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Solvent-free optical recording of structural colours on pre-imprinted photocrosslinkable nanostructures

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Abstract
Optical digital information storage media, despite their ever-increasing storage capacity and data transfer rate, are vulnerable to the potential risk of turning inaccessible. For this reason, long-term eye-readable full-colour optical archival storage is in high demand for preserving valuable information from cultural, intellectual, and scholarly resources. However, the concurrent requirements in recording colours inexpensively and precisely, and preserving colours for the very long term (for at least 100 years), have not yet been met by existing storage techniques. Structural colours hold the promise to overcome such challenges. However, there is still the lack of an inexpensive, rapid, reliable, and solvent-free optical patterning technique for recording structural colours. In this paper, we introduce an enabling technique based on optical and thermal patterning of nanoimprinted SU-8 nanocone arrays. Using photocrosslinking and thermoplastic flow of SU-8, diffractive structural colours of nanocone arrays are recorded using ultra-violet (UV) exposure followed by the thermal development and reshaping of nanocones. Different thermal treatment procedures in reshaping nanocones are investigated and compared, and two-step progressive baking is found to allow the controllable reshaping of nanocones. The height of the nanocones and brightness of diffractive colours are modulated by varying the UV exposure dose to enable grey-scale patterning. An example of recorded full-colour image through half-tone patterning is also demonstrated. The presented technique requires only low-power continuous-wave UV light and is very promising to be adopted for professional and consumer archival storage applications.

1. Introduction
Optical patterning techniques, owing to their excellent resolution, throughput, and yields, have been at the forefront of the microdevice manufacturing industry for a few decades. To continue scaling down semiconductor devices as predicted by Moore’s law and to enable mass production of novel nanodevices and nanofeatures, intensive research and development have been driven to push the resolution limit into nanoscale. State-of-the-art immersion photolithography equipment implements a deep ultra-violet (UV) light (193 nm wavelength) and high numerical aperture lens immersed in liquid for volume production at the sub-10 nm node [1]. A plasmonic lens can be used to focus light into a tight hot spot much smaller than the diffraction limit to expose the photore sist film that is accurately positioned within the optical near-field [2, 3]. Resist kinetics are modulated through a writing beam and an assisting confining beam to fabricate deep subwavelength patterns [4–7]. Despite continuous breakthroughs in patterning resolution, the high equipment cost and complicated system construction have limited their practical applications to those industries that require super-high-resolution and ultra-low defect rate, such as leading-edge CMOS microchip manufacturing.
In applications where the defects are relatively less critical and a high-speed, large-volume and low-cost fabrication process is indispensable, nanostructures can be patterned by combining conventional photolithography with other high-throughput nanoscale patterning techniques. Nanoimprint lithography (NIL) can rapidly replicate surface-relief nanostructures from a stamp, by mechanical moulding of polymer through a thermal or UV nanoimprint process [8, 9]. NIL in roll-to-roll schemes, owing to its continuous and high-speed processing, and low manufacturing cost, has already been widely adopted to replicate nanostructures for mass production [10, 11]. Cheng and Guo have introduced a combined-nanoimprint-and-photolithography (CNP) to fabricate residue-free high aspect ratio nanopatterns by placing a light-blocking metal layer on top of the mould protrusions [12]. The metal layer functions as a photomask in the photolithography process to enable complete removal of negative-tone photoresist after exposure and development. Zhang et al have demonstrated the imprinting of high aspect ratio micropillars onto SU-8 film with pillar height controlled through capillary force [13]. They also reported a unique photolithography patterning method incorporating a solvent-free thermal development process: after photolithography exposure on SU-8 micropillars, the sample is baked above the glass transition temperature of SU-8 to flatten unexposed SU-8 micropillars using thermoplastic flow. In previous work of our group, we introduced a structural colour printing technique using photolithography to fabricate residue-free high aspect ratio nanostructures by placing a light-blocking metal layer on top of the mould protrusions [14]. A desirable colour image can be formed based on the corresponding nanostructures, which are selected through the patterned blocking layer, using UV NIL.

Optical storage, as one of the most widely used optical patterning techniques, optically records and reads out high-density information on storage media. Traditional optical storage media, usually in disc format (blu-ray discs, for example), are inexpensive and removable, and allow random access to data with a reasonable data transfer rate. In the past few decades, the data storage capacity of optical discs has been progressively improving, primarily through applying smaller pits in a higher density and recording data on more stacked layers. Nowadays, a blu-ray disc with a track pitch of 320 nm and minimum pit size of about 117 nm, can store 32 gigabytes of data per layer and up to four layers per disc [15]. For the next-generation main-stream optical storage technique, one most promising candidate is 3D optical storage, where ultra-high-density data are stored in a 3D volume of a recording medium. 3D optical bit storage [16] and volume holographic data storage [17] are two examples. 3D optical bit storage uses pulsed or continuous-wave laser beams to record data in multiple layers of a 3D recording medium. The recording process usually implements a two-photon process to modify the optical property of the recording material that is localised to the focal volume of the laser beams. The binary data in bit wise are essentially stored as the laser-induced contrast in optical properties, for example, laser-bleached fluorescence [18, 19], laser-induced fluorescence [16, 20–23], and laser-induced change in refractive index [24]. The storage density of 3D optical bit can be further extended by multiplexing data using other orthogonal dimensions. Photothermal patterning has been used to reshape plasmonic nanorods that are selective to wavelengths and polarisations to enable 5D optical storage [25, 26]. Self-assembled nanogratings written by ultra-fast lasers in fused silica exhibit birefringence and the slow axis orientation and strength of retardance have been used to encode data in addition to three spatial dimensions [27, 28]. Storage capacity of 360 terabytes per disc (recorded in 1200 layers in a standard-sized disc with 1.2 mm thickness) has been claimed [28]. Holographic data storage records page-wise binary data in volume holograms using interference between a data-encoded signal beam and a reference beam [17, 29]. Multiple data pages, with each page containing more than a million bits, can be superimposed within the same volume to achieve ultra-high storage density (theoretical density of about 40 terabits inch$^{-2}$) [29]. A holographic drive with a data storage density of 712 gigabits inch$^{-2}$, using monocular architecture and a blue laser, has been demonstrated for consumer applications [30].

Long-term optical archival storage is in high demand for preserving important information for at least 50 years, or more preferably for several centuries, without the necessity of frequent refreshing or migration of the information onto new storage media. Nowadays, in the information age, industries and organisations such as financial institutions, health services, governments, and cloud data centres handling huge amounts of data and internet information, require high-level information security. Hence, a colossal volume of valuable data and information must be reliably stored on off-line backups to minimise the risk of loss or alteration due to internet-based attack, unstable storage environment, or other potential dangers. Optical archival storage requires removable write-once–read-many (WORM)-type media. For conveniently accessing the stored information and preserving the information offline for security purposes, the archival storage media must be removable. The characteristic of write-once can prevent altering or erasing the stored information. Ordinary WORM-type optical discs implement organic dyes in recording layers [31–33]. However, degradation and breakdown of the dye materials under light, heat, and humidity pose serious risks in losing data after no more than one decade [34]. Specially formulated archival-grade discs, such as Verbatim MDisc blu-ray discs, implement a ‘stone-like’ inorganic recording layer (very resistant to light, heat, and humidity) capable of preserving data for 1000 years [35]. The aforementioned 3D optical bit storage in fused silica can remain thermally stable up to 1000 °C and
therefore has a virtually unlimited life-time at room temperature [28]. Holographic data storage with a projected life-time of more than 50 years is also an emerging candidate for archival storage [29].

All of the above-mentioned digital-type optical archival storage media, either commercially available or under on-going development, have one serious drawback in common, i.e. being vulnerable to technological obsolescence [36, 37]. Information stored in purely digital forms must be read out using special hardware and software. Due to the fast progress in computer technology, newly developed hardware and software seldom possess multi-generational backward compatibility. As a result, digital information stored in the best archival storage media nowadays will very likely turn inaccessible after decades (even though the data can be kept completely intact), simply because the appropriate reader device or software becomes obsolete. For this reason, a huge volume of data must be periodically refreshed or migrated onto up-to-date storage media and digital formats to keep pace with the technological advance of storage techniques. For information of a purely digital nature, such challenges are unavoidable and have to be overcome with a permanent and sustainable solution, which is still unclear. For other types of information, which originally appear in other forms, but are digitised for computer processing or digital storage purposes, an apparent and seemingly long-term solution is to store such information on eye-readable optical archival storage media [36, 38]. The term ‘eye-readable’ denotes that the stored information can be directly viewed by human eyes or with the assistance of a magnifying lens, without using other special hardware or software. For example, snapshots of historical manuscripts and pictures, government records, legal papers, photographs, and motion pictures can be stored into eye-readable media to be preserved for centuries. Such stored information can always be accessed by future generations whenever needed, which is of vital importance for preserving cultural, intellectual, and scholarly resources for the sake of human civilisation.

One technical challenge in eye-readable archival storage is the difficulty in storing colours, which requires recording colours with high resolution and fidelity, and, in the meanwhile, preserving colours for the very long term. Eye-readable colours can be directly recorded onto photographic colour microfilms for archival purposes. However, the storage life-time is sensitive to the storage condition due to photobleaching. For example, positive colour archival microfilm Ilfochrome (also known as Cibachrome) was projected to preserve colours for over 500 years if stored under dark and cold conditions. However, if such films are kept displayed under ambient environment with light, colours begin to fade after about 29 years, according to Wilhelm et al [39]. Other existing eye-readable archival storage with a longer life-time can only record grey-scale black and white images. Black and white microfilms, based on high-resolution photographic emulsion, have been used for archiving since the year 1938, and are projected to last for hundreds of years, according to the National Archives (United States) [40]. The digital optical tape system (DOTS), an archival storage in optical tape format developed by Group 47 Inc., uses a special phase-change material, mainly composed of alloy of antimony and tin, to store digital data and black and white images for at least 100 years [38, 41, 42]. These black and white storage media can be used for recording information of colours by separating colours into red, green, and blue channels and storing channels individually [42]. However, such recorded colours are not directly eye-readable and require special reader devices or software to be reconstructed from three channels. Some 3D optical bit techniques are capable of displaying colour images in the readout, but only single fluorescent colour is available [22, 23].

Considering the limitations in existing archival storage techniques, a better solution in recording and preserving eye-readable full colours is in high demand. We believe structural colour printing holds the promise for realising long-term full-colour eye-readable optical archival storage. Unlike colours from dyes or pigments, structural colours originate from the interaction of light with physical structures in microscale or nanoscale shapes, rather than the colours associated with the material itself. Structural colours, by nature, are very resistant to oxidation and other environmental influences, and can enable never-fading colours [43–46]. For eye-readable full colours, resolution and colour fidelity are two key aspects. Resolution is mainly determined by the fabrication technique and colour fidelity relies on the pixel chromaticity for a chosen colour space. Structural colours possess appealing advantages in terms of resolution [43], chromaticity [47], and being eco-friendly [45]. In order to apply structural colours in eye-readable archival storage media, the major hurdle is the lack of an inexpensive, rapid, reliable, and solvent-free recording technique. The solvent-free feature is usually mandatory for a storage technique to be widely adopted for practical use. Direct patterning of structural colours requires fabrication tools with nanoscale resolution. Electron beam lithography (EBL) can pattern structural colours in ultra-high resolution (about 100 000 DPI) [43]. However, the writing speed is too slow for archival storage purposes. Direct optical nanopatterning techniques can potentially record structural colours with sufficient throughput [4–7]. However, the adoption of such expensive systems for archival storage purposes remains impractical in the near future. Other scalable techniques capable of printing full-colour structural colours, including laser interference [48], photolithography in combination with other techniques [14, 49, 50], colloidal crystallisation [49, 51, 52], colloidal assembly [53], and inkjet printing [54–56], all require certain wet chemical processing.
To enable structural-colour-based long-term eye-readable optical archival storage, efficient structural colour recording techniques, essentially patterning techniques of nanostructures, must be invented and studied. In this article, we introduce a solvent-free, optical, and thermal 2D patterning technique for recording structural colours on pre-imprinted nanostructures using the photocrosslinking and thermoplastic flow of SU-8. This technique combines high-throughput NIL and photolithography to enable scalable and cost-effective patterning of nanostructures. For the sake of convenience, this technique is termed as ‘NETT’, where the acronym stands for the main steps in the recording process: nanoimprint, exposure, and thermal treatment.

2. Overview of NETT recording process

As shown in figure 1, a NETT recording process consists of five major steps as described below: (1) a master stamp with a surface relief of nanowell arrays on quartz is fabricated, as shown in figures 1(a) and (e). (2) Nanocone arrays are replicated from the stamp onto an SU-8 film using thermal NIL (figures 1(b) and (f)). The nanocone arrays used in this work function as 2D gratings to display diffractive colours. By adjusting the grating periods, nanocone arrays can display red, green, or blue diffractive colours. The pattern of imprinted nanocone arrays is comprised of periodic arrays of R, G, and B pixel bands, which have nanocone arrays for red, green, and blue diffractive colour, respectively. Such a pattern is generic for all recordable colours through the mixing of red, green, and blue primary colours, a similar strategy used in [14, 55–57]. (3) Photolithography using UV light exposes a user-defined pattern, according to the desirable colour pattern, onto the nanocones (figure 1(c)). Photolithography exposure can be carried out through masked exposure from a UV lamp or a scanning UV laser beam. (4) In this step, which is the key to NETT, thermal development and reshaping (TDR) of the nanocones takes place by heating the sample (figures 1(d), (g) and (h)). TDR utilises crosslinking of UV-exposed SU-8 and thermoplastic flow of SU-8 when heated above its glass transition temperature. Under an ambient environment, unexposed (uncrosslinked) SU-8 has a glass transition temperature \( T_g \) of about 50 °C, while fully crosslinked SU-8 is higher than 200 °C [58]. When the sample temperature is above 50 °C, unexposed SU-8 nanocones flow into a flat film (figure 1(h)), while UV-exposed SU-8 is crosslinked under heat and those exposed nanocones remain on the sample surface (figure 1(g)) [13]. Compared to those as-imprinted nanocones (figure 1(f)), the exposed and crosslinked nanocones (figure 1(g)) are reshaped into shorter nanocones due to the very viscous flow of SU-8 before it is fully crosslinked. As a result of TDR, the generic pattern of nanocone arrays turns into a customised pattern to store user-defined colours in R, G, and B pixel bands. It should be noted that the height of the reshaped nanocones depends on the heating procedure and UV exposure dose, which will be presented in detail in later sections of this article. (5) The final step (not shown in figure 1) fixes the pattern of nanostructures using flood UV exposure followed by baking to fully crosslink the entire SU-8 film. No structural change occurs in the already photocrosslinked nanocones during the final step.

![Figure 1. NETT recording on SU-8 nanostructure arrays. (a) A quartz master stamp with surface relief of nanowell arrays. (b) SU-8 nanocone arrays imprinted from the master stamp using thermal NIL. (c) Photolithography exposure on the nanocone array using UV light. (d) Thermal development and reshaping by heating the sample. The UV-exposed nanocones are crosslinked and reshaped into shorter nanocones, while unexposed nanocones flow into a flat film. Atomic force microscope (AFM) image of (e) a nanowell array on the master stamp, (f) an imprinted SU-8 nanocone array, (g) an exposed and crosslinked SU-8 nanocone array, and (h) a thermally-flattened unexposed nanocone array. The colour bars from black to white in the AFM images span linearly from 0–450 nm in height. (e)–(h) were acquired from the nanocone arrays in the G pixel band, which gives green diffractive colour at the default lighting and viewing angle. (g) and (h) were acquired from the fully exposed and unexposed region, respectively, from a sample that was treated with two-step baking after exposure.](image-url)
3. Methods

Detailed experimental conditions and procedures used in studying the NETT recording process are provided in this section.

3.1. Nanoimprint of SU-8 nanocone arrays

A schematic of the fabrication process of SU-8 nanocone arrays is shown in figure 2. A nanostructured quartz stamp was first fabricated using laser interference lithography (LIL) and reactive ion etching (RIE). A quartz wafer was cleaned and evaporated with 100 nm thick aluminium (Al) film. A photoresist layer was spin-coated on top of an Al layer (step (i)) and then exposed with 2D periodic nanopatterns using LIL (step (ii)). After developing the photoresist (step (iii)), the patterned photoresist layer was used as a mask to transfer the pattern into the Al layer using RIE (step (iv)). After stripping the photoresist using oxygen plasma (step (v)), the patterned Al layer was used as a mask to etch into the quartz surface using RIE (SF6/CHF3/O2 gas, step (vi)).

Owing to the lateral erosion of the Al mask during the etching process, the nanoholes in the Al layer were gradually enlarged and nanowells of tapered sidewalls on a quartz surface were obtained. After RIE, the nanostructured quartz stamp was thoroughly cleaned with chemicals and oxygen plasma (step (vii)).

The fabricated quartz stamp surface was then treated with an anti-adhesive layer of perfluorodecyltrichlorosilane for easy release in thermal NIL to be used in later steps. SU-8 2005 (MicroChem Corp.) was spin-coated onto a silicon wafer and soft-baked at 95 °C for 30 min to evaporate all solvents (step (viii)). The film thickness was about 5 μm. Thermal NIL was used to imprint the quartz stamp onto the SU-8 film (step (ix)). The thermal NIL process was carried out in an air cushion press system (NX-2000, Nanonex Corp.). The stamping condition was 40 PSI pressure and 95 °C temperature for 3 min. After thermal NIL, the quartz stamp was separated from the SU-8 film to obtain an SU-8 nanocone array (step (x)).

Figure 3(a) shows the schematic layout of the R, G, and B pixel bands in the thermally imprinted SU-8 nanocone arrays. The pixel bands are repeated in a 1D periodic array with 25 μm centre-to-centre distance. Each effective pixel with a size of 75 × 75 μm consists of three subpixels (R, G, and B subpixels) with each being 25 × 75 μm. As shown in the reflection microscope image (figure 3(b)), there are slight variations in the width of individual pixel bands, which is an artefact of the LIL process. An AFM image of the as-imprinted nanocone arrays on the R, G, and B bands is shown in figures 3(c), (d), and (e), respectively. The as-imprinted 2D nanocone arrays have grating periods of 650, 560, and 465 nm, nanocone height around 300, 224, and 188 nm, and nanocone base diameter around 630, 560, and 460 nm for the R, G, and B pixel bands, respectively.

Nanocone arrays used in this work function as 2D gratings to diffract light of a certain spectral band into the directions determined by the grating orders. As shown in figure 3(f), consider a white light incident at an angle α from a medium of refractive index n (usually air, n = 1) and a nanocone array having grating period λ. Light of wavelength λ carried in the mth grating order is diffracted into the angle β. The relationship of λ and β is given.
by \( n \Lambda (\sin \alpha - \sin \beta) = m \lambda \). The grating periods of the nanocone arrays are tuned so that at a given lighting and viewing angle, the R, G, and B nanocone arrays gives red, green, and blue diffractive colour, respectively, at the same angle. Consider light incident angle \( \alpha = 60^\circ \) and viewing angle \( \beta = -7^\circ \). By calculation under this configuration, the nanocone arrays on the R, G, and B bands have first-order diffraction peak wavelengths at 642, 553, and 459 nm, respectively.

3.2. UV exposure
Grey-scale UV exposure onto SU-8 nanocone arrays was carried out using a laser writer (μPG101, Heidelberg Instruments) equipped with a UV diode laser (375 nm wavelength, 18 mW maximum power). The writing process implemented an energy factor equal to 1 and the maximum exposure dose was about 400 mJ cm\(^{-2}\). A grey-scale exposure pattern was defined in a grey-scale bitmap image where each pixel is an unsigned 8-bit integer with value from 0–100 to define the percentage of the exposure dose. For example, a pixel with a value of ‘80’ is to be exposed to 80% of maximum dose.

Contact photolithography UV exposure on SU-8 nanocone arrays was carried out using a mask aligner (ABM Inc.). The photomask pattern was generated using a custom-written MATLAB script, as demonstrated in supplementary figure S2 available online at stacks.iop.org/NANOF/1/025001/mmedia. For UV exposure, the photomask was aligned with the pixel bands and the pattern was exposed onto SU-8 nanocone arrays using i-line (365 nm wavelength) with an exposure dose of about 336 mJ cm\(^{-2}\).

3.3. Thermal treatment
Thermal treatment was done on a hotplate surface to bake the sample at the set temperature for the set amount of time. Two different baking procedures have been experimented: (1) one-step direct baking; (2) two-step progressive baking. For one-step direct baking, the sample was directly loaded onto a hotplate stabilised at 95 °C to bake for 10 min. For two-step progressive baking, the sample was first baked at 45 °C for 2 h and then the temperature of the hotplate was raised at a ramp rate of about 20 °C min\(^{-1}\) to 95 °C to bake the sample for another 10 min at 95 °C. All thermal treatment processes were carried out inside a class 100 cleanroom environment with room temperature around 20 °C and relative humidity about 45%.

3.4. Optical characterisation
Prior to optical characterisation, the sample surface with crosslinked SU-8 nanostructures was first coated with 35 nm thick Al film using sputter coating to enhance diffraction. Figure 3(g) shows a schematic of the optical setup for measuring diffraction efficiency. The sample is mounted on a rotation stage to control the light
incidence angle and light collection angle. Broadband white light from a fibre-connected light source is collimated by collimator C1. The output parallel beam is then incident onto the sample surface and the diffracted light is collected by a microscope objective lens (4X Olympus Plan Achromat Objective, numerical aperture = 0.10, working distance = 18.5 mm). Behind the objective lens, an iris II reduces the numerical aperture to about 0.025. The diffracted light is split by a beam splitter BS (50:50 split ratio). Half of the diffracted light is recorded by a digital colour camera to give a microscope colour image of the diffractive colours. The other half is first focused onto an iris I2 for selecting a circular spot from the sample surface and then the transmitted light is coupled into a fibre-connected spectrometer to record an intensity spectrum \( I_s(\lambda) \). The reference spectrum \( I_{ref}(\lambda) \) is measured by loading a flat mirror under the objective lens and recording the mirror reflection of the source beam. The diffraction efficiency from a spot selected by iris I2 is given by

\[
\eta_{ROI} = \frac{I_s(\lambda) - I_{ref}(\lambda)}{I_s(\lambda) - I_{dark}(\lambda)},
\]

where \( I_{dark}(\lambda) \) is a dark spectrum recorded when the light source is switched off. The normalised diffraction efficiency is given by \( \eta_{norm} = \frac{\eta_{ROI}}{R_A} \), where \( R_A \) is the area ratio that the nanostructures occupy within the selected spot. \( R_A \) is calculated by image processing of the collected microscope colour image. \( \eta_{norm} \) is a property of a nanostructure array, independent from the array size. In all optical characterisation results presented in this article, the light incident angle \( \alpha = 60^\circ \) and viewing angle \( \beta = -7^\circ \).

Colour photos of the samples were captured using a digital camera (Canon 5D0) with a 50 mm lens. The aperture of the camera was set to be \( f/16 \) to match closely with the numerical aperture of the optical measurement setup. The sample was mounted onto a rotation stage. The camera and a halogen light source were fixed at a distance of about 40 cm from the sample.

4. Results

4.1. Thermal development and reshaping

In conventional photolithography patterning, a flat and featureless SU-8 thin film is used as a negative-tone photoresist. Upon the absorption of UV photons in SU-8, photoacids are generated. A post-exposure baking for a few minutes, usually conducted at 95 °C, crosslinks the exposed SU-8 under catalysis of photoacids. The baked SU-8 film is further developed in propylene glycol methyl ether acetate to selectively dissolve unexposed SU-8. Such a chemical development process is based on the contrast between the solubility of crosslinked SU-8 and uncrosslinked SU-8. This catalysis of photoacids. As a result, the degree of crosslinking and property under heating; when the heating process of exposed SU-8 begins, the crosslinking is initiated under the catalysis of photoacids. Consequently, the behaviours of exposed SU-8 nanocones depend on the procedures used in heating the sample.

We have experimented with two different heating procedures for studying TDR. In one-step direct baking, the sample was directly baked on a hotplate stabilised at 95 °C to bake for 10 min. In two-step progressive baking, the sample was first baked at 45 °C for 2 h and then the temperature of the hotplate was raised to 95 °C at a ramp rate of about 20 °C min\(^{-1}\), while keeping the sample on top. After the hotplate temperature reached 95 °C, the sample was baked for another 10 min at 95 °C. Figure 4(a) shows a schematic of the two baking procedures. In experiments, three samples of as-imprinted SU-8 nanocones were first prepared using thermal NIL. Two samples were aligned with a binary photomask and exposed using UV illumination in a mask aligner. The exposure dose is sufficiently high to make those illuminated nanocones fully exposed. After exposure, each sample has both fully exposed and unexposed nanocones for comparative studies. One sample was treated with one-step direct baking, while the other with two-step progressive baking. The third sample was not exposed or baked at all and served as a reference for studying the optical properties of as-imprinted nanocones.

AFM imaging was used to scan the profiles of the nanocones to elucidate the effects of TDR. Although there are three different types of nanocone arrays on the sample surface, for the sake of brevity, only AFM scans of the nanocone arrays in the G band are shown in figures 1(f)–(h) and figure 4(b). The results of the nanocones in the R and B bands are provided in supplementary figure S1. Figure 1(f) shows as-imprinted nanocones, which are nanocones right after thermal NIL without any further processing; figure 1(g) shows fully exposed nanocones treated with two-step progressive baking; figure 1(h) shows unexposed nanocones treated with two-step progressive baking. The cross-sectional plots, horizontally cutting through the centre of the nanocones, are plotted in figure 4(b) for conveniently comparing the surface profiles before and after baking. Also included in figure 4(b) is a cross-sectional plot of fully exposed nanocones treated with one-step direct baking.
As shown in figures 1(h) and 4(b) (green curve), the unexposed nanocones under two-step baking completely flowed into a flat film. Another AFM scan on the unexposed nanocones under one-step baking showed no noticeable difference. As expected, the thermoplastic property of the unexposed SU-8 was not affected by the heating procedures because no crosslinking occurred. The flattening of the unexposed SU-8 was solely determined by the final baking temperature and baking time.

For fully exposed SU-8 nanocones, the one-step direct baking significantly diminished the nanocones. As shown in figure 4(b), the nanocones were reshaped from about 224 nm (as-imprinted nanocones, black solid curve) into about 10 nm (nanocones after one-step baking, red dash-dot curve) in height. Once the sample was loaded onto a hotplate surface at 95 °C, which was well above \( T_g \) of uncrosslinked SU-8, the nanocones already flowed significantly before SU-8 could be sufficiently crosslinked. Eventually, the exposed SU-8 was crosslinked and the flow stopped, because the \( T_g \) of crosslinked SU-8 increased to above the hotplate temperature. However, the nanocones had already been diminished too much before the flow stopped. In contrast, the two-step progressive baking reshaped the fully exposed nanocones into slightly shorter cones (about 185 nm in height, blue dash curve in figure 4(b)) with ‘smoothed’ surface. The low-temperature baking at 45 °C during the first step for 2 h allowed the exposed SU-8 to partially crosslink without any flow, because the temperature was below the \( T_g \) of uncrosslinked SU-8. This partial crosslinking effectively increased the \( T_g \) of exposed SU-8. The temperature was slowly raised during the second step, partially crosslinked SU-8 began to flow after the hotplate temperature reached its \( T_g \). Since the \( T_g \) of partially crosslinked SU-8 was above that of uncrosslinked SU-8, more time was allowed for SU-8 to reach a higher degree of crosslinking before flowing could occur. When the flow of SU-8 started, the flow was slow, because the viscosity was increased with the higher degree of crosslinking. As a result, the fully exposed nanocones were mainly preserved, but slightly reshaped into shorter nanocones due to the small amount of flow of SU-8 during the second step of baking. The surfaces of the nanocones were also smoothed due to the thermoplastic flow.

As shown in figures 1(h) and 4(b), the nanocones under two-step baking completely flowed into a flat film. Another AFM scan on the nanocones under one-step baking showed no noticeable difference. As expected, the thermoplastic property of the unexposed SU-8 was not affected by the heating procedures because no crosslinking occurred. The flattening of the unexposed SU-8 was solely determined by the final baking temperature and baking time.

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The diffraction efficiency of the nanocone arrays before and after thermal treatment was measured and analysed. The diffraction spectra shown in figure 4(c) compared the as-imprinted reference sample with the sample fully exposed and treated with two-step baking. Both samples were coated with 35 nm thick Al film to enhance diffraction before measurement. The lighting and viewing angle measurements are specified in figure 4(d). The diffraction peaks around 550 nm wavelength marked with letter ‘G’ correspond to the diffraction from the nanocone arrays in the G band. After reshaping the nanocones, the peak diffraction efficiency of the array increased from 0.15–0.18. For nanocone arrays in the R band, the nanocones were reshaped from 300–213 nm in height and the peak diffraction efficiency (peaks around 645 nm wavelength, marked with letter ‘R’) decreased from 0.23–0.18. For nanocone arrays in the B band, the nanocones were reshaped from 188–128 nm in height and the peak diffraction efficiency (peaks around 465 nm wavelength, marked with letter ‘B’) barely changed around 0.13. The change in diffraction was not significant in fully exposed SU-8 after two-step baking. On the other hand, diffraction measurement on the unexposed sample revealed that the thermally-flattened surface gives negligible or no diffraction. Therefore, using the strong contrast between fully exposed and unexposed SU-8 nanocones, binary colour patterns can be reliably recorded and read out as ‘on’ and ‘off’ of diffractive colours.

4.2. Grey-scale dose-dependent patterning

Since two-step progressive baking can effectively preserve nanocones, in the following sections of this article, only two-step progressive baking is applied to heat the sample after UV exposure. In this section, we show that with the same heating procedure, thermal reshaping can also be controlled by varying the UV exposure dose, which in fact determines the concentration of photoacids generated in SU-8. Such dose-dependent thermal reshaping allows us to control the height of the reshaped nanocones as well as the diffraction efficiency of the array.

In our experiments, we implemented a UV laser writer to expose a grey-scale pattern onto SU-8 nanocones and then applied two-step progressive heating. The process is schematically shown in figure 5(a). In total 11 squares were exposed onto the sample with each square being 1.6 mm in side length and the laser power was increased from 0%–100% of the maximum power (18 mW) in steps of 10%. After the NETT recording process, the sample was sputtered with 35 nm thick Al film. A photo of the sample is shown in figure 5(b). Each big square in the photo actually covers multiple R, G, and B pixel bands and thus displays a grayish colour by mixing the red, green, and blue diffractive colours. Clearly, a higher exposure dose yielded a brighter square comprised of nanocone arrays.

The reshaped nanocones were further characterised using SEM, AFM, and diffraction measurements. For the sake of brevity, only the characterisation results of reshaped nanocones in the G band are shown in figure 5. Figures 5(c)–(i) show SEM images (tilted at 40°) of reshaped nanocones exposed to laser power from 40%–100%. The reshaped nanocones exposed to doses below 40% were too short and gave negligible diffraction. The height of the reshaped nanocones obtained from AFM scans is plotted in figure 5(j). The normalised pixel brightness is calculated by integrating the measured diffraction efficiency within the wavelength range 525–575 nm (around the diffraction peak in green colour) and plotted in figure 5(g). As the exposure dose increases from 40%–100%, the height of the reshaped nanocones increases from about 10 to about 180 nm. The diffractive pixel brightness increases with laser power monotonically. In particular, the dose range between 70%–100% gives almost linear relationship, which allows linear modulation of diffractive colour brightness.

4.3. Half-tone recording of full-colour images

As a proof of concept, we implemented contact photolithography with a binary photomask to record a full-colour image onto imprinted SU-8 nanocone arrays. As shown in figure 6(a), the as-imprinted nanocone arrays are arranged into R, G, and B pixel bands, which display red, green, and blue diffractive colour, respectively, at the default lighting and viewing angle. A binary photomask was generated according to the input digital image and the layout of the pixel bands. One colour pixel given in a digital colour image is translated into a set of three separate apertures on the R, G, and B subpixels. The aperture size defines the area of a subpixel to be exposed and in fact determines the area of nanocone arrays that can remain on the sample surface after TDR. The visual colour displayed by each effective pixel is mixed by appropriate brightness of the red, green, and blue subpixels, similar to a colour LCD display device. The brightness of one subpixel is proportional to the area of the nanocone array as determined by the aperture size in the photomask. As schematically shown in figure 6(a), to mix into a colour defined as (R, G, B) = (50%, 25%, 100%), the aperture on the R, G, and B subpixels should open 50%, 25%, and 100% of the maximum area of the corresponding subpixel, respectively. More details in generating exposure pattern are provided in supplementary figure S2. Since the UV exposure is in a binary pattern and the brightness of an individual pixel is controlled by the size of the nanocone arrays, this patterning
is half-tone in nature, similar to the photolithography-based patterning \cite{14} and inkjet-based MIONS printing \cite{55, 56}.

In the experiments, the photomask was manually aligned to the corresponding pixel bands to expose the SU-8 nanocone arrays. After exposure, the sample was treated with two-step progressive baking. After completing the NETT recording process, the sample was coated with 35 nm thick Al film. Figure 6(b) shows a photo of the produced image with the size of 2 × 1.5 cm. The coat-of-arms logo of Simon Fraser University is represented on the image with excellent colour and resolution. The display resolution is about 338 pixel per inch (PPI), which is close to the resolution limit of human eyes. Characterisation results of red colour marked as ‘spot #1’ and blue colour marked as ‘spot #2’ are shown in figures 6(c)–(k). For different colours, the nanocone arrays on the R, G, and B bands were patterned into the sizes according to the colour of the input image. The quality of the produced image is consistent across the entire sample. The red colour in spot #1 is in fact displayed by a big-area red nanocone array and a small-area blue nanocone array. Its diffraction spectrum (figure 6(k)) shows a strong peak in red colour and a very weak peak in blue colour. The blue colour in spot #2 is displayed by a small-area green nanocone array and a big-area blue nanocone array. Its diffraction spectrum (figure 6(k)) shows a strong peak in blue colour and a second peak in green colour. These experiment results prove that a full-colour image can be accurately patterned onto SU-8 nanocone arrays using binary UV exposure in a NETT recording process.

5. Discussion

NETT is above all a scalable, high-throughput, cost-effective, and versatile manufacturing process for 2D patterning of surface-relief nanostructures. It implements a top-down strategy: thermal nanoimprint lithography at the beginning to prepare a surface covered with nanostructures and then UV photolithography followed by TDR to ‘machine’ those imprinted nanostructures into the desirable form. The nanoimprint can be implemented through a roll-to-roll scheme for very low-cost production of nanostructures. The as-imprinted nanostructures are generic for different structural colour patterns or other information, so that every offspring replicated from the same master stamp can be used to record customised or personalised information. The only
expensive procedure is the upfront cost in origination of a master stamp, which requires fabrication techniques in nanoscale resolution, such as EBL and LIL. However, the cost in originating one master stamp can be effectively diluted by the significant number of recordings that can be made from it. The pattern on a master stamp is generic, and the layout and optical properties of generic nanostructures could be specifically tailored for each particular application category. Only one master stamp needs to be originated for each application category and all colour patterns or information, belonging to the same category, can be recorded onto nanostructures imprinted from the same stamp.

In terms of implementations, NETT is an adaptive and convenient technique for the commercial production of featured nanostructures for optical storage devices. First, master stamp origination and thermal nanoimprint of generic nanostructures can be completely separated from other recording steps. From an industry production line, pre-imprinted generic nanostructures as recordable media can be manufactured in massive quantities. Such recordable media can potentially appear in the format of tapes, discs, or sheets, and be delivered to individual users to record colour patterns using optical exposure and thermal treatment. In addition, NETT recording is solvent-free, which is an advantage for consumers and professional users, as it does not require any wet chemical processing equipment or facility. Furthermore, to expose a pattern on generic nanostructures, NETT implements a low-cost, low-power continuous-wave UV diode laser beam or a UV lamp, rather than expensive and delicate high-power lasers or ultra-fast lasers.

The NETT process shows attractive advantages for long-term eye-readable optical archival storage. We distinguish three main advantages: (1) both full-colour structural colours and data can be recorded onto pre-imprinted nanostructures. The recorded information can be binary (half-tone) or grey-scale (continuous-tone) or a combination of both. In this work, a full-colour image was recorded using binary exposure to pattern nanocone arrays into various sizes on individual subpixels. It should be noted that, using grey–scale exposure, full-colour images can also be recorded by varying the UV exposure dose (figure 5). The diffraction efficiency of nanocone arrays and thus the brightness of individual subpixels can be modulated with a grey-scale exposure pattern, which is generated according to an input colour image. Unfortunately, the laser writer used in this work is not compatible with manual alignment between exposure pattern and pixel bands. In our future work, grey-scale recording of full-colour images will be explored once the limitation in equipment is overcome. The grey-
scale recording can also enable multiplexing binary data using light intensity, similar to the grey-scale fluorescent storage [23]. For example, using the linear dependence range (figure 5(j)), if 16 levels of grey can be differentiated in optical readout with sufficient signal-to-noise ratio, each exposed spot can effectively store 4 bits of data. (2) Information recorded onto SU-8 nanostructures can potentially be preserved for a very long time period, because fully crosslinked SU-8 has excellent mechanical, thermal, and chemical stability at the same time: Young’s modulus about 4–5 GPa, degradation temperature about 380 °C, and strong resistance to many chemicals [58]. In addition, information recorded using NETT is physically represented by reshaped nanostructures with stable surface profiles (after crosslinking). Information is actually embedded into nanostructures rather than pits burned into a recording layer. It can be fairly projected that the optical archival storage based on NETT recording can last for a very long period. In our future work, experimental testing on the storage stability over time will be investigated. Although NETT requires thermal treatment, the gain in the durability of stored information is still very appealing. (3) Due to the surface-relief nature of nanostructures, a final product out of a NETT process can serve dual functions: a stand-alone storage device or a stamp for replicating the device. The latter function, to the best of our knowledge, is not available in any commercially available WORM-type recordable medium. It should be clarified that pre-recorded optical discs for distributing digital content, such as music, motion pictures, and computer games, are manufactured using replications. In the manufacturing process, a master stamp is first originated with the data recorded as binary surface-relief nanostructures using electron beam writing [59–62] or deep UV laser beam writing [63–66] and then pre-recorded discs are rapidly replicated from the stamp in large quantities. Our NETT recording technique could potentially enable direct origination of master stamps for pre-recorded information from pre-imprinted nanostructures.

Existing eye-readable archival storage media, such as colour microfilms, black and white microfilms and DOTS, display information based on the modulated absorption of light in the recording material. In archival storage media based on NETT recording, quite differently, so-called structural colours are generated through the interaction of light with physical structures. In this work, diffractive colours from 2D nanocone arrays were used to demonstrate the NETT recording process. Due to the grating nature, the colours shift as the lighting or viewing angles are changed. Such a characteristic is very useful in producing optical variable devices (OVDs) for security and authentication applications [55]. Commercially available OVDs are usually mass produced through roll-to-roll embossing and all OVDs produced from the same master stamp carry identical features. Using NETT recording, OVDs with personalised and customised information can be produced cost-effectively and provide high-level security features specifically tailored for the individual entity to be authenticated. The diffractive colours in this work are generated through first diffraction order with diffraction efficiency between 15%–25%. In our future work, the diffraction efficiency can be further enhanced by improving the design of nanostructures. For eye-readable colour archival storage purposes, the fidelity of recorded colours is of primary importance and requires angle-independent colours. Plasmonic colours based on hybridising metallic nanoholes and nanodisks are very promising candidates for improving the angle robustness of colours [45]. The resolution achieved in this work (338 PPI) is sufficient for direct-viewing eye-readable storage. However, for storing colours in a fashion similar to microfilm, the pixel size must be scaled down in the future.

NETT recording can be viewed as a manufacturing technique combining photolithography and NIL. In particular, NETT uses a thermal development process to flatten unexposed features. In comparison, the CNP technique introduced by Cheng and Guo implements a nano-patterned light-blocking metal layer and solvent-based development to remove unexposed residue in the imprinted photoresist layer [12].

In this work, although no solvent has been used in the NETT recording process, a metal thin film needs to be deposited onto the SU-8 nanocones after recording to enhance the diffractive colours. This deposition process significantly increased the cost of recording each colour pattern. In the future development of the NETT technique, such a drawback can be avoided by implementing a NETT process on SU-8 nanocones that are pre-coated with Al film. Thin polymer foils with thermally imprinted generic SU-8 nanocones through a roll-to-roll process can be first evaporated with very thin Al film inexpensively and then the NETT recording process can be implemented to record colour patterns on these pre-coated SU-8 nanocones. Since the Al film is very reflective for UV light, exposure must be carried out through the backside. Provided the Al film is sufficiently thin, the thermoplastic flow of SU-8 can still potentially enable effective thermal development and reshaping with Al film on top during the thermal treatment step.

The two-step progressive baking procedure used in this work is a fairly slow process. The thermal reshaping is a result of time-dependent competition between the hotplate temperature and the effective glass transition temperature of SU-8 in the process of being crosslinked. A much faster baking procedure is possible through better experimental control of the thermal process by boosting crosslinking, while suppressing flow. It should be noted that shrinkage of SU-8 induced by crosslinking can also contribute to the reshaping of the nanocones. The reshaped green nanocones, which were fully exposed and baked with the two-step process, shrink in height from 224–185 nm, with a linear shrinkage of about 17%. The volume shrinkage of SU-8 upon crosslinking is known.
to be about 7.5% and the corresponding linear shrinkage is less than 3% [58]. Therefore, the thermoplastic flow of SU-8 is still the fundamental cause of reshaping. Since the thermoplastic flow of SU-8 is of great interest for thermally reshaping of these imprinted nanostructures, numerical studies can be used for studying and controlling the thermoplastic flow in nanostructures. Our preliminary work towards this direction is shown in supplementary figure S3.

6. Conclusion

We demonstrated a solvent-free optical and thermal patterning technique for recording structural colours on pre-imprinted SU-8 nanostructure arrays for long-term full-colour eye-readable archival storage applications. The nanocone arrays in pixelated bands of red, green, and blue colours were thermally replicated from a pre-fabricated stamp and then UV photolithography exposure was used to define a pattern on how nanocones should be reshaped during thermal treatment. Unexposed SU-8 nanocones were completely flattened after being sufficiently baked above their glass transition temperature. Exposed SU-8 nanocones survived and were reshaped into shorter and smoother nanocones. We found that the results of thermal reshaping were governed by the thermoplastic flow and photocrosslinking of SU-8 together, which is controllable through the heating procedures. Applying a direct one-step baking only diminished nanocones to negligible heights and destructed any associated diffractive colour. Using two-step progressive baking, the reshaping of nanocones can be controlled through UV exposure dose. With fully exposed nanocones, the shrinkage in height is about 17%, which is much larger than what would be otherwise expected from the intrinsic shrinkage of SU-8 caused by photocrosslinking alone. Grey-scale recording of diffractive colours by modulating the nanocone height was achieved using a UV laser writer and almost linear modulation of diffractive colour brightness was achieved between 70%–100% of laser power at 18 mW (375 nm wavelength). A full-colour image was recorded onto pixelated nanocone arrays using a half-tone patterning through contact photolithography. Excellent colour representation in resolution of 338 PPI can be retrieved at the desired lighting and viewing angle. The stored full-colour information was clearly eye-readable and projected to last for a long time on the crosslinked SU-8 nanostructured storage media.

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