Direct Imprint Patterning of 2-D and 3-D Nanoparticle/Polymer Hybrid and Crystalline Metal Oxide Structures for Printed Optical, Electronic, and Energy Devices

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Abstract

Nanoimprint lithography (NIL) offers high precision patterning of structures as small as 50 nm using wafer-based or roll-to-roll process platforms, however current resist systems offer little functionality. We developed hybrid UV-NIL resists containing up to 90 wt. % nanoparticles with excellent optical transparency for direct patterning of device structures including a readily scalable print, lift, and stack approach for producing large-area, 3D photonic crystal (PC) structures and optical gratings. We have also extended the NIL approach to directly print dimensionally stable metal oxide nanostructures using inks containing high concentrations of crystalline nanoparticles.

Introduction

The development of additive or direct patterning techniques for polymer/nanoparticle composites with tuned properties and for inorganic metal oxide and semiconductor structures, particularly using approaches that are scalable for continuous production and operate at ambient pressure and modest temperatures, would be enabling for the low cost production of fully functional printed electronics and for devices that require large active areas. Significant challenges to realizing these goals include fabrication rate and integration density. Many printing approaches, including ink jet and aerosol jet printing, yield structures with minimum features sizes of tens or hundreds of microns, while acceptable performance thresholds often require features in the deep sub-micron range. For example, features below 250 nm are typically required for the manipulation of visible light while features below 1 micron are required to realize high integration density electronics or efficient sensors.

Nanoimprint lithography was developed more than twenty years ago and offers high resolution pattering with excellent feature resolution.[1] To date the field has largely relied on polymer-based substrates, resists and inks. Thermal imprint lithography uses heat and pressure to transfer a pattern from a rigid master to a thermoplastic substrate in a manner akin to hot embossing. UV-assisted NIL in contrast relies on optical curing of a liquid polymer or pre-polymer resist in contact with a patterned master. Both approaches have been scaled to roll-to-roll production.[2] While NIL patterning of polymers offers excellent precision and high rate, its direct utility for device fabrication is constrained by the limited functionality of the polymers used in the imprinting process. It is therefore advantageous to extend the principles of NIL to directly pattern materials that can perform a specific function in a printed device. These could include polymer/nanoparticle composites with tuned refractive index, dielectric constant or magnetic permeability and patterned inorganic dielectrics, conductors and semiconductors.

NIL Patterning of Polymer/Nanoparticle Hybrid Materials

Well-dispersed polymer/nanoparticle composites provide an opportunity to tune physical properties through simple variations of nanoparticle composition, size and loading. Recently we demonstrated effective refractive index tuning of elastomers with high extensibility and of acrylate based nanoimprint lithography resists by controlling the loading of well-defined zirconia and titania nanoparticles at compositions of up to 90 wt.% nanoparticles while maintaining excellent optical transparency.[3,4] Nanoparticle-filled NIL resists can then be used to print optical elements including Bragg gratings and 3-D photonic crystals.[3] Figure 1 shows refractive index tuning of an acrylate-based NIL resist by controlling the loading of anatase nanoparticles. By controlling interactions between the particles and the resist, excellent dispersion and optical transparencies of more than 90% are maintained at nanoparticle loadings as high as 90 wt.%. These modified resists can then be used for direct printing of optical elements. Figure 2 shows a Bragg grating printed using a hybrid resist containing 90 wt.% anatase nanoparticles.

We are now creating hybrids for high dielectric constant applications using $BaTiO_3$ particles and for magnetic applications using NP magnets.

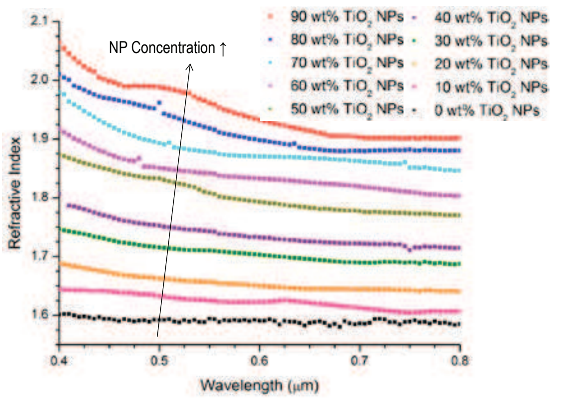

Figure 1. Refractive index as a function of wavelength for the indicated concentrations of TiO_2 nanoparticles in an acrylate-based NIL resist.[3]

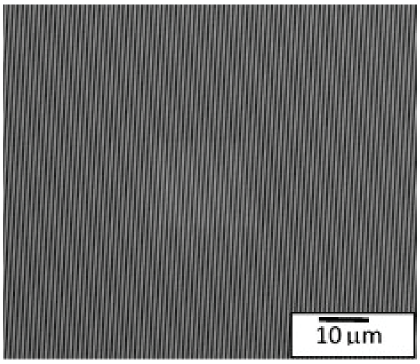

Figure 2. Grating structure printed using a 90 wt.% TiO_2 / 10 wt.% acrylate hybrid NIL resist. The pattern dimensions are 400 nm line width (LW) and a 1 µm pitch.

NIL Patterning of Crystalline Metal Oxides

Patterned metal oxide and semiconductor films are highly desirable for functional devices. The ability to directly and rapidly "print" such structures with high fidelity and sub-micron resolution could open the door to low cost and high performance device fabrication. We have found that robust 1-D, 2-D and 3-D high aspect ratio crystalline metal oxide nanostructures can be fabricated using soft nanoimprint lithography with inks comprised of nanoparticle (NP) dispersions in solvent or in sol-gel precursors for the metal oxide. The use of high loadings of nanoparticles (70-80 wt.%) dispersed in thermally or UV curable sols maintains fluidity and enables imprinting at low solvent concentrations in the ink.[5] The ability to mix and match nanoparticles, the nature of the sol-gel precursor and other additives enables tuning of the ultimate structure composition. Moreover, residual layer free direct imprinting can be achieved by choosing the resist with the appropriate surface energy to ensure dewetting at stamp-substrate interface. 3-D nanostructures can then be created by deploying a layer-by-layer imprint strategy. 1-D, 2-D and 3-D ITO and TiO2 structures can be fabricated for their potential use in electronic and photonic devices, respectively.[5] Here we demonstrate the fabrication of 1-D and 3-D CeO_2/TiO_2 composites for use as high surface area electrodes for biosensors.[6] The ink was comprised of 5 nm crystalline CeO_2 nanoparticles and titanium diisopropoxide bis(acetylacetonate) dispersed in a mixture of IPA and propane diol. For these experiments the ink composition was tuned to yield a 80:20 Ce to Ti ratio in the oxide structure post calcination. A line grating pattern of 1 micron pitch was produced using the ink and a cross-linked PDMS master stamp. The printed line pattern was then leveled using a polymer-based planarization layer and a second line pattern was printed onto the planarized surface. Calcination at 500 ^{0}C yields a 3-D grid structure. The number of grid layers was increased simply by increasing the number planarization and print cycles. Figure 3 shows a four-layer electrode stack. Note that the grid lines are self-supporting and defect free.

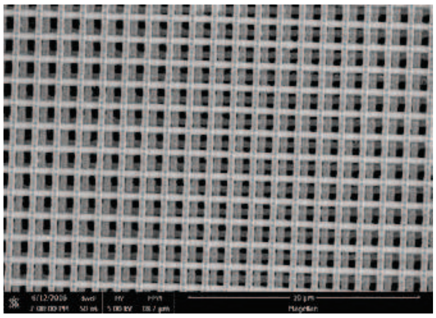

Figure 4. Four-layer stacked CeO_2/TiO_2 nano-array electrode fabricated using nanoimprint lithography with a pitch of 1 micron. The electrode is used in a biosensor.[6]

Conclusions

We demonstrate that nanoimprint lithography can be extended for the direct fabrication of functional device architectures through the use of hybrid polymer/nanoparticle and crystalline nanoparticle based inks and resists.

Acknowledgments

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