Highly transparent poly(glycidyl methacrylate-co-acryloisobutyl POSS) for 100 µm-thick submicron patterns with an aspect ratio over 100†

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This is the first report on the fabrication of defect-free submicron structures with more than 100 µm thickness and an aspect ratio over 100. Highly transparent poly(glycidyl methacrylate-co-acryloisobutyl POSS) (PGP) was synthesized via radical polymerization. The mechanical properties of the PGP submicron structure displayed a Young’s modulus of 6.09 GPa and a hardness of 0.16 GPa, 4.2 and 8 times, respectively, than those of SU8 nanopatterns. These enhancements enable the utilization of ultrathick 2D-/3D-submicron structures as an ideal platform for microelectromechanical systems, big data storage systems, energy devices, etc.

Two- or three-dimensional (2D, 3D) structures with a periodicity of a submicron scale have received significant interest for a wide range of applications, including photonic/phononic crystals, energy devices, data storage, and sensors. 1–5 Submicron structures fabricated via various fabrication methods such as self-assembly, photolithography, and nanoimprint lithography have been broadly studied for the aforementioned applications. 6,7 Recently, ultrathick micro-/nano-structures with a high aspect ratio and high resolution have shown a broad range of applications in dynamic tuning of nanointerfaces for surface wetting/dewetting, biomechanics, opto-

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PGMs, PGPs, and poly(acryloisobutyl POSS) (PAP) were prepared via free radical polymerization using azobisisobutyronitrile (AIBN) as an initiator in sealed ampoules under a vacuum atmosphere. A 20 wt% solution in THF of GMA and A1-POSS with 1 mM AIBN was heated to 65 °C in a sealed ampoule under a vacuum atmosphere. After 6 h, the polymer was precipitated into isopropyl alcohol (IPA). The precipitated polymer was collected by filtration, washed with IPA, and dried in a vacuum overnight to obtain a white powder.

Fig. 1a shows a schematic of a one-step synthesis of PGP via free radical polymerization. Glycidyl methacrylate (GMA), an epoxy functionalized monomer, and POSS-containing acrylate monomer are copolymerized with AIBN as an initiator with variation of the feed-ratio in weight. The polymerization results of PPGs with various amounts of POSS are shown in Table S1 (ESI†). GMA with a controllable number of epoxy groups was utilized as a crosslinkable negative-type photoresist upon exposure and an acryloisobutyl POSS monomer with –Si–O1.5–cube-octameric frameworks was introduced to improve the transparency, contact angle (Fig. S4, ESI†), and mechanical properties of the prepared polymer. PGMA resin has been widely used for coatings, printing inks, recording materials, photoresists, and printing plates due to its good mechanical properties and high chemical resistance. We utilized PGMA as a backbone photoresist polymer since it exhibits relatively high transparency, low volume shrinkage, and a controllable number of epoxy groups. In order to further enhance the transmittance and mechanical properties of PGMA, the inorganic cage segment of POSS has been incorporated for the fabrication of thick and robust submicron structures.15 However, at the same time, POSS inevitably lowered the glass transition temperature \(T_g\) of PGMA since POSS functional groups serve as inert diluents of the dipole-dipole interaction of GMA molecules as shown in Fig. S1 (ESI†).16 It is very important for the photoresist to remain in a solid phase to be applicable to various lithography methods since a liquid-type photoresist (polymers that are not solidified even after evaporating the solvent) causes registration problems such as distortion of the incident light through flux matter and unfavourable contact between the mask and the resist. Besides, the low \(T_g\) value of the photoresists is not favored since it promotes several adverse effects during the high temperature process (e.g. PEB) including acid diffusion, pattern distortion, and limited resolution. In order to obtain a solid-type and high \(T_g\) photoresist, the POSS content in PGs was controlled in such a way that the maximum transparency is ensured. The thermal properties with varying POSS contents were explored by differential scanning calorimetry (DSC), as shown in Fig. 1b. Compared to the low \(T_g\) value (≈ 2 °C) of the commercially available epoxy-functionalized POSS photoresists, the \(T_g\) values of PGP-2 and PGMA (≈ 72.2 °C and ≈ 76.2 °C, respectively) were much higher than room temperature, indicating that these materials have a solid phase status at room temperature and durability under high temperature processing conditions. TGA data in Fig. S2 (ESI†) show the thermal stability of PGPs up to 250 °C, which is above the processing temperature. The transmittance of the 100 μm-ultrathick PGP-2 film is about 96.6% at 355 nm, as shown in Fig. S3 (ESI†). As shown in the transmittance spectra of the films with various thicknesses in Fig. 1c, the formulated PGP-2 film with thickness as high as 127 μm has higher transmittance than 83 μm-thick PGMA and 50 μm-thick SU8 at 355 nm, which corresponds to the wavelength of the irradiated laser light. Proton nuclear magnetic resonance (\(^1\)H-NMR) and Fourier transform infrared (FT-IR) spectra of the as-prepared samples are shown in Fig. 1d and e. The \(^1\)H peaks of PGP-2 in Fig. 1d are marked at each proton in Fig. 1d and e. According to the DSC data, the Nd:YAG laser (532 nm) was used to photopolymerize the PGP submicron structures. The high refractive index of the cured polymer allows for ultra-high NA lithography with better resolution. Ultrathick (80 μm) polymer was collected by filtration, washed with IPA, and dried in a vacuum overnight to obtain a white powder.
assigned to the C—O stretching of the ester carbonyl groups and the C—H vibration from the main chain of polymers. Typical absorption bands at 910 cm⁻¹ and at 1128 cm⁻¹ corresponding to the epoxy group of GMA and the Si—O—Si linkage, respectively (the peaks are marked by a solid blue square in Fig. 1e), confirm the incorporation of POSS into PGP. The optimized content of POSS to GMA to secure both transparency and a high Tg was about 3.03% of the molar ratio (PGP-2, Table S1, ESI†). The product mole ratios for the GMA monomer were calculated by the intensity of the peak at 0.6 ppm (a blue square in Fig. 1d) and 3.2 ppm (black circles in Fig. 1d) for A1-POSS and GMA, respectively. All product mole ratios are about one-third of the feed ratio because A1-POSS macromonomers reduce the reactivity in free-radical copolymerization due to the steric hindrance of the bulky and rigid moiety. Overall, we found that POSS has a critical influence on the various important properties of PGP as a photoresist, such as transmittance, Tg, and the molecular weight of the final polymer. The incorporation of POSS into the PGMA polymer results in a decreased Tg yet increased transmittance and increased weight average molecular weight in the PGP polymer. Nanodentation was used to investigate the difference in the mechanical properties of the square patterned PGMA and PGP-2 films as shown in Fig. 2. A Berkovich tip was used to indent the square patterned PGMA and PGP-2 films at a constant P/P (nominal strain rate of 0.05 s⁻¹) up to the maximum load of 500 mN. The load–displacement curves of PGMA and PGP-2 patterned structures shown in Fig. 2a were analyzed using the Oliver and Pharr method, which is described in more detail in the ESI.† The resulting Young’s modulus (E) and the hardness (H) are shown in Fig. 2b and c, which were taken from indentation displacement of 1.5 μm, or 15% of the film thickness, to avoid substrate effects. PGP-2 was measured to have E = 6.09 GPa and H = 0.16 GPa, respectively, which are 17% and 10% higher, respectively, than those of the patterned PGMA. The increase in the Young’s modulus and hardness is likely due to the inclusion of the POSS molecules, which is more rigid in comparison to the PGMA. Thus, more inclusion of POSS molecules would translate to the enhancement in the mechanical strength and Young’s modulus while also ensuring the needed transparency as a photoresist. The enhancement in the mechanical properties is in agreement with other studies that reported a similar increase in the mechanical properties by the addition of silica nanoparticles to SU8 nanopatterns. The optimized 3D silica/SU8 nanopatterns displayed E = 3.8 GPa and H = 0.05 GPa, which are factors of 2.6 and 2.5 enhancement, respectively, compared to the bare SU8 nanopatterns, which has E = 1.46 GPa and H = 0.02 GPa. Our PGP-2 submicron patterned structure with E = 6.09 GPa and H = 0.16 GPa would translate to 4.2 and 8 times increase, respectively, compared to the SU8 nanopatterns mentioned above. A homogeneous distribution of the POSS moiety in the PPG photoresist provides a uniform delocalization of the load, resulting in enhanced hardness and Young’s modulus. Overall, compared to PGP, PGP has enhanced mechanical properties as well as transparency as a photoresist by addition of the inorganic POSS moiety. With the addition of POSS, the Young’s modulus and hardness are expected to increase according to its volume fraction, where $E = xA + (1 - x)B$, $H = xA + (1 - x)B$. ‘A’ and ‘B’ are the mechanical properties of POSS and PGMA, respectively, and ‘x’ is the volume fraction of additive POSS in the synthesized PGP.

We hypothesized that the high transmittance and outstanding mechanical properties of optimized PGP would permit the formation of an extremely high-aspect ratio submicron structure over a large area. Ultrathick submicron structures with 105 μm-height and an aspect ratio (height/diameter of the deep hole in the single unit cell) of 131 were successfully fabricated by using PGP as a photoresist via interference lithography (slightly twisted and collapsed morphology at 150 μm-height, Fig. S3, ESI†). Interference lithography using multiple laser beams is a facile technique for realizing defect-free periodic patterned structures over relatively large areas. Here, the samples were fabricated using two-beam interference lithography for large area uniform ultrathick submicron structures. The fabrication involves sequential, double exposure with a 90° rotation of the sample relative to the interference pattern of two laser beams with equal intensity and the transfer of the resultant light intensity pattern into a photoresist via cationic polymerization of epoxy rings (Fig. S7, ESI†). Fig. 3a shows a top-surface image of the periodic submicron structures with a hole diameter of ~800 nm square lattice with a pitch of 1.8 μm. (The limited geometry of the square pattern with holes was determined by the use of a negative-type photoresist and interference lithography.) Fig. 3b shows a cross-sectional image indicating the formation of the ultrathick submicron structure. It reveals an extremely uniform, single crystalline, well-defined cylindrical hole from top to bottom of the 100 μm-thick photoresist layer, achieved by the enhanced transmittance and mechanical properties of the PGP polymer (Fig. 3b). When PGP was applied to another lithographic technique that allows for the fabrication of 3D-submicron structures, namely the proximity field nanopatterning (PnP) method, an 83 μm-thick
3D holographic submicron structure was successfully fabricated, as shown in Fig. S6 (ESI†). This result demonstrates that the PGP photosensitive resin can be applied to other lithography techniques to realize ultrathick submicron structures. The volume shrinkage of the materials was calculated using the following equation using measured thicknesses of films via cross-section views of SEM images before and after patterning steps.

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\text{Shrinkage} = \left( 1 - \frac{\text{thickness of patterned film}}{\text{thickness of unpatterned film}} \right) \times 100 \%
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Shrinkage is the result of the reduction in the intermolecular distance between monomeric units necessary to maintain the thermodynamic equilibrium during the monomer/cross-linked polymer transformation. Large volume shrinkage would cause a significant distortion of the final morphology of structures, reduced critical resolution, and poor adhesion to the substrate. The volume shrinkage of PGP-2 was 2.36%, which is relatively low, while those of SU8 and PGMA were 40.8% and 3.13%, respectively. The additive POSS compound can help reduce volume shrinkage because of the filler strengthening effect of inorganic cages, accompanied by an interpenetrating effect.20 PGP, a novel solid-type photosensitive resin containing POSS with highly transparent, photo-active, and mechanically robust properties was synthesized via free radical polymerization for the fabrication of ultrathick submicron patterns with the thickness higher than 100 μm and an aspect ratio of over 100. The content of the POSS moiety in the PGP polymer was optimized to enhance the transmittance and the \( T_g \) of PGP to optimally serve as a photosensitive for ultrathick submicron structures. The mechanical properties of the film made by the PGP submicron patterns displayed an Young’s modulus of 6.09 GPa and a hardness of 0.16 GPa, constituting improvements as 4.2 and 8 times, respectively, compared to those of SU8 nanopatterns. Furthermore, PGPs composed of PGMA and the POSS moiety have a relatively lower volume shrinkage of 2.36%, while SU8 and PGMA showed 40.8% and 3.13% shrinkage, respectively, suggesting that our material is an excellent substitute to the broadly used SU8. These 3D-ultrathick submicron structures with enhanced mechanical properties can serve as a robust material platform for MEMS, microfluidics, and other applications.

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References