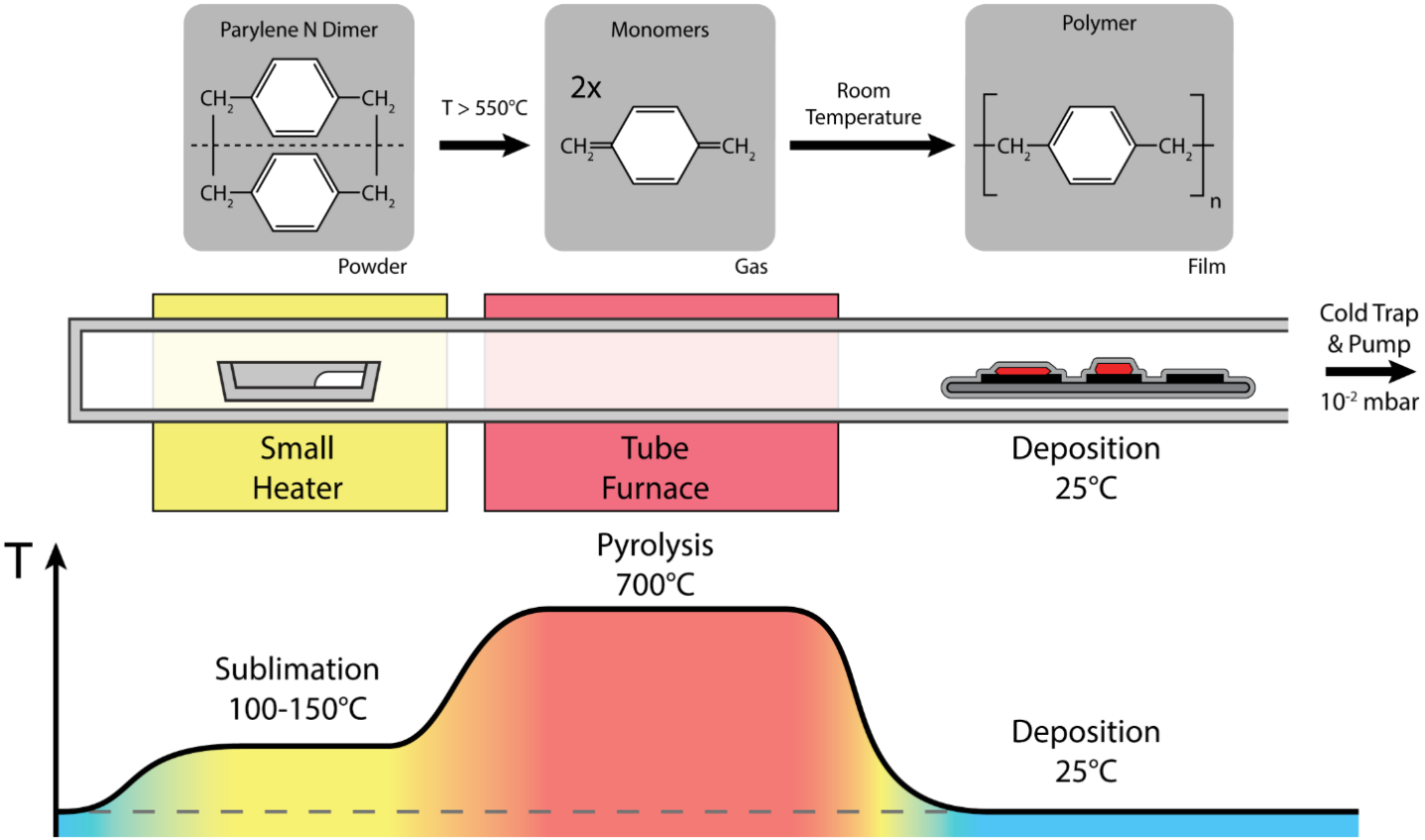
Technical notes on parylene deposition

29 April 2024

V. Bruevich, V. Podzorov,
Department of Physics, Rutgers University, NJ
bruevich@physics.rutgers.edu
podzorov@physics.rutgers.edu

Parylene deposition process:



Useful Refs.:

V. Podzorov, V. M. Pudalov and M. E. Gershenson, Field-effect transistors on rubrene single crystals with parylene gate insulator, *Appl. Phys. Lett.* **82**, 1739-1741 (2003).

R. W. I. de Boer, M. E. Gershenson, A. F. Morpurgo and V. Podzorov, Organic single-crystal field-effect transistors, *Physica Status Solidi (a)* **201**, 1302 (2004).

J. G. Gluschke, F. Richter, A. P. Micolich, A parylene coating system specifically designed for producing ultra-thin films for nanoscale device applications. *Review of Scientific Instruments* **90**, 083901 (2019).

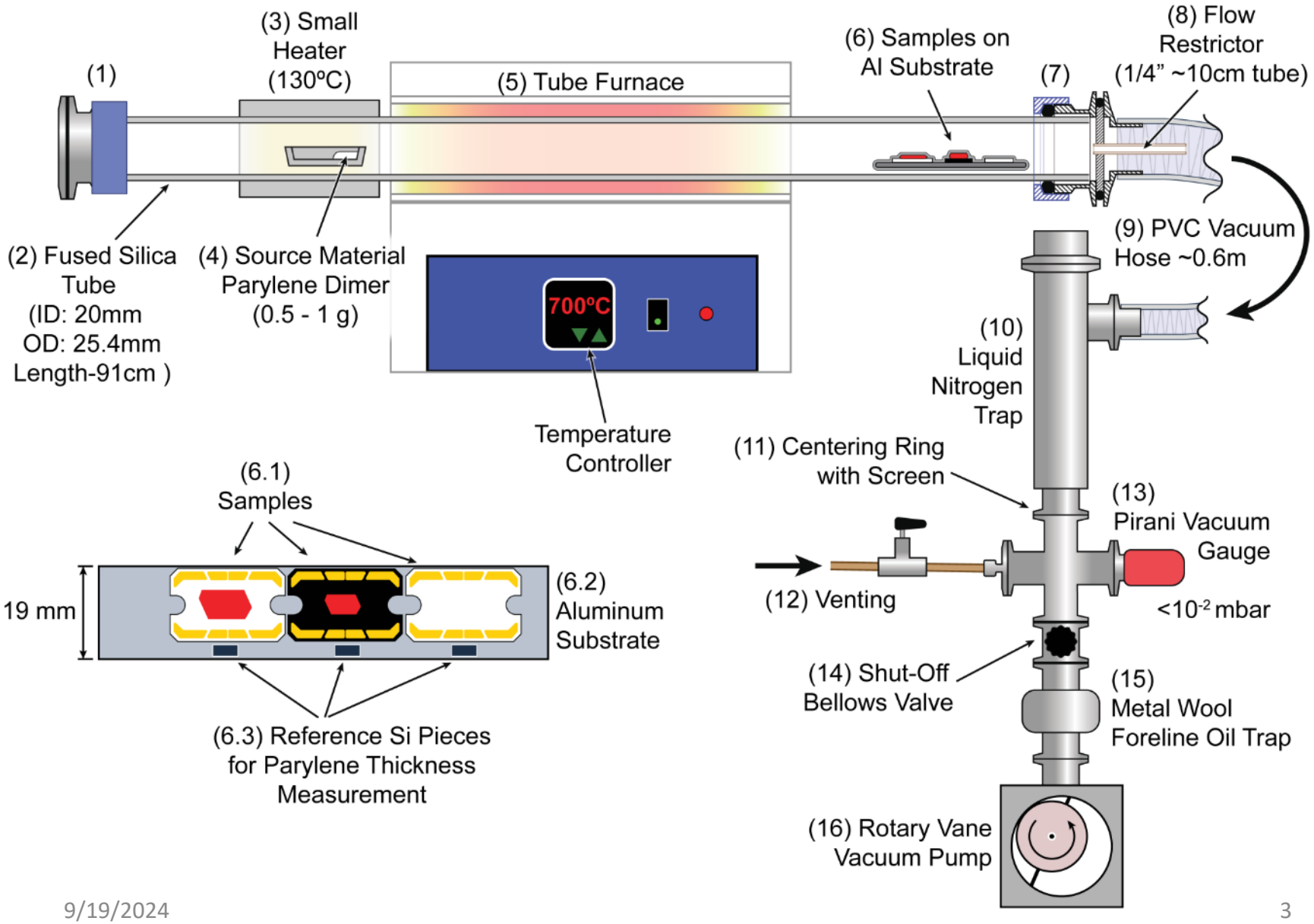
M. Gazicki-Lipman, Vapor Deposition Polymerization of para-Xylylene Derivatives - Mechanism and Applications, *J. Vac. Soc. Jap.* **50**, 601 (2007).

For parylene properties, see:

http://www.physics.rutgers.edu/~podzorov/parylene properties.pdf

https://scscoatings.com/parylene-coatings/parylene-properties/

Parylene deposition setup at RU:



List of setup parts:

(1), (7) Compression Fitting (*Quick-Fit/Swift-Seal*) to **KF25** flange.

(2) Fused Silica Tube: **ID 20 mm**, **OD 25 mm**, **36" length**; both ends enlarged to **OD 25.4 mm** to fit 1" standard compression fitting (see apendix).

(3) Small Heater for evaporation of parylene dimer (typically set to **130 C** for Parylene-N).

(4) Alumina Boat with parylene dimer powder (usually loaded with **0.5-1 g**, but might need more material for thicker deposition, > 2 μm).

(5) Blue-M tube furnace (set to **700 C** for Parylene-N, with the hot zone long enough for all the dimer molecules to undergo pyrolysis (splitting)).

(6) Samples on the Al substrate: samples should be placed closer to the right end of the quartz tube, at room temperature.

(6.1) Samples. Samples can be attached with a double-sided or single sided Scotch tape. Note that parylene coats even deep and very narrow spaces such as **10 μm** wide, **1 cm** deep gaps under samples.[link]

(6.2) Aluminum support substrate. The width of the substrate should be less than the ID of the tube (**19 mm** is perfect).

(6.3) Small pieces of polished silicon wafer needed for monitoring the interference colors (and thus thickness of the growing film) *in-situ* during the growth, as well as to measure the actual thickness of parylene film after the deposition using an ellipsometric setup.

(8) Flow Restrictor, needed to reduce the rate of monomer vapor removal from the reactor (quartz tube). If pumping is very efficient and no flow restrictor is used, then parylene polymerization on the substrates will be too inefficient/slow. In addition, because of the high flow of monomer towards the liquid nitrogen trap (10), too much monomer will condense and accumulate on it, which might lead to a *solid phase addition polymerization* chain reaction triggered during or after the deposition (when the temperature is increased). This reaction occurs as a little explosion (a burst), and, in most cases, can reduce the quality of the parylene film on the sample.[link]

(9) Vacuum-rated 1" steel-spring reinforced PVC hose. The PVC hose should be replaced, when too much parylene is deposited inside.

(10) Liquid nitrogen trap for collecting unreacted parylene monomer and preventing it from reaching the vacuum elements below.

(11) Centering ring with a screen/mesh preventing parylene flakes from falling in the vacuum system below.

(12) An inlet for venting the vacuum system (with a venting valve). It is located below the cold trap to prevent contaminating the valve with parylene. The system should NOT be vented with Ar, because it has a higher temperature of condensation than the temperature of boiling liquid N_2 at ambient pressure. Optimally, venting should be done with a nitrogen gas, with the gas pressure regulator set to **1.1 - 1.3 bar**.

(13) Pirani Gauge. It is located below the cold trap to prevent its contamination with parylene.

(14) Shut-off vacuum bellows valve. Used to isolate vacuum pump from the parylene deposition system.

(15) Metal Wool Foreline Oil Trap (TAR4CS100QF - Kurt Lesker).

(16) Rotary Vane vacuum pump. Trivac D8A (much smaller pump such as Edwards E2M1.5 can be used, if capable of pumping down to 10^{-2} **mbar**).

Parylene deposition steps (short, more details below):

1. Start by turning ON the furnace (5) and the pump (16) for preheating; the furnace should be empty (no quartz tube inside), shifted far back on the table towards the wall; the pump should be shut-off with the valve (14).
2. Attach your samples (6.1) and reference Si pieces (6.3) to the aluminum holder (6.2) using adhesive tape. Load the aluminum holder assembly (6) inside the quartz tube from its right-end side (7).
3. Wipe the boat (4) with dry clean paper wipes; fill in a new portion of parylene dimer powder near the right end of the boat (0.5 - 1 g of the powder for our normal process that results in the parylene thickness in the range 0.5 - 2 μm).
4. Place the boat (4) inside the quartz tube by sliding it in from the left end (1) of the tube. The correct position of the boat is marked on the tube.
5. Slide the small heater (3) and both Quick-Seal connectors on the quartz tube up to the limit and tighten the connectors (hand-tight).
6. Open the shut-off valve (14). The pressure (13) should reach 10^{-2} mbar in a few minutes provided the pump is in good condition. If the pump was already operating for more than an hour it will reach 10^{-2} mbar in less than a minute. If pumping is much slower, try replacing pump oil.
7. Pour liquid nitrogen into the cold trap (10). Wait a minute and add more after boiling receded. Check the vacuum level (13) - it should drop down to $1\text{-}2\cdot10^{-3}$ mbar in a few seconds.
8. Open the furnace (5) and slide it along the table forward (away from the wall), so that its center ends up right under the "*furnace zone*" of the quarts tube; do this while slightly lifting the left end of the tube (1) with your left hand. Once the furnace is in the right position, lower the left end of the quartz tube, close the furnace, and **wait** until the furnace's temperature reading goes back to 700 ^{o}C.
9. Turn on the small heater (3) output (plug its cord into the power supply). Set the temperature (SP1) to 150 C (for parylene-N and parylene-F).
10. A few minutes after the temperature reaches the setpoint (150 C), the color of the reference Si pieces (6.3) will start to change. Change the set temperature of the small heater (3) to 130 C. *Keep observing the changing coloration of the Si pieces.*
11. After the required number of color changes, turn OFF the small heater (3) by unplugging it, shift it leftward to the end (until it props against the Quick-Seal fitting (1), almost touching it), and adjust the external fan to blow on the place with the boat inside (3). This helps to cool the boat faster and stop evaporation of the dimer.
12. After a couple of minutes turn OFF the furnace (5), open it and slide it to the back of the table while lifting the left end of the tube (1) with your left hand.
13. Let the quartz tube cool down completely to room temperature under the blowing fan before venting the system. Immediately after venting, remove the liquid nitrogen trap's insert.
14. Clean the tube if needed: usually, at least each 3rd deposition, or when a substantial contamination/darkening is seen in the furnace zone of the tube.

Various notes:

1. Check the color and level of oil in the glass-tube indicator of the forvac pump. The oil should be transparent, light colored and free of debris. The level (measured when the pump is off) should be between Hi and Lo marks of the indicator.

   Avoid cheap vacuum pump oils, because they tend to contaminate the vacuum system (and your samples), slow down pumping, and degrade much faster. The most important parameter of the oil is its vapor pressure at the working temperature (~ 70 ^{o}C). Synthetic vacuum oils, although expensive, are the best. High-quality mineral oil, like Edwards ULTRAGRADE 19, works well.

2. The sample might get slightly heated by the furnace if placed too close to it. The temperature of the sample zone can be stabilized by blowing air using an external fan, which leads to a more homogeneous distribution of parylene thickness among multiple samples. However, care should be taken to prevent the fan from blowing directly into the furnace's opening or on the liquid nitrogen trap.

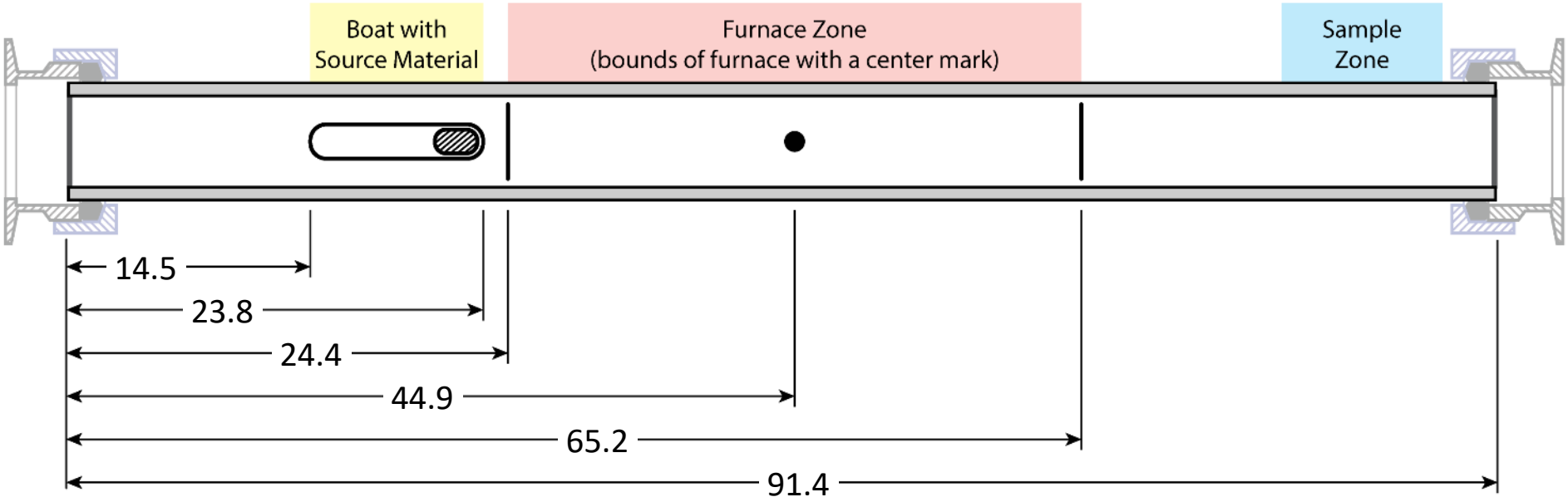
3. Before using the system after a long break, inspect all O-rings, replace the ones with cracks, and clean all O-rings with Kim wipe tissues soaked in isopropanol or ethanol.

4. When pumping air or solvent vapors, open the *gas ballast* of the pump for a few minutes at the beginning to reduce oil contamination of the vacuum system. Close the gas ballast after that and keep pumping.

5. The simplest way to open the reactor is to loosen the Quick-Seal vacuum ports (1, 7) and slide the quartz tube out while gently (and slightly) rotating it around its long axis. Open one Quick-Seal vacuum port at a time.

6. With the quartz tubes having smooth, fire-polished edges used in our system, the Quick-Seal assembly can be put together by pushing the end of the tube into the loosened (unscrewed) Quick-Seal fitting, while slightly rotating the tube around its long axis.

Parylene deposition tube markings:



1. The quartz (fused silica) tube for parylene deposition is marked with a temperature resistant marker (for example, Markal 97303) as shown on the drawing. Black lines are the markings.

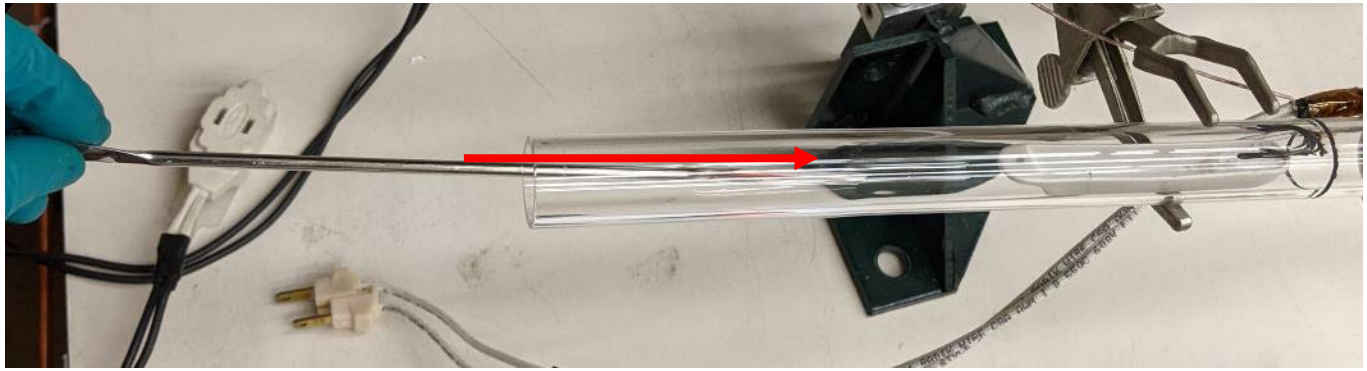
2. New tubes can be marked using this drawing as a guide. The position of each mark is given in cm relatively to the left edge of the tube.

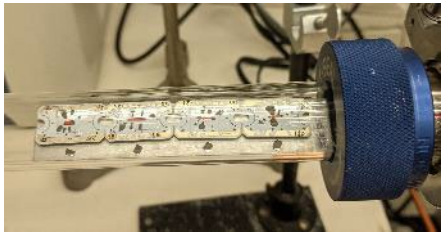
3. The markings can fade after cleaning or mechanically scratching the tube. They should be reapplied if they become too faint.

4. Temperature resistant marker can be dissolved by organic solvents, before it is annealed at high temperature. Thus, it is recommended to first fix the new markings by annealing the entire tube at high temperature (> 200 ^{o}C), before it can be cleaned with organic solvents.

Detailed parylene deposition steps (ref. to # on slide 5):

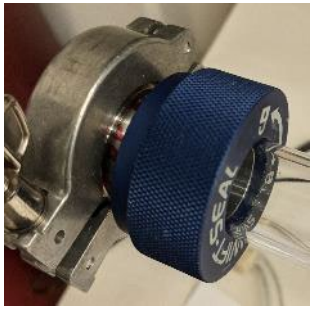
3. The photos show our typical loads of parylene-F (left) and parylene-N (right). The load's weight can be measured with an electronic balance (remember to account for the weight of the empty boat).

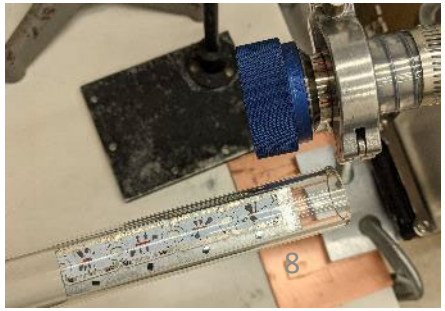




4. Carefully slide the loaded boat inside the quartz tube through the opening on the left, as shown above. It is important to minimize the spilling of the powder. Position the boat according to the black marks on the tube.

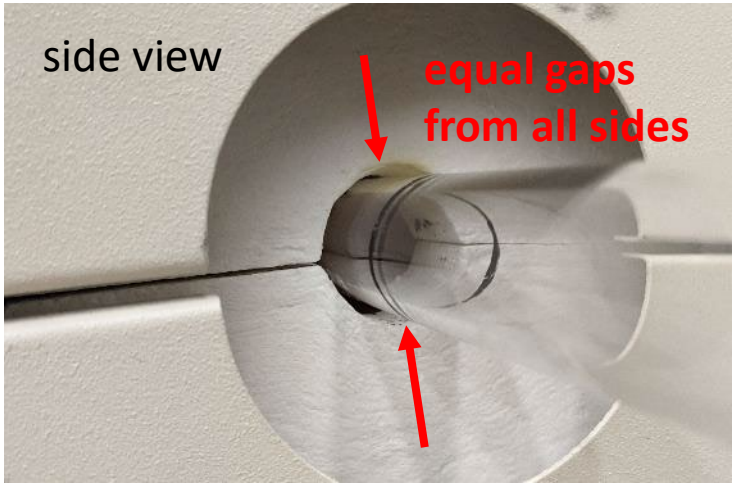
5. Slide on the small parylene heater over the tube's left end. Make sure the samples (on the aluminum holder) are loaded and properly positioned inside, near the right end of the tube. Then, install the Quick-Seal vacuum flanges.



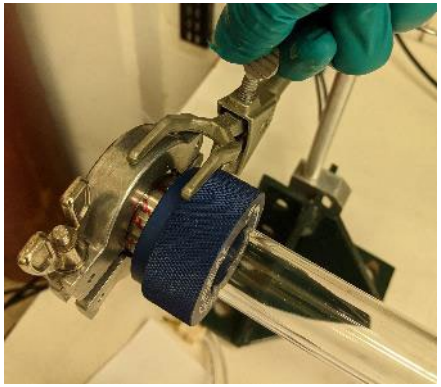


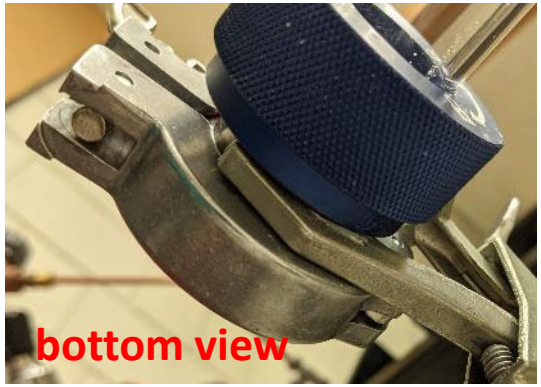
Supporting the tube to fit the furnace:

In the optimal arrangement, the quartz tube should be supported by its both ends and positioned horizontally to fit inside the Blue-M tube furnace's opening *coaxially* and without touching the heaters.

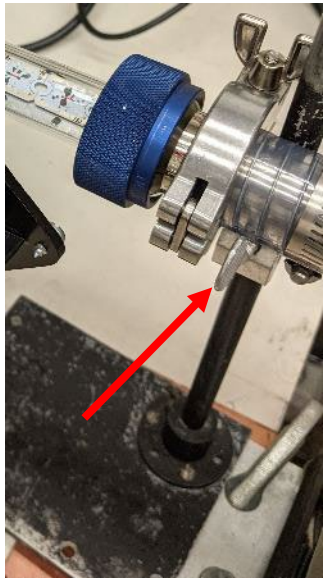


left holder





right holder



The furnace should be freely movable, without scratching/touching the quartz tube, by gently sliding the whole furnace along the table top. Ideally, one should make initial adjustments of the tube's supports before turning the furnace on. Small adjustment can be made after installing the furnace for the experiment.

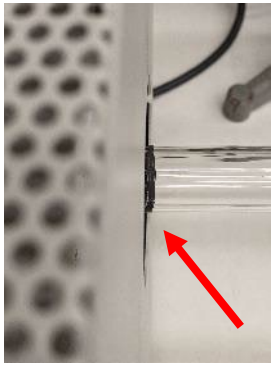
Filling the liquid nitrogen (LN) trap:

7. To fill the LN trap, first, pour some LN into the trap (use a foam cup and a funnel), wait until boiling recedes, then gradually add more to top it off.

During the parylene deposition, keep adding LN from time to time to keep the trap filled. Note that when vacuum in the system is good, boiling of LN subsides. The vacuum level usually falls below $2 \cdot 10^{-3}$ mbar shortly after LN is added to the trap. This pressure also depends on the length of the PVC tube (9), so this tube should not be too long.

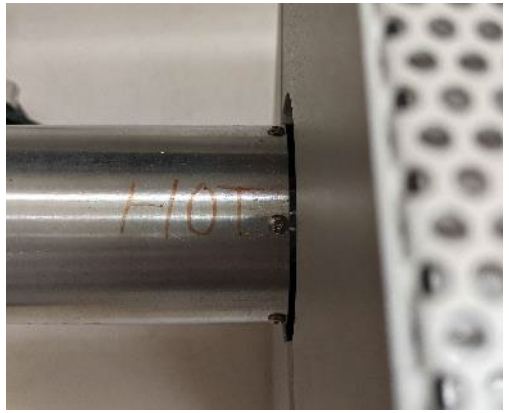
8. After the LN trap is filled and Blue-M reached 700 °C, open the furnace and *quickly but carefully* shift it to its correct position under the quartz tube. Close the furnace and make sure the black marks on the tube are aligned with the furnace's sides, as shown on the photos (refer to tube markings slide above). Once the furnace is in position, wait for its *T* to recover to 700 °C. After that, with the quartz tube and everything inside under vacuum, avoid waiting for too long, because the parylene dimer in the boat on the left may start evaporating due to the heat reaching out from the furnace.

top views



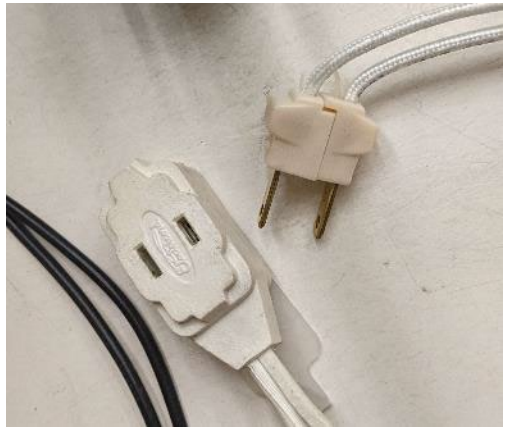
Positioning and using the small heater:

Position the small parylene heater so that its right side is “in-plane” with the left side of the case of Blue-M furnace (its outside metal case) as shown on the photo.

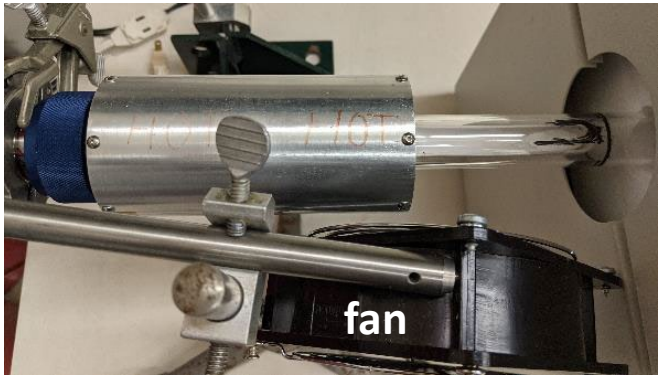


Observe the “HOT” warning sign on the small heater and avoid touching it with bare hands or while wearing regular laboratory gloves. The temperature of the outer surface of this heater may reach > 100 °C, which will cause skin burns on touch.

9. After the heater is properly positioned and the temperature of Blue-M furnace reached 700 °C, with the quartz tube and everything inside under vacuum, turn the small heater on by plugging its power plug into the receptacle of the power output of the *T* controller (shown on the photo). Check the *T* controller’s indicator to make sure that *T* of the small heater is rising and the correct setpoint is set.



11. To abruptly stop the evaporation of the parylene dimer, shift the small heater along the quartz tube to the left, and turn the fan on to blow air onto the exposed section of the quartz tube that contains the boat as shown on the photo (double check that the airflow is directed towards the tube). Turn off the small heater by unplugging its power connector (show on the picture) but leave the Blue-M furnace on for some time to process any remaining vapor of the dymers.

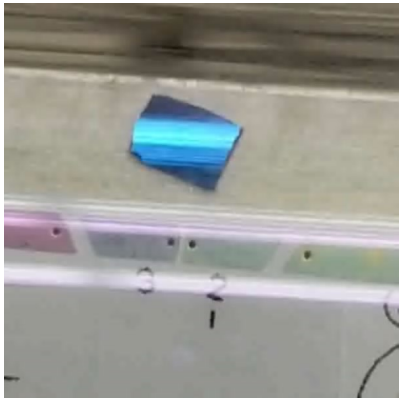


Be careful when plugging/unplugging the small heater, because the plug is made of two parts that can suddenly split exposing your finger to 110 V.

Observing the periodic change in color vs. parylene thickness:

- During the parylene deposition, the thickness of the growing film gradually increases with time. Because the process parameters and conditions, such as the vacuum level, temperature, initial amount of material etc., are hard to control precisely, the thickness of the grown film might be hard to control by these parameters.
- A better way of controlling the thickness is to place a small flat chip of a Si wafer near the sample, inside the quarts tube. By *in-situ* observing the periodic color change of the light reflected off the chip, the process can be stopped when the desired film thickness is reached. When the samples are collected, the exact thickness of parylene can be measured more accurately using an ellipsometric setup (SemiconSoft) or other methods (optical micro interferometry or profilometry).
- The video shows a typical color change timelapse (accelerated) within approx. one period. The thickness can be estimated by counting the number of full color-change periods (best by counting the *violet*) and multiplying this number by 180 nm (if observed at a normal).

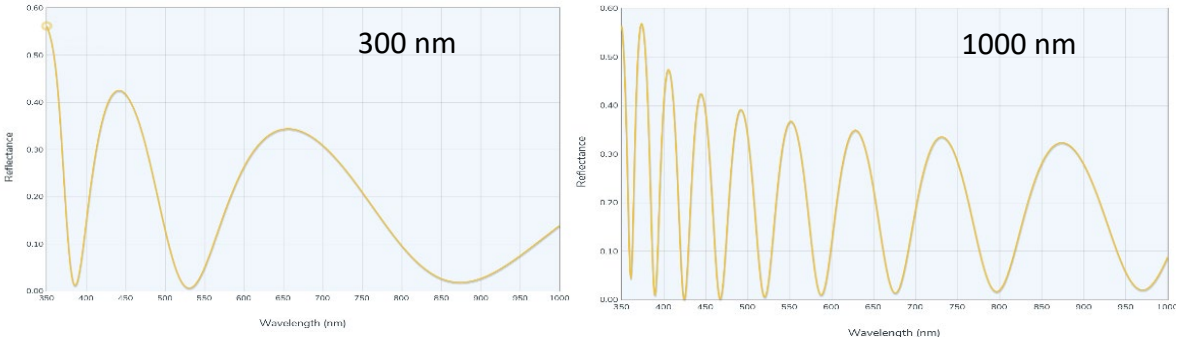
video (accelerated)



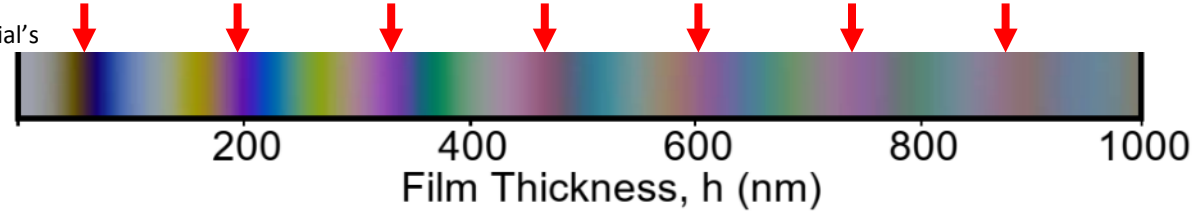
For general information about the phenomenon, see *light interference in thin films*.

This example calculation gives intensity of light reflected off a thin dielectric film (of a thickness indicated) as a function of wavelength. Certain wavelengths are reflected more than others, giving the film its colored appearance when viewed in white incident light. With a growing thickness, a color dominant at one thickness, for instance violet at 200 nm (see below), will periodically extinguish and come back up again at a greater thickness.

Spectral reflectance calculator



An example of a color change of light reflected off a thin film of Si_3N_4 of varied thickness:
Note the steps of violet.
The step size depends on material's refractive index ***n***.



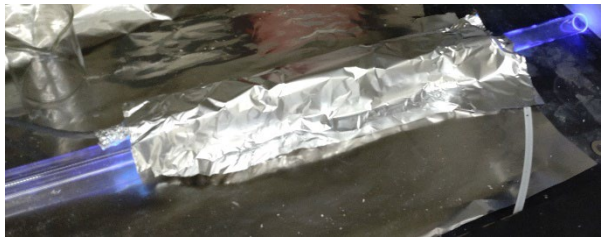
color vs thickness for Si_3N_4 film from reference

Instructions for cleaning the quartz tubes and PVC hose:

1. Cleaning with a UV-ozone lamp (case of (semi)transparent parylene deposits):

If darkening of the quartz tube due to parylene carbonization is not too severe and the tube is still (semi)transparent, the tube can be cleaned using a UV-ozone lamp. We use ozone-generating mercury lamp **ZW 38D 15-Y-375** from Amazon (UV-C with significant 180 nm band). It should produce a significant amount of ozone from air, so (1) check if it does, (2) use it only under a fume hood (*ozone must not be inhaled*). If a low-power lamp is used, it might take > 1 h to clean the deposits.

- Place lamp directly on top of the tube inside the working fume hood (top photo).
- Cover the tube and the lamp tightly with Al foil (bottom photo). In this task, Al foil can be reused.
- Turn on the lamp. Minimize exposure of your eyes and skin to the UV light coming from the lamp. Do not stare directly at the operating lamp. Turn of the lamp every time you want to remove the foil.



2. Cleaning by anneal in a furnace in air (case of very dark and non-transparent carbonized deposits):

If the tube is heavily contaminated by carbonized deposits, making it significantly opaque (non-transparent), so that UV light will not pass through the walls, it can only be cleaned with: (1) heat + oxygen, (2) aggressive chemical cleaning such as a piranha solution (not recommended).

For cleaning the tube with heat, put the open tube into the furnace at 700 °C and shift it gradually (by steps) so that the tube is heated from one end to the other. A fan can be places outside of the tube to force smoke to exit from one end (the end that will be heated the last.)

3. Cleaning the quartz tubes and PVC hose with a brush:

Parylene cannot be dissolved in organic solvents. However, it can be stripped off mechanically (with a long nylon brush) and then washed away with any solvent. This step is recommended prior to methods 1 and 2 above.

PVC hose should be periodically scratched-cleaned with a brush from inside to remove thick parylene deposits that can eventually delaminate off the wall, obstruct the tube during pumping and compromise vacuum.

Deposition of parylene-F:

- We normally use parylene-N as an encapsulant or a gate dielectric material. However, for some projects parylene-F is preferred. Parylene-F has a better thermal stability, lower dielectric constant (2.20), but it is much more expensive and typically less pure.
- Parylene-F can be grown using the same settings as parylene-N: temperatures of the small heater 130 °C, and Blue-M furnace 700 °C.
- Unlike parylene-N, a single run of Parylene-F (or parylene-C) deposition usually results in a very significant contamination of the quartz tube with a black carbonized deposit in the hot zone. Unless a very thin parylene layer (< 300 nm on the sample) is grown, the tube will have to be cleaned after each deposition.
- Perhaps, certain impurities in the parylene-F dimer powder are responsible for the carbonization of the quartz tube. This carbonization leads to a rather quick and noticeable decrease in the monomer concentration downstream, leading to the film growth virtually terminated after a quick initial stage of the deposition. This effect limits the thickness of the grown parylene-F film. If the process is ran further, all evaporated parylene-F material is absorbed by the carbonized walls of the high-temperature zone acting as a catalyst for molecular decomposition.
- Usually after each deposition, the carbon contamination of the tube in the hot zone is too dense to permit UV-ozone cleaning. Deposited carbon absorbs most of the UV light coming from the Hg-lamp outside, preventing the generation of ozone inside the quartz tube. Thus, in this case, the method of heating in air (or oxygen) should be used. This can then be combined, if necessary, with a second-stage cleaning using the UV-ozone method.
- For estimating the thickness of parylene-F layer, the exact same ellipsometric/optical properties (refractive indices) as for parylene-N can be used. Capacitance measurements of parylene-F films show that if the film's thickness is estimated this way, the dielectric constant matches the literature value of 2.20.
- Parylene-F can be ordered from ***Ambeed*** (Parylene F Dimer CAS 1785-64-4 97% 10.00g).

Appendix A. Ordering quartz tubes:

- The quartz tubes required for parylene growth need to be robust, able to withstand strong thermal cycling, and can be easily cleaned.
- To correctly fit into the Quick-Seal vacuum compression fittings, the tube must have an OD required by the Quick-Seal's specifications: 1.00 ± 0.01 inch OD. In addition, both ends of the tube must be firepolished to prevent damaging the rubber O-rings of the compression fittings. These features require additional work by the company selling the quartz tubes, thus adding to the cost. Somehow, closest standard sizes of tubes typically available by default are smaller than OD 1 inch, typically OD 22 mm ± large margin, thus, the company needs to enlarge (flare out) the tube at both ends.
- Thick-wall quartz tubes are highly recommended, because it makes the tubes much more resilient and lasting considering the relatively high cost of these tubes.
- Use the following specification when ordering quartz tubes for parylene growth setup:

  Clear fused quartz tubing 20mm ID x 25mm OD x 36" long.
  2" on each end sized to 1+/-.010" OD to accommodate a 1" compression fitting.
  Both ends firepolished.

Appendix B. Small Heater for parylene dimer evaporation.

The main use of this heater is evaporation of parylene precursor (parylene dimer) of any type.

Technical parameters (nominal):

- Maximum operating temperature (limited by the copper tube supporting the heating element) is 450 ^{o}C. Tested up to 300 ^{o}C. Normally operated at 130 ^{o}C (for evaporating parylene dimers).
- The temperature is controlled with external PID temperature controller. The rate of heating of the inner copper tube is very fast (at the heating cord's power of 125 W), and the *T* overshot is negligible.
- Heat transfer between the copper and quartz tubes is relatively slow, quartz tube's temperature stabilizes in > 30 min.