Generation and detection of a monolayer grating by laser desorption and second-harmonic generation: CO on Ni(111)

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We show that a monolayer grating of CO on Ni(111) can be generated by laser desorption using two interfering laser pulses and detected and characterized *in situ* by surface second-harmonic generation.

Laser-induced dynamic gratings have found many important applications in modern science and technology.[1] They range from phase conjugation for real-time image reconstruction to material studies. In the latter case, monitoring of the time-dependent relaxation of the dynamic gratings in a medium allows us to deduce useful information on the dynamic properties that govern the diffusion of particles, energy, and even phases of coherent excitations in the medium. So far, research in this area has been heavily concentrated on bulk samples. It may seem obvious that the same scheme should be applicable to surfaces or interfaces to yield similar information on surface dynamic properties. However, a surface grating one or several monolayers thick is often difficult to monitor. This is particularly true for gratings composed of monolayers of small molecules. Diffraction of a probe beam by such a grating is easily masked by scattering of the beam from the bulk.

Recently optical second-harmonic generation (SHG) has been demonstrated to be highly surface specific.[2] It can therefore be an ideal method to probe surface monolayer gratings. Indeed, the multiorder diffraction of SHG from a dye monolayer grating can be easily observed.[3] Actually, monolayer gratings composed of large organic molecules can even be detected by linear optical diffraction.[4] For studies of surface diffusion[5] and reactions, however, one is often more interested in small molecules, such as CO, on well-defined surfaces in ultrahigh vacuum. Production and detection of a monolayer grating of such systems are understandably much more difficult. Here we report the first study to our knowledge of controlled generation of monolayer gratings of CO on Ni(111) by laser-induced desorption and the subsequent detection of the gratings by SHG. Surface diffusion of molecules will smear out the monolayer gratings. Time-dependent observation of how a grating disappears allows us to deduce the surface diffusion constant for the adsorbed molecules. This is reported elsewhere.[5]

In our experiment, a 99.998% pure Ni(111) sample 1 cm in diameter and 1.5 mm thick was situated in an ultrahigh-vacuum chamber with an operating pressure of 0.8×10^{-10} Torr. It was mounted vertically with one of its (110) axes oriented 30° off the horizontal plane. Ar^+ sputtering at a beam voltage of 500 V with subsequent annealing in slow cooling was used to prepare a clean, well-defined surface. This was manifested by the negligible impurity traces in Auger spectroscopy and the sharp (1×1) low-energy electron-diffraction pattern. A Chromel–Alumel thermocouple welded to the sample was used to monitor the sample temperature.

For the generation of a CO monolayer grating on the Ni(111) sample, we first cooled the sample to 140 K and then covered its surface with a saturation coverage of $\theta = \theta_s = 0.5$. We then produced the monolayer grating, using the technique of laser desorption by overlapping two 1.06-μm laser beams on the sample. Both beams derived from the same Q-switched Nd:YAG laser had a TEM_{00} mode and a 16-nsec pulse width (FWHM). They were incident in the horizontal plane with incident angles $\phi = \pm 1.5°$ on the sample, as shown in Fig. 1. The beam profiles on the sample surface were given by $I_i(x, y) = I_i(0, 0)\exp[-(x^2 + y^2)/r_0^2]$ $(i = 1, 2)$ with $r_0 = 3.8$ mm, where $\hat{x}$ is taken as the horizontal axis on the surface. We adjusted I_1 and I_2

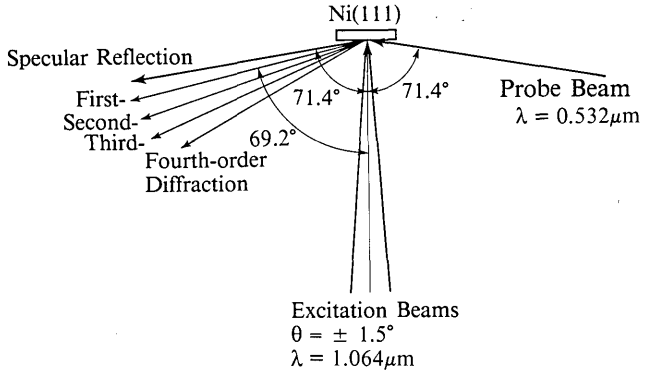

Fig. 1. Schematic of the experimental arrangement for generation and characterization of the monolayer grating of CO on Ni(111) in ultrahigh vacuum.

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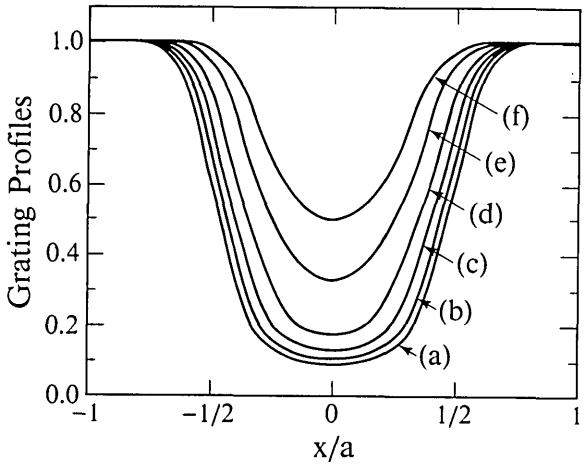

Fig. 2. Calculated groove structure of the monolayer grating at various distances r from the center of the desorption beam: (a) $r/r_0 = 0$; (b) $r/r_0 = 0.1$; (c) $r/r_0 = 0.3$; (d) $r/r_0 = 0.3$; (e) $r/r_0 = 0.4$; (f) $r/r_0 = 0.5$. Here, r_0 is the e^{-1} radius of the Gaussian desorbing beam.

such that the laser intensity profile on the surface had the interference pattern

$$I(x, y) = I_0(1 + 0.55 \cos \Delta k_{\parallel} x)\exp[-(x^2 + y^2)/r_0^2], \quad (1)$$

where $\int I_0 dt = 0.26$ J/cm^2, $\Delta k_{\parallel} = (4\pi/\lambda)\sin\phi$, and $\lambda = 1.064$ μm. From our earlier research on laser desorption of CO from Ni(111),[6] we know that at the center of the beam the CO desorption reached 90% at the interference maxima and less than 1% at the minima. Thus a CO monolayer grating with a grating spacing of $2\pi/\Delta k_{\parallel} = 20$ μm was formed. With the sample at 140 K, surface diffusion of CO on Ni(111) is slow, so that a CO monolayer grating remains essentially unchanged even after many hours.[5]

More quantitatively, knowing $I(x, y)$ and how the local CO surface coverage on Ni(111) should depend on the local laser desorption energy from our previous experiments,[6] we can find the spatial variation of the CO coverage $\theta(x, y)$ after the desorption by $\int_{-\infty}^{\infty} I(x, y)dt$. It has a grating structure with the groove profile slowly varying with x and y, deeper and broader in the center and shallower toward the edge of the desorbing beam spot. This is shown along the x direction in Fig. 2. In terms of a Fourier series, we can write

$$\theta(x, y) = \theta_0(x, y) + \sum_{m=1}^{\infty} \theta_m(x, y)\cos(m\pi x/a), \quad (2)$$

where $2a$ is the grating spacing and θ_0 and θ_m are deduced from the known grating profile.

After the grating was formed, we probed the grating, using the surface SHG technique. The probe beam was at 0.532 μm, obtained from frequency doubling of the same laser used for desorption. It impinged upon the sample with an incident angle of 71.4° and practically covered the whole grating in the $\hat{x}$ direction. The beam profile was Gaussian, with a beam radius of 1.16 mm at the e^{-1} point, and the maximum beam fluence was limited to 30 mJ/cm^2. As indicated in Fig. 1, diffraction of SHG up to the fourth order from the CO monolayer grating could be detected. The specularly reflected SHG, which corresponds to the zeroth-order diffraction, had a signal strength of ~160 photons/pulse. It measured the average surface coverage of CO after the laser desorption. The nth-order diffractions of SHG with $n = 1$–4 appeared at $\Delta\theta = 2.22°$, 4.24°, 6.10°, 7.84°, respectively, off the specular reflection direction, as expected from the phase-matching condition

$$k_{\parallel}(\text{diff}) = k_{\parallel}(\text{inc}) - n\Delta k_{\parallel}. \quad (3)$$

The observed intensities of the diffracted SHG of various orders, relative to that of the specularly reflected SHG, are presented in Fig. 3. They can be compared with the theoretical calculation of SHG diffracted from the CO monolayer grating with the deduced structural profile $\theta(x, y)$ mentioned above. It is known that the surface nonlinear polarization $P_s^{(2)}(2\omega)$, which in our case with CO on Ni(111) and both input and output $\hat{p}$ polarized, can be written as[2]

$$P_s^{(2)}(2\omega) = (\alpha + \beta\theta)E_p^2(\omega), \quad (4)$$

where α and β are constants. One can then easily see that the zeroth-order SHG has a signal strength

$$S_0 = \int (A + B\theta_0)^2 I_p^2 dx dy, \quad (5)$$

and the mth-order diffracted SHG has a signal strength

$$S_m = \int (B\theta_m)^2 I_p^2 dx dy, \quad (6)$$

where A and B are constants and $I_p(x, y)$ is the probe beam intensity on the sample surface. From the measurement of the adsorption dynamics of CO on

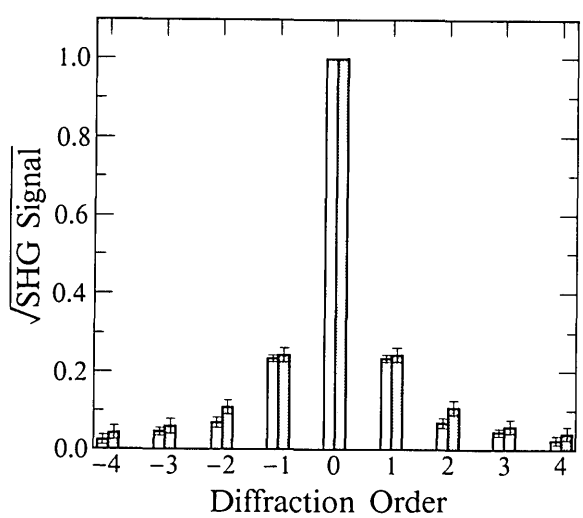

Fig. 3. Measured (unshaded) and calculated (shaded) square roots of various orders diffraction from the monolayer grating of CO on Ni(111).

Ni(111) using SHG similar to those in Ref. 2, we obtained $B/A = -0.68$. Thus the ratio S_m/S_0 can be calculated when $I_p(x, y)$, θ_0, and θ_m are known. The result of our calculation in comparison with the experimental observation is shown in Fig. 3. The agreement is remarkably good. This illustrates our ability to prescribe a monolayer grating by using laser desorption.

In summary, we have succeeded in demonstrating the possibility of using laser desorption to produce, and SHG to detect, a monolayer grating of CO on Ni in ultrahigh vacuum. Probing the time variation of such a grating can yield important information on the dynamics of molecular adsorbates.

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