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Characterization of High-k Dielectrics (HfO_2, Al_2O_3, $HfAlO_x$) with VUV Spectroscopic Ellipsometer (VUV-SE) and Grazing X-ray Reflectometer (GXR)

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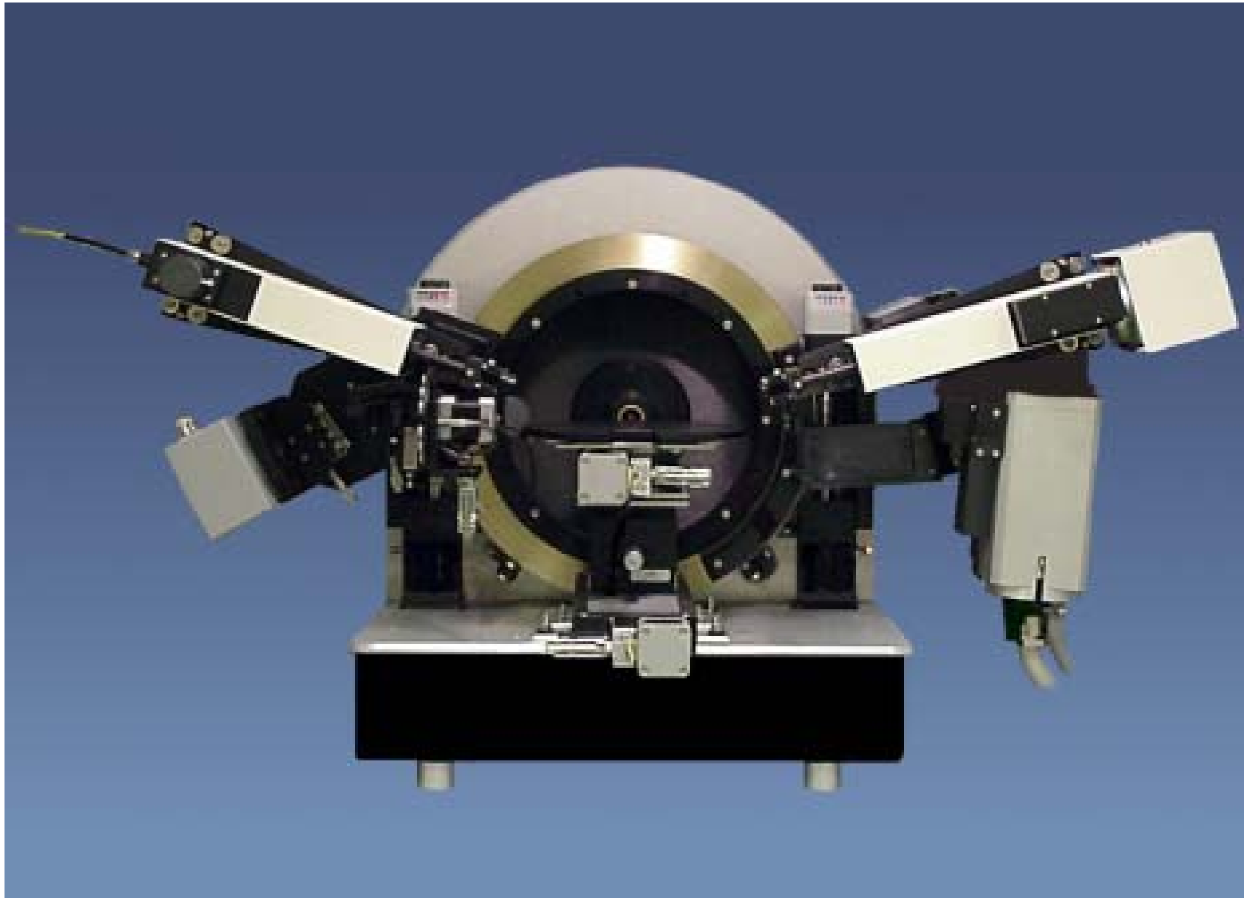
Introduction

- High-k gate dielectrics are required for sub-100nm technology node to reduce gate leakage and improve device reliability.
- For new high-k materials development, processing quality evaluation and control, a nondestructive characterization technique is desired.
- Spectroscopic ellipsometry (SE) is well-known noncontact, nondestrcutive and precise technique for determining thickness and optical properties of thin films. However, it is difficult to obtain these information unambiguously and simultaneously for ultra-thin films because of possible high correlations between them.
- A complementary nondestructive Grazing X-ray reflectometry (GXR) can be used to extract thickness for such ultra thin films. And then, optical properties of these films could be determined with SE.
- Both SE and GXR are compatible and integratible. Extending spectra down to vacuum ultra violet (VUV) could further enhance the capability of using SE for such high k dielectric characterization.

PUV SE System



Combined GXR / SE system

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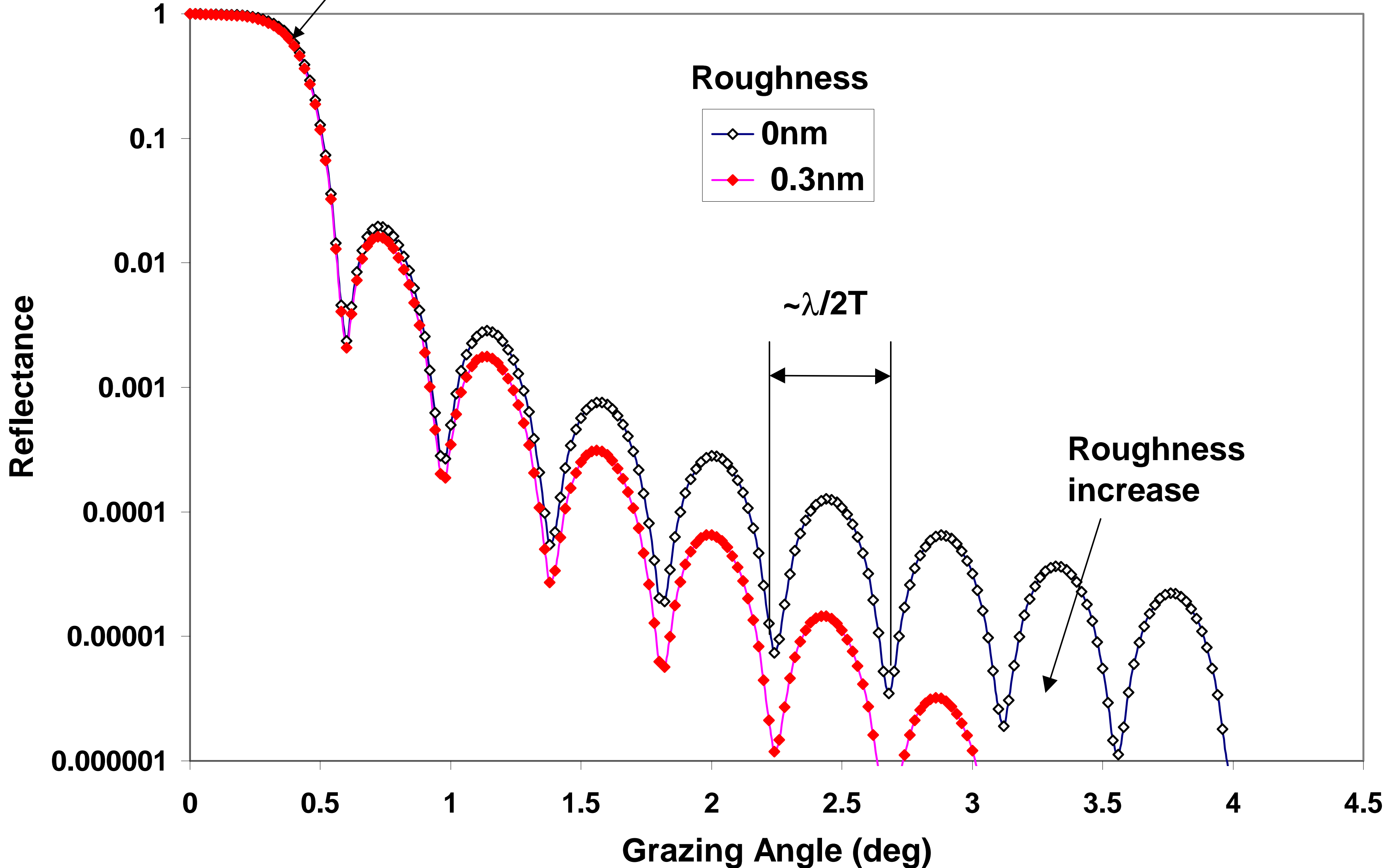
GXR Reflectometry

Grazing x-ray reflectometer is simply a reflection measurement in the hard x-ray range at the grazing angles. At a wavelength of 1.54Å (Cu - Kα), all the materials are quasi-transparent and the optical indices can be expressed by:

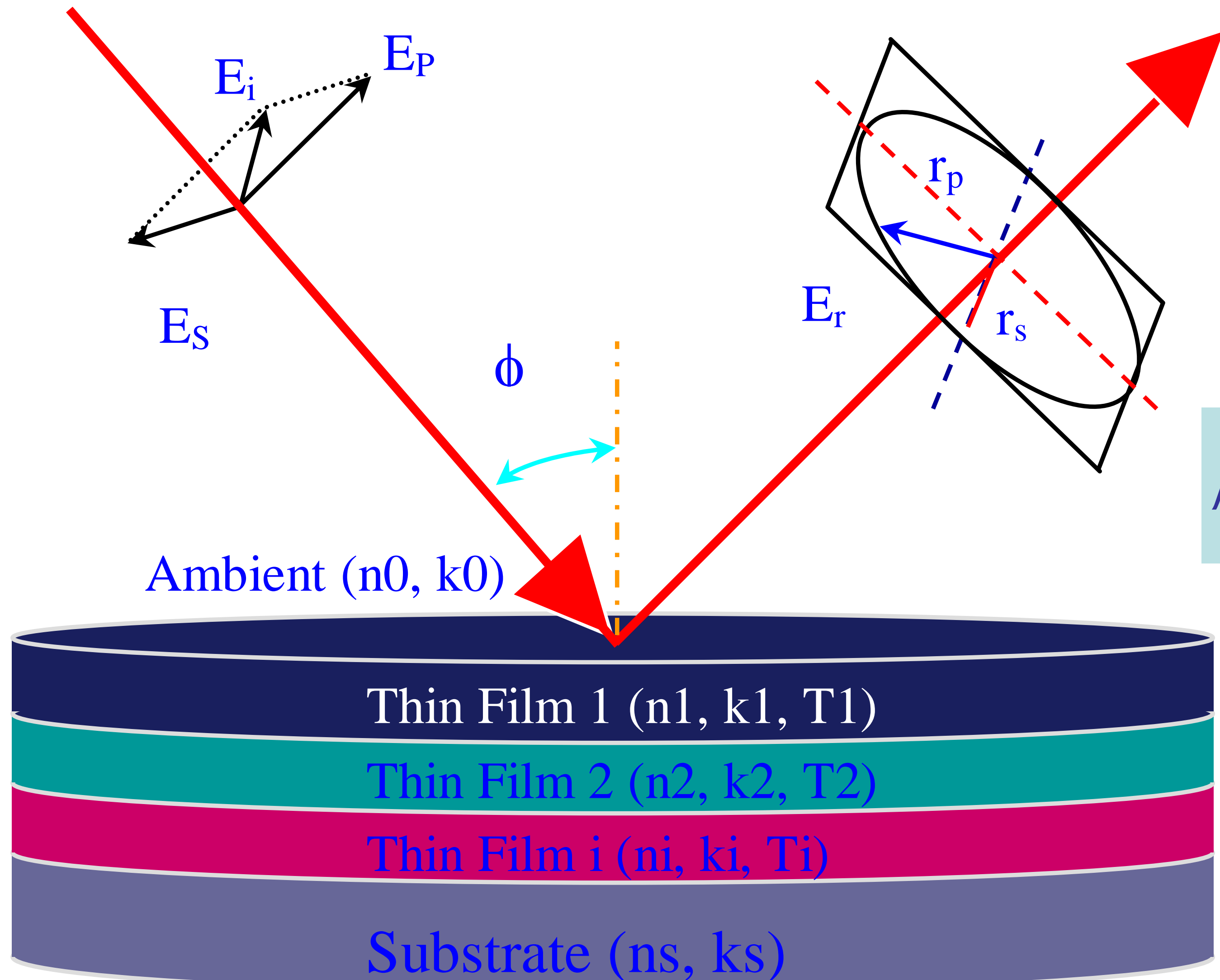
$$n = 1 - \delta - i\beta$$

where δ and β are in the range 10^{-5}-10^{-7}. So position of the interference fringes gives directly the thickness of the layers. The mean roughness is given by the rate of decrease of the reflectance curve.

GXR Basics

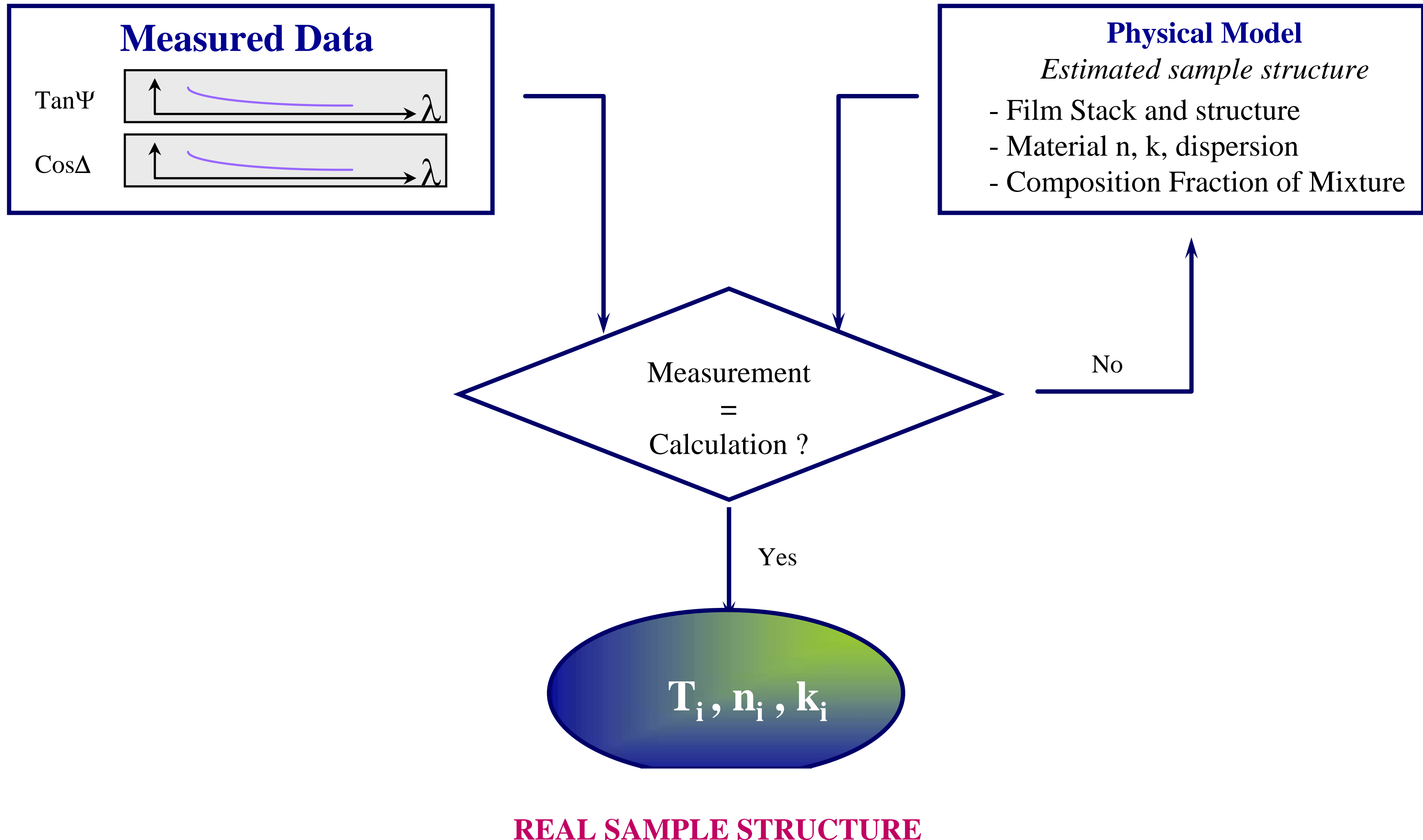


Principle of Ellipsometry



$$\rho = \frac{R_p}{R_s} = Tan\ \psi\, e^{j\Delta}$$

Model and Its Analyses



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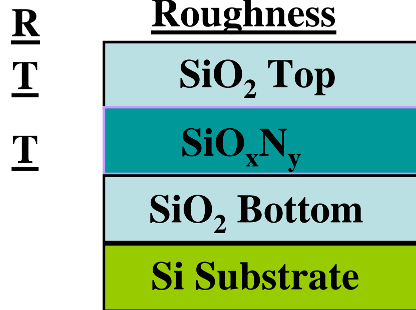
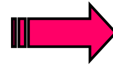
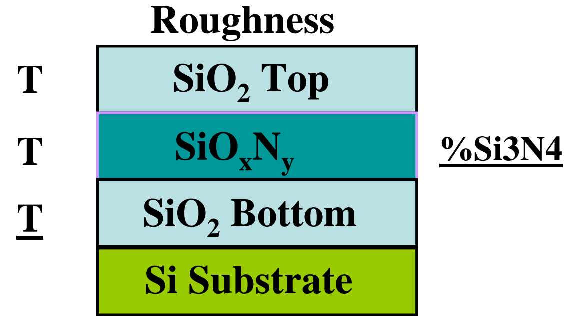
GXR Technique

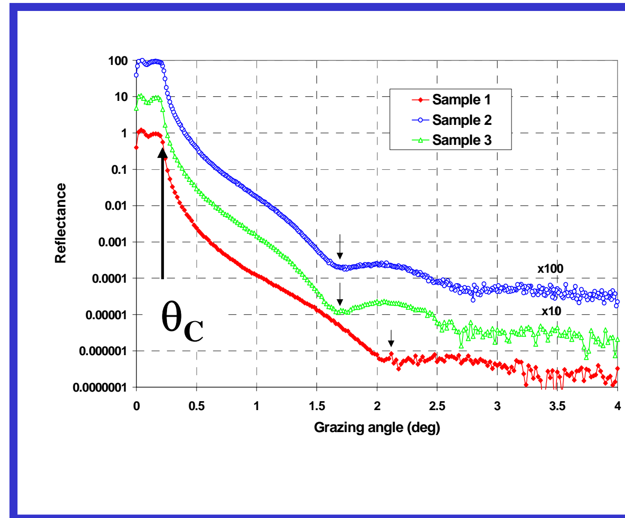




SE Technique



Model structures used for sample analysis; Underscored quantities are determined from regression analyses.



Sample	GXR			SE		XPS
	Top SiO_2 (Å)	SiN_xO_y (Å)	Roughness (Å)	Bottom SiO_2 (Å)	Si_3N_4 content (%)	N/O (%)
Sample 1	5.7±0.4	19.7±0.2	1.5±0.2	8.0±0.4	30±4	38
Sample 2	9.9±0.5	21.2±0.3	1.7±0.2	12.7±0.5	42±5	70
Sample 3	9.1±0.9	22.3±0.8	2.1±0.1	7.1±0.3	54±3	79

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Samples Description

- Films: HfO_2, $HfAlO_x$ and Al_2O_3
- Substrate and Size: (100) silicon wafer and 200mm in diameter.
- Deposition Technique: Atomic Layer Deposition (ALD) technique at IMEC.
- Al concentration in $HfAlO_x$ was varied by changing the relative number of $HfCl_4$ and $Al(CH_3)_3$ cycles (2:1, 1:1 and 1:2).
- Annealing Effect on HfO_2 film: annealed in a nitrogen ambient at 700ºC for 1 min. after the deposition.

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Sample List

Sample number	Type	Hf:Al Cycle Ratio	Total Cycles #	Interface layer	Thermal treatment
1	HfAlOx	2:1	9	1 nm RT0 ASM	none
2	HfAlOx	1:1	10	1 nm RT0 ASM	none
3	HfAlOx	1:2	9	1 nm RT0 ASM	none
4	HfAlOx	2:1	27	1 nm RT0 ASM	none
5	HfAlOx	1:1	28	1 nm RT0 ASM	none
6	HfAlOx	1:2	27	1 nm RT0 ASM	none
7	HfAlOx	2:1	90	1 nm RT0 ASM	none
8	HfAlOx	1:1	90	1 nm RT0 ASM	none
9	HfAlOx	1:2	90	1 nm RT0 ASM	none
10	HfAlOx	2:1	909	Hf last	none
11	HfAlOx	1:1	910	Hf last	none
12	HfAlOx	1:2	909	Hf last	none
13	HfO2	/	100	Hf last	none
14	HfO2	/	100	Hf last	700°C
15	Al2O3	/	1000	Hf last	none

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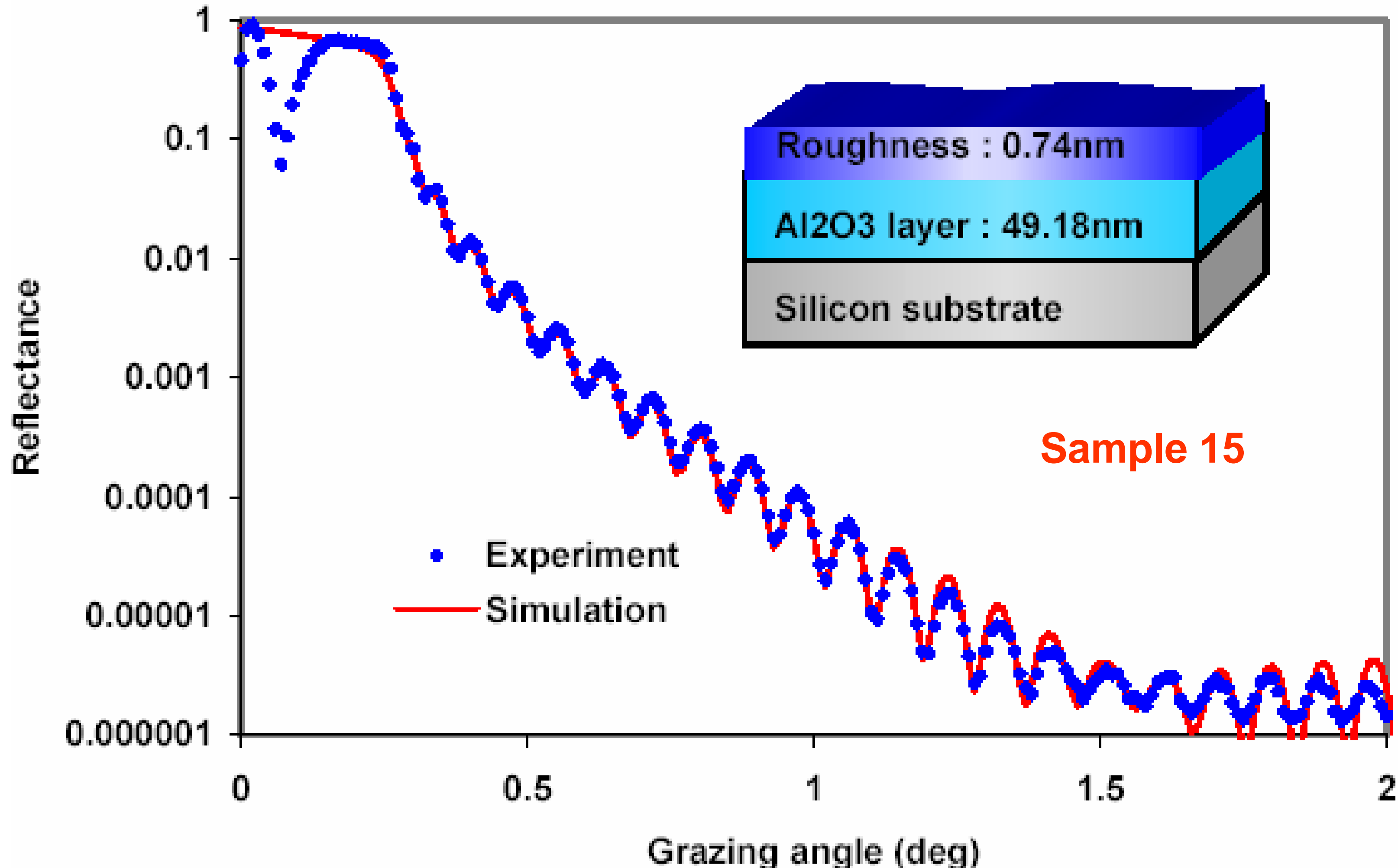
Al_2O_3 Layer Thickness by GXR



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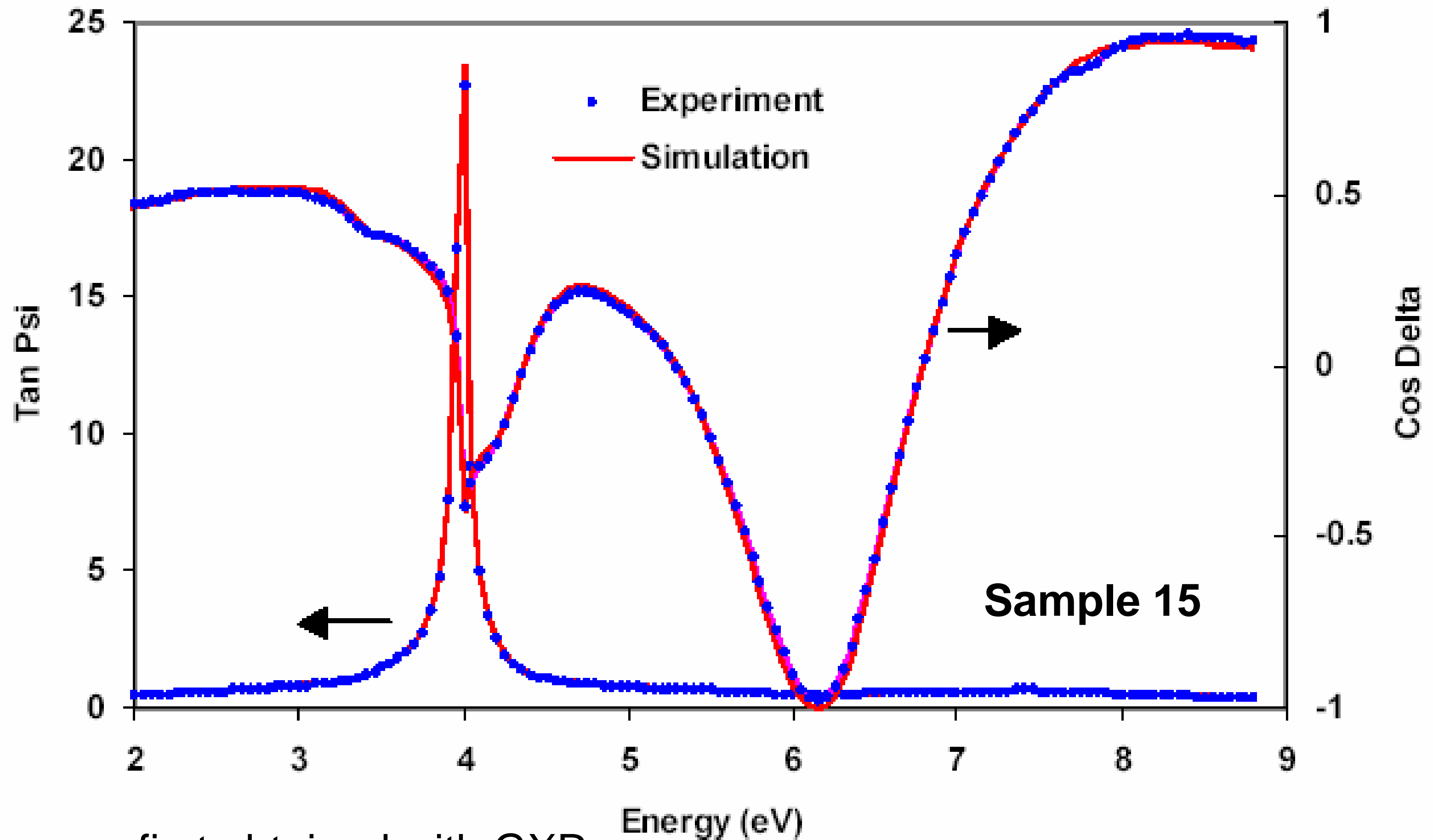
Measured and Fitted SE Spectra

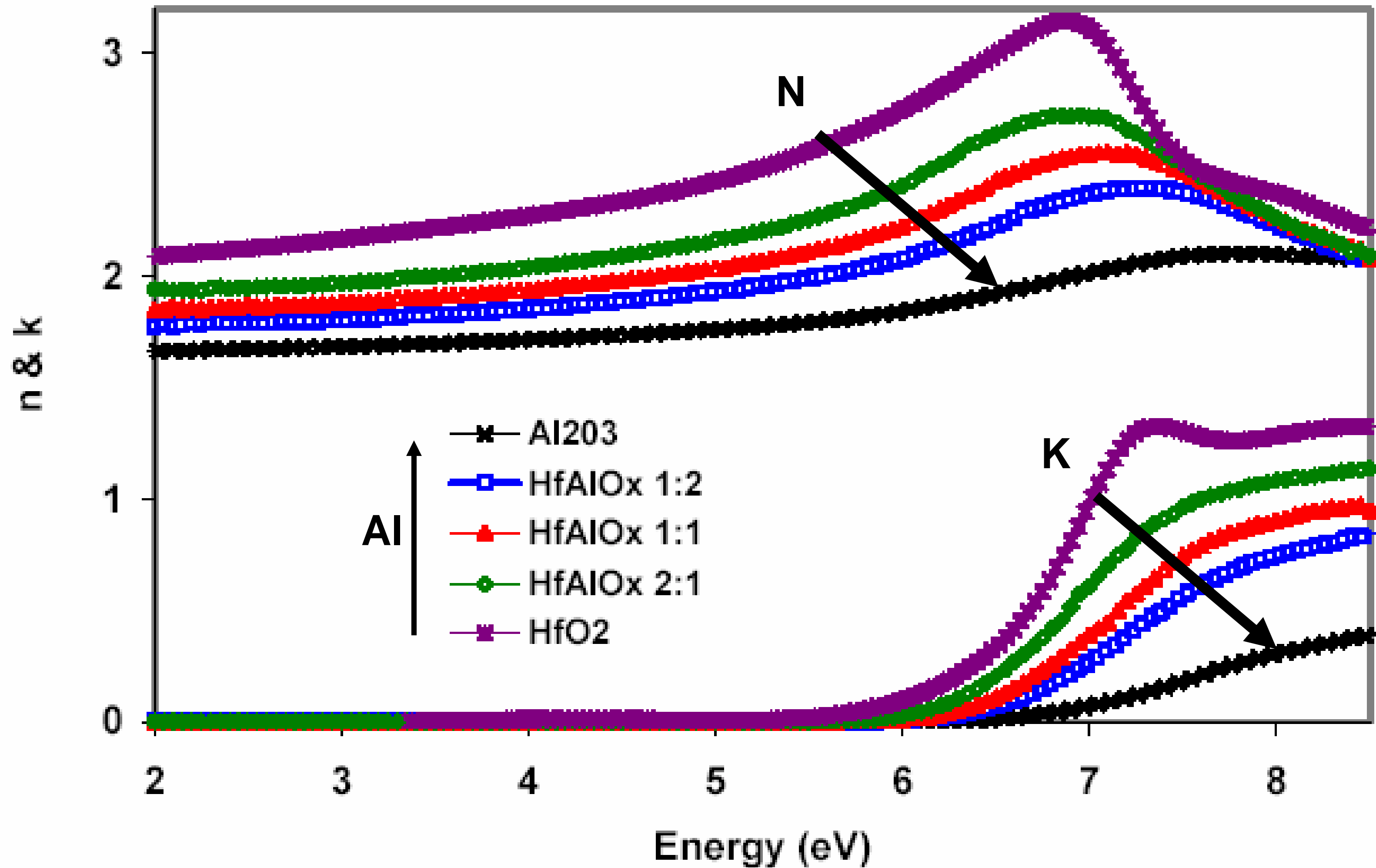


Thickness was first obtained with GXR

Optical constants (N&K) were then obtained through NK calculation from the measured SE spectra.

Obtained thickness and optical constants were confirmed with calculating SE spectra

Optical Constants for Studied Films



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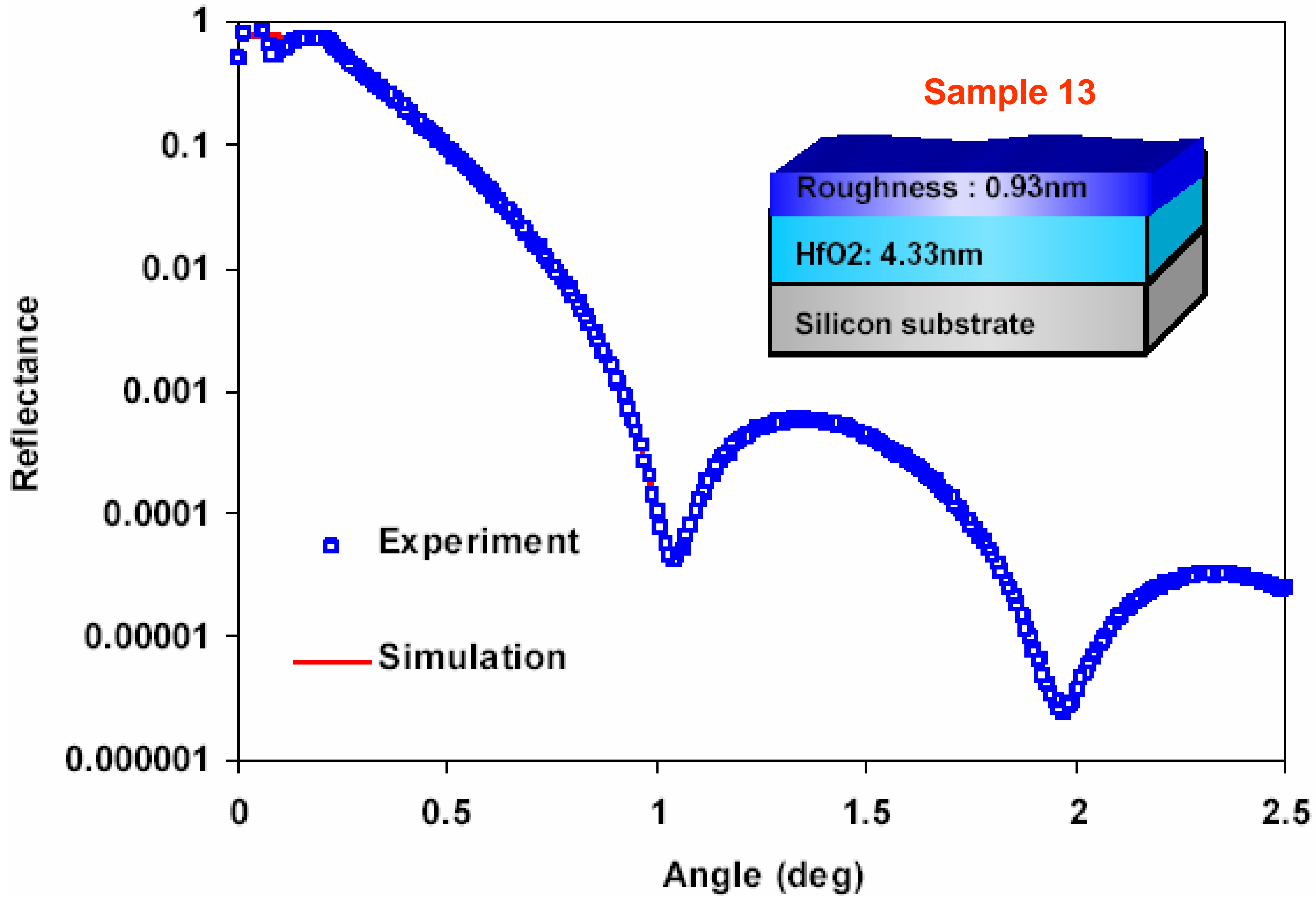
GXR Analysis on HfO_2 Film



Effect of Annealing on Optical Constants of HfO_2 Film

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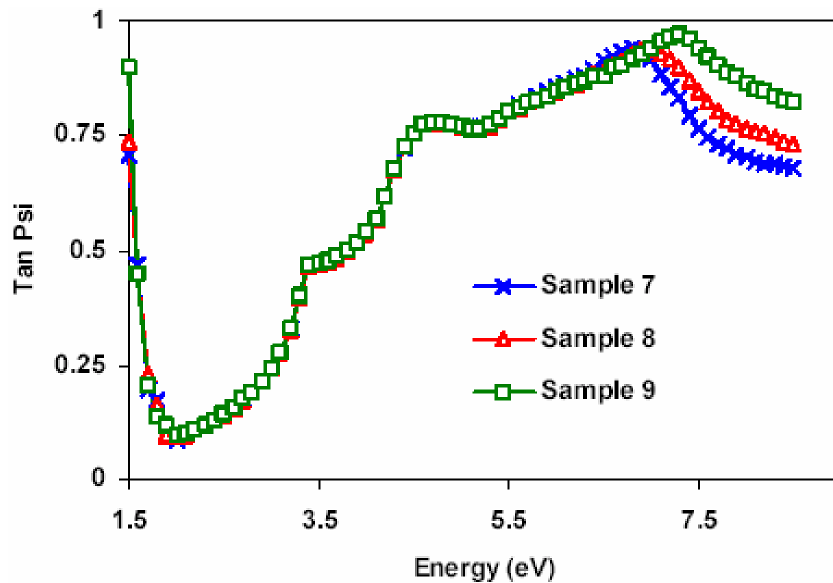
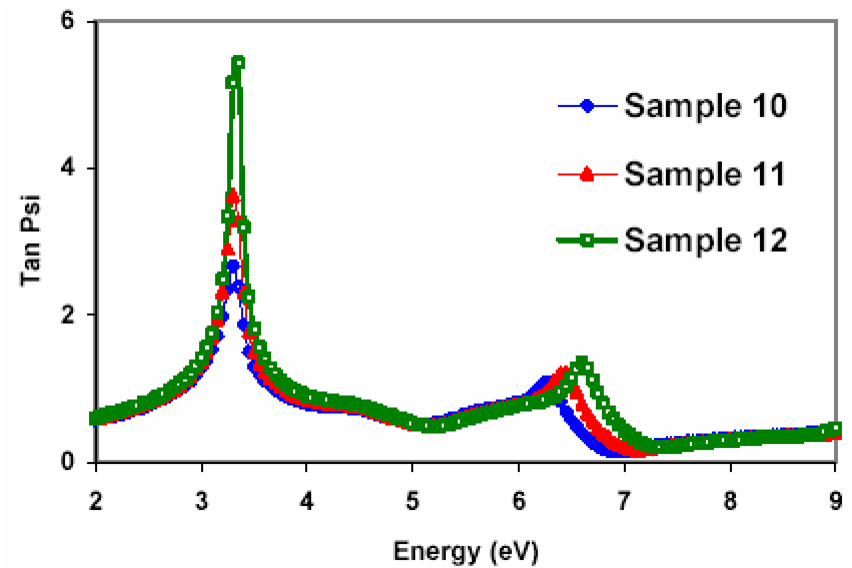
Features in VUV Range





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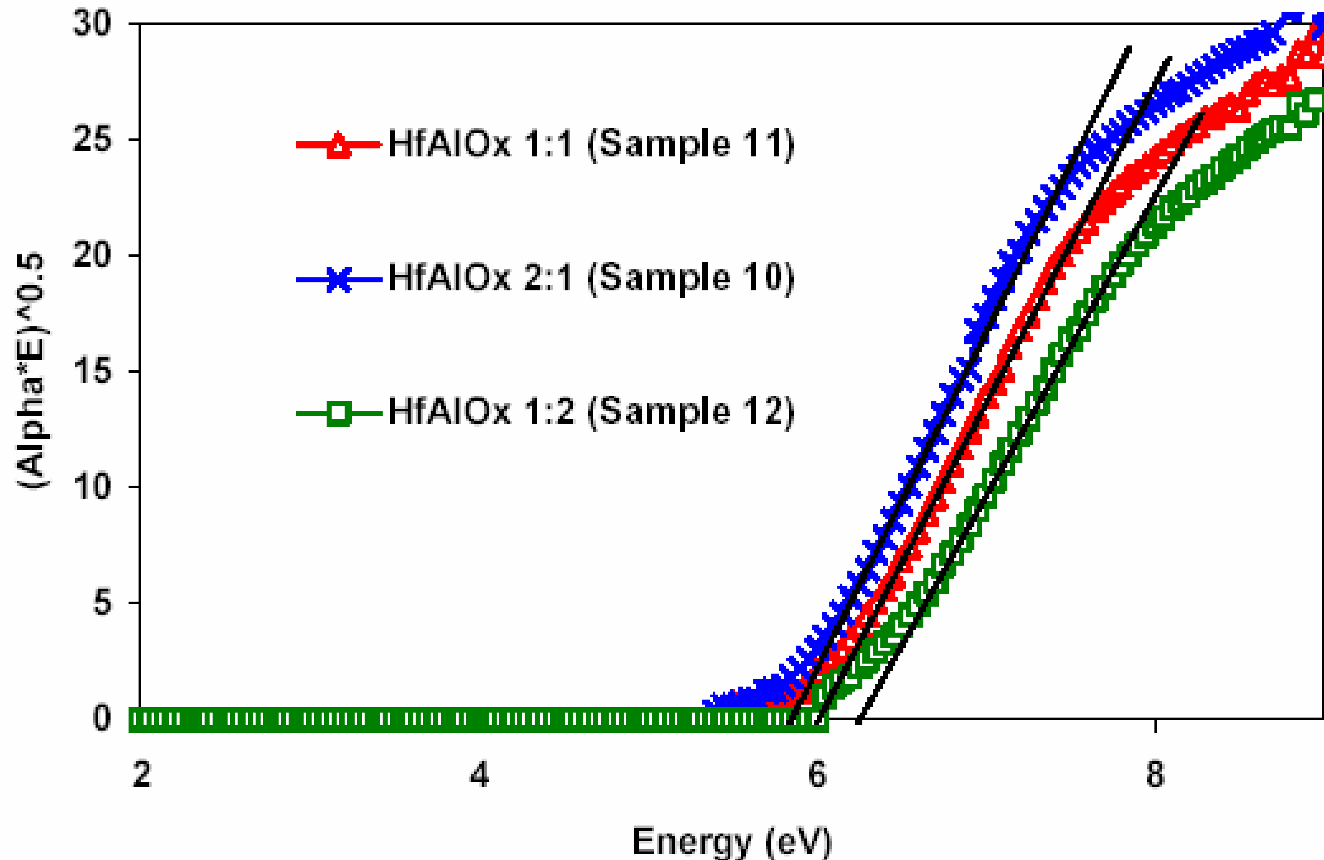
Bang Gaps Determination



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Analysis Results

Sample number	Hf:Al Cycle Ratio	Number cycles	Thickness (nm)	Al2O3 mol fraction	Band gap (eV)
1	2:1	9	0.45±0.03	0.25±0.10	/
2	1:1	10	0.93±0.04	0.44±0.09	/
3	1:2	9	0.91±0.06	0.47±0.13	/
4	2:1	27	1.84±0.05	0.34±0.04	/
5	1:1	28	2.00±0.04	0.41±0.03	/
6	1:2	27	2.10±0.03	0.52±0.03	/
7	2:1	90	5.75±0.06	0.33±0.01	/
8	1:1	90	5.61±0.05	0.41±0.01	/
9	1:2	90	5.88±0.05	0.61±0.01	/
10	2:1	909	53.20±0.05	0.263 (XRF)	5.89±0.01
11	1:1	910	56.10±0.03	0.415 (XRF)	6.00±0.02
12	1:2	909	58.83±0.03	0.594 (XRF)	6.15±0.01

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Summary

- GXR is a nondestructive technique which could be used to characterize ultrathin high-k dielectric films for thickness.
- With thickness information from GXR, optical properties could be then obtained by SE with a high confidence. In addition, relative Al_2O_3 content in the compound $HfAlO_x$ can be estimated based SE spectra from EMA mixture model.
- VUV SE spectra offer more features due to absorption and band gap. It is expected that Al concentration in $HfAlO_x$ could be obtained through monitoring band gap shifting.