Magnetic force assisted thermal nanoimprint lithography (MF-TNIL) for cost-effective fabrication of 2D nanosquare array

Rakesh S Moirangthem
Nanophotonics Lab, Department of Physics, Indian Institute of Technology (ISM), Dhanbad -826004, JH, India
E-mail: moirangthemrakesh@gmail.com

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Abstract
The work presented here describes a simple, low-cost, and unconventional technique to fabricate a 2D nanosquare array using magnetic force assisted thermal nanoimprint lithography (MF-TNIL). The nanofabrication process involves two steps: (i) fabrication of a 2D nanosquare array template on a laminated plastic sheet via sequential thermal nanoimprinting of linear nanograting polydimethylsiloxane (PDMS) stamp, and (ii) reversal imprinting of template on UV curable polymer using soft UV-nanoimprint lithography. Without using an expensive nanofabrication tool, our proposed technique can fabricate nanosquare array over an area of \(1 \times 1 \text{ cm}^2\) with individual nanosquare having a feature size of about \(383 \text{ nm} \times 354 \text{ nm} \times 70 \text{ nm}\). We believe that our proposed MF-TNIL represents a promising nanofabrication technique that will allow fabricating various types of nanostructures for their applications in developing sensors, anti-reflective surfaces, self-cleaning surfaces, etc.

1. Introduction

In recent years, artificially fabricated nanostructures have been employed in various domains of modern technologies like nanoelectronics, optoelectronics, color filler electrodes, security hologram, high-density magnetic storage, nano-electro-mechanical systems (NEMS), energy harvesting, sensing, and diagnostic devices [1–11]. The rapid fabrication of nanostructures over a large area at low-cost remains one of the biggest challenges with traditional nanofabrication techniques, including electron beam lithography, focused ion beam lithography, X-ray lithography, ion projection lithography, deep-UV projection lithography, and so on [4, 6, 12, 13]. Several unconventional nanofabrication techniques have been proposed to overcome the limitations encountered in conventional nanofabrication techniques [14, 15]. These techniques include micro-contact printing (µ-CP), self-assembly, dip-pen lithography, nanoimprint lithography, colloidal lithography, scanning probe microscope lithography, etc [16–24]. Among these techniques, nanoimprint lithography (NIL) represents the most promising, inexpensive and rapid nanofabrication technique that allows nanostructure fabrication over a large sample area. Earlier reports have shown that the NIL technique can fabricate nanostructures having features of lines and dots down to 10 nm resolution [19, 25]. NIL technique typically employed either thermal/light-sensitive polymer film to replicate the nanostructure from the master stamp. Light assisted NIL (i.e., UV-NIL) technique has been extensively employed for nanostructure replication; however, it has limitations to use an opaque master stamp in the replication process [25–29]. Whereas thermal nanoimprint lithography (T-NIL) provide a better alternative to employed both transparent and opaque master stamp to replicate as well as fabrication of nanostructure via sequential imprinting process. T-NIL technique employed thermoplastic materials such as poly (methyl methacrylate) (PMMA), poly (tetrafluoroethylene) (PTFE), polystyrene (PS), polycarbonate (PC), etc as a resist layer to transfer the nanostructures from a hard or soft stamp [28, 30]. Also, T-NIL technique enables to fabricate nanostructures on sol-gel oxide and silica films [31–36]. So far, most of the reported T-NIL techniques have adopted either solid parallel-plate (SPP) press or air
cushion press (ACP) mechanism for pressing the stamp over a thermoplastic polymer film [37]. However, the SPP mechanism suffers drawbacks like high imprint pressure requirements, non-conformal contact, non-uniform applied force, and pressure distribution, stamp-substrate experience share, and rotation stress. Also, the ACP mechanism needs a pressure chamber in the imprinting process, which adds complexity to system design and operation in multilayer alignment and step-and-repeat operation [37]. To address some of the above drawbacks, electrostatic force-assisted nanoimprint lithography (EFAN) was introduced that exploits electrostatic force between a stamp and substrate to pattern the nanostructures on the resist layer coated on the substrate by applying a voltage between them [38]. EFAN technique can patterned grating structure with 200 nm pitch over 100 mm diameter wafer with very high uniformity. However, EFAN technique is only limited to patterned the nanostructure on a resist layer coated on a conducting substrate. Further, the magnetic force was exploited to direct imprint the microstructure pyramids array on PMMA resist placed between a Nickel stamp and a heatable electromagnetic plate [39]. The idea was extended to pattern microstructure grating on UV resin over polycarbonate film using a magnetic PDMS stamp on a continuous roller magnetic platform under UV light [40]. A similar methodology was further adopted in the \( \mu \)-CP technique to print homogeneous and uniform fluorescent ink down to 10 \( \mu \)m linewidth [41]. The magnetic force assisted direct imprint, or \( \mu \)-CP process has the advantage of maintaining uniform imprinting pressure by precisely controlling the magnetic force of the electromagnet. It was reported that the uniform magnetic imprint pressure could overcome uneven press in the SPP technique, and the imprinting process does not require a pressure chamber, unlike the ACP technique. However, the fabrication of highly smooth and uniform nanoscale features on the Nickel stamp involves a prolonged preparation process and careful control. Also, the preparation of a magnetic PDMS stamp demands a homogeneous mixture of highly viscous PDMS polymer with iron particles, which is a big challenge. A non-homogeneous magnetic PDMS stamp will create non-uniform magnetic forces and subsequently affect the uniformity of the imprinted microstructure or ink on the substrate. The limitations mentioned above suggested that it is desirable to have a non-magnetic imprinting stamp in the magnetic force assisted nanoimprinting process, and it has not been realized so far. In this letter, we introduced an in-house developed magnetic force assisted thermal nanoimprint lithography (MF-TNIL) that allows cost-effective fabrication of 2D nanostructure array template with dimension down to 350 nm via sequential imprinting of a linear nanograting PDMS stamp. The fabricated templates were used to prepared highly uniform 2D nanosquare array over an area of \( 1 \times 1 \) cm\(^2\) via soft UV-NIL technique. The minimum feature of the 2D nanosquare depends on the slit-width of the linear nanograting. We believed that by employing very small slit-width linear nanograting, one could achieve a nanostructure feature down to 50 nm, which we intend to do in the future.

2. Materials and methods

2.1. Instrumentation of MF-TNIL

Our proposed MF-TNIL setup consists of a finely polished chrome-plated iron plate (called as iron plate), whose backside is attached to a customized silicone heating pad that can heat up to 250 °C. The surface of the iron plate is attached to a resistance temperature detector (RTD) sensor, which allows controlling the surface temperature of the iron plate. The silicon heater and RTD sensor were connected to a proportional-integral-derivative (PID) controller to set the surface temperature of the iron plate at the desired temperature. The linear nanograting PDMS stamp was prepared from a new DVD purchased from a stationery shop. The replication process and fabrication of the PDMS stamp is given in our earlier report [42]. We use a laminated plastic sheet as thermoplastic material for the fabrication of nanostructure. The laminated plastic sheet has 250 \( \mu \)m thick coating of polyethylene vinyl acetate polymer over a polyethylene terephthalate (PET) sheet. Our proposed MF-TNIL technique exploits the magnetic pulling force of a circular disc Neodymium (N35) magnet having a diameter of 20 mm and a thickness of 15 mm with the iron plate. Considering the thickness of supporting magnetic plate, PDMS stamp, and laminated plastic sheet, the separation distance between the magnet and iron plate was found to be approximately 3 mm. The calculated effective magnetic pulling force to the iron plate surface kept at 3 mm distance away was approximately 31 N. With the contact surface area of about 3.14 \( \text{mm}^2 \), a magnetic pressure of approximately 9.87 N mm\(^{-2}\) is exerted uniformly on the iron plate surface beneath the magnet [43].

Since the diameter of the magnet is 20 mm, without considering the magnetic pressure from the edges of the magnet, it is expected to have uniform magnetic pressure within an area of 10 \( \times \) 10 mm\(^2\) on the iron plate surface. All the components were housed inside a closed vacuum chamber derived by a rotary vacuum pump. The vacuum chamber is optional, and one can simply use an enclosure to prevent the dust particles. The schematic of the proposed MF-TNIL with its components is shown in figure 1. It has to be noted that the use of permanent magnet in the current MF-TNIL setup limits precise control over the magnetic pressure. However,
there is a possibility to precisely control the magnetic pressure by employing an electromagnet in our MF-TNIL setup, which will be implemented in the future.

2.2. Fabrication of 2D nanosquare array

In the typical fabrication process, PDMS stamp, magnetic plate, and laminated plastic sheet were placed between the magnet and iron plate. In the first imprinting process, the temperature of the iron plate was set at 80 °C for 10 min under the mild vacuum of 780 mmHg, followed by another 10 min without vacuum. After that, the heater was cooled down to room temperature, and the PDMS stamp was carefully separated from the laminated plastic sheet. In the second imprinting process, the temperature of the iron plate was set at 60 °C, and the PDMS stamp was rotated about 90 degrees and subsequently pressed onto the pre-patterned linear nanograting structure following the same protocol mentioned above. After the second imprinting process, a 2D nanosquare array template was achieved, which was transferred to a UV-curable polymer film on the glass substrate via reversal soft-UV NIL process to obtained nanosquare array over an area of 1 × 1 cm². Figure 2 provides a schematic of the fabrication steps involved to prepare a 2D nanosquare array using our proposed MF-TNIL technique.
3. Results and discussions

Figure 3(a) shows a FESEM image consisting of both 1D linear grating obtained after the 1st nanoimprint, and 2D nanosquare array template after the 2nd nanoimprinting process. The yellow dotted light in figure 3(a) indicates the border between the 1st and 2nd imprinting process. Figure 3(b) provides a magnified view of the 2D nanosquare array template, and the final 2D nanosquare array prepared by the replication process using the soft-UV NIL process is shown in figure 3(c). The lateral size of an individual nanosquare post obtained from the FESEM image is about 383 nm × 354 nm. The slight mismatched in the lateral dimension of a single nanosquare post might be resulting from inaccurate rotation of PDMS stamp by 90 degrees during 2nd nanoimprinting process.

Figure 3(d) illustrates the larger area FESEM image of the fabricated 2D nanosquare array, and the photographic image of a prepared sample is given in the inset of figure 3(d). It is clearly seen that the light diffracted from 2D nanosquare array appears bluish color whereas the light diffracted from 1D linear grating portion reflects the aqua color. It is observed that the fabricated nanosquare array is highly uniform over a large area with minimal defects. The sharpness of the individual nanostructure features at the edges can be further improved by optimizing the fabrication parameters. Also, the surface topography and height profile of both 2D nanosquare array template and replicated 2D nanosquare array were further characterized using an atomic force microscope (AFM). Figure 4(a) shows the two-dimensional surface topography of the 2D nanosquare array template. The blue and red line in the image indicates two perpendicular axes on the top of the nanograting along which the height profile was measured, and the corresponding height profiles are shown in figure 5(a). The height profile reveals different ripple pattern on the top of the nanograting having an average height of about 60 nm along axis-1 (blue line), and 35 nm along axis-2 (red line), respectively.

Whereas, the height profile in the nanograting valley, i.e., along the axis-1 (green line) and axis-2 (magenta line) in figure 5(b) shows a very close match with an average height of about 70 nm (axis-1), and 60 nm (axis-2), respectively. The three-dimensional AFM topography shown in figure 4(b) illustrates the unequal distribution of heights in our fabricated 2D nanosquare array template. Figure 4(c) shows the AFM image of fabricated 2D nanosquare array (labelled as inverted) prepared by replication from 2D nanosquare array template on UV...
curable polymer via soft UV-NIL technique. Similarly, the height profile determined from the nanosquare post array along axis-1 (blue line) and axis-2 (red line) is shown in figure 5(c). It is seen from figure 5(c) that the height of the nanosquare post array along both axes is relatively equal, with an average height of about 70 nm similar to its template pattern shown in figure 5(b). Further, the height profile obtained in the valley region of figure 4(c) along axis-1 (green line) and axis-2 (pink line) also exhibits different height pattern in figure 5(d), which is indeed an inverted height profile of the template structure shown in figure 5(a).

Thus, our purposed MF-TNIL technique enables us to fabricate a 2D nanosquare array over a sample area of $1 \times 1$ cm$^2$ with an individual nanosquare size of approximately $383 \text{ nm} \times 354 \text{ nm} \times 70 \text{ nm}$ by employing a linear nanograting PDMS stamp on a laminated plastic sheet. By controlling and optimizing the fabrication parameters, the mismatched in height profiles along both perpendicular axes of the 2D nanosquare array template can be overcome. Subsequently, the fabricated 2D nanosquare array will have a uniform height of individual nanosquare post. The size of the nanostructure can be reduced further by using a linear nanograting stamp with smaller slit-width. We have also fabricated other 2D nanostructures consisting of elliptical and diamond shapes by varying the rotational angle of PDMS stamp during the 2nd nanoimprinting process. The results are provided in the supplementary information. The presented work focuses on demonstrating the proof-of-concept to develop the MF-TNIL technique that enables the fabrication of 2D nanostructures over a large sample area by sequential imprinting of a non-magnetic linear nanograting PDMS stamp, which is a rare attempt to the best of our knowledge. In the future, the existing MF-TNIL tool will employ an electromagnet with a magnetic sensor for precise controlling of imprinting pressure, which will help to standardized its efficiency, yield, and resolution.

4. Conclusions

In summary, we have reported the development of a magnetic force assisted thermal nanoimprint lithography that allows the fabrication of nanostructures over a sample area of $1 \times 1$ cm$^2$. The proposed technique allows fabricating 2D nanostructures using a linear nanograting stamp. Further, the size of the fabricated 2D nanosquare structure can be reduced by employing a customized linear nanograting stamp with smaller
slit-width. By employing a PDMS linear nanograting stamp prepared from a DVD, we can fabricate a 2D nanosquare array with an individual feature size of 383 nm × 354 nm × 70 nm on a laminated plastic sheet. We believed that our proposed MF-TNIL technique could be a promising candidate for cost-effective nanostructure fabrication for their potential applications in developing high-performance sensors, self-cleaning surfaces, anti-reflective surfaces, security holograms, supercapacitors, etc. Further, the proposed MF-TNIL technique will be additional NIL techniques reported to date.

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Data availability statement

The data that support the findings of this study are available from the corresponding author upon request.

ORCID iDs

Rakesh S Moirangthem  https://orcid.org/0000-0002-5628-0115

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