Multi-technique Approach for Determination of Crystalline Phase and Electronic Structure of Atomic Layer Deposited $Hf_{1-x}Zr_xO_2$

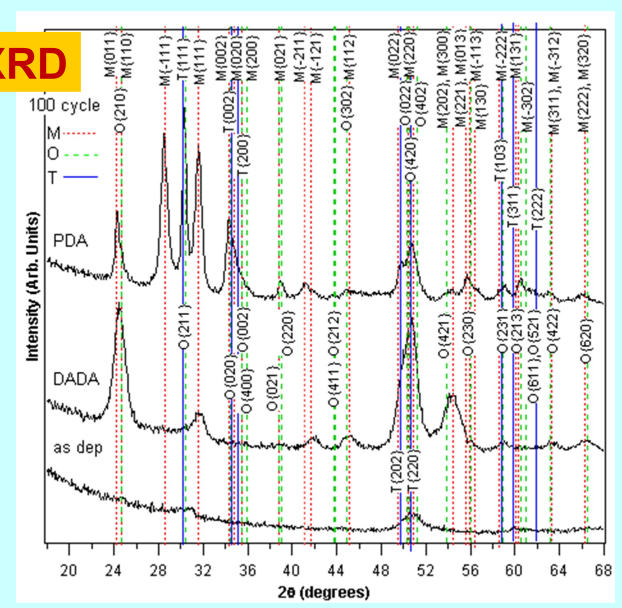
Relja Vasić,[1] Steven Consiglio,[2] Robert Clark,[2] Kandabara Tapily,[2] Shawn Sallis,[3] Bo Chen,[4] David Newby, Jr,[4] Manasa Medikonda,[1] Gangadhara Raja Muthinti,[1] Eric Bersch,[1,*] Gert Leusink,[2] and Alain Diebold[1]

[1]College of Nanoscale Science & Engineering, University at Albany, 257 Fuller Road, Albany, NY 12203, USA
[2]TEL Technology Center, America, 255 Fuller Road, Albany, NY 12203, USA
[3]Department of Physics, Applied Physics and Astronomy, Binghamton University, Binghamton, NY 13902, USA
[4]Department of Physics, Boston University, 590 Commonwealth Avenue, Boston, MA 02215, USA
[*]SEMATECH, 257 Fuller Road, Albany, NY 12203 (present address)

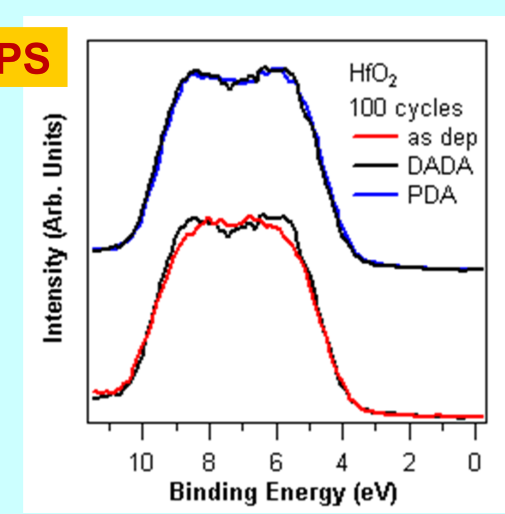
BACKGROUND

- Scaling of MOSFET devices requires decreasing the equivalent oxide thickness of the gate dielectric and/or increasing its dielectric constant (k).
- As a replacement for SiO_2 based gate dielectrics, Hf-based dielectrics have been chosen.[1]
- HfO_2 with an admixture of ZrO_2 has the potential to provide a higher k value via tetragonal phase stabilization as opposed to the thermodynamically preferred monoclinic phase which is typically obtained for HfO_2.[2-3]
- Our previous investigation focused on crystallinity of thin HfO_2 films by a multi-technique approach combining grazing incidence X-ray diffraction (GIIXRD), along with the identification of signature spectral features from X-ray photoemission spectroscopy (XPS) valence band and spectroscopic ellipsometry (SE) measurements which were indicative of crystallinity and/or presence of monoclinic phase.[4]

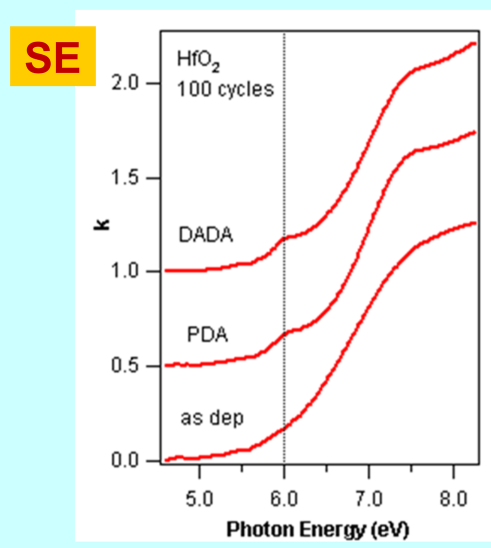
GIIXRD



XPS



SE



peak splitting -> crystalline

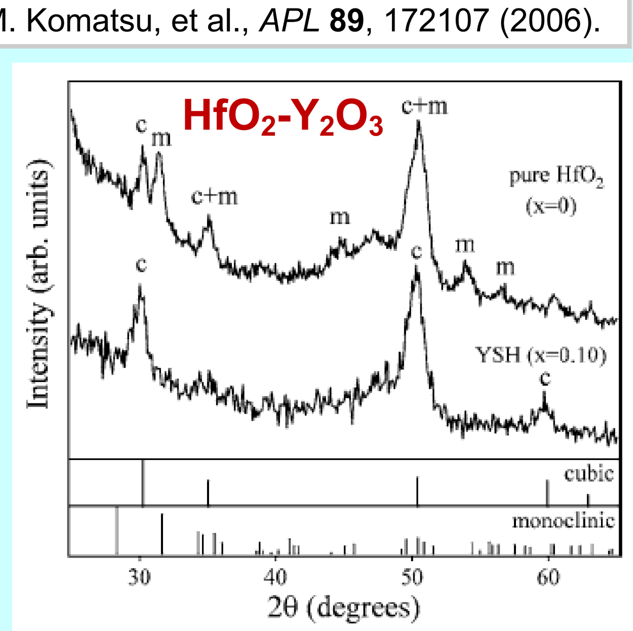
absorption feature at ~6eV -> monoclinic

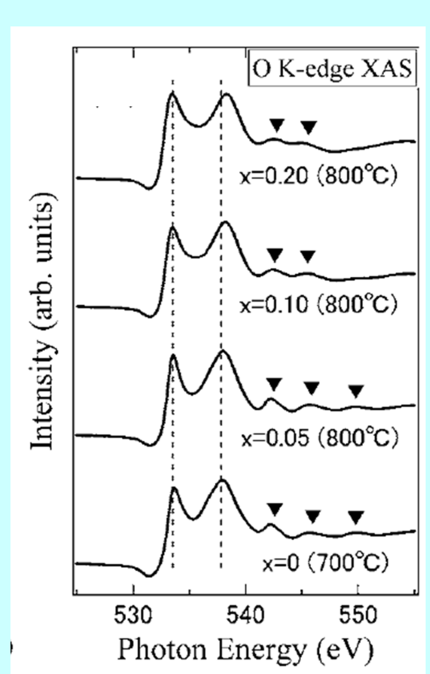
APPROACH/TECHNIQUES

- In this study we extend the multi-technique approach by utilizing X-ray absorption spectroscopy (XAS) to study $Hf_{1-x}Zr_xO_2$ films grown by a cyclical deposition and annealing scheme, which is termed DADA (20 ALD cycles followed by annealing in an inert gas repeated 5 times).[5,6]
- GIIXRD and XAS were performed at beamline X20A and X1B, respectively, at the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory.
- XPS was performed in a laboratory based XPS system with a monochromatized Al Kα source.
- SE was measured for λ range 150–1000 nm using a Woollam vacuum ultraviolet- variable angle SE (VUV-VASE).

CORRELATION OF XAS SPECTRAL FEATURES WITH CRYSTALLINE PHASE FROM LITERATURE.[7-10]:

M. Komatsu, et al., *APL* **89**, 172107 (2006).

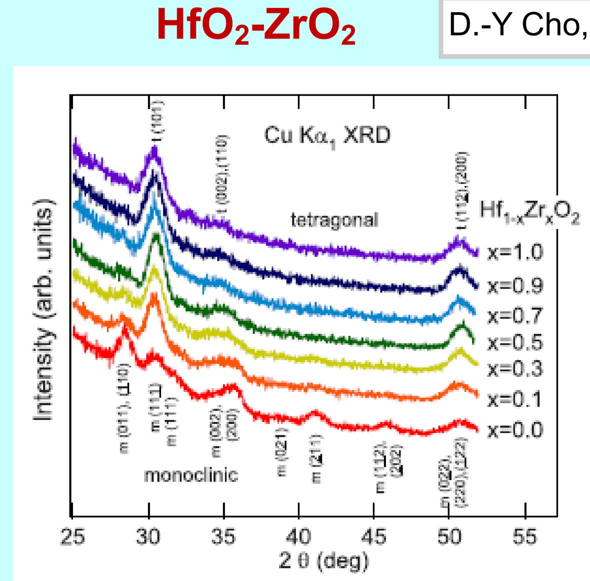


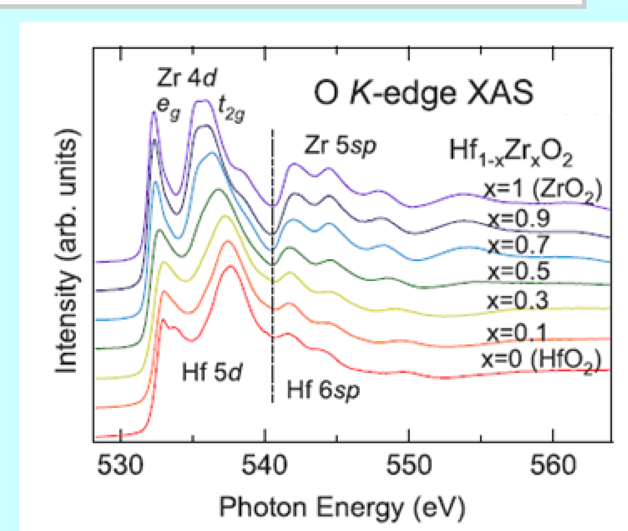


XAS -> 2 peaks = cubic, 3 peaks = monoclinic (to photon energy 555 eV)

HfO_2-ZrO_2

D.-Y Cho, et al., *Phys Rev B* **82**, 094194 (2010).



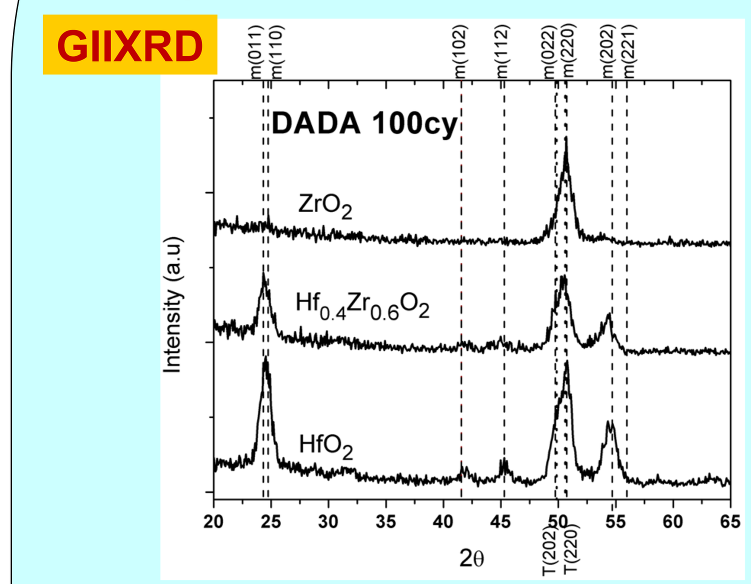


XAS -> 3 peaks = monoclinic, 5 peaks = tetragonal (to photon energy 565 eV)

RESULTS

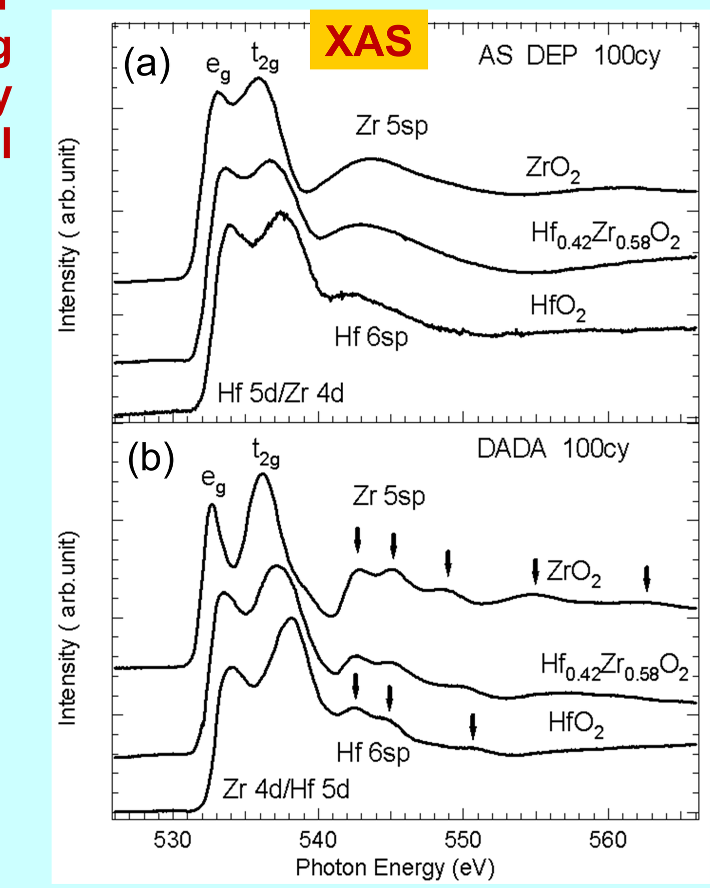
The local bonding order observed by XAS and long range order observed by XRD show the same crystal phases.

GIIXRD



GIIXRD spectra of DADA processed films; m-HfO_2, $Hf_{0.4}Zr_{0.6}O_2$ and t-ZrO_2.

XAS



XAS at O K edge for (a) as deposited and (b) DADA processed films. Arrows show peaks in sp band and extended region. Presence of 3 peaks is signature of monoclinic phase while presence of 5 peaks is signature of tetragonal phase.

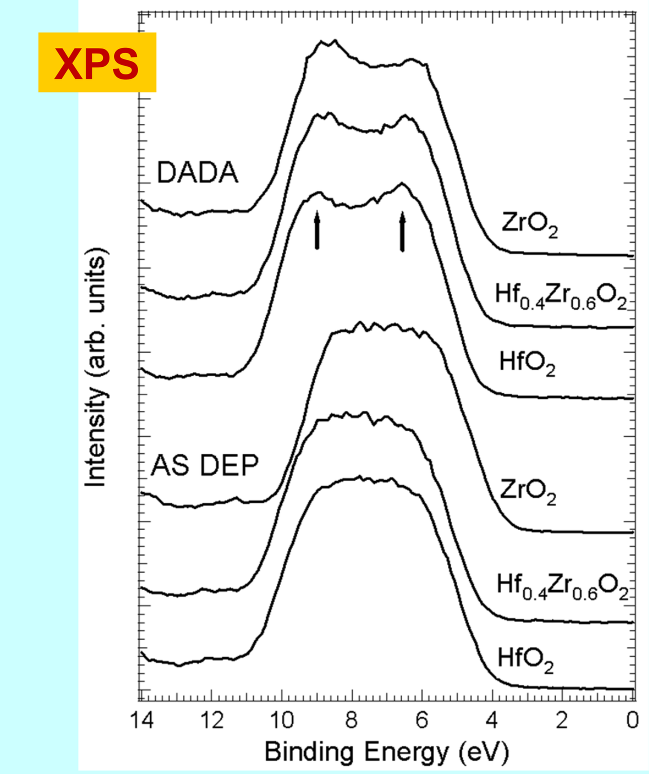
- The XAS spectra show differences in electronic structure and crystalline phase of the HfO_2, $Hf_{0.42}Zr_{0.58}O_2$ and ZrO_2 films for as deposited (no anneal) and DADA processing schemes (annealed).
- The metal d states (e_g and t_{2g} peaks associated with ligand field splitting) show larger splitting for DADA processed films due to the larger crystal field.
- The peaks in the region above ~ 540 eV are more pronounced and sharper in the DADA processed films compared to the amorphous as deposited samples.

TABLE. Conduction band minima (eV) for as deposited and DADA films at O K edge.

Sample	as deposited	DADA
HfO_2	532.0	532.4
$Hf_{0.4}Zr_{0.6}O_2$	531.6	531.9
ZrO_2	531.2	531.4

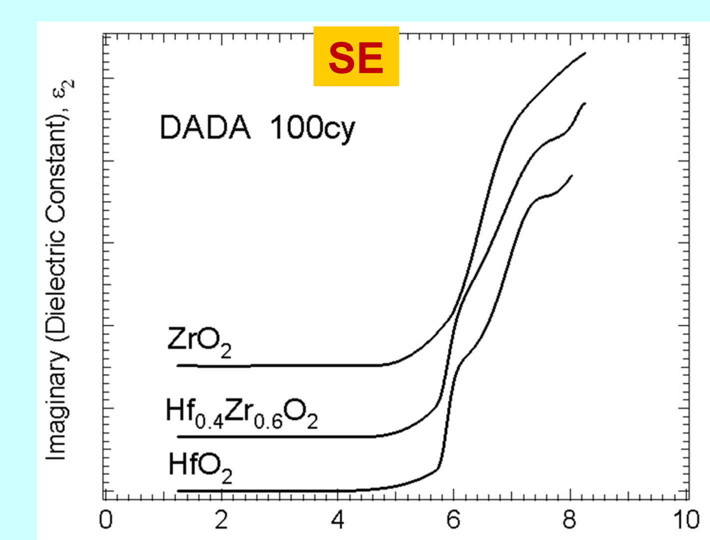
Conduction band minima is reduced by addition of ZrO_2. Relation of barrier height to increased leakage current density needs to be considered.

XPS



Double peak structure due to valence band splitting of O 2p bonding and non-bonding states indicates that the DADA processed films are crystalline. In the case of amorphous films one broad peak is observed.

SE



Absorption feature at 6 eV is unique to monoclinic phase and is absent for t-ZrO_2. Feature is consistent with theoretically predicted self-trapped polaron in monoclinic HfO_2.[12,13]

CONCLUSIONS

- A multi-technique approach was shown to be useful for a thorough determination of the crystalline phase and band structure of $Hf_xZr_{1-x}O_2$ (x=0-1) high k gate dielectric films that were deposited by atomic layer deposition using a cyclical deposition and annealing scheme.
- The combination of XPS of the valence band and SE of the optical band edge can be used to identify crystallinity and the presence of monoclinic phase for thin $Hf_{1-x}Zr_xO_2$ films.
- XAS of the conduction band was used to determine the electronic conduction band structure and corroborate diffraction data for crystalline phase and the crystal phase transformation from monoclinic to tetragonal structure due to the addition of ZrO_2 in HfO_2.

REFERENCES

1. D. G. Schlom, et al., *MRS Bull.* **33**, 1017 (2008).
2. D. H. Triyoso, et al., *J. Vac. Sci. Technol. B* **25**, 845 (2007).
3. J. Müller, et al., *Microelectron. Eng.* **86**, 1818 (2009).
4. E. Bersch, et al., *AIP Conf. Proc.* **1395**, 154 (2011).
5. K. Tapily, et al., *ECS Trans.* **45**(3), 411 (2012).
6. S. Consiglio, et al., *J. Electrochem. Soc.* **159**, G80 (2012).
7. G. Lucovsky, et al., *Microelectron. Reliab.* **46**, 1623 (2006).
8. D.-Y. Cho, et al., *Appl. Phys. Lett.* **89**, 172107 (2006).
9. M. Komatsu, et al., *Appl. Phys. Lett.* **89**, 172107 (2006).
10. S. Toyoda, et al., *J. Appl. Phys.* **97**, 104507 (2005).
11. E. E. Hoppe, et al., *Appl. Phys. Lett.* **92**, 141912 (2008).
12. D. Muñoz Ramo, et al., *Phys. Rev. Lett.* **99**, 155504 (2007).
13. M. C. Cisneros-Morales, et al., Appl. Phys. Lett. **96**, 191904 (2010).

COLLEGE OF NANOSCALE SCIENCE & ENGINEERING
UNIVERSITY AT ALBANY State University of New York

TOKYO ELECTRON

Acknowledgements

-USER CONTRACT ACKNOWLEDGEMENTS. Research carried out in part at the National Synchrotron Light Source, supported by the U.S. Department of Energy, Office of Basic Energy Sciences under Contract No.DE-AC02-98CH10886.
-We thank Professor Kevin Smith and Dr. Jude Laverock at Boston University, supported in part by the Department of Energy under Contract No. DE- FG02-98ER45680.
-We thank Jean-Jordan Sweet (IBM) and Christian Lavoie (IBM) for help with data collection at X20A.