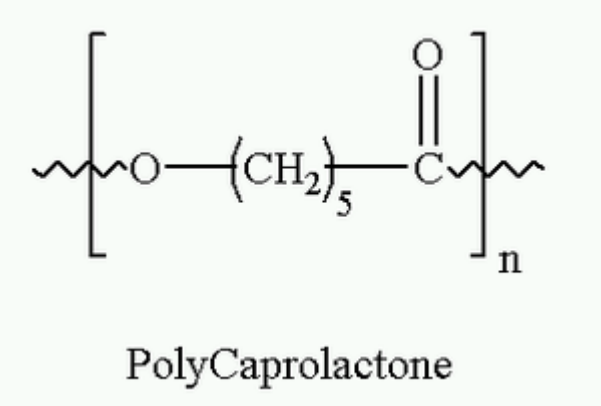
Polycaprolactone (PCL) Film Deposition

Standard Operating Procedure

Faculty Supervisor: Prof. Robert White, Mechanical Engineering (x72210)
Lab Manager: Dr. James Vlahakis (x75155)
Safety Office: Peter Nowak x73246 (Just dial this directly on any campus phone.)
(617)627-3246 (From off-campus or from a cell phone)
Tufts Emergency Medical Services are at x66911.

Revised: July 26, 2018

Goal:
Produce a thin (1-100 micron thick) PolyCaprolactone (PCL) film and release it from the substrate. A thin sucrose film will be used as the sacrificial release layer. See Bettinger, et al, Advanced Materials 2006, 18, 165-169 for more information on the sucrose film process.



(Wikimedia Commons)

1. Material Requirements:

1.1 Equipment and tools: Spin processor, "Dirty" Oven, "Dirty" Hotplate, dedicated graduated cylinder, two dedicated 250 mL glass beakers, one dedicated glass petri dish large enough to hold the silicon substrate, silicon substrate, wafer tweezers, disposable pipettes.

1.2 Chemicals: **Dichloro Methane** (Methylene chloride; Sigma-Aldrich 270997), **Sucrose** (Sigma-Aldrich S0398), **PolyCaprolactone** pellets (Sigma-Aldrich 440744, average molecular weight, M_n=70,000 to 90,000)

1.2.1 Hazards associated with chemicals:

1.2.1.1 Dichloro Methane, also called Methylene Chloride, CAS# 75-09-2, is a suspected carcinogen, and acutely toxic if ingested. It is a mild skin and respiratory tract irritant. It has a boiling point of 40 °C. Not flammable or combustible. Chemically stable under normal conditions. **ONLY WORK WITH Dichloro Methane in the fume hood. Wear gloves at all times.**

1.2.1.2 Sucrose, $C_{12}H_{22}O_{11}$, CAS #57-50-1, is a non toxic, water soluble, biodegradable, biocompatible sugar. It is not flammable. Wear gloves.

1.2.1.3 Polycaprolactone, CAS #24980-41-4, is a non toxic, biodegradable, biocompatible polymer. It is not flammable. It has a melting point of 60 °C. Wear gloves.

1.3 Engineering Controls: **Conduct procedures in the fume hood**. Dispose of chemicals as described at the end of this document.

1.4 Personal Protective Equipment: Nitrile gloves and eye protection required for all procedures.

2.0 Procedure:

2.1 Wafer should be clean prior to starting processing. A Piranha clean (see Piranha clean SOP) and O_2 plasma clean (See March RIE SOP) are suggested.

2.2 Sucrose solution preparation (90% weight by volume; 90 %w/v) [following Bettinger, et al, Adv. Mater., 2006, 18 165-169] :

- **2.2.1** Place the small (~250 mL) solution beaker on the scale.
- **2.2.2** Tare the scale.
- **2.2.3** Add 90 g of sucrose to the beaker (use a small disposable plastic spoon).
- **2.2.4** Measure 100 mL of DI water into the dedicated graduated cylinder.
- **2.2.5** Pour the 100 ml of DI water into the beaker.
- **2.2.6** Mix with the plastic spoon until fully dissolved.
- **2.2.7** Dispose of the spoon in the non-hazardous waste trash can.

2.3 Spin on sucrose layer (following Bettinger, et al, Adv. Mater., 2006, 18 165-169):

- **2.3.1** Line "dirty" spin processor bowl with aluminum foil or fab wipes if desired.
- **2.3.2** Put clean silicon wafer on the "dirty" spin processor and ensure it is center.
- **2.3.3** Load sucrose solution onto the wafer with a disposable pipette. Use enough solution to create a circular puddle approximately 2/3 of the wafer diameter.
- **2.3.4** Dispose of the pipette in the non-hazardous waste solid trash.
- **2.3.5** Spin at 500 rpm for 4 seconds, 3000 rpm for 30 seconds. (Spin speed can be varied to adjust sucrose film thickness. No data on sucrose film thickness is available at the time of writing.) See Laurell Spinner SOP for more information on spin coating.
- **2.3.6** Prebake on the dirty hotplate at 95 ^{o}C for 120 seconds.
- **2.3.7** Postbake in "dirty" convection oven at 120 ^{o}C for 24 hours.

2.4 PCL solution preparation:

- **2.4.1** Place the small (~250 mL) dedicated PCL beaker on the scale.
- **2.4.2** Tare the scale.
- **2.4.3** Add PCL pellets to the beaker to get the desired concentration. [Concentration will affect film thickness after spinning. No data is available at the time of writing. Start with 6 % w/v as a guess for starting point, data will need to be gathered.] Assuming you are using 100 mL Dichloro methane (see next step) then 6 g for 6% w/v, 4 g for 4% w/v etc.
- **2.4.4** Measure 100 mL of Dichloro Methane into the dedicated graduated cylinder.
- **2.4.5** Pour in 100 mL of Dichloro Methane into the beaker.
- **2.4.6** Mix with a plastic spoon until fully dissolved.
- **2.4.7** Dispose of the spoon in the solid solvent waste trash can.

2.5 Spin on PCL film:

- **2.5.1** Line "dirty" spin processor bowl with aluminum foil or fab wipes if desired.
- **2.5.2** Put silicon wafer with sucrose film on the "dirty" spin processor and ensure it is center.
- **2.5.3** Load PCL solution onto the wafer with a disposable pipette. Use enough solution to create a circular puddle approximately 2/3 of the wafer diameter.
- **2.5.4** Dispose of the pipette in the solvent solid waste trash.
- **2.5.5** Spin at 500 rpm for 4 seconds, 3000 rpm for 30 seconds. (Spin speed can be varied to adjust film thickness. No data on PCL film thickness is available at the time of writing.) See Laurell Spinner SOP for more information on spin coating.
- **2.5.6** Remove wafer from the spinner and cover (in a petri dish, box, or other container to avoid particles from dropping on the wafer… leave some vent holes for solvent fumes to escape).
- **2.5.7** Allow wafer to air dry at room temperature for > 6 hours.
- **2.5.8** Additional hotplate, oven, and/or vacuum oven processing may modify film properties. No data is available at the time of writing. Some authors reflow polymers on a hotplate at temperatures near or above melting point (60 ^{o}C for PCL), and some dry in a vacuum at room temperature for as long as 24 to 48 hours. Experiments are needed to determine effects on film properties.

2.6 Releasing the PCL film from the substrate:

- **2.6.1** Pour enough DI water into the glass petri dish to more than cover the sample.
- **2.6.2** Place the wafer with the films into the water.

2.6.3 Allow the sample to soak for 24 hours at room temperature. Sucrose film will dissolve and PCL film should detach from the substrate.

2.7 Cleanup:

2.7.1 Turn off the hotplates and ovens. Throw away any fab wipes or tinfoil in the solvent/photoresist trash.

2.7.2 Remove the hotplates from the hood.

2.7.3 Make sure the spinner has been cleaned according to the procedures in the Spinner SOP.

2.7.4 Pour excess PCL solution into mixed solvent waste (mix with acetone, isopropanol, methanol, etc).

2.7.5 Rinse PCL solution beaker with water 3 times, pouring waste water into mixed solvent waste.

2.7.6 Pour excess sucrose solution into dilute acid/base waste container (5 gallon HDPE jug). Rinse beaker with water 3 times, pouring waste water into the dilute acid/base waste container (5 gallon HDPE jug).

3.0 Storage:

3.1 Dichloro methane should be stored in the solvent cabinet.

3.2 PCL and sucrose precursors should be stored in the photoresist cabinet.

4.0 Waste Disposal:

4.1 Dichloromethane and PCL waste:

4.1.1 Solid waste should go in the solvent/photoresist trash.

4.1.2 Liquid waste should go in the mixed solvent/photoresist liquid waste bottle.

4.2 Sucrose waste:

4.2.1 Solid waste should go into the non-hazardous solid trash.

4.2.2 Liquid waste should go into the dilute acid/base waste jug.

5.0 Accident Procedures:

5.1 Contact: Read MSDS prior to working with any chemical to familiarize yourself with the symptoms of exposure and recommendations for treatment.

5.1.1 Inhalation of Dichloro Methane fumes may make you feel dizzy. If this occurs, turn off the hotplates and leave everything in the hood. Leave the room and get some fresh air. If symptoms persist, contact Tufts health services and inform the lab directory and Tufts health and safety office.

5.1.2 Skin contact from Dichloro Methane, sucrose, and PCL are not critically dangerous. Exit the lab and wash with soap and water in the bathroom.

5.1.3 If Dichloro Methane is ingested, contact Tufts emergency services immediately and ask for an ambulance. Dichloromethane is acutely hazardous if ingested.

5.2 Spill:

5.2.1 If a small, contained spill of Dichloro Methane occurs, such as inside the hood, wipe it up with chemical wipes and dispose of in the solvent trash container.

5.2.2 If a large spill of Dichloro Methane occurs that you are not comfortable cleaning up, evacuate the lab and contact Tufts emergency services (x66911). Also notify the faculty advisor.

5.2.3 Spills of sucrose and/or PCL are not hazardous and can be easily cleaned up and disposed of in the non-hazardous waste.

5.3 Fire:

5.3.1 If a fire starts, use the fire extinguisher to put it out. Evacuate the lab and contact the faculty supervisor.

5.3.2 If you are not able to quickly extinguish the fire using the fire extinguisher, immediately evacuate the lab and call **Tufts Emergency Services at x66911.**

If at any time you feel a situation is dangerous, do not hesitate to call the safety office (x73246, Peter Nowak) or the faculty supervisor (x72210, Robert White).

Report all accidents (injuries, major spills, fires) to the safety office at x73246 (Peter Nowak), the faculty supervisor at x72210 (Robert White), and the lab manager at x75155 (James Vlahakis). For emergencies, call Tufts Emergency Services at x66911.