Direct photo-patterning of thiol-ene thermoset polymer thin film structures by DLP lithography

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Thiol-ene and thiol-ene / acrylate thermoset polymers offer valuable thermo-mechanical properties such as near-zero cure stress, stability up to near 300 ^{o}C processing temperatures, high strain capacity , tunable elastic modulus and more [2004.Hoyle, 2013.Simon], which enables their use as a substrate material or/and as a functional material for flexible electronics and microfluidics. Because their glass transition temperature can be tuned close to body temperature, their application in biomedical implants (i.e. in softening neural interface devices) is being explored [2013.Ware]. Direct micro-patterning of these plastics by photo-polymerization has been studied to a limited extent [2013.Kasprzak, 2012.Karlsson]. These attempts were done with a method referred as "contact liquid photolithographic polymerization" (CLPP), using common photo-masks that make contact to a liquid thin film of the monomer solution. Here, we present our first results on photo-patterning thiol-enes and thiol-ene / acrylates by a contact-less method: projection lithography using digital light processing (DLP) technology. We study pattern development and compare our results to those published using CLPP.

Two different monomer solutions were studied: a primary ene monomer mixed with a secondary thiol, and a primary ene mixed with an acrylate and a primary thiol. These compositions were chosen for specific applications. The monomer solutions behave as a negative resist based on radiation-induced cross-linking reactions. In order to be able to expose using common DLP technology, the solutions were sensitized to visible light using phenylbis(2,4,6-trimethylbenzoyl)phosphine oxide (BAPO) as a photoinitiator. Thin films of 10 to 60 micrometer thicknesses were prepared by spin-coating on 4-inch silicon wafers. After exposure, the patterns were developed by soaking the surface with extra amount of the ene monomer, followed by rinsing with acetone. The patterns were analyzed using optical microscopy, contact profiler mapping, AFM and SEM. We have found that during exposure tall features emerge at the edges of the exposed regions, drawing material from nearby unexposed regions. This is apparently visible in the profiler data, as well as in the optical micrographs shown in Figure 1. We have confirmed that the edge features are not artifacts of DLP image processing, and also appear when a mask aligner is used (with a gap maintained between the mask and the monomer solution), see in Figure 2. Further work is required to study and describe the phenomenon.

References

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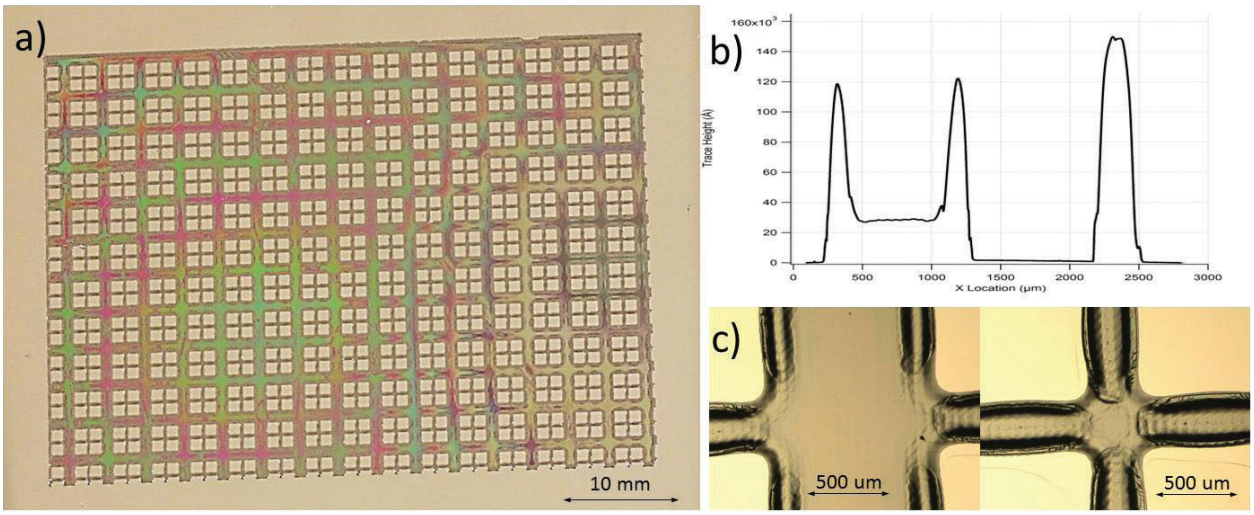

Figure1. Pattern created by projection lithography using DLP technology. A periodic "roughness" on the pattern is observed to correlate with the 70 micrometer DLP pixel size used in this study. The emerged edge features are much taller than the original thickness of the monomer solution.

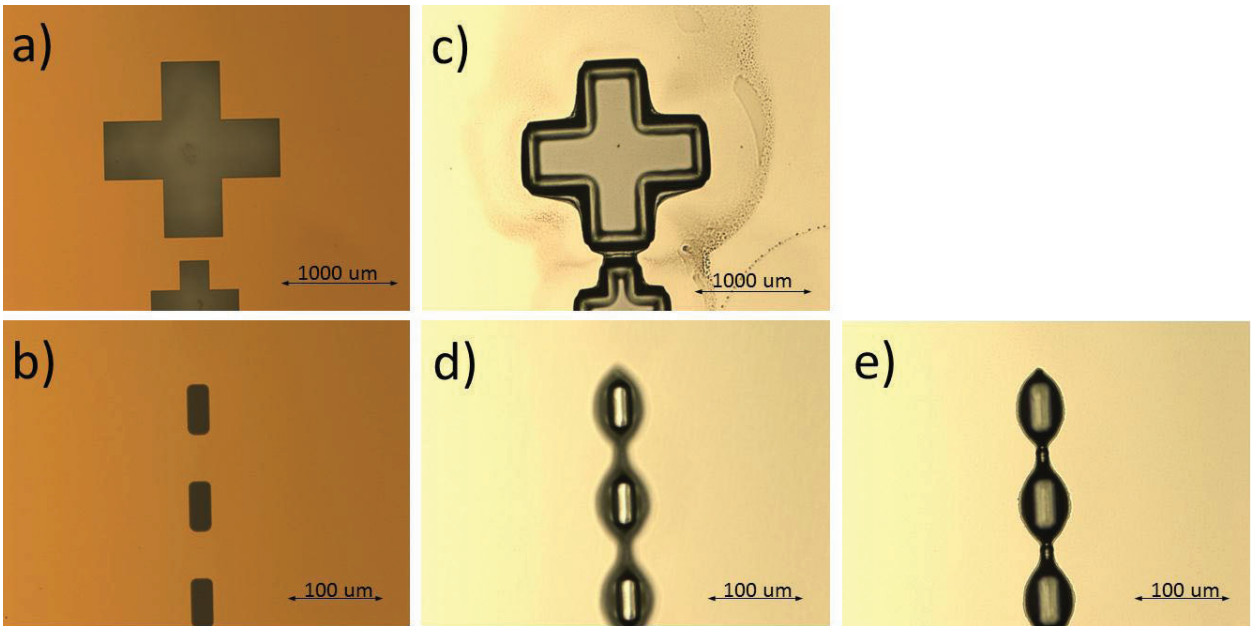

Figure 2. Pattern created by photolithography using a Karl Suss mask aligner and custom spacers that maintained about 100 micrometer gap between the mask and the monomer solution surface during exposure. Optical micrographs of patterns on the mask (a and b) and of resulting patterns of thiol-ene / acrylate (c,d and e) show the edge features emerging on similar length scales to those observed while using DLP technology.