
Low-Surface-Energy Photoresist as a Medium for Optical Replication

Replication of precision surfaces is an inexpensive fabrication method for both small- and large-diameter optical devices. It is useful for producing a wide variety of surface features in polymers for applications ranging from binary or multiple-step diffraction elements and grating structures, to asphere correction layers, lenslet arrays, waveguiding structures, and more.

In these applications, a master surface relief is created by exposing photoresist through a suitably designed grayscale-intensity mask. Development of the resist produces a profiled surface according to the mask transmittance and exposure. Components can be replicated from this master by contact molding; this requires a release layer to insure the master and replicant can be separated without damage to either. Typically, this release layer is an evaporated metal-glucose-metal sandwich structure that allows separation without loss in modulation-function fidelity.¹ Ideally, the on-demand separation between the surfaces occurs at the glucose layer, and by reevaporating the glucose and a single metal layer, the master is ready for repeated use. This is akin to polymer injection molding, where the metal mold (“master”) is also reused for thousands of injection operations before wear requires replacement. In *practice*, however, the metal-glucose-metal release layer disintegrates unevenly or adheres to the master. To save the master for reuse, the release-layer residues must be entirely removed and then redeposited. The former requires chemical etching, which tends to wear the photoresist master, significantly reducing its useful life. In some cases, the production of new-exposure masters or several masters at once can be inexpensive; however, for optical elements of large diameter, such as required by inertial-confinement-fusion lasers, this can require many, costly-to-prepare, precision-polished master substrates. The development of sixty, 30-cm-diam distributed phase plates for OMEGA necessitated the search for a simplified approach to a *deterministic* master-replicant release operation in optical replication. Since surface energy determines the adhesion of contacting surfaces, the solution lies in the development of a photoresist that has a low surface energy, thereby obviating the need for a release layer.

In this article, we describe a first step toward developing, by environmentally benign methods,² a resist that has a low surface energy and maintains the desired photosensitivity. In its first implementation, the combination of photoresist and on-demand, mechanical release action in a single medium is realized as a *guest-host* version. Since this technique is compatible with current technology, it has the potential for widespread acceptance.

Siloxanes and fluorinated alkanes (and more recently fluorinated siloxanes³) have been used as low-surface-energy materials.⁴ *Functionalizing* a poly(styrene), i.e., novolac-like, block with a siloxane block to form a diblock resist for reactive ion etching has also been reported recently.⁵ In Ref. 5, it is also mentioned that such block grafting could be used to fabricate controlled-surface-energy polymers; however, no data are given in support of this assertion. *Doping* of a siloxane or perfluoroalkane into commercial photoresist to lower the surface energy entails two key issues: (1) Is the dopant miscible in the novolac/solvent matrix in quantities necessary to accomplish significant surface-energy reduction, and (2) can the normal resist development process still transfer the mask modulation function in the presence of the dopant? Here we address these two issues and report results for siloxane. The perfluoroalkane systems are currently plagued by poor planarity of surfaces and pore formation during solvent removal. These problems appear to be solvable.

Novolac resin, the major constituent of traditional photoresists, is a highly hydroxylated oligomer that dissolves well in 1,2-propanediol monomethylether acetate, as does the typical photoactive resist constituent diazonaphthaquinone (DNQ). The generally narrow solvent range in which most siloxanes must be processed can be extended to include the novolac/solvent system by adding hydroxyl functionalities to the siloxane. Poly(phenyl, propyl)silsesquioxane is a commercially available, inexpensive siloxane polyol that yields the best miscibility within the Shipley novolac resist families 1400 and S1800 without precipitation up to 40-wt% doping.⁶ The

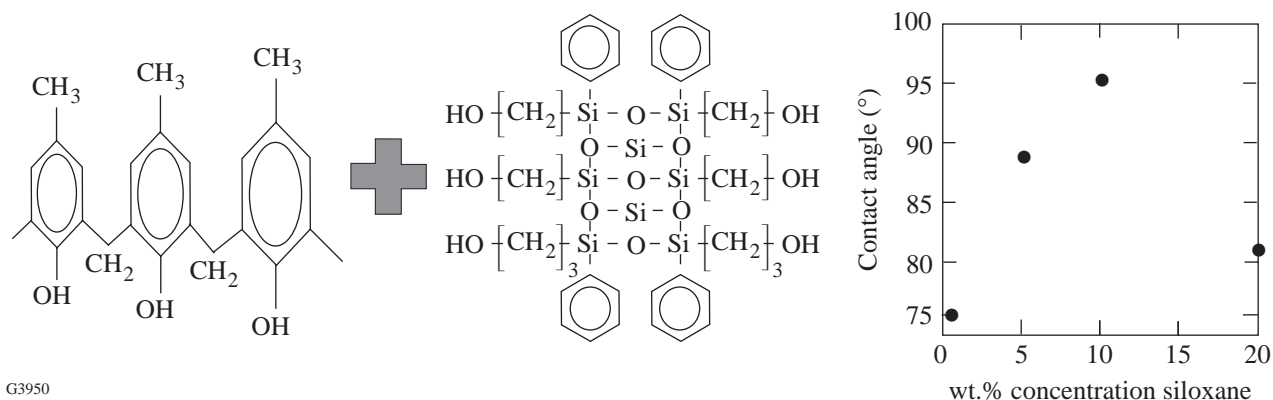
actual precipitation limit for this mixture was not determined. It was merely ascertained that for up to 40-wt% doping, no fluid phase separation occurs for temperatures up to the resist bake temperature (most resists are baked before exposure to UV light). Also, no solid copolymer phase separation was seen under visible-light microscopy after stripping the solvent. The silsesquioxane was used as received, after thin-layer chromatography detected no measurable, low-polarity, UV-detectable or stainable impurities. The molecular-weight dispersity of the silsesquioxane was not measured. Upon completion of dissolution of the silsesquioxane in the commercial resist (Shipley S1800), the mixture was filtered under protective lights through a 0.5- μm pore membrane for particulate (dust) removal.

When irradiated, the DNQ/novolac crosslinking mechanism involves the phenolic O-H sites in novolac.⁷ We surmise that the silsesquioxane O-H sites are equally eligible for ketocarbene attachment reactions, especially since the propyl spacer reduces the silane influence. For this reason, the term *copolymer* or *polymer blend* seems justified for the mixture reaction product.

The effect of siloxane concentration on the polymer surface energy was determined by static contact-angle measurements using 18-M Ω water as reference fluid. Samples containing different silsesquioxane concentration were spin coated on fused-silica substrates, air dried for solvent removal, irradiated (without mask) under a Hg lamp (365-nm output), and developed by standard methods. Under microscope observation,⁸ water droplets were placed on the sample surfaces, using a

Hamilton microdispenser. Within 5 to 10 s after placing the drop on a respective surface, the image of the droplet was captured, and the contact angle at the surface was measured. In Fig. 66.38 the measured contact angles are plotted against weight-percent concentration of polysilsesquioxane. Errors in both angle measurement and concentration are smaller than the data points indicated. As Fig. 66.38 shows, there is a range of concentrations where the copolymer surface energy can be minimized, i.e., the contact angle reaches a peak. This concentration interval is well below the 40-wt% dopant concentration previously mentioned.

To test the surface-relief-generation capability of the copolymer, a 10-cm-diam sample, with 10-wt% concentration of poly-silsesquioxide, was irradiated under an Ar-laser interference (holographic) grating (364 nm) and developed in the same manner as an undoped resist (i.e., in an aqueous alkaline developer—Shipley MF-312 CD-27). The sinusoidal irradiation and the developer parameters were chosen so that the grating aspect ratio was within the resolution of atomic force microscopy (AFM) with a 70° probe-tip angle. For a 700-nm groove spacing, a 150-nm groove depth was chosen. The tradeoff in grating efficiency intrinsic to shallow gratings was of no concern here. The grating carries all spatial frequency features commensurate with the design goal. On thinner, 38-mm-diam, borosilicate-glass substrates, witness films were spin cast for flat-field illumination and subsequent refractive-index measurements using waveguide refractometry.⁹ Doping the hydroxylated silsesquioxane into the photoresist at 10 wt% lowered the 632-nm refractive index from 1.60(8) to 1.59(4). Both average numbers carry ~2% errors.



G3950

Figure 66.38

Contact angle for 18-M Ω water on photoresist/silsesquioxane blends as a function of silsesquioxane concentration

The results for this grating development are shown in the AFM map in Fig. 66.39(a). A $10\text{-}\mu\text{m} \times 10\text{-}\mu\text{m}$ raw-data scan output¹⁰ depicts, in a head-on view, the grating structure whose profile is shown as a lineout oriented orthogonally to the grating grooves [Fig. 66.39(b)]. In this instance, the lineout orientation is inclined by $\sim 15^\circ$ to the scan direction. To accommodate the large sample size, a stand-alone AFM model was used in contact mode.¹¹ Modification of the sample (due to material drag) during scanning in this mode (a phenomenon

frequently encountered with soft, organic thin films¹²) was avoided by minimizing the force used and by reducing the scan speed. The sinusoidal groove depths derived from Fig. 66.39(b) are in reasonable agreement with those obtained from grating transmission efficiency measurements using several-millimeter-diameter optical-probe beams at 543 nm and 1054 nm. The grating efficiency was modeled using an electromagnetic code called SIGMA.¹³

To determine whether microphase separation occurs upon photoinitiated crosslinking, and to identify a possible cause for the weakly irregular grating edges depicted in Fig. 66.39(a), several flat-field samples were also mapped by AFM. This series comprised three samples: one in which the initiator dye and DNQ were removed¹⁴ such that no photopolymerization could take place; one that was irradiated but not developed further; and one that was fully developed. As shown in Fig. 66.40(a), the 10-wt% mixture of initiator-free, DNQ-free photoresist with silsesquioxane yields pinhole-free, smooth films after spin coating and air drying. The irradiated film

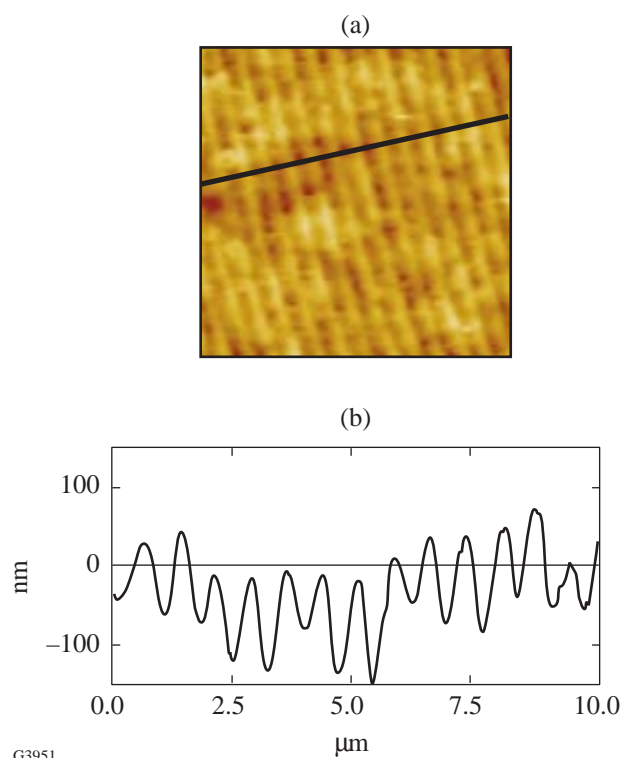


Figure 66.39

(a) Atomic-force microscopy map of $10\text{-}\mu\text{m} \times 10\text{-}\mu\text{m}$ grating area. The straight line across the image indicates the orientation of the lineout depicted in Fig. 66.39(b). Short horizontal features are indicative of soft material being dragged by the probe tip into grating grooves. (b) Orthogonal lineout through grating structure depicted in Fig. 66.39(a).

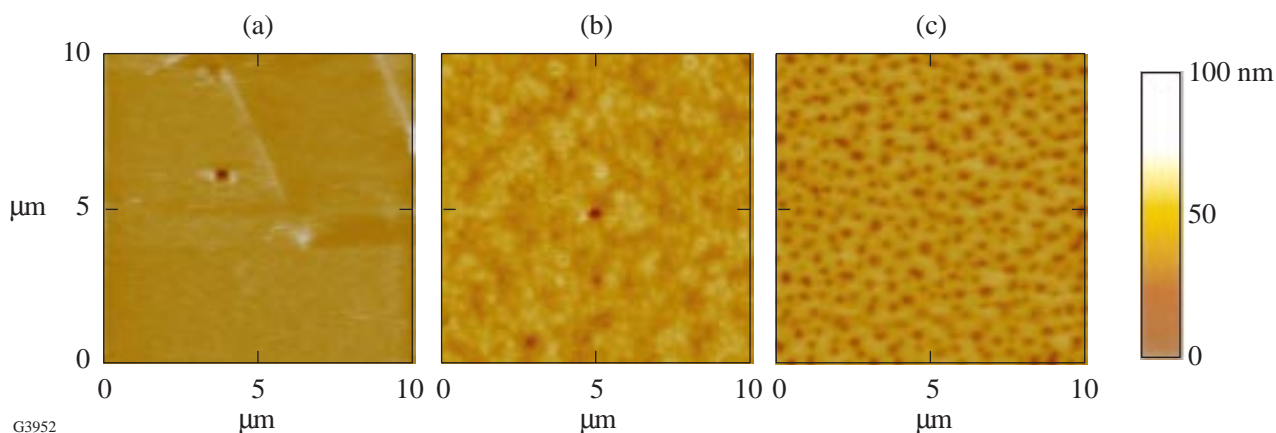


Figure 66.40

(a) AFM scan of unactivated blend of photoresist and 10-wt% silsesquioxane. Except for one pinhole, the surface is smooth (3.1 nm rms). (b) $10\text{-}\mu\text{m} \times 10\text{-}\mu\text{m}$ AFM scan of irradiated blend of composition as in Fig. 66.40(a). Submicron-sized clusters have formed, leading to a roughened surface (5.2 nm rms). (c) Development of the blend in aqueous-alkaline developer removes the near-surface clusters, leaving a slightly porous surface behind (7.0 nm rms).

[Fig. 66.40(b)] shows slight clustering, with clusters protruding up to 20 nm above the film top-surface average. Upon development [Fig. 66.40(c)], these clusters appear to be preferentially attacked, leaving 20- to 30-nm-deep voids. Since AFM does not offer universal speciation capability, it was impossible to determine from these images the stoichiometry of these clusters, and no strict inference about their formation mechanism could be made.

In summary, a silsesquioxane/photoresist mixture has potential as a combined resist/release medium with low surface energy for simplified optical replication. The guest-host mixture can be developed using normal aqueous-alkali resist developer and established procedures. The tendency of such a mixture to form, upon irradiation, phase-segregating clusters that are preferentially removed by the developer is an application impediment for fine-line-transfer replication. It explains the grating-edge roughness observed in Fig. 66.38. After these first trials, neither the mechanism for the cluster formation nor the optimum exposure conditions for suppressing this cluster formation are known. As a typical feature of guest-host systems, this phenomenon can be avoided entirely by resorting to *functionalized-siloxane-polyol* additions.

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