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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Contents

- Introduction
- Grazing X-ray Reflectometry and Spectroscopic Ellipsometry
- Sample Preparation and Characterization
- Results and Discussion
- Summary

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

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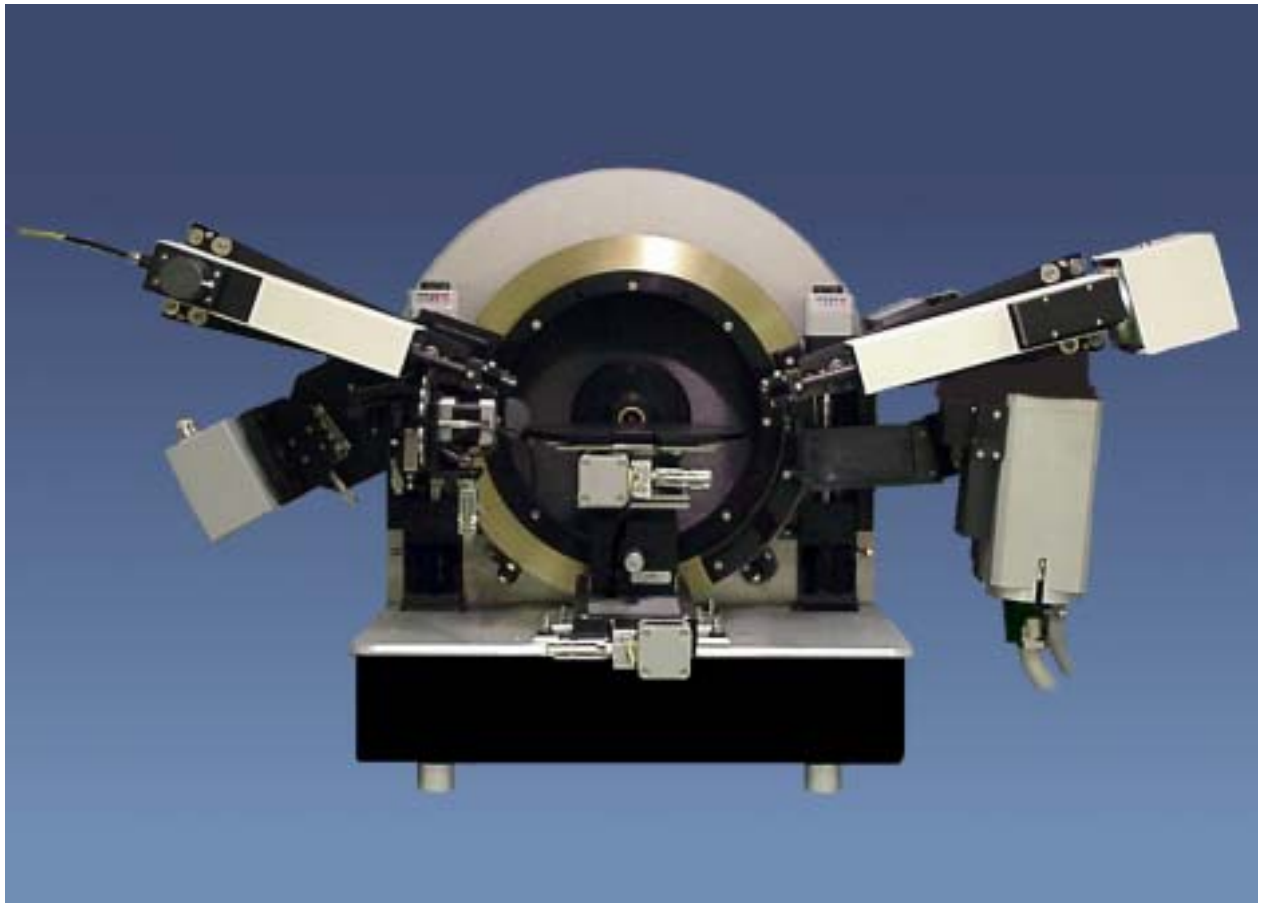

Combined GXR / SE system

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GXR Reflectometry

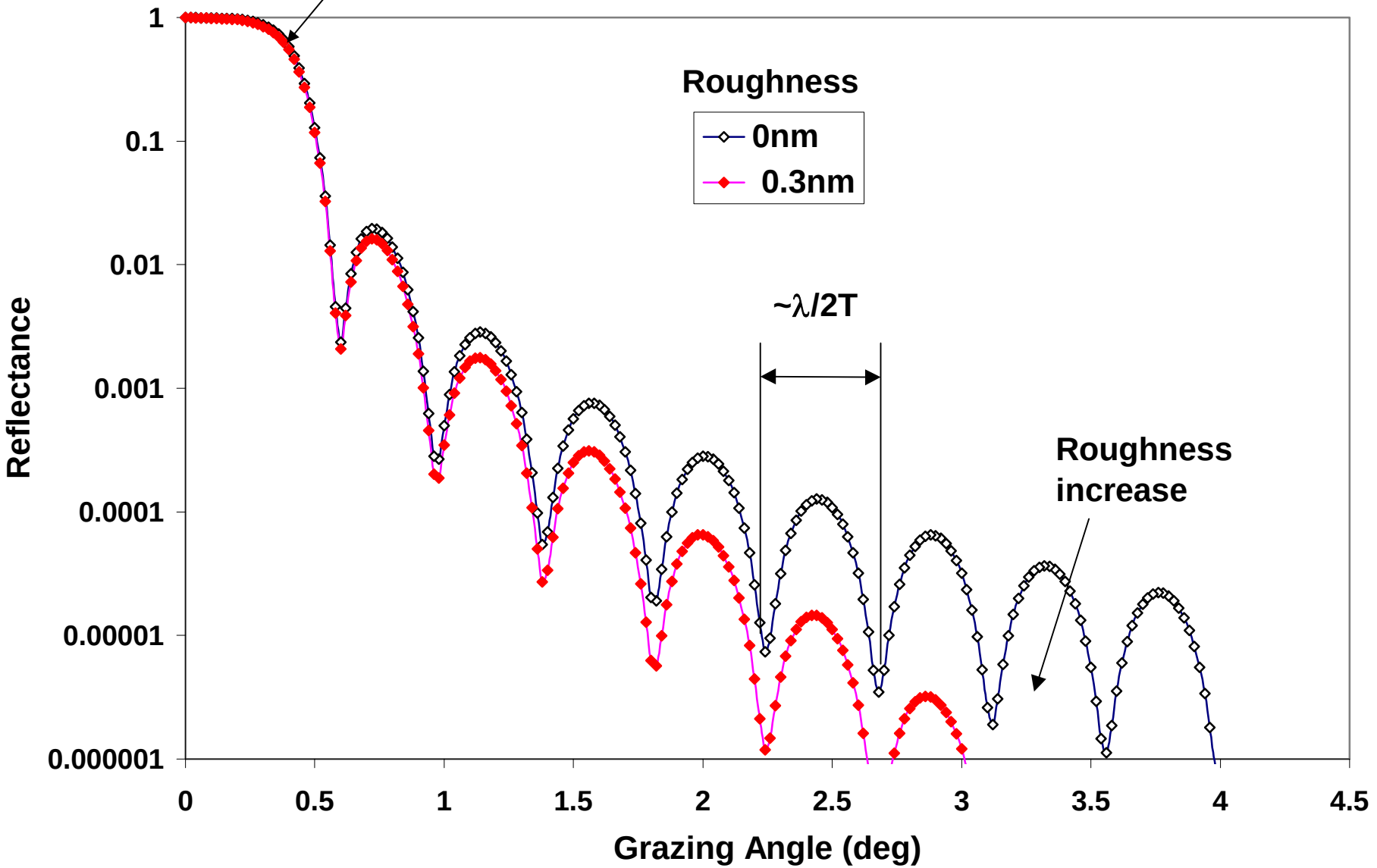
Grazing x-ray reflectometer is simply a reflection measurement in the hard x-ray range at the grazing angles. At a wavelength of 1.54Å (Cu - Kα), all the materials are quasi-transparent and the optical indices can be expressed by:

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

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

$$\theta_c \approx \sqrt{2\delta}$$



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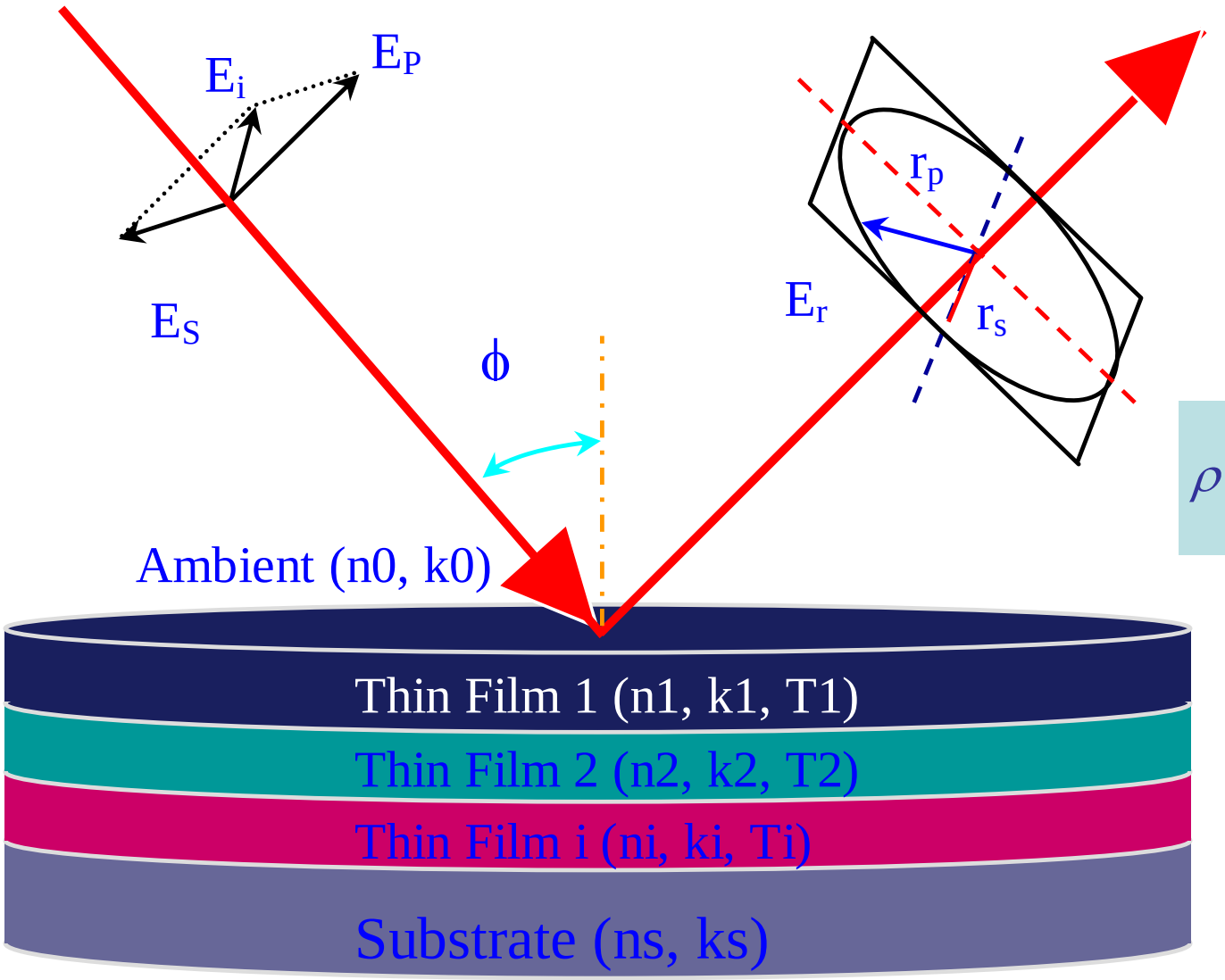
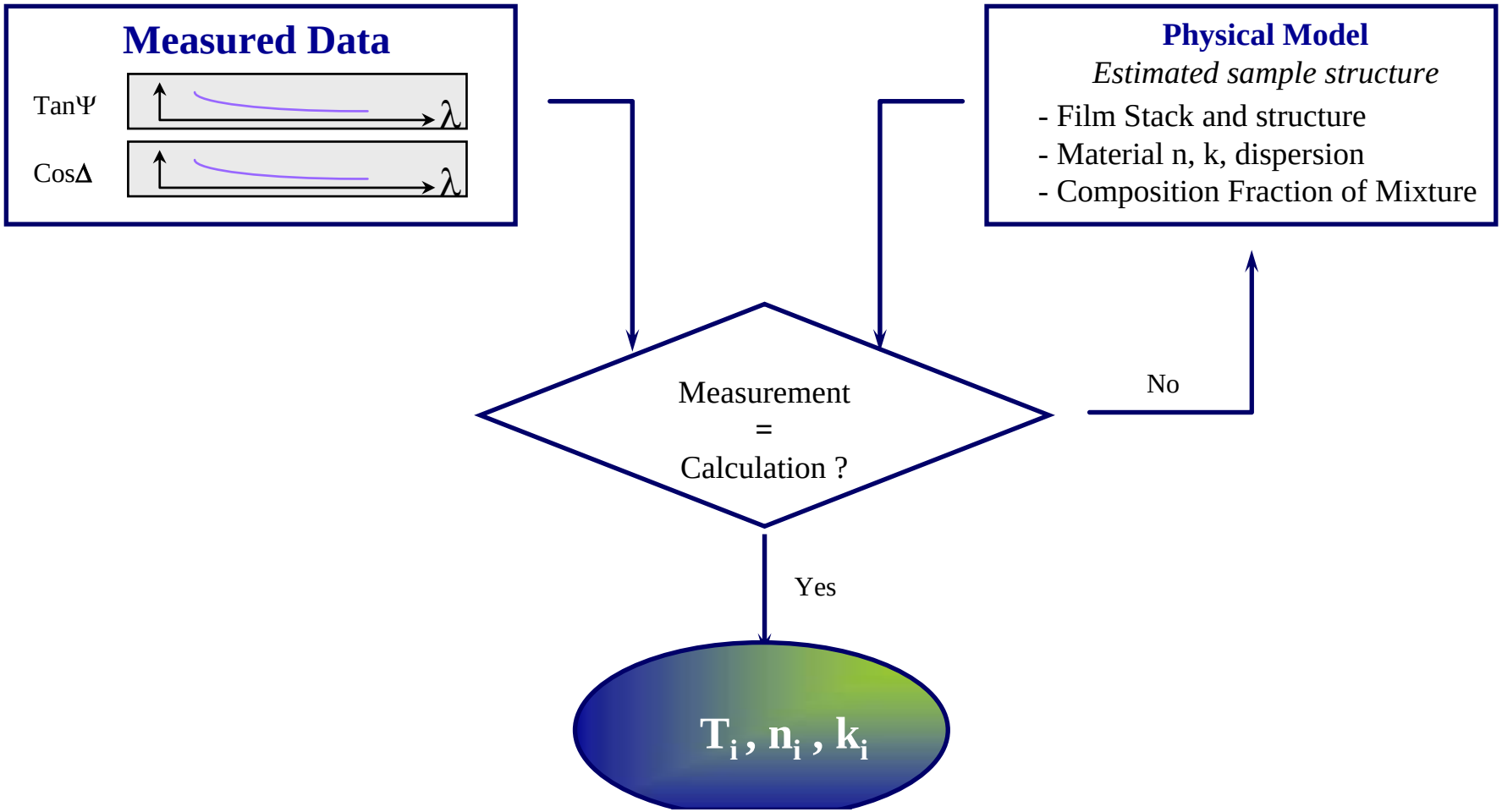
Principle of Ellipsometry

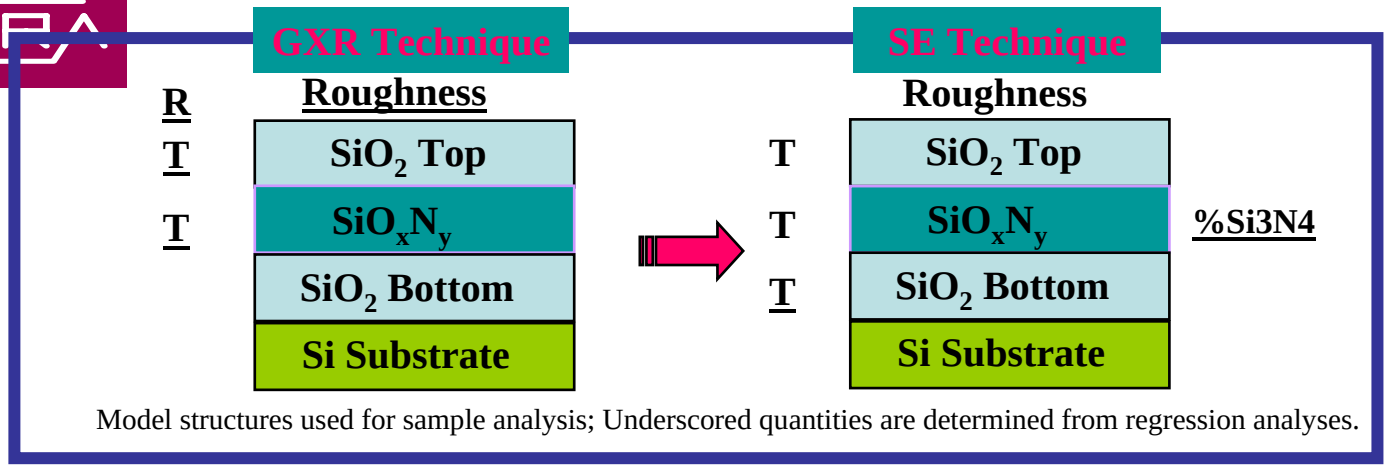


$$\rho = \frac{R_p}{R_s} = Tan\ \psi\, e^{j\Delta}$$

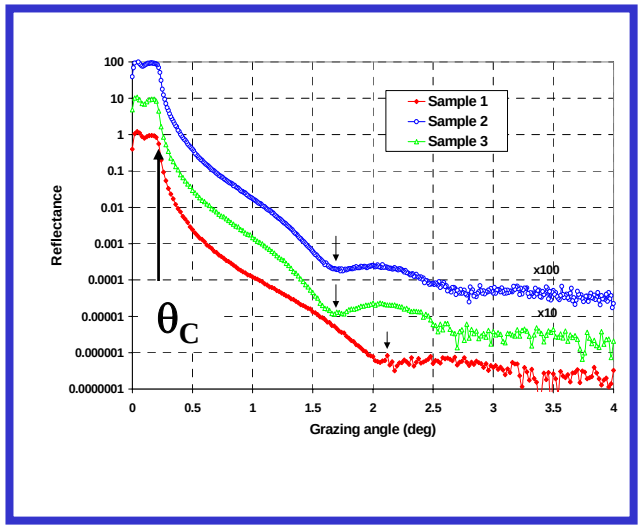
Model and Its Analyses



REAL SAMPLE STRUCTURE



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

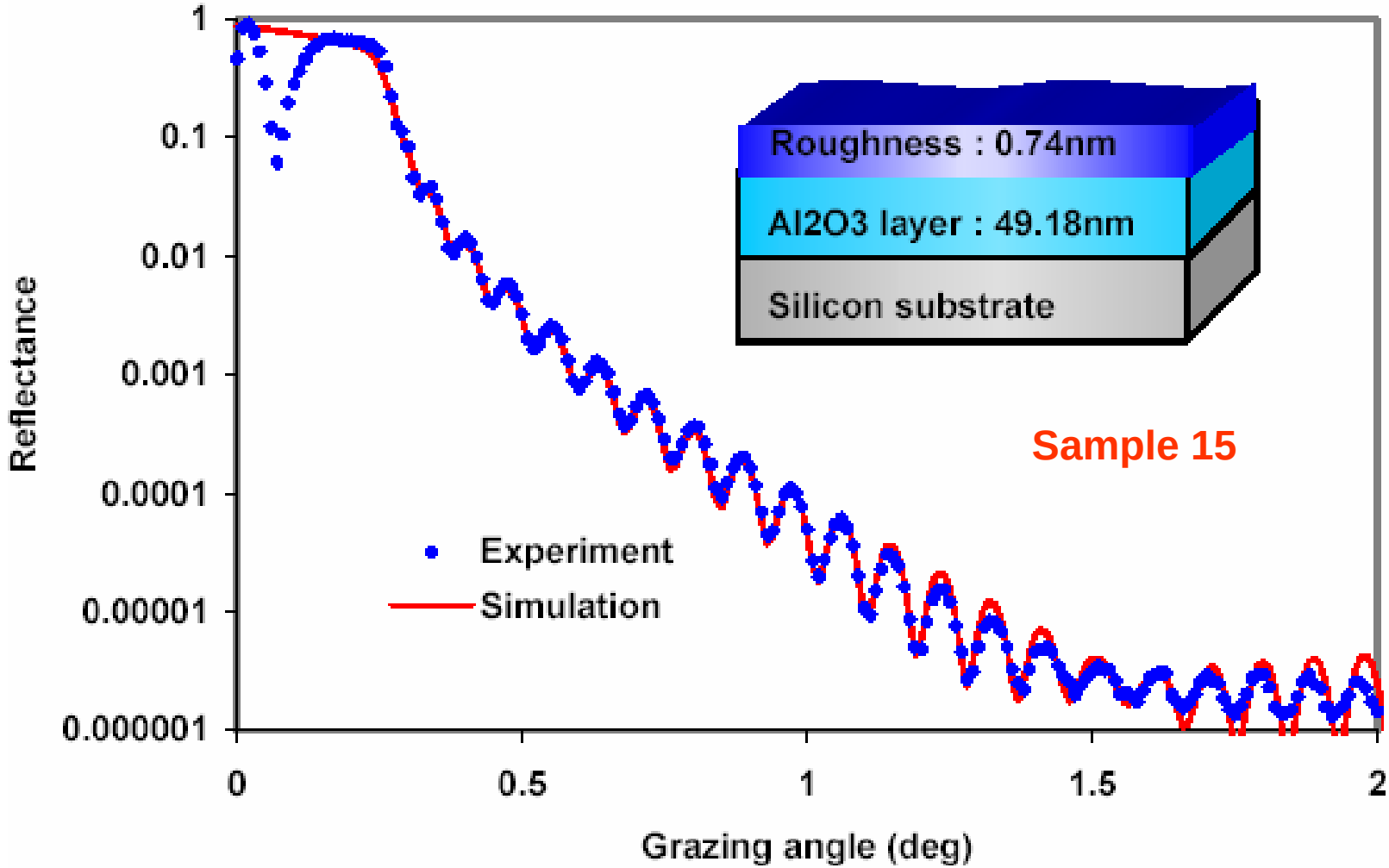
Samples Description

- 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.

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

Al_2O_3 Layer Thickness by GXR



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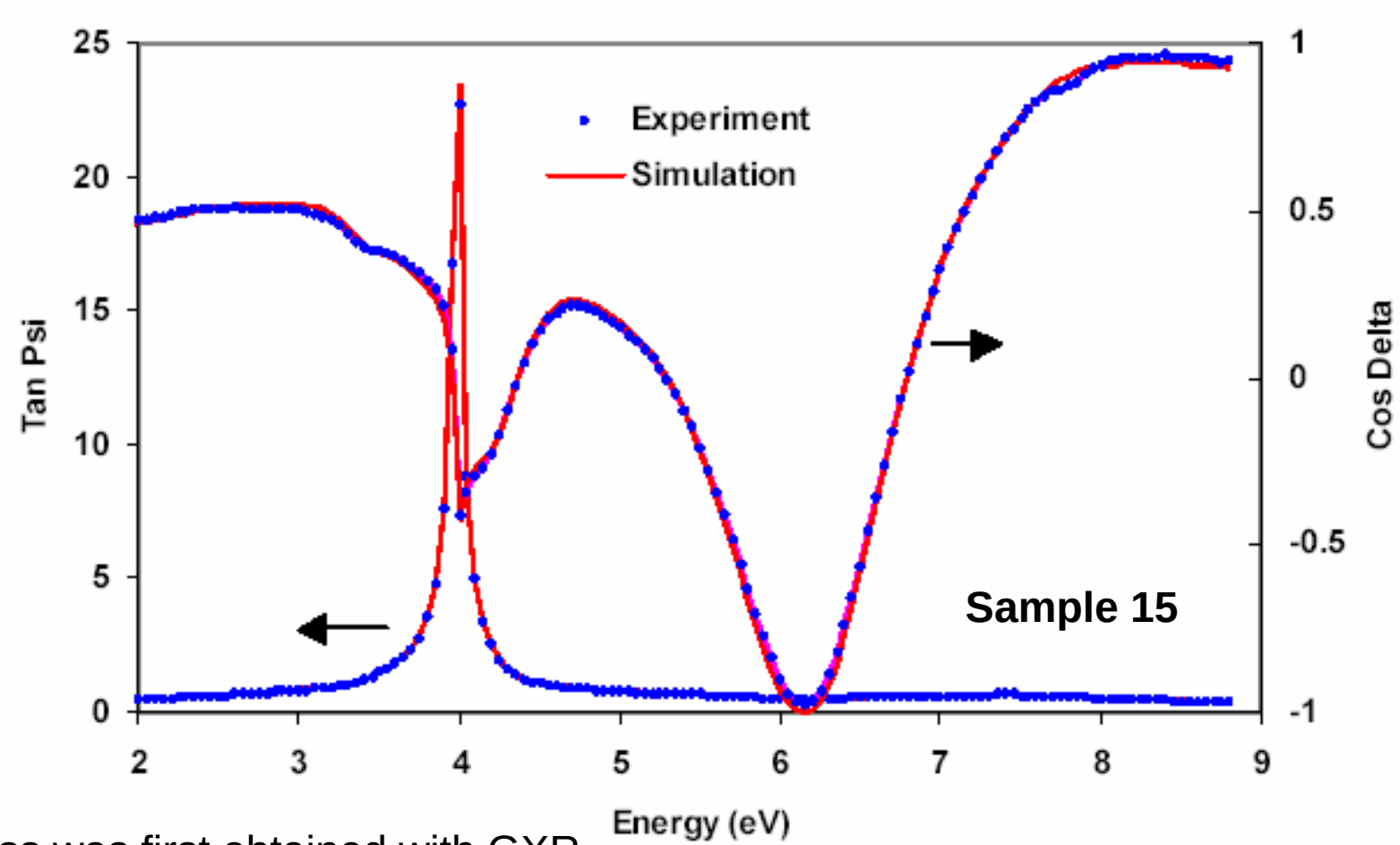
Measured and Fitted SE Spectra



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

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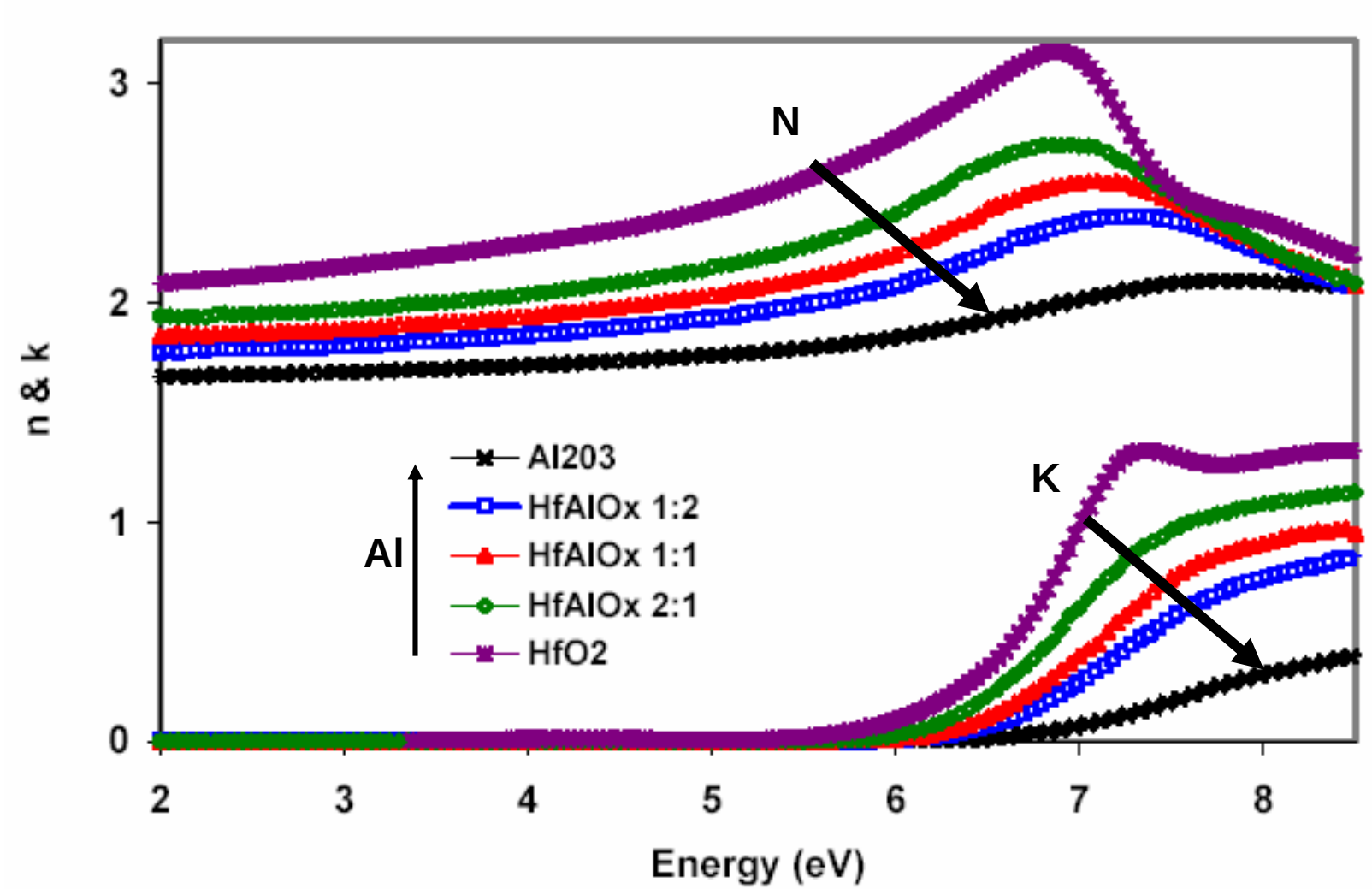
Optical Constants for Studied Films



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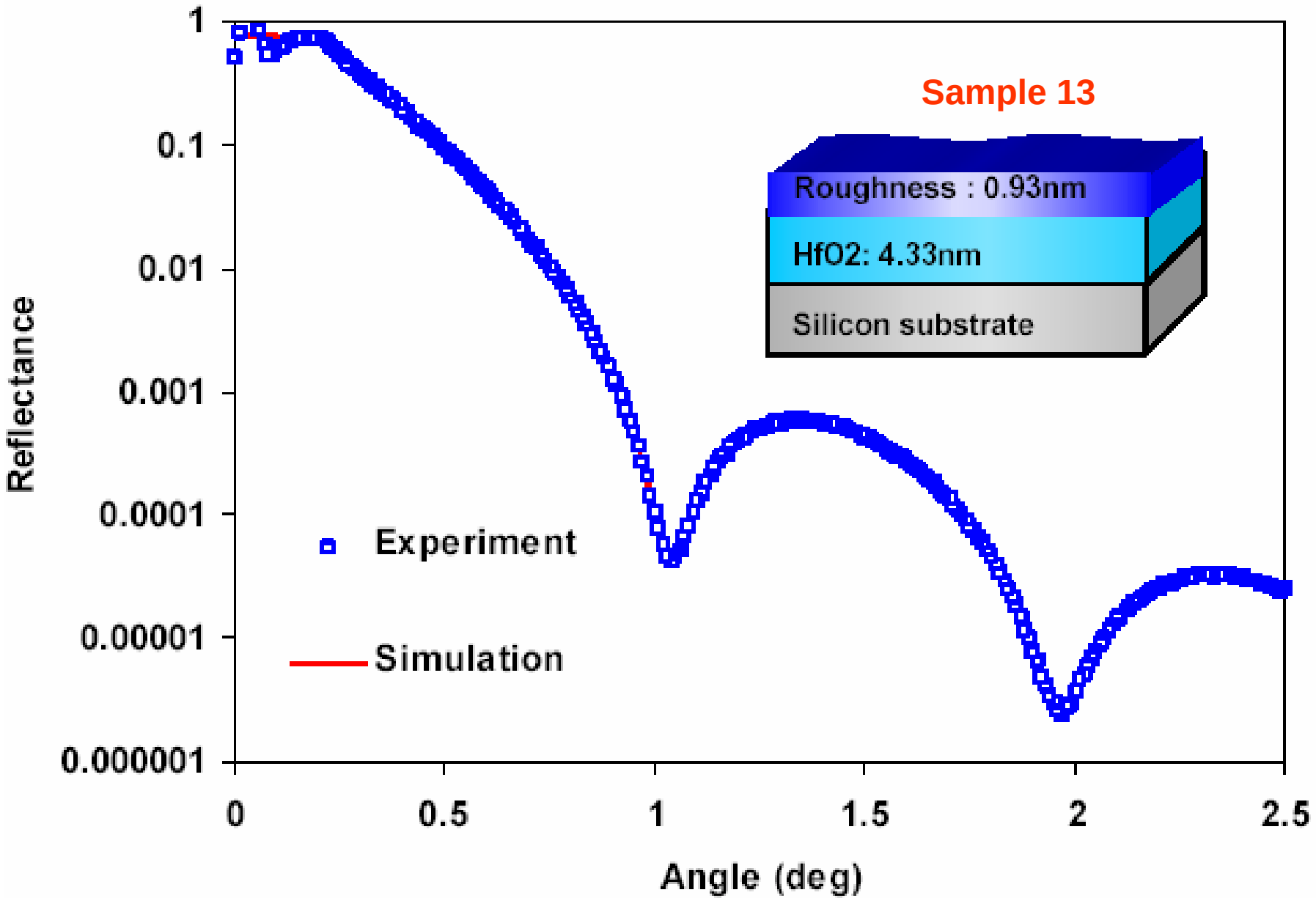
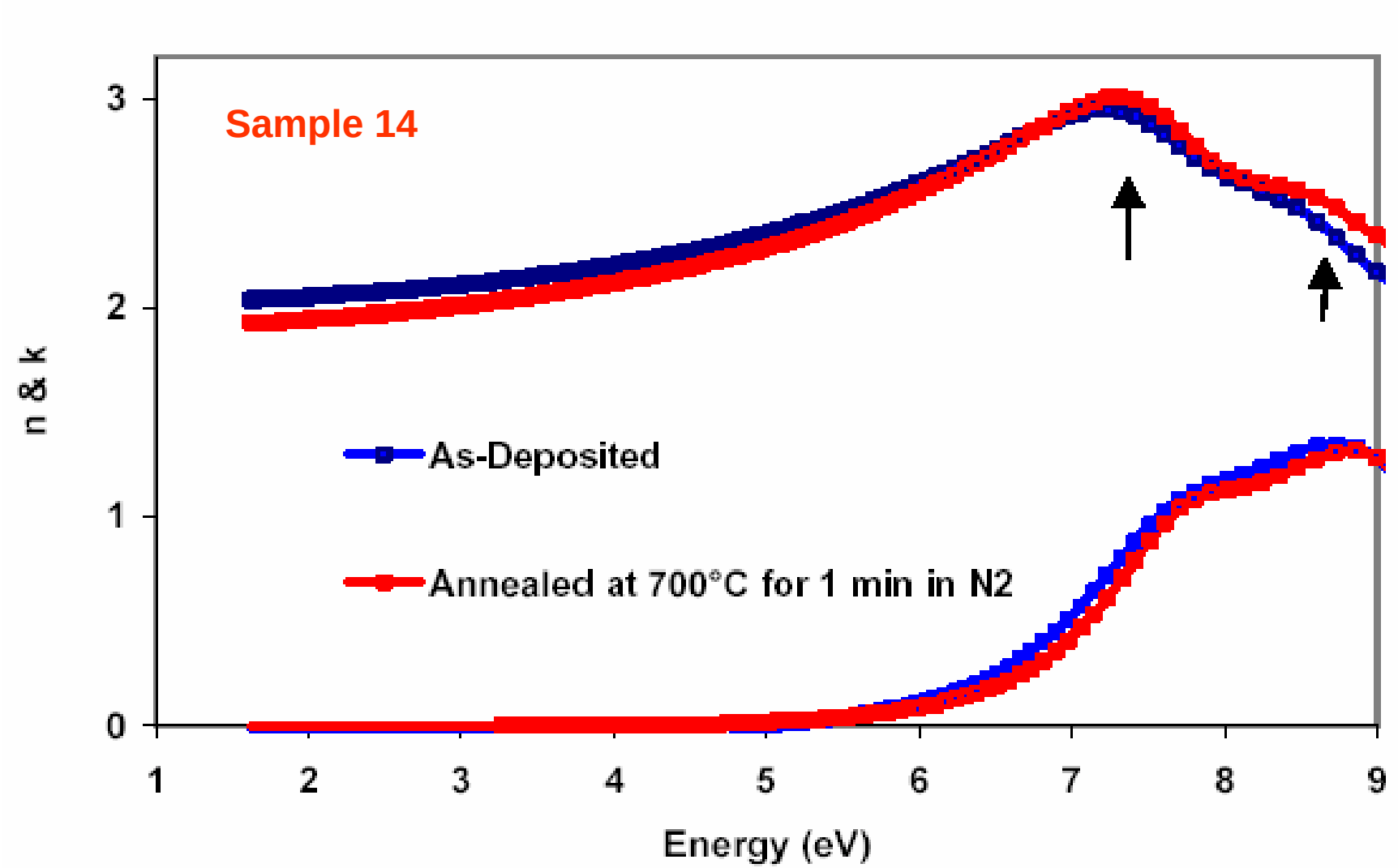
GXR Analysis on HfO_2 Film



Effect of Annealing on Optical Constants of HfO_2 Film



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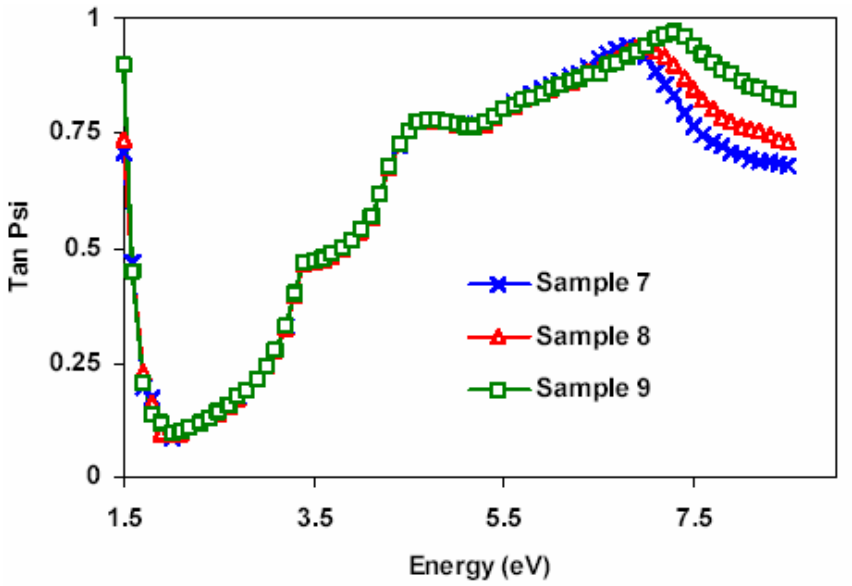
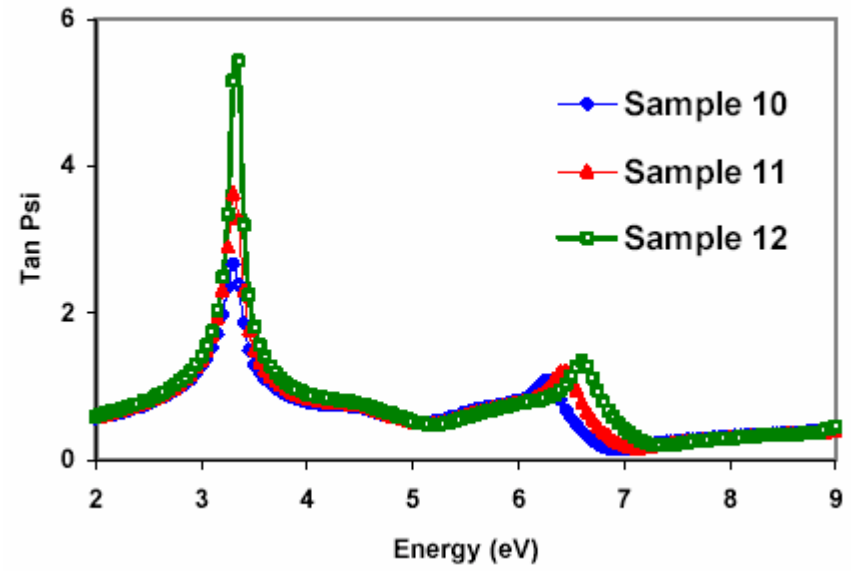
Features in VUV Range





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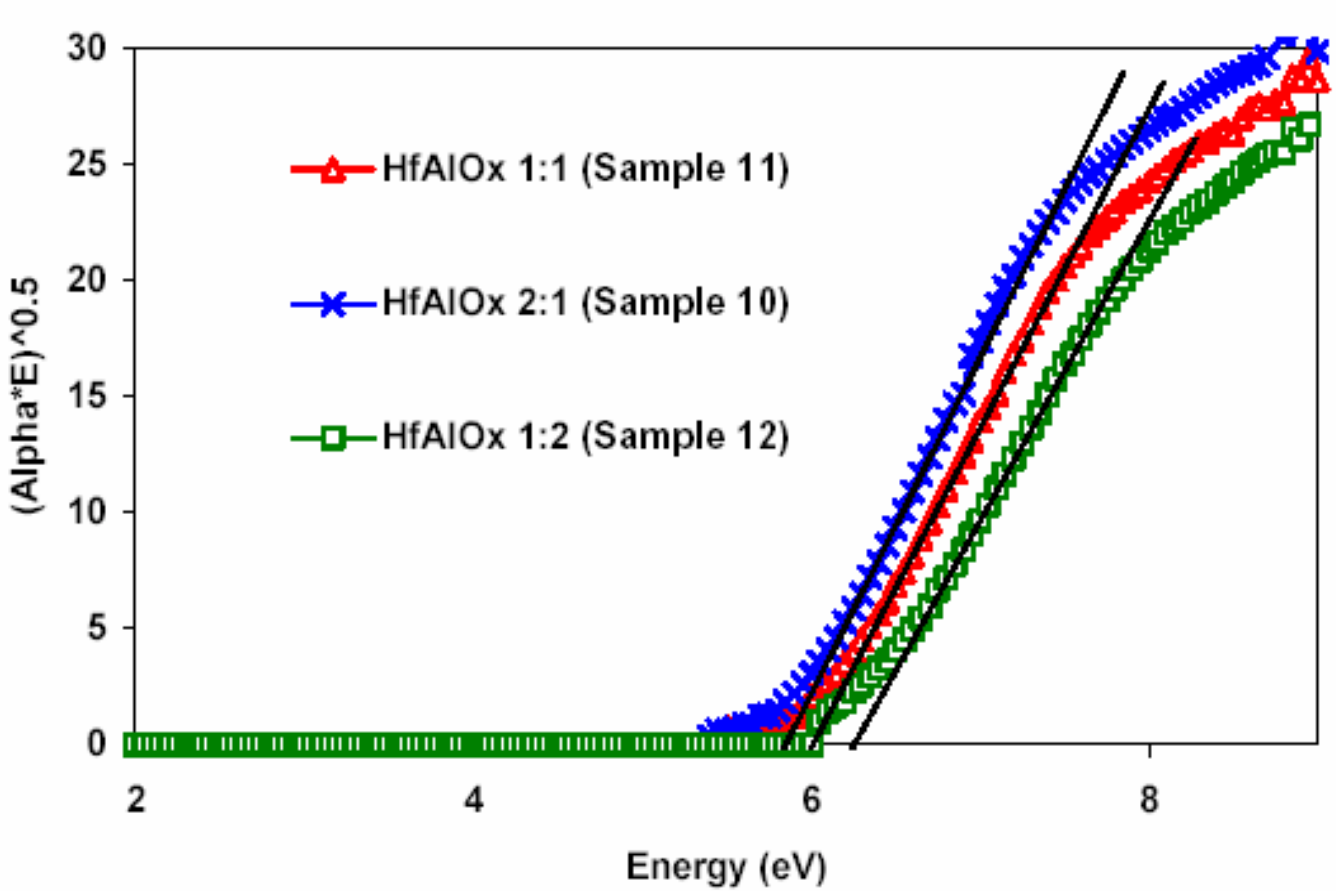
Bang Gaps Determination



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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

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.