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An Ultraviolet-Curable Mold for Sub-100-nm Lithography

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This communication introduces a novel ultraviolet (UV) curable mold that enables one to fabricate densely spaced sub-100-nm structures with a high aspect ratio in a short time on a large area. The radiation curable mold has a modulus of 40 MPa, thereby providing the stiffness for replicating fine patterns. It also allows for flexibility when the mold is prepared on a flexible support. This flexibility makes it suitable for large area replication. In addition, it has excellent inertness to chemicals and solvents such that it does not cause deformation or swelling problems.

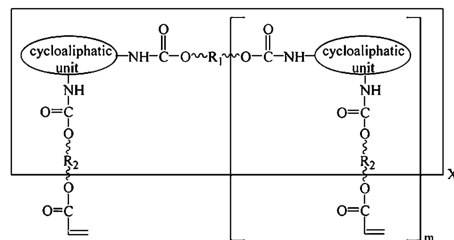
The ability to fabricate nanostructures is essential to modern science and technology.[1] While the conventional methods such as photolithography and electron-beam lithography can be used for the fabrication,[2] they are too costly to use in many applications. In contrast, unconventional methods such as imprint lithography[3] and soft lithography[4] are simple and cost-effective. However, they still have certain drawbacks. The imprint lithography based on a hard mold provides a resolution down to 10-nm feature size, but it requires applying a high pressure for the patterning and a flat surface.[3] On the other hand, the soft lithography based on a soft mold, typically made of poly(dimethylsiloxane) (PDMS), does not necessarily require a pressure or a flatness, but its resolution capability is quite limited.[5] In submicrometer range, the PDMS mold loses its mechanical integrity and deforms into unexpected shapes, resulting in the failure of pattern replication.[6] To overcome these problems, several approaches have been taken such as step and flash method in imprint lithography (SFIL)[7] and utilizing composites or new mold materials in soft lithography.[8,9] Nevertheless, some basic problems still remain, such as use of an expensive quartz mold in SFIL and pattern collapse in soft lithography when densely spaced small features are patterned.

The UV-curable mold in this communication consists of a functionalized prepolymer with acrylate group, a photoinitiator, and a radiation-curable releasing agent for the surface activity. The mold material should have a number of desirable properties such as mechanical rigidity, flexibility, small shrinkage, and light transmittance to UV. Scheme 1 gives the chemical formulas of the species involved and the reaction route to preparing the mold material. The excellent characteristic properties of the mold suggested in this study are a result of the fact that the prepolymer contains both cycloaliphatic and linear long chains.[10] The former provides the rigidity while the latter does the flexibility. Therefore, the material is adequately hard and yet flexible enough for molding. The tensile modulus of the material is 40 MPa (cf. 1.8 MPa for 184 PDMS or 8.2 MPa for hard PDMS), and the elongation at break is 31% (UTM analysis).

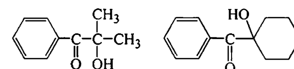
It is important for the cured mold to have a low surface energy for the mold to be removed easily and cleanly after replicating. For this purpose, a releasing agent is utilized to promote the releasing property. Although silicon-based oils are widely used in

Scheme 1. Preparation of a UV-Curable Mold and Reaction Route[a]

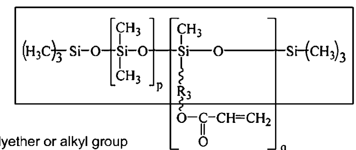
Functionalized prepolymer with acrylate group



Photoinitiator
(Hydroxyphenylketone or
1-Hydroxycyclohexylphenylketone)

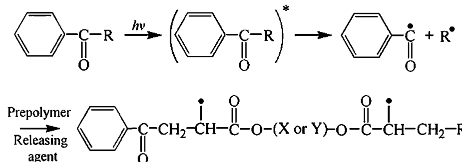


Releasing agent
(Organo-modified
silicone acrylate)



R1, R2, R3 ~ polyether or alkyl group

Reactions



[a] X and Y denote the unchanged fragments during the photopolymerization process.

coating industry, their incompatibility and nonreactivity make them unsuitable as a releasing agent for this UV-curable mold. TEGO Chemie Service has commercialized acrylated organo-modified polysiloxanes (Rad 2200N) that are compatible with the UV curability. These additives contain not only polyether or alkyl pendants substituted with some methyl groups for compatibility but also reactive acrylate functional groups for radiation curability. Even at 0.4 wt % loading of the additive in the mold composition, the surface energy of the cured mold decreases to around 23 dyn/cm, comparable to that of PDMS (~21.6 dyn/cm), which is sufficiently low enough for clean release.[11] Therefore, simply introducing a small amount of the additive (1 wt %), which participates in the reaction, serves the purpose of lowering the surface energy while not affecting other properties.

Shown in Figure 1 is the procedure for replicating the mold. The liquid composite material is drop-dispensed on a master pattern. A flexible and transparent support made of polyurethane elastomer or soft epoxy resin is brought into contact with the coated composite liquid. Subsequently, it is exposed to UV ($\lambda = \sim 250-400$ nm) for a few tens of seconds through the transparent backside (dose = 100 mJ/cm^2). After the UV curing, the mold is removed from the master by being peeled. Trimming the edges completes the preparation of the first replica mold, which is the negative of the

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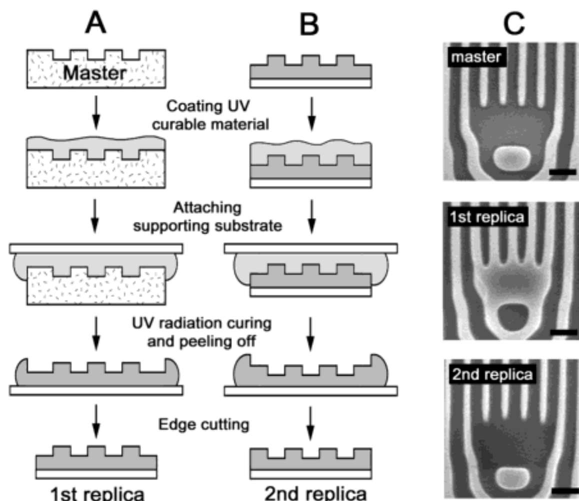

Figure 1. Schematic illustration of the molding process. The lighter shaded regions represent the prepolymer and the darker ones represent the cured polymer. (A) The first replica is the negative replica of the master pattern. (B) Process of self-replication. The second replica is the positive replica. (C) SEM images, from the top down, of the master, the first replica, and the second replica. Bar scale is 500 nm.

master. In Figure 1C, the features in the first replica look rounded because of the discordance between the top and bottom shapes of the master, but the shape is recovered in the second replica.

One notable feature of the mold material is that it allows self-replication of the mold even for very fine features (less than 100 nm), which is difficult to achieve with other molding materials because of the pattern collapsing problem arising from their low mechanical strength. For the self-replication, trapped polymer radicals and remaining unsaturated acrylate in the first replica need to be removed by excessive exposure to UV and/or heat treatment at an elevated temperature (~60 °C), usually for several hours.[10] Then the same procedure as in Figure 1A is repeated for the fabrication of the second mold (Figure 1B), which restores the negative to the positive original master pattern. Scanning electron microscopy (SEM) images in Figure 1C for a pattern with 100-nm line width and 250-nm spacing show that the replica and the self-replicated second replica can readily be fabricated by the preparation procedure. However, one can observe some shrinkage after the self-replication, as shown in Figure 1C. Although the bulk shrinkage of the material is 0.7%, a little less than that of PDMS, the shrinkage effect is concentrated on the protruding parts of the mold, especially for very fine features, because the strong binding with the support suppresses the lateral shrinkage.

Inertness to chemicals and solvents is an important attribute. The prepolymer does not have particularly reactive polar groups such as epoxide ring and hydroxy group, which tend to interact with other chemicals or solvents. Preliminary results showed that the mold material is inert to some representative polar and nonpolar solvents (see Supporting Information). The mold is also durable in that 500 replication cycles did not result in notable degradation of the mold.

To show the replication capability of the mold for sub-100-nm feature, a 75-nm wide polarizer pattern (MOXTEK, Inc) was used. The SEM micrographs in Figure 2A for the master and Figure 2B for the replicated pattern with the mold demonstrate the replication capability. The replication carried out over an area of 3×5 cm^2 was flawless. Another example of the replication is shown in Figure 2C for a 100-nm equal-spaced line and space pattern with a step height of 330 nm. This result demonstrates the capability to replicate patterns with a high aspect ratio. Shown in Figure 2D is a flexible

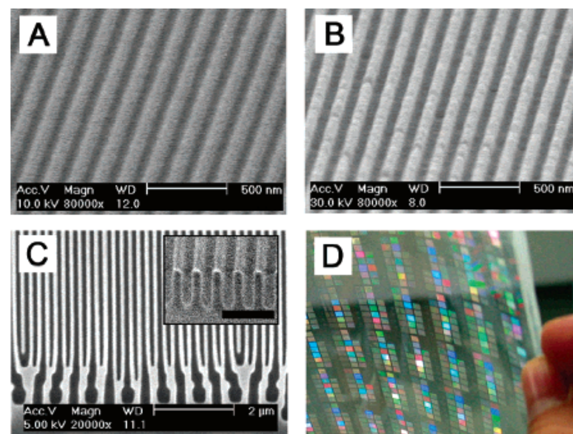

Figure 2. SEM and optical mocroscopic images of replication results. (A) Master pattern of 75-nm line/space polarizer. (B) Replicated pattern of (A). (C) Replicated pattern of a 100-nm line/space circuit pattern. Inset is the cross-sectional SEM image. Bar scale in the inset is 500 nm. (D) Example of large area replication of hologram gratings.

mold made from a silicon wafer master (half an 8-in. wafer) gratings that consist of groups of equal-spaced line and space patterns ranging in size from 250 to 800 nm, which shows the applicability to large area replication.

In summary, this communication describes a novel UV-curable mold that is stiff enough for replicating dense sub-100-nm features. It also allows for flexibility such that large area replication can be accomplished. The composite material is inert to chemicals and is durable for repeated UV curing. The surface energy is made low with a releasing agent such that the mold can be removed easily and cleanly after patterning. These unique features of the material should make the mold quite useful for various patterning purposes.

Supporting Information Available: Experimental details on the specific chemical structures, formulations, and swelling (durability) tests. Stress−strain relationship for the mechanical analysis (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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