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TITLE:

Fabrication of large-area ultrathin polymer films

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SHORT ABSTRACT:

We describe a method for the fabrication of large-area (up to 10 cm diameter) and ultrathin (as thin as 10 nm) polymer films. Instead of using a sacrificial interlayer to delaminate the film from its substrate, we use a self-limiting surface treatment suitable for arbitrarily large areas.

LONG ABSTRACT:

We describe a method for the fabrication of large-area (up to 10 cm diameter) and ultrathin (as thin as 10 nm) polymer films. Instead of using a sacrificial interlayer to delaminate the film from its substrate, we use a self-limiting surface treatment suitable for arbitrarily large areas. Typically, ultrathin films are prepared using either sacrificial layers, which may damage the film or affect its mechanical properties, or they are made on freshly cleft mica, a substrate that is difficult to scale. Further, the size of ultrathin film is typically limited to a few square millimeter. In this method, we modify a surface with a polyelectrolyte that alters the strength of adhesion between polymer and wafer. The polyelectrolyte can be shown to remain on the wafer using spectroscopy, and a treated wafer can be used to produce multiple films, indicating that at best minimal amounts of the polyelectrolyte are added to the film. The process has thus far been shown to be limited in scalability only by the size of the coating equipment, and is expected to be readily scalable to industrial processes. In this study, the protocol for making the solutions, preparing the wafer surface, and producing the films is described.

INTRODUCTION:

Free-standing thin polymer films are used in a variety of applications including sensors,¹⁻³ MEMs, catalysis or filtration,⁴ and tissue engineering.⁵⁻⁸ They are also used for fundamental studies exploring the behavior of polymers under confinement.⁹⁻¹³ A free-standing film is one that is supported on a non-continuous substrate such as an annular ring or hoop as opposed to a silicon wafer or glass slide. This work describes a simple, repeatable fabrication procedure for ultrathin free-standing polymer films that is suitable for large-area films or high-throughput production. It is compatible with a variety of different polymers, including poly(vinyl formal), polystyrene, and poly(methyl methacrylate). It can be used to fabricate free-standing films that are as large as 13-cm diameter or as thin as 10 nm.

The fabrication of free-standing polymers consists of three basic steps: 1) **deposition** of polymer

film onto a traditional substrate such as a wafer or slide, 2) **release** of the film from the substrate, and 3) **capture** of the resultant film onto a support.

Deposition can be achieved by any number of basic polymer thin film technologies such as spin-coating, vapor deposition, or dip-coating. In this work, we utilize standard spin-coating techniques.

The “lift off-float on” technique is the most common method for releasing an ultrathin film from its substrate.¹⁴ In this technique, the film and substrate are immersed in a suitable solvent bath. The solvent swells the film and induces spontaneous delamination, releasing the film and allowing it to float to the top of the bath. There minimum film thickness that can be released using lift off-float is determined by balancing the interfacial peeling energy with the swelling-induced strain energy:¹⁵

$$L > 2 \frac{(1+\nu_f)}{(1-\nu_f)} \frac{\gamma}{E(\xi-1)^2} \quad (1)$$

Where L is the film thickness, ν_f is the Poisson’s ratio of the film, E is the Young’s modulus of the film, ξ is the swelling ratio of the film, and γ is the interfacial energy of peeling. The typical way to bypass the limitation imposed by Eq. (1) is to deposit a sacrificial interlayer between the film and the deposition substrate.¹⁶⁻¹⁹ When this interlayer dissolves in a solvent bath, the film is released and can be captured on a support. A related method is the sacrificial overlayer method, which utilizes mechanically peeling the film onto a sacrificial layer prior to dissolution.²⁰

The use of sacrificial materials has several chief drawbacks. First, the addition of an extra process material and step may require a compromise between optimal film fabrication conditions and sacrificial material processing conditions. Second, sacrificial materials may be difficult to deposit without affecting the mechanical properties or purity of the final free-standing film. Third, the process for depositing the sacrificial material must be optimized and monitored for quality as an operation in the overall free-standing film fabrication.²¹

In this work, we describe a surface modification technique that decreases the interfacial peeling energy, enabling the lift off-float technique to be used for ultrathin films. The deposition substrate is modified by assembling a self-limited, self-optimizing monolayer of polycation. Because of the strength of the binding between the polycation and the substrate, this surface modification is robust to subsequent process steps. The self-limiting and self-optimizing nature of the monolayer formation requires practically zero optimization and is easily scalable to large areas.

Following removal, the film floats to the top of the solvent bath where it is captured on a hoop-like support. While not given much attention in the extant literature, in this work we will describe techniques for capturing large-area films on supports that reduce the probability of tearing or otherwise damaging the film.

PROTOCOL:

1. Solution preparation

1.1) Prepare a polyvinyl formal solution by adding 0.3 g of polyvinyl formal (Vinylec E, SPI) to 60 g of ethyl lactate that was filtered through a 0.20 μm filter. Place the solution into the oven at 50 $^{\circ}\text{C}$ for 4 hours. Shake the vial gently to see if the polymer has dissolved completely. If the dissolution process is not complete, return the vial to the oven for another 2 hours. Note: this recipe is for a 0.5% polymer solution, which is typically used for film thicknesses around 30 nm.

1.2) Prepare a PDAC solution by weighing 1.0 g of PDAC reagent (Sigma-Aldrich 409014) in a 20 mL volumetric flask and filling the flask to the measuring line with DI water. Swirl the solution gently before transferring it to a storage container.

2. Substrate preparation

2.1) CAUTION. Pour 60 ml conc. sulfuric acid into a clean 250 ml beaker. slowly add 20 ml of 30% hydrogen peroxide. Wait until fuming subsides, then swirl the solution gently. The solution and the beaker will become very hot and the mixture is corrosive.

2.2) Place a 150 mm petri dish onto the hot plate and pour the acid into the dish. Set the hot plate to 100 $^{\circ}\text{C}$. Place a 4" silicon wafer into the acid with the polished side up. Gently push the wafer down in the middle with a pair of tweezers to make sure the entire surface is wetted. Leave the wafer in the acid for 30 min.

2.3) Remove the wafer from the acid and rinse the front and back of the wafer thoroughly. The water should sheet off in a regular pattern. Dry the wafer in a clean bench.

2.4) Preheat a hotplate to 50 $^{\circ}\text{C}$. Rinse a disposable 3 ml syringe and a 0.2 μm filter first with DI water and then with PDAC solution by drawing the liquid into the syringe, mounting the filter, and then pushing the liquid out through the filter.

2.5) Mount a cleaned wafer in the spin coater. Dispense 1.0-1.2 ml of PDAC solution onto the middle of the wafer. Spin at 4000 rpm for 15 s, then transfer the wafer to the hotplate and let it sit for 30 s.

2.6) Rinse the dried PDAC layer off with DI water and dry in the clean bench.

3. Film fabrication

3.1) Place a dry PDAC-treated wafer onto the spin coater.

3.2) Rinse a disposable 3 ml syringe and a 0.45 μm filter with the ethyl lactate solution using the procedure under 2.4).

3.3) Deposit 2.5 ml of the ethyl lactate solution with the syringe in the middle of the wafer and spin for 10 s at 200 rpm, then for 3 s at 1700 rpm (dependent on desired film thickness). There should be a uniform liquid film on the wafer.

3.4) Let the film dry in the spin coater until it is visibly dry (typically 10-15 minutes), then place it on the hotplate for 10 minutes.

3.5) Scribe the dry film with an Exacto blade to cut the film into squares. Use low pressure to avoid producing particles.

3.6) Fill a 190 x 100 mm culture dish with DI water. Clamp the wafer by the large flat to a rack-and-pinion mounted to a tilt stage and slowly lower it into the DI water. The film should separate from the wafer at the water line. Continue lowering the wafer at a rate that gives the film enough time to separate from the wafer, rather than pushing the lift-off interface below the water line. When the first row of squares has detached from the wafer and is floating on the surface, pause the lowering and lift off the films with a film holder.

3.7) Immerse the head of the film holder into the water and move it underneath the film. Line up the handle edge of the hoop with one of the film edges and touch the hoop with the film. If successful, the film will stick to the hoop. Retract the hoop slowly from the water at an angle of 35°. For films less than 20 nm thick, increase the angle after about half of the film has been pulled from the water to avoid pulling the film through the holder. When the hoop is fully retracted, place it to the side to dry. Make sure the bottom of the hoop is free of drops before putting the hoop down, and use a curved surface (such as a wafer tray) to avoid created a liquid seal between hoop and surface.

3.8) After all films from the row have been lifted out, continue lowering the wafer into the water and repeat the process above for the other rows.

3.9) Let the films dry over night.

Literature recipes for spin coating thin polymer films from solution can be used in this process with minor adjustment of the spin coating parameters. An example of a solution and spin coating recipe for polystyrene and poly(methyl methacrylate) that was adapted for this protocol is given in Ref. [22].

REPRESENTATIVE RESULTS:

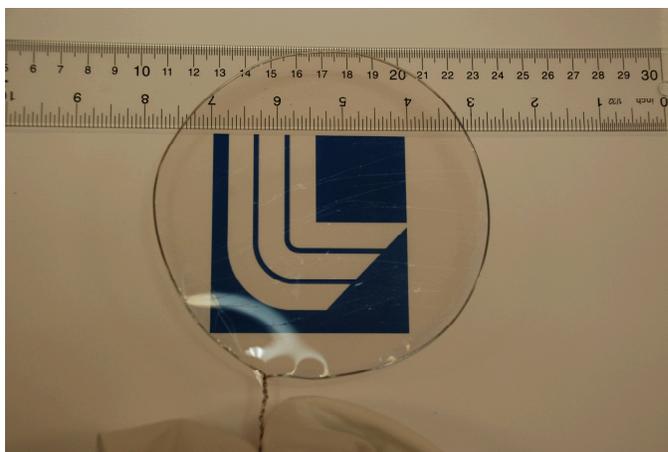


Figure 1. A polyvinyl formal film of 50 (?) nm thickness mounted on a 5" diameter steel hoop. Reprinted with permission from [21]. Copyright 2014 American Chemical Society.

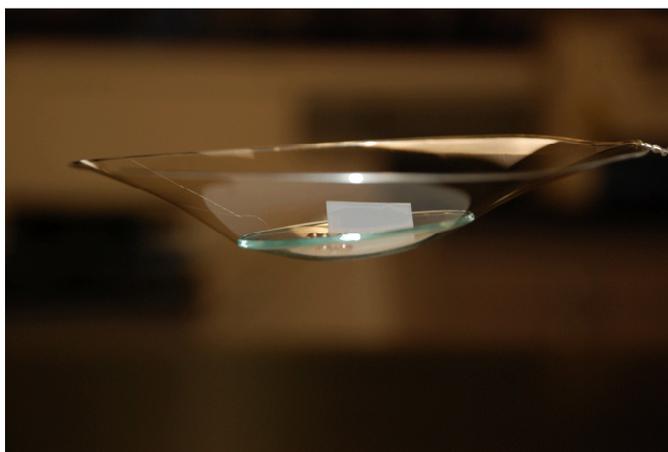


Figure 2. A 22 nm thick, 5" diameter polyvinyl formal film loaded with a watch glass and copper beads. The total mass supported by the film is 10.5 g, while the mass of the film is estimated to be 0.336 mg.



Figure 3. A 30 nm thick, 7 cm diameter polyvinyl formal film supporting a 4 g ball.

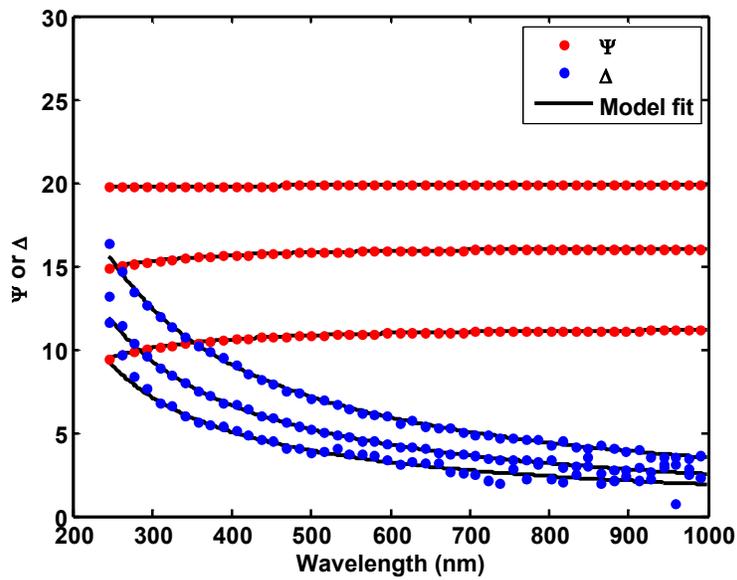


Figure 4. Spectroscopic ellipsometric data on a free-standing film collected at 65°, 70°, and 75° angles of incidence. The model fits are generated using standard ellipsometric software (CompleatEase, JA Woollam) using an air-Cauchy-air stack. The best-fit thickness for this film is 8 nm.

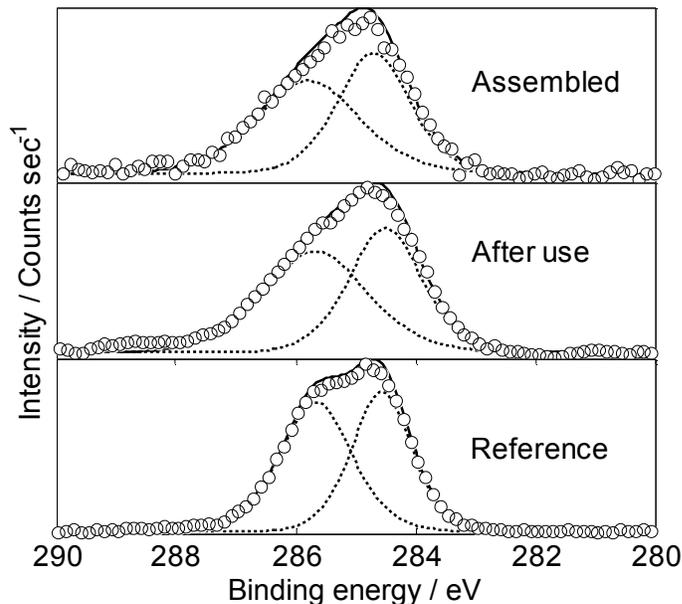


Figure 5. XPS data of wafers coated with PDAC before and after liftoff. The spectrum is largely unchanged, indicating that little if any PDAC is removed during the process. Reprinted with permission from [21]. Copyright 2014 American Chemical Society.

Figure Legends:

Figure 3. A polyvinyl formal film of 50 (?) nm thickness mounted on a 5" diameter steel hoop. Reprinted with permission from [21]. Copyright 2014 American Chemical Society.

Figure 4. A 22 nm thick, 5" diameter polyvinyl formal film loaded with a watch glass and copper beads. The total mass supported by the film is 10.5 g, while the mass of the film is estimated to be 0.336 mg.

Figure 3. A 30 nm thick, 7 cm diameter polyvinyl formal film supporting a 4 g ball.

Figure 4. Ellipsometric data on a free-standing 10 nm film

Figure 5. XPS data of wafers coated with PDAC before and after liftoff. The spectrum is largely unchanged, indicating that little if any PDAC is removed during the process. Reprinted with permission from [21]. Copyright 2014 American Chemical Society.

DISCUSSION:

The swelling-induced delamination of thin polymer films from their deposition substrate is limited by the strain energy in the swollen film. This limitation results in a minimum thickness that can be delaminated as shown in Equation (1), a limitation which is usually circumvented by the use of sacrificial materials. In the protocol described here, no sacrificial materials are

necessary because the interfacial peeling energy has been lowered by the use of PDAC to modify the deposition substrate. Using this technique, we have delaminated polyvinyl formal films as thin as 10 nm, which is a factor of ten thinner than what is possible without the PDAC treatment. An ellipsometric measurement of a free-standing 10 nm film is shown in Figure 4.

[Place figure 4 here]

The PDAC is effective because it decreases the interfacial peeling energy between the deposition substrate and the polymer. It is not a sacrificial layer, as evidenced by XPS spectra in Figure 5 showing its presence on the deposition substrate both before and after delamination. In fact, once treated with PDAC, a substrate can be utilized to deposit and delaminate films multiple times (up to ten) without any noticeable change in performance. The strong binding of the PDAC to the substrate is due to the strong electrostatic interaction between the positively charged polyelectrolyte and the negatively charged silicon substrate.^{23,24}

[Place figure 5 here]

Despite its strong binding to the substrate, the PDAC binds only weakly to the overlying polymer thin film. We have used the protocol described here to delaminate and fabricate free-standing thin films of polystyrene, polymethyl methacrylate, and polyvinyl butyral. The quaternary amine side chains of PDAC likely limits the interaction between the treated substrate and the thin polymer film to weak van der Waal's forces, a mechanism which is evidently applicable to a number of different polymer thin films.

The polyelectrolyte adsorbs to the substrate surface based on self-limiting electrostatic interactions, meaning substrates of any size can be easily treated provided that they are negatively charged (e.g., silicon or glass). Figures 1-3 shows very large thin films (up to 13 cm in diameter) fabricated using this protocol, with the only change being the volume of reagents used. The ultimate achievable size appears to be limited only by the deposition and delamination equipment or the ultimate strength of the polymer used to fabricate the free-standing structure.

While the former is clearly a practical issue, the latter is not a simple reflection of the intrinsic strength of the polymer. We have found that evaporation rate during spin coating and solvent selection –among other factors – can determine the film strength (data not shown).

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DISCLOSURES:

The authors have nothing to disclose.

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