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Soft UV Nanoimprint Lithography: A Versatile Tool for Nanostructuration at the 20nm Scale

Andrea Cattoni[1], Jing Chen[1], Dominique Decanini[1], Jian Shi [2] and Anne-Marie Haghiri-Gosnet[1]
[1]*Laboratoire de Photonique et de Nanostructures, LPN (CNRS-UPR20), Marcoussis*
[2]*Ecole Normale Supérieure de Paris, Paris*
France

1. Introduction

1.1 Why soft UV nanoimprint lithography?

Since the pioneering work of Whitesides and coworkers on microContact Printing (mCP) and Soft Lithography (Kumar & Whitesides (1993)) (Xia & Whitsides (1998)), considerable progress has been made in the last years and Soft Lithography is now a well consolidated technology utilized in academic and industrial laboratories (Rogers & Nuzzo (2005)). These printing methods use a flexible elastomer material named PDMS (poly(dimethylsiloxane)) to transfer molecules on a surface thus creating localized chemical patterns (Cerf & Vieu (2010)). The PDMS stamp inked with the desired molecules is placed in contact with the substrate to perform the molecular transfer. mCP has received large attention for biological applications since this soft transfer occurs in a gentle manner which allows the biomolecules to be transferred without any damage. In addition, this powerful technique is cheap because the soft PDMS stamp can be replicated an indefinite number of times by simply pouring the PDMS prepolymer onto a single expensive silicon master mold that contains micro or nanostructures. Since the flexibility of the elastomeric stamp ensures a perfect conformal adhesion within the substrate, thus allowing replication on large areas up to several tens of cm^2, the use of such flexible PDMS stamps was also efficiently applied to another low-cost and high-throughput manufacturing technique called Soft UV Nanoimprinting Lithography (Soft UV-NIL). This technique creates a thickness contrast by embossing thin polymeric films, highlighting the advantages of using a flexible PDMS stamp.

Historically, Nanomprint Lithography (NIL) in its original version was proposed by Stephen Chou in 1995 (Chou et al. (1995)) as an alternative technique for the embossing of high resolution patterns in thermoplastic materials. The patterning of features as small as 10 nm has been demonstrated from the beginning (Chou (1997)). This nanoimprint process, usually referred to as thermal-assisted NIL (T-NIL), is based on the use of a hard mold, namely a silicon wafer. As schematically shown in Figure 1, this hard mold containing nanoscale surface-relief features is pressed at high pressure (50-100 bar) onto a thin polymeric resist film. The resist is held some 90-100 °C above its glass-transition temperature (T_g) for few minutes to allow the flowing of the polymer in the mold nanocavities. The thin residual layer of polymer intentionally left to prevent the direct contact between the substrate and the rigid mold is

then removed by reactive ion etching (RIE) to complete the resist pattern transfer. T-NIL uses a very simple experimental set-up, which results in a very short process time, from seconds to minutes.

In contrast to conventional lithography methods based on exposure and development of a resist, nanoimprint lithography is based on mechanically embossing a thin polymer film under a mold that contains micro or nanopatterns. For this reason, limitations imposed by light diffraction or beam scattering in conventional lithography techniques can be overcome. As a second advantage, NIL provides parallel processing with high throughput, which is suitable for large-scale patterning with very high resolution. Another important benefit is the low cost of the NIL equipment, which compared with the processing cost of classical lithography techniques like deep UV optical lithography or Electron Beam Lithography (EBL). Nanoimprinting lithography has rapidly received a lot of attention from both the research community and industry, so much so that MIT's 2003 Technology Review named nanoimprint lithography as one of the "ten emerging technologies that will change the world." Additionally, NIL has been added into the International Technology Roadmap for Semiconductors (ITRS) for the next 22 nm node.

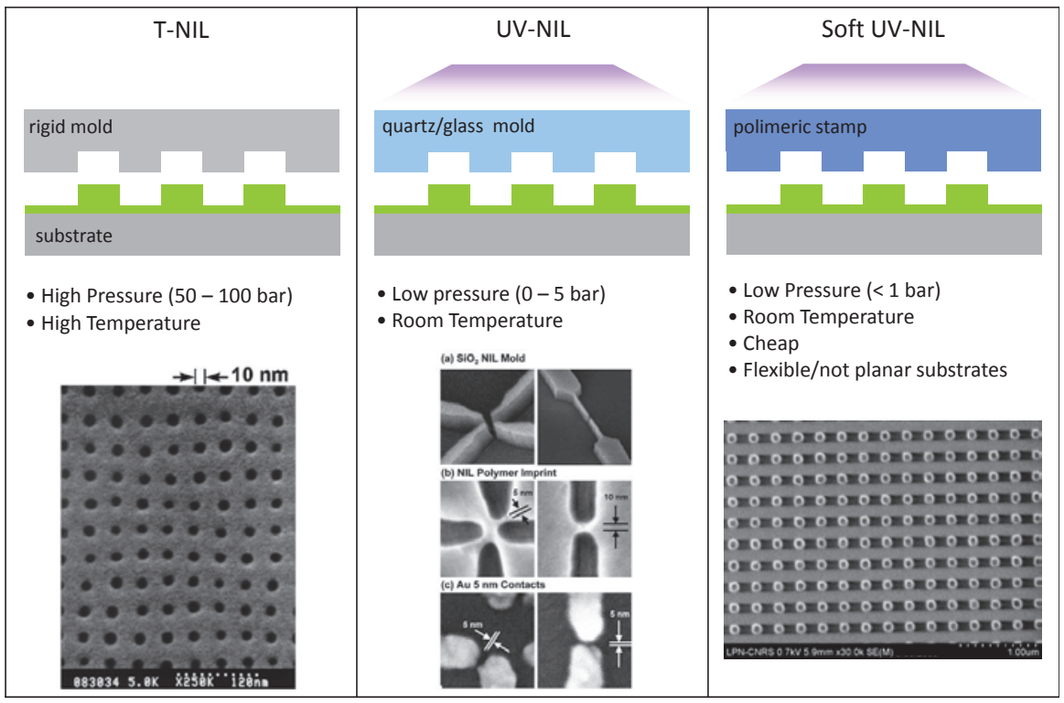

Fig. 1. Left panel: schematic of the T-NIL process proposed by S.Y. Chou in 1995 with a SEM image of 60 nm deep holes imprinted into PMMA which have a 10 nm minimum diameter and a period of 40 nm. Reprinted with permission from (Chou (1997)). Copyright 1997 American Vacuum Society. Central panel: schematic of the UV-NIL process and relative SEM image of the imprinted resist after UV curing with feature sizes as small as 5 nm. Reprinted with permission from (Austin et al. (2004)). Copyright 2004 American Vacuum Society. Right panel: SEM image of imprinted Amonil resist (AMO GmbH Aachen, Germany) of 100 nm square dots with 300 nm pitch after Soft UV NIL with PDMS stamp replicated by a Silicon master mold.

Although there are no apparent resolution limitations for T-NIL due to its purely mechanical embossing nature, this technology is unable to meet the stringent requirements of semiconductor IC manufacturing. In particular, the high pressure and temperature required during the process limit its use to few applications. UV-NIL (Haisma et al. (1996); Ruchhoeft et al. (1999)), which appeared quickly after T-NIL, is considered to be the most attractive variant for semiconductor IC manufacturing (Figure 1). With this variant, a transparent quartz mold is pressed at room temperature with a lower pressure on a liquid precursor that can be cured by UV light before the release of the mold. Industry quickly adopted UV-NIL, particularly Step and Flash Imprint Lithography (SFIL) which replicates nanostructures on a large area by patterning several fields (Bailey et al. (2002)). This industrial approach consists of dispensing a drop of the low viscosity photopolymerizable liquid resist on each field surface prior to the imprinting process. This allows for the patterning on the whole wafer area, much like a stepper lithography tool does.

As an alternative to UV-NIL, Soft UV-NIL has recently been proposed as a means to reduce the cost of master fabrication. Soft UV-NIL uses a flexible transparent stamp normally made of poly(dimethylsiloxane) (PDMS) or other flexible polymers that can be easily replicated from a single Silicon master mold. This Silicon master mold is fabricated with conventional lithography techniques, like EBL, which are more time consuming and expensive. The flexibility of the Polymeric stamp ensures contact with the surface substrate on large surfaces at low pressures, even on curved or flexible substrates. In particular, PDMS exhibits attractive properties like low interfacial free energy ($\sim$21.6 dyn/cm), chemical stability and high optical transparency. Moreover, its permeability prevents problems caused by trapped air bubbles in the resist layer when imprinting at ambient pressure. Soft UV-NIL is considered today to be the most promising variant to replicate patterns in the sub-50 nm range for mass production at low cost. Soft UV-NIL is currently being applied in a large spectrum of emerging area like Flexible Electronics, Photonics, Biotechnology and Nanomedicine.

In this paper we will discuss the ability to use PDMS based stamps, as candidates for nanoimprinting lithography in the sub-20nm scale on large surfaces and at very low pressure (< 1 atm). In terms of resolution, the replication of features with sizes as small as 2 nm has been demonstrated by using a unique carbon nanotube as a template and a modified PDMS material for the stamp (Hua et al. (2004)). These recent experiments demonstrate that PDMS properties, and specifically the density of cross-links, are important parameters that can influence the ultimate resolution. In this context, testing the resolution limits for soft UV-NIL with flexible stamps and for real applications appears very challenging.

In the frame of the European Project TERAMAGSTOR (EU funded FP7 STREP project) for the production of the next generation of perpendicular magnetic storage media with an areal density greater than 1 Tbit/inch^2, our group has been working on the feasibility to apply Soft UV-NIL for the nanofabrication of bit pattern media at ultra high resolution in the sub-10 nm scale. Our optimized approach for the fabrication of the silicon master mold using classical electron beam lithography will be presented with different fabrication techniques and resists. Due to the high cost of the master mold fabrication by EBL, we will propose new routes for the replication and/or inversion of the master mold at the whole wafer scale based on T-NIL. Once the hard mold with highly resolved patterns is obtained, the second challenge concerns the replication of the PDMS stamp. It should exhibit enough local hardness for the replication of nanometric features, and at the same time, preserve a global flexibility to ensure conformal contact at low imprinting pressures. The description of our bilayer hard-PDMS/PDMS stamp will be detailed and we will demonstrate the replication of 20 nm features under specific

experimental conditions. To conclude with real application, we will present the fabrication by Soft UV NIL of plasmonic nanostructures for biosensing applications with superior optical performances directly related to their high quality and uniformity on the whole pattern area.

2. Master mold fabrication

The whole replication process of the nanostructures by Soft UV NIL is composed of three separate steps: the fabrication of the master mold, the replication by this master of the polymeric stamp and the imprinting in the UV curable resist by using this replicated polymeric stamp. Together, these steps affect the quality of the final replication in terms of resolution and line edge roughness of the nanostructures.

The first challenge is obtaining an accurate fabrication of the master mold; particular care has to be placed in order to achieve high resolution with low roughness features. Compared to other lithography techniques, the quality of the master mold is very important since the PDMS stamp will replicate any eventual imperfections with precision. These constraints can be relaxed, for instance, in the fabrication of the UV photomask for projection optical lithography, in which a demagnified image can be projected onto the photoresist (4:1). This allows for the patterning of smaller features as well as the reduction of mask damages and imperfections (Cui (2008)). For this reason, the fabrication process of such a master mold is more often based on electron beam lithography (EBL), which provides flexibility and high resolution.

The resolution limit of EBL is determined by proximity effects inside the resist, which are due to the scattering of electrons within the substrate. Working with a high energy electron beam (above 50 KeV) and with a thin resist layer reduces these proximity effects. We will compare standard processes based on a PMMA resist with direct etching, a lift-off process and a process based on a Hydrogen-silsesquioxane (HSQ) resist. Once the template is fabricated, it can be used many times, either as a mold for direct nanoimprint in T-NIL or UV-NIL, or as a master mold for the replication of polymeric stamps. In practice, both silicon and quartz templates can be damaged during these processes and it is thus highly desirable to develop a low cost solution for large area replications. Conventional methods such as EBL are time consuming and unsuitable for mass production. Other high throughput lithography techniques developed for the semiconductor industry, like immersion optical lithography and extreme UV lithography, include complicated processes and expensive equipment. To overcome this issue, we will describe a master mold replication process based on the combination of T-NIL and reactive ion etching.

2.1 EBL processes for high resolution patterns

Among the high resolution resists available for EBL, PMMA (polymethyl methacrylate) was one of the first polymeric materials to be studied for this purpose. The most prominent features of the PMMA resist are its high resolution, its wide process latitude, and its high contrast associated with its low sensitivity. Master molds have been fabricated by two EBL processes based on the PMMA resist: a conventional single-step process with PMMA exposure and direct Silicon etching (Figure 2 - Process 1(A)), and a multi-step process with PMMA exposure combined with metallic lift-off and Si reactive ion etching (Figure 2 - Process 1(B)).

In the first process, EBL exposure at 100 KeV is performed in a 430 nm thick layer of PMMA (950PMMA A5, MicroChem Corp.), spin coated on a Silicon wafer and baked at 180 °C for 30 minutes. The sample is developed in a methylisobutylketone (MIBK)/isopropanol (IPA)

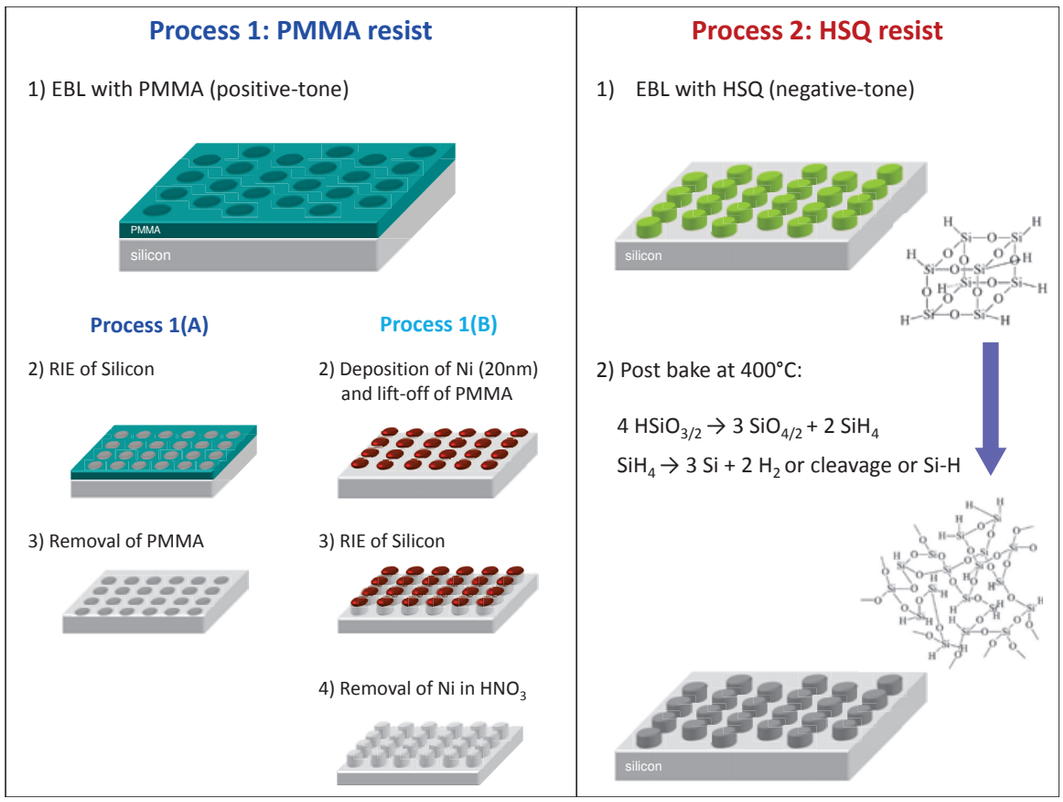

Fig. 2. Schematic of the Process 1, based on positive-tone PMMA resist and of the Process 2, based on negative-tone HSQ resist.

solution at 20 °C for 35 sec, rinsed in IPA for 10 s and then dried with a nitrogen gun. Pattern transfer in the Silicon substrate is then performed with a highly anisotropic RIE process based on $CHF_3/SF_6/O_2$, and the PMMA resist is finally removed with acetone. This process allows for the fabrication of high resolution and low sidewall roughness structures, as shown in the Figure 3 (a and b).

Since PMMA is a positive tone resist, an inverted pattern can be obtained either by exposing the complementary area, which is time consuming, or by a multi-step process with metal lift-off. In order to test the PMMA performance and the feasibility of this second process, we have carried out a challenge exposure of nanodots in a hexagonal pattern with a nominal diameter of 20 nm and a pitch of 60 nm, in a 80 nm thick PMMA resist (950PMMA A2, MicroChem Corp.). After the sample was developed as described in process 1 and lifted off of the 15 nm Ni mask, the dot patterns were transferred into the silicon wafer by reactive ion etching. The Ni mask was then removed by chemical wet etching in a HNO_3 acid solution.

The Figure 3 (c) shows a SEM image of the Si master molds after the Ni mask was removed. The inset shows a distribution graph of the area of the dots, including the standard deviation and the relative average diameter of the dots. In general, this process is suitable for the fabrication of structures up to the 100 nm scale, but it is not reproducible on sub-20 nm scale structures. This is due to the multiple intermediate steps which introduce broadening of the structures, defects and sidewall roughness. In order to improve shape uniformity and sidewall roughness, we have developed an alternative process based on negative-tone resist, Hydrogen Silsesquioxan (HSQ). HSQ is a new non-chemically amplified resist for EBL

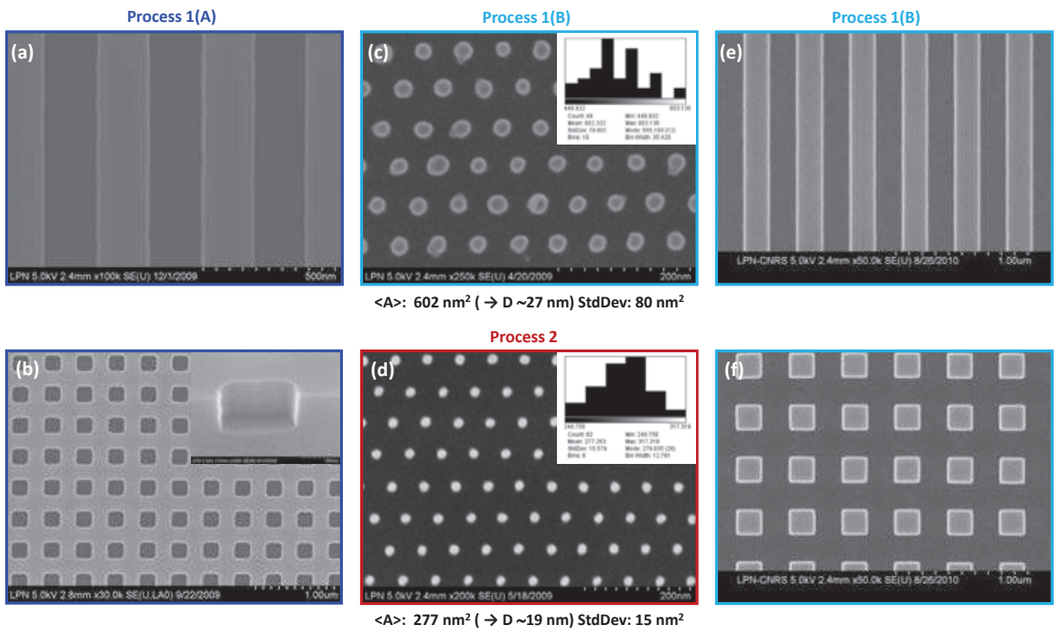

Fig. 3. SEM images recorded on Si master molds that have been processed with the PMMA process 1 (a-c) and with the HSQ process 2 (d-f). In particular, (c) and (d) show the results obtained for the processes 1(B) and the processes 2 respectively, by exposing nanodots with the same nominal diameter of 20 nm (pitch of 60 nm) in a hexagonal geometry. The correspondent dot area (A) distributions in the insets, shows that the HSQ master displays smaller dots with a better shape and area uniformity with a mean diameter (D) of 19 nm compare to the broadened mean diameter of 27 nm obtained with the multiple step process 1 (B).

which has been widely investigated in recent years (Chen et al. (2006); Falco & van Delft (20); Grigorescu & Hagen (2009); Namatsu et al. (1998)). It offers ultra-high resolution with linewidth fluctuations lower than 2 nm (Word & Adesida (2003)) and high stability and strength that can be improved by a thermal post-baking (Yang & Chen (2002)). In this second process, EBL exposure at 100 KeV is carried out on 40 nm thick HSQ (XR 1541, Dow Corning, 2% solids) spin coated on a silicon wafer. In order to avoid any change in the structure of the HSQ and possibly reduce the resist contrast, no pre-baking was conducted and the wafer was simply left for one day at room temperature to remove the solvents. The wafer is then developed in a potassium hydroxide (KOH) based solution at 20°C for 30 sec, rinsed for 2 min in deionised water, and gently dried with pure nitrogen gas. Finally, the post thermal curing of HSQ was performed at 400°C. By comparison with the multi-step fabrication process 1(B), this single step process results in a superior resolution and uniformity of the nanodots (Figure 3 (d)). The post-baking treatment induces a silica-like network redistribution of the HSQ which can be directly used, after anti-sticking treatment, as a master mold for replication of a bi-layer hard-PDMS/PDMS stamps.

2.2 Performances of the HSQ EBL process at the 10 nm scale

Even though a sub-10 nm resolution has already been achieved on a HSQ resist for isolated structures (Grigorescu & Hagen (2009)), one of the biggest challenges in nanofabrication is the patterning of high resolution and high density structures. Bit patterned media for magnetic

data storage is one of the most important applications of this technology, and it was actually one of the first applications for which NIL was proposed and studied (Chou (1997)). Patterned media by means of Nanoimprinting is one of the most promising approaches pursued by global companies like Hitachi and Toshiba in order to overcome the superparamagnetic limit of current perpendicular magnetic storage media. Our group has been working within the framework of the European project "'Teramagstor"' [www.teramagstor.com], in which the main goal of the consortium is the demonstration of a Bit pattern media prototype for the next generation of disk drivers with an areal density greater than 1 Tbit/in^2 fabricated by EBL and Soft UV NIL. In contrast to writing on conventional media, where the bits can be placed everywhere on the medium, a key challenge of writing on nanodot arrays of a bit patterned media is that the write pulses must be synchronized to the dot period and a perfect displacement of the dots is compulsory. Figure 4 shows a Silicon master mold fabricated utilizing the HSQ process with 15 nm dots and a 60 nm pitch (corresponding to an areal density of 180 Gbit/in^2), and 15 nm dots and a 30 nm pitch (corresponding to an areal density of 720 Gbit/in^2), with perfect dots displacement on the whole area. At the moment, we are working on further process optimization in order to achieve 1 Tbit/in^2 which corresponds to a 27 nm pitch and will eventually demonstrate higher areal density.

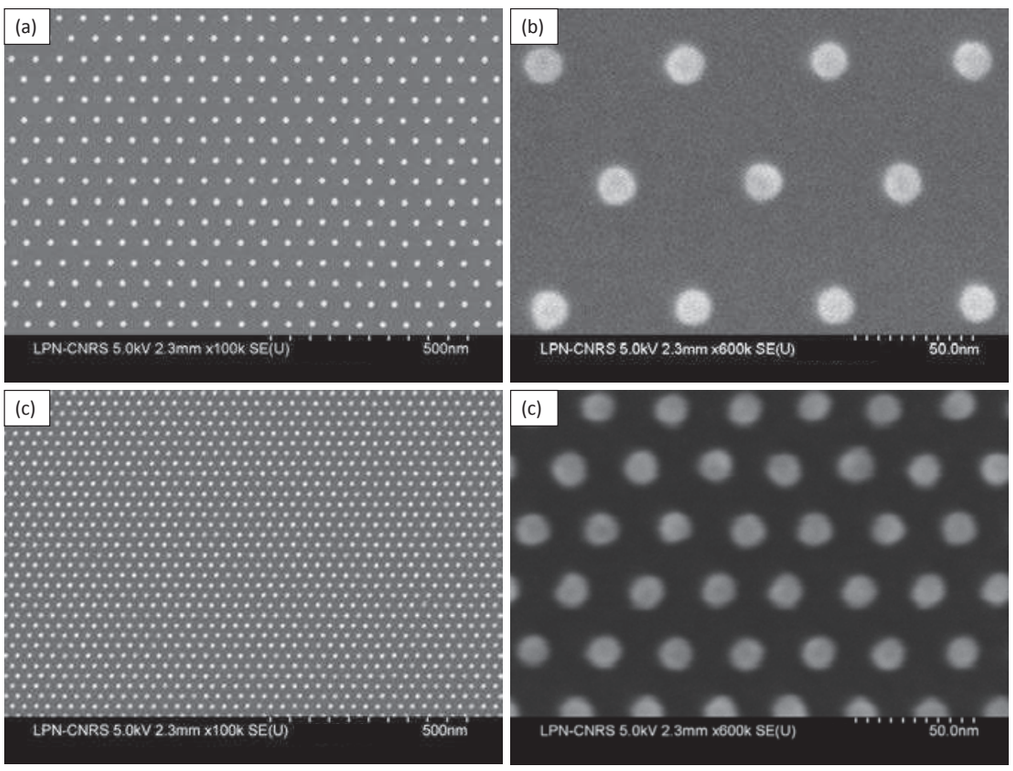

Fig. 4. SEM images recorded on Si master molds fabricated by HSQ Process 2, after annealing at 420 °C of (a-b) 15 nm dots, 60 nm pitch (corresponding to an areal density of 180 Gbit/in^2) and 15 nm dots, 30 nm pitch (corresponding to an areal density of 720 Gbit/in^2). The thickness of the resist is 25-30 nm.

2.3 The whole wafer inversion based on T-NIL

We have recently proposed and developed a T-NIL based process to replicate and invert an EBL master mold (Chen et al. (2010)). The inversion by means of T-NIL allows for the fabrication of a silicon mold with inverted features, so that pillars in the original master mold become holes in the daughter mold (Figure 5). We have studied how each pattern transfer process can affect feature size, pattern shape and homogeneity. Sub-200nm nanostructures have been inverted with good reproducibility and homogeneity on field as large as 1cm^2.

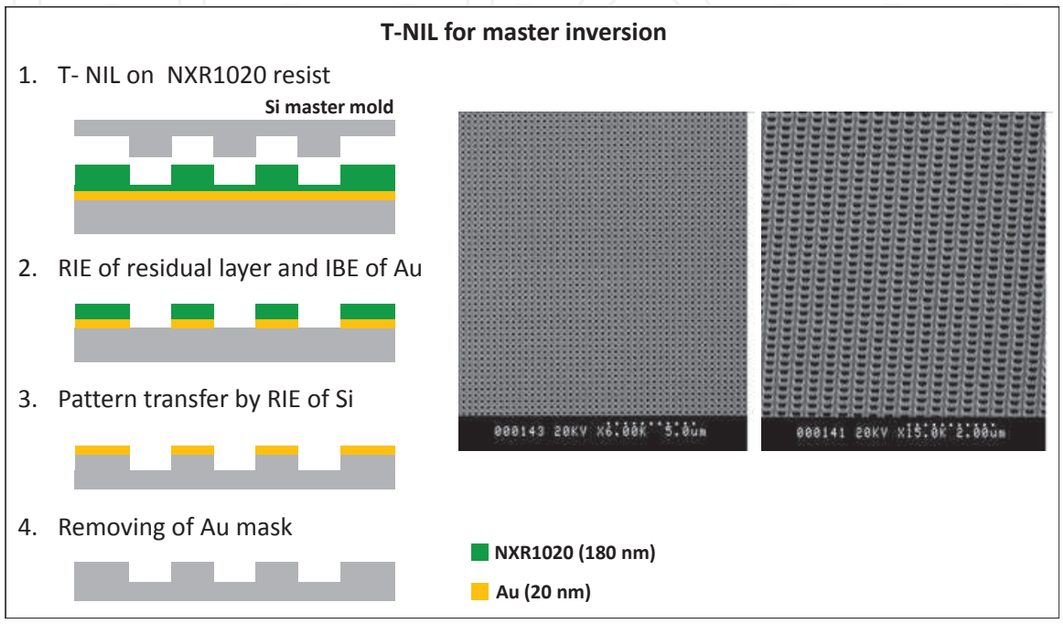

Fig. 5. (a) Schematic of master mold inversion based on T-NIL and SEM images of daughters molds

A schematic of this inversion process is presented in Figure 5. A thin gold layer (20nm) is first deposited on the silicon wafer. The thermal imprints are then performed on the NXR-1020 resist (Nanonex), spin coated at a thickness of 180 nm on Au/Si wafers. These resist films are annealed at 120°C for 10 minutes to remove the solvents. The Si master mold is gently placed in contact with the resist substrate and sandwiched between the two membranes of the NXR-2500 Nanonex, which provides optimal uniformity over the whole imprinted field. Imprinting is carried out at 130°C in two successive steps: 10 sec at 120 PSI (8 Bars) followed by 30 sec at 200 PSI (14 Bars). The imprinting tool is then cooled down below the estimated glass transition temperature of the resist, before carefully demolding the master. After removing the residual NXR1020 resist layer with O_2 plasma at a rate of 30 nm/min, the thin Au mask layer is etched by ion beam etching (IBE). The resist layer is then simply removed with acetone. Finally, the patterns are transferred into the silicon wafer with a standard Si reactive ion etching process using the Au mask, obtaining hole arrays. A trichloromethylsilane (TMCS) anti-sticking treatment is then applied to the daughter Si mold. With this process, we demonstrated that inversion is feasibile at the whole wafer scale. Figure 5 shows the SEM images of a 2 inch silicon wafer inverted daughter mold. It was patterned on a surface of 1 cm^2, with 200 nm-wide hole arrays. A good homogeneity was observed over the whole imprint field. These results clearly show the ability of the process to reach a resolution of 100 nm.

For feature sizes smaller than 100 nm, a small broadening of the pattern size is observed, even though the general shape is maintained (Chen et al. (2010)). An average broadening of 20 nm is observed for patterns (nanoline and nanohole) with feature sizes above 70 nm, while the broadening of feature sizes smaller than 50 nm become bigger (30 nm). This broadening originates from a loss of etch resistance of the NXR1020 mask resist during Ar IBE at high energy. Possible solutions to improve accuracy will be explored by using a thinner metallic underlayer or a T-NIL resist with a larger IBE resistance.

3. Fabrication of the replicated soft stamp

3.1 Polymeric stamp materials

The first unquestionable advantage of using a polymeric replica of the original master mold in the nanoimprint process is the cost reduction. As previously stated, from a single and expensive master mold, it is possible replicate a large number of polymeric stamps to use in the nanoimprint process. This prevents damages to the original master mold if it is directly used in the nanoimprint process. Moreover, the long range flexibility of the elastomeric material used for the stamp ensures the contact between the stamp and the substrate on large surfaces at low pressures (tens of bars) and on curved or flexible substrates. Several kind of polymeric materials have been tested as candidate for stamp replication including polycarbonate resins (Posognano et al. (2004)), cross-linked novolak based epoxy resin (Pfeiffer et al. (2002)), fluoropolymer materials and tetrafluoroethylene(PTFE) (Kang et al. (2006)). Nevertheless, poly(dimethylsiloxanes) (PDMS) still offers numerous attractive properties as a stamp elastomer. First of all, PDMS ensures a conformal adhesion of the stamp with the substrate on large areas without applying any pressure. To stress this point, Soft UV NIL performed with PDMS based stamps was recently renamed as UV enhanced Substrate Conformal Imprint Lithography (UV-SCIL) by Philips Research and SUSS MicroTec (Ji et al. (2010)).

Additionally, PDMS offers numerous other attractive properties: (1) its flexible backbone enables accurate replication of relief shapes in the fabrication of the patterning elements, (2) its low Young's modulus ($\sim$750 KPa) and its low surface energy enable conformal contact with the substrate without applied pressure and nondestructive release from patterned structures, (3) its good optical transparency down to a light wavelength of approximately 256 nm, (4) its commercial availability in bulk quantities at low cost. While PDMS offers some advantages, there are a number of properties inherent to PDMS which severely limit its capabilities in soft UV-NIL. First, its low Young's modulus limits the fabrication of features with high aspect ratios due to collapse, merging and buckling of the relief structures. Second, its surface energy ($\approx$ 22-25 mNm^{-1}) isn't low enough to replicate profiles with high accuracy. Third, its high elasticity and thermal expansion can lead to deformation and distortions during the fabrication. Finally, it shrinks by $\sim$1% after curing and can be readily swelled by some organic solvents. In general, long range deformations can be avoided by the introduction of a thin glass backplane which preserves a global flexibility. On the other hand, short range deformations can be avoided only by increasing the elastic modulus of PDMS, as we will discuss in deepth in the next paragraph. Therefore, compared to hot-embossing lithography (HEL) and UV-NIL which use rigid molds, it is particularly important to control the mold deformation as much as possible for the soft UV-NIL.

3.2 Basic PDMS stamp fabrication process

Simple PDMS stamps 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 the nanostructured master molds and degassed in a dessicator. 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 due to thermal shrinkage. Longer curing times and higher temperatures allow up to twice the elastic modulus and hardness of the polymer, but can also lead to higher roughness and deformations. The stamps are left to cool to room temperature, carefully peeled off from the master mold and treated with silane based antisticking treatment to further reduce the low PDMS surface energy. These stamps are not suitable for the replication structures at the sub-100 nm scale or with a high aspect ratio because of the low elastic modulous of PDMS. To address this issue, a modified PDMS with a higher elastic modulus was already proposed 10 years ago.

3.3 Improved hard-PDMS/PDMS bilayer stamp fabrication process

In 2000, Schmid et al. (Schmid & Michel (2000)) used a modified PDMS with higher elastic modulus (hard-PDMS) to extend the range in which conventional soft lithography could be applied. The hardening of the PDMS was accomplished by decreasing the chain length of the prepolymer. Increasing the elastic modulus of PDMS allows for the replication of smaller features in the 100 nm range, but it results in poor flexibility and an increase in the brittleness of the stamp. To overcome this problem, Odom et al. (Odom et al. (2002)) proposed a composite stamp of hard-PDMS and standard PDMS which combined the advantages of a rigid layer to achieve a high resolution pattern transfer and an elastic support which enabled conformal contact even at a low imprint pressure. Another important property of hard-PDMS is the lower viscosity of its prepolymer in comparison to PDMS. PDMS prepolymer cannot completely fill up the recessed nanoareas of the master mold due to its high viscosity, and the height of the soft stamp nanostructures will thus be lower than the height of the master patterns resulting in a poor inprinted thickness contrast. The decreasing of the chain length in the preparation of the hard-PDMS prepolymer, produce a lowering of its viscosity with a consequent higher ability of hard-PDMS prepolymer to replicate with accuracy the original master mold especially for high dense and small patterns.

The importance to reduce the viscosity of the prepolymer for an accurate replication of the master mold have been reported by other two groups (Kang et al. (2006); Koo et al. (2007)). In this case the viscosity of the PDMS prepolymer was reduced with the introduction of a solvent to the mixture, together with the use of an excessive amount of modulator to delay the cross-linking. The improved stamp replication process resulted in a better more accurated imprinting process, as shown in 8.

In Figure 7 is summarized the procedure for the replication of the bi-layer hard-PDMS/PDMS stamp. The hard-PDMS prepolymer, prepared by following a recepie similar to the one proposed by Schmid (Schmid & Michel (2000)), is spin coated onto a master at 5000 rpm for 30 sec and then degassed in vacuum for 10 min (the thickness of the hard-PDMS is about 5-8 μm). A mixture of conventional PDMS (1:10) is then poured on the spin coated hard-PDMS layer curing at 60 °C for 24 hours, the bi-layer stamp can be peeled off from the master and it is treated with trichloromethylsilane (TMCS).

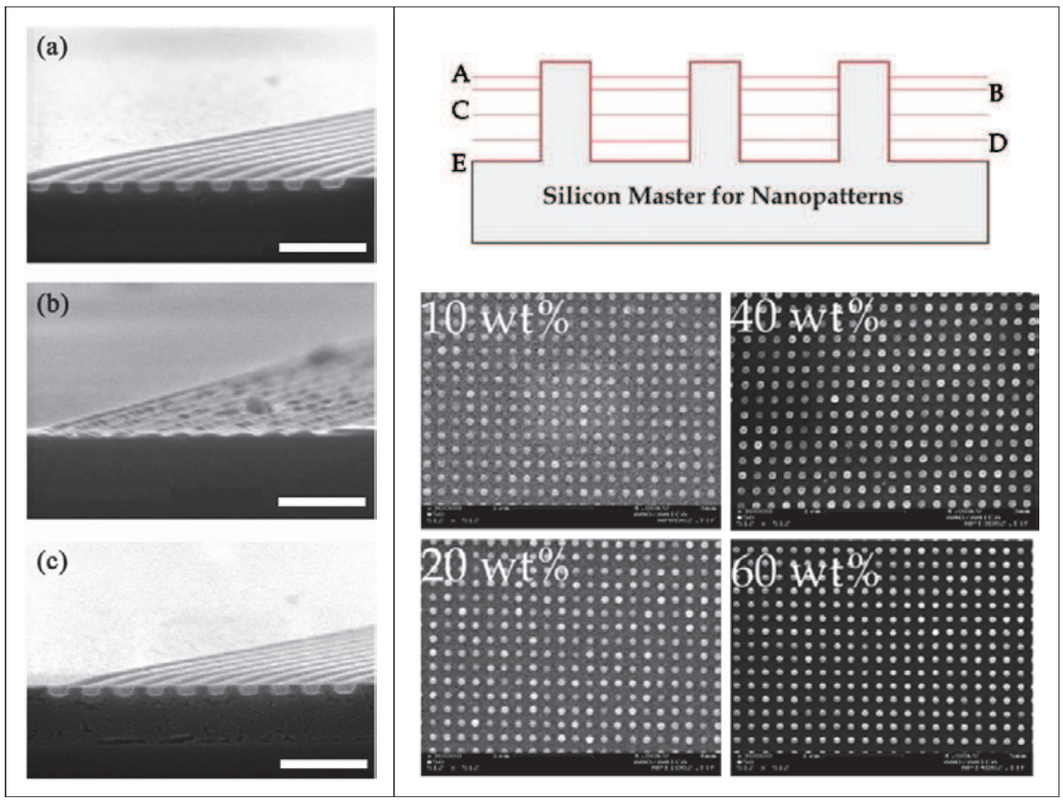

Fig. 6. Left panel: SEM images of (a) a 100 nm line of the master pattern, (b) patterned polymer with the composite stamp prepared by the method proposed by Schmid and Odom and (c) by the improved method with toluene as solvent for hard-PDMS (the scale bar is 500 nm). Reprinted with permission from (Kang et al. (2006)). Copyright 2006 IOPP Publication. Right panel: schematic of the influence of the material viscosity on the penetration depth into the master cavities for nanostructures. Exemplary SEM pictures of an 50 nm dots array imprinted with diluted PDMS molds prepared with toluene concentration of: A: 10 wt%, B: 20 wt%, C: 40 wt% and D: 60 wt% whom correspond to a pattern height increases from 10 nm (A) up to 70 nm (D). Reprinted with permission from (Koo et al. (2007)). Copyright 2007 Elsevier.

4. Soft imprinting process

4.1 Minimization of pressure and dimension control

In order to achieve an accurate pattern replication, it is important to control the eventual broadening and deformations of the replicated structures. During T-NIL and UV-NIL processes, a parallel and uniform surface contact between the hard mold and the substrate is obtained by applying high pressure, and the replicated structures preserve a high accuracy when compared to the original ones in the master mold. During the Soft UV NIL process, the flexibility of the PDMS stamp ensures a conformal adhesion with the substrate at low pressure. On the other hand, the low elastic module of PDMS can produce deformations of high aspect ratio structures when too much pressure is applied. If it is not possible to completely avoid these deformations, it is important to control and reduce them under appropriate values, depending on the specific application. Because soft UV-NIL is a very recent variant of NIL,

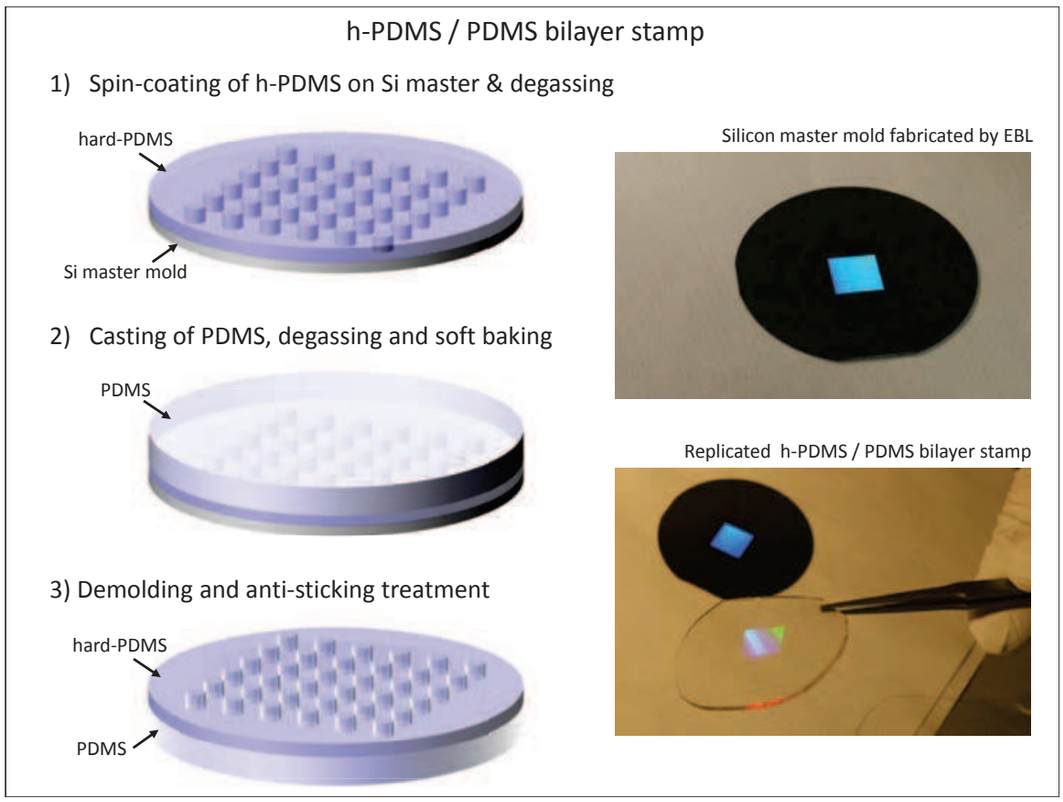

Fig. 7. Schematic of the fabrication process of a hard-PDMS/PDMS bilayer composite stamp and a pictures of a Silicon master mold and of a bilayer stamp after peeling off.

such a resolution study has been conducted by only a few groups. For instance, KarlSuss GmbH has recently demonstrated the replication of nanoholes with a diameter of 340 nm ($\pm$5%) and a minimized residual layer thickness of 36 nm in the Amonil resist with a pitch uniformity of 2 nm over a surface area of 6 inches (Ji et al. (2010)).

The pressure applied during imprinting directly influences the flow of the resist and determines the accuracy of the imprinted nanoscale structures. The first step consists of minimizing the imprinting pressure to reduce local distortions while ensuring a complete resist filling in the stamp nanocavities. We have shown that this pressure can be largely reduced to 0.7 bar (10 PSI) (Cattoni et al. (2010); Shi et al. (2009)). Combined with a UV exposure of 10 min (dose of 2 Jcm^2) at 365 nm wavelength, patterns with a high quality shape can be obtained (Figure 8(a)). To quantify the accuracy of the control dimension, we investigated the changes in pattern size on a two-inch wafer scale under this optimum pressure (10 PSI). Nanodot patterns with two different diameters (215 nm and 310 nm) have been chosen for this study. Each field size is 200 um x 200 um on the wafer. The critical dimension of the nanodot patterns on the mold and replicated in the resist were then measured using a high-resolution scanning electron microscopy (Fig. 8(b)). Black and blue points correspond to the measured diameters on the EBL master mold whereas red points correspond to measured diameter in the Amonil resist after nanoimprinting. We observe a broadening of the dot diameter, which never exceeds 10 nm, corresponding to a standard deviation of less than 5%.

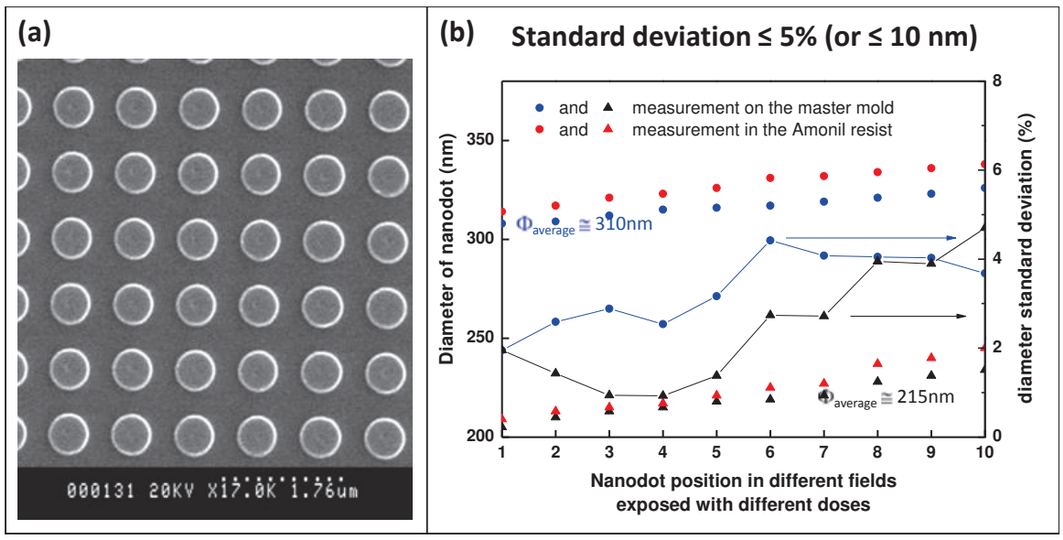

Fig. 8. Control dimension fidelity after soft UV-NIL at optimized pressure: (a) SEM image of 310 nm-diameter pillar array recorded in the Amonil resist and (b) comparison of the diameter values measured on the master mold and in the Amonil thickness contrast, with the relative calculated diameter standard deviation.

4.2 Minimization of the thickness of the resist residual layer

A second important point of the nanoimprint process concerns the removal of the residual layer of the resist. Because T-NIL and UV-NIL use rigid mold and high pressure, a thin residual layer of resist is normally left between the protrusions of the mold and the substrate. It acts as a soft cushion layer that prevents direct impact of these fragile nanostrucures and the substrate. This residual layer is normally removed by reactive ion etching (RIE) which can largely affect the original shape and size of the pattern. Soft UV NIL uses flexible stamps and this residual layer can be reduced as much as possible by simply adapting the initial resist thickness to the depth of the stamp (height of patterns). Figure 9(b) shows a SEM cross-section image of the imprinted structures at a optimized pressure of 0.7 bars, with a 25 nm thick residual layer, obtained by adjusting the initial thickness of resist. These results can be compared to the recent ones from AMO that are presented in Figure 9(a).

Finally, in order to validate the ultra-high resolution HSQ process for EBL and our improved hard-PDMS/PDMS bilayer stamp fabrication process, we have carried out Soft UV NIL in the sub-100 nm scale. Figure 9 (b-c) shows the thickness contrast in the Amonil resist after Soft UV-NIL, at 10 PSI and at room temperature, by using the bi-layer mold hard-PDMS/PDMS for 50 nm dots with a pitch of 100 nm and 20 nm dots with a pitch of 60 nm. The high and uniform contrast thinknesses obtained on the whole pattern area demonstrate the ability of Soft UV NIL with hard-PDMS/PDMS stamps to replicate nanostructures in the 20-nm scale. We believe than our current limitations in achieving higher resolution, specifically for the replication of highly dense structures, are essentially due to the replication of the bilayer stamp. It will be necessary to work on this stamp replication process, in particular by further reducing the viscosity of the hard-PDMS prepolymer and by controlling the effects of the thermal curing process, which results in a isotropic volume shrinkage of the hard-PDMS that becomes more and more important at the sub-20 nm scale.

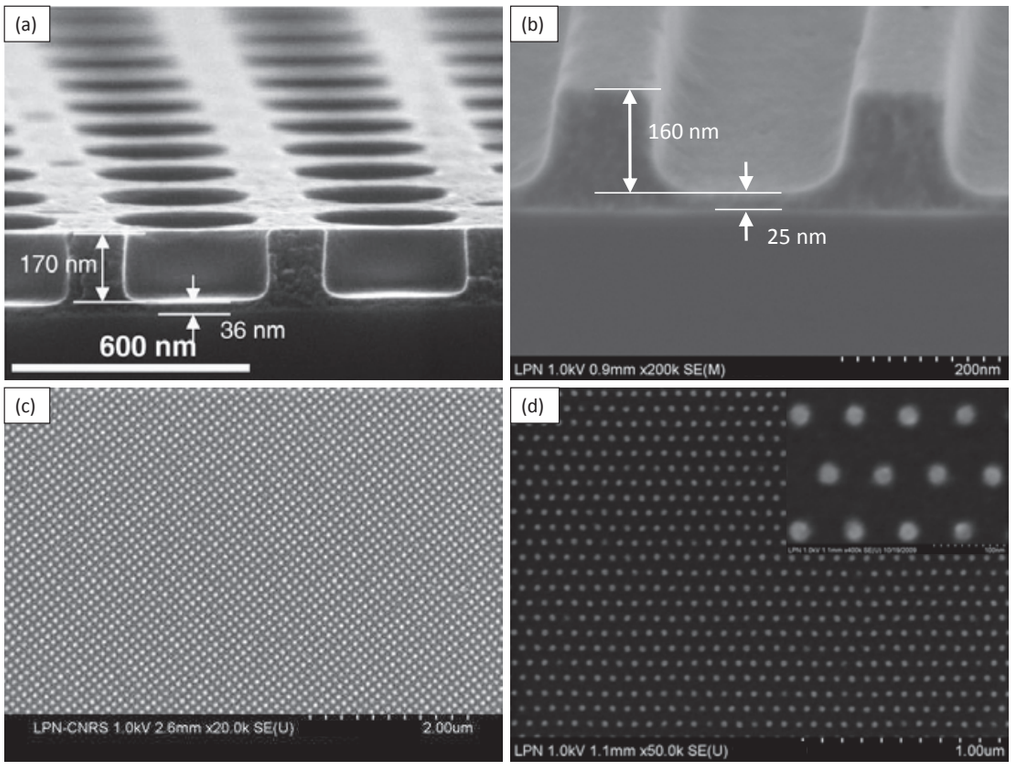

Fig. 9. SEM images of: (a) imprinted structures into AMONIL resist, the structure depth is 170 nm and the residual layer is 36 nm. Reprinted with permission from (Ji et al. (2010)). Copyright 2007 Elsevier. (b) imprinted structures into AMONIL resist, the structure depth is 160 nm and the residual layer is 25 nm. (c-d) High resolution replication at the 50 nm and at the 20 nm range in AMONIL resist.

5. Soft UV NIL for plasmonic biosensing: a real case application

Surface plasmon resonance (SPR) based sensors are a well established technology utilized for label-free bio-chemical sensing in different applications, from immunoassay and medical diagnostics, to environmental monitoring and food safety. Localized Surface Plasmon Resonance (LSPR) based sensors have different advantages and constitute a promising alternative to the SPR sensor (Stuart et al. (2005)). Because LSPR based biosensors are by design very sensitive to changes in the characteristics of nanoparticles (uniformity in nanoparticle size, shape and composition) the standard approach for the fabrication of LSPR based sensor is Electron Beam Lithography (EBL) which provide an extreme control over nanoscale size and shape of the nanoparticles thus improving sensitivity and reliability of the sensor. On the other side this is an expensive and time-consuming technique, consequently not suitable for mass production.

We have successfully realized a LSPR biosensor based on $\lambda^3/1000$ plasmonic nanocavities fabricated by Soft UV Nanoimprint Lithography 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 (Cattoni et al. (2011)).

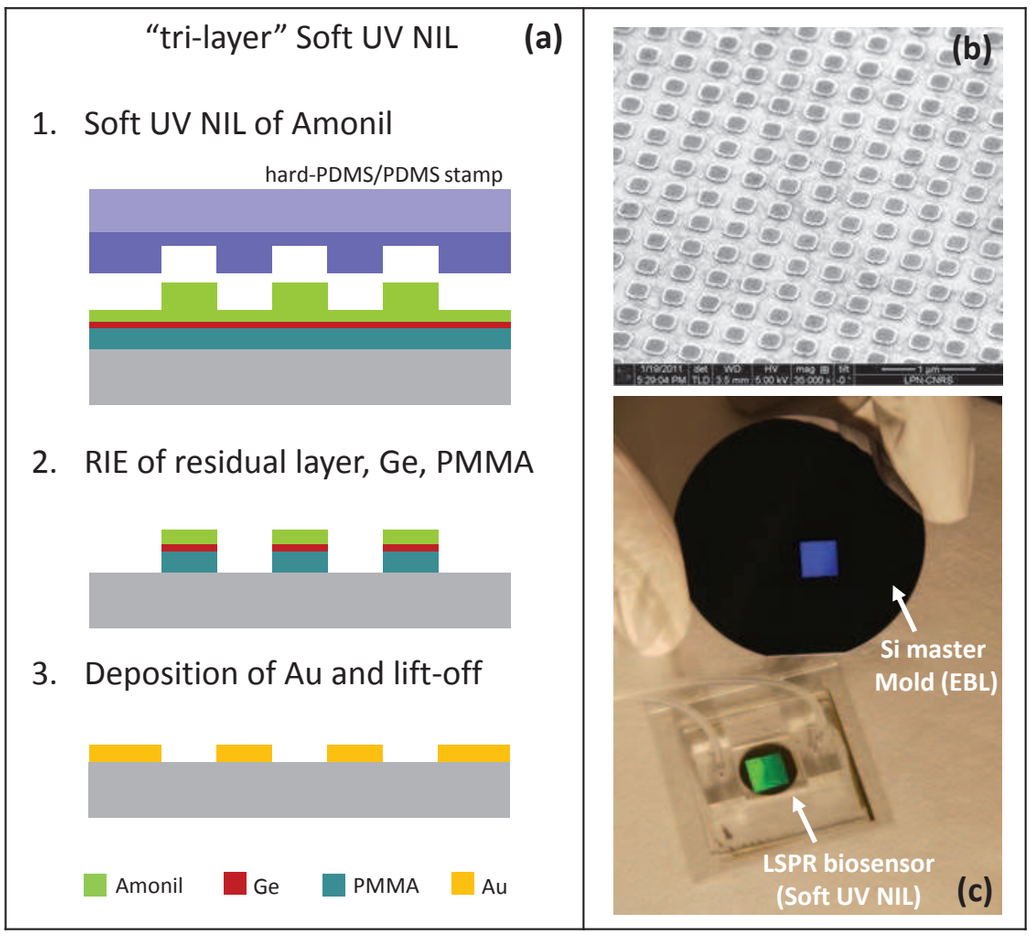

Fig. 10. (a) Schematic of the tri-layer Soft UV NIL process, (b) SEM image of square gold nanoparticle (size = 200 nm, pitch 400 nm) realized with this method and lift-off, (c) the LSPR biosensor fabricated by Soft UV NIL, integrated in a microfluidic channel with its original Silicon master mold fabricated by EBL.

The basic element of the nanocavities array (not shown) is composed by lower thick gold film acting on a glass substrate, a thin dielectric layer forming the gap of the optical antenna and an upper gold nanoparticle realized by "tri-layer" Soft UV imprint lithography and standard lift-off. In figure (a) is shown the concept of the tri-layer system on a generic substrate: typical UV NIL resists (like Amonil) are not soluble in solvents and a lift-off process is possible by using a PMMA layer under the UV NIL resist. In our process a further 10 nm Ge layer is insert between the thick PMMA layer and the thin UV NIL resist (Amonil) to improve the selectivity of the former one over the PMMA layer. After imprinting with a UV light and separation, the top layer structure is transferred into the bottom layer by a sequential reactive ion etching. The high aspect ratio tri-layer so obtained can be used directly as etching mask or for the lift-off of metals. In Figure 10 (b) is shown a SEM image of square gold nanoparticle (size = 200 nm, pitch 400 nm) realized by "tri-layer" Soft UV imprint lithography. Figure 10 (c) shows the LSPR biosensor based on $\lambda^3/1000$ plasmonic nanocavities fabricated by Soft UV Nanoimprint Lithography and integrated in a glass/PDMS/glass fluidic chamber for the

optical index sensing experiments together with its original Silicon master mold fabricated by EBL.

6. Conclusion

As we have shown, the replication process of nanostructures by Soft UV NIL it is composed by three separate processes: the fabrication of the master mold, the replication of the soft polymeric stamp from this template, and the imprinting process by using this stamp. All these steps contribute equally at the quality of the final result, in terms of resolution and line edge roughness of the nanostructures. In this manuscript we have presented a detailed master mold fabrication process based on EBL. The performances of two EBL resists (PMMA and HSQ) for the replication of high density patterns (pitch=30 nm) have been discussed for ultra high resolution at the 15 nm scale. In addition a process combining T-NIL and etching has also been proposed for the cheap and fast replication of master molds. We have then detailed the replication of the polymeric stamp, based on a composite hard-PDMS/PDMS bilayer. Finally for the last third critical imprinting step, we have demonstrated the ability of Soft UV NIL to replicate nanostructures at the 20 nm scale with high uniformity at the whole pattern area. We do believe that Soft UV NIL will have in the near future an important role as a powerful and versatile tool for nanofabrication. To validate this statement, we conclude by presenting an example of a real case application, i.e. the fabrication by Soft UV NIL on large area (1 cm^2) of gold plasmonic nanostructures with outstanding optical and biosensing performances.

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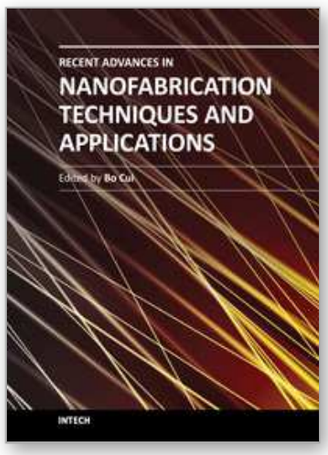

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Nanotechnology has experienced a rapid growth in the past decade, largely owing to the rapid advances in nanofabrication techniques employed to fabricate nano-devices. Nanofabrication can be divided into two categories: "bottom up" approach using chemical synthesis or self assembly, and "top down" approach using nanolithography, thin film deposition and etching techniques. Both topics are covered, though with a focus on the second category. This book contains twenty nine chapters and aims to provide the fundamentals and recent advances of nanofabrication techniques, as well as its device applications. Most chapters focus on in-depth studies of a particular research field, and are thus targeted for researchers, though some chapters focus on the basics of lithographic techniques accessible for upper year undergraduate students. Divided into five parts, this book covers electron beam, focused ion beam, nanoimprint, deep and extreme UV, X-ray, scanning probe, interference, two-photon, and nanosphere lithography.

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