UV-Curable Nanoimprint Resist with Liquid Volume-Expanding Monomers

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Nanoimprint lithography (NIL) has been regarded as one of the most promising large area nanofabrication technology due to its low cost and high throughput. For UV-curable NIL, the resist volume shrinkage during curing not only influences the pattern fidelity but also induces defects in the demolding process. Many methods have been employed to reduce the shrinkage, including inorganic additives and polymer precursors with bulky side groups. Previously, we achieved zero volume shrinkage by mixing common epoxy monomers with spiro-orthocarbonate monomers. Spiro-orthocarbonate is a monomer that undergoes volume expansion upon cationic ring-opening polymerization. However, the spiro-orthocarbonte monomer is in solid crystalline form at room temperature due to its highly ordered structure. This is inconvenient for formulating the resist because UV-curable resist needs to be in liquid form with low viscosity for best performance.

In this work, we develop a new nanoimprint resist that utilizes liquid volume-expansion monomer and assess its various performance parameters. The resist formulation contains an epoxy resin, a volume expanding monomer and a photo initiator (shown in Fig.1). 3,9-diethyl-3,9-bis(allyloxymethyl)-1,5,7,11- tetraoxastetraoxaspiro [5.5] undecane (DB-TOSU) is liquid at room temperature and it undergoes volume expansion upon polymerization. DB-TOSU was synthesized through the reaction of trimethylolpropane allyl ether with TEOC. DB-TOSU polymerizes at room temperature under UV light and at the presence of photo-generated acids. The relationship between the resist volume shrinkage and the weight ratio of DB-TOSU is shown in Fig. 2. When DB-TOSU reaches 50 wt%, the resist shrinkage is almost zero. A mechanical tester (MTS) was used to measure force/displacement responses during demolding after UV nanoimprinting. The relationship between the demolding force and the weight ratio of DB-TOSU in resist is shown in Fig. 3. When the DB-TOSU content reaches 50%, the demolding force is cut in half.

The zero volume shrinkage will leave no residual stress in imprinted micro and nanostructures, which potentially reduce pattern defects in UV nanoimprint by significantly lowering demolding forces. In addition, the introduction of fluoride epoxy resin can further reduce the demolding force. Thus the new resist formulation has the potential to significantly reduce patterning defects in UV nanoimprint.

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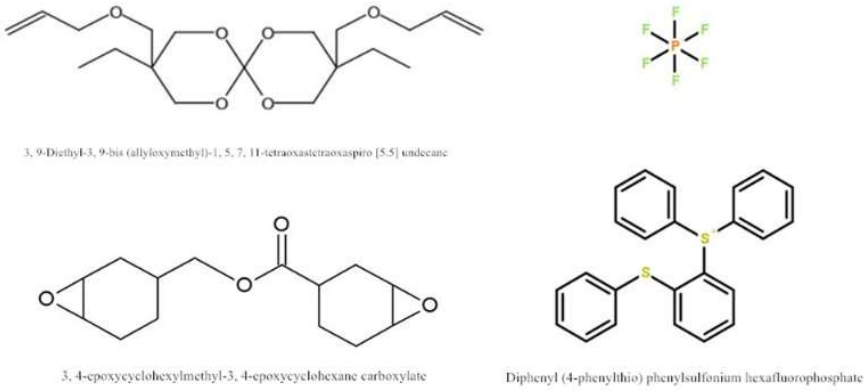

Fig. 1. Chemical structures of the resist components. DB-TOSU and 3, 4-epoxycyclohexylmethyl-3, 4-epoxycyclohexane carboxylate as the base (oligomer), and diphenyl (4-phenylthio) phenylsulfonium hexafluorophosphate as the photo-initiator.

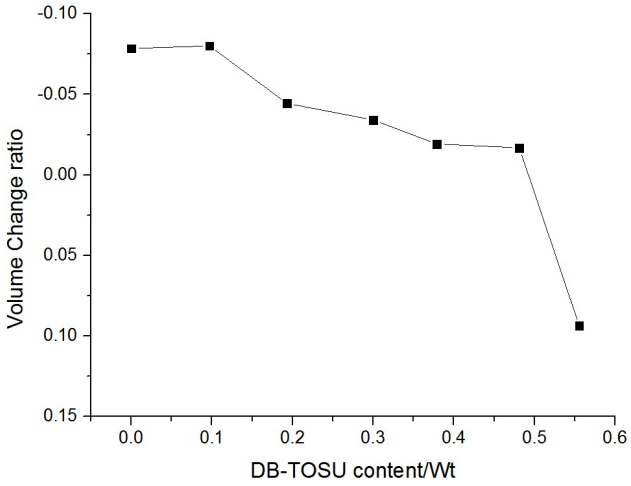

Fig. 2. Volume change ratios for different weight ratios of DB-TOSU in resist.

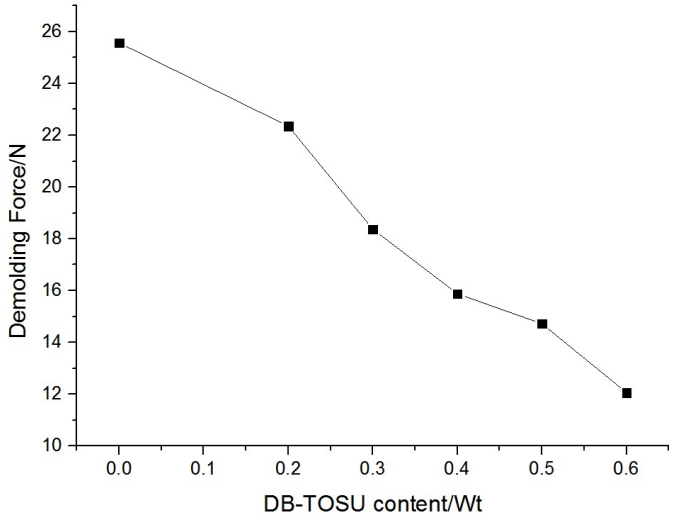

Fig. 3. Demolding force change for different weight ratios of DB-TOSU in resist.