Large-Scale Multiplexed Azopolymer Gratings with Engineered Diffraction Behavior

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The diffraction of polychromatic light from periodic superficial structures is often responsible for the structural colors observed in Nature. Similarly, engineered microtextures fabricated on metallic or dielectric surfaces can be used to design diffracted optical patterns with desired shapes and colors. To this aim, advanced diffraction gratings with exceptional design and functionality are continuously proposed, and new fabrication methods follow to stay abreast with the improving design capabilities. Multiplexed surface reliefs, acting as complex gratings with tunable diffraction behavior, can be readily produced on films of azobenzene containing materials by exposing the surface to controlled sequences of holographic interference patterns. This work fully investigates, both theoretically and experimentally, the use of light-induced surface relief on azopolymers for the realization of large-scale multiplexed gratings with optimized diffraction performances.

The reconfigurable diffraction gratings able to diffract polychromatic light in the same direction with controllable relative color intensities by tuning exposure parameters in a switchable two-beam interference setup are designed and fabricated. The results can be generalized to more complex diffractive devices, usable in emerging display application areas.

1. Introduction

The morphology at micro and nanoscales strongly influences surface functionality. Optimized surface textures with advanced effects on wettability, friction, adhesion, and visual appearance have been developed by evolution in natural world to ensure survival. In particular, the bright and shiny colors of many animals and plants often originate from the diffraction of light from sophisticated periodic structures present on their surface. Understanding and controlling surface geometry for structural colors is the subject of many research efforts in material science, chemistry, and physics, that aim to fabricate artificial light modulating devices with advanced optical and chromatic functionalities by improving the design and the fabrication of diffraction gratings.

Diffraction gratings are optical components made of grooves periodically arranged on the surface of metallic or dielectric substrates. A diffraction grating splits incoming monochromatic light in multiple emerging waves, referred to as diffraction orders. The diffraction angle for each order depends on the wavelength of incoming light and on grating periodicity, while the shape and the depth of surface profile (e.g., sinusoidal), together with the optical properties of the grating material (refractive index, metallic coating, etc.), influences the amount of light diffracted in each specific order.

Diffraction gratings of different geometries including periodicity, orientation, groove depth and surface profile can be overlaid to realize a single combined and complex grating (referred to as multiplexed grating). A similar grating produces a complex diffraction pattern, simultaneously dependent on the combined geometry and chromatic behavior of each composing grating. Engineering the geometrical parameters of the superposition gives control on the emerging light distribution. For example, a multiplexed grating can be designed to diffract light of different wavelengths into a same diffraction order, eventually partially re-balancing the angular spreading of polychromatic light that single gratings would produce alone due to chromatic dispersion. When the superimposed gratings have sinusoidal profiles, the multiplexed structure is often referred to as an Optical Fourier surface.
The fabrication of this class of advanced diffraction gratings requires highly accurate surface structuration techniques. Standard fabrication methods for diffraction gratings include direct machining technology, in which a ruling engine\cite{9} or an ion beam\cite{23} makes grooves on a grating plate, and holographic photolithography, in which the periodic structure of sinusoidal diffraction gratings is produced by interference lithography on a photosensitive\cite{22} that is successively developed and transferred on a dielectric or metallic support via chemical etching or vapor deposition. However, grating multiplexing with these standard methods is either impossible or it requires multiple complex lithographic steps.\cite{30}

Recently, holographic inscription of sinusoidal gratings, directly achieved as surface reliefs on azobenzene-containing polymers (azopolymers), has been demonstrated to be a powerful approach for the realization of multiplexed gratings with engineered directional\cite{23–25} and chromatic\cite{19} diffraction behavior. The azopolymer structuration process is sensitive directly achievable as surface reliefs on azobenzene-containing polymers (azopolymers), has been demonstrated to be a powerful approach for the realization of multiplexed gratings with engineered directional\cite{23–25} and chromatic\cite{19} diffraction behavior. The azopolymer structuration process is sensitive to intensity and polarization distributions of the irradiated field.\cite{26–27} so that both intensity and polarization interference pattern can be used to produce the sinusoidal surface relief gratings (SRGs).\cite{28–30} The dimension of the structured area depends only on the diameter of the interference beams, and SRGs on areas as large as several cm$^2$ can be realized in single lithographic steps. The use of azopolymers as materials for diffraction components\cite{26,31} is further incentivized by the possibility to make the grating reconfigurable and then usable for multistep structuration processes. The surface structuration of azopolymers is a nondestructive two-beam process that, conversely to the chemical etching of standard photolithography, involves a light-driven directional\cite{32–35} polymer mass transport,\cite{36,37} that generates surface relief with the same geometry of the illumination pattern (e.g. sinusoidal for the two-beam interferogram).\cite{38,39} The polymer can be transported back to restore the original state both optically or thermally, erasing then the surface pattern, or moved again by a new lithographic illumination step which combines the preexisting texture with a new one.\cite{29,40,41}

We recently explored the light-induced dynamical and reversible behavior of azopolymer surfaces by directly structuring small areas of a polymer film through structured digital holography illumination and optical erasing, achieving advanced state-of-the-art reconfigurable diffractive gratings and lenses, which we applied in operating devices as motionless monochromators and reconfigurable imaging systems.\cite{16}

Here we extend the use of dynamical surface reliefs on the azopolymer to design and characterize large-scale multiplexed gratings realized via sequential two-beam interference lithography. To this aim, we first analyze the theoretical aspects of the diffraction from a general multiplexed grating made of superposition of sinusoidal reliefs, providing a solid and practical framework for the design of these devices. Then we specify our analysis, by means of theory, simulations, and experiments, to a large-scale onedimensional multiplexed grating that diffracts red (R), green (G), and blue (B) light, in a fixed common diffraction order. We recently explored the light-induced dynamical and reversible behavior of azopolymer surfaces by directly structuring small areas of a polymer film through structured digital holography illumination and optical erasing, achieving advanced state-of-the-art reconfigurable diffractive gratings and lenses, which we applied in operating devices as motionless monochromators and reconfigurable imaging systems.\cite{16}

For a monochromatic plane wave of wavevector $k_0 = 2\pi/\lambda_0$ propagating along the $z$ axis and incident perpendicularly on the dielectric grating, the phase delay resulting from the modulation reads as:

$$\varphi(x, y) = k_0 \times (n - 1) h(x, y)$$  \hspace{1cm} (1)
Equation (1) is at the basis of the design general diffractive optical components and constitutes the operative relation between the geometry \( h(x,y) \) of the dielectric surface and the optical functionality for any generic diffractive optical element (DOE),\(^{[50]}\) including single or multiplexed sinusoidal surfaces. The case of a DOE made of a 1D single sinusoidal surface relief is of particular interest for the present analysis, also because some of the relevant properties in the diffraction behavior of generic DOEs are easily generalized from this simple case.

Figure 1A shows the schematic representation of a dielectric sinusoidal grating of period \( \Lambda \) and amplitude modulation depth \( h \), described by the one-dimensional surface relief function \( h(x) = h_0 \sin(2 \pi x / \Lambda) / 2 \). This grating diffracts the incoming light field into a finite number of propagating diffraction orders (plus an infinite set of evanescent orders), identified by an integer number \( m = 0, \pm 1, \pm 2, \ldots \), emerging from the surface at the angles \( \theta_m \) determined by light wavelength \( \lambda_0 \) and grating periodicity \( \Lambda \) (Figure 1B) via Bragg’s relation (see also Supporting Information):

\[
k_0 \sin \theta_m = m \frac{2 \pi}{\Lambda}
\]

For this grating, the diffraction efficiency (DE) \( \eta_m \), which is a measure of the amount of the incident light power converted in the \( m \)th propagating order, is related to the maximum phase modulation depth \( \beta = k_0 (n - 1) h \) induced by the sinusoidal surface relief according to the relation (Figure 1C):

\[
\eta_m = \left| J_1 \left( \frac{\beta}{2} \right) \right|^2
\]

Here \( J_m \) are the Bessel functions of first kind of order \( m \). For a given material and light wavelength, the parameter \( \beta \) is directly proportional to the grating amplitude \( h \), which is then the actual structural parameter to be eventually tuned to achieve specific distribution of light power among the diffraction orders in the pattern generated by a sinusoidal grating (Figure 1B). For example, the behavior of \( \eta_{2\Lambda} \) is approximately linear in respect to \( h \) for relatively small modulation depths (Figure 1C).

Bragg’s relation in Equation (2) can be alternatively interpreted in terms of the direction of the wavevector \( k_m = (k_x,m, k_z,m) \) for the \( m \)th diffraction order emerging from the dielectric grating (Figure 1B). Diffraction theory (see also Supporting Information) requires indeed that a propagating order \( m \) must have an in-plane wavevector component \( k_{x,m} = k_0 \sin \theta_m \) that is an integer multiple of the grating vector \( g = (g_x,g_z) = (2 \pi / \Lambda, 0) \) of the diffraction grating or, equivalently, borrowing well-known concepts of solid state physics, that \( k_{x,m} \) must be a vector of the reciprocal lattice of the surface.\(^{[50]}\) As the reciprocal lattice only depends on the in-plane surface morphology (for a 1D sinusoidal grating, the reciprocal lattice is entirely known by specifying only the grating periodicity \( \Lambda \), the geometry of the entire diffraction pattern is completely defined by the grating vector \( g \) (which is a base in the reciprocal space). Such considerations, apparently more complicated than Bragg’s law for a single sinusoidal grating, are particularly useful in the analysis of the diffraction patterns produced by more complex gratings, like the diffraction gratings obtained as superposition of \( N \) sinusoidal gratings (multiplexed grating)

\[
h(x) = \sum_{m=1}^{N} h_m \left( 1 + \sin \frac{2 \pi x}{\Lambda} \right) / 2
\]

each having periodicity \( \Lambda_m \) (grating vector \( g_m = (2 \pi / \Lambda_m, 0) \)) and surface modulation amplitude \( h_m \). While the results for the scalar diffraction theory could be extended to diffractive surfaces described by Equation (4) (see also Supporting Information), the relevant features of their diffraction patterns can be understood by generalizing the concepts developed for the single sinusoidal grating in the interpretation of Equations (2) and (3).

Diffraction orders produced by a multiplexed grating propagate, following a generalized Bragg’s law, at directions \( \theta_a \) (where \( \alpha = (\alpha_x, \alpha_z, \ldots, \alpha_N) \) is an array of integer numbers) which make the in-plane component of the diffracted wavevector \( k_{x,a} \) a vector of the reciprocal lattice of the total surface:

\[
k_0 \sin \theta_a = \sum_{m=1}^{N} \alpha_m \frac{2 \pi}{\Lambda_m} = \sum_{m=1}^{N} \alpha_m g_m
\]

Properly tuning the periodicities \( \Lambda_m \), which, analogously to the case of the single sinusoid, completely defines the spatial distribution of the spots in the diffraction pattern, and the modulation amplitudes \( h_m \), that control the relative intensity of those spots, complex diffraction functionalities (and eventually engineered chromatic behaviors) can be directly encoded in the geometry of a multiplexed grating designed as the superposition of Equation (4).

These concepts are here used for the design of the RGB multiplexed grating, which generates different perceived light color in a specific direction as weighted superposition of three diffraction orders of a three-components multiplexed grating simultaneously illuminated with light at red, green, and blue wavelengths.

2.2. Design of a RGB Multiplexed Grating

Figure 2 describes the design of a RGB multiplexed grating that diffracts light of wavelengths \( \lambda_1 = 633 \) nm (red), \( \lambda_2 = 532 \) nm (green), and \( \lambda_3 = 488 \) nm (blue) at the common angle, arbitrary chosen as \( \theta_{\text{target}} = 18.5^\circ \) (see also Figure S2, Supporting Information). The periodicities \( \Lambda_1 = 2.00 \) mm, \( \Lambda_2 = 1.68 \) mm, and \( \Lambda_3 = 1.54 \) mm of the three sinusoidal diffraction gratings composing the multiplexed grating are calculated by solving the equation \( \sin \theta_{\text{target}} = \lambda_1 / \Lambda \), obtained from Equation (2) with \( m = 1 \), and graphically represented in Figure 2A.

The effect of multiplexing for these sinusoidal gratings is simulated in Figure 2B, in which the morphology of the single components \( G_i \) is rendered by grayscale topographic images, that overlay in a linear even superposition \( (h_1 = h_2 = h_3 = h/3) \) to compose the multiplexed surface of the RGB grating according to Equation (4). For clearer visualization, the simulated surface profiles are also presented in Figure 2C.
According to Equation (5), the diffraction pattern produced by the multiplexed grating is characterized, even under illumination with monochromatic light, by several diffraction spots spatially distributed in the directions of the reciprocal lattice. For a total grating amplitude \( h = \sum h_l \) comparable to the incident light wavelength (e.g. \( h = 500 \text{ nm} \)) and refractive index \( n = 1.7 \), most of the diffracted light is contained in three first orders (defined as the orders for which \( |\alpha| = 1 \) in Equation (5)), one of which is the target RGB order of our design (see Figure S2, Supporting Information). To better visualize the spatial distribution of light in the diffraction pattern produced by the multiplexed RGB grating under simultaneous illumination of the three design wavelengths, Figure 2E shows the simulated diffraction pattern that the dielectric surface produces, on a screen placed at large distance \( z_s = 50.0 \text{ mm} \), in the configuration schematized in Figure 2D.

Details about the simulation are given in Experimental Section. The simulated diffraction pattern clearly shows the presence of a white diffraction spot, in which the three colors are spatially superimposed, confirming the design principle of the RGB grating and, more in general, of the multiplexing approach to engineer a complex diffraction pattern via the tailored superposition of sinusoidal surfaces. The simulation is also able to calculate the effects of having eventual different amplitude weights for \( h_l \). Additionally, it should be noted the presence in the pattern also of the other diffraction orders predicted by the reciprocal lattice. In principle, these orders could be spatially filtered out because they propagate at different angles in respect to the design RGB direction. However, their presence should not be neglected in the definition of the operation performances of real devices based on the multiplexed design, because, even not compromising the overall device functionality, they necessarily reduce the DE of the grating in the target diffraction order.
3. Results and Discussion

3.1. Large-Scale Dynamical and Multiplexed Azopolymer Gratings

To experimentally implement the designed multiplexed RGB gratings over large scales, we realized a switchable two-beam interference setup able to sequentially irradiate an azopolymer film with p-polarized sinusoidal intensity interferograms having accurately controlled periodicities. This illumination configuration, largely used for efficient surface relief inscription in azopolymers,[26,31,44–47] has been demonstrated to provide very accurate structural control and high inscription efficiency for our azopolymer.[25]

The principle of the design of our setup is to have a stable interference system, in which the desired interferogram periodicity can be chosen by alternatively selecting one couple of interfering beams between three possible configurations with minimum mechanical movement, while simultaneously monitoring the dynamical diffraction behavior of the developing surface grating by means of a diffracting probe beam. The schematic representation of the setup is presented in Figure 3A.

A horizontally polarized beam from a solid-state laser (Cobalt Calypso) at 491 nm was divided a first time by 70:30 (R:T) beamsplitter (BS1 in Figure 3A). The direction of beam reflected by BS1 (Beam 0) defines the optical axis of the system. Before impinging orthogonally over an area of ≈2 mm in diameter on the azopolymer surface placed in the sample plane, Beam 0 was divided a second time by a 50:50 beamsplitter (BS2). To produce the three interferograms of different periodicity in the sample plane, Beam 0 was alternatively recombined with one of the three other beams (namely, Beam 1; Beam 2; Beam 3) represented in Figure 3A. The angle $\gamma_i$ between Beam 0 and each of the three beams was accurately controlled by means of micrometric rotating mirrors. A movable mirror (MM in Figure 3A) was used to switch between the configurations with Beam 1 and Beam 3. Tunable neutral density filters were finally used to equilibrate the incident intensity for each beam and improve the visibility of the p-polarized interference pattern in the sample plane. A constant total average intensity of 0.14 W cm$^{-2}$ in the interferogram was used in the experiments.

To monitor in real-time the diffraction produced by the developing surface relief gratings during the inscription process, a horizontally polarized He-Ne laser beam at wavelength of 633 nm was irradiated at normal incidence (transmitted through BS1 and BS2) in the structuring sample area. Three photodiodes (PD1; PD2; PD3), properly placed along directions predicted by Bragg's law, were used to record the time-dependent diffraction efficiency for the probe beam at $\lambda = 633$ nm recorded by PD1, PD2, and PD3 during a typical inscription experiment (exposure time 240 s) of the gratings G1, G2, and G3, respectively. E–J) Atomic force microscope (AFM) micrograph and relative topographic profile of the azopolymer surface resulting from the three illumination configurations.

Figure 3. Switchable interference setup for SRGs of engineered periodicity. A) Schematic representation of the setup. In each exposure step, only one couple of the illustrated beams (Beam 0 + Beam i, with $i = 1$, 2, 3) is irradiated on the sample. B–D) First order time-dependent diffraction efficiency for the probe beam at $\lambda = 633$ nm recorded by PD1, PD2, and PD3 during a typical inscription experiment (exposure time 240 s) of the gratings G1, G2, and G3, respectively. E–J) Atomic force microscope (AFM) micrograph and relative topographic profile of the azopolymer surface resulting from the three illumination configurations.
evolution of probe light diffracted in the +1 order for each of the three periodicities. DE was calculated by dividing the time-depended photodiode signal produced by the evolving grating by the signal transmitted through the flat sample surface before starting the writing process. A notch filter, placed right after the sample, discards light of the writing beam from the detection space. An additional circularly polarized collimated beam from a diode laser at the wavelength of 405 nm (referred to as assisting beam), and intensity ≈0.4 W cm⁻² incident on the sample from the substrate side, was also included in the structuration process. This beam, highly absorbed by our azopolymer,[34,36] improves the grating inscription rate by redistributing the orientation of azobenzene molecules, which otherwise tend to be realigned perpendicular to the polarization of the writing beams, with a resulting gradual reduction of absorption probability and overall relief inscription efficiency.[26,48–50] We extensively studied the influence of this beam on the writing dynamics of our azopolymer in our recent work.[36]

Figure 3B–D shows the diffraction curves recorded in 240 s inscription experiments of the gratings G1, G2, and G3, realized to have the periodicities \( \Lambda_i \) (\( i = 1, 2, 3 \)) calculated above. The approximate linear behavior observed in the rising of the first diffraction order efficiency can be used to eventually control the height of the surface relief gratings, by properly tuning the exposure time.[16,46] Additionally, the stable signal recorded also when the writing interferogram is switched off (Figure 3B–D) demonstrates a diffraction behavior dominated by the stable surface relief grating, with only small contributions from the eventual birefringence grating typically observed in the interference-based photostructuration of azopolymers due to the photoalignment of the chromophores.[19,26,31]

Figure 3E–J reports the atomic force microscope (AFM) images and the relative topographic profiles of the three azopolymer surfaces at the end of the grating inscription process. The periodicities of the sinusoidal gratings measured by the AFM were in perfect agreement with the design (see also Figure S3, Supporting Information), confirming the highly accurate control over grating periodicities achievable in our switchable interference configuration.

In the experimental configuration of Figure 3A, both reconfigurable and multiplexed large-scale surface relief gratings can be easily realized and eventually tuned in real-time by using the monitored diffraction of the probe beam as indirect measure of the surface relief amplitude. Figure 4 presents the results of a dynamical experiment in which the grating G2 was inscribed, erased, and re-inscribed on the surface before a multiplexed grating was realized by adding to it the grating G1 in a successive exposure step. The dynamical evolution of the surface was characterized by simultaneously monitoring the signal of the two photodiodes PD2 and PD1, detecting the +1 diffraction order of G2 and G1, respectively. The diffraction curves are reported in Figure 4A, together with the AFM micrographs (in the insets) of the azopolymer surface after the first writing of G2 (i), after its erasing (ii) and after its rewriting (iii), which clearly show the connection between the surface topography and its dynamical diffraction behavior. The erasure of the surface from (i) to (ii) was realized by means of the 405 nm laser beams in the configuration of Figure 3A, but with higher intensity (≈0.9 W cm⁻²), as characterized in detail in our previous work.[16] At the instant (iii), the interference pattern was switched to the configuration for G2, so that a multiplexed grating with the geometry G2 + G1 started to develop on the azopolymer surface.

The exposure time in the final step was chosen to make the diffraction efficiencies for G2 and G1 approximately the same (difference less than 1%), which, according to the diffraction analysis in this surface modulation regime, would correspond also to approximated similar weight \( h_1 \) and \( h_2 \) for the sinusoidal components of the multiplexed grating in the Equation (4). This is confirmed by the AFM analysis presented in Figure 4B, where a very good agreement between the experimental topographic profile and the theoretical profile, obtained by overlaying the two sinusoidal functions with experimental periodicity and equal amplitudes, is observed.

The possibility of empirically selecting the appropriate exposure time to realize a target balance in diffraction efficiencies (in our case, approximately equal DE) is a clear advantage of direct dynamic efficiency monitoring during grating inscription, which avoids a priori calibration of surface relief heights in respect to the exposure time. This calibration has been demonstrated to be a difficult task for 1D topographies realized as sequences of exposures on azopolymer films because...
pre-existing grooves on the surface can affect the inscription efficiencies for gratings in the following steps of the multiplexing sequence. Additionally, we also observed a possible influence of inscription efficiency in subsequent exposures on the specific order of the sequence (see also Figure S5, Supporting Information), which further weakens the feasibility of an approach based on a priori grating depth calibration for the realization of reliable and repeatable multiplexed gratings.

3.2. RGB Grating on Azopolymer Film

For the realization of the designed multiplexed RGB grating, three sequential exposures of the polymer film were used. In our experiment, we aimed not only at achieving the correct superposition of sinusoidal reliefs that produces the common (white) diffraction spot for the design wavelengths simulated in Figure 2E, but also at realizing multiplexed structures with controllable relative weight of the superimposed components. For the latter goal, real-time monitoring of the probe beam DE for the three gratings and empirical tuning of the exposure time for each component were used. Figure 5A shows the time evolving diffraction curves recorded during the inscription of a RGB grating, designed to have approximately equal final DE in the first orders of the superposed sinusoidal reliefs at \( \lambda = 633 \, \text{nm} \), which again directly correlates with having approximately equal amplitude weights in the multiplexed structure.

In the inscription process described in Figure 5A, after the first structuration step (grating G2) lasting until the instant \( t_1 \), the interference configuration was switched in the second one (grating G1) and the irradiation of the sample continued until the empirically selected instant \( t_2 \), when the DE for the second grating reached approximately the same maximum level of the first exposure step. At that instant, the last grating component (grating G3) was superimposed in the third illumination step, which continued until all the three first-order diffraction efficiencies were similar at the time \( t_3 \). The AFM micrograph of the final azopolymer surface is show in Figure 5B, while the comparison of its experimental profile with the theoretical profile (calculated as equal-weight superposition of the sinusoidal components) is presented in Figure 5C. Similar to the analysis of two-component multiplexed grating of Figure 4B,C, the empirical tuning of exposure times in the multiplexed superposition by real-time diffraction monitoring, produced also for the
three component RGB grating an experimental profile in very good agreement with the target one. It should be noted that a similar exposure sequence, with a-priori definition of exposure times\cite{13} (for example equal exposure times for all Gi), provided a worst structural result in terms of final component balance (see Figure S5, Supporting Information).

Finally, the diffraction pattern produced by the azopolymer multiplexed RGB grating under simultaneous irradiation of three collinear laser beams at design wavelengths (see Experimental Section), is shown in Figure 5D. The spatial distribution of the diffraction orders quantitatively matches the simulated pattern calculated for the ideal multiplexed surface in Figure 2 (see also Supporting Information), with the presence of a white diffraction spot in which the three diffraction orders at the three colors (Figure 5E) are angularly superimposed. This confirms the validity of diffraction analysis, design principle, and experimental implementation we used for the realization of the azopolymer grating, which could be eventually extended to other multiplexed large-scale diffraction devices, realized as superposition of sinusoidal surface reliefs with controlled periodicity and relative amplitude weights.

4. Conclusions

In this work, we used sequential inscription of sinusoidal surface relief gratings on the surface of an azopolymer film to realize diffraction gratings with overlayed morphology, having engineered structural and chromatic behavior. A multiplexed grating that diffracts polychromatic light in the same direction has been designed from the accurate analysis of the results that scalar diffraction theory provides for light modulation from dielectric surfaces. The periodicity of the superimposed gratings plays the crucial role in the definition of the diffraction pattern produced by the multiplexed grating: excellent agreement between theory and experiments has been obtained by taking advantage from a stable switchable interference setup realized to inscribe SRGs with accurate periodicity control. Real-time diffraction monitoring has been used to optimize the superposition of the single sinusoidal components in the experiment, providing an empirical but powerful approach for the tuning of relative sinusoidal weights of the superposition. Our results could be used to engineer perceived color saturation in RGB diffractive devices, realized as superposition of sinusoidal surface reliefs with controlled periodicity and relative amplitude weights.

5. Experimental Section

Azopolymer Synthesis, Characterization, and Film Preparation: The material used in this work for the realization of dielectric surface relief gratings is an azobenzene-containing polymer (azopolymer) in amorphous state. The details about the synthesis and structural, thermal, and optical characterizations have been extensively reported in the previous works.\cite{25,34,38}

The solution for film fabrication was prepared by dissolving 70 mg of the polymer in 0.50 mL of 1,1,2,2-tetrachloroethane and filtered on 0.2 μm PTFE membrane filters. Amorphous thin films were prepared by spin coating the solution on 24 × 60 mm cover slides at 300 rpm for 4 min, obtaining typical film thickness of 1.0 ± 0.1 μm. Before photostructuration experiments, the samples were kept under vacuum at room temperature for 24 h to remove solvent traces. Refractive index of the fabricated film was measured via ellipsometry. Measured values at the device operating wavelengths (633, 532, 488 nm) are: \(n_{633} = 1.70\); \(n_{532} = 1.74\); \(n_{488} = 1.78\). After synthesis and holographic structuring, the azopolymer samples are stored at room temperature. The topological analysis and optical analysis were repeated also after several months from fabrication, showing no degradation effects for both the material and the surface structure over time.

Morphological Surface Characterization: The topographic analysis of the structured surfaces was performed by AFM (WITEC Alpha RS300) operating in tapping mode with a cantilever of 75 kHz resonance frequency. Analysis and elaboration of AFM data was accomplished by means of the open-source software "Gwyddion."

Simulations of Diffraction Patterns: To simulate the diffracted field from the structured azopolymer surfaces, incident plane waves of unitary amplitudes were considered. In the calculations the incident field is assumed to be phase modulated in the plane at \(z = 0\), in which the structured dielectric surface is placed. The field transmitted just behind the phase mask is equal to \(\mathbf{U}_{\text{out}}(x, y) = e^{i \phi(x, y)}\). The diffracted field \(\mathbf{U}(x, y, z)\) in each transverse plane, orthogonal to the optical axis \(z\) behind the surface is evaluated by solving the Helmholtz scalar wave equation (see also Supporting Information), considering the Rayleigh–Sommerfeld diffraction integral in Fresnel approximation:\cite{10,52}

\[
U(x,y,z) = \frac{e^{ikz}}{kz} \int \mathbf{U}_{\text{out}}(x', y') \exp \left\{ \frac{i}{2z} \left( (x - x')^2 + (y - y')^2 \right) \right\} dx' dy' \tag{6}
\]

A discretized form of this integral was implemented coding a MATLAB script. In the case of RGB diffraction, the Fresnel integral was calculated for each wavelength and then the results were summed according to optical field superposition principle.

Experimental Imaging of RGB Diffraction Patterns: The experimental diffraction patterns produced by the azopolymer single (see Figure S4, Supporting Information) and multiplexed RGB gratings were obtained by illuminating the structured sample with three collimated and collinear laser beams, incident normally from the substrate side. The beams had the same wavelengths of the theoretical analysis (\(\lambda_1 = 633\); \(\lambda_2 = 532\), and \(\lambda_3 = 488\) nm) and were produced by three different laser sources (He-Ne, Nd: YVO4 frequency-doubled laser, and a Cobalt Obis diode laser, respectively) which were made propagating along a common optical axis by a proper combination of mirrors and beam splitters. The three beams were tuned to have the approximately same intensity before the sample (9.5 × 10^−3 W cm^2). Low intensity ensures that the green and blue light (which are absorbed by the azopolymer) do not significantly affect the surface pattern. The transmitted diffraction pattern was collected on an opaque screen placed at 205 mm from the sample and recorded by a color reflex CCD camera.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.
Data Availability Statement
The data that support the findings of this study are available from the corresponding author upon reasonable request.

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