

Electronic and electrical properties of functional interfaces studied by hard x-ray photoemission

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Outline

- **Introduction**
- **Effective WF of metal in contact with dielectric**
 - Fe/Gd/Al₂O₃/Si
- **Measurements of band line-up at metal/ferroelectric interface**
 - Fe/BaTiO₃
- **Charge redistribution in MOS stacks upon *ex situ* biasing**
 - Pt/HfO₂/Si
- **Planned experiments**

Introduction

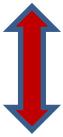
“...interface between the different materials plays an essential role in any device action. Often, it may be said that the interface is the device.”

H. Kroemer, Nobel lecture (2000)

- The scaling of the device lateral size → shrinking of individual layer thicknesses in the functional structure down to 1-10 nm scale
- Numerous non-volatile memory concepts taking advantage of the electric resistance switching in a ~10 nm thick multilayers



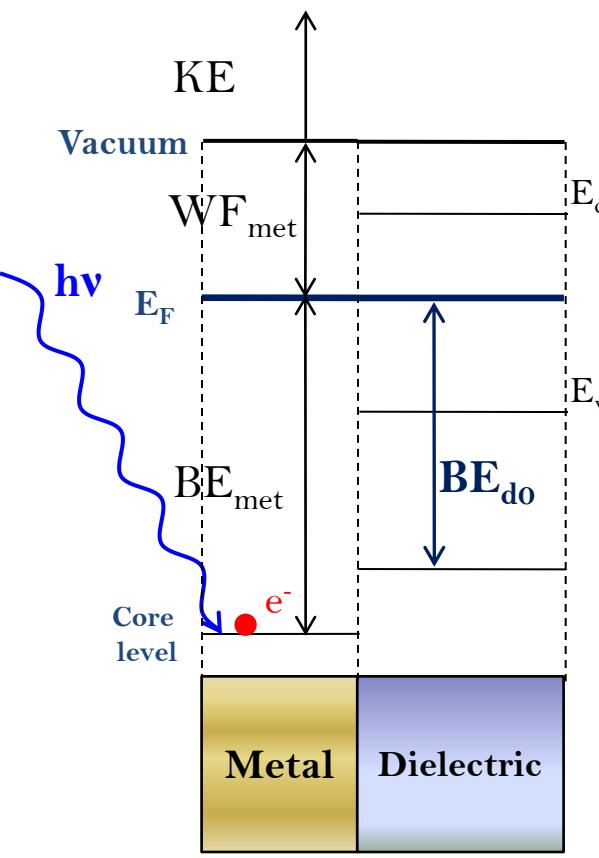
HAXPES has emerged as a powerful tool to assess the chemical and electronic properties of buried interfaces in such functional multilayered structures



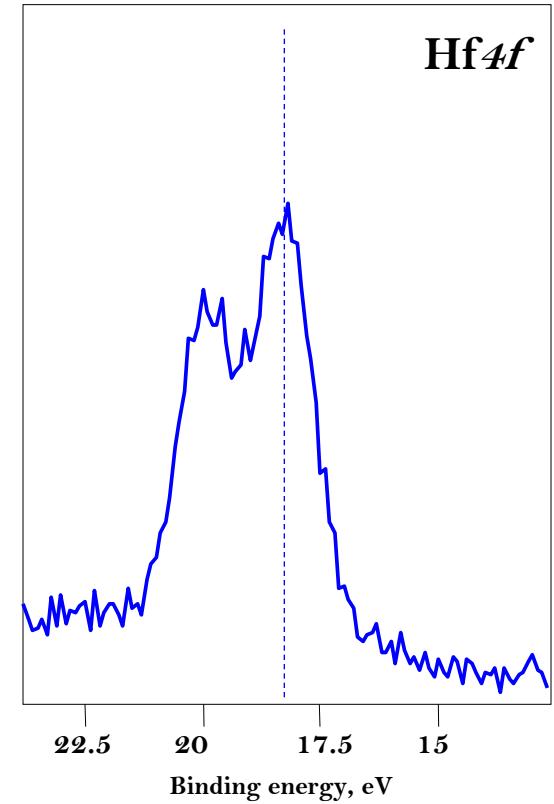
“...for most metal-semiconductor systems the determination of interface band bending from core-level photoemission lines is difficult if not impossible”

W. Monch, “Electronic properties of semiconductor interfaces”, Springer (2004)

Monitoring of interfacial electric dipole changes by PES

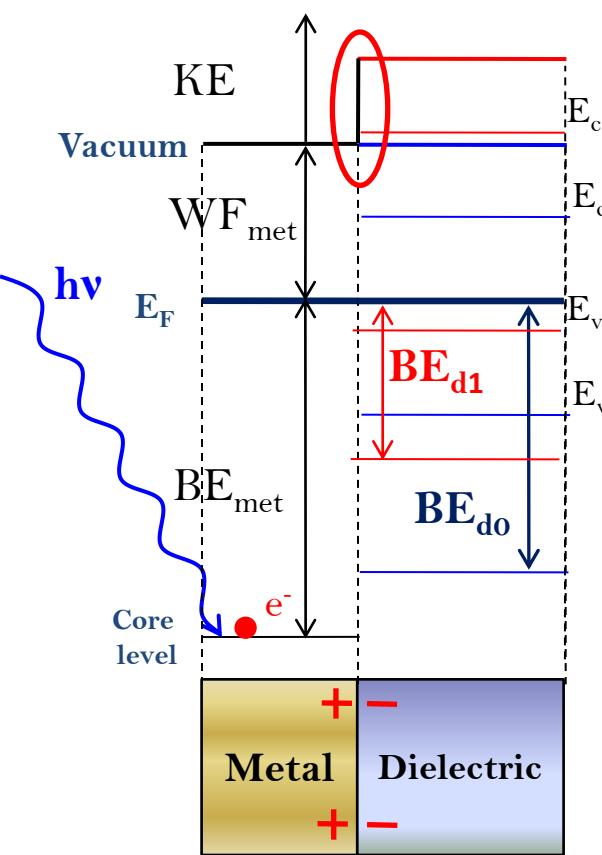


$$BE = h\nu - KE - WF$$



- XPS: core level binding energy (BE) is measured wrt. E_F
- interface electric dipole → shift of dielectric BE wrt. metal gate E_F

Monitoring of interfacial electric dipole changes by PES

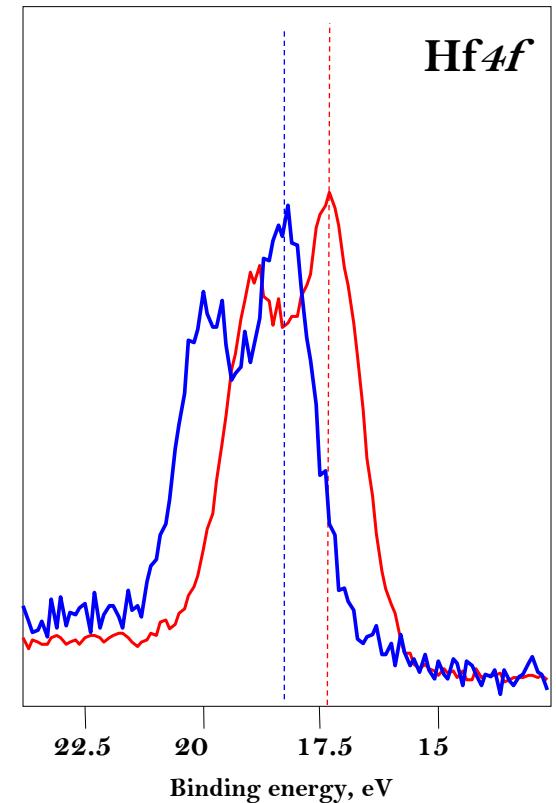


$$BE = h\nu - KE - WF$$

Δ interface dipole

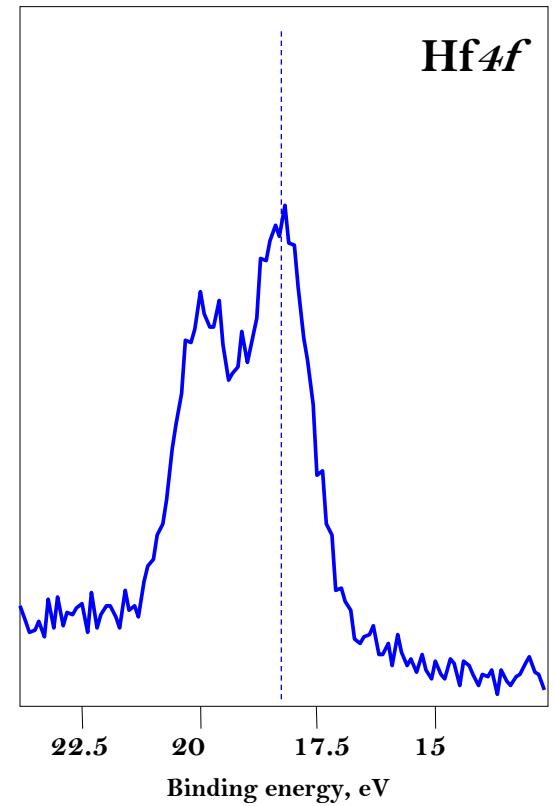
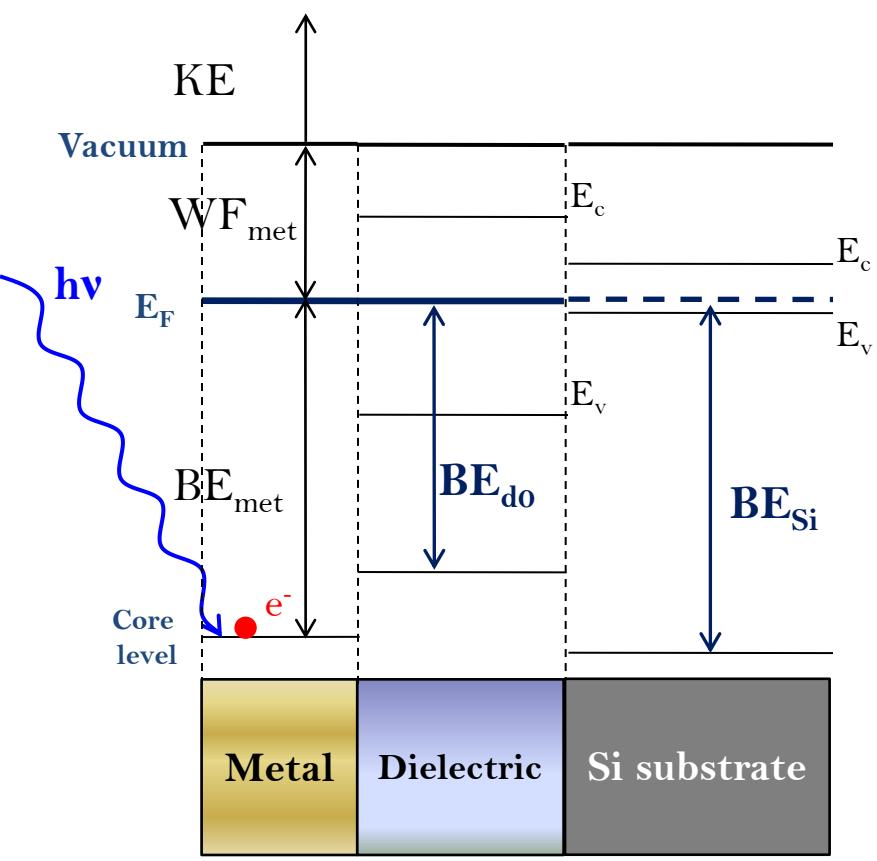


$$\Delta BE = BE_{d0} - BE_{d1}$$



- XPS: core level binding energy (BE) is measured wrt. E_F
- interface electric dipole → shift of dielectric BE wrt. metal gate E_F

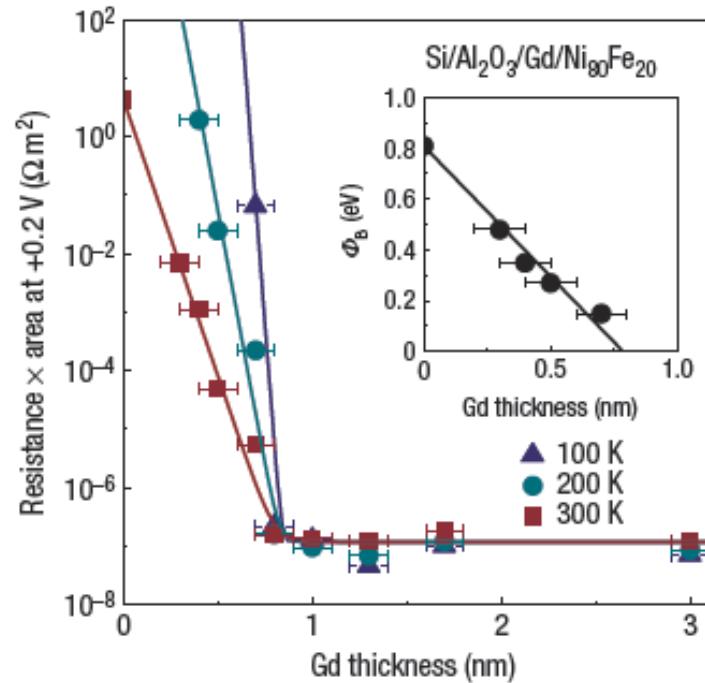
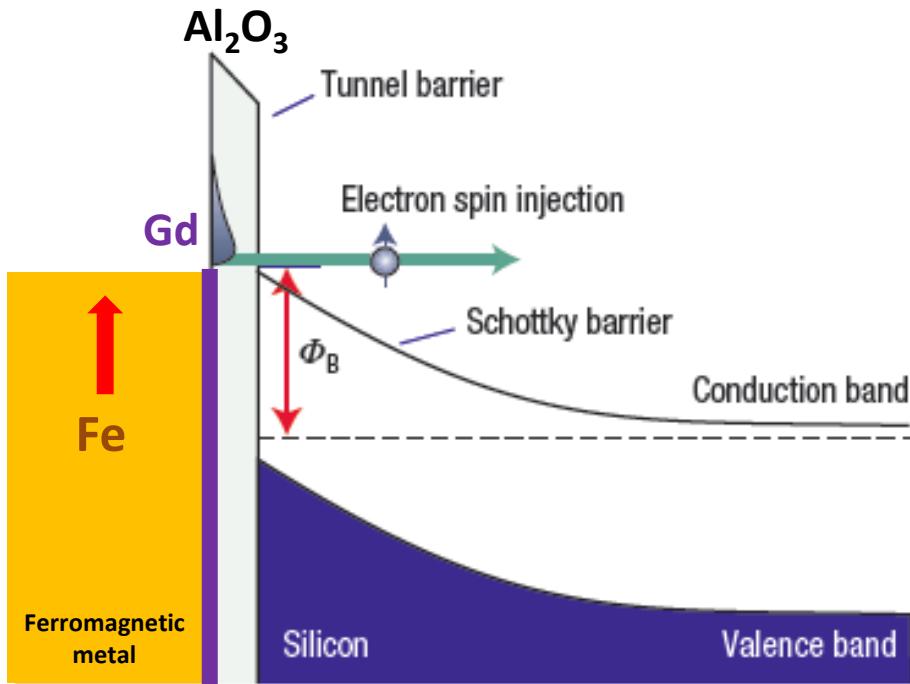
Monitoring of interfacial electric dipole changes by PES



- Realistic MOS stack is too thick for laboratory XPS analysis ($d \sim 5$ nm)
↓
- Hard X-ray photoemission spectroscopy (HAXPES): $d \sim 20$ nm →
an opportunity to analyze electronic conditions in a MOS stack

HAXPES on Fe/Gd/Al₂O₃/Si stack: motivation

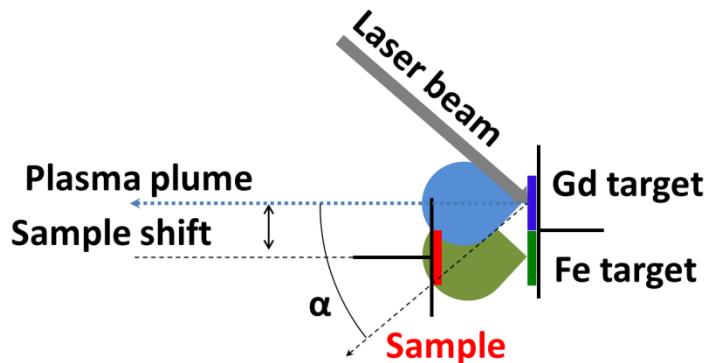
Injection of spin-polarized electron into Si



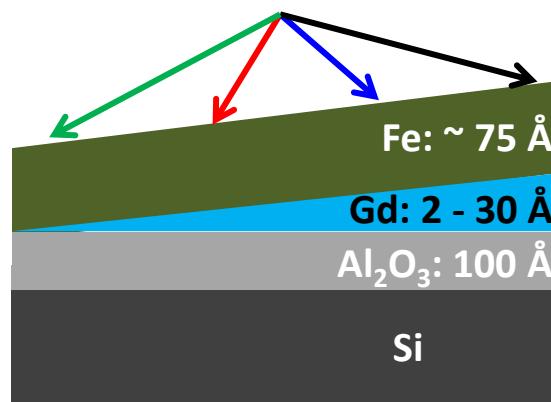
* B.-C. Min, K.I Motohashi, C. Lodder, R. Jansen "Tunable spin-tunnel contacts to silicon using low-work-function ferromagnets", Nat. Mat. 5 817 (2006).

Samples preparation, HAXPES analysis

Samples: PLD

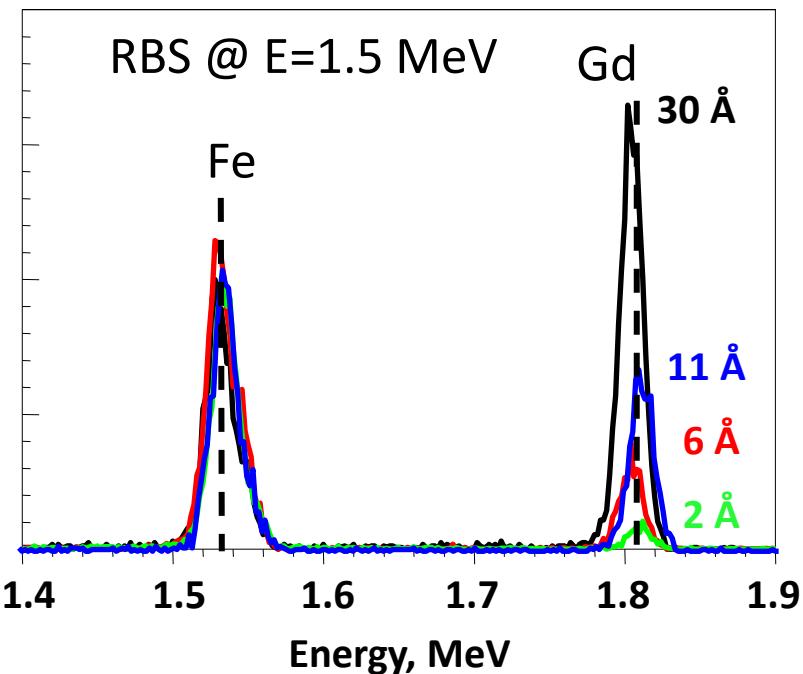


Points of RBS & HAXPES analysis

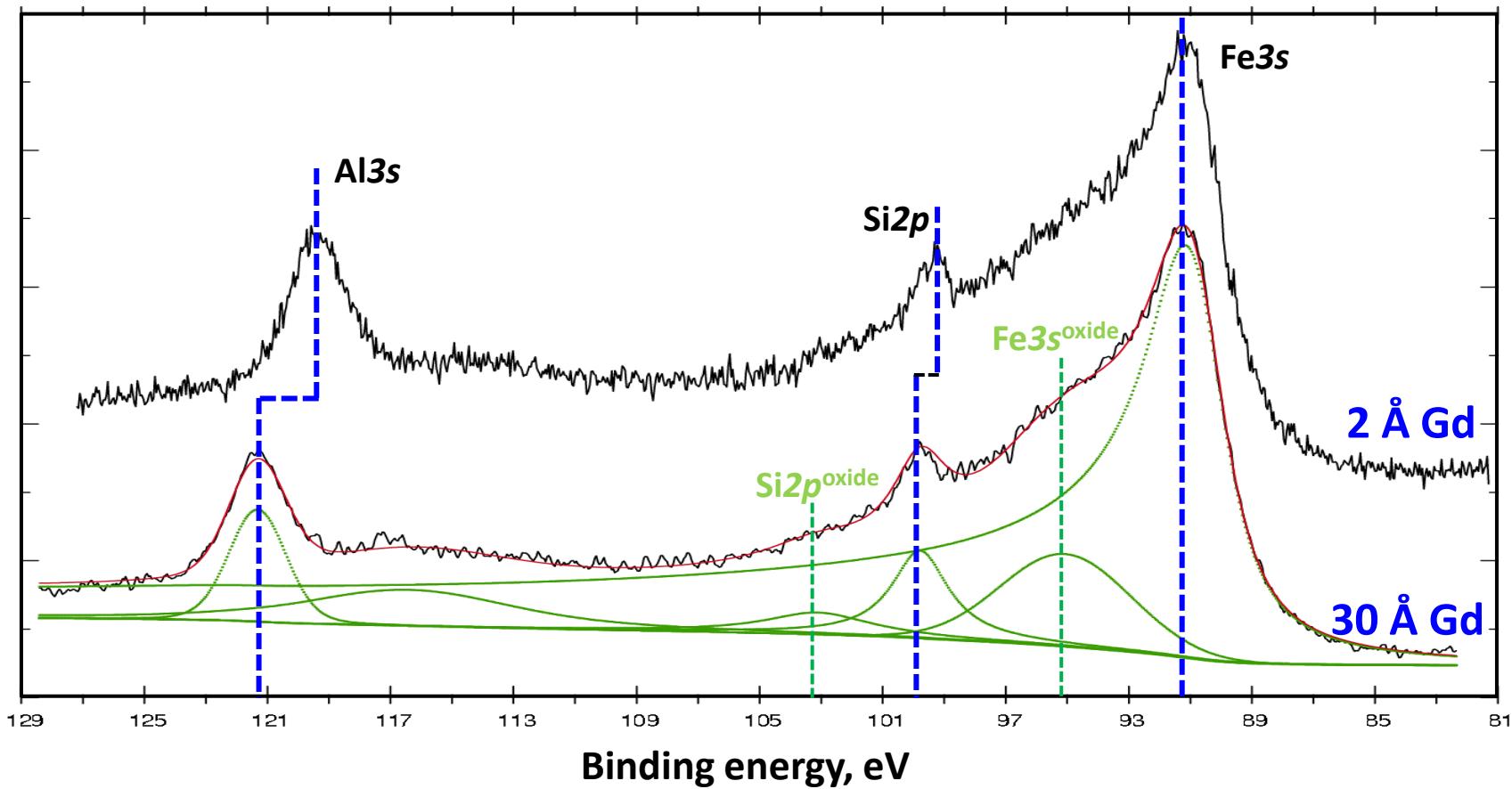


- HAXPES @ DESY: BW2 (DORIS III) and P09 (PETRA III) stations

- ✓ E = 4.5-6 keV
- ✓ normal emission

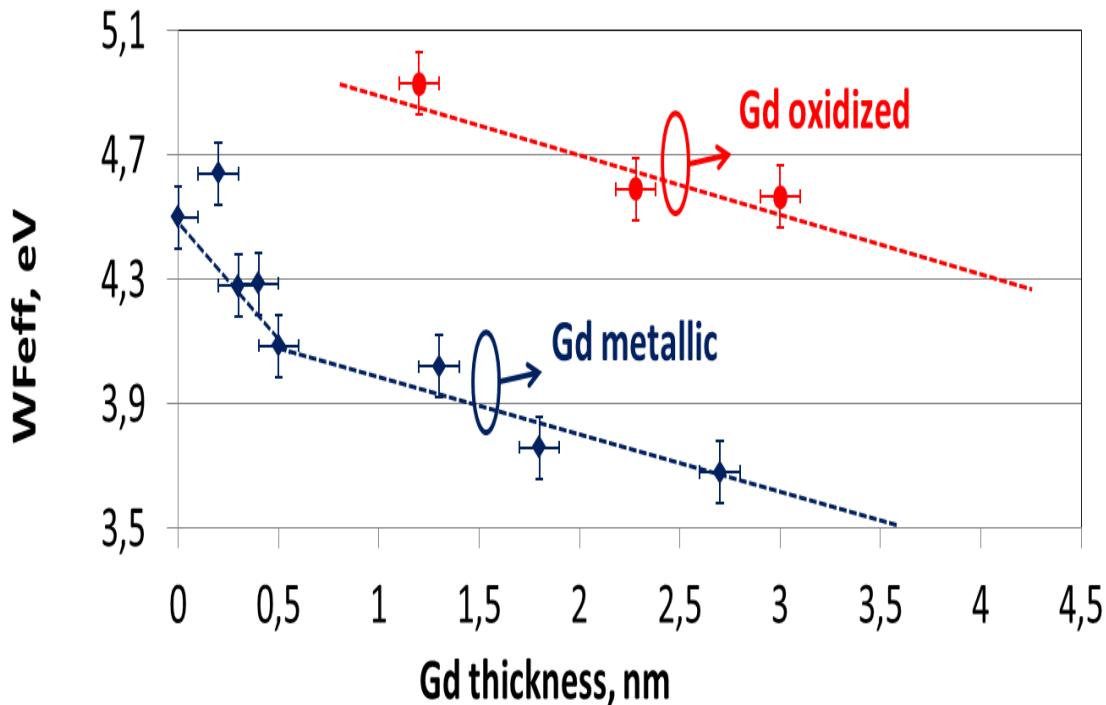
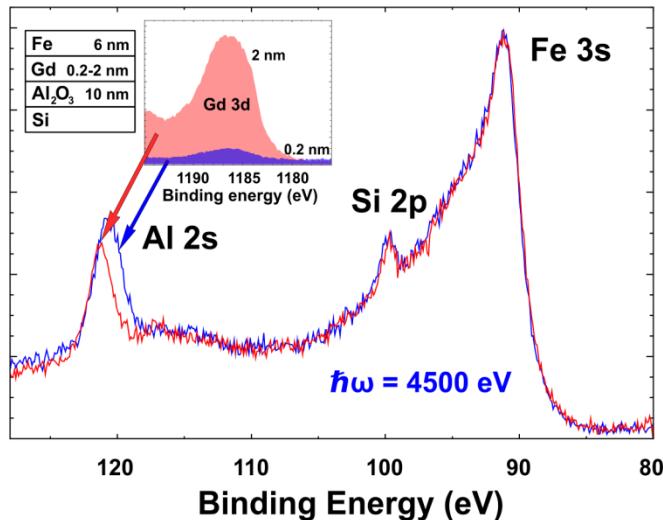


HAXPES on Fe/Gd/Al₂O₃/Si based MOS stack



- *the band alignment change at the Fe/Al₂O₃ interface is clearly visible in the Al 2s peak shift wrt. Fe 3s depending on the Gd thickness*

Effect of Gd marker on W_{eff} of Fe in contact with Al_2O_3



- *Gd IL thickness changing 0 - 3 nm in Fe/Gd/ Al_2O_3 /Si → decrease of Fe $W_{\text{eff}} = 4.5 - 3.7 \text{ eV}$*

To be submitted to JAP.

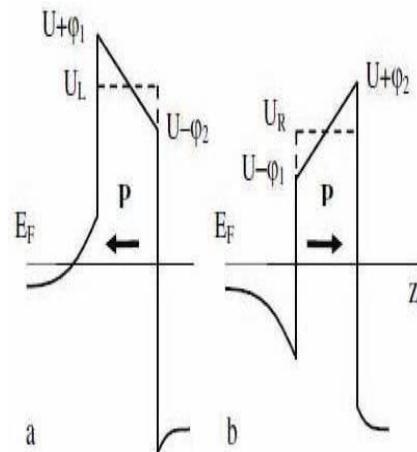
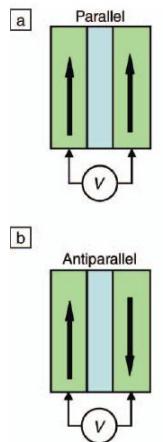
MTJ

→

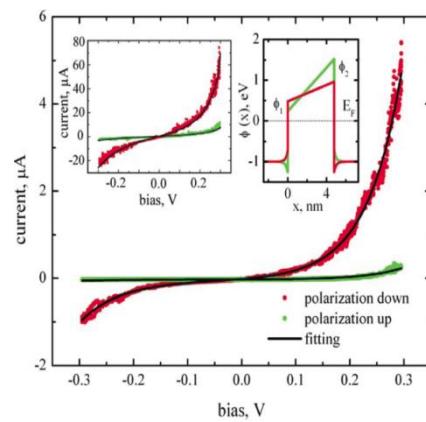
FTJ

→

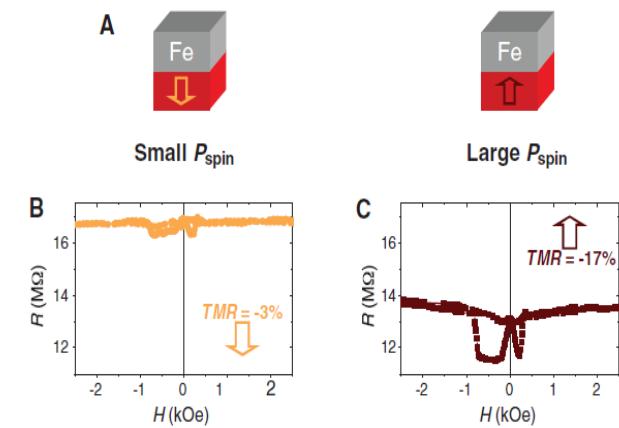
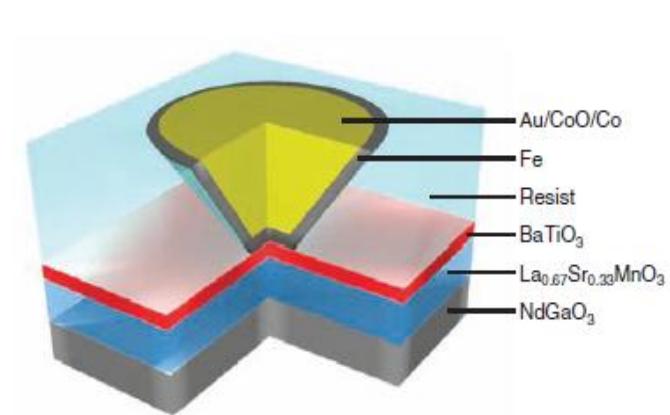
MFTJ



M. Ye. Zhuravlev, et al. Phys. Rev. Lett. 94, 246802 (2005).

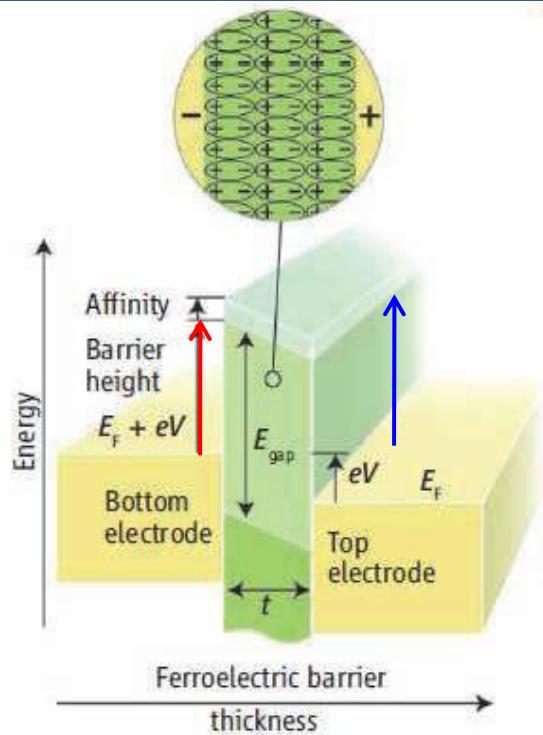


A. Gruverman, et al. Nano Lett. 9 3539 (2009).

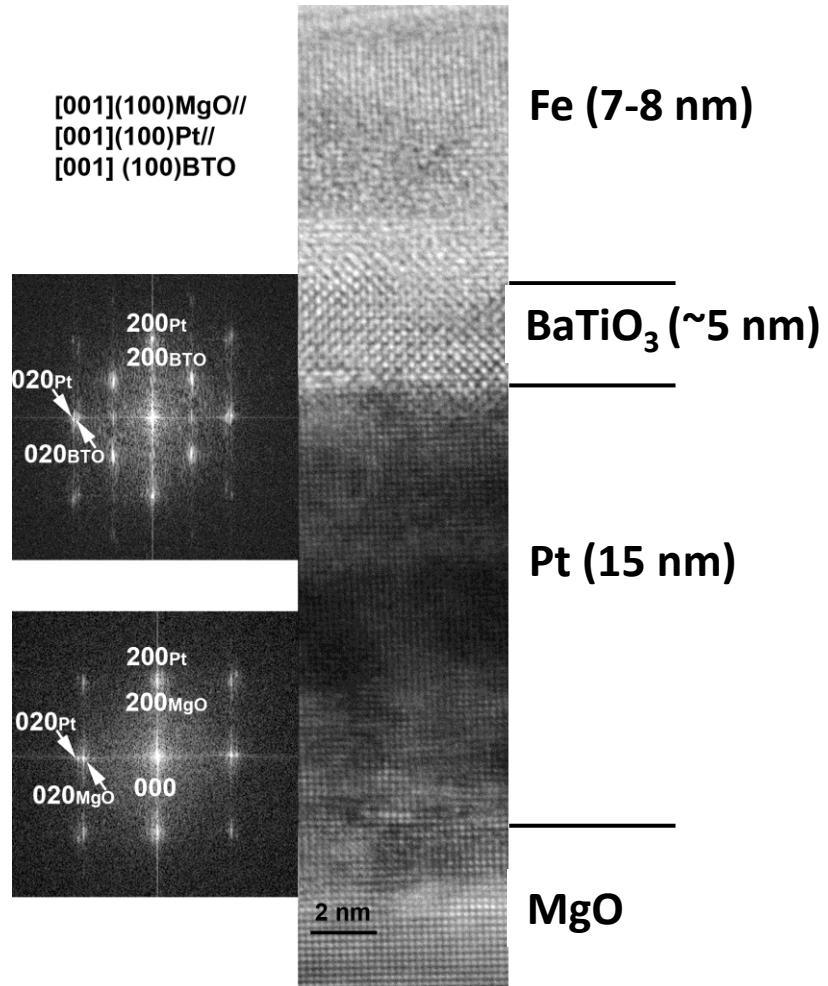


V. Garcia, et al., Science 327, 1106 (2010).

Band line-up at FM/FE interface



E. Y. Tsymbal, et al., Science 313, 181 (2006).

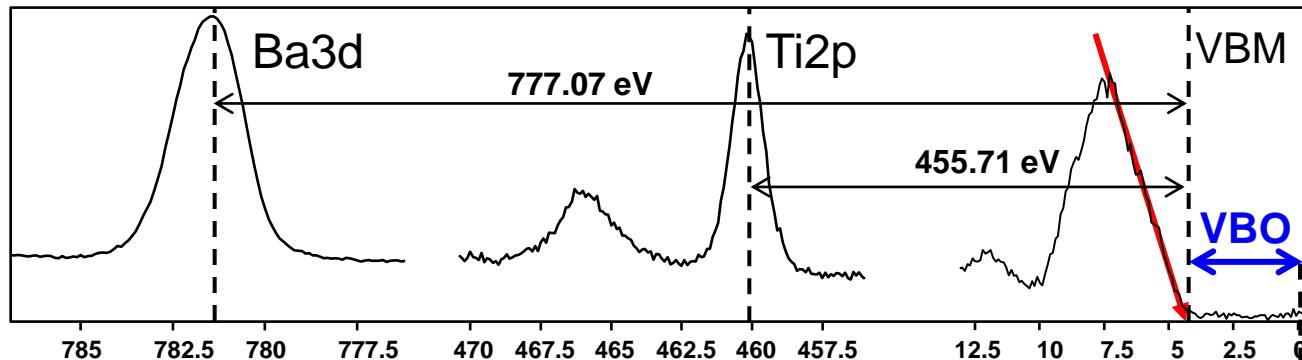


- **Motivation:** to characterize the electronic properties at Fe/BaTiO₃ interface

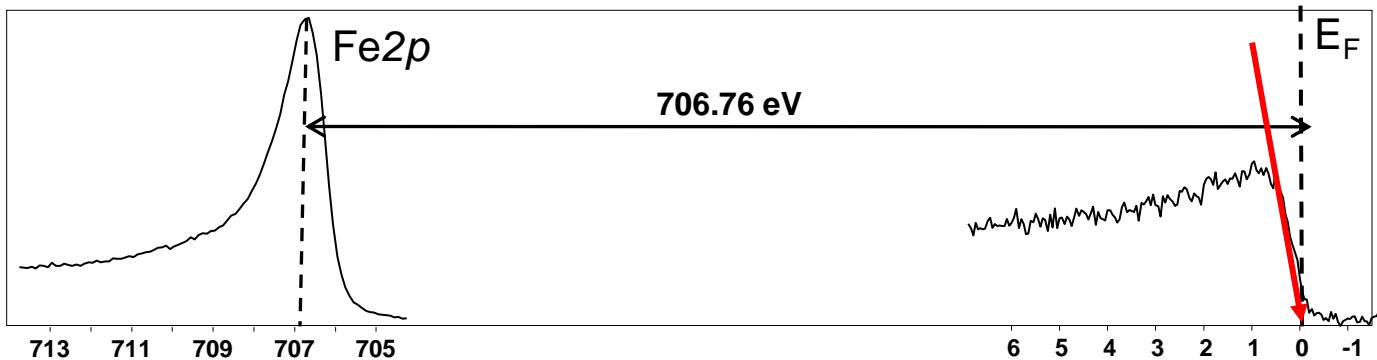
Band line-up at BTO/Fe interface probed by HAXPES

$$VBO = (E_{Fe2p} - E_{Ti2p})_{Fe/BTO} - (E_{Fe2p} - E_F)_{Fe} + (E_{Ti2p} - VBM)_{BTO}$$

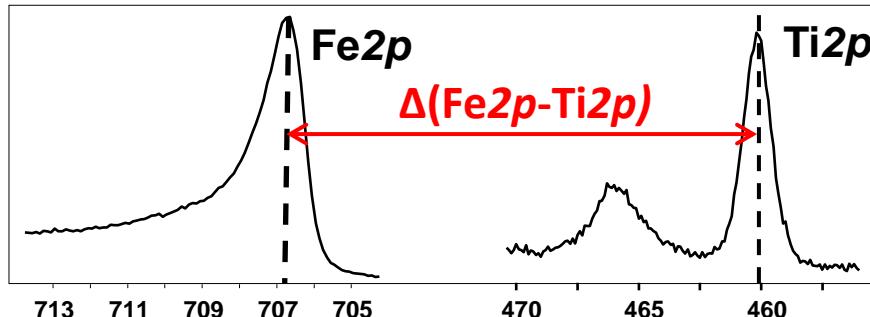
BTO (15 nm)
STO:Nb(100)



Au(5 nm)
Fe(15 nm)
MgO(100)



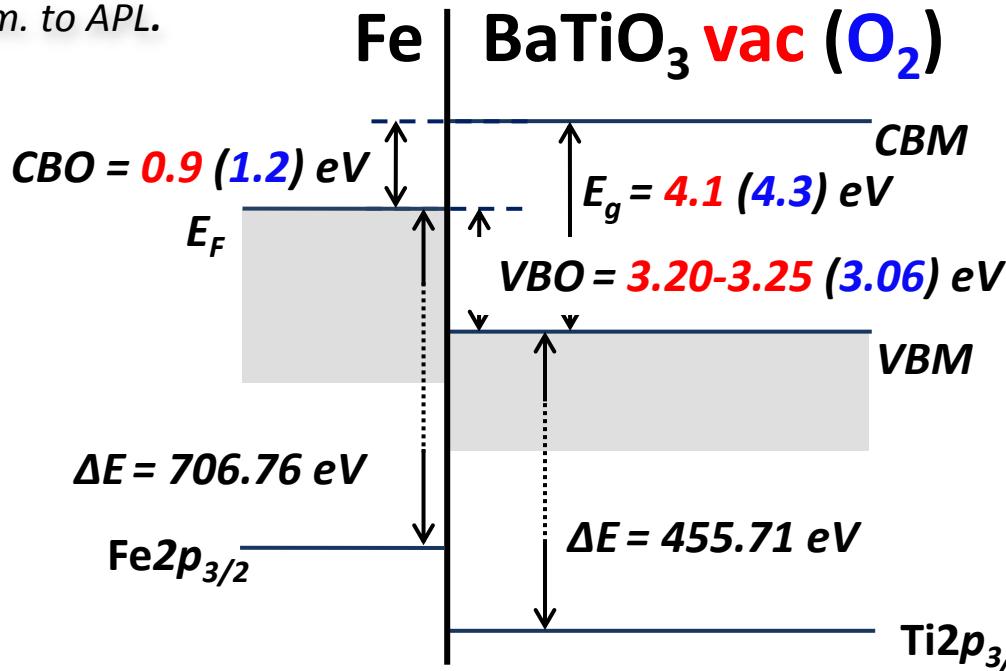
BTO_y(5 nm)
Fe(15 nm)
MgO(100)



Band line-up at BTO/Fe interface*: summary

	$(E_{Fe2p} - E_{Ti2p})_{Fe/BTO}$ ± 0.05 eV	VBO, ± 0.05 eV	$E_g, \pm 0.1$ eV (REELS)	CBO, ± 0.1 eV
MgO/Fe/BTO _V	247.85	3.20	4.1	0.9
STO/BTO _V /Fe	247.81	3.25	4.1	0.9
STO/BTO _O /Fe	248.00	3.06	4.3	1.2

* A. Zenkevich et al., *subm. to APL.*



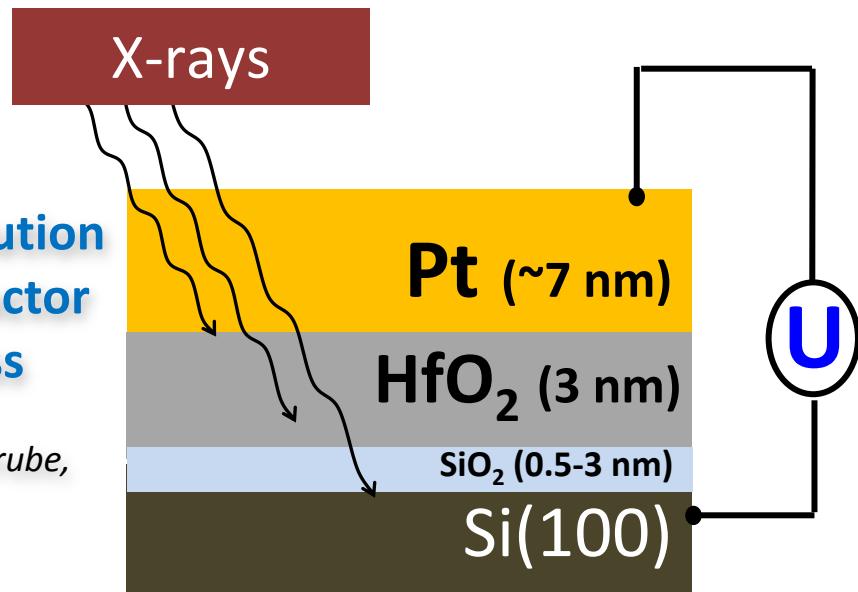
- **CBO= 0.9-1.2 eV depending on O vacancies concentration in BaTiO₃**

Role of oxygen vacancies in HfO_2 : Pt/ HfO_2 /Si stack

- Pinning of E_F^*
- Precursors of resistive switching phenomena**
- Charge trapping upon bias-temperature stress (BTS)***

Idea: to monitor by HAXPES the re-distribution of charges across metal-oxide-semiconductor stack following bias-temperature stress

A. Zenkevich, Yu. Matveyev, Yu. Lebedinskii, S. Thiess and W. Drube, ME 88 1353-1356 (2011).



* E. Cartier et al. Symp. on VLSI Techn., (2005), p.230

** L. Goux, et. al., APL 97 (2010) 243509

*** E.-A. Choi and K. J. Chang., APL 94 (2009) 122901

Motivation: to better understand mechanisms of oxygen vacancies formation/migration in Pt/ HfO_2 /Si stacks

Bias-temperature stress on Pt/HfO₂/Si stacks

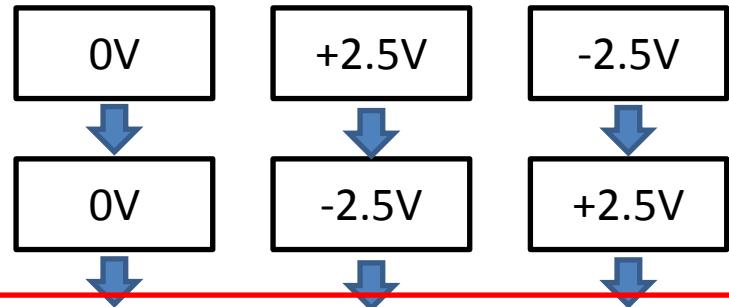
series #1: single treatment

3 areas (T=350°C):



series #2: cyclic treatments

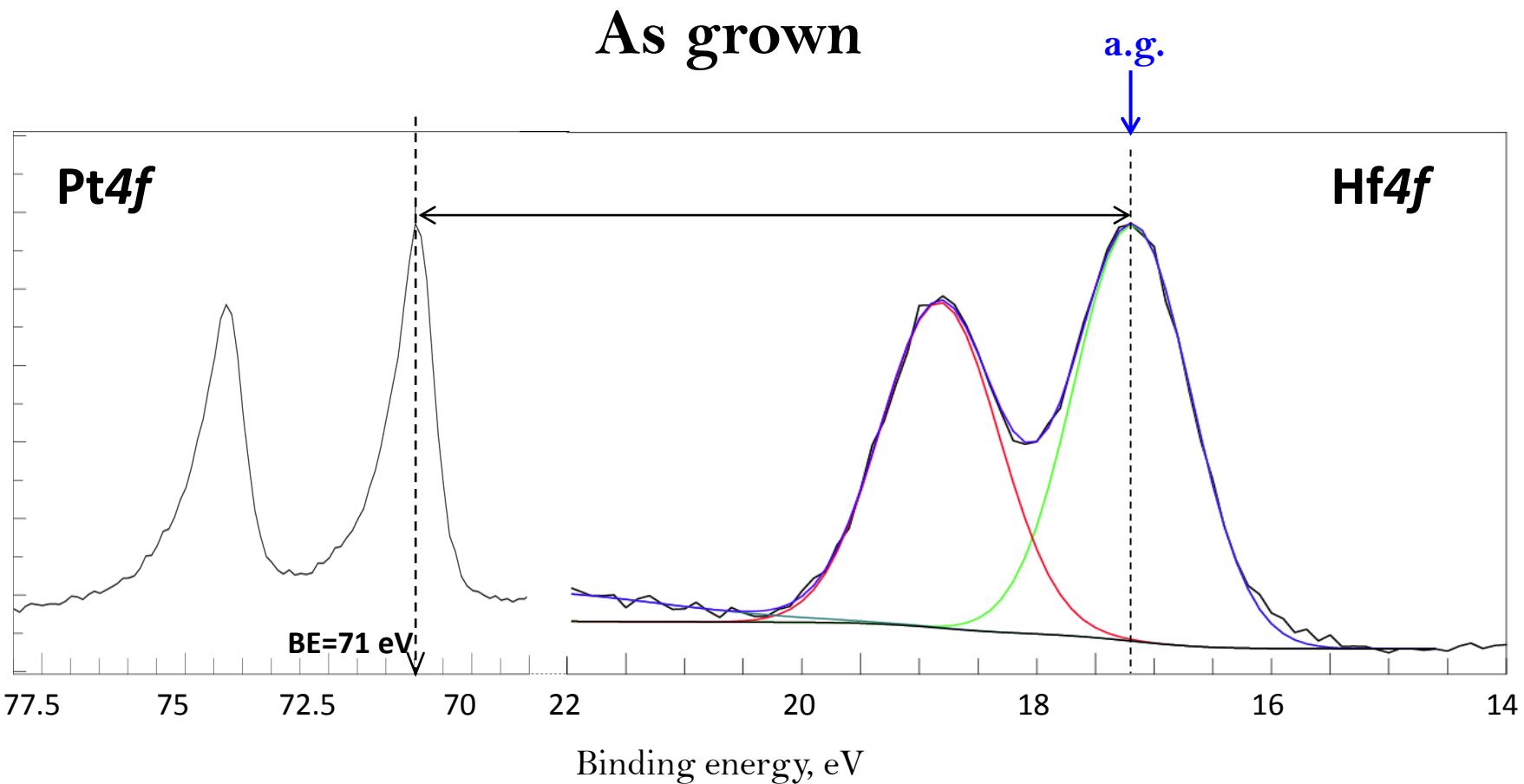
3 areas (T=350°C):



HAXPES

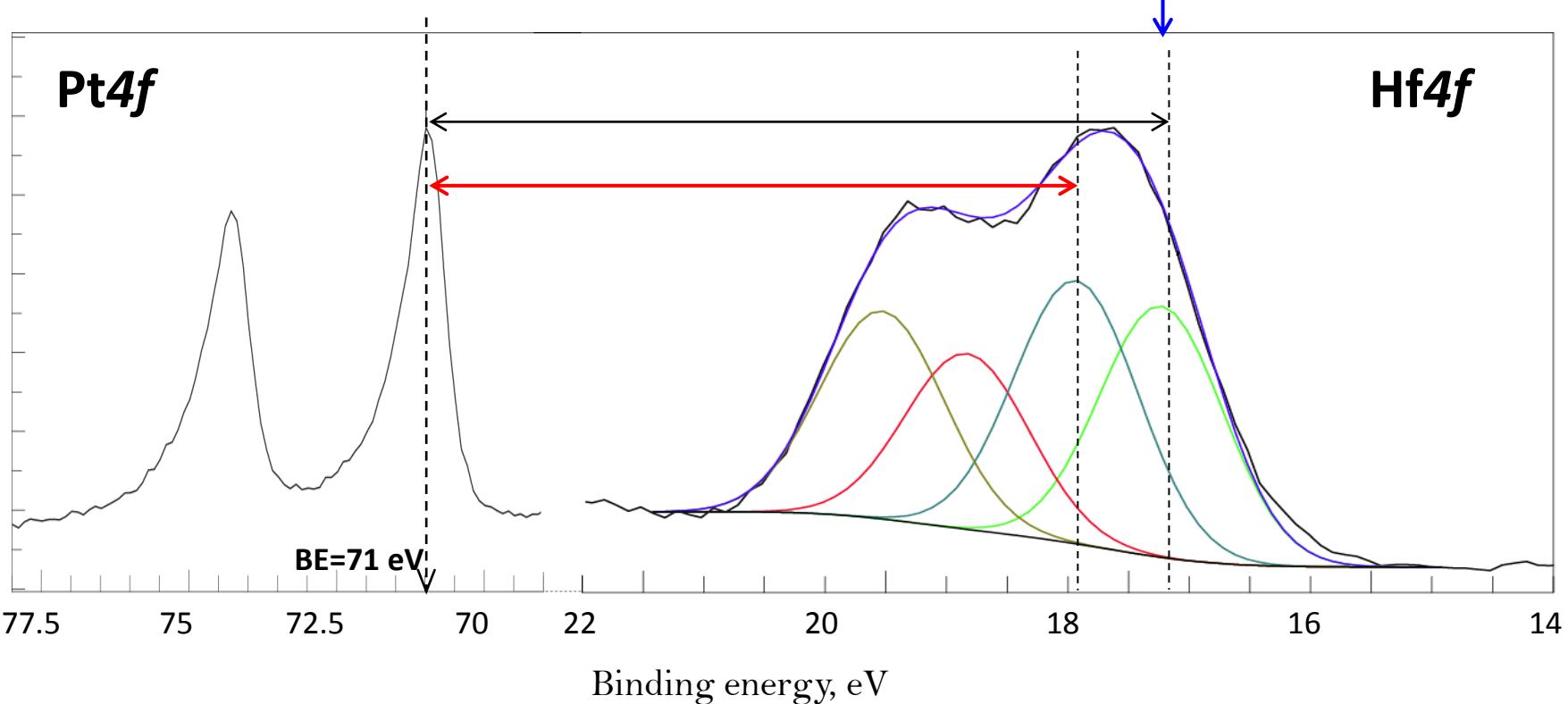
- Comparative *ex situ* HAXPES analysis on three areas

HAXPES: evolution of potential distribution across HfO_2



HAXPES: evolution of potential distribution across HfO_2

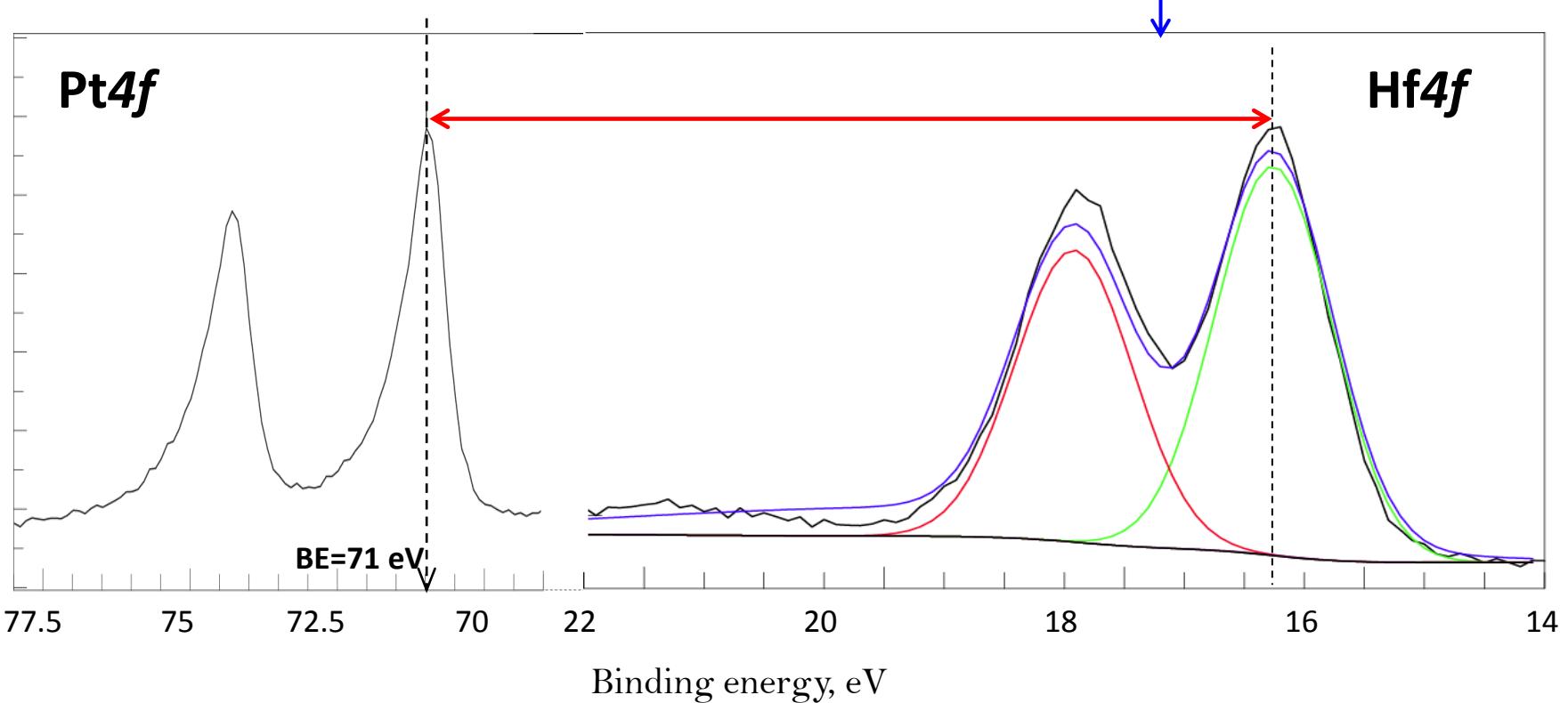
Upon T=350° C



- Upon heating to T=350°C Hf4f line broadens (additional doublet in the fit)
- BE \nearrow \rightarrow positive charge at the HfO_2/Si interface

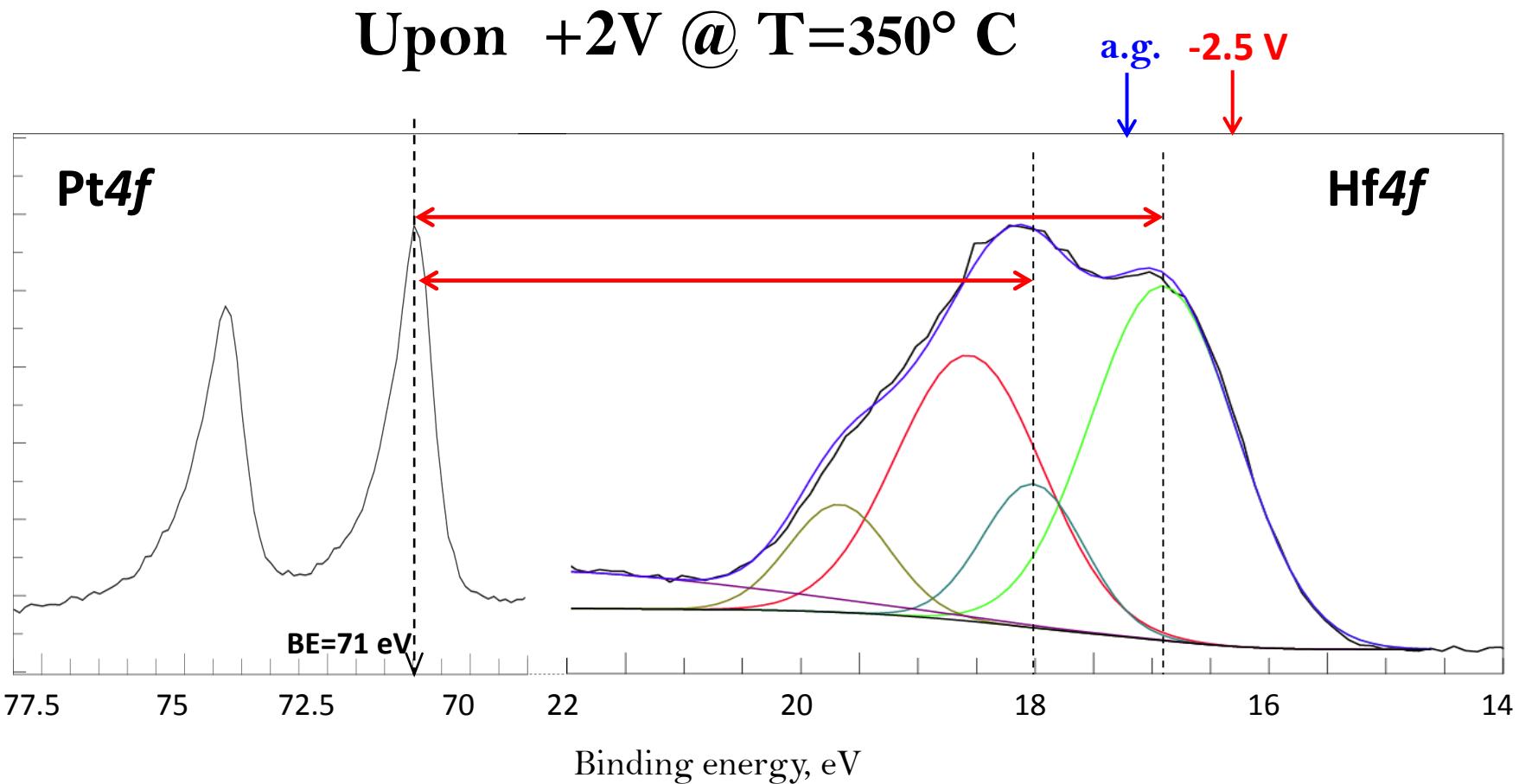
HAXPES: evolution of potential distribution across HfO_2

Upon -2V @ T=350° C



- Negative BTS step (-2V; T=350°C): additional doublet vanishes + Hf4f line shifts to lower BE → negative charge in HfO_2

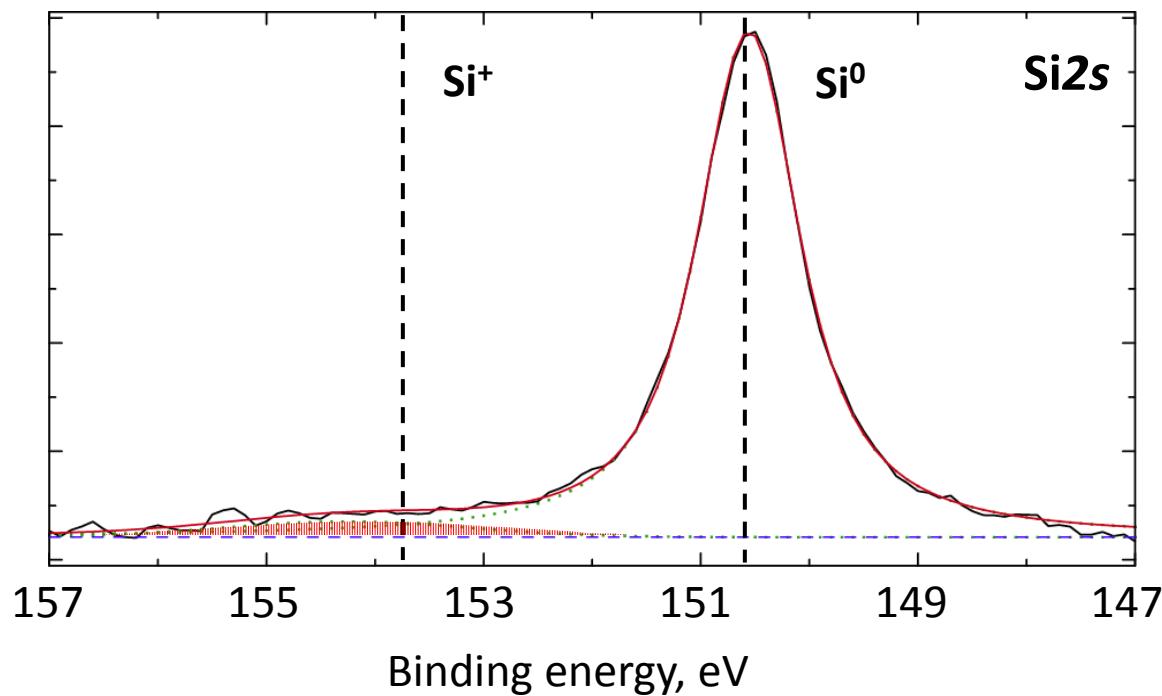
HAXPES: evolution of potential distribution across HfO_2



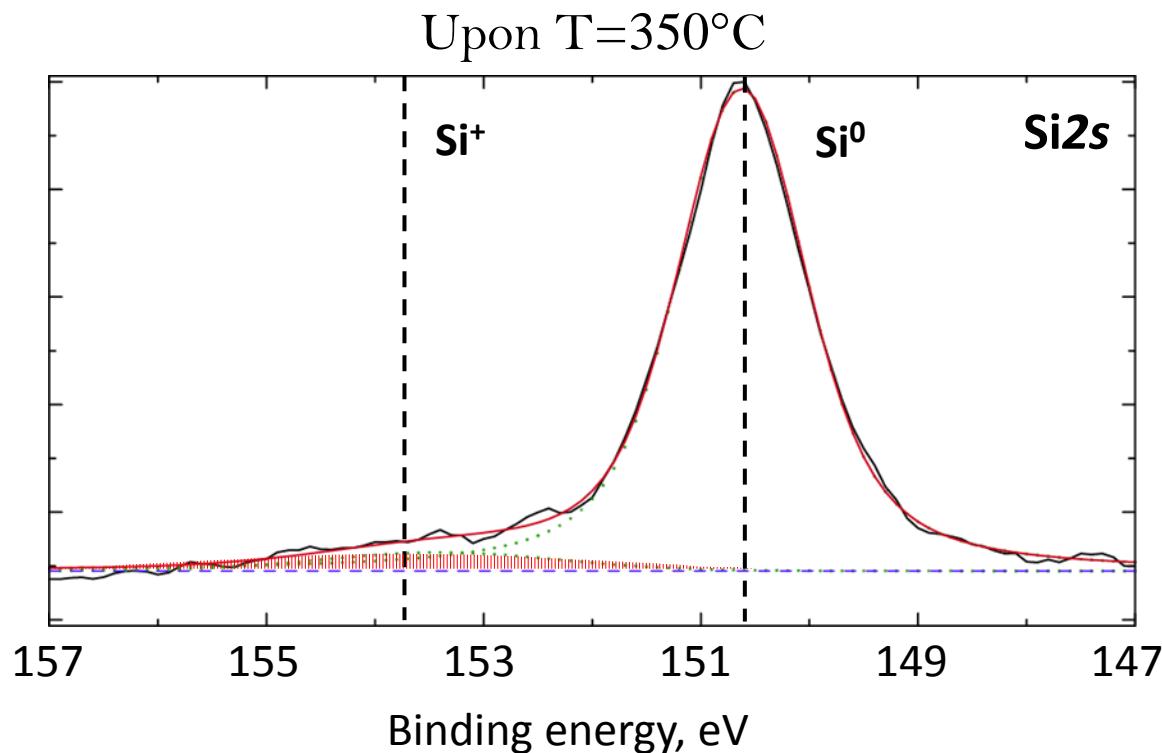
- Positive BTS step (+2V; T=350°C): Hf4f line shifts to higher BE and broadens → positive charge in HfO_2 , mostly at the bottom interface (angular dependence – not shown)

Evolution of SiO_x thickness at HfO_2/Si interface

As grown sample

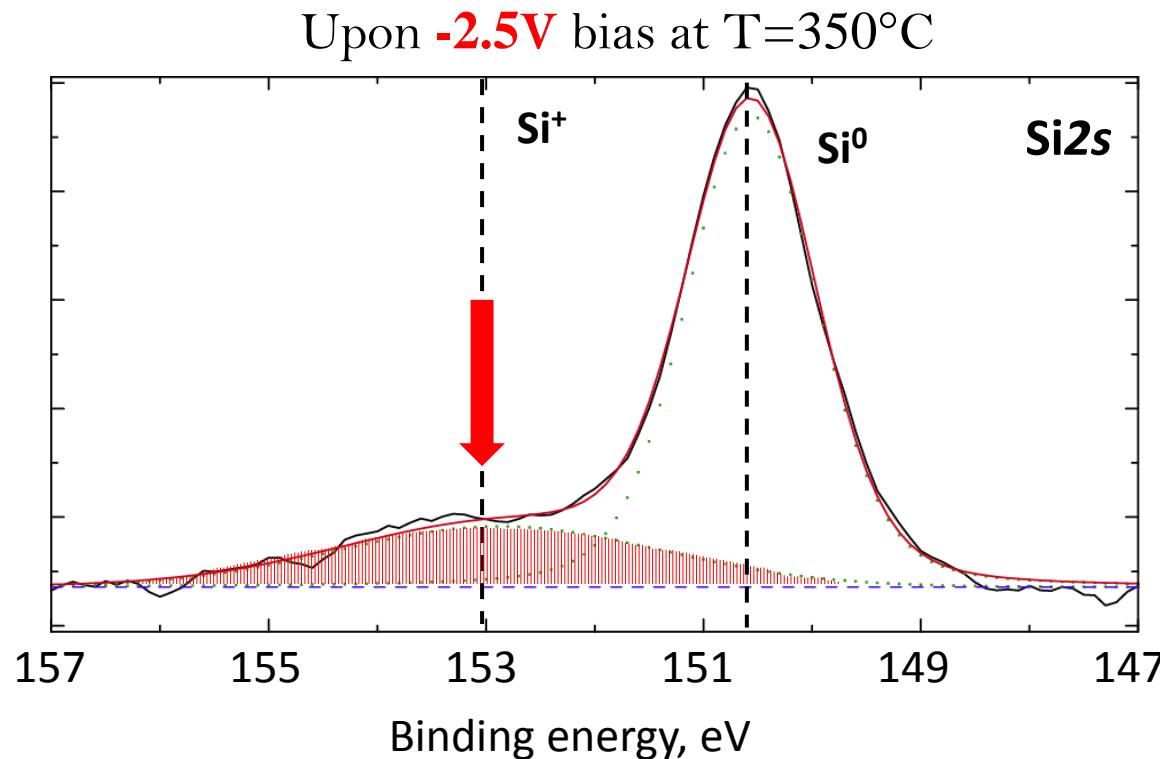


Evolution of SiO_x thickness at HfO_2/Si interface



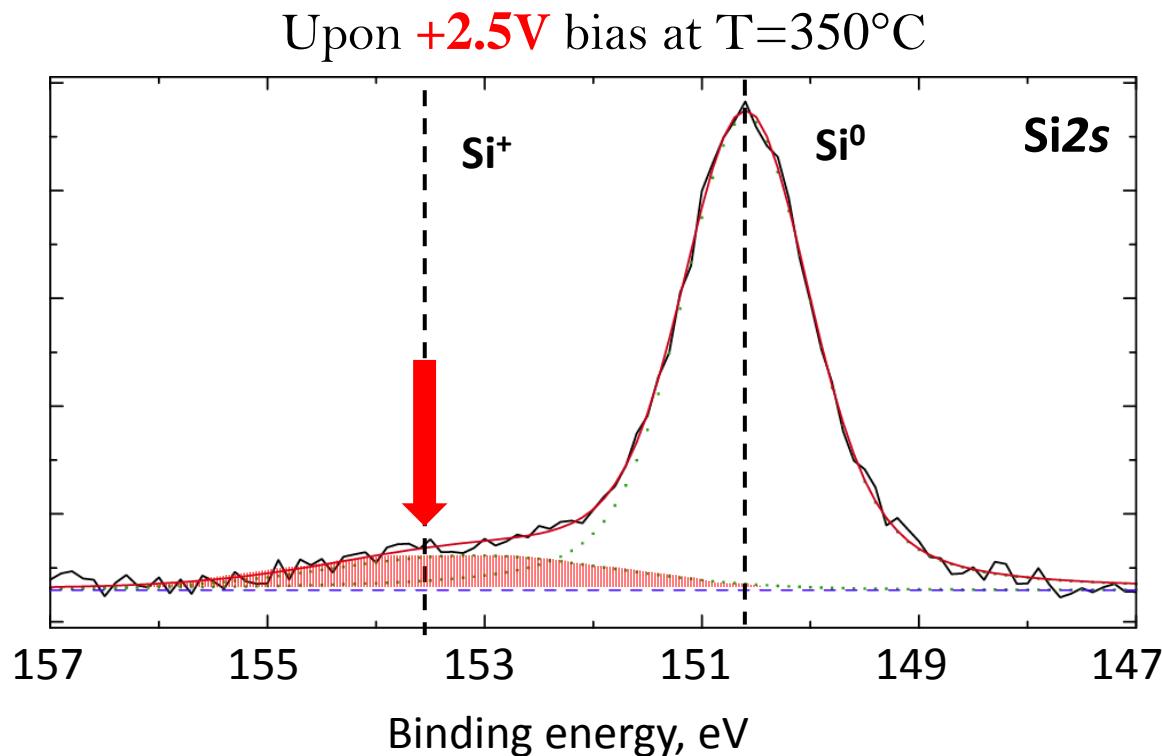
Small increase of the SiO_x at HfO_2/Si interface

Evolution of SiO_x thickness at HfO_2/Si interface



Growth of the SiO_x layer at HfO_2/Si interface up to 3.8 nm in thickness

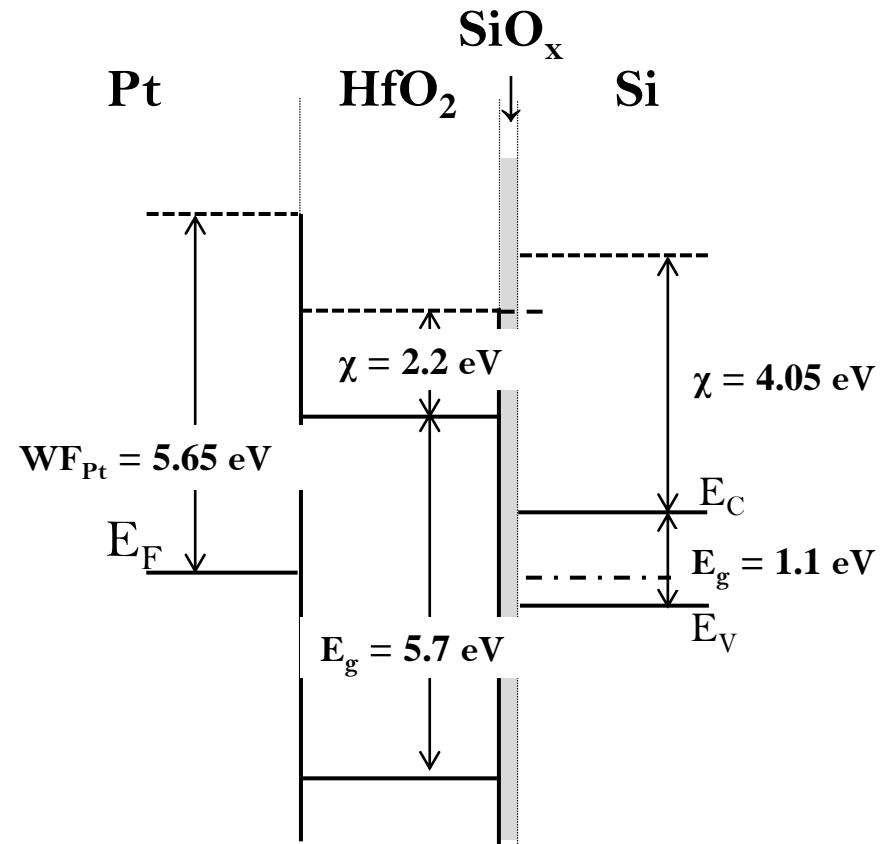
Evolution of SiO_x thickness at HfO_2/Si interface



Further positive BTS step: the thickness of SiO_x decreases down to 2 nm

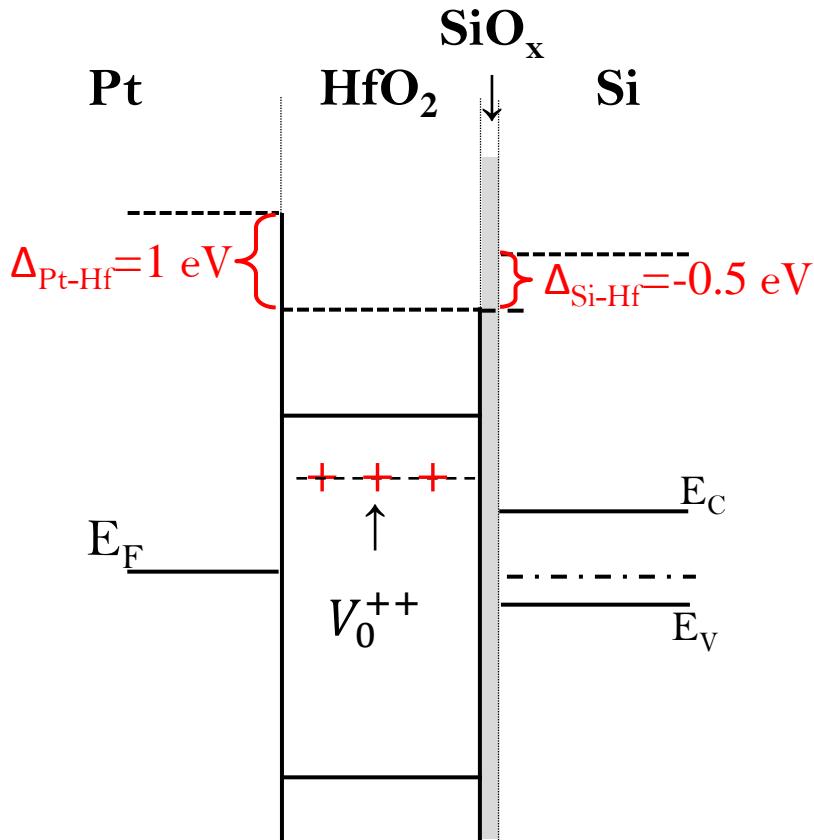
Electronic band diagram for Pt/HfO₂/Si stack

As grown

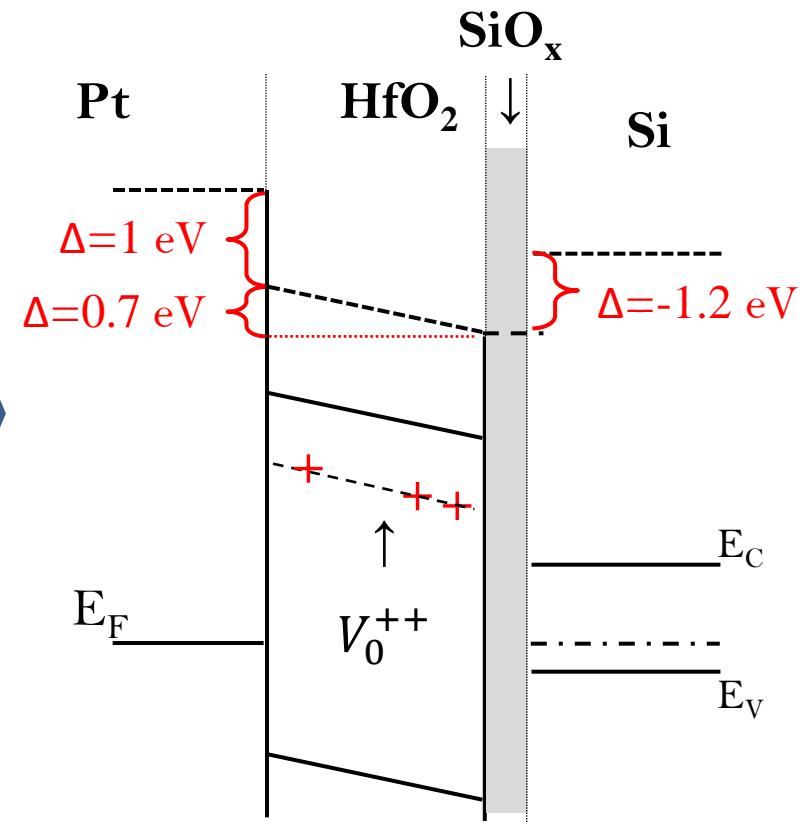


Electronic band diagram for Pt/HfO₂/Si stack

As grown

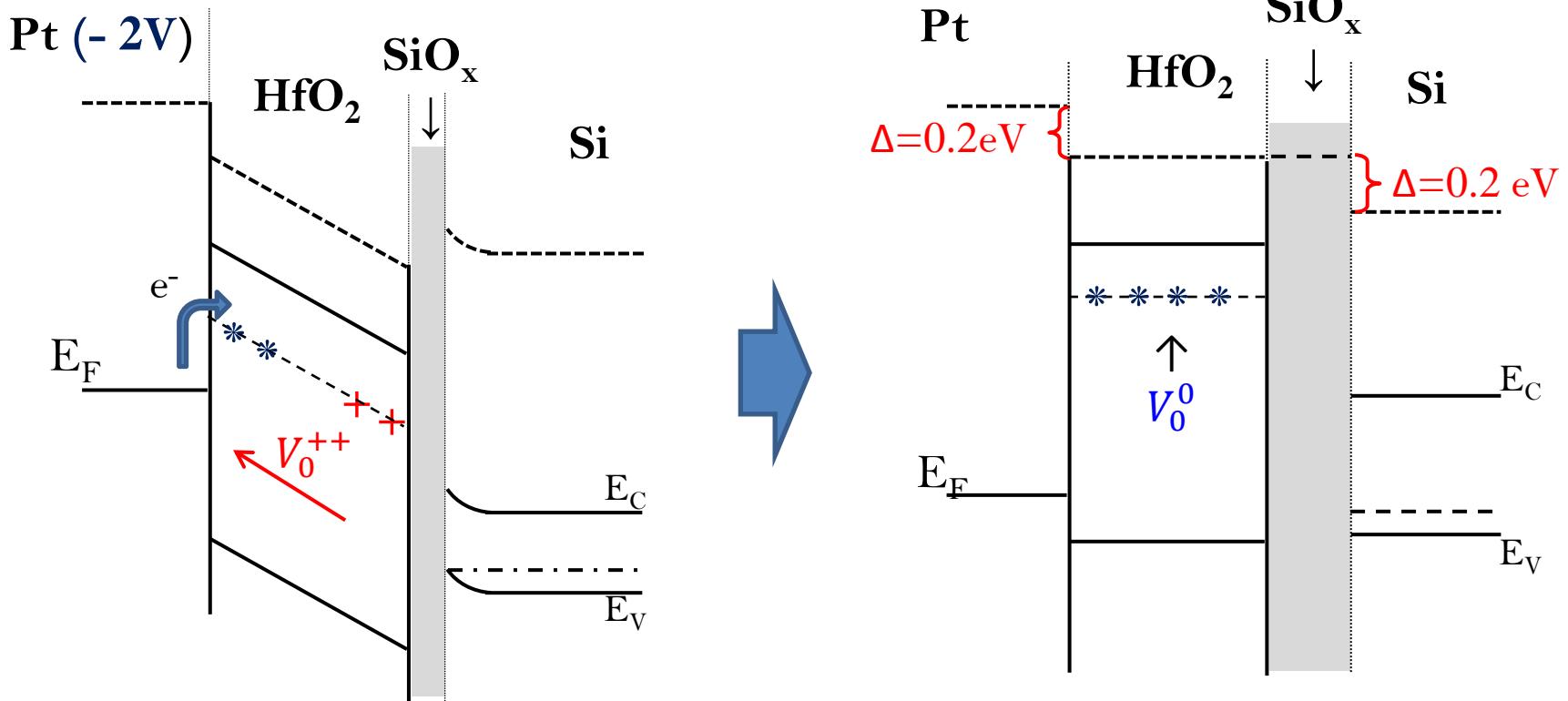


Upon T=350°C



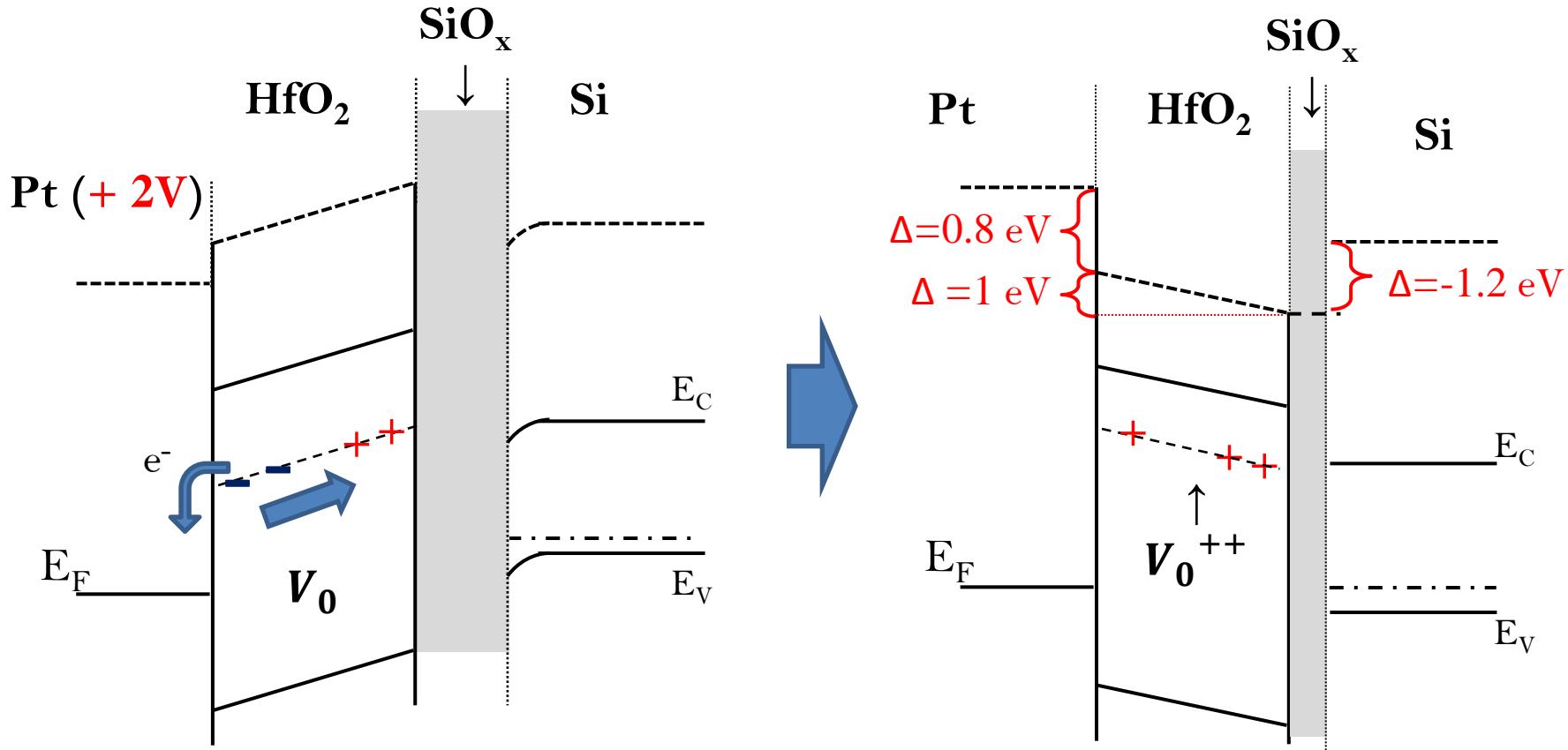
- chemical reaction at bottom interface → formation of additional SiO_x
 - formation of additional V_0^{++} in HfO₂ close to Si

Electronic band diagram for Pt/HfO₂/Si: negative BTS



- V_0^{++} move to upper interface \rightarrow concentration at the bottom interface \searrow
- \downarrow
- renewal of HfO_2 -Si reaction \rightarrow further growth of SiO_x
 - at the top interface vacancies neutralize from Pt $\rightarrow V_0^0$

Electronic band diagram for Pt/HfO₂/Si: positive BTS



1) V_0^0 at the top interface drop electron to the gate and become V_0^{++}

2) V_0^{++} move to the bottom interface → capture oxygen from SiO_x → decrease SiO_x thickness

Planned experiments

- *In situ* HAXPES on “*devices under operation*” (P09 @ PETRA III):
 - monitoring of resistance switching (memristive?) phenomena in MIM stacks
 - potential re-distribution across M-FE-M following the switching of polarization direction in ferroelectric
 - valence band changes at FM/FE interfaces upon FE polarization; magnetoelectric effects?

Thank you for your attention!



Experiment is in progress... at 5 a.m. (at DORIS III: BW2)