Second-harmonic diffraction from a monolayer grating

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Diffracted surface second-harmonic radiation emerging in several orders has been observed from a periodically modulated monolayer of adsorbed dye molecules. The molecular grating was produced by laser-induced desorption in the field of two crossed beams. An elementary theory is presented that relates the characteristics of the second-harmonic diffraction pattern to the spatially varying properties of the surface and is applied to infer the adsorbate density profile of the spatially modulated grating. The density profile is compared with the predictions of a model of grating formation based on thermal desorption.

Induced grating techniques have proved of great value for investigating the bulk properties of materials.[1] As a rule, however, these methods lack sensitivity to surface properties and have not been suitable for use in examining surfaces and interfaces. The nonlinear optical processes of second-harmonic (SH) and sum-frequency generation, on the other hand, have been developed as powerful tools for probing surfaces with monolayer sensitivity.[2] In this Letter we present results of a study that combines the capability of second-harmonic generation (SHG) for probing surface properties with the possibility of producing a grating structure by means of interfering laser beams. We demonstrate that a grating of monolayer thickness can be produced by exposing an adsorbed molecular layer to interfering laser beams and that such a grating can give rise to observable second-harmonic radiation in several diffracted orders. As we show, the SH diffraction can be related to the spatial variation of the nonlinear susceptibility along the surface. For the case of a grating in adsorbate density, produced in this study by laser-induced desorption, we are able to infer the spatial profile of the adsorbate concentration. Further, as we discuss in this Letter, this information can be used to develop a model for the desorption process. In an independent study, Reider et al.[3] have reported SH diffraction in first order from periodically modulated structures formed by a direct writing scheme. Zhu et al.,[4] in a different recent work, have monitored surface diffusion of adsorbed molecules by measuring SH radiation in the first-order diffracted beam.

First we present some general considerations regarding SHG from structures with periodically modulated surfaces. The response of the surface is characterized by the surface nonlinear susceptibility tensor $\chi_s^{(2)}$, relating the nonlinear source polarization per unit area to the pump electric field in the surface plane. For a grating with variation only along the x spatial coordinate, the surface nonlinear susceptibility can be written in a Fourier expansion as $\chi_s^{(2)}(x) = \sum_{n=-\infty}^{\infty} \chi_s^{(2)}(n)\exp(ink_gx)$, where k_g is the wave vector characterizing the grating of period $l_g = 2\pi/k_g$. Under laser excitation at a frequency ω, a surface nonlinear polarization is induced with

$$\mathbf{P}_s^{2\omega}(x) = \sum_{n=-\infty}^{\infty} \chi_s^{(2)}(n){:}\mathbf{E}_s^\omega\mathbf{E}_s^\omega \exp[i(2k_x^\omega + nk_g)x]. \quad (1)$$

Here $\mathbf{E}_s^\omega$ is the pump electric field at the surface, and the sample is assumed to be oriented so that the component of the pump wave vector in the surface plane is $k_x^\omega\hat{\mathbf{x}}$, i.e., with the lines of the grating perpendicular to the plane of incidence. This nonlinear polarization will lead to SH radiation emerging not only in the usual transmitted and reflected directions ($k_x^{2\omega} = 2k_x^\omega$) but also in diffracted directions specified by the relation $k_x^{2\omega}(n) = 2k_x^\omega + nk_g$, with $n = \pm1, \pm2, \pm3, \ldots$. The angular spacing between the different diffracted beams for SH radiation will be half as great as for the linear diffraction of the pump radiation, as noted previously by Wokaun et al.[5] for SH diffraction from periodic arrays of silver microparticles.

The expression for the strength of the radiated SH fields can be obtained by considering a polarized sheet[6] for each Fourier component of the nonlinear susceptibility. The nth-order diffracted SH field $\mathbf{E}^{2\omega}(n)$ polarized along $\hat{\mathbf{e}}^{2\omega}$ is given by

$$\hat{\mathbf{e}}^{2\omega}(n) \cdot \mathbf{E}^{2\omega}(n) = 4\pi i\omega c^{-1} \sec\theta(n)$$
$$\times [\mathbf{e}_s^{2\omega}(n) \cdot \chi_s^{(2)}(n){:}\mathbf{e}_s^\omega\mathbf{e}_s^\omega][E^\omega]^2. \quad (2)$$

In this relation, $\theta(n)$ is the angle of the diffracted SH radiation, the vectors $\mathbf{e}_s^\omega$ and $\mathbf{e}_s^{2\omega}$ refer to the polarization of the pump and detected radiation after transformation by the Fresnel factors appropriate for propagation to the surface, and $\mathbf{E}^\omega$ is the electric field of the pump laser. For SH radiation appearing only in a narrow range of angles, the SH electric field in each diffracted beam will, according to Eq. (2), be proportional to the corresponding Fourier component of the effective surface nonlinear susceptibility. It should be noted that the simple relation between the Fourier components of the surface nonlinear susceptibility and the radiated SH fields applies only in the limit of a thin diffraction grating. A more complex analysis is required for surfaces with a corrugation approaching the scale of a wavelength of light,[7] since propagation effects will lead to multiple scattering. For the case of modulated molecular monolayers considered here, the

approximation of Eq. (2) should be valid. The lack of multiple scattering from these structures is substantiated by the low efficiency observed for linear diffraction.

Diffracted SH radiation will result from any periodic modulation of the surface properties influencing the surface nonlinear susceptibility tensor. Such gratings might arise from changes in molecular composition, orientation, or excitation in an adsorbed layer. In the present study we are concerned with a variation in adsorbate density. Under the neglect of local-field corrections, Eq. (2) yields a simple relation between the amplitude of radiated SH fields (for a given combination of pump and detected polarizations) and the Fourier coefficients of the adsorbate density:

$$E^{2\omega}(n)/E^{2\omega}(0) = N_s(n)/N_s(0). \qquad (3)$$

This equation holds even for a complex surface nonlinear susceptibility, as one would observe for a resonant response.

We have investigated SH diffraction from a periodically modulated monolayer of Rhodamine 6G dye molecules adsorbed on a fused-silica substrate.[8] In the data reported here, the average density of the dye molecules was roughly $7 \times 10^{13} \text{ cm}^{-2}$, as deduced from linear absorption measurements for the $S_1 \leftarrow S_0$ transition. The surface gratings were formed by means of photodesorption in the field of two crossed beams. For this purpose, the frequency-doubled output of a Q-switched Nd:YAG laser (6-nsec pulses at a wavelength of 532 nm) was split into two beams, which were brought together on the surface at $\pm 2.0^\circ$ from the surface normal ($l_g = 7.6 \ \mu\text{m}$). The gratings were probed by pump radiation from a dye laser, which produced pulses of nanosecond duration at 690 nm. The pump wavelength was chosen to take advantage of the enhanced nonlinear response from the $S_2 \leftarrow S_0$ transition at the SH frequency.[8] [Since this feature is quite broad, we do not anticipate that resonant excitation will increase the sensitivity of the molecules to the local environment, a factor that has been implicitly

neglected in Eq. (3).] The SH light in the reflected direction was detected with a photomultiplier and conventional gated electronics. Different diffracted SH beams were selected by rotating the sample about an axis perpendicular to the plane of incidence.

Typical results of a SH diffraction measurement are shown in Fig. 1(a). The dashed curve represents the SH intensity from a homogeneous film of Rhodamine 6G molecules adsorbed on fused silica. Only a single peak in the SH signal is observable as a function of sample rotation, corresponding to the detection of the reflected SH wave with an angle of incidence and an angle of reflection of 45°. The solid curve in Fig. 1(a) displays the SH intensity from the molecular layer after a grating has been formed by photodesorption with a (spatially averaged) fluence of 1.8 J/cm² at the surface. In addition to the sharp decrease in the reflected SH signal, associated with the decrease in the average density of the adsorbed molecules, diffracted peaks are now visible. The predicted positions of the diffracted SH beams follow immediately from the relation $k_x^{2\omega}(n) = 2k_x^\omega + nk_g$, with $n = \pm 1, \pm 2, \ldots$. In our experiment, we expect to observe diffraction peaks spaced by $\delta\theta \approx 1.83^\circ$, as indicated in the figure. The data in Fig. 1 were obtained for SHG with p-polarized pump and detected radiation. Other combinations of polarization gave equivalent diffraction patterns, in line with expectations for a grating in the adsorbate density. To show the diffracted radiation more clearly, we have plotted in Fig. 1(b) the SH electric field strength corresponding to the solid curve in Fig. 1(a). Three diffracted orders of SH radiation are readily identified.

We now turn to the question of reconstruction of the spatial profile of the adsorbate density $N_s(x)$ of the surface gratings from the observed SH diffraction pattern. From the signal strength in each diffracted order n and Eq. (3), we can determine the relative magnitudes of the Fourier components of the adsorbate spatial distribution: $|N_s(n)/N_0|$, where N_0 denotes the density of the film before the formation of the grating. In general, this information is insufficient to permit the spatial profile to be determined completely, since we do not know the signs of the different Fourier components. In these studies we had only a few signs to determine, and we were able to do so by imposing the constraint that the inferred adsorbate profiles lie between 0 and N_0. The reconstructed adsorbate densities (solid curves) are shown in Fig. 2 for one period of the grating. The strongly modulated profile was inferred for a grating formed with a desorption fluence of 1.6 J/cm²; the weakly modulated case corresponds to a desorption fluence of 1.1 J/cm². In the figure we have scaled the profile to be unity in the region of low desorption, in agreement, within experimental accuracy, with the results based on a comparison of signal strengths from the homogeneous film before formation of the grating.

Each adsorbate density profile in Fig. 2 can be considered a simultaneous measurement of adsorbate density for exposure of the surface to differing laser intensities and, as such, contains information about the desorption process. Here we outline an elementary model of the formation of the grating based on a
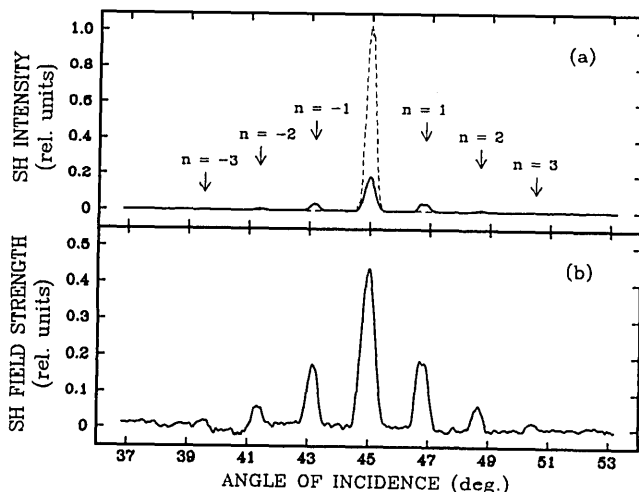

Fig. 1. Diffracted SH signals from a molecular monolayer as a function of sample rotation. (a) SH intensity from the monolayer before (dashed curve) and after (solid curve) the formation of a grating. (b) SH field strength from the grating.
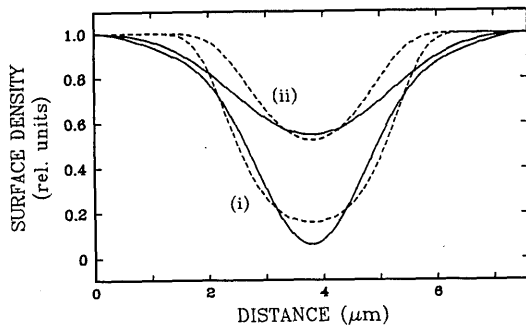
Fig. 2. Average surface densities for the monolayer gratings compared with the original densities of the homogeneous monolayers as a function of spatial position. The solid curves are based on the experimental diffraction patterns, and the dashed curves are obtained from the thermal desorption model. Grating (i) was formed with a desorption fluence of 1.6 J/cm^2; grating (ii) with a fluence of 1.1 J/cm^2.

thermal desorption process.[9] A more detailed discussion is provided elsewhere.[10] The spatially varying surface temperature is calculated from the thermal diffusion equation, assuming that all the heat is deposited in the surface. The desorption process is then described by first-order kinetics with a preexponential factor ν and an activation energy E_a. This leads to a density profile for the adsorbed molecules after the formation of the grating given by $N_s(x) = N_0 \exp\{-\nu\tau \exp[-E_a/k_B T_s(x)]\}$. To obtain this analytic form, we have made the approximation that the desorption rate is significant only (for a time τ) while the surface is near its peak temperature $T_s(x)$.

The dashed curves in Fig. 2 are calculated from the thermal desorption model presented above. The two adjustable parameters ν and E_a were fixed by fitting the strongly modulated profile. The weakly modulated profile was then predicted strictly from experimental parameters. Reasonable qualitative agreement is obtained. In this treatment we have, however, neglected any potential optical saturation of the adsorbed molecules during the desorption process. When this effect is introduced into the model, good agreement with the experimental density profiles is still obtained over a wide range of saturation behavior, and an activation energy for desorption of $E_a \sim 1.5$ eV can be inferred for the dye molecules. On the other hand, the choice of saturation intensity strongly influences the value of the preexponential factor ν (from 10^{10} to more than 10^{17} sec^{-1}), precluding a meaningful estimate of this quantity. For systems in which the surface temperature can be determined more accurately, the method presented here should permit a complete determination of the kinetic parameters.

In conclusion, we have demonstrated that SH diffraction to several orders may be observed from a periodically modulated molecular monolayer. An analysis was developed to relate the spatial variation of the adsorbate density and the characteristics of the SH diffraction pattern. The inferred spatial variation of the adsorbate density was found to be compatible with a model for formation of the grating based on laser-induced thermal desorption. We expect the method presented here to be widely applicable, since high SH diffraction efficiency is exhibited by any system with a significant modulation in the surface nonlinear susceptibility. It should be emphasized, moreover, that SH diffraction is not limited to density gratings. It will result from any periodic modulation of the characteristics of the surface reflected in the nonlinear response, such as the chemical composition and environment, alignment, and electronic or vibrational excitation of adsorbed molecules.

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Note added in proof: Since submission of this paper, higher-order diffraction has also been reported by X. D. Zhu and Y. R. Shen, Opt. Lett. **14**, 503 (1989).

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