

Vacuum-based long-term thermal stability evaluation of metal-organic precursors for atomic layer deposition

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ABSTRACT

Understanding the long-term thermal stability of metal-organic precursors is critical for maintaining consistent and reliable atomic layer deposition (ALD) performance. Conventional evaluations, such as thermogravimetric analysis (TGA) and bulk long-term thermal stability tests in sealed containers, do not reproduce the vacuum exposure and pressure fluctuations encountered under practical ALD process environments. In this work, we developed a vacuum-based long-term stability evaluation platform that reproduces process-relevant pressure cycling while enabling extended thermal treatment and periodic, atmosphere-free sampling of liquid precursors. Using tetrakis(ethylmethylamino)hafnium (TEMAHf) as a model precursor, we compare non-pumping, 6-h cyclic pumping, and 1-h cyclic pumping environments and track degradation using colorimetry, TGA residual mass, viscosity, and vapor pressure. More frequent pressure cycling accelerates degradation, evidenced by stronger color changes, increased non-volatile residue accumulation, higher viscosity, and reduced vapor pressure. These results indicate that non-vacuum, non-cycling tests can underestimate process-relevant long-term degradation and highlight the need for vacuum- and pressure cycling-based protocols to screen precursor stability and guide precursor and process optimization in ALD.

1. Introduction

Atomic layer deposition (ALD) is a thin film deposition technique that relies on self-limiting surface chemical reactions. It offers precise control of film thickness at the atomic scale, operates at relatively low temperatures, and produces uniform films with excellent conformality [1–3]. These advantages have established ALD as a widely used technique in semiconductor manufacturing and in advanced materials research [4–6]. In ALD, thin films are formed through chemical reactions between precursors and co-reactants on the substrate surface [7]. The physicochemical properties of these precursors critically influence process parameters and ultimately determine the film characteristics. Therefore, thorough characterization of precursor properties is essential for process control and optimization. Among these properties, thermal behavior—including vapor pressure and thermal stability—plays a key role in achieving consistent and reproducible deposition [8].

During deposition, precursors are continuously exposed to thermal stress to maintain sufficient vapor pressure [9]. In practical applications, precursors may be stored for several weeks or months; therefore, they must exhibit sufficient thermal stability to avoid decomposition at elevated temperatures over extended periods [10]. Maintaining thermal stability throughout processing and storage is thus imperative to prevent decomposition that would compromise precursor purity. Decomposition leads to variations in precursor properties, which cause batch-to-batch fluctuations in thin film quality and hinder process reproducibility [11]. Consequently, the thermal stability of precursors in ALD processes has a significant impact on process optimization and the properties of the resulting films. Clarifying this behavior is crucial for selecting suitable precursors, addressing film degradation issues, and improving the overall efficiency of thin film deposition processes. However, detailed long-term data remain scarce, and further research is required [12,13]. In particular, process-relevant long-term stability data remain limited, partly because conventional evaluation methods do not reproduce

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canister-level environments in ALD operation.

The thermal properties of precursors are typically measured using thermogravimetric analysis (TGA) under either atmospheric or vacuum conditions [9,12]. A single-step mass loss without subsequent degradation generally indicates excellent thermal stability. However, TGA measures small sample amounts over short timeframes, which differ significantly from actual ALD process conditions where larger precursor amounts undergo prolonged thermal exposure under vacuum [13]. In addition, precursors must remain stable at process temperatures for days or weeks, whereas TGA measurements are completed within hours, making them unsuitable for long-term thermal stability evaluation. Bulk long-term thermal stability tests in sealed containers are also widely used: precursor properties are compared before and after extended heating to assess degradation [12,14]. However, these tests are conducted under static, non-vacuum conditions that differ from actual process environments, which involve prolonged vacuum exposure and dynamic pressure fluctuations. Despite their widespread application, such conventional approaches may introduce critical inaccuracies, underscoring the urgent need for evaluation methods that better replicate actual processing conditions. Indeed, discrepancies in decomposition behavior between sealed and vacuum conditions have been reported in thermal decomposition studies of organic materials, indicating that the evaluation environment for precursor thermal stability should closely mimic actual process conditions [15]. In practical canisters, repeated vapor generation and removal can continuously perturb the headspace composition and pressure, potentially altering the apparent long-term degradation behavior compared with static sealed thermal treatment.

Nevertheless, existing thermal stability evaluation methods for metal-organic precursors fail to represent the vacuum-based pressure variations characteristic of actual ALD operation. To address this gap, we summarize representative evaluation methods in terms of (i) environment (vacuum vs non-vacuum), (ii) sample amount, (iii) duration, and (iv) the presence of pressure cycling. Therefore, Table 1 compares conventional methods with a novel thermal stability measurement approach that more closely replicates actual process conditions.

In this work, we developed a vacuum-based platform for evaluating long-term thermal stability of ALD precursors under ALD process-relevant vacuum exposure and dynamic pressure cycling. It enables periodic, atmosphere-free sampling of the liquid phase during extended thermal treatment. As a demonstration, we apply this platform to tetrakis(ethylmethylamino)hafnium (TEMAHf), a widely used hafnium precursor for high-k HfO_2 thin film deposition [16–18], and quantify the impact of pumping interval on long-term degradation using colorimetry, TGA residual mass, viscosity, and static vapor pressure measurements. By isolating the effect of pressure cycling, this study highlights that non-vacuum, non-cycling evaluations may underestimate process-relevant precursor degradation and provides a practical route

for stability screening and process/precursor optimization.

2. Materials and methods

2.1. Sampling apparatus for precursor thermal stability evaluation

Fig. 1 shows a schematic of the sampling apparatus developed in this work. The system includes a heat treatment chamber to heat the sample, a sampling section that collects precursor samples at predetermined times without exposure to the external atmosphere, a pumping system that removes precursor vapor and volatile decomposition products generated during heating, and a control unit for managing the heaters and valves. This apparatus enables thermal treatment of metal-organic precursors used in atomic layer deposition (ALD) under conditions representative of actual process environments. It also supports continuous thermal treatment required for long-term stability assessment and allows sample collection at specific intervals without contact with the outside environment.

The body and lid of the sample canister were connected with a CF flange and a copper gasket for sealing. The lines and sample canister used in the apparatus were constructed of stainless steel 316L and connected with VCR® metal gasket face seal fittings and metal gaskets, providing leak-tight sealing from vacuum to positive pressure. After assembly, the apparatus was leak-tested using a helium leak detector by the equipment manufacturer at the time of assembly, and the leak rate was confirmed to satisfy the manufacturer's acceptance criterion of

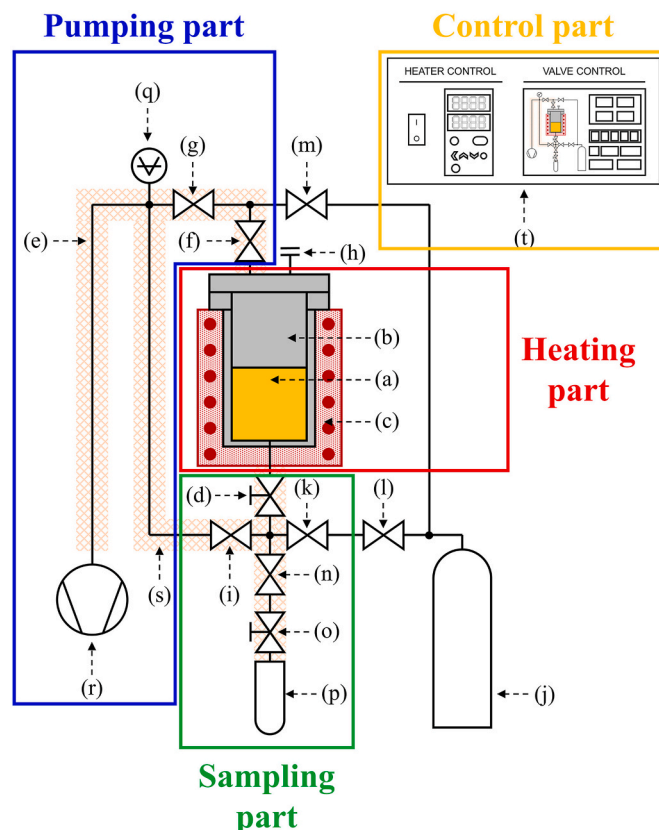


Fig. 1. Schematic of the sampling system for thermal stability evaluation under simulated ALD process conditions: (a) sample; (b) sample canister; (c) heater; (d) manual valve (for sample canister); (e) pumping line; (f)–(g) pneumatic valve (for sample pumping); (h) extra port; (i) pneumatic valve (for sampling line pumping); (j) inert gas cylinder; (k)–(m) pneumatic valve (for gas purging); (n) pneumatic valve (for sampling); (o) manual valve (for sampling cell); (p) sampling cell; (q) vacuum gauge; (r) vacuum pump; (s) line heater; (t) heater and valve controller.

Table 1
Comparison of thermal stability evaluation methods for metal-organic precursors.

Evaluation method	Evaluation environment	Sample amount	Evaluation duration	Pressure variation
Thermogravimetric analysis (TGA)	Non-vacuum or vacuum	Very small (few mg)	Short-term (several hours)	Constant (no pressure cycling)
Bulk thermal stability test (Sealed container)	Non-vacuum	Adjustable (3 mL ~)	Long-term (several days to weeks)	Constant (no pressure cycling)
This work	Vacuum-based	Adjustable (70, 100 mL)	Long-term (several days to weeks)	Variable (vacuum-based cyclic pumping)

5.0×10^{-9} Torr·L/s.

2.2. Sampling procedure under cyclic pumping

The process begins with a heat treatment step. During this step, the interior of the sample container is periodically evacuated to simulate process conditions. Next, the samples are collected at desired time points without exposure to the external atmosphere. Finally, any residual precursor remaining in the sampling line between the sample container and the sampling cell is removed through a purging step.

2.3. Materials and characterization methods

TEMAHf (SK Trichem Co., Ltd., Republic of Korea) was used as the metal-organic precursor. The volume of TEAHf loaded into the sample canister was 70 mL for the non-pumping condition and 100 mL for both the 6-h and 1-h cyclic pumping conditions. Each sample collected via the sampling part was approximately 10 mL. Precursor samples were subjected to heat treatment at 393 K for 15 days using the developed sampling apparatus, with sampling performed every three days. The heat treatment temperature of 393 K was selected as an accelerated condition to highlight differences in precursor stability and decomposition under varying pumping environments. This temperature exceeds the typical canister temperature used in actual processes (approximately 323–333 K) but remains below the thermal decomposition temperature of TEAHf (413 K) [11]. The temperature was monitored at the heater element of the sample canister. To verify the actual liquid temperature, a calibrated resistance temperature detector (RTD) probe was immersed in the TEAHf liquid inside the sample canister. At a heater set-point of 393.15 K, the liquid temperature stabilized at 392.85 K, a deviation of 0.30 K.

The experimental design consisted of three groups to evaluate the effect of vacuum exposure and cyclic pumping interval on precursor stability: (i) a non-vacuum condition with no pumping applied during heat treatment (non-pumping TEAHf), (ii) a vacuum-based cyclic pumping condition with pumping applied for 3 s every 6 h (6-h cyclic pumping TEAHf), and (iii) a similar vacuum-based cyclic pumping condition but with pumping applied for 3 s every hour (1-h cyclic pumping TEAHf). A rotary vane vacuum pump (W2V40, WooSung Co., Ltd., Republic of Korea) was used for evacuation. The base pressure before each cyclic pumping evaluation was 6.8 mTorr for the 6-h condition and 3.5 mTorr for the 1-h condition. When the pumping lines were heated to 403 K to prevent condensation of precursor vapor, the base pressure was 30.0 mTorr for the 6-h condition and 14.9 mTorr for the 1-h condition.

Color changes in the precursors before and after heat treatment were analyzed using a spectrophotometer (Colormate, SCINCO, Republic of Korea). Precursors were placed in quartz cuvettes with a 10 mm optical path length, sealed with lids, and the transmitted color was measured. Physical properties were characterized by thermogravimetric analysis (TGA), viscosity measurements, and vapor pressure assessment. TGA was conducted using an STA 449 F3 instrument (NETZSCH, Germany). Approximately 10 mg of sample was heated from room temperature to 773 K at a rate of 10 K/min under a high-purity nitrogen atmosphere, with a carrier gas flow of 60 mL/min and a protective gas flow of 20 mL/min. Viscosity measurements were conducted using a viscometer (SV-1A, A&D Company, Japan) after calibration with water. Measurements involved vibrating a sensor over about 2 mL of precursor. Vapor pressure measurements were carried out using a static vapor pressure apparatus. Approximately 3 mL of sample was loaded into a triple-walled canister connected to a thermostatic bath (RE1050S, LAUDA, Germany) with a temperature stability of ± 0.02 K. Silicon oil (Kryo 51, LAUDA, Germany), reliable over 233–393 K, served as the heat transfer fluid. All sample preparations were performed in a glovebox under an inert atmosphere with O_2 and H_2O concentrations maintained below 1 ppm. TGA and viscosity measurements were also conducted inside the

glovebox.

3. Results and discussion

3.1. Conventional (non-pumping) vs. vacuum-based cyclic pumping evaluation

To clarify how the conventional non-pumping system compares with the developed vacuum-based cyclic pumping system in terms of long-term precursor degradation, we first examined color changes and yellowness index under the three environments defined in Section 2.3.

As shown in Fig. 2(a), photographs illustrate the color changes of non-pumping TEAHf, 6-h cyclic pumping TEAHf, and 1-h cyclic pumping TEAHf over the heat treatment period. In all three conditions, the color becomes progressively darker with increasing heat treatment time. This color change is attributed to the formation of TEAHf thermal decomposition products, analogous to color changes reported for thermally degraded metal-amide ALD precursors [19].

To quantify these color changes, a spectrophotometer was used to measure the transmitted color and evaluate yellowness, as shown in Fig. 2(b). For non-pumping TEAHf, the yellowness remained relatively constant beyond approximately 6 days. In contrast, both the 6-h and 1-h cyclic pumping conditions showed a continuous increase in yellowness over the entire 15-day period. In particular, the sample subjected to 1-h cyclic pumping for 15 days exhibited the highest yellowness, indicating the most severe degree of color change among the tested conditions, suggesting significant accumulation of thermal decomposition products in the precursor liquid.

3.2. Effect of cyclic pumping interval on degradation

Since Section 3.1 established a clear difference in long-term degradation behavior between the conventional non-pumping method and the developed vacuum-based cyclic pumping method, we next focused on the developed platform to examine how the pumping interval affects degradation kinetics.

Changes in physical properties were investigated to assess differences in the decomposition behavior of the precursors. Fig. 3(a) and (b) present the thermogravimetric (TG) curves of TEAHf subjected to 6-h and 1-h cyclic pumping conditions. The residual mass in the TG curves reflects the extent of precursor decomposition [20]. Under 6-h cyclic pumping, the residual mass increased from $\sim 1.8\%$ for non-heated TEAHf to approximately 3.8% after 15 days of heat treatment. Under 1-h cyclic pumping, it increased more markedly to about 6.1% after 15 days, indicating the formation of increased residual decomposition products compared with both the 6-h condition and the non-heated TEAHf. Such decomposition can alter key precursor properties such as viscosity and vapor pressure, potentially affecting thin film quality and overall device performance [21].

3.3. Effect of long-term thermal treatment on the viscosity and vapor pressure

Because long-term degradation can alter physical properties that directly affect precursor delivery, we further examined viscosity and vapor pressure under the 1-h cyclic pumping condition. The viscosity of TEAHf increased progressively with heat-treatment time, from 4.34 cP (non-heated) to 4.49, 4.46, 4.60, 4.77, and 5.00 cP after 3, 6, 9, 12, and 15 days, respectively. This trend is consistent with the enrichment of heavier and/or more strongly interacting species in the liquid phase as decomposition proceeds.

Fig. 4(a–c) show the vapor pressure-time profiles of TEAHf measured using a static vapor pressure apparatus at 333–343 K, for a non-heated sample and samples subjected to 1-h cyclic pumping for 9 and 15 days. For the non-heated TEAHf, the saturation pressure measured at the beginning of the experiment remained essentially

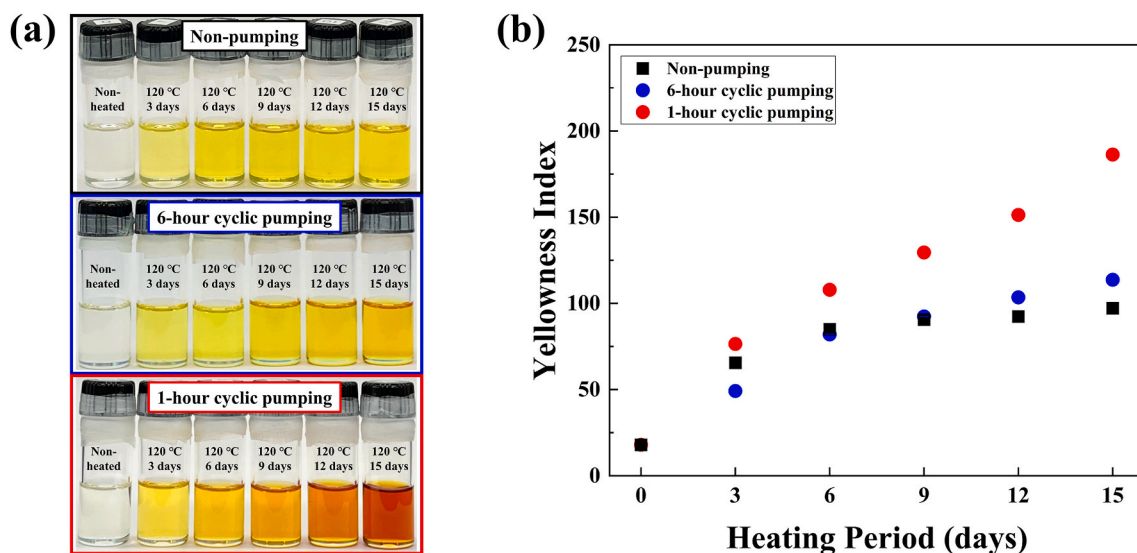


Fig. 2. (a) Photographs showing color changes during heat treatment of TEMAHf under non-pumping, 6-h cyclic pumping, and 1-h cyclic pumping conditions. (b) Change in yellowness of TEMAHf as a function of heat treatment period under different pumping conditions. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

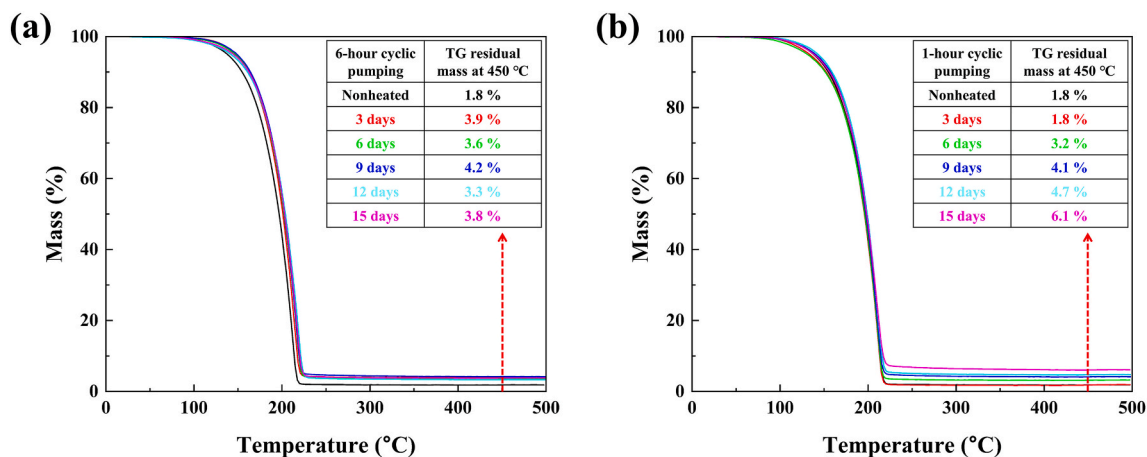


Fig. 3. TGA curves of TEMAHf as a function of pumping period: (a) 6-h cyclic pumping TEMAHf; (b) 1-h cyclic pumping TEMAHf.

constant throughout the test. In contrast, TEMAHf subjected to 1-h cyclic pumping exhibited a lower initial vapor pressure than the non-heated sample. At 9 days, the final vapor pressure was approximately 0.5–0.8% lower than the non-heated sample at each temperature point, whereas at 15 days, the final vapor pressure was approximately 1.6–2.1% lower (Fig. 4(d)). The vaporization enthalpy, obtained from the slope of $\ln(P)$ vs. $1/T$ at these three temperatures, remained nearly unchanged between the non-heated sample and after 9 days (66.39 and 66.84 kJ/mol, respectively), but decreased to 64.35 kJ/mol after 15 days—a reduction of about 2.04 kJ/mol relative to the non-heated sample.

Although TGA and viscosity measurements already showed a clear increase at 9 days (residual mass from 1.8% to 4.1%; viscosity from 4.34 to 4.60 cP), this degree of change did not produce a proportionally significant effect on vapor pressure or vaporization enthalpy at the same time point. This suggests that the residue concentration at 9 days, while detectable by TGA and viscosity, had not yet reached a level sufficient to meaningfully affect the vapor–liquid equilibrium properties, and that a more pronounced effect on vapor pressure and enthalpy emerges only after further residue accumulation, as observed at 15 days.

3.4. Possible origins of the degradation divergence under cyclic pumping

Under identical heat treatment conditions (393 K, 15 days), the vacuum-based cyclic pumping TEMAHf conditions exhibited more pronounced degradation-related signatures than the non-pumping TEMAHf condition. This section examines the possible origins of this divergence.

We first exclude the possibility of H_2O or O_2 ingress. Based on measurements of TEMAHf taken between 323 K and 348 K in 5 K increments, the extrapolated vapor pressure at 393 K is approximately 5.04 Torr. In comparison, the base pressure of the pumping line was 14.9–30.0 mTorr, higher by a factor of approximately 167 to 338. Gas flow through the valve is therefore always directed outward from the canister, preventing ambient moisture or oxygen from entering through this path. A leak in the canister body itself would affect both the non-pumping and cyclic pumping conditions equally, and therefore cannot account for the condition-dependent divergence observed here.

TEMAHf undergoes thermally driven ligand dissociation, generating volatile byproducts (e.g., free and Hf-complexed EMA species) as well as less-volatile or non-volatile residues formed via N-bridged oligomerization over time [11]. Because the reversibility of this initial

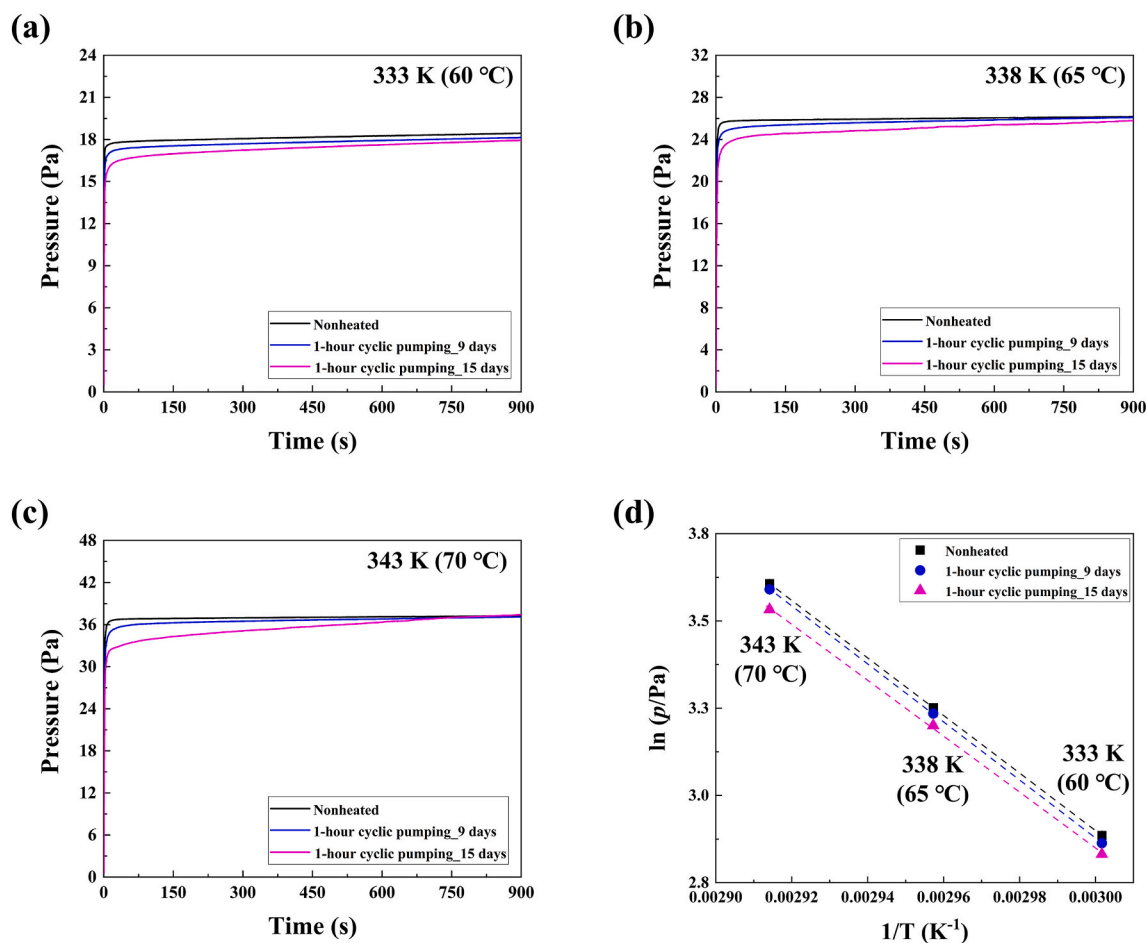


Fig. 4. Vapor pressure curves of TEMA hf measured using a static vapor pressure apparatus at (a) 333 K, (b) 338 K, and (c) 343 K. Data are shown for a non-heated TEMA hf sample and TEMA hf heat-treated at 393 K under 1-h cyclic pumping for 9 and 15 days. (d) Comparison of vapor pressure at each temperature. Black squares and a black dashed line denote non-heated TEMA hf, whereas blue circles and pink triangles denote TEMA hf heat-treated for 9 and 15 days, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

dissociation step for TEMA hf cannot be determined from the present data, both possibilities are considered below.

If the dissociation step is reversible, free EMA retained in the head-space under the non-pumping condition can re-associate with the dissociated fragment, limiting the net rate of decomposition. Under cyclic pumping, continuous removal of free EMA and unreacted TEMA hf vapor suppresses this re-association, allowing decomposition to proceed further at a given elapsed time and thereby resulting in a genuine increase in the decomposition rate under cyclic pumping.

If the dissociation step is irreversible, the decomposition rate is the same under both conditions. Cyclic pumping nonetheless preferentially removes volatile components (unreacted TEMA hf and volatile byproducts), thereby increasing the relative concentration of non-volatile oligomeric residue in the remaining liquid over successive cycles. At a given elapsed time, the cyclic pumping condition therefore appears more degraded than the non-pumping condition even without any change in the underlying rate.

Neither scenario can be distinguished based on the present data; both are equally consistent with the observed degradation-related changes — color change, increased non-volatile residue, elevated viscosity, and reduced vapor pressure — under cyclic pumping relative to non-pumping. In either case, these results suggest that conventional thermal stability tests may underestimate process-relevant long-term degradation, highlighting the need for vacuum- and cyclic pumping-based thermal stability screening that better reproduces actual ALD process environments.

4. Conclusions

We developed a vacuum-based long-term thermal stability evaluation platform that systematically reproduces process-relevant vacuum exposure and dynamic pressure cycling while enabling periodic, atmosphere-free sampling of metal-organic precursors. Using TEMA hf as a model precursor, we demonstrated that cyclic pumping leads to more pronounced long-term property changes compared with non-pumping conditions, and that shorter pumping intervals lead to more severe property drift. After 15 days of treatment at 393 K, the 1-h cyclic pumping condition exhibited stronger color changes, increased TGA residual mass (from ~1.8% to ~6.1%), elevated viscosity (from 4.34 to 5.00 cP), and reduced vapor pressure (1.6–2.1% decrease at 333–343 K).

Overall, the results indicate that conventional non-vacuum, non-cycling stability tests may underestimate process-relevant degradation, and that vacuum- and pressure-cycling-based protocols, such as the present platform, provide a practical route for realistic long-term stability screening of ALD precursors.

CRediT authorship contribution statement

Jaewuk Lim: Writing – review & editing, Writing – original draft, Investigation, Data curation, Conceptualization. **Hayeong Kim:** Writing – review & editing, Writing – original draft, Investigation, Data curation, Conceptualization. **Seonjeong Maeng:** Investigation, Data curation. **Jong-Man Kim:** Formal analysis. **Ju-Young Yun:** Supervision, Project

administration.

Declaration of competing interest

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: Hayeong Kim has patent Sampling device for evaluation of thermal stability in vacuum environment of organometallic precursors for deposition process and method thereof issued to Korea Research Institute of Standards and Science (KRISS). Seonjeong Maeng has patent Sampling device for evaluation of thermal stability in vacuum environment of organometallic precursors for deposition process and method thereof issued to Korea Research Institute of Standards and Science (KRISS). Ju-Young Yun has patent Sampling device for evaluation of thermal stability in vacuum environment of organometallic precursors for deposition process and method thereof issued to Korea Research Institute of Standards and Science (KRISS). If there are other authors, they declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Data availability

Data will be made available on request.

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