PHYSICAL ELECTRONICS
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Application Note

Monitoring ALD Thin Film Coverage & Growth by XPS Structure Modeling with *Strata*PHI

Overview:

Atomic layer deposition (ALD) is often treated as a layer-by-layer process, but the first few cycles can deviate strongly from ideal linear growth. For ultra-thin films, the key question is not only how thick the deposited material is, but also how completely it covers the substrate.

*Strata*PHI structure modeling software uses XPS peak intensities and attenuation-based thin-film models to evaluate ALD-deposited layers. For Al_2O_3 deposited on SiO_2/Si substrate, *Strata*PHI was used to calculate both Al_2O_3 thickness and fractional surface coverage as a function of ALD cycle number from the same XPS data set.

Classical thin-film growth is commonly described by three limiting modes: Frank-van der Merwe layer-by-layer growth [1], Volmer-Weber island growth [2], and Stranski-Krastanov intermediate growth [3]. Layer-by-layer growth is favored when deposited material wets the substrate. Volmer-Weber growth occurs when the deposited material nucleates as three-dimensional islands instead of forming a continuous, wetting layer. Al_2O_3 island growth has been reported on low-reactivity surfaces such as hydrogen-terminated silicon [4] and graphene [5], whereas hydroxyl-rich oxide surfaces are generally expected to nucleate efficiently and grow layer-by-layer [6].

In the present study, *Strata*PHI analysis of Al_2O_3 deposited on the oxygen plasma-treated SiO_2/Si substrate from a trimethylaluminum precursor is consistent with Volmer-Weber-like island growth consisting of three-dimensional islands at sub-monolayer coverage rather than a uniform layer.

Results

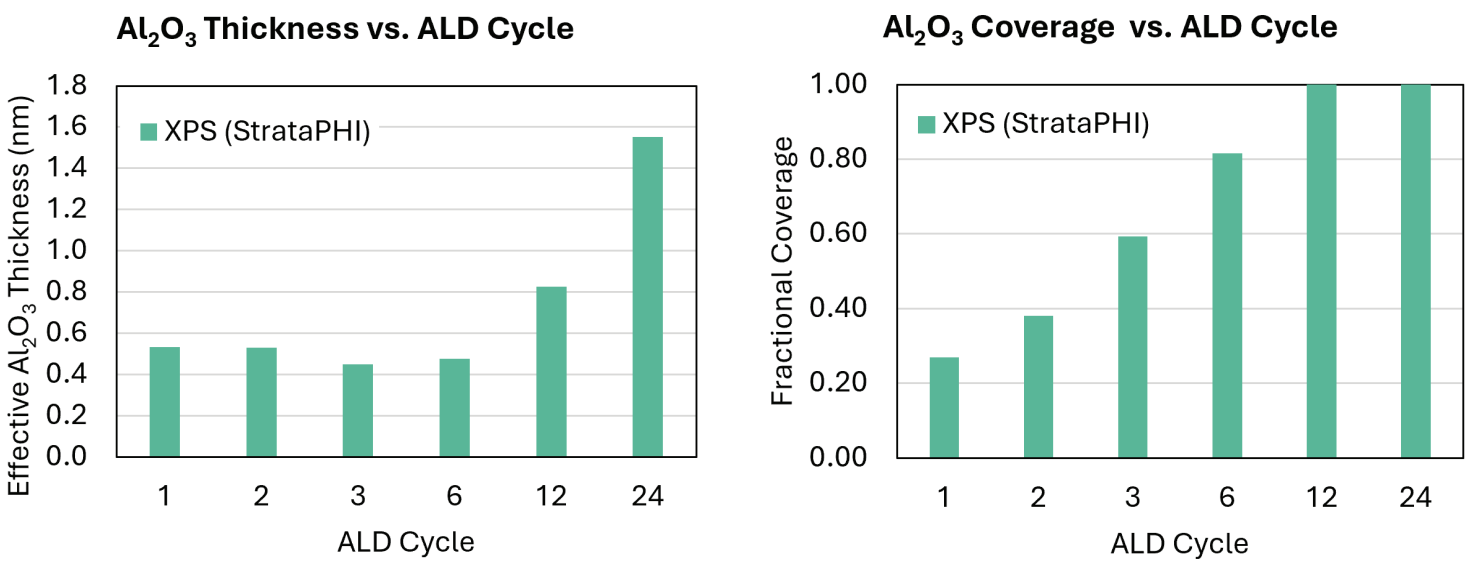


Figure 1: *Strata*PHI-calculated Al_2O_3 thickness and fractional coverage on SiO_2/Si substrate as a function of atomic layer deposition (ALD) cycle number.

Figure 1 shows the *Strata*PHI-calculated Al_2O_3 effective thickness (left) and fractional coverage (right) as a function of ALD cycle number. For the partially covered samples, *Strata*PHI returned a nearly constant effective Al_2O_3 thickness of about 0.5 nm for the covered regions from cycle 1 through cycle 6, while fractional coverage rose from roughly 27% to 82% over the same range.

Because the X-ray beam was rastered over a length of 1.4 mm, the 0.5 nm thickness represents an average over a large island population and is an effective thickness rather than a uniform island height.

When the surface approaches closure between cycles 6 and 12, vertical film growth becomes the dominant growth mechanism. Thickness increases from 0.8 nm at cycle 12 to 1.6 nm at cycle 24, consistent with a transition from island coalescence to more uniform film growth.

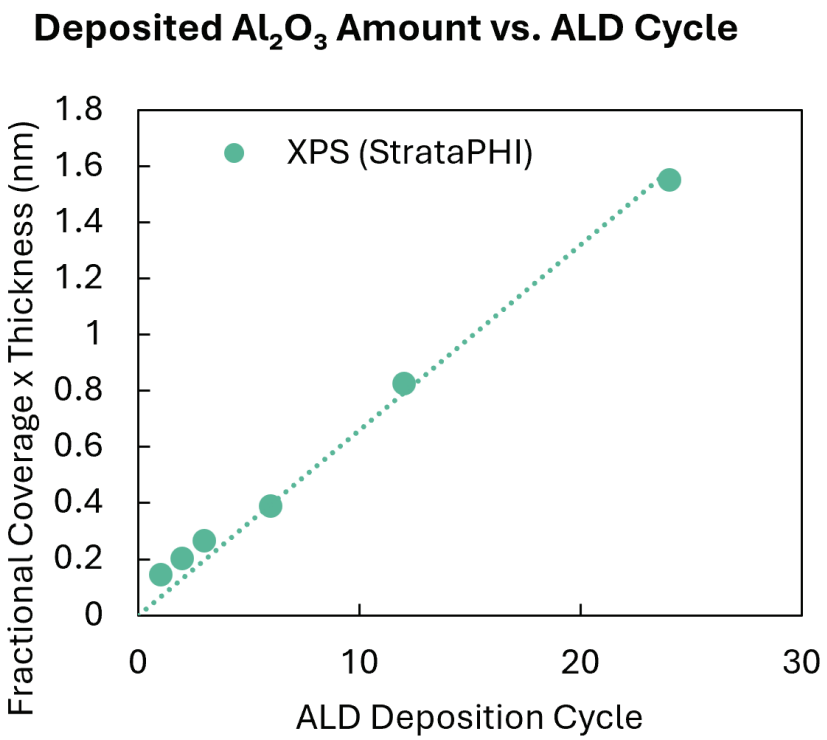


Figure 2 - Deposited Al_2O_3 amount expressed as the product of fractional coverage and thickness using XPS and *Strata*PHI

The combined coverage and thickness data support Volmer-Weber-like island growth transitioning into a continuous film. Two processes occur during early ALD cycles for the Al_2O_3/SiO_2 system: 1) new Al_2O_3 nuclei form on uncovered SiO_2 substrate and 2) existing Al_2O_3 islands spread laterally. As shown in Figure 2 with the product of Al_2O_3 thickness and coverage as derived from XPS and *Strata*PHI, the deposited amount increases approximately linearly with cycle number across the measured range, indicating a roughly constant deposition rate across the transition from island growth to a closed film as expected for a saturating ALD process.

The key observation is that the film does not get thicker on average while coverage is still incomplete. This is consistent with preferential lateral spreading before vertical growth resumes. Once the surface reaches near-complete coverage, subsequent cycles add material to a continuous Al_2O_3 layer. The behavior is described in Figure 3.

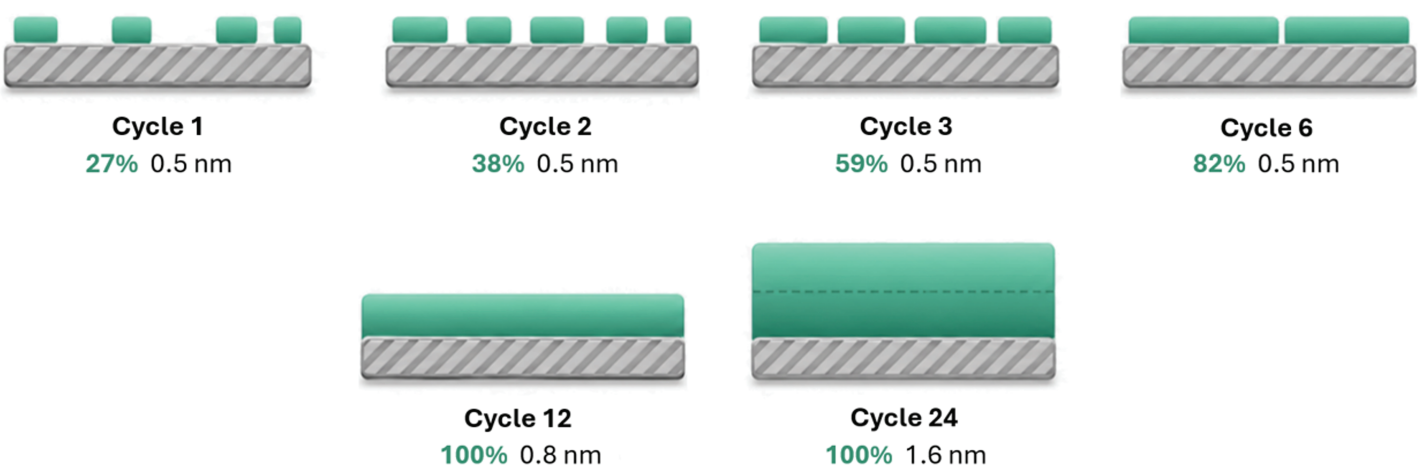


Figure 3: Schematic of proposed ALD growth mechanism for Al_2O_3 on SiO_2/Si substrate: island nucleation followed by lateral coalescence and continued post-closure film growth.

ALD Cycle	*Strata*PHI Analysis	Interpretation
1	0.5 nm, 27% Coverage	Sparse nucleation on available substrate sites
2	0.5 nm, 38% Coverage	More islands form and existing islands spread laterally
3	0.5 nm, 59% Coverage	Lateral growth dominates over vertical growth
6	0.5 nm, 82% Coverage	Near coalescence; thickness remains unchanged
12	0.8 nm, 100% Coverage	Closed film, vertical growth resumes
24	1.6 nm, 100% Coverage	Continuous film, growth proceeds with cycle number

Table 1 – Description of proposed ALD growth mechanism for Al_2O_3 on SiO_2/Si substrate: island nucleation followed by lateral coalescence and continued post-closure film growth.

*Strata*PHI vs. Ion Scattering Techniques for Fractional Coverage

The fractional coverage values calculated by *Strata*PHI are consistent with independent stand-alone LEIS measurements as shown in Figure 4. This agreement is important because the two approaches are based on different physics: *Strata*PHI models XPS attenuation through a partially covered surface, while LEIS directly probes the outermost surface layer.

The agreement confirms that *Strata*PHI separates two quantities that are often coupled in conventional XPS interpretation: the thickness of the deposited Al_2O_3 features and the fraction of substrate covered by those features. Coverage and thickness are not readily obtained together by a single alternative technique.

The combined thickness and coverage trends support Volmer-Weber-like island growth transitioning into a continuous film by lateral coalescence. Two processes occur during early cycles: new nuclei form on uncovered substrate, and existing Al_2O_3 islands spread laterally. The rapid increase in coverage by cycle 6 suggests that lateral growth becomes dominant as the available bare substrate decreases.

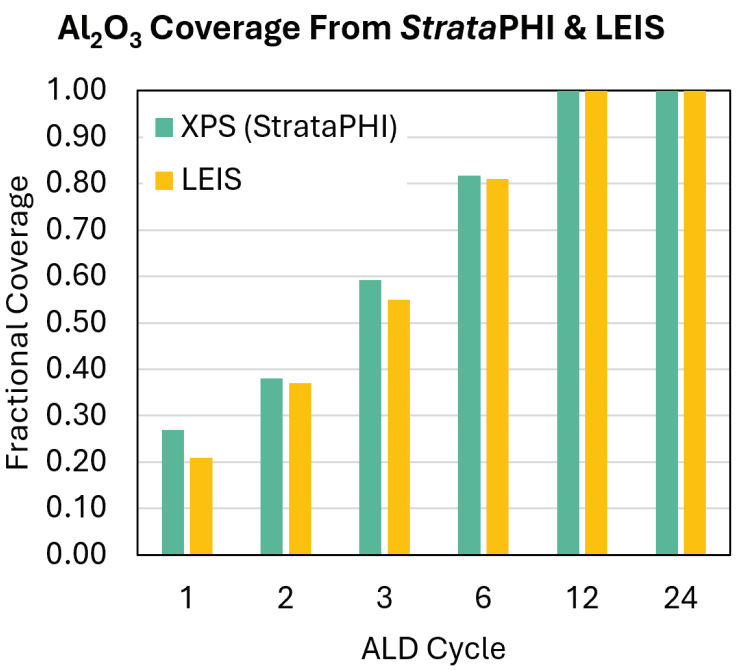


Figure 4 – Validation of StrataPHI fractional coverage by stand-alone low energy ion scattering spectroscopy (LEIS).

		ISS on XPS Instrument	Dedicated HS-LEIS Tool	*Strata*PHI (XPS)
Blank Reference Required		Yes	Yes	No
Elemental/Chemical Separation		Overlap in Elements with Similar Atomic Mass	Reduced Overlap in Elements with Similar Atomic Mass	Elemental & Chemical
Analysis Area		> 1 mm	Micrometers to Millimeter	Micrometers to Millimeter
Surface Contamination		Cleaning Required Before Analysis*	Cleaning Required Before Analysis*	No Cleaning Needed; Included in Structural Model
Simultaneous Fractional Coverage & Thickness	**Surface**	No	On Cleaned Surface (Not As-Received)	Yes
	Buried Layer	No	No	Yes
Maximum Non-Destructive Depth Profile Thickness		N/A	< 10 nm One Overlayer on Substrate (Element Must be Detected on Surface)	< 10 nm (XPS) < 30 nm (HAXPES)** Multiple Overlayers on Substrate
Measurement Impact on Surface		Surface Modification from Heating/Ion Beam Exposure	Surface Modification from Heating/Ion Beam Exposure	Non-Destructive

Table 2 – Comparison of ISS/LEIS as an option on a XPS instrument and stand-alone HS-LEIS and *Strata*PHI (XPS) for fractional-coverage and thickness analysis of ultra-thin films and StrataPHI (XPS) for fractional-coverage and thickness analysis of ultra-thin films. *Gas cluster ion beam (GCIB) or atomic oxygen cleaning, typically 10-35 minutes per sample. **Enabled on PHI XPS instruments equipped with hard X-ray photoelectron spectroscopy (HAXPES) capability.

Low energy ion scattering (LEIS) / ion scattering spectroscopy (ISS) are direct surface coverage methods with practical limitations for routine ALD film evaluation. StrataPHI provides a non-destructive XPS-based alternative that can return both coverage and thickness from the same measurement while retaining XPS chemical-state information.

Conclusions

- *Strata*PHI was used to calculate Al_2O_3 thickness and fractional coverage across ALD cycle number for Al_2O_3 on SiO_2/Si.
- The early cycles show a thickness plateau near 0.5 nm while coverage increases, indicating island nucleation and lateral growth rather than layer-by-layer growth.
- Stand-alone LEIS gives coverage values consistent with *Strata*PHI, validating the XPS-based structure model.
- The growth sequence is consistent with Volmer-Weber ALD behavior: islands of nucleation, lateral coalescence, surface closure, then linear growth.
- Compared with ISS/LEIS, *Strata*PHI resolves elements and chemical states, accounts for hydrocarbon contamination within the structural model rather than requiring its removal, needs no blank reference, and returns coverage and thickness for surface or buried layers from a single XPS acquisition.

Acknowledgment

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