

NANOCONTACT MOLDING OF THIOL-ENE PHOTOPOLYMERS

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Introduction

The preparation of complex patterns in polymer films has been widely explored by classic photolithographic techniques¹ as well as newer methods such as microcontact printing (μ CP) of self-assembled monolayers,² polymer brushes,³ and block copolymer self-assembly.^{4,5} Other non-optical contact patterning techniques including nanoimprint lithography⁶ and "step & flash" imprint lithography⁷ have recently been seriously examined.

Recently we developed novel nanocontact molding techniques for the replication of nm-scale features on surfaces using functional crosslinked polymeric materials.^{8,9} An advantage of this technique compared with other available imprint methods is the control of the chemistry of the nano-molded polymer and the ability to perform surface transformations via the incorporation of reactive functionality into the crosslinked polymers.

The nanocontact molding process relies on the use of a photopolymerizable monomer composition, both for the creation of the molds and the replication of patterns on substrates. We have relied predominately on resin formulations consisting of a crosslinkable meth-/acrylate monomer mixture that undergoes a photoinitiated polymerization when exposed at 365nm.¹⁰ One current area of interest is exploring other photopolymerizable systems for use in the molding process. Our goal is to develop a suite of moldable materials that are tailor made for advanced performance under a number of variable conditions.

The addition of thiols to olefins to form thioethers is a reaction that has been known since it was reported in 1905,¹¹ and the UV-initiated reaction was reported several decades later.¹² Workers at W. R. Grace & Co. reported the first examples of well characterized, photocured thiol-ene polymers¹³ and work in the area has continued for the last 30 years.¹⁴ We felt that thiol-ene photopolymer could be patterned using our nanocontact molding process in place of more commonly used acrylate-based photopolymers. The reported lack of inhibition by oxygen,^{13,15,16} and the wide variety of available thiol and vinyl monomers¹⁷ has made the examination of these materials very attractive. Herein we report the use of thiol-ene photopolymers in nanocontact molding.

Experimental

Materials. Single-side polished 1" Silicon wafers (diameter: (25.4 ± 0.3) mm, thickness: (254 ± 50) μ m), terminated in 20 \AA native silicon oxide, were obtained Virginia Semiconductor, Inc.. Ethoxylated (2) bisphenol A dimethacrylate (Sartomer), 1-vinyl-pyrrolidin-2-one, acrylic acid, 2,2-bis-acryloyloxyethyl-butyl ester, 4-bromostyrene, 2,2'-bipyridyl, 1,5-cyclooctadiene, and propylene glycol methyl ether acetate (PGMEA) (Aldrich or TCI), pentaerythritol tetrakis(2-mercaptoproacetate), and 1,4-cyclohexanedimethanol divinylether and were used as received. 2,2-Dimethoxy-1,2-diphenyl-ethanone (Aldrich) was recrystallized prior to use. Nanocontact molding was performed using a modified Instron 1122 frame equipped with a 400W OAI 365 nm flood exposure system.

Mold Fabrication. Thin glass plates were cleaned by first soaking for 5 min in a solution of *No-Chromix* in concentrated sulfuric acid followed by extensive rinsing with deionized water. These were then washed in an isopropanol vapor bath and dried in an oven. A filtered 5% solution of 3-methacryloyloxypropyl trimethoxysilane in methanol was then dropped on the glass plates and the excess material was spun off. The substrates were then baked at 100 $^{\circ}\text{C}$ for 10 min. A drop of photopolymer resin (ethoxylated bisphenol A dimethacrylate (54.9%), N-vinylpyrrolidone (16.7%), 2-ethyl-2-(hydroxymethyl)-1,3-propanediol trimethacrylate (16.7%), 2,2,2-trifluoroethyl methacrylate (10%), and 2,2-dimethoxy-2-phenylacetophenone (1.8%)) was placed upon a clean, patterned silicon master and a glass backing plate was placed above. The resin was then cured (365 nm, 35 mW/cm², 1 min) and the backing plate carefully removed from the master to produce an exact copy of the master in negative relief.

Nanocontact Molding. A 25% solution of 1 eq of pentaerythritol tetrakis(2-mercaptoproacetate) and 2 eq of 1,4-cyclohexanedimethanol divinylether in propylene glycol methyl ether acetate was spun onto clean silicon wafers (prepared by UV/ozone cleaning, 150 $^{\circ}\text{C}$, 40 min). The mold prepared above was placed in contact with the resin coated wafer and a pressure of 100 psi was applied. The resin was then cured for 2 min with 365 nm light (35 mW/cm²). Removal of the mold yielded a patterned thiol-ene network polymer.

Results and Discussion

We chose a monomer formulation consisting of equimolar amounts of thiol and vinyl ether functionality. The high degree of functionalization per monomer unit ensured the formation of a crosslinked network photopolymer. Accordingly we used 1 eq of pentaerythritol tetrakis(2-mercaptoproacetate) (1) and 2 eq of 1,4-cyclohexanedimethanol divinylether (2), which after photopolymerization yielded a tough, rubbery crosslinked resin. We performed a number of bulk polymerizations in order to determine the curing behavior and exposure time. We found that 2 minutes exposure at 35 mW/cm² was sufficient.

Molds were fabricated as described in our previous studies.^{8,9} These molds consisted of a thin acrylate network photopolymer layer that was cast from etched Si wafers. The mold was supported on a thin glass backplate and stored under N₂ prior to use.

We attempted to contact mold the resin thiol-ene resin by coating clean Si wafers with a pure monomer mixture, but this proved to be too viscous to allow for high resolution patterning. The monomer mixture was diluted with propylene

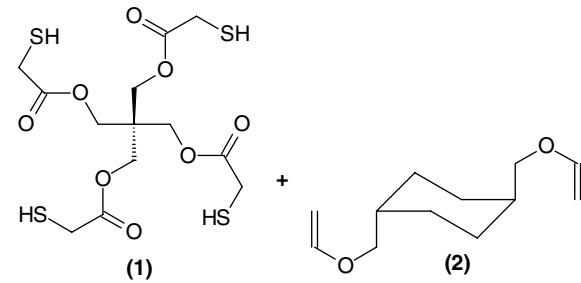


Figure 1. Thiol-ene monomers, pentaerythritol tetrakis(2-mercaptoproacetate) (1) and 2 eq of 1,4-cyclohexanedimethanol divinylether (2).

glycol methyl ether acetate to give a 25 wt. % solution of pentaerythritol tetrakis(2-mercaptoproacetate) (1 eq) and 1,4-cyclohexanedimethanol divinylether (2 eq). This solution was spun-coated onto clean Si wafers (3000 RPM, 10 sec). This resulted in a thin (50-100 nm) layer of photopolymerizable monomer evenly distributed on the Si wafer. This wafer was purged with N₂ and placed in contact with the patterned mold at 100 psi and exposed for 2 minutes at 365 nm. The mold was removed from the wafer, leaving a patterned thin film of cured thiol-ene polymer. Figure 2 shows an optical microscope picture of a 100 x 100 μm test pattern of molded thiol-ene polymer.

Conclusions

We have demonstrated that thiol-ene photopolymers can be successfully used in nanocontact molding. We were able to pattern resins consisting of pentaerythritol tetrakis(2-mercaptoproacetate) (1 eq) and 1,4-cyclohexanedimethanol divinylether (2 eq). This polymerization is initiated in

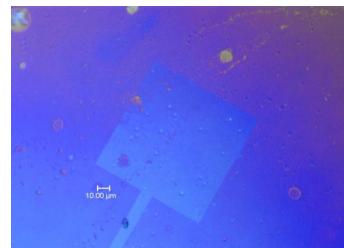


Figure 2. Optical microscope picture of molded thiol-ene photopolymer. Square region is 100 x 100 μm .

the absence of an added initiator, which could enable stable monomer solutions that do not contain added photoinitiator or sensitizers. We are currently exploring the ultimate resolution and performance of these thiol-ene resins and their ability to be utilized as patterned etch resist layers for advanced high-resolution imprint lithography.

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