Low Cost, Durable Masters for Imprint Lithography and Injection Molding by NIL Patterning of Metal Oxides

Feyza Dundar, Vince Einck and James J. Watkins
Polymer Science and Engineering Department
Center for Hierarchical Manufacturing
University of Massachusetts
Amherst, MA 01003
Email: watkins@polysci.umass.edu

Alicia Johansson, Ilja Czolkos and Theodor Nielsen
NIL Technology
Diplomvej 381, DK-2800
Kongens Lyngby, Denmark
Email: theo@nilt.com

Micron-scale and nano-scale patterning of surfaces by imprint lithography, embossing and injection molding are of interest in a broad range of applications including anti-microbial and anti-drag surfaces, structural color, anti-counterfeiting, optical devices, thermal emitters and micro- and nano-fluidics. One challenge, particularly for nanoscale patterning, is the creation of low cost durable masters that can survive tens of thousands and in some case hundreds of thousands of cycles. Typically such masters are created using clean room processing techniques, including optical or e-beam lithography followed by subtractive processing of robust substrates such as Si, quartz and stainless steel. Creation of the masters is not only time consuming, but is also resource and capital intensive, creating barriers to commercialization.

Recently, we developed new materials and approaches for direct imprint patterning of crystalline metal oxides for a variety of applications. A polymer master stamp is used to imprint an ink containing high concentrations of crystalline nanoparticles dispersed in solvent and/or sol-gel precursors to a desired inorganic phase. Residual layer free direct imprinting (without etching) is achieved by choosing an ink with the appropriate surface energy to ensure dewetting at stamp-substrate interface. The technique can be further extended to stack the nanostructures by deploying a layer-by-layer imprint strategy. To date, the imprinted metal oxides have been used directly in devices, including optics, microbatteries and wave-length selective thermal emitters. Here we show that imprinting using metal oxide inks can be used to create low cost "daughter molds" that can be subsequently used as masters for imprint lithography, embossing and injection molding.

We created crystalline zirconia daughter molds (that are subsequently used as masters) by imprint patterning of ZrO_2 nanoparticle-based inks. In one example we replicated a shark-skin anti-microbial surface pattern in polymers using a ZrO_2 master and thermal or UV-assisted nanoimprint lithography. In a second example we replicated a pattern for structural color using a ZrO_2 mold insert for injection molding. The ZrO_2 master, which contained half-pitch gratings with periods of 700-1400 nm and a feature height of 175 nm, was used for more than 100,000 cycles of ABS molding without loss of pattern fidelity. This paradigm, in which durable zirconia masters for nanoscale polymer replication can be created as inexpensively as the polymer imprints themselves, may have a profound effect on the economics and utility of polymer replication at the nanoscale.

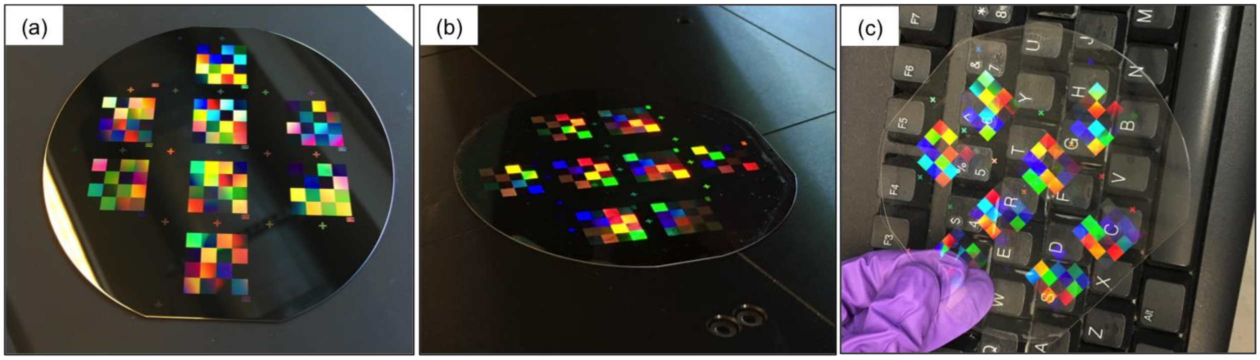

Figure 1: Images of (a) Si master mold. (b) ZrO_2 mold on a Si wafer. (c) PMMA inverse structures of the ZrO_2 master on a PET substrate.

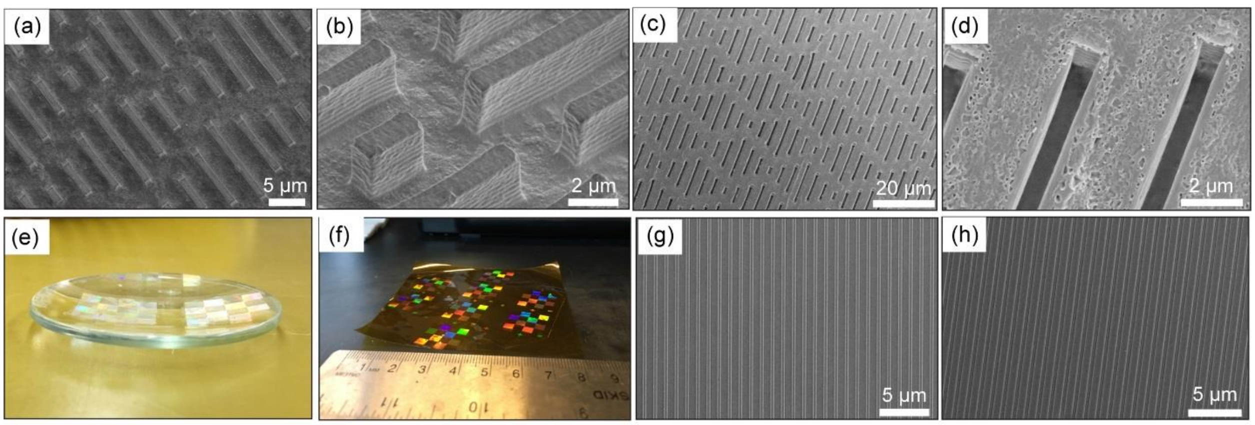

Figure 2: SEM images of (a) patterned ZrO_2 NPs on steel using solvent-assisted soft NIL, (b) higher magnification with 45^o tilt, (c) inverse PMMA structures using hard ZrO_2 mold via thermal NIL, and (d) higher magnification. (f) Digital photos of ZrO_2 imprint on a curved watch glass (e) Digital photo of ZrO_2 master mold on Kapton film. SEM images of (g) patterned metal oxide nanoparticles on Kapton film, (h) and inverse PMMA structures using hard metal oxide mold via thermal NIL.

Reference:

[1] Beaulieu, M.R.; Hendricks, N.R.; Watkins, J.J.; "Large-Area Printing of Optical Gratings and 3D Photonic Crystals Using Solution-Processable Nanoparticle/Polymer Composites" ACS Photonics 2014 1, (9) 799-805.

[2] Arisoy, F. D.; Kolewe, K. W.; Homyak, B.; Kurtz, I. S.; Schi, J. D.; Watkins, J. J. "Bioinspired Photocatalytic Shark-Skin Surfaces with Antibacterial and Antifouling Activity via Nanoimprint Lithography" ACS Appl. Mater. Interfaces 2018, 10 (23), 20055–20063.

[3] Li, W.; Zhou, Y.; Howell, I. R.; Gai, Y.; Naik, A. R.; Li, S.; Carter, K. R.; Watkins, J. J. "Direct Imprinting of Scalable , High-Performance Woodpile Electrodes for Three-Dimensional Lithium-Ion Nanobatteries" ACS Appl. Mater. Interfaces 2018, 10 (6), 5447–5454.

[4] Li, W.; Christiansen, T. L.; Li, C.; Zhou, Y.; Fei, H.; Mamakhel, A.; Iversen, B. B.; Watkins, J. J. High-Power Lithium-Ion Microbatteries from Imprinted 3D Electrodes of Sub-10 Nm LiMn2O4/Li4Ti5O12 Nanocrystals and a Copolymer Gel Electrolyte. Nano Energy 2018, 52, 431–440.

[5] Beaulieu, M. R.; Hendricks, N. R.; Watkins, J. J. "Large-Area Printing of Optical Gratings and 3D

Photonic Crystals Using Solution-Processable Nanoparticle/Polymer Composites" ACS Photonics 2014, 1 (9), 799–805.