Anomalous Mobility of Strongly Bound Surface Species: Cl on GaAs(001)-$c(8 \times 2)$

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Although strongly bound chemisorbates at low coverage readily diffuse on metal surfaces at 300 K, they generally do not diffuse on semiconductor surfaces because of a large corrugation in the adsorbate-surface interaction potential. Chlorine chemisorbed on the Ga-rich GaAs(001)-$c(8 \times 2)$ surface has anomalously fast diffusion even though the chemisorption state is tightly bound and highly specific. Simple Hartree-Fock total energy calculations suggest that this diffusion of strongly bound adsorbates can occur at 300 K because there are multiple nearly degenerate adsorbate sites.

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Adsorbates on metal surfaces are generally bound by delocalized electronic effects, a reflection of the delocalized bonding of the bulk. The adsorption energy is not highly position dependent, leading to low diffusion barriers between nonspecific adsorption sites [e.g., face-centered-cubic and hexagonal-close-packed sites on (111) surfaces]. Facile diffusion at 300 K is common, and thermodynamics plays a large role in system evolution.

In contrast, nonmetallic chemisorbates are bound to semiconductor surfaces by localized and directional bonds [1]. The localized nature of the chemical bonds leads to higher diffusion barriers. Directional bonds lead to highly specific binding sites that are more widely separated. As a result, diffusion in these systems is far slower, with major consequences for the evolution of surface processes. Other than hydrogen (which can tunnel through activation barriers), no atomic nonmetallic chemisorbate on a semiconductor has been directly observed to diffuse spontaneously at room temperature.

There is indirect evidence that atomic chlorine may diffuse at 300 K on GaAs(110) [2]. However, no mechanism has been suggested for this case. In this Letter, we report for the first time the direct observation of room temperature diffusion of a heavy, nonmetallic, atomic adsorbate on a semiconductor surface. We find that this anomalously fast diffusion is due to the presence of nearly degenerate adsorption sites that facilitate atom hops.

Dry etching of GaAs(001) with chlorine is an important process for the semiconductor industry [3]. When molecular halogens interact with polar surfaces of GaAs, chemisorption is controlled by charge transfer between the substrate atoms. The dangling bonds of surface As atoms are filled with two electrons, while Ga dangling bonds are empty. When a diatomic halogen nears the surface, its highest occupied molecular orbital hybridizes with these dangling bonds. At an As atom, the extra electrons must occupy an antibonding orbital, so that the complex is repulsive. The result is a strong chemical selectivity for reaction with Ga [4]. In previous studies of halogen adsorption on the As-rich GaAs(001)-(2×4) [5] and the mixed GaAs(001)-(6×6) [6] reconstructions, initial adsorption was exclusively at second-layer Ga dangling bonds, resulting in gallium monohalide surface species. At higher coverages, the selectivity can be less strong [7].

Using scanning tunneling microscopy (STM) we have found that the low coverage adsorption site of Cl on the Ga-rich GaAs(001)-$c(8 \times 2)$ reconstruction is on the top-layer rows of Ga dimers, with no reaction at the As dangling bonds between the rows. Beyond this chemical selectivity, however, there are significant differences between adsorption on the $c(8 \times 2)$ surface and on other reconstructions of GaAs(001). The apparent adsorption site is not at a single Ga atom; the Cl atom diffuses between two neighboring Ga atoms so quickly that the STM cannot resolve the motion. Moreover, the Cl atoms diffuse relatively rapidly along the Ga rows, whereas there is no diffusion on other GaAs(001) surfaces. This is particularly surprising since the Ga-Cl bond is quite strong, which would normally correlate with a large energy barrier to diffusion. The diffusion takes place via long and short hops at alternating positions on the surface. The long hops occur more frequently than the short hops, facilitated by an intermediate secondary adsorption site with an energy only slightly higher than the primary site.

Epi-ready GaAs(001) wafers (n-type, Si doped at $\sim 2 \times 10^{18}/\text{cm}^3$, miscut $<1°$) were regrown *ex situ* with molecular beam epitaxy to a thickness of ~500 nm and capped with a protective layer of As. In our ultrahigh vacuum system (base pressure $<10^{-10}$ Torr) the As cap was desorbed by heating the sample to 450 °C for several hours. Residual contamination was removed by sputtering the 540 °C sample with 500 eV Ar^+ ions.

This preparation method results in a very well-ordered, $c(8 \times 2)$ reconstructed surface with ~1000 Å terraces, as shown in Fig. 1(a). Images in this Letter were obtained using a Park Scientific STM with a sample bias of −3.5 V and a tunneling current of 0.2 nA. With this bias, the electrons tunnel from filled surface states to the STM tip. Since As is more electronegative than Ga, As atoms appear more prominent than Ga atoms. Our images of the clean surface agree with the most commonly suggested surface structure [8], illustrated in Fig. 1(c), according to the interpretation

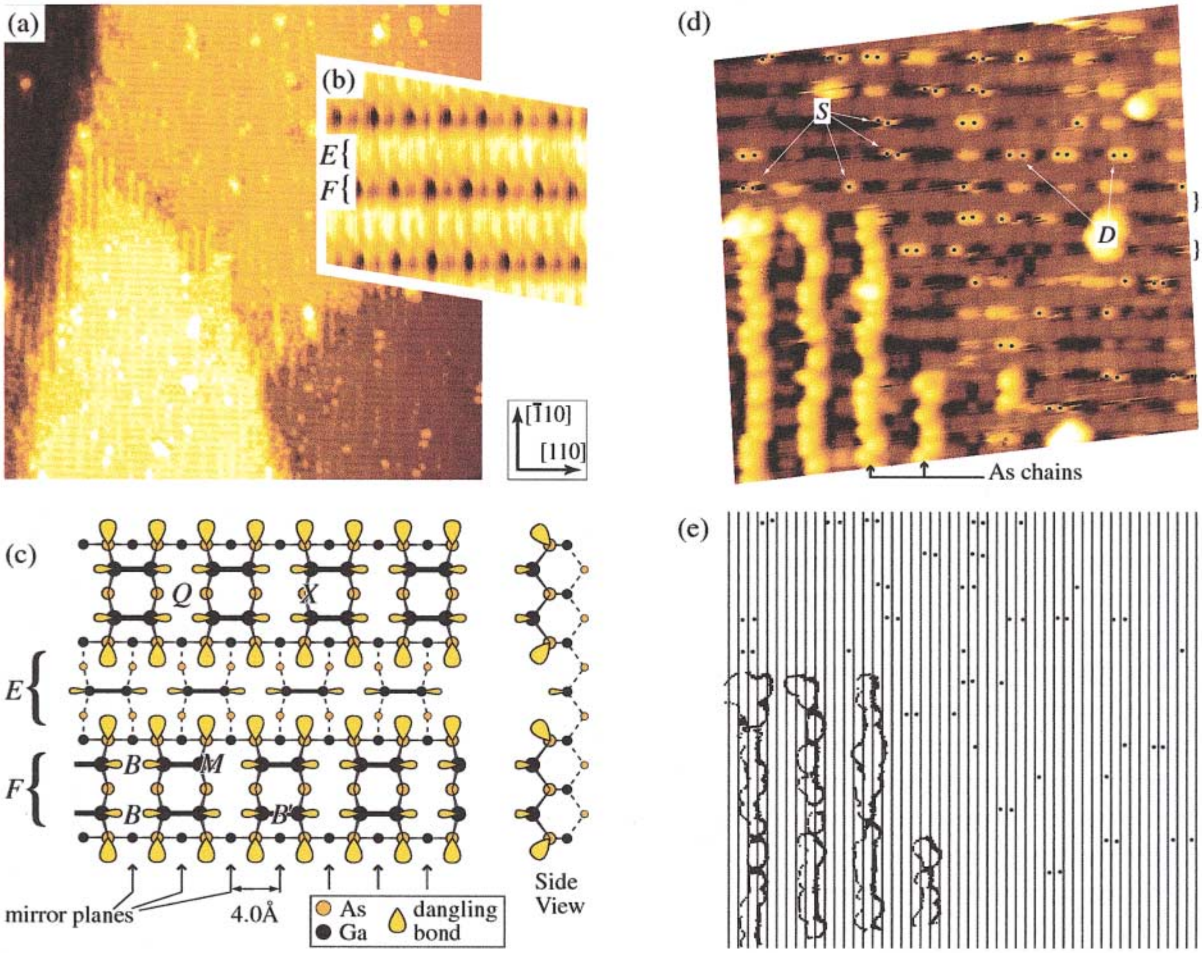

FIG. 1 (color). (a),(b) Filled state STM images of the clean Ga-rich GaAs(001)-$c(8 \times 2)$ surface, of size 1000×1100 Å^2 and 57×45 Å^2. (c) The structure model for this surface, including labels for sites associated with Cl adsorption. (d) A horizontally scanned filled-state STM image of Cl/GaAs(001)-$c(8 \times 2)$, size 200×210 Å^2. Cl positions are marked by black dots. In the lower left is an area with the 6×6 reconstruction. (e) A representation of image (d) showing Cl adsorbate positions and the (110) mirror planes of the $c(8 \times 2)$ surface as extrapolated from the 6×6 surface.

of Xue *et al.* [9]. The surface consists of rows of parallel pairs of Ga dimers separated by trenches with filled As dangling bonds. The bright rows (E) are the filled second-layer As atom dangling bonds. In Fig. 1(b) the dimerization of the first-layer Ga atoms can be clearly seen in the darker rows (F). Note that the clean surface is symmetric about (110) mirror planes occurring every 4.0 Å between the top-layer Ga atoms.

Figure 1(d) shows a surface three hours after dosing with 0.11 eV Cl_2 to a coverage of ~2.5% of a monolayer. New features appear in the dark rows of the $c(8 \times 2)$ surface; they are marked in the figure with small black dots. Their apparent height is 1.1 ± 0.15 Å. The majority are round features 6.5 Å in diameter, labeled S. Larger oblong features, labeled D, appear to be formed of two S features separated by 4.5 Å. Most of the S features have horizontal discontinuities, indicating adsorbate motion as discussed below, and hence are marked with two dots.

The Cl features are in the center of the dark dimer rows F, symmetrically placed along [$\bar{1}$10]. This would seem to indicate an adsorption site along the line between the Ga dimers, such as the sites labeled Q and X in Fig. 1(c). However, all these sites would require unusually high Cl atom coordination and/or very nontetrahedral bonding for the Ga atoms. Such sites could be reasonable if the adsorption interaction were strongly ionic. But even gallium chloride (Ga_2Cl_6) forms molecular crystals, in which Cl atoms make at most two bonds and Ga atoms retain tetrahedral bonding [10]. Therefore, these are unlikely to be the true adsorption sites.

Nearby, chemically more reasonable sites are the inter- and intradimer bridge sites B and B', and the monochloride dangling bond site M [see Fig. 1(c)]. Sites similar to these have been proposed in theoretical work [11]. Halogens adsorb on the GaAs(001)-(2×4) and -(6×6) reconstructions at M-like sites [5,6]. Each of these sites could be consistent with our observations in either of two ways. First, if two atoms were to adsorb at a neighboring pair of these sites, such as the pair of B sites indicated in Fig. 1(c), they could possibly appear as a single feature in STM images. However, the Cl-Ga bonds are quite polar, so that such a pair of adsorbates would experience a strong dipole-dipole repulsion. A second, much more likely possibility is that there is a low energy barrier between such a pair of sites. Then a single Cl atom could rapidly diffuse between them. If this diffusion were fast enough ($\gtrsim$1 kHz), then the adsorbate would appear to the STM to be smeared across the two sites.

The position of the Cl features along the F rows (along $[110]$) is more difficult to determine, since the high resolution exhibited by Fig. 1(b) was only rarely obtained. One method exploits the phase coexistence of the $c(8 \times 2)$ reconstruction with the 6×6, the structure of which is known [6]. The 6×6 features determine the bulk lattice position. Extrapolating from the bright As-dimer chains of the 6×6 [see Fig. 1(d)] gives the positions of the $c(8 \times 2)$ mirror planes to within ± 0.5 Å. Symmetry requirements are used to refine the mirror plane positions relative to the adsorbates. Figure 1(e) shows the result: the adsorption sites (for both S and D features) lie between the mirror planes of the clean surface. The B and B' sites lie on the mirror planes; thus the adsorption must occur at M sites. An S feature is formed by a single Cl atom rapidly hopping along $[\bar{1}10]$ between two M sites.

The Cl atoms also hop along [110], as indicated by the S feature discontinuities. If an adsorbate moves while the STM is imaging that region, an abrupt contrast change results in the image. In Fig. 1(d) all of the adsorbate hops are horizontal, parallel to the F rows and to the STM scanning direction. The S features mostly hop back and forth between just two sites. The length of these hops is 4.5 ± 0.3 Å. Shorter hops of 3.5 Å are occasionally seen, but only between places where the longer hops occur.

Rates of diffusion can be measured by counting discontinuities in images like Fig. 1(d). In fact, we can see that some hops occur while the STM tip is actually over the adsorbate: the adsorbate appears abnormally wide (or narrow) in that scan line, as the adsorbate moved with (or against) the scanning direction. Analysis finds that the adsorbates make long hops at an average rate of 1.4 Hz while the STM tip is over them, and a rate of 0.45 Hz during other times. Short hops occur an order of magnitude less frequently.

Even if all the mobility were induced by the STM, it would still indicate a low barrier to diffusion, relative to the many other systems that are stable under STM imaging. However, there is additional evidence that the Cl adsorbates undergo thermally induced diffusion. At somewhat higher coverages the Cl atoms cluster into short chains along the $[110]$ direction [12]. At a coverage double that in Fig. 1(d), the density of these clusters has been observed to be the same as the adatom density in Fig. 1(d). This can be consistent only with the chemisorbed Cl atoms diffusing from their original adsorption sites to find other adsorbates.

Note that the details of the adsorbate mobility confirm that M is the correct adsorption site. The 4.5 ± 0.3 Å site separation is significantly larger than the surface lattice constant of 4.0 Å. This cannot be consistent with B-type sites. Also, the different hop rates indicate two inequivalent energy barriers, while the adsorbates have the same apparent height at either end of a hop. This agrees well with M adsorption sites at either end of the Ga dimers, separated by hops over and between Ga dimers.

Although mobility at 300 K has been observed on the GaAs(110) surface [2], the large degree of mobility on GaAs(001) is unexpected. Even the prevalence of long hops over short hops defies usual trends in diffusion. The measured bond strength in ClGa diatomic molecules, 5.0 eV, is quite large (compare to 2.2 eV for AsGa and 3.4 eV for Si_2) [13]. For covalently bonded substrates, this is usually correlated with a high adsorption energy, and in turn with a high diffusion barrier. If we assume an Arrhenius expression for the hop rate, $\nu = \nu_0 \exp(-E_b/kT)$, with an attempt frequency of $\nu_0 = 10^{12}$ Hz, then the observed rates correspond to energy barriers of only roughly $E_b \approx 0.7$ eV.

In order to obtain insight into the mechanisms behind the observed behavior, *ab initio* calculations were performed to determine the preferred geometry for small clusters simulating the GaAs(001)-$c(8 \times 2)$ surface. The cluster energy was minimized under the effective core potential scheme of the Hartree-Fock approximation, using the GAUSSIAN 94 [14] computer program with its built-in LanL2MB basis sets [15]. No higher-order corrections (such as Møller-Plesset perturbation) were used. The basic cluster, $Ga_{20}As_{20}H_{32}$, simulates two parallel Ga dimers of the $c(8 \times 2)$ surface, and includes atoms from eight atomic layers. Hydrogen atoms terminate bonds that would connect to the bulk crystal. Note that the calculated energies depended somewhat on cluster size; optimizations for larger clusters were not practical. The results reported here are nonetheless indicative of the system's behavior.

For a single Cl atom there are two, nearly degenerate adsorption sites. The dangling bond M site [Fig. 2(a)] has an adsorption energy of 2.42 eV. Inserting the Cl atom into the Ga dimer forms a bridge bond with an angle of 130° [Fig. 2(b)]. This corresponds to the B' site in Fig. 1(c), and has an adsorption energy of 2.50 eV. Mulliken population analysis indicates that in both cases there is a charge of $Q = -0.5e$ on the Cl atom, and a charge of $+0.32e$ on the nearest Ga atoms relative to their charge of $q = +0.14e$ in the unchlorinated cluster.

The principal deficiency of this size cluster is that on a real surface, an M site Cl would be further stabilized by electrostatic attraction to the nearby positively charged Ga dimers. This stabilization would be of magnitude $\Delta E = kQq/r = -0.25$ eV, where k is Coulomb's constant, $r = 3.97$ Å is the distance from the M-site Cl to the nearest Ga not represented in the cluster, and charges Q and q and

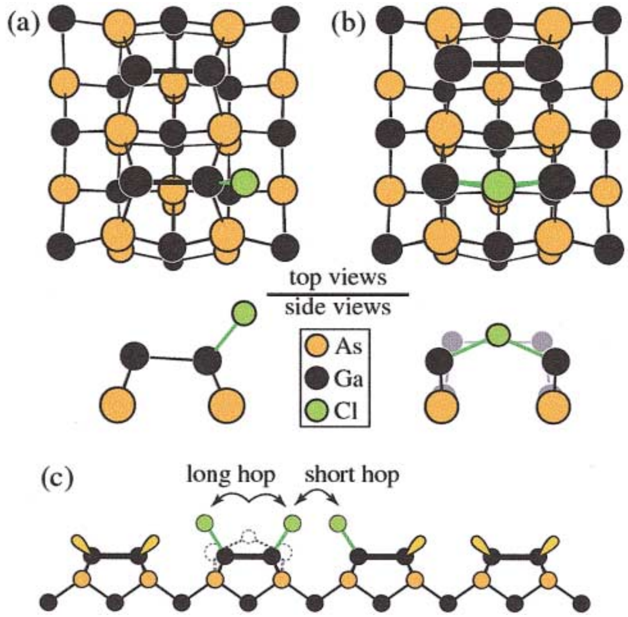

FIG. 2 (color). (a),(b) Optimized geometries of $Ga_{20}As_{20}Cl$ clusters modeling Cl on GaAs(001)-$c(8 \times 2)$. Top-layer Ga atoms and their neighbors are shown in side view (from $[1\bar{1}0]$). Terminating H atoms are not shown. (a) A Cl atom at a dangling bond site. (b) A Cl atom inserted into a Ga dimer to form a bridge bond. (c) A schematic side view of a row of Ga dimers, showing how the intermediate B' bridge site facilitates long hops between M adsorption sites. A short hop is also shown.

the atom positions are obtained from the calculated cluster. Thus theory gives the M site as the true adsorption site, in agreement with experiment.

The most important result is the observation that the M and B' sites are nearly degenerate in energy. This suggests that the B' sites enable the anomalously fast long hops by providing a pathway between M sites at either end of a Ga dimer, allowing frequent long hops as shown in Fig. 2(c). We speculate that short hops may be similarly facilitated by B-like bonding [see Fig. 1(c)]. Of course, the diffusion rate is ultimately determined by the energy barriers between sites. Further optimizations of constrained geometries indicate that the M-to-B' pathway barrier is as low as 0.12 eV for this cluster. While the true barrier is unlikely to be this low, this verifies the feasibility of this mechanism for anomalous diffusion.

We also note that when a second Cl atom is added to the cluster, the only stable configuration has the Cl atoms at dangling-bond M sites on opposite corners of the cluster. This confirms that, due to dipole-dipole repulsion, Cl atoms will not group together closely.

Despite the initial appearance of STM images of Cl adsorbed on the GaAs(001)-$c(8 \times 2)$ reconstructed surface, the Cl atoms are bound as monochlorides at Ga atom dangling bond sites, just as on other GaAs(001) reconstructions. The crucial difference for this surface is the high degree of adsorbate mobility. Because of very rapid diffusion between neighboring sites across the Ga rows, the Cl atoms appear to be centered on those rows. Diffusion along the Ga rows allows for long range mobility of the adsorbates. This diffusion can occur for this tightly bound species because of another, nearly degenerate adsorption site. While we would expect a high energy barrier along the path between the primary adsorption sites, this second favorable configuration lowers the energy along that path and enables the diffusion.

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