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Experiment-based modelling of a vapor draw ampoule used for low-volatility precursors

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Abstract

Delivery of low-volatility precursors is a continuing challenge for chemical vapor deposition and atomic layer deposition processes used for microelectronics manufacturing. To aid in addressing this problem, we have recently developed an inline measurement capable of monitoring precursor delivery. Motivated by a desire to better understand the origins of what is now observable, this study uses computational fluid dynamics and a relatively simple model to simulate the delivery of pentakis(dimethylamido)tantalum (PDMAT) from a commercial vapor draw ampoule. Parameters used in the model are obtained by fitting the performance of the ampoule to a limited dataset of PDMAT delivery rates obtained experimentally using a non-dispersive infrared sensor. The model shows good agreement with a much larger experimental dataset over a range of conditions in both pulsed and continuously flowing operation. The combined approach of experiment and simulation provides a means to understand the phenomena occurring during precursor delivery both quantitatively and qualitatively.

I. INTRODUCTION

Modern microelectronics incorporate increasingly more materials that are being used for an increasing variety of roles. Innovations in physical vapor deposition have allowed it to incorporate many new materials into new process nodes, but the continued scaling of three-dimensional structures like multilayer interconnects,^{1, 2} through-silicon vias,^{3–5} and multi-gate field-effect transistors^{6, 7} has meant that many materials now must be deposited by methods capable of greater conformality. These include chemical vapor deposition (CVD) and atomic layer deposition (ALD). The introduction of new materials and new architectures has therefore necessitated the development of chemical precursors to be used in these processes. While chemistry can be used to modify and improve the properties of precursors,^{8–10} the compounds used in high-volume manufacturing are typically the result of compromises between vapor pressure, thermal stability, reactivity, etc. The ALD and CVD of new materials, therefore, often involves understanding the shortcomings of precursors and then engineering solutions to address them.

Many precursors with otherwise acceptable properties have the undesirable characteristics of being solids and/or having low vapor pressures if they are used at low temperatures that limit

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their thermal decomposition. Problematic delivery of these compounds, selected through compromise, has encouraged the invention of numerous containers meant to increase the concentration of the precursors in a flowing carrier gas.^{11–14} These devices, however, themselves represent compromises: Modifications often introduce practical problems such as difficult maintenance, increased fabrication costs, irreproducible delivery rates, and particulate entrainment. Despite being one of the simplest designs, the vapor draw ampoule, which is essentially a bubbler without a dip tube, remains a common means to deliver solid precursors with low vapor pressures.

In our efforts to quantify precursor delivery, we have developed inline, optics-based measurements.^{15–19} These have an advantage over ultrasonic monitors commonly used for monitoring precursor delivery since low concentrations in low-pressure gas lines can be measured optically whereas ultrasonic sensors are limited to operating pressures > 4 kPa.²⁰ Our measurements have allowed us to study the delivery of industrially relevant organometallic precursors like $\mu^2-\eta^2$ -(*t*-Bu-acetylene)dicobalthexacarbonyl (CCTBA)^{17, 19} and pentakis(dimethylamido)tantalum (PDMAT).¹⁸ Delivery of PDMAT, a solid with a melting point above 100 °C and a reported vapor pressure of 6.7 Pa (50 mTorr) at 55 °C,²¹ exhibits complicated behavior when a vapor draw ampoule is used. While our measurements allow us to observe how the PDMAT flow rate changes in response to our input variables (e.g., pulse timing), the dynamics inside the ampoule that are responsible remain poorly understood. In other words, the ampoule remains a “black box” despite our being able to characterize its performance.

To better understand what is occurring inside the vapor draw ampoule, the work presented here uses simulation to model PDMAT sublimation and transport in a flow of carrier gas. We find that a relatively simple model that includes only the flow of the carrier gas, the flow and diffusion of PDMAT, and a constant PDMAT pressure at its source can account for the trends we observe experimentally. Parameters for this model are obtained from a small set of experimental data, which allow the model to simulate the performance of a broad set of conditions as confirmed by a much larger experimental dataset. This approach is potentially useful for understanding the operation of process equipment, for the design of new delivery devices, and for process development.

II. MODEL

The nominally 1.5 L vapor-draw ampoule [Fig. 1(a)] analyzed in this report is a commercial stainless steel cylinder that includes two 12.7 mm (1/2 inch) gas lines with 9.7 mm inner diameters serving as inlet and outlet. Additionally, an off-center, capped line (the “fill port”) is found on the top of the vessel, but it is neglected in the present analysis. The inlet line is terminated internally with a 90° elbow that directs flow into the nearby wall; the outlet is flush with the top. The internal height of the can is 124.2 mm, and the inner diameter is 127.0 mm. During the experiment, the ampoule contains roughly 200 g of PDMAT, which is included in the simulation by setting the height to 111.6 mm corresponding to an estimated depth of 12.6 mm of PDMAT. The simplified geometry used in the simulation is constructed based on mechanical drawings and is shown in Fig. 1(b).

We initially perform some calculations based on the operating conditions and geometry of the system to determine the Reynolds number $Re = uL/\nu$, where u is the gas velocity, L the characteristic length, and ν the kinematic viscosity. The maximum value of u in the system is located near the inlet tube; the average there is $\bar{u} = Q_{STP}TP_{STP}/T_{STP}PA$ where Q_{STP} is the volumetric flow rate at standard temperature ($T_{STP} = 273.15$ K) and standard pressure ($P_{STP} = 101.325$ kPa), A is the cross-sectional area of the inlet, and P and T are the pressure and temperatures, respectively, inside the ampoule. The value of ν is related to the dynamic viscosity μ and density ρ through $\nu = \mu/\rho = \mu k_B T/Pm$ where the density is determined using the ideal gas law with k_B being the Boltzmann constant and m being the molecular mass of the gas. Combining these equations, the Reynolds number is

$$Re = \frac{Lm}{A\mu} \left(\frac{Q_{STP}P_{STP}}{k_B T_{STP}} \right). \quad (1)$$

The present work uses Ar as a carrier gas. At 60 °C, the value of μ is calculated to be 24.8 $\mu\text{Pa}\cdot\text{s}$,²² so $Q_{STP} = 1$ L/min results in $Re = 3200$ when L is chosen to be one half the circumference of the ampoule. Even using the maximum velocity, the calculated Re is well below the 3.2×10^5 transition value for flow over a flat plate.²³ (The proper choice of L is ambiguous in this case, but dimensions inside the ampoule are on the same order as our choice.) With L chosen to be the inner diameter of the inlet tube, $Re = 150$ is calculated, which is below the 2000 transition value for flow through cylindrical pipes.²³ The flow in the present system, therefore, can be assumed to be laminar.

Simplifying assumptions can be made in constructing the model, which greatly increase computational throughput:

1. **Isothermal conditions.** Ampoules like the one we investigate are typically enclosed in ovens when used in high-volume manufacturing. We have assumed the temperatures of the walls and gas are homogeneous, and both are equal to a one value, T .
2. **Highly dilute conditions.** The vapor pressure of PDMAT²¹ at the maximum temperature examined in this study, 78 °C, is approximately 50 Pa while the outlet pressures are on the order of 1000 Pa. Because of the low concentration of PDMAT in the PDMAT/Ar mixture, the density and viscosity of the gas is taken to be that of pure Ar. This assumption allows details of the flow to be calculated without regard to the composition of the gas.
3. **Ideal gases.** Both Ar and PDMAT are assumed to be ideal gasses. The density of Ar is calculated as $\rho = Pm_{Ar}/k_B T$ where P is the pressure and m_{Ar} is the atomic mass of Ar. Similarly, the molar concentration of PDMAT is given by

$$c_{Ta} = p_{Ta}/N_A k_B T \quad (2)$$

where p_{Ta} is the partial pressure of PDMAT and N_A is the Avogadro constant. The dynamic viscosity μ of the gas is taken from the literature values of the kinematic viscosity ν of Ar²² assuming the ideal gas law: $\mu = \nu Pm_{Ar}/k_B T$.

4. **Symmetry.** Flow is assumed to be symmetric across the plane that includes the inlet and outlet ports. The effects of the fill port are ignored. Additionally, the internal elbow is assumed to be well-aligned. Asymmetry in the physical system would introduce rotation that is not included in this model. The assumption of symmetry allows the ampoule to be split [Fig. 1(b)] so that the number of required elements is halved.
5. **Source assumptions.** Sublimation is assumed to be sufficiently fast so that transport into the Ar carrier gas is limited by diffusion. Furthermore, the only source of PDMAT is assumed to be at the bottom of the ampoule.
6. **Constant pressure.** The pressure at the outlet, P_{out} , is assumed to be constant with time. In reality, measurements downstream of the ampoule reveal that the pressure exhibits minor transients lasting tens of seconds when the carrier gas is switched between flowing through the ampoule and by-passing it. At around 2050 Pa, these transients amount to about 3 % of the long-term value.

With the above assumptions, the mathematical model for transport is constructed and solved using COMSOL Multiphysics v5.3a.²⁴ A mapped mesh based on the simplified geometry of the ampoule [Fig. 1(b)] is applied. Numerical solutions are obtained for differential equations that include the form of the Navier-Stokes equations for the conservation of momentum within a compressible Newtonian fluid

$$\rho \left(\frac{\partial \mathbf{u}}{\partial t} + \mathbf{u} \cdot \nabla \mathbf{u} \right) = - \nabla p + \nabla \cdot \left[\mu (\nabla \mathbf{u} + (\nabla \mathbf{u})^T) - \frac{2}{3} \mu (\nabla \cdot \mathbf{u}) \mathbf{I} \right] \quad (3)$$

where $\mathbf{u}$ is the velocity vector, $\mathbf{I}$ is the identity matrix, and $(\nabla \mathbf{u})^T$ is the transpose of the gradient of the velocity field. Additionally, the continuity equation for the conservation of mass must be obeyed:

$$\frac{\partial \rho}{\partial t} = - \nabla \cdot (\rho \mathbf{u}). \quad (4)$$

Flow at the walls is set to zero, i.e., a no-slip wall boundary conditions are used, which establishes boundary layers in the simulation. The inlet boundary condition is set using the flow Q_{STP} from the experiment. The boundary condition at the outlet is set by a pressure P_{out} (Assumption 6.) This pressure corresponds to the pressure calculated for the ampoule headspace and is based on measured downstream pressures, the Hagen-Poiseuille equation,²⁵ and empirically determined pressure drops from the valves.¹⁵ Flow is forced to be normal at the outlet, and backflow through the inlet is suppressed by allowing the inlet pressure to adjust. Because of Assumption 4, the value of Q_{STP} used for the simulation is half the experimental value.

Assumption 2 allows the fluid flow to be solved independently of the mass transport of PDMAT. Using the flow field $\mathbf{u}$ from the solutions of the above equations, the molar concentration of PDMAT is determined using an equation combining Fick's second law and a convective term:

$$\frac{\partial c_{Ta}}{\partial t} = \nabla \cdot (D_{12} \nabla c_{Ta}) - \mathbf{u} \cdot \nabla c_{Ta} \quad (5)$$

where D_{12} is the binary diffusion coefficient of PDMAT and Ar. The boundary conditions are $c_{Ta} = 0$ at the inlet and $c_{Ta} = c_{Ta,bot}$ at the bottom of the ampoule (Assumption 5). Unfortunately, values of D_{12} for any organometallic vapors are rare in the literature, and none have been reported for PDMAT. We therefore use the Chapman-Enskog theory²⁶ within the simulation:

$$D_{12} = \frac{3}{16} \left(\frac{2\pi k_B T}{m_{12}} \right)^{1/2} \frac{1}{n \sigma^2 \Omega_{12}} \quad (6)$$

where $m_{12} = m_{Ar} m_{Ta} / (m_{Ar} + m_{Ta}) = 6.0330 \times 10^{-26}$ kg is the reduced mass for a collision of an Ar atom with a PDMAT molecule, which has an average mass $m_{Ta} = 6.66414 \times 10^{-25}$ kg. The gas number density n can be determined from the ideal gas law: $n = \rho / m_{Ar} = P / k_B T$. The value of the characteristic length σ and collision integral Ω_{12} in Eq. (6) are unknown. Using published values of D_{12} for nitrogen and Co(tmhd)₃, a similarly sized organometallic compound,²⁷ we use Eq. (6) to estimate $\sigma^2 \Omega_{12} \approx 2 \times 10^{-18}$ m², which we use as a starting point for PDMAT in Ar. Rewriting Eq. (6), we use $D_{12} = d_0 T^{3/2} P^{-1}$ to describe the diffusion coefficient where the lumped parameter $d_0 = (9\pi/128 m_{12})^{1/2} k_B^{3/2} \sigma^{-2} \Omega_{12}^{-1}$ should be approximately 5×10^{-5} kg·m·s⁻³·K^{-3/2}.

The above equations are solved for both time-invariant and dynamic solutions. The time-invariant solutions are meant to model conditions of continuous flow as is typical in CVD. Dynamic solutions are obtained for simulating pulses of precursor like those used in ALD. A pulsed injection is simulated by introducing a time-dependent Q_{STP} that alternates between the full value and zero. To speed computation, the full set of differential equations is solved only for the pulse time and 0.5 s immediately before and after it. Outside of these pulse periods, flow is set to zero and only solutions for diffusion [Eq. (5)] are generated.

The rate of PDMAT delivery is calculated by integrating the normal flux across the outlet aperture. In this study, the delivery rate is expressed in terms of the mass,

$$j(t) = 2m_{Ta} N_A \iint_S -\mathbf{n} \cdot (c_{Ta} \mathbf{u} - D_{12} \nabla c_{Ta}) dS \quad (7)$$

where $\mathbf{n}$ is the normal vector at the outlet aperture. The surface integral is multiplied by a factor of two because of our implementation of symmetry (Assumption 4). The amount of PDMAT injected during a pulse i is the integral of $j(t)$ over the duration of the pulse:

$$J_i = \int_{t_{1,i}}^{t_{2,i}} j(t) dt \quad (8)$$

where $t_{1,i}$ and $t_{2,i}$ are times marking the beginning and end of pulse i .

III. EXPERIMENTAL

The apparatus (see Fig. 2) and methods used to measure the partial pressure of PDMAT are described in detail elsewhere.^{15, 18} Briefly, by utilizing a non-dispersive infrared (NDIR) gas analyzer consisting of a thermal source, optical chopper, bandpass filter, and mercury-cadmium telluride detector, we measure the absorption from PDMAT and its decomposition product dimethylamine (DMA) as they pass through a short-pathlength flow cell. By calibrating the absorption against the PDMAT molar concentration (and accounting for the interferant DMA), we obtain measurements of PDMAT concentration downstream of the vapor draw ampoule.¹⁸ The system includes a mass flow controller upstream of the ampoule to deliver a constant volumetric flow rate (STP) of the Ar carrier gas. Pressures are measured with capacitance manometer gauges upstream of the ampoule and downstream of the flow cell. The pressure is controlled independently of the flow rate by use of a throttle valve before the pump. The ampoule is coupled to the system through the commonly used “five-valve cluster” configuration: Two manual diaphragm valves allow the ampoule and cluster to be isolated from the rest of the apparatus; three pneumatically actuated diaphragm valves alternate the Ar flow between passing through the ampoule and by-passing it.

In some cases, parameters used in the simulation are directly from process measurements made during the experiment. This is the case with Q_{STP} , which is taken from the setting of the mass flow controller, and T , which is from the K-type thermocouple used to control the ampoule heating jacket. Other parameters, however, require calculations based on measurements and detailed understanding of the flow characteristics of the system. In the case of P_{out} , which is the estimated headspace pressure, a downstream pressure measurement is required along with calculations of the pressure drops from valves and lines.¹⁵ Similarly, the simulated values of J_i and $\dot{J}(t)$ are compared to the experimental PDMAT delivery rate as determined from the NDIR measurement, the flow rate of Ar, and the total pressure at the optical cell corrected for the pressure drop between it and the pressure measurement point.¹⁸

IV. RESULTS AND DISCUSSION

Within the model, the delivery rate of PDMAT with a continuous flow of Ar is determined both by the rate of diffusive transport into the carrier gas and by the PDMAT concentration at the bottom of the ampoule. The simulated PDMAT output from the ampoule, therefore, can be matched with experimentally measured values by adjusting the values of D_{12} and $c_{\text{Ta,bot}}$. Unfortunately, the values of D_{12} and $c_{\text{Ta,bot}}$ are correlated parameters: the effect on the output by a decrease in one can be offset by an increase in the other even when other parameters (e.g., Q_{STP} and P) are varied. Only by introducing transients can unique values for D_{12} and $c_{\text{Ta,bot}}$ be obtained. Intuitively, this can be understood if one considers that the partial pressure of PDMAT in the headspace before flow starts should eventually reach the vapor pressure (as reflected by $c_{\text{Ta,bot}}$); how close the system approaches this limit depends on how long it rests between pulses and the rate of diffusional mass transport (as determined by D_{12} .) Thus, simulating pulsed flow with variable timing could be used to determine D_{12} and $c_{\text{Ta,bot}}$ simultaneously through an optimization approach. Unfortunately, simulating transients is time-consuming, and optimizing for two parameters would be more so.

To circumvent these difficulties, we have adopted a strategy that uses modeling of continuous flow as an initial step for the next step of modeling of pulsed operation. We simulate the PDMAT output under continuous flow of Ar and compare it to a single experimental measurement obtained from long pulses (45 s). The datum chosen is the measured 0.242 mg/s of PDMAT delivered from the 75 °C ampoule with a calculated headspace pressure of 6076 Pa from an Ar flow of 1 L/min (STP). Within the model, the PDMAT delivery rate is determined at a series of d_0 values around $5 \times 10^{-5} \text{ kg}\cdot\text{m}\cdot\text{s}^{-3}\cdot\text{K}^{-3/2}$ while varying $c_{\text{Ta,bot}}$; since the output is found to be a linear function of $c_{\text{Ta,bot}}$, a series of (d_0 , $c_{\text{Ta,bot}}$) pairs that produce 0.242 mg/s can be readily determined. These are fit to a function, $c_{\text{Ta,bot}} = f(d_0)$, which limits the model fit parameters to just one, d_0 . The function, in this case, is arbitrarily chosen to be a power law.

Using the empirical relationship $c_{\text{Ta,bot}} = f(d_0)$ obtained from matching the continuous flow simulation with an experimental datum, the continuum of values is then limited to just one by simulating the first pulse obtained after a prolonged idle time. Experimentally, the ampoule was isolated for 3 min at 75 °C, which, we assume, should allow the PDMAT concentration to homogenize through diffusion. (At an estimated $D_{12} \approx 1.1 \times 10^{-4} \text{ m}^2/\text{s}$, the diffusion time $L^2/2D_{12}$ for the internal height $L = 111.6 \text{ mm}$ is calculated to be approximately 1 min.) In the simulation, the c_{Ta} is initially set to be uniformly equal to $c_{\text{Ta,bot}} = f(d_0)$, so by varying d_0 , the J_1 from the first pulse (2 s duration) can be matched with the 2.38 mg experimentally measured from a 75 °C ampoule with a calculated headspace pressure of 3680 Pa and Ar flow of 1 L/min (STP). The value of J_1 is found to be nearly linearly related to d_0 , which allows us to readily determine that $d_0 = 6.34 \times 10^{-5} \text{ kg}\cdot\text{m}\cdot\text{s}^{-3}\cdot\text{K}^{-3/2}$ results in $J_1 = 2.37 \text{ mg}$. (This value for d_0 compares well with the estimate of $5 \times 10^{-5} \text{ kg}\cdot\text{m}\cdot\text{s}^{-3}\cdot\text{K}^{-3/2}$ that we used as a starting point.) The value of $c_{\text{Ta,bot}}$ obtained from $f(d_0)$, is $6.58 \text{ mmol}\cdot\text{m}^{-3}$, which corresponds to a value of $p_{\text{Ta}} = 19.0 \text{ Pa}$ by Eq. (2). This differs significantly from the 34.8 Pa at 75 °C obtained from the Antoine equation for PDMAT:²¹

$$\log_{10} p_{\text{vp}} = A - \frac{B}{T_{\text{PDMAT}}} \quad (9)$$

where $A = 13.390$, $B = 4124.9 \text{ K}$ and the vapor pressure p_{vp} is in units of Pa. Clearly, assuming that $c_{\text{Ta,bot}}$ is simply the concentration corresponding to the vapor pressure at T would lead to results that differ from the experiment; compensating by adjusting D_{12} would lead to a non-physical value. The temperature that corresponds to $p_{\text{vp}} = 19.0 \text{ Pa}$ in Eq. (9) is $T_{\text{PDMAT}} = 68 \text{ °C}$. As will be discussed below within the context of Fig. 7, the model consistently requires the PDMAT source to be at a lower concentration than what is predicted by the vapor pressure curve from Ref. 21.

Using the parameters obtained from fitting two data points that correspond to continuous flow and to the first pulse after a prolonged idle time, the simulation is extended to more pulses and to other conditions. Fig. 3(a) shows the experimental and simulated J_i values for $i = 1$ to 10 at P_{out} values around 3650 Pa and 5950 Pa for pulse lengths of 1 s and 2 s. In all cases, the conditions are $T = 75 \text{ °C}$, $Q_{\text{STP}} = 1 \text{ L/min}$, and the inter-pulse time is 8 s. Good agreement is found generally with the initial pulses being within 9 % of the measured ones

and the tenth pulses being within 6 %. Therefore, two experimentally determined data points is sufficient to allow the model to accurately simulate output.

The simulation is used to examine other timings. With P_{out} around 3650 Pa and $Q_{\text{STP}} = 1 \text{ L/min}$, the pulse and inter-pulse times are varied. Starting with the ampoule at a uniform concentration ($c_{\text{Ta}} = c_{\text{Ta,bot}}$), simulations are made to determine J_5 , which are plotted in Fig. 3(b). As is apparent in Fig. 3(a), the values of J_5 are within 0.05 mg of those from J_{10} , so computation time is halved with only a slight decrease in accuracy. The simulated values in Fig. 3(b) agree with the experimentally determined long-term pulse outputs. In both the experiment and simulation, the output depends strongly on the length of the pulse and less strongly on the inter-pulse times. For ALD process development, both times may need to be considered. For example, varying the pulse timing of the co-reactant and/or the purge times of either half-cycle also changes the amount of PDMAT that is delivered even without changing the PDMAT pulse time. The simulated shapes of the pulse $\check{J}(t)$ also appear to agree qualitatively with the experiment as evidenced by Fig. 4, which shows the first five pulses obtained from 2 s pulses at about 3680 Pa, 75 °C, and 1 L/min (STP). In each case, the first pulse shows a nearly constant amount delivered before the rate decreases. The simulation shows the decrease occurs in two stages while the experiment shows only one. In later pulses, both the simulation and experiment show $\check{J}(t)$ initially increases in two steps. The second, slower increase slows and transitions to a decrease which results in a peak in $\check{J}(t)$. The simulation again shows two steps in the decrease while the experiment shows only one. The point at which the constant delivery rate ends on the first pulse and the time where the peak occurs in latter pulses occurs at an earlier point in the simulation than in the experiment. This may be indicative of a deficiency in the model that perhaps originates from one of the listed assumptions.

Despite the discrepancies between the experiment and simulated results, the simulation can be used to explain the general shape of the pulse. Several points in the simulation are labeled “A” through “G” in Fig. 4, and the corresponding c_{Ta} and velocity streamlines are shown in the cross-sectional plots of Fig. 5. The concentration profile in “A” in Fig. 5 is the result of the four pulses that began with a homogenous profile before the first pulse. Going from “A” to “B,” the flow field develops while gas that has accumulated PDMAT during the inter-pulse period flows outward. This explains the rapid initial increase in $\check{J}(t)$ in Fig. 4. A vortex begins to form near the inlet with some inflowing gas sweeping the bottom of the ampoule before rising along the wall; other gas flows through the central volume of the ampoule. The vortex becomes fully formed going from “B” to “C.” At “C,” the central volume appears mostly depleted of PDMAT, which explains the maxima in Fig. 4. Going from “C” to “D,” the small region near the top of the ampoule is depleted of PDMAT while the vortex region picks up PDMAT. Between “D” and “E,” the vortex region accumulates PDMAT, which is lost slowly to the flow around it. Eventually, the PDMAT vapor is confined to the region above the bottom and along the wall near the outlet as shown in “F.” Together, the transport of PDMAT into and out of vortex explains the complex behavior seen in the simulation. After flow is ceased, the distribution of PDMAT left in “G” evolves to become that immediately before the pulse in “A.”

The above analysis can be used to interpret the general shape of the experimentally measured PDMAT concentration in Fig. 4. The slower increase in concentration that follows the rapid, initial increase is likely due to the establishment of a high-concentration flow that sweeps over the bottom. This flow accompanies a separate flow through the central volume, which is slowly depleted of PDMAT. This depletion is responsible for the long, slow decrease after the maximum. Some of the quantitative differences between the experiment and simulation in Fig. 4 are possibly due to neglecting the fill port since the region above the vortex appears to influence the simulated output. Additionally, the flow leaving the ampoule passes through two diaphragm valves and approximately 82 cm of tubing before reaching the optical cell.¹⁵ These components likely influence the shape of the pulse profile $j(t)$ although the integrated amounts J_i remain the same.

The above discussion has focused on pulsed flow of PDMAT, which simulates ALD processes. In CVD, the flow is continuous, and transients are less important. In Fig. 6, the PDMAT delivery rate using 1 L/min (STP) of Ar is plotted as a function of P_{out} while at 75 °C. The experimental values are obtained from the ends of 45 s pulses. There is good agreement between experiment and simulation. If the results are analyzed using the “bubbler equation,”^{28, 29} which assumes the ratio of the partial pressures of carrier gas and precursor in the headspace equal the ratio of their molar flow rates, then one would expect the delivery rate of PDMAT to be inversely proportional to the Ar partial pressure. Fitting the experimental data to bP^{-1} (see Fig. 6) provides a value of $b = (1450 \pm 30) \text{ Pa}\cdot\text{mg/s}$. (Uncertainties here and elsewhere in this work are expressed at 95 % confidence intervals.) Using this value, the calculated partial pressure of PDMAT in the ampoule would be about 5 Pa (40 mTorr), which, according to Eq. (9), corresponds to 52 °C. This result is 23 °C below the measured ampoule temperature. As discussed below, the simulation utilizes partial pressures that are much closer to what is expected based on Eq. (9) although systematic differences are present.

A separate experiment is conducted in which the output from 45 s pulses is measured with the ampoule temperature varied between 60 °C and 78 °C with the output pressures nearly constant in the range of (6009 to 6091) Pa. Using the value for d_0 that we obtain from the 75 °C data, the value of $c_{\text{Ta,bot}}$ is adjusted in the simulation to match the experimental delivery rates at each temperature. To facilitate the evaluation of the fitted $c_{\text{Ta,bot}}$ values, they are used to calculate equivalent partial pressures [Eq.(2)], which are plotted against the vapor pressure of PDMAT [Eq.(9)] in Fig. 7. At the highest ampoule temperature of 78 °C, the simulation requires the PDMAT partial pressure to be a value corresponding to 70 °C in Eq. (9). At 60 °C, the equivalent partial pressure in Eq.(9) is obtained at 58 °C. The difference at 75 °C, which is the temperature at which the data in Fig. 6 is obtained, is 8 °C. Fitting the simulation values in Fig. 7 to the functional form of Eq.(9), one obtains $A = 10.3 \pm 1.2$ and $B = (3154 \pm 453) \text{ K}$. The temperature-dependent value of the 0063 concentration of PDMAT in the model can be expressed as

$$c_{\text{Ta,bot}}(T) = (N_A k_B T)^{-1} 10^{10.3 - 3154/T}. \quad (10)$$

Delivery of the liquid Co precursor CCTBA from a bubbler has also shown a lower partial pressure than what was expected from its reported vapor pressure.¹⁹ The causes for the

suppressed outputs for CCTBA and PDMAT are not known. Possibly, a neglected physical effect explains the discrepancy between the expected values and the experiment (e.g., cooling from the heat of sublimation.) However, for PDMAT, a possibility exists that the method used to determine the vapor pressure may have inadvertently included the decomposition product DMA in the measurement. If that is the case, then the vapor pressure of PDMAT actually may be closer to the simulation inputs. Recent work in determining the vapor pressures of slowly decomposing compounds (including one alkylamide similar to PDMAT) could provide a means to rule out systematic measurement errors.^{30, 31}

Finally, we extend our model to demonstrate how it might be used to predict long-term precursor delivery. By varying the height of the ampoule in the simulation, the effect of varying the fill level of precursor can be examined. The flow of Ar is 1 L/min (STP), the pressure is 3650 Pa, and the temperature is 75 °C. Fig. 9 shows that the delivery rate of PDMAT decreases by about one-third as the level decreases from 100 mm, which is just below the elbow in Fig. 1(b), to the 12.6 mm used in the rest of this study. Compensating for this decrease could be accomplished by increasing the temperature (Fig. 7) or by decreasing the pressure (Fig. 6) in the ampoule while maintaining the flow rate (STP) of carrier gas. (Maintaining the flow rate in this way minimizes the disturbance of the process downstream of the precursor delivery system.) Precursor monitoring would likely become necessary if such a method were utilized to stabilize precursor delivery. This strategy would provide another solution (besides better container design) to the problem of low-volatility precursor delivery.

V. CONCLUSIONS

A model of a vapor draw ampoule was constructed using a limited dataset of experimental data obtained from an inline NDIR gas analyzer and from calculations based on detailed knowledge of the flow system under consideration. For the case examined, two parameters, one for the gas-phase concentration of the source and one for the diffusion coefficient, were sufficient to model PDMAT delivery in both pulsed and continuously flowing operation over a wide range of conditions. Adapting this model to other geometries and conditions could be accomplished using these empirically determined parameters. The accuracy of the simulated results suggests the model may be potentially useful for equipment design and process development. Furthermore, we find the unusual shape of the experimentally observed pulse profiles could be qualitatively explained based on the simulation. These findings illustrate the potential in combining process measurements and modeling to understand what is occurring in the “black boxes” found upstream of ALD and CVD reactors.

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Fig. 1. Schematic drawings of the vapor draw ampoule: (a) the physical dimensions (in mm) of the actual ampoule and (b) the simplified model used in the simulation.

Fig. 2. Schematic diagram of the apparatus used to measure the PDMAT concentration from the vapor-draw ampoule. MFC = mass flow controller, P1 and P2 = upstream and downstream capacitance manometer pressure gauges, and FC = flow cell.

Fig. 3. Experimental and simulated values compared. (a) The mass of PDMAT delivered from a series of pulses of 1 s and 2 s duration with 8 s inter-pulse periods. Two ampoule pressure regimes (around 3650 Pa and 5950 Pa) are examined. (b) The long-term output per pulse varying the pulse and inter-pulse lengths at around 3650 Pa.

Fig. 4. Experimental and simulated injection rates of the first five pulses of PDMAT determined for 2 s pulses with 8 s inter-pulse periods. The pressure is 3650 Pa. The labeled points in the simulation correspond to the data displayed in Fig. 5.

Fig. 5. Simulated PDMAT concentrations and streamlines in the cross-section of the ampoule. Letter labels correspond to the points in Fig. 4. Yellow denotes higher concentrations while navy blue is lower.

Fig. 6. Experimental and simulated PDMAT mass flow as a function of the ampoule outlet pressure using 1 L/min (STP) of Ar. The experimental data is fit to the function bP^{-1} with $b = 1450$ Pa·mg/s.

Fig. 7.

Partial pressures of PDMAT at the bottom of the ampoule used to simulate the delivery rates over a range of temperatures. The reported vapor pressure from Ref. 21 is plotted for comparison. The fit line for the simulation data uses Eq.(9) with $A = 10.3$ and $B = 3154$ K.

Fig. 8. Simulated PDMAT mass flow as a function of the depth of PDMAT in the ampoule. The flow of Ar is $Q_{\text{STP}} = 1$ L/min, the pressure is 3650 Pa, and the temperature is 75 °C.