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A versatile pattern inversion process based on thermal and soft UV nanoimprint lithography techniques

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ABSTRACT

Si master molds are generally patterned by electron-beam lithography (EBL) that is known to be a time-consuming nanopatterning technique. Thus, developing mold duplication process based on high throughput technique such as nanoimprint lithography can be helpful in reducing its fabrication time and cost. Moreover, it could be of interest to get inverted patterns (holes instead of pillars) without changing the master EBL process. In this paper, we propose a two step process based on thermal nanoimprint lithography (T-NIL) (step 1) and soft UV assisted nanoimprint lithography (UV-NIL) (step 2) to invert a master EBL mold. After the two inversion steps, the grand-daughter Si mold exhibits the same pattern polarity as the EBL mold. For step 1, pattern transfer using ion beam etching (IBE) of a thin metallic underlayer is the critical step for dimension control due to the low NXR1020 resistance. For step 2, the optimized reactive ion etching (RIE) step allows transfer with good anisotropy even for nanostructures at the 50 nm-scale. For structures larger than 100 nm, this inversion process has been successfully applied to large field replication (up to 1.5 cm^2) on whole wafer.

1. Introduction

The ability to fabricate nanostructures of high resolution and high density at low cost and over large area is of importance for both fundamental research and industrial applications including optoelectronics, sub-wavelength optical nanostructures, high density magnetic data storage, and bio-sensors [1–4]. Electron-beam lithography (EBL) [5] and focused ion beam (FIB) lithography [6] are the most common nanolithographies used for sub-100 nm scale patterning, but they are not suitable for mass production because of their long writing time and expensive equipments. In this context, unconventional lithographic techniques advance dramatically in the past decades. Compared to traditional methods, they are much simple, fast and cheap. In addition, they offer a better process flexibility and compatibility for biology and chemical applications such as biomolecular patterning and multifunctional microfluidic chips [7]. Among these recent techniques, nanoimprint lithography (NIL) has been demonstrated to be one of the most promising alternative techniques for producing dense periodic nanostructures on large areas at reasonable cost [8,9]. With intensive developments from materials (i.e. resists, mold) to imprinting tools, now, NIL has passed a barrier from a laboratory scale to industrial preproduction [10,11].

However, one NIL key parameter for both resolution and pattern smoothness concerns the fabrication of the master mold. Since NIL allows faithful pattern duplication even of nanometer variations on a pattern sidewall, it is important to fabricate NIL master molds of high resolution over large area and with minimal sidewall roughness. These molds are thus generally patterned using EBL at high energy. To reduce both writing time and fabrication time, developing other strategies for master replication and/or inversion at the whole wafer scale is important. In this work, we propose a two steps process that allows pattern inversion at each step. The first step combines thermal nanoimprint lithography (T-NIL), ion beam etching (IBE) and reactive ion etching (RIE) for pattern transfer, whereas the second step is based on soft UV nanoimprint lithography (UV-NIL) associated only with reactive ion etching (RIE). In this paper, we study how each pattern transfer process will affect feature size, pattern shape and homogeneity. Sub-200 nm nanostructures have been inverted with good reproducibility and homogeneity on field as large as 1 cm^2. Two successive inversions were finally performed in order to quantify changes in both line width and pattern shape between the original EBL Si master mold and the grand-daughter Si mold (step 2) replicated from the daughter mold (step 1) by soft UV-NIL.

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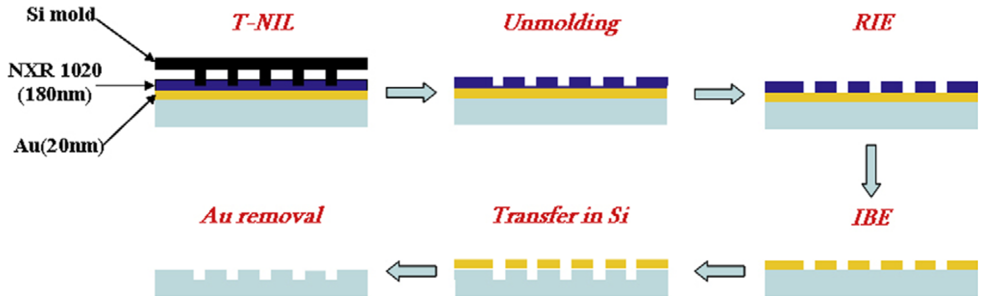

Fig. 1. The mold inversion process based on T-NIL and ion beam etching. The daughter mold exhibits holes arrays instead of pillars on the EBL master.

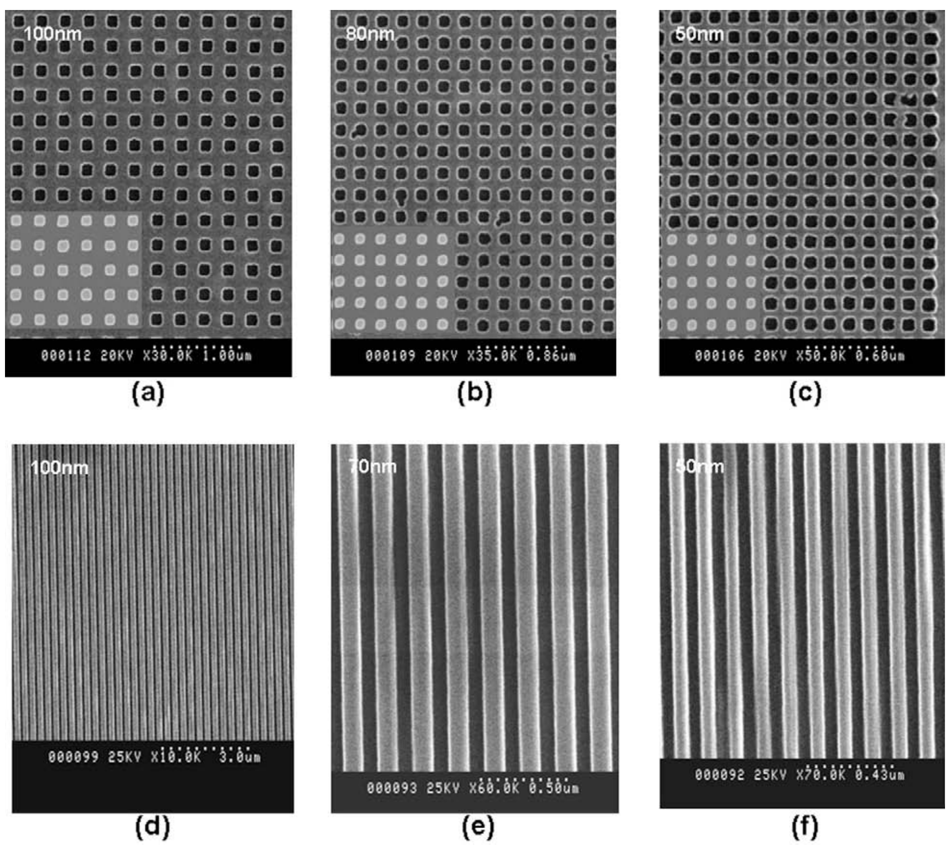

Fig. 2. SEM images of (a) NH1: d = 100 nm, (b) NH2: 80 nm, (c) NH3: d = 50 nm, gold nanoholes arrays (d) NL1: line width is 100 nm, (e) NL2: line width is 70 nm and (f) NL3: line width is 500 nm nanolines arrays after thermal nanoimprint lithography, reactive ion etching of the residual resist and ion beam etching for inversed replicating patterns. The inset of (a), (b) and (c) show a nano-square dots gratings on the Si master after high resolution EBL, Ni lift-off and anisotropic RIE with CHF_3–SF_6.

2. Materials and experiments

T-NIL and soft UV-NIL were performed on our commercial Nanonex NXR-2500 imprint tool. The fabrication process can be divided in two parts: (Fig. 1) T-NIL combined with IBE and RIE is first used to invert an EBL master mold (step 1). Then soft h-PDMS/PDMS transparent stamps are casted on the daughter Si to perform UV-NIL (step 2 – Fig. 4a). Finally, after RIE pattern transfer, the grand-daughter Si mold exhibits the same pattern polarity as the original EBL master.

2.1. Master mold fabrication

Each pattern field on the silicon masters (mother molds) used in this work contains either nanopillars arrays or nanolines arrays. These master patterns are defined by electron-beam lithography at 100 keV in a resist layer (ZEP520 or PMMA depending of the pattern size) and transferred into a silicon wafer by anisotropic reactive ion etching (RIE) with CHF_3–SF_6 gas [12,13], resulting in sub-100 nm features with a depth of 100 nm. Finally, the surface of the patterned silicon mold was treated with trichloromethylsilane (TMCS) as release agent.

2.2. Thermal nanoimprint lithography (T-NIL) inversion process

First, T-NIL is used to invert the Si master mold, for example to get holes arrays starting from pillars arrays (Fig. 1). A thin gold layer (20 nm) that will act as the mask during IBE pattern transfer is first deposited on the silicon wafer. The NXR-1020 resist (Nanonex) is then spin coated to get a thickness of 180 nm on Au/Si wafers and is finally annealed on hotplate at 120 °C during 10 min to remove the solvent. The Si master mold is gently placed in contact with the NXR-1020/Au/Si sample and sandwiched between the two membranes of the NXR-2500 Nanonex, which provides optimal uniformity over the whole imprinted field [14]. Imprint is performed at 130 °C in two successive pressuring steps: 10 s at 120 psi (8 bars) followed by 30 s at 200 psi (14 bars). The imprint tool is cooled down below the estimated glass transition temperature of the resist, before careful unmolding of the master.

After T-NIL step, the residual NXR1020 resist layer is removed under O_2 plasma at a rate of 30 nm/min, and the thin Au mask layer is etched by Ar ion beam etching (IBE) at high energy (350 V). This IBE step is crucial for pattern dimension control as it will be discussed later in Section 3.1. The resist layer is then simply removed in acetone. Finally, the patterns are transferred into silicon wafer with standard Si RIE process [12,13] and the Au mask is removed in a KI + I_2 solution. At the end of this step 1, inverted patterns are obtained in the daughter Si mold (for example holes as shown in Fig. 2).

2.3. UV nanoimprint lithography (UV-NIL) replication process

In soft UV-NIL [1], patterns are replicated in a low viscosity UV-curable polymer from a flexible transparent mold that offers many advantages. This polydimethylsiloxane (PDMS) soft stamp can be easily cast more than twenty times on the same master mold. Moreover this cheap stamp is sufficiently flexible to be in perfect conformal contact during printing [10]. Here we used our specific h-PDMS/PDMS bi-layer transparent stamps [12] to perform replications in the sub-100 nm range.

These arrays (for example pillars) are replicated by soft UV-NIL in an Amonil/Ge/PMMA tri-layer system that allows pattern transfer with high aspect ratio (Fig. 4) [13]. PMMA bottom layer is first spin coated with a thickness between 150–300 nm and pre-baked at 180 °C for 10 min. A 10 nm-thin intermediate germanium (Ge) is then deposited by electron-beam evaporation. Finally a 180 nm thick Amonil resist (AMO-MMS4) layer is spin coated on the top of the Ge layer. UV-NIL is realized at room temperature using the optimized pressure of 8 psi (0.55 bars).

UV imprinted patterns (for example holes arrays) in Amonil resist are then transferred using three successive RIE steps with O_2/CHF_3, SF_6 and O_2 plasma [12]. A 20 nm-thin Ni layer is deposited by electron-beam evaporation and lifted in acetone. The final patterns (pillars in that case – see Fig. 4) are etched in Si with our standard CHF_3/SF_6 gas mixture. The Ni mask is then removed with nitric acid (HNO_3). After this whole process, the grand-daughter Si mold exhibit pillar arrays similarly to the original EBL master mold.

3. Results and discussion

Unlike other conventional lithography, nanoimprint lithography replicates patterns by producing a 3D topography in a thin resist film. Such pattern contrast can be obtained either by embossing a thermoplastic resist at an elevated temperature (T-NIL) or by curing with UV a resist precursor at room temperature (UV-NIL). In order to achieve high resolution pattern over wafer-scale area, applying a uniform pressure is a key parameter. After imprinting to maintain both feature size and pattern shape, pattern transfer by etching is a key step that has to be optimized. The ability of each etching step to properly transfer patterns (IBE or RIE) will be discussed below.

3.1. Master inversion by using T-NIL

Pillars and lines arrays of different sizes ranging from 70 nm to 1 μm have been selected as test structures to investigate the replication performances of T-NIL.

Typical results after T-NIL and both RIE and IBE are presented in Figs. 2a–g. SEM images of Fig. 2a–c show respectively nanohole array of 100, 80 and 50 nm. Each inset shows the SEM image of the corresponding Si master for direct comparison. Fig. 2d–f presents the line gratings with a linewidth of 100, 70 and 50 nm. These results show clearly the ability of the process to reach resolution to 100 nm. However, for feature size smaller than 100 nm, even if the general shape is maintained, the pattern size can be affected. As shown in both Fig. 2a and d, the shape of the 100 nm wide structures is similar as the master one, even if a small broadening is observed. Lines even at small width do not exhibit significant lateral defects. However, for the smaller nanoholes with diameter of 70 nm and below, defects appear and the general squared shape of the hole is not well preserved as it can be seen in Fig. 2b and c. To analyze more precisely changes in pattern width (or diameter), these SEM images have been analyzed using the "Image J" software that extracts contrast and pattern outline. The feature size distribution can thus be calculated from the listed area distribution. Table 1 gives the different mean feature size values recorded on both Si master fabricated by EBL and the daughter inverted Si mold. An average broadening of 20 nm is observed for patterns (nanoline and nanohole) with feature size above 70 nm; while for smaller feature (50 nm), the broadening becomes bigger (~30 nm).

This broadening originates from a loss of etch resistance of the NXR1020 mask resist during Ar IBE at high energy. If the first oxygen RIE step for residual layer removal of NXR1020 does not affect feature size, the IBE transfer of the resist pattern inside the intermediate Au layer is more critical. Thus, in order to minimize the loss of etch resistance of NXR1020, it would have be possible to both decrease NXR1020 and Au thicknesses to reduce more IBE etching time. Finally, for this step 1, the IBE etching resistance of the NXR1020 resist has thus to be improved in the future to avoid any size broadening.

We have also applied this T-NIL inversion process to field as large as 1.5 cm^2 for 200 nm-wide pillar arrays and for 150 nm-wide line arrays. For these dimensions higher than 100 nm, the inverted replication worked more successfully in faithfully keeping the profile and dimension. Fig. 3 show images of 2 in. silicon inverted replication molds (daughter molds). The first one has been patterned on 1 cm^2 field with 200 nm-wide holes arrays (top) and the second one on a 1.5 cm^2 patterned area with 150 nm-wide line arrays (down). A good homogeneity and uniformity can be observed over the whole imprint field up to 1.5 cm^2. SEM images also show that a good uniformity can be obtained on the whole large field without noticeable variation in critical dimension, sidewall roughness. This turns out that larger than 100 nm patterns can be replicated with a well controlled process and then be transferred into the substrate by direct etching.

Table 1
Summarized results of feature size (for nanohole array the dimension refers to the diameter and for nanoline array the dimension refers to the width). The first table line gives dimensions on the Si master mold and the second line gives dimensions measured on the inverted mold fabricated by T-NIL and IBE.

Nanopatterns	NH1	NH2	NH3	NL1	NL2	NL3
Pattern size (nm)on the master	100	80	50	100	70	50
Pattern size (nm) on the inverted mold	120 ± 4	102 ± 5	80 ± 6	120 ± 2	90 ± 5	80 ± 5

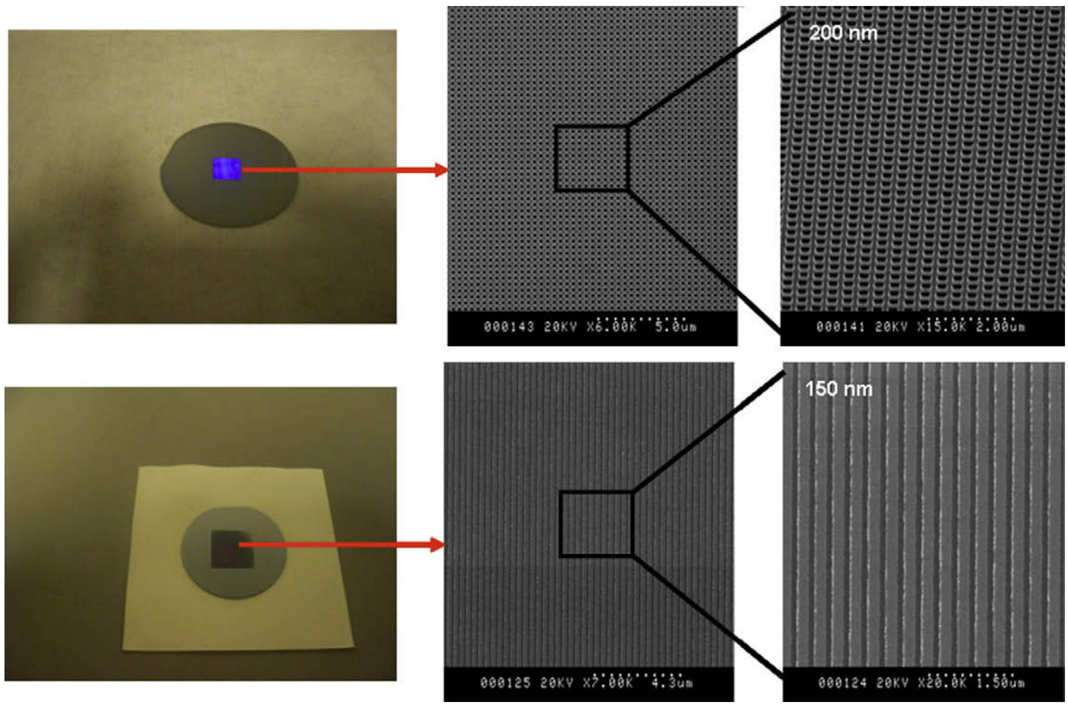

Fig. 3. Images of 2 in. Si inverted replication molds (daughter molds) with (top) a 1 cm^2 hole array ($d = 200/p = 400$ nm) and (bottom) a 1.5 cm^2 line array ($d = 150/p = 300$ nm) fabricated based on thermal NIL and IBE.

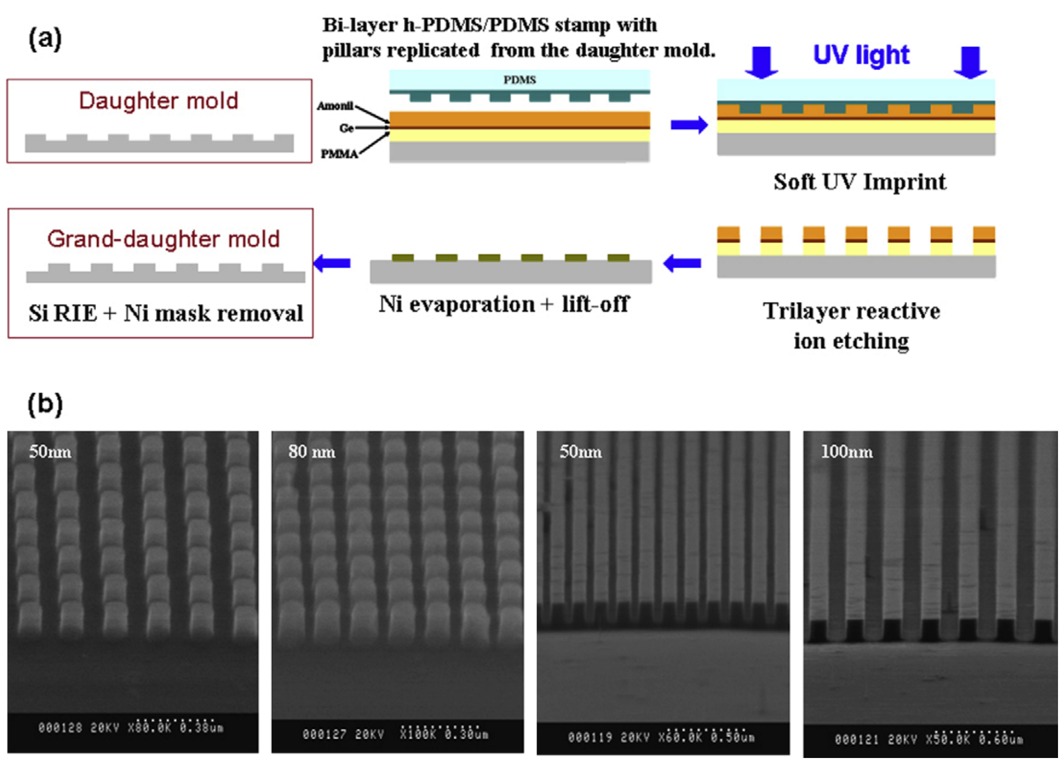

Fig. 4. (a) Schematics of the soft UV nanoimprint process; (b) SEM images of the grand-daughter mold with different diameter pillars and linewidth lines gratings based on the proceeding fabrication procedure: soft UV-NIL with the h-PDMS/PDMS bi-layer stamp obtained from the Si daughter mold patterned with 200 nm-wide nanohole arrays, tri-layer etching, lift-off and transferred into Si.

3.2. Soft UV-NIL imprint and transfer

In order to test pattern shape and feature dimension control of the inverted daughter silicon molds, bi-layer hard PDMS/PDMS flexible stamps have been used. Fig. 4a shows the fabrication sequence with the soft h-PDMS/PDMS stamp replicated from the daughter mold by using soft UV-NIL. Soft UV-NIL has been performed in the Amonil/Ge/PMMA tri-layer stack. Note that the hard bi-layer h-PDMS/PDMS stamps used in this study can guaranty a good contact between mold and the substrate, thus producing a homogeneous replication on the whole large area. After the three RIE steps and the metallic lift-off, we obtain similar nanostructures than those on the initial EBL master mold. Fig. 4b shows tilted SEM images of both nanopillars arrays and nanolines gratings with different feature size. We observed a small widening of both the pillars and lines, which can be minimized to 10 nm by optimizing the parameters of three continuous etching steps as follows: (1) removal of the Amonil residual layer inside the nanopatterns with O_2 and CHF_3 mixture at a 40 nm/min etching speed, (2) etching of the thin Ge layer using SF_6 plasma and finally, and (3) O_2 plasma etching of the thick PMMA underlayer. If the first Amonil etching step (1) has to be well optimized to get faithful pattern profile compared with the original pattern, the last PMMA etching step (3) allows perfect control of the feature size.

Finally, the verticality of the pattern profiles observed on the SEM images of the grand-daughter Si mold (Fig. 4) proves that this inversion process based on several etching steps is sufficiently controlled in terms of anisotropy.

4. Conclusion

In summary, we have successfully demonstrated the fabrication of 100 nm nanostructures by combining T-NIL, soft UV-NIL and optimized RIE processes. Two successive mold inversions have been realized at the whole wafer scale. The good shape homogeneity and size uniformity of the replicated nanostructures over field as large as 1.5 cm^2 proves that the Air Cushion Press System of the Nanonex imprinting tool is well adapted for faithful replications at the 100 nm scale. For nanostructures with dimensions ranging from 100 to 50 nm, after the T-NIL/IBE step 1, an average width broadening of 20 nm is systematically observed due to a loss of IBE resistance of the NXR1020 resist whereas it is reduced to 10 nm after the UV-NIL/RIE step 2. However, even at this scale, a good homogeneity in pattern shape is observed. For patterns larger than 100 nm, our two step inversion process appears as a reliable technique for replicating and inverting expensive EBL master molds.

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