# Electronic Supplementary Information

## One-Step Fabrication of Hierarchically Ordered Structures on Photoresponsive Azobenzene-Containing Polymers with Phase Masks

Si Wu, and Jintang Huang
Max Planck Institute for Polymer Research, Ackermannweg 10, 55128 Mainz, Germany
E-mail: wusi@mpip-mainz.mpg.de; huang@mpip-mainz.mpg.de

## Experimental Section

*Materials:* The synthesis of the azopolymer poly(2-(4-((4-nitrophenyl)diazenyl)phenoxy)ethyl methacrylate) ($P2NO_2$) is according to our previous work.[1, 2] The molecular weight ($M_n$) and polydispersity index of $P2NO_2$ are $3.2 \times 10^3$ g/mol and 2.27, respectively. Thin films (~215 nm) of $P2NO_2$ were prepared by spin-coating the solution of $P2NO_2$ in cyclopentane (4 wt %) at 1000 rpm on silicon wafers.

*Fabricating PDMS phase masks:* Masters of line patterns and hexagonal islands were fabricated by interference laser ablation on polyimide foil according to our previous work.[3] The mixture of PDMS pre-polymer and curing agent (Sylgard 184, 10:1 by weight) was degassed in a vacuum oven at room temperature. The degassed mixture was then poured onto a master in a Petri dish. Then, the Petri dish was transferred into a vacuum oven and degassed. The PDMS prepolymer was cured at 70 °C in the oven for 3 h. After it was fully cured, the PDMS phase mask was released from the master.

*Fabricating hierarchical structures with phase masks:* The PDMS phase mask was put on the surface of the $P2NO_2$ film without additional pressure. We used a continuous wave coherent cube diode laser (COHERENT Inc.) at 446 nm with the energy ~39.2 mW and the diameter ~2 mm as the light source. The $P2NO_2$ films are irradiated for 10 min. The morphology of the $P2NO_2$ film after irradiation was observed by SEM.

*Measurements:* SEM images of the samples were obtained with a LEO Gemini 1530 system. AFM images of the phase mask were obtained on a Dimension 3100 system with tapping mode.

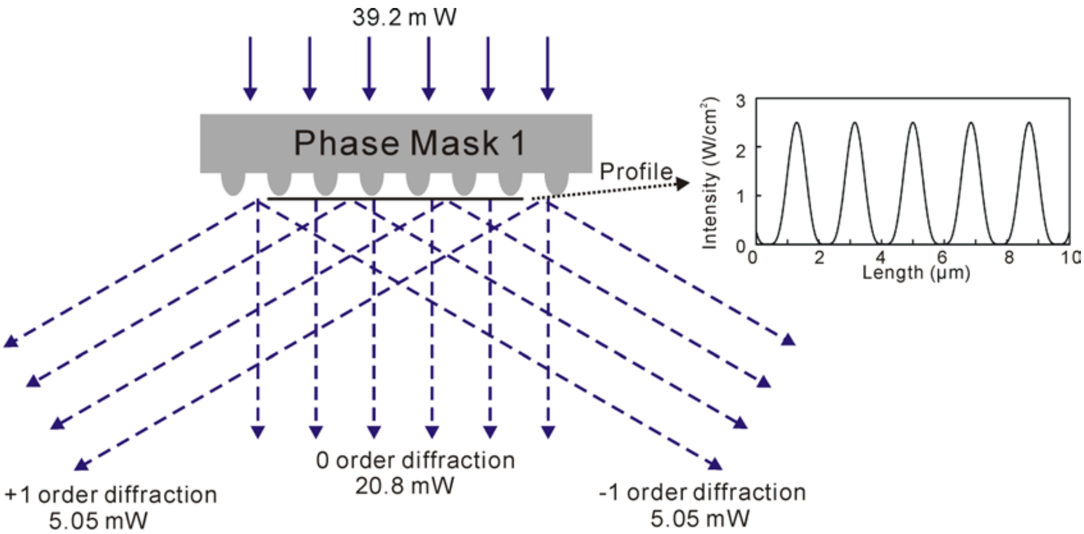


Figure S1. Schematic illustration of the phase mask and the simulated intensity distribution by the method reported previously.[3-5] The interference pattern is generated by the interference of diffracted beams.

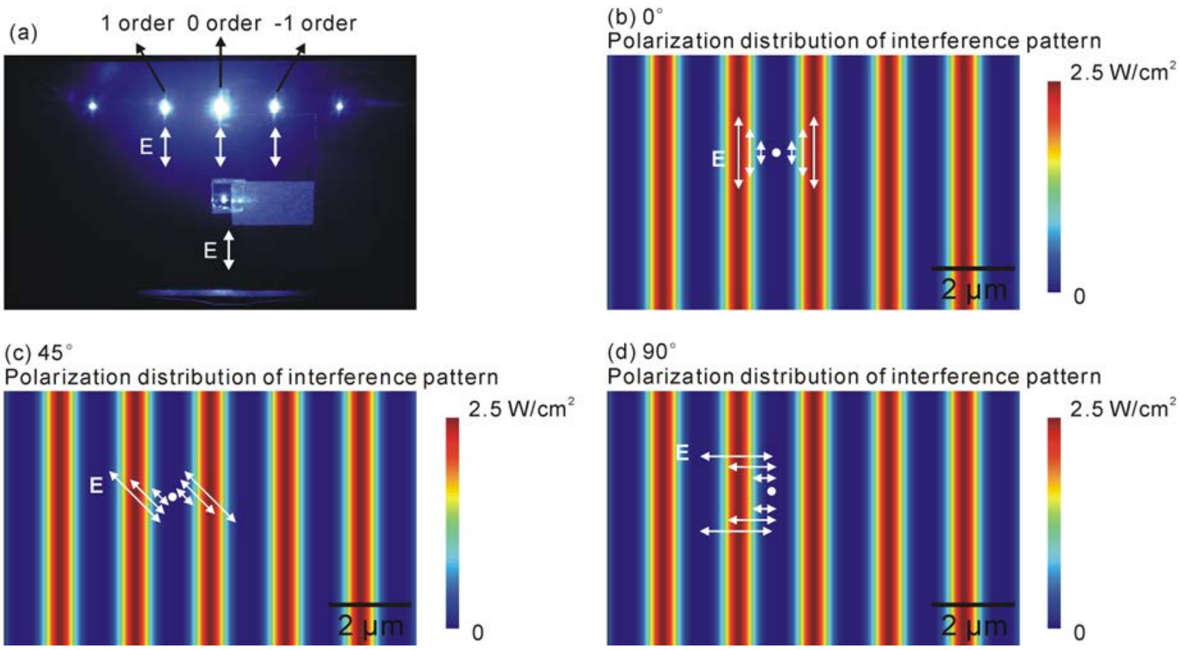


Figure S2. (a) Photograph of a laser beam passes through Mask 1. The arrows indicate the polarization directions of the incident beam and the diffracted beams. (b)-(d) Simulated 2D intensity and polarization distributions of interference patterns when a laser beam passes through Mask 1. The polarization of the laser to the grating direction of Mask 1 are 0° (b), 45° (c), and 90° (d). The arrows indicate the polarization directions. The interference patterns are simulated according to the previous work.[3-5]

In Figure S2 (a), the polarization direction of the laser is parallel (0°) to the grating direction of Mask 1. We measured the polarizations of the incident laser beam and the 0, and ± 1 order diffracted beams. The polarizations of the diffracted beams are the same with the polarization of the incident beam.

We also changed the polarizations of the incident beam to 45° and 90° to the grating direction of Mask 1. The polarizations of the diffracted beams are also the same with the polarization of the incident beam.

According to the measured polarizations of the diffracted beams, the polarization distributions of interference patterns are shown in Figure S2 (b)-(d).

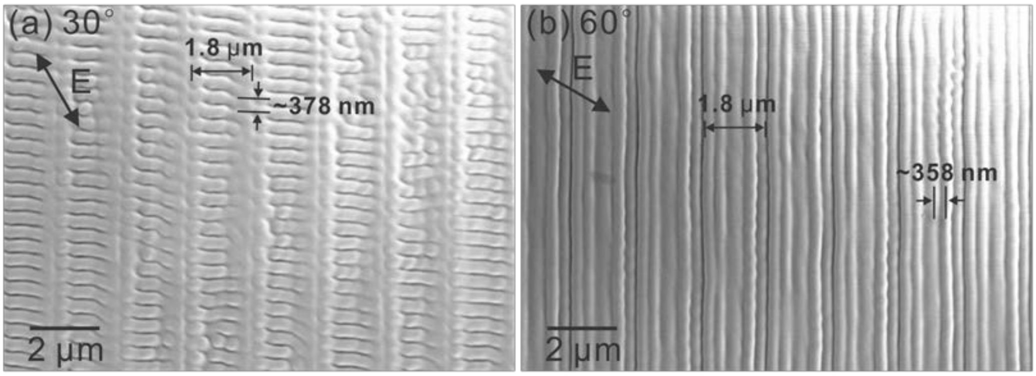


Figure S3. SEM images of hierarchical structures on P2$NO_2$ fabricated by the linearly polarized laser with different polarizations (E vector). (a) 30°, (b) 60°. The pattern in (a) is similar to patterns in Figure 3d and 3e in the manuscript. The pattern in (b) is similar to the pattern in Figure 3f in the manuscript.

**Table S1.** Summary of periods and directions of the nanoripples fabricated at different irradiation conditions.

| SEM image | Phase mask / Laser polarization | Period of nanoripples (nm) | Angle between nanoripples and laser polarization (°) |
|---|---|---|---|
| Figure 2 | No phase mask | 391 ± 13 | 60 ± 4 |
| Figure 3d | Mask 1 / 0° | 359 ± 4 | 89 ± 4 |
| Figure S3a | Mask 1 / 30° | 378 ± 8 | 88 ± 3 |
| Figure 3e | Mask 1 / 45° | 375 ± 11 | 45 ± 4 |
| Figure S3a | Mask 1 / 60° | 358 ± 8 | 90 ± 3 |
| Figure 3f | Mask 1 / 90° | 368 ± 23 | 90 ± 2 |
| Figure 4d | Mask 2 / 0° | 377 ± 17 | 58 ± 9 |

References

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