

High-K Dielectric with nanoscale thickness studied by Spectroscopic Ellipsometry & FTIR-ATR



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High-K dielectrics are under investigation to replace the conventional SiO_2 or SiO_xN_y gate dielectric in many applications of Complementary Metal Oxide Semiconductor (CMOS) devices.

Hafnium aluminium oxides (HfAlO) were investigated in this study as they fulfill the physical properties required for such applications. The structure and composition of hafnium aluminate films as well as the HfAlO / Si interface play a very important role for the optimization of CMOS devices.

For this study complementary optical techniques were used. VUV Spectroscopic ellipsometry and infrared spectroscopy (FTIR-ATR) provide accurate characterization of thin film thickness and optical properties near and above the bandgap.

Introduction

The standard inter-poly dielectrics (IPD) of Flash memories are reaching their lower thickness limit due to the reduction in size of the devices. However, high-K dielectric materials can be used to replace the standard Oxide/Nitride/Oxide (ONO) IPD stacks of Flash memories in order to maintain a high coupling ratio (due to the low equivalent oxide thickness) while reducing the leakage current through the IPD.

The physical properties that high-K materials must exhibit are:

- High dielectric constant
- Wide band gap
- Good thermal stability with silicon
- Good interface quality, morphology and reliability

Hafnium aluminium oxides (HfAlO) are promising candidates for this role as they combine the high dielectric constant of HfO_2 and the large barrier height and good thermal stability of Al_2O_3 materials.

Experimental Details

A batch of eight HfAlO mixed layers was deposited on silicon substrates at 300°C by atomic layer chemical vapor deposition (ALCVD), using H_2O , HfCl_4 (hafnium tetrachloride) and $\text{Al}(\text{CH}_3)_3$ (trimethylaluminium) as precursors. Different compositions were obtained by controlling the ratio of HfCl_4 and $\text{Al}(\text{CH}_3)_3$ in the deposition cycle. This procedure allows the hafnium content to be varied from 0% to 100% with an average layer thickness of 6 nm.

Table 1: Hf and Al ratios of the as-deposited alloys

HfCl ₄ : Al(CH ₃) ₃ deposition cycle ratio	Hf ratios (%)	Al ratios (%)
0:1 (Al ₂ O ₃)	0	100
1:9	27	73
1:6	30	70
1:4	31	69
1:3	40	60
1:2	57	43
9:1	94	6
1:0 (HfO ₂)	100	0

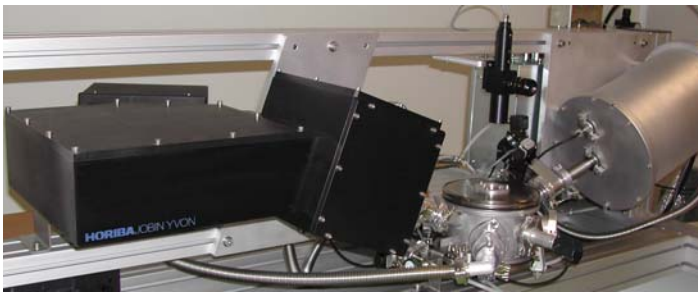
- **Fourier Transform Infrared Spectroscopy - Attenuated Total Reflection (FTIR-ATR)**

FTIR measurements using an ATR configuration were performed to enhance the infrared signature of the thin aluminate films.

A Fourier transform infrared spectrometer was used to probe the sample through a germanium prism in contact with the sample to ensure total reflection at the Ge/Si boundary. Spectra were recorded between 600 and 2000 cm^{-1} and the prism spectrum was taken as a reference. The penetration depth of the evanescent wave in the top layers of the sample was evaluated to a few tens of nanometers.

- **Vacuum Ultraviolet Spectroscopic Ellipsometry (VUV-SE)**

As high-K absorption signatures are below 190 nm, measurements were performed using the UVISEL VUV phase modulated spectroscopic ellipsometer from HORIBA Jobin Yvon. Ellipsometric measurements were collected across the spectral range 1.5 – 8 eV (155 - 826 nm), in steps of 0.02 eV, at an angle of incidence of 70°.



Results

- **FTIR-ATR Results**

ATR absorbance spectra of the aluminates films are shown in Fig.1.

Three chemical bond signatures appear in the range between 600 and 1300 cm^{-1} . The Si-O bond around 1190 cm^{-1} is due to the interfacial SiO₂ layer and does not vary with the hafnium content indicating a stable interface. The second absorption peak at around 950 cm^{-1} indicates the Al-O bond. With increasing hafnium content the Al-O peak shifts towards 700 cm^{-1} relative to Hf-O bond. Finally the two Hf-rich samples (9:1 and 1:0) seem very similar showing that a small amount of aluminium does not change the large absorption band attributed to the Hf-O stretching vibration.

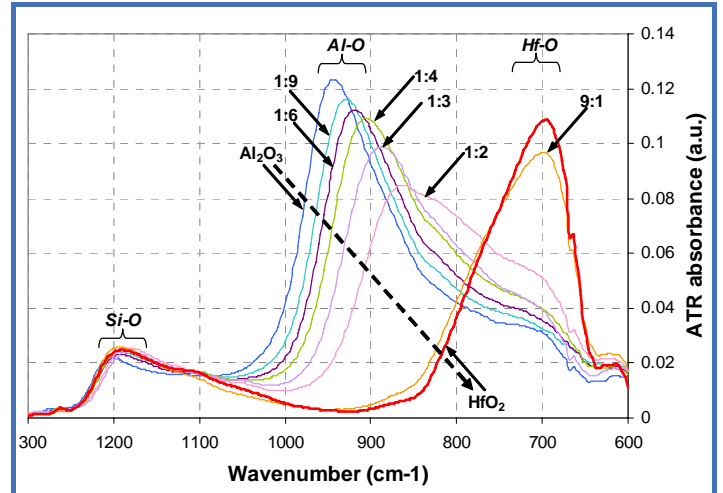


Fig.1 – Infrared spectra of HfAlO films

- **Spectroscopic Ellipsometry Results**

A two layer model was used to describe these samples. It consists of a HfAlO film, and a 7 Å SiO₂ interface on top of the silicon substrate.

HfAlO	Determined thickness
SiO ₂ Interface	7 Å
c-Si substrate	

The fitting process determined simultaneously the HfAlO thickness and optical constants, while the SiO₂ interface thickness was fixed.

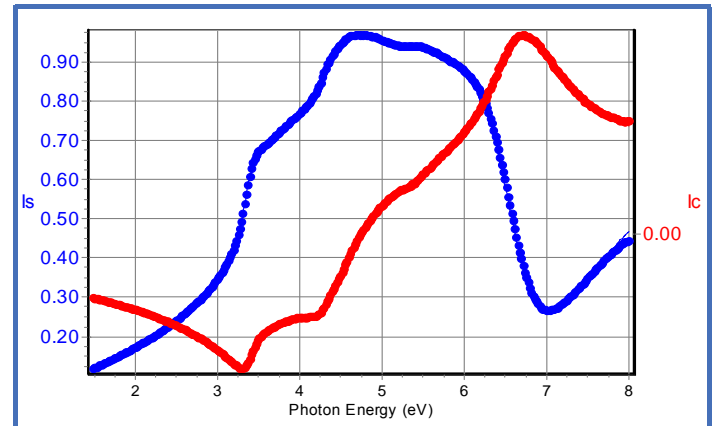


Fig.2 – Experimental & generated ellipsometric data

The table below summarizes results obtained for the different Hf/Al ratios.

	HfO ₂	Hf/Al 9:1	Hf/Al 1:2	Hf/Al 1:3	Hf/Al 1:4	Hf/Al 1:6	Hf/Al 1:9	Al ₂ O ₃
[Hf]	1	0.945	0.575	0.4	0.313	0.3	0.272	0
Th (Å)	69.70	71.98	63.66	63.56	64.98	65.89	62.67	69.15
Eg (eV)	5.64	5.65	5.91	6.05	6.19	6.28	6.32	6.38

The optical properties of HfAlO were determined using a Tauc Lorentz dispersion law with 2 oscillators (Fig.3).

The optical bandgap was extracted from the linear variation of $\sqrt{\alpha(E) \cdot E}$

where α is the absorption coefficient (expressed as $\alpha = \frac{4\pi k}{\lambda}$), by DeltaPsi2 software.

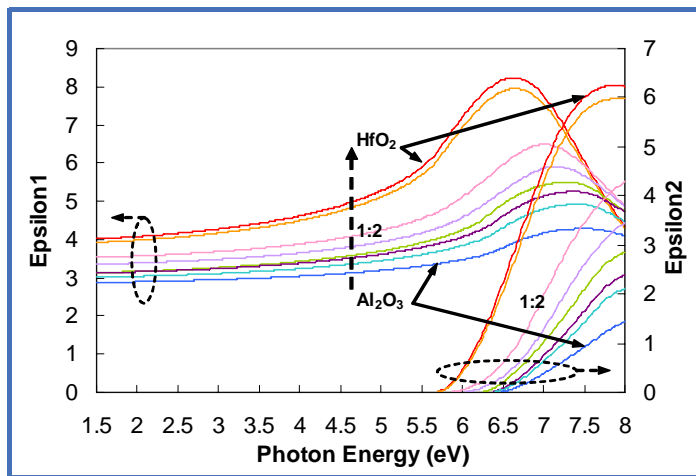


Fig.3 – Dielectric functions of HfAlO films

As previously observed the 9:1 and HfO₂ as-deposited films are very similar. All HfAlO dielectric functions are well distributed between HfO₂ and Al₂O₃.

The shift of the optical bandgap is correlated with the hafnium content and ranges linearly from 6.4 eV, for pure Al₂O₃, to 5.6 eV, for pure HfO₂ (Fig.4).

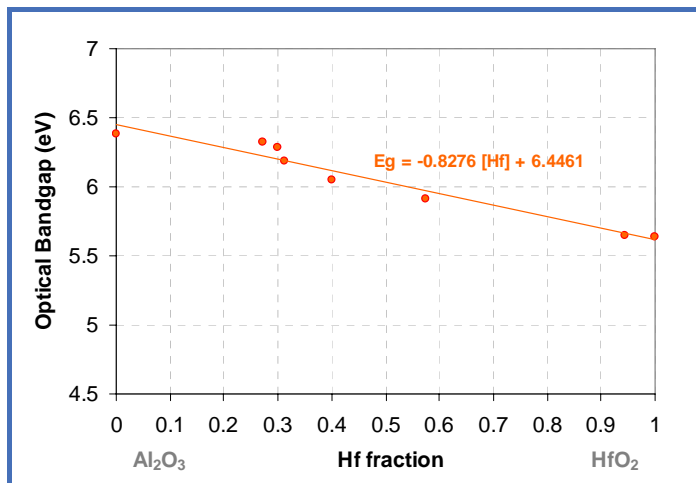


Fig.4 – Plot of the bandgap of HfAlO films

Conclusion

Optical characterization techniques proved to be complementary to optimize high-k materials used in microelectronic applications.

This note shows that the VUV wavelength range of the UVISEL Phase Modulated Ellipsometer is particularly suitable for the accurate characterization of high-k film thickness and interfaces with nanoscale dimensions as well as optical properties and bandgap.

Reference

For more information, read the article:

Coupling of Advanced Optical and Chemical Characterization Techniques for Optimization of high-k Dielectrics with Nanometer Range Thickness

C. Licitra, E. Martinez, N. Rochat, T. Veyron, H. Grampeix, M. Gely, J. P. Colonna, and G. Molas, AIP Conf. Proc. 931, 292 (2007)

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