

From the surface characterization of the ^{28}Si -sphere to the semiconductor ultra-thin film using X-ray metrology



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CMS/ITRI has established a system for kilogram realization via the XRCD method, comprising a ^{28}Si -enriched sphere and an XRF/XPS surface analysis system to measure the Si-sphere's surface layer mass. The core parameters, including lattice structure and isotope ratio, are highly stable and determined from prior measurements, enabling the mass determination of the Si-sphere. The XRF/XPS technique quantifies the Si-sphere's surface composition, distinguishing oxide, carbonaceous, and chemisorbed water layers. By analyzing mass deposition and atomic fractions, this method accurately determines surface layer properties. Beyond kilogram realization, this technique extends to semiconductor ultra-thin film analysis. Applied to an ALD-deposited HfO_2 film, it successfully measured composition and thickness, with results validated by Cs-TEM. These findings highlight the potential of XRF/XPS for sub-nanometer thin film characterization, paving the way for further applications in semiconductor materials.

Introduction

Since 2019, the definition of the unit of mass, the kg, is redefined by a fixed value of Planck constant $h = 6.626\,070\,15 \times 10^{-34} \text{ J s}$. CMS/ITRI adopts the XRCD method for kg realization and establishes the XRF/XPS surface analysis system for surface layer mass measurement. Combined with the surface layer mass with the Si-sphere's predetermined core mass, the Si-sphere's mass was determined to be 1000.078400(36) g. Beyond kilogram realization, the XPF/XPS technique also extends to semiconductor ultra-thin film analysis.



Fig.1 The ^{28}Si -enriched sphere "Sikg2803a" at CMS/ITRI

Experimental

Conventional techniques

Nondestructive testing

- ✓ XRR $\rightarrow$ 1.2 nm ~ 200 nm
- ✓ SE $\rightarrow$ 1.5 nm ~ 1000 nm
- ✓ XRF $\rightarrow$ Above 10 nm

Destructive testing

- ✓ SEM/TEM $\rightarrow$ Below 1 nm

XRF/XPS surface analysis system

$\rightarrow$ 0.1 nm ~ 10 nm

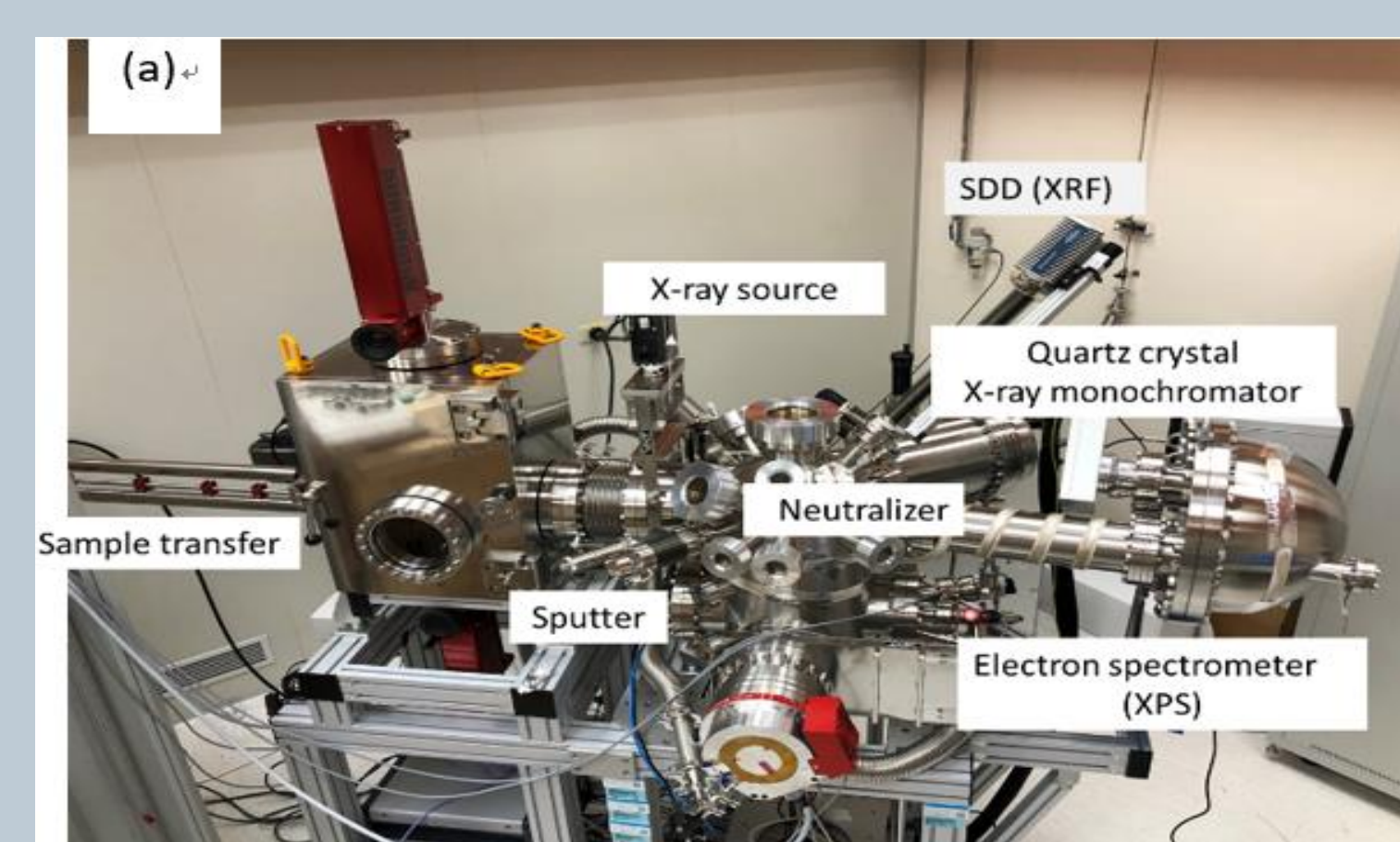
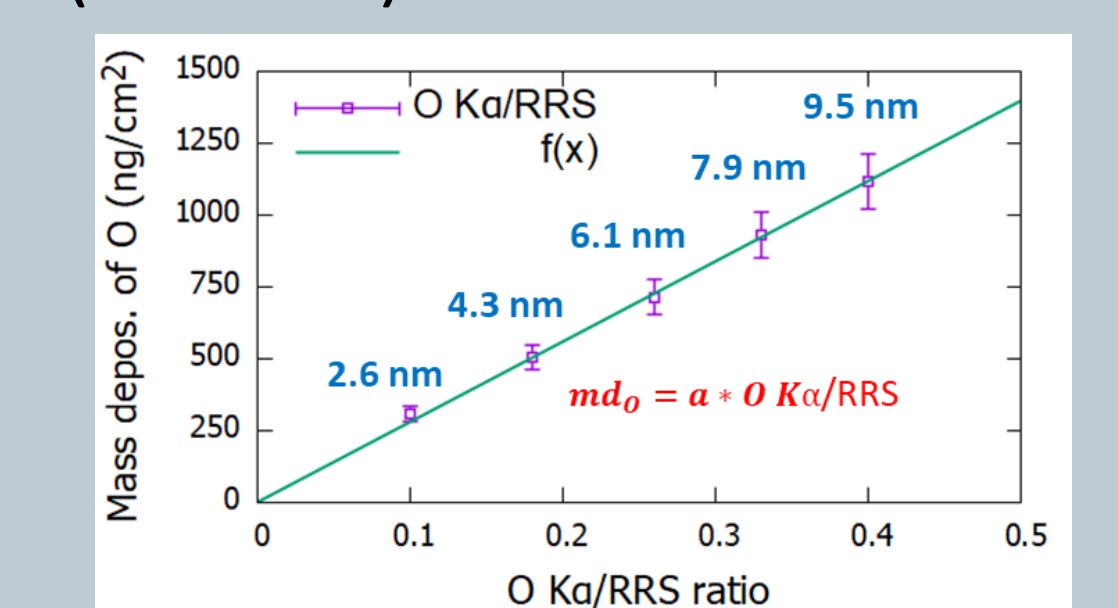


Fig.2 XRF/XPS surface analysis system

XRF :

to quantify the mass deposition of oxygen (md_o) on the surface layer based on the SiO_2 reference samples (2-10 nm).

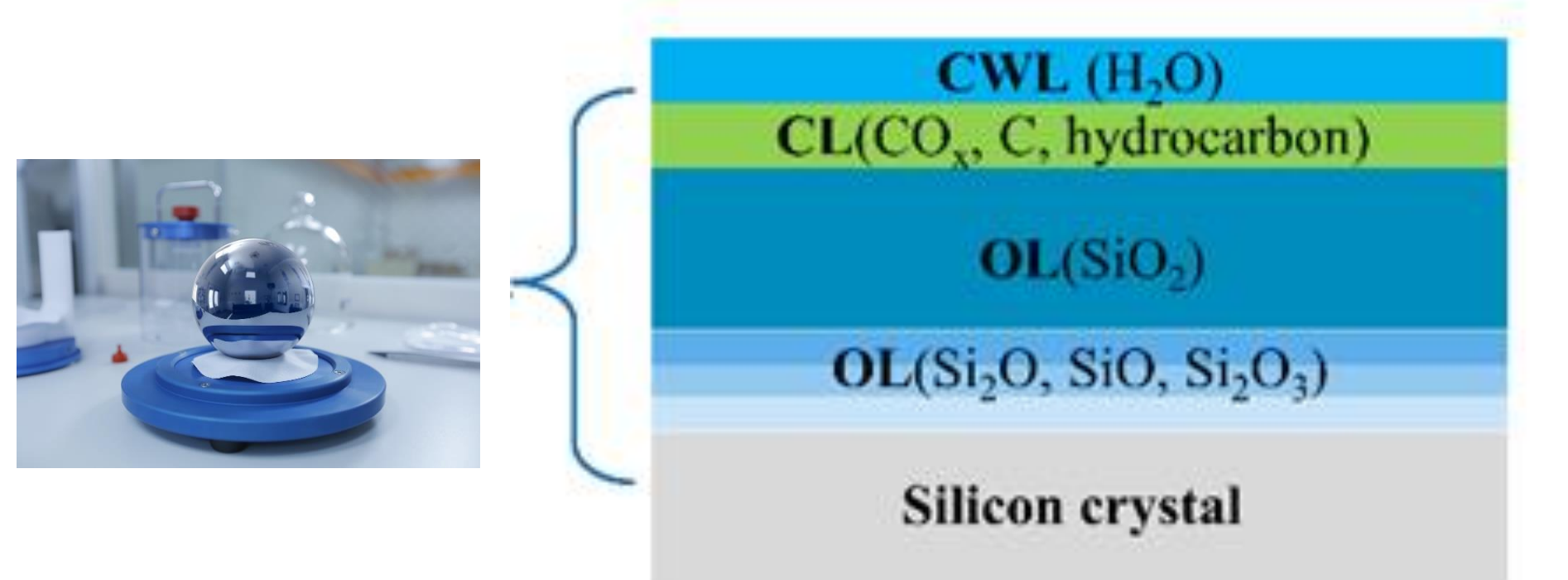


XPS :

provides relative atomic fractions and the chemical state in each layer by integrating the signal peaks of each element.

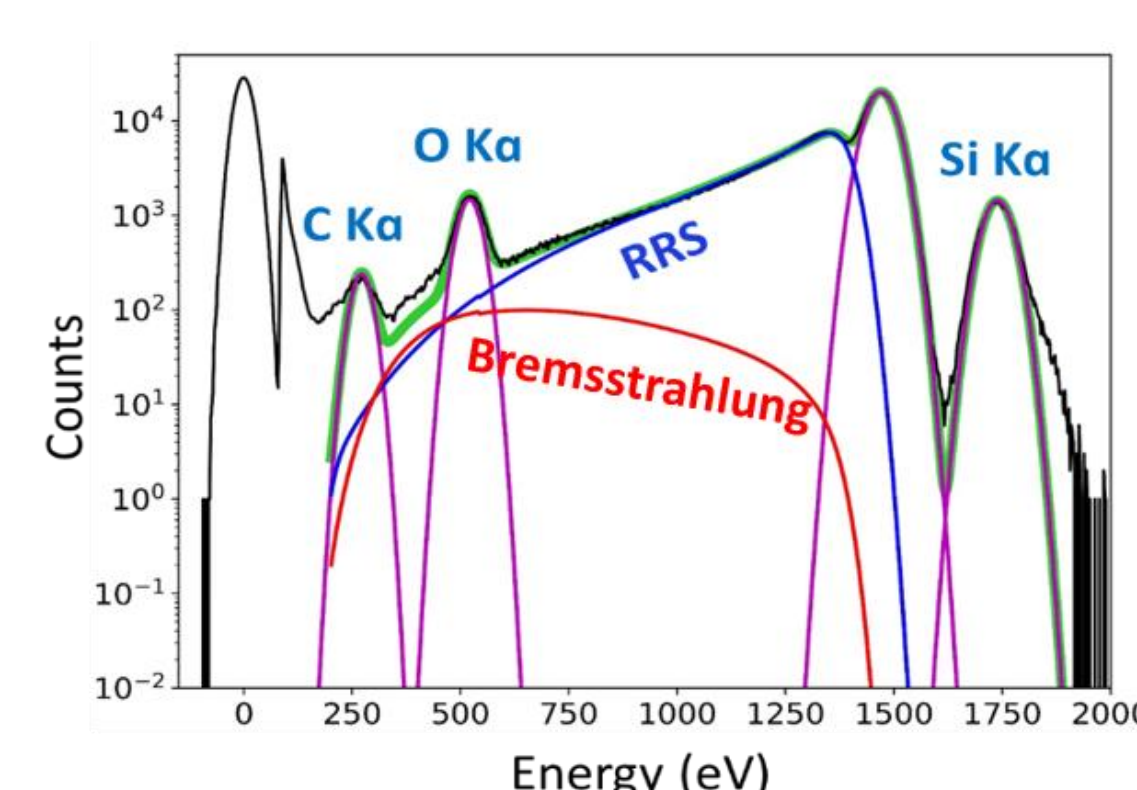
The deposition mass of surface thin film

Data analysis and discussion (Si- sphere and semiconductor thin film)

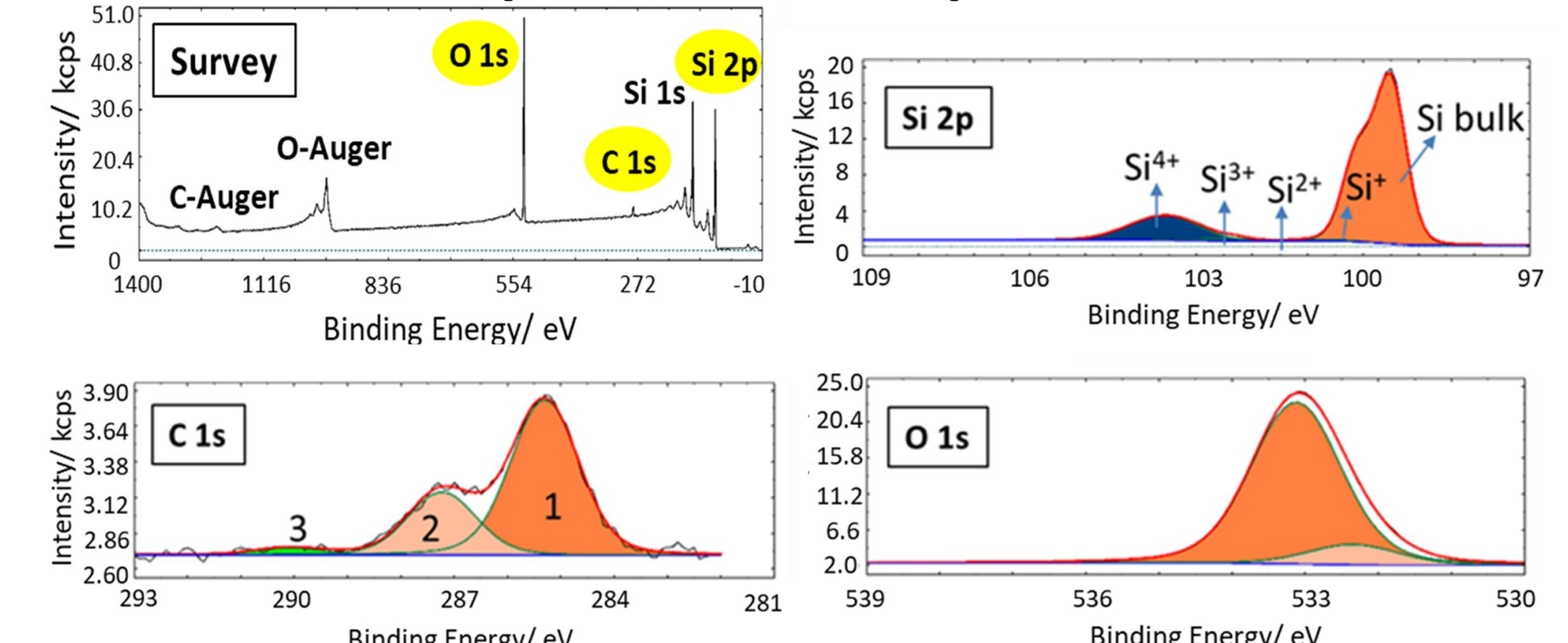


Surface layer mode of Si- sphere

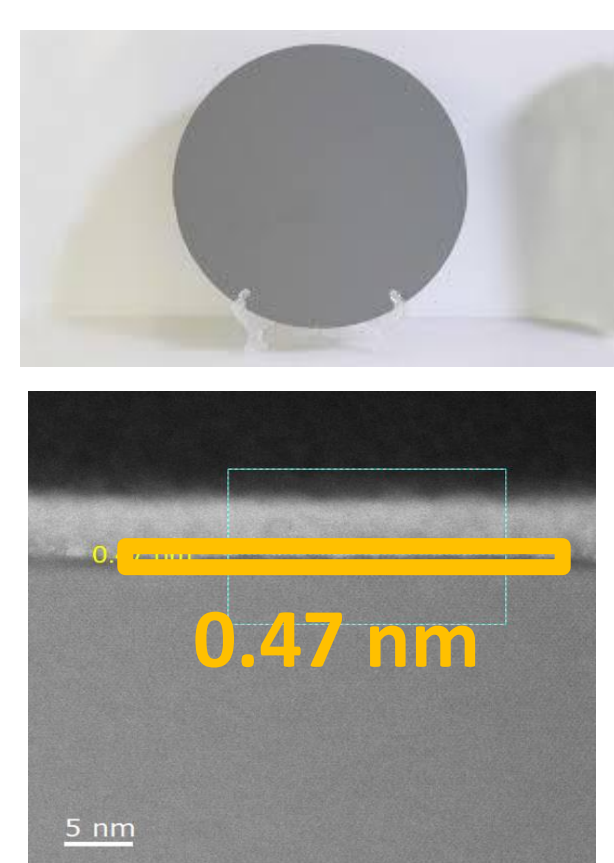
XRF spectrum of Si sphere



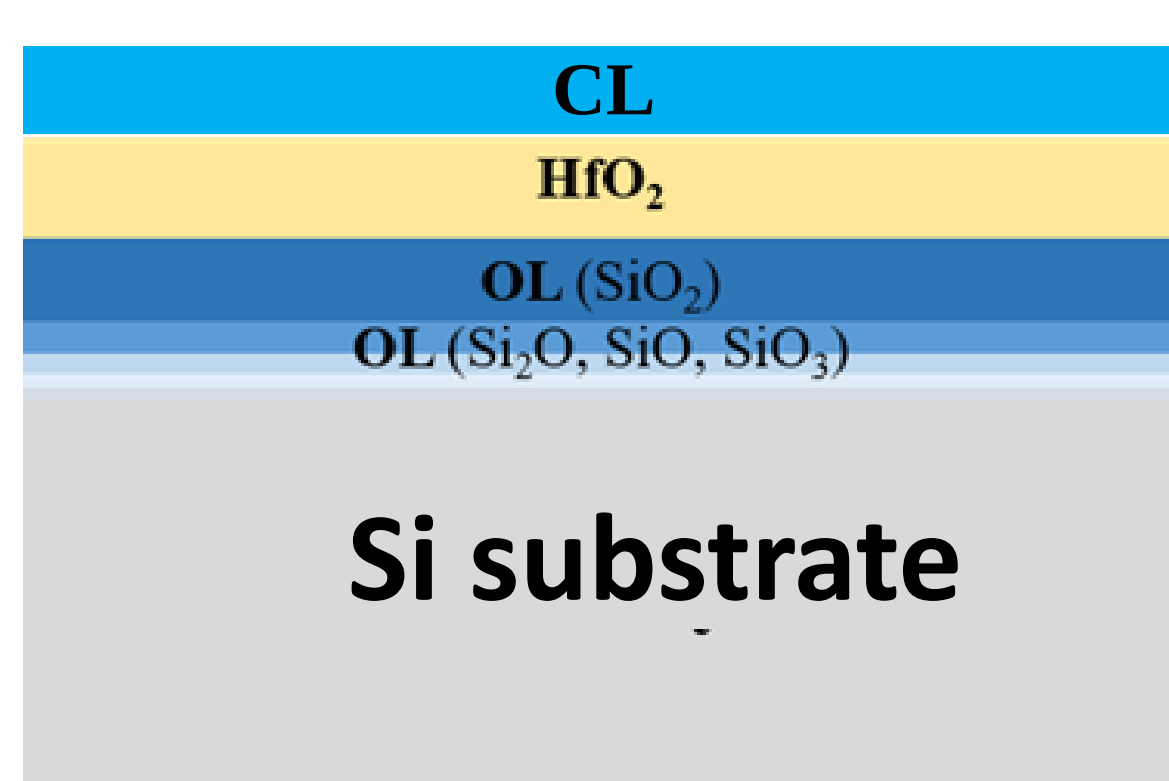
XPS spectrum of Si sphere



Sample	md_o by XRF	Atomic ratio by XPS	Mass deposition (ng/cm^2)	Thickness
Si-sphere	145(13) ng/cm^2	$C_{\text{Si}} : C_{\text{C}} : C_{\text{O}} = 25.3\% : 11.7\% : 62.9\%$	$md_{\text{C}}:20(15), md_{\text{Si}}:102(11), md_{\text{H}}:3(1)$	OL: 1.05(12) nm, CL :0.24(16) nm, CWL: 0.38(9) nm
HfO_2	99(10) ng/cm^2	$C_{\text{Si}} : C_{\text{C}} : C_{\text{O}} : C_{\text{Hf}} = 16.3\% : 28.0\% : 53.7\% : 2.0\%$	$md_{\text{Hf}}: 49, md_{\text{Si}}:55$	OL: 0.54 nm, (Due to acid clean process before ALD) HfO_2 : 0.48 nm (Cs-TEM: 0.47 nm)

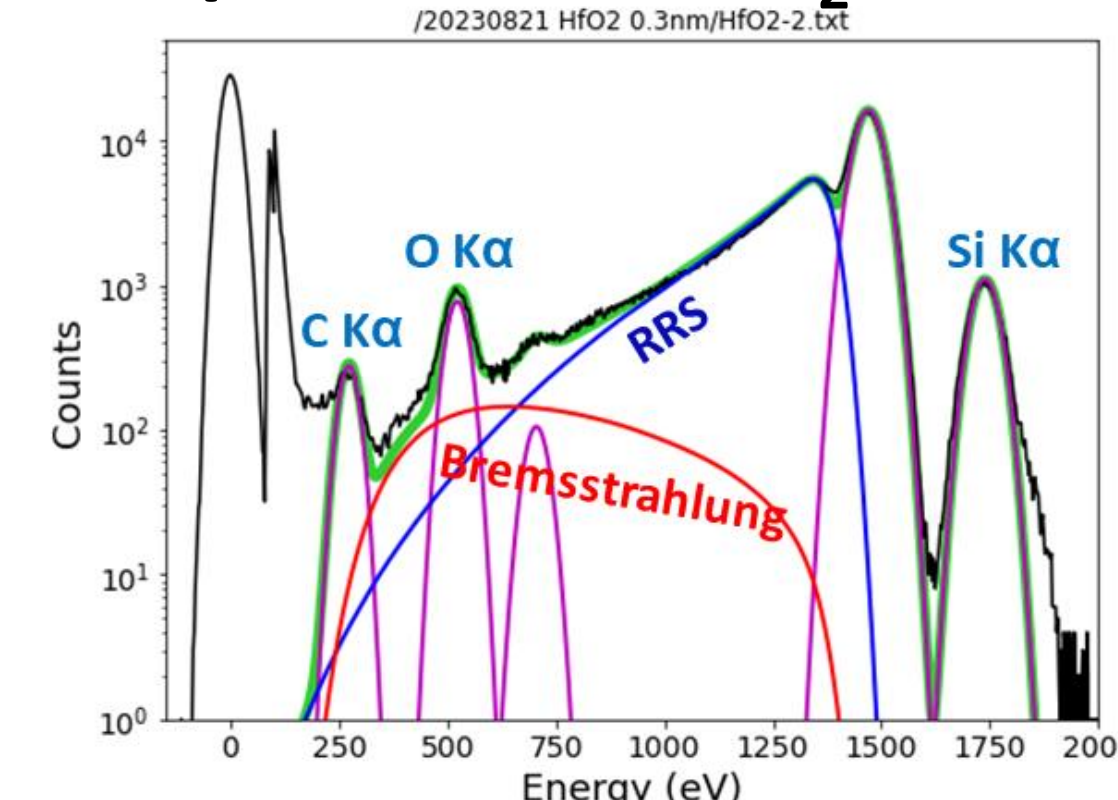


Cs-TEM

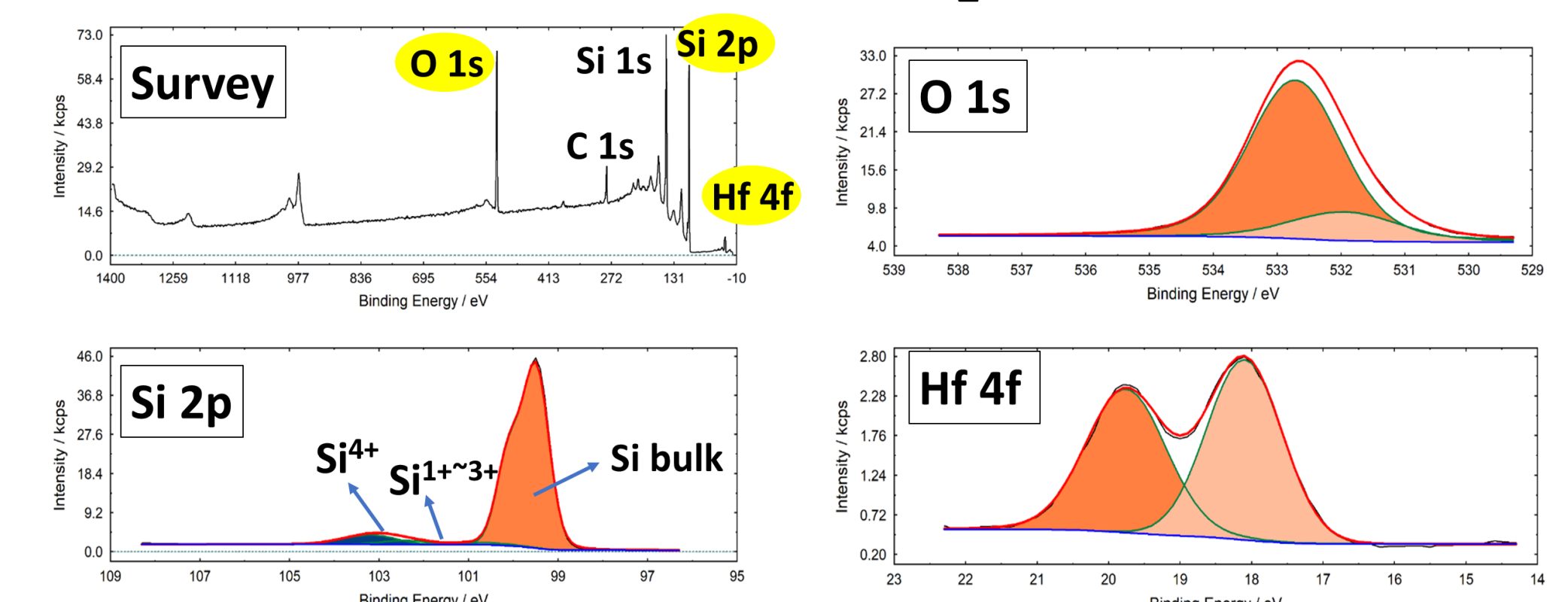


Surface layer mode of HfO_2 thin film

XRF spectrum of HfO_2 thin film



XPS spectrum of HfO_2 thin film



Conclusion

The quantitative analysis using XRF and XPS enables the determination of the mass of each element in HfO_2 , which can be converted into film thickness based on density. The measured thickness shows a high degree of consistency with the results obtained from TEM. From these results, this quantitative XRF/XPS surface analysis technique shows its potential for applications in ultrathin film analysis (thickness below 1 nm) in the semiconductor industry. Applications to different thin film materials will be our next challenge.