Silica Nanoparticles-Containing Replica Resin Molds for Step-and-Repeat UV Nanoimprinting

Shunya Ito, Takahiro Nakamura, and Masaru Nakagawa

Institute of Multidisciplinary Research for Advanced Materials (IMRAM), Tohoku University
2-1-1 Katahira, Aoba-ku, Sendai, Miyagi 980-8577, Japan

E-mail: masaru.nakagawa.c5@tohoku.ac.jp

Introduction: UV nanoimprint lithography (UV-NIL) has attracted much attention especially in the field of semiconductor and optical devices owing to the cost-effective process with high resolution. Synthetic quartz molds are widely used for this technology, while the cost of the molds increases the process cost because the molds are fabricated by electron beam lithography. The use of replica resin molds is one of the solutions to reduce the process cost (Figure 1). The replica resin molds require high transmittance of UV light and high reliability in step-and-repeat UV nanoimprinting. The improvement of mechanical strength of the replica resin molds is necessary for the mold performances of stable critical dimension and lifetime during repeated molding and demolding processes because the replica resin molds show remarkably lower mechanical strength than synthetic quartz molds. In this study, we developed UV cured hybrid materials made from silica nanoparticles and a photopolymerizable monomer from the standpoint of mechanical strength, to demonstrate step-and-repeat UV nanoimprinting using the replica mold with 45-nm-width line patterns.

Experimental: Methacrylate-terminated silica nanoparticles (mean diameter of 14 nm) and diacrylate monomers of AC10 and MC10 were selected as shown in Figure 2. The UV cured films with and without the silica nanoparticles were prepared by wire-bar coating method. The mechanical strength of the films was evaluated by nanoindenter with a Berkovich indenter. The replica molds with and without the silica nanoparticles were fabricated from a fluorinated resin mold with 45-nm-width line patterns. The replica resin and silica nanoparticles-containing resin molds modified with a fluorinated release layer were applied to step-and-repeat UV nanoimprinting. The molds after the UV nanoimprinting were observed by field-emission scanning electron microscopy (FE-SEM).

Results and Discussion: The addition of the silica nanoparticles of 60 wt% into AC10-based resin improved mechanical strength of the cured films. The Young's modulus of the film was increased from 1.6 GPa to 4.4 GPa, which was almost the same value as polyimide. The silica nanoparticles-containing AC10 hybrid mold with 45-nm-width lines could be available for step-and-repeat UV nanoimprinting in 128 cycles, while the AC10 resin mold showed morphological changes in the lines after 76 cycles (Figure 3). We demonstrated that the improvement of mechanical strength lengthened the lifetime of the replica molds with 45-nm-width lines in step-and-repeat UV nanoimprinting.

Our group has investigated the viscosity of diacrylate monomers in nano-gaps between silica surfaces,[1,2] and recently revealed that the viscosity of AC10 began to increase at a longer surface-surface distance between acryloyloxy-terminated monolayers than that between methacryloyloxy-terminated monolayers owing to homology of chemical structure causing strong molecular interactions.[3] According to this insight, the bulk viscosity of solution containing the monomer (AC10 or MC10) and the silica nanoparticles was investigated. The addition of the silica nanoparticles increased the viscosity of both AC10 and MC10 solutions. The AC10 solution showed fluidity at contents of the silica nanoparticles of no more than 60 wt%. In contrast, the MC10 solution lost its fluidity at the content of 15 wt%. This result suggested that the strong interactions of MC10 with the silica nanoparticles caused the increase in viscosity at a lower content owing to homology of terminated functional groups.

Reference: [1] S. Ito, et al., *ACS Appl. Mater. Interfaces* **9**, 6591 (2017). [2] S. Ito, et al., *Langmuir* **34**, 9366 (2018). [3] S. Ito, et al., *Chem. Lett.* accepted (2019).

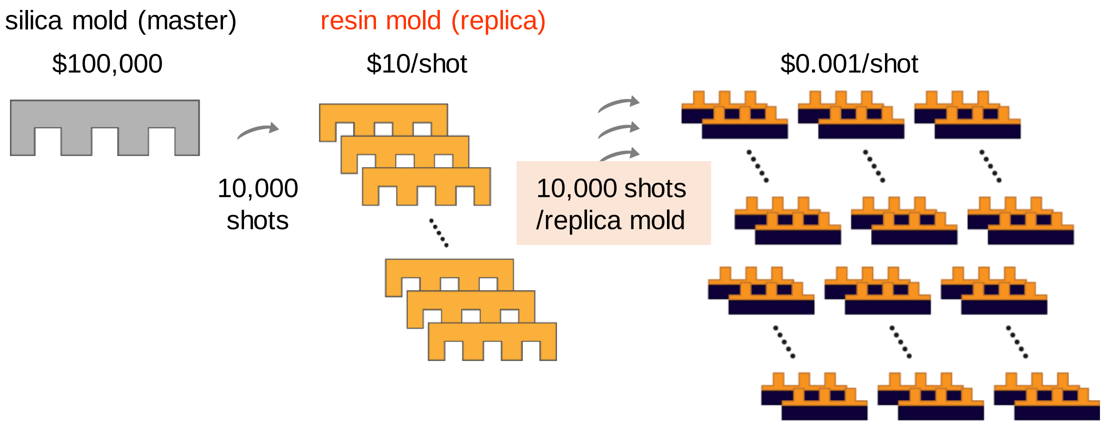

Figure 1. Schematic illustration of reducing process cost by use of replica resin molds.

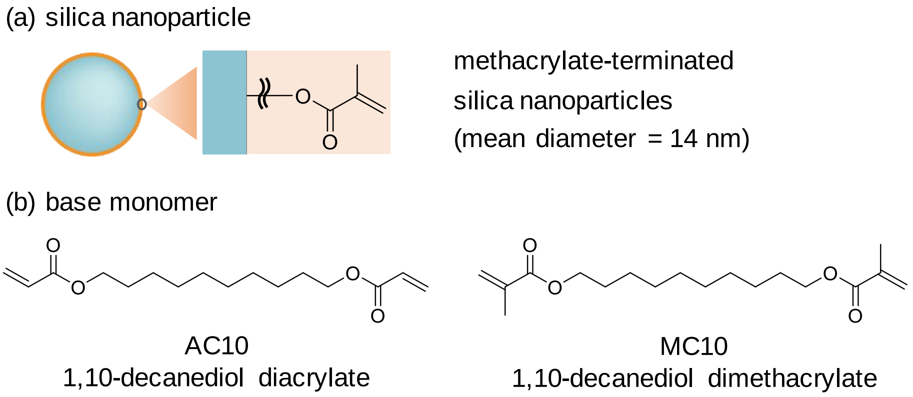

Figure 2. Materials for hybrid molds. (a) Methacrylate-terminated silica nanoparticles and (b) base monomers of 1,10-decanediol diacrylate (AC10) and 1,10-decanediol dimethacrylate (MC10).

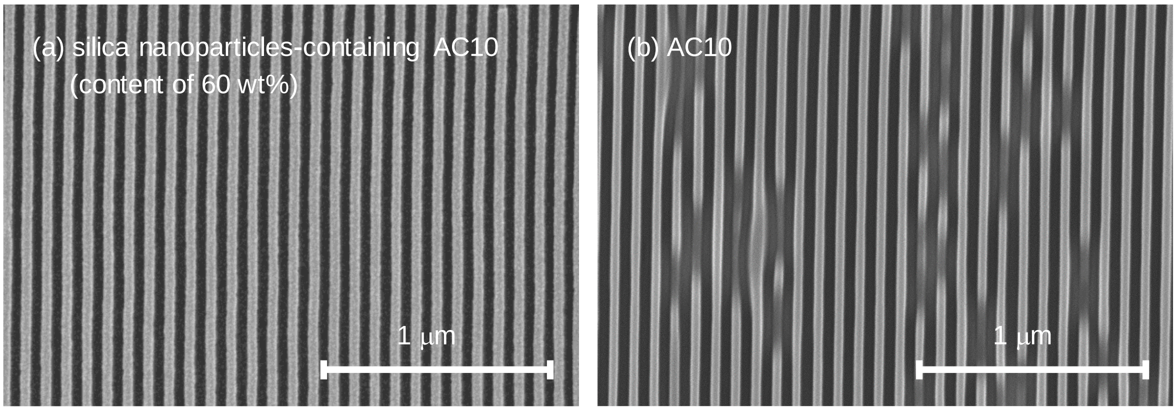

Figure 3. FE-SEM images of (a) silica nanoparticles (60 wt%)-containing AC10 hybrid mold and (b) AC10 resin mold after step-and-repeat UV nanoimprinting in 128 and 76 cycles, respectively.