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Ultrafast volume holography for stretchable photonic structures

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Abstract: Stretchability and flexibility are two key requirements for manipulating the propagation of light in compact and high-performance lab-on-a-chip systems. These requirements are best met by embedding stretchable and flexible tuning elements such as volume phase gratings (VPGs) in polydimethylsiloxane (PDMS), making them attractive alternatives to conventional rigid optical elements. However, fabrication of these PDMS VPGs is a challenge, requiring extensive modifications to PDMS or complex multi-step processes that require long processing times. In this context, we propose the concept of “ultrafast volume holography” for the fabrication of stretchable photonic structures such as tunable VPGs directly in unmodified PDMS. Our concept translates insights in heat regulation via fs repetition rate control into volumetric patterning, forming periodic refractive index modulation of $1.95 \times 10^{-4}$ in the PDMS without post-processing. VPGs formed are further demonstrated as active beam steering units and tunable spectroscopic optical elements.

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1. Introduction

Manipulating the propagation of light using optical elements is the fundamental basis of research and applications in optics. Development of these optical elements follow trends and needs of researchers, and increasingly the need for flexible and stretchable (and therefore tunable) optics has grown. This growth follows the expansion of research on beam manipulation in compact lab-on-a-chip devices, particularly in beam steering [1] and spectroscopy [2]. In this regard, the attractiveness of tunable, flexible and optically transparent holographic devices is well established. Polydimethylsiloxane (PDMS), due to its tunable elasticity and high transmission in the visible wavelength range can be a promising flexible transparent substrate for developing such tunable optical elements. Various nanofabrication techniques have been developed and demonstrated to fabricate such structures on and in PDMS. These conventional processes include e-beam lithography [3], imprint lithography [4], standard UV photolithographic techniques [5], femtosecond direct laser writing (fsDLW) [6,7] and interference patterning of photosensitive PDMS [8]. Diffractive components such as gratings can be fabricated with these processes, but they are mainly limited to forming surface relief or thin diffraction gratings, which are less suitable for beam steering and spectroscopic applications. These thin diffraction gratings exhibit Raman-Nath diffraction [9], with many unwanted diffraction orders that result in reduced diffraction efficiency ($\eta$). For increased efficiency in tunable beam steering and spectroscopic applications, volume phase gratings (VPGs) are desired instead. VPGs are able to exhibit up to $\eta = 100\%$ through Bragg diffraction [9]. However, fabricating VPGs or any sort of holographic pattern directly in PDMS is much more challenging and less widely reported.
To the best of our knowledge, only two methods to fabricate VPGs in PDMS have been reported so far. Using slow focused fsDLW, Watanabe et al. [10] formed VPGs directly in PDMS. They first allowed femtosecond filaments to form through the PDMS under a slow focusing condition, before writing across the PDMS. These filaments then induced refractive index changes along itself. In this manner, instead of a 1D line at the beam focus, a 2D ‘sheet’ of altered refractive index was formed through the thickness of the PDMS. By drawing multiple parallel sheets with a fixed period, a VPG, instead of a diffraction grating as reported by other researchers working on fsDLW [6,7] can be fabricated. However, femtosecond filamentation is still poorly understood and there are challenges in controlling the depth and quality of the grating. Furthermore, this method also faced the same issues as other fsDLW methods such as low resolution and higher grating width due to the diffraction limit spot size of the beam focus. Being a serial writing process, the uniformity of grating linewidth was also adversely affected by the cumulative error across a single line due to variations in fluence ($F$). Therefore, slow focused fsDLW is not a good method to form high resolution holographic patterns.

As an alternative to the fsDLW of unmodified PDMS, other researchers have varied the content of photosensitive compounds incorporated in PDMS instead, so that the existing holographic methods could be used to fabricate VPGs. Ryabchun et al. tuned the photosensitivity of PDMS and other elastomers [11] by varying the content of benzophenone (BPh) photoactive molecules, before using standard holographic methods to pattern volume gratings directly into the modified PDMS [12,13]. With an optimal percentage of BPh added, they fabricated various VPGs using both laser interference patterning and mask patterning. These VPGs were then demonstrated to tune the diffraction spectrum of an incident white light source. However, by making PDMS more photosensitive to the UV spectrum, the transparency of the modified PDMS is effectively reduced in that spectrum. This reduction in transparency has the potential limitation of reduced efficiency in beam steering and reduced spectral range for spectroscopy in the UV range. Furthermore, one of the key advantages of using unmodified PDMS is the wide availability of information on physical and chemical properties, enabling ease of use across a spectrum of applications. Modified PDMS in contrast does not have known physical and chemical characteristics readily available, which would limit the use of this technique. Lastly, the additional material processing step included also introduces complexity to the overall fabrication process. Therefore, there is a definite need of a method to directly fabricate high resolution VPGs in unmodified PDMS for stretchable and flexible optics.

In order to subdue these above-mentioned drawbacks, we propose a concept termed ‘ultrafast volume holography’ based on femtosecond (therefore ultrafast) laser-assisted precise refractive index modulation ($\Delta n$) that can directly form high resolution VPGs in unmodified PDMS. Our concept builds on applying and translating the insight of heat energy regulation via femtosecond repetition rate ($f$) control. A similar insight was previously reported for direct laser writing to form waveguides [14,15] in fused silica and other dielectric materials. However, instead of using focused fs pulses, we modulate heat energy accumulation across a volumetric holographic pattern via fs pulse interference, and by controlling $f$ we precisely induce periodic $\Delta n$ in unmodified PDMS. Furthermore, other femtosecond pulse parameters such as number of pulses ($N$), fluence ($F$) and wavelength ($\lambda$) provide us with additional degrees of freedom, which are used to determine an optimal processing region to form VPGs with higher efficiency and minimal material damage for the proposed beam steering and spectroscopy.

2. Fabrication and characterization of VPGs

Our approach is based on interfering counter propagating 343 nm femtosecond pulses directly on the PDMS film as shown schematically in Fig. 1(a). The laser used is a linearly polarized Yb-fiber femtosecond laser (Amplitude Systems Satsuma HP) with 220 femtosecond pulse duration. The third harmonic (343 nm) is used for fabrication, as PDMS has a slightly higher linear absorption coefficient in the UV range compared to other wavelengths. The laser beam
is first collimated and then split equally into two parts by a plate beam splitter. The two collimated beams then interfere at the sample stage where PDMS films are mounted. Each beam is 0.50 mm in diameter at the interference plane with fluence of each pulse within 2% of each other. The details of the PDMS film preparation are included in Appendix A. Interference of these femtosecond laser pulses (with intensity \( I_0 \) and phase difference \( \delta \)) forms a grating pattern consisting of a periodic \( \Delta n \) following a cosine-squared distribution \( I = 4I_0 \cos^2(\delta/2) \). The patterned areas on the PDMS film are shown in Fig. 1(b), diffracting the visible spectrum when held against a white LED source. The PDMS film after the fabrication can directly be mounted and stretched as shown in Fig. 1(c) without any further post-processing. In this way, the period of the VPG can be tuned (as shown schematically in Fig. 1(a)) for the proposed applications.

Unmodified PDMS provides a high transparency, 89.6% and relatively high absorption coefficient, 4.734 cm\(^{-1}\) (at 343 nm) in the UV spectral range compared to longer wavelengths. This property enables us to pattern the PDMS film through its entire thickness when exposed to 343 nm wavelength radiation. We demonstrate that we can fabricate VPGs instead of surface...
relief gratings, by investigating the diffraction regime of our gratings. Depending on the wavelength ($\lambda$) of incident light, the periodicity ($\Lambda$) of the grating formed and the interaction length or thickness ($t$) of the grating, either Raman-Nath or Bragg diffraction may be exhibited. If the length of interaction $t \gg (\Lambda^2 n_0)/(2\pi\lambda)$, then the grating is said to be in the Bragg diffraction regime [9]. Thus, the thickness of the grating should be much greater than 795 nm for diffraction to occur in the Bragg regime, considering $\lambda = 532$ nm, $n_0 = 1.415$ and $\Lambda = 1370$ nm. If we consider the length along the optical axis (normal to the PDMS surface) of two beams of 0.50 mm diameter, we find that the length of the pulse overlap area where the interference will occur is about 2.88 mm and 3.98 mm for an interference angle 10.0° and 7.2° respectively. This value is more than an order of magnitude larger than the thickness of our PDMS samples. Based on this reasoning, we can assume that Bragg diffraction will be observed from our gratings. To validate it, we have compared the theoretically calculated ($\sin \theta_B = \lambda_0 / 2\Lambda$) Bragg angle with the experimentally measured Bragg angles for two different periodicities 1370 nm and 987 nm (interference angles 7.2° & 10.0°). 1370 nm and 987 nm were chosen so that light in the visible spectrum (400–700 nm) can be diffracted for our two proposed applications. We used two different lasers with wavelengths at 532 nm (diode-pumped solid-state (DPSS) continuous wave (CW) laser from Laserglow Technologies LRS-0532) and 638 nm (fiber-coupled CW laser diode from Thorlabs 638 nm Fiber Pigtailed Laser Diode) and the results are tabulated in Table 1. Both lasers have a fixed output power in the range of 40–45 mW. From these results, we therefore conclude that, we can fabricate VPGs directly into the bulk of the PDMS film that follows the Bragg diffraction formula very closely.

Table 1. Comparison of calculated and measured Bragg diffraction angles at 532 nm and 638 nm for sample periodicities of 1370 nm and 987 nm

<table>
<thead>
<tr>
<th>Sample period $\Lambda$</th>
<th>Calculated $\theta_B$ (532 nm)</th>
<th>Measured $\theta_B$ (532 nm)</th>
<th>Calculated $\theta_B$ (638 nm)</th>
<th>Measured $\theta_B$ (638 nm)</th>
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<tr>
<td>1370 nm ($\theta_f : 7.2^\circ$; $\lambda_f : 343$ nm)</td>
<td>11.20°</td>
<td>12.06°</td>
<td>13.46°</td>
<td>13.98°</td>
</tr>
<tr>
<td>987 nm ($\theta_f : 10.0^\circ$; $\lambda_f : 343$ nm)</td>
<td>15.63°</td>
<td>15.62°</td>
<td>18.86°</td>
<td>19.00°</td>
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3. Parametric studies of fs pulse on the VPG formation

These VPGs are formed mainly due to the accumulation of thermal energy (as discussed in next section) in PDMS which has a high thermo-optic coefficient of $-4.5 \times 10^{-4}$ per °C [16]. Since repetition rate ($f$) is known to regulate thermal energy accumulation in materials [14], the first step to maximize $\Delta n$ is to investigate the key effect of $f$ on VPG formation. $f$ from 10 kHz to 500 kHz are investigated. Samples are fabricated with fixed number of pulses, $N = 50 \times 10^6$ per beam and fluence, $F = 3.5 \times 10^{-4}$ Jcm$^{-2}$. It is to be noted here that enough care is taken to ensure that samples are kept free of dust, bulk impurities or surface damage, to minimize the impact of light scattering on grating formation. The obtained result is shown in Fig. 2(a). It can be inferred from Fig. 2(a), that, the efficiency ($\eta$) values vary with respect to $f$. At $f = 500$
kHz, $\eta$ is measured to be 9.32% and reduces to 7.43%, 7.15%, 5.99% and 1.13% at 250 kHz, 100 kHz, 75 kHz and 50 kHz, respectively. We observe a sharp increase in $\eta$ above 100 kHz which indicates that high values of $f$ are important in the formation of efficient VPGs. The high $f$ (500 kHz) values not only increases $\eta$, but also requires less exposure time to record the pattern that can increase the fabrication speed up to an order of magnitude higher than that for the lower $f$ (50 – 100 kHz) values. The sharp increase in $\eta$ above 100 kHz is possibly due to the transition from thermal diffusion (to the rest of the material) to heat accumulation (to induce more $\Delta n$ in the beam interaction area), similar to the results reported by Eaton et al. in poorly conducting materials [15].

In the thermal diffusion regime, which is observed to be below 100 kHz in PDMS, thermal diffusion occurs during femtosecond pulse-material interaction before much heat can be accumulated in the material to induce refractive index changes. However, at 100 kHz and above, the decrease in the length of time between pulses allows a greater amount of heat accumulation. Therefore, a larger refractive index change is induced in the material, as observed in the increase in $\eta$ (to be discussed in next sections). On the other hand, too much heat accumulation at higher $f$ is expected to form damage in PDMS along the beam path. This degrades the performance of fabricated VPGs due to increase in beam distortion through scattering losses. A good balance can therefore be found between $\eta$ and scattering loss. Such control over thermal accumulation is difficult with long pulse lasers (and impossible with CW lasers), because heat accumulation can already occur during the longer pulse-material interaction irrespective of $f$ [17], which can lead to scattering and burning damage even at low $f$.

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![Fig. 2. Optimization of VPGs with ultrafast volume holography. (a) Change in diffraction efficiency with repetition rate, with fixed number of pulses ($N$) at $1.75 \times 10^{-4}$ Jcm$^{-2}$. (b) Fluence ($F$) and $N$ (or exposure time) thresholds for formation of VPGs, scattering damage and burn damage. The optimal processing region is marked separately with dashed lines. (c) Relationship between exposure time (x-axis) and $F$ (series) with Bragg diffraction efficiency ($\eta$) of VPGs.](image-url)
While increased $f$ regulates thermal energy accumulation by reducing the amount of heat that can diffuse out of the local interaction region between two consecutive pulses, thermal energy needs to be transferred to the PDMS sample via individual pulses. Samples are fabricated for different $F$ values ranging from $0.25 \times 10^{-4}$ Jcm$^{-2}$ to $1.75 \times 10^{-4}$ Jcm$^{-2}$ per beam and exposed from 10 s to 500 s. Therefore, increasing $F$ and $N$ incident on PDMS (at a fixed $f$) is expected to increase the amount of thermal energy transferred into the PDMS. To probe this relationship in greater detail, we vary the effect of $F$ and $N$ at $f = 500$ kHz.

The results we obtain are summarized in Fig. 2(b). From our results, we identify an optimal processing region (marked by the black dotted line), where holographic patterns are formed with comparatively high efficiency and minimal scattering damage. This optimal region covers region 2 and the lower half of region 3. Identifying this optimal processing region is important to optimize tunable beam steering and spectroscopic performance while reducing the beam shape distortion and scattering losses. Outside of this optimal range, we identify three other regions as follows: Below the lowest threshold, no gratings are observed to have formed (Region 1). The lack of grating formation is experimentally verified, as there is no Bragg diffraction at the expected Bragg angles or at any other angles of incidence. No other permanent changes are also observed for samples under a confocal optical microscope (Keyence VK-250 Confocal Microscope) at 50X.

Between the first and second thresholds, a second region (Region 2) can be described, where VPGs are formed without any optical or scattering damage. In Region 3 between the second and third threshold, VPGs are observed along with scattering damage within the exposed area. In the upper half of region 3, $\eta$ is found to decrease beyond certain exposure time (e.g., 300 s and 100 s for $1 \times 10^{-3}$ Jcm$^{-2}$ (green) and $1.25 \times 10^{-4}$ Jcm$^{-2}$ (purple) as shown in Fig. 2(c)).

The reason for this decrease is explained in the next section. Optical or scattering damage is determined through direct microscope observation at 50X and are characterized by the formation of ‘tracks’ induced by both beams (details discussed in Appendix B). Above the third threshold (Region 4), the PDMS films simply burn, catch fire and spread rapidly across the film if not extinguished in time. Determining this third threshold is a bit challenging, as any surface or bulk impurities in the PDMS films would cause the PDMS to catch fire even before the actual threshold. However, with adequate dust and impurity control measures, this threshold can be determined for native PDMS. We note that the above regions are to some extent analogous to the thresholds of damage formation in transparent materials proposed by Schaffer et al. [18] and observed in fused silica by Onda et al. [19].

4. Mechanism of refractive index modulation

A deeper analysis is necessary to understand the formation mechanism of $\Delta n$ (that lead to the formation of the VPGs) and the observed damage features in the optimal processing region described above. Unlike conventional femtosecond interactions, we expect and verify that the observed refractive index changes in PDMS are mostly due to linear single photon absorption and heat accumulation from high repetition rate patterning [20,21]. Z-scan experiments (details in Appendix C) that we perform at comparable $F$ and conditions do not show any significant result for nonlinear focusing and defocusing from electronic effects. This result is expected as the pulse intensities (maximum 0.8 GWcm$^{-2}$) in use are far below the expected terawatts (or higher) [17] range to induce any significant nonlinear interaction. Therefore, the nonlinear effect of the highly intense pulse is expected to give negligible contribution (although cannot be ruled out completely) to the refractive index change of PDMS. While the photon energy from our laser is selectively absorbed only by the Si-C bonds, heat accumulation is required to break the stronger Si-O backbone (detailed mechanisms of energy absorption in PDMS are discussed in Appendix D) and forming monomers. Basically, the refractive index change ($\Delta n$) is proportional to the number of monomers formed. Thus, following the cosine square intensity distribution, a maximum change in the refractive index ($\Delta n$) will occur at the maxima region.
(crest) and the change gradually decreases towards the minima (trough) of the pattern. A schematic representation of such \( \Delta n \) in the VPG is as shown in Fig. 3.

The magnitude of \( \Delta n \) depends on the \( F \) of each beam, the exposure time (equivalent to \( N \)) and \( f \) of the fs laser. When \( F \) of both beams increase equally (with all other parameters unchanged), the amplitude of the cosine-square variation increases more in the areas of constructive interference (crests) than the destructive interference (trough region) as shown in Fig. 3(a). Thus \( \Delta n \) will be maximum at the crest region and minimum at the trough. Thus, \( \Delta n \) will increase with increasing \( F \). On the other hand, when \( N \) of each beam increases (\( F \) being fixed), the amplitude of the intensity at crest does not increase as shown in Fig. 3(a). However, more number of photons interact with PDMS with time and results in an increase in \( \Delta n \) at the crest relative to the trough region. Thus, the increase in both \( F \) and \( N \) increases \( \Delta n \) of the grating. To calculate \( \Delta n \), we use the Kogelnik’s formula \( [22] \) and from our experiments, we find that our most efficient gratings (fabricated at \( 1.75 \times 10^{-4} \) J cm\(^{-2} \) and 100 s, Fig. 2(a)) have an efficiency of 9.32%, corresponding to a \( \Delta n \) of \( 1.95 \times 10^{-4} \).

From Fig. 2(c), we had observed that there is a decrease in efficiency (noted in the previous section) after certain extended exposure. Here we note that since power is normalized for both 0th and 1st order diffraction efficiency calculations, this decrease in efficiency cannot be due to scattering losses and/or beam distortion by the damages in the sample. This observed decrease in efficiency is instead due to the interplay of two convoluted phenomena; duty cycle (d.c.) and \( \Delta n \) between crest and trough of the grating. To explain the observed decrease in efficiency, we look to an analogous decrease in \( \eta \) observed in binary gratings, due to the changes in the duty cycle \([23]\). As the duty cycle increases beyond 50\%, \( \eta \) of binary gratings decreases. In a similar fashion, the observed decrease could be due to the expansion of the crest (Fig. 3) beyond a certain point (without a change in period) when the refractive index at the crest reaches a saturation value. Therefore, the refractive index distribution will deviate from the original cosine square distribution. In addition to this effect, when the refractive index at the crest regions saturate, we can expect that refractive index will still increase at the trough regions. Therefore, a second phenomenon could occur, where \( \Delta n \) between crest and trough would decrease after saturation is reached (Figs. 3(a) and 3(b)).

![Fig. 3. Proposed mechanisms of VPG formation with ultrafast volume holography. (a) Effect of fluence (\( F \)) on \( \Delta n \) and width of \( n_{max} \) where \( I_1 < I_2 < I_3 \). RI saturated from \( I_2 \) onwards. (b) Effect of number of pulses (\( N \)) (or exposure time) on refractive index modulation (\( \Delta n \)) and width of maximum refractive index (\( n_{max} \)), where \( x < y < z \). RI saturated from \( y \) number of pulses onwards.](image-url)

To gather some insights on the effects of both these phenomena, we perform FDTD simulations \([24]\) by modelling the above described refractive index profile as described in Appendix E. The obtained FDTD simulation results support our explanation, showing a...
decrease in efficiency due to a decrease in $\Delta n$ and increase in crest width $(a)$ when the d.c. $(= a/P$, see Appendix E, which is defined as the saturated crest width with respect to period) value of the grating is in the range of 0.5 – 0.6. These results indicate that both changes are present. While we can hypothesize that both the decrease in $\Delta n$ and the increase in the width of crest (region of higher refractive index change) contribute to the decrease in $\eta$, the relative contributions cannot be determined, as neither the variation of $\Delta n$ nor the variation of the d.c. with time can be independently verified in our experiments. One possible method to tackle our hypothesis would be to use a high resolution differential interference contrast (DIC) method like the one developed by Rollinson et al. [25] or Ali et al. [26] for future investigations.

5. Tunable beam steering and spectroscopic applications

We demonstrate the stretchability and flexibility of our VPGs for tunable beam steering and spectroscopic applications in free space. Beam steering devices are important to quickly and accurately change the beam path for applications in laser communications, laser detection and ranging, and there is a need for compact beam steering devices [27], of which tunable Bragg-type gratings are the most heavily researched [11,13,28–30].
Fig. 4. Tunable beam steering and spectroscopy demonstrated with stretchable and flexible VPGs in PDMS. (a) Schematic of VPG as a free space beam steering device via rotation and stretching for a single wavelength (532 nm). (b) Change in Bragg angle in relation to strain (%). Dotted line indicates the expected Bragg angle, while the plotted points indicate the measured angles. (c) Schematic of VPG as free space transmission-based spectroscopic grating with a white light source. (d) Change in peak wavelength and spectral dispersion in relation to strain (%). (e) Demonstration of the tunable spectroscopic transmission grating using a supercontinuum (SC) laser. (i) 0th order and 1st Bragg order diffracted beam. (ii) & (iii) Close-up of diffracted spot before and after stretching, marked in white. Visualization 1 shows the spectrum change as the sample is stretched and rotated.

To demonstrate the use of a PDMS VPG as a tunable beam steering device, we mount our VPG with period = 987 nm onto a mechanically actuated stretcher set on a high precision micrometer-actuated rotation stage (angular resolution of 0.02°). The same 532 nm laser as used previously is used for this demonstration. The Bragg diffraction direction is measured by noting the maximum power read by a power meter. The incident beam is fixed in position, and the stage is manually rotated and shifted to keep the beam incident directly on the grating, as
the sample is stretched in different steps (Fig. 4(a)). Bragg angle values are taken from 0% to 20% strain at 5% intervals, and a graph of Bragg angle versus strain is obtained (Fig. 4(b)). Losses in \( \eta \) are not considered for this short demonstration. From our results, there is a good fit between our obtained Bragg angle results (red dots), and the theoretical Bragg results (red dotted line), with a maximum error of 3.23% at 10% strain. The observed error is expected, as we noted that there is some slipping of the PDMS out of the stretching mechanism, resulting in a consistently larger Bragg angle than otherwise expected. Other sources of error also include deviation from expected non-uniform stretching over the grating, as other researchers have observed [31]. Therefore, by simple rotation and mechanical stretching, we are able to show a relatively precise Bragg angle change of 2.42° over 20% strain, for beam steering applications.

Secondly, we demonstrate a tunable transmission-based spectroscopic grating, using our fabricated VPG (Fig. 4(c)). A collimated beam from a supercontinuum laser (NKT Photonics SuperK Extreme) is incident on VPG of period of 987 nm and manually stretched at the fixed Bragg angle of 13.60°. The diffracted spectrum is collected via a fibre coupler into the spectrometer (Ocean Optics USB4000 UV-VIS Spectrometer). To investigate the changes in the diffracted spectrum, spectrometer readings are taken at different strain percentages from 0% to 9%, and the results are plotted in Fig. 4(d). Each spectrum measurement is normalized with respect to the peak spectrum data of that measurement for ease in comparison and compensating losses due to decrease in thickness or additional scattering from non-uniform stretching [12]. We observe that across 0% to 9% strain, the peak \( \lambda \) linearly shifts from 644 nm to 770 nm, while the FWHM of the peak gradually increases. The spectrum also indicates that there is minimal out-of-band transmission at each Bragg angle with minimal side-lobes. Visually, a similar spectrum change (at a different Bragg angle) is captured by the shift from a peak in the green range to the red range (Fig. 4(e)). A video is provided (see Visualization 1) that shows the spectrum change as the sample is stretched and rotated. While not optimal, we can conclude that our fabricated VPGs could be potentially used as a tunable transmission-based spectroscopic grating.

6. Conclusion

In conclusion, we demonstrate a novel concept of fabricating tunable and flexible VPGs for active beam steering units and tunable spectroscopic optical elements. By applying and translating the insight of heat energy regulation via femtosecond repetition rate (\( f \)) control, we show that our single step ultrafast volume holographic patterning process is able to directly pattern VPGs into unmodified PDMS. Patterning is therefore achieved by modulating heat energy accumulation across a volumetric periodic pattern. Using this process, we could achieve \( \Delta n \) of \( 1.95 \times 10^{-4} \) in unmodified PDMS with less than 1 \( \mu \)m periodicity, which is not reported elsewhere. Further work can be done to independently verify the relative contributions of the variation of both the \( \Delta n \) and duty cycle with time. Furthermore, there are a few disadvantages in the current work such lower diffraction efficiency, smaller pattern area, higher fluence requirement and longer fabrication time that have to be overcome before the results of the work can be applied more widely. It is to be mentioned that these demonstrated applications in free space could well be extended to PDMS based flexible and compact lab-on-a-chip systems with the addition of more reliable and compact non-mechanical stretching systems to control PDMS tuning. Other potential applications such as in hybrid optics can be envisioned by conformally laying our fabricated VPGs over rigid optical components such as lenses. Furthermore, by using multiple pulse trains at different angles simultaneously with additional provisions for sample scanning, our method opens the door for facile fabrication of large area tunable 2D and 3D photonic crystals and metamaterials. This demonstrated single step method will be useful to a larger audience seeking efficient techniques for integrating complex periodic patterns into compact lab-on-a-chip photonic systems.
Appendix A: PDMS film preparation

PDMS (Dow Corning Sylgard 184) films are prepared in a 10:1 (base: binding agent) weight ratio. The base/binding agent mixture is first thoroughly mixed in a petri dish for 1 to 2 minutes before being degassed for an hour under vacuum. The degassed mixture is then spin-coated on an acrylic plate to form thin and uniform PDMS films. Finally, the thin films are cured in an oven at 80°C for 4 hours. After curing, the PDMS films are measured to be 180 μm. The cured PDMS films are then cut into approximately 15 × 15 mm and mounted flat onto cut-out acrylic holders. These films are secured tightly on three edges, leaving both the front and back of the sample in free space such that fabrication won’t be affected by reflection or absorption of laser energy by the acrylic holder. Before exposure, PDMS films and acrylic holders are cleared of dust and organic contaminants using adhesive tape and ethanol.

Appendix B: Damage formation in PDMS

To quantify the region threshold parameters discussed in Section 3 above, we measured the transmittance of the grating regions under normal incidence. The same laser of wavelength 532 nm used previously (DPSS CW laser from Laserglow Technologies LRS-0532) with λ = 532 nm is incident on the patterned area and the transmitted power is measured by a power meter. The obtained result of normal incidence transmission measurement is shown in Fig. 5(a). From Fig 5(a), we can see that the transmitted power decreases with increasing exposure time, irrespective of F. This reduction in transmission with exposure time is due to the increased absorption and/or scattering loss of the incident beam by the grating region of the PDMS. The rate of decrease in transmission (slope of the curve) is less for lower F (0.5 × 10⁻⁴ J cm⁻² and 0.75 × 10⁻⁴ J cm⁻²) compared to the higher ones (0.875 × 10⁻⁴ J cm⁻² and 1.0 × 10⁻⁴ J cm⁻²). This is because, at lower F there are lesser number of photons available to break the chemical bonds and to form monomers (discussed in Appendix C) that could have caused scattering loss. This trend can also be observed from Fig. 2(b) where (in Region 1) only minor scattering is expected for 0.5 × 10⁻⁴ J cm⁻² and 0.75 × 10⁻⁴ J cm⁻² even towards 500 s exposure time. With higher F, more thermal energy can be accumulated even at very low exposure time to start breaking the polymeric backbone of PDMS, causing much larger refractive index changes (Region 2) and scattering losses due to damage (Region 3) throughout the exposed area. The damage is characterized by ‘tracks’ that follow the path of the beam as shown in Fig. 5(b) (top view). These tracks, which are formed by unwanted changes in refractive index follow the individual beam path through the PDMS film and cross at the point where the two beams cross with each other. The magnitude of damage formation has its effect from minor refractive index changes (without any observable changes in optical transmission) to scattering losses and even to void formation (Fig. 5(b), inset) along the tracks. These void formations happen at higher F and exposure times where explosive ablation takes place within the PDMS bulk. This damage leads to a drastic loss in transmission, starting from 200 s for 0.875 × 10⁻⁴ J cm⁻² (green dashed line) and even earlier (100 s) for 1.0 × 10⁻⁴ J cm⁻² (purple dotted line). With continued accumulation of photothermal energy with exposure time, the PDMS films then start to burn and char (Fig. 5(c)), as observed in Region 4 in Fig. 2(b).
Fig. 5. Damage features through ultrafast volume holography. (a) Relationship between transmitted power, fluence ($F$) and exposure time (equivalent to number of pulses ($N$)). (b) 10X Confocal microscope image of scattering damage induced by femtosecond holographic patterning. Inset: 20X optical microscope image of voids formed along scattering damage tracks. (c) 10X Confocal microscope image of burn damage induced by femtosecond holographic patterning. All microscope images are viewed normal to the PDMS surface.

Appendix C: Z-scan

We conducted a series of Z-scan experiments to investigate potential mechanisms for pulse-material energy transfer. A standard Z-scan set-up is used, with identical reference and measurement biased photodiodes connected to the same oscilloscope (Rigol MSO1104Z Digital Oscilloscope) for voltage measurements and comparison. The same third harmonic generated (THG) beam used for fabrication is used for the Z-scan experiments for consistency. The THG beam is split into two via a plate beam splitter, with one directed towards the reference photodiode, and the other directed towards a plano-convex focusing lens (150 mm focal length). Un-patterned PDMS films of the same thickness (180 $\mu$m) are mounted on a sample stage that is manually scanned across 20 mm on either side of the beam focus. Two excitation conditions are investigated: 100 pulses (50 Hz) of fluence one order of magnitude larger compared to fabrication are captured every mm in a closed aperture scan, and 50,000,000 pulses (500 kHz) of the same fluence are captured almost every mm in both open and closed aperture scans, to simulate fabrication conditions. The fluence used for the z-scan experiments was $8.37 \times 10^{-4}$ Jcm$^{-2}$, which is in the same order of magnitude as fluences under parametric study. The low repetition rate experiments are done to investigate purely electronic nonlinear effects due to pulse fluence (at fabrication conditions), while the high repetition rate experiments are done to investigate the combination of electronic and thermal nonlinearities (from the accumulation of thermal energy at high repetition rates), at conditions close to the fabrication parameters used.
Fig. 6. Z-scan at high and low repetition rates. (a) Normalized signal from Z-scan done at 50 kHz, using the 343 nm fs laser used for VPG fabrication. The averaged signal from 100 pulses were taken at each position. (b) Normalized closed and open aperture signals from Z-scan done at 500 kHz, using the 343 nm fs laser used for VPG fabrication. (c) Normalized and adjusted aperture signals from Z-scan done at 500 kHz, using the 343 nm fs laser used for VPG fabrication. The averaged signal from 500,000 pulses were taken at each position.

The closed aperture Z-scan at low repetition rates (Fig. 6(a)) show no significant changes in the transmitted intensity across the focal area, indicating lack of significant electronic nonlinearities. This result is as expected because no significant electronic nonlinear effects are involved in the absorption of pulse energy (in the range of $10^8 \text{ Wcm}^{-2}$) [17]. Since no significant effects are observed in the closed aperture scan, we did not follow up with an open aperture scan. In the closed aperture Z-scan at high repetition rates (Fig. 6(b)), a significant change in transmission is observed, with a rising edge and a peak, followed by a shorter peak as the sample is scanned towards the detector to the right. Since the result of this scan is inconclusive, an open aperture Z-scan is conducted using the same parameters to investigate the effect of nonlinear absorption. A second curve is obtained (Fig. 6(b)), which indicates some measure of saturable absorption (peak) offset from the center. An adjusted Z-scan curve (closed divided by open aperture) (Fig. 6(c)) then reveals an asymmetric curve, offset from the center. This result indicates that there is nonlinear change in refractive index due to thermal effects (i.e. thermal lensing) where $n_2$ is negative. It is to be noted that the sample undergoes a permanent refractive index change during the high repetition rate irradiation, and this is the main cause for the shift and asymmetry in the Z-scan curves. Therefore, we conclude that thermal accumulation from high repetition rate pulses is the main mechanism of refractive index change and damage formation in PDMS.

Appendix D: Mechanism of energy absorption in PDMS

PDMS is mostly transparent (89.6%) to the UV wavelength. Thus, only up to 10% of the photons (not considering reflectance) can interact with the PDMS. These photons are absorbed...
by the polymeric chains that make up PDMS, comprising of a repeating Si-O backbone with two pendant methyl groups bonded to the Si atom. Energy absorption by the chemical bonds leads to chemical changes in PDMS due to photochemical and/or photothermal mechanisms [20]. In the photochemical process, chemical bonds break when the incident photon energy is higher than the binding energy of that covalent bond [21]. In PDMS, the binding energies of Si-C, Si-O & C-H bonds are 3.3 eV, 4.7 eV, 4.3 eV respectively [21]. Since the incident photon energy of our laser (343 nm) is 3.6 eV, only the Si-C bonds can directly absorb these photons and liberate the methyl groups from the Si-O backbone via the photochemical process. From Fig. 2(b) (in the paper), we can observe that there is a threshold for photochemical changes alone at a fluence of $0.25 \times 10^{-4}$ Jcm$^{-2}$, where only grating formation without scattering damage is observed in fabricated VPGs. On the other hand, the other two bonds having higher binding energies cannot absorb these photons. Breaking the Si-O backbone, which would cause breakdown of the entire polymer into smaller chains, would require energy from the accumulation of heat energy instead. These bonds are broken via a photothermal mechanism, where the heat energy absorbed by PDMS from pulse-material interaction accumulates and overcomes the covalent binding energy [21]. When bonds are broken, monomers or radicals such as crystalline Si (c-Si) [21] could be formed. As a result, the refractive index of PDMS changes along with damage formation or ablation in the sample.

Furthermore, since there is a breakdown of the PDMS polymer skeleton, we would expect some degradation in mechanical properties across the exposed regions (supported by the surface ablation observed around the VPGs). However, across small areas, any mechanical degradation resulting from VPG would not be expected to impact performance significantly. Accordingly, this issue of mechanical degradation could have more significant effect on the VPG performance if they were fabricated over a larger area. This degradation issues could be explored as part of future work.

**Appendix E: FDTD simulation**

To gather some insights to the phenomenon described above for the saturation of refractive index change and increase in width of the maximum intensity region (crest), we performed FDTD simulations on this type of refractive index modulation. It is not straight forward to mimic exactly such kind of refractive index modulation that would have formed when saturation takes place at the crest region. However, we tried to make a simulation model that could represent approximately such kind of refractive index modulation. We generated two material blocks with cosine square variation of refractive index having minimum refractive index of 1.45 (for native PDMS) and maximum refractive index equal to ‘1.45 + Δn’ as shown in Fig. 7(a). Here the cosine square refractive index modulation is represented by gradient of color where deeper color represents maximum refractive index value and vice versa. The thickness of these two blocks are denoted as $t_L$ and $t_R$ for the left and right block respectively.

This cosine square refractive index modulation is generated by writing a script and then imported as an object for the simulation. Then we created another block of uniform refractive index ‘1.45 + Δn’ and width ‘a’ and inserted in between the first two blocks as shown in Fig. 7(b). The uniform color of the block in Fig. 7(b) represents a constant refractive index throughout the whole block. These three blocks together form a unit cell of width ‘$t_L + t_R + a$’ that is equal to the period (P) of the VPG. Here we have taken period $P = 1370$ nm as per our fabricated sample. In the next step, we repeat this unit cell periodically with a lattice constant of 1370 nm as shown in Fig. 7(c). We define a parameter d.c. where $d.c. = a / P$ and varied its value by changing the width (a) of the middle block keeping the value of P fixed.
Fig. 7. FDTD simulation elements and results. (a) Imported objects with cosine square refractive index variation where the color gradient represents such refractive index variation with deeper color indicating higher refractive index & vice versa. (b) Unit cell with a uniform block of refractive index $1.45 + \Delta n$ sandwiched between the left and right block. (c) VPG formed by periodic repetition of the unit cell having period $P = t_l + a + t_r$. (d) Variation of efficiency ($\eta$) with d.c. defined by $d.c. = a / P$. (e) Far field diffraction pattern for varying d.c. (f) Variation of $\eta$ with $\Delta n$.

Using this model of VPG, we analyzed the Bragg diffraction for a monochromatic plane wave source at an angle of incidence equal to the Bragg angle $11.19^\circ$. The variation of efficiency ($\eta$) with d.c. as obtained from the simulation is provided in Fig. 7(d). As can be seen from Fig. 7(d), the efficiency ($\eta$) increases with d.c. from 0.3 towards the range of 0.5 – 0.6 and then decreases afterwards. Although this is not the exact representation of the actual refractive index modulation, we still got an approximate validation for the decrease in efficiency as per the experimental observation. The 0th order and the Bragg diffracted peaks for each d.c., obtained from the simulated far field diffraction, is also shown in Fig. 7(e). It shows that the efficiency of the Bragg diffracted spot is maximum for d.c. = 0.5 and less for other values. It should be noted here that, in simulation we have taken finite number of such unit cells to form the VPG and used perfectly matched layer (PML) boundary conditions for the calculation of far field diffraction pattern. Thus, the accuracy of the result is limited by the memory requirements of the computer.

The next part of simulation is to study the sole effect of refractive index modulation on the diffraction efficiency. For this purpose, we keep the cosine square intensity distribution, and changed the refractive index modulation ($\Delta n$) between the maximum (crest) and minimum (trough) point in the range from $1 \times 10^{-4}$ to $9 \times 10^{-4}$. The obtained simulation result is shown in Fig. 7(f). As can be seen from Fig. 7(f), $\eta$ decreases as $\Delta n$ decreases from $9 \times 10^{-4}$ to $1 \times 10^{-4}$. Thus, the reason for the decrease in $\eta$ beyond certain number of pulses can be the convolution of two effects as postulated in the paper and is validated by the simulation results.

One challenge however is that neither change can be directly observed optically, in contrast to binary gratings etched or developed physically via photolithography. Therefore, while we can hypothesize that both the decrease in $\Delta n$ and the increase in the width of greater refractive index change contribute to the decrease in $\eta$, the relative contributions of either cannot be determined. Neither the variation of $\Delta n$ nor the variation of the pattern width (d.c.) with time.
can be independently verified in our experiments. One possible method to tackle our hypothesis would be to use a high resolution differential interference contrast (DIC) method like the one developed by Rollinson et al. [25] or Ali et al. [26] for future investigations.

**Author contributions**

TNCY, along with SPK, KYJ and MVM conceived the idea and designed the experiments. Instrumentation and sample fabrication is done by TNCY, while simulations are done by SPK. Characterization and all other experiments are performed by both TNCY and SPK. MVM and KYJ supervised the research and corrected the manuscript. All authors reviewed and approved the final manuscript.

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