Behind Closed Doors – What You Don't Know About Your CVD Chamber

Sean Clancy, Ph.D., Robert Askin, HZO, Inc.
Morrisville, NC, USA
sclancy@hzo.com

Abstract

Purpose

One of the challenges of larger parylene chemical vapor deposition (CVD) chambers is what seems to be unpredictable material behavior throughout the working volume. The tight parameters on the state of the substrates, adhesion promoter, and parylene deposition process require informed engineering, even when industry best practices produce problematic distributions of materials.

Results

Transient electrical failures, among other unexpected behavior, that recover over time can be influenced by the method of adhesion promoter introduction, the volume of adhesion promoter used the state of cleanliness of the substrates, the total volume of substrate outgassing, circuit design as well as other factors. Related case studies on the effects of the state of the substrate and conditions before and after coating will be addressed. With very similar products, the same process has worked without issue, countless times.

Outcome

Controlled experiments that vary each of the critical factors have shown how they affect the coating process and product performance. Cross-sectional analysis, FTIR spectroscopy, adhesion tests, process modifications, and substrate concerns will be discussed to illustrate how high-reliability products can be produced in a high-volume manufacturing process using parylene conformal coatings.

Background

Principles of parylene chemical vapor deposition (CVD)

Poly(*para*-xylylenes) are a family of polymers more commonly known as parylenes. Parylenes made through chemical vapor deposition were first reported by Szwarc through the pyrolysis of p-xylene in 1947.[1,2] Later in 1966, Gorham found that the p-xylene dimer, [2.2]paracyclophane, could be used as a precursor for these polymers through CVD and without any byproducts.[3] In the decades since, parylenes have been used as a protective coating on a wide range of products, including electronics,[4] medical devices,[5] and organic light-emitting diodes (OLEDs),[6] as well as to aid in the preservation of historic artifacts and specimens.[7]

Parylene coatings are applied under vacuum, which means that products are placed inside the deposition or coating chamber, the dimer precursor is loaded into the vaporizer, the system is closed, the air is removed, and the coating process begins. As illustrated in Figure 1 below, when the system is under vacuum, the dimer precursor is heated to around 150 to 200 °C, during which the dimer sublimes from a solid to a gas. The vacuum pump pulls the dimer gas through a pyrolysis zone that's heated to around 550 to 700 °C, which "cracks" the dimer into two active monomers, still in a gaseous state. The vacuum continues to pull this monomer gas into the coating chamber, which is typically at or very close to room temperature, and these monomer molecules bounce around and land on everything within the chamber, including the products. When monomers land close to one another, they combine to form the polymer coating. The parylene coatings are fully cured at the end of the coating process. Other features of parylene include that they're free of catalysts, solvents, and volatile organic compounds (VOCs), and don't generate harmful pollutants.

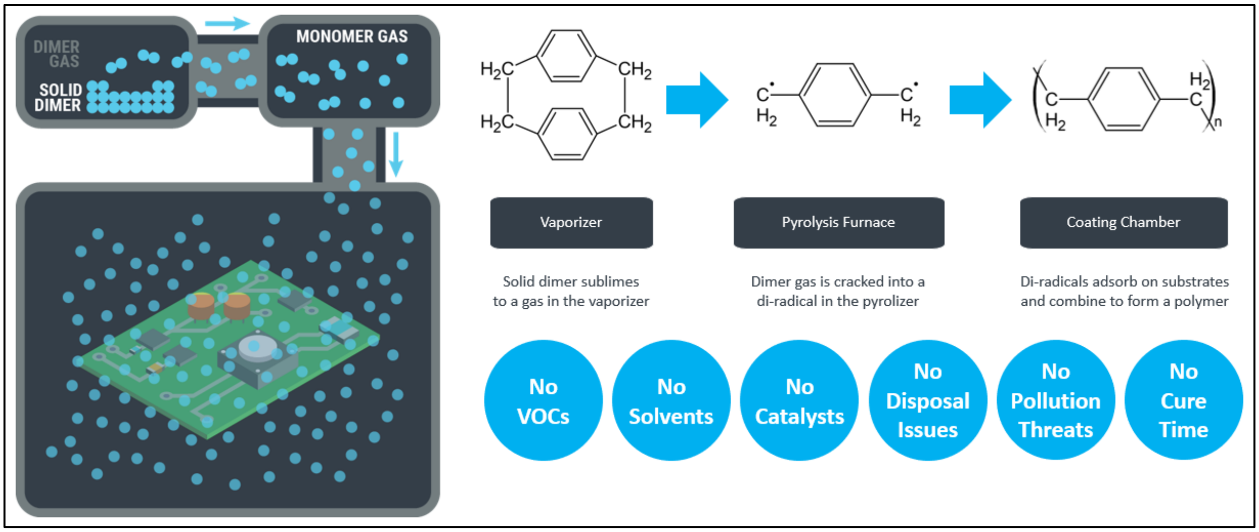


Figure 1. Overview of the parylene chemical vapor deposition (CVD) deposition and polymerization process.

Principles of Silane A-174 adhesion promotion with parylene

Some applications of parylene require assistance in preventing delamination, which may require different levels of surface preparation, such as various cleaning methods, plasma activation with argon or argon and oxygen, and/or using an adhesion promoter.

Adhesion promoters, such as Silane A-174, work best when there are oxygen functional groups on the surface of the substrate, which can usually be determined by how wettable a surface is with just a water drop, water-break test, dyne pens, or a water contact angle measurement.

Failure to power on phenomena was observed in user assemblies across multiple builds. These failures were isolated to something inherent in the CVD coating process, and the most likely candidate was the adhesion promoter (AP). The AP was the aforementioned Silane A-174, which has two functional ends, with the “feet” bonding to oxygenated sites on the substrate, and the “head” a methacrylate monomer that bonds to parylene monomers through a free radical reaction, as illustrated in Figure 2 below.

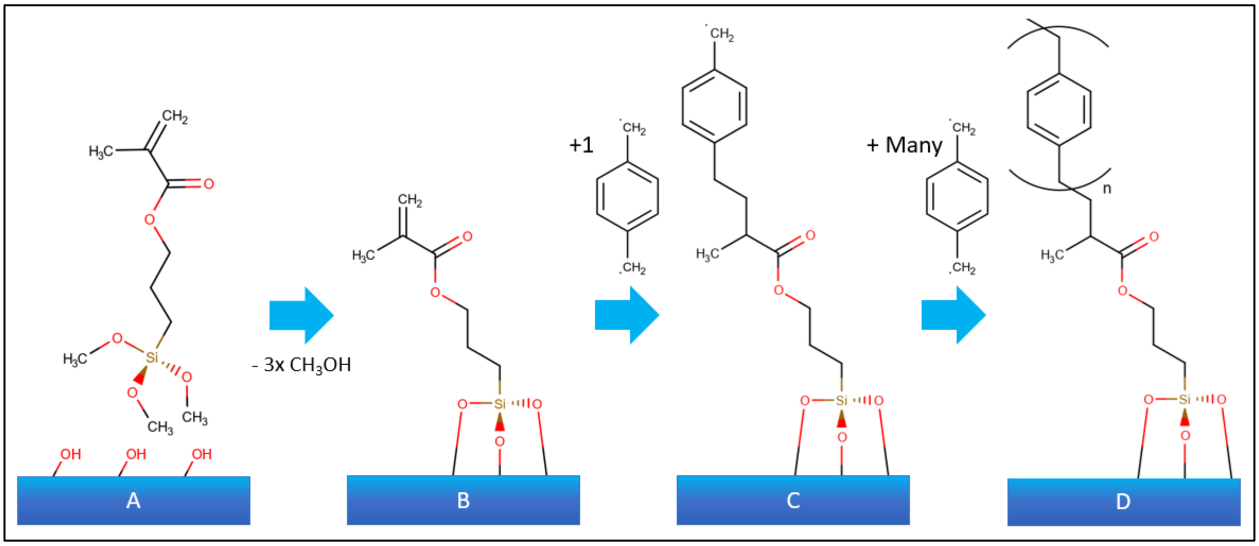


Figure 2. Overview of the adhesion promoter mechanism for chemically bonding parylene to a substrate.

Case Study #1 – Intermittent and transient failures at FATP, or a series of unfortunate events

Up until this issue was observed, AP was applied via a sponge method in which a small volume of AP was added to an inert foam and placed at the top of the CVD chamber. The issues that were observed are summarized in Table 1 below.

Table 1. Summary of parameters and observations for product failures.

Test Results Soon After Process	Test Results After 24+ h	Relative Amount of Adhesion Promoter	Product Loading in Chamber	Observed Oily Residue	Observed "Wrinkled" Masking Tape
Pass	Pass	Low	High	No	No
Fail	Pass	High	Low	Yes	Yes

Failures in the CVD chamber were associated with an oily residue and "wrinkling" (solvent-induced swelling and relaxation) of PVC masking tape liners, which were located in a highly repeatable region in the chamber, between the AP sponge and the pump outlet, indicating a predictable viscous flow that results in areas of unequal condensation and deposition of the AP.

In another CVD chamber that was used for the previous generation product, the oily residue was reproduced when loading only 20 boards in the chamber. Much lower volumes of AP produced good and uniform cross-hatch adhesion test results on glass coupons throughout the chamber, but that wasn't a direct comparison to the amount of AP needed to ensure adhesion to PCBA substrates but did indicate how much could provide an even distribution.

The failures were electrical and localized to the power management integrated circuit (PMIC)/clock oscillator region of the assembly, which was sensitive to input impedance and capacitance. We and a third-party laboratory were both able to induce failures by adding excess AP manually to this region. We observed recovery of the circuit after several days and noticed that any oily residue was gone, which indicated either evaporation or polymerization of the AP. The user also induced failures by adding high impedances (10s to 100s of MOhm) between points in this part of the circuit.

Both ethanol and methanol, which have similar chemical structures to the "feet" of the AP, were observed to quickly dissolve "no-clean" flux residues on the boards. Consultation with industry contacts reported that AP was capable of dissolving or softening flux residues temporarily.

A coated assembly from the lot that experienced issues was cross-sectioned and evaluated for any issues of concern, especially around the PMIC component, and highlighted in Figure 3 below.

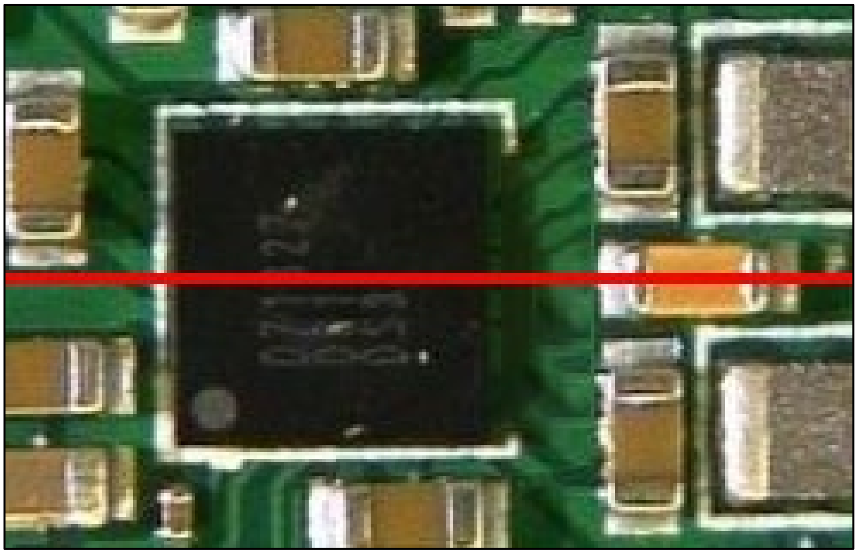


Figure 3. Location of the cross-section of the PMIC component on the PCBA.

A separate adhesion promoter (AP) layer wasn't observed with SEM-EDS even under much higher magnification, which was a good indicator of non-excess deposition on this assembly. No unusual elements were observed to be present during elemental analysis with SEM-EDS.

In Figure 4, the parylene coating appeared separated from the base of the BGA solder joints, which was likely due to the presence of flux residue that was coated over by the parylene and removed during the grinding, polishing, and requisite rinsing processes involved in cross-sectional sample preparation.

If desired, flux residue can be minimized by reducing the aperture size in the solder stencil, which will allow for a smaller amount of solder paste transferred to this component's location. A sufficient amount of solder paste and flux will still be needed to ensure good quality solder joints, as were observed on this assembly.

A smaller amount of flux residue would also be less likely to induce electrical shorts due to electrochemical migration (ECM) or dendritic growth, since less ionic residue would be present, whether it was solubilized in excess AP, moisture exposure, etc.

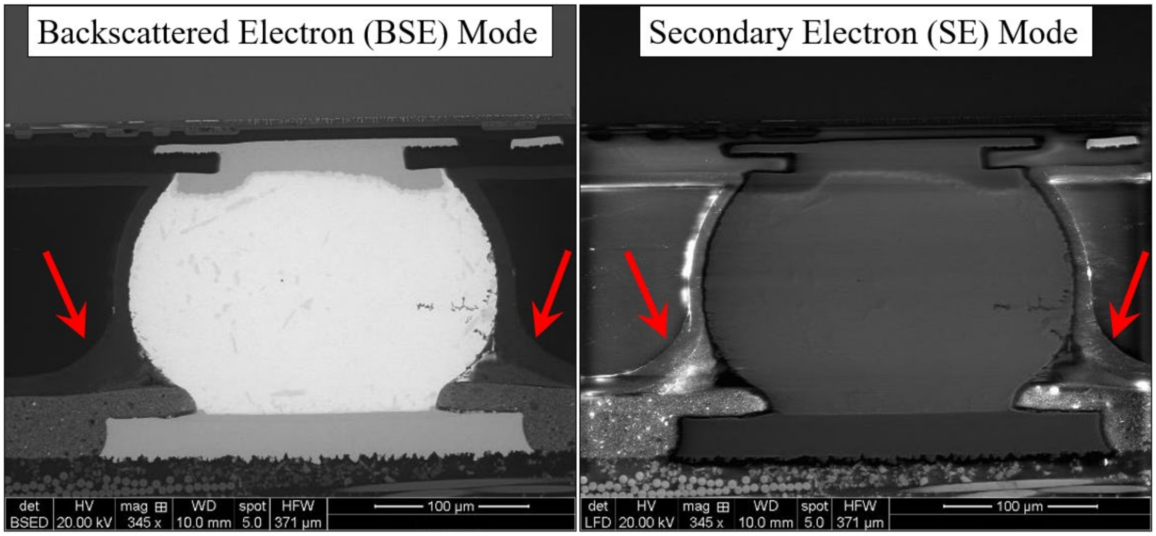


Figure 4. Scanning electron microscopy (SEM) images in backscattered-electron (BSE; left) and secondary electron (SE; right) modes, showing pockets at the base of the ball-grid array (BGA) solder joint, which likely covered from "no-clean" flux residues.

An example image of a cleaned PCBA that's been coated with parylene is shown in Figure 5 below, in which the coating completely conformed around the component body, solder joint, and the board, with no evidence of flux residues present.[8] Since flux residues weren't present, the coating didn't spread out and separate from the base of the joint.

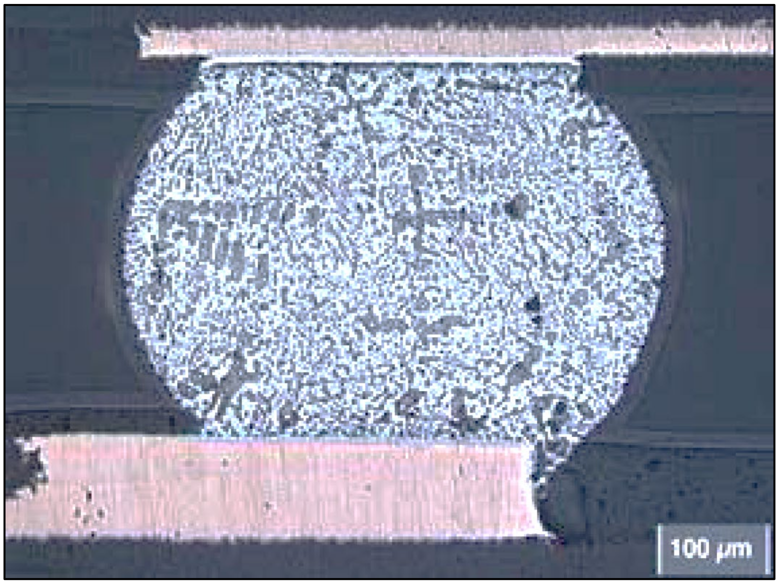


Figure 5. Metallographic microscope image of parylene-coated BGA solder joint from a cleaned PCBA.

An uncoated board from the same lot was evaluated for solvent-soluble residues using IPC TM-650 Method 2.3.38C – Surface Organic Contaminant Detection Test and IPC TM-650 Method 2.3.39C – Surface Organic Contaminant Identification Test (Infrared Analytical Method).

The PCBA was rinsed in different locations with methanol and Silane A-174 and separately collected on aluminum-coated glass slides. Immediately after collecting all of the rinse solutions, each of the four slides: 1. Methanol control, 2. Methanol product-rinse, 3. Silane A-174 control, and 4. Silane A-174 product rinse were noted to have a meniscus of liquid and were left in a chemical hood with the sash pulled most of the way down to allow the solvents to evaporate. After 16 hours, the slides were examined and the methanol slides were dry and had visible residue, while the Silane A-174 slides still had a visible meniscus and were given additional time to dry. Figure 6 shows images of the methanol control and product rinse slides, where residue was observed on both. Note that it was unusual to see the residue on the methanol solvent control.

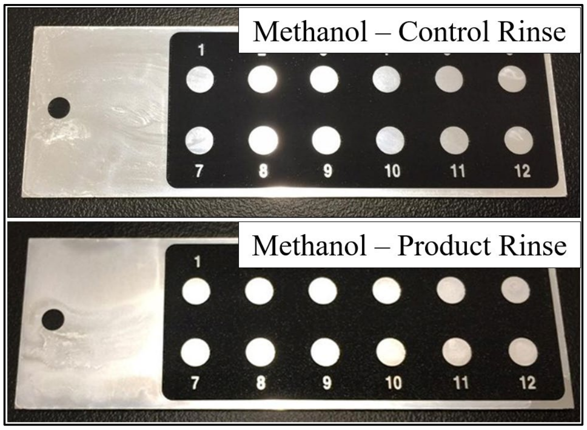


Figure 6. Residues were observed on both the methanol control and product rinse slides for Surface Organic Contaminant Detection Test. Relatively more residue was seen on the product rinse as compared to the control slide.

Fourier transform infrared (FTIR) spectroscopic analysis was performed with a Thermo Nicolet iS50 FTIR spectrometer equipped with a Smart iTR attenuated total reflectance (ATR) sampling accessory and germanium ATR crystal with 0.67 µm penetration depth at 1000 cm^{-1}. Thermo Fisher Scientific's "OMNIC" software was used for capturing and processing spectral data and "OMNIC Specta" software was used for multicomponent spectral search with material databases. The FTIR spectra for the control and product rinse samples are shown in Figure 7.

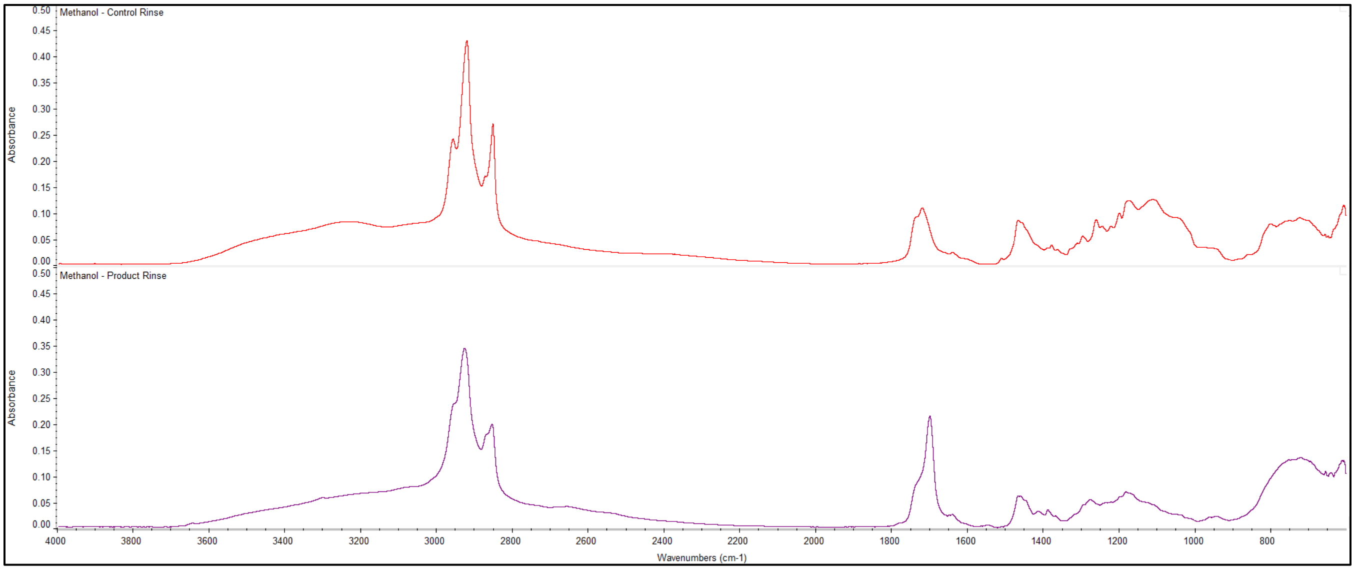
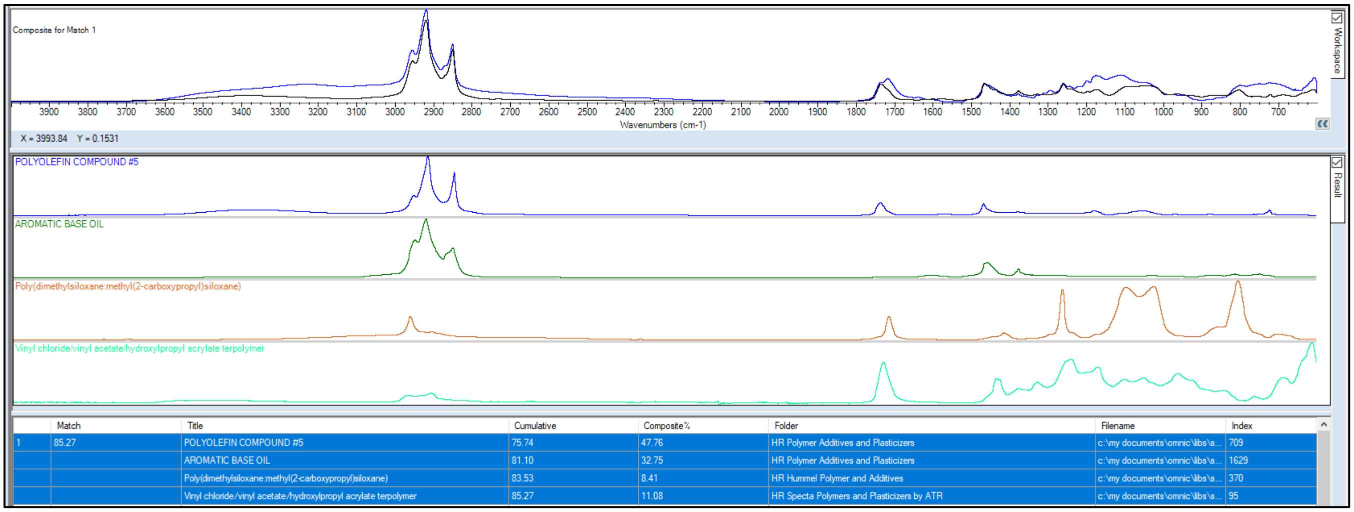


Figure 7. FTIR spectra of the residue on the control rinse and product rinse slides.

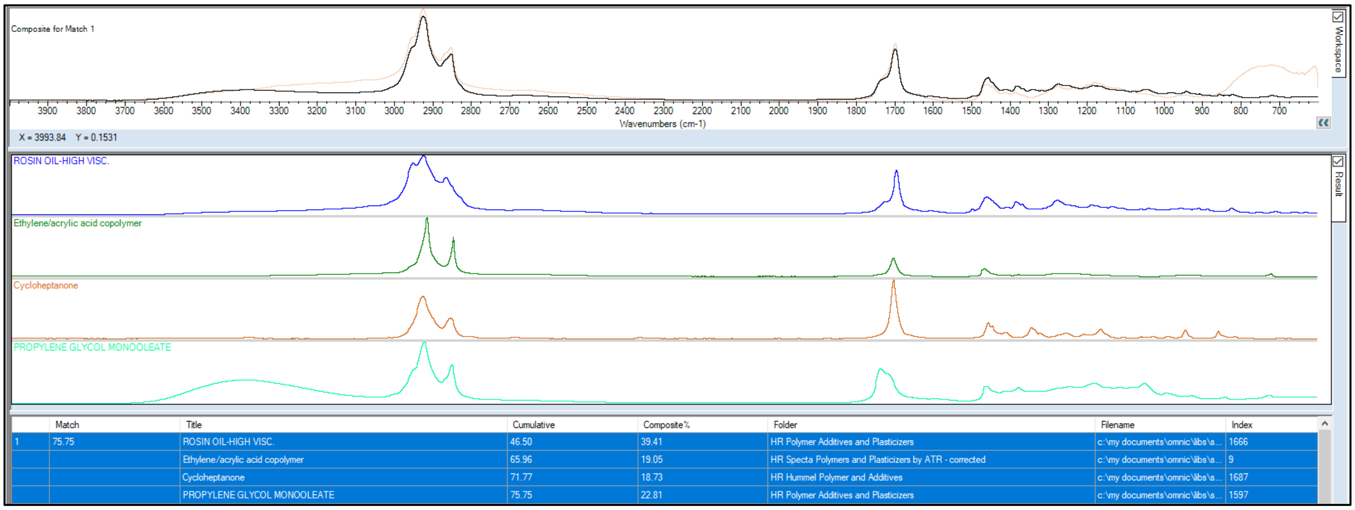
The FTIR analysis of the methanol control rinse sample showed peaks similar to oily, siloxane, and acrylic components (Figure 8), which were highly suggestive that the Silane A-174 contaminated the methanol slides through evaporation and re-deposition within the chemical hood. Future analyses would be repeated with a fresh solvent, a different product assembly, and away from the AP to mitigate any contribution from it.



	Match	Title	Cumulative	Composite%	Folder	Filename	Index
1	85.27	POLYOLEFIN COMPOUND #5	75.74	47.76	HR Polymer Additives and Plasticizers	c:\my documents\omnic\libs\s...	709
		AROMATIC BASE OIL	81.10	32.75	HR Polymer Additives and Plasticizers	c:\my documents\omnic\libs\s...	1629
		Poly(dimethylsiloxane:methyl(2-carboxypropyl)siloxane)	83.53	8.41	HR Hummel Polymer and Additives	c:\my documents\omnic\libs\s...	370
		Vinyl chloride/vinyl acetate/hydroxylpropyl acrylate terpolymer	85.27	11.08	HR Specta Polymers and Plasticizers by ATR	c:\my documents\omnic\libs\s...	95

Figure 8. FTIR spectrum multicomponent search results for the "Methanol – Control Rinse" sample.

The FTIR analysis of the methanol product rinse sample showed the presence of a rosin material (Figure 9), which is a common ingredient in solder paste fluxes.



	Match	Title	Cumulative	Composite%	Folder	Filename	Index
1	75.75	ROSIN OIL-HIGH VISC.	46.50	39.41	HR Polymer Additives and Plasticizers	c:\my documents\omnic\libs\s...	1666
		Ethylene/acrylic acid copolymer	65.96	19.05	HR Specta Polymers and Plasticizers by ATR - corrected	c:\my documents\omnic\libs\s...	9
		Cycloheptanone	71.77	18.73	HR Hummel Polymer and Additives	c:\my documents\omnic\libs\s...	1687
		PROPYLENE GLYCOL MONOOLEATE	75.75	22.81	HR Polymer Additives and Plasticizers	c:\my documents\omnic\libs\s...	1597

Figure 9. FTIR spectrum multicomponent search results for the "Methanol – Product Rinse" sample.

The user shared the safety data sheet (SDS) for the solder paste that was used, and the findings from the product rinse agreed with the listed composition of the flux in the solder paste, which is listed in Table 2. The last three rows are the flux in the solder paste. Upon researching the CAS numbers, both the rosin and resin components are rosin-based compounds. The activator was a collection of various length, medium-chain carboxylic acids, which along with the rosin and resin, serve as the flux.

Table 2. Composition and information on ingredients on the user's "no-clean" solder paste.

Substance Name	CAS No.	EC. No.	Concentration or Range of Concentration (Component %)	Classification and Pattern of Substance
Metal Alloy	/	/	Surplus Quantity	
Tin (Sn)	7440-31-5	231-141-8	Surplus Quantity	Metal Content (Homogeneous Mixture)
Silver (Ag)	7440-22-4	231-131-3	3.0 ± 0.5	
Copper (Cu)	7440-50-8	231-159-6	0.5 ± 0.2	
Metal Component	/	/	11.50 ± 0.30	
Hydrogenated Rosin	65997-06-0	266-041-3	4.0 to 11.5	Paste Content (Homogeneous Mixture)
Resin	65997-05-9	500-163-2	3.5 to 6.5	
Activator	65937-72-4	273-084-1	2.4 to 5.2	

The rosin was stated to be soluble in ketones, esters, hydrocarbons, alcohols, and chlorinated solvents, and insoluble in water. If desired, to successfully clean residue from this component of the flux, a detergent or surfactant cleaning agent would likely need to be used along with heated, deionized water.

Root Cause Statement

The power-on failures were caused by excessive AP deposition, which led to high impedance shorts by dissolving or softening flux residues that remained on the assemblies after the SMT reflow process. The presence of excess AP was correlated to an excessive volume of AP applied for low board volumes while maintaining an equivalent surface area within the chamber, the outgassing volume to buffer the partial pressure of the AP, and the adequate dispersion of the AP via molecular diffusion.

Discussion of Root Cause Development

The volumes of AP used in chambers for the investigation were previously validated in chambers filled mostly with aluminum coupons, on several substrates, and to the level that improved adhesion that observed with the cross-hatch test. For the products that experienced failures, there was a possibility that the starting volumes of AP were excessive for the very low loading levels of the product's engineering builds. These volumes, at the time they were introduced to the previous revision product's manufacturing line, were successful for board loads of several hundred pieces. With these two pieces of information, there was no reason to suspect that the volume applied to the revised product was excessive. The user's deposition process was updated, particularly for low loading levels.

Prevention

For subsequent runs, the ratio of PCBA surface area to the volume of AP being used was monitored, as well as implemented other mechanisms for introducing AP into the chamber. The loading levels of PCBAs provide the surface area and the degree of air, moisture, and potential masking material outgassing in the chamber that all together provide a buffer that facilitates adequate molecular diffusion of the AP throughout the chamber.

Given that the AP acted as a solvent that partially solubilized the flux residues, enough at least to have a conductive path between test points and/or solder joints, minimizing the flux residues that may interact with AP would be very helpful as well. That request though is more challenging for high volume, consumer electronics manufacturing, where the "no-clean" process has already been accepted, and cleaning is an added, unplanned cost.

Case Study #2 – "Water is a contaminant, too, especially under vacuum", or "evaporative cooling can be great, just not usually in your coating chamber"

For another project, there was an issue that led to a low failure rate with undesirable coating thickness variation over small lateral distances and on materials with high thermal conductivity, including metal pins in connectors and shield cans. Generally, when there were issues, they were associated with thicknesses that were much higher than the target. In this case, a thin coating was being used for a "connect through" application on a board-to-board (B2B) connector, so the connector mating process removed the parylene and enabled full functionality without having to mask before and de-mask after the coating was applied.

When a thicker coating was present at that location, the connector mating process wasn't able to remove the coating and exhibited an electrical failure.

No changes occurred with the parylene precursor and lot that was used, as well as the same equipment operators, deposition equipment, and the process of record (POR). Besides the new lots of samples that were being coated, the factors that were eventually tracked down were the time of year and ambient conditions in which the product was being manufactured and stored.

The first two rounds of prototype builds took place in winter and the early transition to spring and proceeded without incident. Issues began to occur during the subsequent manufacturing phase of the engineering validation test (EVT), which took place in the summer. The coating process was installed in an area in the manufacturing facility with well-controlled temperature and humidity, while the assembly manufacturing and storage areas had fewer environmental controls.

Contamination is the key to most issues in coating and process issues, and moisture can be a contaminant, too. When moisture is on a substrate and placed under vacuum, the water will quickly boil, which will use the energy in the water itself, until enough energy is lost and the residual water freezes.

A set of experiments were performed to evaluate how long it would take for water to freeze during the CVD chamber pump down process, as well as incorporating pauses at varying pressure levels to evaluate the water removal process. An example setup is shown in Figure 10, where a 4-channel thermocouple data logger was placed to run in the chamber with 3 thermocouples placed in small cups of water and 1 thermocouple serving as a control.

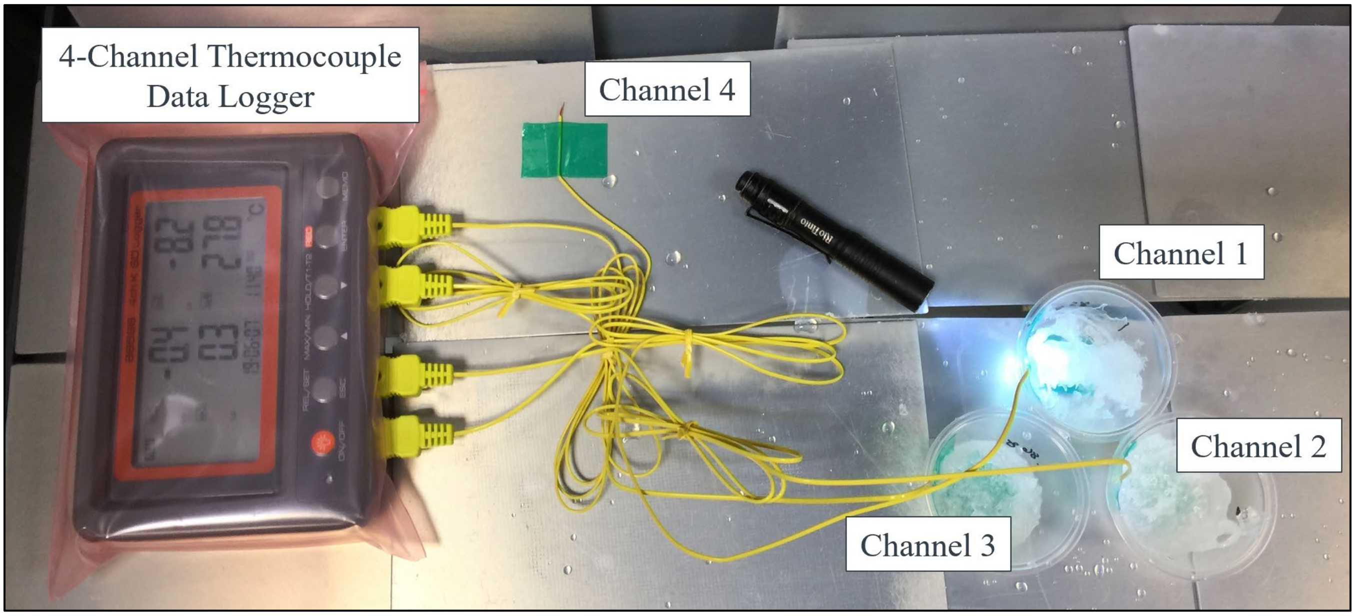


Figure 10. Experiment setup with thermocouple data logger with three thermocouples (Channels 1 through 3) placed in small cups of water, one thermocouple as a control on Channel 4, and a small flashlight to serve as a light source for viewing through the chamber's viewport.

The thermocouple data were plotted as the time-series temperature data shown in Figure 11. The control thermocouple showed a slight increase in temperature over time, while the three thermocouples that were in the water experienced temperatures below -50 °C.

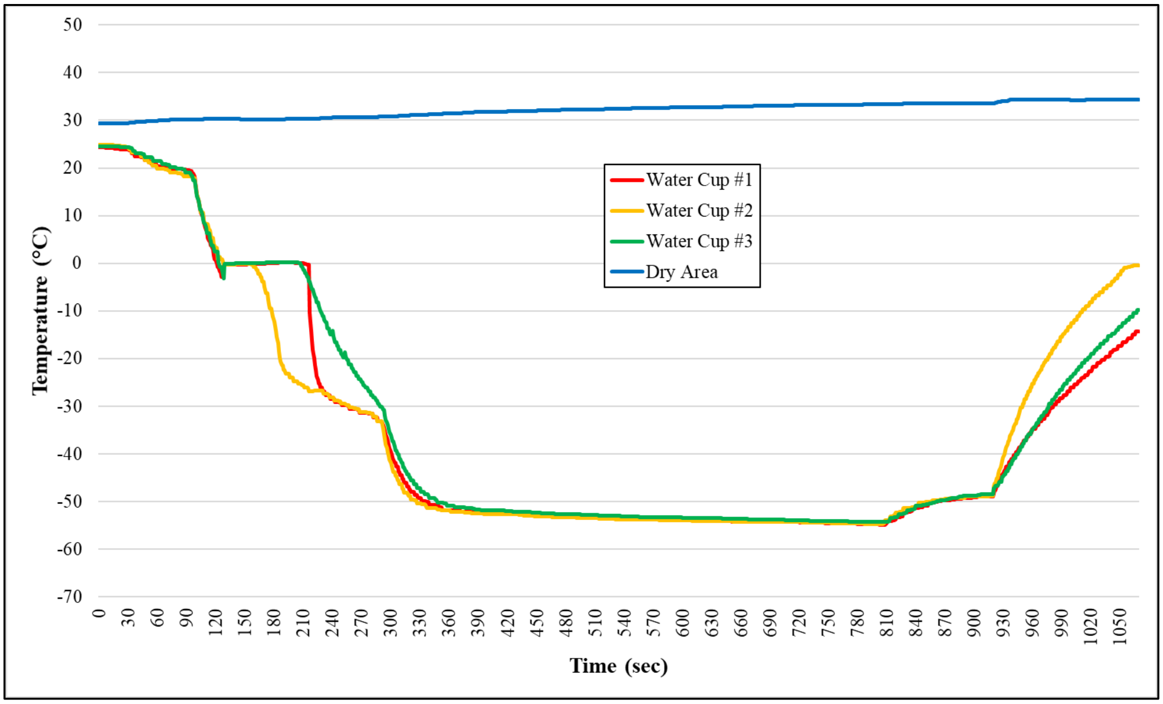


Figure 11. Time-series temperature for the three thermocouples placed in small cups of water and one serving as a control.

A camera was observing the process through the chamber's viewport and a video was captured for the process. Figure 12 shows a series of still frames with a time code starting when the system started to pump down from atmospheric pressure. By the 2 minute mark, the water was boiling vigorously, while by 3 minutes the water appeared frozen. The temperature continued to drop with no major visible differences observed.

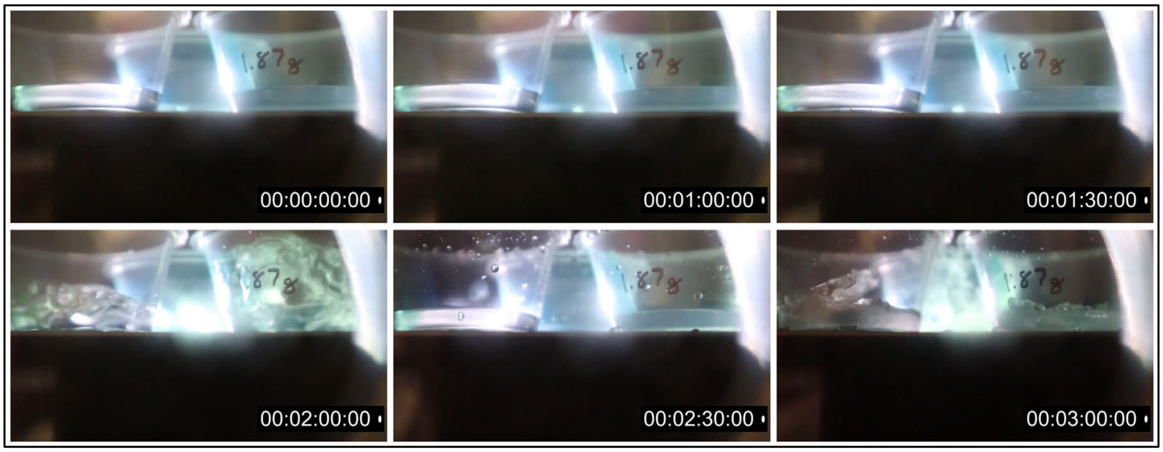


Figure 12. A series of snapshots from the video that was captured through the parylene CVD chamber's viewport. Water boiled vigorously by the 2-minute mark and appeared frozen by 3 minutes.

Additional experiments were performed with four different substrates: an FR4 PCB, a stainless steel panel, an aluminum panel, and a glass slide, with and without water present to evaluate the effects of the evaporative cooling. Figure 13 shows the dry samples with no appreciable difference, as was expected. Figure 14 shows the samples which had 5 mL of water placed on each substrate, with significant changes observed and temperatures again reaching below -50 °C. Representative pressure curves were included on each plot to show the changes in pressures achieved during this process.

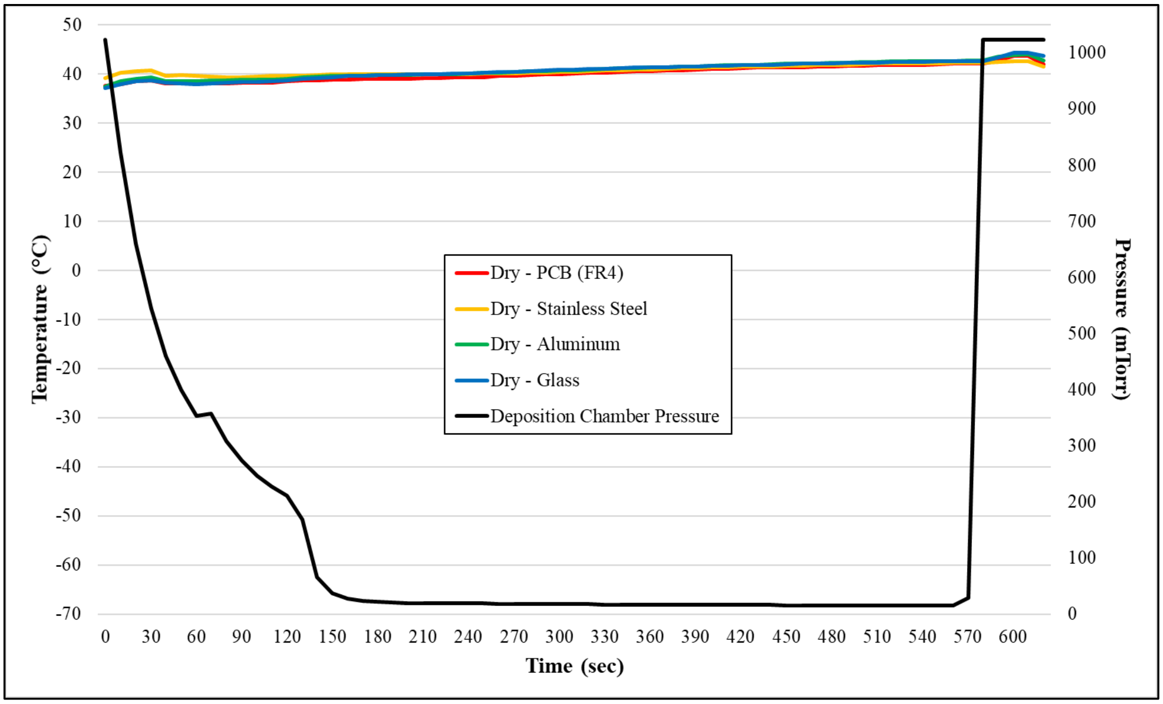


Figure 13. Temperature vs time study of four different dry substrates during the chamber pump down process. No appreciable difference was observed for each material type: FR4 PCB, a stainless-steel panel, an aluminum panel, and a glass slide.

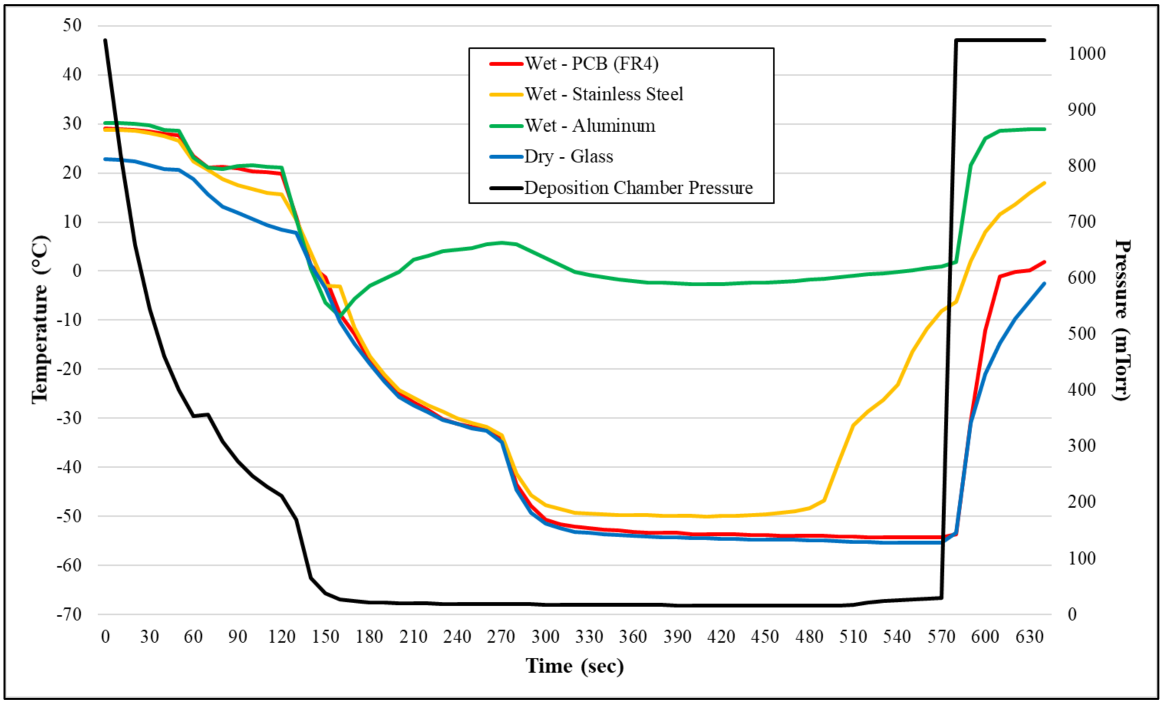


Figure 14. Temperature vs time study of four different wet substrates during the chamber pump down process. No appreciable difference was observed for each material type: FR4 PCB, a stainless-steel panel, an aluminum panel, and a glass slide. Note that the aluminum sample likely had ice break off of the thermocouple area, so the temperature didn't reach the lowest values.

Once the water was frozen and still under vacuum, the ice then sublimes from a solid to a gas, enabling the temperature to remain low, and eventually freeze-drying the product. A phase diagram for water is shown in Figure 15,[9] with labels on each of the phase transitions.

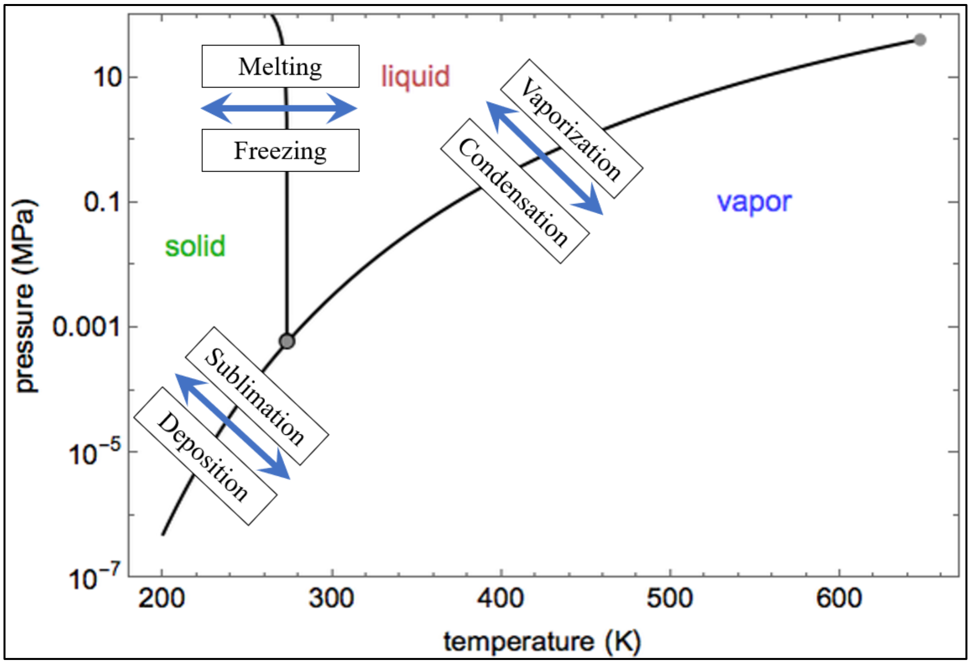


Figure 15. Pressure-temperature phase diagram for water with each of the transitions labeled.

One of the properties of parylenes is that there's an increase in the deposition rate with the corresponding decrease in substrate temperature. Examples of this relationship are illustrated in Figure 16 at two different deposition pressure regimes.

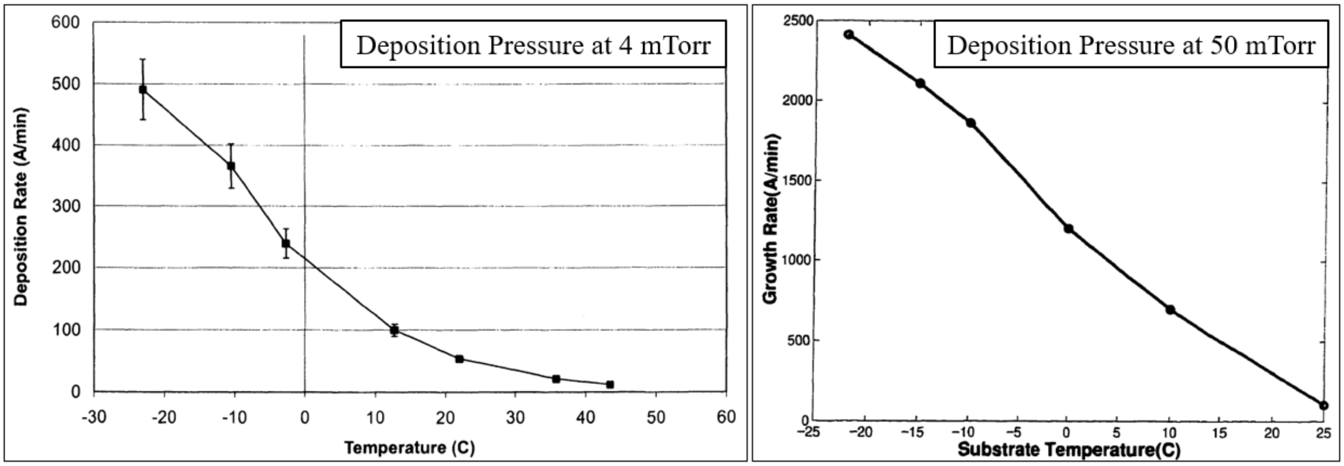


Figure 16. Deposition rate vs temperature of parylene N for example deposition systems operating at 4.0 mTorr[10] and 50 mTorr[11] deposition chamber pressures.

Root Cause Statement

It was concluded that the vacuum process, along with the environmental variations in relative humidity and water adsorption, led to significant evaporative cooling of substrates. Once these parts were cooled in a vacuum, they stayed cold due to lack of convection. Additionally, with rapid vacuum introduction on small loads and using a large vacuum pump, we observed frost or ice formation on the parts. This frost then sublimates slower than liquid would evaporate, reaching a much lower minimum temperature than ice at atmospheric pressure and increasing the likelihood that parts are cold at the start of deposition. As noted above, the polymerization of parylene N occurs more rapidly at lower substrate temperatures and would result in thicker coatings in colder regions.

Discussion of Root Cause Development

The higher moisture content in the assemblies led to degassing and evaporative cooling during the vacuum deposition process. The target coating thickness was achieved on non-thermally conductive parts, such as board and connector bodies, while metallic areas, such as connector pins and shield cans had significantly more coating than intended. Various mechanisms were developed with the client to assist with drying and degassing the parts before the start of the parylene deposition. Besides excess moisture, under-cured adhesives in the localized areas were identified by the user, which led to similar evaporative cooling behavior.

Prevention

For subsequent runs, the pump down sequence at the beginning of the deposition process was adjusted to mitigate the degassing issue. Ideally, manufacturing and storing assemblies in a well-controlled environment, as well as baking out the assemblies according to the JEDEC and IPC standards before coating would improve the overall deposition process and repeatability, which in turn would ensure the quality of the coating and the reliability of the coated product. The introduction of a baking step and enhanced environmental controls were challenging for this high volume, consumer electronics manufacturing facility, and would have added unplanned costs and build schedule time to the user.

Conclusions

There's a reason behind the push for high levels of cleanliness, along with low moisture content in components and assemblies, for high-reliability products in critical use applications. Through careful management of materials, equipment, and process, parylene CVD coatings can overcome the need to remove moderate levels of "no-clean" flux residues and less than ideal degassing of assemblies for users who don't want the added costs of cleaning, baking, and storing under industry recommended conditions, and still deliver a quality product that passes rigorous testing criteria. It was possible to control for the interactions and solvation effects of adhesion promoters with flux residues and managed degassing of moisture from assemblies through modifications of the coating deposition equipment and processes.

Acknowledgments

The authors would like to thank the Materials Characterization Laboratory in the Materials Science and Engineering Department at the University of Utah for assisting with the scanning electron microscopy analysis, as well as the HZO Application Engineering, Operations, Process Engineering, and Technology groups in the US and China for the team efforts that executed on these projects.

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Authors:

Sean Clancy, Ph.D. and Dusty Askin, HZO, Inc.

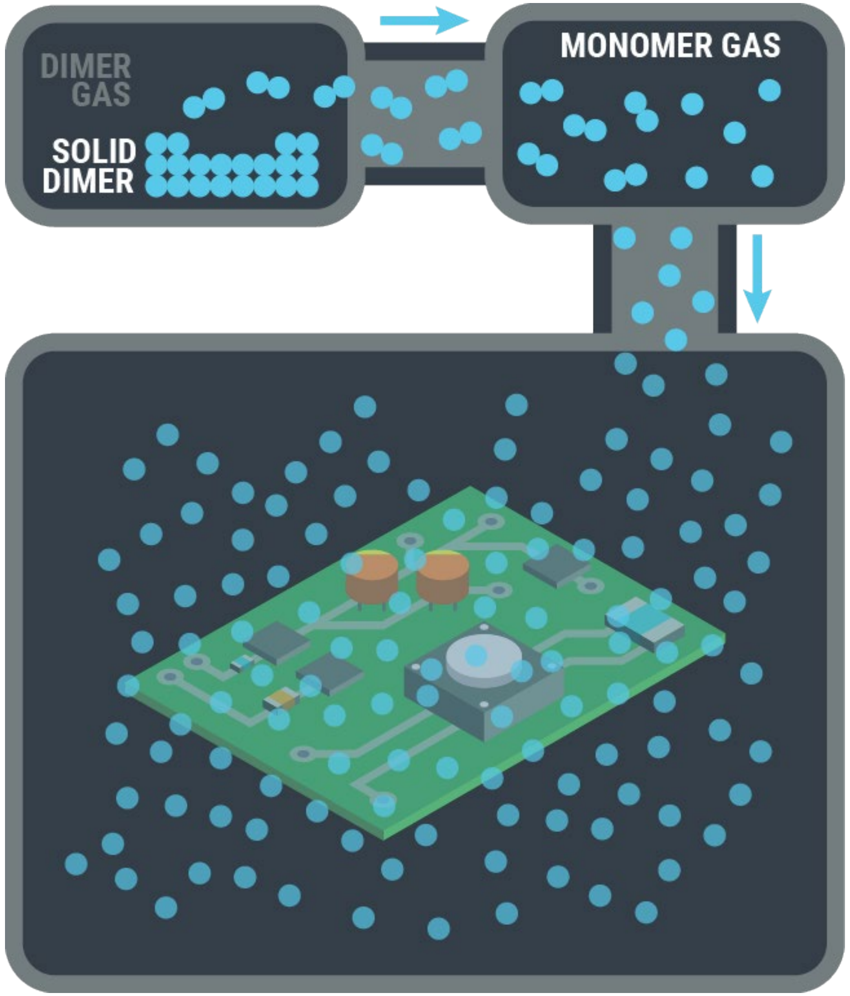
Morrisville, NC, USA

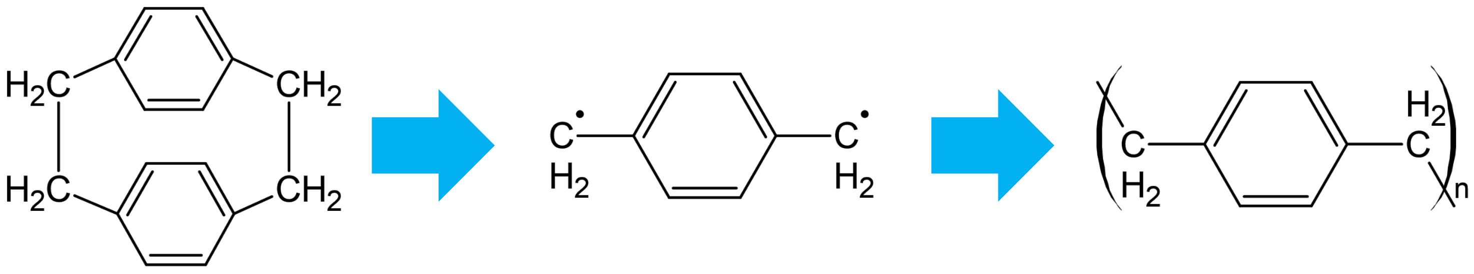
sclancy@hzo.com

Agenda

- Background
  - Principles of Parylene chemical vapor deposition and adhesion promotion (AP)
- Case Studies and Process Improvements
  - #1
    - Transient electrical issues occurred immediately after coating
    - Caused by AP-contaminant interactions and substrate outgassing
  - #2
    - “Connect through” issues with unintended increase in thickness
    - Caused by contaminant degassing and evaporative cooling
- Conclusions

Parylene Chemical Vapor Deposition (CVD) Process



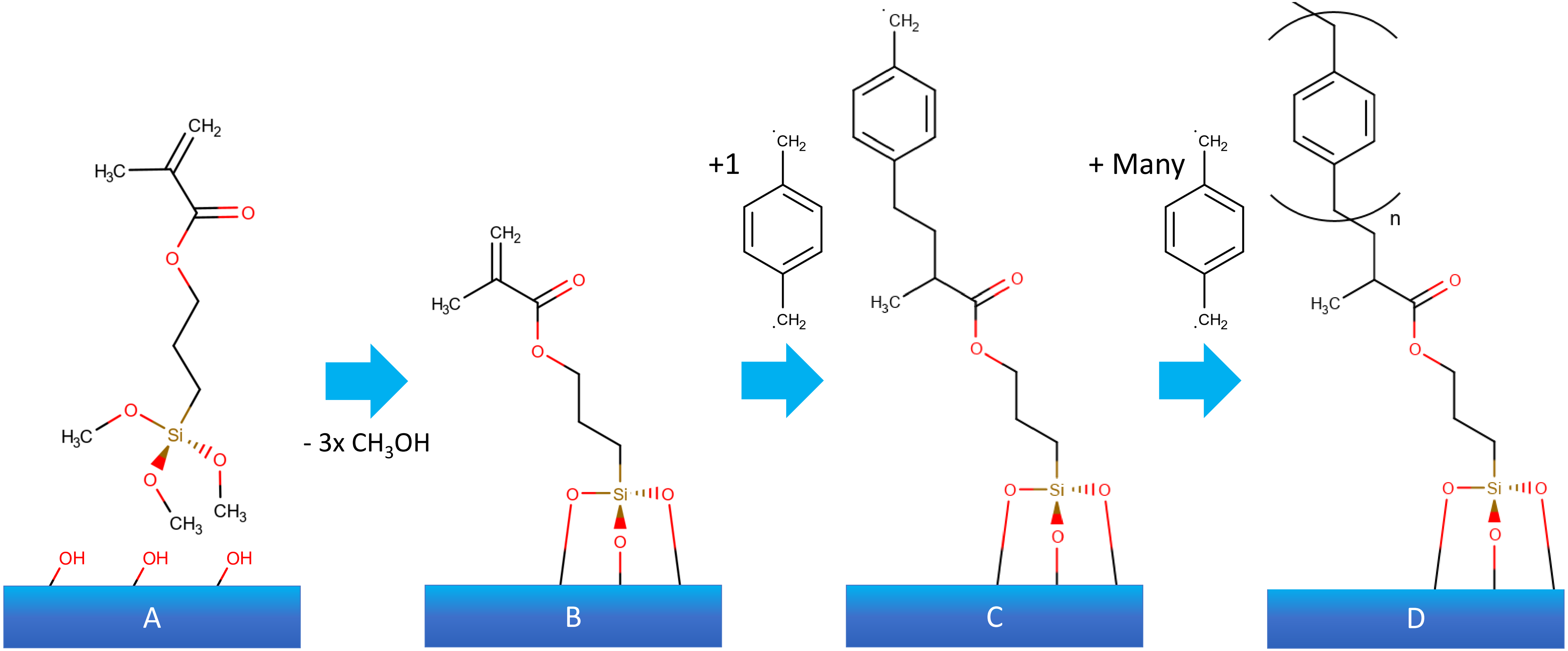


Vaporizer	Pyrolysis Furnace	Coating Chamber
Solid dimer sublimes to a gas in the vaporizer	Dimer gas is cracked into a di-radical in the pyrolizer	Di-radicals adsorb on substrates and combine to form a polymer

- **No VOCs**
- **No Catalysts**
- **No Disposal Issues**
- **No Pollution Threats**
- **No Cure Time**

Adhesion Promoter Mechanism

- 3-(Trimethoxysilyl)propyl methacrylate, a.k.a. Silane A-174



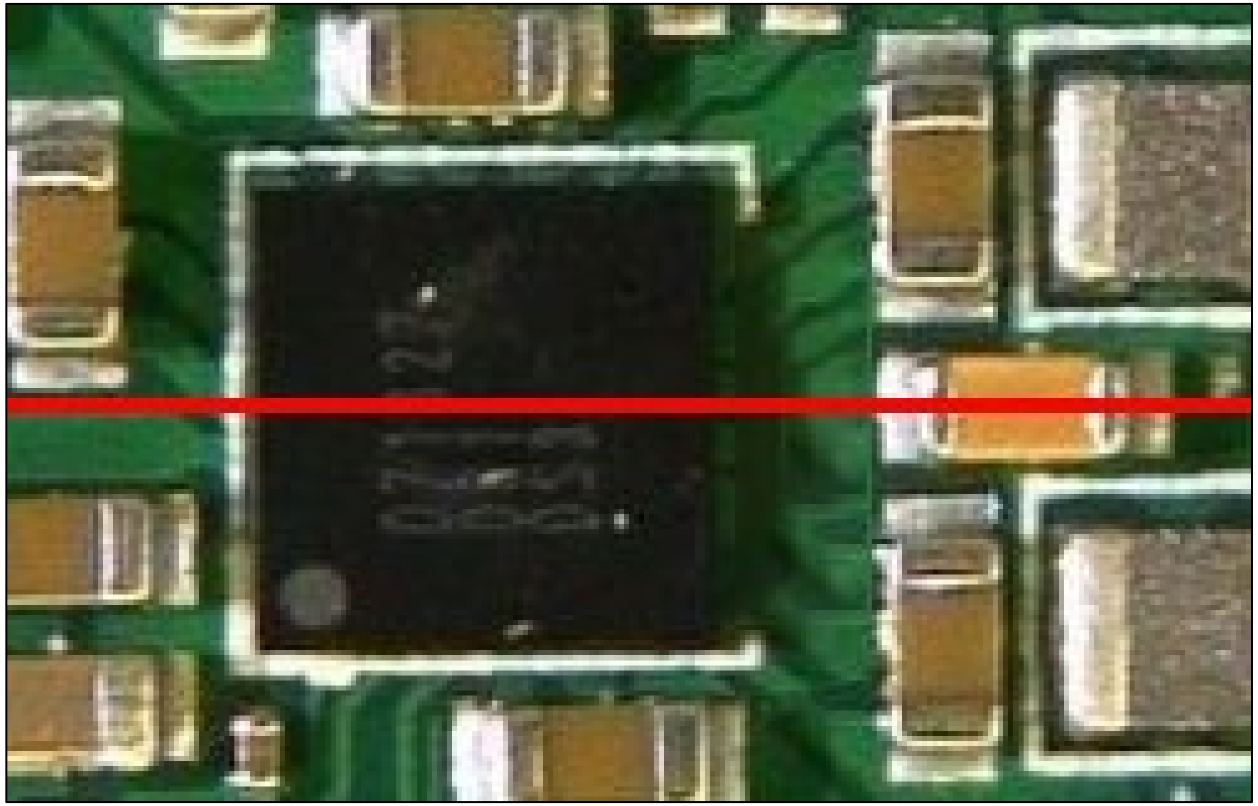
Case Study 1 – Intermittent & Transient Failures at FATP

Test Results Soon After Process	Test Results After 24+ h	Relative Amount of Adhesion Promoter	Product Loading in Chamber	Observed Oily Residue	Observed “Wrinkled” Masking Tape
Pass	Pass	Low	High	No	No
Fail	Pass	High	Low	Yes	Yes

- Electrical failures focused on power management integrated circuit (PMIC) component
- Failures triggered on uncoated products by manually adding excess AP in the PMIC region
- After AP was removed and/or allowed to react for several days, the product recovered

CS#1 – Location of the Cross-Section

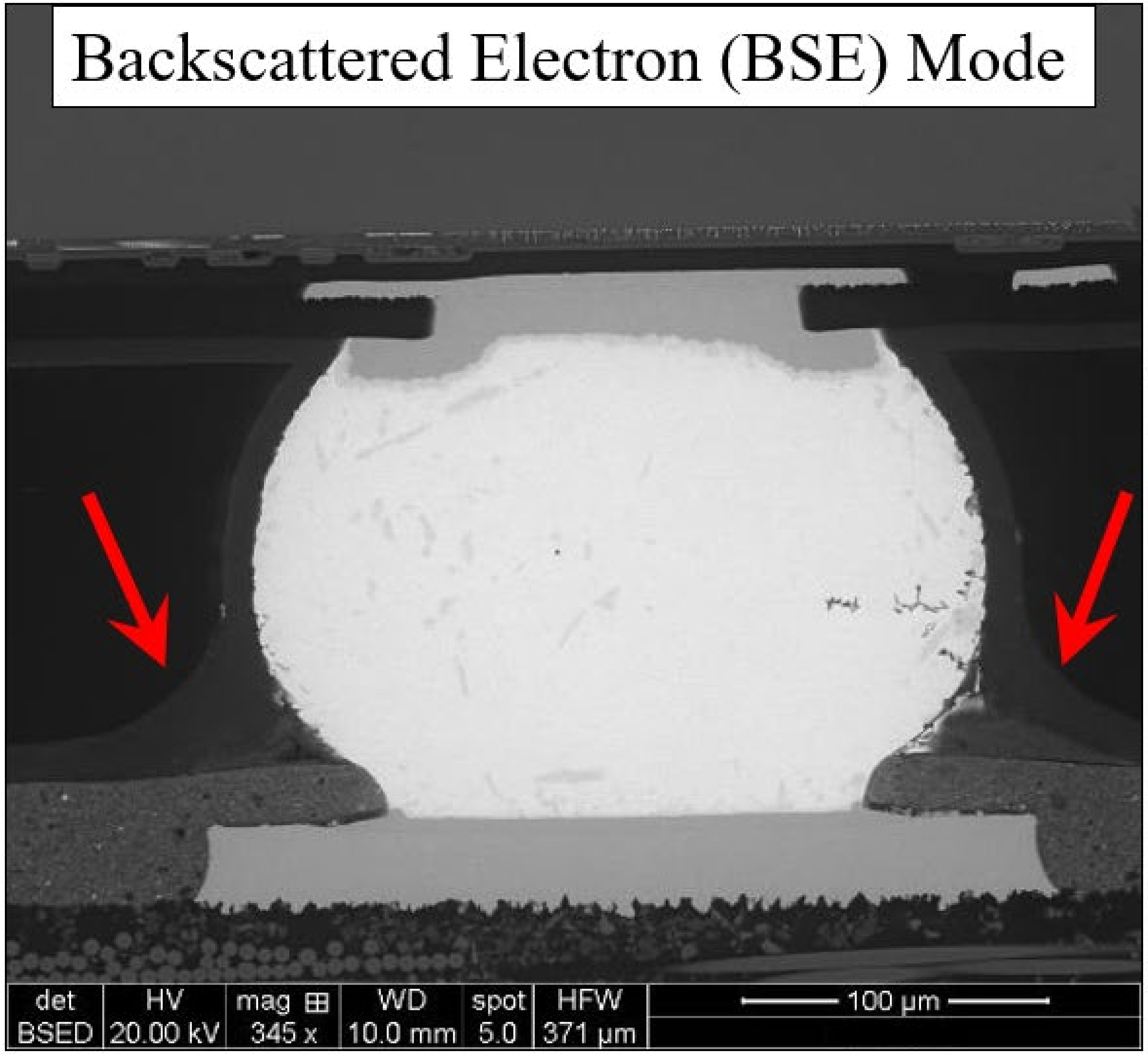
- Cross-sectioned coated PMIC with location noted with red line

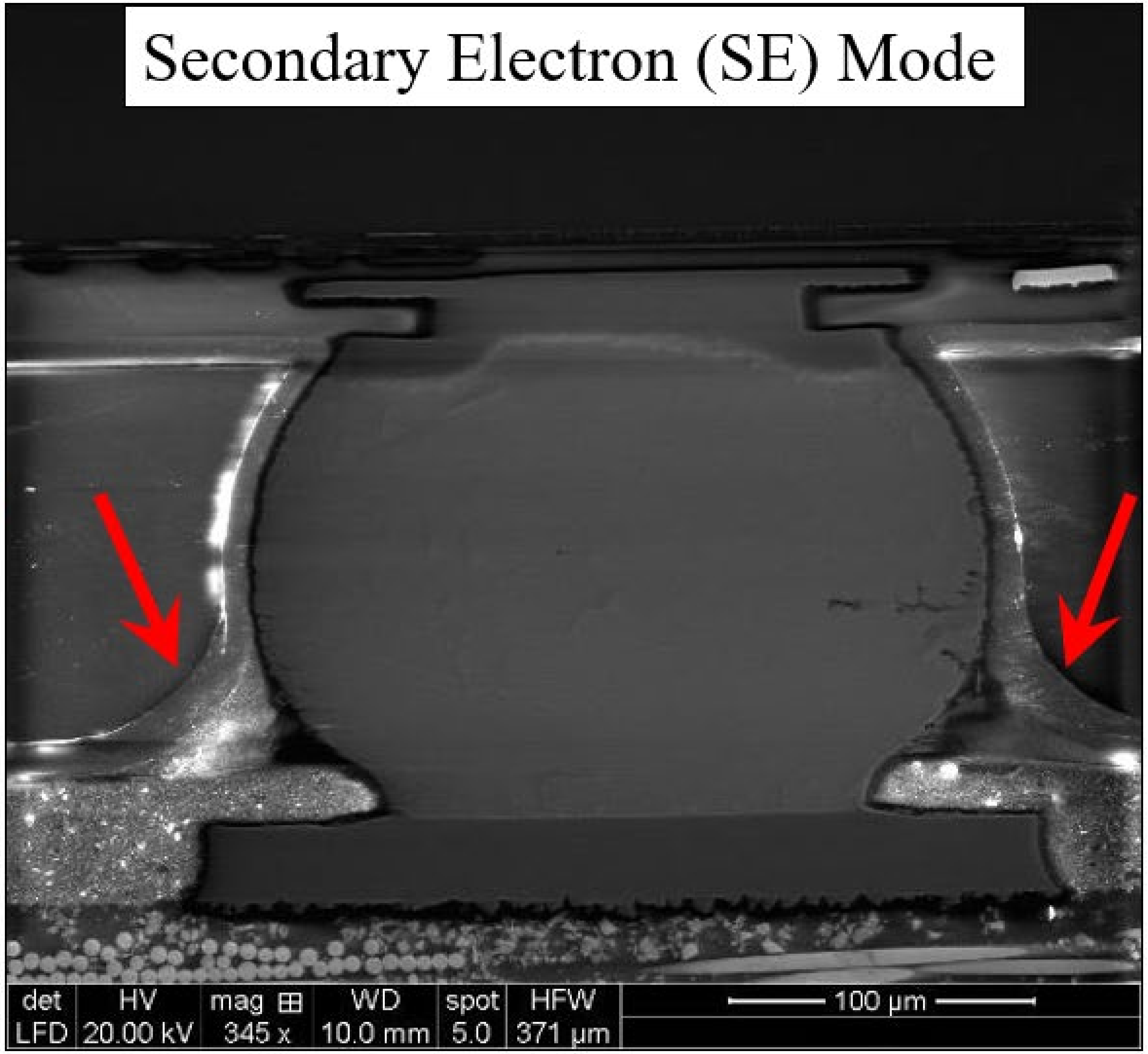


CS#1 – PMIC Component Cross-Section – Optical Microscopy

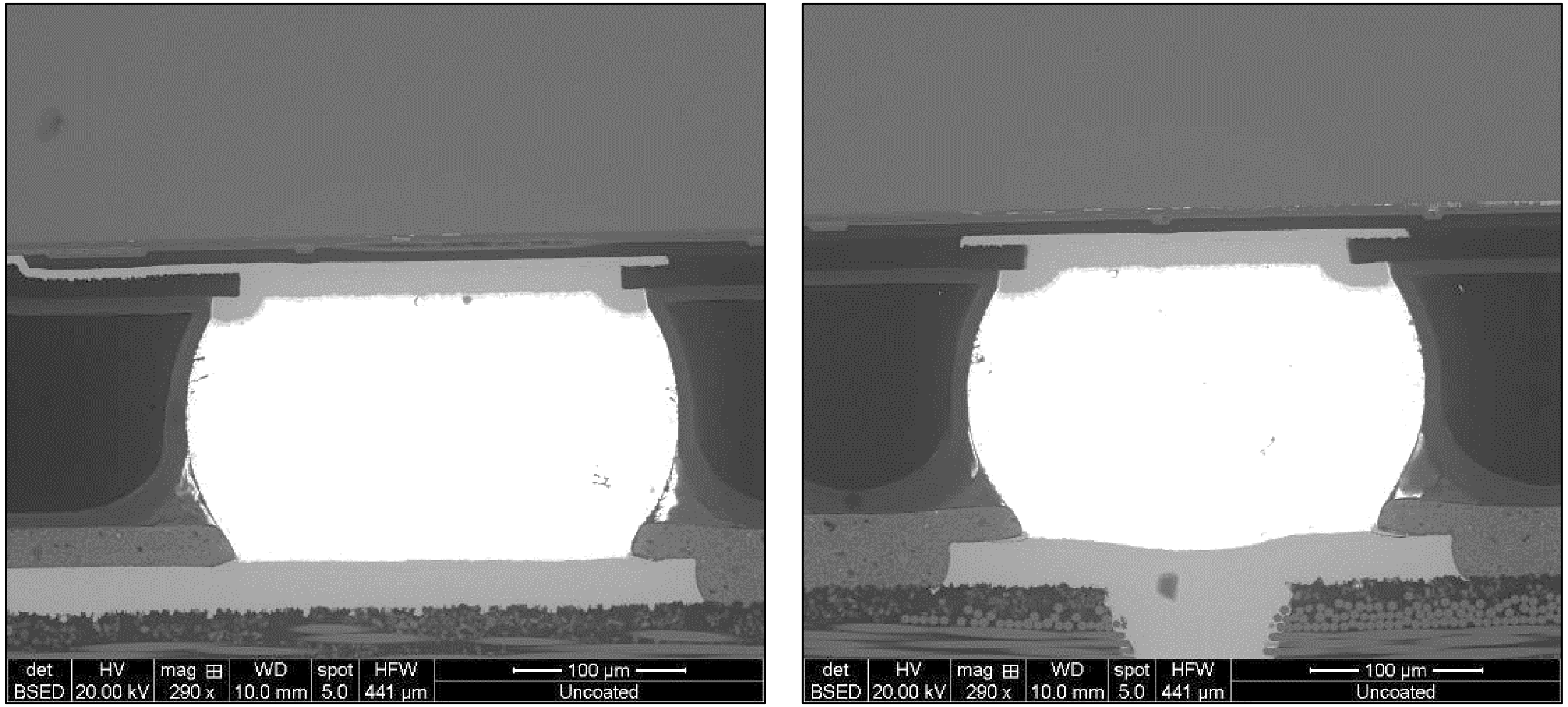
- Parylene conforms to all surfaces
- Pockets were observed at the base of the BGA solder joints
- Pockets were most likely the result of “no-clean” flux residues

CS#1 – PMIC Component Cross-Section – SEM Imaging

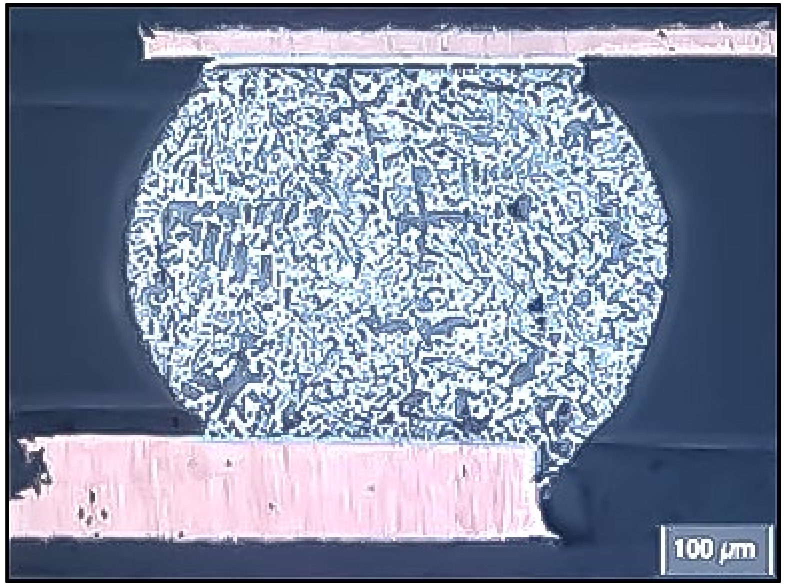




CS#1 – Coating Conformality – “No-Clean” vs Clean



- Pockets at BGA solder joints on “no-clean” assembly



- No pockets on BGA solder joints on cleaned assembly
- Ref.: R. Wilcoxon, D. Hillman, D. Pauls, D. White, “The Impact of Improper Conformal Coating Processes on BGA Solder Joint Integrity”, *Proc. of SMTA International Conference*, ***2015***, 870.

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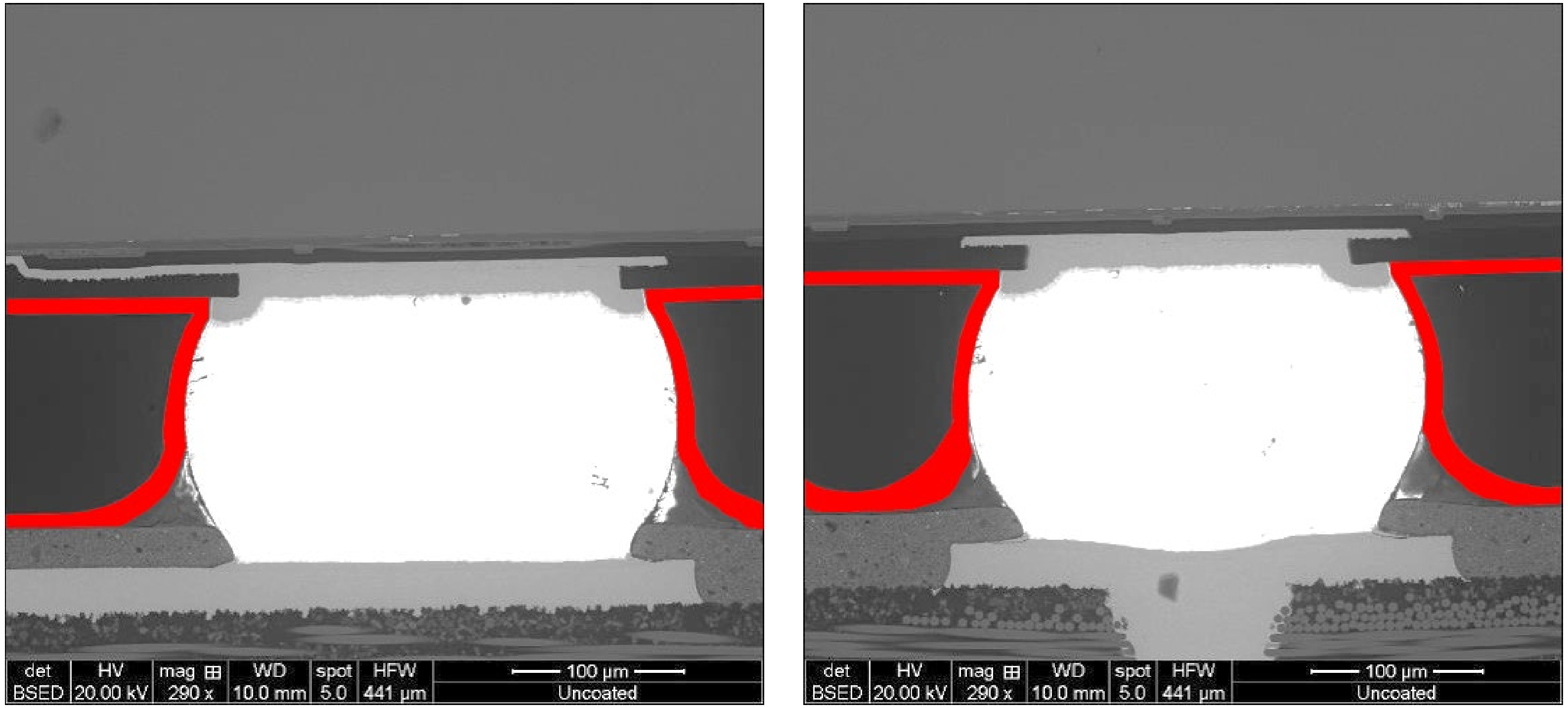

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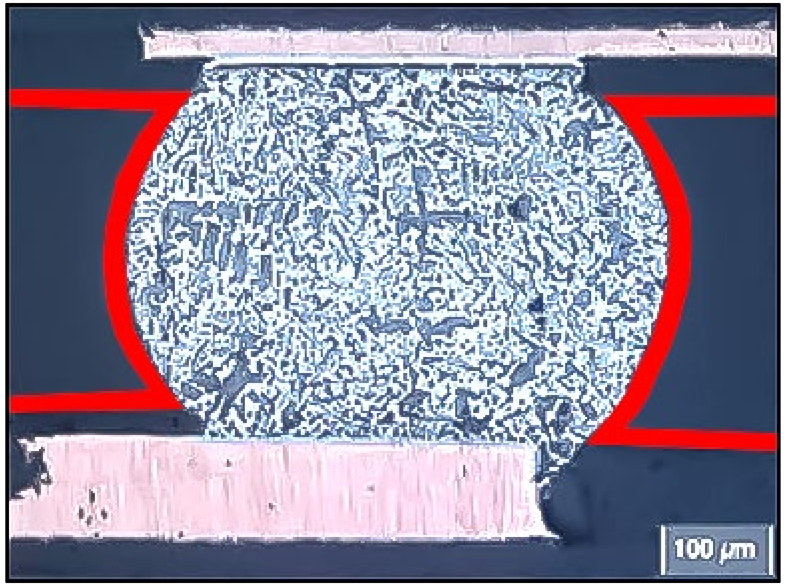

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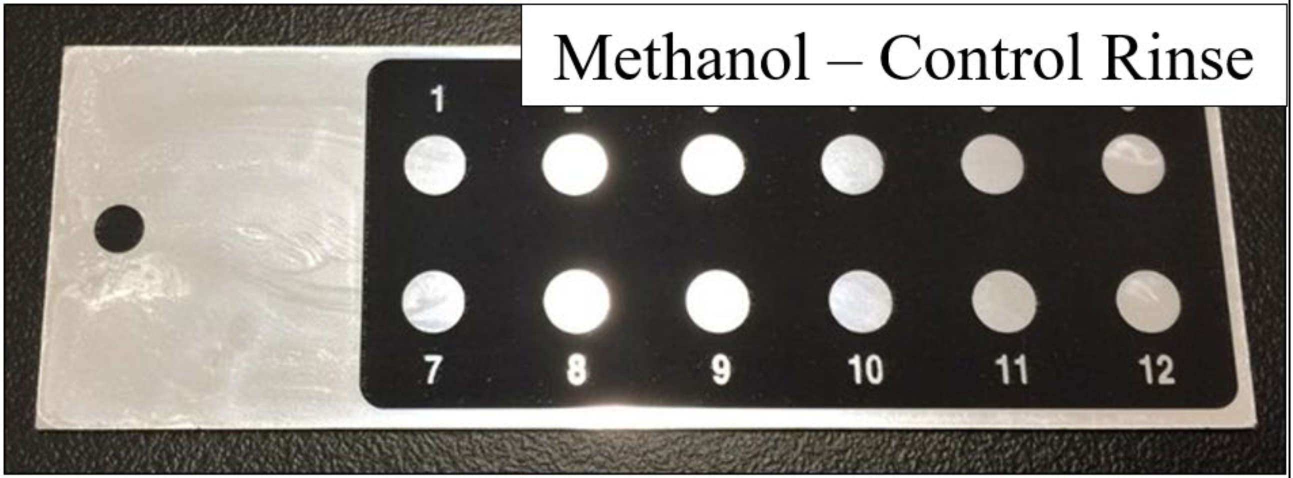
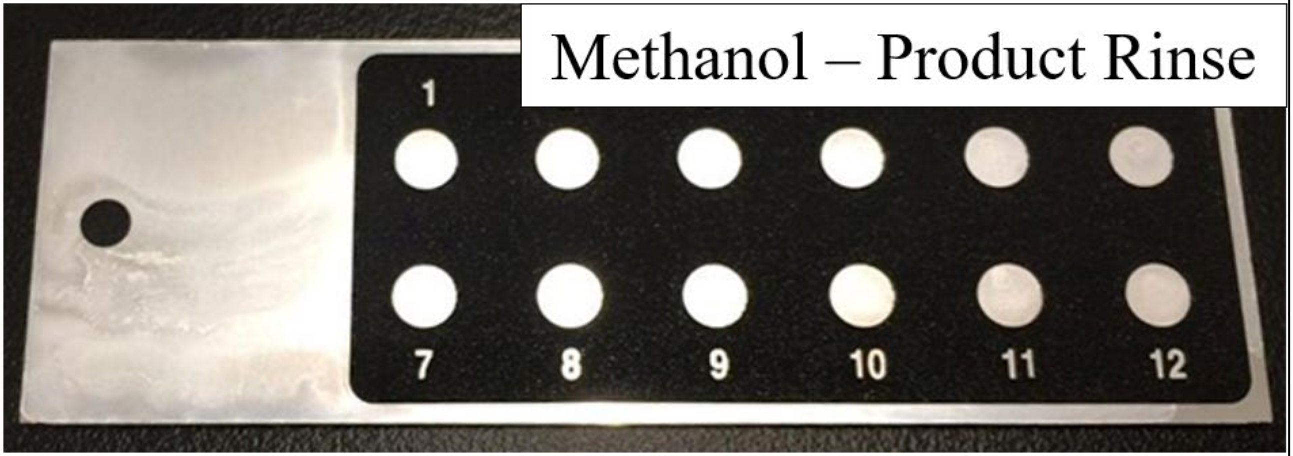
CS#1 – Surface Organic Detection & Identification Tests

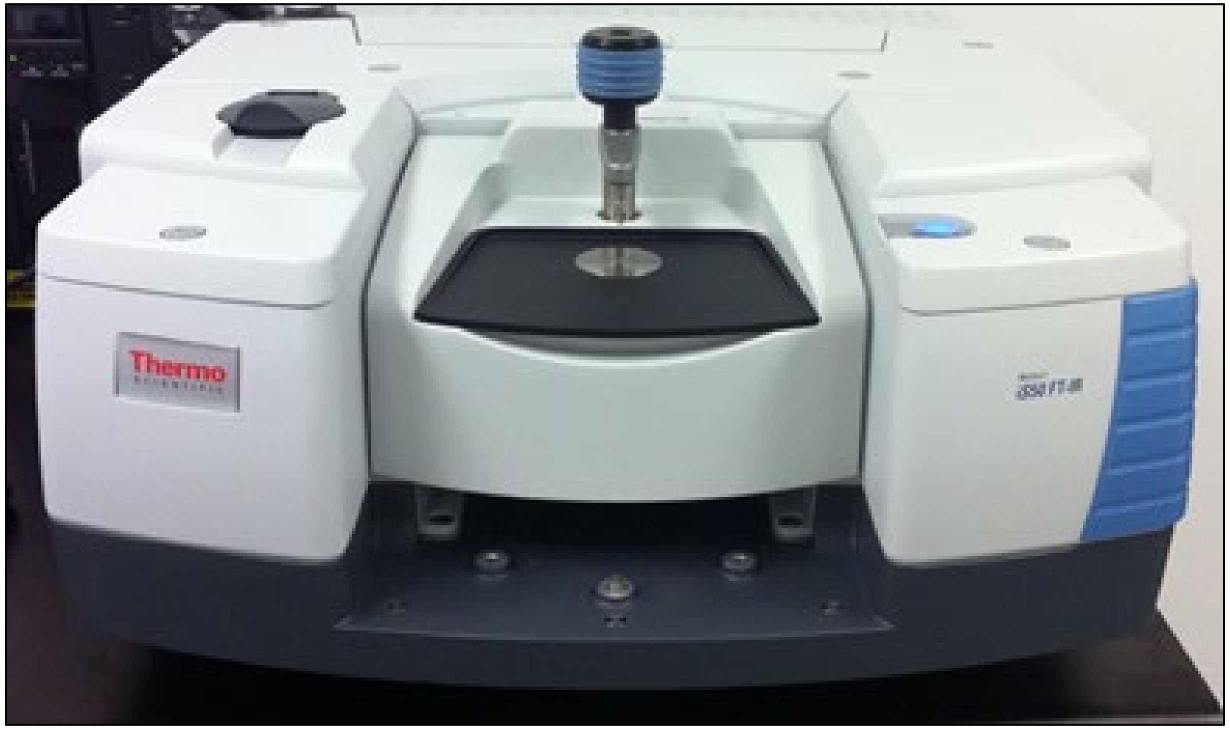
- Test methods:
  - IPC TM-650 Method 2.3.38C – Surface Organic Contaminant Detection Test
  - IPC TM-650 Method 2.3.39C – Surface Organic Contaminant Identification Test (Infrared Analytical Method)
- Two solvents:
  - Methanol
  - AP (Silane A-174) - *Issues*
- Residues on both slides
- More residue on product rinse slide.



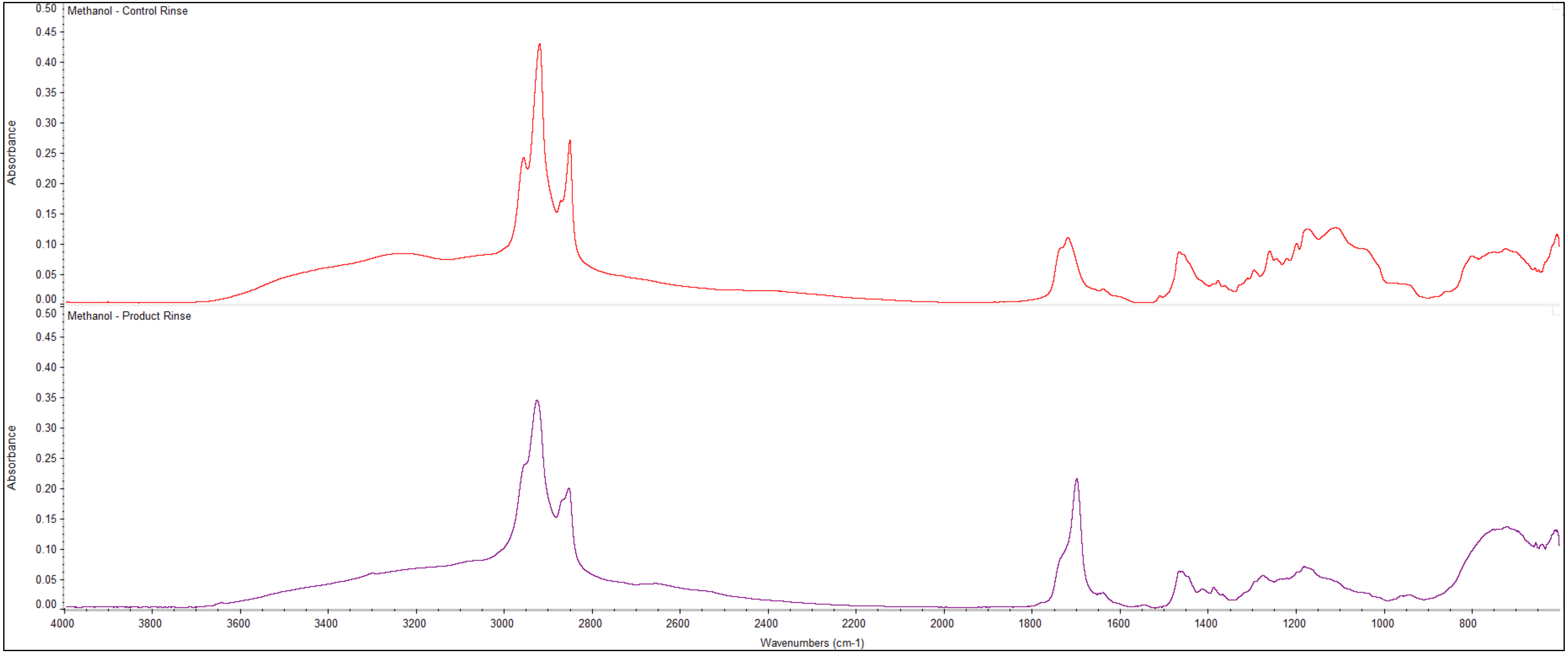


CS#1 – FTIR Spectroscopy

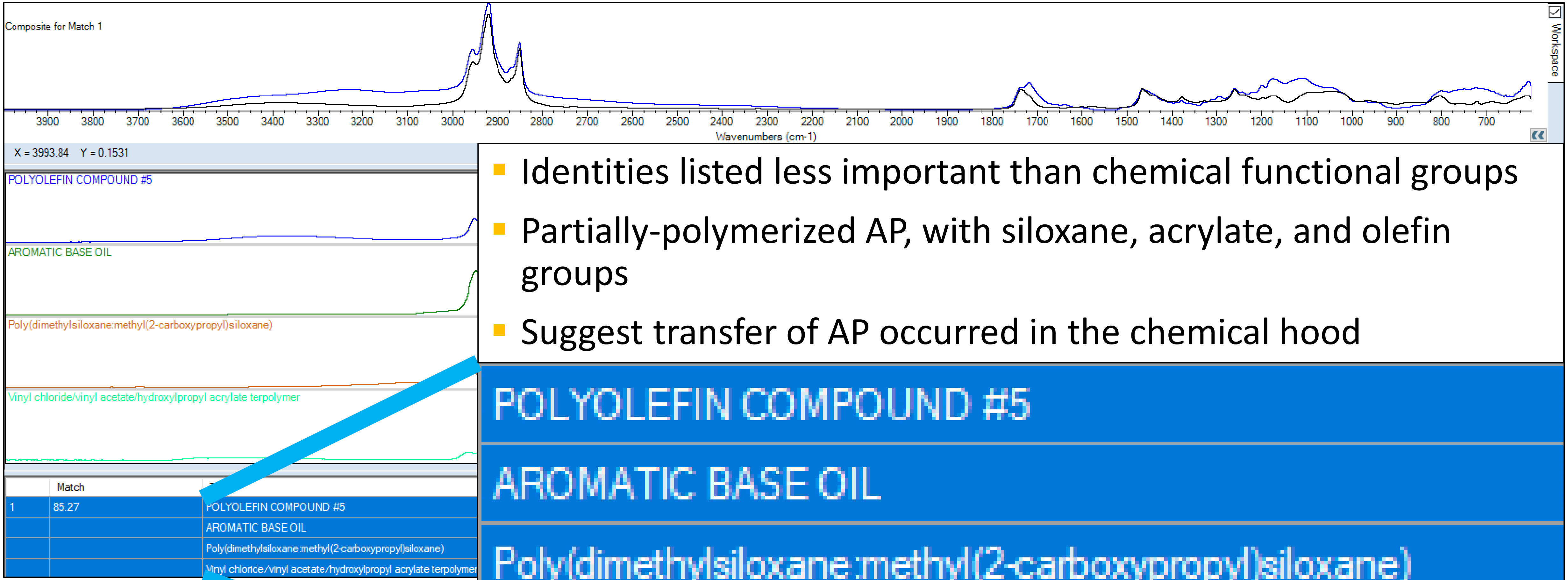
- Fourier Transform Infrared Spectroscopy
  - Instrumentation:
    - Thermo Nicolet iS50 FTIR Spectrometer
    - Smart iTR ATR Accessory
    - Germanium ATR Crystal
  - Software:
    - OMNIC – Capturing/processing data
    - OMNIC Specta – Multicomponent spectral search with material databases



CS#1 – Methanol Control vs Product Rinse Residues



CS#1 – Methanol Control Slide – Multicomponent Search



	Match	
1	85.27	POLYOLEFIN COMPOUND #5
		AROMATIC BASE OIL
		Poly(dimethylsiloxane:methyl(2-carboxypropyl)siloxane)
		Vinyl chloride/vinyl acetate/hydroxylpropyl acrylate terpolymer

- Identities listed less important than chemical functional groups
- Partially-polymerized AP, with siloxane, acrylate, and olefin groups
- Suggest transfer of AP occurred in the chemical hood

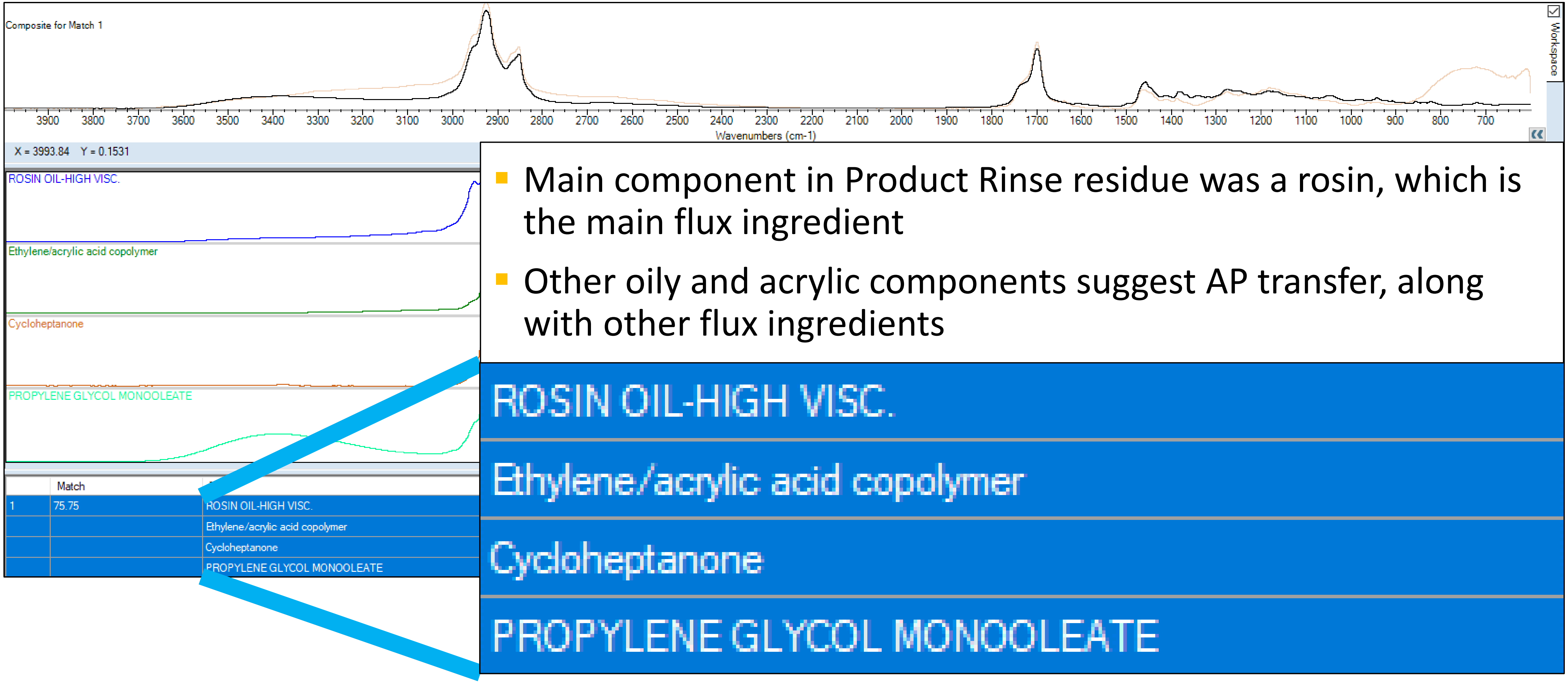
POLYOLEFIN COMPOUND #5

AROMATIC BASE OIL

Poly(dimethylsiloxane:methyl(2-carboxypropyl)siloxane)

Vinyl chloride/vinyl acetate/hydroxylpropyl acrylate terpolymer

CS#1 – Methanol Rinse of Product Slide – Multicomponent Search



X = 3993.84 Y = 0.1531

	Match	
1	75.75	ROSIN OIL-HIGH VISC.
		Ethylene/acrylic acid copolymer
		Cycloheptanone
		PROPYLENE GLYCOL MONOOLEATE

- Main component in Product Rinse residue was a rosin, which is the main flux ingredient
- Other oily and acrylic components suggest AP transfer, along with other flux ingredients

ROSIN OIL-HIGH VISC.
Ethylene/acrylic acid copolymer
Cycloheptanone
PROPYLENE GLYCOL MONOOLEATE

CS#1 – Composition of Customer’s No-Clean Solder Paste

Substance Name	CAS No.	EC. No.	Concentration or Range of Concentration (Component %)	Classification and Pattern of Substance
Metal Alloy	/	/	Surplus Quantity	
Tin (Sn)	7440-31-5	231-141-8	Surplus Quantity	Metal Content (Homogeneous Mixture)
Silver (Ag)	7440-22-4	231-131-3	3.0 ± 0.5	
Copper (Cu)	7440-50-8	231-159-6	0.5 ± 0.2	
Metal Component	/	/	11.50 ± 0.30	
Hydrogenated Rosin	65997-06-0	266-041-3	4.0 to 11.5	Paste Content (Homogeneous Mixture)
Resin	65997-05-9	500-163-2	3.5 to 6.5	
Activator	68937-72-4	273-084-1	2.4 to 5.2	

- The last three rows are the flux in the solder paste.
- CAS numbers show both rosin and resin components are rosin-based.
- Activator is a collection of various length (C4 to C11) dicarboxylic acids.

CS#1 – Root Cause & Process Improvements

- Root Cause
  - ***Excessive AP deposition led to high impedance shorts with "no clean" flux residues.***
  - Excess AP was correlated to:
    - Low PCBA volumes while maintaining an equivalent surface area within the chamber
    - Outgassing volume from PCBAs buffers partial pressure of AP & influences dispersion of AP
  - The volume of AP previously validated in chambers filled with mostly aluminum coupons, as well as in loads with larger PCBA volumes.
  - ***The loading levels of PCBAs provide the surface area and the degree of air, moisture, and potential masking material outgassing in the chamber that all together provide a buffer that facilitates adequate molecular diffusion of the AP throughout the chamber.***
- Prevention
  - Updated the customer's deposition process, especially for low loading levels.
  - Monitored ratio of PCBA surface area to volume of AP used, as well as implemented other mechanisms for introducing AP into the chamber.
  - Recommended reducing the amount of flux residues on the PCBAs.

Case Study 2 – Unexpected Thickness Variations

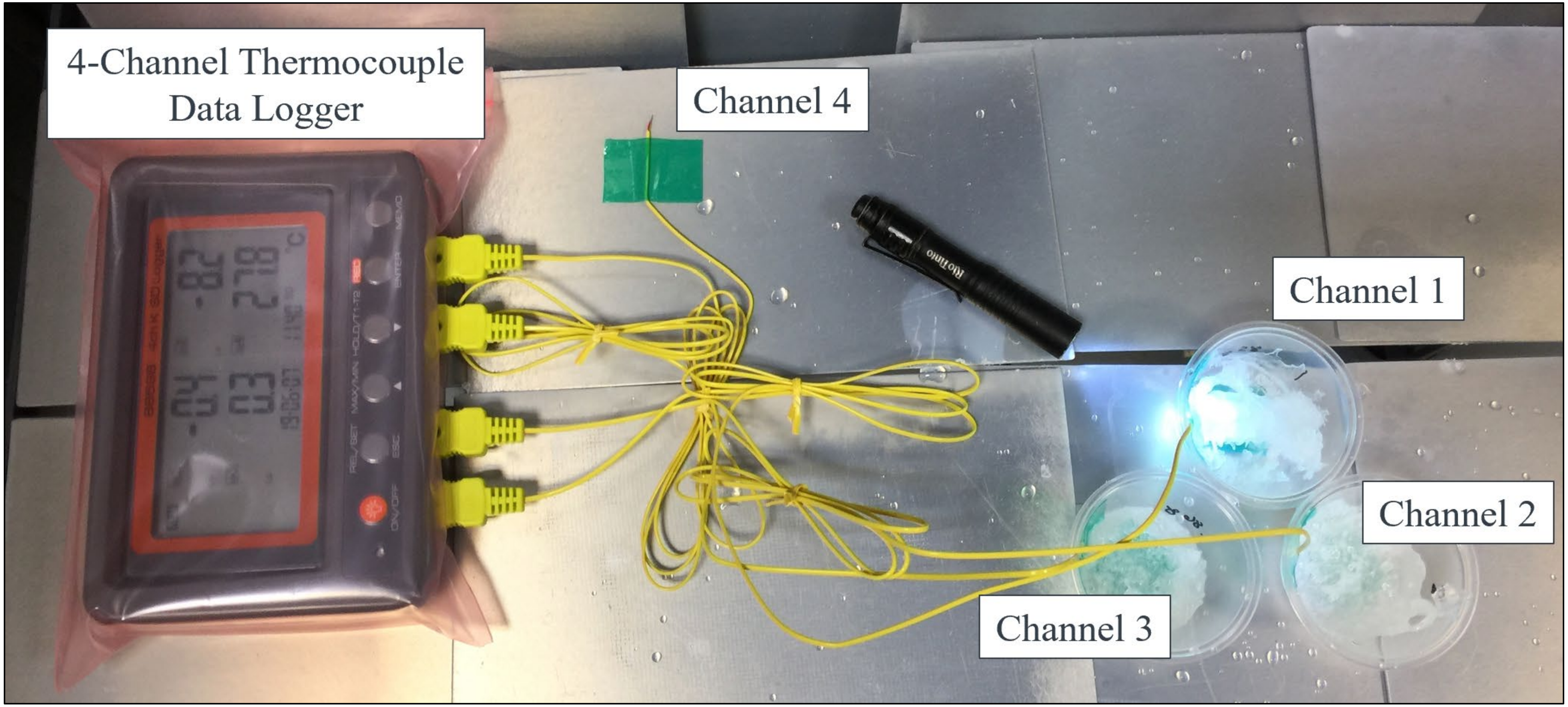
- Electrical failures localized to B2B connectors and increased thickness on shield cans
- Thin coating was being used for a “connect through” application on a B2B connector
- Thicker coating exhibited an electrical failure at final assembly

- Failures occurred in warmer, more humid months
- No changes in machines, materials, methods, and personnel

- Coating process was installed in area with well-controlled temperature and humidity
- Manufacturing and storage areas had fewer environmental controls

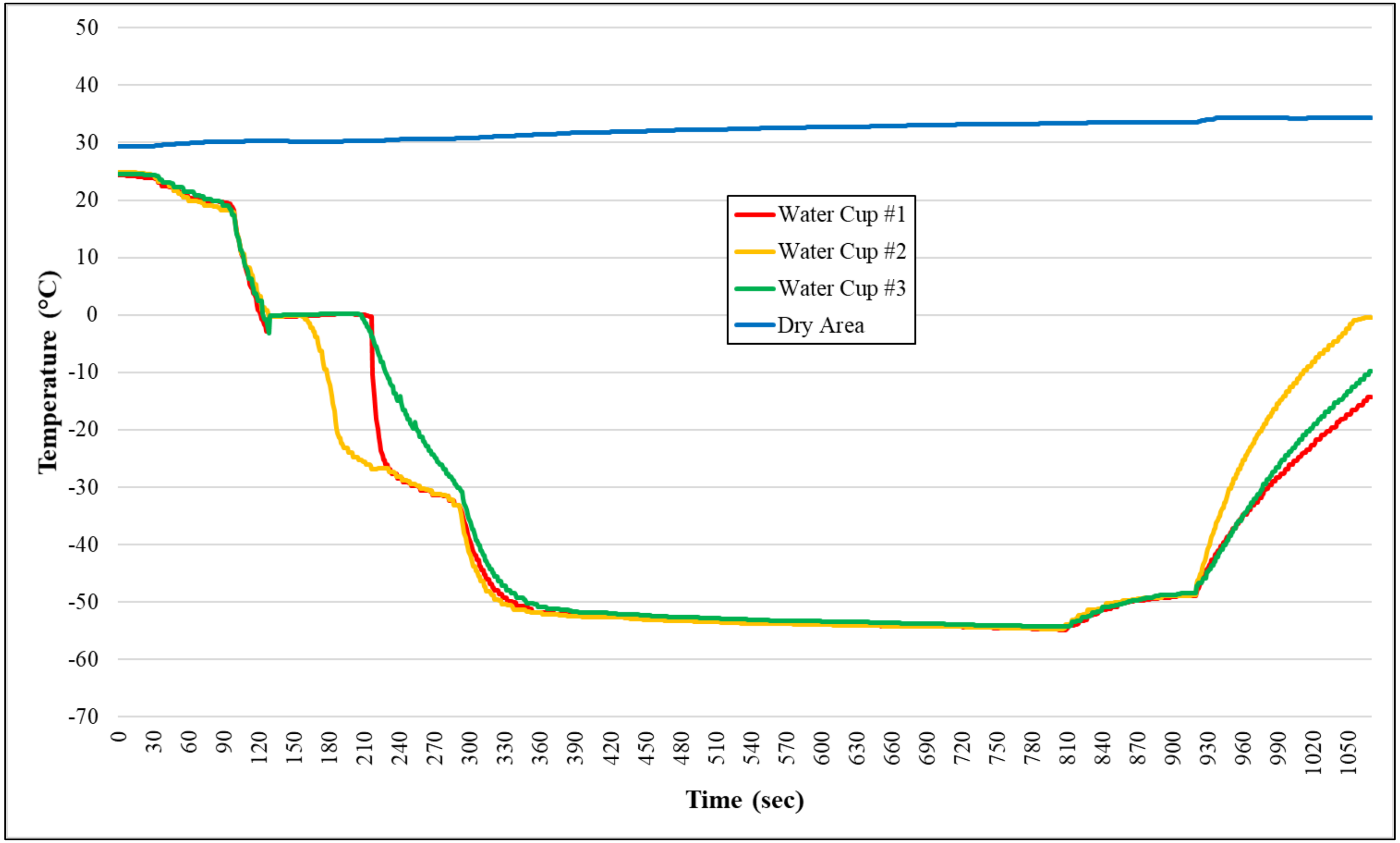
- Contamination from moisture was a concern, especially its ability for evaporative cooling

CS#2 – Experiments to Time Freezing of Water in CVD Chamber



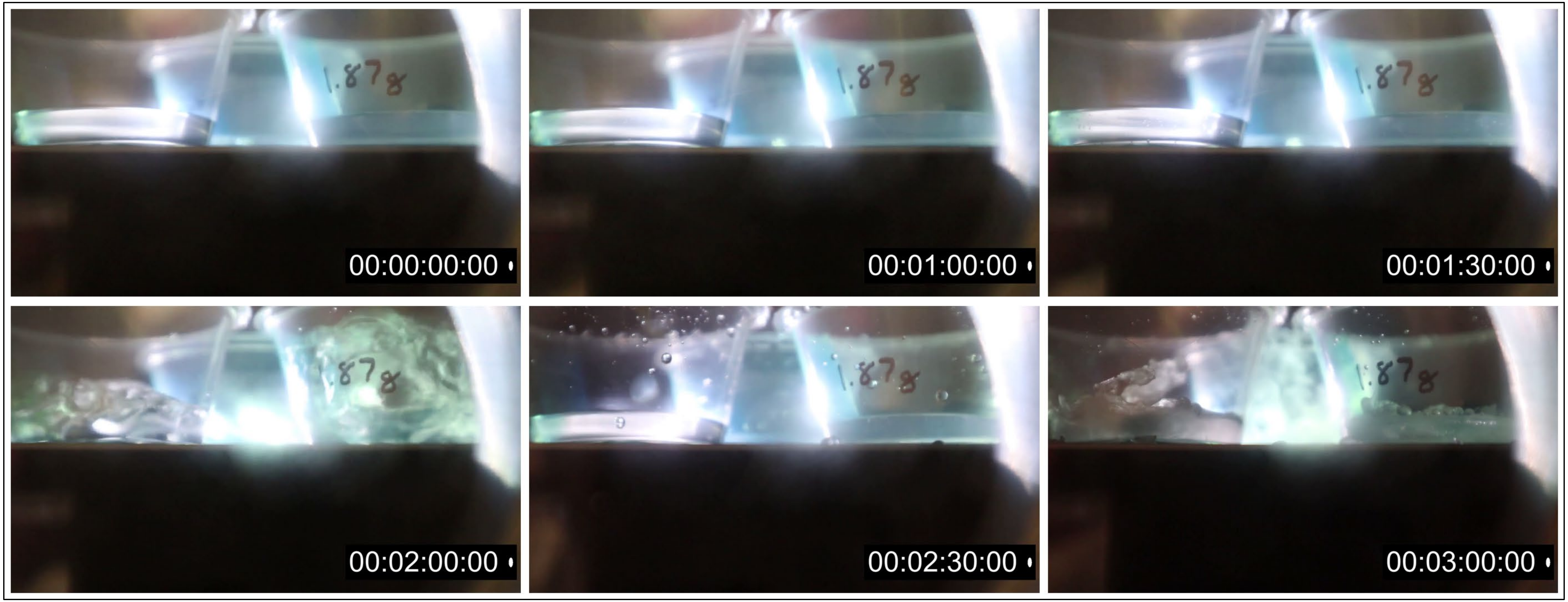
- Thermocouple Channels 1 through 3 in water and Channel 4 as control
- Flashlight as a light source for viewing through chamber’s viewport

CS#2 – Experiments to Time Freezing of Water in CVD Chamber



- Water froze within 2 to 3 minutes
- Water temperatures went below -50 °C within 5 to 6 minutes

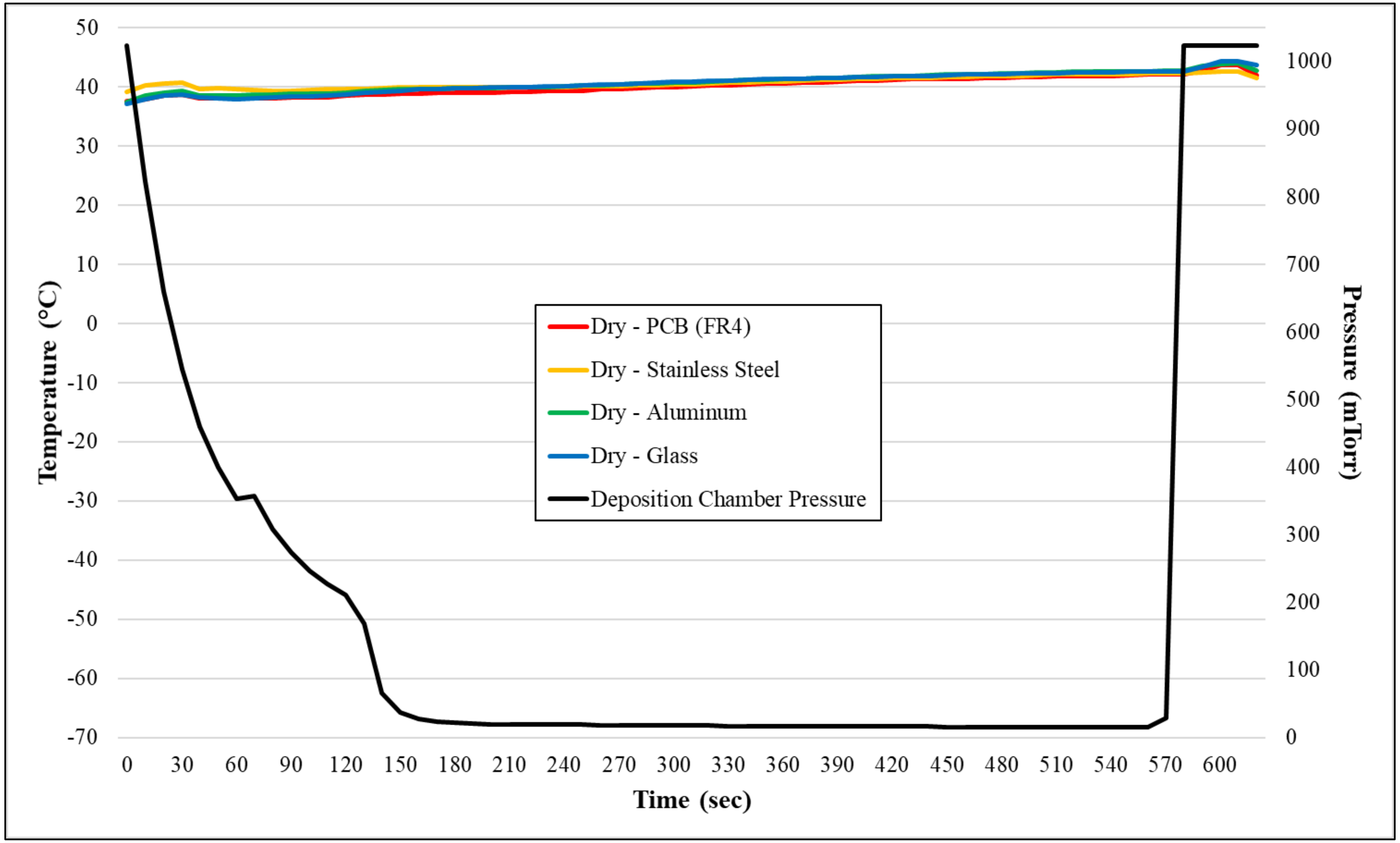
CS#2 – Experiments to Time Freezing of Water in CVD Chamber



- Snapshots from video captured through the Parylene CVD chamber's viewport
- Water boiled vigorously by the 2-minute mark and appeared frozen by 3 minutes

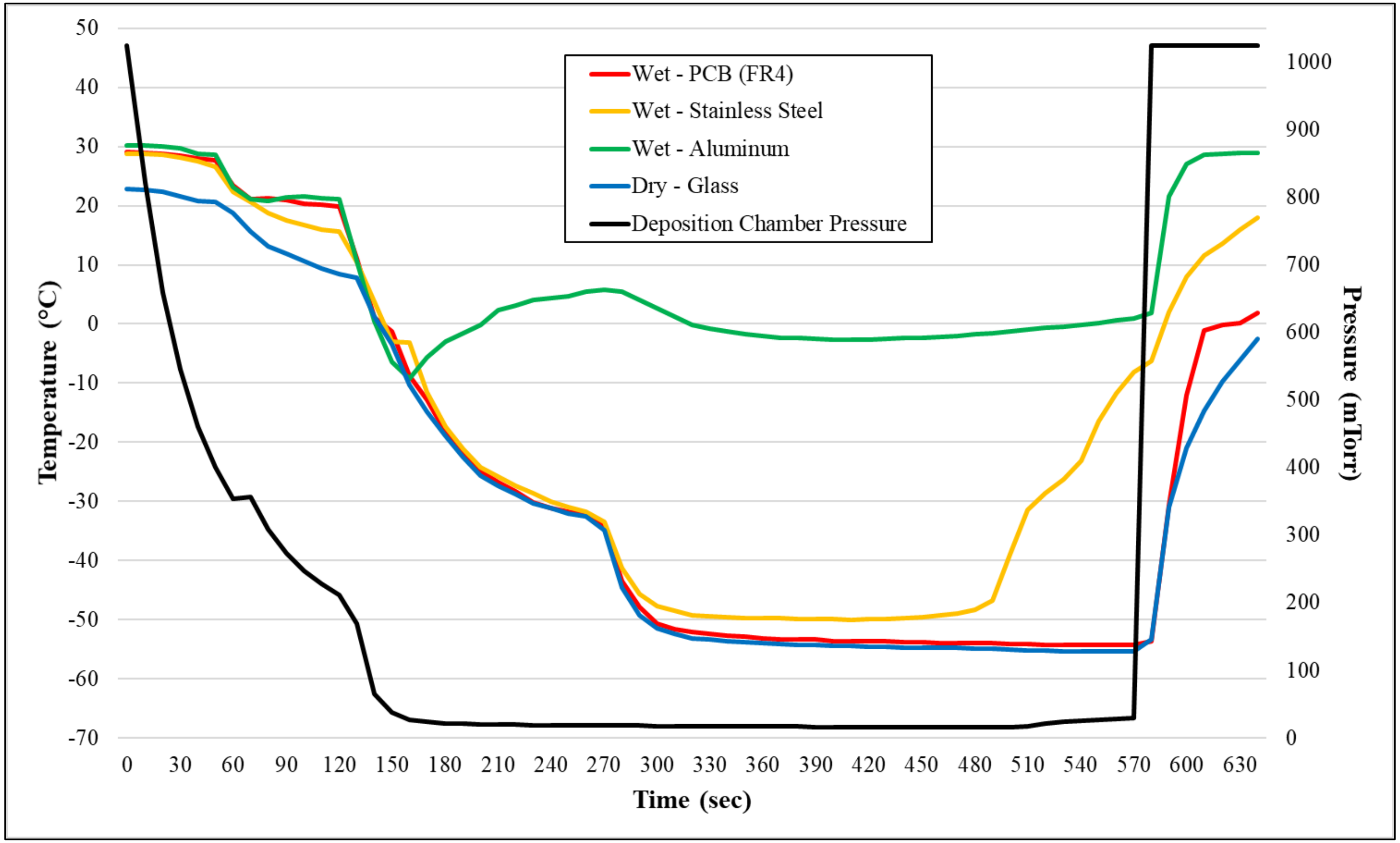
CS#2 – Video of Water Freezing in CVD chamber at 10x Speed

CS#2 – Temperature vs Time for Dry Substrates



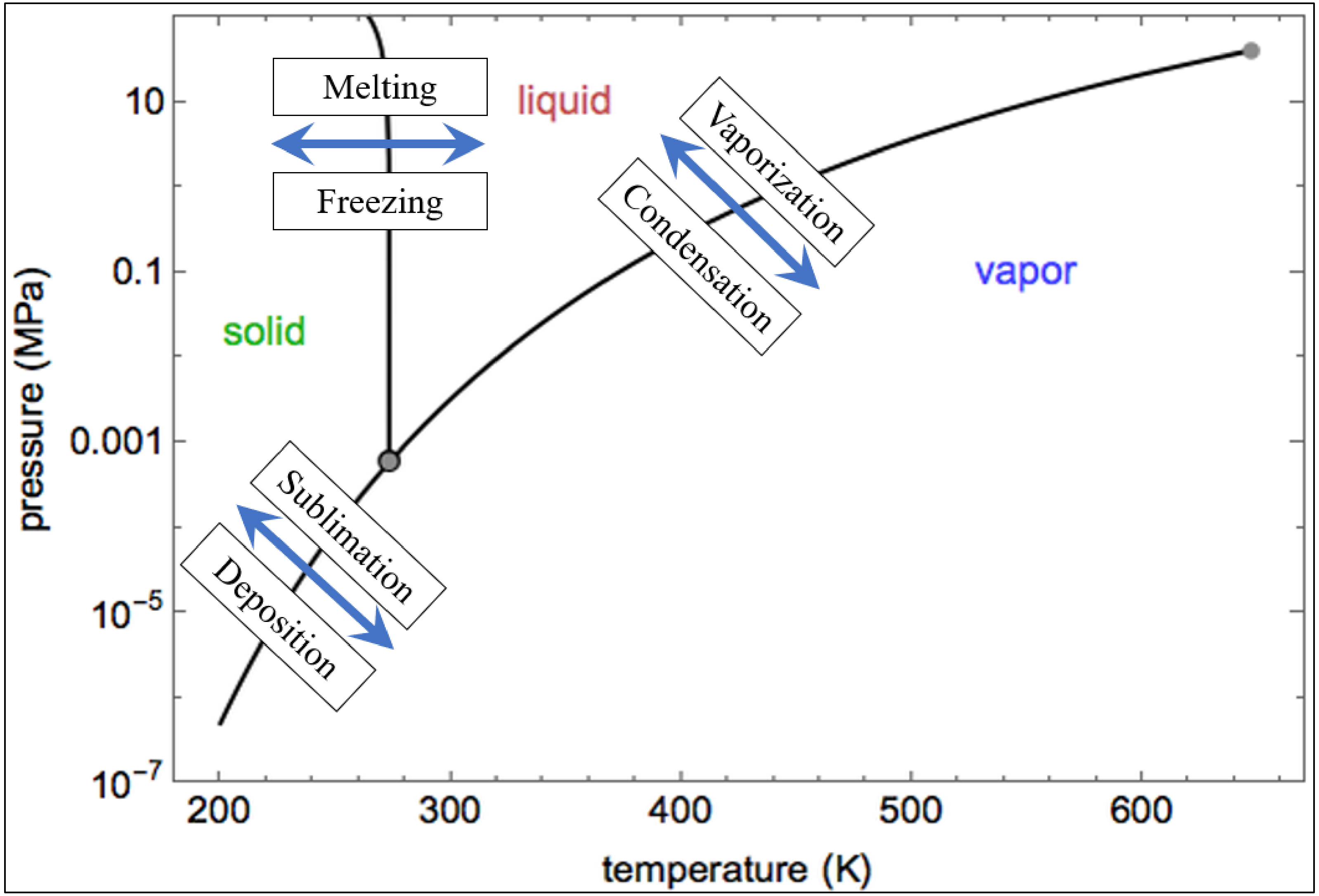
- Four different dry substrate materials were evaluated during pump down
- No appreciable difference was observed

CS#2 – Temperature vs Time for Wet Substrates

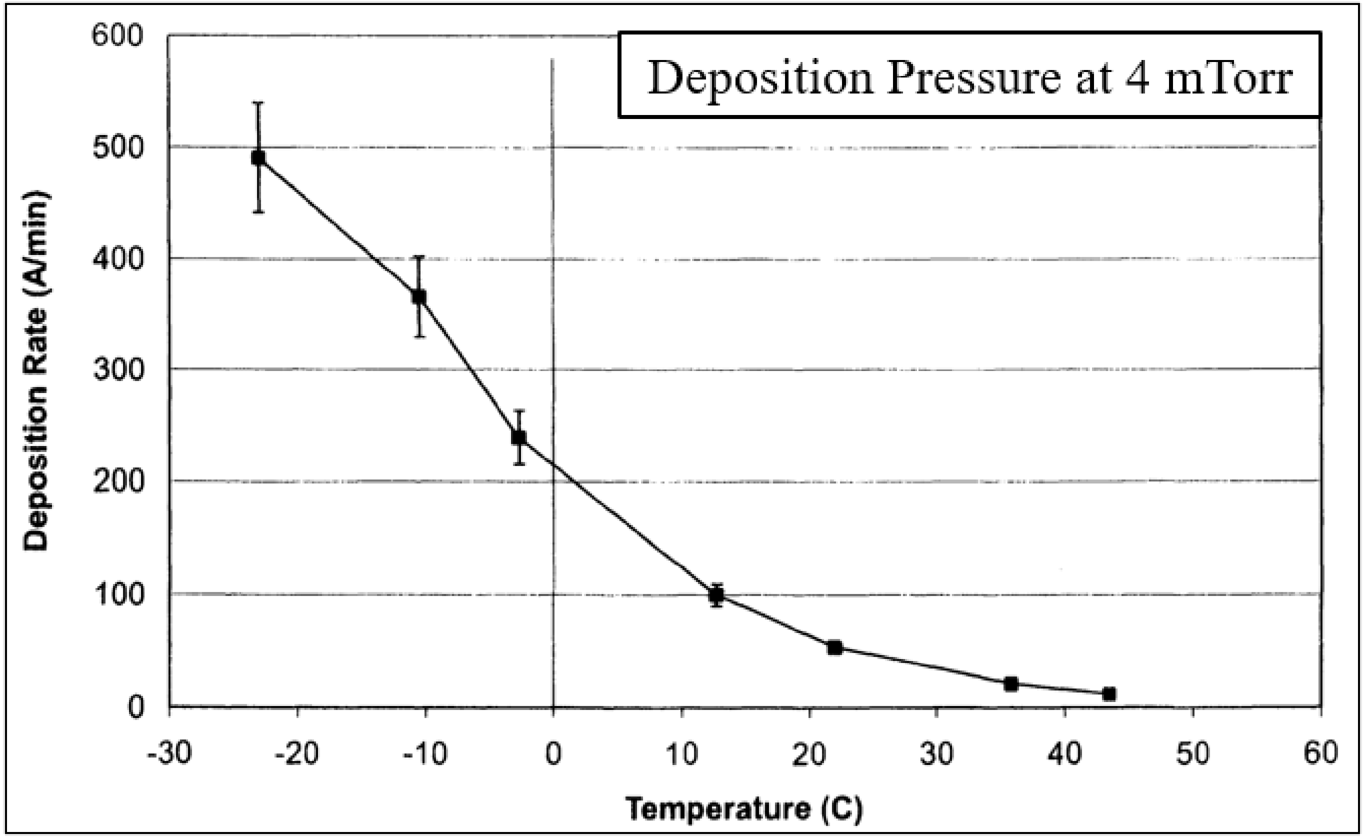


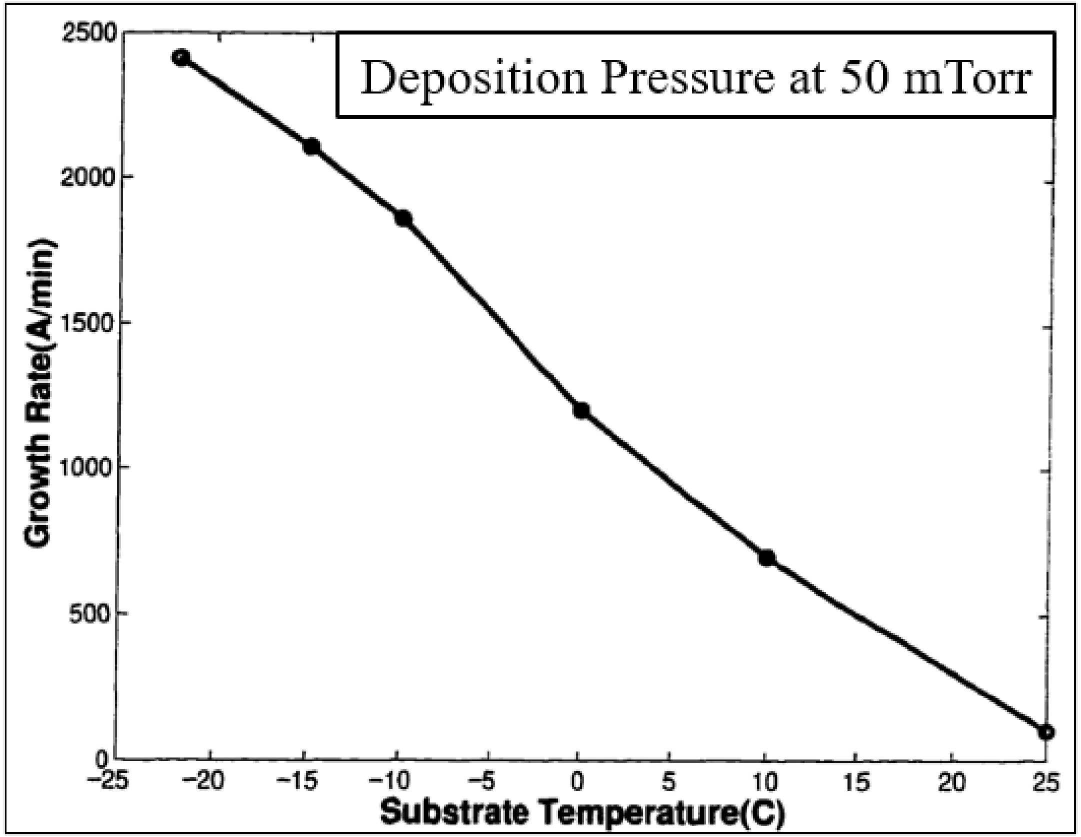
- Water added to different substrate materials and pumped down again
- Aluminum likely had ice form and break off thermocouple, so the lowest temperatures weren't reached

CS#2 – Pressure-Temperature Phase Diagram for Water



CS#2 – Deposition Rate vs Substrate Temperature for Parylene N





- Many studies have shown increased deposition rates with lowered substrate temperatures

- Ref.: (Left) J. B. Fortin, T.-M. Lu. "Chemical Vapor Deposition Polymerization: The Growth and Properties of Parylene Thin Films", Springer, New York, **2004**, p. 45. (Right) S. Ganguli, "Step Coverage of Metals and Interlayer Dielectrics in Multilevel Metallization." Rensselaer Polytechnic Institute, Troy, NY, **1997**, p. 130.

CS#2 – Root Cause & Process Improvements

- Root Cause
  - ***Higher moisture content in PCBAs led to degassing and evaporative cooling during the vacuum deposition process.***
  - Target coating thickness was achieved on non-thermally conductive parts, such as board and connector bodies, while metallic areas, such as connector pins and shield cans had significantly more coating than intended.
- Prevention
  - Various mechanisms were developed with the customer to assist with drying and degassing the parts before the start of the Parylene deposition.
  - Worked with customer to adjust the pump down sequence at the beginning of the deposition process to mitigate the degassing issue.
  - Recommended manufacturing and storing assemblies in a well-controlled environment, as well as baking the assemblies before coating.

Conclusions

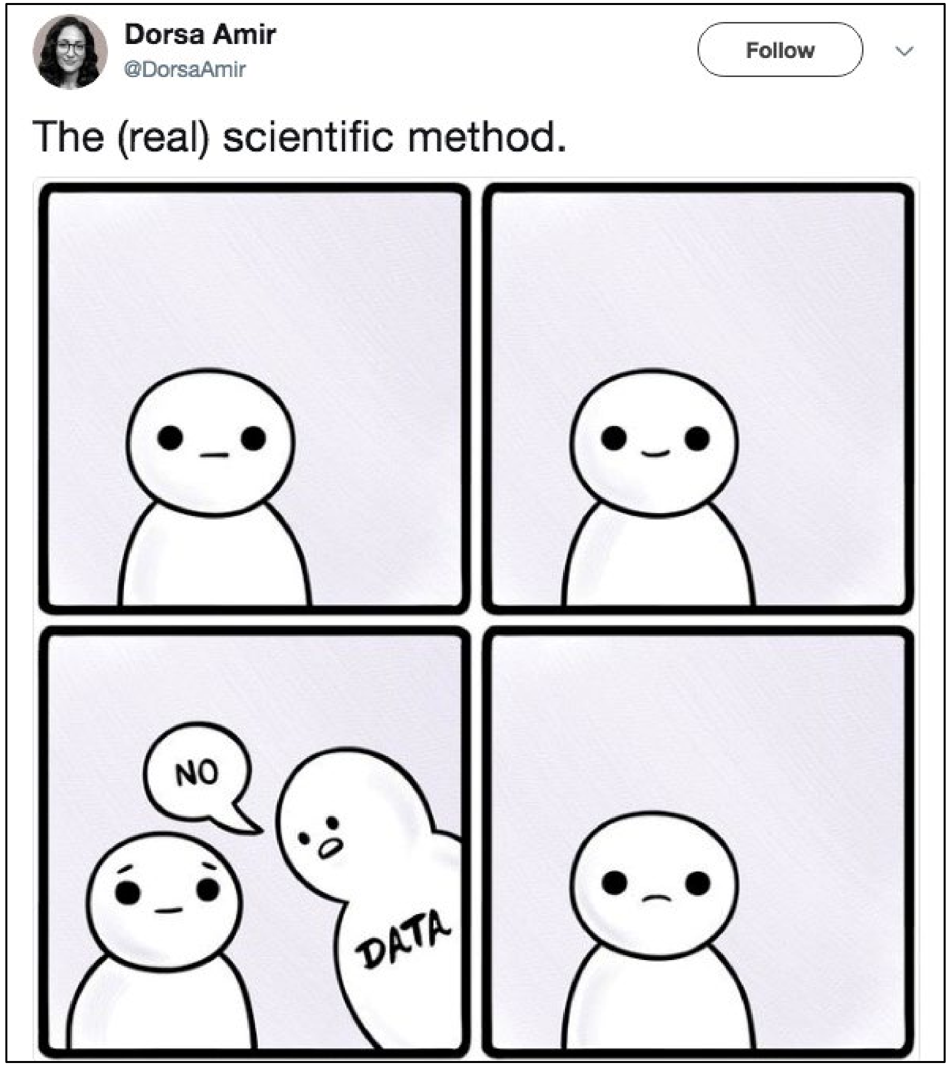
- There’s a reason behind the push for high levels of cleanliness, along with low moisture content in components and assemblies for high-reliability products in critical use applications.
- Evaporative cooling isn’t limited to water and can include any phase change material, such as reaction products in glues and other types of under-cured masking materials.
- The costs of cleaning, baking, and storing under industry recommended conditions, are not acceptable for many customers, we’ve helped their products pass rigorous testing criteria.
- Lessons were learned and through careful management of materials, equipment, and process, helps Parylene CVD coatings overcome moderate levels of “no-clean” flux residues and less than ideal degassing of assemblies on consumer electronics and other moderate-reliability products.

Acknowledgments

- HZO’s Global Team Members in the Application Engineering, Operations, Process Engineering, and Technology groups

- Scanning electron microscopy (SEM) was performed at the Materials Characterization Lab in the Materials Science & Engineering Department and the Surface Analysis Lab in the Utah Nanofab at the University of Utah

Q&A Session – Any questions?



Dorsa Amir
@DorsaAmir

The (real) scientific method.

Thank you!

Questions?