(Al)GaN/high-k oxide interface formation: Insight from time-resolved synchrotron studies

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The (ultra)wide bandgap semiconductors gallium nitride (GaN) and aluminum gallium nitride (AlGaN) are the materials of choice for enabling power electronic devices with very high switching frequency and superior energy efficiency. Such devices are based on metal-oxide-semiconductor (MOS) gate stacks, where downscaling and leakage control require gate oxides with high dielectric constant, so-called high-k oxides, such as HfO_2 [1]. However, device performance and especially switching frequencies are often limited by the insufficient quality of the (Al)GaN/high-k interface. Ultrathin, conformal high-k layers can be synthesized using atomic layer deposition (ALD), where the choice of oxide material, pre-ALD cleaning methods, and ALD parameters strongly influence film and interface quality. Many important details about the physics and chemistry of the interface formation still remain unknown. Furthermore, until now all efforts to explore the high-k oxide film formation have been based on ex situ approaches, meaning that film deposition and characterization of the resulting interface occur in separate steps.

Here, we present a first time-resolved investigation of the ALD reactions of HfO_2 on (Al)GaN. For this, we implemented the ALD process in a synchrotron ambient-pressure X-ray photoelectron spectroscopy (AP-XPS) setup [2]. Thus, we mapped surface chemistry and electronic properties *in situ* during subsequent ALD half-cycles, which consisted of tetrakisdimethylamido-hafnium (TDMA-Hf) and water deposition. We observed a rather inefficient first ALD cycle, compared to previous semiconductor ALD studies [2], which improved with increasing aluminum content. Thickness and chemical composition of the resulting Hf-oxide film varied strongly if the order of the precursors was changed. Both observations are against the established ligand-exchange ALD model and highlight the importance of in-depth studies for improving the quality of high-k layers on (Al)GaN.

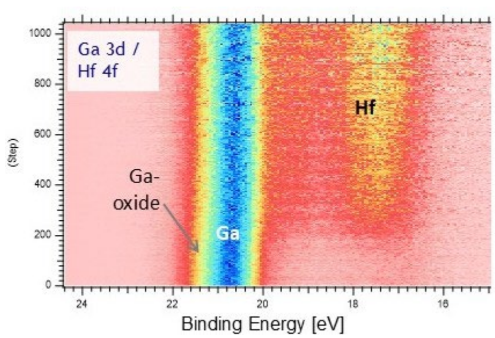

Figure 1: Time-resolved XPS during the first half-cycle of HfO_2 ALD on GaN.

In addition, we have used XPS to systematically investigate the electronic properties and chemical composition of the interface between different (Al)GaN substrates and HfO_2 or Al_2O_3 high-k oxide films, for different ALD temperatures, where HfO_2 resulted in less interfacial oxide. The choice of pre-ALD cleaning methods (HCl or HF etching) was also found to be of importance, which can enhance ALD efficiency but also result in significant interface contamination. We will discuss how our structural results can be implemented to improve device performance.

[1] P. Gribisch,…, V. Darakchieva, E. Lind, … *Fully-Vertical GaN FinFETs,* IEEE Trans. Electron Dev. 70, 4101 (2023)
[2] G. D'Acunto, …, and R. Timm, *ALD of HfO_2 on InAs: Insights … in situ studies,* ACS Appl. El. Mat. 2, 3915 (2020).

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Suplementary Pages (Optional)

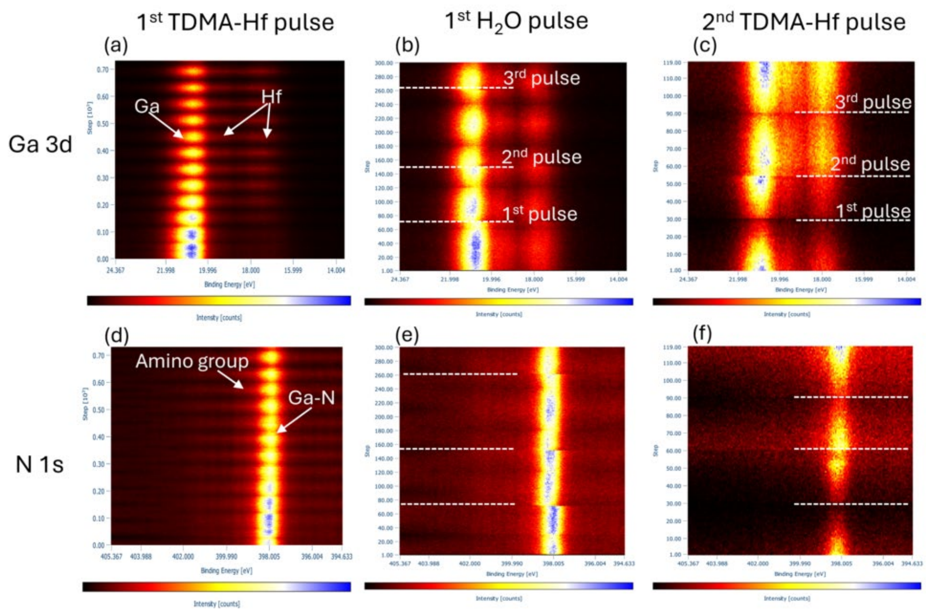

Figure S1: Time-resolved XPS data of HfO_2 ALD on GaN, with color-coded intensity from (a-c) Ga 3d and Hf 4f, which are overlapping in energy, and (d-f) N 1s core levels, obtained in snap-shot mode during (a,d) the 1st TDMA-Hf deposition, (b,e) the 1st water deposition, and (c,f) the 2nd TDMA-Hf deposition. Individual precursor pulses, using Ar as carrier gas, can induce shifts in binding energies. Periodic fluctuations of the intensity occur as the sample is continuously scanned through the X-ray beam, in order to avoid X-ray induced reactions, moving it slightly in and out of focus.

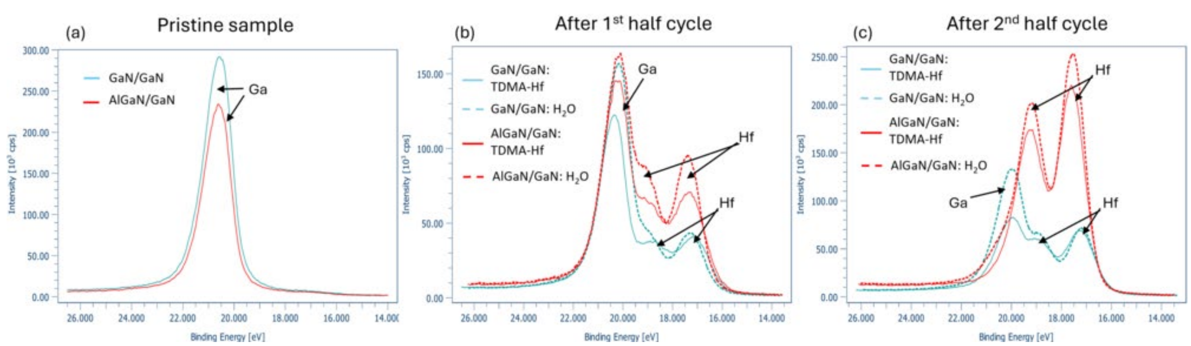

Figure S2: Ga 3d/Hf 4f XPS core-level spectra from a GaN and an $Al_{0.06}Ga_{0.94}N$ sample before (a) and after 1^{st} (b) and 2^{nd} (c) ALD cycle. Ga 3d and Hf 4f core-level peaks are partially overlapping. More Hf is found on the AlGaN sample. Note that in (c) the Ga peak has almost vanished for the AlGaN sample due to strong attenuation by the Hf-containing surface layer.

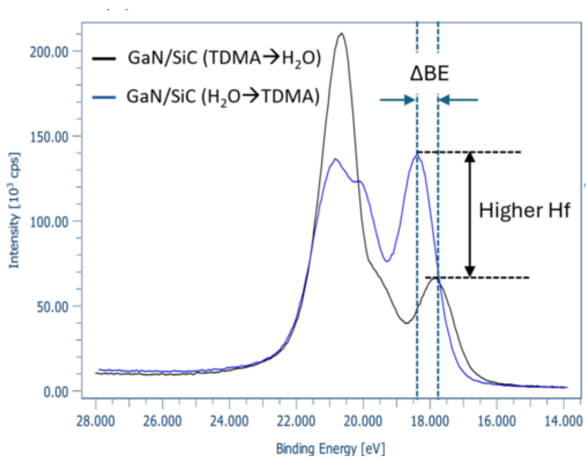

Figure S3: Ga 3d/Hf 4f XPS core-level spectra from a thick GaN film grown on SiC, obtained after one full HfO_2 ALD cycle, with either TDMA-Hf precursor first and water second (black curve) or vice versa (blue **curve**). In the latter case, we observe not only a much higher Hf intensity, but also a significant shift in the binding energy of the Hf peaks, indicating oxygen-deficient Hf-oxide.

		Ga-O/Ga-N XPS peak ratio
GaN reference		28.0 %
GaN/**HfO_2**	**HCl** pre-treatment	9.5 %
	HF pre-treatment	16.2 %
GaN/**Al_2O_3**	**HCl** pre-treatment	18.7 %
	HF pre-treatment	20.8 %

Table S1: Ratio of Ga-O and GaN XPS peak sizes, indicating different amounts of native oxide, for a GaN reference sample and for GaN samples with HfO_2 and Al_2O_3 ALD layers and HCl or HF pre-ALD treatment.

References:

(Al)GaN MOS structures with *ex situ* characterization of the (Al)GaN/high-k interface:

- R. Stoklas et al., *Characterization of interface states in AlGaN/GaN metal-oxide-semiconductor heterostructure field-effect transistors with HfO_2 gate dielectric grown by atomic layer deposition*, Appl. Surf. Science 461, 255 (2018).

Examples from our work within (Al)GaN/HfO_2-based devices:

- P. Kühne, …, and V. Darakchieva, *Enhancement of 2DEG effective mass in AlN/$Al_{0.78}Ga_{0.22}N$ high electron mobility transistor structure determined by THz optical Hall effect,* Appl. Phys. Lett. 120, 253102 (2022)
- P. Gribisch, …, V. Darakchieva, and E. Lind, *Capacitance and Mobility Evaluation for Normally-Off Fully-Vertical GaN FinFETs,* IEEE Trans. Electron Dev. 70, 4101 (2023).

Examples from our previous *in situ* studies of HfO_2 ALD on narrow bandgap semiconductors:

- R. Timm,_et al., *Self-cleaning and surface chemical reactions during HfO_2 atomic layer deposition on InAs*, Nature Communications 9, 1412 (2018).
- G. D'Acunto, …, and R. Timm, *Time evolution of surface species during the ALD of high-k oxide on InAs*, Surfaces and Interfaces 39, 102927 (2023).