

Translational Energy Distribution of Si Atoms Desorbed by Laser-Induced Electronic Bond Breaking of Adatoms on Si(111)-(7 × 7)

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The desorption of Si atoms caused by the laser-induced electronic bond breaking of adatoms of Si(111)-(7 × 7) was studied upon exciting the surface with nanosecond and femtosecond laser pulses. The translational energy distribution of desorbed Si atoms is characterized by a peak energy of 0.06 eV with an onset energy of 0.02 eV; the feature is independent of wavelengths, fluences, and temporal widths of excitation laser pulses. This energy distribution, as well as other characteristic features of the process, is well described by a proposed model of phonon-kick mechanism following the two-hole localization on adatom sites. [S0031-9007(98)08226-X]

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Laser interaction with semiconductor surfaces has been studied extensively, motivated both by applications in materials processing and by basic research in light-matter interaction [1,2]. As a result of the interaction, changes in surface atomic structures are often induced, and the electronic processes have been shown to play important roles in the change when laser intensities are below melt threshold [3–5]. Recently, it has been demonstrated by scanning tunneling microscopy (STM) observation that adatoms of the 7 × 7 structure of clean Si(111) surfaces are removed selectively by an electronic process under irradiation of nanosecond (ns)-laser pulses in the visible region [5]. It has also been shown that Si atoms are ejected from the surface in the electronic ground state as a direct consequence of the electronic bond breaking of adatoms. This electronic bond breaking on Si(111)-(7 × 7) is featured by the efficiency which is strongly site sensitive, resonantly wavelength dependent, and highly superlinear with respect to the excitation intensity [5]. Based on these results, it has been suggested that the two-hole localization on adatom sites plays an important role in this electronic process.

As evidenced by several previous studies on desorption processes, the translational-energy distribution of desorbed species gives essential information on mechanisms of bond breaking processes at surfaces [6–8]. In this Letter, we present measurements of the translational-energy distribution of Si atoms desorbed by the electronic bond breaking of adatoms by exciting the surface with different types of laser light, which includes a ns laser in ultraviolet (UV) range and a femtosecond (fs) laser, together with a ns laser in the visible region. It is shown that the energy distribution shows a common feature of a peak energy of 0.06 eV with an onset energy of 0.02 eV, irrespective of different characteristics of excitation laser light. Based on this result and its analysis, together with the other features revealed previously [5], a model is proposed of the mechanism of the electronic bond breaking of adatoms on Si(111)-(7 × 7).

The 7 × 7 surfaces of a *p*-type Si(111) wafer were prepared and characterized as before [5]. STM observation of the surface revealed typical 7 × 7 images in which almost no atomic-scale defects were included. Three different types of lasers were used to generate laser pulses for exciting the surface. An excimer-laser-pumped dye laser (Lambda Physik, Model EMG201MSC, and FL3002) generated laser pulses of 20-ns temporal widths at wavelengths from 400 to 700 nm. A *Q*-switched Nd:YAG laser (Spectra Physics GCR130) was used for generating 532-nm (5 ns) and 266-nm (4 ns) laser pulses. And a mode-locked Ti:sapphire laser (Coherent Mira 900F) with a regenerative amplifier (BMI α -10) was employed for generating 403-nm (200 fs) and 269-nm (300 fs) laser pulses. The laser pulses were guided to the UHV chamber precisely on the same optical path determined by using several apertures, and were incident at 45° from the normal of the surface. Desorbed Si atoms were resonantly two-photon ionized by laser pulses of 251.23 nm, generated by a *Q*-switched Nd:YAG laser-pumped dye laser (Lambda Physik, Scanmate 2B), which were guided to pass parallel to the sample surface with a distance of 3.30 mm. Si⁺ ions thus ionized were collected by a negatively biased (−120 V) drift tube, and then detected by a microchannel plate placed in a shield box behind the drift tube.

Any of the laser beams used here had a near-Gaussian beam profile, and the typical beam radius at the sample surface was 0.20 mm for ns-laser pulses and 0.10 mm for fs-laser pulses, respectively. Laser irradiation was made with fluences below 300 mJ/cm² for ns-laser pulses and 30 mJ/cm² for fs-laser pulses [9]. The formation of vacancies at mostly individual adatom sites, without any trace of surface recrystallization and melting, was revealed by STM observation of irradiated surfaces for the fluence range used.

When the 7 × 7 surface was excited by 266-nm laser pulses or fs-laser pulses of 403 and 269 nm, Si atoms were emitted in the electronic ground state as the major product of desorption. In the fluence range studied, the

yield (Y_d) of desorption changed as much as 3 orders of magnitude, with showing similar superlinear dependence on the fluence of excitation laser to that for previous ns-laser excitation. The time-of-flight (TOF) spectra of desorbed Si atoms were measured by changing the time interval between laser pulses for surface excitation and those for ionizing desorbed Si atoms at several fluences of each type of laser light. The TOF spectra are characterized by a given velocity distribution and a peak at flight time of $2.05 \mu\text{s}$, neither of which depends on wavelengths, fluences, and temporal widths of laser light.

In order to have deeper insight into the bond breaking process, we evaluated the number density $N(\varepsilon)$ of atoms with translational energy ε from a TOF spectrum. In this evaluation, a phase space factor of ν^2 was taken into account (ν is the speed) [6,8], to compare experimental data with consequences of a one-dimensional model which will be discussed later. The result is shown in Fig. 1. The distribution shows a steep increase after an onset energy of about 0.02 eV (shown by the arrow) to form a peak at 0.06 eV, associated with the high-energy tail up to 0.6 eV. Although the peak flight time of $2.05 \mu\text{s}$ in TOF spectra corresponds to the translational energy of 0.15 eV [5], the peak translational energy of 0.06 eV in $N(\varepsilon)$ is obtained after the phase-factor correction, which enhances significantly number densities at low-energy parts [6,8]. Since the amount of Si atoms desorbed by one pulse is at most 10^{-4} monolayer (ML) [5], any effects of gas-phase collision after desorption can be neglected [10]. Therefore, the energy distribution seen in Fig. 1 is characteristic of the bond breaking process at the surface.

One of the important features seen in Fig. 1 is that the energy distribution is identical with each other for different types of laser light with different characteristics.

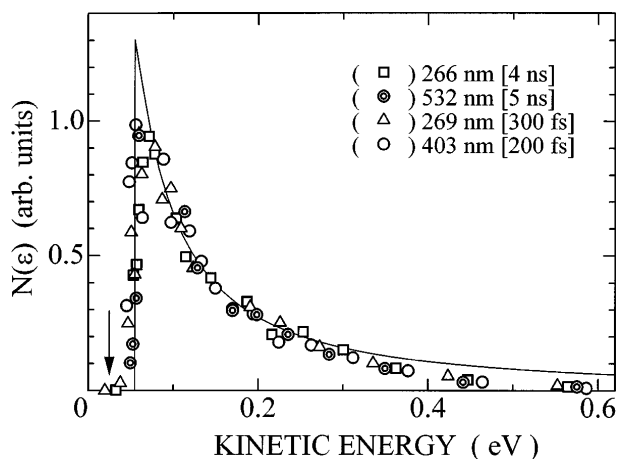


FIG. 1. Translational energy distribution of Si atoms desorbed by the laser-induced electronic bond breaking of adatoms of Si(111)-(7 × 7). Surface excitation was made at 300 K with laser pulses of different characteristics in wavelengths, fluences, and temporal widths. Data for different types of laser light are normalized to the same peak height. The solid curve is the calculated distribution by the simple model presented in the text.

This feature indicates clearly that the final step of the bond breaking which governs the energy partition to Si atoms is common for any type of excitation. It implies that the same localized excited state (which will be hereafter called the reactive state) is formed at adatom sites with a formation yield which is dependent on several characteristics of excitation laser light. Below, we briefly discuss some characteristics of the yield of forming this reactive state in a few cases.

In Fig. 2, we show the result of Y_d induced by 266-nm ns-laser pulses. It shows a clear superlinear dependence, although the yield is much smaller than that for 532-nm ns-laser pulses (and hence than that for 600-nm ns-laser pulses [5]). The previous study revealed a strong peak at 2 eV in the wavelength dependence of the efficiency of desorption, and the peak was attributed to the optical transition(s) in the surface electronic states [5]. An alternative assignment may be argued that the peak is related to the two-photon absorption transition in the bulk electronic states, based on the fact that the direct band gap of Si crystals is 4.185 eV [11], and on the feature of the nearly quadratic dependence of Y_d at weak fluence regime [5]. However, the superlinear dependence of Y_d for excitation by 266-nm laser, the photon energy (4.66 eV) of which is above the direct band gap, definitely excludes this alternative. We interpret the result as follows: the 4.66-eV photons can induce optical transitions in which surface electronic states are involved [12], and the holes in the surface band thus formed are still responsible for the two-hole localization to form the reactive state. In fact, the dependence shown in Fig. 2 is well described by the equation derived in the two-hole localization mechanism [13], as shown by the solid curve in the figure. The lower yield for 266-nm excitation may be attributed to a weaker optical-absorption strength and/or

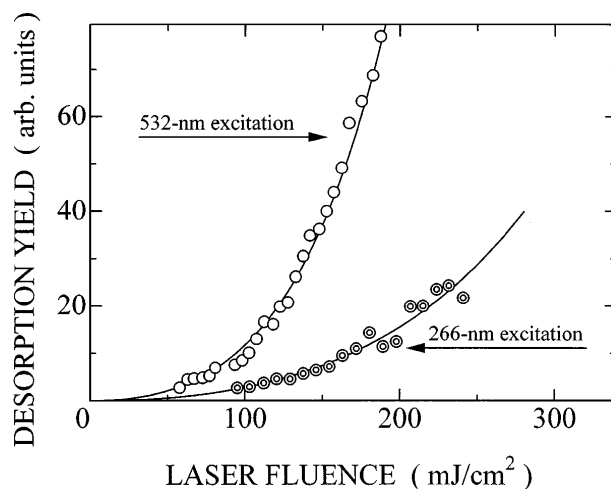


FIG. 2. Fluence dependence of the yield of Si-atom desorption induced by irradiation with ns-laser pulses of 266 nm. The dependence for 532-nm ns-laser pulses is also shown for comparison. The solid curves are the best fit of the formula derived from the two-hole localization mechanism (Refs. [5] and [13]).

efficient pathways which compete with the reactive-state formation in the deexcitation process of free holes generated by 266-nm excitation.

The yields of desorption by fs-laser pulses of both 403 and 269 nm also depend superlinearly on fluences. However, the fluence which gives the same amount of Si-atom desorption was reduced to about $\frac{1}{10}$ of that for a ns laser of a similar wavelength. In the case of excitation with fs-laser pulses, temporal widths of which may be much shorter than the lifetimes of surface excited species generated, one-hole and two-hole localized states may be formed in time-dependent ways during the lifetime of the free holes in the surface band. We formulated the equation for such a time-dependent hole localization, and evaluated the yield of two-hole localized states. The enhanced yield due to higher densities of holes generated in a short time period and the superlinear dependence for the fs-laser excitation are well described by this equation [14].

Thus, in the cases of UV-laser and fs-laser excitation, the desorption yields are well described by the two-hole localization mechanism, similar to the previous studies [5]. The two-hole localization assumes the first-hole localization on the surface. Since the adatom-vacancy formation is not related at all to any preexisting defects on the surface [5], an intrinsic process of the first-hole localization has to be assumed. In contrast to the valence electronic state of Si crystal showing a large delocalization energy B , which can be measured as a half of the bandwidth, some of the occupied surface states on Si(111)-(7 × 7) show much narrower bandwidths (the width is as small as 0.05 eV for the surface band S_2) [15]. Although no theoretical estimates on the lattice relaxation energy for the holes on this surface have been available, the small B of the surface electronic state and restricted freedom of carrier motion [16] may make the self-trapping of holes possible on the surface. Therefore, the two-hole localization at intrinsic adatom sites may be applied for the bond breaking of adatoms on this surface.

We now discuss the mechanism of the electronic bond breaking of adatoms. The peak energy of 0.06 eV seen in Fig. 1 is much smaller than photon energies of excitation laser light. This low translational energy may exclude any desorption models which assume simple repulsive potential energy surfaces leading to ε of the order of eV. Also, the fluence-independent velocity distribution of desorbed Si atoms indicates clearly that the mechanism of desorption induced by multiple electronic transition (DIMET), often argued for desorption processes on metal surfaces [7,17], is not the case for the bond breaking of adatoms on this surface.

Experiments [18] and *ab initio* calculations [18–20] have shown a significant charge delocalization of dangling bond state of the adatoms, which results in a bonding interaction between adatoms and the Si atoms directly below them. Therefore, upon hole localization at adatom sites, bonding property of the adatom may be affected seriously to weaken the bond and to induce a strong

adatom vibration. Based on this consideration, together with an important role of the two-hole localization described above, we propose here the phonon-kick mechanism of the bond breaking of adatoms on Si(111)-(7 × 7). Defect reactions induced (or enhanced) by transiently generated violent lattice vibration (phonon kick) upon the carrier localization at defect sites are well documented in semiconductors [21]. In the present case, “defect sites” are the first-hole localized sites, and the violent vibration leading to the bond breaking is induced only upon the second-hole localization along the reaction coordinate Q_R of vibrational motion of adatoms normal to the surface.

This process is schematically portrayed in Fig. 3, where a group of parabolas denoted by V_1 represents the state of the second hole staying in the free state with the first-hole localized, V_2 the state of two-hole localized, and V_f the final state of the bond breaking, respectively. In the bond breaking process, the adatom electronic state of a perturbed sp^3 -like configuration is finally transformed into the free-atom s^2p^2 state in V_f . We assume that this electronic transition, a key of the bond breaking, takes place on V_2 at a critical point R with an energy E_R and a distortion Δ_R on Q_R .

The phonon-kick process can be described as follows: the packet formed on the coordinate with a mean total energy E_i ($\geq E_R$) passes the critical point n times with the energy E ($\leq E_i$) during relaxation, induces the transition with a probability P at each passage, and is dissipated finally. The Si atoms desorbed by the packet with E have ε given by $\varepsilon = E - E_0$, where E_0 is the energy of V_f measured from the bottom of V_2 . The number density $N(\varepsilon)$ is determined by the product of n and P ,

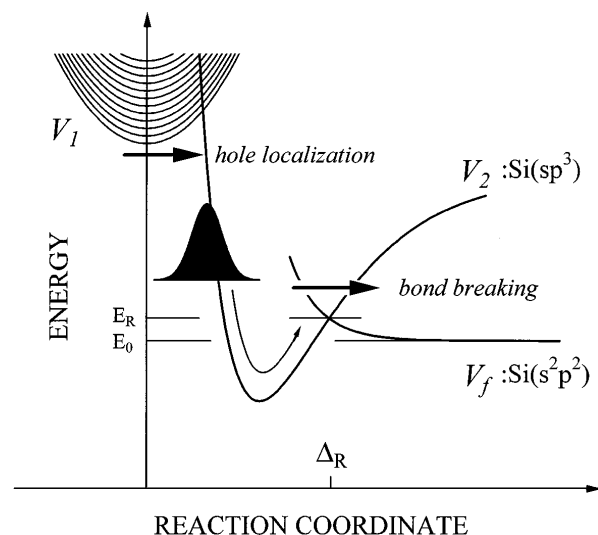


FIG. 3. Schematic of the model of the phonon-kick process following two-hole localization at adatom sites. Adiabatic potentials V_1 , V_2 , and V_f show the state of the second hole staying in the free state in addition to the first localized hole, that of two-hole localized, and that of the final state of the bond breaking including a Si atom in the electronic ground state in vacuum, respectively.

both of which are dependent on E . As a crude guide of the dependence, when we assume a simple damping oscillator as the packet, n is inversely proportional to E . And, when P is evaluated by Landau-Zener formula [22] of $P_{LZ} = \{1 - \exp(-2\pi T^2/\hbar\nu_R|F_R|)\}$, where T is the transition matrix element, $|F_R|$ is the change of the energy separation of the surfaces at R , and ν_R is the velocity of the packet at R , respectively, it takes the largest value for $\nu_R = 0$ (i.e., $E = E_R$), with a sharp cutoff for $E \leq E_R$. For $E > E_R$, P decreases with increasing E .

In view of this model, the peak energy of 0.06 eV in $N(\varepsilon)$ shows that E_R is higher by about 0.06 eV than E_0 . A sharp cutoff is, in fact, observed $E < E_R$, and $N(\varepsilon)$ decreases with increasing ε as expected from the dependence of both n and P on E . The highest energy of E_i which determines the highest ε is estimated to be about 0.6 eV + E_0 in Fig. 1. Thus, the proposed model describes well the qualitative features of the experimental result. The solid curve in Fig. 1 is the energy distribution calculated by this simple model of $N(\varepsilon) \propto nP_{LZ}$ with assuming ν_R to be proportional to $\sqrt{E - E_R}$ and a constant E_i . It describes the overall features of the experimentally determined energy distribution of Si atoms, although it shows some discrepancies, the origins of which are pointed out below. In the packet dynamics, theoretical study shows that the transition probability deviates significantly from that evaluated from P_{LZ} to reduce it in the region where $\nu_R = 0$ [23], which may be related to the distribution around the peak energy. A finite amount of desorption in the range of $\varepsilon < 0.06$ eV is a clear indication that the packet with $E \leq E_R$ can induce transition via quantum tunneling [21], giving the onset energy of 0.02 eV from E of 0.02 eV + E_0 . The discrepancy in the region of ε above 0.4 eV may originate from anharmonic properties of V_2 which give significant effects on the dynamics of packets with higher E , responsible for the desorption in the region. A possible distribution of E_i may also affect the distribution in the higher- ε region. More sophisticated evaluation of $N(\varepsilon)$ with taking these aspects into account is certainly desired for full quantitative description of the result, which will be published elsewhere [24].

In conclusion, the features of the translational energy distribution of desorbed Si atoms and the other characteristics, including the resonantly wavelength-dependent and highly superlinear efficiency of the bond breaking, are explained satisfactorily by the model of the two-hole localization followed by the phonon-kick process at adatom sites. The site dependence of the bond breaking efficiency is presumed to be related to the different bonding properties of the center- and corner-adatom sites, which have been revealed by STM-tip extraction experiments on this surface [25,26].

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