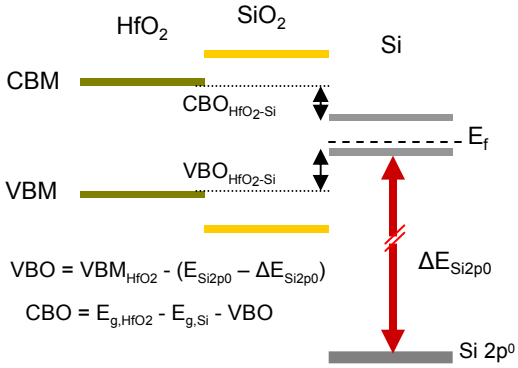
XPS Characterization of Hf-based High-k/SiO_2/Si Film Stacks

E. Bersch*, (ebersch@uamail.albany.edu), M. Di*, S. Consiglio**, R. Clark**, G.J. Leusink**, A.C. Diebold*
*College of Nanoscale Science and Engineering, Albany, NY
**TEL Technology Center, America, LLC, Albany, NY

Motivation

- In a traditional MOSFET the gate oxide is SiO_2
- Recently, a gate oxide of high-k oxide/SiO_2 has been used to
  - reduce gate leakage current
  - maintain a low equivalent oxide thickness (EOT)
  - preserve carrier mobility in Si
- For ultra-thin gate oxides, leakage current depends on band offsets with respect to Si (should be >1eV)

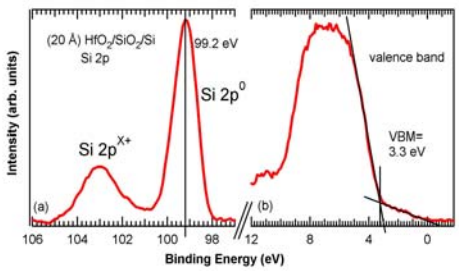
Band Offsets



$VBO = VBM_{HfO2} - (E_{Si2p0} - \Delta E_{Si2p0})$

$CBO = E_{g,HfO2} - E_{g,Si} - VBO$

VBO measured by XPS

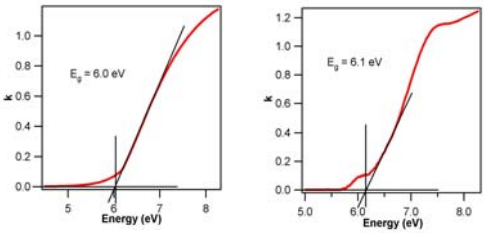


ΔE_{Si2p0} = 99.0eV (measured from sputtered Si)

$VBO = VBM_{HK} - (E_{Si2p0} - \Delta E_{Si2p0})$

VBO = 3.3eV- (99.2eV - 99.0eV) = 3.1eV

E_g measured by Spectroscopic Ellipsometry-CBO can be determined



$CBO = E_{g,HfO2} - E_{g,Si} - VBO$
CBO = 6.0 - 1.1 - 3.1 = 1.8eV

$CBO = E_{g,HfO2} - E_{g,Si} - VBO$
CBO = 6.1 - 1.1 - 3.5 = 1.5eV

Unannealed HfO_2/SiO_2/Si

Thickness (Å)	Band Gap (eV)	VBO (eV)	CBO (eV)
0	n/a	n/a	n/a
20	6.0	3.1	1.8
30	6.0	3.1	1.8
40	6.0	3.2	1.7

Annealed HfO_2/SiO_2/Si

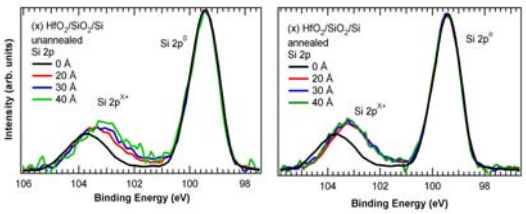
Thickness (Å)	Band Gap (eV)	VBO (eV)	CBO (eV)
0	n/a	n/a	n/a
20	6.1	3.5	1.5
30	6.1	3.5	1.5
40	6.0	3.5	1.4

Unannealed (20 Å) $Hf_xSi_{1-x}O_2/SiO_2$/Si

Composition (x=)	Band Gap (eV)	VBO (eV)	CBO (eV)
0.7	6.1	3.8	1.2
0.55	6.3	3.9	1.3
0.4	6.5	4.0	1.4

SiO_2 Layer Chemistry

unannealed annealed



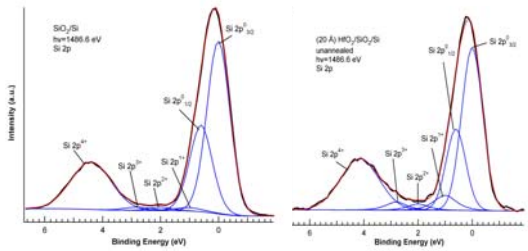
Deposition of HfO_2 layer alters the Si 2p oxide ($2p^{X+}$) peak
- increase in intensity and width
- decrease in binding energy relative to the Si $2p^0$ peak

Annealing the HfO_2/SiO_2/Si stack alters the Si $2p^{X+}$ peak
- peaks become narrower and are nearly the same for all HfO_2 thicknesses

Peak fitting is needed to obtain a more quantitative analysis
- Results from the literature: Si 2p 1+, 2+ and 3+ binding energies relative to the Si $2p^0_{3/2}$ are widely agreed upon*
- Si 2p 4+ binding energy can vary based on SiO_2 thickness

Approach: use established Si 2p 1+, 2+ and 3+ energies and allow 4+ energy to vary to optimize fit

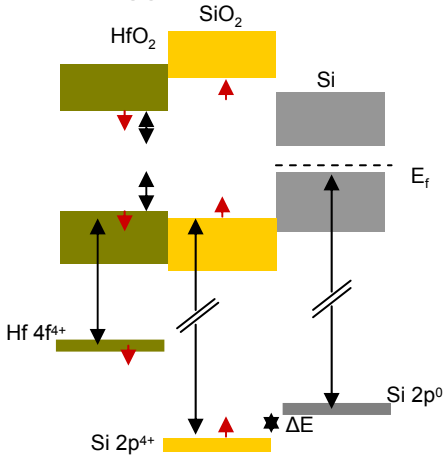
*F. Himpsel *et al.*, *Phys. Rev. B*, **38**, 6084,1988



Si $2p^{4+}$ is 4.4 eV below Si $2p^0_{3/2}$ Si $2p^{4+}$ is 4.1 eV below Si $2p^0_{3/2}$

- Growth of HfO_2 layer shifts Si $2p^{4+}$ relative to Si $2p^0_{3/2}$ and increases relative suboxide intensity by a factor of 3

Energy Level Shifts



- Shift in Si $2p^{4+}$ and increase in HfO_2-Si VBO after annealing may be due to changes in the chemistry at the interfaces

Angle Resolved XPS

Beer-Lambert Law:
thin film

$$I = I_o(1-\exp(-d/\lambda\cos\theta))$$

substrate covered by a thin film

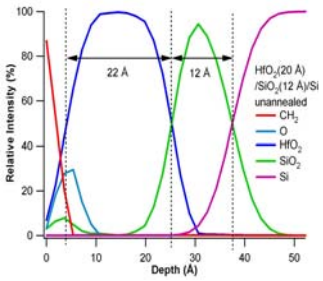
$$I = I_o\exp(-d/\lambda\cos\theta)$$

Attenuation length (λ)
λ can be calculated using the method described in NIST Standard Reference Database 82

www.nist.gov/srd/nist82.htm

Input ARXPS core level spectra into maximum entropy algorithm to generate depth profile

(20 Å) HfO_2/SiO_2/Si



Comparison between SE and ARXPS Thickness Measurements

Nominal HfO_2 Thickness (Å)	Annealed?	SE thicknesses (Å) HfO_2	SE thicknesses (Å) SiO_2	ARXPS thicknesses (Å) HfO_2	ARXPS thicknesses (Å) SiO_2
0	no	n/a	13	n/a	13
20	no	24	14	22	13
30	no	34	14	31	14
40	no	45	13	35	12
20	yes	20	14	20	12
30	yes	30	14	30	12
40	yes	41	13	34	12

Conclusions:
- XPS and SE can measure VBO and CBO
- HfO_2-Si VBO increases with annealing
- Deposition of HfO_2 and annealing of film stack both alter SiO_2 layer chemistry and energy level alignment
- ARXPS depth profile gives HfO_2 and SiO_2 film thicknesses that agree with SE