

Utilizing PRINT™ Technology to Create Precision Nanopatterned Films

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ABSTRACT

We describe the use of a new, enabling class of materials for performing precise, nano-scale imprint lithography for patterned film replication. These low surface energy, minimally adhesive, room-temperature photocurable perfluoropolyether (PFPE) elastomers, trademarked as Liquidia's Fluorocur™ resin series, are a unique class of fluoropolymers that are liquids at room temperature that can be functionalized and cured to form transparent "Teflon®-like" elastomers. Molds made from Fluorocur™ materials exhibit the favorable properties of both rigid and soft materials in that they are rapidly made and disposable, yet maintain the chemical resistance and performance of rigid materials such as quartz. Liquidia's proprietary PRINT™ technology (Pattern Replication in Non-wetting Templates) utilizes molds of these materials to create nano-scale pattern replication with sub nanometer resolution.

Keywords: nanoscale patterned film, optical film, photovoltaics, displays, specialty coatings

1 INTRODUCTION

New materials for high-throughput precision molding technologies are needed in order to truly enable the nanotechnology industries to come to fruition.[1-4] Imprint lithography and the related fields have the potential to offer viable, cost-effective alternatives to photolithography for manufacturing highly precise optical components and other patterned films and membranes having sub- μm features.[1-3]

Polydimethylsiloxane (PDMS) based networks have served as the material of choice for much of the work in soft lithography.[5] The use of soft, elastomeric materials like PDMS offers numerous attractive properties in several lithographic techniques. PDMS is highly UV-transparent and has a very low Young's modulus which gives it the flexibility required for conformal contact. Mold flexibility facilitates easy release from masters and replicates without cracking and allows the stamp to endure multiple printing steps without damaging fragile sub-100 nm features. Rigid materials such as quartz, glass, and silicon have also been utilized to generate stamps for imprint lithography and hot embossing techniques. [3,6,7] Such materials are superior

to PDMS stamps in modulus and swelling resistance but lack flexibility and therefore conformal contact.

While both PDMS and rigid materials such as quartz glass and silicon offer advantages, there are a number of properties inherent to these materials that limit their utility. One particular drawback is that PDMS elastomers significantly swell when exposed to most oil-soluble organic compounds.[8] Since most polymer resist materials will swell PDMS-based elastomers, this severely limits material and solvent choices for this technique. Other limitations of PDMS include the surface energy which requires fluorination for mold release and the low modulus (~1.5 MPa) of the commercially available form of the material (Dow Corning's Sylgard 184®), which results in sagging and bending of features.[1] To date, researchers have had marginal success in pushing soft lithographic techniques with high fidelity below 1 micron size features using PDMS-based materials. Rigid masters (glass, quartz, and silicon) are chemically robust and solvent resistant, but the lack of flexibility creates problems when releasing the master from a rigid replicate.[3,5] Other serious disadvantages of rigid materials used as stamps include the necessity to use fluorination steps to lower surface energy of the stamp [3], and the cost of the master itself due to the complexity of the manufacturing and short lifetime associated with using the master to directly imprint materials, rather than making a disposable polymeric replica.

We have previously demonstrated the use of the PRINT technology in patterning dense, 70nm features with a precision of ± 1 nm[9] using high fidelity molds made from photocurable perfluoropolyethers (PFPEs). These PFPE-based materials are liquids at room temperature and can be photochemically cross-linked to yield tough, durable, elastomers. The materials are highly fluorinated and thus exhibit remarkable resistance to swelling by organic liquids, allowing for the patterning of a variety of organic resins including etch resists, optical adhesives, inorganic sol-gels, and conducting polymers. Herein, we further demonstrate the capability of these materials in the rapid patterning of dual damascene structures for electronics, microlens structures for displays and optics, highly ordered structures for photovoltaics, and other patterns for a variety of applications.

2 METHODOLOGY

The synthesis of the perfluoropolyether dimethacrylate (PFPE DMA) has been reported previously [10]. AFM micrographs were recorded in tapping mode on a Digital Instruments D3100 atomic force microscope. SEM images were performed on a JEM 6300 scanning electron microscope made by JEOL, Inc. Optical microscopy images were recorded on a Zeiss Axioskop 2 MAT Incident Light Microscope. The dual damascene master was acquired from International Sematech. The microlens master was made using laser ablation. Masters used for photovoltaics applications were acquired from Benchmark technologies and were made using photolithography (200 nm features) and anodized aluminum oxide was made using equipment at the University of North Carolina (<200 nm features).

2 RESULTS AND DISCUSSION

The PRINT™ technology has been used to replicate sub 100-nm lines, holes, and posts, three dimensional features, and micro- and nanolens structured films with precise, nanometer scale control over pitch, sidewall angle, and surface roughness. The PRINT™ process, enabled by Liquidia's proprietary fluorinated polymeric materials, allows Liquidia to address unmet market needs through precise design and commercial-scale manufacturing of micro- and nano-structured materials, including particles, arrays of particles and patterned films, allowing for a high-throughput, high-fidelity method essential to fabricating these complex 3 dimensional structures.

Dual damascene technology has been a key aspect of IC feature minimization, as it lowers the number of processing steps, eliminates metal etch, reduces production cost, and minimizes problems with lithographic overlap tolerance [11]. Although this technology reduces the number of overall processing steps, there are still about 20 steps associated with each layer. Imprint lithography methods provide a straightforward way to reduce these steps; when the imprinted material is a functional dielectric, the number of steps can be reduced by a third [12]. To demonstrate our ability to pattern dual damascene structures, we have fabricated PFPE-based molds and created TMPTA replicates of complex, 3D structures, building a platform for more functional imprinting of dielectric materials. Figure 1 shows molding and replication of a trench and via dual damascene structure. The variation in color shows the depth of field. These particular dual damascene structures are larger (100's of nanometers) to simplify initial process development and eventual electrical testing. The PFPE-based Fluorocur™ materials generated excellent, high fidelity replica molds of the nanoscale features on the patterned silicon wafer master. The trenches of the Fluorocur™ replica mold had an average height of 580 nm which was in excellent agreement with the measured 581 nm height of the features in the silicon master

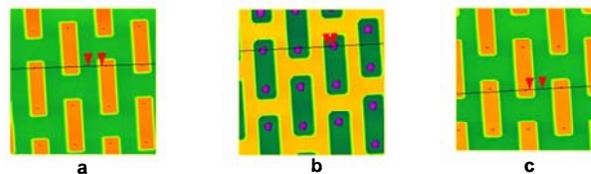


Figure 1: High Resolution AFM images of a silicon master with trenches and vias (left column); Fluorocur™ stamp with the inverse image (middle column); TMPTA replicate made with the fabricated Fluorocur™ stamp (right column).

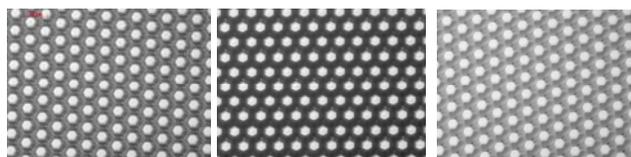


Figure 2: Optical Microscopy images of parylene master (left), Fluorocur™ mold (middle), and optical replicate (right) of a microlens feature utilized for a display application. The replicate created was precise enough to match theoretical calculations of light output from the designed lens structure.

Additionally, the PRINT™ technology was used to replicate micro- and nanolens structured films with precise, nanometer scale control over pitch, sidewall angle, and surface roughness (Figure 2). These structures are designed to guide light in a specific direction; thus spacing, sidewall angle, and surface flatness are critical to maintain on the nanometer scale, despite the fact that the feature size is several microns. The parylene master was laser etched to specifications described in molecular modeling. The replicate film created using a Fluorocur™ mold was tested for the equivalent specifications—the replicate film demonstrated light output efficiencies from 90-96%, matching theoretical values. The flat panel display market is aggressively seeking technologies which can reduce the overall cost to consumers. A scalable method for producing nanostructured films can increase display brightness in the desired direction, which significantly reduces the need for expensive and bulky light sources

Liquidia's PRINT™ process has also been used to create BHJ organic solar cells having unique engineered geometries. The efficiency of solar cell devices is generally related to the organization or structure, on a nano-scale, of the materials that make up the solar cell. Inexpensive organic solar cells devices have low efficiency because excitons do not dissociate readily in most organic semiconductors. In order to favor exciton dissociation, the concept of heterojunction was proposed, which uses two materials with different electron affinities and ionization potentials.[13] In order to obtain effective light harvesting

and exciton dissociation, bulk heterojunction (BHJ) was employed where the distance an exciton must diffuse from its generation to its dissociation site is reduced in an interpenetrating network of the donor and acceptor materials. However, lack of nano-scale morphology control and random distribution of the donor and acceptor materials can lead to charge trapping in the conducting pathways to the electrodes. [14]

Several methods have been used to make BHJs: (1) control of blend morphology through processing conditions; (2) Synthesis of donor-acceptor copolymers; (3) Use of porous organic and inorganic films as templates; (4) Self organization; (5) Cosublimation of small molecules to from graded donor-acceptor heterostructures.[15] Due to immiscibility of solid state materials, limited synthesis methods and high cost, these methods lack nano-scale morphology control and can not be used for large area device fabrication. Thus, there is a need for solar cells that overcomes these drawbacks. Here we report methods to make PV devices with unprecedented level of morphology design and control, unlimited selection of donor and acceptor materials, and capability to fabricate large area devices.

Typical photovoltaic cells utilize a BHJ between anatase TiO_2 and a conducting polymer such as a polyphenylvinylene or polythiophene derivative. The PRINTTM process has successfully been used to fabricate highly ordered 2-D arrays of anatase TiO_2 nano-features using PFPE molds of 200 nm pillars etched on silicon wafers. A patterned perfluoropolyether (PFPE) mold is generated from a master having 200 nm x 200nm features. Separately, an ITO glass substrate is pre-treated with acetone and isopropanol in an ultrasonic bath followed by cleaning for 10 minutes with oxygen plasma. The ITO substrate is then treated with a non-wetting silane agent and an adhesion promoter. Following this, a sample of titanium oxide sol gel is placed on the treated ITO substrate and the patterned PFPE mold is placed on top of it. The substrate is then placed in a molding apparatus and a small pressure is applied to ensure conformal contact and to push out excess donor material. The entire apparatus is then subjected to heat while under a nitrogen purge. The PFPE mold is separated from the treated ITO substrate. The patterned material is baked at 110 °C, then calcinated at 450 °C. A solution of the electron acceptor material is spin coated onto the electron donor material and heat is applied to decrease the viscosity of the material to allow for cavity filling. This step is followed by deposition of a metal cathode onto the electron acceptor material. Patterned titania features on a TCO (Transparent Conductive Oxide) are shown in Figure 3.

Future directions for this project include the use of novel materials, specifically new low bandgap polymers, as well as novel device architectures, using smaller features (<100nm) and photonic trapping films. In addition to controlling the morphology of the active layer, we are using PRINTTM technology to create novel light management

structures. These films use nanostructures to manipulate light either concentrating more light to a PV cell or making more of the spectrum usable by the cell. These structured films can be made similar to those described in the above section on optical lenses.

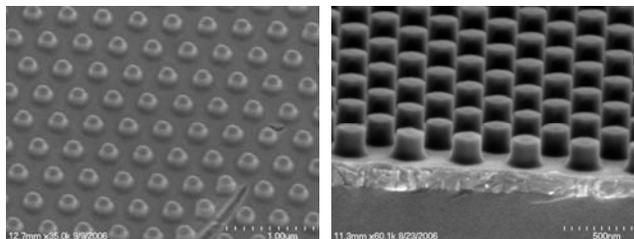


Figure 3: Patterned 200 nm TiO_2 structures on a TiO_2 film

4 CONCLUSIONS

In summary, we have proven the capabilities of PFPE-based elastomers as ideal materials for advanced, high-performance organic molding applications. These highly fluorinated materials enable many soft lithographic techniques because they have an extremely low surface energy, are elastomeric, are solvent and chemically resistant, can be easily fabricated, and are durable enough to be used in a continuous manner. We have shown that PFPE-based materials could be used as stamps to imprint and mold complex, dual damascene structures with no signs of limitations for miniaturization as well as micron scale optical films with nanometer scale precision. In addition, the transparent, elastomeric PFPE-based materials allow for a novel method for photovoltaic active layer design, making it an exciting new approach to use in the rapidly growing alternative energy sector.

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