Electronic Properties of (2×1) and $c(4 \times 2)$ Domains on Ge(001) Studied by Scanning Tunneling Spectroscopy

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The surface electronic structure of Ge(001) was studied by scanning tunneling spectroscopy. The measured surface densities of states unequivocally reveal the presence of a metallic state on the (2×1) domains, which is absent on the $c(4 \times 2)$ domains. This metallic state, so far observed only in integral measurements, is attributed to the flip-flopping dimers that constitute the (2×1) domains. Our data also reveal a set of previously unresolved surface states, in perfect agreement with published theoretical predictions.

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The electronic structure of semiconductor surfaces has been the subject of numerous studies. Among all, Si(001) is the most intensively studied surface along with Ge(001). In particular, the latter attracted quite substantial attention after the observation of a metalsemiconductor transition on the surface as a function of temperature [1,2]. The metallic properties of the Ge(001) have been pursued further in other studies, using angle resolved photoemission (PES) and inverse photoemission studies [3,4], besides a dc field effect study [5].

Despite many experimental and a few theoretical studies on the metallicity of a Ge(001) surface, there is still no consensus about the metallic density of states [1,2,4,6-9]. In their initiating work, Kevan and Stoffel [1] suggested that this metallicity may be due to the (2×1) domains. In these domains, the dimers are flip-flopping above a critical temperature and passing through a symmetric state during their switching between two buckled states [10,11]. Showing that the state does not exist at low temperatures-when all the dimers are frozen in a buckled state-Kevan and Stoffel [1] have associated this metallic state to symmetric dimers. Nevertheless, they could not exclude the possibility that this state may be due to defects. Later on, Kipp et al. [4] suggested that this state is due to the band formed by partially occupied dangling bonds (π) of the dimers forming the well ordered (2×1) domains.

Following the PES experiments of Kevan and Stoffel [1], Kubby *et al.* [7] carried out scanning tunneling spectroscopy (STS) measurements on a Ge(001) surface. However, by its nature, the metallic state of Ge(001) lies near the Fermi level (E_F). It is well known that maintaining a stable tunneling at a gap bias falling into the band gap of semiconductors is difficult, if not impossible. This in-turn makes it difficult to obtain reasonably noise-free *I-V* measurements at energies corresponding to a band-gap region of the particular semiconductor. Since E_F corresponds to V = 0 gap voltage, the energy resolution of reported STS measurements could not provide the

information about the existence of a metallic state at E_F . Consequently, the surface electronic structure of Ge(001) was not resolved in STS experiments in the band gap of Ge(001) [7]. Moreover, the *ab initio* studies for calculating the surface local density of states (LDOS) of Ge(001) at the Γ point [6] do not seem to comply with the STS measurements for almost all surface related states [8]. Apparently, the studies focusing on both the electronic structure of the Ge(001) surface in general and the studies about the metallicity of the Ge(001) surface, in particular, are short of a common agreement.

After detailed STM measurements on extremely clean Ge(001) surfaces it has been observed that Ge(001) exhibited a striped $(2 \times 1)/c(4 \times 2)$ domain pattern at room temperature [12-14]. The development of this ordered pattern lies in the strain relaxation of the dimerized surface [11,12]. This property of the Ge(001) surface gave us the opportunity to study the electronic structure of both (2×1) and $c(4 \times 2)$ domains simultaneously using room temperature STS. In this Letter, we report the spatially resolved electronic structure of the Ge(001)surface obtained by room temperature scanning tunneling spectroscopy experiments. We present the best resolved STS data reported so far, demonstrating that the metallic state is undoubtedly due to symmetricappearing, flip-flopping, dimers of (2×1) domains. Moreover, we present previously not observed peaks, and discuss these spectra in view of existing theoretical predictions.

We have performed our experiments in a UHV system with a base pressure $\leq 5 \times 10^{-11}$ mbar. Our main analysis technique was a room temperature OMICRON STM-1, with SCALA electronics. The Ge(001) samples were cut from a nominally flat, 3 in. by 0.5 mm, single side polished, almost intrinsic (25 Ω cm), *n*-type wafers and were mounted on clean Mo holders. After cleaning the samples by 800 eV Ar⁺ ion sputtering and direct current annealing cycles, we obtained sharp 2 × 1 reflection high-energy electron diffraction patterns and STM revealed clean surfaces (for further details of our setup and sample preparation see [15]).

Tunneling spectroscopy is performed simultaneously with topography measurement at every point of the surface that is imaged by STM. Typically, the sample bias is set to -1.8 V, and tunneling current to 0.45 nA for the feedback loop. The *I-V* curves are taken in -1.7 to 1.7 V range with steps of 40 mV. Each spectroscopy point is averaged over 640 μ s and the delay between two points is 200 μ s. Every data file contains 2500 *I-V* curves taken at each of the 2500 points of the surface region, along with the topographic image of the region (with 1 Å steps).

In Fig. 1(a), the surface region, on which the STS data have been taken at every point in a 50 Å \times 50 Å matrix, is shown. Figure 1(b) shows the atomistic model of the (2×1) and $c(4 \times 2)$ domains. The *I-V* curves, taken at every pixel in each rectangle drawn on the image, are averaged separately. Figure 2(a) shows the numerically determined differential conductivity (dI/dV) of the $(2 \times$ 1) and $c(4 \times 2)$ domains. From these curves, the band gap of the Ge(001) surface at the Γ point is measured in the range of $0.72(\pm 0.05)$ eV to $0.9(\pm 0.05)$ eV, the latter being mainly on $c(4 \times 2)$ domains. Figure 2(b) is a zoom-in view into the near E_F region of the dI/dVcurves. To the left of E_F there is a peak in the differential conductivity data taken over the (2×1) domain, where dimers appear symmetric. However, the same peak is missing in the data of the $c(4 \times 2)$ domain, where the dimers are asymmetrically pinned in the buckled state.

Although the differential conductivity curves are quite useful for the determination of the band gap of semiconductors, they give only an overall idea about the surface LDOS at the Γ point. Nevertheless, one can numerically calculate the LDOS, through the normalization process of (dI/dV)/(I/V) (i.e., $d\ln I/d\ln V$) [7,16]. Figure 3 shows the LDOS curves calculated this way. The



FIG. 1. (a) STM image of a 50 Å \times 50 Å region of the Ge(001) surface. At every pixel (1 Å apart) an *I-V* curve is taken. Patches of (2 \times 1) and $c(4 \times 2)$ domains are visible. The rectangles mark the data regions for averaging (see text). (b) A model of Ge(001) with (2 \times 1) and $c(4 \times 2)$ domains. Atoms in the (2 \times 1) domain are drawn equally sized. In the $c(4 \times 2)$ domain, buckling is represented by one big and one small appearing atom for each dimer (see also Fig. 4).

differences between the LDOS of the (2×1) and the LDOS of the $c(4 \times 2)$ domains are quite evident.

Before starting to discuss the peaks observed in Fig. 3, we make an overview of the surface states that would be expected due to the dimer formation and the buckling registry on the Ge(001) surface. Figure 4 represents a buckled-dimer profile. Each atom of the dimer has a free dangling bond. In this case the dimer is buckled so it has an upward buckled bond $(D_{\rm up})$ due to which the $D_{\rm up}$ surface band forms. The dangling bond of the downward buckled atom is named as $D_{\rm down}$ and forms the $D_{\rm down}$ surface band. Also the dimer bond (σ) forms two bands, D_i (σ -bonding band) and D_i^* (σ^* -antibonding band). Because of the lower energy, the $D_{\rm up}$ bond is relatively more populated than the $D_{\rm down}$ bond [11].

Several peaks are identified for each domain, in Fig. 3. First of all, the LDOS curve of the (2×1) domain clearly has a metallic state crossing the E_F (V = 0), where $c(4 \times 2)$ does not show a similar state. From left to right, the first peak at -1 eV occurs in both the (2×1) and the $c(4 \times 2)$ domains. Both domains show a filled state at the same energy. Again, both domains occupy a



FIG. 2. (a) The differential conductivities calculated using the *I-V* curves measured over the (2×1) and $c(4 \times 2)$ domains, and averaged over every pixel within the rectangles shown in Fig. 1(a). (b) Zoom-in view near the E_F .



FIG. 3. LDOS of (2×1) and $c(4 \times 2)$ domains calculated through the normalization process of [(dI/dV)/(I/V)].

state around -0.8 eV. Moreover, the $c(4 \times 2)$ domain seems to have another state closer to E_F , around -0.5 eV. Again, both domains occupy a state at ~ 0.5 eV, and another state at $\sim +0.8$ eV. Finally, only in $c(4 \times 2)$ domains, there seems to be a state around 0.6 eV, which is missing in (2×1) domains.

The LDOS curves show that four of the states are common to both of the domains. While the $c(4 \times 2)$ domains seem to possess two additional states, the (2×1) domains have one extra state. First, the state at -1 eV is well resolved in both domains, but the state around -0.8 eV is clearer on the $c(4 \times 2)$. In case of the pinned-buckled dimers of the $c(4 \times 2)$ domain, the D_{up} bonds are relatively more populated with respect to the D_{down} bonds. In the case of the symmetric-appearing dimers in the (2×1) domains, the D_{down} and D_{up} bonds are almost equally populated—in a time averaged manner-due to the high frequency of the flip-flopping of the dimers between two buckled states [10,17]. Consequently, a band that would form due to D_{up} bonds can be expected to appear sharper in $c(4 \times 2)$ domains, while the same band in (2×1) would look more smeared or attached to a nearby, high-intensity, state as a shoulder. But a state that would either be originating from the bulk or be due to the dimer bond (for instance, the σ bond) would have similar sharpness in both domains. The -1 eV state is equally sharp in both domains but the 0.8 eV state is sharper in the $c(4 \times 2)$ domain. In line with the data and the arguments



FIG. 4. The buckled-dimer model.

above, we can attribute the state at -1 eV to the σ band and the state showing up at -0.8 eV to the D_{up} band [18].

Continuing to look at the common states in the (2×1) and the $c(4 \times 2)$ domains, we encounter the states at 0.5 and 0.8 eV. The sharpness of these states in both domains are similar, but the additional state showing up in the $c(4 \times 2)$ domain around 0.6 eV causes the two states of the $c(4 \times 2)$ domain to blur. Nevertheless, the state at 0.8 eV keeps its sharpness in both domains the same. Following the argument we made for -1 eV state, we can assign this peak to the dimer bond. Since it resides in the empty states, it should be due to the dimer bond antibonding band. Moreover, looking at the peak positions and their existence in both domains, we may assign the state at 0.8 eV to the σ^* band and the state at 0.5 eV to the D_{down} band.

Following the discussion over the common states, we also address the domain specific states. First, the broadening of the -1 eV peak in the $c(4 \times 2)$ domain is due to both the D_{up} state at -0.8 eV and an extra peak closer to E_F at around -0.5 eV. Such a broadening is predicted by the calculations [6], in which all the dimers are considered to be in the $b(2 \times 1)$ state; like in the pinned-buckled dimers of the $c(4 \times 2)$ domains. However, a specific state around -0.5 eV is not predicted, probably because the $c(4 \times 2)$ higher order reconstruction is not incorporated in the calculations, which in itself gives rise to higher order resonances. So, this additional state at -0.5 eV occurring only in the $c(4 \times 2)$ domains is linked to the higher order reconstruction on the Ge(001) surface due to the buckling registry, for the moment.

The metallic state, crossing the E_F only in the symmetric-appearing (2×1) domains, may have two origins. First, it is well established that the (2×1) domains are composed of nonfrozen/flip-flopping dimers [10,11,17]. Theoretically, the dimers are shown to be frozen as buckled due to an energy gain [19,20]. The lack of the geometrically symmetric state of dimers in the $c(4 \times 2)$ domains and, at the same time, the observation of the metallic peak only within the (2×1) domains suggest that the observed metallic state can be attributed to a band formed by the symmetric state of the dimers. The other explanation can be the continuous charge transfer between the dangling π bonds during the flip-flop motion, generating a free-electron-like effect, which may appear as a metallic state. We note that this metallic state cannot be due to the D_{up} state as reported before by Kipp et al. [4], because it does not appear in the spectra of the $c(4 \times 2)$ domains, which should have a more intense $D_{\rm up}$ character. Nevertheless, the other state at around -0.5 eV on $c(4 \times 2)$ domains can be associated with the D_{up} band. This may sound like a contradiction with the final sentences of the previous paragraph, but the following argumentation offers a way out of this contradiction: The D_{up} bonds in the $c(4 \times 2)$ domains are always more filled than the $D_{\rm up}$ bonds in (2×1) domains, over a time average. This, in turn, may generate an additional surface state due to the differences in the local charge densities on the surface. For instance, a state may form as a result of more than half filled π bonds. Because of the flip-flopping of the dimers in the (2×1) domains, more than half filled bonds are existent only in absolutely pinned $c(4 \times 2)$ domains. So, the state at -0.5 eV can also be related to more than half filled $D_{\rm up}$ bonds. In line with these arguments, the additional state between σ^* and $D_{\rm down}$ states in $c(4 \times 2)$ domains is probably also due to the higher order reconstruction, or because of the $D_{\rm up}$ bonds.

Using the results at hand and looking at the literature, some solutions to several problems are suggested besides the definite assignment of the metallic state crossing the Fermi level to (2×1) domains. First, Kubby *et al.* [7] measured the spectra in a broader energy range. They assigned the -1 eV peak to the σ band as we do, but the states closer to E_F could not be resolved, because of the unavailability of the data in the -0.8 to 0.8 eV range. Second, the metallic peak measured by Kipp et al. [4] around 30 meV cannot be attributed to the D_{up} band. Our data show that the intense metallic state is originating from the (2×1) domains, but does not originate from the $c(4 \times 2)$ domains, which should have a stronger D_{up} state due to the pinned formation of the dimers. Finally, our observations agree very nicely with the *ab initio* calculations of Pollmann et al. [6]. This agreement is better than expected (and mentioned, in view of previous measurements). The D_{down} state is closer to the Fermi level, as well as the σ^* state, and they are not far apart from each other. Also the broadening of the -1 eV state in the $c(4 \times$ 2) domains is apparent in our data in accordance with the theoretical predictions, in which the dimers are considered in pinned-buckled state. One final but important point before summarizing has to be touched upon. The state at -1 eV exists in all the experiments under all conditions, almost independent of the experimental parameters. This indicates that, at this energy, not only a surface related state but also a bulk derived, more intense state exists. This is also in line with the calculations [6].

In summary, spatially resolved tunneling spectroscopy data collected on the Ge(001) surface provides an unprecedented and detailed insight on the electronic properties of the (2×1) and the $c(4 \times 2)$ domains (especially on their differences). It is possible to identify the spatial location from where the previously reported metallic state originates [1]. The (2×1) domains are shown to host this state, while the $c(4 \times 2)$ domains do not. This indicates that the metallic state is either due to the symmetric orientation of the dimer bond or due to the charge transfer between the two dangling bonds of the dimer during the flip-flop motion of the dimer. Moreover, the spectra presented here agree in detail with the theoretical LDOS calculations of the Ge(001) surface at the Γ point of the Brillouin zone.

Our results, while shedding new light onto several decade long problems, can also be generalized to similar semiconductor surfaces like GaAs(001) and Si(001), in order to resolve the local differences on the surface electronic structure at the dimer level. Moreover, the electronic structure data we present here would be relevant for Si/Ge superlattice growth studies for obtaining local chemical information at the dimer level.

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