Solving an old puzzle: fine structure of diffraction spots from an azo-polymer surface relief grating

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Abstract
We report on the experimental and theoretical interpretation of the diffraction of a probe beam during inscription of a surface relief grating with an interference pattern into a photo-responsive polymer film. For this, we developed a set-up allowing for the simultaneous recording of the diffraction efficiency (DE), the fine structure of the diffraction spot and the topographical changes, in situ and in real time while the film is irradiated. The time dependence of the DE, as the surface relief deepens, follows a Bessel function exhibiting maxima and minima. The size of the probe beam relative to the inscribed grating (i.e., to the size of the writing beams) matters and has to be considered for the interpretation of the DE signal. It is also at the origin of a fine structure within the diffraction spot where ring-shaped features appear once an irradiation time corresponding to the first maximum of the DE has been exceeded.

Graphic abstract

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Extended author information available on the last page of the article
1 Introduction

Azobenzene containing polymer thin films can develop significant opto-mechanical stress under irradiation with spatially modulated light [1, 2] which results in the macroscopic deformation of the surface. The deformation ranges from elongation or contraction in one direction during irradiation with linear polarized light [3] to a fine vortex-like topographical response to a complex shape of the inscribing beam [4–6]. Special relief structures can be generated by applying illumination with an interference pattern, where the incoming light shows a periodic variation of the magnitude or local orientation of the electrical field vector [7, 8]. The dynamical responsive of these polymeric materials is such that the topography deforms on time scales of seconds to minutes, mimicking the optical meric materials is such that the topography deforms on time scales of seconds to minutes, mimicking the optical

periods as small as 125 nm for a certain polarization pat-
demonstrated that such topographical gratings can have

torus or temperature softening, under rather low intensity circular polarization, the other beam left-handed) [14,

amplitude typically exceeds around 100 nm. The explana-
the inscribed grating area in size, one finds a fine structure in the spatial profile of the diffraction spot, which has been reported earlier by other groups [38]. The spatial profile of the diffraction spot changes as a function of the SRG height starting from a Gaussian to a hollow ring (“donut” like) and finally to a ring structure with a bright center. The hollow ring appears at the moment where the total DE signal decreases, while the ring with the bright center sets in when the DE signal starts to increase again. On the example of two different polymers, at fixed size of the writing and probe beams, we show that the decrease in the DE signal and the variation of the fine structure of the beam profile of diffraction spot starts at the same SRG height. For a very small probe beam diameter, the diffraction efficiency follows the

Bessel function and can be explained using a time-depend-
ent model based on the Raman–Nath diffraction theory [26]. It has been reported, indeed, that the diffraction efficiency is not monotonously increasing as a function of irradiation time, but can drop in the course of grating development [27–32]. However, the DE signal contains information about bulk and surface gratings, and requires a quite involved de-convolution model to separate the contributions of both gratings to the time-dependent DE signal [33–36].

Recently, we have proposed a set-up where one can directly separate birefringence and surface gratings by measuring the development of DE signal and topography simultaneously and in situ, i.e., during irradiation [37]. The set-up consists of three parts (see Scheme 1): (1) a two-beam interference system for generating a well-defined intensity or polarization interference pattern; (2) a probe laser with a set of photodiodes for recording the diffraction efficiency, and (3) an atomic force microscope (AFM) for acquiring the change in surface topography during irradiation. The DE and AFM data are taken simultaneously over time scales of seconds to minutes, while the SRG grows in amplitude in the presence of the interference pattern. In this paper, complementing the above-described set-up, we report on data taken with an additional component that acquires the spatial intensity profile of the diffraction spot. Moreover, we explain a maximum and subsequent decrease in the DE that appears during the development of the SRG when its amplitude typically exceeds around 100 nm. The explanation is supported by calculations using a “reflecting phase screen” model in the Raman–Nath approximation,26 and is based on the fact that the profile of the writing beam has a Gaussian shape. The corresponding modulation depth of the SRG changes over the inscribed area (see Fig. 4b below): the grating has a maximal amplitude in the center of the writing spot which drops radially to periphery. The size of the probe beam that records the SRG growth, relative to the inscribed area, determines the conditions where the DE signal peaks occur. Using a wide probe beam, which matches the inscribed grating area in size, one finds a fine structure in the spatial profile of the diffraction spot, which has been reported earlier by other groups [38]. The spatial profile of the diffraction spot changes as a function of the SRG height starting from a Gaussian to a hollow ring (“donut” like) and finally to a ring structure with a bright center. The hollow ring appears at the moment where the total DE signal decreases, while the ring with the bright center sets in when the DE signal starts to increase again. On the example of two different polymers, at fixed size of the writing and probe beams, we show that the decrease in the DE signal and the variation of the fine structure of the beam profile of diffraction spot starts at the same SRG height. For a very small probe beam diameter, the diffraction efficiency follows the
prediction for a homogeneous grating of infinite area (given by squares of ordinary Bessel functions).

2 Experimental part

2.1 Materials and methods

Poly[1-{4-(3-carboxy-4-hydroxyphenylazo)benzenesulfonamid]-1,2-ethanediyl, sodium salt] (Pazo) and Poly[(methyl methacrylate)-co-(Disperse Red 1 acrylate)] (poly(MMA-co-DR1A)) are purchased from Sigma-Aldrich. The Pazo polymer solution is prepared by dissolving 170 mg Pazo in 1 ml solution containing a mixture of 95% methoxyethanol and 5% ethylene glycol. The poly(MMA-co-DR1A) polymer is dissolved in chloroform to get a concentration of 60 mg/ml.

Sample preparation The polymer films are prepared by spin casting at 3000 rpm for one minute of 100 μl of the polymer solution on a thin glass slide. The film thickness is measured from the cross-sectional profile of atomic force microscope (AFM) micrographs along a scratch within the polymer film.

2.2 Methods

Home-made set-up for studying SRG formation in situ The set-up consists of three parts: (1) two-beam interference lithography, (2) atomic force microscopy (AFM) and (3) diffraction efficiency (DE) measurement (Scheme 1). The two-beam interference lithography with a continuous-wave diode-pumped solid-state laser (Cobalt Calypso, λ = 491 nm) allows generating well-defined spatiotemporal interference patterns by changing the polarization of two interfering beams in a controlled way. In this part of the set-up, the laser beam is spatially expanded and then collimated with a pair of focusing and collimating lenses and a pinhole (Scheme 1). The beam diameter is set to 4 mm and the total intensity is varied between 100 mW/cm² and 200 mW/cm². Additionally, a 50:50 beam splitter is added to separate the initially single beam into two beams of the same intensity. These two beams pass through a set of wave plates and polarizers allowing independent control of intensity and polarization. For instance, adding a half-wave plate to each of the beam paths of the interference set-up (H3, H4), one with an angle of +22.5° and the second with an angle of −22.5° with respect to the optical axis, results in the ±45° interference pattern (IP). This is a polarization interference pattern with constant intensity in the sample plane, but spatially varying distribution of polarization.

The second part of the home-made set-up is an atomic force microscope (AFM, PicoScan (Molecular Imaging) AFM operating in intermittent contact mode) enabling measurements of the polymer topography changes in situ and in real time, i.e., under varying irradiation conditions. The scan speed of the AFM is set to 1 Hz with a scan area of 10 x 10 μm and a resolution of 512 x 512 pixel. Commercial tips (Nanoworld-Point probe) with a resonance frequency of 130 kHz, and a spring constant of 15 N/m are used. The sample is oriented with the polymer surface pointing towards the AFM tip, such that irradiation is “from below”, i.e., through the glass substrate (Scheme 1).
SRG amplitude is determined from the plot of the surface profile of the AFM scan by measuring the difference in height between topography maximum and minimum. A plot of this value as a function of time gives the growth kinetic of the SRG. To obtain at the same time information about the alignment of the azobenzene side chains in the polymer film, a red probe laser beam (Uniphase, HeNe, 633 nm) with a tunable beam diameter from 1 mm to 3 mm (I = 30 mW/cm²) is integrated into the set-up. The wavelength of 633 nm is outside the absorption band of both polymers studied in
Fig. 1 a, c In situ-recorded SRG height and diffraction efficiency (DE) under irradiation of a Pazo film with a ±45° interference pattern (IP) of λ = 491 nm light (I = 200 mW/cm², Δ = 2 μm grating period, thickness d = 1 μm); a 1st h of irradiation; c irradiation during 6 h. Note the non-monotonous increase and decrease in the first-order DE (red curve), while the SRG height increases continuously (black dots). The inset depicts the chemical structure of the Pazo polymer. b Spatial profile of the first-order diffraction spot for three irradiation times (camera images, scale bar 1 mm). The shape is Gaussian, until the maximum DE signal (SRG height of 100 ± 10 nm, micrograph marked by I) is reached. When the DE starts to decrease, there is a noticeable change in the beam profile (micrographs marked by II and III). The intensity in the center of the diffraction spot decreases, resulting in a ring-shaped distribution (II). Further irradiation changes the spot shape to a ring structure with a bright center (III). d Parametric representation of the data in e: DE (optical data) as a function of SRG height (AFM data). e In situ-recorded SRG height (dots) and 1st order DE (solid line) for two irradiation intensities: 200 mW/cm² (red) and 100 mW/cm² (blue). f Plot of the data of e as a function of fluence (intensity multiplied by time)

this work and its intensity is weak enough not to affect the polymer film, as proved by AFM measurements. To calibrate the DE, a beam splitter with a ratio (T/R = 90:10) is used in the DE set-up, such that 90% of the light arrives on the sample (intensity I₀) and 10% on a photodiode. The signal of this photodiode is recorded during the whole measurement for controlling the stability of the probe beam during the experiment. The diffraction efficiency is defined as the ratio of the intensity of diffraction order (Iₙ) and the intensity of the incoming light (I₀): \( \eta_d = \frac{I_d}{I_0} \), where I₀ is 90% of the total intensity of the probe beam. The DE set-up additionally includes a quarter-wave plate converting the polarization of the probe beam from linear to circular. The polarization state of the probe beam can be set by adding a polarizer afterwards. The probe beam is P-polarized for all measurements discussed in this paper. The detector D2 measures the P-polarized component of the 1st order DE signal.

The three different set-ups: two beam interference, AFM and DE acquisition are controlled and operated with a software (Profilab-Expert, Abacom) specifically designed in the laboratory to record signals of the photodiodes, control the irradiation shutter and to synchronize DE set-up with the AFM. A computer-generated signal regulates the irradiation with the help of an AD/DA converter (Kolter Electronic, PCI-AD12 N-DAC2), which also records the signals of the photodiodes. This irradiation signal is sent to the diffraction efficiency set-up as well as to the AFM by recording the signal with the aux-input of the AFM controller, which enables to synchronize the different components.

The set-up is aligned in such a way that the AFM probe is placed in the center of the two interfering beams, using as a reference spot the red laser of the AFM optical lever focused on the cantilever. Afterwards, the probe beam is aligned to the center of the IP and AFM probe.

Silicon detectors (Thorlabs DET 100A/M) are used in the diffraction efficiency (DE) set-up to measure the intensity of the diffracted probe beam. A 600-nm long-pass filter is placed in front of each photodiode to be only sensitive to the probe beam. The intensity of the diffracted light is recorded every 200 ms.

The change in the beam profile of the first-order DE is recorded with a CMOS Camera (Thorlabs DCC1545 M) with a sensor size of 6.7 x 5.3 mm and resolution of 1280 x 1024 pixel (pixel size 5.2 μm). For these measurements, the photodiode is replaced by the CMOS camera; alternatively, the camera can be placed in the direction of the -1 diffraction order (see Scheme 1).

All experiments are carried out under yellow light in the laboratory (to avoid undesirable photo-isomerization) and under ambient conditions, i.e., at room temperature with a relative humidity of 55%. The whole set-up is covered with a non-transparent encapsulation to avoid any influence of the environment on the measurement (parasitic light, air circulation and vibration).

3 Results and discussion

Figure 1 shows a typical curve recorded during irradiation of the azobenzene containing polymer film (Pazo) with the ±45° interference pattern (IP). The SRG height (black dots in Fig. 1) increases continuously, while the DE signal (1st order, red curve in Fig. 1a) has a Bessel function shape where several maxima and minima appear. Indeed, the DE signal first increases within 10 min of irradiation followed by a decrease when the SRG height reaches 100 ± 10 nm. In the course of irradiation during 6 h two maxima of the DE signal (at SRG height of 100 ± 10 nm and 300 ± 10 nm) and two minima (at 200 ± 10 nm and 400 ± 10 nm) develop (Fig. 1c, d). Similar behavior is observed for other polymers, here illustrated with poly(MMA-co-DR1A) (Figure S1b, Supporting Information). The extremal points of the DE signal appear at the same positions relative to the SRG height, although the SRG kinetic growth is much faster for the poly(MMA-co-DR1A) (Figure S1a, Supporting Information).

The DE signal typically measured is the integrated value over the whole detector area, i.e., the entire diffraction spot. The analysis of spot profile in the 1st order reveals, however, a time-dependent intensity modulation resembling “donut” structure. As long as the DE signal grows (1st 10 min of irradiation), the beam profile has a Gaussian shape (micrograph I in Fig. 1b). At maximum DE signal (the SRG height is 100 ± 10 nm), the intensity in the center of the laser spot (micrograph II in Fig. 1b) starts to decrease (appearance of the “donut”). Further irradiation with an interference pattern will modify a spot profile further into a ring structure with
a bright center (after 45 min, micrograph III in Fig. 1b). The time evolution of diffraction spot profile is shown in a video (see Supporting Information, Figure S2). The DE slightly decreases when the pump beam is switched off (after 60 min of irradiation), while the SRG amplitude and the spatial profile of the first-order diffraction spot do not change. This indicates directly the relaxation of the birefringence grating. When the irradiation intensity is reduced in two times (from 200 to 100 mW/cm²), a similar behavior of the DE signal is observed (blue curve in Fig. 1e), but at longer irradiation time where the SRG has reached the height of 100±10 nm. This behavior scales with the energy fed into the system, as illustrated by the collapse of the DE and SRG data when plotted as a function of the product of intensity and irradiation time (insert in Fig. 1f).

At constant irradiation parameters, the kinetic of the SRG growth and the maximal SRG height depends on the thickness of the polymer film. Figure 2 shows a comparison of the first-order DE and SRG height for different thicknesses of the Pazo polymer film and a fixed irradiation time of 1 h. In the case of 1-μm-thick polymer film (Fig. 2a), the DE signal increases until the SRG height of 100±10 nm (13 min of irradiation at I = 200 mW/cm²) is reached. The inset of Fig. 2a shows the in situ-recorded AFM micrograph during irradiation. The micrograph depicts the temporal evolution of the polymer topography with the vertical direction from top to bottom (red arrow at the bottom right corner) corresponding to the irradiation time. The AFM scanning starts in dark (flat topography), at the position marked by the dashed white line; the irradiation with ±45° interference pattern (IP) is switched on. The distribution of the electric field vector relative to the topography maxima and minima is shown by the white arrows (Fig. 2a). In the case of a 750-nm-thick polymer film, the kinetics of the SRG growth is slower. The final SRG height is 160 nm after 1 h of irradiation (see also the inset in Fig. 2b, showing the final in situ AFM micrograph). The peak in the DE appears also at the SRG height of 100±10 nm (after 17 min of irradiation). Further reduction of the Pazo polymer film and a fixed irradiation time of 1 h.

Fig. 2 In situ-recorded SRG height (black dots) and diffraction efficiency (1st order DE, red curve) as a function of time during irradiation with ±45° IP for different thicknesses of the Pazo polymer film: a 1 μm, b 750 nm, c 500 nm and d 200 nm. The inset in a shows the in situ AFM micrograph of the polymer film deformation during irradiation. The direction of scanning (indicated by the red arrow at the bottom right corner) is from top to bottom showing the temporal evolution of film topography. The AFM scanning starts without irradiation (flat film), and at the position marked by the dashed white line, the irradiation (λ = 491 nm, I = 200 mW/cm², ±45° configuration, A = 2 μm) is switched on. The local polarization of the electric field relative to the topography maxima and minima is shown by white arrows. The insets in b–d illustrate the topographies of the final SRG measured by AFM.
of the film thickness to 500 nm results in a drop of the final SRG height to 120 nm (Fig. 2c). In the DE, a saturation level at the characteristic height of 100 ± 10 nm is reached. In the case of 200-nm-thick polymer film, the maximal SRG height after 1 h of irradiation is 22 nm (Fig. 2d) and the DE signal does not show any drop.

In the following, we explain that the distribution of the intensity within the diffraction spot is the result of the integration of light diffracted at different SRG modulation depths (different positions). Indeed, the grating does not have a constant modulation amplitude, $u$, over the inscribed area, but rather a circular shape set by the profile of the writing beams (see schematic representation in Fig. 4b), due to the Gaussian profile of the writing beam. Since the spot sizes of the writing (4 mm) and the probe beam (3 mm) are comparable, the DE signal is acquired from the whole irradiated area where the probe beam is diffracted at spatially inhomogeneous modulated SRG amplitude.

To compare the data with a theoretical model, we have computed the diffracted light wave in the far field and the near field (see Appendix for details). The basic idea is to “shrink” the azo-polymer film into a phase grating that is observed in reflection. For our setup, the intensity of the diffraction spot in the $n=1$ order is given by:

$$I_n \propto \frac{\sin^2 \left( \frac{n \pi u}{w} \right)}{\left( \frac{n \pi u}{w} \right)^2}$$
The function $u(r)$ is proportional to the phase front modulation amplitude imprinted at position $r$ by the film, and $\exp(-r^2/\sigma^2)$ gives the intensity profile of the probe beam. The diffraction efficiency $\eta$ is obtained by integrating Eq. (1) over $r$ followed by normalization. The results of this calculation are illustrated in Fig. 3. The angular profile of the diffraction spot is shown in Fig. 3a, assuming that the probe beam diameter ($\sigma$) is similar in size to the SRG-inscribed area ($w = \sigma$). As the grating amplitude grows (from bottom to top), a “dark ring” appears in the spot profile starting at black curve, $u = 3.5$, in Fig. 3a).

This happens when the total diffracted intensity is beyond its maximum, as shown in Fig. 3b (dots on the red curve). There, we also show the influence of the probe beam size: a narrow beam ($\sigma = 0.5w$) diffracts similar to a homogeneously grating, with an efficiency related to the Bessel function $|J_n|^2$ that oscillates beyond its first the maximum. For a much wider beam, the diffraction efficiency increases monotonously.

We finally estimate the SRG height that corresponds to the first maximum of the first-order DE. In the reflection screen model, the optical path length permits to estimate the phase as $2\pi n' L / \lambda$, where $n'$ is the (real) refractive index at the probe wavelength. The probe beam passes from the substrate to the polymer–air interface and back. The relevant modulation depth of the path length $L$ is, therefore, twice the SRG height $\delta h$. This gives a phase modulation depth

$$u = \frac{4\pi n' \delta h}{\lambda}$$

The maximum of the Bessel function $J_1$ appears at $u_{\text{max}} \approx 1.84$ so that we get a peak-to-bottom amplitude $2\delta h_{\text{max}} \approx 108$ nm in reasonable agreement with the experimental value $100 \pm 10$ nm ($n'_{633 \text{nm}} = 1.7$). The agreement would become better (smaller value for $\delta h_{\text{max}}$) if we took into account a volume grating in the film which also contributes to the optical DE. Such an analysis will be presented in another paper.

We confirm experimentally the theoretical predictions shown in Fig. 3. The spot size of the probe beam is reduced to 1 mm and the DE signal, as well as the SRG amplitude, is recorded during irradiation at different position along the irradiated area (Fig. 4b): at the center of the irradiated area (red curve in Fig. 4aI), 1 mm and 2 mm away (red curves in Fig. 4aII, III). Here, the probe beam is still centered with respect to the AFM probe, but the center of the pump beam is shifted stepwise with respect to the AFM cantilever. As can be seen from Fig. 4a with increasing the distance from the center, the height of the SRG decreases due to the Gaussian envelope of the writing beam intensity. The DE signal recorded in the center (I) has similar shape as in the case presented in Fig. 1, but the extrema of curve (maxima and minima) are shifted to smaller SRG height as predicted in Fig. 3b. At 1 mm off center, the SRG height is smaller and the DE curve shifts to later times (red curve in Fig. 4aII). The last measurement is performed 2 mm away from the center at the edge of the illumination spot (see Fig. 4aIII); here, the intensity is weak, and thus the maximal SRG height is 70 nm, so that no drop in the DE became noticeable.

### 4 Conclusions

We demonstrated that during continuous irradiation of a photosensitive polymer film with an interference pattern, the diffraction efficiency (DE) of a probe beam changes in a non-monotonous way, showing several maxima and minima; while the amplitude of the surface relief grating (SRG) is monotonously increasing. We used the Raman–Nath theory to compute the fine structure in the spatial profile of the diffraction spot that appears clearly when the DE goes through its maximum. The reason for this fine structure is that the spatial profile of the inscribed grating differs from an infinitely extended grating because of the Gaussian envelope of the irradiation pattern. Using a probe beam which matches the irradiated area in size, the profile of the diffraction spot changes as a function of the SRG height from a Gaussian through a hollow beam (“donut”) to a ring structure with a bright center. For a narrow probe beam, the DE follows the theory for an infinite grating (squared $n$th oder Bessel function), with a maximum first-order DE appearing for SRG heights around ~ 100 nm. In deeper reliefs, the DE is distinctly different from the Bessel function when the probe beam size is not much narrower than the irradiated area. These results are based on a simple reflecting phase screen model that combines the SRG and the birefringence grating in the bulk of the film into one complex reflection function [39]. These findings are confirmed in the experiment by probing the DE with a probe beam diameter much smaller than the inscribed area and aiming the probe at different positions of the SRG, while measuring the SRG amplitude simultaneously with an AFM. Only probe beams with sizes as narrow as half the waist of the writing beams ($\sigma = 0.5 w$) diffract similar to an infinite grating with homogenous modulation depth. The Raman–Nath-based model we propose also comprehensively explains the fine structure within the diffraction spot.

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Appendix

We get a tractable calculation of the diffraction efficiency and the spot profile, when the sample is modeled as a reflecting phase screen. This means that the light wave, after (partial) reflection from the sample, is given by a complex reflection function that contains a spatially modulated phase \[39\]

\[
\psi_{\text{out}}(r) = R \exp\left[i \varphi(x,y)\right] \psi_{\text{in}}(r)
\]

where \(R\) is the overall reflection amplitude and \(x, y\) are coordinates parallel to the screen [we write \(R\psi_{\text{in}}(r)\) although this wave has actually a reversed propagation direction due to reflection from the non-modulated screen (specular order)].

We first compute the diffraction pattern in the far field: it is given in the Fraunhofer–Kirchhoff approximation, by

\[
I(q) = \left| \tilde{\psi}_{\text{out}}(q) \right|^2
\]

where \(\tilde{\psi}_{\text{out}}(q)\) is the the 2D Fourier transform of \(\psi_{\text{out}}(r)\). We consider first the simple case of an infinitely extended phase grating where \(\varphi(x,y) = \sin(\mathbf{G} \cdot \mathbf{r})\) and \(\mathbf{G}\) is the grating vector. Then, the outgoing wave is

\[
\psi_{\text{out}}(r) = R \exp[iu \sin (\mathbf{G} \cdot \mathbf{r})] \psi_{\text{in}}(r)
\]

The first factor (the phase modulation) is periodic in \(r\) along the direction \(\mathbf{G}\) with period \(\Lambda = 2\pi/\mathbf{G}\). It can be expanded in a Fourier series

\[
\exp[iu \sin (\mathbf{G} \cdot \mathbf{r})] = \sum_n J_n(u) \exp(in \mathbf{G} \cdot \mathbf{r})
\]

with coefficients \(J_n(u)\) given by Bessel functions (Jacobi–Anger expansion). If the incoming wave is a plane wave, \(\psi_{\text{in}}(r) = \sqrt{i_n} \exp(i \mathbf{k}_0 \cdot \mathbf{r})\), the outgoing wave contains the wave vectors

\[
\mathbf{k}_n = \mathbf{k}_0 + n \mathbf{G}
\]

We may choose the \(x\)-axis along \(\mathbf{G}\) and introduce the diffraction angle \(\theta_n\) via \(k_n = k \sin \theta_n\) with the wavenumber \(k = 2\pi/\lambda\). The discrete diffraction orders appear under the angles (Bragg–Laue condition)

\[
\sin \theta_n - \sin \theta_0 = \frac{n \mathbf{G} \lambda}{2\pi}
\]

where \(\lambda\) is the wavelength of the wave. For an infinite grating, the diffraction efficiencies are thus given by the squared coefficients in Eq. (6):

\[
\eta_n = \frac{I_n}{I_{\text{in}}} = \left| R \right|^2 \left| J_n(u) \right|^2
\]

In the experiment, the grating does not have a constant modulation amplitude \(u\), but rather a circular shape set by the profile of the writing beams. We assume here a Gaussian grating profile

\[
\varphi(x,y) = u(\rho) \sin Gx \quad u(\rho) = u e^{-\rho^2/2w^2}
\]

with \(\rho^2 = x^2 + y^2\). The width \(w\) is much larger than the grating period \(\Lambda\). This motivates an approximate evaluation of the Fourier transform \(\tilde{\psi}_{\text{out}}(q)\) (the far field)

\[
\tilde{\psi}_{\text{out}}(q) = R \sqrt{I_{\text{in}}} \int dx dy e^{iu(\rho) \sin Gx} \exp[i(q_\text{in} - q) \cdot \mathbf{r}]
\]

that we explain in the following. We split the integral along \(x\) into periods of size \(\Lambda\) centered at \(x_i = l\Lambda\) and replace \(x \rightarrow x_i + x\) with \(-\Lambda/2 \leq x \leq \Lambda/2\) and \(l = 0, \pm 1, \pm 2, \ldots\). We also focus on a far-field direction close to the \(n\)th order and set \(q_x = k_n + nG + \delta q\) with \(\delta q \ll G\) (angular fine structure of the diffraction spot). Observe that \((q_x-k_n)(x_i+x) \equiv \delta qx_i + (nG + \delta q)x\mod 2\pi\). We apply a multiple-scale approximation and assume that the grating modulation \(u(\rho)\) varies slowly across the grating period \(\Lambda\). This means that we can set

\[
u(\rho) \approx u(\rho_l), \quad \rho_l^2 = x_i^2 + y^2
\]

The integral along \(x\) over one grating period then gives

\[
\int_{-\Lambda/2}^{\Lambda/2} dx e^{iu(\rho_l) \sin Gx} \exp[-i(nG + \delta q)x] \approx \Lambda J_n^2(u(\rho_l))
\]

where a small phase \((|x\delta q| \leq \Lambda \delta q)\) was neglected. (This will be justified from the end result Eq. (15) below.) The sum over the grating periods is replaced back by an integral

\[
\tilde{\psi}_{\text{out}}(q) \approx R \sqrt{I_{\text{in}}} \sum_l \Lambda J_n^2(u(\rho_l)) e^{-i\delta q \cdot r_l}
\]

This is the key result of the calculation: the shape of the diffracted beam (as measured by the angular deviation \(\delta q\) from the \(n\)th order) is the Fourier transform of the local diffraction amplitude (the Bessel function \(J_n^2(u(\rho_l))\)).

We finally compute the near-field profile of the diffraction spot. It is easy to read off the back Fourier transform from Eq. (14). We get for the beam shape in the \(n\)th order:

\[
\psi_n(r) = R \sqrt{I_{\text{in}}} J_n(u(\rho))
\]

This proves Eq. (1) in the main text.

To evaluate Eq. (14), one simplification is possible by switching to polar coordinates: \(\exp(-i\delta q \cdot r) = \exp(-i\delta q \cos \phi)\). The \(\phi\) integral gives \(2\pi J_0(\rho \delta q)\), and we finally get

\[
\tilde{\psi}_{\text{out}}(q) \approx 2\pi R \sqrt{I_{\text{in}}} \int_0^\infty \rho d\rho J_n\left(ue^{-\rho^2/2w^2}\right) J_0(\rho \delta q)
\]
For large $\rho \gg w$, the Bessel function $J_\rho$ becomes proportional to $e^{-\rho^2/2\sigma^2}$ so that the integral converges for $n > 0$. Its numerical evaluation presents no difficulties. We can estimate its typical width as a function of the scattering wave vector as $\delta q \sim 1/w$. Since we assumed a scale $w$ for the grating profile much wider than the period $A$, the phase neglected in Eq. (13) is at most $O(A/w) \ll 1$.

Finally, we consider the case that incident and specular beams have a Gaussian profile

$$\psi_{in}(r) = R \sqrt{I_{in}} e^{i k x} \exp \left( -\rho^2 / 2\sigma^2 \right)$$

(17)

We assume that the waist of the probe beam $\sigma$ is also larger than the grating period. The preceding calculation can be carried through, and we get Eq. (16) with an additional factor $\exp(-\rho^2 / 2\sigma^2)$ under the integral. The predictions of this theory are illustrated in Fig. 3. The angular profile of the diffraction spot is shown in Fig. 3a, assuming that the probe beam is matched in size to the grating covered area ($\sigma = w$). As the grating amplitude grows (from bottom to top), a “dark ring” enters the spot profile (top curves). This happens when the total diffracted intensity is beyond its maximum, as shown in Fig. 3b (dots on the red curve). There, we also show the influence of the probe beam size: a narrow beam ($\sigma = w/2$) diffracts similar to an infinite grating, with an efficiency related to the Bessel function $|J_\rho(0)|^2$ that oscillates beyond the maximum efficiency. For a much wider beam ($\sigma \gg w$), the diffraction efficiency increases monotonously. An analytical proof of this property is given in the Supporting Information.

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