We here designed a new hybrid resist for UV-NIL based on the thiol-yne photopolymerization. The hybrid resist is comprised of bifunctional polyhedral oligomeric silsesquioxane containing octyl and mercaptopropyl groups (POSS-OA-SH) and difunctional alkyne. The obtained hybrid resists possess numerous desirable characteristics for UV-NIL, such as great coating ability, high thermal stability, low surface-energy, low bulk volumetric shrinkage (0.8~4.8%), and excellent oxygen-etch resistance. Because of the click reaction characteristics of thiol-yne photopolymerization, the hybrid resists can be photo-cured within seconds under UV exposure at room temperature. Finally, through the double-layer resist approach for pattern transfer onto silicon substrate, the transfer pattern with the height of about 3 times more than that of the original NIL pattern can be obtained due to excellent oxygen-etch resistance of the etch barrier material. These results provide the thiol-yne hybrid resists as an alternative for UV-NIL.

Key words: UV nanoimprint lithography (UV-NIL), hybrid photoresist, thiol-yne, polyhedral oligomeric silsesquioxane (POSS)

1. Introduction

Due to the feasibility to perform at facile condition, cost-effective and high throughput in production, ultraviolet nanoimprint lithography (UV-NIL) have abstracted much attention as a next-generation patterning technique UV-NIL technology, and have been successfully used in fabrication of electric [1-3], optical[4, 5] and biological devices [6]. Despite the great achievement in the NIL technology, its progress is limited to the availability of the suitable resist materials. At present, the UV curable photoresists include (meth)acrylate[7-9], vinyl ether [10-12], epoxy resin[13-15]. Although such materials have presented good performance for patterning high resolution feature, it still face some challenges in UV-NIL process. Acrylate-based resist is still inevitable to form edge defects of the pattern due to the inherent flaws of oxygen inhabitation, and the volume shrinkage in the UV imprint process is another problem for the pattern transfer of micro & nano sized original features. The high viscosity of the epoxy component leads to some undesired consequences, which limited its wide application. Vinyl ethers also find some disadvantages due to their high separation force and the limitation of commercial availability.

Recently, thiol-ene photo-curing technology has been of great interest in design of new types of photoresist for UV-NIL[16-18]. Thiol-ene based photoresists possess many desirable attributes for UV-NIL, such as extraordinary resistance to oxygen inhibition,[19, 20] lower shrinkage [21, 22] and rapid polymerization kinetics. Moreover, their step-growth nature produces a homogeneous, cross-linked material with uniformly distributed alkyl sulfide functional groups through out the network [23, 24]. Due to their volatility, however, thiol-monomers of low-molecular weight might bring up unsuitable odor. We recently presented a novel hybrid resist for UV-NIL based on thiol-ene photopolymerization, which was comprised of arylate and mercaptopropyl polyhedral oligomeric silsesquioxane (POSS-SH) as inorganic component [25, 26]. The incorporation of POSS-SH into photoresist of UV-NIL leads to two obvious advantages. Firstly, because of its high molecular weight and ultra-low volatility, POSS-SH can avoid the unpleasant odor of other thiol monomers. Secondly, POSS-SH can lead to the ultra-high etching resistance and excellent
2. Experimental

2.1 Materials

POSS-OA-SH was synthesized according to the previous report [34]. Other materials are commercial and used as received except as noted.

2.2 Measurements

$^1$H NMR and $^{29}$Si NMR spectra were recorded on a Varian Mercury Plus-400 nuclear magnetic resonance spectrometer (400 MHz) using CDCl$_3$ as deuterated solvents. FTIR spectra were recorded on a Perkin-Elmer Paragon 1000 FTIR spectrometer. The samples were prepared as KBr disk. Atomic force microscopy (AFM) images were taken with a Nanoscope III AFM Multimode camera (Digital Instruments, USA) under ambient conditions. The AFM was operated in the tapping mode using silicon cantilevers with a force constant of 40 N/m. Scanning electron microscopy (SEM) images were obtained using a Hitachi S-4800 microscope operating at 20 kV. Thermo gravimetric analysis (TGA) was performed in nitrogen with a Perkin-Elmer TGA 2050 instrument at a heating rate of 10$^\circ$/min. For each measurement, the samples were maintained at 100$^\circ$C vacuum for 12 h to evaporate the solvent in the sample before measurement. The viscosities of hybrid resists were determined at 25 $^\circ$C using a NDJ-79 rotational viscometer. Measurements were acquired on 10–15 mL samples at a rotation speed of 5-75 rpm. The Young’s moduli of the cured resists were measured at room temperature with a commercial nanoindentation system (Hysitron TI-900 TriboIndenter; USA). According to ISO 3521, a pycnometer was used to measure the density ($\rho$) of uncured and cured resist specimens. The bulk volumetric shrinkage was calculated using the formula:

$$\text{Shrinkage } \Delta V\% = \left(1 - \frac{\rho_{\text{uncured}}}{\rho_{\text{cured}}} \right) \times 100\%$$

2.3 Mold and Substrate Modified

The molds were modified with the fluorinating agent (tridecafluoro-1,1,2,2-tetrahydrooctyl) trichlorosilane (Cl$_3$SiCH$_2$CH$_2$(CF$_2$)$_5$CF$_3$, TDFOCS) by vapor deposition. The silicon substrate was cleaned in a 1:3 mixing solution (30% H$_2$O$_2$: 98% H$_2$SO$_4$, Caution: be careful using “piranha” solution as it is very dangerous) at 150 $^\circ$C for 3 h. After washed and dried, it was soaked inside 0.2 wt% MAPTES (3-(methacryloxy) prop-ytrimethoxysilane) in toluene for 4 h. After thermal stability of the cured resist, which allows for good transfer of pattern with high resolution onto silicon substrate. As continuous work on developing the novel photoresist for UV-NIL, we here designed a new type of POSS containing resist based on thiol-yne photopolymerization. Because each alkyne in a radical polymerization is difunctional and reactive to two thiol groups to form two new bond, thiol-yne polymerization often results in materials with the relatively higher crosslinking density and moduli, in comparison to the monofunctional step-growth of thiol-ene polymerization [27, 28]. To still maintain other advantageous characteristics of thiol-ene polymerized materials, therefore, the thiol-yne polymerization can address some intrinsic limitations of the thiol-ene reaction, and is expected to find potential in the photoresist for UV-NIL. Because of the very recent investigation of the thiol-yne photopolymerization [29-33], however, the practical application of the thiol-yne system in photo-cured materials is less reported.

In this work, a bifunctional POSS containing mercaptopropyl and octyl group (POSS-OA-SH) was incorporated into an alkyne system to form hybrid polymer network through thiol-yne photopolymerization. The whole photocrosslinked mechanism is illustrated in Scheme 1. Instead of POSS-SH, bifunctional POSS-OA-SH possesses good compatibility with alkyne monomers. The resultant hybrid materials based on thiol-yne photopolymerization possess many desirable properties for UV-NIL, such as great coating ability, high thermal stability, ultra-fast photo-curing speed, low bulk volumetric shrinkage, and excellent O$_2$ etch resistance. In the presence of poly(styrene) (PS) as the transfer film, the transfer pattern on the silicon substrate with the height about 3 times more than that of the original NIL polymer. To the best of our knowledge, this is the first time to report for the thiol-yne based hybrid photoresist, which can provide an alternative for designing the novel resist for UV-NIL.

![Scheme 1. Whole strategy for the hybrid resist based on thiol-yne system.](link)
the substrate was removed from the solution, it was cleaned thoroughly with fresh toluene in an ultrasonic bath and dried in nitrogen gas.

2.4 Surface energy characterization

Hybrid photoresists (Table 1) were spin-coated on a silicon wafer at 3000 rpm for 30 s, then it was covered by the flat mold and exposed under UV light for 10 min to achieve uniformly coated surfaces for contact angle measurements. Advancing and receding contact angles were measured using OCA20 goniometer (Dataphysics, Germany) with ~5 μL droplets of various liquids (purchased from Aldrich and used as received).

| Components            | Mole ratio | Viscosity (cP) | Shrinkage (%) | Surface energy (mJ·m⁻²) | Hard (MPa) | Young's modulus (MPa) |
|-----------------------|------------|----------------|---------------|--------------------------|------------|-----------------------|
| 1 PTMP/DDY            | 1:1        | 60             | 9.6           | 44.6                     | 8.7        | 29.3                  |
| 2 POSS-OA-SH/HDDA     | 1:2        | 87             | 4.8           | 34.9                     | 10.3       | 16.5                  |
| 3 POSS-OA-SH/DDY      | 1:1        | 127            | 4.9           | 36.2                     | 21.3       | 72.4                  |
| 4 POSS-OA-SH/DDY/PPGY | 1:0.75:0.25| 142            | 2.9           | 32.3                     | 16.5       | 26.2                  |
| 5 POSS-OA-SH/PPGY b   | 1:0.5:0.5  | 158            | 1.4           | 29.7                     | 4.3        | 17.3                  |
| 6 POSS-OA-SH/PPGY     | 1:0.25:0.75| 177            | 0.8           | 27.3                     | 3.7        | 13.5                  |
| 7 POSS-OA-SH/PPGY     | 1:1        | 198            | 0.6           | 25.2                     | 3.0        | 6.8                   |

Table 1. The components and some physical properties of the hybrid resists.

a: The weight of the photoinitiator I-907 is 5 wt% of the whole resist.
b: The composition of the hybrid resist is a typical formula in our experiment, which is named as JTHC-c1.

filter before spin-coating. The Si substrates were then spin-coated with a thin film (ca.200 nm thickness) of 2 wt% PS diluted in toluene at 3000 rpm for 20 s, followed by prebaking on a hot plate at 80°C for 1 hour to evaporate the solvent. Then, the resists employed for UV-NIL were prepared by spin-coating on the transfer film at 3000 rpm for 20 s. The thickness of the obtained film was nearly 300 nm.

2.5 Preparation of Transfer Film and Thin-Film resist.

The components of the hybrid resist are shown in Scheme 2. Formulation study was conducted to determine the optimal concentration of the POSS-OA-SH with good thermal stability and etching selectivity. The formulation with the mole ratio of POSS-OA-SH, DDY and PPGY is 1:0.5:0.5 was chosen for spin-coating, in which the weight ratio of POSS-SH is 51.3%. This hybrid resist was named as JTHC-c1. The final hybrid resist JTHC-c1 is diluted to 20 wt% in CH₂Cl₂ solution, and filtrated through a 0.25-μm filter before spin-coating. The Si substrates were then spin-coated with a thin film (ca.200 nm thickness) of 2 wt% PS diluted in toluene at 3000 rpm for 20 s, followed by prebaking on a hot plate at 80°C for 1 hour to evaporate the solvent. Then, the resists employed for UV-NIL were prepared by spin-coating on the transfer film at 3000 rpm for 20 s. The thickness of the obtained film was nearly 300 nm.

2.6 The Process of NIL and Graphic-Transfer.

The whole process of UV-NIL (a) and fabrication nanostructure pattern on Si substrate by RIE (b) is illustrated in Scheme 2. The resist layer was covered by the quartz mold, and the sandwich sample was then put in vacuum chamber to expel the trapped air bubble. The sample was exposed under UV-light for 3 min (2000 mJ/cm²) after a pressure of 0.2 bar was applied for 10 min. The sample was removed from the nanoimprinter and the mold was then detached from the substrate. The photoresist was imprinted by the IL-NP04 imprinter [35].

The transfer film was used to increase the aspect ratio. After the initial oxygen break through etch, an SF₆ etch was used to transfer patterns directly into the underlying silicon substrate. The residual resist was removed by O₂ plasma. The etching time of these bilayer films was determined by measuring the film thickness change with a Dektak surface profilometer.
Results and Discussion

3.1 The components of the hybrid resist and physical properties

The functions and structures of different components in our hybrid resist are shown in Scheme 3. DDY and PPGY were used as the difunctional alkyne monomers. Instead of POSS-SH, POSS-OA-SH was used as inorganic component due to its good compatibility with DDY and PPGY. The compatibility between the hybrid components is an important factor to the performance of the final crosslinked material. The mixtures of POSS-OA-SH and DDY and PPGY are homogenous, while the mixtures of the pure POSS-SH and DDY and PPGY are turbid, indicating that the incorporation of the n-octyl chain into POSS can enhance the compatibility of POSS and DDY and PPGY. For comparison, thiol monomer PTMP and difunctional acrylate monomer HDDA are kept as references. In order to find the optimal components of the hybrid resist, a series resist of various components were prepared (Table 1). All of the resultant hybrid resists are a homogeneous, transparent and low viscosity system. The viscosities of these hybrid resists were controlled between 127 and 198 cP , which was appropriate in UV-NIL[36, 37].

One of major advantageous characteristics of the hybrid resist as UV-NIL material is its lower volumetric shrinkage. After the incorporation of the POSS-OA-SH in resist, the volumetric shrinkage decreased obviously. Compared with the PTMP/DDY resist, the bulk volume shrinkage (~4.8%) of the hybrid resist POSS-OA-SH/DDY was lower than that of PTMP/DDY system (9.6%). The lower shrinkage of the hybrid resist may be attributed to the nature of the incorporation of POSS-OA-SH [26, 38]. And with the decreasing of the crosslinking density in these ternary systems from POSS-OA-SH/DDY to POSS-OA-SH/PPGY, the shrinkage decreased from 4.8% to 0.6%. Another advantage for the hybrid resist is the low surface energy, the surface energy for the cured POSS-OA-SH/DDY is 36.2mJ/m², which is lower than that of PTMP/DDY (44.6mJ/m²). With the increasing content of PPGY in the hybrid resist, the surface energy decreases from 36.2 to 25.2 mJ/m², which is almost close to that of PDMS (Sylgard 184). The static water contact angles of the optical cured PTMP/DDY, POSS-OA-SH/DDY and POSS-OA-SH/PPGY, are 70°, 95° and 103°, respectively, and the lower surface energy is helpful to demold.

3.2 The reaction kinetics of the hybrid thiol-yne photoresist

Real time IR (RT-IR) was used to study the polymerization kinetics of thiol-yne systems because of its inherent advantage of being able to measure thiol and yne conversions independently and simultaneously. RT-IR spectra of the typical hybrid resist POSS-OA-SH/DDY and POSS-OA-SH/PPGY exposed for different time are shown in Figure 1, in which peaks at 3313 and 2110 cm⁻¹ are attributed to yne and 2550 cm⁻¹ is ascribed to -SH, respectively. According to the local amplification RT-IR spectra, the disappearance of both thiol and yne groups is rapid, suggesting the fast photopolymerization of thiol-yne. During the process of photopolymerization, the vinyl sulfide intermediate product (1609 cm⁻¹) can not be found, which is consistent with previous studies on thiol-yne systems.[27, 28] The whole photopolymerization of these hybrid resists was
almost finished in two minutes, and the final conversion of thiol groups was higher than 80%, suggesting the efficient thiol-yne photoreaction.

The thermo gravimetric analysis (TGA, Figure 3) was carried out to obtain information regarding the thermal stability of the hybrid resist. For the PTMP/DDY based resist, the initial decomposition occurred at 346°C and the resulted polymer was completely decomposed at c.a. 500°C. The hybrid resist POSS-OA-SH/DDY possessed a higher initial temperature of degradation at about 369°C, indicating that the incorporation of POSS enhanced the thermal stability very significantly. With increasing soft segment (PPGY) ratio in this ternary system, T_d decreased from 369°C to 345°C. These results demonstrate the feasibility of changing the structure of monomer component to the thiol-yne system.

3.3 The performance of the cured hybrid resist

Figure 2 shows the Young’s modulus of the cured hybrid resists as a function of the contact depth. The minimum Young’s modulus and hardness for several photoresists are summarized in Table 1. The Young's modulus and hardness of POSS-OA-SH/DDY film was higher than that of PTMP/DDY. These results demonstrate the feasibility of adding a POSS component to the thiol-yne system, which can enhance the mechanical strength. Compared with thiol-ene reference of POSS-OA-SH/HDDA, the Young's modulus (72.4 MPa) and hardness (21.2 MPa) of POSS-OA-SH/DDY are much higher, which might be ascribed to the higher crosslinking density of thiol-yne photo-cured system. With increasing PPGY ratio in this ternary system, the modulus decreased from 72.4 to 6.8 MPa due to the increasing of the soft segment in the structure of system. The value of Young's modulus is still higher than that of Sylgard 184 PDMS (1.8 MPa) [39]. These results implied that the imprinted nanostructures with these POSS-based formulations would be rigid enough to resist failures, resulting in the potential for UV-NIL.
Hybrid photoresists of different formulations were processed to determine etching rate and selectivity as a function of etch barrier. Figure 4 presents the O$_2$ and SF$_6$ RIE etching rate of the cured hybrid resists, in which the mole ratio between yne and thiol is fixed at 1:2. The high silicon content of the POSS-OA-SH materials provides a greatly improved etch resistance to O$_2$ plasma. This result is consistent to our previous studies.[25] And it was also found that the SF$_6$ etching rate gradually decreased due to the lower resistance of silicon oxide by nature. Based on these studies, the optical formulation of these resists is the mole ratio between POSS-OA-SH, DDY and PPGY is 1:0.5:0.5, which is named as JTHC-c1. The oxygen etching rate is 0.30 nm/s, which is much slower than that of PTMP/DDY cured polymer (2.8 nm/s).

![Figure 4](image1)

Figure 4. The effect of POSS-SH-OA content on O$_2$ and SF$_6$ gas etching rate

3.4 UV-NIL for the hybrid resist and Graphic-Transfer

Figure 5 presents the typical SEM images of the quartz molds and the replica molds with different features. The hybrid resist could be easily imprinted over large areas and there are almost no obvious bugs or distortions in the replica pattern. Due to the good coating properties and low viscosity, the hybrid resist could be easily imprinted from micro to nano-scale features, which was further confirmed by AFM images (Figure 6). It should be noted that the resolution is limited generally by the mold design, but not by the hybrid resist itself. The Young's modulus based on thiol-ynie photocurable systems could be tuned 1.1 GPa to 70 MPa at room temperature [32, 33]. So the mechanical strength of the cured hybrid resist could be tuned further through changing the monomer. Although the Young's modulus in our system is relatively low, it is strong enough to break. The resultant high throughput pattern with excellent resolution and shape indicated that the hybrid resist is very potential to UV-NIL.

![Figure 5](image2)

Figure 5. SEM images of (a-c) the quartz mold and (e-f) NIL patterns of JTHC-c1 with different feature sizes: (a, d) 200 nm, (b, e) 400 nm, (c, f) 700 nm.

![Figure 6](image3)

Figure 6. (a) AFM image of the NIL JTHC-c1 film and its corresponding phase diagram, (b) cross section SEM of the JTHC-c1 polymer.

The photo-cured hybrid resist is optically clear and transparent, and its morphology was studied by AFM and SEM (Figure 6). The AFM contrast phase images exhibited a very homogeneous surface without any noticeable domains, suggesting no obvious phase separation. The toughness of the patterned surface is less than 3 nm. The SEM micrographs also showed a featureless morphology, indicating no phase separation and homogenous dispersion of POSS.
This should be ascribed to the good compatibility between POSS-OA-SH and yne monomer. Our POSS functionalized with four thiol groups is cross-linked with yne monomer at a molecular level.

Because of the high resistance of the O₂ etching, the hybrid resist is very attractive to a double-layer approach for graphic transfer. Usually, the silicon-rich, photocurable film is applied in UV-NIL on top of another thicker polymer layer (transfer layer). This topcoat serves as an etch mask, providing high etch selectivity during the pattern transfer process to produce higher aspect ratio patterns. One important issue regarding nanostructure stability of double-layer method is the surface mobility at the interface of the two layers. To enhance the interaction force between curing resist and the PS, the hybrid resist solution is spin-coated directly over at the film of polystyrene on a silicon substrate. With the wetting and infiltration of CH₂Cl₂ agent to the surface of PS film, which could bring the resist infiltrate in PS film, and increase the amount of interfacial force, although there is slightly etching with PS film. Table 2 summarizes the parameter of RIE etching rate of the NIL layer and the underlying transfer film polystyrene. The O₂ etching selectivity between transfer layer and NIL layer more than 7.0 can be easily achieved with the hybrid resist JTHC-c1. Although the SF₆ etching selectively between silicon and transfer layer is slightly smaller than other commercial resist, the significant improvement of O₂ etch resistance is beneficial to graphic-transfer. Thus, the hybrid resists could be excellent candidates for imprinting resist materials. Figure 7 shows the AFM and sectional profile images of samples as (a) the original NIL pattern, (b) the Si pattern after etching. The height of the resultant silicon structure is about 300 nm, which is 3 times higher than that the original pattern (c.a. 100 nm) in this case. Therefore, the hybrid resist containing POSS is suitable for transferring graph onto Si.

Table 2. The RIE etching rate of the hybrid resist in comparison to other materials. Parameters were 20 sccm SF₆, 60 mTorr, 40 W; 20 sccm O₂, 20 mTorr, 20 W.

| Etching rate (nm/s) | Etching Selectivity |
|---------------------|---------------------|
| O₂                  | SF₆                |
| Transfer layer      | Vₐ<sub>Transfer layer</sub> | Vₐ<sub>NIL layer</sub> | Vₐ<sub>Si</sub>/Vₐ<sub>Transfer layer</sub> |
| PS                  | 2.3                | 4.8                | -      | 2.9                |
| Watershed 11110     | 2.1                | 4.4                | 0.8    | 3.2                |
| mr-NIL 6000         | 4.5                | 8.1                | 0.4    | 1.7                |
| PTMP/DDY            | 2.8                | 7.5                | 0.8    | 1.9                |
| JTHC-c1             | 0.30               | 11.3               | 7.6    | 1.3                |

Vₐ<sub>Transfer layer</sub>: the etching rate of the transfer layer by O₂;
Vₐ<sub>NIL layer</sub>: the etching rate of the NIL layer by O₂;
Vₐ<sub>Si</sub>: the etching rate of the Si substrate by SF₆; the etching rate of the Si substrate is 14.2 nm/s.
Vₐ<sub>Transfer layer</sub>: the etching rate of the NIL layer by SF₆.

Figure 7. The perspective AFM and sectional profile images of (a) imprinted, (b) after bilayer etching with PS as transfer film.
4. Conclusion
In summary, we have developed a new hybrid resist containing POSS based on thiol-yne system, which is demonstrated as the suitable material for advanced, high-performance UV-NIL applications. The addition of POSS-OA-SH can enhance the thermal properties and $O_2$ etching resistance ability of the cured polymer. It can also reduce the shrinkage and improve dimensional stability. The hybrid resist based on thiol-yne photopolymerization possess numerous desirable characteristics for UV-NIL, such as fast UV-curing speed, high thermal stability, low surface-energy, low bulk volumetric shrinkage (0.8–4.8%), and excellent oxygen-etch resistance. Because of excellent oxygen-etch resistance of the etch barrier material, the transfer pattern with the height of about 3 times more than that of the original NIL pattern can be obtained through the double-layer resist approach for pattern transfer onto silicon substrate. Considering these excellent characteristics, the hybrid resists based on the thiol-yne photopolymerization is firmly believed to be a novel alternative for UV-NIL instead of (metha) acrylate, thiol-ene, vinyl ether or epoxy systems.

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