Fabrication of large-area stamps, moulds, and conformable photomasks for soft lithography

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Abstract: Low-cost fabrication is essential to the successful introduction of organic electronics and reel-to-reel manufacturing processes. Here it is proposed that extending flexography into the micrometre-size resolution regime may provide an economical commercialization path for plastic devices. Flexography is a high-speed technique commonly used for printing onto very large-area flexible substrates. Although low resolution and poor registration are characteristics of today's flexographic process, it has many similarities with soft lithographic techniques. This work shows that large (12 in × 12 in), high-resolution printing plates appropriate for use on small tag and label flexographic presses can be prepared using simple and inexpensive flexographic-compatible processes. This paper illustrates the use of these plates for three representative soft lithographic processes: microcontact printing, replica moulding, and phase-shift lithography.

Keywords: low-cost, large-area stamp, flexography, soft lithography

1 INTRODUCTION

Flexography and microcontact printing (μCP) have basic similarities and ample differences. They both use flexible elastomeric printing plates and are 'inked' with a slightly raised image, which is transferred onto a substrate. Flexography [**1**] can be briefly described as a reel-to-reel, high-speed printing process. It uses fast-drying inks for printing large areas (greater than 1 m^2) on plastic, foil, acetate film, brown paper, and other materials used in the packaging industry with modest resolution (30 μm). In contrast, microcontact printing (μCP) [**2**, **3**], a representative soft lithographic technique, has a demonstrated ability to pattern sub-micrometre features of Au and other metals, typically over small areas with potential applicability to large areas. It is well suited for the fabrication of conducting layers in high-performance electronic devices such as backplanes for electrophoretic displays [**4**]. Numerous groups around the world have demonstrated that this and other techniques are viable for printing electronic devices [**5–7**]. Source/drain levels of thin film transistors (TFT) with small channel lengths have been printed using μCP [**4**], thermal printing [**5**], ink-jet printing [**6**], and photolithography [**7**]. Commercializing high-performance flexible displays might be achieved in a reel-to-reel process in which large-area μCP plates are used in a flexography-like process. A starting point on such an ambitious path, and the heart of this work, is learning how to produce flexible plastic printing plates that offer high resolution over large areas at a reasonable cost.

In this work, it is demonstrated that 12 in × 12 in polydimethylsiloxane (PDMS) stamps with micrometre-size features can be fabricated via a simple procedure. The size was chosen to fit the plate size requirements of small commercial tag and label flexographic presses. Stamps were used to pattern micrometre-size Au lines onto 12 in × 12 in Mylar substrates using standard thiol chemistry for the inks. The large PDMS stamps were constructed via a straightforward and inexpensive process. A standard photoresist (PR) coating was used to create relief structure in a master. The PR was exposed through a glass photomask using a standard exposure unit, which is nearly collimated over a 30 in × 40 in area and commonly available in printing shops. A PR master with lines and spaces (L/S), 1–10 μm wide was then used to produce the 12 in × 12 in PDMS

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stamps. The stamps were inked using established thiol chemistries and micrometre-size Au lines were then patterned onto a Mylar substrate. This simple, low-cost approach to photoresist exposure allows the fabrication of masters up to 30 in × 40 in in size with micrometre resolution without complex photolithography set-ups that are typically used in semiconductor manufacturing or research facilities. It is also shown that these same stamps can be used as moulds for replica moulding of photopolymers and as phase masks for exposing photoresist layers [**8**].

2 EXPERIMENTAL RESULTS

Since most anticipated applications of plastic electronics systems cannot bear high processing costs, the scale-up of μCP presented here is based on simple, low-cost manufacturing steps. First, a large master for the PDMS stamp was fabricated using standard PR technology. A Shipley 1805 PR was coated onto a 14 in × 12 in clean glass sheet (Corning 1737) to 1 μm in thickness using a Meyer rod (Fig. 1(a)). After pre-baking at 115 °C for 2 minutes, a chrome glass photomask (g-PM, Advance Reproductions) was used to pattern this resist. The features in the g-PM included sets of source and drain electrodes with 1, 1.5, 2, 3, 5, and 10 μm channel lengths with lines measuring 500 μm long and 250 μm wide. Four imaging steps were performed using a small, inexpensive 5 in × 5 in g-PM in order to expose the 12 in × 12 in PR area. The mask was sequentially positioned at the four corners of the PR. At each position, the PR areas not in direct contact with the photomask were masked. Having established a vacuum contact between the g-PM and PR, the PR was exposed for 13 s. The PR was exposed using light from an ultraviolet (UV) source (L1261-OLEC lamp). This system (Douthitt) is commonly used in the printing industry for the exposure of large analogue photopolymer plates (30 in × 40 in) used in colour proofing (Fig. 1(b)). The bulb's spectral range and energy density are 360–385 nm and $3.8 \pm 0.1\ \mathrm{mW/cm^2}$ over the exposure area, respectively. After having completed the exposures, the PR was post baked at 115 °C for 2 min prior to its development in MF-319 developer (Shipley) for 1 min (Fig. 1(c)). With this approach, large masters with 1 μm features can be achieved without an I-liner imaging.

The developed PR was then used as a master to fabricate the PDMS stamp (Fig. 2). A fluorinated silane self-assembled monolayer was first applied to the master to aid in the separation of master and stamp. The stamp was formed using one of the following procedures. For thinner stamps, PDMS (Sylgard 184) pre-polymer mixture (1:10) was poured over the PR master and a 250 μm thick,

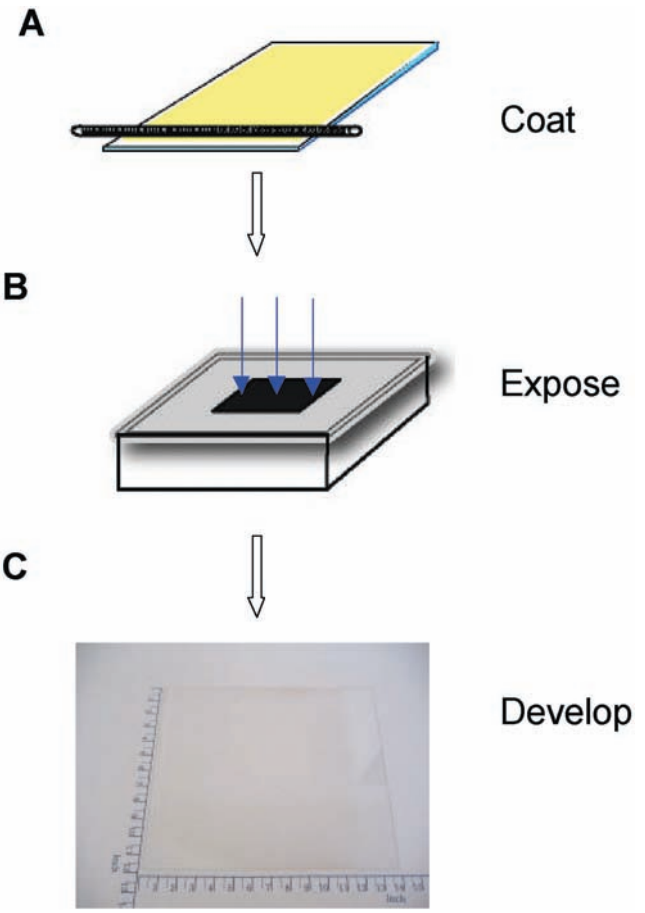

Fig. 1 Schematic illustration of steps for making 12 in × 14 in glass master. (a) A clean 12 in × 14 in × 0.7 mm glass sheet was coated with diluted PR using a Meyer rod to a 1.3 μm thickness and pre-baked for 2 min at 115 °C. (b) Large-area UV exposure unit, contact between photomask (glass or plastic) and glass sheet is done by vacuum. (c) Completed glass master after development in MF-319 developer (Shipley) for 1 min and post baked at 115 °C for 2 min

13 in × 13 in Mylar film was placed on top of the liquid PDMS. The pre-polymer was evenly spread to less than 50 μm in thickness by rolling a Meyer rod over the surface of the Mylar backing film. Pre-polymer of PDMS was cured by holding down the edges of the slightly oversized Mylar backing film using a vacuum plate at 67 °C on a hotplate for 18 h. Thicker plates were fabricated as follows. In order to assure that the PDMS stamp were absolutely flat and uniform, two PDMS pre-polymer mixture (1:5) layers were coated and put in contact via lamination. Thus, a 25 μm thick layer of PDMS pre-polymer was directly coated using a Meyer rod on the PR master surface and another 25 μm thick layer was deposited onto the stamp's Mylar backing (Figs 2(a) and (b)). The two pre-polymer layers were then laminated prior to the curing step. Adhesion between the Mylar backing and the PDMS stamp was enhanced by pre-treating

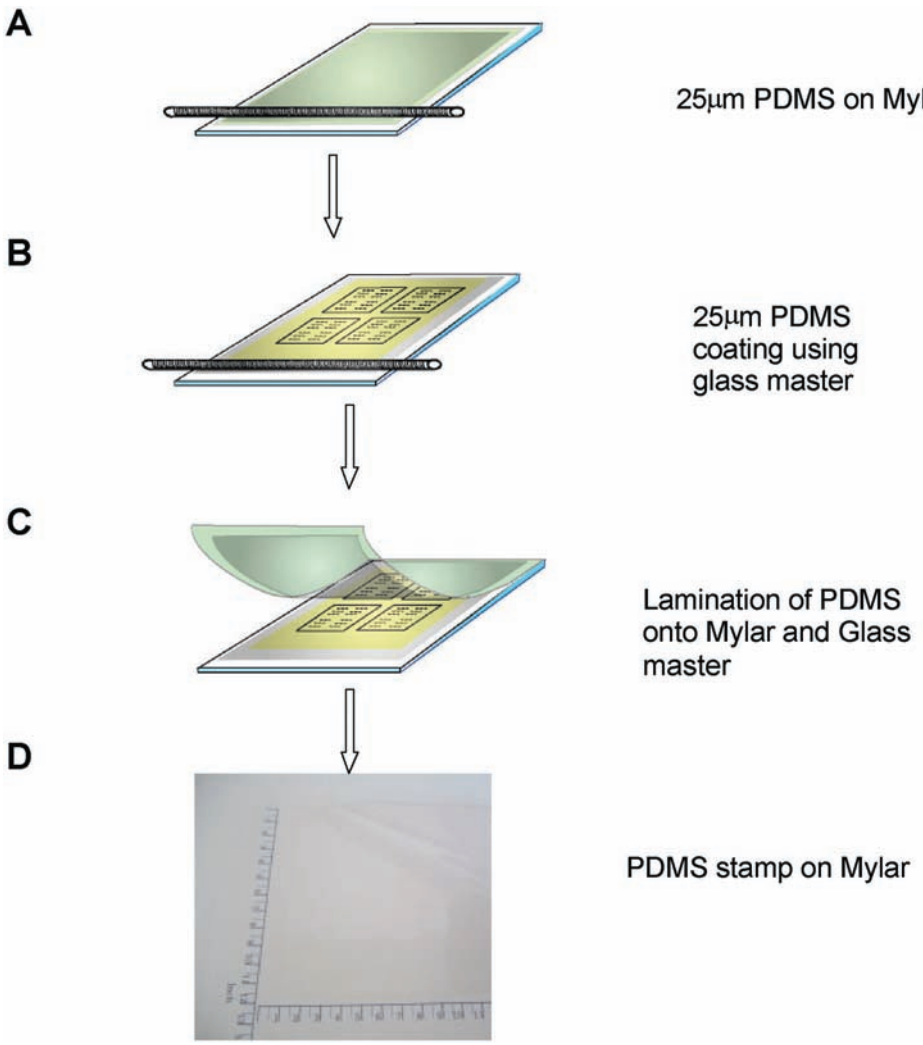

Fig. 2 Schematic illustrations of steps for PDMS stamp fabrication: (a) 25μm 1 : 5 mixture of Sylgard 184 coated onto 250 μm Mylar; (b) 25 μm 1 : 5 mixture of Sylgard 184 coated onto glass master after silane vapour treatment; (c) lamination of PDMS-coated Mylar and glass master; (d) 12 in × 12 in PDMS stamp on Mylar cured at room temperature for 48 h

the Mylar surface with an adhesion promoter (1205, Dow Corning). Curing laminated PDMS stamp at room temperature for 48 h followed by delaminating from glass master completed the stamp fabrication. The thickness of the cured PDMS layer obtained by following the latter procedure is approximately 50 μm (Figs 2(c) and (d)). Atomic force microscopy (AFM) images of the developed PR are shown in Figs 3(a) and (b). Since PDMS stamps are soft, a mould was fabricated (with Norland optical adhesive (NOA 73)) and used for the AFM analysis (Fig. 3(c)). A 25 μm NOA 73 photopolymer film was first coated onto a 12 in × 14 in glass sheet and laminated onto a PDMS stamp. The replication was completed by cross-linking the NOA 73 via a UV exposure and removing the PDMS stamp. AFM images of the Au lines on a Mylar substrate fabricated using μCP from the stamp are shown in Fig. 3(d).

To demonstrate the use of the resulting stamp, μCP was performed on a layer of Au on plastic. In particular, Ti/Au (2 nm/20 nm) film was deposited onto a 12 in × 12 in Mylar film (250 μm thick) using an e-beam evaporator. After the stamp had been inked with a 1 mM hexadecanethiol solution, the stamp was gently brought into contact with the Au-coated Mylar surface. The contact between the stamp and the Mylar was established in a gradual way in order to control the propagation of the wetting front (from top to bottom) and avoid the formation of trapped air bubbles. The thiol molecules were transferred from the raised regions of the stamp that come into contact with the Au surface. An aqueous ferro/ferri cyanide etchant was then used to etch away the Au in the areas unprotected by the thiol molecules [**2**].

In addition, the stamps are phase masks that can be used to produce submicrometre features of

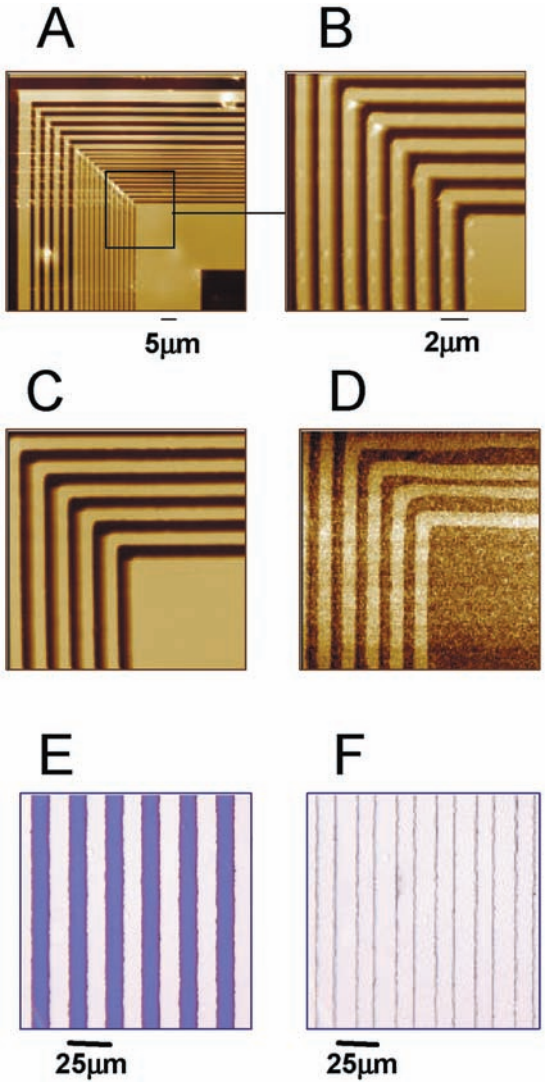

Fig. 3 (a) AFM of 1 and 2 μm line and spacing of developed photoresist on Kapton; (b) detail AFM of 1 μm L/S of image (a); (c) AFM 1 μm line and spacing of replicated NOA 73 mould from PDMS stamp; (d) AFM 1 μm line and spacing of etched Au after thiol stamping using PDMS stamp; (e) optical micrograph 12 μm line and spacing of photoresist on glass master; (f) optical micrograph submicron lines on glass master after phase-shift lithography using PDMS photomask made from master (e)

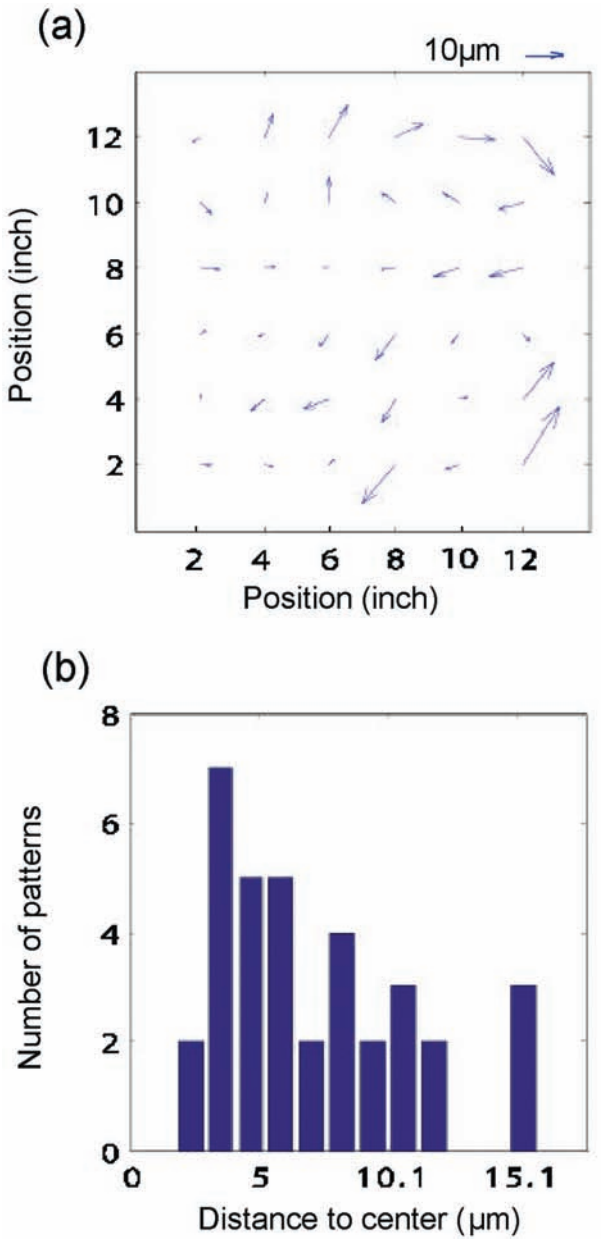

Fig. 4 Distortion measurements collected at 36 points equally spaced across a 12 in × 12 in stamp supported by a 250 μm thick Mylar backing. In this case a vacuum plate was used to hold down the Mylar backing on the glass master during the composite stamp curing step (67 °C on a hot plate for 18 h). (a) The top frame shows a vector diagram of misalignments between the stamp and its master (overall translational, rotational misalignments, and isotropic shrinkage of the stamp are subtracted). (b) The bottom frame shows a histogram plot of the lengths of the vectors illustrated in the top frame. The median distortion is approximately 6.5 μm

photoresist via near-field exposure [**8**]. In this case, a 12 in × 12 in plastic photomask on 250 μm thick Mylar sheet having 12 μm lines and spacings throughout was purchased from Advance Reproductions. A 12 in × 12 in PR layer was coated using a Meyer rod (measured thickness of 500 nm), followed by a prebake at 115 °C for 2 min. The developed PR was used to fabricate the PDMS stamp with 12 μm lines and spaces. The height of the lines relative to the trenches was 500 nm. The adhesion of photoresist to the 12 in × 12 in glass plate was improved by priming the glass with hexamethyl-disilazane (HMDS). The HMDS was vacuum deposited on the glass and baked at 150 °C for 30 min prior to the PR coating. The patterned stamps were placed in contact with

the unexposed PR-coated glass (thickness 500 nm) and exposed for 5 s in the Douthitt exposure system. After post-baking at 115 °C for 2 min, exposed regions were developed with MF-319 developer for 30 s to make sub-micrometre line patterns (Figs 3(e) and (f)).

Deformations in the stamps can cause difficulties in alignment and registration. To quantify these deformations, the exact positions of the features on the stamp were compared with those on the PR master [**9**]. Although absolute distortions are important, relative distortions between multiple prints of the same pattern are enough to prove the feasibility of using the μCP technique for printing multilayer structures. The measurement begins by placing the PDMS stamp on its master and then recording with an optical microscope the offsets between the positions of 36 features of the master and stamp in an array of 6×6 patterns equally spaced across the $12\,\text{in} \times 12\,\text{in}$ area. Figure 4 shows displacement offset vectors after subtracting the effects of rigid translations and rotations and isotropic shrinkage of the stamp (root mean square (RMS) value of residual distortion = 22 p.p.m. (6.5 μm over 30 cm) for a stamp cured at 67 °C hot plate). The stamp used for this experiment consisted of a 50 μm thick PDMS layer supported by a 250 μm thick Mylar sheet. The algorithm used to perform these corrections was similar to that used by Menard *et al.* in the case of thin PDMS stamps backed with two Kapton layers [**10**]. The residual distortions have a median value of 6.5 μm. The approximate accuracy of the measurement method is estimated to be 1.5 μm.

3 RESULTS AND DISCUSSION

One of the factors that may facilitate the successful introduction of plastic electronics would be to provide a clear differentiation between any new approach being brought into the marketplace and the well-established Si technology. Regarding plastic electronics as technologically capable of producing electronic devices over large areas, with high throughput, onto flexible substrates and perhaps with a reel-to-reel printing process would clearly emphasize the distinction. The aim of this work was to support this idea by proposing that μCP could perhaps be the starting point for the development of μ-flexography.

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