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30. Mn was transferred to the tip from either the CuN or bare Cu surface by moving the tip into point contact with the atom and then withdrawing the tip while applying +2 V. The atom was then transferred to the CuN by repeating this procedure with –0.5 V. Mn atoms can bind to the CuN atop either a Cu or N atom, with the Cu site being more stable.
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34. The conductance steps at low fields on Mn atoms and trimers are too narrow to resolve the flat bottom that clearly differentiates an IETS line shape from the Fano line shape that characterizes the Kondo effect (*15*, *16*). Because this flat bottom is seen on longer chains, we consider the Kondo interpretation to be unlikely for the shorter chains as well.
35. Because H_N is represented as a $(2S_A + 1)^N \times (2S_A + 1)^N$ matrix, numerical diagonalization becomes computationally expensive for larger S_A and N. We therefore limited our calculations to $N \leq 6$.
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39. STM topographic images were processed using WSxM (www.nanotec.es). We thank D. M. Eigler for mentoring and stimulating discussions; B. J. Melior for expert technical assistance; and C.-Y. Lin and B. A. Jones for stimulating discussions.

Supporting Online Material

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Fig. S1
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Desorption of H from Si(111) by Resonant Excitation of the Si-H Vibrational Stretch Mode

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Past efforts to achieve selective bond scission by vibrational excitation have been thwarted by energy thermalization. Here we report resonant photodesorption of hydrogen from a Si(111) surface using tunable infrared radiation. The wavelength dependence of the desorption yield peaks at 0.26 electron volt: the energy of the Si-H vibrational stretch mode. The desorption yield is quadratic in the infrared intensity. A strong H/D isotope effect rules out thermal desorption mechanisms, and electronic effects are not applicable in this low-energy regime. A molecular mechanism accounting for the desorption event remains elusive.

Photon-stimulated desorption is a powerful tool to study fundamental processes in adsorbate-surface systems, as well as to achieve selective surface reactions for controlled surface processing (*1*–*4*). Photons are easily directed and tuned in energy to induce transitions in atomic and molecular states, with high spatial and temporal precision. Direct adsorbate-surface bond breaking by electronic excitation using ultraviolet light has been reported (*5*, *6*). However, visible and infrared (IR)–stimulated desorption processes studied so far generally involve indirect mechanisms (*7*, *8*), such as light-induced substrate heating (*9*) and, in physisorbed systems, energy transfer from internal molecular excitation to molecular translational motion away from the surface (*10*, *11*). Selective bond scission at these lower energies is desirable but has proven challenging because of rapid energy delocalization from the mode of excitation (*1*). Here we report resonant photodesorption of H from a Si(111) surface using IR radiation. We show that the process is resonant with the Si-H vibrational energy and displays an unusual and surprising dependence on excitation intensity, which cannot be explained by either thermal or electronic processes. Successful elucidation of this fundamental excitation mechanism would be a major advance in surface science, and its implementation could lead to site-selective desorption at low temperatures.

The H/Si(111) structure is a well-characterized adsorbate system, ideal for the study of fundamental surface processes. The Si-H bond is perpendicular to the Si(111) surface, with a bond energy estimated to be between 3.15 and 3.35 eV (*12*) and a vibrational stretch energy of 0.26 eV at the terrace sites (*13*). In our experiments, the Si-H vibrational stretch mode was resonantly excited by IR photons. The Si substrate was transparent to mid-IR illumination, minimizing electronic excitation and direct laser-induced heating. Although this paper deals with the basic mechanisms of the desorption process, there could be important technological applications. Because H desorption is an important component of Si chemical vapor deposition, modifying the H desorption mechanism can have a large impact on growth. In particular, the vibrational energy of an Si-H bond at the terrace site of the Si(111) surface differs from that at the step site by 51.8 cm^{-1} (*14*), opening the possibility of site-selective desorption of H adatoms by IR irradiation. Such a photolytic process could efficiently treat a large area and modify the type of sites available for epitaxial growth. This might be compared to nanoscale lithography of H on Si achieved using the scanning tunneling microscope (STM) (*15*, *16*).

Our experiment was performed in an ultrahigh-vacuum (UHV) system at room temperature. The base pressure was $\sim 3.0 \times 10^{-10}$ Torr. The sample was prepared in air, using hydrofluoric acid etching to protect the Si surface from oxidation and contamination, and then cleaned by direct-current heating in the UHV chamber. The clean surface was verified by the strong Si(111)-7×7 low-energy electron diffraction (LEED) pattern. Ultrahigh-purity H_2 gas was introduced into the UHV chamber. A tungsten filament at 2000 K was used to dissociate H_2 molecules, thus efficiently forming

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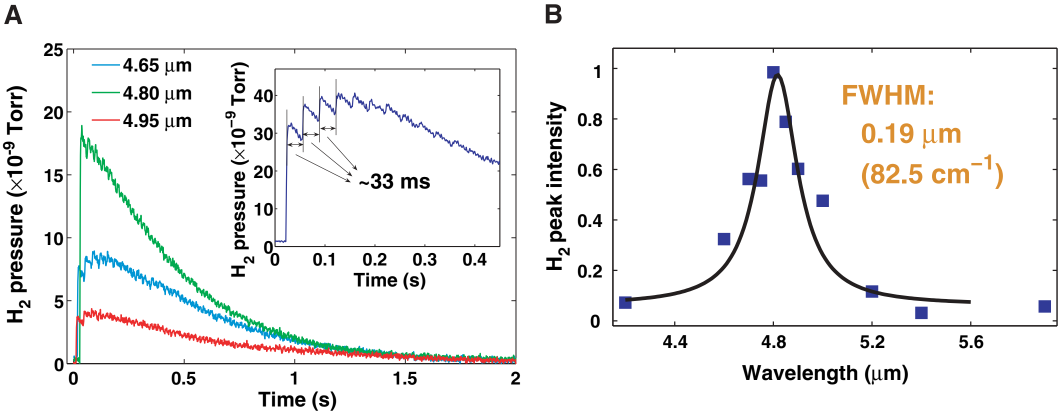

Fig. 1. (**A**) Typical curves of desorbed H_2 signal as a function of time at three wavelengths. The background pressure has been subtracted. The FEL fluence was 0.8 J/cm^2 per macropulse. The inset shows the fine structure of a desorption curve. The step rises are due to desorption by individual FEL macropulses. The 33-ms interval corresponds to the 30-Hz repetition rate of the macropulse. (**B**) Wavelength dependence of the desorption yield. Data were normalized to 1. The solid curve is a Lorentzian fit to the data.

the Si-H bonds at the Si(111) surface. After a hydrogen dose of 3×10^{-6} Torr for 120 s, an area of Si surface measuring 5 by 4 mm was uniformly covered with H atoms, as evidenced by the Si(111)-1×1 LEED pattern and the uniform desorption behavior at different spots when all other desorption conditions were kept the same. Thermal desorption spectra showed only one peak at ~820 K, indicating that H was adsorbed exclusively as a monohydride phase on the Si surface (*17*).

The free-electron laser (FEL) at Vanderbilt University provides a maximum of 100 mJ per macropulse at a repetition rate of 30 Hz. Each macropulse is composed of $\sim 10^4$ micropulses of 1 ps duration, spaced 350 ps apart. The spectral width of the FEL emission is ~50 to 90 cm^{-1}. The IR radiation was guided into the chamber through a CaF_2 viewport and focused onto the sample with a spot size of 0.8 mm. Its power and polarization could be adjusted with an attenuator and polarizer outside the chamber. The sample surface was positioned to make a 30° angle with the linearly polarized beam. The total electric field above the Si surface is the sum of the incident and the reflected fields. For the Si substrate with refractive index 3.42 and this incident angle of 60°, the direction of this total electric field is close to the surface normal; namely, the direction of the Si-H bond. The field projection in this direction is $(1 + r_p)E\cos\theta\cos30°$, with E being the incident field, r_p the reflection coefficient of the p-polarized component, and θ the angle between the FEL electric field and the incident plane. The effective FEL fluence in the direction of the Si-H bond can be varied by changing either the incident intensity E^2 or the polarization angle θ.

The sample was exposed to the FEL illumination at room temperature, and the desorbed H was pumped away by the ion pump at the same time. An IR pyrometer focused on the sample detected no temperature rise during desorption, showing no FEL-induced heating of the bulk sample, though not ruling out a local transient temperature increase. A quadrupole mass analyzer was employed to record the H_2 partial pressure as a function of time once the FEL shutter was open. After desorption, an experimental parameter, such as the FEL wavelength or polarization, was varied, and the FEL focus was moved to a new sample position that had not been exposed to the FEL illumination. When the FEL beam was not incident on the Si surface, no desorption signal was measured, indicating that there was no contribution from scattered FEL radiation.

To study the wavelength dependence of H_2 photodesorption, we monitored the H_2 partial pressure as a function of time over a range of FEL wavelengths, with the fluence kept fixed and the polarization set to $\theta = 0°$ (Fig. 1A). The signal quickly rose to its peak, then decayed exponentially with a rate that was in agreement with the pumping speed of the vacuum system. The fine structure of the desorption curves (inset, Fig. 1A) features step-like increases. The interval of 33 ms is in good agreement with the 30-Hz repetition rate of the FEL macropulse, indicating that these increases resulted from desorption by each FEL macropulse. Finer temporal structure due to FEL micropulses could not be resolved by our instrumentation. The H_2 partial pressure is a measure of the total number of H_2 molecules in the UHV chamber. Therefore, the magnitude of each jump is taken as a measure of the number of H_2 molecules desorbed by each macropulse; that is, the desorption yield.

The desorption yield peaked at a wavelength of 4.8 µm (Fig. 1B), corresponding to 0.26 eV, the energy of the vibrational stretch mode of the Si-H bond at the terrace sites of the Si(111) surface. A Lorentzian fit yielded a full width at half maximum (FWHM) of 0.19 µm (82.5 cm^{-1}), close to the FEL linewidth, which is the limiting factor in resolving wavelength. Because the vibrational energy of the Si-H bond at the terrace site differs from that at the step site by 51.8 cm^{-1}, this resonance effect suggests that wavelength-selective site desorption (*18*) would be readily possible with an incident beam of appropriately narrow linewidth. In addition, desorption was unobservable when the wavelength was far from resonance, ruling out a desorption mechanism due to simple, direct laser heating.

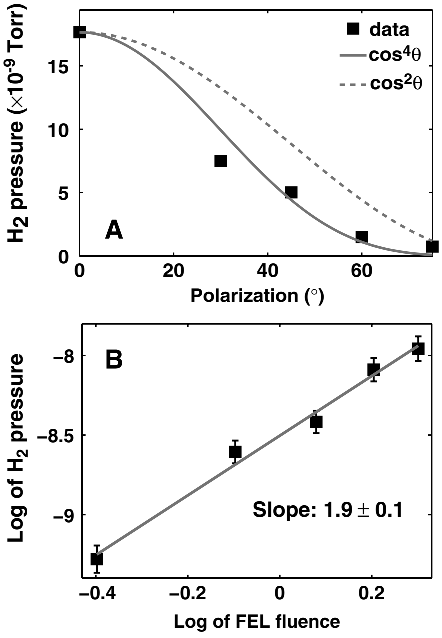

Fig. 2. (**A**) Polarization dependence of the desorption yield (squares). The FEL fluence was kept at 0.8 J/cm^2 per macropulse for all polarizations. (**B**) Log-log plot of desorbed H_2 versus FEL fluence. A linear fit yields a slope of 1.9 ± 0.1. The polarization was 0° for all fluences, and the wavelength was tuned to 4.8 µm.

A study of the polarization dependence of the desorption yield provides further insight into the desorption mechanism. For bulk-like thermal processes, possibly because of impurities or defects, the desorption yield is not expected to be very sensitive to the polarization angle. For direct bond-breaking processes via electronic excitation, the yield should be a simple quadratic function of the FEL electric field projected in the direction of Si-H bond (*5*) (that is, a linear dependence on the incident intensity) and follow a $\cos^2\theta$ curve as illustrated (Fig. 2A). In our experiment with constant FEL fluence, however, the desorption yield scales with the incident polarization as $\cos^4\theta$ (Fig.

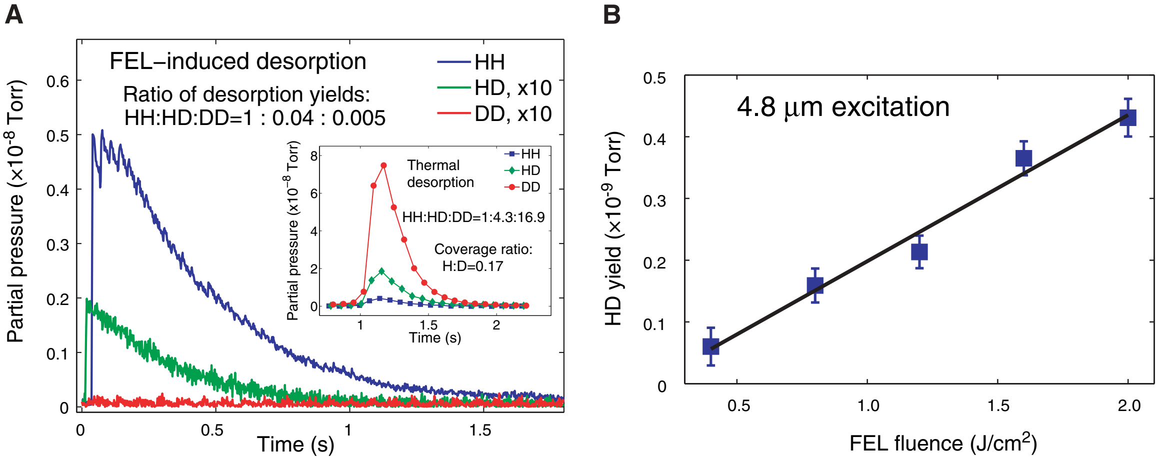

Fig. 3. (**A**) Partial pressures of H_2, HD, and D_2 as a function of time arising from FEL-induced desorption. The fluence was 1.6 J/cm^2 per macropulse. The FEL data for HD and D_2 are magnified by 10 times. The inset shows the partial pressures in a single thermal desorption. Data were obtained by continuous cycling of an atomic mass unit scan from 0.5 to 5.5, with a period of 75 ms. The temperature began to rise at 0.9 s, from room temperature to the terminal temperature of ~950°C. (**B**) Desorption yield of HD as a function of FEL fluence when excited at 4.8 μm. A linear relationship is observed.

2A). This behavior indicates that the observed desorption does not result from a thermal process caused by direct laser heating, but from the direct interaction between the incident field and the Si-H bonds. Furthermore, the $\cos^4\theta$ dependence implies a quadratic dependence on the incident intensity, as verified in a measurement of the yield dependence on the FEL fluence (Fig. 2B). This quadratic dependence is significantly different from the ~ninth-order dependence observed in multiple vibrational excitations of H on Si(100) by the STM (*19*).

To further probe the nature of the desorption mechanism, the thermal desorption and IR-induced desorption of a coadsorbed mixture of H and D were also measured. H and D adatoms were coadsorbed and then the desorption yields of different species were measured (Fig. 3A). For thermal desorption, the ratio of the yields was H_2:HD:D_2 = 1:4.3:16.9. In the FEL-induced process, with the same H/D coverage and the wavelength tuned to the Si-H stretch at 4.8 μm, the desorption ratio was found to be 1:0.04:0.005, in stark contrast to the thermal data. Furthermore, the HD desorption yield was linear in photon flux (Fig. 3B) over the same range in which the H_2 yield was seen to be quadratic. These results support the idea that there are very different mechanisms for thermal desorption and IR-induced desorption.

The underlying mechanism that may account for the observed desorption behavior is not immediately obvious. Related phenomena include laser-induced thermal desorption and vibrational ladder-climbing. Direct laser heating of the substrate (*9*) can clearly be ruled out as the dominant mechanism, based on the wavelength and polarization dependencies of the desorption yield and our experimental measurement of the bulk temperature. Another type of thermal mechanism, resonant local heating, refers to a process in which the Si-H vibrational stretch mode is resonantly excited by the IR photons and then couples to local substrate phonons, causing a local temperature increase and eventually thermal desorption. The measured isotope effect in this FEL-induced desorption rules out such local heating, because the FEL-induced desorption yields are drastically different from thermal desorption yields. In the vibrational ladder-climbing mechanism, Si-H bonds may be continuously excited to higher vibrational states by either multiphoton adsorption (*10*) or dipole-dipole coupling of Si-H bonds (*20*). We estimate that an H adatom must climb to approximately the fifth vibrational energy level of the Si-H stretch mode in order to overcome either the diffusion barrier of 1.5 eV (*21*) for enhanced diffusion or half of the activation energy of 2.4 eV (*22*) in a thermal activation scheme. The quadratic power dependence observed in the H_2 desorption and the linear dependence in the HD desorption might not necessarily suggest a two-photon or one-photon process. Multiphoton processes often display a much lower order of dependence on the photon flux than the number of photons absorbed (*23*). For example, if the absorption cross section increases when the system has absorbed one or two photons, the excitation rate will be determined by these initial photons. Consequently, the measured power dependence will be low-order, even though the process requires additional photons. In such a multiphoton process, the higher energy states would have slightly different absorption energies because of anharmonic effects. However, the FEL linewidth is broad enough to allow the excitation of some number of levels. As a result, these considerations make vibrational ladder-climbing a possible mechanism to explain the experimental observations. New mechanisms that are consistent with the data might also be considered and further investigated.

The experimental findings reported above are unprecedented and unexpected. The precise underlying mechanism is still to be identified. An important intention of this work is to stimulate future studies on the basic mechanisms of surface dynamics, both experimentally and theoretically.

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