# Dependence of the thickness and composition of the $HfO_2/Si$ interface layer on annealing

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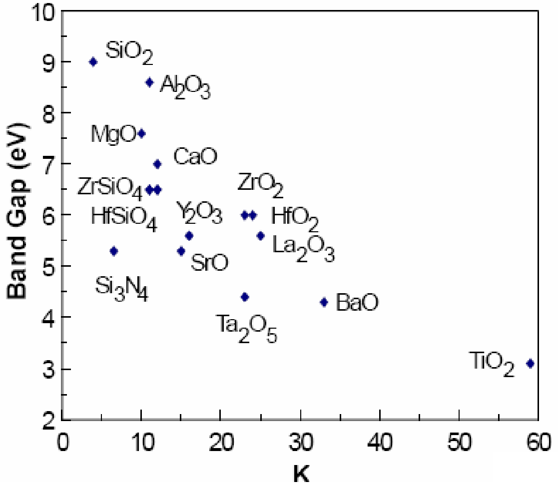
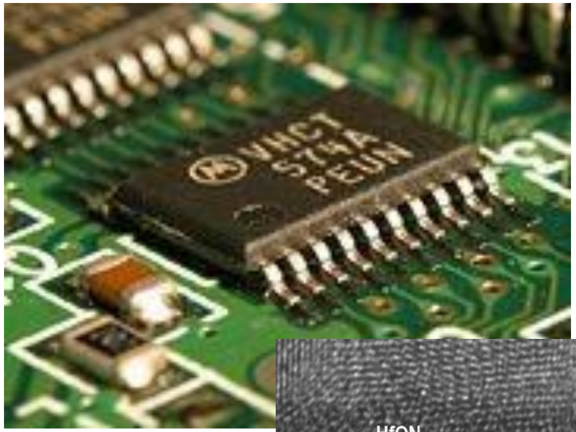
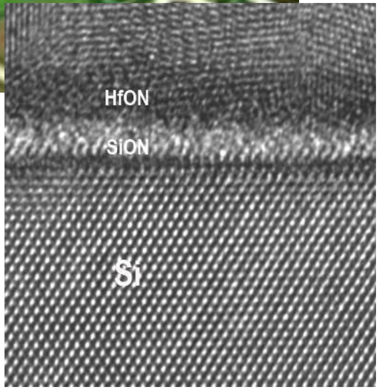
# background

- Introduction
  - ALD
  - DC Sputtering
  - XPS
    - ARXPS
- Growth of $HfO_2$ films by ALD
  - Caracterization by XPS
- Growth of TaN films by DC sputtering
  - Caracterization by XPS
- Annealing of $Si/HfO_2/TaN$
  - Removed TaN
  - Charaterization by XPS
- Conclusions

# Introduction



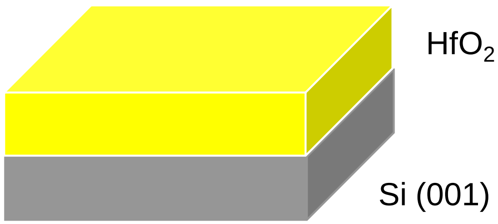



- *High thermal stability and high dielectric constant.*

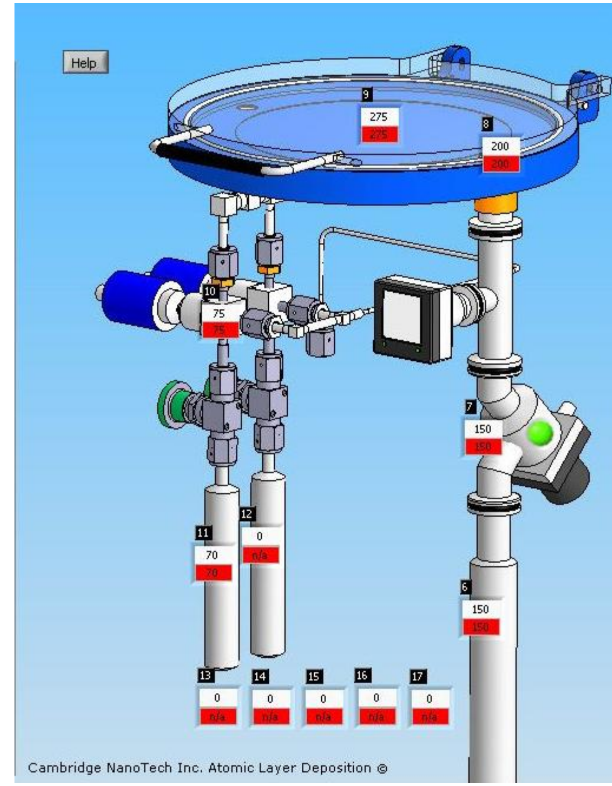
- *Get the composition and thickness of the $HfO_2$/Si interface.*

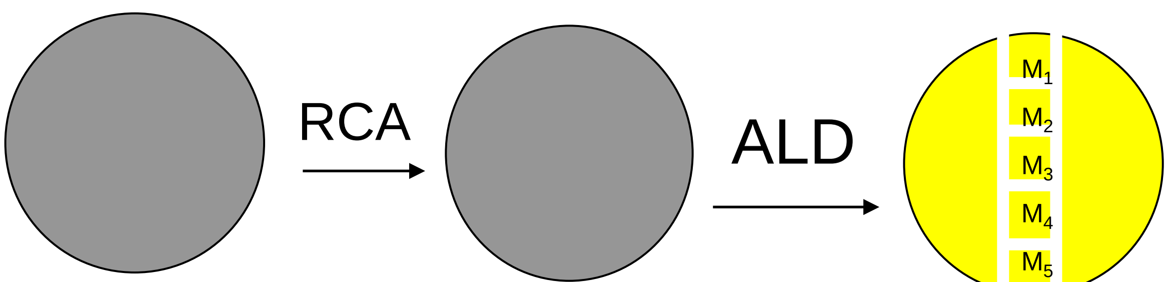
# ALD (atomic layer deposition)

Si/$HfO_2$




Si (100)

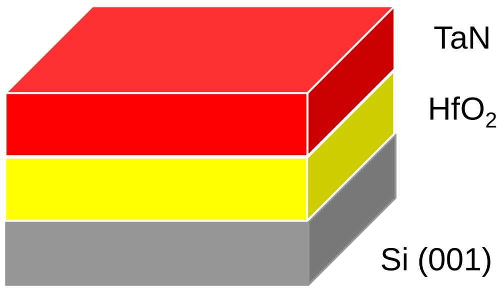


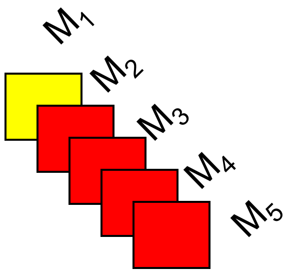



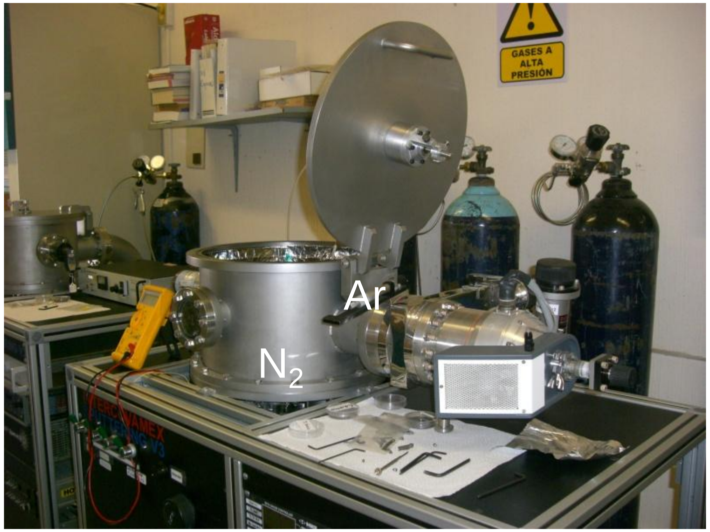

| | Pulse (seg) | Drain (seg) |
|---|---|---|
| $H_2O$ | 0.1 | 7 |
| TDMA-Hf | 0.08 | 7 |

# DC sputtering

Si/$HfO_2$/TaN




$P_B$= 6.4X10$^{-6}$ torr

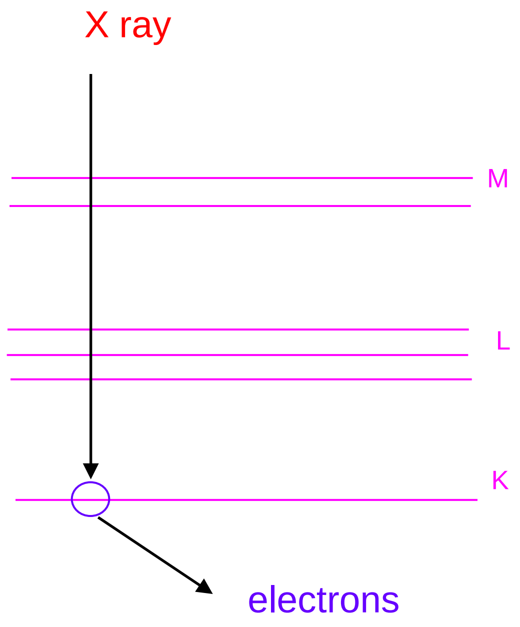
## X-ray source

Al Kα no-monochromatic

$h\nu$ = 1486.6 eV

Mg Kα no-monochromatic

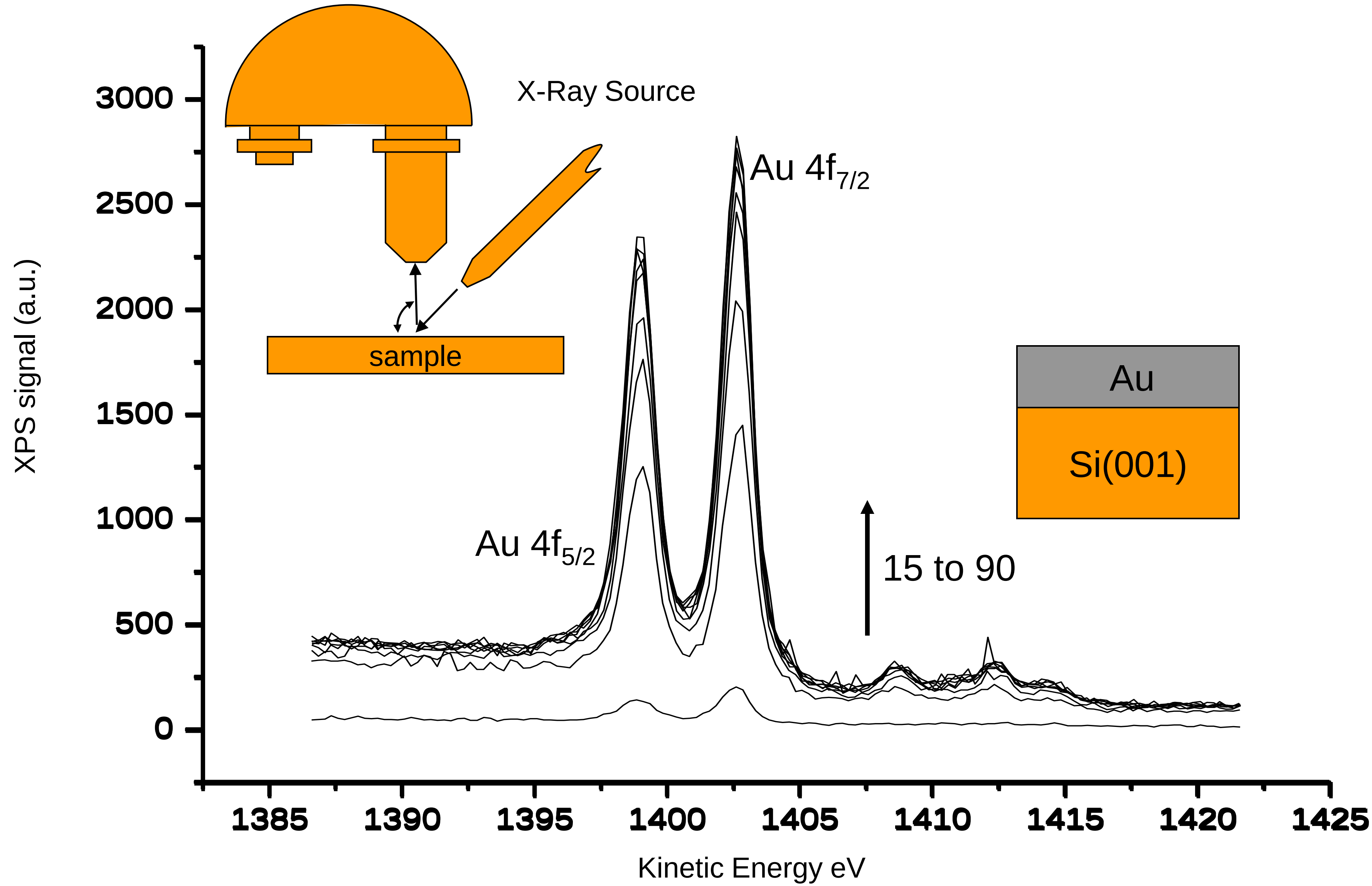
$h\nu$ = 1253.6 eV




$$E_K = h\nu - E_B$$

# ARXPS

concentric hemiespheric analyzer



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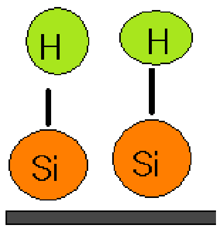
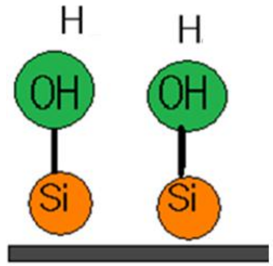
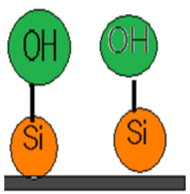
# Growth of $HfO_2$ in silicon wafer by ALD

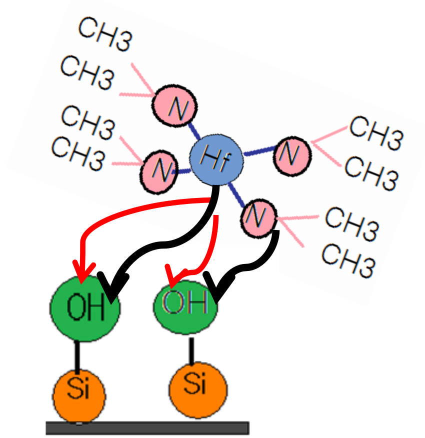



$H_2O$ (DI)

TDMA-Hf (Tetrakis dimetilamino-Hf)



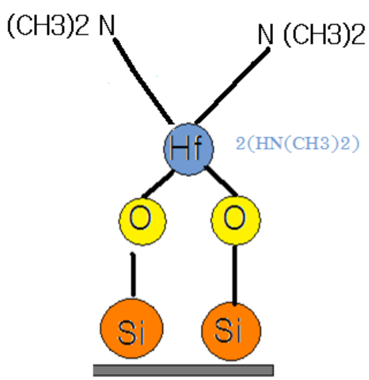

## Growth condition

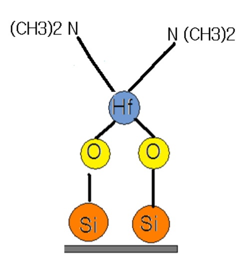
$P_i$= 2.039x10$^{-1}$ torr

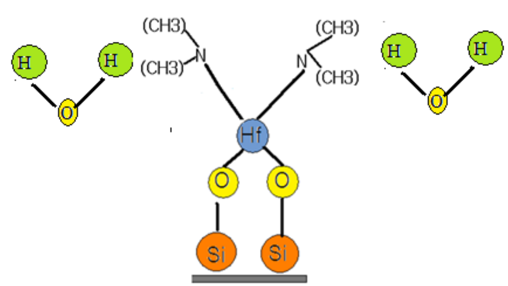
275 °C on the substrate

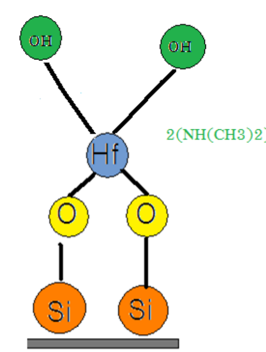
200 °C on the wall

70 °C on the cylinder TDMA-Hf

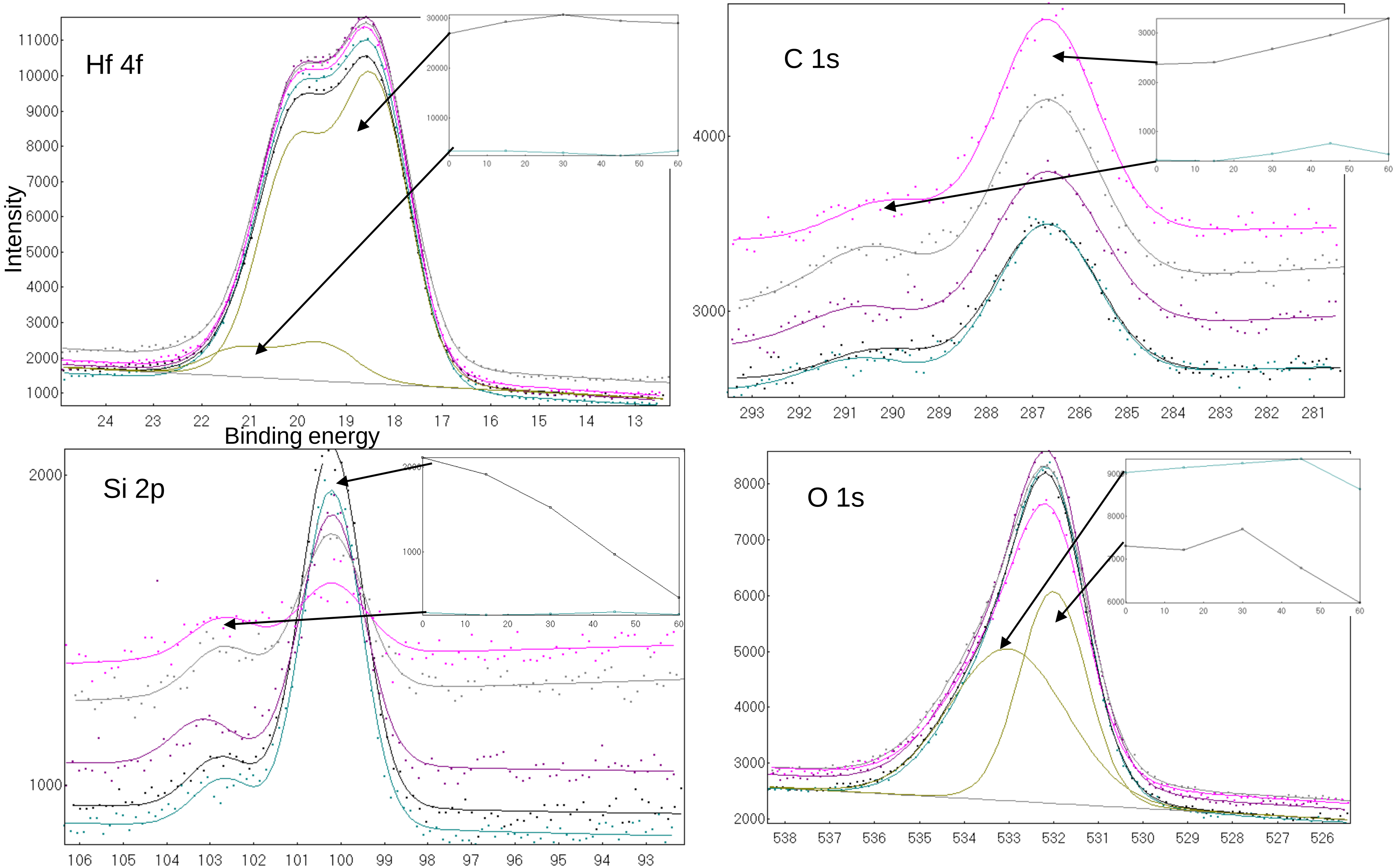


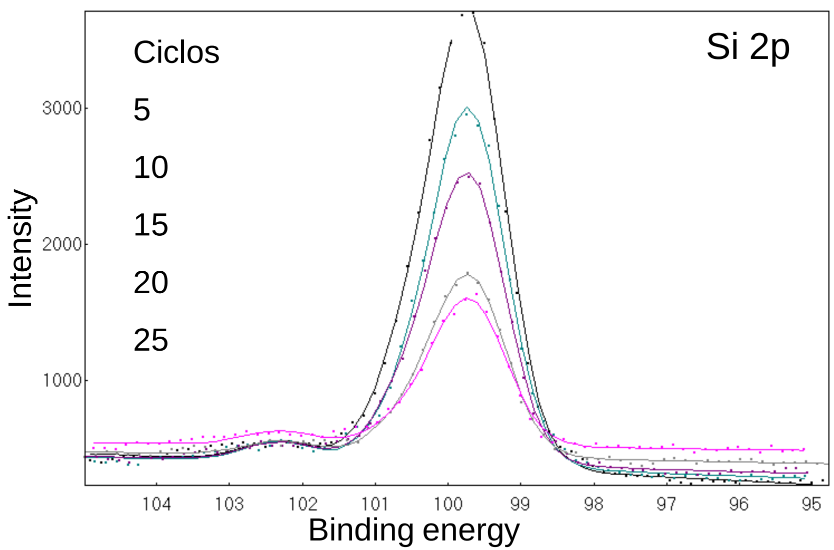



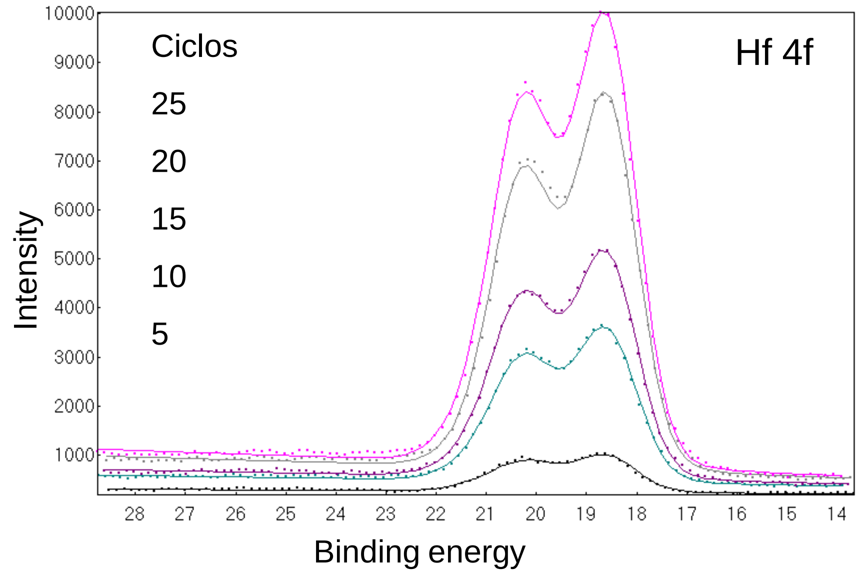



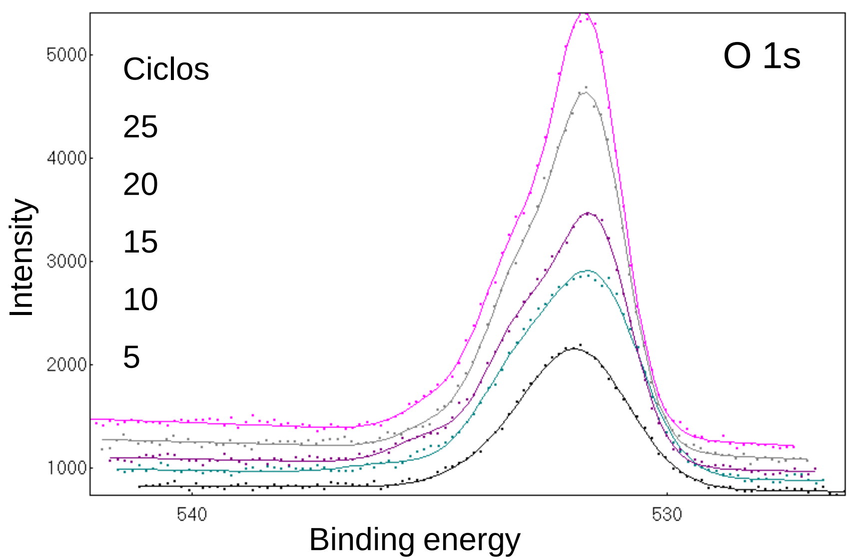
# ARXPS in sample with 30 cycles



# Growth of $HfO_2$/Si varying the number cycles



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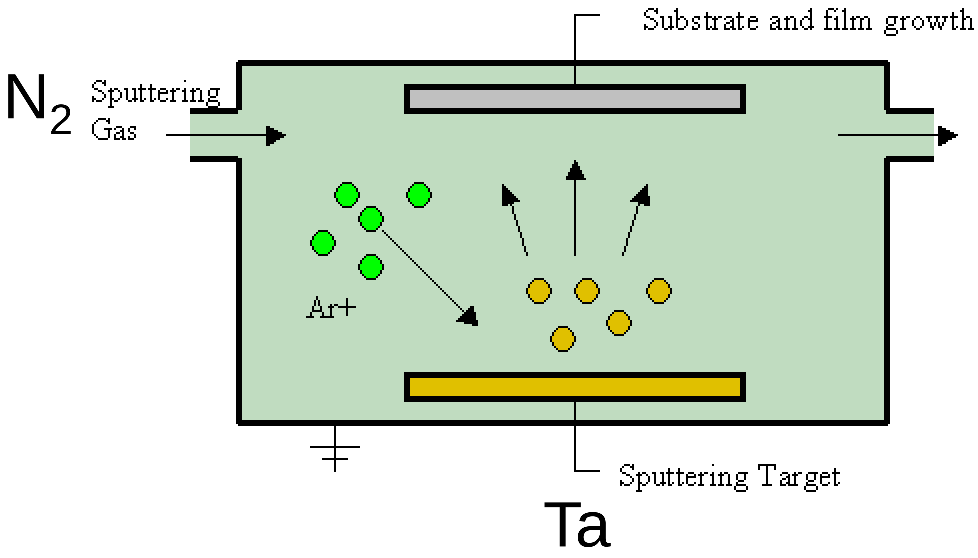
# TaN film grown by DC sputtering



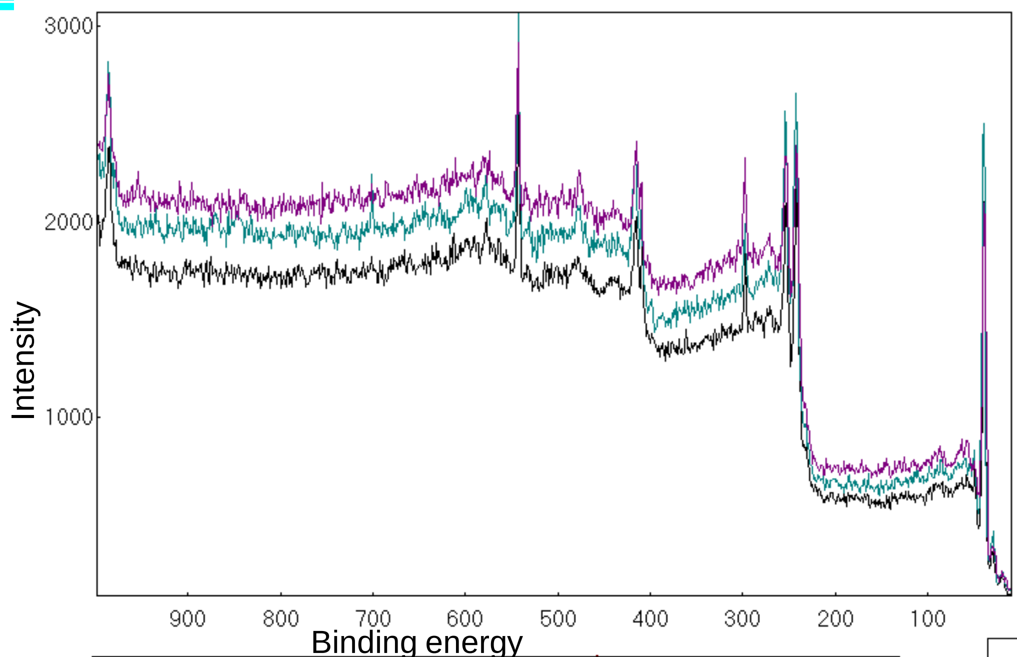

$P_T$= 2.6X10$^{-4}$ torr

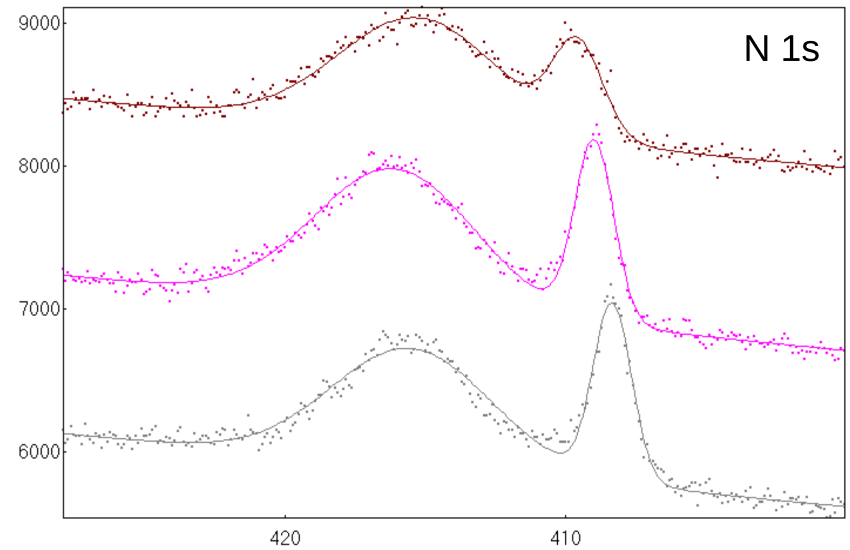
t= 4 min

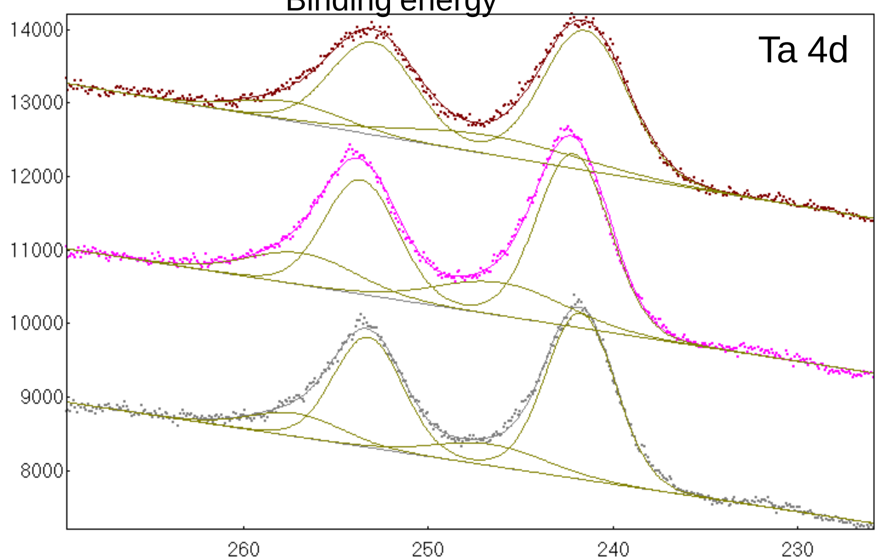
P= 100 W

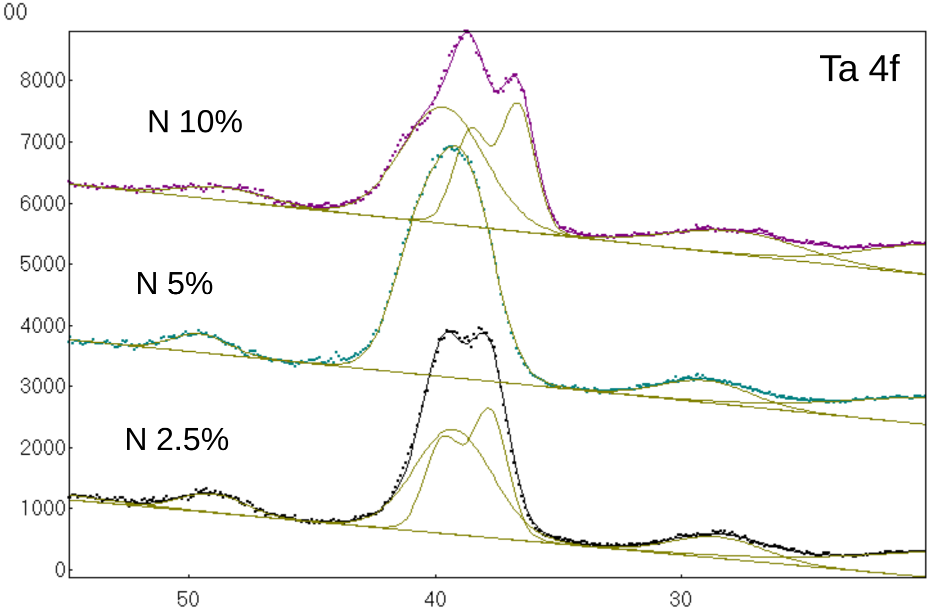
Thickness= 1000 Å

# Characterization XPS in TaN films

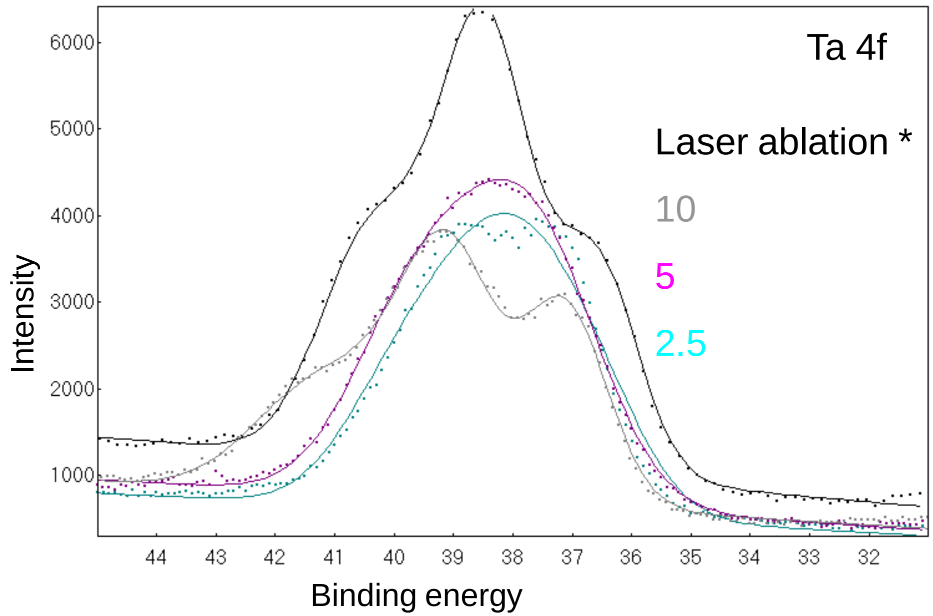


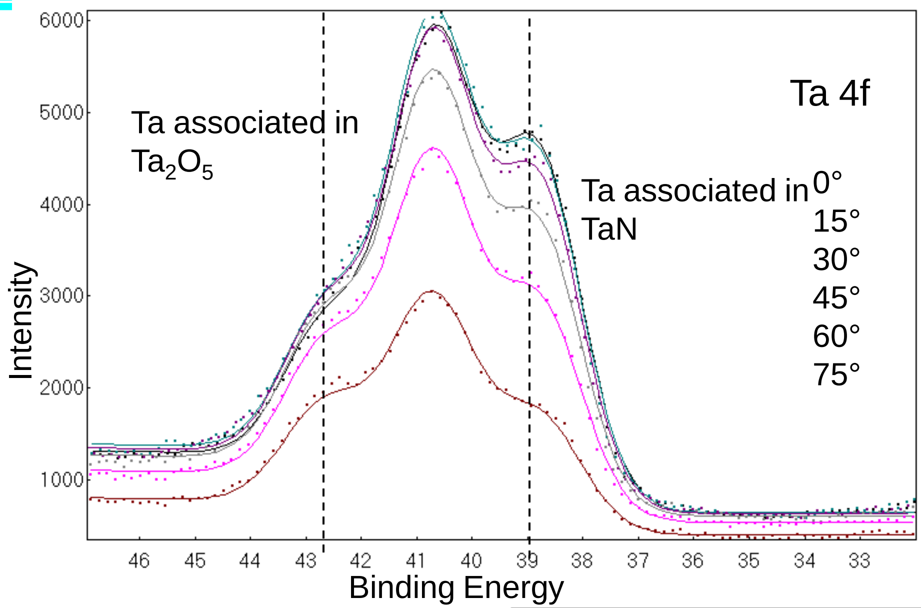
# Comparing TaN films grown by laser ablation and DC Sputtering

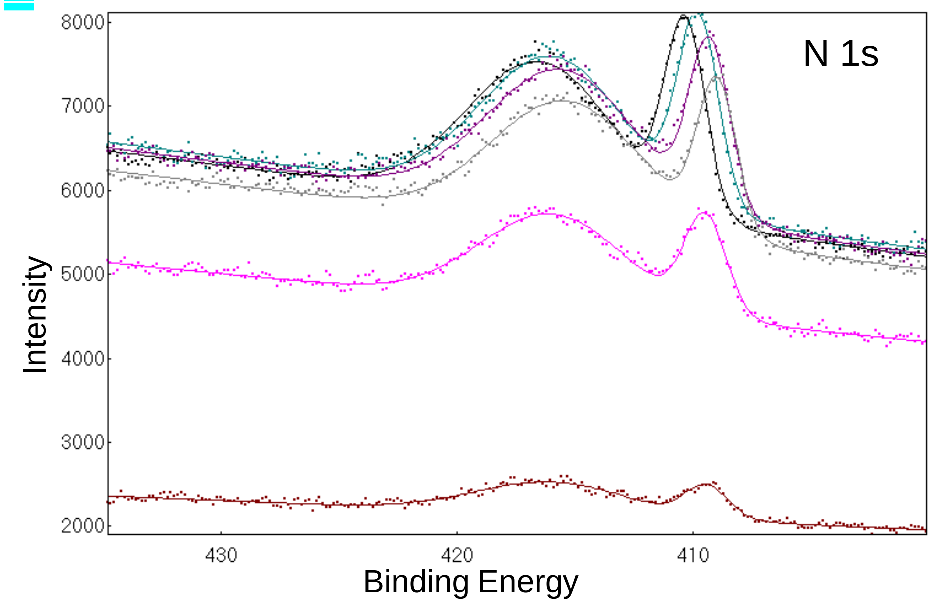


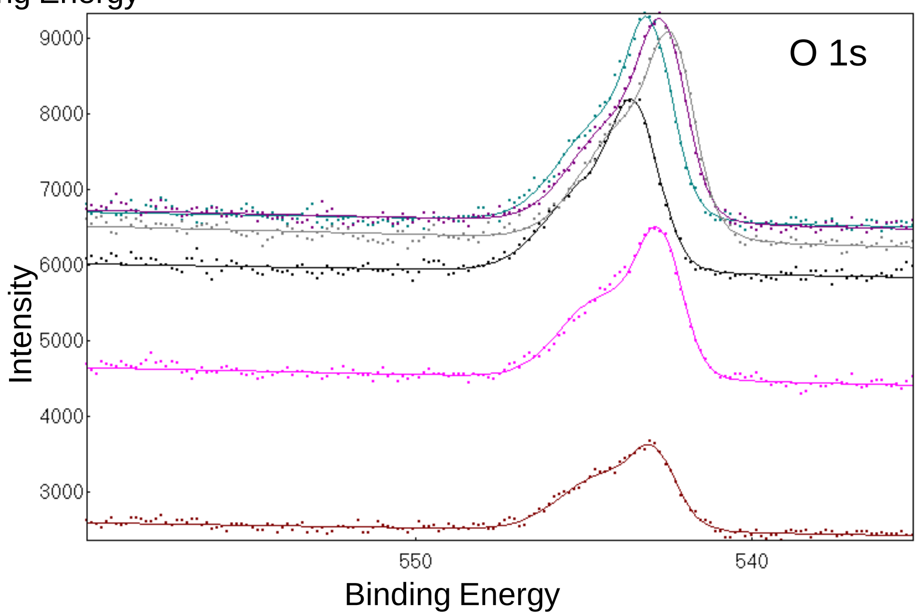

| N flow (%) | Ar flow (%) | N ($cm^3$) | Ar ($cm^3$) | Thickness (Å) | Resistivity (Ω cm) | |
|---|---|---|---|---|---|---|
| 2.5 | 97.5 | 0.6 | 24.4 | 1464 | 1.596E+02 | |
| 5 | 95 | 1.3 | 23.7 | 1090 | 7.358E-02 | |
| 10 | 90 | 2.5 | 22.5 | 1087 | 6.36E-04 | |
| | | | | 1000 | 3.73E-04 | Laser A. |

* Dr. Wencel de la Cruz (CNyN)

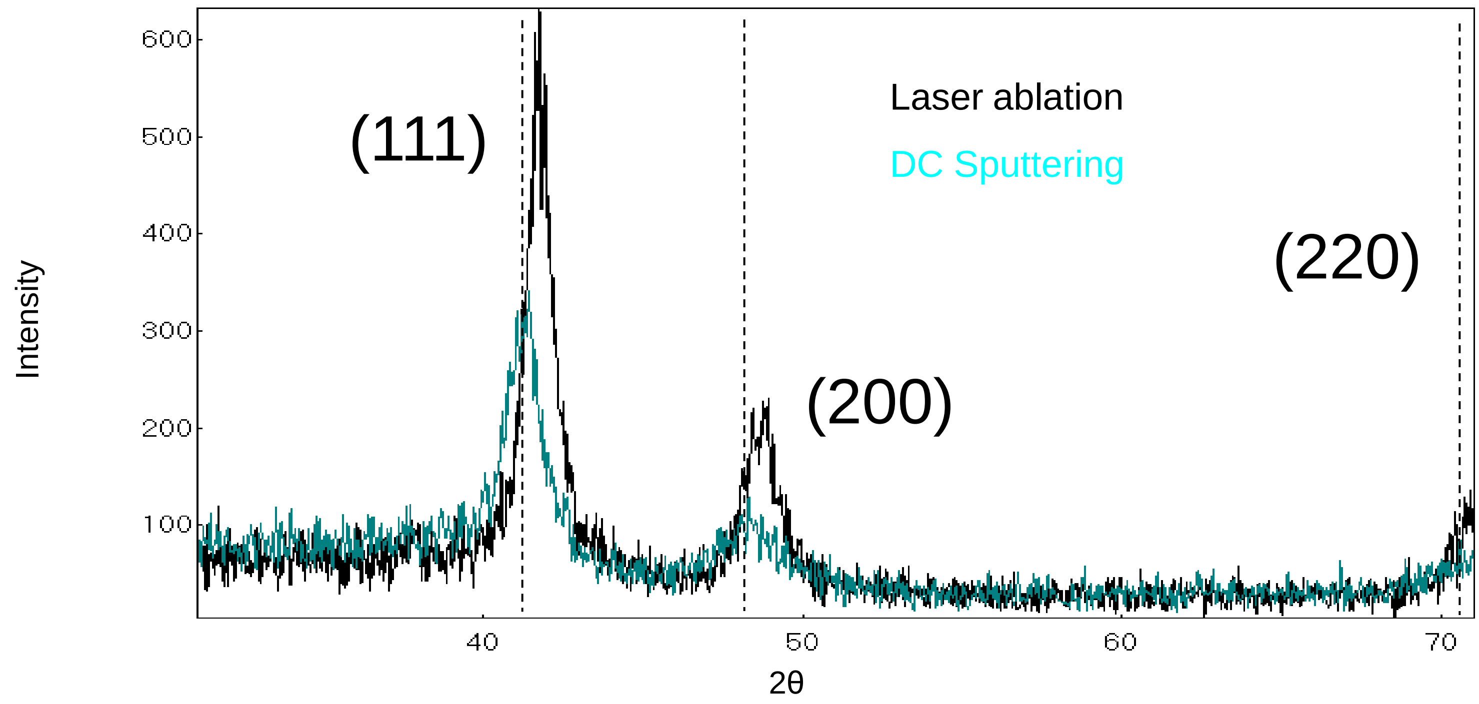
# ARXPS in TaN films



# Characterization XRD for TaN films



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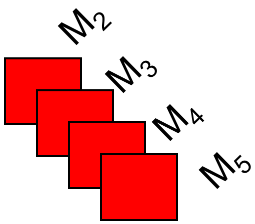
# Thermal annealing and removed TaN for $Si/HfO_2/TaN$

$N_2$


*T=700-1000 °C*
*10 seg*

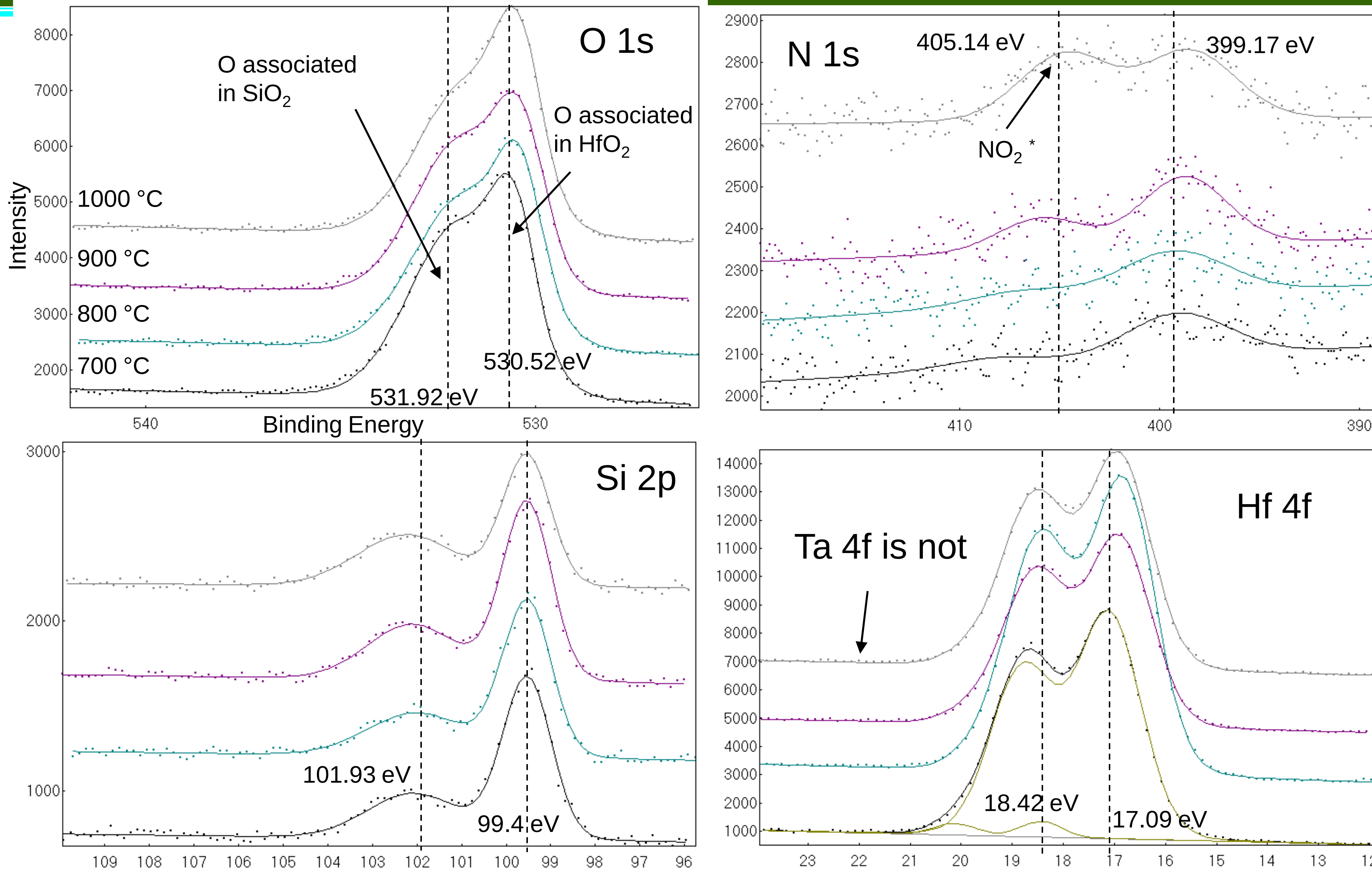



Removed TaN

$NH_4OH:H_2O:H_2O_2$

10:1:1 to 85 °C

# XPS after removed TaN film




* V.B. Wiertz, P. Bertrand, *Identification of the n-containing functionalities introduced at the surface of ammonia plasma treated carbon fibres by combined TOF SIMS and XPS*, Unité de Physico-Chimie et de Phys. Des Mat., Univ. Louvain 1348 Editor, Louvain.

# Thickness calculation

Equations (model) and parameters employed in the calculations

$$I_S(\theta,\mathbf{r}) = X(\mathbf{r})\,A(\theta)\,\sigma_S\; s_S\; \frac{1-\exp\left(-\dfrac{d_S}{\lambda_S\cos\theta}\right)}{1-\exp\left(-\dfrac{a_{S\perp}}{\lambda_S\cos\theta}\right)} \prod_{i}^{\substack{\text{layers}\\ \text{above S}}} \exp\left(-\frac{d_i}{\lambda_{S,\mathrm{i}}\cos\theta}\right)$$

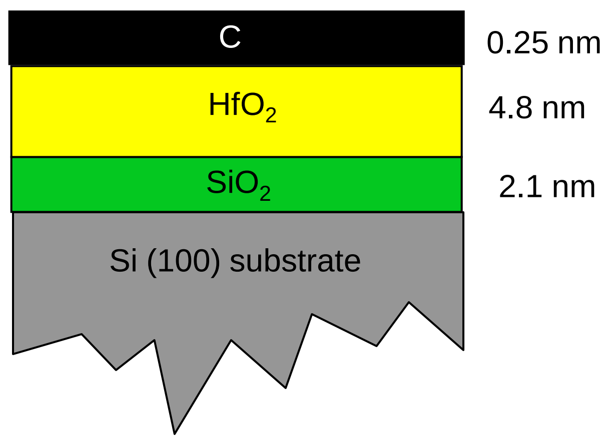
$$A(\theta) \sim \frac{1}{KE}$$ (not exactly, but close)

$$\frac{I_C(\theta,\mathbf{r})}{I_{Si}(\theta,\mathbf{r})} = \frac{\sigma_C\; s_C}{\sigma_{Si}\; s_{Si}}\; \frac{\dfrac{1-\exp\left(-\dfrac{d_C}{\lambda_C\,\mathrm{sen}\theta}\right)}{1-\exp\left(-\dfrac{a_C}{\lambda_C\,\mathrm{sen}\theta}\right)}}{\dfrac{1}{1-\exp\left(-\dfrac{a_{Si}}{\lambda_{Si}\,\mathrm{sen}\theta}\right)}\exp\left(-\dfrac{d_{SiO2}}{\lambda_{SiO2}\,\mathrm{sen}\theta}\right)\exp\left(-\dfrac{d_{HfO2}}{\lambda_{Hf}\,\mathrm{sen}\theta}\right)}$$

# Parameters

| | | | | effective attenuation lengths | | | |
|---|---|---|---|---|---|---|---|
| | **cross section** | **assymetry** | **KE** | **Si** | **SiO2** | **HfO2** | **Carbon** |
| **Si 2p** | 0.11 | 1.1 | 1153.95 | 29.2 | 35.2 | 17.2 | 33.4 |
| **Hf 4f** | 0.118 | 1.02 | 1236.36 | | 36.9 | 18 | 35 |
| **N 1s** | 0.024 | 2 | 854.511 | | 28.4 | 13.9 | 27.2 |
| **O 1s** | 0.04 | 2 | 722.75 | | 25.5 | 12.5 | 24.4 |
| **C 1s** | 0.013 | 2 | 967.76 | | 31 | 15.1 | 29.5 |
| | | | **Thickness** | | 21.0038668 | 47.9606174 | 2.59638606 |

The thicknesses were varied to reproduce the anions' (Si, Hf and C) data



# Conclusions

- The annealing present a different phase of $SiO_2$ and $HfO_2$ moved the binding energy.
- increasing the cycles number, the signal of O assotiated to $HfO_2$ increase.
- TaN is not present after of removed in the samples annealing
- With annealing the N is going to entrance to lattice of the $HfO_2$
- N 1s present a peak of correspond to $NO_2$ is possible to introduce of HfON, SiON or both of them.
- The thickness was calculated with the equation

# Conclusiones

- Increase the $SiO_2$ peak with annealing
- The suboxide in the Si 2p to continue increase with the temperature.
- We have a uniform and control in the grown of $HfO_2$ films but is formed a $SiO_2$ in the interface of $HfO_2$/Si.
- is possible to see the contribution of TaO and TaN respect the angle resolution the $Ta_2O_5$ is on the surface and N of the TaN is depth.