Local Hydride Formation of the Si(111)-(7×7) Surface by Hydrogen Atoms Deposited from a Scanning Tunneling Microscope Tip

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The Si(111)-(7×7) surface can be locally hydrized at the nanometer scale by depositing H atoms from the tip of a scanning tunneling microscope. The H atoms to be deposited are continuously supplied to the tip made of Pt (20% Ir) from an ambient H_2 molecule gas through dissociative adsorption ($H_2 \rightarrow 2H$) and are deposited onto the Si(111)-(7×7) sample surface one by one by field evaporation; although the ambient H_2 molecules are not adsorbed on the Si(111)-(7×7) surface, the H atoms from the tip are adsorbed on the surface.

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The scanning tunneling microscope (STM) invented by Binnig and and Rohrer [1] is a promising tool for the manipulation of single atoms. In a pioneering work, Becker, Golovchenko, and Swartzentruber [2] made an atomic-scale protrusion on a Ge(111) surface using an STM tip. Eigler and Schweizer [3] demonstrated that Xe atoms weakly physisorbed on a Ni(110) surface could be moved over the surface with an STM tip; later, Eigler, Lutz, and Rudge [4] succeeded to pick up such an Xe atom with the STM tip and redeposit it onto the surface repeatedly ("atom switch"). Lyo and Avouris [5] extracted and redeposited single Si atoms chemically bonded on the Si(111) surface using an STM tip. Such a redeposited Si atom can be displaced with an STM tip as demonstrated by Uchida *et al.* [6]. Hosoki, Hosaka, and Hasegawa [7] successfully extracted single S atoms from a $MoS_2(111)$ surface to form a predetermined pattern. However, another mode of STM atom manipulation is required in order to use this technique for various applications such as the creation of novel nanometer-scale electronic devices. Namely, we want to continuously supply foreign atoms to an STM tip and deposit them onto a sample surface one by one.

In this paper, we demonstrate such atom manipulation by taking H atoms as the foreign atoms. The H atoms were supplied to a Pt (20% Ir) tip from an ambient H_2 molecule gas through dissociative adsorption ($H_2 \rightarrow 2H$) [8-11] and were deposited onto a Si(111)-(7×7) sample surface one by one by field evaporation [12]. We note that although H_2 is not adsorbed on the Si(111)-(7×7) surface [13], H is adsorbed on the surface [14].

A Si(111) sample ($15 \times 7 \times 0.3$ mm^3) was cut from a P-doped *n*-type Si wafer (0.1 Ω cm) and mounted on a sample holder of an STM (JEOL JSTM-4000XV) operated in ultrahigh vacuum (UHV) of about 6×10^{-11} Torr and cleaned by repeated heating at 1200 °C in UHV better than 1×10^{-10} Torr to obtain the (7×7) reconstructed structure. Image observation and structure modification of the Si(111)-(7×7) surface by the STM were done either under UHV conditions or 1×10^{-7} Torr of H_2 using a Pt (20% Ir) tip. In both the image observation and the structure modification, the tunneling current was always 0.6 nA. It was essential in the present work to use a clean tip. The final cleaning of the tip was done by electron-bombardment heating followed by removal of residual contamination by field evaporation in UHV.

First we imaged a 10×10 nm^2 area of the Si(111)-(7×7) sample surface at the normal scanning voltage of +1.0 V to the sample in UHV. Then we scanned the Pt tip in a centered area of 5×5 nm^2 in UHV at a higher voltage of +3.5 V to the sample. The scan speed was 195 nm/s and the number of scan lines was 512, so the duration of the higher voltage, τ, was 13 s. STM images before and after the higher voltage scan are shown in Figs. 1(a) and 1(b), respectively, the 5×5 nm^2 area mentioned above being shown by a square in Fig. 1(b). In this paper, an arrow in STM images indicates a natural defect as a marker. If we compare Fig. 1(b) with Fig.

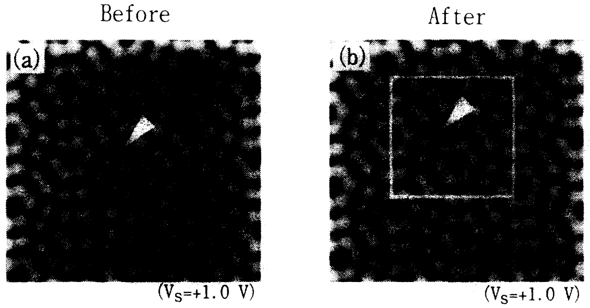

FIG. 1. STM images of an area of 10×10 nm^2 of the Si(111)-(7×7) sample surface (a) before and (b) after scanning a clean Pt tip in a 5×5 nm^2 area shown by a square in (b) with a voltage of +3.5 V being applied to the sample at a tunneling current of 0.6 nA. The image was made at a sample voltage of +1.0 V and a tunneling current of 0.6 nA. Arrows indicate a natural defect as a marker.

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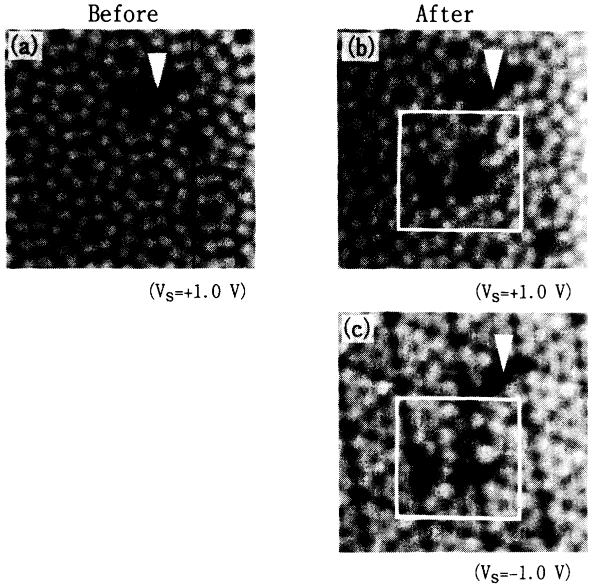

FIG. 2. STM images of an area of 10×10 nm^2 of the Si(111)-(7×7) sample surface (a) before and (b),(c) after scanning a Pt tip in an area of 5×5 nm^2 shown by a square in (b) and (c) in 1×10^{-7} Torr of H_2 with a voltage of +3.5 V being applied to the sample at a tunneling current of 0.6 nA. The image was made at a sample voltage of +1.0 or −1.0 V as indicated and a tunneling current of 0.6 nA. Arrows indicate a natural defect as a marker.

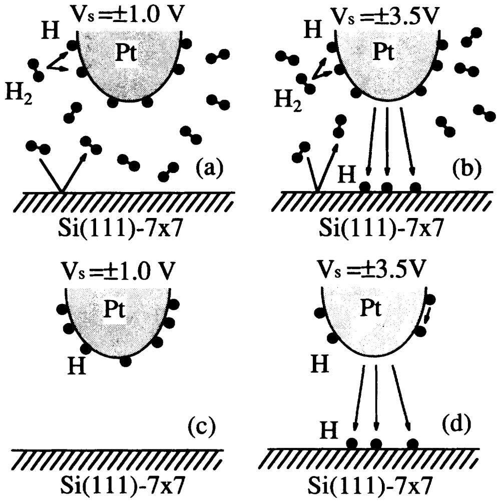

FIG. 3. Upper panel: Schematic figures of a Pt tip and the Si(111)-(7×7) surface placed in H_2 gas. It is shown that H_2 is dissociatively adsorbed on the Pt tip ($H_2 \rightarrow 2H$) but not adsorbed on the Si(111)-(7×7) surface. No apparent change occurs on the sample surface provided that the sample voltage is small enough as shown in (a), but H atoms on the tip are deposited onto the sample surface through field evaporation if the sample voltage is increased to +3.5 V as shown in (b). Lower panel: Schematic figures of a Pt tip previously exposed to H_2 gas and the Si(111)-(7×7) surface placed in UHV. The tip has H atoms on it due to the exposure to H_2 gas as shown in (c). The H atoms on the tip are deposited onto the sample surface through field evaporation when the sample voltage is increased, as shown in (d).

1(a), there is no essential difference between them. This result indicates that the voltage applied to the sample, +3.5 V, is less than the critical voltage for extracting Si atoms from the sample surface through field evaporation, in agreement with previous studies [15–17].

Next, we repeated the experiment in 1×10^{-7} Torr of H_2. STM images before and after this experiment are shown in Figs. 2(a) and 2(b), respectively. In both figures, the (7×7) structure is clearly observed, despite these images being taken in the H_2 gas. This is consistent with the fact that H_2 is not adsorbed on the Si(111)-(7×7) surface at room temperature [13] [Fig. 3(a)]. If we compare Fig. 2(b) with Fig. 2(a), the former exhibits Si atom sites which are darker than others, on the lower left of the natural defect. Figure 2(c) shows an image of the same area but was taken with the opposite polarity of sample voltage. The darker Si atom sites in Fig. 2(b) are also darker in Fig. 2(c). These darker Si atom sites are due to the adsorption of H atoms deposited from the Pt tip, as discussed later. This is reasonable because H_2 is dissociatively adsorbed on Pt surfaces [8–11] [Figs. 3(a)], also the adsorbed H atoms can be field evaporated under a strong field [12] [Fig. 3(b)], and H atoms can be adsorbed on the Si(111)-(7×7) surface [14] [Fig. 3(b)].

In order to confirm that the darker Si atom sites in Figs. 2(b) and 2(c) are due to adsorbed H atoms, we exposed the Si(111)-(7×7) surface to gaseous H atoms produced in H_2 gas by heating a W filament placed in front of the sample. In STM images taken after this exposure, the adsorption of H atoms was observed to create Si atom sites that are darker than others at both polarities of sample voltage, in agreement with previous studies [18,19]. In addition, the voltage dependence of the image contrast of these sites agreed with that of the darker Si atom sites observed in Figs. 2(b) and 2(c). Namely, as the sample voltage increased (decreased) beyond about +1.5 V (−1.5 V), the Si atom sites became brighter.

If, as we propose, the deposition of H atoms from the Pt tip is due to field evaporation, such deposition should occur even in UHV provided that the Pt tip has been previously exposed to H_2 to coat it with H atoms [see Fig. 3(c)]. In order to confirm this, we exposed the Pt tip to 9×10^{-5} Torrs of H_2 and made the same experiment in UHV with this tip. Figure 4(a) shows an STM image before the experiment and Figs. 4(b) and 4(c) show images after the experiment measured at positive and negative sample voltages, respectively. As we see in Figs. 4(b) and 4(c), the expected deposition of H atoms [Fig. 3(d)] is observed on the upper left of the natural defect, the number of deposited H atoms being comparable to that in

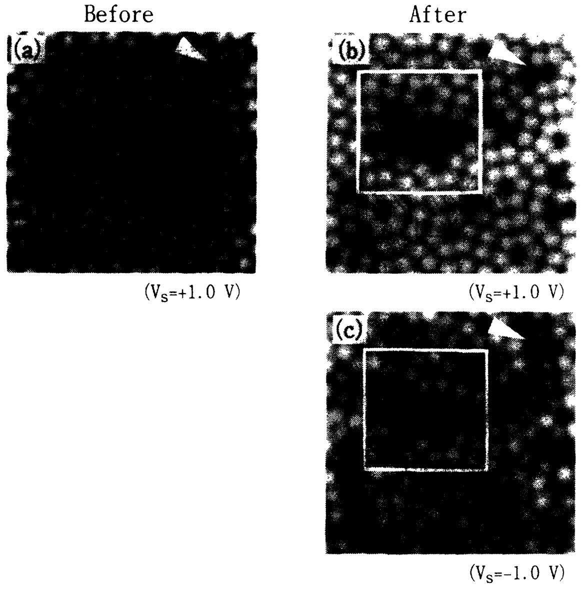

FIG. 4. STM images of an area of 10×10 nm^2 of the Si(111)-(7×7) sample surface (a) before and (b),(c) after scanning a Pt tip, which was previously exposed to 90 L of H_2, in an area of 5×5 nm^2 shown by a square in (b) and (c) in UHV with a voltage of $+3.5$ V being applied to the sample at a tunneling current of 0.6 nA. The image was made at a sample voltage of $+1.0$ or -1.0 V as indicated and a tunneling current of 0.6 nA. Arrows indicate a natural defect as a marker.

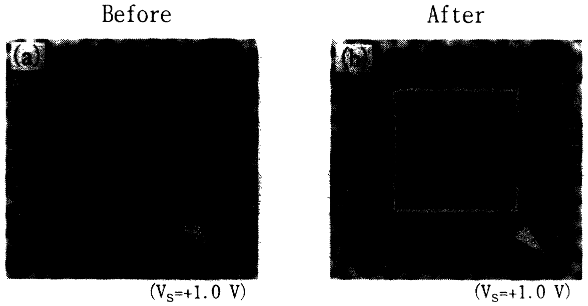

FIG. 5. STM images of an area of 10×10 nm^2 of the Si(111)-(7×7) sample surface (a) before and (b) after scanning a Au tip, which was previously exposed to 90 L of H_2, in an area of 5×5 nm^2 shown by a square in (b) with a voltage of $+3.5$ V being applied to the sample at a tunneling current of 0.6 nA. The image was made at a sample voltage of $+1.0$ V and a tunneling current of 0.6 nA. Arrows indicate a natural defect as a marker.

Figs. 2(b) and 2(c). This result eliminates the possibility that the deposition of H atoms could be due to a field induced dissociation of H_2 molecules. After repeating this experiment many times (~100 times, although it depends on tips), the deposition of H atoms did not occur any longer, presumably because H atoms on the Pt tip were exhausted (~1000 H atoms were deposited in total). These results indicate that the deposited H atoms were definitely supplied from the Pt tip by field evaporation.

We made the same experiment using a Au tip previously exposed to H_2. STM images before and after this experiment are shown in Figs. 5(a) and 5(b), respectively. If we compare Fig. 5(b) with Fig. 5(a), there is no apparent change, as expected from the fact that H_2 is not adsorbed or dissociated on a Au surface [20]. This result confirms that the deposition of H atoms observed for the Pt tip is due to the dissociative adsorption of H_2 molecules onto the Pt tip.

In the case of the Pt tip, although we uniformly scanned the tip in the 5×5 nm^2 area, the deposited H atoms were not uniformly adsorbed in the area but formed a few small aggregates consisting of 5–10 H atoms in total, as seen in Figs. 2(b) and 2(c) and Figs. 4(b) and 4(c). This can be explained by assuming that (i) the number of deposited H atoms was not large enough to cover the whole area and (ii) the deposited H atoms migrated to form the aggregates. Regarding (ii), Boland [18] has made detailed STM observations of H atom adsorption on the Si(111)-(7×7) surface and found that adsorbed H atoms form aggregates even at small coverages. As for (i), the deposition of H atoms is confined in the 5×5 nm^2 area in which the tip was scanned, as we see in Figs. 2(b) and 2(c) and Figs. 4(b) and 4(c), so it is reasonable to think that the effective minitip responsible for the process of concern has a diameter much less than 5 nm, say less than ~1 nm. If we assume that the minitip has a pyramidal shape, the number of Pt atoms on the minitip is therefore smaller than ~10. Since the saturation coverage of H atoms on Pt surfaces is ~0.25 per exposed Pt atom [8,9,21–24], the number of H atoms adsorbed on the minitip, n, is smaller than ~2.5; this number is constant during field evaporation since we observed that the number of deposited H atoms increased linearly with time. The rate of field evaporation of the adsorbed H atom, R, is therefore estimated to be $\sim0.2\ \mathrm{s}^{-1}$ because 5–10 H atoms were deposited in 13 s from the minitip. Such a small value of R is typical in field ion microscopy [12].

This raises the question of how the H atoms are continuously supplied to the minitip. Is it directly from the ambient H_2 gas or through surface diffusion from other places? First we consider only the direct supply from the ambient H_2 gas. In this case, n changes with time t according to $dn/dt=-nR+(n_0-n)a$ $(a=pPS/n_0)$, where n_0 is the initial value of n at $t=0$ (smaller than ~2.5 as already discussed), p the sticking probability of H_2 on Pt surfaces (~0.1 [8,9,21–24]), P the number of H_2 molecules hitting a unit area of the minitip per unit time (1.4×10^{14} cm^{2}s^{-1} at the 1×10^{-7} Torr), and S the surface area of the minitip (less than ~2 nm^2). From this equation, the number of deposited H atoms, N, is

$$N=\int_0^{\tau} nR\,dt$$
$$=n_0[R^2/(R+\alpha)^2]\{1-e^{-(R+\alpha)\tau}+\alpha\tau(R+\alpha)/R\}\lesssim 2. \qquad (1)$$

This number is much smaller than our experimental value, 5–10, indicating that the H atoms are predominantly supplied through surface diffusion. The surface diffusion can be taken into account by replacing α in (1) with $\alpha+\beta$ ($\beta=Q/n_0$), where Q is the number of H atoms supplied to the minitip per unit time through surface diffusion when the minitip has no H atoms. In order to have an N comparable to 5–10, $\beta\gtrsim 0.4$ s^{-1} and so $Q\gtrsim 1$ s^{-1}, indicating that H atoms on the Pt tip are vigorously migrating in our experiments in an applied field.

In this paper, we have discussed only the case of a positive sample voltage of +3.5 V, but we observed the deposition of H atoms also for a negative sample voltage of −3.5 V. For positive and negative sample biases, H atoms should be field evaporated as negative and positive ions, respectively. According to a recent theoretical study by Sawamura, Tsukuda, and Aono [25], a H atom on a tip can be field evaporated as a positive or negative ion depending on the polarity of the field.

To summarize, in an STM, if we scan a PT tip in an area of the Si(111)-(7×7) sample surface at an appropriately high sample voltage in a H_2 gas, we can locally hydrize the surface. This local hydrization occurs because H atoms dissociatively adsorbed on the Pt tip are field evaporated toward the sample surface.

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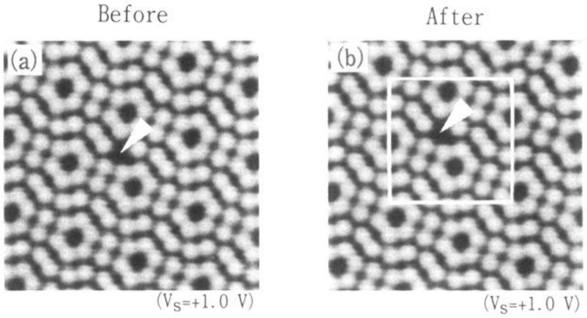

FIG. 1. STM images of an area of 10×10 nm^2 of the Si(111)-(7×7) sample surface (a) before and (b) after scanning a clean Pt tip in a 5×5 nm^2 area shown by a square in (b) with a voltage of +3.5 V being applied to the sample at a tunneling current of 0.6 nA. The image was made at a sample voltage of +1.0 V and a tunneling current of 0.6 nA. Arrows indicate a natural defect as a marker.

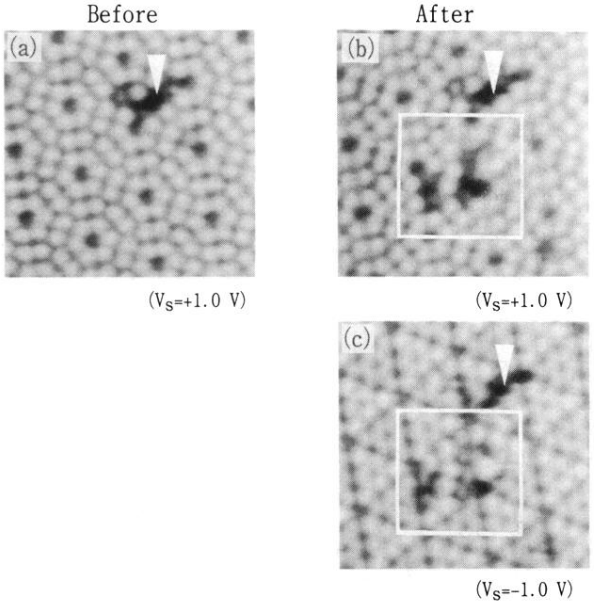

FIG. 2. STM images of an area of 10×10 nm^2 of the Si(111)-(7×7) sample surface (a) before and (b),(c) after scanning a Pt tip in an area of 5×5 nm^2 shown by a square in (b) and (c) in 1×10^{-7} Torr of H_2 with a voltage of +3.5 V being applied to the sample at a tunneling current of 0.6 nA. The image was made at a sample voltage of +1.0 or −1.0 V as indicated and a tunneling current of 0.6 nA. Arrows indicate a natural defect as a marker.

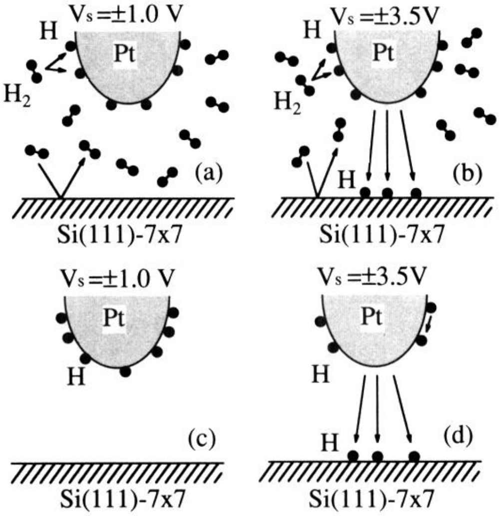

FIG. 3. Upper panel: Schematic figures of a Pt tip and the Si(111)-(7×7) surface placed in H_2 gas. It is shown that H_2 is dissociatively adsorbed on the Pt tip ($H_2 \rightarrow 2H$) but not adsorbed on the Si(111)-(7×7) surface. No apparent change occurs on the sample surface provided that the sample voltage is small enough as shown in (a), but H atoms on the tip are deposited onto the sample surface through field evaporation if the sample voltage is increased to +3.5 V as shown in (b). Lower panel: Schematic figures of a Pt tip previously exposed to H_2 gas and the Si(111)-(7×7) surface placed in UHV. The tip has H atoms on it due to the exposure to H_2 gas as shown in (c). The H atoms on the tip are deposited onto the sample surface through field evaporation when the sample voltage is increased, as shown in (d).

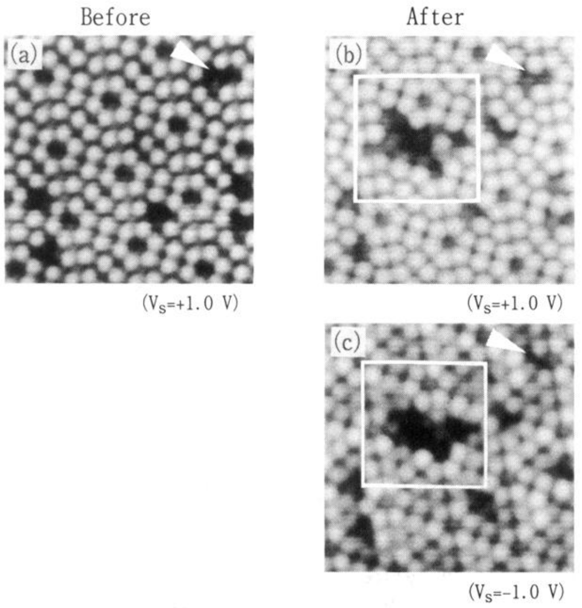

FIG. 4. STM images of an area of 10×10 nm^2 of the Si(111)-(7×7) sample surface (a) before and (b),(c) after scanning a Pt tip, which was previously exposed to 90 L of H_2, in an area of 5×5 nm^2 shown by a square in (b) and (c) in UHV with a voltage of +3.5 V being applied to the sample at a tunneling current of 0.6 nA. The image was made at a sample voltage of +1.0 or −1.0 V as indicated and a tunneling current of 0.6 nA. Arrows indicate a natural defect as a marker.

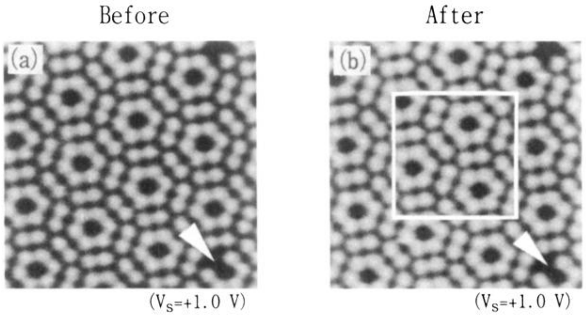

FIG. 5. STM images of an area of 10×10 nm^2 of the Si(111)-(7×7) sample surface (a) before and (b) after scanning a Au tip, which was previously exposed to 90 L of H_2, in an area of 5×5 nm^2 shown by a square in (b) with a voltage of +3.5 V being applied to the sample at a tunneling current of 0.6 nA. The image was made at a sample voltage of +1.0 V and a tunneling current of 0.6 nA. Arrows indicate a natural defect as a marker.