Photoinduced Structural Instability of the InP (110)-(1 × 1) Surface

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A scanning tunneling microscopy study reveals the removal of P and In atoms at intrinsic surface sites of InP (110)-(1 × 1) through an electronic mechanism under ns-laser excitation. Femtosecond nonresonant ionization spectroscopy detects desorption of P and In atoms associated directly with the bond rupture, and shows their translational energies characteristic of electronic bong breaking. The rate of P-atom removal is 4 times higher than that of In-atom removal, revealing a prominent species-dependent effect of structural instability under electronic excitation on semiconductor surfaces.

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Laser interaction with solid surfaces has been studied extensively motivated by interest in both applied and basic research into light/matter interactions [1]. Under low-intensity irradiation, laser-induced electronic excitation plays crucial roles in structural modifications on semiconductor surfaces. Recent studies have revealed that Si atoms at perfect surface sites on several reconstructed Si surfaces are the subject of bond rupture under valence photoexcitation [2–4]. Whether the intrinsic structural instability under valence excitation is a feature common to covalent semiconductor surfaces in general is an important issue to be explored in laser interaction with the surfaces.

The structural instability under valence excitation has been suggested theoretically for III-V semiconductor surfaces composed of binary constituents of metallic and nonmetallic atoms [5,6]. Although the theoretical studies have predicted inherent instability of metallic-atom sites, the species dependence in the instability on these surfaces has yet to be clearly elucidated. However, the mechanisms of laser-induced processes on the surfaces are still controversial [7–11], and consequently the species-dependent property has remained as an open question. The controversy results partly from low sublimation energies of these surfaces; laser-induced heating plays some roles even well below the surface melting temperature [7]. Also, strong activities of surface defects in atomic processes under photoexcitation [8–10] often prevent us from unambiguous observation of intrinsic processes on surfaces. By using scanning tunneling microscopy (STM), it has been shown that bond rupture at perfect surface sites on GaAs (110) is induced by low-energy electron-beam interaction with surfaces [9]. However, it has been claimed that ns-laser irradiation leading to the valence excitation does not induce bond rupture at perfect sites on GaAs(110) [9], leaving the role of valence excitation unclear for III-V semiconductor surfaces.

In this Letter, we demonstrate that the intrinsic structural instability leading to bond breaking for both metallic and nonmetallic atoms at perfect surface sites of InP (110)-(1 × 1) is induced by low-intensity ns-laser pulses. By combining the results based on STM study that elucidates structural changes at the atomic level and on femtosecond nonresonant ionization spectroscopy (FNRIS) study that probes desorption processes with high sensitivity, we demonstrate a prominent species-sensitive bond breaking rate in the instability under valence excitation of this surface.

A nondoped n-type InP crystal with a carrier concentration of $\sim 4.5 \times 10^{15}$ cm^{-3} (resistivity of ~ 0.5 Ω cm) was mainly used. Specimens with a cross section of 0.2 mm × 5 mm were cleaved in an ultrahigh vacuum (UHV) chamber with a base pressure of 5×10^{-11} Torr. Characterization of surface-atomic structures by an UHV-STM system (UNISOKU STM-U2) and desorption studies were carried out *in situ.* Laser pulses of 5-ns temporal width, generated with a YAG-laser pumped dye laser (Lambda Physik Scanmate 2B) with 10-Hz repetition rate, were used to excite the surface at wavelengths ranging from 550 to 420 nm at 296 K. In desorption measurements, 80-fs-laser pulses of 800 nm, generated with a regenerative-amplified Ti:sapphire laser (BMI alpha-10), were used to ionize desorbed neutrals. For clear mass resolution in FNRIS technique described in Ref. [10], use of InP was more advantageous than GaAs because of the large mass ratio between In and P.

Figure 1 presents STM images acquired before, (a), and after, (b) and (c), irradiation with 460-nm laser pulses at a pulse fluence of 2.8 mJ/cm^2. Images (a) and (b) represent P-atomic images, while image (c) shows the In-atomic image. As seen in image (a), the concentration C_0 of surface defects (mostly monovacancies at P- and In-atomic sites) before irradiation is less than 0.1% for a 0.2×0.2-μm^2 wide single domain terrace of our cleaved surfaces. On the other hand, we observe in images (b) and (c) several dark spots newly generated at both P and In sites after laser excitation. We identify the dark spots to vacancies formed at P and In sites, because the P and In atoms desorbed from the surface are quantitatively corre-

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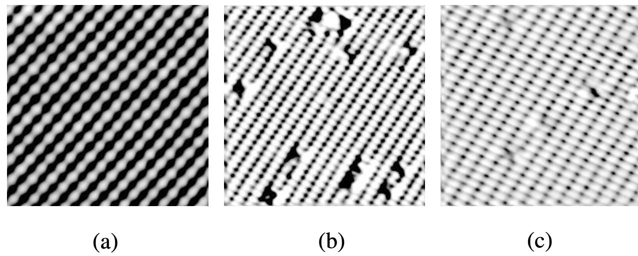

FIG. 1. STM images of In(110)-(1 × 1) before, (a), and after, (b) and (c), irradiation with 460-nm laser pulses at 2.8 mJ/cm^2. P-atomic images were acquired with a positive tip-bias voltage of +2.3 V in (a) and (b), and the In-atomic image with a negative voltage of −2.5 eV in (c).

lated with the densities of dark spots observed at P and In sites, as will be shown below.

In image (b), P vacancies take the forms of monovacancies (V_M's) and vacancy clusters, while In vacancies are mostly monovacancies as seen in image (c). Statistical analysis, of the images surveyed over 50 000 surface sites, showed that V_M's were generated predominantly in low dose regions and that larger P-vacancy clusters grew progressively at higher doses. Therefore, the primary step is monovacancy formation at originally perfect sites. Vacancy clusters are formed subsequently by bond rupture at sites near existing monovacancies. Dual-bias imaging for the same spot on the surface revealed that there is no spatial correlation between monovacancy sites of P and In atoms. Therefore, removal of P and In atoms takes place as a separate event to generate monovacancies at respective sites.

For quantitative analysis of the growth of vacancies, we introduce two quantities: the number density N_j and the vacancy size V_j for a vacancy clusters consisting of j vacancy sites. The N_j is registered simply as a count of vacancy clusters irrespective of their size. The V_j is registered as j, the number of sites, in an individual vacancy cluster. Any bond ruptures at sites nearest preexisting vacancies enhance the magnitude of the total vacancy size $V\ (=\sum_j V_j)$, but do not change the total number density $N\ (=\sum_j N_j)$. Therefore, N represents purely the concentration of new vacancies formed at originally perfect sites. In Fig. 2, we plotted N and V as a function of irradiation time t, defined as the product of pulse width and number of laser shots. Both N and V increase with t, but with decreasing rates. The increasing N for P vacancies and V for In vacancies up to above 0.5%, far above C_0, reveal that the vacancy formation takes place at intrinsic P and In sites) [12].

Upon excitation of the surfaces with ns-laser pulses, three different neutral species were desorbed; these were monatomic P, diatomic P_2 and monatomic In, as shown in the mass spectrum inset to Fig. 3(a). Monatomic P is the major desorbed species with the yield higher than the In yield. InP molecules were not detected, and no ions were

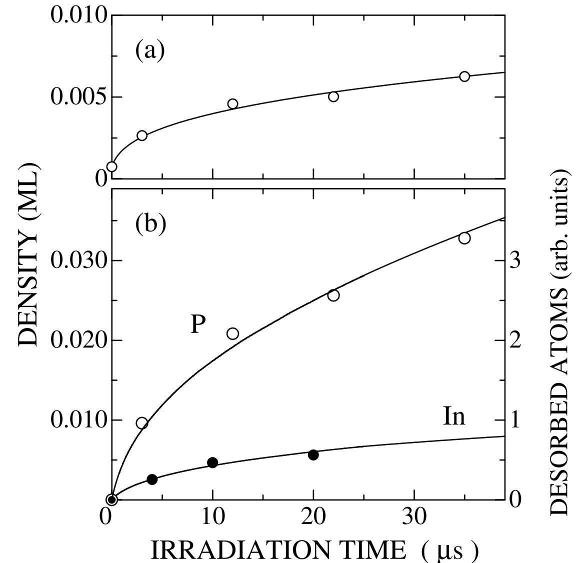

FIG. 2. Growth of the total number density of P vacancies, (a), and those of total vacancy sites of P and In vacancies, (b), upon excitation by 460-nm laser pulses. The solid curves in (b) are the time-integrated desorption yields of P and In atoms measured simultaneously by FNRIS (see the text).

emitted. Figures 3(a) and 3(b) show the desorption yield of P and In, measured simultaneously as a function of t. Although the yields of both species decrease with t, the yield of In relative to that of P remains constant irrespective of sharp drop in total yield during irradiation, suggesting that the same mechanism induces desorption of both species. Time-of-flight (TOF) of P and In atoms from the surface to the ionization volume were measured by changing time delay between the excitation pulses and fs-laser pulses for ionization at the region showing slower reduction after t of 5 μs. The TOF spectra of P and In atoms shown in the inset of Fig. 3(b) are characterized by the peak flight times of 0.6 and 1.0 μs, which correspond to the translational energy E_T of 0.2 and 0.3 eV, respectively. The different flight times of P and In atoms exclude the possibility of dissociative ionization of InP molecules desorbed, and show clearly that these atoms are desorbed separately, consistent with the STM observation that monovacancies at P and In sites are formed during separate events.

We correlate quantitatively the yield of desorption with the size V of vacancy sites. For the bond-rupture rate $g(t)$ at time t, the desorption yield is proportional to $g(t)$, while V is given by the integral of $g(t)$ over t. Then, we compare the time-integrated desorption yield $Y(t)$ (solid curves) with V in Fig. 2(b) for P and In atoms. It is evident that these two quantities show essentially the same dependence on t. Therefore, the desorption is the direct consequence of the bond rupture of P and In atoms on the surface.

In order to study the characteristics of monovacancy formation on pristine surfaces, the desorption is exam-

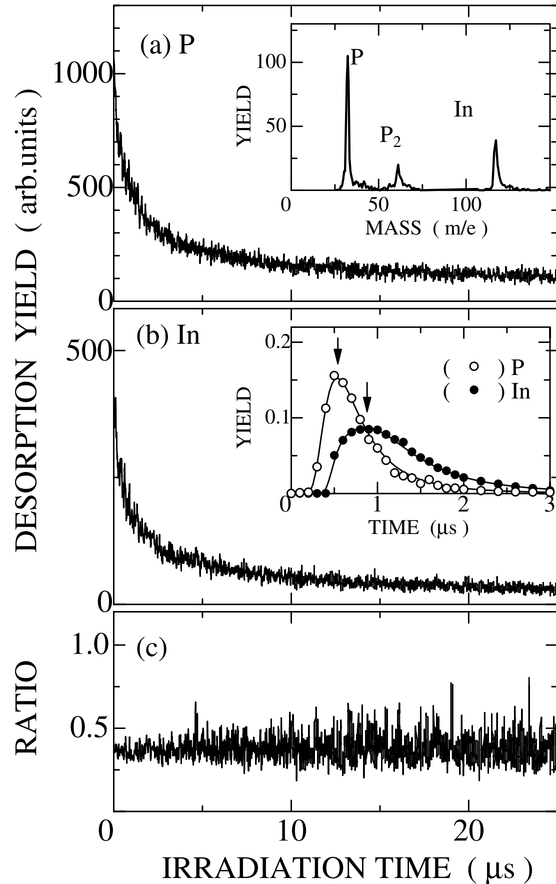

FIG. 3. Desorption yields of P atoms, (a), and In atoms, (b), and the ratio of the yield of In relative to that of P atoms, (c), as a function of irradiation time of 460-nm laser pulses at 2.8 mJ/cm^2. The inset of (a) shows the mass spectrum of neutral desorbed species, and the inset of (b) shows the time-of-flight spectra of P and In atoms.

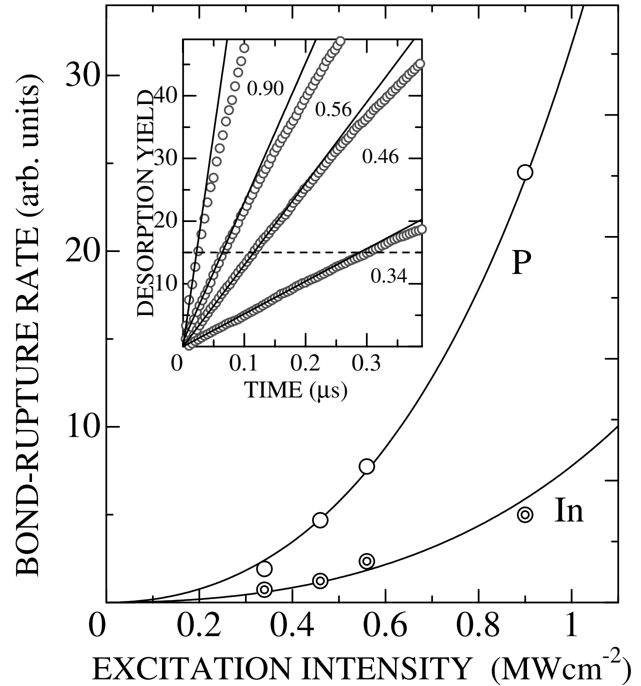

FIG. 4. The bond-rupture rate of P and In atoms as a function of excitation intensity of 460-nm laser light. The solid curves are the best fit of the two-hole localization model. The inset shows the time-integrated yields of desorbed P atoms as a function of irradiation time for four different excitation intensities.

ined only for *the first* few hundred ns, thus avoiding any contributions from bond rupture near preexisting vacancies. In the inset of Fig. 4, we show $Y(t)$ of P atoms as a function of t in this initial region. For any curves measured at different excitation intensities ϕ's, Y increases linearly until a certain critical value of Y, above which the growth rates start to decrease. The slope of the initial part can be taken as $g(0)$ at perfect sites on the surfaces with low C_0. The rates thus determined are plotted as a function of ϕ in Fig. 4; it depends superlinearly on ϕ. The bond-rupture rate of In, determined by a similar analysis, shows a similar nonlinear feature.

P monovacancies can be formed thermally more efficiently on p-type than n-type InP(110)-(1×1) [13,14]. Although the rate of this thermal process is negligible at 296 K, a possible temperature rise ΔT by laser heating might enhance the rate. The ΔT upon ns-laser irradiation, estimated from the standard formula of laser heating [15], is less than 30 K even for the maximum fluence of 5 mJ/cm^2. At the estimated highest temperature (326 K), the rate of about 1.3×10^{-7} ML/s can be interpolated by published data for p-type InP, which is too low to account for the P vacancies formed by laser excitation. Therefore, it is evident that the bond rupture induced by laser excitation is not due to laser-induced heating. This conclusion is substantiated definitely by the results of FNRIS. It has been shown that neutral atoms and molecules are desorbed by laser-induced heating with the translational energies E_T's corresponding to the surface temperature. A surface temperature of about 400 K has been deduced for GaAs under 532-nm laser irradiation at fluence of 80 mJ/cm^2 [7]. On the other hand, E_T's as high as 0.2 eV, corresponding to more than 2000 K, are imparted to P and In atoms under excitation at fluence as low as 2.8 mJ/cm^2 that can result in ΔT less than 15 K. Therefore, the desorption is not due to thermal mechanism, but is due to electronic processes following laser excitation.

The essential features of the electronic process described above are the case for broader excitation-wavelength range from 550 to 420 nm, where laser irradiation results mainly in the valence excitation of InP. Therefore, the intrinsic structural instability is induced by valence excitation on InP(110)-(1×1). The instability is featured first by local bond rupture at perfect surface sites, followed by subsequent bond rupture near vacancies. It also shows the second feature of the bond breaking rate dependent superlinearly on ϕ for both In and P

atoms, with a much higher rate for P atoms on the surface. In view of the first feature, the mechanism may be most appropriately described as a localization of electronically excited species at respective surface sites. Among several models proposed so far, the two-hole localization (THL) mechanism [5] provides the most reasonable description of these observations. Qualitatively, the THL mechanism requires that a valence hole first localizes at a surface site through the surface occupied band consisting of s-like orbitals on surface P atoms. Localization of a second-hole near the same P-atom site, under a dense excitation, leads to bond rupture between the P atom and the nearest In atoms with the two holes separated from each other on both sides of the ruptured bond. Then, the Coulomb repulsion between the two localized holes and associated lattice relaxation results in the ejection of either P or In atoms with a certain branching ratio.

Quantitatively, the THL mechanism predicts the desorption rate $g(0)$ given by $g(0) = A\{\exp(N_s/Z) - 1\}^2$, where A is a constant, N_s is the density of free holes confined in the two-dimensional surface region, and Z is the effective number of free holes at temperature T [5]. When we assume N_s proportional to ϕ, then $g(0) = A\{\exp(\beta\phi) - 1\}^2$, where β is a constant [2,5]. The solid curve in Fig. 4 is a fit of this equation to the experimental results; it describes satisfactorily the superlinear desorption yield for both P and In with the same value of β. The best-fit value of β suggests N_s/Z of 0.6 at the intensity of 1 $\mathrm{MW/cm^2}$. We estimate the magnitude of N_s to be the hole density per unit atomic plane from the density N_v of bulk holes. The N_v is approximately $N_v \approx \alpha\tau\Phi$, where α is the absorption coefficient, τ is the lifetime of the free hole, and Φ is the photon fluence. We find that $N_s/Z = 0.6$ is satisfied if $\tau \geq 300$ ps [16], which is reasonable based on the results of surface electron dynamics studies [17]. On damaged surfaces, however, τ may be reduced by efficient trapping of the holes at vacancy sites thus to reducing N_s. In view of the superlinear yield dependence, a small reduction of N_s results in a strong reduction of $g(0)$. Therefore, a decreasing growth rate of N and V and decreasing desorption yield of P and In may result, as shown in Figs. 2 and 3. The analysis in Fig. 4 shows that the constant A is species-dependent such that A is 4 times larger for P-atom desorption than for In-atom desorption. This difference most likely results from the branching between P and In atoms in the desorption mechanism following two-hole localization. The microscopic theory to describe the branching is an important issue to be explored in the future.

A recent STM study for n-type GaAs (110)-(1×1) has shown that both As and Ga atoms are removed electronically from originally perfect sites under excitation of ns-laser pulses (450–550 nm) at intensities below 1 $\mathrm{MW/cm^2}$, and that vacancies are formed by about 3 times more efficiently at As sites than In sites [18]. Therefore, the structural instability with a species-dependent rate of bond rupture appears to be common for III-V semiconductor surfaces.

In summary, we have shown that the intrinsic structural instability is induced under valence excitation on InP (110)-(1×1). The instability on this binary-component surface is featured by a prominent species-dependent rate of the bond rupture and by the superlinearly dependent rates of bond breaking on the excitation intensity. The results suggest that the intrinsic structural instability under valence excitation is one of the characteristic features of covalent semiconductor.

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