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2013 Nanotechnology 24 505307
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Large-area, continuous roll-to-roll nanoimprinting with PFPE composite molds

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Received 1 July 2013, in final form 24 September 2013
Published 27 November 2013
Online at stacks.iop.org/Nano/24/505307

Abstract
Successful implementation of a high-speed roll-to-roll nanoimprinting technique for continuous manufacturing of electronic devices has been hindered due to lack of simple substrate preparation steps, as well as lack of durable and long lasting molds that can faithfully replicate nanofeatures with high fidelity over hundreds of imprinting cycles. In this work, we demonstrate large-area high-speed continuous roll-to-roll nanoimprinting of 1D and 2D micron to sub-100 nm features on flexible substrate using perfluoropolyether (PFPE) composite molds on a custom designed roll-to-roll nanoimprinter. The efficiency and reliability of the PFPE based mold for the dynamic roll-to-roll patterning process was investigated. The PFPE composite mold replicated nanofeatures with high fidelity and maintained superb mold performance in terms of dimensional integrity of the nanofeatures, nearly defect free pattern transfer and exceptional mold recovering capability throughout hundreds of imprinting cycles.

Online supplementary data available from stacks.iop.org/Nano/24/505307/mmedia

(Some figures may appear in colour only in the online journal)

1. Introduction
Nanoimprint lithography (NIL), an advanced lithographic technique for patterning of polymer nanostructures, has made a substantial impact in the last decade due to ease of fabrication process, high throughput, high resolution nanoscale patterning capability and the need for only simple instrumentation for the process compared to conventional patterning techniques such as photolithography and electron beam lithography, etc [1–3]. These advantages generated a great interest in nanoimprinting technology among both academia and industry, and have led to significant developments in associated techniques, methods and materials. Researchers have been exploring the potential of the nanoimprinting technique over the last several years and the research efforts have resulted in numerous applications in Si electronics, organic electronics, photonics, magnetics, separation process, microfluidics and biology [1]. However, the cycle time required for the completion of either the UV or the thermal batch nanoimprinting process has remained a weakness for the high throughput manufacturing sector. Several concepts were put forward by investigators to overcome this issue, namely roller nanoimprinting [4], reverse nanoimprinting [5], and nanotransfer printing [6] etc all of which have yet to provide a solution to overcome the bottleneck towards high throughput aspirations. The continuous UV roll nanoimprinting process
proposed by Ahn et al was the first successful attempt towards a continuous large scale micro- and nanopattern replication on rigid and flexible substrates in which they used a roll stamper made by direct machining on an aluminum roller as mold [7]. Later, Guo et al developed the process and platform for the implementation of the high-speed, large-area continuous roll-to-roll/roll-to-plate (R2R/R2P) nanoimprinting process on both flexible and rigid substrates [8, 9]. One significant advantage of the R2R nanoimprint lithography (R2R NIL) technique is that it inherited the high resolution pattern fidelity benefit from the traditional NIL technique with a drastically increased throughput. Also, the R2R patterning technique required much smaller force since it proceeds in a small area perpendicular to the web moving direction. The possibility of defect generation during the mold–substrate separation process is considerably lower in the R2R NIL technique due to the peeling fashion in which the web separates from the R2R mold assembly as compared to the conventional NIL technique [10]. Along with these significant advantages, there remain certain challenges associated with the lack of new materials having the necessary properties required for R2R molds and resists. Future advances in R2R nanoimprinting and its utilization in commercial applications strongly depends on the development and fabrication of new R2R mold and resist materials that can maintain the fidelity of the replicated features and deliver an almost defect free pattern transfer for long process cycles in a high volume manufacturing process. Unlike the batch process, during the R2R NIL process the mold material undergoes a severe test of its reliability, durability, robustness, mold recoverability, and the ability to maintain the fidelity of pattern transfer throughout the continuous process. Therefore the mold is one of the most important components that can determine the outcome of the entire process. There are several options for the fabrication of molds for the R2R process, and most of them are difficult. One option is to generate the pattern directly on the embossing roller which can be either quartz or metal, either by machining or by lithographic/plating processes [7, 11]. Such fabrication processes are generally more complex and the feature size is limited to the micrometer regime. Fabrication of elastomeric cylinder molds from a thermal/UV curable precursor is one other option that needs a patterned cylinder master or a large sized master mold. Another option is to wrap a flexible mold or mold assembly made of a polymer or metal shim around the embossing roller [12]. So far only a few materials including ethylene-tetrafluoroethylene (ETFE) [8, 9], Sylgard 184 (crosslinked PDMS elastomer) [13], Teflon® [13, 14] and nickel shim [11, 15–17] have been investigated and used as molds for R2R NIL process. A mold material that can provide a clean and smooth mold release without generating defects, and is also capable of maintaining the fidelity of the pattern transfer over hundreds of imprinting cycles can be considered as suitable for the R2R NIL process. Molds made of polymeric materials are easy to fabricate when compared to nickel shims, especially when the features are at sub-100 nm dimensions. Continuous nanoimprinting with ETFE molds was demonstrated by Guo et al [8, 9]. However, the use of ETFE molds in the R2R NIL process required the substrate to be treated with oxygen plasma and deposited with adhesion promoter to avoid defect generation and mold contamination during the process. The addition of surfactants may also be needed in the case of replicating higher aspect ratio features [8]. Even though the ETFE seems to have several characteristics required for a R2R NIL mold, it is still prone to resist contamination during successive imprinting cycles. Moreover, once it is contaminated during the continuous imprinting process, the possibility of mold recovery is unlikely and often results in the spreading of the contaminated area. This necessitates a frequent replacement of molds with new ones and therefore this is not a desirable scenario during a continuous process. Siloxane based elastomeric molds (PDMS and h-PDMS) are also not reliable for sub-100 nm R2R NIL processes due to their low modulus and poor chemical resistivity. Air permeability of the mold material becomes important when imprinting patterns with complex geometry that can lead to trapped air bubbles and result in incomplete filling of features [13]. Molds made of ETFE, Teflon® and Ni shim suffer from this shortcoming due to their poor/nonexistent air permeability. On the other hand fluorinated elastomers offer a promising alternative to ETFE and siloxane based molds due to their low surface energy, solvent resistance, chemical stability, transparency and tunable modulus. These characteristics make perfluoro(polyether) (PFPE) acrylates promising mold materials for R2R patterning of micron to sub-100 nm features [18–21]. Previous studies have shown that the resolution of fluoroelastomer molds can be enhanced by increasing the crosslink density or by adding small percentages of additives like trimethylolpropyl triacrylate (TMPTA) without sacrificing the low surface energy [19]. Tunability of the modulus without compromising the surface energy of the fluoroelastomer molds offers a substantial advantage for overcoming some failures such as roof collapse, buckling, lateral collapse, smoothing, delamination, and edge roughness often encountered in elastomeric molds used in soft lithography.

Stamp life is an important factor that has to be taken into consideration in a continuous patterning process. Materials that undergo structural disintegration and surface deterioration due to lack of chemical stability, mechanical strength and low surface energy are considered to be not suitable for continuous nanopatterning. These properties are critical in determining stamp life. Incorporating low surface energy groups in the NIL resist to induce smooth mold release and functional groups that provide better adhesion to the substrate can significantly improve the stamp life to a greater extent. Ease of fabrication of PFPE molds as thin films with simple process steps on a flexible backing make them durable and easy to handle [20].

In this paper, we investigate the reliability, durability, long term performance and efficiency of the PFPE composite mold in replicating nanostructures in a dynamic R2R process. To the best of our knowledge, the present work represents the first reported use of PFPE based molds in a dynamic R2R process.
2. Experimental section

2.1. Materials

Polyethylene terephthalate (PET) roll (ST 505, 125 μm thick, DuPont) was purchased from Tekra Corporation, WI, USA. Polyvinylpyrrolidone (PVK30) was purchased from ISP Technologies, INC, NJ, USA. Norland Optical Adhesives, NOA 81 and NOA 74 were purchased from Norland Products, NJ, USA. Perfluoropolyether acrylate (PFPE acrylate) (CN4001) was purchased from Sartomer Company, USA. Vertraf XF (DuPont) solvent was supplied by Cornerstone Technology, Inc, USA. Benzoin methyl ether, propylene glycol monomethyl ether acetate (PGMEA) and 2-butanol were purchased from Sigma-Aldrich Company and were used as received.

2.2. Fabrication of the PFPE acrylate composite mold

The PFPE acrylate was thoroughly mixed with photoinitiator Benzoin methyl ether (BME) (2 wt%) using Vertraf XF solvent for 1 h. A 10 wt% of Solvay Solexis MD 700 (PFPE urethane methacrylate) was added to CN4001 in the case of preparing molds with higher aspect ratio features. A plasma treated PET sheet was spin coated with a thin layer of NOA 74 (as adhesion promoter) and thereafter cured under UV light for 3 min. The fluoro-acrylate mixture was spin coated on the non-fluorinated Si master mold (1000 rpm, 45 s). The PET with cured NOA 74 layer was placed on top of the spin coated Si master with the adhesive layer facing the master mold and the entire assembly was placed in the Nanonex Nanoimprinter (NX 2000) for UV curing under nitrogen atmosphere for 20 min. Manual peeling off completed the mold fabrication where the crosslinked PFPE acrylate remained adhered to the PET backing layer.

2.3. Roll-to-roll nanocoating

In order to improve the wetting properties of the resist and enhance the adhesion to the PET substrate, we coated the substrate with 1 wt% solution of polyvinylpyrrolidone (PVP) in 2-butanol using the Mayer rod coating station, dried and re-wound on to the rewind roller with an interleaf. The corona treatment was not necessary for the PVP coated substrate for resist coating. A 35 wt.% solution of NOA 81 in propylene glycol monomethyl ether acetate (PGMEA) was used as coating solution for resist coating. The speed ratio of the coating roller was kept at one and the web speed was synchronized with the speed of the embossing roller. The Mayer rod (no. 2.5) rotation was kept at 10 rpm throughout the entire process. The solvents were removed at the drying station above the coating unit.

2.4. Roll-to-roll nanoimprinting

Several pieces of PFPE composite molds were taken on a double-sided tape and wrapped around the embossing roller having 6 in in diameter and width. A rubber cushion layer was placed between the roller and the mold to ensure conformal contact during the process. When the resist coated web was fed into the embossing roller, the two vacuum rollers on either side of the embossing roller applied web tension and the pinch roller pressed the coated web against the roll-to-roll mold assembly on the embossing roller. The resist was cured by the UV light source (Omnicure 2000, EXFO) placed at 5 to 7 mm distance from the embossing roller and operating at 90% opening. The web speed was maintained between 9–12 in min\(^{-1}\). The cured resist and web were continuously separated from the mold at the release roller as the web moves forward.

2.5. Characterization

Cross-section samples were prepared by depositing a thin layer of gold on patterned surface and then embedding the substrate in epoxy. After curing overnight, the surface was polished in cryogenic condition using a diamond blade. Scanning electron microscopy images were taken using FEI Magellan 400 SEM and JEOL JSM-7001F SEM. The modulus of the cured PFPE acrylate and cured NOA 81 resin were measured by nanoindentation technique using Hysitron Triboindenter.

3. Results and discussions

Figure 1 shows the custom built R2R Nanoimprinter, R2R Nano Emboss 100, (Carpe Diem Technologies, MA, USA) and schematic representations of R2R nanoimprinting processes namely resist coating, imprinting and curing. The R2R NanoEmboss tool consists of five sections, namely unwind, coating, imprinting, metrology/coating, and rewind (for a more detailed diagram of the tool see supplementary information stacks.iop.org/Nano/24/505307/mmedia). The coating, imprinting, and metrology sections are suspended on an inbuilt air cushion for the isolation of surrounding mechanical vibrations. The coating section has interchangeable Mayer rod and gravure rod coating units, a corona surface treater, and a drying station. We used the Mayer rod coating technique throughout this work. The R2R NanoEmboss tool is equipped with specially designed vacuum rollers to regulate web tension and ultrasonic sensors for precise web tracking and positioning.

Continuous patterning of higher aspect ratio features requires good adhesion between the resist material and the PET substrate. A thin layer of polyvinylpyrrolidone (PVP) was coated on the PET substrate before coating the resist. Coating with PVP has two advantages: first, PVP improved the wetting properties and adhesion between resist and substrate, and as a result provided a uniform coating of resist. Second, the water soluble PVP layer can also be used as a lift-off layer for R2R device fabrication processes that involve reactive ion etching, metal deposition, and lift-off. The PVP coated web was re-wound on to the rewind roller with interleaf and brought back to the unwind section for UV resist coating, imprinting, and curing. A schematic illustration of the R2R nanoimprinting process is shown in figure 1(b).
The PFPE acrylate composite molds were fabricated by thoroughly mixing PFPE acrylate (CN4001, Sartomer) with a photoinitiator, and afterwards the mixture was spin coated on a patterned silicon master mold. An adhesive layer coated PET backing sheet was placed on top of the spin coated master with the adhesion layer facing the master, and the whole assembly was UV cured under nitrogen atmosphere for 20 min. Peeling off the composite daughter mold from the master completed the mold fabrication. Dozens of different molds were made in the same manner. The modulus of the cured PFPE acrylate film was measured to be 45 MPa. Before starting the process several pieces of PFPE composite molds were taken on a double-sided adhesive tape and adhered to a rubber cushion layer wrapped around the embossing roller. A picture of a fabricated PFPE composite mold as well as several molds wrapped around the embossing roller is shown in figures 2(a) and (b).

A commercially available fast curing photocurable resin, Norland Optical adhesive 81 (NOA 81) was used as the resist material in the present work. Photocurable resists that can be imprinted at room temperature and low pressure are preferred over resists that need high temperature or pressure to imprint for high volume nanofabrication. It is known that the imprint resist must have a high enough modulus to avoid collapse of dense high aspect ratio structures, and deformation of features during the substrate peeling off in the roll-to-roll process [22]. The suitability of several Norland Optical adhesives as UV NIL resist for replicating sub-100 nm features was well established by numerous earlier reports [23–26]. These thiol-ene based resists accurately replicated nanofeatures with high fidelity during pattern transfer. Even though the exact chemical composition of NOA resins are withheld due to proprietary reasons, it is presumed to consists mainly of urethane-containing tetrafunctional allyl ether and its thiol counterpart trimethylolpropane tris(2-mercaptoacetate) [23]. NOA 81 has high enough modulus (1.08 GPa) to achieve a good pattern definition and moderate viscosity to obtain lines with sharp edges. NOA 81 cured quickly under UV light (2 J cm\(^{-2}\)@365 nm) and didn’t require oxygen free environment. Resists that require long curing times and oxygen free atmosphere are not as suitable for R2R UV nanoimprinting.

A 35 wt.% solution of NOA 81 in propylene glycol monomethyl ether acetate (PGMEA) was used as coating
solution. As the web moved forward, the coating roller transferred resist solution to the PET substrate and the turning Mayer rod (No. 2.5) removed excess resist material from the substrate. The Mayer rod coating station used a wire-wound metering rod in which the diameter of the wire can vary for different coating thickness. The grooves between the wire coils determined the precise amount of resist material that passed through the Meyer rod as the web moved over it. The other factors that can influence the actual coating thickness were viscosity of the coating solution, concentration, web tension, web speed and wetting properties of the resist. After the resist passed through the Mayer rod, the initial shape of the resist was a series of stripes, spaced apart according to the spacing of the wire windings. Almost immediately, the surface tension of the resist film pulled these stripes together, providing a uniform coating (∼5 µm thickness) with a flat and smooth surface. Solvent was fully removed at the drying station in the coating section.

The embossing section in our R2R nanoimprinting system consists of two vacuum rollers, an embossing roller, a pinch roller, a release roller and a UV curing station. When the resist coated web moved in to the imprinting section, the pinch roller pressed the web against the R2R mold assembly wrapped around the embossing roller. Under the web tension provided by two vacuum rollers and pressure exerted by the pinch roller, resist filled into the nanopatterns via the capillary force, and thereafter was cured by a high power UV source (Omnicure 2000, EXFO). The UV light (wavelength 365 nm) was illuminated through PET by a 4 in wide splitter with a narrow slit opening. The intensity of UV light at a 5 mm distance was measured to be 2 W cm⁻². The cured nanofeatures were continuously peeled off from the embossing roller/R2R mold assembly at a speed of 12 in min⁻¹ on the release roller.

Grating patterns having periodicities 980 nm (line width 500 nm), 550 nm (line width 230 nm) and 130 nm (line width 70 nm) and pillars having diameters 1 µm, 700 nm, 500 nm and 350 nm were successfully imprinted. Figure 2(b) shows the imprinted substrate as it leaves the release roller and these films display strong light diffraction from the nanoimprinted gratings. This strong light diffraction revealed the high quality of the replicated nanofeatures. SEM images of the Si master mold and the cross-section image of nanofeatures on imprinted PET are shown in figures 2(c) and (d). The exact replication of the patterns even to minute detail points to the fact that the resist was able to completely fill the trenches of the nanofeatures at the process speed and was cured immediately by the UV light. The imprint speed can be increased by using either multiple UV sources or higher intensity source. The speed was chosen to avoid wasting large amounts of materials and substrates for the purpose of development.

Accurately replicated NOA 81 patterns should have the same geometry as in the Si master mold because the PFPE composite mold has the exact inverse patterns of the master mold. Comparison of the original master mold and the replicated patterns on NOA 81 showed excellent pattern replication. A several foot long piece of nanoimprinted web coming out of embossing section is shown in figure 3(a). Top down SEM images of 500, 230 and 70 nm gratings

Figure 2. (a) Picture of the fabricated PFPE composite mold, (b) molds on the embossing roller and imprinted features separating at the release roller, (c) tilted SEM image of 230 nm grating Si master, (d) cross-section SEM image of the R2R imprinted 230 nm gratings on PET.
are shown in figures 3(b)–(d). The SEM images confirmed the capability of the PFPE composite molds to faithfully replicate sub-micron to sub-100 nm features in a dynamic situation with high fidelity on a continuous process platform. Suitability of various polymeric materials as molds for R2R nanoimprinting processes depend on their ability to faithfully replicate features even after several hundreds of imprinting cycles. The low surface energy of the PFPE composite mold enabled smooth mold release without defect generation and self-cleaning during the successive imprinting cycles. The good chemical resistivity of the PFPE prevented the swelling of the nanofeatures on the mold even after several hundreds of imprinting cycles. Swelling would have caused the loss of critical dimensions of the nanofeatures that ultimately results in release failures.

Good adhesion between resist and substrate, easier release of features from the mold and better self-cleaning (recovering from contamination) capability of the PFPE composite mold allowed the continuous replication of the nanofeatures with exact dimensions over hundreds of imprinting cycles. Careful inspection of the used PFPE composite molds with SEM after several hundreds of imprinting cycles showed no noticeable defects, surface deterioration, contamination, swelling, deformation and collapse of features. The SEM images of these used molds and imprinted gratings after approximately 300 imprinting cycles are shown in figures 4(a)–(d). The 230 nm grating PFPE composite mold shown in figure 4(b) was used for imprinting where the gratings were orthogonal to the moving web direction. The high aspect ratio (2.1) mold showed no noticeable deformation at all and replicated features with high fidelity throughout the entire process. There have been questions as to whether orientation of patterns parallel or orthogonal to the moving web would affect pattern release and quality. We observed no difference in our experiments. Moreover, the SEM images of the gratings features taken from sections on imprinted web after ∼300 imprinting cycles were comparable to the features imprinted at the early cycles. The results were similar with respect to the quality of the R2R imprinted 2D structures.

As shown in figure 5, pillars having diameters 1 µm, 700, 500 and 350 nm were accurately replicated throughout the entire imprinting cycles. The height of all the 2D features was 500 nm. In this case the release characteristics of the mold are crucial in determining the quality of the continuously imprinted micro and sub-micron pillars. Molds with poor release properties can lead to missing pillars on the imprinted substrates. The SEM images of the R2R imprinted 2D
features showed no evidence of missing pillars and deformed structures. Exceptional mold recovering capability, chemical stability and low surface energy were necessary to keep the mold clean and usable after hundreds of imprinting cycles. The structural integrity of the mold remained intact during the entire process. The PFPE remained adhered to the backing.
layer as there was no sign of delamination from the PET. Our results showed that the PFPE based composite mold is a promising candidate and reliable material as mold for the R2R manufacturing of nanofeatures for various applications. The larger issue of metrology, both real time and static, forms the basis of a substantial body of research [27–30]. The systematic analysis of defects, factors that contribute to defects and ways to overcome those issues are currently under investigation by our group and others skilled in metrological science and will be addressed in future studies.

4. Conclusions

In summary, we have shown the efficiency, reliability, and durability of the PFPE based composite molds in replicating 1D and 2D micron to sub-100 nm features with high fidelity over successive imprinting cycles in a dynamic large-area high-speed roll-to-roll nanoimprinting process that required only a simple roll-to-roll substrate treatment step using a custom built R2R nanoimprinter. The coating of the PVP layer provided enhanced adhesion between the substrate and the resist which was very critical in determining the quality of pattern transfer in a R2R nanoimprinting process. The smooth and clean mold release as well as the better mold recovering capability of the PFPE composite mold allowed the continuous replication of the nanofeatures without defect generation over hundreds of imprinting cycles. SEM images of the PFPE composite molds taken after the process showed no noticeable defects, deformation of features, surface deterioration, swelling, contamination, and collapse of features. These observations as well as the ease of fabrication of the mold on a PET backing by using only a few drops of PFPE render the PFPE composite mold a cost effective, durable, robust, and large-area mold highly suitable for a R2R Nanopatterning process.

Acknowledgments

This work was fully supported by the NSF Nanoscale Science and Engineering Center for Hierarchical Manufacturing (CHM) at the University of Massachusetts-Amherst (Grant No: CMMI-1025020). The authors express their gratitude to Boston Research Laboratory for kind support. Raboin are also acknowledged for providing assistance during this research work. We acknowledge Lightsmyth Technologies, OR for providing a silicon master mold used in this work. Dr. Alexander Ribbe, John Nicholson and Louis Raboin are also acknowledged for providing assistance with characterization facilities. KRC also thanks the Panasonic Boston Research Laboratory for kind support.

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