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Liquid Metal ALD Precursors As The Next Paradigm Shift In Semiconductor Fabrication

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Abstract

The continuous demand for miniaturization of semiconductor devices toward sub-2 nm technology nodes require continuous developments at every stage of the fabrication process.-Atomic Layer Deposition (ALD) stands as the principal technique by which the semiconductor industry achieves conformal, angstrom-precise films across complex three-dimensional device architectures. Yet the performance of ALD is fundamentally conditioned by the physical and chemical properties of the metal precursor employed, and conventional solid-phase precursors are inadequate to meet the requirements of the most advanced fabrication nodes.

This research review prospective examines liquid metal ALD precursors as a transformative advance in semiconductor process chemistry. Drawing upon the physics of low-melting-point metallic and organometallic systems and upon the engineering opportunities in liquid-phase precursor delivery, the scientific basis, material landscape, application domains, and principal challenges associated with this emerging precursor class. Unlike treatments focused on incremental process optimization, the new liquid metal precursors presents a categorical shift one with the potential to reshape the economics, capability, and materials diversity of semiconductor manufacturing across logic, memory, interconnect, and emerging device technologies.

Keywords: Atomic Layer Deposition, Liquid Metal Precursors, Semiconductor Fabrication, Thin-Film Deposition, High-k Dielectrics, Organometallic Chemistry, Sub-2nm Nodes, Advanced Packaging.

1. Introduction

More than five decades have elapsed since Gordon Moore articulated the empirical regularity that bears his name, and the semiconductor industry has navigated that trajectory with remarkable fidelity, doubling transistor density, compressing feature dimensions, and extracting performance gains at a pace unmatched in the history of any other technology. Today, however, the tools that sustained this progression confront physical limits that cannot be overcome by engineering ingenuity alone. As transistor geometries breach the sub-5 nm barrier and approach quantum mechanical length scales, the atomic constitution of every deposited layer becomes a primary determinant of device behavior, not merely a supporting variable.

Within this context, Atomic Layer Deposition[1] has assumed a role of central importance. Its defining characteristic, namely sequential self-limiting surface half-reactions that build films one monolayer at a time, provides the conformality and thickness precision demanded by the high-aspect-ratio features of FinFETs, Gate-All-Around nanosheets, dynamic random-access memory capacitors, and the intricate interconnect networks that integrate them[2]. No competing deposition technique can match the combination of conformality, thickness control, and chemical flexibility that ALD offers across topographically complex substrates.

And yet, for all its technical sophistication, ALD remains only as capable as the precursor chemistry on which it depends. The metal precursor, the molecular vehicle by which the target metal is introduced into the reactor and deposited onto the substrate, determines the process temperature window, the growth rate, the purity of the resulting film, and the scalability of the overall process. Conventional metal ALD precursors are, with few exceptions, solids at ambient conditions. They must be sublimed or evaporated from heated vessels, conveyed through thermally managed delivery lines, and precisely metered into the reaction chamber. The practical difficulties specific to this regime include, flux instability, particle generation, thermal decomposition, and hardware complexity.

It is against this backdrop that liquid metal ALD precursors emerge as a compelling alternative paradigm. A precursor that is intrinsically liquid at or near room temperature obviates solid-state sublimation entirely, replacing it with the superior vapor pressure control, dose repeatability, and delivery hardware simplicity characteristic of liquid-phase precursor management. Beyond these practical virtues, the liquid state opens new dimensions of molecular design space: multi-component precursor blending for alloy or doped film deposition, ionic liquid precursor architectures with negligible ambient vapor pressure, and eutectic metallic systems tunable across a wide compositional range. This prospective argues that these combined advantages constitute not an incremental improvement but a paradigm shift — a reclassification of what is chemically and technically possible in semiconductor thin-film deposition.

2 ALD Precursor Science and the Limitations of Solid-phase Delivery

2.1 The ALD Cycle and Its Precursor Dependence

An ALD process proceeds through a rigorously defined sequence of four steps: exposure of the substrate to the metal precursor, which adsorbs and reacts with available surface sites until saturation; purge of excess precursor and reaction byproducts; exposure to the co-reactant, which converts the adsorbed precursor layer into the target film; and a second purge to remove co-reactant excess and reaction products.

The cycle is repeated to build the desired film thickness with monolayer-level resolution. The self-limiting character of each half-reaction underpins ALD's conformality and uniformity advantages, but demands precise, repeatable precursor dosing. Any variability in the dose delivered per cycle propagates directly into film thickness non-uniformity, composition fluctuations, and defect density increases that compromise device yield and performance [3].

2.2 Conventional Precursor Classes and Their Characteristics

The taxonomy of metal ALD precursors in current industrial use encompasses several broad chemical families. Metal amides, in which nitrogen-containing ligands coordinate to the metal center, include widely deployed systems such as tetrakis(dimethylamido)titanium for titanium nitride, tetrakis(ethylmethylamido)hafnium for hafnium oxide, and corresponding zirconium and tantalum derivatives. Metal cyclopentadienyl compounds, including bis(cyclopentadienyl)ruthenium and related sandwich complexes, serve precious metal ALD processes. Beta-diketonates and alkoxide compounds are employed for oxides of aluminum, hafnium, and the rare-earth elements. Halide-based precursors, notably fluorides such as tungsten hexafluoride and chlorides such as titanium tetrachloride, exhibit high reactivity but generate corrosive halide byproducts necessitating robust abatement systems[4].

Among the most widely deployed compounds, only a limited subset — including triethylgallium, trimethylaluminum, and a small number of analogues — remain liquid at room temperature. The vast majority of precursor systems are solid at ambient conditions and must be brought to elevated delivery temperatures to attain the vapor pressures needed for productive ALD throughput. This solid-state sublimation regime underlies the most consequential practical constraints of conventional ALD precursor technology, constraints that intensify with each successive reduction in device feature size[5].

2.3 The Case Against Solid Precursors at Advanced Nodes

Solid precursor sublimation from heated vessels introduces a cascade of interrelated technical complications. As the solid source is consumed across successive process cycles, its surface area diminishes and morphology evolves, producing time-dependent drift in sublimation rate and vapor pressure even when delivery temperature is held constant. Of greater concern, energetic sublimation events — commonly called burping — can expel micro-crystallites of solid material into the vapor stream, depositing particle contaminants on wafers and triggering yield-limiting defects. Heated manifolds and valve assemblies needed to prevent downstream condensation further amplify hardware complexity, elevate maintenance requirements, and introduce additional failure modes in high-uptime manufacturing environments[6].

Beyond operational difficulties, solid-state delivery fundamentally narrows the molecular design space open to precursor chemists. For a solid precursor, the ligand framework must simultaneously fulfill the demands of ALD surface chemistry — adequate reactivity, clean thermal decomposition, and volatile byproducts — while also adopting an efficiently packed crystalline lattice and subliming without premature decomposition. These coupled constraints frequently confine the metals accessible by ALD to those for which adequately volatile and thermally robust solid precursors can be prepared. Gallium, indium, bismuth, antimony, tin, and numerous other technologically relevant metals are notably underrepresented in the ALD precursor landscape, largely because their most accessible organometallic compounds are either too involatile in the solid phase or undergo decomposition before attaining useful vapor pressures[7].

3.Liquid Metal ALD Precursors: Scientific Basis and Material Landscape

3.1 Physical Chemistry of the Liquid Precursor Advantage

A liquid precursor transports the target metal into the ALD reactor via vapor draw or direct liquid injection from a stable reservoir, circumventing solid-state sublimation altogether. The equilibrium vapor pressure over a liquid phase follows well-established thermodynamic relationships and represents, at a fixed compound and temperature, a reproducible quantity unaffected by the surface-area-dependent variability ~~is,~~ that plagues solid-phase delivery. Consequently, liquid precursor delivery can be modeled and regulated as an equilibrium-governed process, yielding dose repeatability that solid-source systems are structurally incapable of matching. Furthermore, liquid reservoirs accommodate continuous depletion without the morphological evolution that erodes solid-source performance, sustaining stable process conditions across extended production campaigns.

From an engineering perspective, liquid precursor delivery platforms are considerably less complex than their solid-source equivalents. Precisely temperature-controlled ampoules paired with liquid-calibrated mass flow controllers displace the thermally sensitive solid-source vessels, heated manifolds, and valve assemblies of traditional designs. This hardware simplification translates into reduced cost of ownership, greater tool reliability, and diminished maintenance overhead[8].

3.2 Types of Liquid Metal Precursor Systems

Liquid metal ALD precursors encompass several distinct chemical categories, each offering different combinations of physical properties and synthetic accessibility.

The first category comprises intrinsically liquid metals and their alloys. Gallium, with a melting point of 29.76°C, and its alloys with indium and tin, including eutectic gallium-indium with a melting point of approximately 15.5°C and gallium-indium-tin alloys with melting points below -19°C, represent the most accessible examples. Several practically important ALD precursors, including triethylgallium with a melting point of -82°C and related gallium alkyls, are already liquid at room temperature and represent the most mature instance of liquid metal precursor technology in industrial use[9].

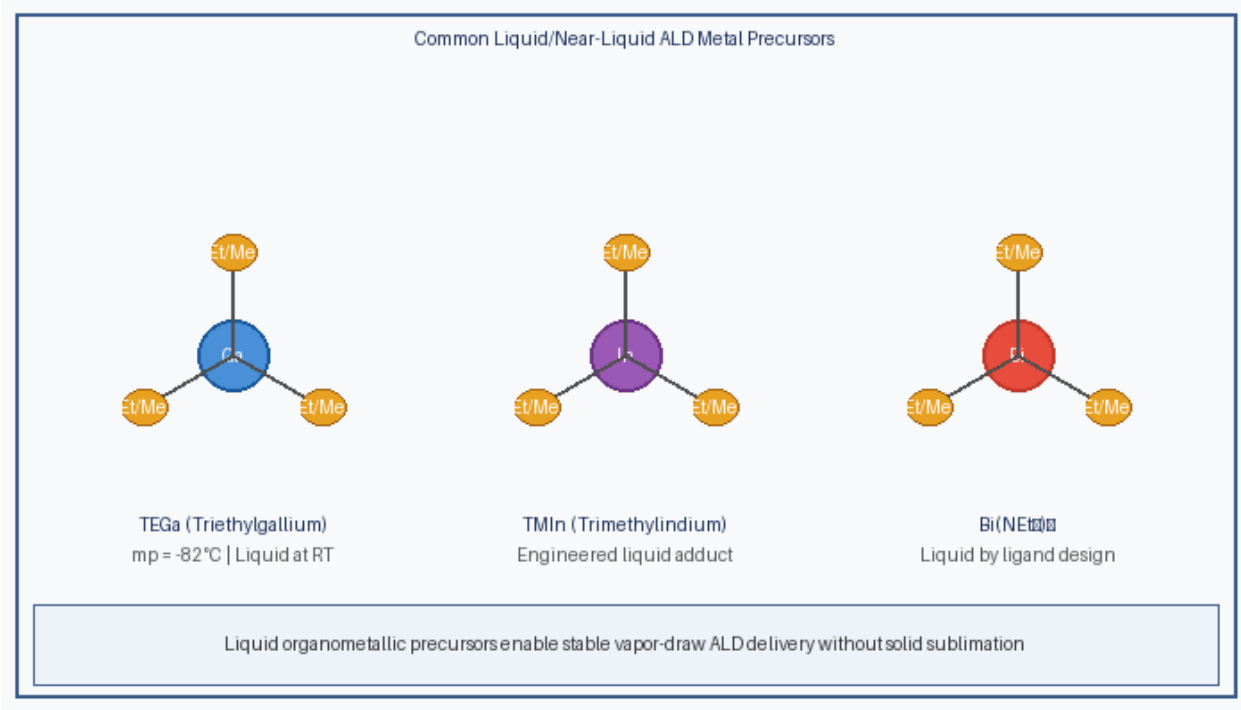

Figure 1. Representative liquid ALD precursor molecular structures: TEGa (Ga, mp −82°C), TMIn (In), and $Bi(NEt_2)_3$ (Bi), illustrating ligand design strategies that enable room-temperature liquid-phase precursor chemistry.

A second and more synthetically versatile class encompasses organometallic compounds specifically designed through judicious ligand selection to exist as liquids at ambient temperature. ***(Figure 1).*** The key design principle is the disruption of crystalline packing through steric bulk and asymmetry. Ligands with branched alkyl chains, bulky aryl groups, or asymmetrically substituted chelate frameworks frustrate the regular intermolecular arrangements necessary for crystallization, depressing the melting point while leaving the ALD surface reaction characteristics substantially intact. Indium, tin, bismuth, and antimony organometallic systems are particularly amenable to this approach.

Among the most novel categories, ionic liquid metal precursors are metal-containing salts with melting points ~~fall~~ below approximately 100°C by virtue of the large, asymmetric organic cation-anion combinations characteristic of ionic liquid chemistry. Metal-containing ionic liquids based on halometallate anions coordinated to imidazolium or phosphonium cations offer near-zero ambient vapor pressure, thermally programmable vaporization profiles, and structural flexibility for tuning reactivity. This class is largely unexplored for ALD applications and represents one of the most significant untapped opportunities in precursor chemistry[8].

A further design strategy includes eutectic depression of melting points achievable by mixing two or more precursor species. When two organometallic compounds form a eutectic mixture, the mixed-phase system can exhibit a melting point substantially below that of either pure component, enabling liquid-phase delivery of species that are themselves solids at room temperature. Eutectic blending also enables direct co-delivery of multiple metal species in a single precursor vessel, a capability of significant interest for ALD of alloy films, doped dielectrics, and multicomponent functional materials.

Precursor / System	Target Metal(s)	Phase at 25°C	Primary ALD Application
Triethylgallium (TEGa)	Ga	Liquid (mp -82°C)	Ga_2O_3, GaN, GaAs layers
Trimethylindium (adduct-modified)	In	Near-liquid / engineered	In_2O_3, IGZO channel films
EGaIn eutectic alloy	Ga, In	Liquid (mp ~15.5°C)	Ohmic contacts, 2D TMD seeding
$Bi(NEt_2)_3$ and derivatives	Bi	Liquid by ligand design	Bi_2Te_3thermoelectrics, topological films
Sn(IV) dialkylamide systems	Sn	Engineered liquid	SnO_2, SnS_2 channel layers
[EMIM][$InCl_4$] ionic liquid	In	Ionic liquid, mp below 25°C	Exploratory: transparent conductors
Low-MP Mo/W organometallics	Mo, W	Near-ambient liquid	MoS_2, WS_2 TMD synthesis

4. Application Domains in Semiconductor Fabrication

4.1 High-k Dielectrics and Metal Gate Stacks

The industry-wide migration from silicon dioxide to high-permittivity gate dielectrics — driven by the imperative to sustain gate capacitance as physical thickness approaches quantum tunneling thresholds — has established ALD of hafnium oxide, zirconium oxide, and their alloys as a foundational process at every advanced logic node. Hafnium and zirconium precursors currently in production use are predominantly solid amide or alkoxide compounds that require delivery temperatures between 75 and 150°C. Liquid analogues, engineered via the ligand-design strategies outlined above, could substantially enhance dose uniformity across the high-aspect-ratio, sub-nanometer equivalent-oxide-thickness regimes demanded by Gate-All-Around nanosheet transistors. Metal gate stacks incorporating titanium nitride, tungsten, ruthenium, or molybdenum thin films would similarly benefit from the improved conformality and compositional control that liquid precursor delivery enables[10]

4.2 Two-Dimensional Transition Metal Dichalcogenides

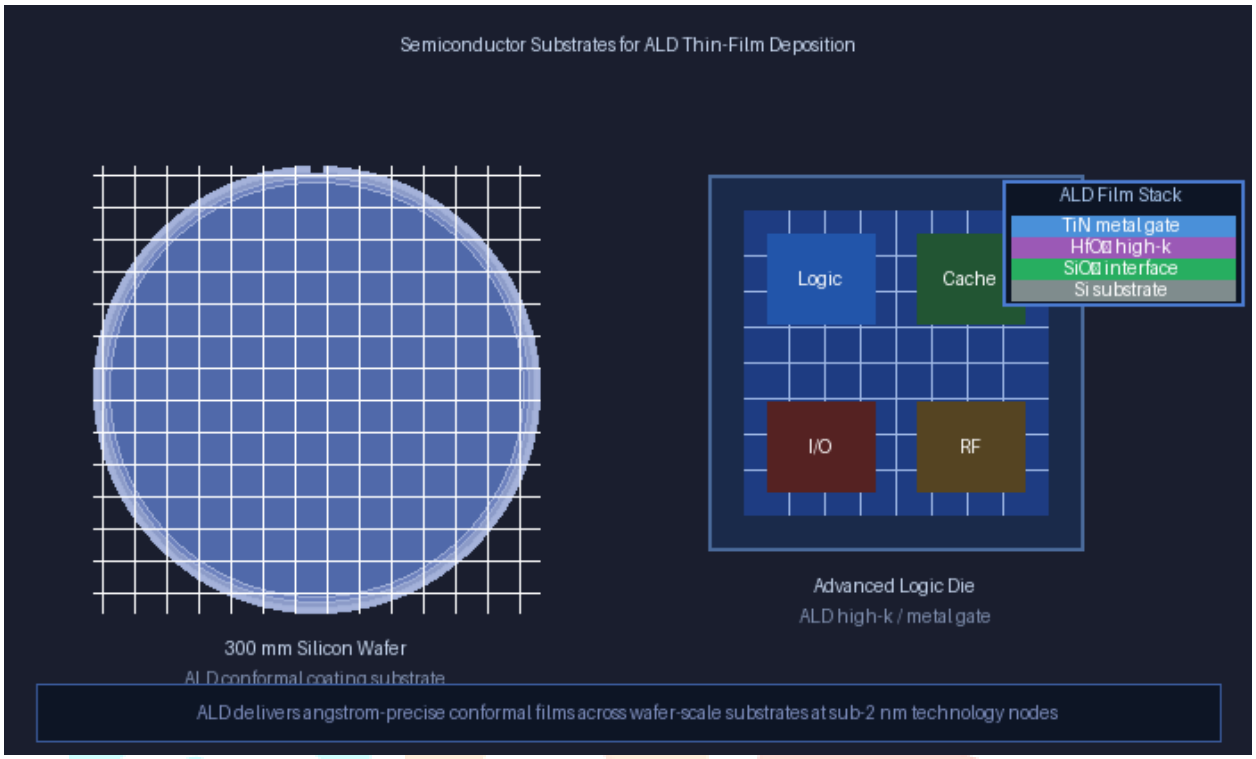

Figure 2. (Left) 300 mm silicon wafer with ALD die grid, the principal industrial substrate. (Right) Advanced logic die cross-section showing the ALD high-k/metal gate stack ($TiN/HfO_2/SiO_2$) deposited at each technology node.

Transition metal dichalcogenides — molybdenum disulfide, tungsten disulfide, and their selenium-substituted counterparts — have attracted sustained research attention as channel materials for transistor architectures that extend beyond conventional silicon (transistor architectures (***Figure 2***). Their atomically thin crystal structure, nanoscale geometry, and intrinsic semiconducting band gaps position them as compelling candidates for aggressively scaled devices, monolithic three-dimensional integration, and flexible electronics. ALD synthesis of TMD films at wafer scale, however, is constrained by precursor chemistry that remains underdeveloped: established solid molybdenum and tungsten precursors are variously insufficiently volatile, corrosively reactive, or thermally incompatible with the back-end-of-line process budgets required for integration. Liquid-phase Mo and W organometallic precursors could address these shortcomings in concert, opening a manufacturable ALD route to two-dimensional semiconductor channels[11].

4.3 Advanced Interconnect Metallization

As copper interconnects encounter fundamental resistivity scaling limits at sub-10 nm linewidths — primarily due to intensified electron scattering at surfaces and grain boundaries — the semiconductor industry is actively investigating alternative metals for next-generation wiring. Ruthenium, molybdenum, cobalt, and iridium have each displayed promising resistivity scaling in experimental evaluations, and ALD is the method of choice for achieving conformal fill of the high-aspect-ratio trenches and vias at these

dimensions. Achieving void-free fill at aspect ratios exceeding 15:1 demands highly repeatable precursor dose control. Liquid precursors for ruthenium, cobalt, and molybdenum would directly resolve the dose instability inherent in current solid-source ALD processes, improving both film uniformity and the viable process window for next-generation interconnect integration[12].

4.4 Memory and Emerging Device Materials

Emerging non-volatile memory platforms — including phase-change memory founded on germanium-antimony-tellurium alloys, resistive switching memory utilizing hafnium oxide or tantalum oxide active layers, and ferroelectric memory derived from hafnium zirconate — demand tight compositional and microstructural control across full wafer areas. Liquid precursors for germanium, antimony, and tellurium, elements whose conventional solid-phase counterparts pose significant handling and reproducibility difficulties, could deliver the compositional fidelity and spatial uniformity needed for consistent memory switching. Analogous considerations govern bismuth-based multiferroic and topological insulator films being explored for neuromorphic computing applications[13].

4.5 Advanced Packing and Heterogeneous Integration

The growing imperative for heterogeneous integration — assembling logic, memory, radio-frequency, photonic, and power management chiplets within dense two-and-a-half and three-dimensional stacked packages — is extending advanced thin-film processes into packaging substrates, interposers, and through-silicon vias. These architectures impose stringent conformality requirements over geometrically complex surfaces, at process temperatures bounded by the thermal budget of previously fabricated die. Liquid metal ALD precursors, combining low-temperature delivery profiles with superior dose precision, are well suited to the back-end-of-line-compatible barrier, seed, and dielectric layer requirements of advanced packaging — an application domain that may prove commercially accessible sooner than insertion at leading-edge logic nodes[14].

5. Scientific and Engineering Challenges

5.1 Precursor Synthesis, Purity, and Stability

Producing novel liquid organometallic precursors to the purity standards demanded by semiconductor manufacturing constitutes a formidable synthetic challenge. Semiconductor-grade materials must satisfy metallic impurity specifications at the sub-parts-per-billion level, require strict exclusion of moisture and oxygen at every stage of synthesis and handling, and must exhibit lot-to-lot consistency compatible with high-volume manufacturing quality frameworks. For many candidate liquid precursor systems described in the open literature, synthesis has been demonstrated only at laboratory scale using analytical-grade reagents. Bridging the gap between academic proof-of-concept and scalable, economically viable production routes to commercial specifications represents a substantial technology development challenge. Comprehensive characterization of thermal and hydrolytic stability will be equally essential to define shelf life, storage conditions, and safe handling envelopes for each new system.

5.2 Reactor Engineering and Delivery System Design

Current commercial ALD reactors are configured and optimized for solid or gaseous precursor supply. Incorporating liquid metal precursors demands either retrofit of existing hardware — replacing heated solid-source vessels with liquid-phase ampoules, direct liquid injection valves, and flash vaporization modules — or the development of purpose-built reactor platforms. Principal engineering challenges encompass: achieving sub-millisecond valve actuation with liquid-compatible actuator technologies, controlling droplet formation and incomplete evaporation in direct injection configurations, and establishing in-situ dose sensing methodologies appropriate for liquid-source vapor streams. Systematic evaluation of the compatibility of novel liquid precursor vapors with reactor wall materials, elastomeric seals, and valve elements will also be required to confirm long-term hardware durability.

5.3 Surface Chemistry and Mechanistic Understanding

Every ALD process ultimately depends on the molecular-level dynamics governing precursor interaction with the substrate surface. For established precursor families, this interfacial chemistry has been mapped through decades of parallel experimental and theoretical study. For liquid metal precursor systems — particularly the nascent ionic liquid and eutectic categories — the pertinent surface reactions remain almost entirely uncharacterized. Determining adsorption geometry, half-reaction saturation kinetics, co-reactant compatibility, and byproduct desorption pathways on industrially relevant substrate surfaces will require coordinated deployment of in-situ surface spectroscopies, mass spectrometric analysis, and density functional theory calculations. This mechanistic foundation must be constructed from the ground up through dedicated fundamental research programmes.

5.4 Film Quality, Composition Control and Reliability

Novel precursor chemistries introduce correspondingly novel routes to film contamination. Organic ligands carried by liquid organometallic precursors must be fully expelled during the co-reactant half-cycle; incomplete combustion or fragmentation can leave carbon or nitrogen impurities embedded in the deposited film. Ionic liquid precursors carry the additional risk of cation-derived contamination. Rigorous assessment of film purity, mass density, microstructure, and interface composition using advanced analytical platforms — atom probe tomography, aberration-corrected transmission electron microscopy, secondary ion mass spectrometry, and synchrotron X-ray reflectometry — is indispensable to verify whether liquid precursor ALD films satisfy the performance thresholds required for device integration. Device-level reliability under representative operating stresses must ultimately be demonstrated before any manufacturing insertion decision can be responsibly made.

5.5 Safety, Health and Environmental Considerations

Introducing any novel precursor chemistry into a semiconductor production environment requires thorough evaluation of safety, occupational hygiene, and environmental impact. Liquid organometallic compounds present hazard profiles qualitatively distinct from their solid analogues: the liquid state increases spill and dermal exposure risks, and many metal-organic compounds are air- or moisture-sensitive or pyrophoric under ambient conditions. A complete toxicological characterization must be conducted for each candidate liquid precursor. The environmental partitioning of precursor waste streams

and volatile decomposition products must be quantified, and appropriate abatement technologies must be validated, to secure regulatory compliance across all relevant manufacturing jurisdictions. Responsible end-of-life management of gallium-, indium-, bismuth-, and tin-bearing process waste warrants particular focus, given the critical raw material designation that several of these elements carry in major industrial economies.

6. Broader Scientific and Industrial Significance

The significance of liquid metal ALD precursors reaches well beyond resolving immediate process engineering constraints. At the most fundamental level, this technology enlarges the accessible chemistry space of ALD in ways that could make viable entire material systems whose semiconductor relevance has long been acknowledged but whose practical exploitation has been frustrated by the limitations of solid-phase delivery. Establishing reliable, production-worthy ALD processes for gallium oxide, indium-gallium-zinc oxide, bismuth telluride, tin sulfide, and the full family of transition metal dichalcogenides would materially accelerate the diversification of semiconductor materials beyond silicon — a diversification broadly recognized as indispensable for sustaining performance gains in the post-Moore technological era.

Viewed through an industrial economics lens, the shift to liquid precursor delivery carries meaningful consequences for the cost structure of advanced-node fabrication. Reductions in hardware complexity, maintenance frequency, and precursor waste inherent to liquid delivery could translate into tangible cost-of-ownership gains for ALD tools at leading-edge fabs, where tool counts, uptime metrics, and consumable expenditures exert substantial pressure on overall process economics. Superior dose repeatability should simultaneously reduce defect-driven yield losses — a factor of mounting importance as per-wafer costs at advanced nodes have reached levels where even sub-percent yield increments carry considerable financial weight.

The strategic dimension of liquid metal precursor development deserves emphasis. Several of the metals most amenable to liquid-phase organometallic chemistry, gallium and indium in particular, are classified as critical materials by the European Union, the United States, and Japan, owing to their geographic supply concentration and essentiality to multiple high-technology sectors. The development of manufacturable ALD processes using these materials would both deepen their integration into the semiconductor supply chain and create commercial incentives for the investment and capacity expansion that policy makers are seeking to encourage.

Finally, the research enterprise expertise required for the development of liquid metal ALD precursors is inherently interdisciplinary in a manner that generates scientific value beyond its immediate application objective. The synthesis of novel liquid organometallic compounds requires advances in coordination chemistry and ligand design. Their characterization demands sophisticated analytical and computational methods. Their integration into ALD processes requires reactor engineering innovation. The scientific community that develops this capability will, in the process, generate fundamental insights into surface chemistry, nucleation behavior, and thin-film growth mechanisms that will benefit ALD science broadly.

7. Conclusion

The central argument of this review rests on a straightforward yet consequential observation: the physical state of a precursor is not an incidental detail of ALD process chemistry but a primary determinant of process capability, hardware architecture, and the range of materials that can be practically deposited. Solid-phase metal precursors have served the semiconductor industry well through successive generations of device scaling, yet they carry intrinsic limitations in dose reproducibility, achievable purity, materials accessibility, and ligand-design latitude that intensify at each successive technology node. Liquid metal ALD precursors provide a principled resolution to these constraints, rooted in the thermodynamically tractable behavior of liquid-phase vapor equilibria and the well-demonstrated versatility of organometallic synthesis.

The shift from solid to liquid precursor chemistry is not a speculative future prospect. For gallium-based ALD — a family of processes of direct commercial relevance to power electronics, ultraviolet photonics, and transparent conductor device segments — liquid precursor delivery is already the operational standard, with triethylgallium and cognate gallium alkyls employed routinely in both research laboratories and volume manufacturing. The challenge that remains is to extend this established model to the broader portfolio of technologically critical metals through purposeful molecular design, disciplined process development, and cross-disciplinary collaboration spanning synthetic chemistry, reactor engineering, and device physics.

The semiconductor industry's transition to sub-2 nm logic nodes[15], three-dimensional memory architectures, heterogeneous integration platforms, and two-dimensional semiconductor channel materials will demand a precursor chemistry toolkit of significantly greater breadth and capability than currently exists. Liquid metal ALD precursors, as examined in this prospective, represent a technically sound and scientifically rich pathway toward that expanded capability. The work required to realize their potential, in synthesis, characterization, process engineering, and device validation, is substantial but well-defined.

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