Molecular $\chi^{(2)}$ gratings via electron-beam lithography

Jorge Luis Domínguez-Juárez,¹ Roberto Macovez,¹ María Ujue González,² and Jordi Martorell^{1,3,a)}

¹ICFO-Institut de Ciències Fotoniques, Mediterranean Technology Park, 08860 Castelldefels (Barcelona), Spain

²Instituto de Microelectrónica de Madrid-IMM (CNM-CSIC), Tres Cantos, 28760 Madrid, Spain

³Departament de Física i Enginyeria Nuclear, Universitat Politècnica de Catalunya, 08222 Terrassa, Spain

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We show that the nonlinear optical activity of an organic molecule may be quenched by electron irradiation. Exploiting this effect, we inscribe periodic $\chi^{(2)}$ patterns in the molecular films by means of a scanning electron microscope. The second harmonic diffraction efficiency of the resulting $\chi^{(2)}$ gratings is measured. The relative intensity of the diffraction orders observed agrees with the expectations for a sheet of nonlinear dipoles with a periodic modulation. No linear diffraction is seen. The present method allows realizing any type of two-dimensional $\chi^{(2)}$ pattern with a resolution only limited by the electron beam patterning capabilities. © 2010 American Institute of Physics. [doi:10.1063/1.3464161]

High-resolution patterning of ultrathin films by means of electron-beam lithography is an important tool in nanotechnology, which has been established for several types of organic films on various substrates. The effect of electron-beam irradiation on organic molecules at surfaces is not always known, and usually varies depending on parameters such as substrate temperature, electron kinetic energy and irradiance, and composition of the organic film. Electron irradiation may entail for example total or partial desorption of the film,^{1,2} selective damage to a part of the organic molecule,^{2,3} or electron-induced reactions,⁴ leading to a modified chemical reactivity or optical activity or, as we show here, to quenching of the nonlinear optical response of a molecular film.

Systems displaying a periodic modulation of the quadratic nonlinear susceptibility $\chi^{(2)}$ allow simultaneous generation and separation of the second harmonic wave from the fundamental input field.⁵ Such $\chi^{(2)}$ patterns can operate as couplers⁶ into waveguide structures and enable resonance-enhanced wavelength conversion, e.g., in nonlinear grating waveguides,^{7,8} and are key elements for integrated optics in distributed feedback lasers.⁹ For quasi-phase matched second harmonic and difference frequency generation, periodic patterning of the nonlinear optical susceptibility without modification of the linear refractive index is required. Usually, this purely nonlinear modulation is obtained by periodic poling.¹⁰

In this paper, we expose thin films of a nonlinear organic chromophore deposited on glass substrates under the electron beam of a scanning electron microscope (SEM) and find that the nonlinear optical response of the dye is quenched as a consequence of electron irradiation. This allows us to pattern molecular films of nanometer thickness on a transparent dielectric substrate, thereby achieving a nonlinear $\chi^{(2)}$ grating without modification of the linear refractive index of the medium. It is known that patterned molecular (and atomic) layers on surfaces may give rise to nonlinear diffraction^{11–13} despite their extremely small thickness compared to the

wavelength of the light. Second harmonic diffraction from monolayer gratings has allowed the study of surface phenomena such as adsorption^{13,14} or diffusion^{12,15} without the interference of substrate effects.¹¹ These structures have been, however, achieved with low-resolution methods such as light-induced desorption in the cross field of two interfering beams.^{11,13} The electron-lithography technique presented here offers several advantages as it produces higher-resolution, precisely aligned, homogeneous patterns, while at the same time allowing for different kinds of two-dimensional patterning also on nonflat surfaces.¹⁶

Thin molecular films of a nonlinear chromophore (crystal violet) were deposited onto microscope quartz slides from a 8×10^{-4} molar solution in 1-propanol. For homogeneity and reproducibility, a motorized stage was used for controlled immersion and retrieval, while the choice of solvent enhanced wetting and evaporation in the meniscus region. One side of the substrates was carefully cleaned leaving the organic film only on one side. The absorption intensity of the molecular films as measured by extinction spectroscopy indicates that their thickness is of few molecular layers.¹⁷ The electron beam of an SEM designed for lithography purposes was focused, as shown schematically in the inset of Fig. 1, to write a grating onto the molecular film. The electron kinetic energy of the electron beam was set to 10 keV. Preliminary experiments showed that the grating quality was virtually independent upon the impinging electron energy in the range between 5 and 30 keV. During these experiments, we noticed that exposure to SEM illumination in imaging mode, i.e., with a relatively low electron dosage, was already sufficient to determine a reduction in second harmonic generation from the molecular film. To obtain the gratings, the beam was scanned to draw a series of parallel stripes, few microns wide and 2 mm long (see inset of Fig. 1), leaving in between a nonexposed stripe of either the same width or three times as large, so that the period δ was twice or four times the width α of the irradiated stripe. The nonirradiated film areas constitute a one-dimensional (1D) $\chi^{(2)}$ grating. Typical gratings presented in this work had a size of two square millimeters and period ranging from 4 to 40 μm . For our second harmonic generation experiments, we used an amplified

a)Electronic mail: jordi.martorell@icfo.es.

FIG. 1. (Color online) Schematic view of the experimental setup used for measuring the diffracted second harmonic light (TS stands for translation stage). Inset (left): writing of a periodic $\chi^{(2)}$ pattern onto the molecular film by SEM. The nonlinear activity of the molecule is quenched by e-beam irradiation.

Ti:sapphire laser emitting a 1 kHz train of 150 fs pulses centered at 800 nm in wavelength. The beam was focused using a 50 cm focal distance lens to increase the energy density at the sample, which was placed before the focal point to avoid any damage. The substrate formed an angle of 45° with respect to the laser beam as depicted in Fig. 1. The beam size at the position of the sample was of few hundreds microns.

The measured surface second harmonic signal at $\lambda=400$ nm in specular reflection geometry is shown in Fig. 2 at different points of a sample containing several gratings. The sample was displaced in steps of 0.025 mm using a micrometric mount in the direction parallel to the plane of the film, i.e., at 45° with respect to the laser beam, thus maintaining constant the position of the reflected beam during the scan. Curve (a) was acquired near a pristine region of the film and curve (b) was measured scanning a region with two gratings of same period but different irradiated width α , equal, respectively, to one half and one fourth of the period ($\delta=40$ μm), as shown in the schematics of Fig. 2. Both

FIG. 2. (Color online) Second harmonic (SH) generation scans across different film regions (measured in reflection) as indicated in the drawing: (a) pristine film; (b) film region with two gratings of same period but different width α of the exposed stripes. Inset: dependence of the SH signal upon the irradiated area ratio.

curves display a vanishing intensity on the left-hand side followed, toward the right, by an abrupt onset of the signal in correspondence with the film edge. The almost vanishing signal in the part of the substrate that is not covered by the dye indicates that second harmonic generation from the clean glass surface is almost negligible under our experimental conditions. As visible in the central part of curve (b) in Fig. 2, the inscription of gratings with 25% or 50% irradiated area ratio leads to a lowering in the second harmonic intensity in specular reflection. The reduction in second harmonic intensity from the grating is indicative of the presence of undamaged molecular areas in the grating region, which shows that spatially-selective irradiation is achieved. For comparison, we have irradiated extended regions of molecular films grown from the same solution using the same SEM settings. In this case, we have seen that the second harmonic signal in reflection is comparable with that of the clean glass substrate, indicating that electron irradiation results in almost total quenching of the nonlinear activity of the dye.

As shown in the inset of Fig. 2, the measured second harmonic signal in reflection is approximately proportional to the ratio α/δ , or, which is the same, it is linearly proportional to the average molecular density in the grating region. This is surprising, since from the quadratic dependence of the second harmonic intensity upon molecular density¹⁴ one would expect that the intensity of the zero-order of diffraction in the grating region should be approximately proportional to the square of the nonirradiated area. This discrepancy might be due to a nonlinear interference effect upon generation. It is well known that second harmonic generation is strongly dependent on momentum (or phase) matching conditions; in the present case the generation of second harmonic light from a molecular stripe occurs in the presence of the (near) field generated by neighboring stripes. Given the arbitrariness of the grating period chosen, the phase relationship between the second harmonic fields from different stripes does not give rise to a perfect addition of the second harmonic near-fields, which might explain the less than quadratic dependence of the far field signal upon molecular density. A linear dependence upon domain density is for example observed in the case of second harmonic generation from random 1D structures.¹⁷ Further investigation is needed to confirm this hypothesis.

The second harmonic diffraction patterns obtained with grating periods of $\delta=40$, 20, and 10 μm and area coverage of 50% are shown in Fig. 3(a). The diffraction intensities were acquired displacing the detector using a linear motorized stage, as shown in Fig. 1. The angular position of the +1 or -1 diffraction orders agree well with diffraction theory for the second harmonic wavelength where the angular position of the various second harmonic diffraction orders in reflection is given by $\sin \gamma_m = \sin \theta_i + m(\lambda/\delta)$, ($m=0, \pm 1, \pm 2, \dots$). It can be observed that the intensity of +1 or -1 diffraction orders is approximately the same for all three gratings, which shows that the diffraction efficiency is not dependent upon the period. This is perhaps not surprising as the second harmonic wavelength used is much smaller than the periodicity of the grating. Figure 3(b) shows the pattern obtained with a period of $\delta=4$ μm . The first order of diffraction which indicates a proper grating formation is clearly visible in the figure. Despite the relatively high intensity of the fundamental infrared beam, no linear diffraction

FIG. 3. (Color online) Second harmonic diffraction patterns from gratings of different period [(a), $\delta=40, 20, 10 \mu\text{m}$; (b) $\delta=4 \mu\text{m}$], with the fundamental beam impinging at 45° . The angular spacing between the diffraction peaks matches the expectations for second harmonic diffraction at a wavelength of 400 nm for the various periods used for the lithography. The intensity of the specular ($m=0$) order saturated the detector.

was detected for any of the gratings. This demonstrates that the observed diffraction is not a geometrical effect due to surface corrugation induced by the lithography process but is only the result of the spatial modulation of the hyperpolarizability. From an applied point of view, the absence of diffraction of the fundamental beam is interesting for applications that require the separation of the fundamental and second harmonic beam while avoiding loss of fundamental power into several diffracted orders.

In conclusion, we have shown that electron irradiation effectively quenches the second-order nonlinearity of crystal violet molecules adsorbed on a glass substrate. The exact effect of electron beam irradiation on the molecules is still unknown. The quenching of second harmonic generation

could be due to a modification of the electronic or chemical configurations, or to desorption or destruction of the whole molecule. The achieved $\chi^{(2)}$ gratings were characterized by second harmonic diffraction, while no linear diffraction was detected. Possible applications of these structures are phase matched second harmonic generation in waveguides coated with a nonlinear grating,¹⁸ exploiting the patterning capabilities of SEM to implement two-dimensional quasi-phase matching mechanisms¹⁹ or the suppression or enhancement of second harmonic generation at interfaces through Wood's resonance anomalies.^{20,21} The method presented might moreover be useful to perform selective nonlinear spectroscopy of dyes at or close to nanostructures.

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