3D patterning by means of nanoimprinting, X-ray and two-photon lithography

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Abstract

Two lithographic techniques suitable for fabricating complex 3D structures with high spatial resolution are presented and discussed. The first one is based on the combined use of nanoimprint and X-ray lithography. Its technological potential has been demonstrated by patterning several types of structures with X-ray lithography on hexagonal array of hemispheres obtained previously by nanoimprinting. These consecutive steps give rise to an intersection-structure where the overall profile of high aspect ratio structures is enveloped by the original 3D imprinted profile. The second technique, two-photon lithography, is an intrinsic 3D lithography and has the highest potential for structuring 3D in the widest sense. The principle of this technology and experimental results in the field of nanomechanics and photonics will be presented.

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In the fast run toward device miniaturization, microelectronics has relied on planar lithography and layering of essentially 2D structures. Technological advances in micro- and nanoelectrome-
In the search for methods for 3D structuring of matter at sub-micron resolution level, several lithographic techniques have been explored. Electron beam lithography (EBL) for example can generate “gray-scale” profiles by control of the exposure dose. High resolution X-ray lithography (XRL) can replicate multilevel mask amplifying the thickness profile [8] and can generate complex 3D structures with multiple exposure at tilted angles [9]. Focused ion beam (FIB) lithography has shown capability for direct milling and for growth of hard materials [10]. Nanoimprint lithography (NIL) can mould 3D profiles [11].

All lithographies above have their own peculiarities and potentialities which in many cases are not completely exploited and cannot cover the entire spectrum of the fabrication needs.

In this paper, we present results about two techniques, the first based on the combined use of nanoimprinting and X-ray lithography and the other based on two-photon induced photopolymerization. Two-photon lithography has recently been established as a powerful tool for laser precision microfabrication since its first proposal [8] by which various 3D photonic devices and micro/nanomachine systems have been readily produced.

In this work, the combination of nanoimprint and X-ray lithography has been employed for fabricating non-conventional 3D polymer structures. The technological potential of this method is demonstrated by patterning with X-ray lithography several types of structures on hexagonal arrays of hemispheres previously obtained by nanoimprinting. The overall profile consists of high aspect ratio trenches and/or pillars modulated by slowly varying 3D structures defined by imprinting.

Both imprinting and X-ray lithography possess their own 3D patterning capabilities. NIL is a high resolution (sub-10 nm), low cost, high throughput technique that has intrinsically 3D replication potentiality. Fig. 1 shows for example an array of PMMA hemispheres closely packed in a 20 μm hexagonal lattice. The master used for NIL was fabricated by isotropic etching of a fused silica substrate to form an array of hemispherical cavities. The imprinting step was carried out onto a 6 μm thick 950 K poly(methyl-methacrylate) film on silicon, at a pressure of 20 MPa and a temperature of 210 °C. The imprinted structures are correctly reproduced on the entire area of the stamp (Fig. 1).

This result illustrates the capability of NIL to form smooth curved surfaces over large areas. Obviously, a large variety of master profiles can be transferred into polymers by NIL. However, some principle and practical limitations exist for arbitrary structures. For example, it would be difficult to fabricate arrays of pillars oriented in any direction differing from the normal to the substrate or any structure having overhanging parts. Their presence would make it impossible to separate the mould from the polymer in a non-destructive way. A second limitation to the 3D NIL patterning capabilities is related to the aspect ratio of the structures. Due to stresses produced by shear and tensile forces at the surfaces of micro- and nanostructures during the release of the master, high aspect ratio structures suffer high mechanical stresses and may easily break. At present, the highest aspect ratios that can obtained by NIL are ~3.

XRL does not share these limitations of NIL. In this respect, XRL is well known to provide aspect ratios attaining values of ~20 (for structures with μm scale resolution), and resolution that at its present status of development can go below 50 nm. Geometrically, the structures obtainable by XRL can be described as the intersection of the volume shadowed by a 2D pattern defined on a mask, with the volume of the resist film. As the 2D pattern of the mask can be projected in arbitrary directions with respect to the resist film, XRL allows defini-
tion also of tilted structures. Furthermore, by performing single or multiple exposure at tilted angles it has been possible to build complex 3D structures containing voids and overhanging parts [9].

In this paper we showed that performing a step of imprinting into a thermoplastic film and utilizing that pre-patterned polymer layer as a resist for X-ray lithography provides a flexible method to fabricate a wide class of complex small-scale 3D structures which easily overcomes most of the limitations of both NIL and XRL. All experiments described below have been carried out on PMMA since this is a very common material both as a resist for X-ray lithography and for imprinting. After the imprinting of an array of hemispheres as described above, X-ray exposure was performed selecting a medium hard spectrum energy window (from 800 to 2.3 keV, peaked at 1.6 keV) in order to facilitate the full exposure of the thickest (9 μm) part of the hemispheres. This ensures that the depth of the XRL patterning is completely independent of the local resist thickness. The X-ray masks consisted of 2 μm thick Si₃N₄ membranes carrying a variety of gold structures (array of dots, lines, zone plates) electroplated to a thickness in the range from 400 to 800 nm. The XRL exposures were performed at LILIT beam line [12]. Two examples of the combined use of NIL and XRL are shown in Figs. 2 and 3 where the mask patterns were exposed on the array of PMMA hemispheres (Fig. 1) with an aerial dose of 4000 mJ/cm². The structures were developed in a solution of methylisobutyl ketone (MIBK) and isopropyl alcohol (IPA) (1:3) for 4 min. The interesting aspect of this method is the possibility of superimposing structures with different spatial frequencies by the consecutive use of the two techniques. In particular we show the result of patterning high spatial frequency features by X-ray lithography onto low spatial frequency nanoimprinted 3D structures. Fig. 2 clearly show that the envelope of high aspect ratio pillars arranged on a 2 μm pitch square array precisely outlines the shape of the pre-patterned array of hemispheres. In a closer view (Fig. 2(c)) it appears that the pillars consist of a central column and an external ring with details at 100 nm scale and aspect ratios exceeding 10. This emphasizes that the local profile of the original NIL structure is preserved at the scale of single structures, as it

![Image](image_url)

Fig. 2. High spatial frequency features defined by XRL on low spatial frequency structures by NIL.

![Image](image_url)

Fig. 3. Zone plate structure superimposed to the 3D profile of an array of hemispheres.
can be easily recognized from the slope of the top of the pillars. We present also the results of the X-ray exposure of a zone plate (Fig. 3) on an imprinted array of hemispheres. The X-ray mask consisted of a 2 \( \mu \)m thick silicon nitrate membrane with 500 nm gold in the absorbing regions, giving a transmitted intensity contrast of 15:1 between transparent and absorbing regions. The high penetration depth of the X-rays makes the lithographic image almost insensitive to the thickness modulation of the pre-existing structure.

Although, Fig. 3(a)–(c) shows the results of a process that could be considered just as a lithography test, it shows that special optical elements containing refractive and diffractive components could be produced.

The second technology considered in this paper is two-photon photopolymerization. The basic idea is tightly focusing a femtosecond (fs) laser into a photopolymerizable resin and directly writing 3D patterns by focus or sample scanning. Due to the quadratic dependence of two-photon absorption (TPA) rate on laser power, photopolymerization (solidification) occurs only at the close vicinity of the focal spot. Then following the scanning locus, a solidified skeleton will be formed, which remains after the removal of un-solidified liquid resin [13]. With this method, various micromachines [14,15] and photonic crystals [13,16,17,19] have been readily produced with near-diffraction-limit 3D spatial resolutions.

Starting liquid materials could be converted into solid phase upon light exposure by photopolymerization [18,20]. Photopolymerization is usually concerned with creation of a polymer through a chain reaction initiated by light. Since most monomers and oligomers commonly employed do not possess initiating species with a sufficient quantum yield upon light exposure, it is necessary to introduce low-molecular-weight molecules called photoinitiators that start polymerization. A photosensitizer is also generally used, which has a large light absorbance and transfers the excitation to a photoinitiator. For all fabrications presented in this research, we used resins consisting of urethane acrylate monomer/oligomer and radical initiators. Photopolymerization is a photochemical reaction that occurs when photon energy is provided. Electronic transition energy for most initiator molecules corresponds to UV spectral range.

In particular, benzoyl chromophor is sensitive to near UV wavelength, and has a good photochemical reactivity, therefore utilized as common UV radical initiators. If the irradiation photon fluence is sufficiently high, e.g., by tightly focusing a fs laser, the probability of an electron simultaneously absorbing two photons is increased, and then TPA becomes practically useful.

Typical cross-sections for one- and two-photon processes are \( 10^{-6} \) cm\(^2\) and \( 10^{-50} \) cm\(^4\) s/photon, respectively. For producing sufficient photon flux density, it is essential to tightly confine laser pulses in both spatial and time domains. This, for the work presented in this article, was accomplished by a homemade system. A Titanium:Sapphire laser that operated in mode-lock at 76 MHz and 780 nm with a 150-fs pulsewidth is utilized as the exposure source. A two-galvano-mirror set moves the laser beam in the two horizontal dimensions, and a piezo stage moved the laser focus vertically, both controlled by a computer. The laser is focused into the resin by a high numerical aperture (NA \( \sim 1.4, \) oil immersion) objective lens. The single-lens focusing geometry naturally satisfies the requirement of pulse overlapping in both time and spatial domains. In this system, the utilization of short pulsewidth and tight focusing are critical for exciting sufficient amount of TPA and for achievement of high accuracy of fabrication. An average focal spot power of 1 mW under a 150 fs pulsewidth and 76 MHz repetition rate corresponds to a transient peak power of 20 GW/cm, or a photon flux density of \( 8 \times 10^{12} \) photon s\(^{-1}\) \( \mu \)m\(^2\).

Laser scanning is the step to convert pre-designed CAD pattern to a resist structure. We used two basic modes for direct laser scanning, i.e., raster-scan mode and vector-scan mode. In the raster mode, all voxels in a cubic volume that contains the microstructure are scanned by the actual/virtual focal spot, depending on the shutter ON/OFF (actual/virtual). In the vector mode, the laser focus directly traces the profile to be defined, and requires a smaller number of voxels. Depending on structures, alternations and combina-
tion of the these two basic scanning modes could be used. Experimentally we fabricated the same object using the two modes. The microbull in Fig. 4(a) was produced using a layer-by-layer raster-scanning scheme, i.e., all voxels consisting of the bull were exposed point-by-point, line-by-line, and layer-by-layer by a two-photon process. As a result, it took 3 h to complete the manufacturing. If we make a detailed analysis on the bull structure, it is found that the entire bull consists of $2 \times 10^6$ voxels. However, the bull profile can be well defined with only 5% of them. As a test, the bull was written once more by using the vector scanning. Astonishingly, we find it possible to depict the same structure within 13 min (Fig. 4(b)). In both cases the scanning step in 3D was 50 nm, the latter, however, the fabrication time in vector scan was reduced by more than 90%. The TPA produced bull crust was self-supported, standing on glass substrate either in liquid or in air. To avoid possible distortion, we further solidified the structure under a mercury lamp, which is a single-photon exposure process.

Two-photon photopolymerization becomes conspicuous in the race for developing 3D photonic crystals (PhCs) due to its intrinsic 3D processing capability [17,19,22] and the potential to comprise materials of various properties like fluorescence emission and refractive index tuning for device functions. Since the demonstration of a photonic bandgap (PBG) in two-photon photopolymerized PhCs [18,20] much research effort has been attracted to laser nanofabrication of polymer photonic lattices [21,23]. However, most efforts result in no presence of the PBG effect. To solve this problem, a high-reproducibility and high-fidelity writing scheme was recently proposed. It utilizes finely quantified pixels and subdiffraction-limited voxels to precisely depict the shape and size of elements, and employs a pre-compensation method to correct the structural deformation brought on by polymerization shrinkage. In order to maximize the PBG effect for given component materials, more complicated lattices are generally required for the purpose of tailoring the density of photon states. For example, rod overlapped fct, diamond, and distorted diamond open the largest full band gap between the second and the third photonic bands [24]. Realization of these structures with sub-micron feature sizes is arduous by conventional techniques, but within the scope of two-photon photopolymerization since more complicated 3D nanomachines have been created [17,19,26,27]. However, related work has not been reported yet. As the first step toward arbitrary-lattice 3D PhCs, we herein report a covalent-bond type diamond crystal with pronounced band-gap effect. Fig. 5(a) illustrates the diamond structure, which is composed of two interpenetrating fcc lattices, one displaced 1/4 of a lattice constant, $L$, in each direction from the other. Each atom is tetrahedrally coordinated with four other atoms in the other sublattice. Examples of electronic crystals with the diamond crystal structure are diamond, silicon, and germanium. In PhCs, the crystal atoms are represented as photonic atoms.

Fig. 4. (a) SEM images of a microbull structure produced by raster scanning, where all voxels were formed by two-photon exposure. (b) The same structure but produced by vector scanning. Only the crust was defined by the two-photon process and the inside was solidified by illumination under an mercury lamp.
Different from the case in a solid matrix [28], inside which atoms are inlaid or, in situ fixed where they are positioned, photonic atoms polymerized from liquids need connection. The linking bridges, or covalent bonds in a stick-and-ball molecular model, are actually the major component in attained crystal configuration. Rather than image observation, the accomplishment of high-quality PhCs has been confirmed by their band-gap effect. Shown in Fig. 6 are the transmission spectra of the demonstrated structure (Fig. 5(c)) as well as a similar lattice with \( A = 3.0 \) \( \mu \)m, both normalized to the transmission of a featureless solidified resin bulk. The transmission minima are at 3790 cm\(^{-1}\) (\( \lambda = 2.6 \) \( \mu \)m) and 3100 cm\(^{-1}\) (\( \lambda = 3.2 \) \( \mu \)m), respectively. They occur at the identical normalized frequency of 1.05, as defined by \( \lambda / A \) showing the linear scaling performance of the diamond lattices. This implies that the band-gap effect of 1.55 \( \mu \)m-lattice PhCs, of which the fabrication is, in principle, of no problem due to the 100 nm lateral spatial resolution, should occur approximately at the communication wavelength of 1.55 \( \mu \)m. A complete PBG is not expected from these crystals since the refractive index contrast (\( \Delta n = 1.5 \)) is far lower than that necessary for the current lattice to open a full band gap (\( \Delta n = 2.0 \)) [25], however, the single-period transmission attenuation as large as 35% indicates the necessity to select a suitable lattice type for a strong PBG effect. A natural extension of this work is the enhancement of refractive index of photopolymerizable materials to above 2.0, which has been proved possible from our preliminary research.

The techniques explored in this paper allows the realization of a very broad class of 3D micro- and nano-objects. In absolute, the technique that allows the fabrication of the most general topologies and morphologies is two-photon lithography. Unfortunately, it suffers from a low throughput due to the sequential nature of the laser scanning process. In order to limit this problem, ongoing efforts are devoted to increasing the parallelism of the technique, as for example by using dynamic diffractive optics to generate and scan a distribu-

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**Fig. 5.** Stick-and-ball model of unit cells of diamond lattices. (a) Schematic illustration, and (b) two-photon photopolymerized \( 2 \times 1 \) primitive. Letters denote vertical atomic coordinates: \( A(0), B(1/4), C(1/2), D(3/4) \), and \( A'(4/4) \). (c) Two-photon photopolymerized diamond PhCs. A \( 8 \times 8 \times 2 \) period crystal, from which a PBG was measured.

**Fig. 6.** Transmission spectra of diamond-lattice PhCs with periods of 2.5 and 3.0 \( \mu \)m. The gray curve is from the uniformly polymerized resin film, to which the two spectra were normalized.
tion of independent focal points. The other techniques considered in the paper, nanoimprint, X-ray lithographies and combination thereof are instead parallel techniques. In particular, while maintaining their individual characteristics of highly parallel high-throughput methods the consecutive use of nanoimprint, X-ray lithographies greatly enlarges the possibilities for 3D structuring. Although, still this combination cannot compete with the versatility of two-photon lithography they could become in future very useful in several domains of micro- and nanotechnology. It would make it possible for example to conceive and to realize new innovative devices that exploit diffractive and refractive phenomena for a better tailoring of the light propagation.

In the next future it will be attempted the combination of NIL, XRL and TPA. In fact due to the alignment capabilities already available in XRL steppers, it is in principle possible to write very complex 3D structures in a mix and match strategy by using all three fabrication techniques.

Photonics, microfluidics for diagnostic biophysics and drug delivery, new hybrid optics, will be the fields where we will first attempt the merging of these three fabrication methods.

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