Chapter 7

Soft UV Nanoimprint Lithography and Its Applications

Hongbo Lan

Additional information is available at the end of the chapter

http://dx.doi.org/10.5772/56186

1. Introduction

Large-area nanopatterning technology has demonstrated high potential which can significantly enhance the performance of many devices and products, such as LEDs, solar cells, hard disk drives, laser diodes, display, etc [1]. For example, nano-patterned sapphire substrates (NPSS) and photonic crystals (PhC) have been considered as the most effective approaches to improve the light output efficiency (internal quantum efficiency and external quantum efficiency) of LEDs and beam shaping [2,3]. The solar cells with sub-micro anti-reflective coating exhibited higher photocurrent and higher power conversion efficiency compared to those without nanostructures [4]. Moreover, the ability to produce large-area micro- and nanostructures on non-planar surfaces is of importance for many applications such as optics, optoelectronics, nanophotonics, imaging technology, NEMS, and microfluidics [5]. However, creating large-area nanostructures on curved or non-planar surfaces are extremely difficult using existing patterning approaches. Furthermore, a variety of existing nanopatterning technologies such as electron beam lithography (ELB), optical lithography, interference lithography (IL), etc., cannot cope with all the practical demands of industrial applications with respect to high resolution, high throughput, low cost, large area, and patterning on non-flat and curved surface. Therefore, new high volume nanomanufacturing technology strongly needs to be exploited and developed so as to meet the tremendous requires of rapid growing markets.

Nanoimprint lithography (NIL) has now been considered as a promising nanopatterning method with low cost, high throughput and high resolution, especially for producing the large-area micro/nano scale patterns and complex 3-D structures and as well as high-aspect-ratio features. Due to these outstanding advantages, it was accepted by International Technology Roadmap for Semiconductors (ITRS) in 2009 for the 16 and 11 nm nodes, scheduled for industrial manufacturing in 2013. Toshiba has validated NIL for 22 nm and beyond. NIL has also been listed as one of 10 emerging technologies that will strongly impact the world by

MIT's Technology Review. The resolution potential has been demonstrated by the replication of 2.4-nm features. It is expected to play a critical role in the commercialization of nanostructure applications [6-8].

Compared to other NIL processes (thermal NIL or hot embossing, UV-NIL with rigid mold) and nanopatterning methods, soft UV-NIL using a flexible (or soft) mold has been proven to be a very promising approach for making large-area patterns up to wafer-level in the micrometer and nanometer scale, fabricating 3-D micro/nano structures and high-aspect-ratio features, especially producing large-area patterns on the non-planar surfaces even curved substrates at low-cost and with high throughput. Since the soft mold (stamp, template) is adopted, the soft UV-NIL process has some unique advantages compared with the traditional UV-NIL with rigid mold. These strengths include: (1) Cost reduction. Cheap soft molds can be easily replicated from one expensive master, significantly reducing cost of the master template fabrication. (2) Conformal contact. Conformal contact between the undulated (or curved, waviness, bow, warp) substrate and the mold can be achieved over large areas without applying high external pressure. (3) Insensitive to particle contaminants. Particle contaminants are less problematic as the soft mold can locally deform around a particle avoiding damage to the mold or substrate which lead to improve the yield of the process and to extend the application fields. (4) Avoiding anti-adhesive layer due to the low surface energy of flexible mold materials. (5) Low imprinting and demolding force. (6) Utilizing gradually sequential micro-contact and "peel-off" separation method for thin film type molds. However, soft UV-NIL process has also some inherent drawbacks. (1) Deformation and distortion of soft molds. Due to the relatively low Young's modulus, the deformation of soft molds under pressure remains a major issue which limits the resolution, uniformity and reproducibility of imprinted patterns. High aspect ratios structures and dense patterns are not stable and tend to collapse. (2) Poor dimensional stability. Due to the poor solvent resistance as well as deformation of pressure and thermal expansion, the dimensional stability of imprinted patterns is determined and degraded. (3) Short mold lifetime. Since the hardness and resistance to solvent are poor, soft molds have relatively low mold lifetime. These limitations must be solved and overcame for extensive applications [8-13].

Currently, full wafer imprint up to 300mm, and 12.5nm resolution patterns have been achieved by using the soft UV-NIL. Soft UV-NIL has been considered as one of the most promising solution implementing mass production of micro/nanostructures over large areas at low cost for the applications in compound semiconductor optoelectronics and nanophotonic devices, especially for LED patterning [2, 14].

As an emerging cost-effective nanopatterning technique, soft UN-NIL involves two basic aspects: fundamental investigation and application research. The fundamental investigation comprises of theoretical basis and key enabling techniques including process, mold (material, fabrication of working stamp and master template), material (resist, functional material, etc.), tool. The application research mainly covers a variety of practical applications suitable for soft UV-NIL, such as LED patterning, optical components, nanophotonics, biological applications, etc. Author proposed an infrastructure of soft UV-NIL, as shown in Figure 1.

http://dx.doi.org/10.5772/56186

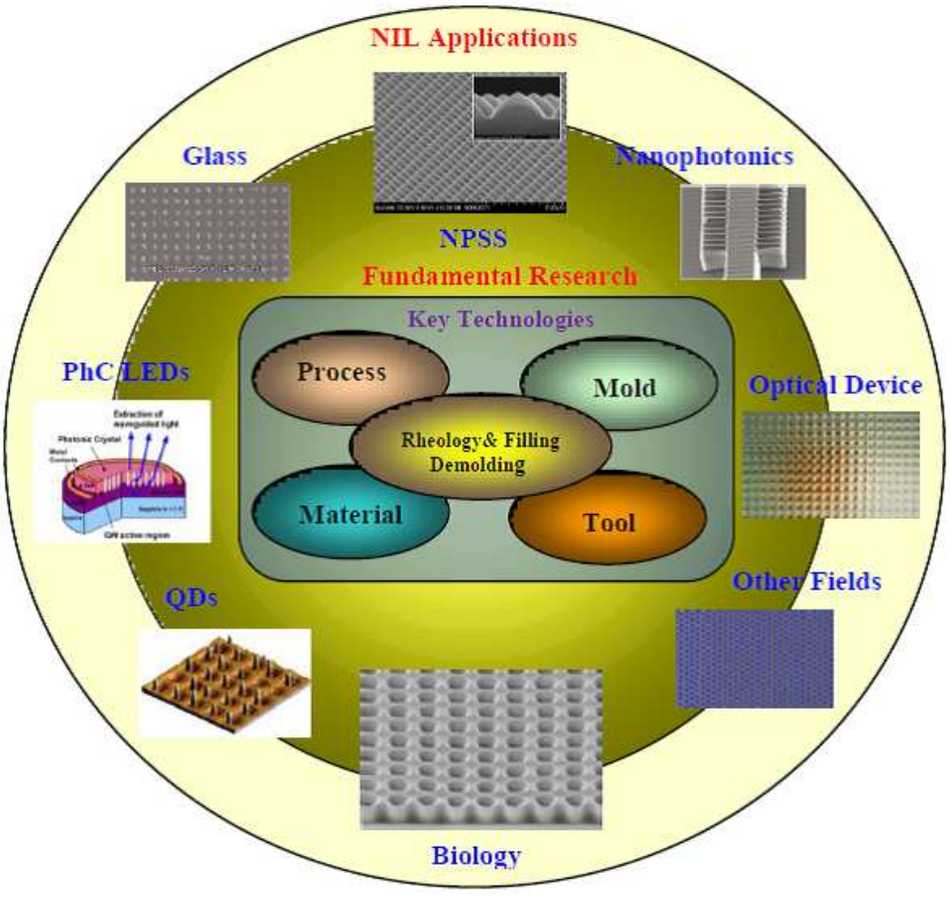

Figure 1. An infrastructure of soft UV-NIL process

2. Principle and process of Soft UV-NIL

2.1. Principle and process flow

The whole process flow of forming micro/nanostructures by soft UV-NIL is composed of four steps: the fabrication of a master template, the replication of a soft mold (or working mold) by this master template, the imprinting in the UV curable resist using the replicated soft mold, and the replicated patterns transfer form UV curable resist to the substrate or functional materials by etching or lift-off process. Together, these steps affect the quality of the final replica in terms of resolution, uniformity, fidelity, patterning area, and line edge roughness.

A master template is firstly fabricated by EBL, IL or other patterning technologies (e.g. block copolymers, AAO, FIB, photolithography, etc.). Then, the surface of the master is treated forming an anti-adhesive layer. The liquid mold material is spin coated or casted the master template to duplicate a patterning layer. Subsequently, a backplane or a flexible layer is bonded to the patterned layer. After cured thermally or UV curing, the soft composite mold is peeled off form the master template. The soft mold obtained is a negative copy of the master template.

The fabrication process of soft UV-NIL includes four steps (as shown in Figure.2): (a) Firstly, a UV-curable resist, which is liquid at room temperature, is spin-coated or dispensed on the substrate. (b) Subsequently, the soft mold is pressed into the resist on the substrate with a low pressure, and adjusts to the waviness or curvature of the substrate until completely conformal contact is achieved. Due to high flexibility, the soft mold can well adapt its shape to the waviness of the substrate obtaining good conformal contact between the non-flat substrate and the mold. (c) After filling all cavities or trenches of the mold, UV curing that solidifies the liquid resist due to cross-linking is carried out by a UV light source. (d) Finally, the soft mold is released, leaving the UV-curable resist patterned. Low viscosity UV-curable resist, commonly comprised of a low molecular weight polymer and photoinitiator, is significantly essential for easily filling the nanocavities of the mold [8-9, 15].

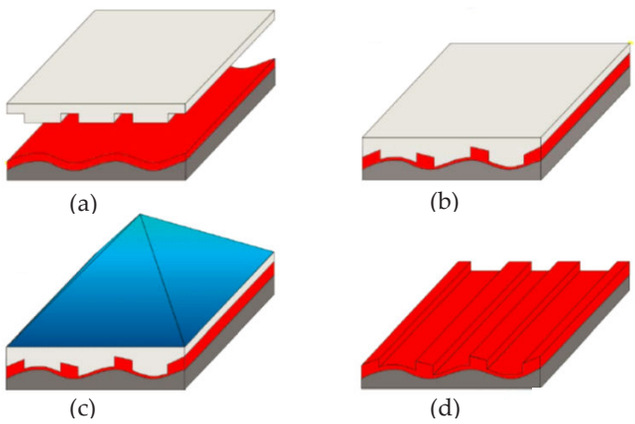

Figure 2. Process flow of soft UV-NIL [15]

The removal of the residual layer is typically performed by using a reactive ion etching (RIE) process with an oxygen plasma. The molded resist can then serve as a mask for further processing steps or be used as a functional layer itself. The most common methods for further processing are using the structured resist as an etch mask for patterning the substrate or as a mask for a lift off process for structuring of functional materials like metals. Besides using the structured resist as a mask for further processing, the resist pattern can also be used directly as a functional layer [16, 17].

2.2. Variations of soft UV-NIL

Some variations of soft UV-NIL have been proposed and developed, e.g., SCIL (Substrate conformal imprint lithography) and UV-enhanced SCIL developed by Philips and SUSS, Soft Molecular Scale Nanoimprint Lithography (SMS-NIL) developed by EVG, and full wafer soft UV-NIL, etc. Verschuuren *et al*. [1, 14, 18-19] proposed substrate conformal imprint lithography (SCIL), which combines the advantages of a soft composite mold for large area patterning with the advantages of a rigid glass carrier for low pattern deformation and high resolution. SCIL is based on a combination of the sequential imprinting method and the sol-gel resist. Figure 3 presented the schematic illustration of the SCIL imprint and separation sequences. To achieve

http://dx.doi.org/10.5772/56186

a substrate conformal contact between a working mold and a substrate, SCIL process relies on a sequential imprinting process. The approaching of the flexible mold starts from one side and spreads to the whole mold subsequently by releasing the vacuum in the grooves step by step and applying a small over pressure of 20 mBar on the mold (step 1 to 3). After conformal contact over the entire substrate is carried out, the imprint resist is cured by UV exposure or in case of using imprint sol-gel based resists diffusion of the sol-gel solvent into the PDMS mold (step 4). The automatic separation of the mold from the substrate is performed by switching on the vacuum in the grooves consequently, which is opposite to the imprint process (step 5 to 7). This results in a low force peeling action which removes the stamp from the patterned resist layer and avoids damage to mold or transferred patterns. SCIL has demonstrated sub-10nm resolution over 150mm-diameter substrates. The SCIL technology can well cope with non-ideal substrates and implement full wafer imprinting in a single step. For the SCIL process, the curing of sol-gel resist relies on the diffusion of solvents into the PDMS mold. Depending on the operation and preparation conditions, the curing time varies from 5 to 15 minutes. In order to improve throughput (reducing curing time) and repeatability of the process, a UV enhanced SCIL process using UV curable resist has been developing. Fader *et al*. recently introduced UV-SCIL with purely organic UV-curing materials showing curing times of 17s [20]. The excellent performance of SCIL in respect to substrate conformity and pattern fidelity over large areas makes this imprint technology a powerful tool, especially for applications like LED/VCSEL, optical elements or patterned media [21].

Author developed a full wafer soft UV-NIL with a tri-layer composite mold. The composite mold includes a thin layer of fluoropolymer-based material as the patterning layer, a thick layer of *s*-PMDS as intermediate flexible or cushion layer, and a thin glass sheet as the support layer. Figure 4 illustrated the schematic diagram of the proposed full wafer soft UV-NIL process. The imprinting process is performed by a sequential and micro-contacting solution starting from the center to two sides of the mold. The separation process employs a continuous 'peel-off' demolding mode starting from two sides to the center of the mold. Compared to the SCIL, the distinct advantages of the process include: (1) The imprinting and demolding procedure take the mold center as axis of symmetry, are carried out at the same time on two sides with higher throughput and easier eliminating trapped air bubble. (2) An enhanced demolding approach is adopted. (3) Since the imprinting procedure is performed under a low vacuum pressure environment, it can better remove the trapped air bubbles and provide completely conformal contact [22].

There is a big difference for the imprinting and demolding mode between soft UV-NIL using flexible mold and NIL with rigid mold. Using gas-assisted imprinting method can easily achieve uniform distribution of applied pressure over the entire substrate, gradually and exactly load imprint force. The sequent contact mechanism prevents the flexible mold from trapping air bubbles and therefore ensures that the mold follows exactly the undulating topography over whole substrate surface. A combination of the sequent micro-contact and gas-assistedmprinting can ensure to achieve uniform pressure and good conformal contact, avoid the trapped air bubble defects, reduce the deformation of soft mold. The peel-off

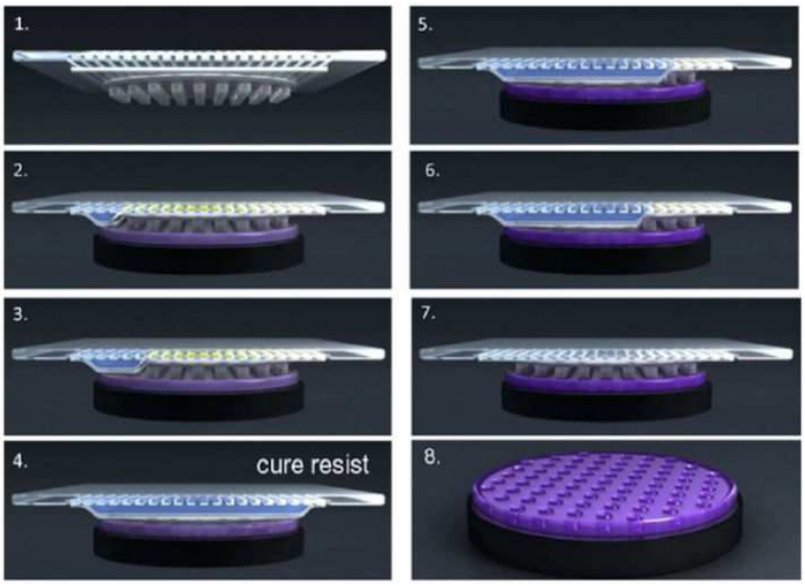

Figure 3. Schematic of substrate conformal imprint lithography (SCIL) [1]

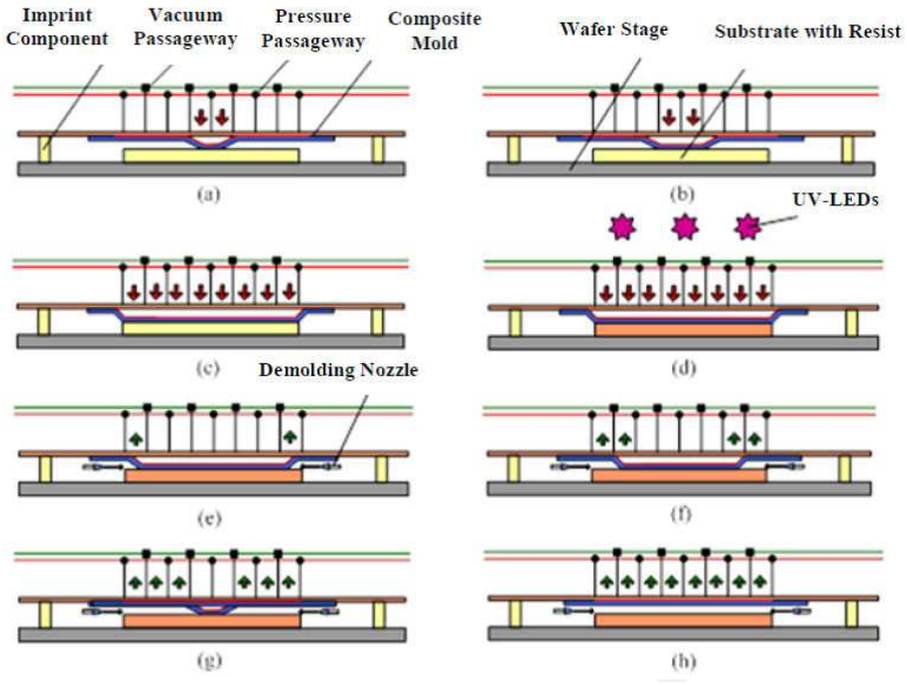

Figure 4. Schematic of a full wafer soft UV-NIL process for non-ideal substrates

demolding approach can be utilized which results in a low separating force that avoids damage to the patterned resist as well as to the mold, and improving the mold lifetime [18, 23].

In order to satisfy the demands of a variety of practical applications, lots of new soft UV-NIL processes have been being proposed and developed. Here only presents some principal and typical variants of soft UV-NIL processes. As the progresses in the soft UV-NIL and continu-

ously growing application needs, much more innovative processes or methods regarding soft UV-NIL will emerge in the future.

3. Various types of soft molds

The flexible mold is the most important elements for soft UV-NIL. The performance of flexible mold has a decisive effect on the soft UV-NIL in term of resolution, patterning area, throughput, uniformity of the imprinted patterns and the residual layer, and reproducibility of imprinted structures.

Since the soft UV-NIL was introduced, various structural types or configurations have been developed and employed. The most common type of the soft mold is a bi-layer structure which is composed of a rigid glass backplane for mechanical stability (optional) and a patterned soft PDMS (the commercially available PDMS brand Sylgard 184, also known as soft-PDMS or *s*-PDMS from Dow Corning Inc.) imprint layer that adapts perfectly to the waviness or bow of a substrate [12, 24-26], illustrated in Figure 5(a). However, due to the low Young's modulus, high viscosity and swell problem of *s*-PDMS, hard-PDMS (*h*-PDMS) which has higher Young's modulus (a Young's modulus of around 9 MPa) and lower viscosity, has been developed as patterned layer material. Figure 5(b) illustrated such a composite mold, in which a thin *h*-PDMS layer with relief structure is supported by a thick layer of *s*-PDMS. The thin layer of *h*-PDMS is able to ensure a good replication of the nanostructures due to his higher Young's modulus, the thick commercial *s*-PDMS top layer maintains a global flexibility of the whole mold allowing perfect conformal contact even for a non-flat substrate at low imprint pressure [27-28]. Figure 5(c) showed a tri-layer composite flexible mold which includes a thin glass backplane, a soft PDMS flexible layer and a *h*-PDMS patterned layer. Although the *h*-PDMS stamp worked well for replication, there were still limitations in using *h*-PDMS as a patterning layer, such as cracking during the mold fabrication step and degraded conformal contact with the substrate compared with the PDMS material normally used. *X*-PDMS, which has a higher Young's modulus up to 80 MPa, the highest cross linking density and lower diffusion, has been developed by Philips and SUSS as a patterned layer for the tri-layer mold for the SCIL and UV enhanced SCIL applied. The composite mold includes a *X*-PDMS patterned layer, a low modulus PDMS intermediary layer, a thin glass sheet, as shown in Figure 5 (d). The in-plane stiffness of the mold avoids pattern deformation over large areas, while out-of-plane flexibility allows conformal contact to underlying surface features [18, 29]. In Figure 5(e) offers the fifth structure of the flexible mold. The first layer is a 2-mm thick cushion layer cast from PDMS. The second layer is a thin flexible plate attached to the PDMS cushion using plasma-activation, which results in an irreversible strong bond between the glass and the PDMS. The third layer is a thin layer of *h*-PDMS spin-coated onto the master. One of the advantages of this composite mold is the reduction of the lateral deformation since the patterned layer is closely anchored to the rigid glass plate [12].

In order to improve Young's modulus of a patterned layer for enhancing the resolution of replicated pattern, PMMS is also used to be a structured layer material. A tri-layer mold

configuration was proposed which consists of a rigid carrier, a PDMS buffer layer (Young Modulus E = 0.75 MPa) and a PMMA patterned layer (E = 5.2 GPa), as shown in Figure 5 (f). The introduction of a thin layer of hard material over the PDMS buffer ensures a good hardness for stamping all types of patterns and a reduced pattern deformation over a large area because of the flexibility of PDMS buffer layer. In order to overcome the cracks and fractures during the imprinting and detaching process for high modulus elastomers, a UV cured rigid polymer has been used as the patterning layer. The hybrid mold composed of a thin (100-200 nm) photocured feature layer and the thick (~2 mm) elastic PDMS support. An interpenetrating polymer network was formed between the interface of the UV-cured rigid patterning layer and the flexible PDMS substrate to provide excellent adhesion of the two distinct materials [30].

Due to the excellent properties of fluorinated materials for an flexible mold used in soft UV-NIL such as low surface energy, excellent mechanical property, high UV-transparency, low viscosity, high chemical durability, thermal stability, etc., fluorinated materials (e.g., PTFE, ETFE, Teflon,) have been considered as the most promising candidate material of patterning layer. Figure 5 (g) and (h) demonstrates a composite mold including a thin layer of PFPE (*a*-PFPE) as the patterning layer and a thin, flexible, polyethylene terephthalate (PET) sheet as the flexible backing layer. The mold has the ability to fabricate high dense and sub-20 nm feature patterns without cracking or tear-out defects that typically occur with high modulus elastomers [31-33].

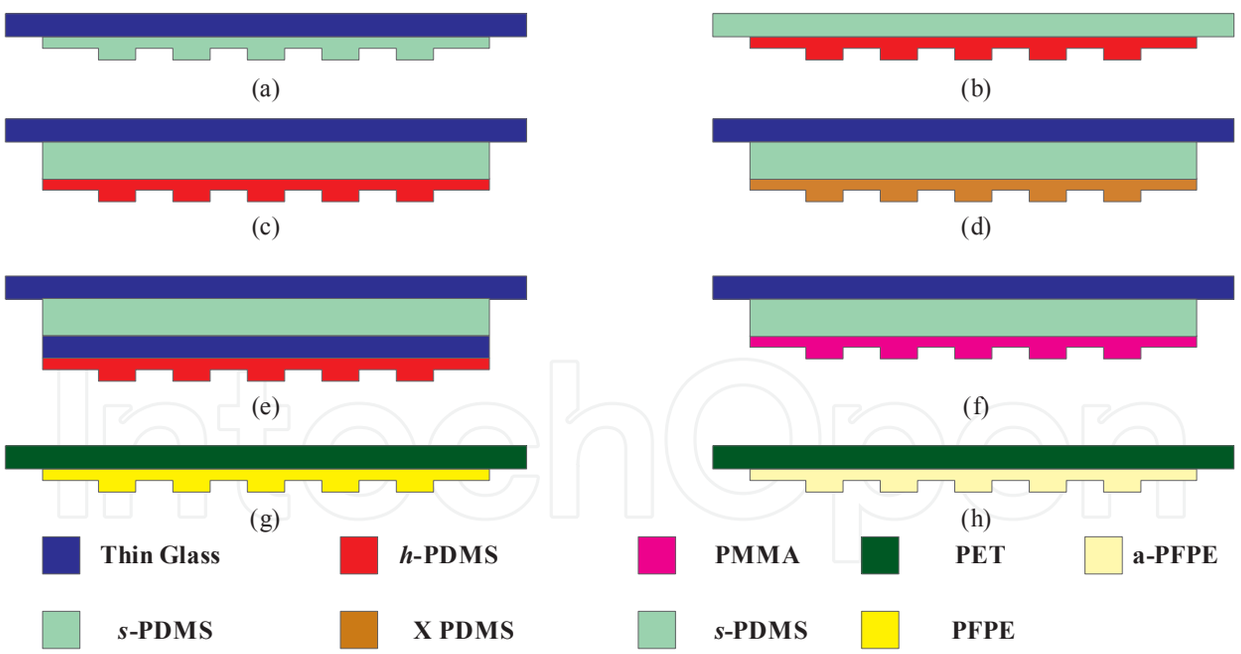

Figure 5. Various types of soft molds used by soft UV-NIL

Based on the presentations and analysis above, we can generalize a structural model of a common soft mold, as shown in Figure 6. It commonly comprised of three layers: a patterning layer, a buffer layer, and a support layer. The fundamental properties of the patterning layer involve the low surface energy, excellent mechanical property, high UV-transparency, low

http://dx.doi.org/10.5772/56186

viscosity, and thermal and chemical stability. The buffer layer is an intermediate cushion layer which has high flexibility to ensure the intimate conformal contact between the non-flat substrate and the mold. The support layer has mainly twofold: avoiding the lateral dimension of the mold and attaching or fixing the stamp to holder (or chuck). High Young's modulus materials with proper flexibility commonly need be adopted, such as a thin glass backplane or a PET sheet. Of course, there are more variations following the basic configuration. The composite mold should have global flexibility and local rigidity for achieving high resolution patterns over large areas.

Figure 6. Structural model of a common soft mold

A flexible thin-film (or membrane) can provide better conformal contact with the non-flat substrate (or large area surface) to be patterned without applying large pressure during the imprinting. A further benefit is that demolding can be achieved by peeling the mold from the substrate with an effectively smaller demolding area and low release force. This is much easier than the detaching of a rigid mold, where the hard mold needs to be separated from the substrate as a whole in a parallel way. Therefore, apart from the structure and material used of a flexible composite mold, the thickness of each layer of the mold is also be optimized.

4. Materials used and fabrication methods for a variety of soft molds

Apart from the structural style discussed in Section 3, the performances and capabilities of soft molds are largely dependent on the properties of the materials used. Nowadays, a wide variety of materials have been utilized to fabricate flexible molds [7, 8, 10]. This section primarily discusses the various material used for flexible molds.

4.1. PDMS-based materials

4.1.1. s-PDMS

Up to now, PDMS is undoubtedly the most widely used soft mold material. There are several reasons that PDMS emerged as a kind of standard material for the soft mold. It has a low Young Modulus and low surface energy that allows for conformal contact and easy release from both a master template and imprinted patterns. It is a durable material with fair chemical resistance and has good optical transparency down to a light wavelength of approximately 256 nm. It is a relatively tough material with a high elongation at break (> 150%) that allows for significant deformation before failure during patterning conditions. It can be easy handled and has high

gas permeability. Most importantly, *s*-PDMS (Sylgard™184 from Dow Corning) is commercially available in kits that allow for inexpensive fabrication of flexible molds from polymer precursors. However, there are some inherent disadvantages to *s*-PDMS which severely limit its capabilities in soft UV-NIL. The low Young Modulus below to 2.0 MPa limits the replication of both the high-density and high resolution features and is also a detriment for forming high-aspect ratio structures as fabricating such features will be apt to collapse, merge, or buckle. Moreover, *s*-PDMS tends to absorb organic solvents and monomers. This leads to fluctuations in the resist composition and swelling issue of the mold. This becomes a serious problem when trying to pattern certain biological materials or for the fabrication of functional nanostructures with controlled surfaces. Its poor solvent resistance has a serious effect on reproducibility due to degradation in the course of patterning repeatedly. Its high elasticity and thermal expansion can lead to deformation and distortions during the fabrication can result in loss of critical dimensions. The surface energy of *s*-PDMS is not low enough to duplicate profiles with high fidelity. In addition, the *s*-PDMS remains its high viscosity (for Sylgard 184, this is 3900 mPa s). As a consequence, 3D nanostructures and fine features of a master mold are difficult to be fully filled which results in a loss of feature height and some defects and uniformity of replicated patterns. Besides, the dimensional change (i.e., thermal shrinkage) due to thermal expansion after thermal curing makes it difficult to apply it for large-area mass production, especially multilevel pattern registration over a large area [10, 12, 13, 26, 34-37].

Simple PDMS molds are typically replicated by first mixing two commercial PDMS components: 10:1 PDMS RTV 615 (part A) siloxane oligomer and RTV 615 (part B) cross-linking oligomers (General Electric). The mixture is then casted on a master template and degassed in a low pressure vacuum chamber. A curing time of 24 h and a curing temperature of 60 °C are usually recommended in order to reduce roughness and to avoid a build up of tension because of the thermal shrinkage. The replicated mold is left to cool to room temperature, carefully peeled off from the master template. In the subsequent fabrication step the unstructured backside of the PDMS layer was treated with oxygen plasma for 30 s in order to temporarily increase the surface energy and thereby ensure a stable bonding of the PDMS layer to the quartz or glass backplane. Sometimes, the mold is also treated with silane based anti-sticking treatment to further reduce the low PDMS surface energy. During the fabrication, curing times and temperatures, which have large effect on the elastic modulus and hardness of the replicated soft mold, must be exactly controlled. The vacuum degree in degassing phase is also a key process parameter. The previous results have indicated that a higher vacuum degree and a lower temperature are the favorable conditions to get better comprehensive physical properties of a PDMS-based soft mold [13, 26].

4.1.2. h-PDMS

An obvious way to overcome unwanted deformations is to use a mold with a higher Young's modulus. Therefore, there have been attempts to utilize materials of high Young's modulus for flexible molds. *h*-PDMS was developed at IBM as early as 2000 [36]. They tried to formulate a better imprint material by trying different combinations of vinyl and hydrosilane end-linked polymers and vinyl and hydrosilane copolymers, with varying mass between cross-links and

junction functionality. A nanoimprint resolution record of 2 nm has been achieved by using soft molds based on *h*-PDMS [37]. Viheriälä *et al*. described a formulation of *h*-PDMS [12].

The procedure for producing a bi-layer *h*-PDMS/*s*-PDMS mold is illustrated in Figure 7. The *h*-PDMS prepolymer, prepared by referring to the formulation in [12], is spin coated onto a Si master template fabricate by EBL at 5000 rpm for 30 sec and then degassed in vacuum for 10 min (the thickness of the *h*-PDMS is about 5-8μm). A mixture of conventional *s*-PDMS (1:10) is then casted the spin coated *h*-PDMS layer curing at 60 °C for 24 hours, the bi-layer soft mold can then be peeled off from the master template and it is treated with trichloromethylsilane (TMCS) [13].

In addition, Pei *et al*. presented a *h*-PDMS-based tri-layer composite mold and its fabrication process for nanostructured amorphous silicon photovoltaics [38]. Although the *h*-PDMS-based mold worked well for replication, there are still some limitations for its applications: (1) releasing it from the master caused cracking across the face of the mold; (2) external pressure is required to achieve conformal contact with a substrate, which created long-range, nonuniform distortions over the large areas of contact [39, 40].

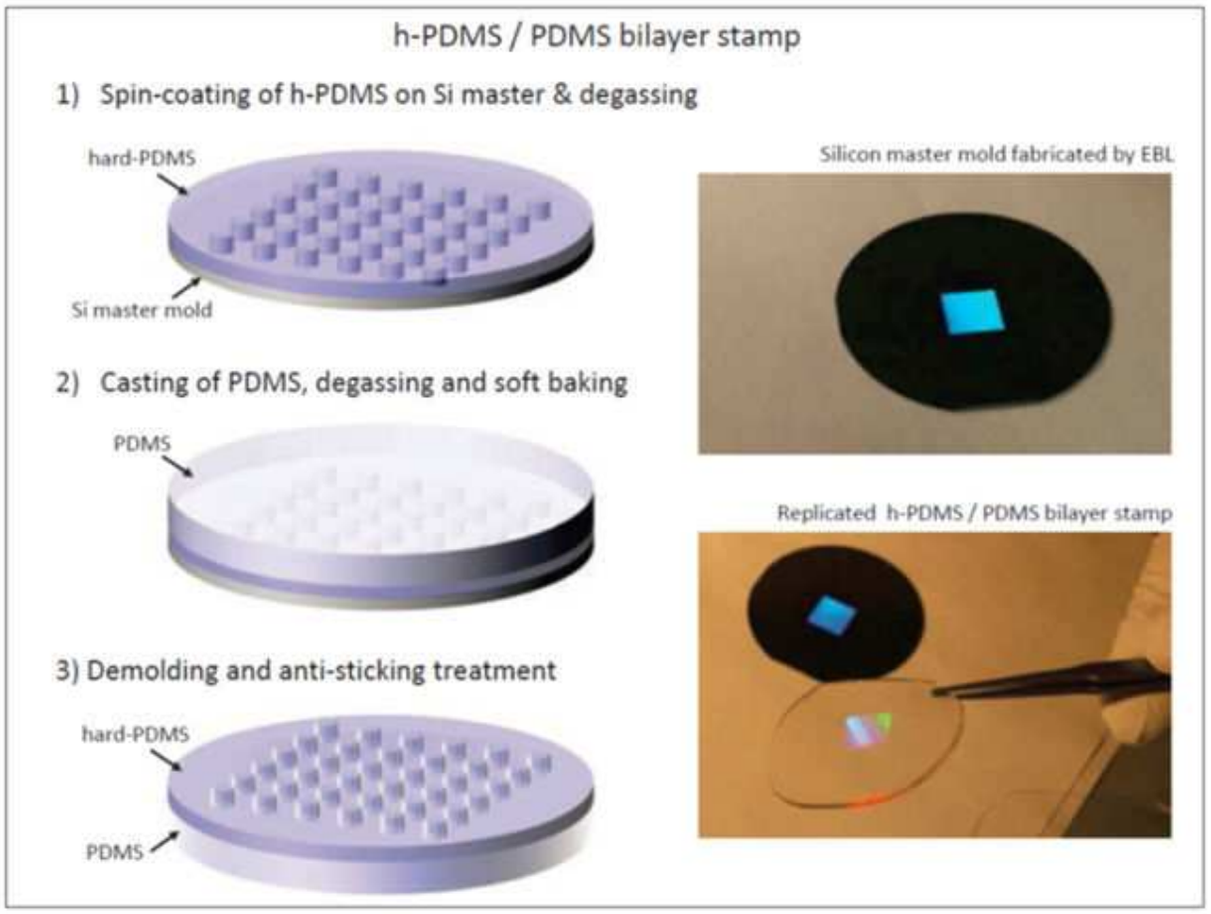

Figure 7. Schematic of the fabrication process of a *h*-PDMS/*s*-PDMS bilayer composite mold and a pictures of a Silicon master template and of a replicated soft mold after peeling off [13]

4.1.3. X-PDMS

Phlips and SUSS developed a new high modulus silicone rubber (*X*-PDMS) which is made from combination of vinyl-modified linear di-methyl-siloxanes and vinyl-modified quaternary siloxanes. The latter component increases the intrinsic crosslink density in the rubber and thereby the Young's modulus. The mixture is cross linked with hydride modified linear siloxanes using a platinum catalyzed vinyl-hydride addition reaction. By changing the linear to quaternary siloxane ratio, they synthesized rubbers with Young's Modulus up to 80 MPa. The rubber material with the highest attained stiffness allows the faithful replication of dense sub-10 nm features while still providing conformal contact over a full wafer [18, 29].

4.1.4. hv-PDMS

Conventional PDMS requires a long, thermal cure under pressure which is very time consuming and can take many hours. Photocurable PDMS (*hv*-PDMS) can overcome deformations associated with thermal curing of conventional PDMS. *hv*-PDMS also provides a tensile modulus higher than that of *s*-PDMS and an elongation at break that is much higher than that of *h*-PDMS, which makes it easier to handle than *h*-PDMS and to be less susceptible to mechanical deformation. Choi and Rogers developed a photocurable PDMS system [41]. *h*ν-PDMS has been used as a mold material to successfully replicate 300 nm width by 300 nm spacing by 600 nm height lines which could not be replicated in either *s*-PDMS(feature collapse failure) or *h*-PDMS (fracture failure).

4.1.5. Diluted PDMS

The main drawback of conventional *s*-PDMS materials is the high viscosity, which is for Sylgard 184 (Dow Corning) 3900 mPa.s. It is extremely difficult for high viscous s-PDMS to fill the nanocavities of the master template for fabricating high resolution soft molds. Thus, the resolution of the soft mold is limited by an inappropriate material flow for pattern geometries within the sub-100 nm regime. To overcome this problem, using triethylamine, toluene and hexane as solvent to low the viscosity of *h*-PDMS has been reported and demonstrated the imprinting of 75 nm lines with a pitch of 150 nm. koo *et al*. have reported an improved mold fabrication process using Sylgard 184 diluted with toluene. Dots with a resolution of 50 nm are well replicated and an excellent imprint homogeneity across a 4 inch wafer with one imprint step only has been demonstrated [42].

4.2. Fluorinated polymer materials

Fluorinated polymer offers an ideal material for soft molds. Compared to other materials used by soft molds, Fluorinated polymer materials have many outstanding advantages: extremely low surface energy, suitable Young's modulus (10Mpa~2GPa), high gas permeability, good mechanical strength, solvent resistance, chemical stability, visible transparency, and tunable modulus. These characteristics open up the possibility of fabricating high performance flexible molds for soft UV-NIL to pattern a wide variety of nanostructures and materials for real applications [43,44].

4.2.1. Perfluoropolyether (PFPE)

Recently perfluoropolyether (PFPE) and its derivatives have gained popularity as flexible mold materials. PFPE is the main component of fluoropolymer that is composed of only carbon, fluorine and oxygen [44]. The pre-polymer mixture is a liquid at room temperature, and can be cross-linked under UV exposure or thermal annealing. The PFPE-based materials contain several distinctive properties such as high chemical resistance, extremely low surface energy, high gas permeability, high solvent resistance, high elastic recovery and good mechanical strength. In particular, the modulus of the elastomer can be easily tuned by changing the molecular weight between crosslinks of the precursor allowing for higher fidelity molds, and are formed via UV curing in several minutes [45-49].

4.2.1.1. HPFPE

HPFPE is a copolymer resin of a perfluoropolyether (PFPE) and a hyperbranched polymer (HP). The HPFPE exhibited low viscosity, high Young's modulus, and lower surface energy, and enhanced stability. The low surface energy of the HPFPE resist resulting from the acrylic acid functional groups on the backbone of the fluorinated polyether precludes any adhesion of the polymer to the mold. By adjusting the weight percent of the multifunctional HP and diluter, 1, 6-hexanediol diacrylate (HDDA), it is possible to modify the viscosity of the obtained HPFPE copolymer resist and yield a HPFPE copolymer resist with a high Young's modulus. By optimizing the soft UV-NIL process with this flexible HPFPE mold, the imprinting results exhibited near zero residues at the bottom of the resist grooves, and no sticking over a large area, and patterning a 50 nm linewidth and a 200 nm period [50].

4.2.1.2. a-PFPE

Unlike certain PFPE formulations described earlier, which have a Young's modulus of around 4 MPa, the Young's modulus of acryloxy PFPE (denoted as *a*-PFPE) is 10.5 MPa. The low surface energy (~18.5 mN m^{-1}) as well as the chemical inertness of *a*-PFPE eliminates the necessity of treating the surfaces of the masters with fluorinated silanes to avoid sticking during casting and curing of the mold. Figure 8 illustrated the fabrication of a composite *a*-PFPE mold using backing layers of *s*-PDMS or polyethylene terephthalate (PET). The photocurable fluorinated acrylate oligomer CN 4000 is mixed with 0.5 wt % of a photoinitiator (Darocurr 4265, Ciba Specialty Chemicals) and filtered through a 0.22 μm syringe filter. A thin layer (~2 μm) of the *a*-PFPE resin is spin coated (4000 rpm, 30 s) on the master and cured in UV light (350–380 nm, 4 mW cm^{-2}) under nitrogen purge for 2 *h*. Then a layer (~4 mm) of Sylgard 184 PDMS (*s*-PDMS) is poured onto the *a*-PFPE layer and cured at room temperature for ~48 *h* or at 65°C for 2 *h*. The *a*-PFPE/*s*-PDMS composite mold is peeled off from the master [51]. The high resolution capabilities of *a*-PFPE, together with other properties such as resistance to swelling, chemical inertness, and photocurability make it a promising alternative to PDMS for soft UV-NIL.

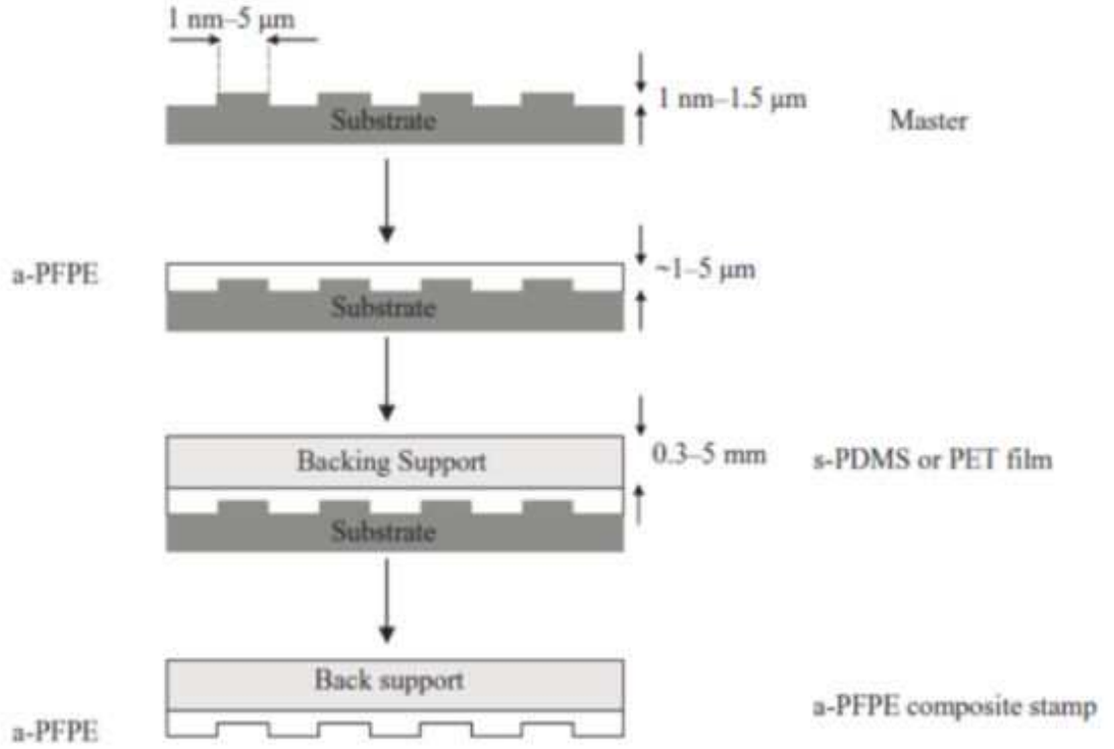

Figure 8. Fabrication of a composite a-PFPE mold with either s-PDMS or PET films as backing supports [51]

4.2.1.3. PFPE-DMA (Photochemically curable fluoropolymer)

The a-,w-methacryloxy functionalized PFPE (PFPE-DMA) is a photochemically curable fluoropolymer. A commercially available hydroxy-terminated PFPE (Solvay Solexis, *Mn*=3800 $gmol^{-1}$) with isocyanato ethyl methacrylate (Aldrich) is used to yield a methacryloxy-functionalized polymer which is a pourable liquid of low viscosity (0.36 Pas) at room temperature. A photoinitiator, 1-hydroxycyclohexyl phenyl ketone (1 wt%, Aldrich), is dissolved into the PFPE-DMA to make a photocurable liquid resin. The PFPE-DMA based mold involves the following features: easy fabrication, the ability to make conformal contact, remarkably low surface energy, resistance to swelling by small organic molecules, and enduring multiple printing procedures. It is able to replicate sub-100-nm sized features with no indications of limits to going to even smaller in size [52].

4.2.2. Ethylene(Tetrafluoroethylene) (ETFE)

The ETFE is a copolymer of ethylene and tetrafluoroethylene. It has some outstanding properties: an exceptional toughness and flexibility, a relatively high stiffness (elastic modulus ~ 1.2 GPa), a high thermal stability (a high melting point in the range of 255–280 °C). ETFE has superior mechanical properties compared to Teflon AF in pressure assisted imprinting at high temperatures. The flexibility and low surface energy of ETFE provide a clean mold release without fracture or deformation of the embossed structures. Patterning over large areas is

made possible because of the good conformal contact originating from the high flexibility and low-adhesion of the ETFE mold. ETFE-based molds also provide a high fidelity of reproduction. ETFE is transparent in the visible and in the UV spectrum (91–95% transmittance in the 200–800 nm range for a 25μm sheet), it can be used to structure a photocurable polymer and to solidify it by irradiation with UV light at room temperature, providing a cheap alternative to quartz or other transparent inorganic mold materials.

Combined with the advantage of their low adhesion and flexibility, ETFE molds can therefore be used to replace brittle and expensive inorganic materials, as well as deformable elastomers and other plastic molds which lack strength when pressure is applied. The strength and robustness of ETFE molds is essential for embossing large microstructures as well as small nanostructures with lateral dimensions approaching 10 nm. Some commercial ETFE products including Fluon ETFE, Tefzel® ETFE resin, have been directly utilized [53].

4.2.3. Teflon

Teflon AF 2400 form Dupont has been adopted as a typical rigiflex mold material. Teflon AF 2400 is a copolymer of 2,2-bistrifluoromethyl- 4,5-difluoro-1,3-dioxole and tetrafluoroethylene. The polymer has a tensile modulus of ca. 1.6 GPa (almost a thousand times harder than the elastomeric PDMS material), which is stiff enough for patterning small features without mold deformation. It can be used for UV-NIL in place of a quartz mold. This material has a low surface energy of ~16 mN m^{-1} which can be used as a mold material without any surface treatment. It is inert to all solvents except for perfluorinated solvents (3M, FC-77) such that there is no swelling problem. It is also inert to all chemicals. Therefore, the inert nature with a low surface energy makes it easy to demold after the imprinting process without any surface treatment and without deterioration in surface properties over many imprinting cycles. In addition, it is transparent to light in the region between deep UV and near infrared. It has high gas permeability. The property can eliminate the trapped air bubble during full wafer imprinting. Teflon® AF (amorphous fluoropolymer by Dupont) can have a life greater than 1000 impressions in a very clean environment. There are two ways of preparing the Teflon mold: solvent-casting method and compression molding [24, 54-56].

4.2.4. Others fluoropolymer materials

A typical concern for high modulus materials is their tendency to crack and break due to their brittle nature. Choi *et al*. fabricated a fluorinated organic-inorganic hybrid mold with high modulus of 115 MPa by using a nonhydrolytic *sol-gel* process which can produce a crack-free mold without leaving any trace of solvent. Various nanometer scale patterns including sub-100 nm patterns have been obtained using the fluorinated hybrid mold [56]. A new commercially fluorinated mold material has been developed by AGC Chemicals Co. The fluoropolymer material has good durability (>250 J/cm^2) against UV irradiation, good transparency at UV region (>95% at 375 nm wavelength), high tensile modulus (1.2GPa), CTE (70–80 ppm/K), and low surface energy. *Tg* of this fluororesin is about 110°C. The thickness of the fluororesin could be controlled from 60 nm to 15 μm by changing concentration and spin coat conditions. Furthermore, it has high chemical durability [57-58]. Haatainen *et al*. demonstrated the

fabrication of the F-template by combining the fluorinated mold material and thermal step and stamp nanoimprint lithography (SSIL) method, as well as presented imprinted results using the F-template. The patterns including gratings with 50 nm features and dot arrays of 350 nm diameter features have been achieved [59].

4.3. UV curable materials

4.3.1. Poly(Urethaneacrylate) (PUA)

The PUA based materials exhibit higher rigidity and better impact strength compared with PDMS without significant compromises in flexibility enabling micro-and nanopatterning when the PUA mold thickness is below 50 mm. It is almost impermeable to gases, inert to chemicals and solvents such that there is no swelling problem, and it is transparent to light in the UV and visible regions. However, the rigidity of PUA material is not enough high. It is necessary to further improve the Young's modulus of PUA for fulfilling higher resolution pattern replication. The mechanical properties of PUA based materials largely depend on their cross-linking density, UV-exposure time, UV light wavelength/intensity, as well as the PUA precursor composition. According to the optimizing results of mechanical properties (hardness and effective modulus) form Kim, the PUA replica mold demonstrated very high mechanical properties of hardness (0.15 GPa) and elastic modulus (2.7 GPa) due to the increased cross-linking density of the PUA precursor at an optimized UV-exposure time of 600 s. The PUA replica mold demonstrated potential for the fabrication of multi-scale line-and-space patterns with sizes of 350 nm or less with good uniformity and reproducibility over large areas [48, 60-61].

4.3.2. Modulus-tunable UV-curable materials

A UV-curable mold material which consists of a functionalized prepolymer with acrylate group for cross-linking, a monomeric modulator, a photoinitiator, and a radiation-curable releasing agent for surface activity, has been developed. The mechanical properties of the mold can be tailored by the chain length of an acrylate modulator in the cross-linking reaction. This tunability can be utilized to obtain a proper balance that is needed for a given patterning technique between the rigidity requirement (tensile modulus of 320 MPa) of a mold for patterning a fine structure and the flexibility requirement (tensile modulus of 19.8 MPa) for a conformal contact [62].

4.3.3. UV-curable inorganic–organic hybrid polymer — Ormostamp

Both the transparency and the thermal stability are principal material properties for flexible molds used in soft UV-NIL. A facing challenge in the UV-NIL process is the high transparency of the mold material in the UV-range, which is the characteristic wavelength range for the majority of photo initiators used in photoresist materials. The novel mold material system based on a – Ormostamp – offers high UV-transparency even after thermal exposure at 270 °C. In this case 90% transparency remains at 350 nm. The elasticity and hardness of the mold material are also critical factors for the transfer of nanostructures and dense patterns as well

as high-aspect-ratio features. Physical properties of Ormostamp are modulus of elasticity of 0.650 GPa, hardness of 0.036 GPa, liquid viscosity of 0.75 Pa s. The values of Ormocomp modulus of elasticity and hardness are sufficient for patterning both micro- and nanostructures without any cracks and fractures (too brittle material) or deformations (too soft material). In addition, the relatively low viscosity of Ormostamp is important for efficient filling of the master template cavities and allows various deposition techniques, which make the material handling and further processing easier [12, 63-65]. The Ormostamp working mold possesses high transparency and thermal and UV stability which are essential for soft UV-NIL. Up to now, only quartz stamps exhibited all these features. Excellent pattern transfer fidelity has demonstrated for 100 nm structures.

4.4. Summary and discussion

In order to meet various differently functional demands of the soft UV-NIL process, applied materials of soft molds should possess a number of desirable properties such as physical rigidity for high resolution, flexibility for intimate conformal contact, low surface energy for high quality demolding, high UV transparency for fast curing resist, low viscosity for easy and fast filling into the nano-cavities or features of a master at low pressure to achieve a high resolution mold, small curing-induced shrinkage for dimension accuracy and stability, and chemical inertness for mold durability, as well as thermal stability, easy material processing and high pattern transfer fidelity, etc. A proper balance between the mold rigidity required for patterning a very fine and dense structure and the flexibility needed for a conformal contact with the substrate is at the core of the successful applications. Table 1 summaries these mold materials.

Various fluorinated polymer materials with ultra-low surface energy and suitable rigidity have received enough attention to become ideal materials of flexible molds for soft UV-NIL. The crack and too friable issues for some materials (such as Teflon) with high Young's modulus should be overcome. A composite mold combining a rigid patterning layer using fluoropolymer-based materials and a flexible support layer shows better performance with higher resolution, easy demolding and intimate confocal contact capability as well as longer mold lifetime. Furthermore, the discovery of newly suitable materials (mold and resist) and control their properties will play a critical role for enhanced soft UV-NIL process.

5. Applications of soft UV-NIL

Soft UV-NIL has been employed to fabricate various micro/nanostructures and devices for nanoelectronics, optoelectronics, nanophotonics, optical components, glass, biological applications, etc. It has become a perfect match for some emerging application fields that are in great need of large area patterning of submicro and nano scale features at a low cost, such as patterned magnetic media, light emitting diodes, optical metamaterials and plasmonic devices for chemical and bio-sensing applications, etc. In particular, this technique has demonstrated great commercial prospects in several market segments, LEDs, laser diodes,

Item	Sub-class		Young's Modulus (MPa)	Surface Energy (mN/m)	Viscosity (mPa.s)	Curing mode
PDMS-based materials	*s*-PDMS		< 2	21-24	~3900	Thermal
	h-PDMS		8-12	~20	Tunable	Thermal
	X-PDMS		~80			Thermal
	hv-PDMS		~3-4	~20		UV-Light
Fluorinated polymer materials	PFPE-based materials	PFPE	4	12		UV-Light
		HPFPE	4-5.4	17-22	300-900	UV-Light
		a-PFPE	10.5	~18.5	60 cps at 25 °C	UV light
		PFPE-DMA	4	16.3	360	UV light
	ETFE		~1.2GPa	15.6		Thermal
	Teflon AF 2400		1.6 GPa	~16		Thermal
UV curable materials	PUA		2.7 GPa	23		UV light
	Modulus-tunable UV-curable materials		Tunable 19.8-320			UV light
	Ormostamp		650		750	UV-curable

Table 1. Summary of various soft mold materials

solar cells, optical elements, patterned media, flat panel displays, micro-lens, and functional polymer devices [7-12, 15-17].

5.1. LED patterning

Light efficiency enhancement and manufacturing cost reduction have always been regarding as the two most crucial issues in LED industry, particularly for the large-scale realization of solid state lighting. Compared to other technologies improving the LED performance, two emerging techniques, photonic crystals (PhC) and nanopatterned sapphire substrate (NPSS), have shown higher potential in output efficiency enhancement and beam shaping. NPSS and Photonic Crystal based LEDs have been considered as the most promising solutions for high brightness LEDs. The typical characteristics of LED epitaxial wafers and sapphire substrates are with large variation in wafer topography (varying TTD), high bow and warp, surface roughness with surface protrusions with micron size, and particle contaminations, etc. And these materials tend to be fragile or brittle. Due to the non-planar and rough nature of the LED epitaxial wafer and substrate, existing nanopatterning technologies cannot well meet the requirements of producing these nanostructures in both technology and cost level which mainly originated form the new challenging issues form LED patterning. Due to a very small depth of focus, optical lithography techniques have insufficiently fidelity for LED patterning. As warpage increases with larger wafer sizes, the ability of the photolithography tool to compensate for substrate warpage becomes even more critical. Interference lithography is

http://dx.doi.org/10.5772/56186

another method of generating periodic patterns over large areas at low cost. Although the patterns made by IL are highly uniform and have superior long-range order, these patterns are usually in very simple geometric forms of grating lines and 2-D dots, and their dimensions are difficult to reduce to sub-100 nm due to light diffraction. Furthermore, it is unsuitable for high volume production processes because the optical configuration has to be modified to realize different patterns. In addition, this approach requires a strict control of the environment to maintain stable fringe patterns. Soft UV-NIL with flexible mold has the capability of nanopatterning on non-flat surface over large areas and is less-sensitive to the production atmosphere. Compared to ICs industry, the LED application is much more relaxed than IC's for overlay and defect density. Therefore, soft UV-NIL has been considered as one of the most suitable solution for LED patterning. Due to its cost-effectiveness combined with superior processing performance, soft UV-NIL will play a crucial role in moving the LED industry into a new realm of nanopattered LEDs with ultra-high efficiency [2, 14, 17, 65]. Figure 9 showed some cases related to LED patterning using soft UV-NIL. In addition, some commercial companies such as SUUS, Obducat, EVG, Toshiba, Aurotek, Luminus, etc. have been developing the process and equipment of soft UV-NIL for high volume producing PhC LEDs and NPSS.

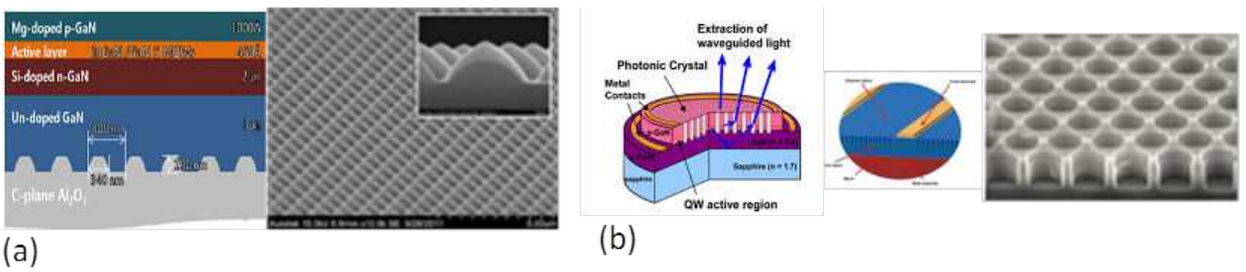

Figure 9. LED patterning using soft UV-NIL [2, 14, 66, 67] (a): NPSS-based LEDs; (b): PhC LEDs)

5.2. Nanophotonic devices

Nanophotonics is a rapidly growing field with great commercial potential. It is a wide field covering many interesting applications branching from cutting edge science including plasmonics, metamaterials, cavity quantum electrodynamics in high-Q cavities all the way to applied sciences like silicon nanophotonics for on chip optical interconnections and single frequency semiconductor light sources. Most of the practical device demonstrations in these fields utilize nanopatterned surfaces. Applications require patterning of nanoscopic gratings, photonic crystals, waveguides and metal structures. Viheriälä *et al*. demonstrated soft UV-NIL nanophotonics applications including distributed feedback laser diodes, plasmonic nanostructures, and patterned facets of optical fibres. Soft UV-NIL will play a critical important role in the commercialization of many nanophotonic applications since it offers excellent cost effectiveness and requires relatively low capital investment. High-density plasmonic nanostructures have been realized on a large area (1 mm^2) using the soft UV-NIL technique. The obtained dimensions of the nanodisks are 65 nm in diameter, 180 nm in periodicity and 25 nm

in height with the soft *h*-PDMS/*s*-PDMS mold. Cattoni *et al.*, have successfully realized a Localized Surface Plasmon Resonance (LSPR) biosensor based on $\lambda^3/1000$ plasmonic nanocavities fabricated by Soft UV-NIL on large surfaces (0.5-1 cm^2). These structures present nearly perfect omnidirectional absorption in the infra-red regime independently of the incident angle and light polarization and outstanding biochemical sensing performances with high refractive index sensitivity and figure of merit 10 times higher than conventional LSPR based biosensor [12, 13, 18, 68-71]. Figure 10 presented some nanophotonic devices made using soft UV-NIL.

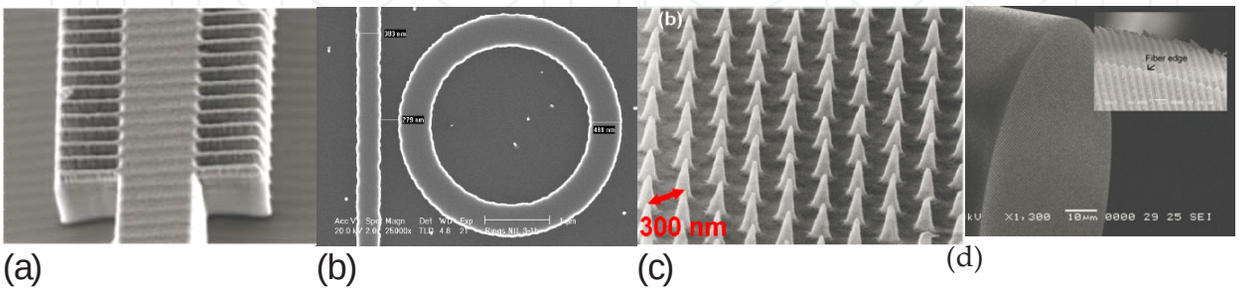

Figure 10. Nanophotonic devices made using soft UV-NIL [12, 13, 72] (a: DFB-laser diodes; b: Silicon microring resonators; c: Metal nanostructures; d: Optical fibre with the imprinted blazed grating)

5.3. QDs-based devices

Quantum dot (QD) arrays have now been attracting tremendous attention due to the potential applications in various high performance devices (e.g., QD lasers, 3rd generation solar cells, single photon emitters, QD memories, etc.), the fundamental investigation of quantum computing and quantum communication, and in the exploration or observation of novel physical phenomena. Currently, the major challenging issues in commercialized application of QD arrays include fabrication of large-area, defect-free, highly uniform and ordering QDs, accurate positioning for individual QD nucleation site, and reproducibility in size and spatial distribution, which all crucially determines optoelectronic performance and consistency for these QDs-based functional devices and the investigation of fundamental physical properties for QDs. In order to accurately control the size, position, density and composition of epitaxially grown self-assembled quantum dots, a variety of strategies including buried stressor dislocation networks, multiple-layer heteroepitaxy structures to control the stress distribution, quantum dots growth on patterned substrates using various nanofabrication techniques have been proposed in the past decade. Among these, the QDs growth on patterned substrates has been considered as the most straightforward approach to control the size, density and position of QDs so as to achieve highly uniform and ordering QD arrays. Furthermore, growing QD arrays on the patterned substrates has the ability to control the absolute lateral position of quantum dots on a long-range scale. Compared to other nanopatterning approaches, soft UV-NIL technique has high potential to create large-area, low defects patterned substrates with low cost and high throughput. Tommila *et al.* reported on the development of UV-NIL process for patterning GaAs substrates, which are used as templates in seeded S–K growth of QDs.

http://dx.doi.org/10.5772/56186

Soft UV-NIL has also been used to pattern GaAs (1 0 0) substrate into periodic nucleation sites for the growth of InAs site-controlled quantum dots. The incorporation of soft UV-NIL and MOCVD may be a promising method of forming large-area, site-controlled, highly uniform and ordered arrays of quantum dots with low-cost and high throughput to satisfy the requirements of mass production for QDs and QD arrays [73-76].

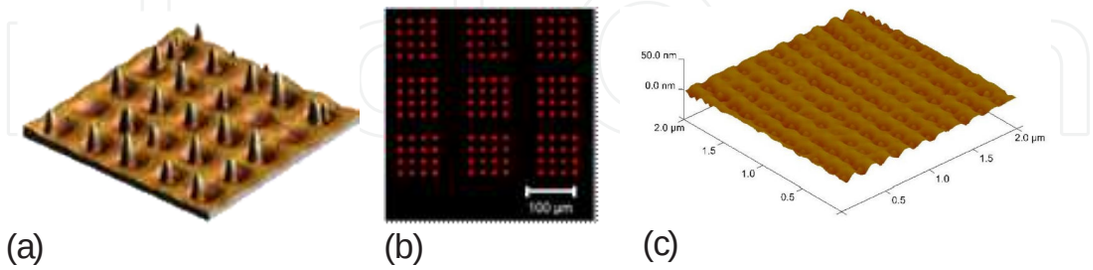

Figure 11. QDs-based devices fabricated using soft UV-NIL [73-76] (a: Site-controlled InAs QDs on UV-NIL patterned surface; b: Nanoimprinted QD arrays for sensing and detecting biomolecules; c: Quantum dot optoelectronics fabrication using soft UV-NIL)

6. Conclusions

Soft UV-NIL by using a flexible mold has been proven to be a cost-effective high volume nanopatterning method for large-area structure replication up to wafer-level (300mm) in the micrometer and nanometer scale, fabricating complex 3-D micro/nano structures, especially making large-area patterns on the non-planar surfaces even curved substrates at low-cost and with high throughput. In particular, it provides an ideal solution and a powerful tool for mass producing micro/nanostructures over large areas at low cost for the applications in compound semiconductor optoelectronics and nanophotonic devices, especially for LED patterning. That opens the way for many applications not previously conceptualized or economically feasible.

Soft UV-NIL has been regarded as the closest process for the industrial application of NIL. In particular, the applications in LED patterning and wafer level micro optics have demonstrated significantly commercial prospect. Soft UV-NIL and its variations (e.g., Roll-type nanoimprint using soft molds) will become more and more important for these applications in large area patterning, fabricating 3-D micor/nanostructures and forming patterns on the non-planar or curved surface. There is a plenty of room to enhance the resolution, patterning area, mold lifetime, yield for the promising patterning method.

Acknowledgements

This work was financially supported by National Science Foundation of China - Major Research Plan “Fundamental Study on Nanomanufacturing” (Grant No. 91023023) and Program for New Century Excellent Talents in University (Grant No.NCET-11-1029).

Author details

Hongbo Lan[1,2*]

Address all correspondence to: hblan99@gmail.com

1 Nanomanufacturing and Nano-Optoelectronics Lab, Qingdao Technological University, Qingdao, China

2 Qingdao Bona Optoelectronics Equipment Co., Ltd., Qingdao National High-Tech Industrial Development Zone, China

References

[1] Verschuuren, M A, & Sprang, H A. Large-area Nanopatterns: Improving LEDs, Lasers, and Photovoltaics. SPIE. http://spie.org/x87355.xml.(2012).

[2] Lee, Y C, & Tu, S H. Improving the Light-emitting Efficiency of GaN LEDs Using Nanoimprint lithography. In: Cui B. (ed.) Recent Advances in Nanofabrication Techniques and Applications. Rijeka: InTech; (2011). , 173-195.

[3] Baek, J H, Kim, S M, & Lee, I H. Control of Characteristic Performance by Patterned Structure in Light-emitting Diodes. Proc. of SPIE (2011). B.

[4] Yang, Y, Mielczarek, K, & Aryal, M. Nanoimprinted Polymer Solar Cell. ACS NANO (2012). , 6(4), 2877-2892.

[5] Farshchian, B, Amirsadeghi, A, & Hurst, S M. Soft UV-nanoimprint Lithography on Non-planar Surfaces. Microelectronic Engineering (2011). , 88-3287.

[6] Chou, Y, Krauss, P, & Renstrom, P. Imprint Lithography with 25-nanometer Resolution. Science (1996). , 272(5258), 85-87.

[7] Schift, H. Nanoimprint lithography: An Old Story in Modern Times? A Review, J. Vac. Sci. Technol. B. (2008). , 26(2), 458-480.

[8] Lan, H, Ding, Y, & Liu, H. Nanoimprint Lithography Principles, Processes and Materials. Nova Science Pub Inc.; (2011).

[9] Guo, J. Recent Progress in Nanoimprint Technology and its Applications. Journal of Physics D: Applied Physics (2004). RR141., 123.

[10] Guo, J. Nanoimprint Lithography: Methods and Material Requirements. Advanced Materials (2007). , 19(4), 495-513.

[11] Bender, M, Fuchs, A, & Plachetka, U. Status and Prospects of UV-Nanoimprint Technology. Microelectronic Engineering (2006). , 83-827.

[12] Viheriälä, J, Niemi, T, & Kontio, J. Nanoimprint Lithography- Next Generation Nanopatterning Methods for Nanophotonics Fabrication. In: Kim K. (ed.) Recent Optical and Photonic Technologies (2010). , 275-298.

[13] Cattoni, A, Chen, J, & Decanini, D. Soft UV Nanoimprint Lithography: A Versatile Tool for Nanostructuration at the 20nm Scale. In: Cui B. (ed.) Recent Advances in Nanofabrication Techniques and Applications Rijeka: InTech; (2011). , 139-156.

[14] Ji, R, Hornung, M, & Verschuuren, M. UV Enhanced Substrate Conformal Imprint Lithography (UV-SCIL) Technique for Photonic Crystals Patterning in LED Manufacturing. Microelectronic Engineering (2010).

[15] Glinsner, T, Plachetka, U, & Matthias, T. Soft UV-based Nanoimprint Lithography for Large Area Imprinting Applications. Proc. of SPIE (2007).

[16] Hiroshima, H. Nanoimprint with Thin and Uniform Residual Layer for Various Pattern Densities, Microelectronic Engineering (2008).

[17] Lan, H, & Ding, Y. Nanoimprint lithography. In: Wang M. (ed.) Lithography Rijeka: InTech; (2010). , 457-494.

[18] Verschuuren, M. A. Substrate Conformal Imprint Lithography for Nanophotonics. PhD thesis. Utrecht University; (2011).

[19] Hornung, M, Ji, R, & Verschuuren, M. Inch Full Field Wafer Size Nanoimprint Lithography for Photonic Crystals Patterning. (2010). th IEEE Conference on Nanotechnology. , 2010, 339-342.

[20] Schmitt, H, Duempelmann, P, & Fader, R. el at. Life Time Evaluation of PDMS Stamps for UV-enhanced Substrate Conformal Imprint Lithography. Microelectronic Engineering. (2012). S., 275-278.

[21] SUSShttp://www.suss.com/index.php,(2012).

[22] Lan, H. A full wafer-scale UV Nanoimprint Lithography Process and Tool for Patterning Photonic Crystal for HB-LEDs. BIT's 1st Annual world congress of Nano-S&T-2011. Oct. Dalian; (2011).

[23] Hiroshima, H. Release Force Reduction in UV Nanoimprint by Mold Orientation Control and by Gas Environment. J. Vac. Sci. Technol. B. (2009). , 27(6), 2862-2865.

[24] Rogers, J A, & Lee, H H. Unconventional Nanopatterning Techniques and Applications. John Wiley & Sons, Inc.; (2008).

[25] Plachetka, U, Bender, M, & Fuchs, A. Comparison of Multilayer Stamp Concepts in UV-NIL. Microelectronic Engineering (2006). , 83-944.

[26] Bender, M, Plachetka, U, & Ran, J. High Resolution Lithography with PDMS Molds. J. Vac. Sci. Technol. B. (2004). , 22(6), 3229-3232.

[27] . Bilayer Transparent Molds for High Resolution Soft UV Nanoimprint Lithography. http://jnte08.trans-gdr.lpn.cnrs.fr/FILES/p12.pdf.

[28] Barbillon, G. Plasmonic Nanostructures Prepared by Soft UV Nanoimprint Lithography and Their Application in Biological Sensing. Micromachines (2012). , 3-21.

[29] Verschuuren, M A, & Brakel, R. van de Laar H W J J., *et al*. VCSEL, LED, Thin-film PV production by Substrate Conformal Imprint Lithography. International Conference on Micro and Nano Engineering Berlin; (2011).

[30] Roy, E, Kanamori, Y, & Belotti, M. Enhanced UV Imprint Ability with a Tri-layer Stamp Configuration. Microelectronic Engineering (2005).

[31] Williams, S S, Retterer, S, & Lopez, R. High-resolution PFPE-based Molding Techniques for Nanofabrication of High-pattern Density, Sub-20 nm Features: a Fundamental Materials Approach. Nano Lett. (2010). , 10-1421.

[32] Gilles, S, Meier, M, & Prömpers, M. UV Nanoimprint Lithography with Rigid Polymer Molds. Microelectronic Engineering (2009). , 86-661.

[33] Choi, D G, Jeong, J H, & Sim, Y. Fluorinated Organic-inorganic Hybrid Mold as a New Stamp for Nanoimprint and Soft Lithography. Langmuir (2005). , 21-9390.

[34] Choi, W M, & Park, O O. Soft-imprint Technique for Submicron-scale Patterns Using a PDMS Mold. Microelectronic Engineering (2004).

[35] Koo, N, Plachetka, U, & Otto, M. The Fabrication of a Flexible Mold for High Resolution Soft Ultraviolet Nanoimprint Lithography. Nanotechnology (2008).

[36] Schmid, H, & Michel, B. Siloxane Polymers for High-resolution, High-accuracy Soft Lithography. Macromolecules (2000). , 33-3042.

[37] Hua, F, Sun, Y, & Gaur, A. Polymer Imprint Lithography with Molecular-scale Resolution. Nano Letters (2004). , 4(12), 2467-2471.

[38] Pei, L, Balls, A, & Tippets, C. Polymer Molded Templates for Nanostructured Amorphous Silicon Photovoltaics. J. Vac. Sci. Technol. A. (2011).

[39] Li, Z, Gu, Y, & Wang, L. Hybrid Nanoimprint-soft Lithography With Sub-15 nm Resolution. Nano Lett. (2009). , 9(6), 2306-2310.

[40] Odom, T W. Christopher Love J., Wolfe D.B., *et al*. Improved Pattern Transfer in Soft Lithography Using Composite Stamps. Langmuir (2002). , 18-5314.

[41] Choi, K M, & Rogers, J A. A Photocurable Poly(dimethylsiloxane) Chemistry Designed for Soft Lithographic Molding and Printing in the Nanometer regime. J. AM. CHEM. SOC. (2003). , 125-4060.

[42] Koo, N, Bender, M, & Plachetka, U. Improved Mold Fabrication for the Definition of High Quality Nanopatterns by Soft UV-Nanoimprint Lithography Using Diluted PDMS Material. Microelectronic Engineering (2007). , 84-904.

[43] Boday, D. J. The State of Fluoropolymers. In Smith D (ed.) Advances in Fluorine-Containing Polymers. ACS; (2012). , 1-7.

[44] Con, C, Zhang, J, & Jahed, Z. Thermal Nanoimprint Lithography Using Fluoropolymer Mold. Microelectronic Engineering. (2012). In press.

[45] Williams, S, Retterer, S, & Lopez, R. High-resolution PFPE-based Molding Techniques for Nanofabrication of High-pattern Density, Sub-20 nm Features: a Fundamental Materials Approach. Nano Lett. (2010). , 10-1421.

[46] Gilles, S, Diez, M, & Offenhausser, A. Deformation of Nanostructures on Polymer Molds During Soft UV Nanoimprint Lithography. Nanotechnology (2010).

[47] Mühlberger, M, Bergmair, I, & Klukowska, A. UV-NIL with Working Stamps Made From Ormostamp. Microelectronic Engineering (2009).

[48] Kim, J K, Cho, H S, & Jung, H S. Effect of Surface Tension and Coefficient of Thermal Expansion in 30 nm Scale Nanoimprinting with Two Flexible Polymer Molds. Nanotechnology (2012).

[49] Jayakumar, P, Ho, Y T, & Soo, H. Adhesion Force Measurement Between the Stamp and the Resin in Ultraviolet Nanoimprint Lithography-an Investigative Approach. Nanotechnology (2009).

[50] Zhu, Z, Li, Q, & Zhang, L. UV-based Nanoimprinting Lithography with a Fluorinated Flexible Stamp. J. Vac. Sci. Technol. B. (2011).

[51] Truong, T T, Lin, R, & Jeon, S. Soft Lithography Using Acryloxy Perfluoropolyether Composite Stamps. Langmuir (2007). , 23(5), 2898-2905.

[52] Rolland, J P, Hagberg, E C, & Denison, G M. High-resolution Soft Lithography: Enabling Materials for Nanotechnologies. Angew. Chem. Int. Ed. (2004).

[53] Barbero, D R, Saifullah, M, & Hoffmann, M. P., *et al*. High-resolution Nanoimprinting with a Robust and Reusable Polymer Mold. Advanced Functional Materials (2007). , 17(14), 2419-2425.

[54] Kim, M J, Park, J E, & Song, S. Simple "Solutal" Method for Preparing Teflon Nanostructures and Molds. J. Vac. Sci. Technol. B. (2007). , 25-1412.

[55] Khang, D Y, & Lee, H H. Sub-100 nm Patterning with an Amorphous Fluoropolymer Mold. Langmuir (2004). , 20-2445.

[56] Khang, D Y, Kang, H, & Kim, T. Low Pressure Nanoimprint Lithography. Nano Lett. (2004). , 4-633.

[57] Choi, D G, Jeong, J J, & Sim, Y S. Fluorinated Organic-inorganic Hybrid Mold as a New Stamp for Nanoimprint and Soft Lithography. Langmuir (2005). , 21-9390.

[58] Kawaguchi, Y, Nonaka, F, & Sanada, Y. Fluorinated Materials for UV Nanoimprint Lithography. Microelectronic Engineering (2007). , 84-973.

[59] Haatainen, T, Mäkelä, T, & Ahopelto, J. Imprinted Polymer Stamps for UV-NIL. Microelectronic Engineering (2009). , 86-2293.

[60] Kim, J Y, Park, H S, & Kim, Z S. Fabrication of Low-cost Submicron Patterned Polymeric Replica Mold With High Elastic Modulus Over a Large Area. Soft Matter. (2012). , 8-1184.

[61] Suh, D, Choi, S J, & Lee, H H. Rigiflex Lithography for Nanostructure Transfer. Advanced Materials (2005). , 17(12), 1554-1560.

[62] Yoo, P J, Choi, S J, & Kim, J H. Unconventional Patterning with a Modulus-tunable Mold: From Imprinting to Microcontact Printing. Chem. Mater. (2004). , 16-5000.

[63] Klukowska, A, Kolander, A, & Bergmair, I. Novel Transparent Hybrid Polymer Working Stamp for UV-imprinting. Microelectronic Engineering (2009). , 86-697.

[64] Mühlberger, M, Bergmair, I, & Klukowska, A. UV-NIL with Working Stamps Made From Ormostamp. Microelectronic Engineering (2009).

[65] Byeon, K J, Hong, E, & Park, H. Full Wafer Scale Nanoimprint Lithography for GaN-based Light-emitting Diodes. Thin Solid Films (2011). , 519-2241.

[66] Hung, R. Luminus Devices, Inc. (2012).

[67] Uhrmann, T. Patterned Sapphire Substrates (PSS): Making LEDs Brighter and Cheaper. (2012).

[68] Jukka, V, Milla-riina, V, & Juha, H. Soft Stamp Ultraviolet-nanoimprint Lithography for Fabrication of Laser Diodes. Proceedings of the SPIE (2009). O.

[69] Shi, J, Chen, J, Decanini, D, et al. Fabrication of Metallic Nanocavities by Soft UV Nanoimprint Lithography. Microelectronic Engineering (2009).

[70] Barbillon, G. Soft UV Nanoimprint Lithography: A Tool to Design Plasmonic Nanobiosensors. In : Kostovski E (ed.) Advances in Unconventional Lithography. Rijeka: InTech; (2011). , 3-14.

[71] Weng, Y J, Weng, Y. C, & Yang, S Y. Fabrication of Optical Waveguide Devices Using Gas-assisted UV micro/nanoimprinting with Soft Mold. Polymers for Advanced Technologies (2007). , 18(11), 876-882.

[72] Spillane, S, Xu, Q, & Fattal, D. Fabrication of Nanophotonic Structures for Information Processing. Proc. of SPIE (2008).

[73] Lan, H, & Ding, Y. Ordering, Positioning and Uniformity of Quantum Dot Arrays. Nano today (2012). , 7(2), 94-123.

[74] Meneou, K. Pathways for Quantum Dot Optoelectronics Fabrication Using Soft Nanoimprint Lithography. Dissertation, University of Illinois at Urbana-Champaign; (2010).

[75] Oh, Y, Lee, K, & Ko, S. Quantum Dot Arrays Patterned by Direct Nanoimprint. The 10th International Conference on NNT, Shilla Jeju, Korea, (2011).

[76] Tommila, J, Tukiainen, A, & Viheriälä, J. Nanoimprint Lithography Patterned GaAs Templates for Site-controlled InAs Quantum Dots. Journal of Crystal Growth (2011). , 232(1), 183-186.

IntechOpen

IntechOpen