Primary Processes of Laser-Induced Selective Dimer-Layer Removal on Si(001)-(2 × 1)

J. Kanasaki,[1] M. Nakamura,[2] K. Ishikawa,[2] and K. Tanimura[2]

[1]*Department of Intelligent Materials Engineering, Osaka City University, 3-3-138 Sugimoto, Sumiyoshi, Osaka 558-8585, Japan*
[2]*The Institute of Scientific and Industrial Research, Osaka University, Mihogaoka 8-1, Ibaraki, Osaka 567-0047, Japan*

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Excitation with nanosecond-laser pulses at fluences well below the melt threshold removes Si dimers on the Si(001)-(2 × 1) surface and induces atomic-Si desorption through an electronic mechanism. The rate of this photoinduced reaction depends superlinearly on the excitation intensity, and is enhanced resonantly at the photon energy where the optical transition injects holes into the dimer backbond surface-band state. The results reveal the crucial role of surface holes and their nonlinear localization in the bond rupture of Si dimers on this surface.

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Extensive studies have been carried out on the interaction of laser light with solid surfaces motivated by interest in both applied and basic research into light/matter interactions [1]. Recent studies by means of high-sensitive detection of desorbed species [2–4] and of direct atomic imaging of irradiated surfaces by scanning tunneling microscopy (STM) [5–9] have proven that electronic processes induce structural changes on many semiconductor surfaces at laser intensity below the melt threshold. The structural response under electronic excitations, the excitation-induced instability, is a characteristic feature of semiconductor surfaces, and depends on several surface properties. Therefore, detailed atomic level knowledge of laser-induced surface processes is required to develop the mechanistic understanding desired in both applied and basic research.

The Si(001)-(2 × 1) surface is a typical example of a reconstructed Si surface, and is the most technologically important semiconductor surface. For this surface, Xu *et al.* have shown that the excitation with 532-nm laser pulses induces selective removal of the topmost dimer layer to generate a new "1 × 1"-like surface phase that has never been prepared by other methods [6]. This phenomenon is of significance to both basic surface photochemistry research and laser-induced material modification research aimed at generating new photoinduced phases. However, the mechanism of the primary photoinduced process remains an open question. Laser-induced desorption from this surface was studied previously [10,11], but no clear correlations between desorption and Si-dimer removal were established. Here we performed a comprehensive study on the excitation-induced instability on the Si(001)-(2 × 1) surface by combining STM, to elucidate surface structural changes at the atomic level, and femtosecond nonresonant ionization spectroscopy (FNRIS), to probe [4] desorption processes with high sensitivity. We show that the nonlinear localization of surface holes, optically injected in the occupied surface state consisting of Si-dimer backbond orbitals, induces the removal of the dimers through ejection of neutral Si atoms.

Boron-doped p-type Si(001) wafers were cleaned by methanol, and then mounted onto a sample holder in an ultrahigh vacuum (UHV) chamber with a base pressure of 5×10^{-11} Torr. The 2 × 1 dimerized surface layer was prepared by flashing the sample at 1450 K following prolonged annealing at 750 K. Surface-atomic structures were characterized by using a commercial UHV-STM system (UNISOKU STM-U2). Laser pulses of 3-ns temporal width, generated with a YAG-laser pumped optical parametric generator (Coherent, Infinity XPO), were used to excite the surface at wavelengths ranging from 355 to 800 nm at 300 K. In desorption measurements, laser pulses of 800 nm with 70-fs temporal width, generated with a regenerative-amplified Ti:sapphire laser (BMI alpha-10), were aligned parallel to the sample surface at a distance of 1 mm, and focused above the irradiated spot. Desorbed neutrals were ionized by the fs-laser pulses, mass separated in a negatively biased (− 120 V) drift tube, and detected with a microchannel plate (Hamamatsu, F4665). The system sensitivity is estimated to be 10^{-7} ML (monolayer) per excitation-laser pulse. [4].

STM images were acquired systematically for the Si(001)-(2 × 1) surfaces irradiated at pulse fluences, Φ, below 100 mJ/cm^2 and wavelengths from 700 to 355 nm. These STM images were analyzed statistically for over 10 000 unit cells in the irradiated region to examine the removal of Si dimers quantitatively. Before irradiation, the surfaces were prepared with dimer-vacant site (DVS) concentrations less than 3%. When we excited the surface with laser pulses at a constant intensity, the concentration of DVS increased with increasing dose. In this process of DVS formation, we found that DVSs were generated mostly at perfect (2 × 1) sites while the concentration of DVS was lower than 10%. However, Si dimers near preexisting vacancies were removed predominantly at DVS concentrations greater than 10%.

The inset of Fig. 1 shows the growth of DVS as a function of laser pulse number at a wavelength of 532 nm and a fluence of 35 mJ/cm^2. It is clear that the concentration increases in proportion to the dose. Based on the linear relation, we determine the rate of Si-dimer

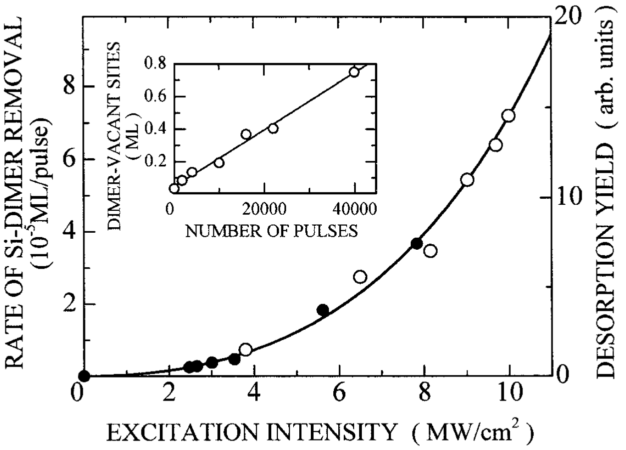

FIG. 1. The rate of Si-dimer removal (solid circles) and the yield of atomic Si desorbed from the surface (open circles) as a function of the excitation intensity of 532-nm laser pulses. The inset shows the concentration of dimer-vacant sites as a function of dose of 532-nm laser pulses at fluence of 35 mJ/cm^2.

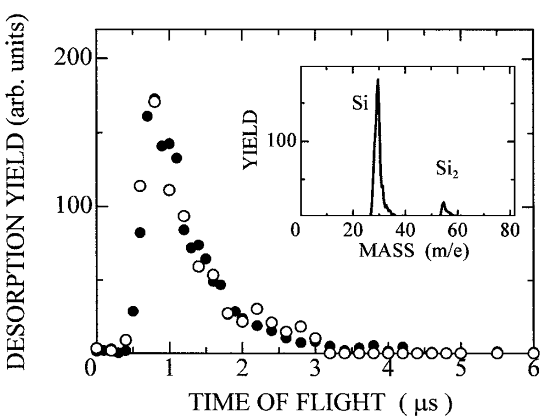

FIG. 2. Time-of-flight distribution of desorbed atomic Si upon exciting the Si(001) surface with a 532-nm laser pulse at 68 mJ/cm^2 (open circles) and with 355-nm laser pulses at fluence of 30 mJ/cm^2 (solid circles). The inset shows the mass spectrum of desorbed neutrals under 532-nm laser excitation.

removal from the slope of the straight line; it is about 2×10^{-5} ML per pulse in this case. The fluence of 35 mJ/cm^2 is far below the melt threshold. It is estimated that the laser irradiation increases the temperature in the heat diffusion length layer by only about 160° at this fluence [12]. Since the dimer structure of the (2×1) surface is stable up to 700 K [13], we conclude that laser-induced removal of Si dimers, in our case, is not due to surface melting, but is due to an electronic excitation mechanism.

We carried out similar measurements and analysis for different excitation wavelengths and intensities and determined the removal rate as a function of the excitation intensity, ϕ, for a given excitation wavelength. For each measurement, the surface was freshly prepared with a DVS concentration less than a few percent. Therefore, the removal rate thus determined is representative of the process on the (2×1)-reconstructed structure. Solid circles in Fig. 1 show the result under 532-nm excitation. The removal rate shows superlinear dependence on ϕ. Similar results of superlinearly dependent rate on ϕ were observed at excitation wavelength from 600 to 355 nm, although the magnitude of the rate depends strongly on the wavelength.

In order to have more insight into the process of excitation-induced Si-dimer removal, we studied desorption of neutral particles. To identify simultaneously all desorbed neutral species, we applied FNRIS. The inset of Fig. 2 shows a typical neutral mass spectrum under 532 nm excitation, displaying major Si and minor Si_2 features. The relative ratio of desorbed Si_2 to atomic Si is about 8×10^{-2}. This ratio was the case for different intensities of fs-laser pulses used for ionizing neutral species; dissociative ionization of Si_2 was not significant as in the case of N_2 ionization [4]. No ionic species were observed in the absence of the fs ionization laser pulse at the laser wavelengths and fluences used here. Therefore, we conclude that the neutral Si atom is the primary product of desorption induced by laser excitation.

In Fig. 1, the yield, Y, of Si atoms desorbed by excitation at 532 nm is plotted (open circles) as a function of ϕ and is compared with the rate of dimer removal evaluated from the STM studies. It is clear that both quantities show the same superlinear dependence on ϕ and that desorption of atomic Si is a direct consequence of dimer bond breaking on this surface. The superlinear dependence on ϕ indicates that electronic bond breaking on the Si(001)-(2×1) surface is primarily induced by nonlinear processes.

The velocity profiles of desorbed Si atoms were measured by changing the time delay between excitation and ionization laser pulses. The normalized yields under 532 and 355-nm irradiation are shown in Fig. 2. The velocity profiles are identical for two different wavelengths with a common peak-flight time of 0.9 μs, corresponding to a translational energy of 0.18 eV. Since the yield of Si atoms desorbed by a single laser pulse is at most 10^{-4}ML, any effects of gas-phase collision after desorption can be neglected [3,4]. Therefore, the velocity profiles shown in Fig. 2 are characteristic of the bond-breaking process leading to the neutral Si desorption. The peak-flight time and velocity profile were identical within errors for all laser intensities and wavelengths examined (from 355 to 650 nm). These results indicate that desorption of Si atoms is not due to thermal effects and that the final step of the desorption process is the same regardless of excitation wavelength.

The superlinear $Y - \phi$ relation shown in Fig. 1 held for all excitation wavelengths ranging from 355 to 650 nm. However, the Si yield is strongly dependent on wavelength at a given excitation-laser fluence. In considering this wavelength-dependent emission yield, the usual definition of efficiency cannot be applied because of the superlinear yield. Therefore, we introduce a practical "desorption efficiency," ξ, to be the inverse of ϕ at which the desorption yield shows a given level [14]. In Fig. 3, the magnitude of ξ is plotted as a function of photon energy of excitation-laser light. The efficiency is negligibly low below 1.9 eV, forms a peak at 2.4 eV, and increases again gradually above 2.6 eV. Under excitation with laser pulses of wavelengths longer than 650 nm (650–800 nm), the desorption yield of Si atoms was extremely low for Φ lower than 200 mJ/cm^2. Si atoms were detected for Φ around 200 mJ/cm^2, but with different characteristics from those for shorter wavelengths than 650 nm. Therefore, we conclude that the electronic bond breaking is essentially inactive for the photon energy region below 1.9 eV [10].

None of the bulk-optical properties of Si display a peak around 2.4 eV. Therefore, the result in Fig. 3 suggests strongly that the peak at 2.4 eV comes from a surface-specific electronic optical transition. The surface optical properties of Si(001)-(2 × 1) have been studied experimentally and theoretically. The surface-specific reflection spectrum shows peaks at 1.5 and 2.4 eV. These bands have been assigned, respectively, to the optical transition from the bonding (π) to the antibonding (π^*) dangling-bond states of the dimer and to that from the backbond state of the Si dimer, which is located at -1.4 eV near the K point, to the π^* state [15]. The peak in the efficiency of Si-atom desorption in Fig. 3 coincides with the peak at 2.4 eV in the surface reflection spectrum. Therefore, we conclude that the optical transition from the dimer backbond state to the π^* state can induce Si-bond rupture.

This surface transition at 2.4 eV injects electrons into the π^* state and holes into the backbond state. Which surface species is crucial to the desorption process can be judged by examining the consequence of the other surface transition around 1.5 eV. The efficiency of the Si-atom desorption below 1.9 eV is extremely low, although the reflection spectrum shows comparable oscillator strengths for both transitions [15]. This result indicates that electron injection into the π^* state does not induce bond rupture of Si dimers. Therefore, we can conclude that injection of holes into the occupied backbond state is crucial in the process.

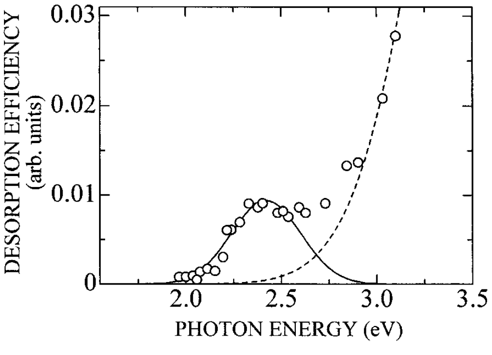

FIG. 3. The efficiency, ξ, of Si-atom desorption as a function of the excitation-laser photon energy. For the definition of ξ, see the text and Ref. [14].

Since surface holes are generated as delocalized waves by photoexcitation, hole localization is an important step in bond rupture at Si-dimer sites. The superlinear dependence of the dimer removal rate on the excitation intensity suggests that the localization is a nonlinear process; a single-hole localization cannot induce the bond rupture. Sumi studied the mechanism of bond rupture theoretically in terms of two-hole localization. He formulated the rate, P, of the bond rupture for successive localization of two holes at a given site; P is given by $P = A[\exp(n_h) - 1]^2$, where A is a constant, and n_h is the steady-state normalized concentration of photogenerated surface holes [16]. In the case of ns-pulse excitation, n_h can be regarded as constant during excitation and is proportional to the excitation intensity [4]. Then, for a given ϕ of the excitation pulse, P is described as $P = A[\exp(\beta\phi) - 1]^2$, where β is a constant that is proportional to the absorption cross section.

Results of experimentally obtained $Y - \phi$ relationships were compared with this equation, using A and β as fitting parameters. The solid curve in Fig. 1 is the best fit of this equation; it is clear that the rate predicted by the two-hole localization can describe satisfactorily the experimental results for the whole range of the excitation intensity. Thus, we conclude that localization of two holes is responsible for the electronic-induced bond breaking of dimers on the Si(001)-(2 × 1) surface.

The superlinear dependence of Y as a function of ϕ for the whole wavelength range of excitation was successfully described by the rate given by the two-hole localization mechanism. An important finding in this analysis is that the best-fit value of A is common for the whole wavelength range. Since A is a sensitive function of the properties of surface holes, as well as the electron-phonon interaction around the side where the first hole is localized [16], this result indicates that the free holes to be localized are in the same surface band for the whole range of the excitation wavelengths. Therefore, the increase of the efficiency of Si-dimer removal above 2.6 eV also originates from the holes injected in the dimer backbond band, although the surface reflection spectrum does not show such an increase. We presume that the increase above 2.6 eV comes from transfer of free holes in the bulk-electronic states into the surface state due to electron-electron scattering and/or electron-phonon interaction. For this transfer, bulk-optical transitions must generate holes in the projected bulk states located deeper than the surface backbond states. When we examine the energy and momentum overlap between the surface and bulk-electronic states on the Si(001)-(2 × 1) surface [15,17], we find the onset that satisfies this condition occurs around 2.6 eV. Therefore, holes generated beyond this onset in the bulk valence bands can contribute to the Si-dimer removal via the transfer onto the surface-hole state. This also explains why Si-dimer removal is not induced upon excitation at photon energies less than 1.9 eV, although the bulk-electronic transition is significant for energies greater than 1.1 eV.

In summary, we have proved the crucial role of photogenerated holes in a surface-valence band in the excitation-induced instability on the Si(001)-(2 × 1) surface. Also, we have shown that the nonlinear localization of surface holes induces bond breaking of Si atoms in the dimer configuration, leading to desorption of atomic Si and selective dimer-layer removal.

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[14] This definition of the efficiency is mainly due to an experimental limitation of our dynamics range in the desorption measurement. However, it also has a physical meaning as a measure of the cross section of hole injection when we apply the two-hole localization mechanism. In this mechanism, the rate of bond rupture is given by $P = A[\exp(\beta\phi) - 1]^2$ (see the text). The quantity β is proportional to the absorption cross section to generate surface holes. Then, for a constant P_0 induced by a given ϕ_0, the inverse of ϕ_0 equals $\beta/\ln(1 + \sqrt{P_0/A})$, being proportional to β.

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