

Thin Film Users Group NCCAUS

Analysis of high-k HfO_2 and HfSiO_x dielectric films

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n **Introduction**

n Hafnium oxide and hafnium silicates are among the leading contenders for new high-k gate dielectric films. A number of papers have been published regarding characterization of these films, in which several early publications have shown depth profile data analyzed using Auger Electron Spectroscopy (AES), Quadrupole Secondary Ion Mass Spectroscopy (Q-SIMS), and X-ray Photoelectron Spectroscopy (XPS)¹⁻³. These profiles exhibited apparent extensive diffusion or migration of Hf into the Si substrate. However, further investigation using various profiling techniques indicates that this migration may be an artifact of the analysis.

n **Results and Discussion**

n Hafnium oxide films of different thickness and methods of production were analyzed using XPS, AES, Time-of-Flight Secondary Ion Mass Spectrometry (TOF-SIMS), and Q-SIMS. Depth profiling conditions were varied to evaluate the effect of changes in sputter ions, energies, currents, and angles.

n 'Chemical state' profiles from XPS show that the HfO₂ films are decomposing or dissociating (analogous to Ta₂O₅ films), leaving Hf suboxides and Hf metal. Substantially different sputter rates for Hf metal, Hf suboxides, and Si produce a highly roughened sputter crater and the appearance of Hf diffusion into the Si substrate. In addition, effects such as electron beam current and energy (AES) appear to result in increasing the apparent Hf diffusion into the Si substrate.

n Backside SIMS was employed to verify the presence of Hf within the Si substrate. In this method, a substantial amount of the Si substrate is removed from the back of a sample, and a SIMS profile is acquired from this thinned backside through the remainder of the Si substrate, through the Hf oxide film. This profile clearly shows that the Hf does not exist within the Si at the depths suggested by AES, XPS, or standard 'frontside' SIMS.

n Hafnium silicate films with different ratios of Hf to Si were examined by different techniques under varying analytical conditions. Depending on method of preparation and on Hf:Si ratios, the profile results exhibit vastly different behavior^{4,5}. At Hf:Si ratios of less than 1, scavenging of O from the silicate occurs to form HfO₂, leaving elemental Si within the bulk of the film. At Hf:Si ratios $\gg 1$, no elemental Si is observed within the profile. In both cases, at the silicate-Si interface, elemental Hf (metal) begins to appear, and the artifact of 'tailing' of Hf into the Si is observed.

n **Conclusions**

n It is apparent that 'standard' analyses techniques that work well for older or current gate materials such as SiO₂ and/or SiON, must be used with caution on high-k dielectric materials. Artifacts, especially in depth profiling techniques can give misleading results, as shown in these results. Work is currently under way to try to understand the fundamental reasons for these artifacts and to find effective way to measure relevant material parameters such as thickness, composition, etc.

Outline

- n Background and driving forces
- n High-k composition
- n Depth Profiles:
 1. HfO₂ high-k anomalies
 2. HfSiO_x materials
- n Conclusions
 - (other anomalies – time permitting)

Background Info

- n New high-k materials for next generation gate dielectrics are being tested in a number of companies.
- n Materials properties and characterization are being tested to verify theories, ascertain best-candidates, etc.
- n The preferred tests are with actual devices, i.e. make transistors & devices using high-k gate materials
- n Costs and time for electrical tests are too high (requires nearly complete device production cycle), therefore earlier in-process tests are performed.
- n Typical testing includes thickness, composition, profiles, dopant diffusion, impurities, etc.

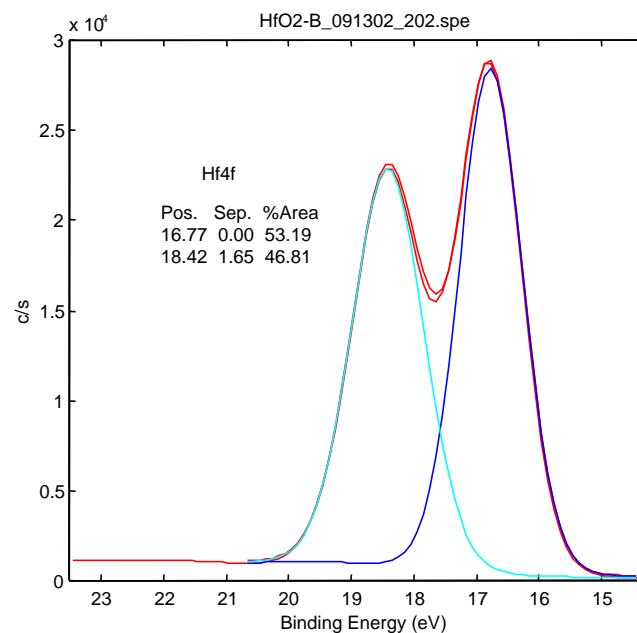
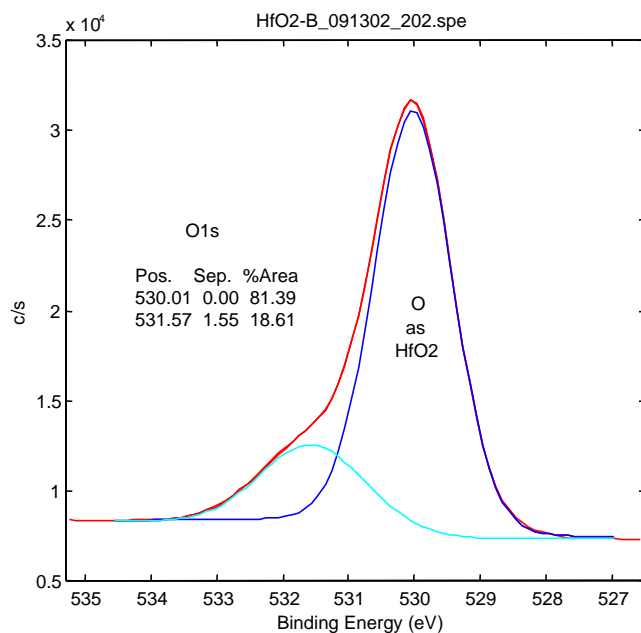
Determining and Measuring Composition and Stoichiometry of Hafnium Oxide (HfO_2) Films.

Composition and Stoichiometry

- n Some techniques (in general mode) may not be able to provide sufficient information for correct composition or stoichiometry coefficients.
 - Examples;
 - RBS may not be able to distinguish between surface O or O as interfacial SiO_2
 - \ O : Hf ratio is likely >2
 - AES may not be able to separate metal oxide from organic or other oxides P O : Hf >2 .
 - XPS may not distinguish between organic O, O as SiO_2 , or O as HfSi_xO_y P O : Hf : Si ratio \neq correct.

Composition and Stoichiometry

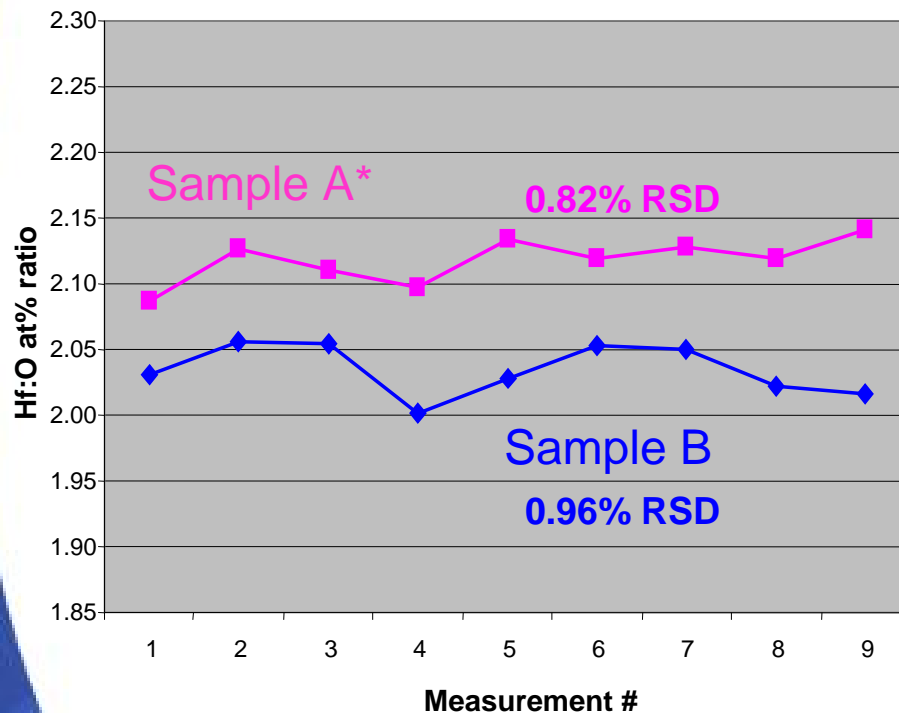
Simple measurement of O and Hf does not give correct O-Hf ratio.



O1s		C1s	Hf4f	Ratio	
63.6		11.7	24.8	Total O:Hf =	2.57 (~Hf ₂ O ₅)
51.6	12.0	11.7	24.8	Corr. O:Hf =	2.09 (~HfO ₂)

Hf:O Atom Concentration Ratio: corrected repeatability measurements.

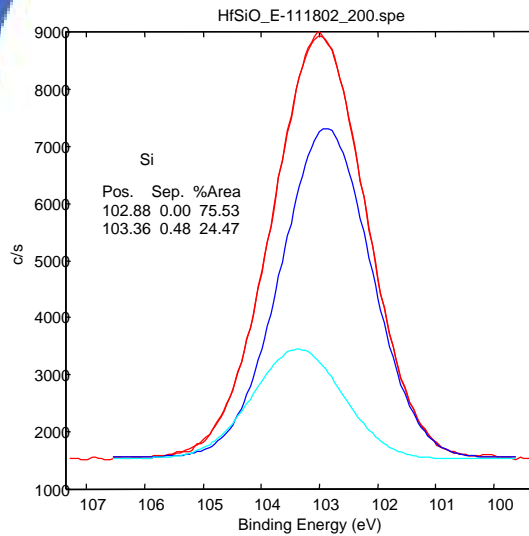
Hf:O corrected repeatability



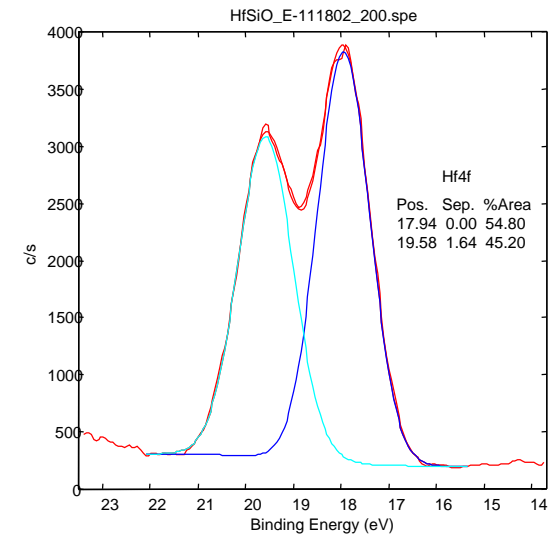
*Sample A contains appreciable Zr

- 10 measurements each
- S/N set for <0.3% precision
- Largest error from O1s curve fit repeatability.
- Data for films >9nm and pure HfO₂.
- Precision decreases with interfacial oxides, silicates, and oxidized impurities.
- IMFP/EAL correction not applied.

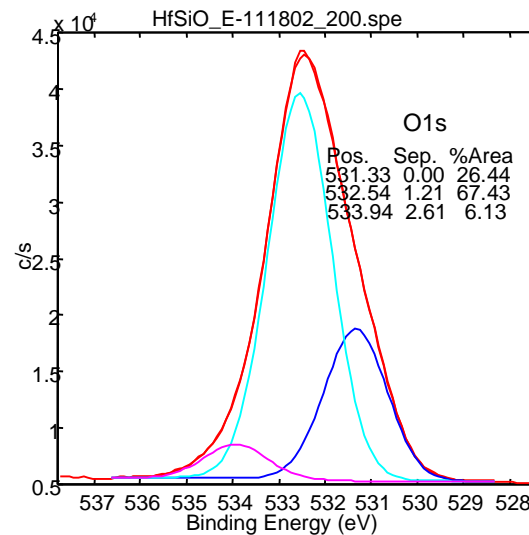
Composition and Stoichiometry



Composition and stoichiometry of HfSi_xO_y films are much more difficult to determine.



n	Atomic %
n	O1s 63.7
n	Si2p 20.8
n	C1s 10.6
n	Hf4f 4.9

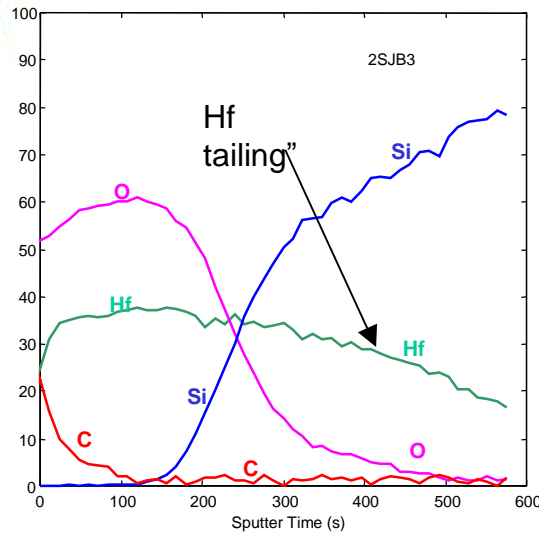


- Non-silicate O unclear
- Si suggests either
 1. 2 silicate forms
 2. Silicate + SiO_2
- Hf4f indicates single Hf state

Profiling Behavior

- n Some dielectric materials profile in a stable consistent manner & congruent sputtering e.g. SiO_2 and Al_2O_3
(i.e. profile stoichiometrically, but do not sputter stoichiometrically).
- n Profiling some materials are problematic at best. (e.g. Ta_2O_5 , GaN, InP, etc.)
 - Dissociative sputtering
 - Differential sputtering
 - Reactive sputtering
 - ...

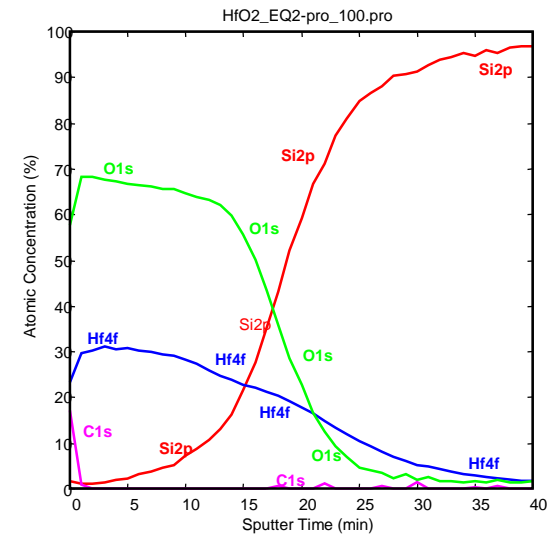
Depth Profiles of HfO₂



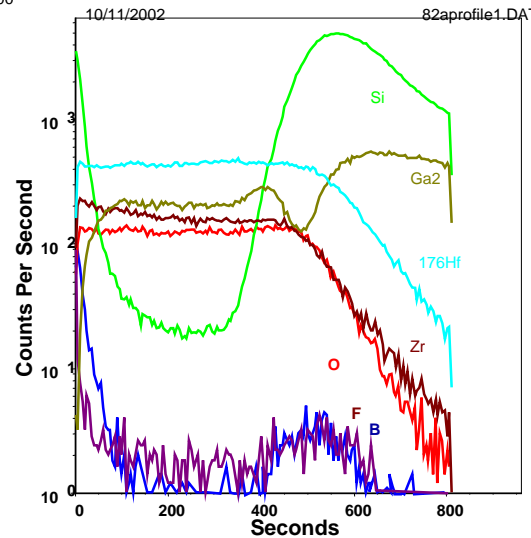
AES profile, 5keV
e⁻ 4 keV Ar⁺

TOF-SIMS profile
15keV ⁶⁹Ga

Profiles of ~8.6nm
HfO₂ film on Si
(with interfacial
SiO₂ layer)



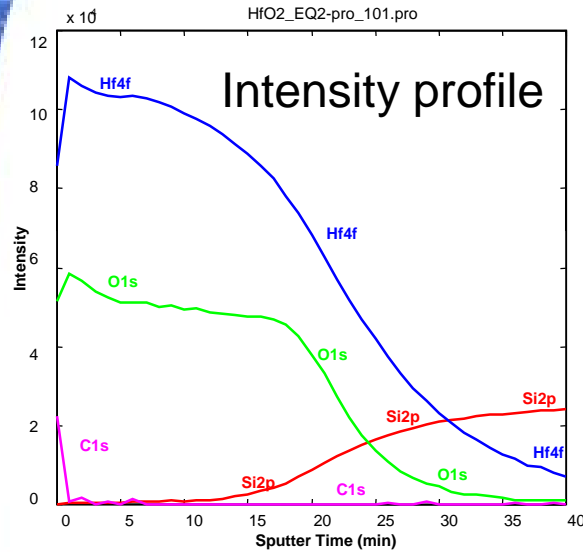
XPS profile
4keV Ar⁺



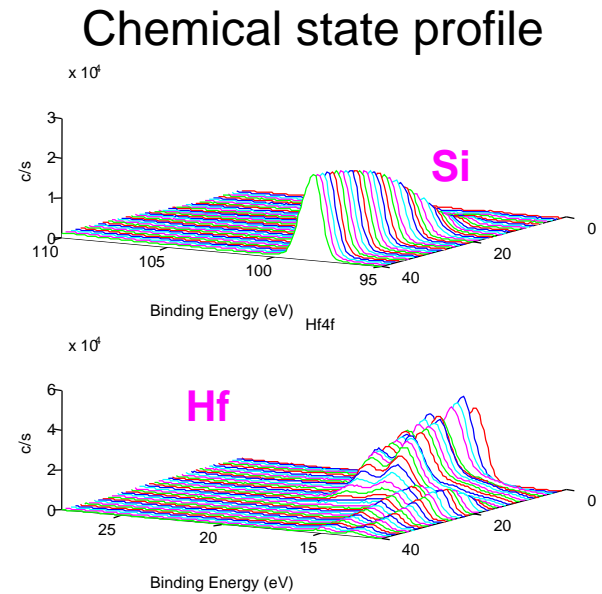
TFUG Apr. 03; WRN-CEA

All techniques exhibit
severe 'tailing' of the
Hf into the Si substrate.

XPS Depth Profiles of HfO₂



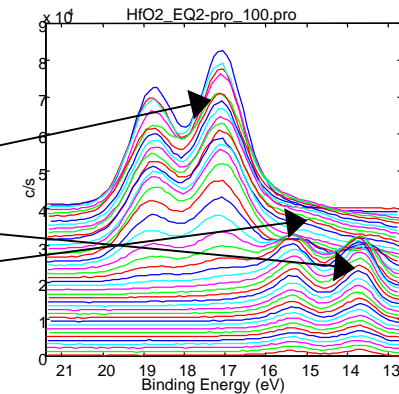
Hf metal appears at/near the Si-HfO₂ Interface.



XPS profiles of 86Å HfO₂ clearly show the presence of Hf⁰ in the Si substrate.

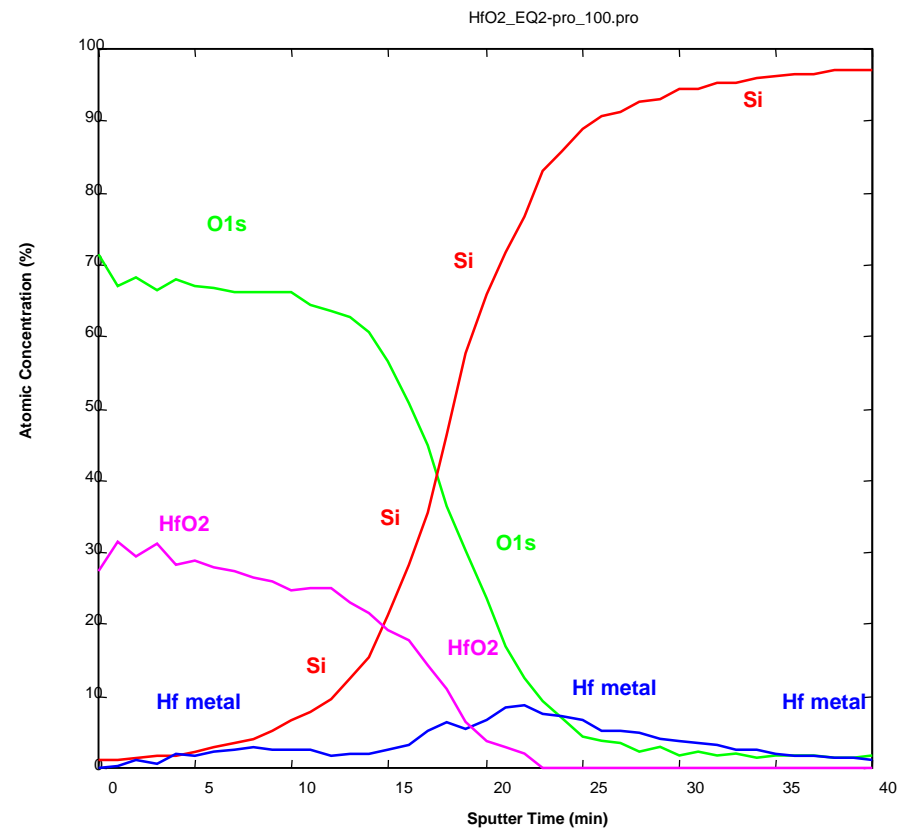
Is this real?

B.E. are consistent with HfO₂, Hf⁰, Hf sub-oxides.



Chemical State XPS Profile of 86Å HfO₂ film on Si.

- n NLLS fit using Hf4f as HfO₂ (@16.3eV) + Hf4f as Hf⁰ (at 13.8eV)
- n Thin interfacial SiO₂ estimated at 5-7Å present (but not shown for clarity)
- n Hf-sub oxides present in HfO₂ film shortly after sputtering starts. Sub-oxide component partially overlaps Hf⁰ component within layer.



Implications and Questions from HfO₂ Depth Profiles

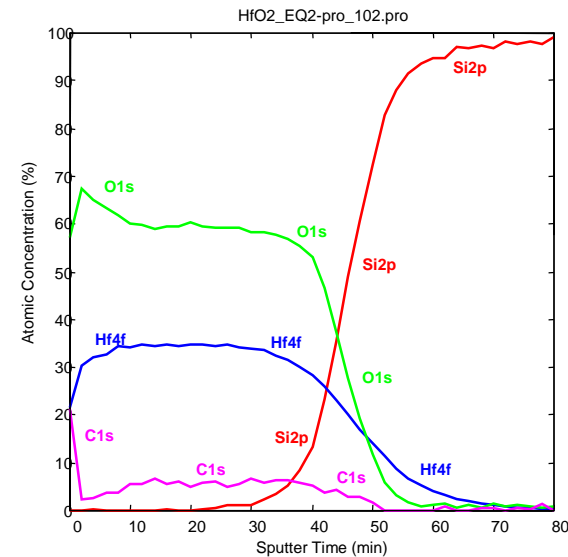
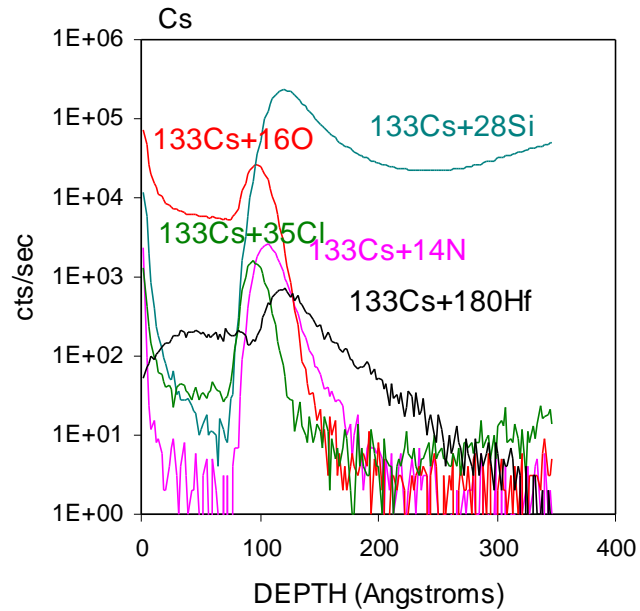
- n Presence of Hf metal is obviously not a desirable property for gate dielectric.
- n LLS fits and selective m/e can force profile to appear 'normal', i.e. no tailing.
- n Can we confirm/prove that metal formation is an artifact?
- n Is the artifact dependent on technique, acquisition method, ion species, K.E., etc.
- n Does this effect occur for doped HfO₂ or HfSiO?
- n Is there any way to avoid this if it is an artifact?

(Refer also to the presentation at AVS 2002 by C. Gondran, J. Bennet, and M. Beebe from Sematech)

Hf 'tailing' in HfO₂ profiles.

- n Extent of 'tailing' is not a function of HfO₂ thickness
(see Sematech AVS presentation)
- n 'Tailing' effect appears to depend somewhat on dopants and/or impurities in dielectric film.
- n Ion species, energy, & angle-of-incidence do not affect presence or extent of 'tailing' appreciably.

Examples



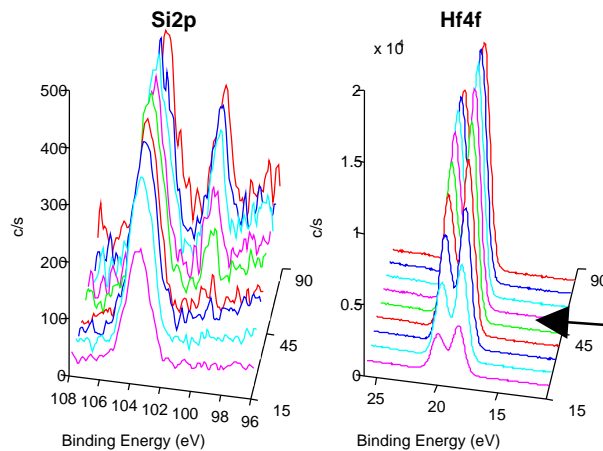
n SIMS

- CsM⁺ shows strong tail,
- M⁺ has less pronounced tail.
- M+O is self-fulfilling profile

n XPS

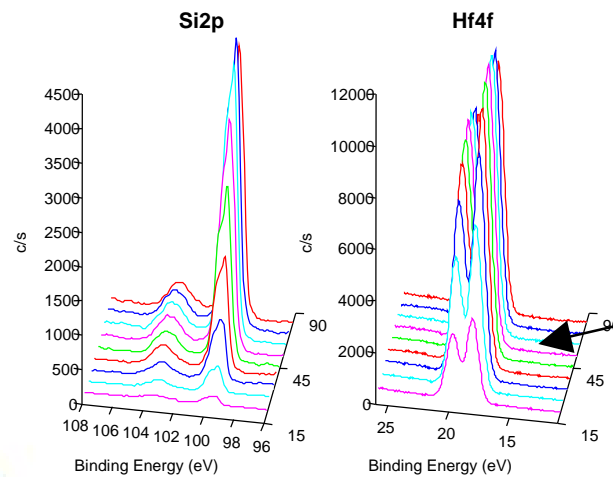
- ALD film with high C content
- w/ C, tail extent is reduced (compare to no C).
- Tailing inversely proportional to N doping?

Is 'tailing' real or not? Test 1



n Angle-resolved XPS of 86Å HfO₂ film, profiled also by XPS, TOF, SIMS.

v No evidence of Hf metal in the Si (or at all).



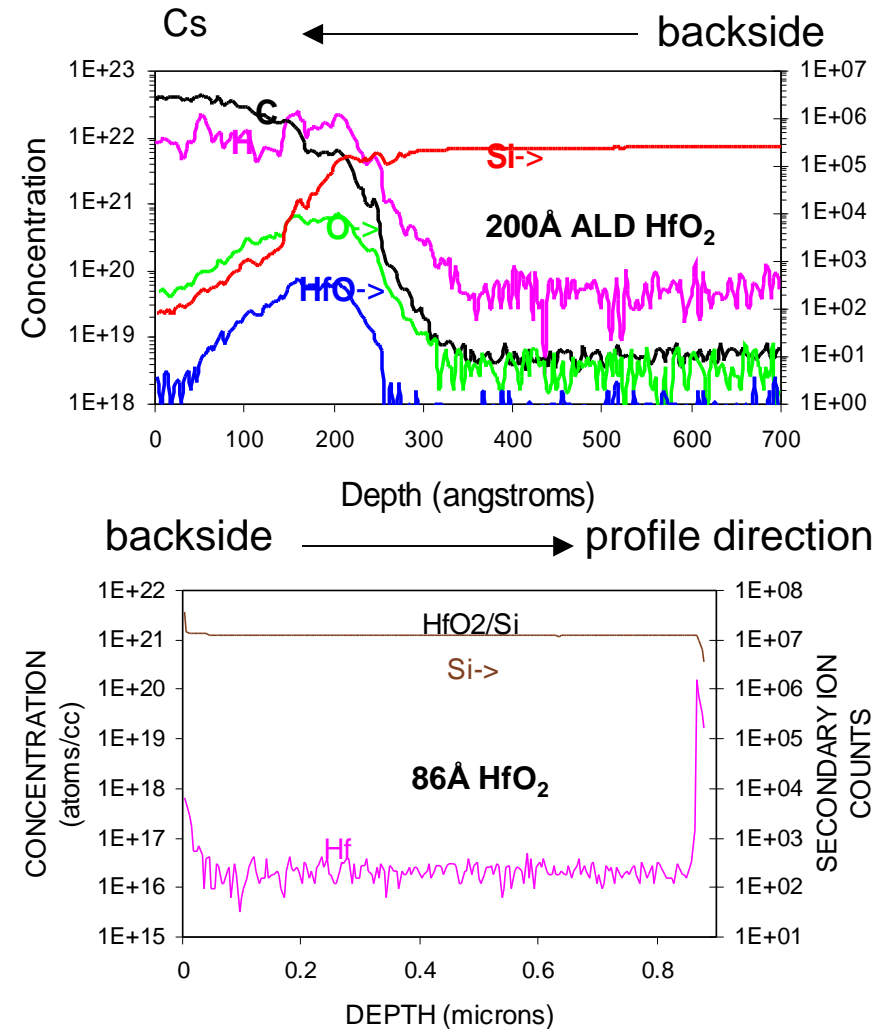
n ARXPS of 40Å HfO₂ layer.

v No evidence of Hf metal present in the sample.

Is 'tailing' real or not? Test 2

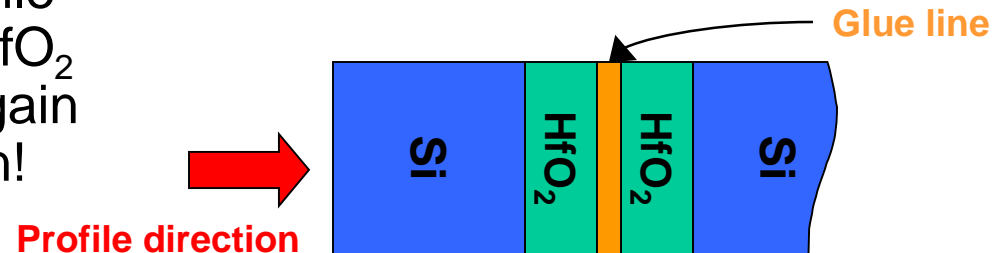
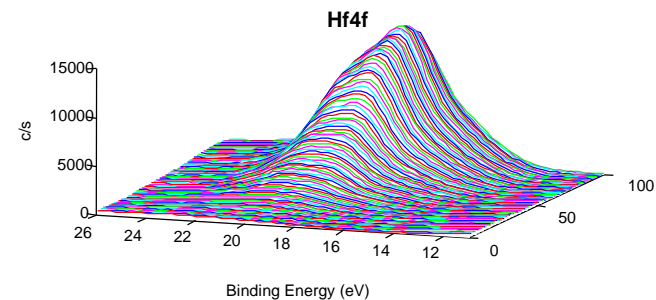
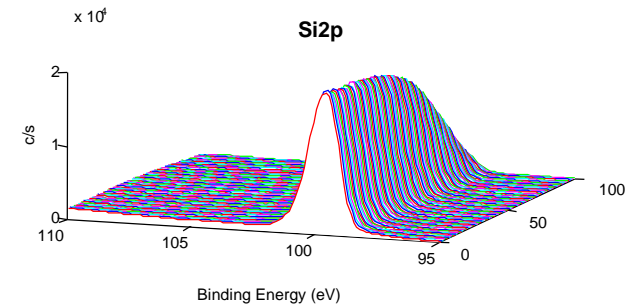
- n Backside SIMS, i.e. a reverse profile from the Si substrate into the HfO_2 film.
- n Requires special sample preparation a'la TEM x-section; thin HfO_2 films on Si are glued face-to-face then backside thinned.

∅ **Backside SIMS shows no Hf in the Si substrate!!**



Is 'tailing' real or not? Test 3

- n *Coup de grace* is XPS backside profile of HfO₂ film.
- n No Hf metal is observed in the Si substrate.
 - Note however, that due to DOI (IMFP, EAL), Hf as HfO₂ begins to appear within Si region.
- n Continuation of profile through glue line, HfO₂ layer, and into Si again shows Hf⁰ formation!

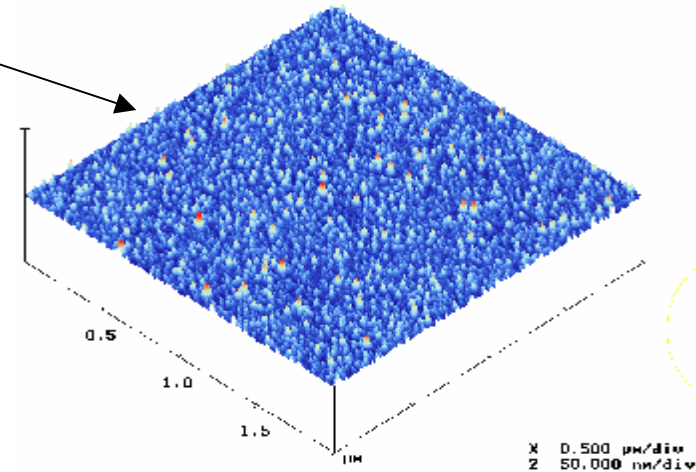
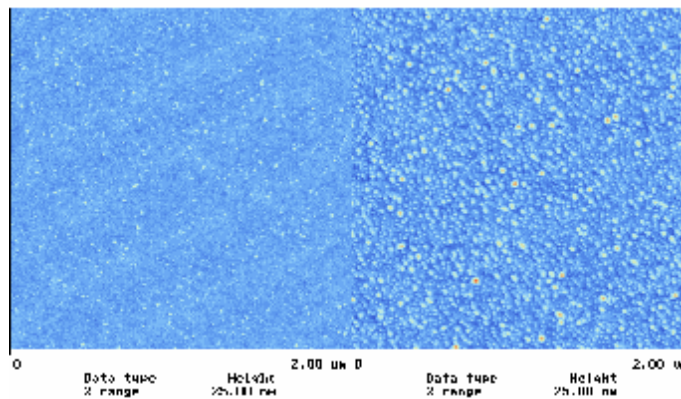


Conclusion #1

- n 'Tailing' of Hf into the substrate in ion sputter profiles is simply an artifact of the sputtering process.
- n ARXPS of thin HfO₂ films demonstrates that there is no metallic Hf present at or below the interface, but ion sputter profiling of the same sample shows extensive Hf metal tailing.
- n Backside SIMS demonstrates (with superior detection limits to XPS) that Hf does not exist in the Si substrate.

Causes for 'tailing'?

Top of sample Bottom of crater.



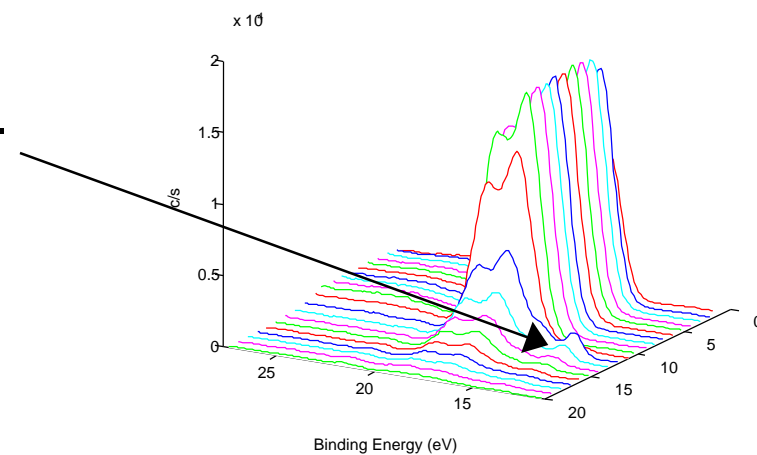
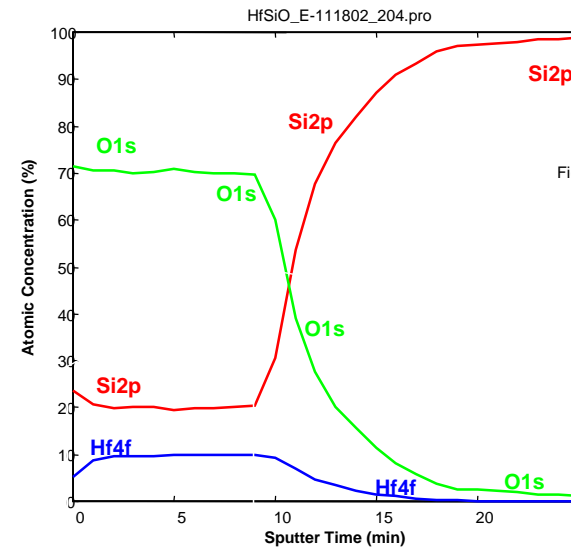
$$R_a = 0.53\text{nm}$$

$$R_a = 2.52\text{nm}$$

- Roughening by the ion sputter process does not account for the long depth of penetration by the Hf into the Si. (see also Sematech AVS presentation).
- Large mass difference between Hf and Si plus large differential sputtering, knock-on, localized heating, etc. may result in Hf 'dissolving' into Si. Analogous to Au on Si profiles.

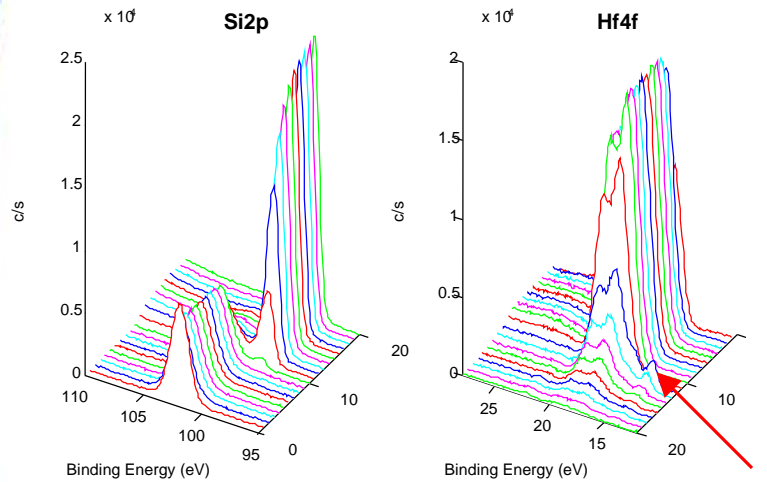
Addition of Si: Profiles of HfSiO

- n Profiles of thin hafnium silicate layers behave differently than HfO₂
- n Behavior depends on Hf-to-Si ratio
- n Regardless of Hf:Si ratio, at interface, Hf metal is seen but tail extent is usually small. (compare to HfO₂ profile).



HfSiO Profile Behavior

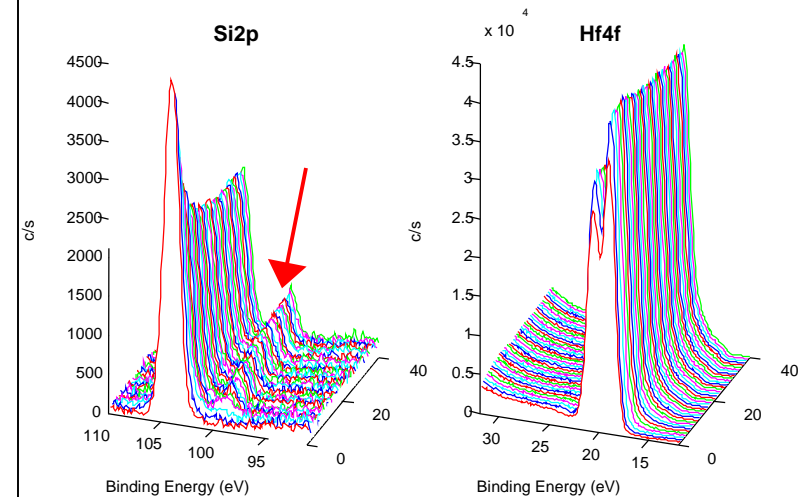
Hf:Si \approx 1:2



n At Hf:Si <1:

- Hf remains as HfSiO₄ through the film.
- **Hf forms Hf⁰ at interface but tailing is usually short.**
- Si as silicate (102.5eV) is ~const. through film.

Hf:Si \approx 2:1

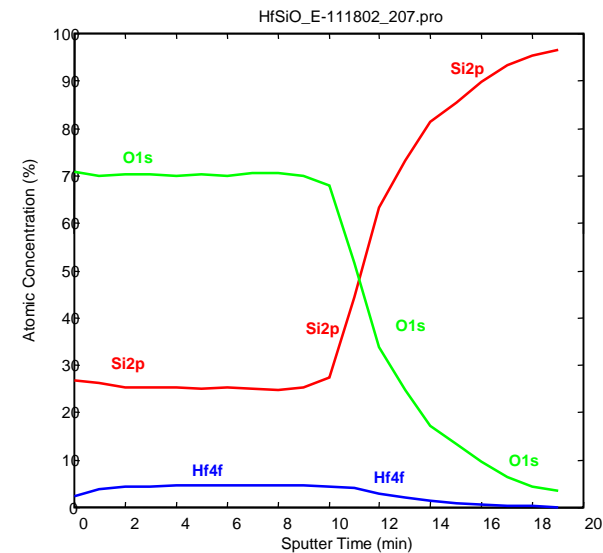
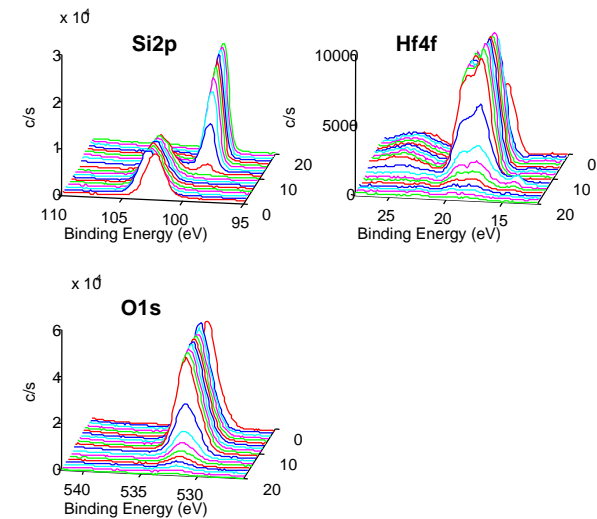


n At Hf:Si >1 (?):

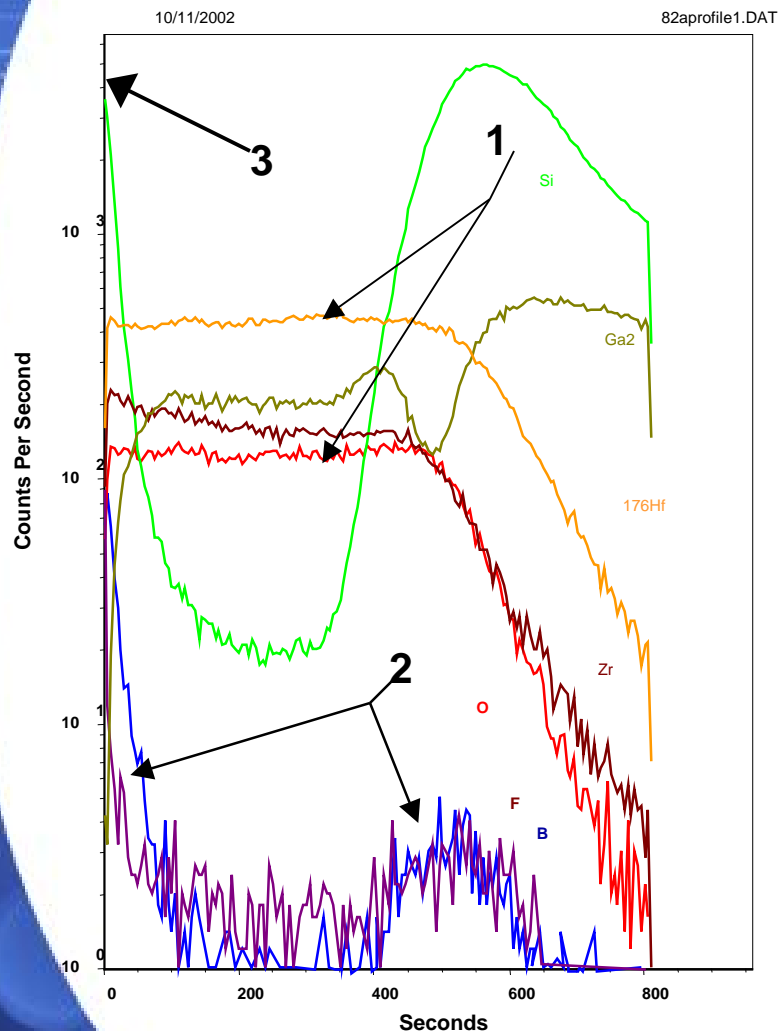
- Hf remains as HfSiO₄ through the film w/ small sub-oxide.
- **Shortly after sputter, Si shows silicate/oxide + Si⁰!!**
- **Hf scavenges O from Si to maintain HfSiO₄!!!**

Conclusion #2 HfSiO_4

- n Profile anomalies in silicates not well understood yet.
- n For $\text{Hf:Si} < 1$ (?)
 - Film is probably $\text{HfSiO}_4 + \text{SiO}_2$
- n For $\text{Hf:Si} > 1$ (?)
 - Film is likely $\text{HfO}_2 + \text{HfSiO}_4$
- n Insufficient range of Hf:Si sample to determine sputter process chemistry.

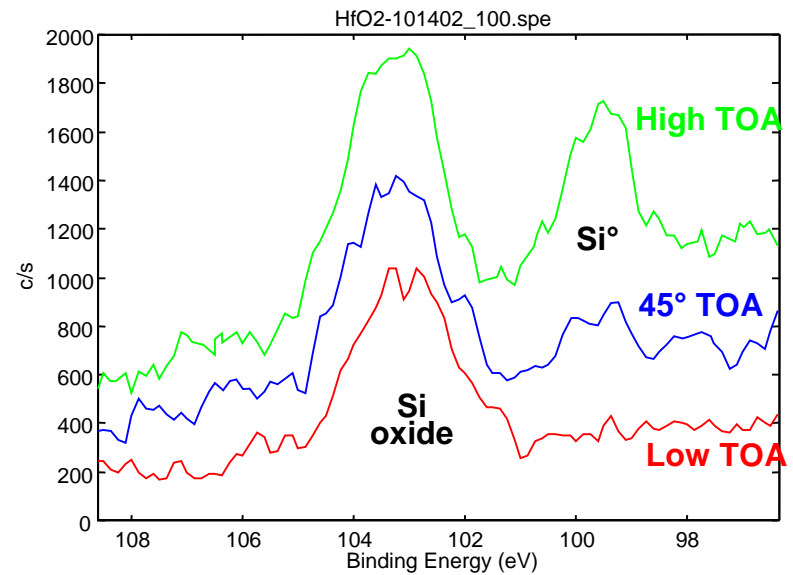
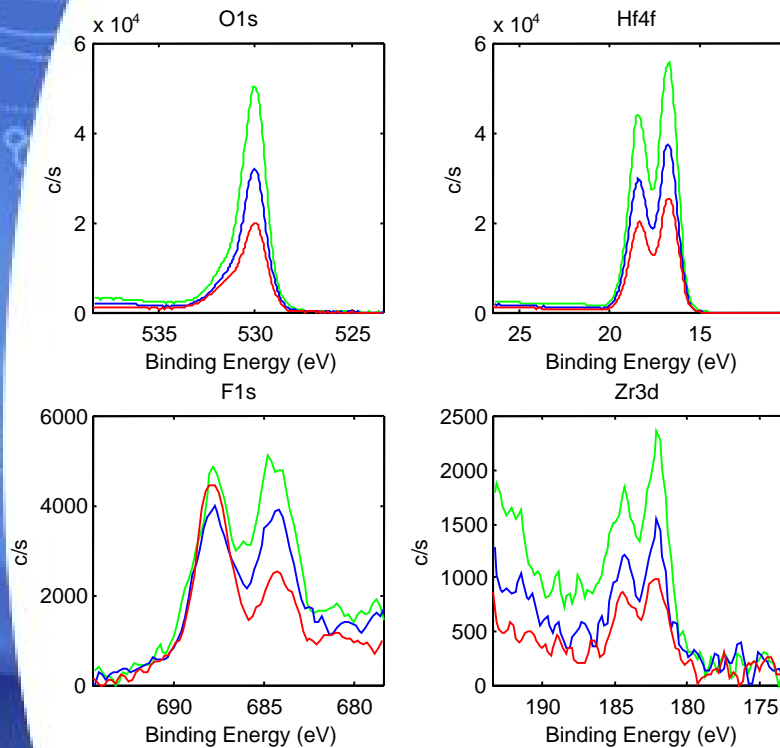


Other 'artifacts': Anomalies in TOF-SIMS of HfO₂



- n Nominal 86Å HfO₂/Si film (by MOCVD?).
- n Test of TOF for profiling composition:
 1. Hf and O are flat through the layer – minimal matrix problems - maybe.
 2. TOF shows a surface and interfacial F layer + high Zr impurity.
 3. (anomalously high) TOF suggests that there is a high surface Si concentration.
 4. Acquisition conditions not optimized?

Other 'artifacts': ARXPS of HfO₂



XPS shows Zr and F.
ARXPS confirms surface
and interface F layer.

XPS composition shows much lower surface Si than expected from TOF.

TOA	O1s	Si2p	Hf4f
30	71.1	1.8	27.0
45	71.4	1.4	27.2
75	71.8	1.6	26.6

Acknowledgements

- n Gary Goodman, SIMS group
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- n Gordan Chao, SPM
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