Crucial roles of holes in electronic bond rupture on semiconductor surfaces

J. Tsuruta, E. Inami, J. Kanasaki *, K. Tanimura

The Institute of Scientific and Industrial Research, Osaka University, 8-1 Mihogaoka, Ibaraki, Osaka 567-0047 Japan

ABSTRACT

Structural changes on cleaved (110) surfaces of InP, induced by tunneling carriers from the tip of a scanning tunneling microscope, were studied. Bond rupture takes place at intrinsic P-sites only at negative sample voltages (i.e., under hole-injection conditions), resulting in the formation of P-vacancies, while injected electrons induce no structural change. The rate of bond rupture, showing a prominent threshold sample voltage at −2.2 V, is a quadratic function of the tunneling current. Nonlinear localization of two holes injected into surface bands is crucial as the primary step in the electronic bond rupture on semiconductor surfaces.

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1. Introduction

Excited carriers generated in semiconductors induce atomic dynamics on the surfaces which have opened unique opportunities for sophisticated material processing. The carrier-induced atomic dynamics exhibit a variety of forms, including dissociation [1,2], desorption [3–8], phase transitions [9,10], polymerization [11], displacement and diffusion of surface atoms [12,13], depending on the properties of the materials and excitation conditions. Among the several available excitation sources, scanning tunneling microscope (STM) has two principle advantages: it allows injection of excited carriers at a predetermined surface site from the metal tips, as well as direct observation of the triggered structural changes. The STM is thus expected to advance our understanding of the fundamental processes of atomic dynamics. Shen et al. have revealed that field-emitted and tunneling electrons from the STM tips induce the desorption of hydrogen atoms from H/Si(001), which has been successfully described by two distinct mechanisms based on the inelastic energy loss of incident electrons [4]. At sample biases above 6.5 V, the authors found a strong desorption at a nearly constant rate, independent of either the sample voltage or current. In this regime, incident electrons possess an available excess energy large enough for the electronic transition from bonding to anti-bonding states of local Si – H bonds, which can induce desorption. Below the threshold voltage, on the other hand, the rate is several orders of magnitude smaller and strongly voltage- and current-dependent. Although the excess energy of tunneling electrons becomes too small to cause the

electronic transition, incident electrons can excite Si – H bonds into highly vibrationally-excited states either resonantly or non-resonantly to break the bond. These inelastic energy loss mechanisms, based on the electronic and vibrational excitations of the surface local bond, have also been applied to explain desorption not only by electron injection but also by hole injection [7].

The inelastic energy loss of tunneling carriers brings about the atomic-scale desorption of adsorbates just below the STM-tip, due to the limited spatial extent of the tunneling junction. In contrast, several studies have found the flip of surface atoms away from the injection point [9,12]. Also, the remotely-induced flip showed anisotropic distribution of events with the spatial spreads characterized by the mobility of surface electronic bands. These results demonstrate clearly that the carriers in the surface bands can induce atomic dynamics after the injection.

So far, different excitation sources have also been used to generate excited carriers in the surface and bulk bands in semiconductors. Recent laser excitation studies have reported that photo-generated carriers induce bond rupture at intrinsic atomic sites on semiconductors, leading to desorption [14–17]. The laser studies have proposed that nonlinear localization of two holes is necessary to break the multiply-coordinated back-bonds at intrinsic surface sites. Nevertheless it is difficult to clarify the relative importance of surface and bulk holes in the bond rupture and to eliminate any possible effects of electrons and/or excitons concomitantly generated by photons. STM allows us to inject either electrons or holes selectively from the tips and to select the electronic states to which the carriers are dominantly injected. The controllability of carrier injection from STM tips is an important advantage in elucidating the relative roles of excited species in the carrier-induced dynamics. Therefore, the bond rupture induced by STM tips can be a crucial test in determining

the carriers responsible for the structural instability on semiconductor surfaces.

In this study, we used tunneling carriers from the STM tips to induce the bond rupture at surface atomic sites on semiconductor surfaces. Direct STM observations of the carrier-injected InP(110) 1×1 surfaces revealed that bond rupture takes place at intrinsic P-sites only at negative sample voltages, corresponding to hole-injection conditions. The rate of bond rupture shows a prominent threshold at a sample bias voltage of -2.2 ± 0.2 V and is a quadratic function of the tunneling current. Based on the experimental findings, we can definitely demonstrate that the localization of the two holes injected into the surface electronic band plays a crucial role in the carrier-induced bond rupture, as has been suggested for the laser-induced bond rupture. This study develops a unified model that can be applied to explain the electronic bond rupture on various semiconductor surfaces, irrespectively of excitation sources.

2. Experimental

All experiments were performed at room temperature in an ultra-high vacuum (UHV) chamber under a pressure $< 7 \times 10^{-9}$ Pa. An STM (UNISOKU USM-1100S) was used both to inject electrons or holes and to characterize directly induced structural changes. The (110) surfaces of InP with a cross section of 0.2 mm $\times$ 5 mm were obtained by cleaving n-type (Sn-doped: 8×10^{16} cm^{-3}) and p-type (Zn-doped: 5×10^{18} cm^{-3}) wafers in UHV. The cleaved surface showed a large terrace size of several hundred nanometers, and contained very few defects: the initial density of the P-vacancy was typically 0.1% relative to the total density of P-sites on this surface. The number density of tip-induced vacancies was measured over the probed area by analyzing STM images before and after the tip-scans.

3. Results

Fig. 1(a)–(d) shows a series of constant-current images probed at the same area of the (110) surface of an n-type sample. The images were acquired under repeated scans of a tungsten tip at a sample bias voltage of $Vs = -2.8$ V, which corresponds to the hole-injection condition. On this surface, no reconstruction is induced but the surface atoms forming the In-P zigzag chains relax significantly to get the anions (cations) raised (lowered) from their bulk-terminated positions [18]. Oval-shaped protrusions running from the lower-left to upper-right in the images show surface P-atoms along the In-P chains, while dark features represent P-vacant sites. The image at the 1st scan, (a), shows no

vacancy in the probed area. Although no vacancy was formed in the wide area until the 5th scan, one monovacancy was first formed at a surface P-atomic site after the 6th scan, (b): the results demonstrate the tip-induced bond rupture at the intrinsic P-site, not the migration of a pre-existing P-vacancy. The 7th scan, (c), showed the removal of one more P-atom from a site neighboring the vacancy to form a divacancy on the same chain. By the end of the 20th scan, three more P atoms were removed around the di-vacancy, (d), resulting in a vacancy string including five P-vacant sites. Thus the continuous tip-scan produced P-vacancy strings elongated along In-P chains, and the rate of formation was significantly higher than that expected from the statistics of the random distribution of the same number densities of vacancies.

Fig. 1(e) shows both P- and In-site images observed at the same area including a tip-induced P-monovacancy, at sample bias voltages of $Vs = -2$ V and $+2$ V, respectively. As clearly shown in the In-site image, two In atoms adjacent to the P-vacancy exist, though the P-vacancy depresses the contrast of the two neighboring In atoms as compared to other sites. Thus the primary process in the observed structural change is the bond rupture at the intrinsic P-site, followed by the sequential removal of neighboring atoms.

In order to compare quantitatively the rate of bond rupture under different injection conditions, similar STM observations were conducted at different sample voltages and tunneling currents. We defined here the rate of bond rupture at intrinsic P-sites as the number density of P-vacancies formed by a single 35-second tip-scan over a 10 nm $\times$ 10 nm area. The bond rupture rates thus determined were measured at several sample biases ranging from -3.0 to $+3.0$ V with a constant tunneling current of 350 pA. Fig. 2(a) shows the averaged rates obtained by the images probed over fifteen different spots on n-type samples. For negative sample voltages (hole-injection conditions), the rate shows a prominent threshold at $Vs = -2.2 \pm 0.2$ V, and then increases steeply as the sample voltage is changed to $Vs = -3.0$ V. In contrast to the strong sample voltage dependence for $Vs < 0$, the rate was kept at nearly zero for $Vs > 0$ up to $+3.0$ V (electron-injection condition).

The bond rupture rate was also measured as a function of the tunneling current I_t. The solid circles plotted in Fig. 2(c) are the rates measured at a fixed sample voltage at $Vs = -2.5$ V. The rates clearly show superlinearity with respect to I_t. The solid curve in the figure shows the best fit of the experimental data using a power function of I_t: the best fit to the data yields a rate proportional to I_t^N with $N = 1.9$. Although the rate strongly depends on Vs, the magnitude of N is almost constant at 2.0 ± 0.2, at several sample voltages.

Similarly to the case of the n-type sample, we observed a bond rupture at the intrinsic P-site on the p-type sample at negative sample
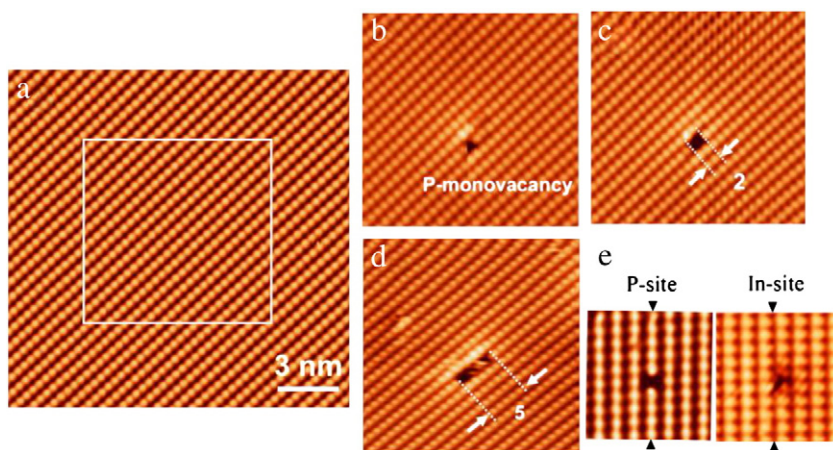

Fig. 1. A series of occupied-state STM images, (a)–(d), of n-type InP(110) 1×1 under repeated scans over the same area at a sample bias voltage of $V_S = -2.5$ V. The tunneling current during the tip-scan is constant at 350 pA. Image (a) shows a wide view of 17×17 nm^2 of the probed surface acquired at the 1st scan. Images (b)–(d) are enlarged views of the area indicated as a square in (a), acquired at the 6th scan (b), 7th scan (c), and 20th scan (d), respectively. The images in (e) are the P- and In-site images of the same area including a tip-induced P-monovacancy, observed at $V_S = -2$ V and $+2$ V, respectively.