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**MICRO- AND NANO-SCALE POLYMER-ON-POLYMER STAMPING OF THE
POLYELECTROLYTES SPS AND PDAC**

by

Shoshana Ruth Gourdin

B.S. Chemistry
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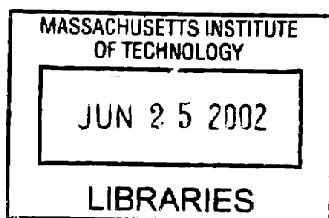
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Shoshana Ruth Gourdin

Submitted to the Department of Chemical Engineering
on May 16, 2002 in Partial Fulfillment of the
Requirement for the Degree of Masters of Science

ABSTRACT

Micro-contact printing has emerged as a promising new technique for patterning micron scale features with a wide variety of materials. Most of the materials examined have been small, reactive molecules patterned on surfaces they are chemically attracted to, like thiols on metals or silanes on glass and metal oxides. Our group has introduced a new approach to surface patterning by using polymers to pattern polymeric surfaces. To further expand the options of charged surfaces, we decided to study strong polyelectrolytes, and their optimal stamping conditions when printed onto polymer platforms, particularly multilayer surfaces. The size of the features that could be produced was also examined.

The success of printing strong polyelectrolytes onto polymer layers depends on the properties of the ink solution as well as the properties of the polyelectrolyte used. SPS is best printed from a concentrated aqueous solution including a large amount of salt. PDAC can be stamped from either concentrated ethanol based inks or from a dilute aqueous one. The more concentrated ink produces prints faster and more reliably, but causes more damage to the stamps used. PDAC can also be used to print nano-scale features, using a concentrated aqueous ink.

Thesis Supervisor: Paula T. Hammond
Title: Associate Professor of Chemical Engineering

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BIOGRAPHY OF THE AUTHOR

Shoshana Gourdin was raised in California. She graduated in 1999 from the University of Chicago, with a BS in chemistry. Her research at MIT was done for the department of chemical engineering, and she is co-author of the paper “Polymer-on-Polymer Stamping: Universal Approaches to Chemically Patterned Surfaces.” Her presentation of this work at the 2002 American Chemical Society Meeting won the “Outstanding Poster Award.”

INTRODUCTION

With an increased demand for miniature devices comes an increased demand for the processing techniques used to produce them. Micro-electronics and biomedical implants, in particular, require patterning techniques that are applicable to a wide variety of materials and a wide variety of production conditions. Cost is also a factor. For any consumer product, lower manufacturing costs permit cheaper products and higher profits, both of which are desirable for the company. What is needed, then, is a flexible and inexpensive patterning method that can reproduce microscopic patterns.

Traditional photolithography relies on patterns of light passed through lenses to reduce the size of the design. The light strikes a resist, which then hardens. A variety of chemical etches can be used to remove the areas unprotected by the hardened resist. This process is reliable and produces excellent micro-scale patterns, but it is not suitable for all applications. For example, it requires a flat surface so that the light is not distorted. Only materials which can withstand the somewhat harsh processing can be patterned, and the apparatus needed is expensive. For an implant, however, you might want to create a small pattern on a plastic cylinder using a process inexpensive enough that the devices could be marketed. As a result, the new field of soft lithography has developed to try and provide alternate methods for micro-scale patterning.

Soft lithography encompasses a wide variety of techniques. Some of these techniques are mechanical, like micromolding or dip-pen nanolithography. [1, 2] Some of them are chemical, like self-assembling monolayers. [3] Some, like micro-contact printing, are both. Contact printing is a simple idea. Cover one surface with ink, and press that surface against a second one. When the two surfaces are separated, the second surface will be printed with a mirror image of the ink pattern on the original. Rubber stamps work by contact printing, as do old fashioned printing presses. Micro-contact printing and nano-contact printing are specialized types of contact printing, defined by the size of the patterns they reproduce, namely micron or nanometer sized features.

Micro-contact printing is a straightforward process. In a key early paper, Whitesides and Kumar introduced the use of rubber stamps that could support micron-scale features without sagging or deforming. The stamps were made of

polydimethylsiloxane (PDMS), molded from an etched silicon master. These stamps could be coated with a thiol ink which could be contact printed onto a gold surface, reliably producing features as small as one micron. [3]

Since then, sub-micron or nano-scale patterns have also become possible. In 1994, Kumar, Biebuyck, and Whitesides reported 200 nm wide lines produced by printing alkanethiols on gold with a PDMS stamp. They specifically noted, however, that the results were not consistently reproducible, and that clean features at such a small scale were exceptions and not the rule. [4] Two years later, Whidden et al. used similar materials and procedures and found that they could produce 300 nm features repeatedly. [5] It was several more years before Pompe et al. reported reproducible 200 nm features, using silanes on silicon wafers and a PDMS “ink pad” to produce the even application of ink demanded. [6] Features as small as 30 nm have been reported by Bao, Rogers, and Katz. [7]

For the smaller features, the materials of the stamp and inks become quite important. The PDMS rubber will deform if the features on it are too thin, producing poor prints. The rubber can be made harder by including more curing agent, but as it becomes stiffer, it is less able to conform to the surface of the material it is printing on, which can also lead to defects. [8] Stamps with an aspect ratio (height of pattern : width of pattern) of about 1 are optimal. PDMS is also quite hydrophobic and as such, will not be wet by many solvents. To use aqueous inks, the stamps must be treated with air plasma or oxygen plasma to ionize the PDMS surface. [9] Without this treatment, the inks will dewet the stamp, producing beads of ink instead of a thin, even coat. This has been used as a patterning technique in its own right [10], but is undesirable for complete reproduction of a complex pattern.

The materials available for micro- and nano-contact printing vary widely, although most of the polymeric materials have been explored within the last few years. The earliest materials used were thiols, designed to form self assembled monolayers on gold and silver surfaces, [3, 5, 11-13] and silanes which were printed on silicon oxide and glass. [6, 14] Both thiol and silane systems are still widely used, and are by far the most studied materials used in micro-contact printing. Palladium colloids have been patterned onto polymer substrates [15] and proteins have been printed on glass. [16] A

variety of polymers, like polystyrene and poly(ethylene oxide) [10] have been used as inks. Our group in particular has studied the behaviors of printed polyelectrolytes and copolymers, like EO-MAL [9], PDAC [17], SPS [17], and a PS-PAA block copolymer [17]. Glass [14, 18], plastic [19], and a variety of metals [5, 6], have been used as substrates. This variety of materials makes micro- and nano-contact printing particularly attractive for areas in which conventional micron scale printing techniques, such as photolithography, are not suitable because they are expensive and possibly destructive to delicate organic molecules. Micro-contact printing has been used to pattern proteins on organic surfaces, for example, where lithographic processing would ruin both the surface and the proteins. [14, 16, 20] Organic transistors have been made with contact printing [19], and could potentially be much cheaper than highly processed inorganic devices. Thus, micro- and nano-stamping are not specialized techniques, but general methods that can help make small-scale patterning available to a variety of fields.

This is particularly true since the patterns made by contact printing can be used to direct additional layers of material. At the simplest level, materials can be selectively adsorbed based on the different chemical properties of the printed material (the ink) and the surface it is printed on (the substrate). A negatively charged substrate will repel negatively charged particles at the same time that a positively charged ink will attract them. As a result, the particles attach only to the printed pattern. [21] Two different materials can also be used to create a template. Thiols with different end groups are often used this way. One thiol is printed onto gold, then the unstamped areas are covered with a second thiol. The difference in the chemical properties of the end groups can cause selective adsorption of ligands or polymers. [9, 22] The techniques can be combined. For example, thiols can be used to direct the deposition of polymers, then another material can be selectively adsorbed onto the polymer surface. [9] In this way, complex surfaces can be created by successive printing and adsorption.

Currently, in micro- and nano-stamping, each ink has a separate set of ideal printing conditions which vary depending on the underlying substrate. Polymers offer a solution to this limitation, in that they can be spun or absorbed onto a wide variety of supports. A stamp placed on the surface of the support will contact only the polymer, and will print based on the ideal conditions between the ink and the polymer, not between the

ink and the underlying material. The same ink could be applied to many different materials using the same conditions, expanding the scope of micro- and nano-stamping.

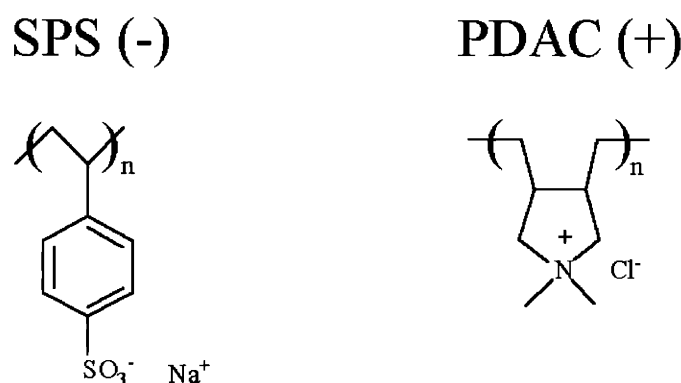
One option for creating polymer interfaces is to use polymer multilayers. Multilayers are single layers of polymer, laid one over the other to form a continuous film. They are usually held together either covalently (as for paired amines and acids) [23] or ionically (as for paired poly-ions) [11]. The top surface of the multilayer determines the surface interactions of the overall substrate.

Multilayers are not new. Iler did the initial work in 1966 when he produced inorganic multilayers out of alumina and silica particles, relying on ionic charge to hold the particles together. [24] The multilayer technique expanded greatly in popularity and utility, however, when it was rediscovered in the 1990's and applied to polymers, creating multilayered organic films. [25, 26] These organic films could be produced by dipping a substrate into solutions of oppositely charged polymers, allowing the molecules to assemble themselves into layers based on the chemical interactions of the materials used. For example, a negatively charged substrate could be placed in a dilute solution of positively charged polymer. The ionic attraction between the polycation and the surface would cause the polymer to deposit on the surface. The substrate could be removed, rinsed to remove any loosely bound polymer, and then placed in a second dilute solution containing a polyanion. The polyanion, attracted to the positive charge of the polycation on the substrate, would deposit on top of it. The substrate could then be covered with a single bilayer, or one layer of each polymer. More bilayers could be laid over the first to create a multilayer film.

Multilayered polymer films are not limited to polyions; they have been used with a variety of materials. Weak polyelectrolytes are common materials. Generally weak polyelectrolyte films rely on the attraction between an acid group (as on PAA) and an amine (as on PAH). These films are quite pH sensitive as a result. [9, 23] Specialized polymers, such as conducting polymers, have been used to form multilayers. [27, 28] Small molecules, such as dyes, have been co-layered with polymers [29] or encapsulated within polymer layers. [30] Even exotic materials like fullerenes have been incorporated into multilayer films. [31]

My work focuses on printing polymer inks onto polymeric and silicon dioxide surfaces. I concentrated on strong polyelectrolytes, and picked the two classic strong polyelectrolytes in the field of multi-layers, SPS (sulfonated polystyrene) and PDAC (poly (diallyldimethylammonium chloride), also abbreviated PDADMAC). SPS is anionic, and PDAC is cationic. (Figure 1)

Figure 1: The polyelectrolytes used and their chemical formulas.



The primary goal of the project was to examine the possibility that SPS and PDAC could be printed atop one another. Stamping techniques can be limited by the substrates they are applicable to. Thiols, for example, are excellent inks when printed on gold, but only when printed on gold. If a stamping technique could be developed that printed onto a polymer surface, then it could print onto that polymer surface regardless of the solid substrate beneath the surface. The ink would only “see” the polymer. Such polymer-on-polymer (POP) printing could be used on a wide variety of materials.

The first requirement of a polymer-on-polymer system is that the materials be able to coat substrates evenly and cleanly. SPS and PDAC were previously shown to form thick, stable bilayers which could be produced simply by dipping the substrate alternately in baths of PDAC and SPS. Their binding was purely ionic, and so depended heavily on the concentration of salt in the dipping solutions. [32] With the correct amount of salt, however, they consistently formed good layers. [32]

Polymer-on-polymer stamping also requires that the two polymers have a strong attraction. For SPS and PDAC, this attraction is ionic. When they form multi-layered platforms, they do not use all of their charged groups to bind to the layer beneath them. Many charged groups are left on the surface. The charged groups on the surface can attract the next layer of the platform from solution or the polymer ink on the stamp.

Finally, the ability to print one polymer on another is not useful if there is no distinction between the two surfaces produced. Differences in the surface properties allow the printed and unprinted areas to be distinguished, and help direct further depositions. SPS and PDAC surface have opposite charges, and this distinction is strong enough that charged dyes can be used to characterize the surface.

The specific printing behavior of SPS and PDAC had not been examined. Therefore, in my work, SPS and PDAC inks were stamped onto multilayers of the same materials in order to find the optimal stamping conditions and examine the films produced at these conditions. For both polymers, the optimal stamping conditions differed widely from the optimal dip-coating conditions used to produce multi-layers. The inks were much more concentrated and in contact with the multi-layer surface for a much shorter time. The solvent used and the salt concentration were also important. SPS turned out to be more sensitive to processing conditions, and hence more difficult to work with, than PDAC.

As a secondary goal, I wanted to see how small a feature could be produced by a polyelectrolyte printed with a PDMS stamp. At such small feature sizes, any defects or deformation in the PDMS rubber stamp could destroy the pattern. Clumping of the polymer or beading of the solvent in the ink could also disrupt the pattern.

To see if stamping such small features with polymers and rubber stamps was feasible, PDAC was stamped onto bare silicon using PDMS stamps having features only about 150 nm wide. In order to get good prints, new stamping techniques were required. A small stamping machine was built to ensure steady placement, and the stamps were spin coated with a different ink solution to produce thin, even coats of ink. [33] Using these methods, the pattern transferred, even at such a small scale.

EXPERIMENTAL

Materials

Poly(diallyldimethylammonium chloride) (PDAC) of MW = 150,000 g/mol was purchased from Aldrich. Sulfonated polystyrene (SPS) of MW = 70,000 g/mol was also obtained from Aldrich. The Sylguard 184 silicone elastomer kit (polydimethylsiloxane, or PDMS) was purchased from Essex Brownell, and the silicon wafers used were bought from Wafer World. The slides used were VWR Micro Slides, made of plain glass and about 1 mm thick. The de-ionized water used was purified with a Milli-Q system, and had a resistance of 18.2 M Ω .

Multilayer Substrate Preparation

The strong polyelectrolytes SPS and PDAC were used to form multilayer platforms on which solutions of the same polymers could be stamped. The platforms were built on glass slides cleaned with a dilute Lysol/water mixture in a sonicator. To start the first bilayer, the slides were immersed for twenty minutes in the PDAC solution (0.02 M PDAC, of MW 100,000-200,000 g/mol in Milli-Q water, with 0.1 M NaCl, filtered through a 0.22 micron mesh). Following a two-minute rinse with a stream of pure Milli-Q water, the slides were placed into the SPS solution (0.01 M SPS, of MW 70, 000 g/mol, in Milli-Q water, with 0.1 M NaCl, filtered through a 0.22 micron mesh) and allowed to sit for 20 minutes. They were rinsed a second time with a stream of pure Milli-Q water and sonicated for three minutes prior to repeating the procedure to make the next bilayer. [32] In later batches of multilayers, the rinsing and sonicating steps were extended to 6 minutes. All platforms were built by a Zeiss DS-50 slide-stainer, programmed and controlled by a computer running HMSPROXA software.

Silicon Substrate Preparation

Bare silicon wafers used for micro-contact printing were cleaned with pure ethanol and blown dry with a stream of nitrogen. Silicon used for nano-stamping was cleaned with a ten-step cleaning procedure in a particulate-controlled area. [34] First, the silicon was sonicated in a 2% solution of Micro 90 soap and de-ionized water and rinsed with a stream of de-ionized water. Then, it was sonicated in de-ionized water for 5 minutes and rinsed with a stream of de-ionized water. This wash and rinse was repeated a second time. Next, the silicon was sonicated in acetone (99.99%, reagent grade) for 5 minutes. It was then washed in two baths of near-boiling trichloroethylene, spending 2 minutes in each bath. Then, it was sonicated in acetone a second and third time, each time for 2 minutes. Finally, the silicon was washed in two baths of near-boiling isopropanol, spending 2 minutes in each bath. The silicon was then blown dry with a nitrogen gun.

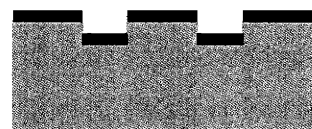
Preparation of the PDMS stamps

The stamps used to make prints on the multilayers were PDMS stamps molded with an etched silicon wafer. The PDMS was from a commercial mix (Sylgard, 184 silicone elastomer kit) and was liquid when prepared. This liquid was placed under vacuum for about an hour to remove most of the gas in it. Then, it was poured over a silicon wafer etched with the desired pattern and placed under vacuum for a few more hours to remove the remainder of the gas. When there were no more bubbles in the liquid, the dish containing the wafer and the liquid was placed in a warm area of the lab, covered, and left to sit for two days. The liquid solidified into a transparent rubber, which could then be removed and cut into pieces of the appropriate size.

Micro-contact Printing

The general stamping procedure is demonstrated in Figure 2, using a polymer multilayer surface as a sample substrate.

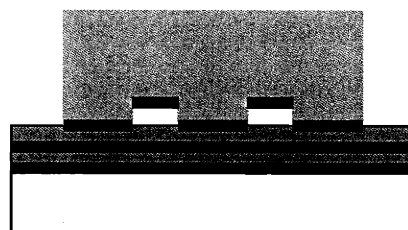
Figure 2: The polymer-on-polymer stamping process.



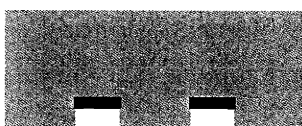
This is a PDMS stamp covered in a thin layer of polymer ink.



This is a multilayer platform. Alternating layers of positively and negatively charged polymer are laid over the glass substrate (the white area). Shown are 2 bilayers.



The inked stamp is placed patterned-side down on the surface of the platform, and allowed to rest there for a period of time.



The stamp is then lifted off the platform, leaving behind a printed pattern where it touched the surface.



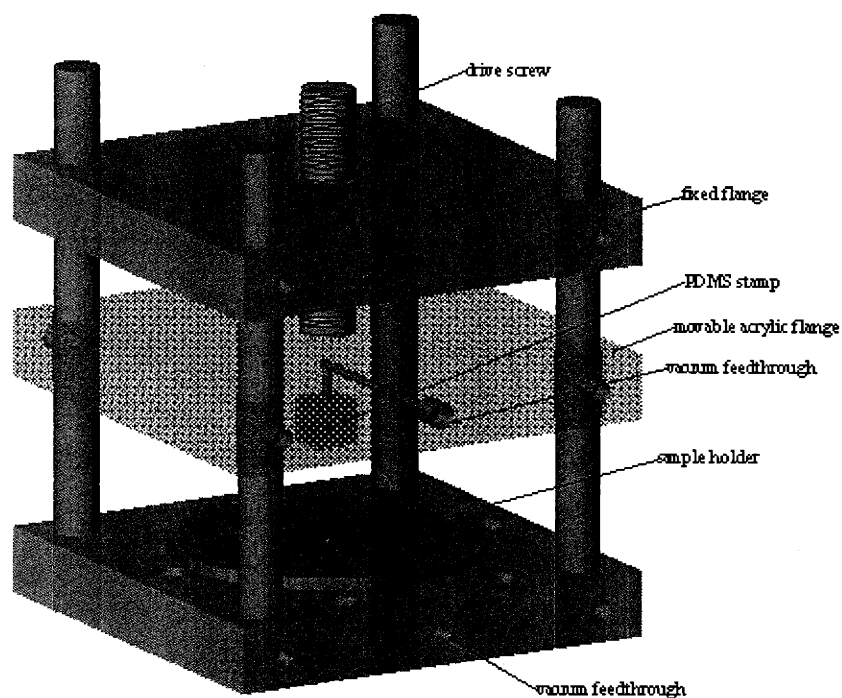
The PDMS stamp surfaces must be made polar before they can be smoothly inked--otherwise, the charged polymer solutions will not wet the hydrophobic PDMS surface. Thus, the clean stamps were placed in air plasma for twenty seconds before ink was placed on them. [17] Then, a cotton swab wet with the ink was brushed over the surface. This thin layer of ink was dried in air or under nitrogen, and the stamp was then placed on the multilayer platform and allowed to sit for a specified amount of time.

Aqueous solutions of 20 mM PDAC and 0.1 M NaCl in water were used to stamp the polymer from aqueous solution. In this case, the stamping times ranged from 30 to 120 minutes. Ethanol/water mixtures were also used as inks. Five solvents of this type were tried: pure water, 75% water, 50% water, 25% water, and pure ethanol. The PDAC inks made with these solvents had concentrations of 0.025 M, 0.1 M, or 0.25 M (by repeat unit). In this study, the stamping times were varied systematically from a few seconds to an hour for each ethanol/water combination. Following the stamping process, the patterned surface was rinsed thoroughly with a stream of Milli-Q water from a solvent squeeze bottle to ensure removal of unbound polyelectrolyte.

Nano-contact printing

The PDMS stamps were spin coated at 1000 rpm – 5000 rpm and 3000 rpm/s – 5000 rpm/s with inks consisting of PDAC in de-ionized water at a concentration of 30 mg/ml (0.19 M). The stamps were allowed to sit for between 1 and 10 minutes prior to being used to make prints. After this delay, the stamps were placed upside-down into the stamper (figure 3) [35] and lowered onto the silicon surface. The stamps were allowed to stay in contact with the surface for 1 minute. This entire procedure was carried out in a particulate controlled environment.

Figure 3: The stamper.



Characterization

Dyes: One of the dyes used was 6-carboxyfluorescein (6-CF). It was purchased from Sigma, and made into solutions of 0.5 mM and 1 mM, using 0.1 M NaOH in Milli-Q water as a solvent. This dye stained the positively charged PDAC surface. The stain looked green when viewed with the fluorescence optical microscope using a FITC filter. [36] The other primary dye was Rhodamine B, which was purchased from Aldrich and dissolved in Milli-Q to produce solutions of concentrations between 0.1 mM and 10 mM. Rhodamine B stained the negatively charged SPS surface and looked red when viewed with the fluorescence optical microscope. For both dyes, the polymers were stained by immersing the stamped platform into a solution of dye for a period of time ranging from a few seconds to a minute.

Ellipsometry: All the ellipsometry measurements were taken with a Gaertner Scientific Corporation ellipsometer, controlled by a Gateway 2000 computer running GEMP, the controlling software.

Fluorescence optical microscopy: All fluorescence optical microscopy was done with a Zeiss Axiovert. The pictures taken were captured by a Hamamatsu C4742-95 digital camera, and processed on a Macintosh G3 computer running Open Lab 2.0.2 software.

Contact angle: Contact angles were measured on a Ramé-Hart goniometer (Ramé-Hart Inc., Mountain Lakes, NJ) equipped with a video-imaging system. Water drops were placed on at least three locations on the surface in the ambient environment and measured on both sides of the drops. Contacting water drops were advanced and retreated with an Electrapipette (Matrix Technologies, Lowell, MA) at approximately 2 μ l/s.

AFM: Samples were examined using the tapping mode of a Digital Instruments Nanoscope III SPM atomic force microscope.

RESULTS AND DISCUSSION

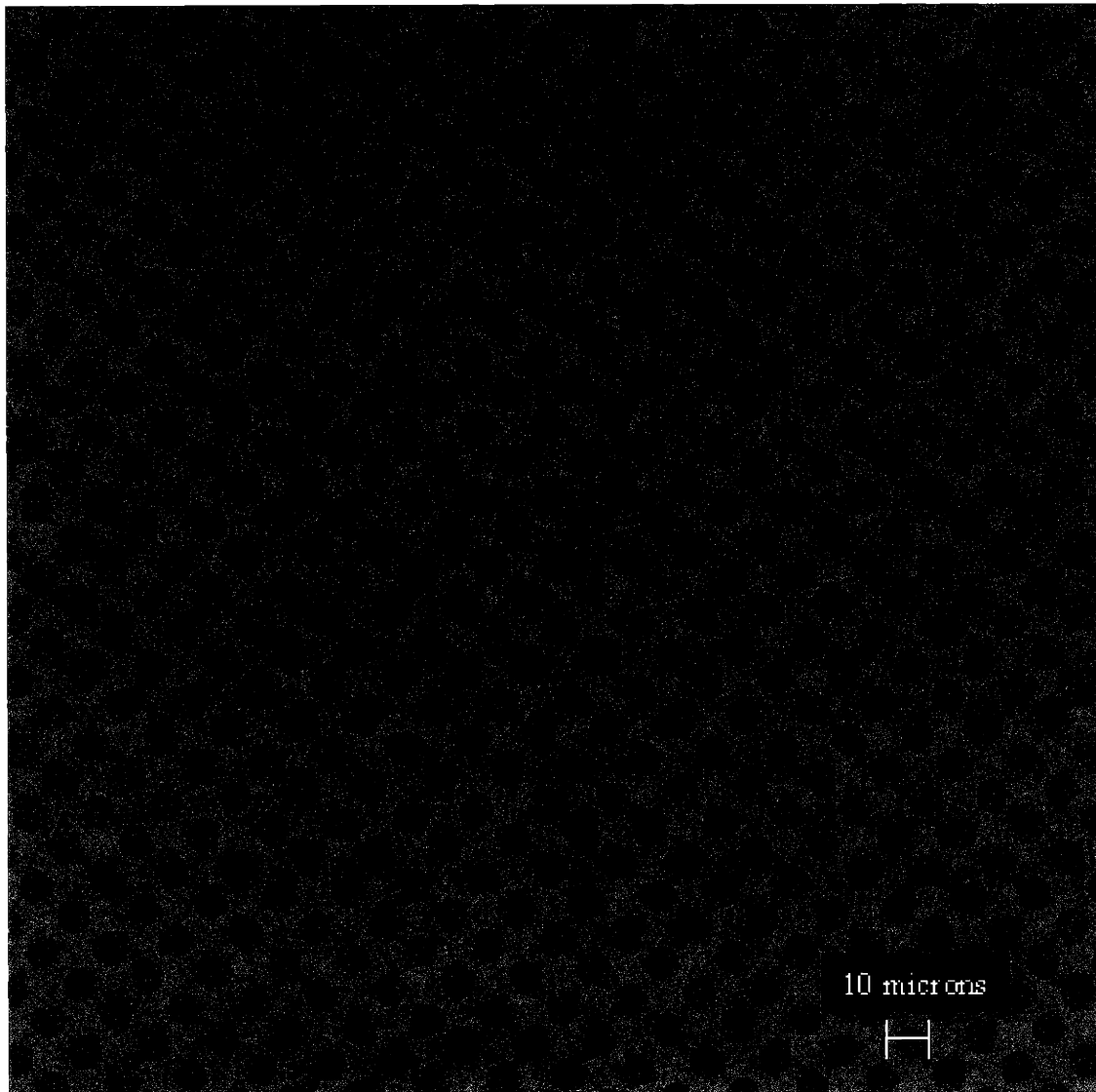
Micro-contact Printing of PDAC onto SPS

Strong, oppositely charged polyelectrolytes such as SPS and PDAC are highly ionized over all or most of the pH range and will only undergo ionic interactions with each other. These systems are ideal for examining the transfer of charged polymers onto oppositely charged substrates. In the first part of this study, PDAC was stamped directly onto SPS/PDAC multilayer films from dilute aqueous solutions and from water/ethanol mixtures at higher concentrations.

To be able to coat the PDMS stamps with such charged or highly polar inks, it was necessary to treat the stamp with air plasma. Plasma times of 20 seconds or longer are sufficient to make the stamp wettable by water and ethanol solutions, as determined by contact angle measurements of a blank PDMS surface which indicates a strong drop in contact angle of the PDMS surface at 15 to 20 seconds. [17] The aqueous or ethanol-based inks spread evenly over a surface treated this way, leading to more even printing.

PDAC could be stamped from aqueous solutions using a dilute ink containing 0.02 M PDAC and 0.1 M NaCl. The stamps needed to be plasma treated for 20 seconds and left in contact with the platform for 30 minutes of stamping time. [17] The prints produced this way had good definition and a fairly large area of coverage. (Figure 4)

Figure 4: Aqueous PDAC print. 0.02 M PDAC and 0.1 M NaCl in Milli-Q water, stamped on a ten bilayer platform, with a stamping time of 30 minutes.

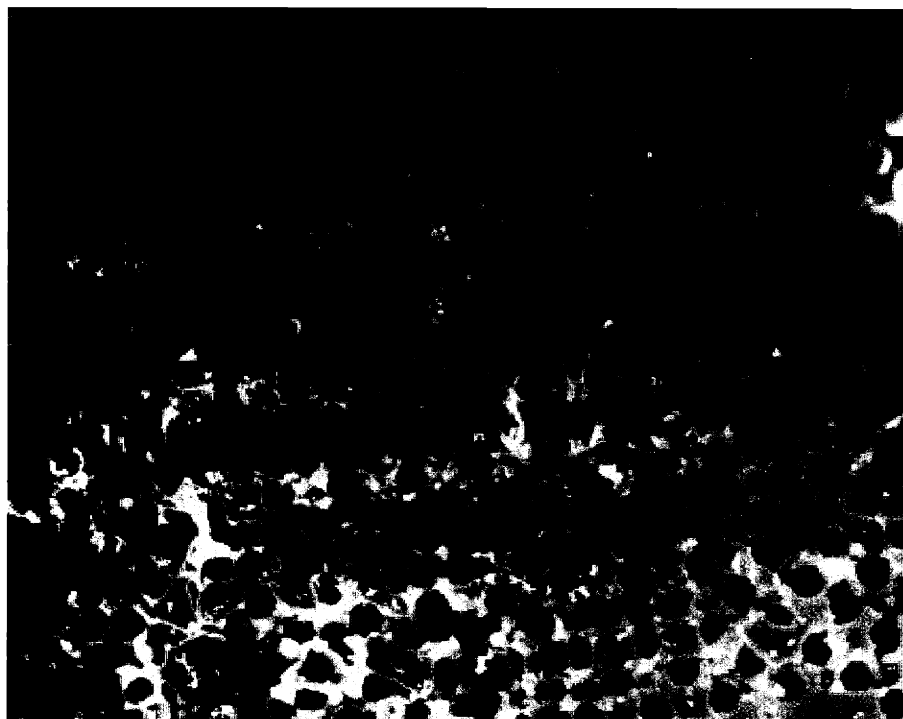


However, this method of printing PDAC was sensitive to processing conditions that could not be easily controlled by hand, such as the exact amount of ink used, or the specific way the stamp touched the platform. As a result, it was sometimes difficult to get complete prints. Parts of the stamp would print well, and other parts would not print at all. The stamping time was also long. Alkanethiols can be printed in a few seconds [4],

and short times are absolutely necessary for the type of reel-to-reel printing needed to make commercial devices. [18]

Some of these drawbacks were be resolved when PDAC was stamped from concentrated solutions in water/ethanol mixtures. Ethanol is a promising solvent because it is at once polar and volatile, so that it can easily solubilize PDAC while evaporating rapidly from the stamp, preventing smudging and “bleed” during the stamping process. Neither pure ethanol nor a 25/75 by volume ethanol-water mixture produced good printing of PDAC. Insufficient coverage by these inks can produce black areas with no transferred film, or areas where only the edges of the pattern were transferred (producing a pattern of rims). This effect is shown in Figure 5.

Figure 5: A PDAC print showing rim defects in areas with insufficient ink. 0.25 M PDAC 50/50 ethanol/water, stamped on a ten bilayer platform, with a stamping time of 40 minutes.



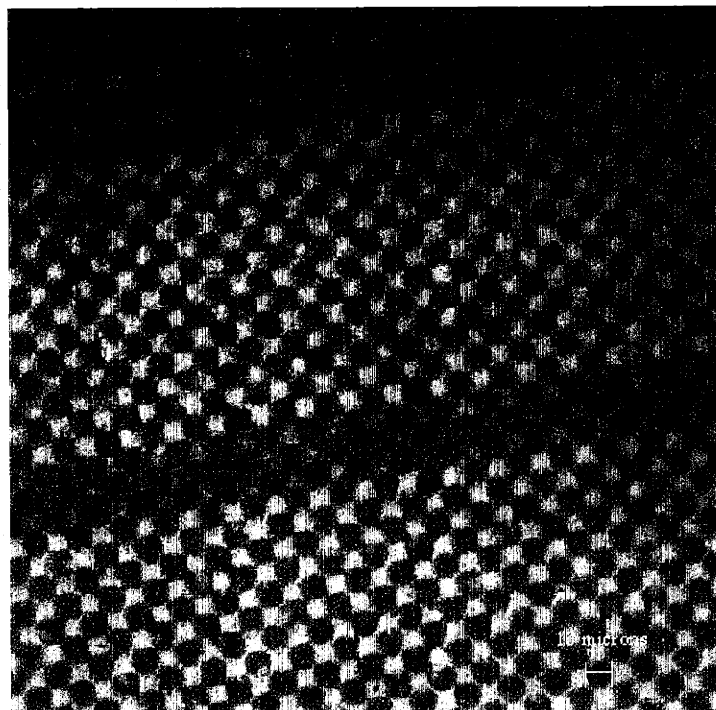
This rim effect may result from the ink collecting on the edges of the pattern where there is more of the hydrophilic, plasma-treated PDMS surface available. If there is not enough

ink to form a complete film (with thicker spots at the pattern's edges), then the ink may accumulate only at the edges, leaving unprinted patches in between. [21]

Solutions made in either 50/50 ethanol/water or 75/25 ethanol/water mixtures performed much better, with the 75/25 mixture giving uniform transferred polymer films, with well defined, clear edges. For most of these solutions, variations in coverage on the stamp during the inking process often produced streaks similar to brush strokes, as pictured in figure 6.

A wide variety of stamping contact times were tried for the ethanol/water mixtures, ranging from a few seconds to an hour. At longer stamping times, the stamp tended to adhere to the platform, making it difficult to remove. Due to this phenomenon, the resulting printed areas often displayed cracked surface regions, as in the printed regions of figure 6. (See figures 7 and 8 for the final prints using the optimal conditions for 75/25 ethanol/water ink.)

Figure 6: A PDAC print showing typical defects, including variation in coloring and a cracked appearance. 0.25 M PDAC 75/25 ethanol/water, stamped on a ten bilayer platform, with a stamping time of 40 minutes.



This adhesion could also damage the PDMS stamps. Shorter stamping times reduced the sticking, as did lighter coatings of ink. At very short stamp times (a few seconds), no PDAC was transferred to the platform. These results indicate that there is an optimal contact time for printing. For PDAC/ethanol solutions, optimal times were found at thirty seconds to one minute. These short times resulted in good prints without great difficulty in removing the stamp.

A number of concentrations of PDAC were tried for each ethanol/water solvent mixture. Low concentrations (0.025 M) produced poor or no transferred prints at all. Moderate concentrations (0.1 M) performed well, but high concentrations (0.25 M) performed best, giving highly uniform stamped regions over large areas. At higher concentrations, the PDAC was less soluble, particularly for the 75/25 ethanol/water mixture that proved most useful. In addition to more PDAC simply being present, it may also be less likely to remain in solution.

Based on the variables discussed above, the optimal stamping condition for PDAC was determined to be a 0.25 M solution of PDAC in a 75/25 ethanol-water mixture, stamped for one minute with a PDMS stamp that had been treated with air plasma for 20 seconds. This set of conditions is markedly different from the successful aqueous stamping conditions, which work best at dilute concentrations and longer stamping times. The mechanism for success may be similar, however. Higher concentration of PDAC, ethanol in the solvent, and the addition of salt all lower the solubility of PDAC and make it less likely to remain in solution. The charged surface of the bilayer platform becomes a more favorable site for the polymer in the ink, causing it to pattern down more regularly. Images are shown for samples stamped using the optimal method in figures 7 and 8.

Figure 7: Optimal PDAC print. 0.25 M PDAC in 75/25 ethanol/water, stamped on a ten bilayer platform, with a stamping time of 1 minute.

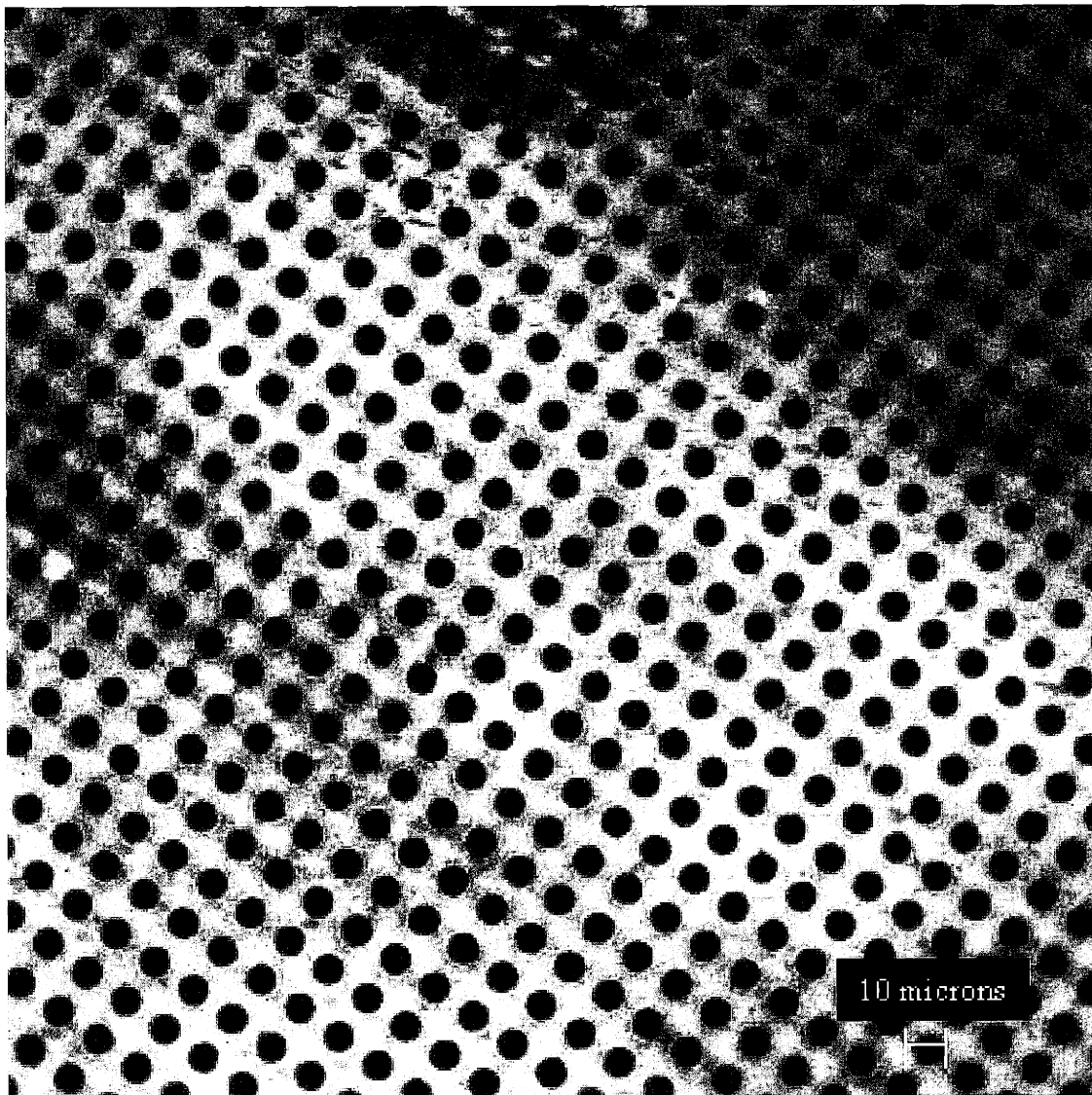
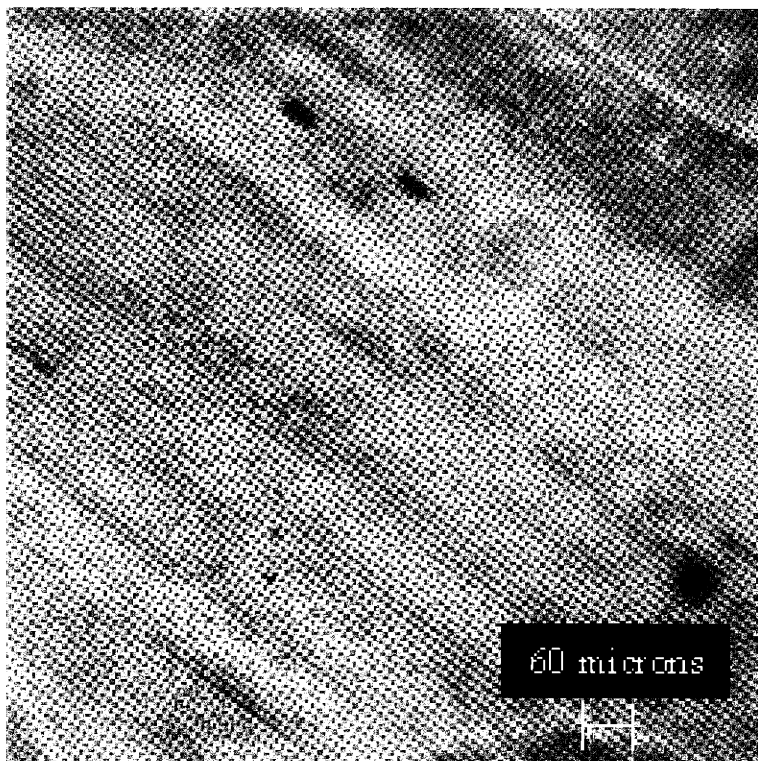


Figure 8: Expanded version of optimal print. This is the same sample as figure 7, but a larger area is shown.



The optimal method has certain advantages over the method used to print dilute aqueous solutions of PDAC. The 0.25 M PDAC in 75/25 ethanol/water solution produced complete prints (prints reproducing the entire surface pattern of the stamp) in 1 minute, instead of producing an incomplete print in 30 minutes. This behavior is much closer to the fast, reliable methods needed in industrial production, suggesting that ethanol based inks may be more commercially viable. The concentrated ink consumes more PDAC than its dilute aqueous counterpart, however, and tends to wear the stamps out faster because of the damage adhesion can cause. Since applying a smaller amount of ink to the stamp diminishes both of these problems, they need not be production hurdles, although some further optimization might be needed to find exactly the right amount of ink for a given process. As discussed below for nano-stamping, the adhesion problem can be eliminated by using more controlled means of inking and stamping.

In all of the images shown, the presence of an alternating pattern of positive and negative regions is made clear by the presence of the green, negatively charged dye on the positive PDAC regions. The dark black regions are the underlying SPS layer, which is not stained by the dye because of electrostatic repulsion. It is clear that there is no bleed or unwanted transfer of PDAC in the SPS regions of the pattern, indicating a clean pattern transfer. A uniform layer such as the one shown can be created over large areas up to approximately a centimeter square area; the possibility of patterning over even larger areas is therefore reasonable using this approach.

The amount of PDAC transferred from the ethanol/water system seems comparable to the amount expected in a monolayer [32], provided the stamped area is well rinsed. To examine this, a gold substrate was coated in a COOH tipped thiol [32] that formed a self assembling monolayer, over which five-bilayer platforms of PDAC and SPS were laid. The thickness of these platforms was roughly 200 Å. (Table 1) On top of these platforms, a print was made from a blank (un-patterned) stamp, using the optimized procedure (0.25 M PDAC, in 75/25 ethanol/water for 1 minute). Prior to rinsing, the layers were both thick and uneven. The variation in thickness was tremendous. (The standard deviation was as large as the average.) After rinsing with a stream of Milli-Q water, the layers were much thinner and more even. The average thickness of the transferred layer was around 22 Å, much closer to the average thickness of the monolayers in the platform. (Table 1)

Table 1: Thickness measurements, in Å. These measurements are averages of measurements taken at three different locations for each of 5 sample platforms. The bilayers were deposited from an aqueous PDAC solution containing 0.02 M PDAC and 0.1 M NaCl and an aqueous SPS solution containing 0.01 M SPS and 0.1 M NaCl. The ink stamped with was 0.25 M PDAC in a 75/25 ethanol/water mixture.

Average thickness of the 5 bilayer platform:	207.21 Å
Average thickness of each monolayer in the 5 bilayer platform:	20.72 Å
Average thickness of the stamped layer, before rinsing:	199.99 Å
Average thickness of the stamped layer, after rinsing:	22.66 Å

These data are consistent with previously reported thicknesses of solution-adsorbed PDAC layers before and after rinsing. [17]

Micro-contact Printing of SPS onto PDAC

Since SPS, like PDAC, is a strong polyelectrolyte requiring a polar solvent, the PDMS stamps required treatment with air plasma in order to print SPS. Fifteen seconds worked better for SPS than the 20 seconds used for PDAC, but the result was much the same. The stamp's surface became more polar and the ink spread more evenly.

SPS proved difficult to stamp. A wide range of solvents, including water, ethanol, DMAC, DMF and methanol, failed to produce good prints. Variations in concentration of SPS from 0.025 to 0.25 M failed to improve the prints. Extending the stamping time, increasing the amount of ink used, and heating the stamp while printing all also failed to improve print quality. Finally, a solution to the difficulties in printing SPS was found in the ionic strength of the ink used.

Aqueous solution of SPS with concentrations of 0.01 M, 0.1 M, and 0.25 M were compared to solutions of the same concentration with 0.1 M of NaCl added. The ones without salt did not produce printed patterns at all. The ones with salt in them produced prints of varying quality. In particular, the most concentrated salted solution, 0.25 M SPS with 0.1 M NaCl gave clear prints with good definition (figures 9 and 10). For the same three concentrations of SPS, 0.5 M NaCl added produced grainy, poorly detailed prints, while solutions with only 0.02 M NaCl added produced no prints at all. Thus the optimal method for stamping SPS onto PDAC uses a stamp that has been plasma treated for 15 seconds, an ink consisting of 0.25 M SPS and 0.1 M NaCl dissolved in Milli-Q water, and a stamping time of 30 minutes. (See figures 9 and 10) The SPS patterns were a bit unstable, even at the best conditions. The lower right hand side of figure 9 has a washed-out look where the printed polymer smeared when washed.

Figure 9: Optimal SPS print. 0.25 M SPS and 0.1 M NaCl in Milli-Q water, stamped on a ten and a half bilayer platform, with a stamping time of 30 minutes.

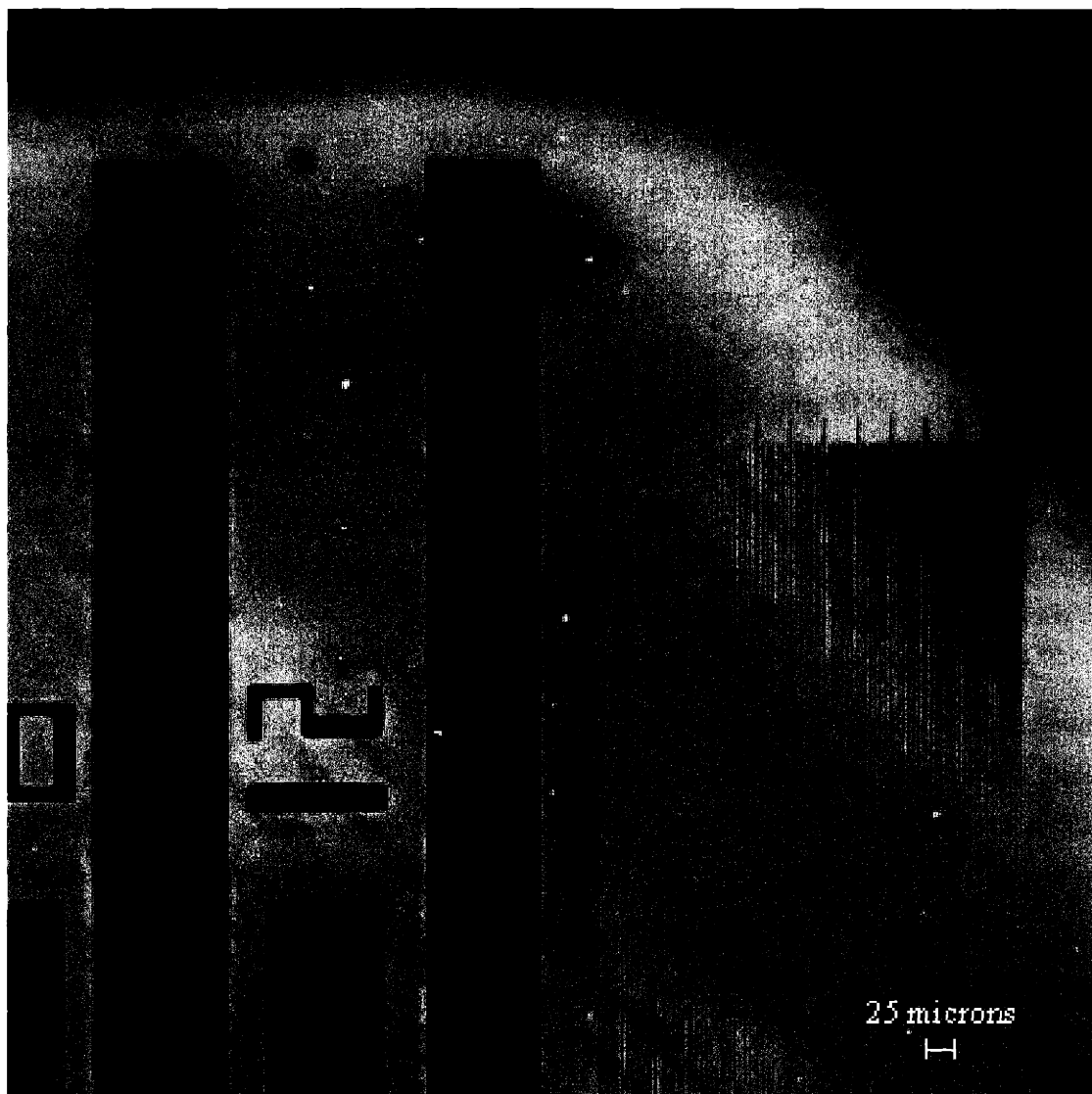
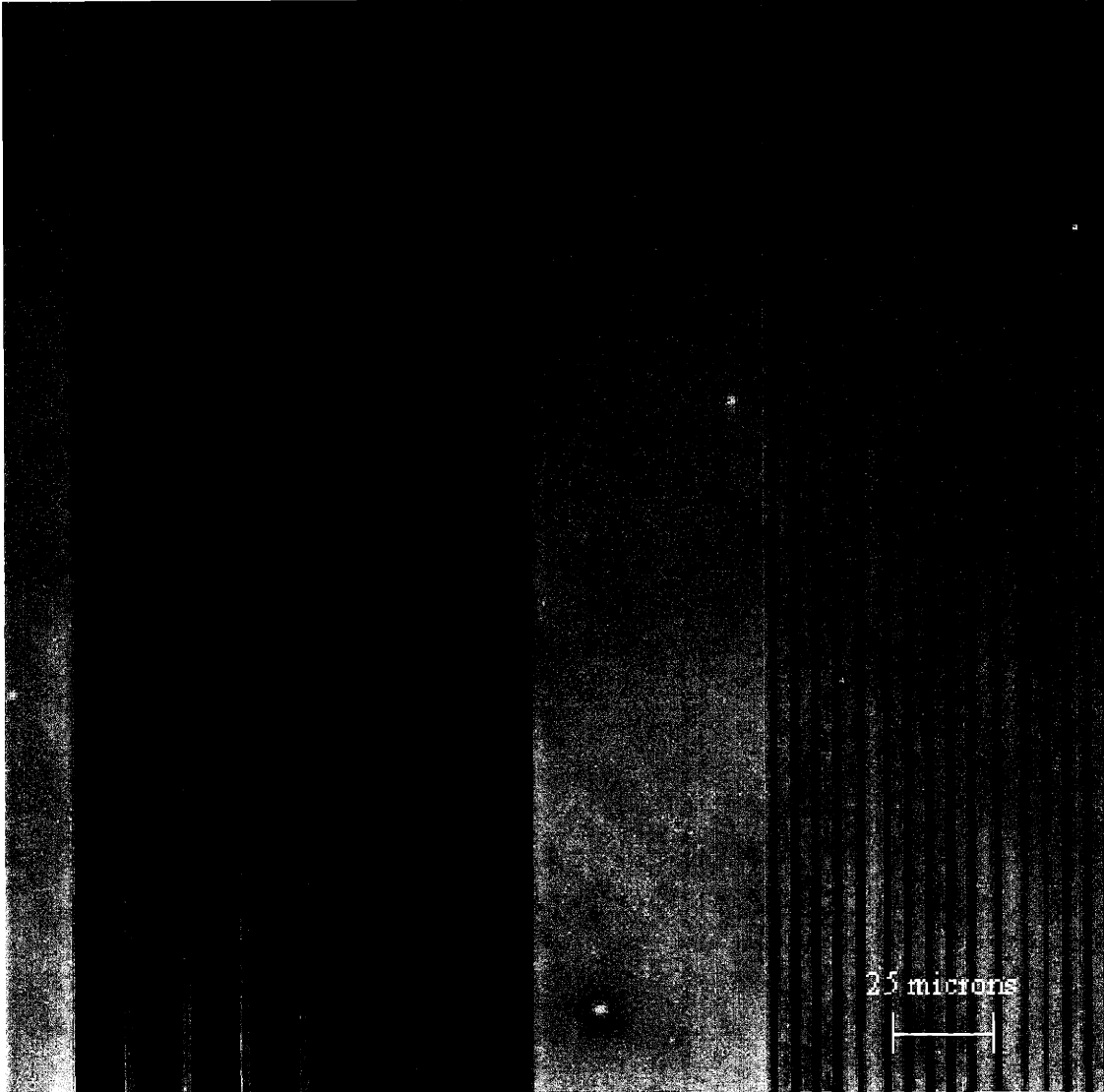


Figure 10: Detail of the optimal SPS print. This is the same sample as figure 9, but a smaller area is shown.



The effects of salt on the success of SPS inks may be related to solubility. The addition of some salt to the solution partially shields the polymer, making it less soluble and thus more likely to settle on the charged surface of the platform. [37] Too much salt will completely shield SPS, making it poorly soluble and unlikely to be electrostatically attracted to the charged surface. 0.1 M is a moderate amount of salt which decreases the

solubility of SPS without negating its charge. Thus, the SPS partitions to the surface of the platform.

In these images, the regions of alternating positive and negative charge are shown with Rhodamine B. The positively charged Rhodamine B stains only the negatively charged SPS, leaving the underlying PDAC dark. It is clear from the detail above (figure 10) that SPS can generate clean, detailed prints.

SPS is very sensitive to the exact conditions of printing, however, even more so than the aqueous PDAC ink. In figure 9, above, there is clearly some blurring on the right hand side. This blurring, on close inspection, turned out to be a result of having too much ink, which washed over patterned areas, obscuring detail. Simply reducing the amount of ink used did not remedy the situation, since only a slight decrease could lead to getting no print at all. The inked stamp itself needed to be placed very carefully, or no print would result. Even when part of the pattern transferred well, the pattern was never complete, but was confined to a relatively small area. Attempts to correct and control these variables failed. Because of these limitations, SPS seems to be a poorer candidate for further stamping research or industrial printing use.

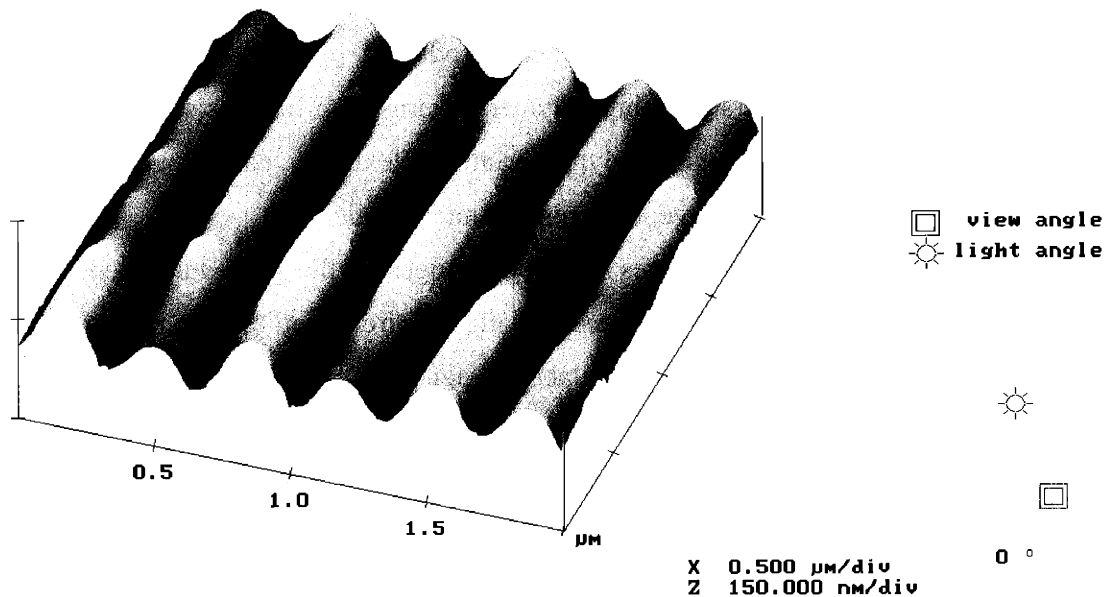
Nano-stamping of PDAC

Contact printing has historically been limited in its uses by the scale on which it can reproduce patterns. The stamps themselves have structural limitations [8], and surface tension and wetting effects can prevent accurate reproduction of fine features [17, 21]. Features smaller than a micron have been produced, [4-7] but with small ink molecules and not large polymers. Printing polymer patterns with features smaller than a micron would extend the advantages of polymer printing (flexibility, ease of use) into the size range most applicable to the burgeoning field of micro-optics.

Stamping with such fine features required changes in the procedure used. The stamps and prints were made in a particulate controlled environment, and the bare silicon used as a substrate was subjected to an elaborate ten-step cleaning process. These additional constraints were designed mainly to ensure cleanliness of the prints, so that we could be sure that the features observed were polymer and not dust from the lab. We also needed to control the inking and stamping processes more carefully, since uneven inking or placement could destroy patterns this small. To that end, stamps were spin coated with ink and placed on the substrates with a stamper. [35] (Figure 3) All the nano-stamping work was done in collaboration with the Bulovic lab at MIT.

At first, however, the optimal conditions for micro-contact printing were simply extended to the nano-contact printing of PDAC on bare silicon. (The stamps were not treated with air plasma, though, lest the plasma destroy the nano-scale features of the stamp.) Little surface patterning was observed; however, in areas with thick concentrations of ink, a molding effect was seen. A thick layer of ink transferred to the substrate, forming a high plateau with a bas-relief copy of the pattern on top. (See figure 11)

Figure 11: A bas relief mold, consisting of PDAC on a bare silicon surface. 0.25 M PDAC 75/25 ethanol/water, stamped on a ten bilayer platform, with a stamping time of 1 minute. The features are approximately 100 nm high.



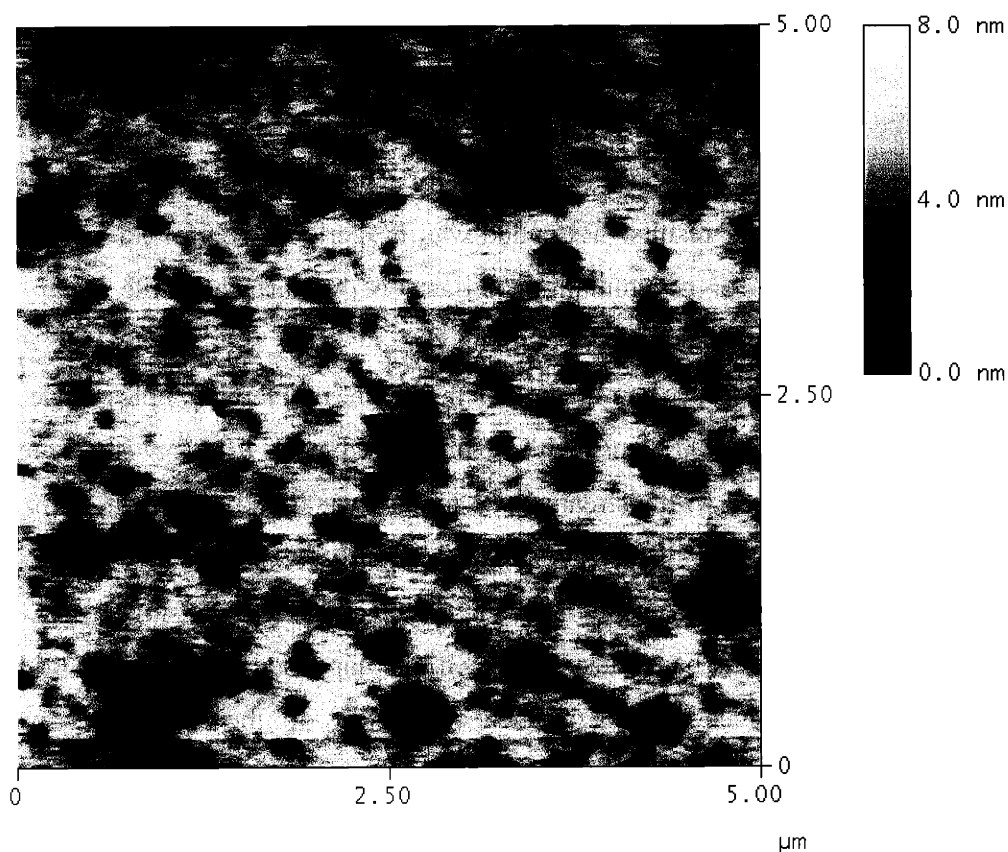
Given the regularity of the structure produced, this type of patterning could be used to generate nano-scale features in a method similar to micro-molding. [38]

In order to produce patterned surfaces (as opposed to three dimensional objects), the methodology needed to change. The ink used was an aqueous solution of PDAC (MW 100,000-200,000 g/mol) at a concentration of 30 mg/ml (about 0.19 M). Stamps were spin coated to produce thin and even coats of inks. Several spin speeds were tried, but the results did not seem to vary with speed. As a standard, then, all stamps used in later prints were spin coated at 3000 rpm and 3000 rpm/s. The inked stamp was placed in the stamper, held in place by vacuum, and lowered slowly onto the cleaned silicon substrate. (Figure 3) It was left in contact with the substrate for a one minute and then raised. The substrate often remained stuck to the stamp, despite being held down by weak vacuum, but a slight tug easily dislodged it. No damage to the stamps or the substrates was observed.

The time elapsed between inking the stamp and pressing it against the substrate had a mild effect on the quality of the prints produced. Samples made with 30 mg/ml aqueous PDAC ink and spin coated at 3000 rpm and 3000 rpm/s were allowed to rest 1.5, 5, or 10 minutes before being placed in the stamper and used to make prints. (1.5 minutes was the shortest time in which we could reliably carry the stamp to the stamper, attach it, and make a print.) The prints made with stamps which had rested for 10 minutes produced poor prints, while the stamps which had rested for 1.5 or 5 minutes produced better prints. The print quality was the same for both a 1.5 and 5 minute delay. The same experiment was done with spin coating speeds of 1000 rpm/1000 rpm/s and 5000 rpm/5000 rpm/s with similar results. Extended waiting periods seem to cause diffusion of the polymer molecules or accumulation of dust on the surface of the stamp. The stamps are better used immediately after being inked.

Rinsing does not improve the quality of the prints. Several samples made with stamps inked at 3000 rpm/3000 rpm/s with 30 mg/ml aqueous PDAC were examined before and after being rinsed with a stream of de-ionized water and dried with a nitrogen gun. Some of the prints showed little change after being rinsed and dried. Others showed decreased contrast between the printed and unprinted areas after rinsing because the polymer was washed onto the bare substrate, much like happened with the SPS printing. (See figure 12) The polymer was not washed completely off the substrate, however, which suggests that the problem is not instability of the adsorbed polymer but loosely bound excess polymer.

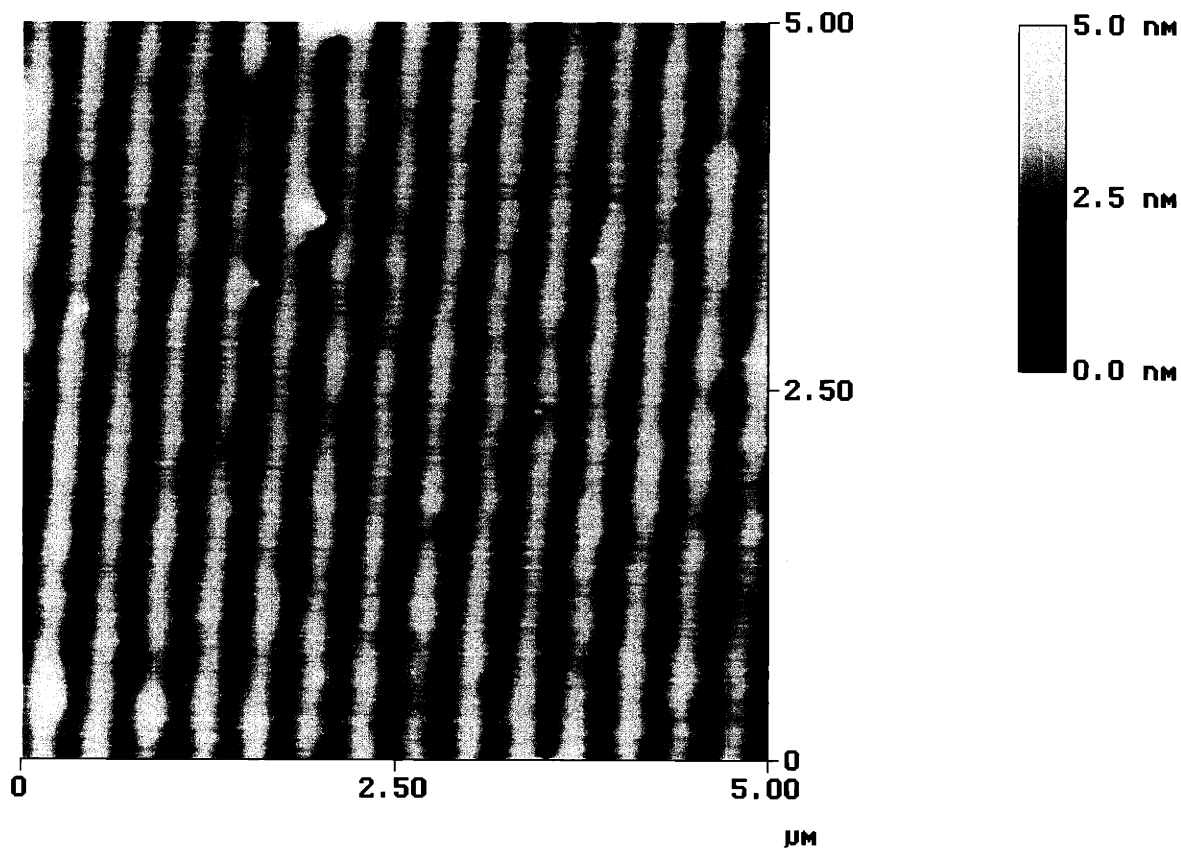
Figure 12: PDAC print, made with a stamp spin coated at 1000 rpm/1000rpm/s with 30 mg/ml (0.19 M) PDAC in de-ionized water and dried for 5 minutes before being stamped for 1 minute on bare silicon. The broken lines of the initial print have been blurred together by rinsing such that only isolated patches of the underlying substrate remain visible.



Furthermore, the printed polymer regions did not become significantly thinner or significantly more even after rinsing. Spin coated stamps produced prints that had 4-8 nm thick layers which had consistent heights over large areas. This height corresponds roughly to the height of a PDAC monolayer [17], suggesting that little more than a monolayer of polymer is deposited under these conditions. For nano-scale polymer printing, it seems more feasible to create monolayers by regulating the amount of ink spun onto the stamp, rather than relying on rinsing to remove excess material deposited (as in micro-scale contact printing).

The best conditions for nano-scale stamping of PDAC thus far rely on spin coating the stamp and using the stamper. The 30 mg/ml aqueous PDAC ink produces fine prints when spin-coated onto a stamp at 3000 rpm/3000 rpm/s, provided that the inked stamp is used promptly and that it is in contact with the substrate for 1 minute. (Figure 13)

Figure 13: Optimal nano-scale PDAC print, using a spin coated stamp and the stamper. 30 mg/ml (0.19 M) PDAC in de-ionized water, stamped on bare silicon, with a stamping time of 1 minute.



There is still much more work to be done on the nano-scale stamping of polymers. Different inks, different pressures, and different processes all still need to be examined, and this work is ongoing. However, figure 13 demonstrates that printing polymers on

this scale is realistic and feasible, and provides hope for further refinements of the nano-contact printing process.

CONCLUSIONS

The success of printing strong polyelectrolytes depends on the properties of the ink solution as well as on the properties of the polyelectrolyte used. SPS is best printed from a concentrated aqueous solution including a large amount of salt. Because of its high sensitivity to processing conditions, SPS is a poor candidate for printing. PDAC can be stamped from either concentrated ethanol based inks or from dilute aqueous ones. The more concentrated ink produces prints faster and more reliably, but causes more damage to the stamps used. PDAC can also be used to print nano-scale features, using a concentrated, aqueous ink.

GLOSSARY

Bilayer—a layer of polymer film consisting of two monolayers bound together. In this paper, “bilayer” generally refers to a monolayer of PDAC paired with a monolayer of SPS.

Feature—each individual part of a pattern. For example, in a pattern of lines, each line is a feature.

Ink—the polymer solution applied to the stamp, and transferred, by printing, to the substrate.

Micro-contact printing—the process of using mechanical stamping or printing to reproduce micron-scale features on the substrate.

Monolayer—a single layer of one particular polymer; half of a bilayer.

Nano-contact printing—the process of using mechanical stamping or printing to produce nanometer-scale features on the substrate.

PDAC— poly (diallyldimethylammonium chloride), a polycation (see figure 1).

PDMS—polydimethylsiloxane, a silicon rubber.

Platform—continuous, un-patterned bilayers onto which the ink is transferred.

Polyanion—a polyelectrolyte with negatively charged groups.

Polycation—a polymer with positively charged groups.

Polyelectrolyte—a polymer with ionic monomers and, hence, multiple charged groups.

Print—the pattern produced by stamping; the transferred image.

SPS—sulfonated polystyrene, a polyanion (see figure 1).

Stamp—the physical device used to make prints (like a rubber stamp that would be used with an ink pad).

Stamper—a simple device used to lower the stamp to the surface of a substrate (see figure 3).

Stamping time—the time the stamp is allowed to sit, patterned side down, on the substrate or platform.

Substrate—the solid surface printed on (if the surface is not coated with bilayers); otherwise, the solid surface under the bilayer platform. In this paper, “substrate” generally refers to a glass slide or a silicon wafer.

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