Supplementary Information

Non-sticky Silicate Replica Mold by Phase Conversion Approach for Nanoimprint Lithography Applications

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Characterization

For solvent resistance of the cured PVSZ, the samples were prepared in the PDMS cast with 1 x 1 cm (width x length) and 1 mm of height and soaked in the diverse solvents such as tetrahydrofuran, ethanol, n-hexane, toluene, and dimethylformamide for 24 hrs after a consecutive curing and hydrolysis. Finally, the resistance of the hydrolyzed PVSZ to solvent-induced swelling was evaluated by calculating the dimensional change. During adhesion force test between the mold surface and the patterned resin, separation force was applied onto the mold-side while keeping the resin side fixed. The maximum amount of force needed to separate the mold from the resin-coated substrate was measured as adhesion strength. The total area under study was 400 mm², crosshead speed was 0.2 mm/min, while the full scale load range was set to 1 kN. For each mold–resin combination, at least five independent experiments were performed for measuring the average maximum force per unit area.

To image the patterned nanostructures, we used an AFM (atomic force microscope)
XE-100, PSIA, Korea) operated in non-contact mode and SEM (scanning electron microscope) (FE-SEM, FEI co., Netherlands). Data were processed using SPIP V3.3.7.0 software (Image Metrology, Lyngby, Denmark). To prevent charging, the samples were coated with a 3 nm platinum layer prior to analysis. The film samples were used for measuring the surface chemistry by attenuated total reflectance infrared spectroscopy analysis (ATR-IR, SensIR Technologies, Travel IR), the surface wettability by water contact angle (KRUSS GmbH, Germany), and the hardness and Young’s modulus by nanoindentation system (Nanoindenter XP, MTS Nano instruments, USA) at room temperature. The mechanical data was presented with the statistical mean values calculated from at least 10 measurements to minimize these position-dependent factors. The powder samples of solid state NMR were obtained either by scratching the film samples on Si wafer. $^{13}$C solid-state NMR with an Unity INOVA 600 MHz NMR spectrometer with a widebore magnet, Varian Inc., U.S.A.). The $^{29}$Si magic angle spinning (MAS) NMR spectra were obtained with a sample spinning rate of 8 kHz, a pulse length of 2 µs corresponding to ~30° flip angle, and a pulse repetition delay of 12 sec. For $^{29}$Si cross- polarization (CP) MAS spectra, contact times of 0.5 and 3.5 ms were used. For $^{13}$C CP MAS spectra, a contact time of 4 ms, a pulse repetition delay of 8 s, and a sample spinning rate of 8 kHz were employed. The $^{29}$Si NMR spectrum of initial PVSZ solution in CDCl$_3$ was acquired with an Unity INOVA 500 MHz NMR spectrometer (Varian Inc., U.S.A.) under proton decoupling.

![Fig. S1 Contact angle of a water droplet on surface of a) the normally cured PVSZ film (UV cured at 365 nm for 15 min and then thermally cured at 150°C for 3 hrs) and b) the hydrolyzed PVSZ film (under aqueous NH$_3$ at 80 °C for 6 hrs) after normal curing process.](image-url)
Fig. S2 Comparative Young’s modulus and hardness of the normally cured PVSZ film (UV cured at 365 nm for 15 min and then thermal cured at 150°C for 3 hrs) and the hydrolyzed PVSZ films (under aqueous NH₃ at 80 °C for 6 or 15 hrs) after curing process.

Fig. S3 UV-Vis transmittance of the normally cured PVSZ film (UV cured at 365 nm for 15 min and then thermal cured at 150°C for 3 hrs) and the hydrolyzed PVSZ film (under aqueous NH₃ at 80 °C for 6 hrs) after curing process.
Fig. S4 Experimental step for the adhesion force measurement in the UV-NIL process (a, b); (a) imprinting the mold onto the uncured resin and UV exposure, (b) fixing the cured setup onto Al jig and measuring the force during demolding step.