Electronic effects induced by single hydrogen atoms on the Ge(001) surface

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The properties of an isolated dangling bond formed by the chemisorption of a single hydrogen atom on a dimer of the Ge(001) surface are investigated by first-principles density functional theory (DFT) calculations, and scanning tunneling microscopy (STM) measurements. Two stable atomic configurations of the Ge–Ge–H hemihydride with respect to the neighboring bare Ge–Ge dimers are predicted by DFT. For both configurations, the unpaired electron of the H/Ge(001) system is found to be delocalized over the surface, rendering the isolated dangling bond of the hemihydride unoccupied. However, local surface charge accumulation, such as may occur during STM imaging, leads to the localization of two electrons onto the hemihydride dangling bond. The calculated surface densities of states for one of the charged Ge–Ge–H hemihydride configurations are found to be in good agreement with atomic-resolution STM measurements on *n*-type Ge(001). Comparison with a Si–Si–H hemihydride of the Si(001) surface shows similarities in structural properties, but substantial differences in electronic properties. © 2008 American Institute of Physics.

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I. INTRODUCTION

Broken (dangling) bonds play an important role in determining the physical and chemical properties of semiconductor surfaces. In particular, semiconductor surfaces minimize their energy by adjusting the positions of their atoms (i.e., undergo reconstruction) to reduce the number of these surface dangling bonds. The dangling bonds that remain after surface reconstruction determine both the chemical reactivity and the electronic properties of the surface. The adsorption of adatoms at the chemically active dangling bond sites is a common way to tailor the properties of semiconductor surfaces for specific applications.¹

Si(001) and Ge(001) are commonly regarded as twinlike semiconductor surfaces. The reconstruction of both of these surfaces is characterized by the formation of buckled dimers within an extended $c(4 \times 2)$ periodicity. The electronic structures of both surfaces are also believed to be very similar.^{2–5} However, there are some intrinsic features of these two surfaces that sometimes result in them exhibiting quite different physical and chemical behavior.⁶ At room temperature, for example, H₂O adsorbs dissociatively on Si(001), while the sticking probability for H₂O on Ge(001) is low.⁷

A prototypical example of chemisorption on a semiconductor surface is its reaction with atomic hydrogen. This reaction is of fundamental importance in understanding the chemistry of these surfaces. Moreover, many reactions at semiconductor surfaces proceed via the cleavage of a single hydrogen atom from a molecule and the subsequent bonding of that H atom to the surface [e.g., H₂O, PH₃, and NH₃ on Si(001) (Refs. 8–10)]. Thus, the adsorption of single H at-

oms, and the effect this has on the electronic properties of the surrounding surface, has broad implications for adsorption to semiconductor surfaces.

In this paper we focus on the properties of an isolated Ge dimer dangling bond formed by the chemisorption of a single hydrogen atom on one of the Ge dimer atoms of an otherwise clean Ge(001) surface. The adsorption of a single H atom breaks the weak π bond of the Ge–Ge dimer and forms a Ge–Ge–H hemihydride. This results in the creation of an unsaturated, isolated dangling bond on the unterminated Ge atom of the Ge–Ge–H hemihydride.

Based on *ab initio* density functional theory (DFT) calculations, we demonstrate that the bare Ge–Ge dimers that are adjacent to a Ge–Ge–H hemihydride have a pronounced effect on both the geometric and electronic structure of the hemihydride. We find that there are two possible structures for an isolated hemihydride on Ge(001). Moreover, the unpaired electron is delocalized on the surface for both of these configurations, rendering the Ge dangling bond of the hemihydride unoccupied.

Calculations of semiconductor surfaces are typically performed assuming intrinsic substrates. However, scanning tunneling microscopy (STM) experiments require conducting surfaces and are therefore of doped substrates. In addition, some local charge accumulation can be expected at the surface under the STM tip due to an electrostatic shifting of the surface bands with respect to the Fermi level (band bending).¹¹ Thus, a more realistic simulation of the experimental conditions can be achieved by increasing the charge contained in the computed unit cell. Our simulations of the surface charge accumulation on the Ge(001) surface yield two additional important findings: (i) the accumulated charge

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FIG. 1. (a) The electronic structure of the clean Ge(001) $c(4 \times 2)$ surface calculated using a (4×4) surface unit cell with six layers in the vicinity of the Fermi level E_F (indicated by the dashed horizontal line). The occupied (π) and unoccupied (π^*) bands of electronic surface states are indicated by the double-headed vertical arrows. (b) Schematic of the irreducible symmetry element of the (4×4) surface Brillouin zone.

is found to spontaneously localise on the hemihydride unsaturated dangling bond for both Ge–Ge–H configurations, and (ii) the hemihydride unsaturated dangling bond can only be doubly occupied or empty. Both of these results are different from those found for the H/Si(001) system where only one of the Si–Si–H hemihydride configurations has the ability to localise the accumulated charge, and the isolated dangling bond of the Si–Si–H can be occupied by zero, one, or two electrons.¹² These results are important as they evidence a clear difference in the electronic properties of the dangling bonds of the topologically similar Si(001) and Ge(001) surfaces.

II. METHODOLOGY

The geometry optimization and electronic structure calculations reported in this study have been carried out using the DFT pseudopotential, plane-wave method incorporated in the VASP computer code.^{13,14} The calculations have been performed using Vanderbilt ultrasoft pseudopotentials,¹⁵ and allowing the up and down spins to be distinct (fully spin polarized calculations). The generalized gradient approximation (GGA) with the parametrization of Perdew–Wang (PW91) has been used for electronic exchange and correlation.¹⁶ The calculations were carried out using a (4×4) surface unit cell, slabs containing either four or six Ge layers, a vacuum region of 11 Å, and a terminating hydrogen layer. This terminating layer was kept fixed, as well as at least one of the immediately adjacent Ge layers. The bulk lattice constant was determined to be 5.77 Å, which is 2% larger than the experimental value of 5.66 Å. The total energy calculations were performed using the calculated bulk lattice constant and four $\mathbf{k}$ points in the irreducible symmetry element of the surface Brillouin zone (SBZ). Tests have been carried out to determine that our choice of parameters, such as the number of $\mathbf{k}$ points, yields reliable results. The electronic band structures have been determined by calculating the eigenenergies at 30 $\mathbf{k}$ points along the Γ -J-K-J'- Γ -K symmetry directions of the (4×4) SBZ (see Fig. 1(b)).

In order to identify the nature of the surface states, three-dimensional (3D) charge/probability density distributions for all of the theoretically predicted surface states have been calculated. A state was considered to be a surface state if virtually all of its charge was contained within the top few surface layers, whereas bulk states have most of their charge confined to deeper layers. The lateral (x - y) distribution of the

electrons has been determined from integrated local density of states (ILDOS) plots. Within the Tersoff–Hamann approximation,¹⁷ these ILDOS plots can be compared directly with the experimental filled/empty state STM images. While one would not expect these ILDOS plots to yield an exact representation of the experimental STM images, they should reproduce all of the important qualitative features. In an effort to reproduce the effects of substrate doping and STM-induced surface charge accumulation due to band bending, we have performed calculations where the total charge contained in the cell was artificially increased. In these calculations, the additional charge was compensated by a uniform background to ensure electrical neutrality within each periodic unit cell.

Experiments were performed using a commercial STM (Omicron Vacuumphysik GmbH) inside an ultrahigh vacuum (UHV) chamber with base pressure $< 5 \times 10^{-11}$ mbar. Germanium wafers (n type) were cleaved and mounted in UHV sample holders. Care was taken to avoid sample contamination by using only ceramic tweezers and sample holders constructed from tantalum, molybdenum and alumina. Samples were degassed at 600 °C overnight, and subsequently prepared by repeated cycles of Ar⁺ sputtering at 1.8 keV and direct current heating. Hydrogen dosing was performed by admitting 99.999% pure molecular H₂ gas to the UHV chamber via a capillary housing a hot tungsten filament. The sample was positioned ~ 50 mm from the hydrogen cracker filament and dosing was performed with the sample at room temperature.

III. RESULTS

A. Ge(001) clean surface

The clean Ge(001) surface was studied for a (4×4) surface unit cell using two surface periodicities, $p(2 \times 2)$ and $c(4 \times 2)$. These two surface configurations were found to have the same dimer bond lengths (2.59 Å) and buckling angles (19.6°). The buckling angle of 19.6° is in good agreement with the theoretical value of 19.0° determined by Yoshimoto *et al.*,¹⁸ and the x-ray diffraction results of $17^\circ \pm 4^\circ$ (Ref. 19) and $19^\circ \pm 1.0^\circ$.²⁰ The predicted dimer bond length of 2.59 Å is 6% larger than the experimentally determined bulk interatomic distance of 2.45 Å.²⁰ The experimental data indicates that the Ge dimer bond length is about 4% longer than the bulk interatomic distance.²⁰ This is consistent with our calculated dimer bond length given that

we have determined the bulk lattice constant to be 2% larger than the experimental value. The energy difference between the $p(2 \times 2)$ and $c(4 \times 2)$ configurations was determined to be quite small (6 meV), with the $c(4 \times 2)$ reconstruction being lower in energy, in accord with other calculations.¹⁸ As a result, the $c(4 \times 2)$ reconstruction was adopted for all of our hemihydride calculations.

Figure 1(a) shows the surface electronic bandstructure for the clean Ge(001) $c(4 \times 2)$ surface calculated for the (4×4) unit cell with six layers. The system is observed to be semiconducting in agreement with recent scanning tunneling spectroscopy (STS) data.⁴ The calculated energy gap at the Γ point of 0.11 eV, however, is somewhat smaller than the experimentally measured surface band gap of 0.3–0.4 eV,^{21,22} due to the well-known deficiency of the DFT method.

The occupied dangling bond states of the up-buckled Ge dimer atoms constitute the narrow π band [see the double-headed arrow lying below the Fermi level E_F in Fig. 1(a)]. This band is located ~ 0.4 eV below E_F and is energetically resonant with the bulk states, in agreement with the measured data. The unoccupied dangling bond surface states for Ge(001) have probability densities that are localized primarily on the down-buckled Ge atoms of the Ge–Ge dimers. These states form three subbands which collectively make up the π^* band [indicated by the double-headed arrow lying above E_F in Fig. 1(a)]. This band is predicted to have a width of 0.9 eV, in good agreement with previous calculations.² The lowest energy subband within the π^* band consists of two states that are dispersive along J - K and J' - Γ (delocalized along the dimer rows) and fairly flat along Γ - J and K - J' (localized in the direction perpendicular to the dimer rows). The next (higher energy) two-state subband is less dispersive, and is located ~ 0.7 eV above the lowest energy subband at the Γ point. The highest energy subband occurs in the upper part of the π^* band and consists of four fairly dispersionless states formed predominantly from the down-Ge atom dangling bond orbitals of every second dimer. The surface states within these two higher energy subbands are in resonance with the bulk states at the bottom of the conduction band. It is some of the unoccupied surface states within the π^* band that are most affected by the creation of the Ge–Ge–H hemihydride.

B. Ge–Ge–H hemihydride on Ge(001)

1. Atomic configurations

The adsorption of a single hydrogen atom on the Ge(001) surface transforms one of the Ge–Ge dimers into a Ge–Ge–H hemihydride leaving one isolated dangling bond on the surface (Fig. 4 N_e schematic). Our total energy DFT calculations show that there are two stable configurations for an isolated Ge–Ge–H hemihydride on Ge(001). These two structures have different buckling configurations of the neighboring Ge–Ge dimers as shown in Fig. 2. In the parallel configuration (HH1), the buckling angles of the adjacent Ge–Ge dimers have the same sign as the buckling angle of the hemihydride [shown in schematics of Figs. 2(c) and 2(d)]. In the antiparallel configuration (HH2), the buckling

angle of the hemihydride has the opposite sign to its two neighboring Ge–Ge dimers in the same dimer row [see schematics in Figs. 2(e) and 2(f)]. The energy difference between these two configurations is determined to be 0.15 eV for a (4×4) surface unit cell, with the antiparallel HH2 geometry being the lower in energy.

For HH1 and HH2 configurations, the buckling angle of the Ge–Ge(H) dimer is slightly different (5.8° and 8.6° , respectively) and significantly less than the buckling angles of the neighboring Ge–Ge dimers ($\sim 20^\circ$). In both cases, the nonhydrogenated Ge atom is the down atom. The bond length of the Ge–Ge(H) dimer of 2.56 Å for HH1 is marginally longer than the corresponding bond length of 2.53 Å for the HH2 configuration. The buckling angles and dimer bond lengths of the neighboring Ge–Ge dimers are very similar for the two geometries and quite close to the values that we calculated for Ge–Ge dimers on the clean Ge(001) $c(4 \times 2)$ surface ($\sim 19.60^\circ$ and 2.59 Å). A value of 1.57 Å was obtained for the Ge–H bond length for both HH1 and HH2 hemihydride configurations.

Both the HH1 and HH2 hemihydride configurations have a single unpaired electron which is shared with the surface atoms. Roling *et al.*² predicted that the unsaturated dangling bond of the hemihydride is half occupied by the unpaired electron and the Ge–Ge–H hemihydride becomes symmetric. The above results show, however, that for an isolated H on Ge(001), the chemisorbed Ge dimer remains buckled, independently of the adopted reconstruction of the neighboring dimers. We will show that this is due to the fact that for both HH1 and HH2, the unpaired electron is delocalized over the surface leaving the unsaturated hemihydride dangling bond empty. We will also show that the different topologies of the adjacent dimers for the HH1 and HH2 configurations result in different delocalizations of the unpaired electron on the surface.

2. Electronic structures

The surface electronic band structures near E_F for the HH1 and HH2 configurations are shown in Fig. 2. Each band is doubly degenerate as the energy of the corresponding majority and minority spin states are the same for these two systems. The energies of the filled Ge–H bonding and empty Ge–H antibonding orbitals are predicted to lie more than 2.0 eV from the Fermi level, and are not shown. Both the HH1 and HH2 configurations exhibit a surface electronic structure in the vicinity of E_F [Figs. 2(a) and 2(b)] that is similar to that of the clean Ge(001) surface shown in Fig. 1(a). However, the energy redistribution due to the chemisorption of the hydrogen atom (and therefore the addition of an electron) results in a relative shift in the Fermi level, which now crosses the lowest energy states within the π^* band. In other words, the H atom increases the number of electrons by one, resulting in an unoccupied band from the clean surface becoming partially occupied. The electronic structure of the HH1 configuration [Fig. 2(a)] also differs from that of both the clean surface and HH2 in that the flat, unoccupied state denoted by open circles lies much closer to

FIG. 2. The surface electronic structure of the (a) HH1 and (b) HH2 Ge-Ge-H configurations calculated using a (4×4) surface unit cell with six Ge layers in the vicinity of the Fermi level E_F (indicated by the dashed horizontal line). The occupied (π) and unoccupied (π^*) bands of electronic surface states are indicated by the double-headed vertical arrows. The stars, empty circles, and filled squares indicate the surface states intrinsic to the Ge(001) substrate that are significantly affected by the chemisorption of a H atom onto one of the Ge-Ge dimers. [(c)–(f)] ILDOS plots for the HH1 and HH2 Ge-Ge-H configurations for the integration range of -0.15 eV [(c) and (e)] and -1.0 eV [(d) and (f)] for the isosurface value $2.0 \times 10^{-4} \text{ e } \text{\AA}^{-3}$. To the right of the ILDOS plots are schematics of the HH1 [(c) and (d)] and HH2 [(e) and (f)] Ge-Ge-H hemihydride configurations. The large shaded circles indicate a Ge up atom and the small shaded circles denote the Ge down atoms. The hydrogen atom of the Ge-Ge-H hemihydride is represented by the small filled circle.

the Fermi level and the higher energy sub-band denoted by stars is more dispersive [compare Fig. 2(a) with Figs. 1(a) and 2(b)].

The spatial distributions of the surface electronic charge for both configurations are illustrated in the integrated local density of states (ILDOS) plots shown in Figs. 2(c)–2(f). These plots show the combined spatial distributions of all the occupied surface energy bands within the adopted ranges of integration. The contrast in the plots is such that the bright regions represent areas of high charge density. Figures 2(c) and 2(e) correspond to integrating from 0.15 eV below the Fermi energy to the Fermi energy. Hence, these two ILDOS plots [Figs. 2(c) and 2(e)] only include contributions from the band that crosses the Fermi energy [filled squares in Figs. 2(a) and 2(b)]. As a result, they show the spatial distribution of the unpaired electron that is generated by the addition of the H atom. For the HH2 configuration [Fig. 2(e)], the unpaired electron is strongly localized in the direction perpendicular to the dimer rows but is delocalized along the dimer row containing the hemihydride. This is evidenced by the observation that the charge is spread along the entire dimer row that contains the hemihydride. The situation for the HH1 configuration [Fig. 2(c)] is similar in that the electron is

again delocalized in the direction parallel to the dimer rows. However, in this case, the electron is found on the dimer row adjacent to that containing the hemihydride.

The ILDOS plots for integrating from 1.0 eV below the Fermi level [Figs. 2(d) and 2(f)] show that the only really bright features are those associated with the doubly occupied dangling bonds of the up-buckled atoms of the bare Ge-Ge dimers. The unsaturated hemihydride Ge atom, by contrast, appears dark. This demonstrates that the unpaired electron is not present in the dangling bond orbital at this site and is delocalized over the surface for both the HH1 and HH2 configurations.

C. The effect of surface charge accumulation

1. Atomic configurations

As stated previously, to produce a more realistic simulation of the Ge(001) surface as it is imaged in STM experiments, we have performed calculations of the surface with increasing charge. In particular, we have carried out geometry optimization calculations for both the HH1 and HH2 configurations in a (4×4) surface unit cell containing one and two additional electrons. We denote these systems as

TABLE I. Hemihydride buckling angles (in degrees) and bond lengths (in angstroms, given in brackets) calculated for the HH1 and HH2 configurations with zero, one and two additional electrons in the (4×4) surface unit cell. A negative buckling angle indicates that the H-bonded Ge atom has become the down atom.

	N_e	N_e+1	N_e+2
HH1	5.8 (2.56)	-10.1(2.63)	-10.4(2.64)
HH2	8.6 (2.53)	7.4(2.52)	-7.9(2.61)

(N_e+1) and (N_e+2) , where N_e is the number of electrons in the neutral cell. The calculated buckling angles and bond length values of the progressively charged HH1 and HH2 surface reconstructions following ionic relaxation are presented in Table I.

We see that the addition of one electron (N_e+1) is sufficient to reverse the buckling of the Ge–Ge(H) dimer in the HH1 configuration, and increase its bond length. However, no further significant structural changes occur with the addition of a second electron (N_e+2). By contrast, the HH2 configuration is seen to remain essentially unaffected by the addition of one electron (N_e+1), but the addition of a second electron (N_e+2) results in a reversal in the buckling and a substantial increase in its bond length. As changes in the buckling angles and bond lengths of dimers indicate changes in the population of their empty dangling bond orbitals, we can conclude that the addition of electrons leads to charge localization for both the HH1 and HH2 configurations. As a result, the buckled parallel HH1 structure is transformed into the buckled antiparallel structure (with the addition of one electron), while the antiparallel HH2 configuration is transformed into the parallel configuration (with the addition of two electrons). These abrupt transitions suggest that the dangling bond of the Ge–Ge–H hemihydride is never singly occupied, but rather accepts electrons only in pairs. This behavior is distinctly different to that of the Si–Si–H hemihydride which, as we have previously shown,¹² can become singly occupied.

Accurate energies for the charged HH1 and HH2 configurations cannot be obtained from VASP, since a reliable theoretical method for determining the energetics of charged semiconductor:adsorbate systems has not yet been developed. However, intuitively one would expect the antiparallel buckling configuration to minimize the surface strain and be lower in energy. Calculations confirmed this for the neutral (uncharged system), showing that the antiparallel configuration, HH2, was lower in energy. Similarly, for the charged systems, one might expect the lower energy state to have an antiparallel configuration. As discussed above, these include the HH2 (N_e+1) system, as well as the HH1 (N_e+1) and (N_e+2) systems for which the buckling of the hemihydride reverses its orientation from that of the original parallel configuration.

2. Electronic structure

The localization of electron pairs on the hemihydride dangling bonds of Ge(001) is clearly seen in the calculated band structures for the (N_e+1) and (N_e+2) HH1 and HH2

configurations shown in Fig. 3. For the HH1 configuration in the (N_e+1) case, the flat unoccupied surface state indicated by the empty circles in Fig. 2(a) has shifted downwards so that it now occurs below E_F as indicated by the filled circles in Fig. 3(a). As a result, two electrons—the unpaired electron and the additional electron—now occupy the hemihydride Ge atom dangling bond orbital. It is this electronic effect that causes the buckling of the hemihydride to reverse its orientation (see Table I) and the system to become semiconducting. With the addition of the second electron, the HH1 system becomes metallic with the extra electron occupying the dispersive low-energy π^* state crossing the Fermi level [filled squares in Fig. 3(c)]. This additional electron is thus delocalized over the surface. As delocalized electrons do not change the structure of a covalent system, the geometry of the HH1 configuration for (N_e+2) is essentially the same as for the (N_e+1) case.

The electronic structures for the charged HH2 configurations are also shown in Fig. 3. In the (N_e+1) case, the system remains metallic as both lower energy surface states within the π^* band now cross E_F [see the filled squares in Fig. 3(b)], and the dangling bond on the Ge–Ge–H hemihydride remains unoccupied. Both the unpaired electron and the added charge are delocalized over the whole surface and the geometry remains essentially unchanged (see Table I). With the addition of the second electron (N_e+2), the unoccupied level associated with the hemihydride dangling bond [open circles in Fig. 3(b)] shifts downward in energy with respect to the π^* band and becomes doubly occupied [indicated by the filled circles in Fig. 3(d)]. It is this electronic effect that causes the buckling of the HH2 hemihydride to reverse (see Table I). One surface state [indicated by the filled squares in Fig. 3(d)] still crosses the Fermi level ensuring that this HH2 configuration remains metallic.

The localization of electron pairs for the HH1 and HH2 configurations is also clearly seen in the series of ILDOS plots shown in Fig. 4. With the addition of two electrons to the dangling bond, the hemihydride unsaturated Ge atom site in both the HH1 and HH2 structures is seen to suddenly brighten from a dark feature (left panels in Fig. 4) to a bright feature comparable in brightness to the doubly occupied Ge dangling bonds of the Ge–Ge dimers (right panels in Fig. 4). For the HH1 configuration, this abrupt transition occurs in going from the (N_e) to the (N_e+1) system, while for HH2 it corresponds to moving from (N_e+1) to (N_e+2).

The above results present compelling evidence that the unsaturated Ge atom of a Ge–Ge–H hemihydride is never singly occupied but rather acts as an attractive center for trapping an electron pair.

D. Comparison to experimental STM images

To determine which of the theoretically predicted hemihydride structures are experimentally observed, we have performed a series of atomic-resolution STM measurements of Ge–Ge–H hemihydrides on the Ge(001) surface. Figure 5 shows a series of filled-state STM images of a single hemihydride on a highly doped *n*-type Ge(001) surface, acquired at different tunneling bias voltages. The $c(4 \times 2)$ static dimer

FIG. 3. Surface electronic bandstructures calculated using a (4×4) surface unit cell with six Ge layers for the [(a) and (b)] (N_e+1) and [(c) and (d)] (N_e+2) charged HH1 and HH2 configurations in the vicinity of E_F (indicated by the dashed line). The hemihydride Ge atom dangling bond states are indicated by the filled and open circles, and the stars. The filled squares denote the surface states partially occupied by the delocalized, unpaired electron. Below the band structures are shown the schematics of the Ge–Ge–H hemihydride. The filled circles represent the electrons of the dangling bond.

buckling of the Ge(001) surface can be observed in each image. Two domains are present with an antiphase boundary separating them as indicated by the arrow. The hemihydride is located in the center of each image. This hemihydride is representative of all hemihydrides observed on the surface in filled-state images, and has been selected because it is well separated from other hemihydrides and intrinsic surface defects. The appearance of the hemihydride is observed to be essentially the same for each sample bias voltage shown in Fig. 5 (–1, –0.6, –0.2, and –0.1 V). Figure 5 shows that the hemihydride feature consists of a bright protrusion located asymmetrically about the dimer row. Inspection of the static buckling along the row containing the hemihydride reveals that the two dimers immediately adjacent to the hemihydride are buckled upwards on the opposite side to the bright protrusion of the hemihydride reflecting an anti-parallel configuration.

The observation that the hemihydride is not imaged as a depression at any bias magnitude rules out both ground-state (N_e) configurations. This is because the hemihydride is expected to be dark for (N_e) for both HH1 and HH2 [see Figs.

2(d) and 2(f)]. A similar argument applies to the (N_e+1) HH2 configuration (see Fig. 4). The doubly charged HH2 (N_e+2) configuration can also be ruled out since the ILDOS plot in Fig. 4 indicates that in this configuration the two neighboring Ge–Ge dimers are buckled upwards on the same side of the dimer row as the hemihydride protrusion. By contrast, both the (N_e+1) and (N_e+2) HH1 configurations produce ILDOS plots in agreement with the experimental STM images. Moreover, as discussed earlier, the buckling of their dimers corresponds to an antiparallel configuration, consistent with our intuition regarding the lowest energy states. We thus conclude that it is the charged version of the HH1 configuration (i.e., HH1 with two electrons localized on the dangling bond) that is observed in our atomic-resolution STM experiments on *n*-type Ge(001). The observation that the hemihydride does not become uncharged even at very low bias values suggests that the occupation of the dangling bond is predominantly due to substrate doping, rather than band bending.

We observe that the Ge–Ge–H hemihydride in the ex-

FIG. 4. ILDOS plots for the HH1 configuration (top row) and HH2 configuration (bottom row) for an integration range of -1.0 eV. The left panels are for the neutral (N_e) systems, the middle panels for one extra electron (N_e+1), and the right panels for the (N_e+2) systems. The isosurface value is $2.0 \times 10^{-4} \text{ e } \text{\AA}^{-3}$.

perimental images appears to be much brighter relative to the up-buckled atoms of the clean Ge–Ge dimers, than what is reproduced in the simulated images [compare, for example, Fig. 5(a) with the (N_e+1) or (N_e+2) HH1 simulated images in Fig. 4]. This is most likely due to the neglect of any energy-dependent tunneling effects in the Tersoff–Hamann approximation. The charging of the hemihydride occurs via occupation of the dangling bond states close to E_F . These states have a smaller barrier through which to tunnel than states deeper in the valence band, and hence would be enhanced by the inclusion of such effects. The features reproduced in the ILDOS plots are relatively insensitive to both the isosurface value and the range of integration (once greater than ~ 0.15 eV), and hence varying these parameters does not produce any significant quantitative changes in the simulated images.

E. Comparison with the H/Si(001) system

In previous work¹² we have shown that the chemisorption of H on Si(001) leads to two Si–Si–H hemihydride structures, similar to those determined in this paper for the

H/Ge(001) system. The buckling angle for the Si–Si–H hemihydride was calculated to be 8.0° for HH1 and 9.6° for HH2. These values are consistent with the corresponding Ge values of 5.8° and 8.6° , respectively. As for Ge, the bond length of the Si–Si(H) dimer was slightly longer for HH1 (2.41 Å) than for HH2 (2.39 Å). For both surfaces, and both configurations, the unpaired electron is found to be delocalized on the surface leading to a metallic state for the system, and some buckling of the Ge–Ge–H and Si–Si–H hemihydrides. The resulting filled-state ILDOS plots show the hemihydride to be dark. Surface charge accumulation, however, causes localization on the hemihydride dangling bond and a significant increase in the brightness of the hemihydride. For the H/Ge(001) system, this transition is abrupt with two electrons now occupying the dangling bond of the nonhydrogenated Ge atom of the Ge–Ge–H hemihydride. For the H/Si(001) system, on the other hand, this brightening is more gradual with the hemihydride dangling bond being progressively populated with first one, and then two electrons.¹²

Differences between the H/Si(001) and H/Ge(001) systems have also been evidenced by the STM images. Our STM measurements have established that the filled-state STM images of a Si–Si–H hemihydride on an *n*-type substrate change from a dark dip-buckled feature to a bright protrusion with increasing bias voltage. A Ge–Ge–H hemihydride on an *n*-type substrate, on the other hand, has been found to image in filled-state as a bright protrusion at any bias voltage. For both systems, it has been found that only the HH1 configuration is consistent with the filled-state images.

It is well known that dangling bonds play a dominant role in determining the behavior and chemical reactivity of semiconductor surfaces. The differences in the behavior of isolated dangling bonds on Si(001) and Ge(001) discussed above could thus explain some of the well-known differences in the properties of these two surfaces.

IV. SUMMARY

In this paper we have studied the nature of isolated, unsaturated dangling bonds that result from the chemisorption of single hydrogen atoms on the dimerised Ge(001) surface. We have shown that there are two different atomic configurations for a Ge–Ge–H hemihydride—buckled either parallel or antiparallel to the neighboring Ge–Ge dimers. We have also shown that the unpaired electron of the H/Ge(001) system is expected to be delocalized over the surface on intrinsic Ge(001) in the absence of effects such as surface charge accumulation due to band bending. The spatial distribution of the delocalized surface charge has been found to depend on the buckling of the surrounding bare Ge–Ge dimers with

FIG. 5. (Color online) Filled-state STM images of a single Ge–Ge–H hemihydride on the Ge(001) surface at sample biases of (a) -1 V, (b) -0.6 V, (c) -0.2 V, and (d) -0.1 V. All images were acquired at ~ 0.8 nA tunneling current and are $\sim 4.5 \times 5 \text{ nm}^2$. The hemihydride is in the center of each image. The arrows indicate the position of an antiphase boundary that separates domains of $c(4 \times 2)$ periodicity.

respect to the hemihydride. In addition, we have established that electrons can be localized on the Ge–Ge–H hemihydride dangling bond by increasing the background electric charge, as occurs with substrate doping and/or band bending. However, the electrons can only occupy this dangling bond in pairs. This is in contrast to the H/Si(001) system where the hemihydride dangling bond can be half occupied. Finally, the Ge–Ge–H hemihydride is a prototype system for the whole family of atomic/molecular adsorbates on Ge(001) which give rise to isolated dangling bonds. We would therefore expect the results presented in this paper to be relevant to many other Ge(001):adsorbate systems.

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