

## Laser-Induced Electronic Bond Breaking and Desorption of Adatoms on Si(111)-(7 × 7)

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Laser-induced structural changes on the Si(111)-(7 × 7) surface were studied for laser fluences below thresholds of melting and ablation. The adatoms of the reconstructed structure are removed selectively by an electronic process, and Si atoms in the electronic ground state are ejected with a peak translational energy of 0.15 eV. The electronic process of this bond breaking of adatoms exhibits the site-sensitive efficiency which shows a resonant wavelength dependence and is highly superlinear with respect to the excitation intensity. [S0031-9007(98)05872-4]

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Extensive studies have been carried out on the interaction of laser light with solid surfaces, motivated both by applications in materials processing and basic research of light-matter interaction [1,2]. Laser-induced effects on silicon surfaces have attracted particular interest, partly for understanding the mechanism of laser annealing phenomena in this material. Becker *et al.* first studied laser-induced structural changes on the Si(111)-(7 × 7) surface using scanning tunneling microscopy (STM), and found a class of new reconstructions of forming  $c$ -(4 × 2) and (2 × 2) structures [3]. The laser fluence  $\Phi$  used was about 1 J/cm<sup>2</sup>, which is certainly above the melting threshold. Consequently, the structural transformation was attributed to laser-induced melting followed by rapid recrystallization. Stritzker, Pospieszczyk, and Tagle measured time-of-flight (TOF) spectra of Si atoms emitted from Si surfaces under the irradiation of laser pulses with  $\Phi$  of 1–2 J/cm<sup>2</sup> [4], and showed that the translational energy of desorbed Si atoms increased with fluence. The observed fluence-dependent translational energy of desorbed Si atoms has been regarded as a consequence of surface melting. Thus, the major structural changes on Si surfaces induced by laser irradiation have been ascribed to laser-induced melting for fluences exceeding a threshold value [5].

On the other hand, it has been suggested that electronic processes are dominant if the laser power is below the melting and ablation thresholds [6–9]. Recently, it has been demonstrated that adatoms of the Si(111)-(7 × 7) structure are removed by irradiation of ns-laser pulses at fluences below the melting and ablation thresholds [8,9]. This laser-induced removal of adatoms on this surface shows a site-sensitive property; the center adatoms are removed more efficiently than the corner adatoms. This feature has been attributed to an electronic process, since the atomic images of the irradiated surfaces do not show any trace of surface melting. In this Letter, we show that the electronic process inducing removal, or bond breaking, of adatoms on Si(111)-(7 × 7) is related directly to the excited electronic states on this surface, and that the efficiency of this electronic bond breaking is strongly site

sensitive, resonantly wavelength dependent, and highly superlinear with respect to excitation intensity. A possible mechanism is proposed based on the experimental results.

A  $p$ -type Si(111) wafer, 5 mm × 15 mm × 0.5 mm in size, was cleaned by ultrasonical rinsing in ethanol and then mounted onto a Ta holder in an ultrahigh vacuum chamber with a base pressure of  $5 \times 10^{-11}$  Torr. After a standard cleaning procedure, the Si(111) surface exhibited a sharp (7 × 7) low energy electron diffraction pattern, and no contaminant was detected by Auger electron spectroscopy. STM observation was performed by using a commercial system (PSI STM-SU2) with tips made of tungsten wire of a diameter of 0.15 mm. Laser pulses of 20-ns temporal widths, generated by an excimer-laser-pumped dye laser (Lambda Physik, Model EMG201MSC and FL3002) were used to excite surfaces at wavelengths from 400 to 700 nm. The magnitude of the photon fluence  $\Phi$  on the surface was evaluated by monitoring the energy per pulse and irradiation radius at which the beam intensity decreased from the peak intensity to  $1/e$ . Si atoms ejected from the surface were detected by resonance ionization spectroscopy (RIS). Laser pulses of 20-ns duration for ionizing desorbed neutral Si atoms, generated by a second excimer-laser-pumped dye laser, were guided to pass parallel to the sample surface with a distance of 2 mm. Si<sup>+</sup> ions ionized by the laser pulses were collected by a negatively biased (−1.0 kV) drift tube, and then detected by a microchannel plate placed in a shield box behind the drift tube.

STM images were acquired systematically for the Si(111)-(7 × 7) surfaces irradiated with dye-laser pulses with fluences below  $\sim 300$  mJ/cm<sup>2</sup> at wavelengths from 400 to 700 nm. It is estimated from a formula provided in Ref. [10] that laser irradiation with the fluence of 300 mJ increases the temperature in the heat diffusion-length layer to about 640 °C, which is well below the melting temperature. In fact, all of the images obtained have shown, as reported previously [8,9], that vacancies are formed by irradiation mostly at individual adatom sites, leaving the (7 × 7) structure essentially unchanged.

No trace of surface melting and no indication of new reconstruction was detectable, which was the case for  $\Phi$ 's below  $\sim 300$  mJ/cm<sup>2</sup> at all wavelengths from 400 to 700 nm. Therefore, we conclude that the adatom-vacancy formation is not due to surface melting.

Statistical analysis was undertaken for these STM images taken over 1200 unit cells in the irradiated region to examine the adatom-vacancy formation quantitatively. In Fig. 1(a), we show the concentration of laser-induced adatom vacancies in units of the fraction of the number of adatom vacancies  $n_L$  relative to the total number  $n_0$  of adatom sites in the region surveyed as a function of the number  $m$  of 600-nm laser pulses incident on the surface under repeated irradiation. The fluence in this case was 23 mJ/cm<sup>2</sup>, far below the melting threshold. It is clear in the figure that  $n_L$  increases linearly with  $m$  up to a level where 6% of the total adatoms have been removed. In Fig. 1(b) is shown the ratio of  $n_L$  at the corner-adatom sites to that at center-adatom sites on the irradiated surface. It shows a constant value of 0.3 irrespective of  $m$ , indicating that the center adatoms are removed about 3 times more efficiently than the corner adatoms. Since this magnitude does not depend on  $m$ , the site-sensitive yield of adatom-vacancy formation is not due to any accumulated effects under repeated irradiation, but is a direct consequence of the process which takes place within each laser pulse.

Results similar to those shown in Fig. 1 were obtained for irradiation at various fluences below  $\sim 300$  mJ/cm<sup>2</sup>

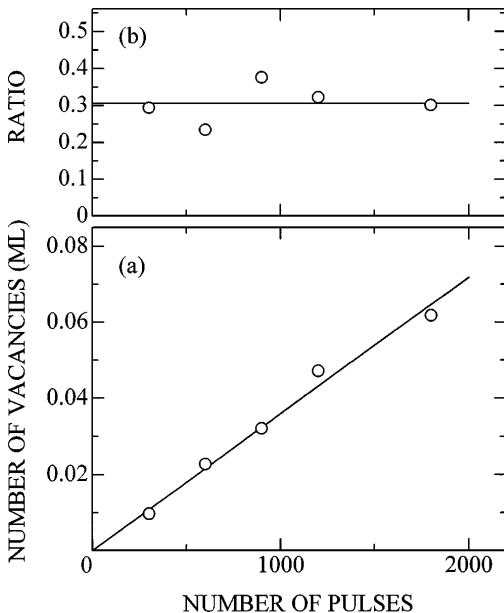


FIG. 1. The concentration of laser-induced adatom vacancies (a), and the ratio of the number of vacancies formed at the corner-adatom site relative to that at the center-adatom site (b), as a function of the number of 600-nm laser pulses with a fluence of 23 mJ/cm<sup>2</sup> under repeated irradiation at a repetition rate of 3 Hz.

and at different wavelengths from 400 to 700 nm. The site-sensitive yield of the adatom-vacancy formation with a ratio of about 0.30 was the case for all of these different excitation conditions. Therefore, the site-sensitive yield is a characteristic of the final step of the bond breaking process, independent of excitation wavelengths. Based on the linear relation between  $n_L$  and  $m$ , we can define the efficiency  $\eta$  of adatom-vacancy formation per single shot of a laser pulse with a given  $\Phi$ . In Fig. 2, the magnitudes of  $\eta$ 's thus determined for 500-nm excitation are plotted by solid circles as a function of  $\Phi$ . The efficiency shows a superlinear dependence on the excitation intensity.

In order to obtain comprehensive information on this bond breaking of adatoms, atoms desorbed by pulsed-laser excitation were identified by using the RIS technique. Without any ionization laser, Si<sup>+</sup> ions were hardly detectable. On the other hand, when ns-laser pulses tuned to the <sup>3</sup>P<sub>0</sub>-<sup>3</sup>P<sub>1</sub> transition energy (4.928 eV) of Si atoms were used, Si atoms were clearly detected. This result shows that the desorbed species is mainly the Si atom in the electronic ground state. The TOF spectra of the desorbed Si atoms were measured by changing the time delay between laser pulses for surface excitation and those

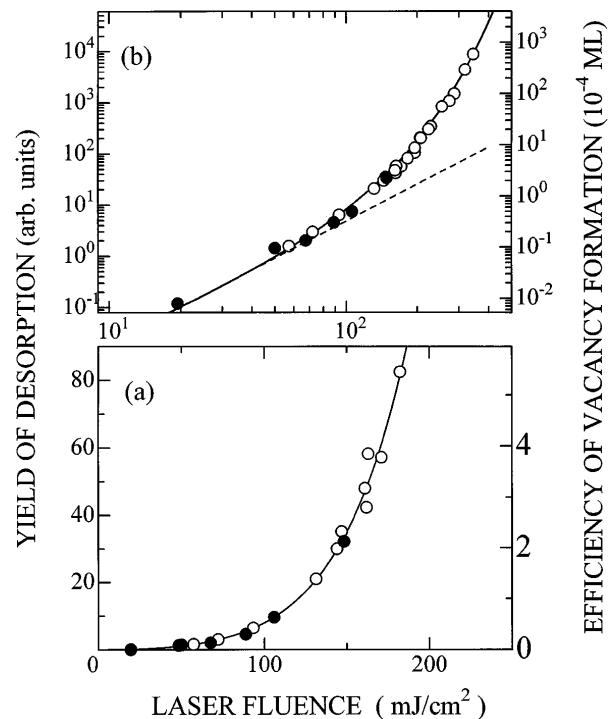


FIG. 2. Fluence dependence of the efficiency of adatom-vacancy formation (solid circle) and the yield of Si-atom desorption (open circle) induced by irradiation with a single shot of a 500-nm laser pulse in (a), linear scale, and in (b), logarithmic scale. Solid curves pertaining to data points in (a) and (b) are the best-fit curve of the formula derived from the two-hole localization mechanism (see the text), while the broken curve in (b) is a power-law function with a power index of 2.3.

for ionizing desorbed Si atoms. Spectra measured for several fluences and for wavelengths from 400 to 700 nm show a common peak translational energy of 0.15 eV and a given velocity distribution, neither of which depends on the fluence or on the wavelength. This fluence-independent translational energy of desorbed Si atoms strongly contrasts to the case of surface melting [4], and indicates that the desorption of Si atoms from this ( $7 \times 7$ ) surface induced by irradiation with laser pulses of  $\Phi$ 's below  $\sim 300$  mJ/cm<sup>2</sup> is not due to surface melting. Also, wavelength-independent velocity distribution of desorbed Si atoms suggests that the final step of the bond breaking which determines the energy partition to desorbed Si atoms is common for all wavelengths from 400 to 700 nm.

In Fig. 2, the yield  $Y$  of Si-atom desorption, measured at the time delay which gives a peak of TOF spectra of Si-atom desorption, is plotted as a function of fluence, and is compared with  $\eta$  as determined by STM studies. We emphasize here two important features. First is that both quantities show the same fluence dependence, demonstrating clearly that desorption of Si atoms is a direct consequence of the bond breaking of adatoms on the ( $7 \times 7$ ) surface. The second is that the dependence is superlinear with respect to the excitation intensity scaled in terms of fluence. As seen in the logarithmic plot in Fig. 2(b), a feature of the dependence is that it depends roughly quadratically on  $\Phi$  for weak fluence regime, but becomes almost exponential for the more intense region. This superlinear dependence of  $Y$  and  $\eta$  indicates that the laser-induced process responsible for the breaking of adatom bonds is superlinear with respect to the excitation intensity.

The yield of Si-atom desorption measured as a function of fluence for wavelengths ranging from 400 to 700 nm showed similar superlinear dependence on  $\Phi$ , but the peak yields were strongly wavelength dependent. In order to examine the wavelength dependence, we introduce a practical definition of the "desorption efficiency" to be the desorption yield at a fixed fluence of 150 mJ/cm<sup>2</sup>, since the usual definition of efficiency cannot be used because of the superlinear behavior. Values of the desorption efficiency thus determined are plotted as a function of the photon energy in Fig. 3. A strong enhancement is evident at 2.0 eV, with weak and broad contribution above 2.5 eV. Qualitatively, similar spectra were obtained by taking yields at different fluences.

Since no such peak at 2.0 eV exists in the absorption spectrum of the Si crystals, the result shown in Fig. 3 suggests that the optical absorption associated with bulk electronic transitions is not effective for the Si-atom desorption. Alternatively, possible optical transitions involving surface electronic states were examined by referring to the extant experimental and theoretical studies of the electronic structure of the Si(111)-( $7 \times 7$ ) surface [11–15]. One finds two possible surface transitions, energies of which fall around 2.0 eV. One is the transition from the surface band ( $S_2$ ) composed of the rest-atom dangling

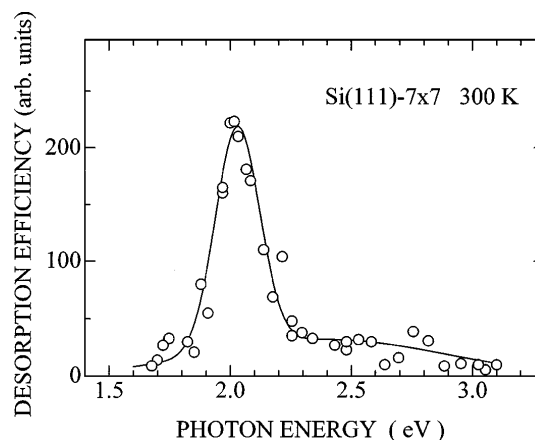


FIG. 3. Photon-energy dependence of the desorption efficiency of Si atoms from the Si(111)-( $7 \times 7$ ) surface for a fluence of 150 mJ/cm<sup>2</sup>.

bond to the band ( $U_2$ ) of the unoccupied adatom back-bond orbital, and the other is that from the band ( $S_3$ ) composed of the occupied adatom back-bond orbital to the band ( $U_1$ ) of the unoccupied adatom dangling bond orbital. Not only these two transitions which coincide well to the peak of the desorption yield, but also other transitions, e.g., from  $S_3$  to  $U_2$ , may be induced above 2.5 eV, where broad but weak contribution of the desorption yield is detected [16]. The beautiful coincidence between the energies of these surface electronic transitions and the peak energy of the desorption enhancement, together with the lack of bulk-transition peaks around 2 eV, leads us to conclude that laser-induced surface electronic transitions affect the bond breaking and desorption of Si adatoms.

Based on the results described above, it is reasonable to conclude that the bond breaking of adatoms on the Si(111)-( $7 \times 7$ ) surface induced by laser irradiation with  $\Phi$ 's below thresholds of melting and ablation is originated from an electronic process where surface excited states are involved. Since the bond breaking takes place at individual adatom sites on the ( $7 \times 7$ ) structure, localization of these photoexcited species onto particular adatom sites is included as an important step. The superlinear dependence of  $Y$  and  $\eta$  on  $\Phi$  shown in Fig. 2 indicates that multiple photogenerated excited species are involved in the localization process [17].

Following the original proposal by Itoh and Nakayama [18], Sumi studied theoretically the two-hole localization process as a possible mechanism of electronic desorption of constituents of semiconductor surfaces, and formulated the rate  $P$  of the two-hole localization onto a particular lattice site [19]. His result of  $P$  can be approximated well by  $P = A[\exp(n_h) - 1]^2$ , where  $A$  is a constant, and  $n_h$  is the concentration of photogenerated holes normalized to the effective number of free-hole states in the surface valence band at a given temperature. The quantity  $n_h$  is presumed to be proportional to the excitation

intensity characterized by  $\Phi$ , so that  $Y$  is given by  $Y = Y_0[\exp(B\Phi) - 1]^2$ , where  $Y_0$  and  $B$  are constants, when the two-hole localization process determines the rate of desorption. The experimental results of  $Y$  and  $\eta$  were compared with this equation with  $Y_0$  and  $B$  being fitting parameters. The solid curve in Fig. 2 is the best fit of this equation to experimental results; it is evident that it describes almost perfectly the results for a whole range of the excitation intensities. In particular, the experimentally observed change from a roughly quadratic dependence at low fluence to an almost exponential dependence at higher fluence can be naturally explained by this equation. The results taken for other wavelengths from 700 to 400 nm could be fitted as well. Therefore, we conclude that the two-hole localization process plays the critical role for inducing the bond breaking of adatoms on the Si(111)-(7 × 7) surface.

By this process, localized excited states may be formed at adatom sites, resulting in the breaking of adatom bonds and the desorption of Si atoms to which a peak translational energy of 0.15 eV is imparted. The site-dependent efficiency of the bond breaking may originate from the localization process and/or the bond breaking reaction. Elucidation of the microscopic structures of the localized excited states may be an interesting future problem.

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 [16] The existing results of the surface electronic states of the Si(111)-(7 × 7) surface suggest also the transition at 3.0 eV from the  $S_3$  band to the  $U_2$  band. The absence of a 3.0-eV peak in the excitation spectrum in Fig. 3 may indicate that generation of holes in the  $S_3$  band does not contribute significantly to the Si-atom desorption.  
 [17] The superlinear yield of desorption has been observed for chemisorbed species on metal substrates when excited by femtosecond-laser pulses, and the mechanism of desorption induced by multiple electronic transitions (DIMET) has been proposed [J. A. Misewich, T. F. Heinz, and D. M. Newns, Phys. Rev. Lett. **68**, 3737 (1992)]. However, this mechanism is specific only to the intense photon field of the femtosecond-laser pulses which induces repetitive excitations within a localized adsorbate-surface system. The fluxes in these femtosecond pulses are higher by a factor of  $10^4$  or more than those of the 20-ns laser pulses used here. Therefore, this DIMET mechanism is not applicable for the present case.  
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