

Bias voltage dependent shift of the atomic-scale structure of the Ge(111)-(2×1) reconstructed surface measured by low temperature scanning tunneling microscopy

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We present the results of our low temperature scanning tunneling microscopy (STM) investigations of the clean Ge(111) surface. We observe bias dependent shifts of the atomic-scale structure caused by the (2 × 1) reconstruction of the Ge(111) surface. A detailed comparison of experimental data with theoretical predictions based on the π -bonded chain model allows us to conclude that inelastic tip-sample interaction plays a significant role in STM imaging of the Ge(111)-(2 × 1) reconstructed surface.

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1. Introduction. It is generally accepted that the cleaved Ge(111) surface can be described in terms of a π -bonded chain model with buckling [1]. Localization of filled/empty surface states on up/down atoms is an intrinsic feature of this model. This implies that, when the tunneling bias voltage is changed from the filled to the empty states range, a shift of dimer rows should occur in the $[2\bar{1}\bar{1}]$ direction in the scanning tunneling microscopy (STM) images. When the buckling becomes sufficiently pronounced and surface states become completely confined around up/down atoms, this shift can be estimated to be around 1 Å [2]. An experimental value of 0.78 Å has been inferred from STM topographical images for the (2 × 1) reconstructed Ge(111) surface at low temperature [3], consistent with the theoretical prediction. On the other hand, one expects a close similarity in the behavior of the surface atomic structures for the Ge(111)-(2 × 1) surface and for the Si(111)-(2 × 1) surface, since the size of the surface unit cells is comparable. It should be possible to use experimental data for the Si(111)-(2 × 1) surface as a reference for measurements on the Ge(111)-(2 × 1) surface. Analysis of the experimental data for the Si(111)-(2 × 1) surface in Ref. [4], see Figs. 5–7, reveals a shift between filled and empty states STM images of the dimer rows in the $[2\bar{1}\bar{1}]$ direction that is as big as 2.5 Å. The shift changes smoothly when varying the bias voltage. However, this shift was observed in images of the local density of states, not in STM topographical images. Experimentally, the con-

trast of STM topographical images can be different from the contrast of STM tunneling current images [5]. Experimental results are also available for the bias dependent shift of individual dimers inside π -bonded chains, i.e. in the $[01\bar{1}]$ direction, for the Si(111)-(2 × 1) surface [6–8]. In this case the phase shift between periodically filled and empty states STM images is equal to π , i.e. maxima in the filled states image are located at positions corresponding to minima in the empty states image.

2. Experiment. The main goal of our STM experiments is to determine in detail the dependence on the applied bias voltage of the surface atomic structure in both relevant directions ($[2\bar{1}\bar{1}]$ and $[01\bar{1}]$) of the (2 × 1) reconstruction.

The investigated samples were cut from a heavily doped (resistivity 1 m Ω · cm) Ge single crystal with n-type bulk conductivity. The doping element is phosphorus, which is a shallow impurity with an ionization energy of 13 meV, and the doping concentration is about $8 \cdot 10^{18}$ cm⁻³. The samples are 1.5 × 1.5 × 3 mm³ slabs with the long axis aligned along the $[111]$ direction. The samples are cleaved *in situ* after cooling the low temperature STM system down to liquid helium temperature. The details of the cleaving procedure and experimental STM setup are described elsewhere [9, 10]. The tunneling bias voltage is applied to the sample, while the STM tip is virtually grounded. According to our experience, the best results can be achieved with PtIr tips cut *ex situ*. Below we present only the STM results that are reliable, i.e. independent of the tip that is used, and reproducible. The thermal and mechanical drifts during

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our measurements are negligible due to good heat exchange between the STM head and the helium bath of the cryostat (Oxford Instruments).

Typical low temperature STM images of the Ge(111)-(2 × 1) surface prepared by *in situ* sample cleavage at liquid helium temperature are presented in Fig.1 for opposite polarities of sample bias voltage.

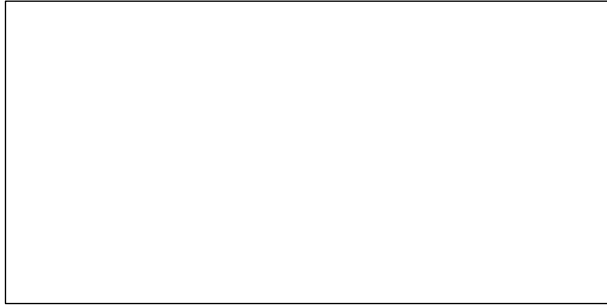


Fig.1. STM images of the Ge(111)-(2×1) reconstructed surface at opposite sample bias voltage. The tunneling current is fixed at 20 pA. The STM image size is $21 \times 21 \text{ nm}^2$. Typical areas used for surface profile averaging are indicated by the black rectangles. Boundaries between surface areas with slightly different atomic arrangement are clearly visible. Movement of a domain boundary, which occurred in between collecting the two STM images, is indicated by the arrows

The images clearly reveal an ordered chain-like surface structure, which in case of the Ge(111) surface is attributed to a (2 × 1) reconstruction with π -bonded chains [11]. Boundaries are present between surface domains with slightly different arrangement of the chains, and the atomic scale structure can be clearly resolved. Domain boundaries are running only in three directions (determined by the threefold symmetry of the surface) relative to the chain-like structure. We also observe changes of the domain boundaries from one scan to another (see Fig.1). As explained in more detail below, we assume that this “movement” can be accounted for in terms of tip-induced (i.e. scanning-induced) excitation of vibrational modes.

It is important to note that in the presence of any type of surface reconstruction the uppermost atoms of the reconstructed surface are behaving differently when compared to all other atoms. The uppermost atoms become more or less separated from the other atoms. Consequently, the standard theory of tunneling often fails to correctly describe processes where tunneling occurs through these uppermost atoms [10]. For the Ge(111)-(2 × 1) reconstruction, the empty surface states band π_{CB}^* almost completely covers the bulk band gap region in the electronic density of states (see Fig.1 in Ref. [10]).

Due to the strong band bending, the surface states band becomes separated from the bulk states by a wide gap. The surface states are localized on *up* and *down* dimer atoms of the Ge(111)-(2 × 1) surface. Consequently, the electronic states corresponding to the uppermost atoms of the reconstructed surface can be easily influenced by the STM tip during the STM measurements. One should therefore be extremely careful when interpreting the STM data.

The procedure we use to determine the bias voltage dependent shifts in the surface structure is quite different for the two relevant directions of the (2 × 1) reconstructed surface: Along the π -bonded chains in the $[01\bar{1}]$ direction, and perpendicular to the chains in the $[2\bar{1}\bar{1}]$ direction. In any case, we first always look for relatively large defect free surface areas in order to be able to perform reliable spatial averaging. This is illustrated in Fig.1, where typical areas of the surface, which we used for surface profile averaging, are indicated by rectangles.

The determination of the shift in the $[2\bar{1}\bar{1}]$ direction is straightforward, because the contrast of STM topographical images is high between different π -bonded chains of the (2 × 1) reconstruction. The STM images only require moderate low-pass filtering in order to clearly distinguish the structure perpendicular to π -bonded chains, while smearing the structure along π -bonded chains.

More difficulties are experienced with the determination of the shift in the $[01\bar{1}]$ direction. The contrast of non-processed STM images for individual dimers along π -bonded chains is not sufficient to allow an accurate determination of the shift within a wide tunneling bias voltage range. Therefore, we have to apply Fourier filtering in order to emphasize the atomic scale structure of the STM image along the $[01\bar{1}]$ direction. The algorithm consists of the following steps: (i) Direct Fourier transformation, (ii) selecting and emphasizing the peaks corresponding to the image structure in the $[01\bar{1}]$ direction, (iii) inverse Fourier transformation and (iv) spatial averaging. Great care has been taken to avoid any artefact that may be induced by the filtering procedure. On the other hand, the periodic atomic structures serve as a very precise intrinsic reference for determining the relative shifts in the images.

3. Discussion. The results of our analysis of the surface profiles along the chains as well as in the transverse direction are presented in Fig.2. Panels (a) and (c) illustrate the shift of the π -bonded chains in the $[2\bar{1}\bar{1}]$ direction when changing the applied tunneling bias voltage. In order to construct panel (a) small stripes have been cut out of the STM topographical images and then glued together. These stripes are taken at an identi-

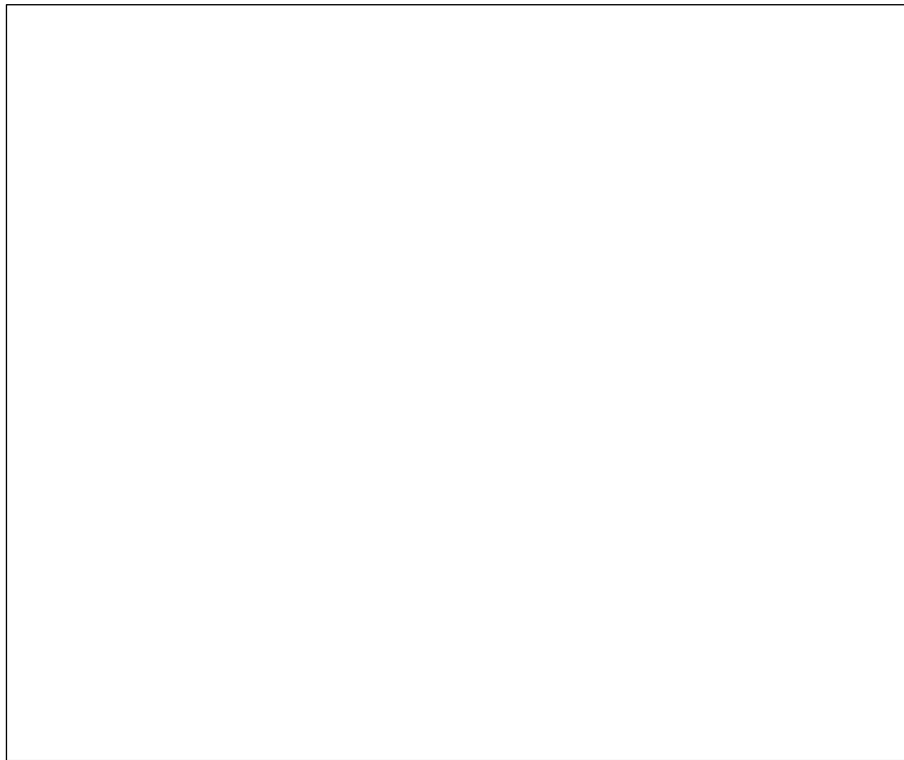


Fig.2. Quantitative information that can be inferred from the STM data for bias dependent shifts of the surface atomic structure. (a), (c): Shift of the π -bonded chains in the $[2\bar{1}\bar{1}]$ direction. (b), (d): Shift of dimers along π -bonded chains, i.e. in the $[0\bar{1}\bar{1}]$ direction. (e): Dependence of the relative shift in the $[2\bar{1}\bar{1}]$ direction (dotted line) and in the $[0\bar{1}\bar{1}]$ (solid line) direction as a function of the applied tunneling bias voltage. The expected position of the surface and bulk energy bands is also shown. In (a) and (c) stripe-like images are collected that have been cut at the same position from different STM images. In (b) and (d) cross-sections of the STM images at the same position are presented. The sequence of bias voltages used for the STM image acquisition are (in V): 2, 1.5, 1.0, 0.7, 0.5, 0.3, -0.3 , -0.5 , -0.7 , -1.0 , -1.5 . The stripe-like images that are displayed in (a) and (c) as well as the cross-sections displayed in (b) and (d) are ordered from top to bottom according to this sequence. The tunneling current is always stabilized at 20 pA

cal position on the STM images acquired at different values of the bias voltage. Panel (c) combines different cross-sections, which are vertically offset for clarity. The cross-sections are also taken at identical positions on the STM images acquired at different values of the bias voltage.

STM images were acquired at the following values of the tunneling bias voltage values: 2, 1.5, 1.0, 0.7, 0.5, 0.3, -0.3 , -0.5 , -0.7 , -1.0 , -1.5 V. The images and cross-sections in panels (a) and (c) of Fig.2 are ordered from top to bottom according to this sequence of bias voltages, i.e. the upper stripe in panel (a) has been cut out of the STM image obtained at 2 V, while the lower stripe has been cut out of the STM image obtained at -1.5 V. Panels (b) and (d) are constructed in the same way as panels (a) and (c), respectively, but the panels (b) and (d) illustrate the bias voltage dependent shift of the dimers along π -bonded chains, i.e. in the $[0\bar{1}\bar{1}]$ direction.

Panel (e) in Fig.2 shows two graphs that summarize the bias voltage dependent shifts discussed above. The dotted line corresponds to the shift of π -bonded chains in the $[2\bar{1}\bar{1}]$ direction, while the solid line corresponds to the shift of dimers along π -bonded chains, i.e. in the $[0\bar{1}\bar{1}]$ direction. The two graphs have been obtained by averaging the shifts inferred from different surface areas, which are sufficiently large to ensure a small error (corresponding error bars are also shown in Fig.2e). The surface band structure (corresponding to the π -bonded chains) as well as the bulk band structure are schematically given next to the two graphs, clarifying the relative position of the experimental data points with respect to the electronic band structure.

Based on the results shown in Fig.2, we arrive at the following conclusions. When varying the bias voltage in the range of empty surface states between +2 V to +0.7 V, the relative shift in the $[2\bar{1}\bar{1}]$ direction is zero within the accuracy of our STM imaging. When the bias

voltage reaches the bulk band gap between +0.7 V and +0.3 V, the shift switches to a value that does not vary considerably and remains close to the mean value of the shift in the $[2\bar{1}\bar{1}]$ direction for bias voltages below +0.3 V (about 1.9 Å, see Fig.2e). Our results therefore indicate that all changes of the relative shift perpendicular to the π -bonded rows occur in the bias voltage range where the surface states are the only states available for tunneling.

Here, we propose to link the rather high value of the relative shift of the surface atomic structure in the $[2\bar{1}\bar{1}]$ direction to inelastic interaction between the tip probe and the sample. The observed behavior of the relative shift of the π -bonded chains can be explained in terms of tunneling current induced excitation of the vibrational modes (optical phonons) of the individual dimers in the π -bonded chains that occurs right below the STM tip. As shown in Ref. [12], the maximum value of the phonon filling number at the typical phonon frequency ω_0 can be estimated as

$$N_{\omega_0 \max} \sim \gamma_L \gamma_R / g^2 \gg 1,$$

where γ_L , γ_R are the tunneling rates governing the transfer of electrons to the leads of the tunneling junction, and g is electron-phonon coupling constant.

The mean square displacement of individual dimer atoms can then be expressed as

$$\langle Q^2 \rangle \sim \frac{\hbar}{M\omega_0} N_{\omega_0 \max},$$

where M is the atom mass. Consequently,

$$\sqrt{\langle Q^2 \rangle} \sim \mu a \sqrt{N_{\omega_0 \max}},$$

where $\mu \sim (m/M)^{1/4}$, m is the electron mass and a is the inter-atomic distance.

The maximum phonon filling numbers can reach values $N_{\omega_0 \max} \sim 30-40$ [12] without destruction of the surface atomic structure, in contrast to the case of individual molecules on a surface. An individual molecule can easily dissociate or leave the surface (be desorbed) at such high local heating of the phonon subsystem. The chain-like rows are apparently more strongly coupled to the bulk than an individual molecule. Therefore, $\sqrt{\langle Q^2 \rangle}$ can become of the order of the inter-atomic distance a . The experimentally observed value of the shift of the π -bonded chains in the $[2\bar{1}\bar{1}]$ direction, which is about 1.9 Å instead of the theoretically predicted shift around 1 Å [2], can be explained in terms of an additional displacement of the dimer atoms from their zero bias equilibrium position because of the excitation of vibrational modes by the flow of the tunneling current. It is important to note that we are referring here to the *measured* values of the shift, i.e. values that can be inferred from the STM images,

and not to *intrinsic* values that are directly related to changes in the electron density of states. Because the tip of the STM is moving according to a raster scan, the local modification of the surface structure, which at any given moment only occurs within the STM tunneling area, is “spread” over the complete scanning area. Consequently, one can understand the discrepancy between the *experimentally observed* relative shift of the surface atomic structure and the *intrinsic* relative shift predicted by the theoretical model calculations.

Recently, it was demonstrated [13] that the relative shift of dimer rows in the STM images of the Si(001) surface is sensitive to the value of tunneling current. This observation fits our interpretation in terms of inelastic tunneling. When changing the value of the tunneling current at fixed bias voltage, one alters the STM tip-sample distance, and consequently also the values of the tunneling rates γ_L and γ_R , which determine the phonon filling numbers.

The experimentally observed shifts of the dimers inside the π -bonded chains, i.e. in the $[01\bar{1}]$ direction, is different when compared to the experimentally observed shifts of π -bonded chains in the $[2\bar{1}\bar{1}]$ direction. In contrast to previous observations on the Si(111)-(2x1) surface [6–8], which in principle should be similar to our observations, we obtain a value for the shift that is almost equal to 4 Å. The dependence of the relative shift in the $[01\bar{1}]$ direction on the applied bias voltage occurs in a smooth way. Above the conduction band minimum the shift is zero within the experimental accuracy, and it smoothly reaches its maximum value at approximately –1 V below the valence band maximum (see Fig.2e).

In Fig.2e the minus sign for the shift refers to the fact that the relative shift of the chains occurs in a direction *opposite* to the $[2\bar{1}\bar{1}]$ direction. In our experiments the exact orientation of the sample is unknown, and the direction of the π -bonded chains was fixed as the reference $[01\bar{1}]$ direction. Therefore, we are unable to distinguish between left and right isomers of the (2×1) reconstruction [1, 3].

We propose to link the observed smooth phase shift inside the π -bonded chains to modifications of the local electronic density of states in the presence of the STM tip. During the tunneling processes the STM tip apex can acquire an additional charge, which is expected to smoothly depend on the tunneling bias voltage. The periodic local density of states inside the π -bonded chains is perturbed by the electrostatic potential of the charged tip apex and acquires a phase shift that is determined by this potential [10]:

$$\rho(r, k(\varepsilon)) \propto \sin[2k(\varepsilon)r + \delta(eV)],$$

where δ is the phase shift determined by the Coulomb potential of the charged STM tip, i.e. by the applied tunneling bias voltage, and $k(\varepsilon)$ is the quasi-one-dimensional wave vector corresponding to energy ε .

The relative shift of the π -bonded chains in the $[2\bar{1}\bar{1}]$ direction reveals a threshold-like dependence on the applied bias voltage. The relative shift of the π -bonded chains rather abruptly changes at the bias voltage where the empty surface states band π_{CB}^* is coming out of resonance with bulk states, i.e. right below the bottom of the bulk conduction band. Starting from this value of the tunneling bias voltage ($\simeq 0.6$ V) and down to the value corresponding to the top of the valence band ($\simeq -0.1$ V) the tunneling current can flow only through the surface states.

The experimentally observed shift in the $[2\bar{1}\bar{1}]$ direction can not be explained in the framework of the standard model of STM imaging. This model assumes that STM is measuring the *non-perturbed* local density of states. Within this simple model all changes in the relative shift perpendicular to the π -bonded chains of the STM images of the Ge(111)-(2 \times 1) surface should occur smoothly within a range of bias voltages that roughly corresponds to the surface band gap range. The experimentally observed behavior of the relative shift of π -bonded chains is also inconsistent with charging effects occurring in the tunneling junction area. In case of charging effects, the relative shift should reveal changes either near the top of the bulk valence band, or near the top of the filled surface states band π_{VB} . In both cases the sample tunneling rate and hence also the charges, which become localized in the tunneling junction area, are expected to change considerably, resulting in a modification of the STM images for this range of bias voltages. Therefore, another model approach has to be used. As indicated above, the observed shift of the STM images in the $[2\bar{1}\bar{1}]$ direction is consistent with the excitation of vibrational modes by the tunneling electrons. The shift of the π -bonded chains in the STM images is not dominated by a transition between filled and empty states images, but it emerges at a *specific threshold value* of the applied bias voltage. We assume that within a narrow bias voltage range around this threshold value strong phonon generation starts and the phonon filling numbers quickly reach their saturation (maximum) values [12], resulting in a saturation of the shift in the $[2\bar{1}\bar{1}]$ direction. A threshold-like behavior for switching on the electron-phonon interaction has also been observed in low temperature STM investigations of quasi-one-dimensional chains of gold atoms [14].

At this point our theoretical model approach is unable to identify the exact details of the physical mech-

anism causing the experimentally observed changes in the STM images. We note, however, that the energy difference between left and right isomers in the Ge(111)-(2 \times 1) reconstructed surface is small (about 6 meV) [15]. Therefore, phonon excitation within the STM tunneling junction area is expected to easily cause some kind of scanning induced motion of the surface dimers, similar to the case of the Si(001) surface [16]. This motion obviously will lead to a modification of the *measured* distribution of the electron density of states, and it is very plausible that these changes in the density of states also alter the *measured* shifts in the STM images.

In contrast to the behavior of the shift of π -bonded chains in the $[2\bar{1}\bar{1}]$ direction, the shift of individual dimers inside π -bonded chains, i.e. in the $[0\bar{1}\bar{1}]$ direction, is consistent with charging of the tip apex. When charging effects are causing the shift, the shift is not governed by a threshold value for the applied bias voltage, and changes occur near the top of the bulk valence band as well as near the top of the filled surface states band π_{VB} .

4. Conclusion. We have presented the results of our STM investigations of the clean Ge(111)-(2 \times 1) reconstructed surface. Our detailed low temperature STM investigations have allowed us to determine the tunneling bias voltage dependent shifts of the atomic-scale structure caused by the (2 \times 1) reconstruction of the Ge(111) surface. Comparing the experimental data to our theoretical predictions, which take into account the π -bonded chain model, leads to the conclusion that inelastic tip-sample interaction plays a significant role in STM imaging of the Ge(111)-(2 \times 1) reconstructed surface.

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