LONG-TERM STORAGE OF NANOLITRE AND PICOLITRE LIQUID VOLUMES IN POLYMER MICROFLUIDIC DEVICES

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ABSTRACT

We introduce uncomplicated nanolitre (23 nL) and picolitre (3.5 pL) liquid volume encapsulation in Off-Stoichiometry Thiol-Ene-Epoxy polymer (OSTEmer™322) wells using spontaneous room-temperature bonding of gold films to thiol and thioether groups present on the surface of the polymer for leak free sealing. First, we show liquid encapsulation within nL, and pL polymer wells by utilizing 100 nm thin Au-film transfer-bonding onto intermediately cured, and micropatterned OSTEmer™322. This approach yielded 3 magnitude orders smaller liquid volume encapsulation than previously reported. Secondly, we show that encapsulated liquid can be stored for >116 h. Finally, we demonstrate encapsulated liquid release by thermopneumatic bursting. We conclude that OSTEmer™322 is excellent for metal-film sealant integration in polymer microfluidic devices.

KEYWORDS: Liquid encapsulation, long-term liquid pre-storage, gold film transfer, bonding, microdevice integration, off-stoichiometry thiol-ene-epoxy

INTRODUCTION

Liquid encapsulation and storage on microsystems has been previously demonstrated in the µL range using blister-packs [1], stick-packs [2], and glass ampules [3], and on Si-based microsystems using Au-based sealing [4-6]; and in the nL range, for polymeric microsystems, using Parylene C sealing, although the latter suffers from liquid loss over time (50 % in 5 h) [7]. Liquid-sealing layers must have good barrier properties but must also be thin enough to allow liquid release, e.g. by bursting using pneumatic pressure [5], electrochemical etching [5], or electrolysis [7], hence only metallic sealing materials should be considered for long-term storage. However, integration of metallic sealing materials to polymeric microsystems is typically complicated, and requires back-end processing. Off-Stoichiometry Thiol-Ene-Epoxy polymers, e.g. OSTEmer™322 (Mercene Labs AB, Sweden), has recently been introduced as a commercial polymer system for manufacturing of lab-on-chip devices as previously reported [8]. These are dual-cure polymers featuring surface-reactive thiol- and epoxy-groups after the first cure, where the thiols spontaneously bonds to Au surfaces [9] and featuring an inert, hydrophilic surface with good water barrier-properties after the second cure [10].

Here we perform uncomplicated transfer-bonding of a 100 nm thin Au-film from an oxidized Si handle-wafer to liquid-filled pL- and nL-well arrays in an intermediately cured OSTEmer™322 substrate. The Au bonds spontaneously to the surface-reactive thiol and thioether groups of the intermediately cured polymer, sealing the liquid-containing wells. nL-wells can be filled by pipetting, whereas transfer bonding of Au on top of pL-wells is performed during liquid submersion of the substrate [11] to avoid evaporation.

EXPERIMENTAL

Au-film wafers were manufactured by sputtering 100 nm Au-layers on SiO₂/Si-wafers, followed by cleaving into ~1-2 cm² chips. Well-arrays of similar area, with well sizes of either 500 µm diameter and 116 µm depth (~23 nL), or 15 µm diameter and 5 µm depth (~3.5 pL) were replica-molded in freshly mixed OSTEmerTM322 using micropatterned PDMS molds, after triggering the first polymerization step with UV-light (OAI, Milpitas, USA, collimated medium pressure Hg lamp model 30, 10mW/cm2 60 s). Well-arrays were obtained via demoulding from the PDMS-molds. For nL-well sealing, the wells were pipette-filled with Rhodamine B solution, and thereafter sealed by gently pressing an Au-film-chip onto the well-array surface, followed by peeling off the well-array (Figure 1 A). For pL-well sealing, Au-film
was first floated on the surface of Rhodamine B solution by spontaneous release of the Au-film from the SiO$_2$-substrate, and thereafter scooped up by the pL-well arrays (Figure 1 B). Au and OSTEmer$^{TM}$322 bonded spontaneously and the second slower thermal cure of OSTEmer$^{TM}$322 occurs spontaneously at room temperature during the following 24-48 h.

**RESULTS AND DISCUSSION**

Liquid-filled wells were successfully sealed by a 100 nm thin Au-film (Figure 2 A and B). The wells were then kept at 24 °C for 116 h. Rhodamine B containing liquid was released from nL-wells after 116 h using thermopneumatic bursting by heating to ~60 °C for 45 min (Figure 3 A and B). Liquid release was verified by fluorescence microscopy (Figure 3 C), where Rhodamine B fluorescence could only be seen in wells that had ruptured. Using method A (Figure 1A) we observed that cracks were created in the Au-film during the peel off step because of stress induced during handling. Cracks could be avoided effectively by using method B (Figure 1 B), as method B significantly reduces stresses on the Au-film. However, method B wasted a large amount of liquid, and the method also resulted in the formation of wrinkles in the gold film during lift-up. The reason for this was that the gold film got stuck to the polymer surface in random places during the lift up, which prevents the fully stretched geometry required for wrinkle free coverage. In turn, these wrinkles provided evaporation pathways for the liquid from the wells. Small air-bubbles were observed in many wells probably due to that air was trapped during the sealing step, or due to evaporation through cracks or wrinkles.

**Figure 1: A) Sealing process using direct transfer of a 100 nm Au-film to patterned and liquid-containing OSTEmer$^{TM}$322 nL-well-array. B) Sealing process of the OSTEmer$^{TM}$322 pL-well-array using Au-film floatation of a 100 nm Au-film.**

**Figure 2: Microscopy of liquid-containing wells seen through Au-film. A) nL-wells. i) air-bubble, ii) liquid. Scale-bar 500 µm. B) pL-wells. Arrow is indicating trapped air. Scale-bar 15 µm.**
CONCLUSION
We conclude that nL and pL liquid volumes in micropatterned OSTEmer™ 322 can be sealed utilizing the spontaneous bonding of nanometer thin Au-films to the thiol functional surface of the intermediately cured polymer. Thanks to the room temperature bonding, this material is a potential candidate for applications where temperature sensitive species, such as biomolecules, are involved. Hence, the proposed method of liquid encapsulation could potentially be applied to long-term pre-store of liquid in bio-arrays of nL-wells or pL-wells of OSTEmer™ 322 polymer.

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