Physisorbed Template for Spatial Patterning of Adsorbates

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The use of physisorbed species as a template for patterning of adsorbate monolayers at surfaces on the micron scale is demonstrated. A physisorbed monolayer is partially removed by laser-induced thermal desorption and serves as a mask during exposure of the final (chemisorbed) adsorbate species, thus acting in a manner similar to a monolayer photoresist. The effect, which has been demonstrated for H/Xe/Si(111)-(7 × 7), permits clean and precise patterning of monolayers of strongly bound and/ or thermally unstable adsorbates. [S0031-9007(97)04325-1]

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Patterning of adsorbate layers with submicron resolution is of importance for a variety of surface science measurements. Among experiments that may benefit from such spatial control of adsorbate density are surface diffusion measurements [1], examination of spatially inhomogeneous chemical processes [2], differential optical probes [3], and film growth processes. For surface science experiments, it is critical to be able to apply patterning to well-defined surfaces in ultrahigh vacuum, to avoid contamination on the level of a fraction of a monolayer, and to control adsorbate density with submonolayer precision. One attractive method for attaining these goals is laser-induced thermal desorption (LITD) [4–7]. The method has the advantage of being applicable to a wide variety of different material systems, since it operates by the common process of thermal desorption and does not rely on any system-dependent mechanism. The approach is suitable for patterning of large areas simultaneously and can achieve resolution on the order of a wavelength of the laser λ. For example, by exploiting interference between two incident laser beams [8,9], one can produce a periodic modulation of the adsorbate density with a grating spacing down to $\lambda/2$ over a broad area of the sample. Moreover, the LITD method is noninvasive, noncontaminating, and relatively easy to implement [10].

Despite these attractive features, the LITD technique suffers from the limitation that it may not be possible to desorb strongly bound adsorbates while maintaining high spatial resolution in patterning. This constraint arises from the fact that the spatial pattern in the laser intensity will be reflected in the temperature profile of the surface only if the laser pulse is sufficiently short for thermal diffusion in the substrate to be ignored. For micron or submicron resolution, this criterion generally requires laser pulses of a duration on the order of nanoseconds or shorter. On the other hand, the short duration of the heating pulse may not allow sufficient desorption to occur at an acceptable surface temperature [11,12]. The peak allowable temperature is obviously constrained by melting the substrate, but may be further reduced by the occurrence of surface damage or defects at lower temperatures. To appreciate the scope of this limitation, one may consider an Arrhenius expression for the desorption rate $R = R_0 \exp(-E_d/k_B T)$. Here R_0 denotes the preexponential factor, E_d is the activation energy for desorption, k_B is the Boltzmann constant, and T is the temperature in K. We may define a characteristic desorption temperature T_d at which desorption occurs under conditions of conventional heating by $R(T_d) = 1 \text{ s}^{-1}$ and a temperature T_p required to desorb on the time scale of 10 ns of many pulsed laser sources. Then for typical values for the prefactor R_0 ranging between 10^{16} and 10^{10} s^{-1}, one may easily show that T_p/T_d varies between 2 and 5 (independent of E_d). While for most physisorbed species T_p is still modest, for strongly bound adsorbates,

with values of T_d above room temperature, the required T_p may easily exceed the threshold for surface damage. A second limitation for the LITD process is the possibility of thermally decomposing a molecular adsorbate rather than (or in addition to) desorbing it. This problem may preclude the use of the LITD technique for patterning of molecular adsorbates that are thermally unstable.

In this Letter, we present a procedure for circumventing the limitations of the LITD technique for patterning such strongly bound or thermally unstable adsorbates. The scheme exploits the use of a physisorbed monolayer as a template for patterning of the desired adsorbate. The physisorbed layer can be readily patterned by LITD without the use of high peak temperatures. The pattern imposed on the physisorbed layer is then transferred to the strongly bound species through the influence of the physisorbed layer on the sticking probability of the strongly bound species. The physisorbed species can be considered as an ultraclean photoresist, which is removed simply by allowing the sample to warm to room temperature. We demonstrate the method by producing a patterned monolayer of H atoms adsorbed on the Si(111)-(7 × 7) surface. In this experiment, a Xe monolayer [13,14] is employed for the physisorbed template and a periodic grating structure is produced by the interference of two laser beams.

The principal steps in the template technique for patterning are illustrated in Fig. 1. The first step is the deposition of a monolayer of the physisorbed species used to form the template. The second step is the patterning of the physisorbed monolayer by LITD. In this step, the local temperature rise from the spatially patterned laser radiation induces a spatially varying surface density of the physisorbed monolayer. In the figure, spatial variation corresponding to a grating structure is shown. In the third step, the physisorbed template serves as a mask to adsorption of the (chemisorbed or thermally unstable) species of interest. This produces a spatially varying pattern for the species of interest that is complementary to the pattern imposed on the physisorbed layer. In the fourth and final step, the physisorbed template is removed simply by heating the sample to its desorption temperature.

The experiment was conducted in an ultrahigh vacuum (UHV) chamber, equipped with capabilities for low-energy

FIG. 1. Scheme for patterning of adsorbed monolayers by the template technique: (1) homogeneous physisorbed layer; (2) spatial profile of template layer after patterning; (3) exposure to chemisorbed adsorbate species; (4) removal of template by thermal desorption.

electron diffraction (LEED) and Auger-electron spectroscopy (AES), at a base pressure below 1×10^{-10} Torr. The sample was cut from a phosphorus-doped Si wafer (10 Ω cm) and mounted on a liquid He-cooled manipulator. The sample could be cooled to 30 K and heated to any desired temperature above this value by direct resistive heating. A clean Si(111)-(7 × 7) surface was prepared by thermal desorption of the native oxide layer at 1260 K. We carefully controlled the peak temperature and the cooling rate (<3 K s^{-1}) to avoid surface roughening and the concomitant increase in scattering in the optical diffraction measurements discussed below. Exposure of the Si(111)-(7 × 7) surface to Xe was performed by simple backfilling of the UHV chamber. The Xe coverage was calibrated by comparison of temperature programmed desorption (TPD) spectra for various exposures with those of Bartha and co-workers [14]. In the experiments, a coverage of 1 monolayer (ML) (defined by saturation of the TPD peak) was used throughout. In order to dose with H atoms, the chamber was backfilled with purified H$_2$, which was dissociated by a hot filament located near the sample. Calibration of the hydrogen exposure was also accomplished by TPD spectra.

LITD on the Xe template layer was performed by a single pulse of a frequency-doubled, Q-switched Nd:YAG laser operating at a wavelength of 532 nm with a pulse duration of approximately 6 ns. We created periodic structures by irradiation of the sample with two overlapping laser pulses. For this purpose, the output of the laser was split into two beams of equal intensity. The two beams were s polarized and directed onto the sample at an angle of ±2.2° with respect to the surface normal, resulting in an interference pattern of 7 μm period. The diameter of the patterned area was a fraction of a centimeter, corresponding to nearly 1000 periods of the grating.

In this experiment, the spatial pattern of both the Xe template and the transferred H monolayers was that of a grating structure. As has been demonstrated by Shen et al. and Zhu et al., such monolayer gratings can be probed very sensitively by means of linear optical diffraction [15]. For this purpose, we employed the cw radiation of an air-cooled Ar$^+$-ion laser at a wavelength of 514 nm and an incident power of 10 mW. The first-order diffracted radiation from the surface was detected by a photomultiplier tube. In order to suppress the background from diffusely scattered light, a modulation scheme was employed: The sample was dithered about its axis, causing the diffracted beam to oscillate slightly in an angle. The angle of the sample was modulated by exciting a torsional resonance of the UHV manipulator at 400 Hz using a scanning stage attached outside of the UHV chamber. This method yields an angular amplitude of oscillation of ≈1 mrad. In combination with an appropriately adjusted aperture in front of the detector and narrow band electronic amplification at twice the vibrational frequency, this simple scheme permitted the
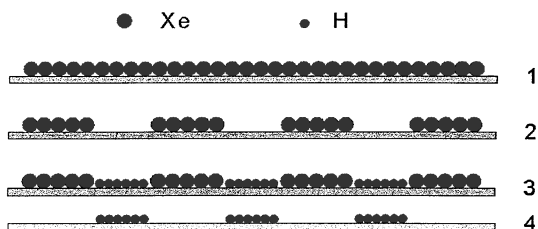
detection of gratings with diffraction efficiencies well below 10^{-9}.

Before turning to a discussion of the actual transfer experiment, a few comments should be made about the physisorbed Xe template layer. The choice of a rare gas for the template layer is natural in view of the chemical inertness of such adlayers. Xe, as a heavy atom, has a nominal desorption temperature of about 80 K in conventional TPD measurements. The calculated desorption temperature for nanosecond LITD of $T_p = 250$ K is still quite low and, indeed, LITD of Xe from metals has been previously reported [16]. The transient LITD temperature peak constitutes, it should be noted, the maximum amount of heating needed to pattern the sample by the template technique regardless of the nature of the chemisorbed species to which the pattern is transferred.

For the Xe monolayer to function effectively as a template, it must be able to significantly decrease the sticking probability of the chemisorbed species of interest. The shielding capability of a homogeneous monolayer of Xe was examined using optical second-harmonic generation (SHG), excited by a Q-switched Nd:YAG laser at 1064 nm, as a probe. While the SHG signal is virtually unaffected by the Xe layer, it is very sensitive to adsorbed hydrogen [17]. The modified sticking coefficient could be determined by normalizing the rate of H uptake relative to the clean surface. The results displayed in Fig. 2 indicate that the sticking coefficient of H is reduced by a factor of 2 for a nominal monolayer coverage of Xe/Si(111)-(7 $\times$ 7) [18]. This reduction is sufficient to allow for a significant spatial modulation of the hydrogen coverage imposed by the physisorbed Xe monolayer, as demonstrated in the grating experiment below. In order to achieve maximum contrast, higher Xe coverages may be used that diminish hydrogen sticking by more than 1 order of magnitude.

Clearly, to transfer the pattern of the Xe template, the adsorbed Xe must not desorb before the H exposure is complete. This criterion can be readily met by maintaining the sample temperature slightly below the nominal TPD desorptio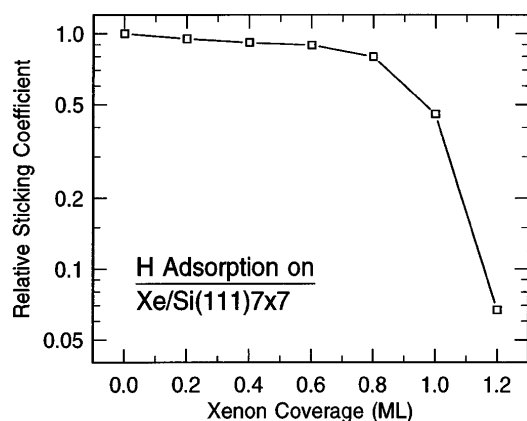n temperature of 80 K. However, it is also necessary to suppress diffusion of the Xe template, since this will wash out its features before the transfer is complete. To achieve this condition requires a significantly lower base temperature. In the experiments described below, the sample was held at 40 K. At this temperature the diffraction efficiency from the Xe grating was found to be stable on the time scale of minutes required to adsorb atomic hydrogen.

Figure 3 traces the steps in the template transfer technique for H/Xe/Si(111)-(7 $\times$ 7) by means of the optical diffraction efficiency from the grating structures. The signal, recorded in real time during the experiment, represents the intensity of the first-order diffraction peak from the 7 μm grating structure. The numbered regions correspond to the different phases of the process delineated in Fig. 1. Initially, there is no appreciable diffraction signal, either from the clean Si(111)-(7 $\times$ 7) surface or from the Si surface covered by a spatially homogeneous monolayer of Xe (step 1). Upon exposing this surface to a pulse of radiation from the two interfering laser beams, we create a grating in the Xe coverage. Since the diffraction measurement is being carried out simultaneously in real time as this grating is formed, we see an abrupt jump in the signal as the Xe grating is established (step 2). The next significant change in the diffraction efficiency occurs upon exposure of the sample to H. The large increase in the diffraction efficiency seen in Fig. 3 was obtained for an exposure of H leading to 0.15 ML of H adsorption on the clean Si(111)-(7 $\times$ 7) surface. The diffraction signal corresponds to a surface covered with interwoven Xe and H gratings (step 3). Up to this point, the sample was held at a temperature of 40 K, preventing appreciable diffusion or desorption of either Xe or H. In the last step, we allow the sample to return to room temperature, which results in the desorption of the Xe template. The diffraction signal drops to the final value for diffraction from the desired H monolayer grating (step 4) [19]. It should be noted that, while a diffraction method has been used as a probe of the

FIG. 2. Relative sticking coefficient of atomic hydrogen on Si(111)-(7 $\times$ 7) as a function of the Xe precoverage.
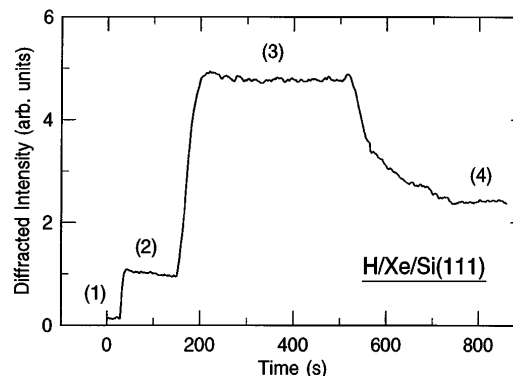

FIG. 3. First-order diffracted light intensity during the patterning process. The time marks indicate the steps in the process corresponding to Fig. 1: (1) exposure to Xe; (2) patterning of Xe by LITD; (3) exposure to H; (4) thermal desorption of Xe template.

grating structure in these experiments, we expect that surface microprobes such as scanning tunneling microscopy should be able to image the grating structures directly in space.

We performed several additional tests to confirm that we had in fact produced a hydrogen grating on an undamaged Si(111)-(7 × 7) surface. First, to establish that the final grating structure was entirely hydrogen, we performed TPD measurements. We found that the diffraction signal vanished just as the hydrogen was being desorbed. We also demonstrated experimentally that the diffraction efficiency could be made to vanish by exposing the surface with the H grating to a further exposure of H, which leads to the elimination of the grating by producing a spatially homogeneous surface with H at saturation coverage. Second, we performed checks to show that the template procedure produced no surface damage. These tests included carrying out the full template procedure with only Xe exposure, only H exposure, and without any gas exposure. As expected, no diffraction signal could be observed at the end of the procedure in any of these cases.

In summary, we have introduced a new and flexible method for the production of precisely controlled adsorbate profiles on surfaces. The method exploits the possibility of patterning a surface with a physisorbed template and then transferring this pattern by the template's influence on the sticking coefficient of the species of interest. Since the removal of the template layer can be accomplished simply by letting the sample come to room temperature, the process is expected (and was demonstrated) to be noncontaminating and damage free. The method is of particular interest for strongly bound and thermally unstable species, which are difficult to pattern by other means. It should also be observed that the physisorbed template may be applied repeatedly to permit the spatial patterning of *two or more* different adsorbed species. Further, while the patterning of the physisorbed template was accomplished using LITD in our present Letter, the approach could clearly be applied to other schemes, such as scanning probe methods, for spatially patterning the template layer.

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[18] Given the large affinity of the dangling bonds to atomic hydrogen (energy gain $\simeq 3$ eV per H atom) and the highly corrugated nature of the Si(111)-(7 × 7) surface, it is not unexpected that the sticking probability of H on one monolayer of Xe/Si(111)-(7 × 7) remains appreciable.

[19] The relative diffraction efficiencies of the different gratings reflect the modulation of the linear susceptibilities of the corresponding layers. Whereas the signal from the Xe grating may simply be attributed to the large polarizability of the adsorbed Xe atoms, the origin of the change in surface susceptibility upon H adsorption is attributed to a reduction of the susceptibility of the Si dangling-bond states. For the case of the Xe + H grating, the high diffraction efficiency can be understood as the combined effect of an enhanced susceptibility in the regions of the surface covered with Xe and a diminished susceptibility in adjacent regions where H has been adsorbed.