A Thiol-ene Degradable Resist for Hybrid Nanoimprint-soft Lithography

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Soft nanoimprint lithography has been developed to overcome the disadvantages of conventional nanoimprint based on rigid mold. A commercial UV transparent elastomer, polydimethylsiloxane (PDMS), is widely used as a mold in soft nanoimprint lithography.[1, 2] However, when it turns to replicating patterns with sub-100 nm scale features, PDMS is unable to avoid pattern distortion due to its low modulus. In our previous work, we developed a hybrid nanoimprint-soft lithography (HNSL) mold with a sub-30 nm resolution, which consisted of a rigid cross-linked patterning layer on an elastic PDMS support.[3] The patterning layer was formed from multifunctional acrylated polysiloxane oligomers which enabled the formation of a rigid polymer network for high imprint resolution. However, oxygen sensitivity of acrylate monomers during polymerization makes mold fabrication time-consuming and complicated. In addition, if the master is stained by silicon-containing resist during hybrid mold replication, it is a great challenge to clean the expensive master without any damage.

In this paper, we design a novel UV-curable resist for HNSL mold fabrication, which is degradable under mild acidic conditions and insensitive to oxygen. The resist system comprises an acid-degradable cross-linker, 2,10-diacryloyloxymethyl-1,4,9,12-tetraoxaspiro[4.2.4.2] tetradecane (DAMTT)[4], and an acyrlated polysiloxane, poly[(mercaptopropyl)methylsiloxane] (PMMS). Its cross-linking mechanism is based on thiol-ene chemistry, so that oxygen sensitivity of acrylate group can be avoided. The cured resist can be decomposed into linear chains through the cleavage of acid-labile ketal links and dissolved in organic solvent when heated in an acidic solution (Scheme 1). The resist possesses necessary properties for mold fabrication and imprinting, including low shrinkage (about 5%), high modulus, high thermal stability, high UV transparency and stability in normal environment. Furthermore, since the cured resist is degradable in acidic media, the stained master can be renewed in a mild condition. Figure 1 shows the SEM images of the patterned degradable resist with nanoscaled features of various sizes and shapes by HNSL molds, which are fabricated from the same resist as a patterning layer.

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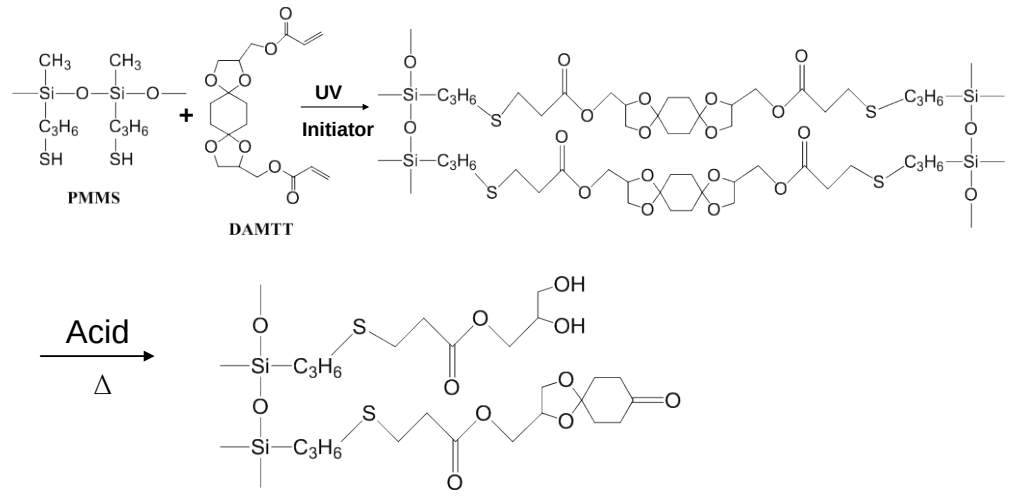

Scheme 1. Mechanism of UV-curing and acid decomposition of the degradable resist for HSNL mold.

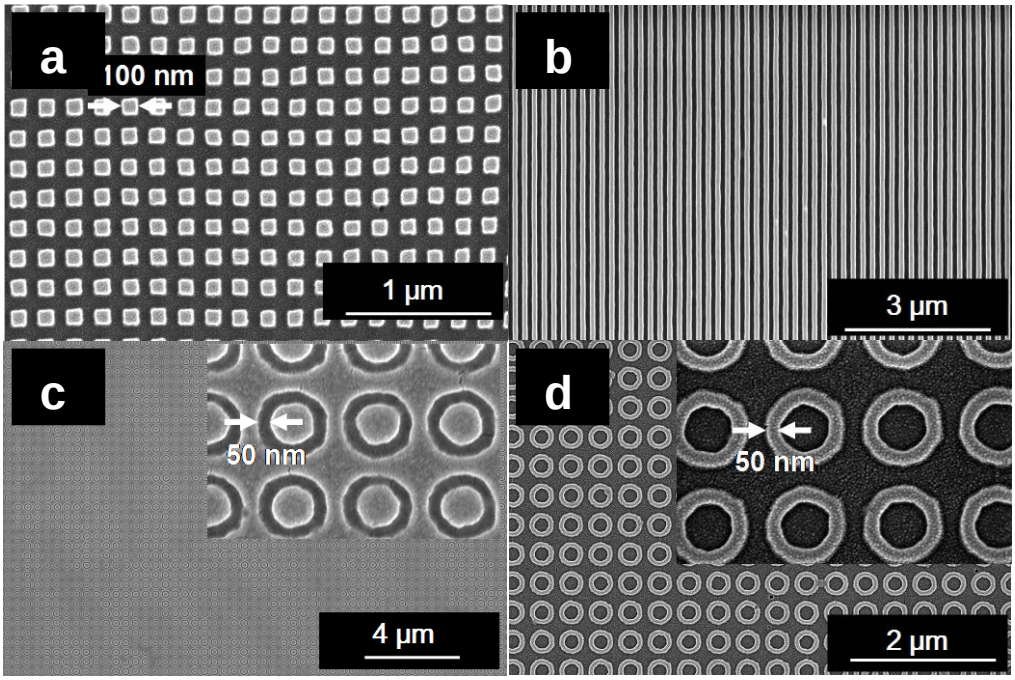

Figure 1. SEM images of imprinted patterns of the degradable resist by HSNL mold fabricated from the same resist: a) square dot arrays with half-pitch of 100nm and side length of 100nm; b) grating patterns with a half-pitch of 100nm; c)-d) notch ring and cam ring arrays with an outer diameter of 300nm, a ring width of 50nm and a periodicity of 400nm.