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37.3: Low Cost Manufacturing of Patterned Films with Nano-Precision
Zhilian Zhou, Ginger Rothrock, Doug Mar, Xiansheng Meng, Jennie Orr, Robert Henn
Liquidia Technologies, Research Triangle Park, NC, USA

Abstract
Much attention has been given to methodologies for patterning optical films with nanoscale precision at the scale and economics required by the Flat Panel Display industry. By using a proprietary mold material, the PRINT™ (Pattern Replication In Nonwetting Template) technology enables low cost manufacturing of precise micro and nanoscale features with single nanometer precision from virtually any material.

1. Introduction
There are many applications of patterned optical films in the display industry, such as brightness enhancement films, diffuser films, and novel backlight units, to name a few. Some recent advances in such patterned films require nano-scale features, while others have micro-scale features requiring complex sub-patterns or nano-scale precision on surfaces, edges, corners, spacing, and angles for effective light manipulation. Much attention has been given to different approaches to achieve such precision at the scale and economics required by the Flat Panel Display industry. New materials and technologies for high-throughput precision molding technologies are needed in order to truly enable cost effective manufacture of these objects over large areas. Imprint lithography and 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 with sub-micron features.

Polydimethylsiloxane (PDMS) based networks have served as the material of choice for much of the work in soft lithography.[1] The use of soft, elastomeric materials such as 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. [2,3,4] Such materials are superior to PDMS stamps in modulus and swelling resistance but lack flexibility and therefore compromise 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.[5] Since most polymer 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.[6] To date, researchers have had marginal success with PDMS-based materials in using soft lithographic techniques to produce <1 micron size features with high fidelity. 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.[1,2] Other serious disadvantages of rigid stamp materials include the necessity of fluorination steps to lower the surface energy of the stamp [2], and the cost of the master itself, due to the complexity of manufacturing and short lifetime associated with using the master to directly imprint materials, rather than making a disposable polymeric replica.

With this work, we report a platform technology, Pattern Replication In Non-Wetting Template (PRINT™), for low cost manufacturing of patterned optical films with single nanometer precision for the display industry.

2. Result and Discussion
The PRINT technology is based on a family of photcurable perfluoropolyethers (PFPE), Liquidia’s Fluorocur™ resin series, as the mold materials. The Fluorocur 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 thermal and chemical stability, as well as very low surface energies. Unlike other molding materials, such as PDMS, Fluorocur-based molds are both non-wetting and non-swelling when exposed to organic and inorganic materials. These characteristics enable the highly precise replication of micro- and nano-features into a variety of organic and inorganic materials. The high-throughput, high-fidelity PRINT process, enabled by Liquidia’s proprietary Fluorocur materials, facilitates precise design and commercial-scale manufacturing of micro- and nano-structured materials, including particles, arrays of particles and patterned films. We have previously demonstrated the use of the PRINT technology in fabrication of monodisperse isolated particles with precise control of size, shape, and composition.[7,8] Herein, we further demonstrate the capability of these materials in the rapid patterning of nano structures for displays and optics, highly ordered structures for photovoltaics, and other patterns for a variety of applications.

In the display industry, semi-conductors and other conducting materials are widely used. The ability of the PRINT™ technology to be compatible with conductive and optical materials has recently been demonstrated in batch scale with UV-curable optical resins, conducting polymers, and inorganic oxides. Figure 1 shows the highly ordered 2-D arrays of cylindrical features of conducting polymer Poly (3-Hexylthiophene) (P3HT), [6,6]-Phenyl C61 butyric acid methyl ester (PCBM) and several commonly used metal oxides. As a general procedure, a Fluorocur™ mold is generated from a master. Following this, a solution of P3HT and PCBM or a sol gel precursor of metal oxides is placed on a substrate (either plastic or glass) and the patterned Fluorocur™ mold is placed into conformal contact with the precursors on the substrate. The liquid precursors then fill the recess areas of the mold by capillary forces. After the precursor material is solidified, the Fluorocur™ mold separates cleanly from patterned features on the substrate. For metal oxides, the
patterned material is annealed to obtain the desired morphology. Alternatively, P3HT can be patterned by a thermal process due to the high thermal stability of Fluorocur™ molds.

Two-dimensional linear gratings with subwavelength pitch have attracted a lot of attention for optics applications including the potential application as wire-grid polarizers. We have done initial work fabricating various nano-wire/line features on films using different organic and polymeric materials. Figure 2 shows SEM and AFM images of several linear patterns at different pitch and length scale.

Beyond their potential value in polarizers, nano-size features have been shown to exhibit anti-reflection properties and increase the transmission of substrates. To demonstrate this effect, we have fabricated 70 nm diameter by 70nm high features using an optical material that matches the refractive index of the underlying glass substrate. Figure 3 shows the AFM image of the patterned features and the transmission of s-polarized light. Compared to a flat substrate, nano-patterning increased the transmission by a few percent in most of the visible region.

PRINT technology also demonstrates the capability of fabricating features of different size, shape, aspect ratio, and packing density in a single step. Figure 4a shows a picture of a complex 8-inch diameter film with 5 different patterns prepared by a single-step PRINT process. Figures 4b-f show the SEM images of the five different features.

3. Conclusions
In summary, the capabilities of PRINT process represent an ideal technology for large area manufacturing of patterned optical films with nanometer-scale precision. The PRINT manufacturing
process for both particles and films is currently in pilot production for high-throughput manufacturing. The PRINT process offers the unprecedented ability to fabricate highly precise micro and nanoscale objects and features from virtually any material. PRINT brings the uniformity and precision of the micro-electronics industry to high volume manufacturing of precision micro- and nano-structures with inherent control over size, shape, orientation and material.

4. References