Nanoscale Film Thickness Measurements by X-ray Fluorescence Spectroscopy for ALD Grown Films

Tarek M. Abdel-Fattah*[1], and Helmut Baumgart[2]

[1]Applied Research Center, Jefferson National Lab and Department of Molecular Biology and Chemistry, Christopher Newport University, Newport News, VA 23606, USA

[2]The Applied Research Center ODU-Jefferson Lab, Newport News, VA 23606 and Department of Electrical and Computer Engineering, Old Dominion University , 231 Kaufman Hall, Norfolk, VA 23529

*Email: fattah@cnu.edu

X-ray fluorescence (XRF) spectroscopy is a powerful quantitative analysis technique [1]. For example, XRF is used for determining the elemental compositions for many of the minerals, rocks, alloys, glasses, cements, polymers and thin films of technological importance [1–3]. Because of XRF is a non-destructive technique, the semiconductor industry used XRF technique as an in-line technique for quality control during the manufacturing process of microelectronic devices such as DRAMs, microprocessors, ASICs [3].

Atomic Layer Deposition (ALD) technology was used in this study for the deposition of Al_2O_3, HfO_2, Pt, TiO_2, ZnO and ZrO_2 nanoscaled films over silicon substrates as described previously [4]. Table 1, summarizes the chemical precursors used for the various films and the ALD deposition temperatures.

Table 1. Chemical precursors and deposition temperature for the ALD Process

Materials	Deposition Temp. (°C)	Precursor I
Al_2O_3	300	Trimethyl aluminum
HfO_2	250	Tetrakis(dimethylamido)hafnium
Pt	300	(Trimethyl)methylcyclopentadienyl platinum
TiO_2	250	Titanium isopropoxide
ZnO	150	Diethyl zinc
ZrO_2	250	Tetrakis(dimethylamido)zirconium

The thickness of a film can be determined by XRF based matching of theoretical intensities and measured intensities. It is important for intensities to be corrected for instrument responses [4]. The empirical coefficient (EC) method (also referred to as a direct method or theoretical influence method) and the fundamental parameter (FP) method are two models that describe the matrix corrections [2, 6].

In this study, we evaluated X-ray fluorescence spectroscopy (XRF) technique for thickness, especially in nanoscale, determination of a variety of single-layer metal (Pt) and metal oxides (Al_2O_3, HfO_2, TiO_2, ZnO and ZrO_2) thin films deposited on silicon substrates. The thickness data generated from XRF analysis is compared for benchmarking with data obtained from ellipsometry, the cross-sectional transmission electron microscopy (TEM) - and scanning electron microscopy (SEM) - imaging analysis from film cleavage sites.

The results indicate that the thickness values obtained from XRF analysis are comparable to film thickness numbers estimated from the experimentally calibrated ALD growth rates in Å/cycles and the known number of ALD cycles used to grow the films as listed in Table 2. This demonstrates the potential of the XRF method for the analysis of deposited high-k transition metal oxides and other technologically important nanoscaled thin films.

Table 2. Thin films thicknesses obtained from ALD synthesis parameters and X-ray fluorescence spectroscopy

ALD Sample Name	Calculated ALD Film Thickness from ALD growth rate in nm	Calculated ALD Film Thickness from XRF analysis in nm
Al_2O_3	30	22.9
HfO_2	60	46.3
TiO_2	21	19.2
ZrO_2	20	20
ZnO	1748	1748
Pt	20	23.6

References:

1. G.R. Lachance and F. Claisse, Quantitative X-Ray Fluorescence Analysis Theory and Application. John Wiley and Sons, Ltd. West Sussex, England. 1995.
2. P.N. Brouwer, in: B. Beckhoff, B. Kanngieβer, N. Langhoff, R. Wedell, H. Wolff (Eds.), Chapter 5 of “Handbook of practical X-ray fluorescence analysis”, Springer Verlag, Berlin, Germany, 2005.
3. C. Wyon, D. Delille, J.P. Gonchond, F. Heider, L. Kwakman, S. Marthon, I. Mazor, A. Michallet, D. Muyard, L. Perino-Gallice, J.C. Royer, A. Tokar, Thin Solid Films 450, 84 (2004).
4. D. Gu, H. Baumgart, T. Abdel-Fattah, G. Namkoong, ACS Nano, 4(2), 753 (2010).
5. L.M. van der Haar, C. Sommer, M.G.M. Stoop, Thin Solid Films 450, 90 (2004).
6. M.H.J. Bekkers, H.A. van Sprang, X-ray Spectrom. 26, 122 (1997).