Low Vapor Pressure Precursor Delivery: A Case Study in MLD of Polyimide

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Introduction

A growing number of precursors are being explored for the development of atomic layer deposition (ALD) and molecular layer deposition (MLD) processes within the SNF. However, precursors with a low vapor pressure present unique challenges to achieving robust precursor delivery. Precursor heating provides a route to increase vapor pressure and may be used in conjunction with bubblers and inert gas boosting to augment precursor dosing. However, increasing precursor temperature requires careful thermal management in order to maintain positive temperature gradients and prevent precursor condensation.

In this report, we present a basic overview of narrow temperature window processes with a focus on recipes requiring precursor heating to > 100 °C. Measurements of the temperature gradient and uniformity across a precursor cylinder assembly are presented. Informed by these measurements, we discuss the thermal limitations of a standard precursor cylinder assembly and insulating jacket used on the MLD, Savannah, and Fiji tools in the SNF.

Two methods to improve thermal performance are evaluated using pyromellitic dianhydride (PMDA) precursor. This low vapor pressure precursor is used in MLD of polyimide, requires heating to >140 °C, and therefore provides an ideal case study to test precursor cylinder assemblies at higher temperatures. We envision that the thermal characterization discussed in this report may serve as a useful reference for process engineers working with other low vapor pressure precursors within the SNF.

Process Temperature Window (excerpt from report by T. English & F. Alfonso, Fall 2014)

The concept of an ALD or MLD window is frequently used to describe the temperature range over which a process yields a reliable self-limiting growth rate. This concept is shown graphically in Figure 1. Deviations in temperature outside the window can lead to either an increase or decrease in the observed growth rate depending on the nature of the limiting process. Therefore, the width of the window, Δ T, plays a critical role in determining the feasibility of an ALD or MLD process.

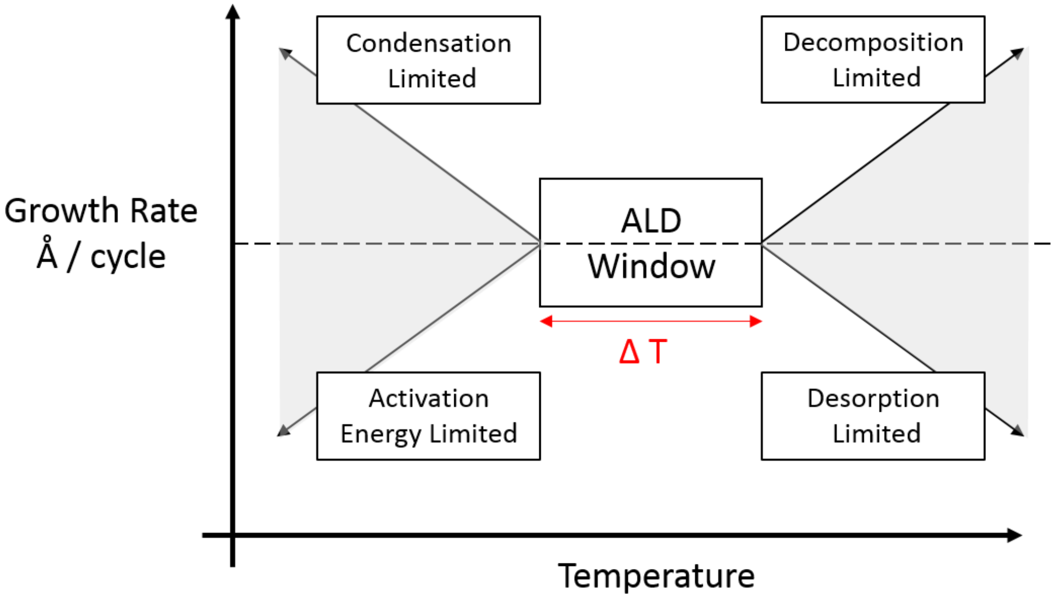

Figure 1: Schematic of an ALD process window.

While a process would ideally have a very large window, such as with TMA/H_2O, many proposed polymer chemistries rely upon precursors with comparatively lower vapor pressures. To achieve sufficient precursor dosing, these precursors are often heated to produce vapor pressures of ~ .1 - 1 torr. However, the range of heating may be limited by thermal decomposition. Additionally, a positive temperature gradient is typically maintained between the precursor source and reactor chamber to minimize precursor condensation which can lead to clogging. Together, the requirements of precursor heating and maintaining a positive temperature gradient can significantly raise the lower temperature limit of an ALD or MLD window as shown in Fig. 2.

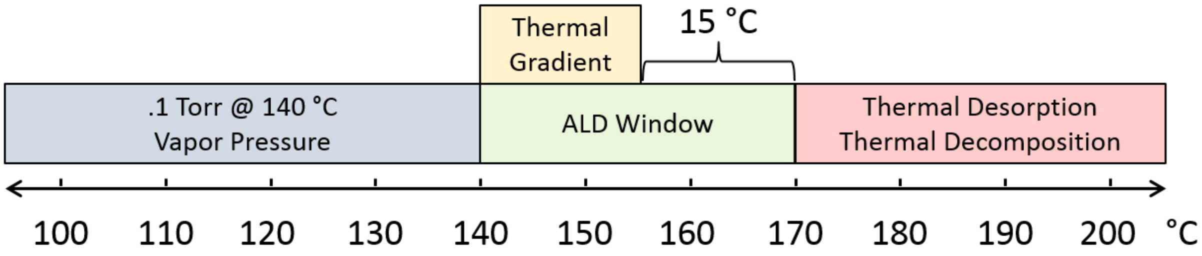

Figure 2: Schematic of narrow temperature window process.

Cutting into the thermal budget leaves a smaller window for deposition. As this window shrinks, unique tool and chemistry challenges appear which strongly govern the feasibility and reliability of an ALD or MLD process. The objective of this report is to document the thermal performance and limitations of a standard precursor cylinder assembly under the constraints of both a high precursor temperature (> 100 °C) and narrow process window (15 °C).

Precursor Cylinder Thermal Management

The graphical user interface (GUI) on ALD and MLD reactors provides an overview of the thermal profile within the tool. For example, Fig. 3a shows the GUI of a Savannah style MLD reactor including the temperature set points for 6 precursor ports across the bottom of the screen. The temperature readings displayed in the GUI and used for closed loop temperature control are measured with a RTD embedded into each precursor heater jacket as shown in Fig. 3b.

While the precursor cylinder has the appearance of being uniformly heated at a single set point temperature maintained by a PID controller, it is important to consider the practical limitations of this isothermal assumption presented to users in the software. Similarly, it is helpful to examine the hardware responsible for the thermal management of precursors.

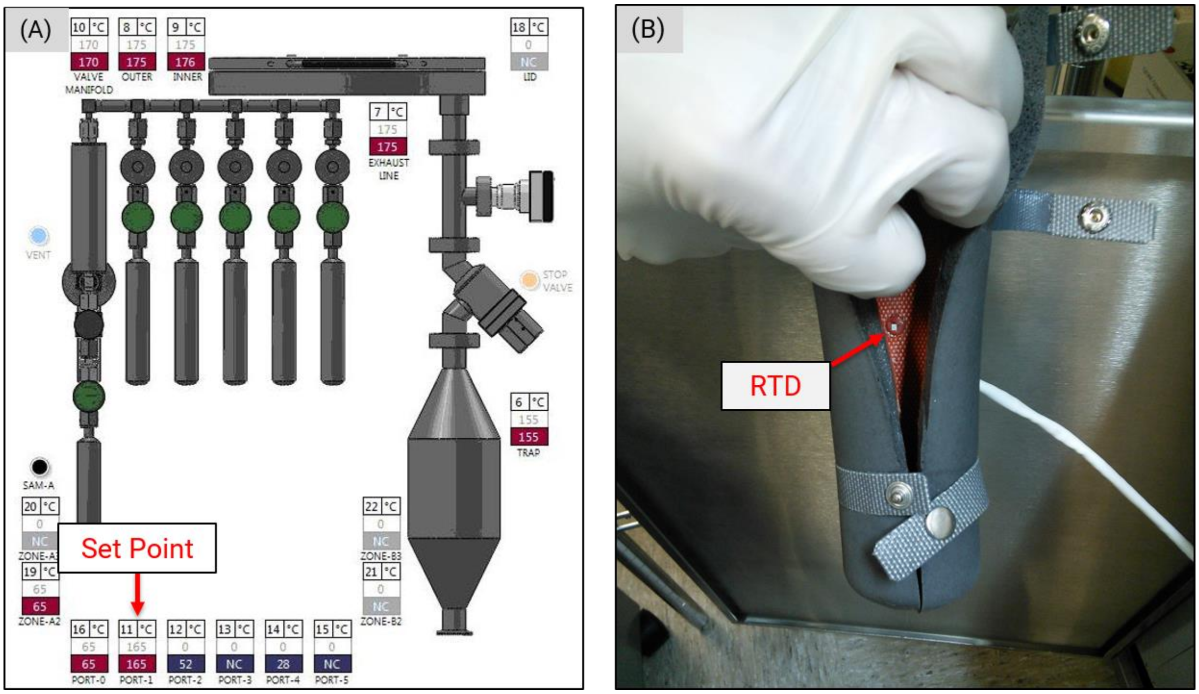

Figure 3: (a) Graphical user interface showing the temperature profile of a MLD reactor, and (b) molded foam precursor jacket with an embedded RTD.

Figure 4a shows a standard precursor assembly consisting of a 50 cm^3 cylinder, manual bellows valve, and a narrower VCR connection in-between. Figure 4b shows a traditional precursor jacket with Velcro fasteners commonly used in the SNF. An opening in the insulation allows the manual valve handle to protrude for access and safety purposes. In contrast to the more loosely fitting Velcro jacket, Fig. 4c shows a molded foam jacket designed to provide improved thermal insulation and temperature uniformity. The wiring leads from each precursor jacket provide electrical connections to the embedded temperature sensor and resistive heater element.

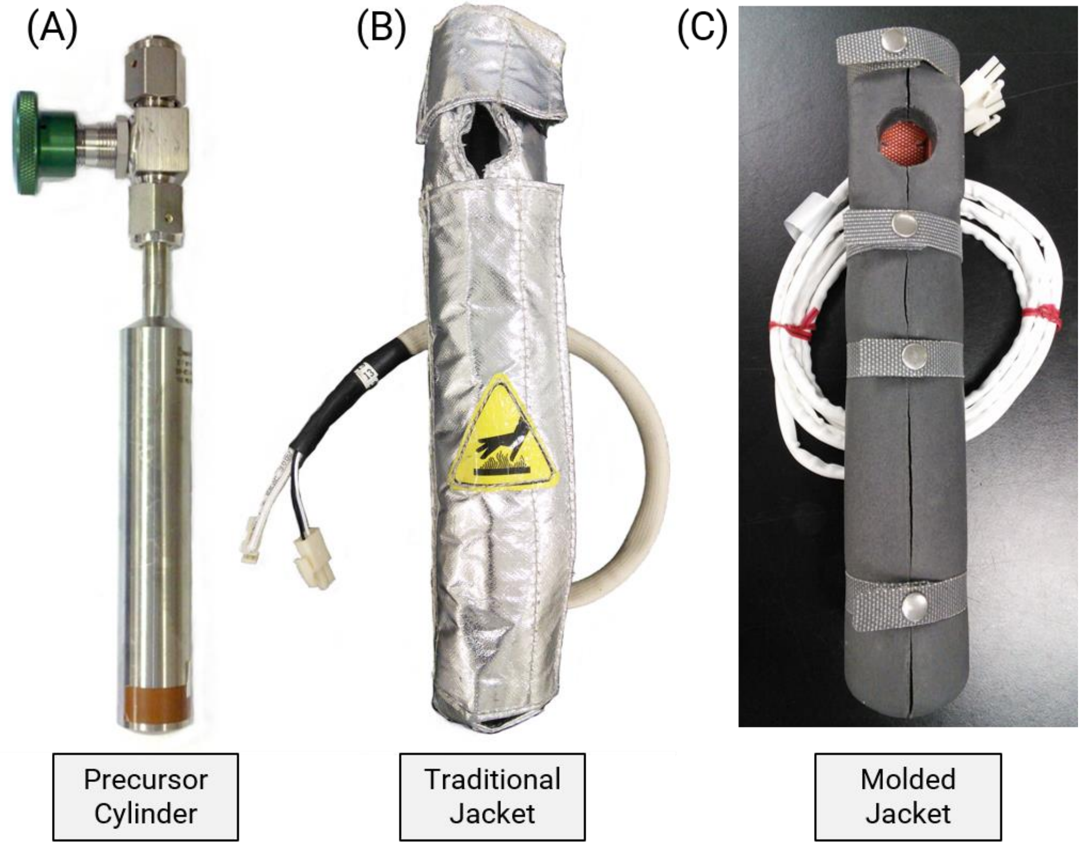

Figure 4: (a) Standard precursor cylinder assembly, (b) Velcro precursor jacket, and (c) molded foam precursor jacket.

Under normal operation, the downstream manifold is maintained at a higher temperature than the precursor cylinder. This condition establishes a positive temperature gradient leading away from the cylinder towards the reactor. However, it is important to note that any surfaces or poorly insulated regions exposed to ambient can disrupt the intended temperature profile, giving rise to cold spots, precursor condensation, and clogging. For example, an exposed manual valve handle provides a large conduction pathway and thermal sink to the ambient environment. Such thermal sinks produce increasing departures from an isothermal condition with increasing precursor temperature, often leading to localized cold spots.

Figure 5 shows an example of precursor clogging in the narrow VCR flange between the precursor cylinder and manual valve. While this clog is confined to the precursor assembly which can be easily removed from the tool, we note that cold spots may also occur downstream of an ALD valve as well. Clogging downstream of the ALD valve carries greater risks because those manifold regions are not designed to be readily accessible or removed for service. Therefore, it is advisable to consider the melting and decomposition temperatures of any new precursors before testing to determine if there is a sufficient thermal budget to clear a clog in less accessible regions of the tool.

Figure 5: Clogging of a precursor cylinder.

Heater Jacket Characterization

A precursor cylinder assembly was outfitted with an array of RTDs to characterize 4 temperature zones defined as the bottom, middle, top, and manual valve regions as shown in Fig. 6a. Thin pads of low thermal conductivity foam insulation were placed on the backside of each RTD and secured with Kapton tape to provide thermal isolation from the electrical heater tape which lines the inside of heater jackets. The cylinder assembly was installed and wrapped with a molded foam jacket as shown in Fig. 6a and 6b, respectively.

The temperature uniformity of a standard precursor assembly and molded foam jacket are characterized with the manual valve handle exposed. This arrangement reflects the best thermal performance a process engineer might expect using standard equipment and installation procedures in the SNF where manual valves are typically left uninsulated. Alternative configurations including insulation of manual valves and standalone temperature controllers will be discussed later in this report.

Temperature measurements are performed by sweeping the precursor cylinder set point in 10 °C increments from no heating (steady state temperature ≈ 36 °C) to 170 °C. The tool was allowed to stabilize for a minimum of 1 hour after reaching each set point temperature. The precursor manifold was set to 170 °C (maximum valve) for all measurements which is limited by O-rings seals used to interface the MLD Savannah tool to a glovebox.

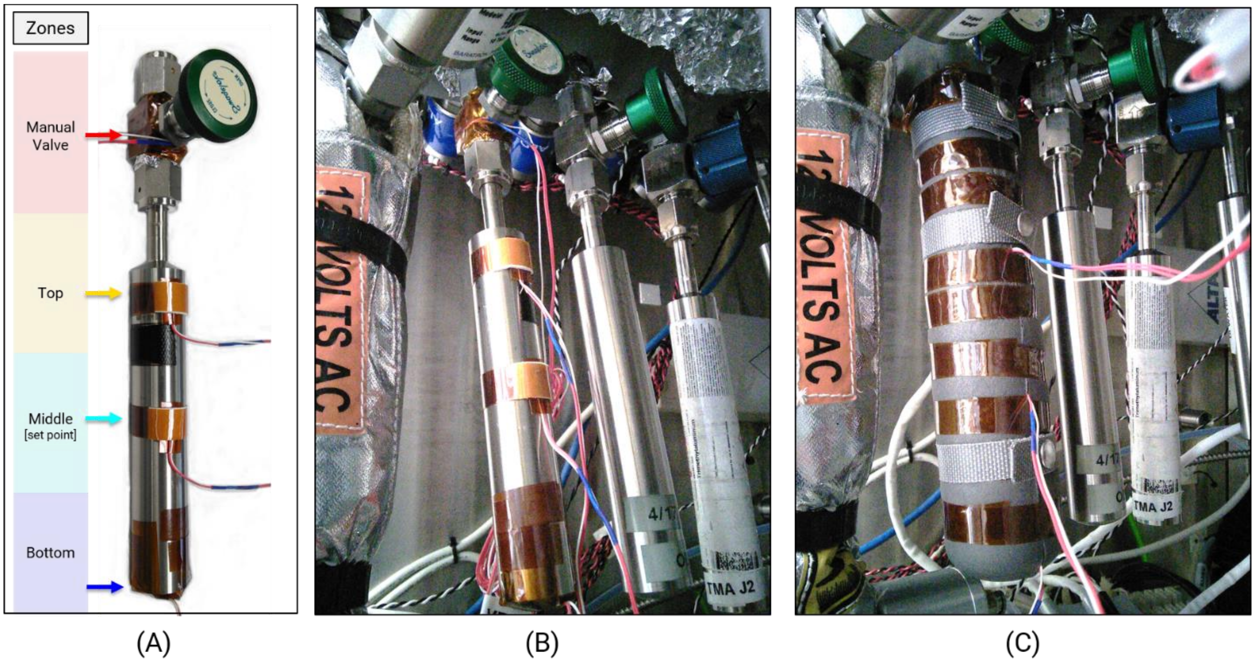

Figure 6: (a) Precursor cylinder assembly with an array of RTDs, (b) installed onto a MLD tool, and (c) after a molded foam jacket is installed. Kapton tape was used to ensure a tight foam seal around the cylinder assembly.

Measurement Data

Figure 7 summarizes the temperature profile measurements acquired at each heater set point. Ideally, the magnitude of temperature gradient from the bottom to manual valve zones would remain constant across temperature set points, maintaining a consistent temperature gradient. However, multiple crossovers are observed, with the lowest occurring at 100 °C and indicating the loss of a positive thermal gradient. The following sections discuss the practical implications of these measurements in greater detail.

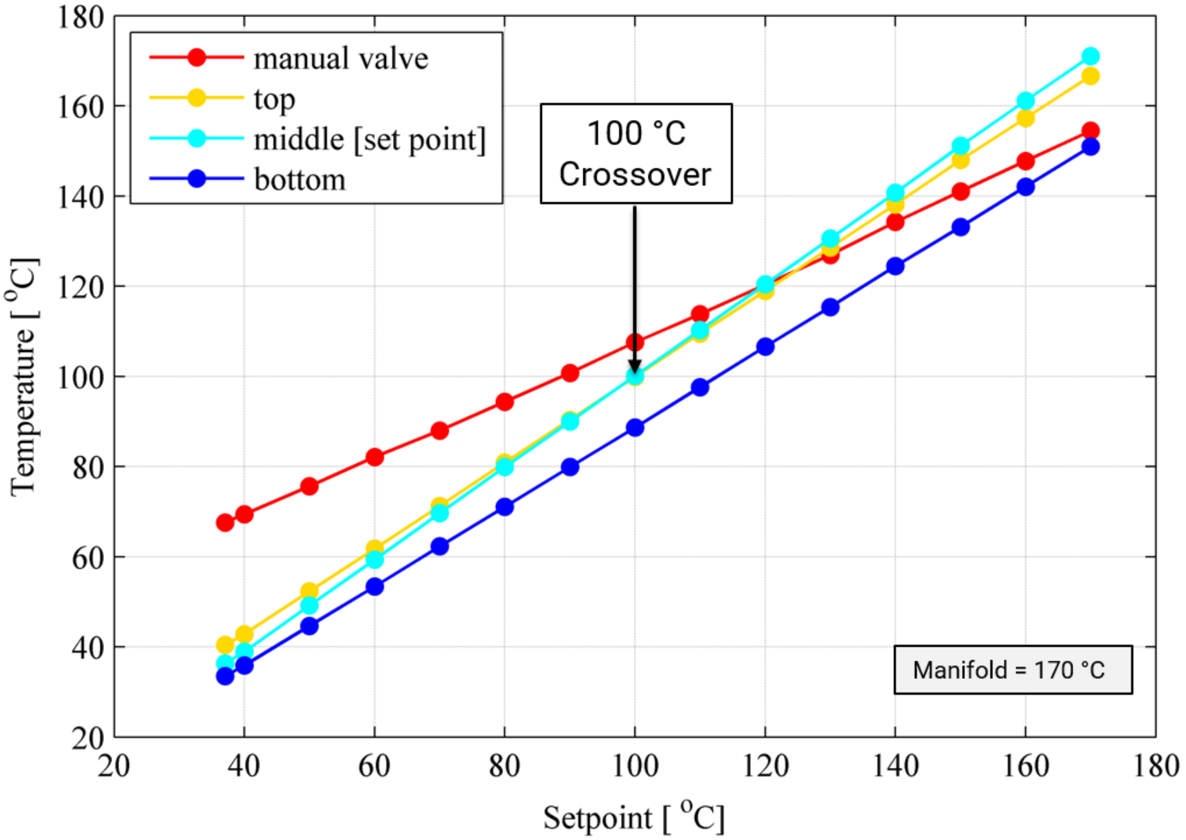

Figure 7: Temperature measurements at each zone in steady state.

Calibration

The middle RTD was placed at the same height on the precursor cylinder as the RTD built into the jacket (see Fig 3b). By choosing this location, a direct comparison between the integrated RTD sensor and our mounted RTD can be made for the purpose of calibration. Figure 8 shows that the middle temperature zone measurements track those of the jacket RTD with a maximum offset error of < 3% of the full scale (max) temperature. This comparison helps verify that we are accurately measuring the temperature of the cylinder itself, and not the local temperature of the adjacent resistive heating elements in the wall of the heater jacket.

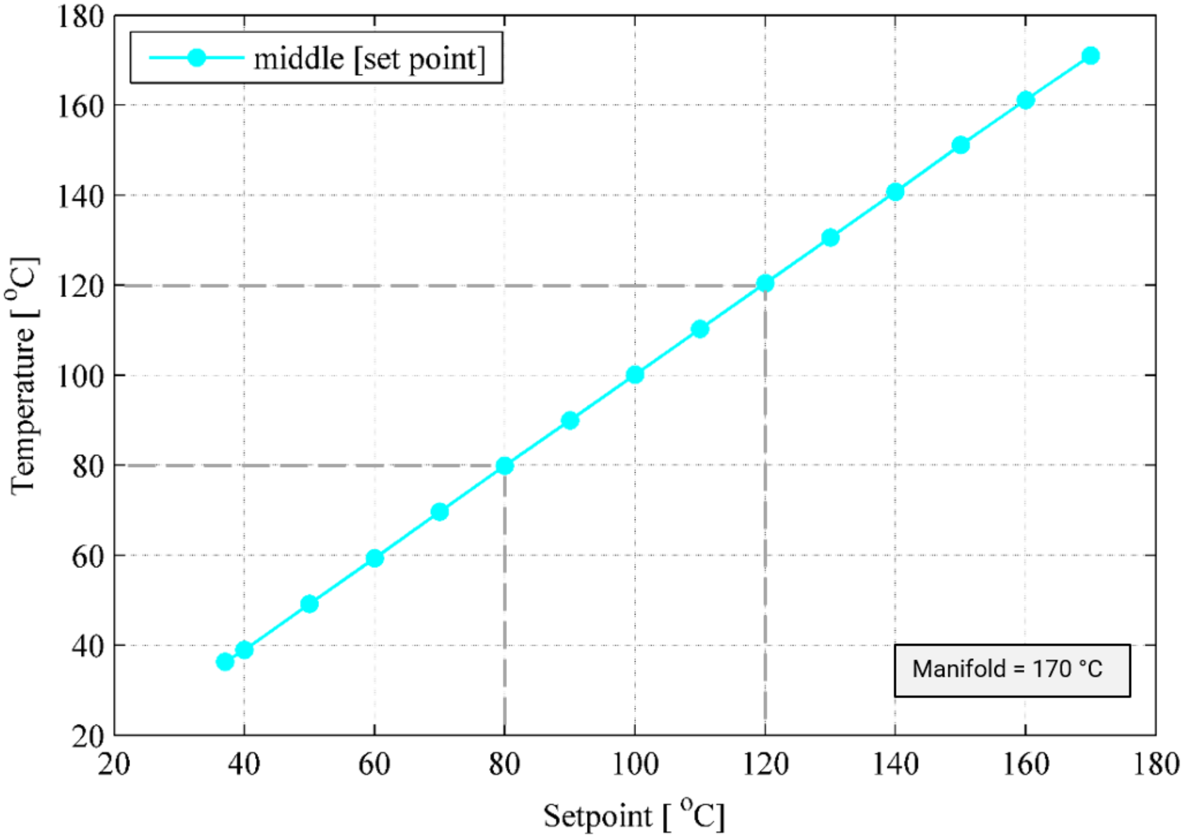

Figure 8: Middle zone vs nominal set point temperature.

Temperature Offset Errors

Liquid and solid precursors are assumed to fill less than half of the cylinder volume and reside at the bottom of the precursor cylinder. The difference between the nominal set point temperature (measured at the middle of the cylinder) and the bottom zone temperature therefore reflects a temperature offset error between the true and intended precursor temperature. While the offset error is comparatively small (< 3 °C) near room temperature, it grows to greater than 20 °C at the maximum precursor temperature tested (170 °C). Errors of this magnitude produce significant offsets in vapor pressure due to the non-linear (Arrhenius type) dependence of vapor pressure on temperature as described by the Clausius-Clapeyron relation.

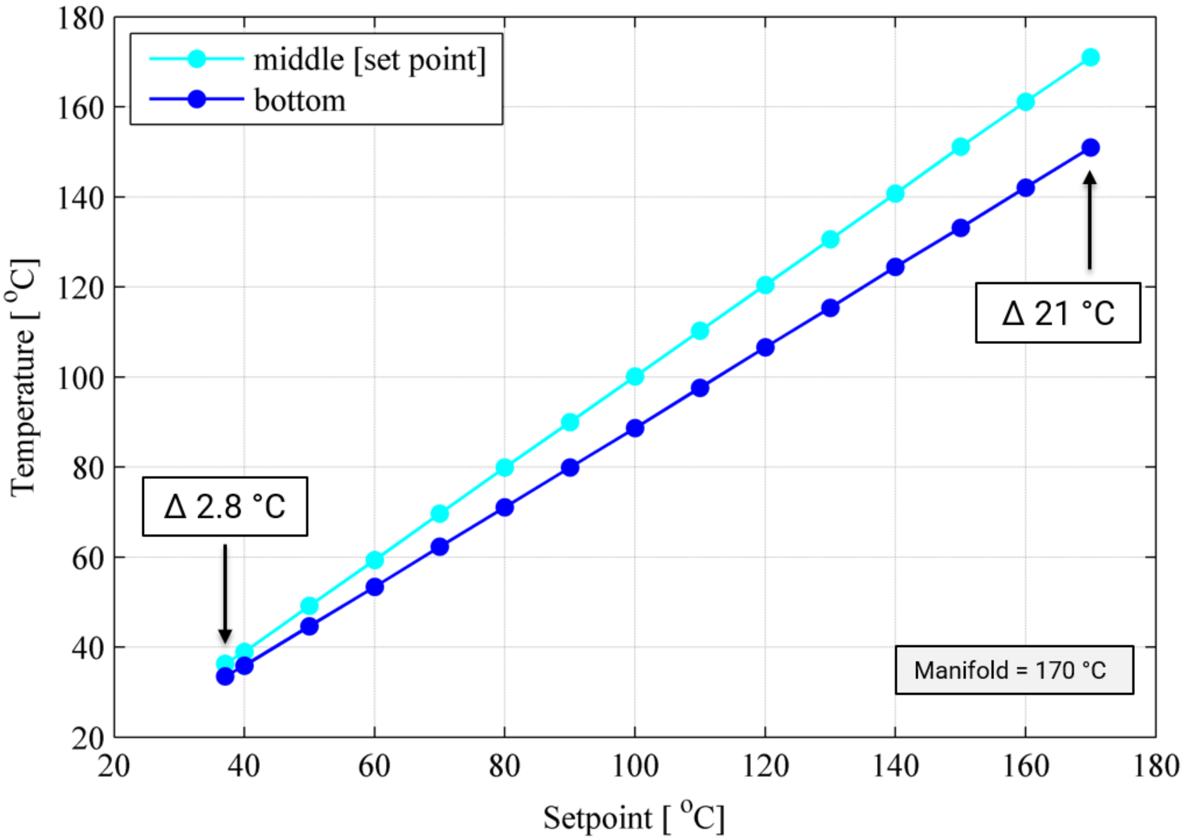

Figure 9: Middle and bottom zone temperatures showing offset errors.

Temperature Gradient Crossover Points

Two temperature crossovers are shown in Fig. 10 associated with the loss of a positive temperature gradient from the bottom of the precursor assembly to the top of the manual valve. While the 100 °C crossover occurs between the middle and top cylinder temperature zones, the 120 °C crossover between the top and manual valve zones creates ideal conditions for clogging in the VCR flange and manual valve. Precursors which are solids at 120 °C are likely to form dense and unrecoverable clogs under these conditions, an example of which is shown in Fig. 5. However, liquid and viscous precursors may experience less severe clogging and clear with sufficient time.

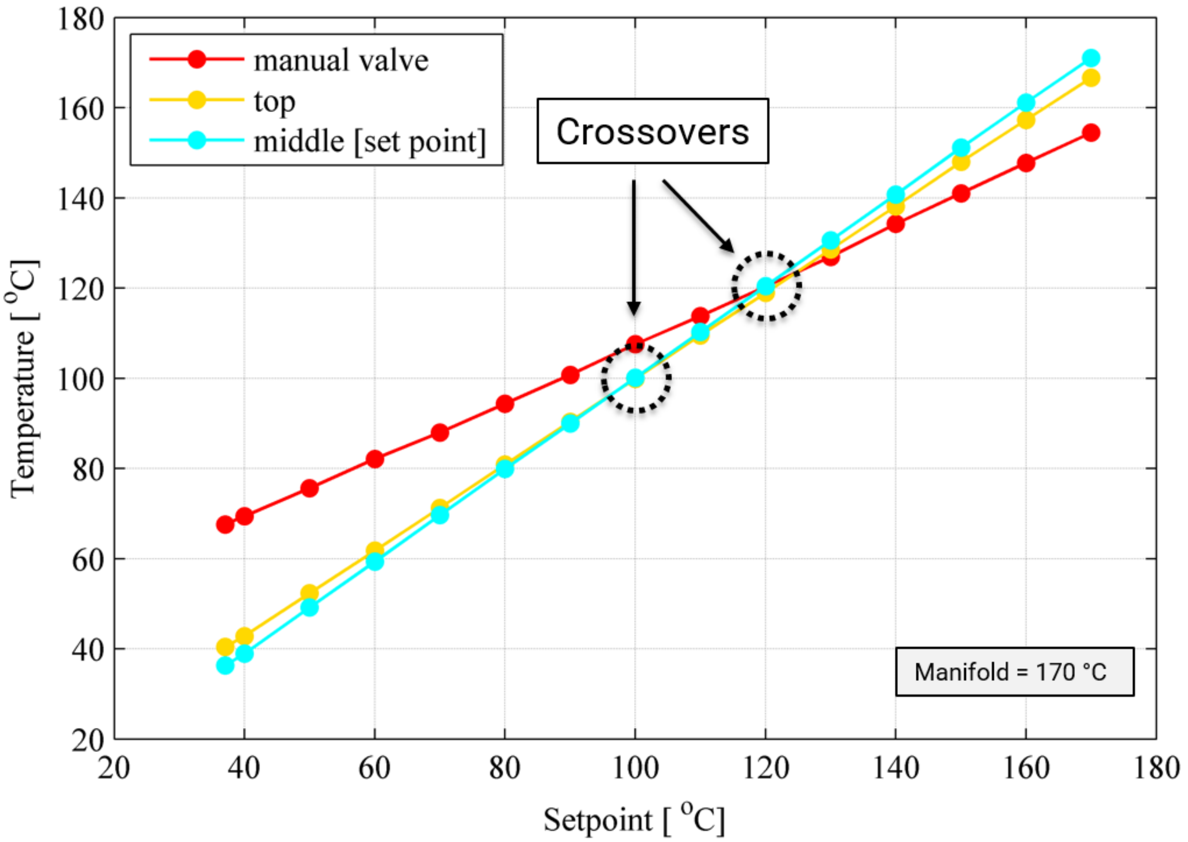

Figure 10: Middle, top, and manual valve zones highlighting the loss of a positive temperature gradient.

Improving Thermal Management

Insulation of the exposed manual valve is expected to improve the thermal performance of the jacket and was found to increase the crossover temperatures shown in Fig. 10 by 10 - 30 °C. However, the degree of improvement depends strongly upon the insulation configuration. Furthermore, in the SNF, precursors are routinely swapped to accommodate user processing requirements given a limited number of precursor ports. Therefore, careful tuning of the insulation around a manual valve is not expected to be an effective solution given the frequency of precursor changes. Additionally, pushing the lowest crossover temperature up to ~ 130 °C is still insufficient to accommodate many precursors for MLD.

An alternative solution is to use independent temperature controllers to establish additional degrees of freedom in the thermal management of the precursor cylinder assembly. Otherwise, it is difficult to obtain the desired temperature gradient at higher temperatures using a single RTD measurement and PID controller provided the jacket heater tape is constant wattage (flux) per unit length. Therefore, a single heater tape cannot provide additional energy input to a localized region (i.e., around the manual valve and VCR flange) to compensate for the larger thermal mass, surface area, and heat sink to the ambient environment.

To evaluate this solution, a polyimide MLD process was tested using a custom reactor outside the SNF. The reactor was outfitted with 6 temperature zones and 4 PID controllers to establish precise control of the temperature gradient across a precursor cylinder assembly filled with PMDA as shown in Fig. 11a. This configuration allows small temperature differences of 2 - 4 °C to be precisely maintained across the precursor assembly with less sensitivity to the arrangement of insulation. A polyimide MLD process outlined in Fig 11b was performed using the single PID controller on the SNF MLD reactor as well as the 4 PID controller configuration on the custom reactor. While depositions were unsuccessful using a single PID configuration and hindered by clogging, the precise temperature control of a 4 PID arrangement enabled successful polyimide deposition onto both –NH_2 and –OH terminated Si substrates with no observable cylinder clogging. A FTIR spectra of a PMDA-DAH polyimide film is shown in Fig 11c.

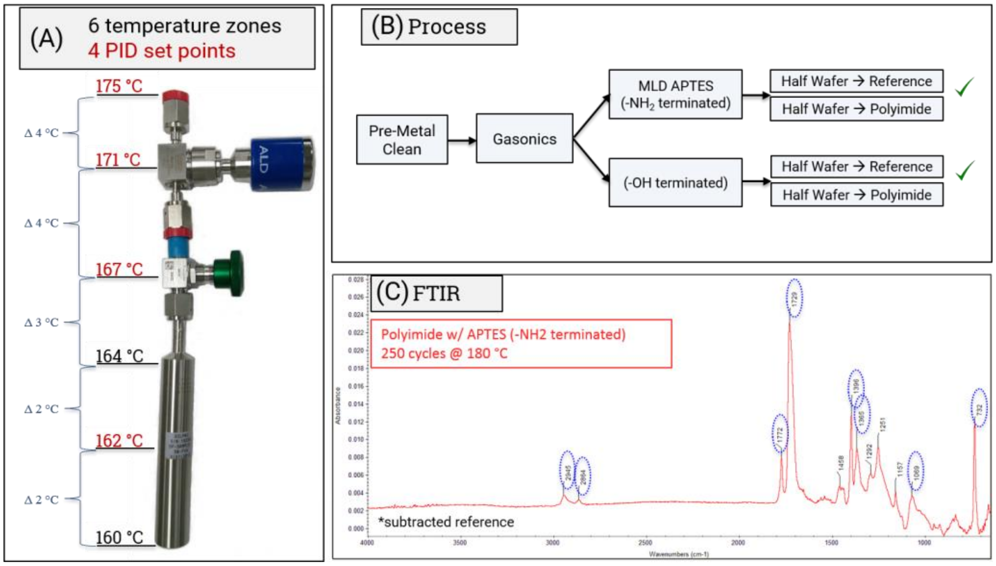

Figure 11: (a) Custom precursor assembly layout using 6 temperature zones with 4 PID controllers, (b) polyimide process overview, and (c) FTIR of 250 cycles PMDA-DAH at 180 °C.

Summary

Low vapor pressure precursors are accompanied by unique thermal management challenges and risks. While the notion of an isothermal precursor cylinder is often conveyed to users through control software, a direct measurement of the temperature profile of a precursor cylinder assembly demonstrates the practical limitations of this assumption. The loss of a positive thermal gradient across a standard precursor cylinder assembly in the SNF is observed at temperatures as low as 100 °C. These thermal limitations, including temperature offset errors and gradient crossovers, can significantly degrade precursor dosing and increase the risk of clogging.

We evaluated these limitations by attempting MLD of polyimides both within the SNF and using a custom reactor offering more flexible thermal management. Precise temperature control using multiple PID controllers and heating elements enabled successful polyimide depositions while a standard precursor cylinder assembly and molded foam jacket within the SNF were found to be insufficient to meet the thermal requirements of the polyimide process.

Finally, we note that the trends presented in Figs. 7 – 10 are generalizable to the MLD, Savannah, and Fiji reactors which use standard precursor cylinder assemblies and (mostly) interchangeable heater jackets. This characterization may therefore serve as a reference and guide for process engineers seeking to develop low vapor pressure precursor recipes for both ALD and MLD tools within the SNF.

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