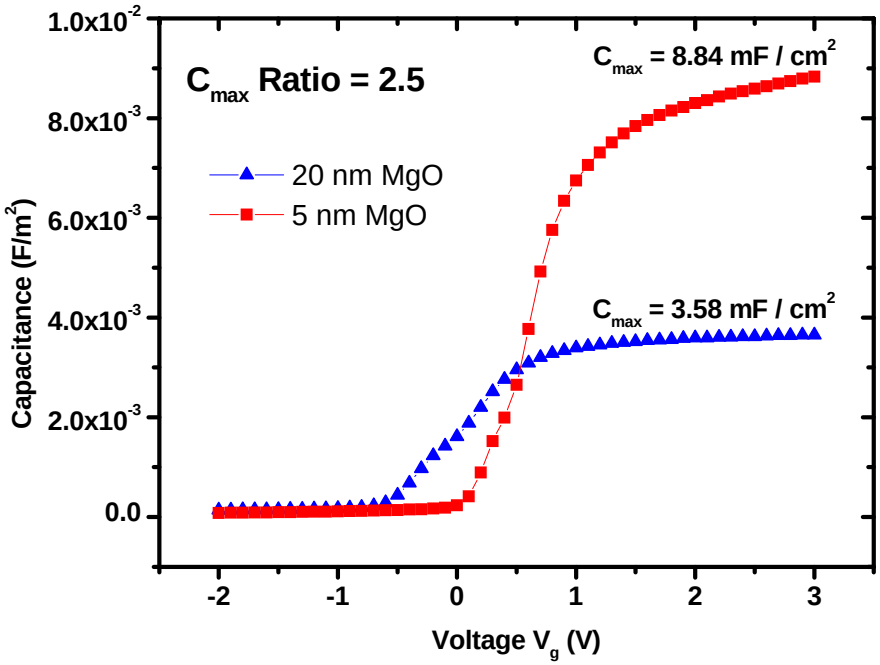
MgO /SiO_x interface formation



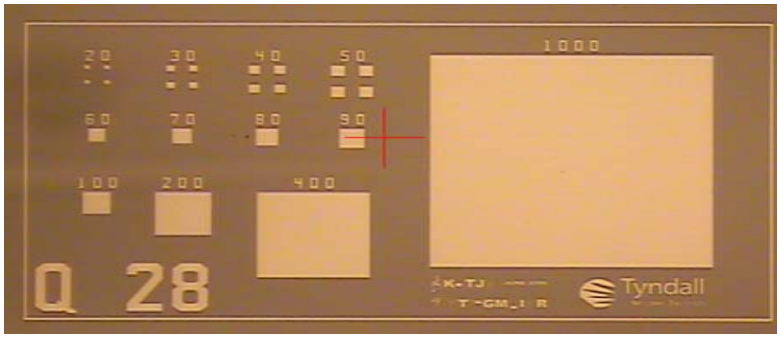


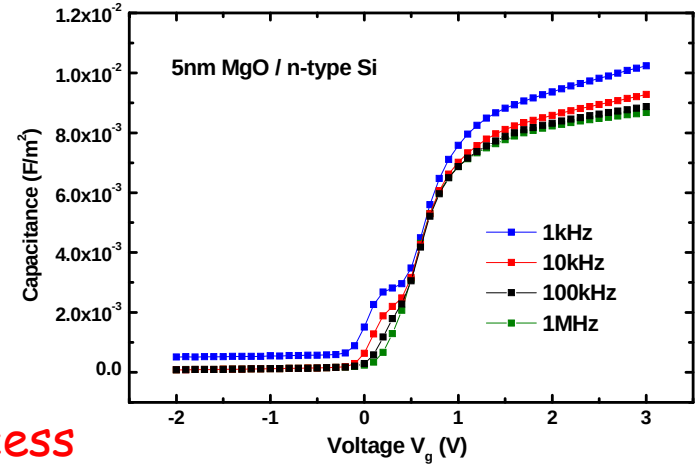
Thickness of interfacial oxide increases as MgO is deposited.
For both HfO_2 and MgO deposition saturation thickness of ~0.6-0.7nm
Original SiO_x/Si interface has been disrupted at RT

Capacitance – voltage measurements MgO on Si



Pd/MgO/Si MOS capacitor structures





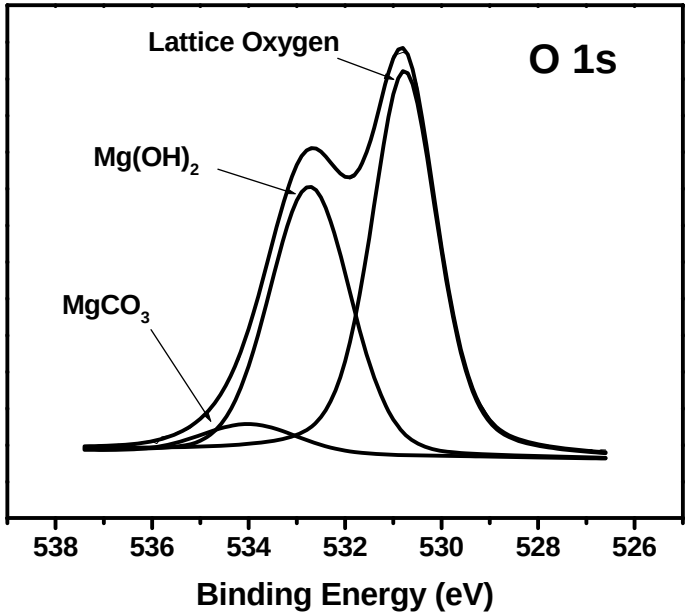
MOS capacitors fabricated by

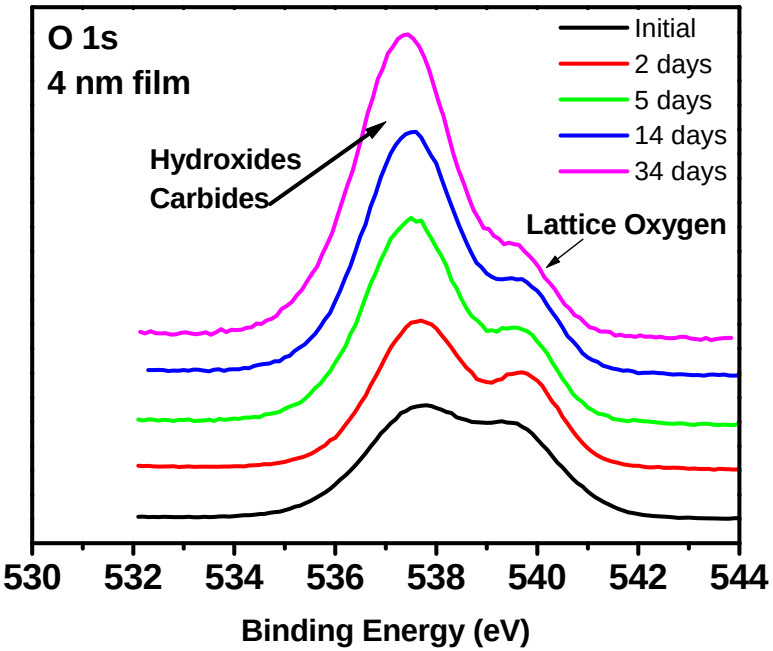
E-beam deposition of MgO on HF etched Si

Ex-situ e-beam deposition of Pd contacts

Pattern defined by wet chemical lift-off process

Ambient degradation of MgO films



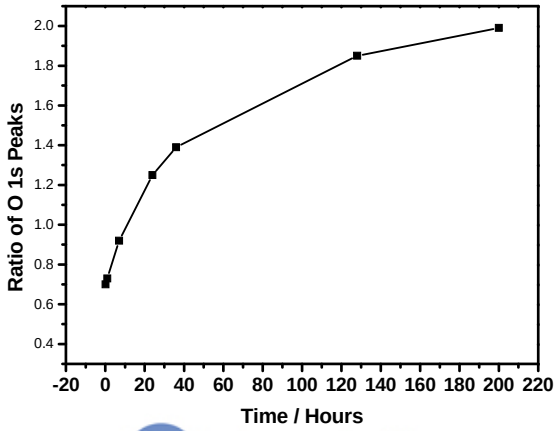


Heats of Formation

$MgCO_3$ = -1113 kJ/mol

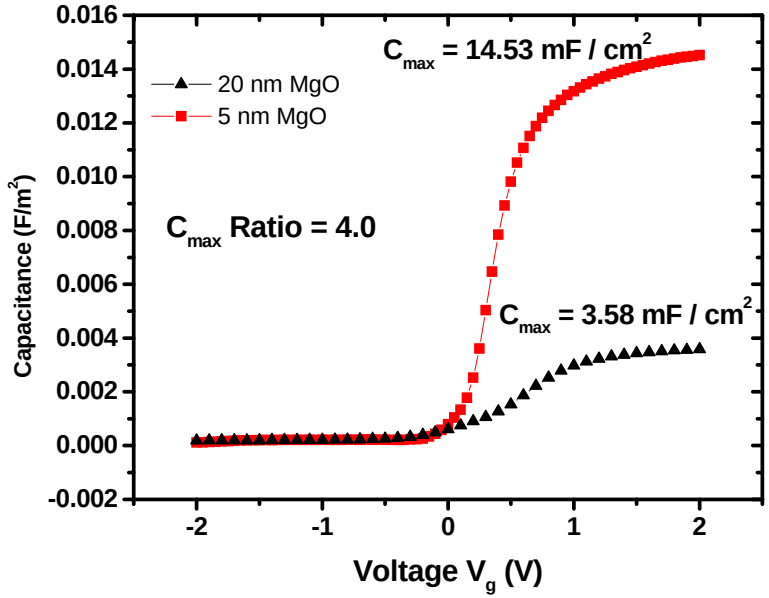
$Mg(OH)_2$ = -924 kJ/mol

MgO = -601.8 kJ/mol



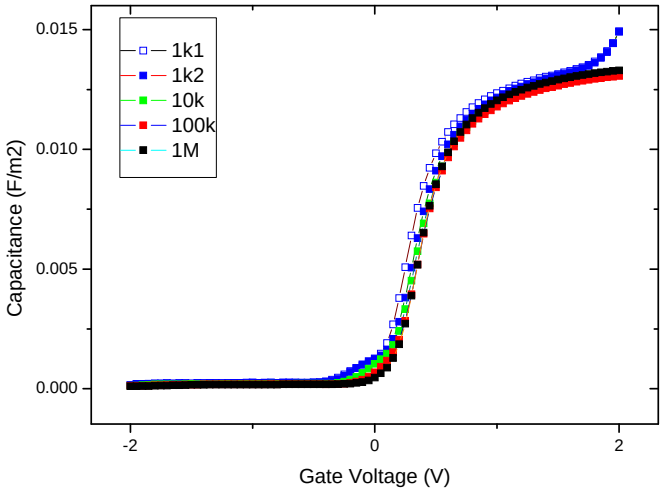
Rate of surface hydroxides and carbide growth

Capacitance for silicide gate process



MgO deposition on Si surface
In-situ Si deposition (100nm) cap
Ex-situ Ni deposition
500°C FUSI anneal

Low frequency dispersion

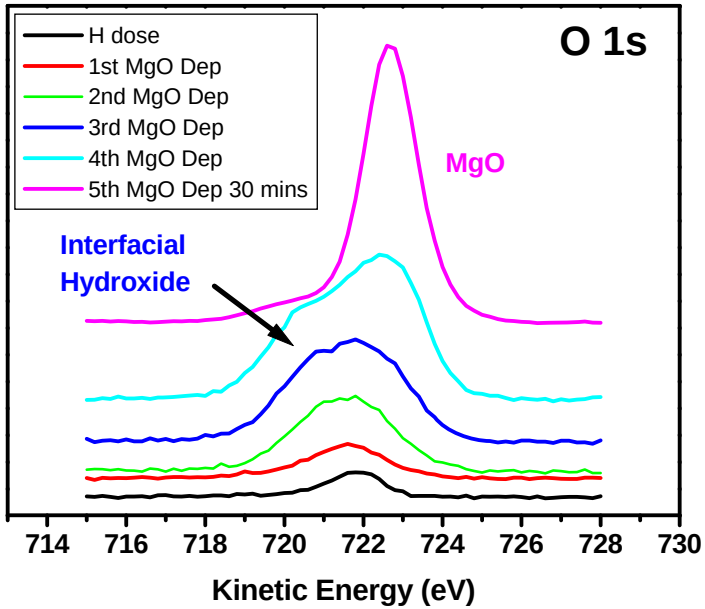


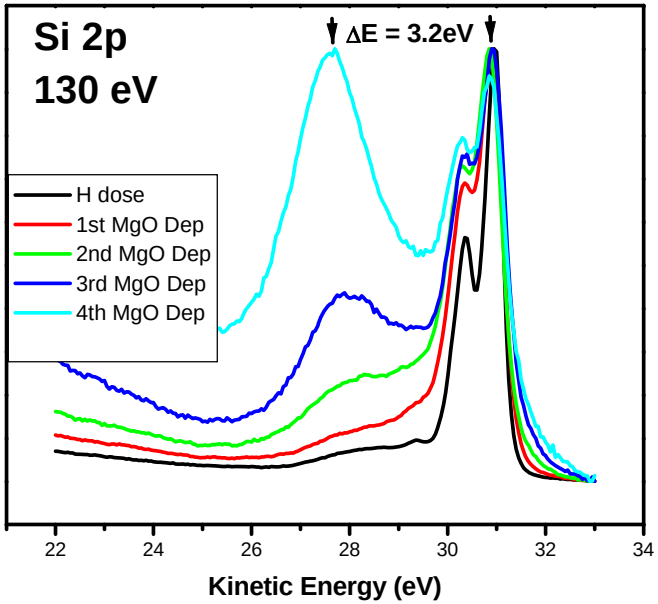
Exact scaling of C_{max} with thickness
Low frequency dispersion
Low interface state densities

Suggests minimal interfacial layer

Si-H MgO interface formation

MgO deposition on H-terminated Si surface in ultra high vacuum





Evidence of magnesium-hydroxy-silicate formation at interface

CV measurements suggest k value higher than SiO_2

Conclusions

- Metal ion catalytic effect induces room temperature oxidation at high-k/Si interface.
- Ultrathin buffer oxide on Si is disrupted by dielectric deposition resulting in roughened interface – impact on mobility.
- Correct capacitance scaling with MgO thickness suggests minimal interfacial oxide layer.
- Photoemission analysis of the MgO/H-terminated Si interface shows the presence of a magnesium-hydroxy-silicate interfacial layer 0.5-0.6nm thick.

Acknowledgements

DCU – Rob O'Connor, Stephen McDonnell, Barry Brennan, Patrick Casey.

Collaborations

Tyndall Institute (Dr Paul Hurley) , Astrid Synchrotron, IMEC.

Funding

Science Foundation Ireland (SFI), Intel Irl.