

Buckling and band gap of the Ge(111)2×1 surface studied by low-temperature scanning tunneling microscopy

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Low-temperature scanning tunneling microscopy is used to study the 2×1 reconstruction of cleaved Ge(111) surfaces. Buckling of the surface atoms is investigated by observations of the corrugation shift between filled and empty states. In the $\langle 2\bar{1}\bar{1} \rangle$ direction, the shift in corrugation maxima from filled to empty states is found to be *negative*, consistent with expectations for the “negatively buckled” model for this surface. A surface band gap of 0.54 ± 0.04 eV is measured by tunneling spectroscopy.

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The 2×1 reconstructions of Ge(111) and Si(111) surfaces have served as prototypical systems for the investigation of surface electronic and optical properties. It is well accepted that the geometry of the surfaces is described by the π -bonded chain model.¹ Many-body effects in the electronic states,² as well as possible *buckling* of the surface chains, are still being investigated.³ In particular, a recent paper by Rohlfling *et al.*⁴ following work by Takeuchi *et al.*⁵ has proposed a model with relatively large “negative buckling” of the chains, based on a comparison of theoretical band gaps with experimental results from photoemission and inverse photoemission spectroscopy^{6,7} (PES/IPES) as well as a comparison of computed optical spectra with experimental data.⁸

In this work we investigate the buckling and the band gap of Ge(111)2×1 surfaces using low-temperature scanning tunneling microscopy (STM). The STM provides a relatively direct means of determining surface buckling (at least for large buckling),^{9,10} as illustrated in Fig. 1. Structural models for positive and negative buckled geometries are shown, taken from Ref. 4. In the π -bonded chains, the surface atoms have one electron per dangling bond. Some charge transfer is expected from the lower to the upper atoms, making them threefold or fourfold coordinated, respectively. Thus, one expects the filled (empty) surface states to be located preferentially on the upper (lower) atoms. Recent theoretical results of Lee and Kang confirm this expectation.³ Thus, if one examines the shift in spatial location from filled to empty states, one expects a shift in the $\langle 2\bar{1}\bar{1} \rangle$ direction for positively buckled chains whereas a $\langle \bar{2}11 \rangle$ shift is expected for negatively buckled chains.

In our results below, we observe a $\langle \bar{2}11 \rangle$ shift in the location of corrugation maxima when going from filled to empty states, which is consistent with a *negatively* buckled surface. In addition, we present detailed results for tunneling spectroscopy, revealing a rich spectrum of surface states and a surface gap of 0.54 ± 0.04 eV. This gap is consistent with that from PES/IPES, and together with the theoretical results of Rohlfling *et al.*⁴ also argues in favor of a negatively buckled surface.

Pieces of {111}-oriented Ge wafers, *p*-type with resistivity of 0.2 Ω cm, were cleaved in ultrahigh vacuum to expose a (111) face. The typical macroscopic appearance of the cleavage face is the same as described in Ref. 11. Cleavage was performed with the sample at room temperature, after which it was immediately transferred to a low-temperature STM (Ref. 12) with base temperature of 12 K. Electrochemically etched tungsten probe tips were used. An *in situ* cleaning step for the probe tips was found to be important for obtaining reproducible spectroscopic results; this was accomplished by making a controlled mechanical contact of the tip to a clean platinum surface and thereby transferring platinum atoms to the end of the tip. Spectra were acquired using the technique of a continuously varying tip-sample separation, $s(V) = s_0 + a|V|$ with values of a of typically 1 $\text{\AA}/V$. Normalization is done by computing the ratio of differential conductance dI/dV (measured with a lock-in amplifier, using

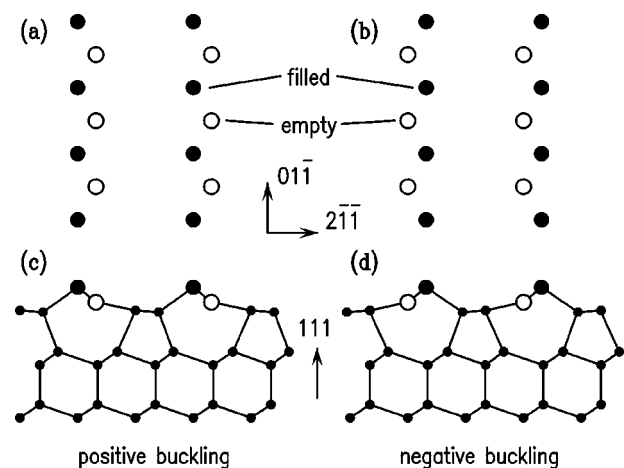


FIG. 1. Structural models for positively buckled [(a) and (c)] and negatively buckled [(b) and (d)] π -bonded chains, following Rohlfling *et al.* (Ref. 4). A side view of the structures is shown in (c) and (d), and a top view of the atoms in the chains is shown in (a) and (b). Surface atoms whose dangling bonds are mainly filled (empty) of electrons are marked by solid (open) circles.

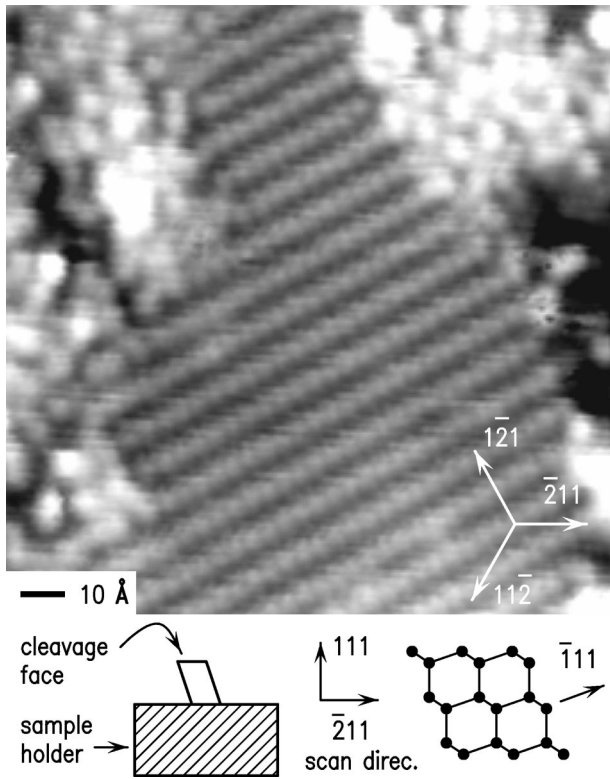


FIG. 2. STM image of cleaved Ge(111) surface. A well-ordered 2×1 domain is seen in the center of the image, with disordered adatom arrangement visible on the right and left sides of the image. The image was acquired with a sample voltage of -1.5 V and constant tunnel current of 1 nA. Gray scale range is 0.9 Å. The lower portion of the figure illustrates the sample mounting geometry, which permits the $\langle 2\bar{1}\bar{1} \rangle$ and $\langle \bar{2}11 \rangle$ surface directions to be easily distinguished.

10-mV modulation) to total conductance I/V , where some broadening is applied to I/V as described below.¹³

Figure 2 shows a typical STM image acquired from our cleaved Ge(111) surfaces. As we have described in previous work, these surfaces consist of ordered 2×1 domains (6.93×4.00 Å² unit cell), interspersed with areas containing disordered adatom arrangements.¹⁴ The surfaces generally contain about 50% of each type of structure. The size of the domains varies from cleave to cleave, but is typically about 5 nm. We note that the ability to establish operable tunneling conditions at low temperature for this surface was found to be no different than at room temperature, indicating that thermally assisted processes are apparently not important in the transport process. One advantage, however, of the low-temperature operation is in the overall stability of the STM operation.

An important aspect of our investigation of the surface buckling is the establishment, with certainty, of the difference between the $\langle 2\bar{1}\bar{1} \rangle$ and $\langle \bar{2}11 \rangle$ surface directions. With the outward surface normal as the cleavage face defined as $[111]$, these two sets of directions are inequivalent. Our method for distinguishing these directions is illustrated in the lower part of Fig. 2. Since the samples are cut out of $\{111\}$ -oriented wafers, two sides of the sample bar are *not* normal

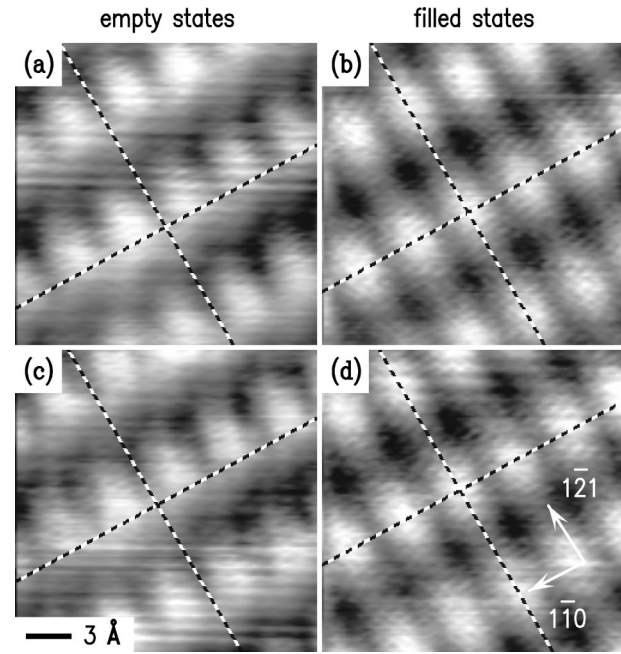


FIG. 3. STM images of the Ge(111) 2×1 surface, acquired at sample voltages of (a) $+0.8$, (b) -0.8 , (c) $+0.8$, and (d) -0.8 V. Dashed lines are located at the same surface locations in each image. Images (a) and (c) are displayed with a gray scale range of 0.3 Å, and images (b) and (d) are displayed with a gray scale range of 0.5 Å. A constant tunnel current of 0.14 nA was used for all images.

to the cleavage face but rather they are oriented at 109.5° to it. Thus, with knowledge of the scanning direction relative to the sample mounting, we can confidently distinguish between the $\langle 2\bar{1}\bar{1} \rangle$ and $\langle \bar{2}11 \rangle$ directions.

Voltage-dependent STM results are presented in Fig. 3. We show four images, which were acquired consecutively (with equal time delay between images). A small amount of drift can be seen between the images. The intersection of the dashed lines on the images has been located on a corrugation maximum in the filled states [Figs. 3(b) and 3(d)], and this intersection point is thus moved slightly in a uniform manner from one image to the next. Examining the images of Fig. 3, we find a shift of half a unit cell (2.0 Å) between empty and filled states in the $[1\bar{1}0]$ direction. This shift is expected according to the inequivalence of the two atoms in the π -bonded chains, as previously observed⁹ and as illustrated in Fig. 1. In the orthogonal direction, we find that the empty states are shifted in the $[1\bar{2}1]$ direction relative to the filled states, by about 0.7 Å. Making repeated measurements of this shift at different surface locations, and for tip-sample voltages with magnitude in the range 0.3 – 0.8 V, leads to an average value for the shift of 0.78 ± 0.08 Å.¹⁵

Our observation of a *positive* $[1\bar{2}1]$ shift of the empty states relative to the filled states (corresponding to a *negative* $\langle 2\bar{1}\bar{1} \rangle$ shift) is consistent, according to Fig. 1, with expectations for *negatively* buckled π -bonded chains. We point out that the interpretation presented in Fig. 1, with filled states on raised atoms and empty states on lowered atoms, is valid

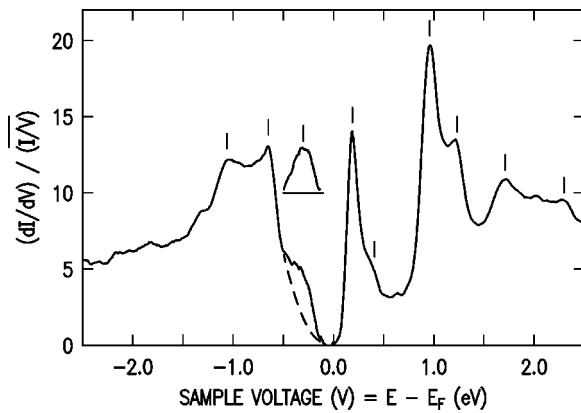


FIG. 4. Tunneling spectrum of the Ge(111)2×1 surface. Peak positions are indicated by vertical lines. The dashed line is an approximate background used for determining the peak position of the feature near -0.3 V, with the difference spectrum shown above raw spectrum. The sample voltage corresponds to the energy of a state relative to the Fermi level (0 V).

only for relatively large amounts of buckling. For small buckling, the empty or filled states will still prefer one atom in the chain or the other (since the two sites are inequivalent), but a detailed computation is required to determine which states are localized on which atom. However, for the case of interest here, viz., large buckling of Ge(111)2×1, we feel that our interpretation presented in Fig. 1 (and explicitly computed in Ref. 3) is valid. Incidentally, we are aware of the recent work by Hirayama *et al.*¹⁶ that provides evidence for regions of different buckling on the Ge(111)2×1 surface. For our results reported here we have restricted our measurements to well-ordered regions near the center of relatively large 2×1 domains, and we have always observed the same sign and similar magnitude of the $\langle 2\bar{1}\bar{1} \rangle$ shift between empty and filled states. Nevertheless, we do acknowledge the possibility of buckling variations near surface defects; indeed, very early STM measurements revealed such effects on the Si(111)2×1 surface.¹⁷ Finally, we note that the corrugation shift between filled and empty states observed here is similar in magnitude to that seen on Si(111)2×1 surfaces, although that agreement may be coincidental.¹⁸

In addition to voltage-dependent imaging, we have also probed the electronic states of the surface using tunneling spectroscopy. Results are presented in Fig. 4, where we show a spectrum consisting of an average of about 15 spectra acquired at various points on a well-ordered 2×1 domain. We plot the ratio of differential to total conductance, where the total conductance provides a normalization quantity. This normalization allows the spectrum to be conveniently viewed on a linear scale. However, as previously discussed, one problem with this type of normalization is that, when a band gap exists, the current goes to zero faster than dI/dV at the band edge, so that $(dI/dV)/(I/V)$ diverges.¹³ This was not a problem in our prior room-temperature spectroscopic measurements on Ge(111)2×1, since a small but non-negligible current was detected throughout the band gap.¹⁴ In the present case, however, no measurable current was detected in

the gap region. We thus apply a small amount of broadening to I/V , forming $\overline{I/V}$ according to Eq. (4) of Ref. 13 using a broadening of $\Delta V = 0.2$ V.

The results of Fig. 4 for the low-temperature tunneling spectrum are in good agreement with prior results obtained at room temperature.¹⁴ The overall appearance of the two spectra are similar, except that the spectral features in the low-temperature case are generally narrower and 2–3 times more intense. Spectral features can be located in Fig. 4 with a precision of typically ± 0.02 eV. The bottom of the empty surface state band appears as the intense peak at 0.19 eV (all energies relative to the Fermi level). A small shoulder is reproducibly seen on the high-energy side of this peak, at about 0.41 eV. The upper part of this band appears as two peaks (only one peak was seen at room temperature¹⁴), at 0.96 and 1.23 eV. Higher-energy peaks, associated with bulk bands, are seen at 1.71 and 2.30 eV. The top of the filled state band is seen as a relatively weak shoulder (similar to the room-temperature results¹⁴), probably because of mixing with valence-band states. Using an approximate background subtraction shown by the dashed line in Fig. 4, we deduce an energy location of -0.30 eV with uncertainty of ± 0.04 eV. Two peaks are seen associated with the lower portions of the filled state band, at -0.65 and -1.06 eV. The remaining small features in the spectrum are at the limit of the residual vibrational noise in our STM, and cannot be reliably identified.

As discussed by Rohlffing *et al.*,⁴ the size of the surface band gap provides an additional measure of the surface buckling. The combination of PES and IPES yields a value of 0.61 eV for the direct surface gap,^{6,7} although some uncertainty exists in this measurement since the results of two experiments (with possibly different Fermi-level positions) must be combined. Theory indicates a direct gap of 0.66 eV,⁴ with an indirect gap which is smaller by about 0.12 eV [taken from Fig. 2(b) of Ref. 4]. Comparing with our measurements above, we find a gap directly from the normalized conductance of 0.49 ± 0.03 eV (combining uncertainties in quadrature). However, a small correction must be applied to this value since the normalized conductance itself slightly underestimates the gap. Based on the analysis of Ref. 19, we estimate a correction of 0.05 ± 0.02 , yielding a gap of 0.54 ± 0.04 eV. This value presumably corresponds to the minimum gap (indirect), and it agrees well with the above PES/IPES and theoretical results. Our prior room-temperature measurements yielded a gap from the normalized conductance of 0.65 ± 0.07 eV.¹⁴ This value is somewhat larger than that observed here, especially considering that the gap should be *smaller* at room temperature [by an amount of about 0.02–0.04 eV, at least for Si(111)2×1 (Ref. 20)]. We feel that this slight decrease in the apparent band gap with reduced temperature, albeit at the uncertainty limit of the experiment, may arise from some nonideal behavior of the probe tips used. Although considerable care in probe tip preparation was used in both the prior and present works, perhaps some residual probe tip effects (which invariably lead to larger observed gaps) were present in the previous work. Further measurements are required to resolve this small discrepancy between the two results.

In summary, we have observed the shift between filled and empty states on the Ge(111) 2×1 surface, and find it to be in the $\langle\bar{2}11\rangle$ direction. This result is in agreement with expectations based on a negatively buckled surface. Measurements of the surface state band gap yield a low-temperature gap of 0.54 ± 0.04 eV, in agreement with prior

experimental results. On the basis of theoretical results,⁴ this relatively small value for the gap is also believed to support the structural model of negatively buckled π -bonded chains.

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¹⁵To quantify the shift between empty and filled states, we fit the images to a function consisting of the sum of two sinusoids, with adjustable phases. The phase shift is found from the difference of the phases between filled and empty states.

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¹⁸The *sign* of the $\langle 2\bar{1}\bar{1} \rangle$ shift between empty and filled state for Si(111) 2×1 surface is uncertain at present. We have carefully reexamined our prior data for this surface, comparing results obtained in different experiments, but we have been unable to unambiguously determine the sign of the shift. Additional measurements are needed in order to determine this quantity.

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