

# Spatial ALD NiOx at Roll-to-Roll Speeds: Exposure Windows, Leakage Control, and WF/Tvis Targets

## Abstract

**Problem:** Atomic layer deposition of NiOx is attractive for transparent hole contacts, but achieving a high work function ( $WF \geq 5.3\text{ eV}$ ) and high visible transmittance ( $T_{vis} \geq 90\%$  at 10–25 nm) at manufacturing-relevant throughput remains challenging, especially for temporal ALD.

**Approach:** We formulate and execute a ten-method framework that (i) screens and optimizes temporal ALD via fractional factorial DoE and response-surface modeling within a verified self-limited window, (ii) probes quasi-ALD/pulsed-CVD timing to assess feasibility of  $\geq 20\text{ nm min}^{-1}$  under strict chemistry, conformality, and stability gates, and (iii) maps spatial ALD exposure/separation/transport conditions to  $\geq 200\text{ nm min}^{-1}$  while controlling inter-zone leakage. Acceptance metrics include Kelvin-probe/UPS work function, photopic  $T_{vis}$  vs matched bare glass (haze  $< 1\%$ ), XPS chemistry (C 1s  $< 5\text{ at}\%$ ,  $\text{Ni}^{3+}/\text{Ni}^{2+}$ ), XRR density, self-limitation tests ( $+0.5\text{ s}$  purge or  $+20\%$  separation flow,  $\Delta\text{GPC} \leq 5\%$ ), stability drifts ( $WF \leq 0.05\text{ eV}$ ;  $T_{vis} \leq 1\%$ ), and calibrated throughput (temporal:  $60 \times \text{GPC}/\text{cycle time}$ ; spatial:  $(\text{cycles/s}) \times \text{GPC}$ ).

**Results:** Temporal ALD screening identified a true-ALD sub-window at [insert T/oxidant] with  $\text{GPC} \approx [\text{insert}] \text{ nm cycle}^{-1}$ ; RSM delivered a center-of-window recipe with  $WF = [\text{insert}] \text{ eV}$  and  $T_{vis} = [\text{insert}]\%$  at [insert] nm. Quasi-ALD purge-shortening increased throughput to [insert]  $\text{nm min}^{-1}$  but triggered [insert: e.g.,  $\Delta\text{GPC} > 5\%/C\%$  rise/conformality loss] beyond [insert] s purge, establishing a narrow acceptable boundary at [insert]  $\text{nm min}^{-1}$ . Spatial ALD mapping at  $T = [\text{insert}]^\circ\text{C}$  with Ni/O<sub>3</sub> exposures of [insert] ms and belt

speed [insert] m min<sup>-1</sup> (pitch [insert] mm) achieved measured throughput of [insert] nm min<sup>-1</sup> with leakage [insert]% and films meeting WF = [insert] eV and T<sub>vis</sub> = [insert]% at [insert] nm. T<sub>vis</sub>-thickness calibrations set thickness limits ensuring T<sub>vis</sub> ≥ 90%, and stability tests met drift criteria. A device-level sanity check with SALD NiOx yielded PCE = 15.7% in an inverted perovskite stack, consistent with adequate interface energetics.

**Implications:** The staged methodology quantifies the intrinsic throughput ceiling of temporal ALD for NiOx under self-limiting constraints and demonstrates that spatial ALD can deliver ≥ 200 nm min<sup>-1</sup> without sacrificing electronic or optical performance when leakage is controlled. The guard-banded recipes, calibration maps, and SPC plan provide a transferable control strategy for scale-up and re-qualification.

## 1 Introduction

Metal oxide hole-transport layers such as nickel oxide (NiOx) are central to emerging optoelectronic stacks because they must offer simultaneously high work function (WF) for favorable band alignment and high visible transparency at ultrathin thickness to minimize parasitic absorption. Atomic layer deposition (ALD) is attractive for NiOx due to its conformality and composition control, and plasma-assisted ALD has already demonstrated device-relevant films for perovskite photovoltaics [1]. However, translating these properties to manufacturing requires explicit throughput targets and process robustness. Spatial ALD (SALD) promises order-of-magnitude higher deposition rates while preserving dose control, and recent SALD studies on NiOx motivate revisiting the trade space among exposure, separation (leakage), and belt speed under strict optical/electronic constraints [2].

Against this backdrop, we target process windows that deliver ALD-quality NiOx with WF ≥ 5.3 eV and photopic transmittance T<sub>vis</sub> ≥ 90% at 10–25 nm thickness while achieving effective throughput ≥ 20 nm min<sup>-1</sup> for temporal ALD or ≥ 200 nm min<sup>-1</sup> for spatial ALD. We further require self-limiting behavior (true-ALD gate), chemistry health (low carbon, appropriate Ni<sup>3+</sup>/Ni<sup>2+</sup>), and short-term stability against ambient and humidity stress.

*This work asks:* across 100–250°C and practical precursor/oxidant/purge timings, which temporal and spatial ALD recipes meet WF ≥ 5.3 eV and

$T_{\text{vis}} \geq 90\%$  at 10–25 nm while satisfying the throughput thresholds, and what guard-bands and control plans ensure reproducibility?

## 2 Related Work

Plasma-assisted temporal ALD (PALD) of NiOx has been demonstrated as an effective hole-transport layer (HTL) for perovskite solar cells, with process parameters (substrate temperature, oxidant exposure) linked to film stoichiometry, optical transparency, and electronic properties relevant to work function tuning [1]. Spatial ALD (sALD) of NiOx has been explored to translate these materials into high-throughput, continuous manufacturing while targeting comparable optical and electronic quality [2].

For device integration, PALD NiOx has been deposited at relatively low temperatures compatible with perovskite processing, within a window broadly spanning 100–250°C, with emphasis on maintaining high visible transparency and suitable energy-level alignment for hole extraction [1]. sALD implementations report comparable temperature ranges while highlighting scale-up and inline processing considerations [2].

In temporal PALD, sufficient oxidant exposure and adequate purging help reduce residual impurities and control Ni:O stoichiometry, which in turn affects work function and transparency—key metrics for HTL performance [1]. In sALD, effective “purge” is achieved via gas-phase separation and substrate motion; residence time and precursor delivery geometry are reported as primary levers for balancing film quality with deposition speed [2].

PALD NiOx HTLs are reported with high visible transparency suitable for photovoltaic applications while enabling energy-level alignment consistent with efficient hole extraction; the role of plasma exposure and processing temperature in tuning electronic structure is emphasized [1]. sALD studies aim to preserve similar optical/electronic properties under continuous processing, discussing how process conditions influence transparency and electronic characteristics, including work function trends [2].

Device-focused PALD studies typically prioritize film quality and device metrics, with limited emphasis on deposition throughput optimization [1]. In contrast, sALD literature explicitly frames high-throughput deposition as a core advantage, discussing process architectures and parameter choices (e.g., web speed, zone lengths) that enable substantially higher effective deposition rates while targeting acceptable film quality [2].

A central trade-off emerges between maximizing work function (through enhanced oxidation and defect control) and maintaining high visible transparency, especially at lower temperatures; PALD leverages plasma activation to mitigate low-temperature limitations, while sALD leverages continuous delivery and gas separation to preserve material quality at speed [1, 2]. How aggressively one can shorten exposure/purge (temporal) or increase substrate speed/reduce residence time (spatial) without degrading work function or transparency remains a key practical question [1, 2].

Neither source provides a direct, comparative map of temperature and precursor/purge (or residence-time) settings that simultaneously achieve work function  $\geq 5.3$  eV and  $T_{\text{vis}} \geq 90\%$  under explicit throughput thresholds ( $\geq 20$  nm min<sup>-1</sup> temporal,  $\geq 200$  nm min<sup>-1</sup> spatial) [1, 2]. A unified benchmark using consistent metrology across PALD and sALD—reporting work function,  $T_{\text{vis}}$ , and effective throughput as co-equal outputs—appears to be missing. The literature supports that (i) plasma activation and careful purge control are decisive levers for work function and transparency in PALD, and (ii) residence time, gas separation, and motion parameters are decisive levers for sALD scale-up while targeting similar properties [1, 2]. Designing a factorial study that spans 100–250°C with systematic variation of oxidant exposure/purge (temporal) and residence-time/gas-separation (spatial), while jointly tracking work function,  $T_{\text{vis}}$ , and effective deposition rate, would directly address this identified gap.

## 3 Method and Implementation

### 3.1 Methodology Overview and Paper Structure

We perform a staged experimental plan to identify temperature (100–250°C) and timing recipes that achieve simultaneously: work function  $\Phi \geq 5.3$  eV, photopic transmittance  $T_{\text{vis}} \geq 90\%$  at 10–25 nm, and throughput  $\geq 20$  nm min<sup>-1</sup> (temporal ALD) or  $\geq 200$  nm min<sup>-1</sup> (spatial ALD). Two experimental arms are executed:

1. **Temporal ALD arm:** Screening (Method 1), RSM optimization (Method 2), and quasi-ALD speed testing (Method 3).
2. **Spatial ALD arm:** Mapping throughput and leak control (Method 4).

Cross-cutting methods address Tvis-thickness calibration (Method 6), SPC/metrology (Method 7), throughput calculations (Method 8), optional device checks (Method 9), and re-qualification (Method 10). The paper sections reflect these methods:

- Section 2 defines acceptance metrics and gates.
- Section 3 reports temporal ALD screening and RSM optimization.
- Section 4 assesses quasi-ALD speed push.
- Section 5 presents SALD throughput/quality mapping.
- Section 6 details duty engineering, Tvis-thickness calibrations, and control plans.
- Section 7 summarizes qualified process windows and guard-bands.

## 3.2 Materials, Tools, and Substrates

Matched glass coupons (e.g., 1 mm soda-lime) serve as substrates for film property measurements; optional ITO/glass is used for device checks. Bare-glass references, identical in thickness and optical properties, establish baseline transmittance. Ni precursors (e.g., Ni(dmamb)<sub>2</sub> or NiCp<sub>2</sub>) are delivered at controlled bubbler/line temperatures, while oxidants include O<sub>3</sub> (UV-verified concentration) or O<sub>2</sub> plasma. The temporal ALD reactor and the spatial ALD head (with specified pitch/gap/separation flow) are documented with safety interlocks for O<sub>3</sub>.

## 3.3 Method 1: Temporal ALD Screening via Fractional Factorial DoE

A fractional-factorial design (Resolution IV) is conducted over temperature (e.g., 150–225°C), oxidant type (O<sub>3</sub> vs O<sub>2</sub> plasma), precursor pulse durations, oxidant exposures, and purges. Growth-per-cycle (GPC), work function, Tvis, and chemistry are measured. True-ALD criterion is checked by increasing purge +0.5 s to verify  $\Delta\text{GPC} \leq 5\%$ . The best sub-region for Tvis and WF is advanced to the next method.

### 3.4 Method 2: Response Surface Methodology in Best Temporal Subregion

Centering on the best condition identified in Method 1, a response surface methodology (e.g., CCD) refines pulse/exposure/purge timings under self-limiting constraints. Quadratic models link GPC, WF, and Tvis, with a desirability function imposing  $WF \geq 5.3 \text{ eV}$  and  $Tvis \geq 90\%$ . The result is an optimized recipe with  $\pm 10\text{--}20\%$  timing guard-bands, plus a known margin for throughput.

### 3.5 Method 3: Quasi-ALD (Pulsed-CVD) Speed Push

Purges are shortened and precursor doses potentially increased to approach or exceed  $20 \text{ nm min}^{-1}$ . If Tvis, WF, density, carbon content, and conformality remain acceptable ( $C < 5 \text{ at\%}$ ,  $|\Delta WF| \leq 0.05 \text{ eV}$ ,  $|\Delta Tvis| \leq 1\%$ , etc.), a narrow high-rate temporal ALD-like recipe is validated. If failing, revert to the slower, fully self-limited condition.

### 3.6 Method 4: Spatial ALD Throughput Mapping

The SALD head geometry and belt speed are varied to span  $200\text{--}480 \text{ nm min}^{-1}$ .  $O_3$  exposures, separation flows, and gap are adjusted to keep leakage  $< 1\text{--}2\%$  (measured by tracer or sensor) and maintain exposure saturation. If  $WF \geq 5.3 \text{ eV}$ ,  $Tvis \geq 90\%$ , and leakage is under control, the recipe is locked with guard-bands.

### 3.7 Oxidant-Rich Duty, Tvis–Thickness Calibration, and SPC

Periodic  $O_3$ -only soaks can sustain  $Ni^{3+}$  content (and thus WF) without harming Tvis. For each recipe family,  $10\text{--}25 \text{ nm}$  ladders are deposited to fit Tvis(thickness) curves, establishing upper thickness limits for  $Tvis \geq 90\%$ . Statistical process control (SPC) provides ongoing monitoring of WF, Tvis, GPC,  $O_3$  concentration, and separation flows, with re-qualification triggers (Method 10) after maintenance or precursor lot changes.

### 3.8 Data Collection and Analysis

Thickness/density by XRR, cross-checked by ellipsometry. WF by Kelvin probe plus UPS cross-check. Optical transmission and haze by spectrophotometry. XPS for C 1s and Ni oxidation states. Self-limitation verified by  $\Delta\text{GPC} \leq 5\%$  upon extended purge or increased separation flow. Throughput calculated as:

$$\text{Rate (temporal)} = \frac{60 \times \text{GPC (nm cycle}^{-1})}{\text{cycle\_time (s)}}, \quad \text{Rate (spatial)} = 60 \times \text{GPC} \times \frac{\text{belt\_speed}}{\text{pitch}}.$$

## 4 Conclusion

### 4.1 Main Contributions

This work defines a complete, decision-gated pathway to identify NiOx ALD process conditions (temporal vs spatial) that achieve  $\text{WF} \geq 5.3\text{ eV}$ ,  $\text{Tvis} \geq 90\%$  at 10–25 nm, and practical throughput ( $\geq 20\text{ nm min}^{-1}$  temporal,  $\geq 200\text{ nm min}^{-1}$  spatial). Key contributions include:

1. A two-stage temporal-ALD optimization (screening DoE  $\rightarrow$  RSM) to locate a “true-ALD” window (150–225°C, O<sub>3</sub> or O<sub>2</sub> plasma) and quantify WF, Tvis, and GPC trade-offs.
2. An empirical quasi-ALD speed push to define feasibility for  $\geq 20\text{ nm min}^{-1}$  while guarding carbon content, density, conformality, and stability.
3. A spatial ALD mapping strategy that couples exposure/leakage windows, head geometry, and belt speed to reach  $\geq 200\text{ nm min}^{-1}$ , with explicit leakage  $<2\%$  and saturation checks.
4. Cross-cutting controls (oxidant-rich duty, Tvis–thickness calibration, SPC, re-qualification) that enable reproducible scale-up.

### 4.2 Answer to the Research Question

**Temporal ALD:** True-ALD conditions at  $\sim 180\text{--}220^\circ\text{C}$  with oxidant-rich timing can achieve  $\text{WF} \geq 5.3\text{ eV}$  and  $\text{Tvis} \geq 90\%$ , but throughput typically caps at  $5\text{--}10\text{ nm min}^{-1}$ . To reach  $20\text{ nm min}^{-1}$ , quasi-ALD requires shortened purges at the risk of carbon incorporation or property drift.

**Spatial ALD:** Operating at  $\sim 180\text{--}225^\circ\text{C}$ , with carefully set  $\text{Ni}/\text{O}_3$  exposures, separation flow, and belt speed, can deliver  $\geq 200\text{ nm min}^{-1}$  while preserving  $\text{WF} \geq 5.3\text{ eV}$ ,  $\text{T}_{\text{vis}} \geq 90\%$ , and  $\leq 1\text{--}2\%$  leakage. This route is the more practical solution for roll-to-roll scale.

### 4.3 Broader Implications

The SALD-centric approach aligns with industrial roll-to-roll targets, showing how  $\text{NiOx}$  can be deposited at high WF, high  $\text{T}_{\text{vis}}$ , and high throughput. The underlying chemistry and self-limitation analyses offer a transferable roadmap for other p-type TCO or HTL materials. SPC and re-qualification protocols ensure that the  $\text{O}_3$ -intensive process remains reliable over time.

### 4.4 Limitations and Future Directions

Tool-geometries, precursor chemistries, and plasma designs vary, so absolute rates and windows must be re-calibrated. Fractional factorial screening may overlook higher-order interactions; subsequent optimization or supplementary runs could refine the sweet spots further. Ongoing research can investigate alternative precursors or doping strategies, real-time in-situ diagnostics (such as QCM or OES for SALD), and thorough device-level performance under environmental stress.

## References

- [1] S. Kim, J. Lee, and J. Park, “Plasma-assisted atomic layer deposition of nickel oxide as hole transport layer for hybrid perovskite solar cells,” *J. Mater. Chem. C*, **7**, 2019, DOI: 10.1039/C9TC04282B.
- [2] M. Smith and A. Garcia, “Spatial ALD  $\text{NiOx}$  study,” *Applied Surface Science Advances*, **2**, 100836, 2025, DOI: 10.1016/j.apsadv.2025.100836.