RAPID COMMUNICATIONS

PHYSICAL REVIEW B VOLUME 44, NUMBER 24 15 DECEMBER 1991-II

Band gap of the Ge(111) 2×1 and Si(111) 2×1 surfaces by scanning tunneling spectroscopy

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(Received 3 September 1991)

The scanning tunneling microscope is used to measure the spectrum of states for the Ge(111)2×1 and Si(111)2×1 surfaces. Detailed spectra, revealing the entire empty and filled state bands for both surfaces are obtained. Band gaps of 0.65 ± 0.09 eV and 0.50 ± 0.05 eV are found for the Ge and Si surfaces, respectively. The results are compared with values for the band gaps obtained from recent quasiparticle calculations.

The 2×1 reconstruction of the Ge(111) and Si(111) surfaces, obtained by cleavage at room temperature, has been the subject of considerable study. Following the initial observation of the 2×1 reconstruction,[1] almost two decades passed before the introduction of the π-bonded chain model,[2] which describes the atomic arrangement of the surface. Based on results from many techniques,[3-7] there is now practically no doubt that this model correctly described the Si(111)2×1 surface. For Ge(111)2×1, however, the situation is not so clear,[8] but the scanning-tunneling-microscopy (STM) results presented in this work provide strong evidence that this surface is also described by the π-bonded chain model. The π-bonded chain structure has been the subject of numerous theoretical computations, presumably because its relatively small size (i.e., compared to the 7×7 structure) makes it amenable to first principles work. Recently, quasiparticle computations have been performed for both the Ge and Si(111)2×1 surfaces.[9,10] The goal of these calculations is to obtain a more accurate value for the band gap separating the filled and empty (π and π^*) surface-state bands.

In this work we report spectroscopic measurements with the STM for the Ge and Si(111)2×1 surfaces. The Si(111)2×1 surface has been the subject of previous STM study.[6] The present results are in excellent agreement with the previous work, notwithstanding the use of somewhat updated spectroscopic methods here. For the case of Ge(111)2×1, no previous STM work has been reported. We present detailed spectroscopic results for this surface. A comparison of the Si and Ge spectra allows a more complete understanding of the various spectral features. In particular, we find that the top of the Ge filled state band can be clearly resolved, even though it lies about 0.5 eV below the top of the bulk valence band. In terms of the band gap between filled and empty surface-state bands, we find values of 0.65 ± 0.09 eV and 0.50 ± 0.05 eV for the Ge and Si surfaces, respectively.

The tunneling microscopes used in this work were contained in ultrahigh-vacuum chambers with base pressures of $\leq 6\times10^{-11}$ Torr. All measurements are performed at room temperature. The Ge and Si samples were p type, with resistivities of 0.2 and 1 Ω cm, respectively. The crystals were cleaved in a $[2\bar{1}\bar{1}]$ direction, exposing a (111) face. Both tungsten and Pt-Ir probe tips were used, and they were thoroughly cleaned by electron bombardment and field emission. Spectra were measured with a continuously varying tip-sample separation, $s(V)$. A modulation voltage of typically 50-mV amplitude and 1-KHz frequency was added to the tip-sample bias voltage, and a lock-in amplifier was used to obtain the conductivity, dI/dV (this conductivity then corresponds to the derivative with respect to voltage at *fixed* tip-sample separation). The data are then analyzed by two methods. First, data are transformed to constant tip-sample separation, $(dI/dV)_s \equiv (dI/dV)\exp[2\kappa s(V)]$, where 2κ is the measured decay constant of the tunnel current. The voltage dependence of κ is found to be small (except in the immediate vicinity of the band edges[6]), and for the purposes of this analysis we use a voltage-independent value, with magnitude in the range 1.0–1.2 Å^{-1}. The second analysis method is to compute the normalized conductivity, $(dI/dV)/(I/V)$. This quantity removes some of the effects of the tunneling transmission term from the measured conductivity.[6]

In Fig. 1(a) we present an STM image of the Ge(111)2×1 surface. Two types of surface areas, with differing atomic structures, are visible in the image. First, there are regions consisting of parallel corrugation rows extending along one of the three $\langle 01\bar{1}\rangle$ surface directions. The spacing of these rows is 7.2 ± 0.4 Å, corresponding to the $2\times$ periodicity of 6.93 Å on Ge(111). Higher-resolution images shown in Figs. 1(b) and 1(c) reveal the $1\times$ spacing along the rows, and display the voltage dependence which is characteristic of the π-bonded chain structure.[6] The second type of surface area consists of Ge adatoms bonded on top of the surface, forming local regions of 2×2 and $c2\times4$ symmetry. These regions are reminiscent of similar disordered adatom structures found on cleaved Si surfaces,[11] except that the coverage of the adatom areas is more than ten times greater for Ge. Typically we find 30%–60% of the surface covered with these structures. The size of a 2×1 domain can be much larger than that shown in Fig. 1, but the adatom covered areas are then correspondingly large. In all cases the adatom areas form at domain boundaries of the 2×1 structure. Historically, there has been some controversy surrounding the 2×1 structure of the Ge(111) surface, with different groups reporting much different photoemission spectra from this surface.[8,12] We believe that the existence of the disordered adatom areas provides an explanation for these results. Depending on the cleavage quality, one can obtain large surface areas covered by the adatoms, and these

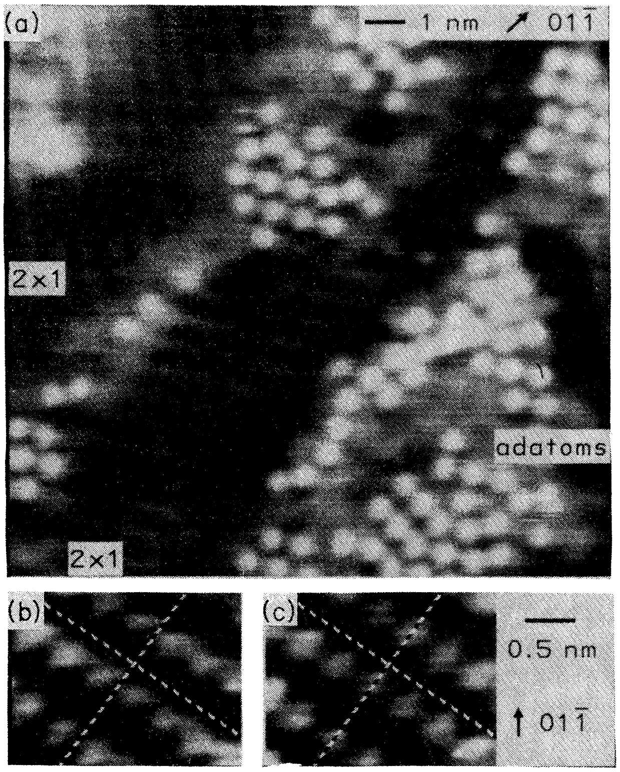

FIG. 1. STM images of the Ge(111)2×1 surface, acquired at sample bias voltages of (a) 1.8, (b) 0.8, and (c) −0.8 V, and at constant tunnel current of 0.1 nA. (a) Regions of 2×1 structure, and adatom covered areas. The cross hairs in (b) and (c) are at identical surface locations, thus revealing the characteristic contrast reversal along the 2×1 rows.

regions will give rise to relatively flat bands as seen in the photoemission spectra.

Spectroscopic results for the Ge(111)2×1 surface are shown in Fig. 2. We observe a rich spectrum, containing numerous features on both the empty state (positive voltage) and filled state (negative voltage) sides. A region of low conductivity is visible, centered at −0.1 eV. We associate this region with the gap between empty and filled state bands. Peaks in the spectrum are indicated by vertical lines in Fig. 2, and the energies of the peak positions are given in Table I. These peak positions are determined by the location of maxima in the spectrum. In cases where the peak lies on a large background, a linear term is subtracted from the spectrum prior to determining the peak position. An example of this procedure is shown for the −0.47-eV peak in Fig. 2, which appears only as a weak shoulder in the spectrum. The uncertainty of the peak positions is estimated to be ±0.03 eV, except for the −0.47-eV peak, which, because of its small size and the large background, is assigned an uncertainty of ±0.06 eV. This level of precision may somewhat overstate the definition of the broad features at 1.25 and 1.54 eV in the spectrum, but in all other cases the peaks are well defined and we believe that they arise from specific features in the surface or bulk band structures.

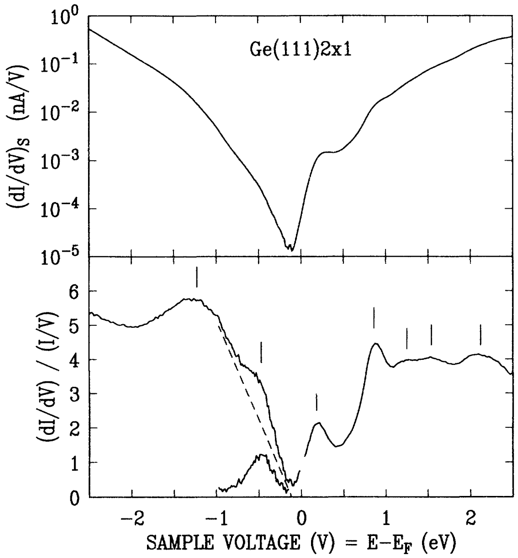

FIG. 2. Spectroscopy of the Ge(111)2×1 surface. The thin dashed line shows an example of the linear background used for determining peak positions, with the resulting difference spectrum shown near −0.5 V. Peak positions are indicated by vertical lines. The sample voltage corresponds to the energy of a state relative to the Fermi level (0 V).

To interpret the Ge(111)2×1 results, it is useful to compare them with the corresponding spectrum obtained from Si. That spectrum has been known for years,[6] but to obtain the highest possible quality and precision of the results we have acquired new spectra for Si(111)2×1. These results are shown in Fig. 3. A region of low conductivity centered at −0.1 eV is observed again, together with various spectral peaks on the empty and filled state sides. The peak positions are indicated by vertical line in Fig. 3, and are listed in Table I. The interpretation of those spectral features is the same as previously specified: the peaks at − 0.34 and −1.08 eV delimit the filled state band, the peaks at 0.16 and 1.22 eV delimit the empty state band, and the peak at 2.36 eV is associated with the lowest-lying conduction band near the L point in the bulk band structure.[6]

We interpret the Ge spectra in a manner analogous to

TABLE I. Peak positions (eV) relative to E_F of STM spectral features for the Ge and Si(111)2×1 surfaces. Uncertainties are ±0.03 eV, except for the −0.47-eV peak, which has an uncertainty of ±0.06 eV.

Ge	Si	Identification
−1.23	−1.08	bottom, surface π band
−0.47	−0.34	top, surface π band
0.18	0.16	bottom, surface π^* band
	1.22	top, surface π^* band
0.86	2.36	bulk Λ_1 band
1.25		surface or bulk DOS feature
1.54		surface or bulk DOS feature
2.12		bulk Λ_1 band

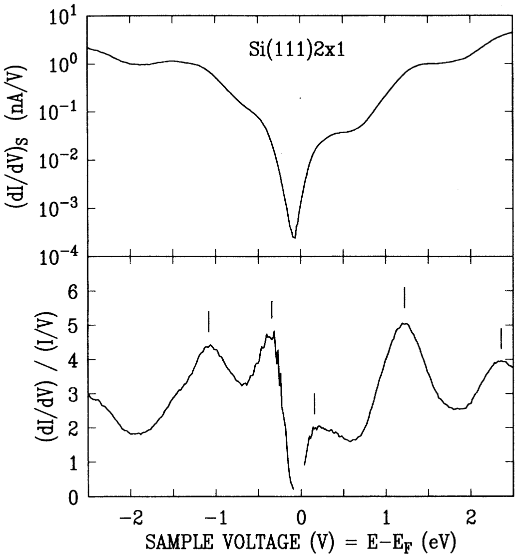

FIG. 3. Spectroscopy of the Si(111)2×1 surface. Peak positions are indicated by vertical lines. The sample voltage corresponds to the energy of a state relative to the Fermi level (0 V).

that for Si. The peaks at − 0.47 and −1.23 correspond to the top and bottom of the filled surface-state band, respectively. The peak at 0.18 corresponds to the bottom of the empty surface band. The top of this band appears to be strongly mixed with bulk states, giving rise to the features at 0.86, 1.25, 1.54, and 2.12 eV. We associate the 0.86-eV peak with the lowest-lying conduction band, Λ_1, which at the L point is the top of the bulk band gap. Following previous work,[13] we take the surface Fermi level and valence-band maximum to be coincident for Ge. Then, our observed 0.86 eV can be compared to the 0.67-eV bulk band gap (at 300 K). The difference between the two is consistent with the expectation that tunneling spectra are not expected to show significant features near critical points in the bulk band structure.[14] Rather, the observed peak arises from some flat portion of the Λ_1 band away from the L point. We interpret the 2.12-eV peak in a similar manner, and we note that analogous peaks at 0.7 and 2.2 eV have been seen in inverse photoemission.[13] The features at 1.25 and 1.54 eV are too broad to permit specific identification, and we associate them generally with density-of-state (DOS) features of the surface or bulk band structures.

Having considered the overall identification of the spectral features, we now discuss the band gap separating the empty and filled surface-state bands for Ge and Si. There is one difference between the gaps for Ge and Si which is not readily apparent in Figs. 2 and 3, but which can be seen by examining a large number of spectra acquired from various spatial locations: For Si, the surface band gap is relatively well defined. Some residual state density associated with defects can tail into the gap[5] (some of which occurs in Fig. 3), but these effects show considerable variation over the surface and thus are not intrinsic to the perfect surface or bulk bands. Alternatively, for Ge, a significant (albeit weak) state density within the gap is always observed at all spatial locations, especially on the negative-energy side. A comparison of the upper panels of Figs. 2 and 3 reveals that the slope of the conductivity on the negative-energy side is significantly less for Ge than for Si. We associate this state density within the gap for Ge with the presence of the top of the bulk valence band (which is expected to occur roughly at 0 eV in Fig. 2). Apparently, the valence band contributes with a weak onset in the spectrum, consistent with the above mentioned expectation for tunneling into bulk states. The observed feature of −0.47 V for Ge is then the top of the filled surface-state band, sitting on top of an increasing background from the bulk valence states. With this identification for the Ge spectrum, we can now be quite confident that the well-defined peak seen at −0.34 V for Si does, indeed, accurately correspond to the top of the filled surface band, without any interfering effects from the bulk valence band. In terms of numerical results for the surface-state band gaps, we obtain from Table I a value of 0.50 ± 0.06 eV for Si. This value is in good agreement with the previous STM results from that surface,[6] thereby allowing us to statistically reduce the uncertainty level to ± 0.05 eV. For Ge, we find a surface gap of 0.65 ± 0.09 eV.

In summary, we have determined the surface-state band gaps on Ge(111)2×1 and Si(111)2×1 by tunneling spectroscopy. In general, tunneling is sensitive to the minimum-size band gap at the surface, which is direct ($\bar{J}$ to $\bar{J}$) for Ge but indirect ($\bar{K}$ to $\bar{J}$) for Si.[9,10,15] Comparing to recent quasiparticle calculations, our result is in agreement with the theoretical direct gap of 0.67 eV for Ge,[10] but is somewhat less than the theoretical indirect gap of 0.58 eV for Si.[9] This difference between experiment and theory for Si might arise from the temperature dependence of the gap. In terms of the direct band gap for Si, the theoretical quasiparticle result is 0.62 eV.[9] Experimentally, we can estimate the direct gap by correcting the STM result by 0.10 ± 0.05 eV for the difference in energy of the π band between the $\bar{K}$ and $\bar{J}$ points as seen by photoemission,[15] yielding 0.60 ± 0.10 eV, in agreement with theory. Our experimental results for the direct single-quasiparticle band gaps are larger than the optical gaps of 0.47 eV for Si (Ref. 16) and 0.50 eV for Ge (Ref. 17) by 0.13 ± 0.10 and 0.15 ± 0.09 eV, respectively. These differences lend support to the possibility of significant excitonic effects on these (111)2×1 surfaces,[9,10] although the uncertainties in the energy differences should not be neglected. The band gaps observed here by STM spectroscopy are consistent with those found by combining direct and inverse photoemission data,[15,18,19] although the STM results are generally more accurate since both empty and filled state bands can be observed in the same spectrum.

The author thanks A. J. Slavin for his participation in the early stages of this project, and D. G. Cahill for motivating the later stages of the work. Discussions with M. S. Hybertsen and J. E. Northrup are gratefully acknowledged.

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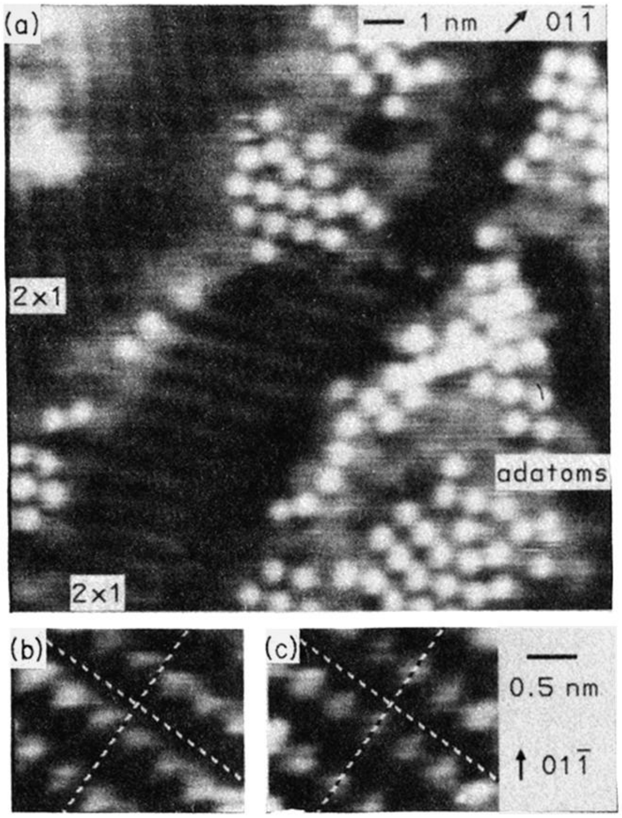

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