Ink dependence of elastomeric stamp in non-photolithography

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Abstract

We describe that an elastomeric stamp of poly(dimethylsiloxane) (PDMS) can modify the surface energy of some surfaces when brought into conformal contact with the number of stamping. We focus on an increase of the hydrophobicity of the patterned surface due to diffusion of low molecular weight (LMW) silicone polymer chains. The transfer of PDMS to the surface during patterning is relevant to and calls for attention by those who are using this method in applications where control of the surface chemistry is of importance for the application.

1. Introduction

Siloxane-based elastomers have found widespread use as sealants, for encapsulation and packaging of electronic components,[1] and, most recently, for soft lithography. [2] In soft lithography, the relief structure of a stamp is used to form desired pattern. The most important tool used in soft lithographic techniques is a transparent elastomeric poly(dimethylsiloxane) (PDMS). PDMS is very soft (Young's modulus ~ 2 Mpa), low surface energy (~ 20 mJ/m^2), chemically cross-linked rubber, which easily established conformal contact with a substrate and exhibits excellent printing (for example, micro-contact printing) characteristics with inks. The conformal contact between the stamp and the surface is ascertained by the interfacial forces and flexibility of the stamp material.

A matter of concern, in some situations where non-conventional lithography with contact process between patterned surface and a PDMS stamp is used, is the risk of the transfer of un-cured or low molecular weight molecules/oligomers from stamp to the patterned surface.

Recent work [3] suggests that organic light-emitting diodes (OLEDs) formed by soft-contact lamination using a PDMS stamp of metal electrodes to form organic electroluminescent (EL) layers. Virtually, the OLEDs had a double cathode device for the efficiency or lifetime of the device. [4] Thus, when metal are deposited on a contaminated surface with un-cured PDMS chains, the resulting degradation of the metal substrates caused film delamination or diffusion into the patterned metal layer, which produced surfaces to which deposited films do not adhere, laminate, or wet.

In this article, we demonstrate that a surface can be changed by PDMS-based lithography and suggest the role that the ink design plays in non-photolithography with contact between the PDMS stamp and ink.

2. Experimental details

The PDMS stamps were prepared by casting the PDMS precursor (Sylgard 184, Dow Corning) on the substrates with a curing agent in the ratio of 10 to 1 against the masters prepared by photolithography and curing at several temperature (from 80 to 230 °C) for 1 h. Soft UV-imprinting was used PDMS stamp cured at 80 °C for 1 h.

The substrate was bare glass (thick ~ 0.7 mm) and cleaned in succession by deionized water and UV/ozone treatment.

The ink was spin-coated onto the bare glass (100 × 100 mm^2) at 1000 rpm for 20 s, and then the sample contacted with stamp (100 × 100 × 3 mm^3) was exposed UV light (365~436 nm, Karl Sűss MA 45). The irradiation power was calibrated to 8 mW/cm^2 at 365 nm. All samples were exposed for 2 min to UV light.

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Advancing contact-angle, surface tension of the used inks, and surface energy of the PDMS stamp measurements were performed using a Krüss contact angle measuring system DSA 100 (KRÜSS GmbH, Germany). Advancing contact angles were taken at approximately 10 sec after the application of the droplet and measured 9 points in 100×100 mm^2 area. The X-ray photoelectron spectroscopy (XPS) spectra were obtained with a VG Scientific ESCA Lab 200R, using a Mg Kα anode X-ray source. The X-ray gun was operated at 300 W (12.5 kV and 20 mA). The pressure in the analysis chamber was maintained at 5×10^{-10} torr. The spectra were referenced to the C 1s peak (binding energy = 284.5 eV) and Au 4f peak (binding energy = 84 eV). The images were obtained by optical microscopy, scanning electron microscopy (SEM), and atomic force microscopy (AFM, operated in non-contact mode).

3. Results and Discussion

The change to a hydrophobic surface of the contacted substrate with PDMS stamps can be explained by simple advancing contact angle (ACA) analysis. Transferring un-cured PDMS chains from the bulk as well as the un-cured PDMS chains of the stamp surface could regenerate the hydrophobic surface as well as allow for repeated stamping with the same stamps.

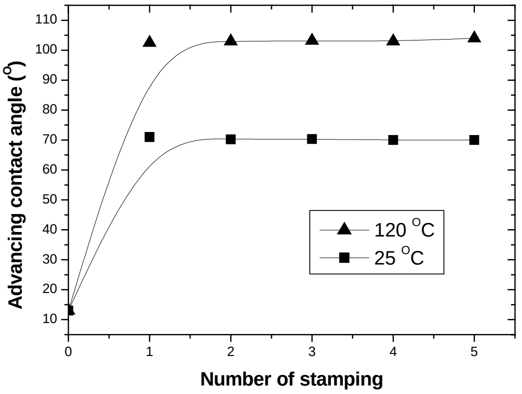

Figure 1. Advancing contact angles of water on the stamped surface as a function of number of stamping annealed for 10 min at 25 °C and 120 °C after contact with bare glass.

As in Figure 1, this was similarly shown for hydrophobic glass surfaces when there was an increase in stamping times and the ACAs were increased with increasing temperature after contact between glass and PDMS stamp. These PDMS chains (LMW molecular or its oligomers) have a low pour point (-40 ~ -50 °C) and glass transition temperature (-123 °C) [5] that enables them to diffuse onto the contacted surface through a pore structure of the free volume of PDMS bulk at ambient temperature. The diffusion of the residue PDMS chains in cured stamp can be increased by increasing the annealing temperature, as well as by a jump in the contact angle at ambient temperature in comparison to bare glass (ACA of water on the cleaned bare glass ~ 13.1°).

Additional experiments were also carried out in order to validate the effect of curing temperature of the PDMS stamp. As shown in Figure 2, however, we could not obtain a decrease of the hydrophobicity by increasing the curing temperature, contrary to other groups' speculations.[6]

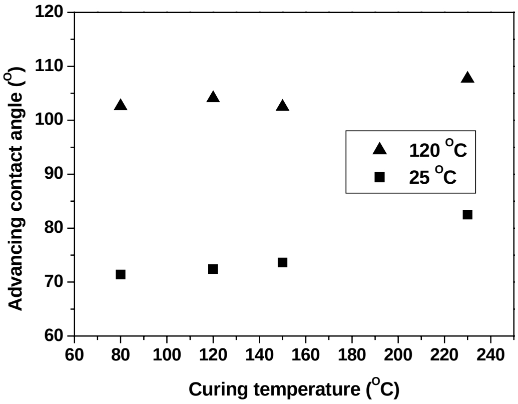

Figure 2. Advancing contact angles of water on the stamped glass surface as a function of the curing temperature of the PDMS stamp and annealed for 10 min at (▲) 120 °C and (■) 25 °C after contact of the PDMS stamp.

Recently, patterning of fluorescent polymer film was achieved by confining polymer solutions on the modified surface, thus using the hydrophobic change due to PDMS stamp.

The results were verified when the transferred PDMS chain on the patterned surface was detected by X-ray photoelectron spectroscopy (XPS) analysis of Si 2p peaks. Figure 3 shows the XPS spectra of the Si 2p region for patterned ink surface using PDMS stamp. The Si 2p peak at 102 eV is assigned to a PDMS. [7, 8] The intensity of the Si 2p peak depends on contacted ink and, in case of ink-1, has no link to contacting time before UV curing after contact PDMS stamp with ink coated glass. The intensity of the PDMS Si 2p peak is increased when contacting time is increased in case of ink-2 and ink-3 (not shown).

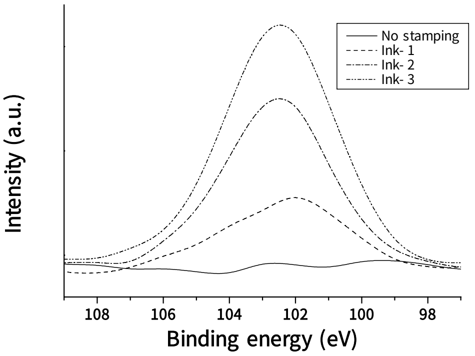

Figure 3. Si 2p spectra (XPS) of samples soft UV-imprinted with flat PDMS contacting for 1 min before UV cured.

4. Summary

In this study, we have shown that the residual PDMS chain in the PDMS stamp is transferred from stamp to the contacted surface during PDMS-based lithography. Through contact angle analysis and XPS, we demonstrate the increase of the diffusion of the un-cured PDMS chain due to the increase in free volume of PDMS stamp bulk by swelling of between the ink and the PDMS chain. Indeed, the ACAs of water on the used PDMS stamps preserved near 110° within all experiments in this work. In other word, the transfer of the low molecular weight PDMS chain due to ink solubility for stamp can be major factor in side of inter-action between the stamp and ink.

5. References

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