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Three modes of inkless micro-contact printing: contact printing, edge spreading, and channel stamping

Ju-Han Kim, Dahl-Young Khang *

Department of Materials Science and Engineering, Yonsei University, 50 Yonsei-ro, Seodaemun-gu, Seoul 120-749, Korea

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ABSTRACT

Three different modes of printing that use recovered siloxane oligomers from a patterned elastomeric stamp, i.e., contact printing, edge spreading, and channel stamping, have been demonstrated. In contact printing mode, the recovered oligomer molecules are transfer-printed on substrate areas with which the protruding pattern features of the stamp are in intimate contact. When the spacing between protruding features becomes large enough, the printing occurs mainly along the pattern edge, or edge spreading mode. If the spacing between protruding features becomes small enough, on the other hand, the printing occurs on areas where the stamp does not make direct contact with the substrate. These three different modes of inkless micro-contact printing with patterned stamp can extend the applicability of the process for generating various pattern features. Also, possible mechanisms for the observed three different modes of printing have been discussed.

1. Introduction

Patterning of materials at micro- or nanoscale is one of the most important steps in diverse fields, and photolithography has long been the choice of method for the purpose. Considering the complex equipments/facilities and expensive materials cost that are needed for photolithography, however, many alternative patterning techniques that can overcome the limitations of photolithography, partially or completely, have been suggested and developed. Among them, soft lithography [1–3], a collective term representing various patterning techniques based on the usage of elastomeric stamp, is a simple yet low-cost process and thus has been widely used in various fields. Micro-contact printing (μCP) [4–6], as one of the soft lithographic techniques, can be considered as a small-scale version of stamping in our daily life, in that an elastomeric soft stamp that has micro/nanoscale topography and has been inked with a self-assembled monolayer (SAM) material prints/transfers ink from stamp onto substrate surface. The molecular-scale thickness of transfer-printed SAM ink has made the process perfectly fit for modifying surface properties, such as chemical heterogeneity and wettability, let alone the method can be used as general-purpose surface patterning technique.

Recently, several studies [7–11] have shown that the μCP process can be done without using substrate-specific, expensive SAM materials as an ink, and the process is termed as "inkless" micro-contact printing (IμCP). The key to achieving IμCP is the use of the hydrophobic recovery [12–21] phenomenon of elastomer, polydimethylsiloxane (PDMS). Even after the typical (60–70 °C, >2 h) curing step, there remain unreacted oligomers of siloxane molecule inside the cured PDMS stamp. These oligomers diffuse out to the surface and make the hydrophilicized stamp surface hydrophobic again, which is well-known phenomenon in electric insulation field. The same phenomenon has been found to occur in μCP process [22–25]; typical μCP with a SAM ink leads to the printing of SAM contaminated with siloxane oligomers, which is in general nuisance in μCP. In IμCP, on the contrary, the recovered siloxane oligomers are utilized as an ink material, instead of substrate-specific, expensive SAM materials in conventional μCP. Here, simple conformal contact with patterned PDMS stamp onto a substrate surface for a given time completes the process. The IμCP has been shown to be used for general-purpose surface patterning [11] or surface modification [7–10].

In this work, we demonstrate other modes of IμCP, in addition to typical contact-printing one. Depending on PDMS stamp properties, such as mixing ratio between base resin and curing agent, contact time, and stamp geometry, the IμCP is found to result in edge spreading or channel stamping. In edge spreading mode, which occurs under low curing agent content and large spacing between pattern features on a stamp, recovered oligomers are printed along the edge of pattern features on the stamp, which is quite similar to edge spreading lithography [26–29]. On the other hand, channel stamping, or oligomer printing on areas where stamp and substrate do not make direct contact, occurs when the pattern spacing on a stamp is small. The channel-stamping mode leads to exactly the opposite replica of a stamp pattern on a substrate, while the contact printing mode results in the same pattern as on a stamp. Further, possible mechanisms for these different printing behaviors are discussed. These different modes of IμCP reported here

* Corresponding author. Tel.: +82 2 2123 5835; fax: +82 2 312 5375.
E-mail address: dykhang@yonsei.ac.kr (D.-Y. Khang).

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can expand the applicability of the process to generate various pattern features from the same master mold, simply by changing the process conditions such as stamp properties and contact time.

2. Experimental details

The elastomeric PDMS stamps (Sylgard 184, Dow Corning) were replicated from patterned photoresist (PR)/Si substrates, which were prepared by photolithography. The 10:1 (or, other mixing ratios) mixture of base resin and curing agent was poured onto PR/Si master substrate, degassed for ~20 min and thermally cured at 70 °C or at room temperature. This patterned PDMS stamp, ~2 cm × 2 cm in size and ~10 mm thick, was kept in contact with cleaned substrates (Si, metals, polymers, etc.) for specific duration.

For the transfer of printed patterns of recovered PDMS onto a substrate, both the wet chemical etching (for Al metal) and the reactive ion etching (RIE; for Si) were used. For the wet chemical etching, uv/ozone treatment of PDMS-printed substrate was applied for 20 min before dipping the samples into wet chemical etchant bath. The wet chemical etchant for Al metal were kindly supplied by Dongwoo Fine Chem., Ltd (MA-SO1B). The plasma-based dry etching was done by home-built RIE system. An atomic force microscopy (AFM; DI 3100, Veeco) in tapping mode was used to image the patterned surface. Finite element analysis was performed using structural mechanics module of Comsol Multiphysics. The PDMS stamp was modeled as a linear elastic material with Young's modulus of 2 MPa and Poisson ratio of 0.48. With 10 mm and 950 kg/m^3 as thickness and density, respectively, the self-weight of the stamp exerted a normal force of ~90 Pa.

3. Results and discussion

3.1. Three modes of IμCP and pattern transfer

Fig. 1 summarizes schematically the three different modes of IμCP, namely, contact printing, edge spreading, and channel stamping. Contact printing is the printing of siloxane oligomers on areas where the stamp contacts the substrate, as usual. The edge spreading is the oligomers printing on both sides of pattern features, with very thin residual layer on the direct contact areas. The degree of this lateral spreading is very small when compared to the size of pattern feature, which enables the fabrication of nanoscale patterns from micron-scale ones. Lastly, channel stamping is the printing of siloxane oligomers on non-contact regions with minute transfer of oligomer on contacted regions, which seems rather counter-intuitive. However, this mode of IμCP is a special case of edge spreading; edge spreading becomes channel stamping when both spreading fronts meet together.

Fig. 2 shows the representative IμCP results and Si substrate surfaces after the pattern transfer using the printed oligomers as an etch mask. In typical contact-printing mode, as shown in Fig. 2a, the recovered siloxane oligomers are printed on areas where the stamp and substrate were in intimate contact. Here, the PDMS stamp used was made under the typical conditions (10:1 weight ratio between base resin and curing agent, cured at 70 °C for >2 h).

After the etching of Si substrate with SF_6 reactive ion etching (RIE), the substrate has the same topography with the stamp used, i.e., protrusions (recessions) on the stamp lead to protrusions (recessions) on the substrate. When the PDMS stamp used for IμCP is made with lower curing agent content, i.e., 20:1 weight ratio, the printing mode changes to channel stamping, as shown in Fig. 2b. In this mode of IμCP, the channel areas, that is, areas where the stamp and substrate were *not* in direct physical contact, were printed with recovered siloxane oligomers. After the SF_6 RIE, now the substrate surface has the opposite topography to that of the stamp used; protrusions (recessions) on the stamp result in recessions (protrusions) on the substrate. Note that the feature sizes on the PDMS stamp were in similar size (1–1.5 μm), the contact time was 4 h and the IμCP was done at room temperature for both samples in Fig. 2a and b. Opposite surface topography was obtained simply by changing the PDMS mixing ratio, under the almost same printing conditions. When the distance between protruding features on the stamp becomes large enough, there are printed siloxane oligomers along the edges of protruding features, as shown in Fig. 2c. This edge spreading mode enables "downscaling" by IμCP, that is, fabricating smaller pattern features on a substrate from larger features on a stamp.

3.2. Time evolution of edge spreading and downscaling

For the above-mentioned downscaling to be practical, the edge spreading should be a controllable process. The edge spreading is believed to be due to surface diffusion of ink materials [6,26–28] on a substrate. Thus, we traced the edge spreading behavior of recovered siloxane oligomers on Si surface as a function of contact time, as

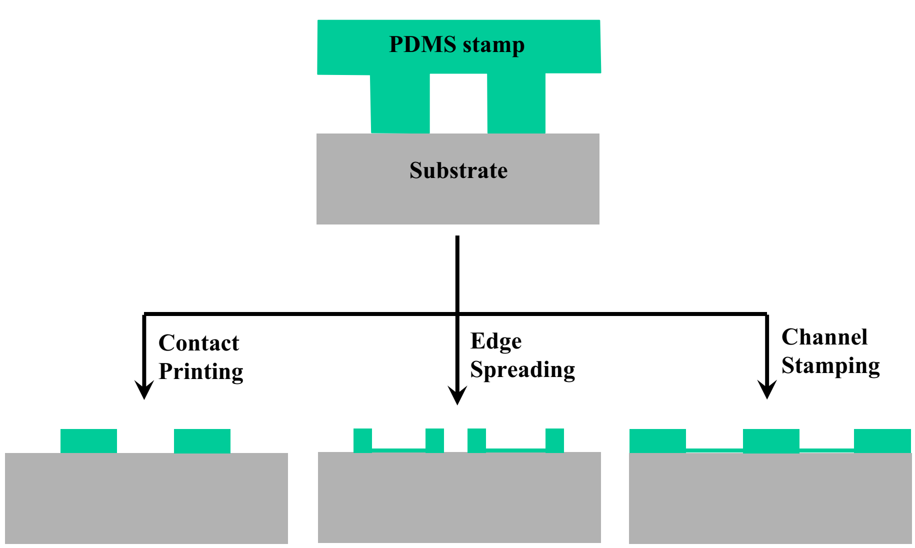

Fig. 1. Three different modes of IμCP of patterned PDMS stamp on a substrate. (Left) Contact printing, that is, transfer of siloxane oligomers where the stamp-substrate contacts are made. (Middle) Edge spreading, a thicker oligomer layers at both sides of protruding stamp features with much thinner layer on contacted areas. (Right) Channel stamping, where the spreading fronts from both sides meet to form thicker layer with much thinner one on contacted regions.