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ALD Precursor Delivery & Debugging: A Case Study in Polymer Development

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Introduction

Polyimide thin films are promising polymeric organic materials for applications throughout the microelectronics and micro electromechanical systems (MEMS) industries. The material exhibits low dielectric constant, high dielectric breakdown, and thermal and mechanical stability.[1] The synthesis of this polymer consists of the condensation reaction between a dianhydride and a diamine. Preparation of polyimide thin films is typically done in the liquid phase by spin coating and the Langmuir-Blodgett technique.[2] It is well documented that solvent affects the quality of the film and substrate by film shrinkage, contamination by residual solvents, and poor control of molecular orientation.[3] An alternative method to deposit thin films is through a process known as vapor-deposition polymerization. The monomers are deposited through a technique known as molecular vapor deposition, in which molecular monomers are heated under vacuum to facilitate the phase transition to the gas, transferred to a main chamber with an inert gas carrier, exposed to the substrate, and evacuated to remove excess vapor. After the deposition of the monomers, thermal annealing leads to cycloimidization resulting in the expelling of water and production of polyimide. A solvent-free deposition of the films allows control of the film properties by manipulating the film thickness and conformity.[4-5] Furthermore the orientation and arrangement of the molecules tend to have a less random distribution due to the stepwise polymerization that occurs.[6] The stepwise polymerization is a result of the self-limiting and surface terminating growth of the organic film.[7]

The objective of this project was to develop a recipe for the deposition of thin films of poly (4, 4' – oxydiphenylene pyromelitimide) through molecular vapor deposition using Pyromellitic dianhydride (PMDA) and 4-aminophenyl ether (ODA). These precursors were chosen due to the high deposition rate (6.7 Å $cycle^{-1}$) reported by Putkonen et al. in comparison to other common polyimide precursors. Due to unforeseen complications in the deposition of the monomers using Savannah S200 from Ultratech/CambridgeNanotech, this work will focus on how to troubleshoot temperature sensitive organic precursors with the goal of describing a broader set of precursor debugging best practices.

Safety

Before continuing, we want to briefly remind the reader that most of the debugging discussed here involves working inside an ALD tool enclosure. This area should only be accessed by SNF staff as there are significant risks posed to anyone operating in this space. These risks include electrical shock, burns from heated surfaces, and exposure to dangerous chemicals.

ALD Window

The concept of an ALD window in Figure 1 is frequently used to describe the range of operating conditions over which an ALD process yields a reliable self-limiting growth rate. Deviations in temperature outside the ALD window can lead to either an increase or decrease in the observed growth rate depending on the physics of the limiting process. Therefore, the width of the ALD window, Δ T, plays a critical role in determining the feasibility of an ALD process in conjunction with precursor selection, temperature gradient requirements within a tool to prevent precursor condensation, and other operating conditions.

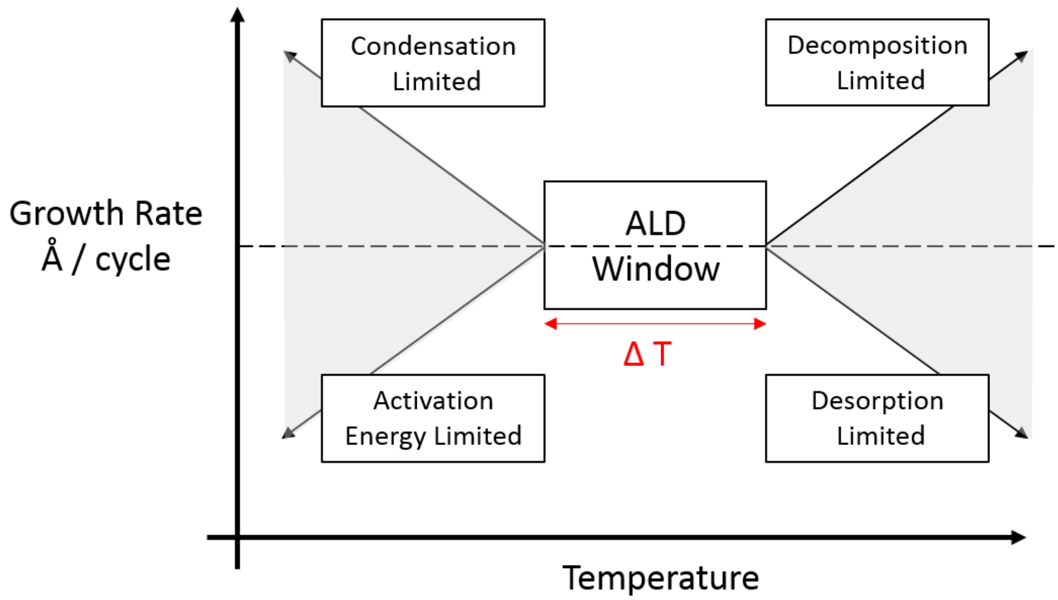

Figure 1: ALD Window

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 ~ 100 -1000 mtorr or higher. However, the range of heating may be limited by thermal decomposition. Additionally, a positive temperature gradient is typically maintained between precursor source and chamber to minimize condensation which can lead to clogging. Heating the precursor to achieve sufficient vapor pressure and maintaining a positive temperature gradient from source to chamber can significantly raise the lower temperature limit of the ALD window as shown in Figure 2.

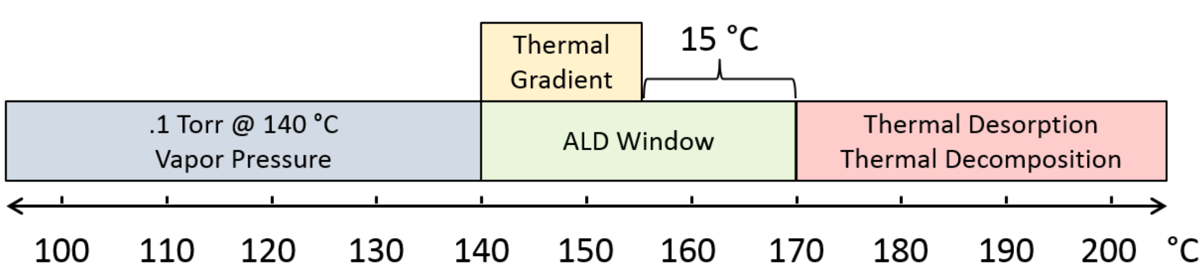

Figure 2: Schematic of narrow temperature window process

Cutting into the thermal budget leaves a smaller ALD window for operation. As this window shrinks, challenges arises from the tool limitations and the chemical and physical properties of the precursor which strongly govern the feasibility and reliability of the ALD process. The objective of this report is to document challenges which appear in such narrow temperature window processes from the practical perspective of a process engineer.

Vapor Pressure

In order to debug narrow temperature windows processes, it is essential to know the vapor pressure, melting temperature, and decomposition temperature of the desired precursors. Examples of vapor pressure plots[9] for precursors used in polyimide depositions are shown in Figure 3.

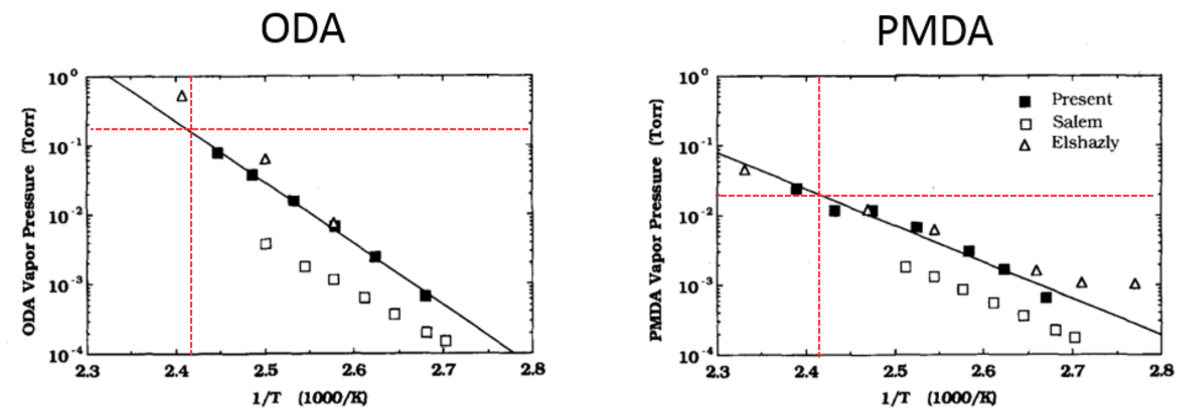

Figure 3: Vapor Pressure of ODA and PMDA

With vapor pressure, one can begin to assess the dose conditions and challenges of delivering precursor to the ALD chamber. For example, vapor pressures of > 1 Torr are ideal and can usually be dosed with standard delivery methods. When 1 Torr > vapor pressure > 100 mTorr, precursor delivery can be aided by Boost™, as system developed by Ultratech/CambridgeNanotech to inject inert gas into the ALD cylinder prior to pulsing in order to agitate the vapor and increase dosing. When vapor pressures fall below 100 mTorr, more complex low vapor pressure delivery systems must be used, which may include bubblers or larger evaporative cells external to the tool.

Cold Spots and Condensation

Precursor condensation at cold spots is a major challenge of working with narrow temperature window processes. If the temperature gradient between precursor source and the main chamber is only 10 – 25 ° C, areas with non-uniform heating can provide a preferential site for precursor condensation and clogging. An example of such clogging is shown in Figure 4.

Careful inspection of the tool design and insulation can help discover and address condensation problems. An example of the SNF MVD Savannah insulation and a current generation Savannah design reproduced from Ultratech/CambriedgeNanotech's website is shown in Figure 5. A few major design revisions are evident. First, new molded precursor jackets are available which improve the insulation and temperature uniformity of precursors, especially in the manual valve and neck regions above the cylinder. These molded precursor jackets fit precursor cylinders more snuggly. In previous tools, heater jackets fit more loosely and leave part of the head space in the port leading to the manifold exposed to air without insulation. Second, improved woven manifold insulation jackets and/or heater blocks are used to minimize the chances of clogging in the new manifold design. However, our earlier generation tool has only foam insulation.

Figure 4: Precursor cylinder clogging

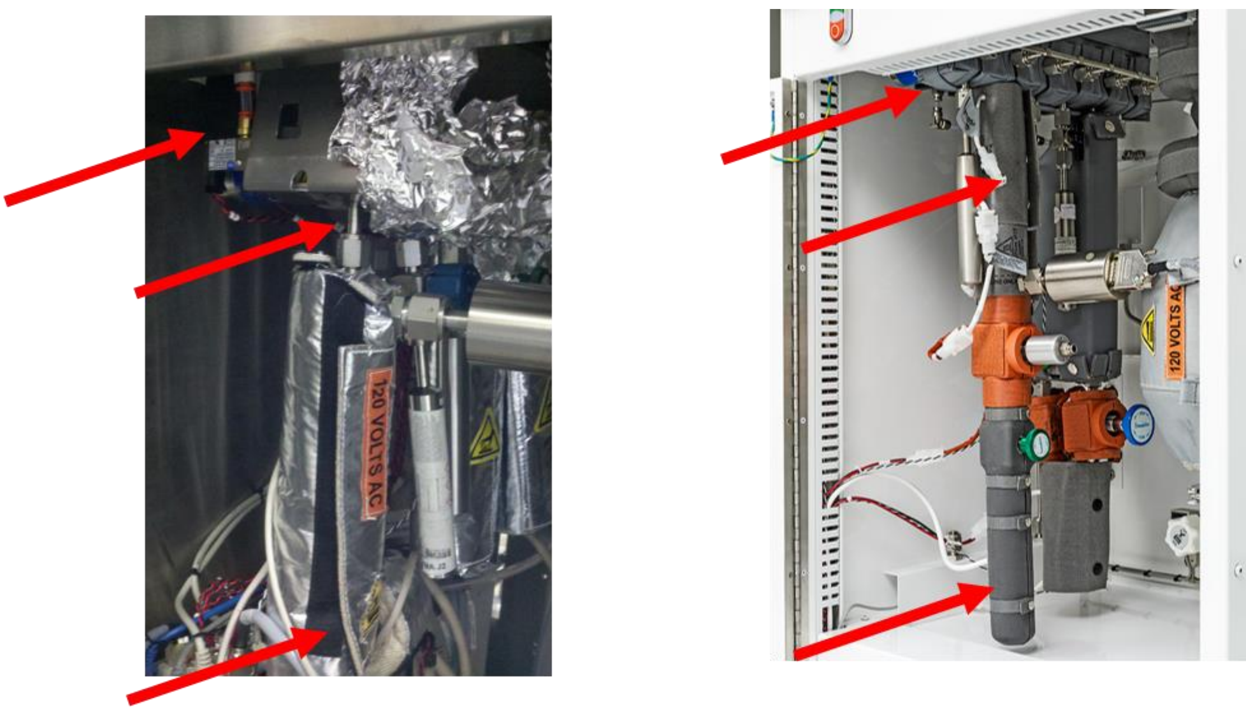

Figure 5: Potential cold spot areas highlighting the differences in insulation design between previous and current generation ALD Savannah Tools

It is noteworthy that clogging was typically observed in the neck and manual cylinder valve regions. This was a likely location for clogging because the valve assembly protrudes from the precursor jacket and serves as a major heat conduction pathway giving rise to cold spots near the neck and valve. To further investigate these issues, we examined manual valves inside a chemical glove box in greater detail. While low temperature manual valves can be used on ALD precursor cylinders, low vapor pressure precursors often require heating and a high temperature bellows valve (SwageLok SS-4H-VCR). While the low temperature valve is constructed with a straight-through ball valve, the high temperature valve implements a bellows valve where direct line of sight and visual confirmation of a clear flow path is more difficult. This is shown in the valve image and cross section in Figure 6.

Figure 6: High temperature manual valve and cross section. A pellet formed by clogging in the bellows region is also shown.

To aid in debugging and evaluating the state of the valves, an inexpensive blower bulb was introduced into the glove box which allowed us to test whether or not there was flow through the valve. In cases where the valve is clogged, sufficient pressure from the bulb was sometimes enough to clear a pellet of condensed precursor from the bellows region as shown in Figure 6.

Pressure Equilibration

We hypothesized that another factor contributing to clogging may originate from the pressure under which precursors are loaded and sealed inside a precursor cylinder assembly. This idea developed from the observation that each of the 3 precursors under evaluation are flaky white powders (granules) with a high sticking coefficient and low density. We experienced the worst clogging from the lowest density precursor despite the fact that it had a higher vapor pressure and allowed for a larger thermal gradient from precursor to chamber. This suggested there may be another physical mechanism responsible for precursor transport to the neck and valve regions. Similarly, the highest density precursor performed best with respect to clogging while having the narrowest temperature window.

We noted that if the precursors are loaded in a glove box above atmospheric pressure and installed on the tool, there exists a tremendous pressure differential between the cylinder and base pressure of the tool even at room temperature and with typical carrier gas flow rates. Therefore, we hypothesized that the large pressure differential may agitate the powder during initial pulsing and cause powder to be drawn towards the neck and manual valve assembly due to the large pressure gradient. Upon heating, this accumulated precursor near the neck could facilitate and accelerate the formation of a clog.

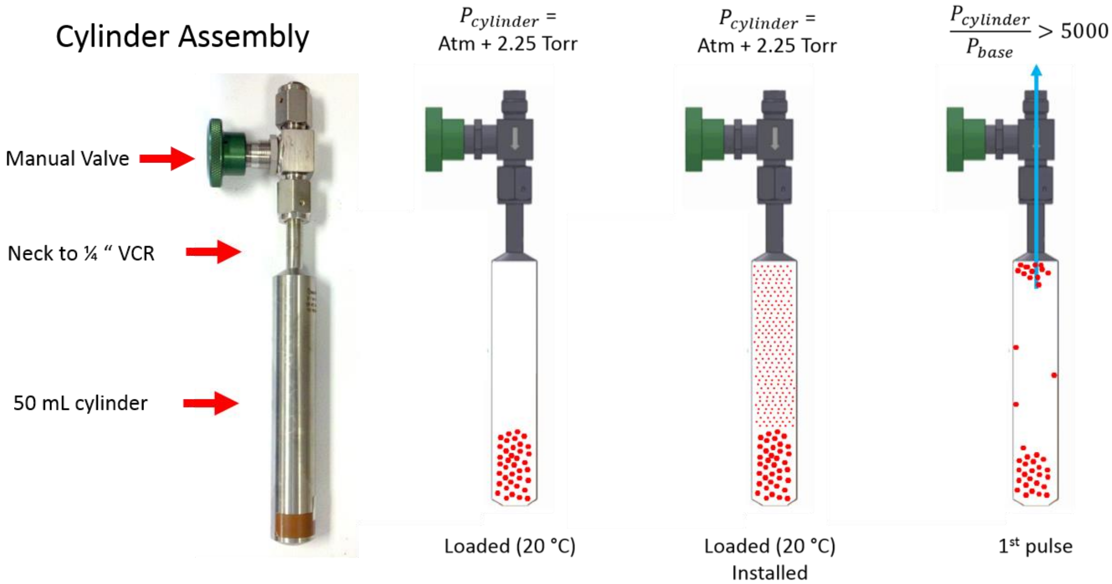

Figure 7: Schematic of cylinder assembly

In an effort to evaluate this hypothesis and reduce clogging, we introduced a cylinder installation protocol using the fastest pulse time (15 ms) to bleed off pressure from the freshly installed ALD cylinder at room temperature. This equilibration process was evaluated using the procedure shown in Figure 8. At each inspection point, the precursor cylinder was remove from the tool, examined within a glove box, re-installed, and the procedure repeated up to the next inspection event. The 15 ms pulse steps 5 and 8 were repeated until pulse heights decayed or stabilized.

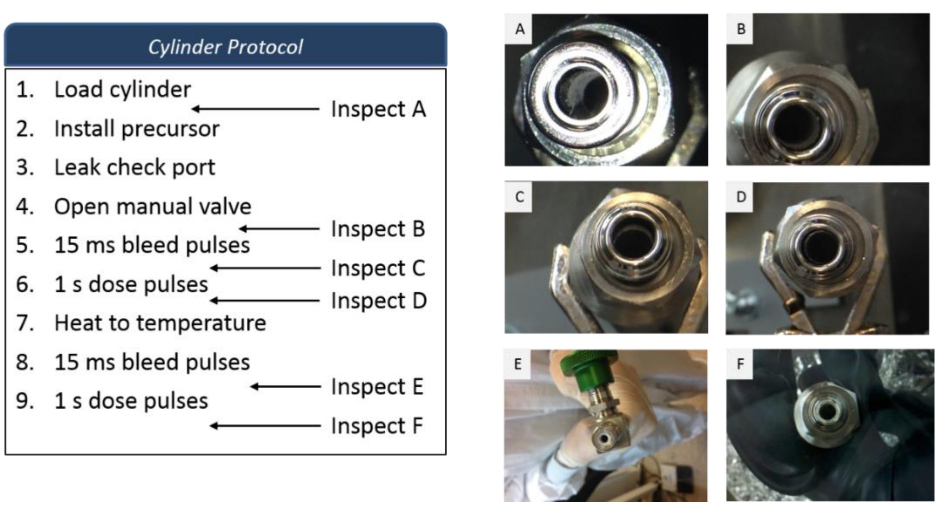

Figure 8: Pressure equilibration protocol and images of the cylinder neck region

Conclusions

The pressure equilibration protocol above was evaluated in conjunction with a new molded heater jacket from Ultratech/CambridgeNanotech. These jackets are shown in the more modern tool in Figure 5 and were found to improve the temperature uniformity of the valve and neck regions of the cylinder as measured with a k-type thermocouple array. To date, this arrangement has allowed for pulsing without clogging. The long term performance of the arrangement has yet to be evaluated, and will provide more definitive answers regarding the effectiveness of this approach to slow or eliminate clogging.

In concluding, we've found several best practices which are believed to improve the delivery and debugging of narrow ALD/MLD window processes, such as those typical in polymer deposition. For future readers, we note that before processing with new precursors which may be prone to clogging, it is advantageous to assess their melting and decomposition temperatures. Does the tool have sufficient thermal budget to clear a clog or would hardware need to be replaced? In the face of low vapor pressure, it is tempting to pulse for longer times or rapidly with many short cycles to increase dosing. However, this may lead to rapid depletion of the available vapor reserve and no additional dosing. Additionally, precursor impurities should be considered, especially when heating a new precursor. Volatile and low vapor pressure impurities can produce significant pressure pulses upon heating. These can be deceiving and give the impression of dosing with strong pulses. Finally, we note that there are many additional issues to consider in precursor debugging beyond what is discussed here. These are just a few of many factors at play. Consulting the literature, SNF staff, and experienced tools users can be a tremendous help when planning a new process or seeking alternative diagnostic tools.

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