Temperature Control of Electronic Channels through a Single Atom

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The elastic electronic channels through a single hydrogen atom adsorbed on a Ge(111)-$c(2 \times 8)$ surface have been investigated by scanning tunneling microscopy and $I(V)$ spectroscopy, whereas inelastic channels have been probed by the vertical and horizontal manipulation of individual hydrogen atoms. The substrate temperature, over the range 30–300 K, has proven to be a powerful parameter to freeze specific electronic channels, offering the possible control of elastic and inelastic channels through a single atom. This opens up very interesting perspectives for controlling the operation of nanodevices.

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The ability of the scanning tunneling microscope (STM) to perform imaging, manipulation, and spectroscopy of individual atoms and molecules adsorbed on a surface relies on the properties of electron transport through a single atomic or molecular adsorbate [1–6]. To fully control this atomic-scale STM engineering, one would like ideally to be able to identify, to isolate, and to choose at will the various electron transport channels through a single atom or molecule. However, this is an inherently complicated task because of (i) the existence of numerous elastic and inelastic electronic channels, (ii) the complex couplings between the electronic and nuclear degrees of freedom of both the adsorbate and the surface, and (iii) the possible quantum interferences between all these electronic channels [7]. Thus far, the surface bias is the main parameter which has been used to probe the electronic channels [8]. The most convincing demonstration of this surface bias control has been the vibrational spectroscopy of individual molecules with the STM [9].

Here we report the use of temperature as a means of controlling the elastic and inelastic channels through a single atom with the aim to discriminate thermally activated from nonthermally activated electronic channels. Individual hydrogen atoms adsorbed on a Ge(111) surface are found to be ideal prototypes for such temperature control experiments. Indeed, the STM imaging of a single hydrogen atom is strongly modified when the temperature is varied between 300 and 30 K. This can be understood by scanning tunneling spectroscopy (STS) which shows that tunneling electronic channels whose energy lies within the Ge(111) bulk band gap are frozen at a low temperature, whereas elastic tunneling electronic channels outside the bulk band gap seem to be unaffected by the temperature change. Another important class of thermally activated electronic channels is evidenced by studying the inelastic electronic channels responsible for the displacement of individual hydrogen atoms. When associated with the vertical displacement of a single hydrogen atom, the inelastic electronic channels are found to have the same efficiency at 300 and 30 K. However, when correlated to more complex hydrogen displacements such as the formation of a "zip" site, the inelastic electronic channels are completely inhibited at 30 K. These temperature effects provide an entirely new insight on the nature and the control of elastic and inelastic electronic channels through a single atom.

Experiments are performed in an ultrahigh vacuum chamber (base pressure 2×10^{-11} torr) equipped with a variable temperature STM. The sample can be cooled down to 30 K using a helium liquid flow cryostat. Clean and well-ordered Ge(111)-$c(2 \times 8)$ surfaces are prepared using the procedure described in Ref. [10]. The germanium sample was p doped with Ga at a concentration of 2×10^{14} atoms per cm^3 giving a resistivity of 15 $\Omega \cdot$ cm. As molecular hydrogen does not adsorb on regular Ge(111)-$c(2 \times 8)$ surfaces [11], the surface was exposed to atomic hydrogen produced by filling the vacuum chamber with molecular hydrogen ($P = 10^{-9}$ torr) and leaving the ion pressure gauge on. Since the efficiency of atomic hydrogen formation with the ion pressure gauge is unknown, all the exposures are given by multiplying the hydrogen pressure by the exposure time.

We will first compare how atomic hydrogen adsorbed on the Ge(111)-$c(2 \times 8)$ surface can be imaged with the STM at room temperature (300 K) and low temperature (30 K). STM studies of atomic hydrogen adsorption at room temperature have been previously reported [11]. At very low coverage, isolated hydrogen atoms are known to adsorb on top of Ge rest atoms and to appear in occupied state STM topographs as "triangles" or "squares" made of the three or four bright adatoms surrounding the occupied rest atoms (see Figs. 1a to 1f). At higher atomic hydrogen coverage, more complicated adsorption sites called "zip sites" have been reported [12]. These zip sites (Figs. 1g and 1h), made of a row of displaced adatoms with one hydrogen atom at each end, can be produced spontaneously when two hydrogen atoms adsorb along the same row of rest atoms separated by distances of 10 nm or more [12]. When the Ge(111) surface is cooled down to 30 K and then exposed to atomic hydrogen, the STM topographs show very different features (Figs. 1b and 1e). The adatoms of the triangle and square sites are no longer bright but appear either normal or slightly darker. Instead, only the dark rest-atom sites, as also seen at room temperature, clearly indicate the adsorption of a hydrogen atom on top of a Ge rest atom.

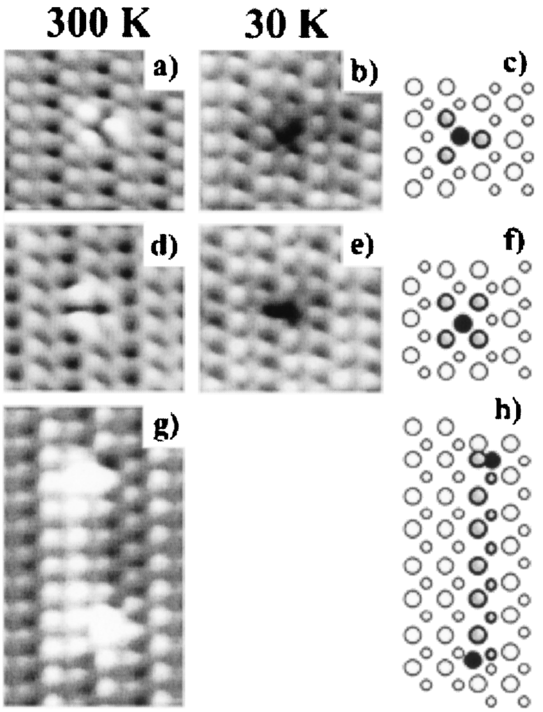

FIG. 1. Adsorption sites of hydrogen atoms on the Ge(111)-$c(2 \times 8)$ surface. The left and center columns show the occupied state STM topographs (-1 V, 1 nA) at 300 and 30 K, respectively. The corresponding atomic diagrams are shown in the right column where the Ge adatoms and rest atoms are represented as large and small light circles, respectively, and adsorbed H atoms as dark circles. The top row, (a)–(c), show a hydrogen atom adsorbed on a Ge rest atom surrounded by three Ge adatoms (triangle site). The middle row, (d)–(f), shows a hydrogen atom adsorbed on a Ge rest atom surrounded by four Ge adatoms (square site). The lower row, (g) and (h), shows a zip site made of two hydrogen atoms.

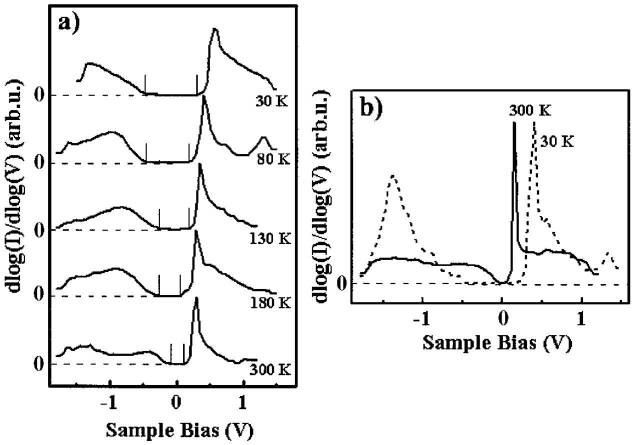

FIG. 2. STM spectroscopy $d(\log I)/d(\log V)$ curves recorded at various temperatures. In (a) clean surface, the tip is positioned on a rest-atom site. In (b) the tip is positioned on one of the adatoms surrounding a hydrogen atom (triangle site). The peak at $+0.2$ V on the 300 K curve is artificially sharp due to the difficulty in numerically calculating $d \log I/d \log V$.

The same behavior is seen when the surface is exposed at 300 K and then cooled down. Experiments have been carried using the same tip at both temperatures and also different tips have been used at 300 and 30 K. This would suggest that the marked difference between the observed sites as a function of the temperature are independent of any tip effect. For the same exposure, similar numbers of adsorption sites were observed at 300 and 30 K. To understand the markedly different STM topographs of H adsorption sites at 300 and 30 K, we performed $I(V)$ scanning tunneling spectroscopy (STS). The results in Fig. 2a show the $d(\log I)/d(\log V)$ curves, calculated numerically from the $I(V)$ curves, at rest-atom sites on the clean surface (without any hydrogen) at various surface temperatures. The spectroscopy curves were obtained using the same bias range (± 1.8 V) and tunnel current (1 nA) at each temperature. Some variation of the tip-sample distance was achieved by changing the setpoint voltage (topography); though, this has no visible effect on the $I(V)$ curves. One clearly observes an opening of the energy gap around the Fermi level from 0.2 eV at 300 K up to 0.7 eV at 30 K, corresponding to the known bulk energy gap of the Ge(111) [13]. We found that the gap increases more on the negative bias side than on the positive bias side ($1.5 \text{ meV} \cdot \text{K}^{-1}$ compared to $0.9 \text{ meV} \cdot \text{K}^{-1}$), and both do so linearly with temperature. This indicates that tunnel electrons which flow through the surface states located inside the band gap need to gain energy by thermal activation either by coupling to the bulk valence or conduction bands or by hopping to neighboring surface sites [14]. The significant widening of the gap (in Fig. 2) observed when cooling from 300 to 30 K considerably exceeds kT (in Fig. 2b, for example, the shift of the band edge at positive bias is about 250 meV or $10kT$). It is unlikely that freezing of the bulk conductance is the dominant effect since the Ga acceptor level is only 0.0108 eV above the valence band so it will *continue* to influence the sample conductivity even below 30 K. This leaves the thermally activated hopping (site to site) through the surface states as the most probable explanation of the results, which would be consistent with the analysis in Ref. [14]. This behavior is also visible when the STM tip is positioned on top of a Ge adatom next to a hydrogen atom (see Fig. 2b). The $d(\log I)/d(\log V)$ curves in Fig. 2b again show that tunneling through surface states whose energy is located inside the bulk band gap is suppressed at 30 K. This suggests that the brightness of the Ge adatoms surrounding an adsorbed hydrogen atom, observed only at 300 K, is related to the tunneling of electrons through adatom surface states inside the bulk band gap. We believe that these thermal effects are limited to the coupling between the adsorbate atom and the substrate as well as the transport of electrons through the substrate and do not affect the coupling between the tip atom and the adsorbate atom. The shift in the band edges cannot alone be explained by any freezing of the electron transfer from the surface state to the bulk bands either directly or indirectly since the probability to activate any process with a barrier of $10kT$ is too small. We believe that, at 30 K, the surface conductivity occurs via lateral site to site hopping within the surface states without any significant interaction with the bulk states. At low temperature the surface conductivity via hopping is frozen out because the barrier to hopping from site to site is about kT. This causes the surface state to apparently disappear with a widening of the gap, since the electrons can no longer be transported across the surface.

Another striking result is that absolutely no zip site could be observed at 30 K, whatever the hydrogen coverage on the Ge(111) surface. This is quite surprising since the movement of the adatom row into the available adjacent metastable T_4 positions [15] producing the zip site was believed to be directly driven by the adsorption of the hydrogen atoms. In particular, the energy required to move the adatom row was expected to come from the energy released during the hydrogen adsorption process. In fact, the absence of zip sites at 30 K indicates that thermal energy is necessary to move the Ge adatom row. The adsorption of two hydrogen atoms on nearby sites along the same rest-atom row is the triggering event which seems to lower the energy barrier for moving the adatom row. However, this energy barrier can only be overcome and the adatom row displaced given sufficient thermal energy.

Zip sites can also be produced by using the STM tip as an atomic manipulator. Two triangle or square sites can be transformed into a zip site by the procedure shown in Fig. 3. The STM tip is positioned over a hydrogen atom (the bottom square site in Fig. 3) and a voltage pulse applied, as previously reported [12]. One of three events can occur: either nothing has changed on the surface, or the hydrogen atom has been transferred to the tip as previously reported [11], or the hydrogen site is transformed into a zip site as shown in Fig. 3. The probability for producing a zip site is given in Fig. 4a as a function of the sample bias voltage V_s. At 300 K, the probability curve has a resonancelike shape with a maximum at $V_s = 4$ V. Quite surprisingly, when performing similar experiments at low temperature (30 K) the probability is always zero whatever V_s (the results in Fig. 4a are reported only for $V_s = 3$ and 6 V where most of the experiments were done). For comparison, we show in Fig. 4b the probability for extracting the hydrogen atom at both 300 and 30 K. Results at 300 K (previously discussed in Ref. [9]) and at 30 K are very similar, indicating that here the temperature has basically no effect on the extraction probability. This is in stark contrast with corresponding experiments on hydrogen adsorbed on Si(100) which showed strong temperature effects on the hydrogen desorption [16] and diffusion [17] efficiencies. When comparing the probability curves at 300 K in Figs. 4a and 4b, it seems that the zip site formation and the H atom extraction are competing processes, since the sharp decrease of the zip site formation probability for V_s higher than 4 V coincides with the strong increase of the H extraction probability. Furthermore, the zip site formation probability was found to be independent of the tunnel current and to increase as a function of V_s in the range 2–4 V. This suggests that, as for the H atom extraction process [11], the zip site formation process involves a direct resonant electronic process via the resonant attachment of tunnel electrons into the σ^*(Ge-H) antibonding orbital located about 4 eV above the Fermi level [11]. However, the ensuing atom dynamics must be very different in nature for the H atom extraction and for the zip site formation. The lack of any temperature effect on the H atom extraction probability indicates that the resonant electronic attachment into the σ^*(Ge-H) orbital is not affected by the temperature. We emphasize that this electronic channel (4 eV above the Fermi level) is well outside the bulk band gap. Therefore it does not require any

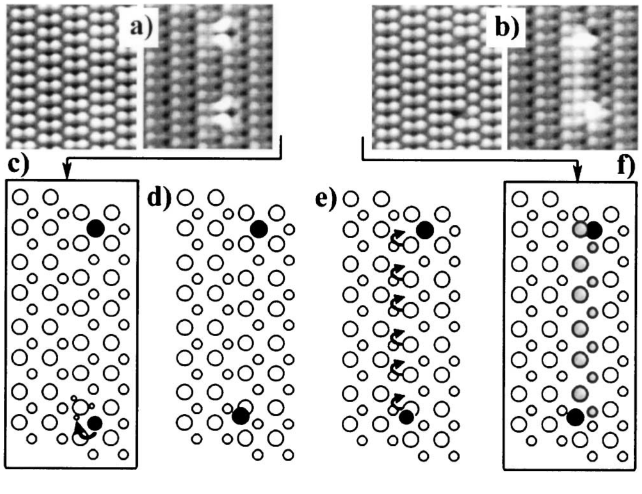

FIG. 3. STM manipulation of a hydrogen atom [lower hydrogen atom in (a)] showing the transformation of two square sites (a) into a zip site (b). Atomic diagrams of the corresponding mechanism are shown in (c)–(f). Atomic symbols are the same as in Fig. 1. From (c) to (d) the hydrogen atom is displaced by electronic excitation with the STM tip from a Ge rest-atom site to a backbond site of a neighbor Ge adatom. From (e) to (f) the row of Ge adatoms is displaced to produce the zip site in (f).

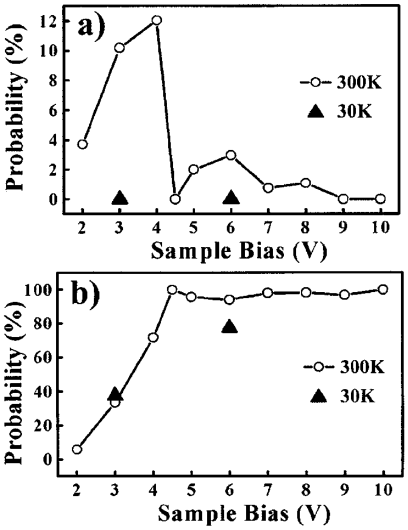

FIG. 4. Probabilities of manipulation of hydrogen atoms at 300 and 30 K: (a) probability of the zip site formation; (b) probability for hydrogen extraction.

thermal energy to be coupled to the bulk electronic states contrary to the electronic channels located inside the band gap (see previously). Furthermore, the H atom extraction must be a direct dynamical process without any coupling with the thermal bath of the surface.

The zip site formation is a much more complicated process since it involves both the resonant electronic attachment into the σ^*(Ge-H) orbital and a thermally activated process to explain its low temperature inhibition. This is schematically represented in Figs. 3c–3f. The process starts with two hydrogen atoms along the same rest-atom row (Fig. 3c). The resonant attachment of electrons into the σ^*(Ge-H) orbital induces a dynamic which can either break the Ge-H bond leading to H extraction or displace the H atom into a metastable site on the surface. As shown in Fig. 3d, this metastable site corresponds to an H atom inserted into the backbond of a neighboring Ge adatom. To reach the stable zip site represented in Fig. 3f, the whole row of six Ge adatoms needs to be pushed up into the intermediate T_4 sites (Fig. 3e). As in the case of spontaneous formation of the zip site by hydrogen adsorption (see below), the displacement of the adatom row in Fig. 3e is believed to be accessible only by thermal activation. It follows that the zip site formation using the STM tip involves both a temperature independent electronic process and a thermally activated one. This raises interesting questions as to why thermal activation is necessary. One could argue that the electronic process does not provide enough energy to overcome the energy barrier for producing the zip site. This is very unlikely since the electronic process inducing the Ge-H bond breaking is believed to have a much higher energy barrier than the zip formation. Furthermore, thermal activation can only provide an energy of the order of kT (25 meV at 300 K). It is more likely that the zip formation may correspond to regions of the potential energy surface of the whole system which cannot be reached by electronic excitation alone, for dynamical reasons rather than energetic ones. The zip formation involving the displacement (probably in a concerted manner) of many Ge atoms may require specific dynamic channels which can be opened only by thermal activation.

In conclusion, exploring the imaging, the spectroscopy, and the manipulation of hydrogen atoms on the Ge(111) surface with the STM at low temperature has yielded several important results. The tunnel electronic channels located inside the band gap are frozen at a low temperature giving rise to new topographic and spectroscopic features. Outside the bulk band gap, elastic electronic channels are believed to be unaffected by lowering the temperature. However, inelastic electronic channels such as the formation of zip sites can be frozen at low temperature even though they are well outside the bulk band gap. These results show that the substrate temperature is a powerful parameter to freeze specific electronic channels. They also demonstrate the existence of two kinds of thermally activated elastic and inelastic electronic channels. The freezing of atomic or molecular electronic channels having energies within the band gap is of special interest. Indeed the decoupling of these electronic channels from the surface or bulk conduction channels of the substrate opens up very interesting perspectives for atomic and molecular nanoelectronics. The evidence of STM manipulations involving the combination of both a temperature independent electronic process and a thermally activated one is also important for the future operation of molecular nanomachines. This type of STM manipulation should be especially relevant for manipulating complex systems having many degrees of freedom. In such cases, a purely electronic excitation is insufficient, and thermal activation is required to trigger the desired dynamic evolution of the system.

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