# Unoccupied surface states on Si(111)$\sqrt{3}\times\sqrt{3}$-Ag

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A nearly metallic surface state band is detected on Si(111)$\sqrt{3}\times\sqrt{3}$ Ag by inverse photoemission, Si $2p$ core level photoemission, and scanning tunneling spectroscopy. The band spans most of the bulk band gap of Si, from the Fermi level at 0.25 eV above the valence band maximum all the way to the conduction band minimum. The Fermi level is pinned over a wide doping range ($7\times10^{18}$ cm$^{-3}$ $p$ type to $1.2\times10^{19}$ cm$^{-3}$ $n$ type). The data suggest that the surface band gap expected from the even electron count is filled in at room temperature, possibly due to thermal disorder or due to the finite domain size of 10–20 nm. A second, prominent surface feature at 2.2 eV above the valence band maximum is assigned to surface umklapp from $\bar{K}$ to $\bar{\Gamma}$ via a $\sqrt{3}\times\sqrt{3}$ reciprocal lattice vector. [S0163-1829(98)03204-4]

## INTRODUCTION

The silver-induced Si(111)$\sqrt{3}\times\sqrt{3}$-Ag surface has become one of the most-studied overlayer structures on semiconductors. It serves as a well-ordered prototype for metal-semiconductor interfaces, it provides an inert substrate for studying semiconductor passivation, and its unusual structure challenges structural techniques. The electronic structure is special as well. It is not even clear whether this surface is metallic or semiconducting, despite a series of photoemission and inverse photoemission studies,[1–7] first principles calculations,[8,9] scanning tunneling microscopy,[10–14] optical spectroscopy,[15] and surface conductivity[16,17] studies. The number of electrons per unit cell is even, suggesting a semiconducting surface. On the other hand, there exists a nearly metallic surface state band that extends throughout most of the band gap of the Si substrate and pins the Fermi level. Our study intends to clarify how such a dilemma can be resolved.

The detailed arguments for a semiconducting $\sqrt{3}\times\sqrt{3}$ surface are the following. The structure consists of a monolayer of Ag atoms embedded into a Si(111) surface truncated between the double layers, a rather unusual truncation with three broken bonds per Si atom. This leaves three Ag atoms with an unpaired $s,p$ electron each and a Si trimer with $3\times3=9$ unpaired electrons in the $\sqrt{3}\times\sqrt{3}$ unit cell. The total number of 12 valence electrons per unit cell is even, such that one might expect a surface with saturated bonds and a band gap, as observed with most adsorbate-covered semiconductor surfaces. Indeed, first principles calculations predict an energy gap of $\approx0.4$ eV (Ref. 8) and 0.54 eV (Ref. 9). These are local density calculations, which typically underestimate the band gap in semiconductors. A surface with paired electrons would also be consistent with the observed inert nature of Si(111)$\sqrt{3}\times\sqrt{3}$ Ag with respect to gas adsorption. Further growth of Ag on top of the $\sqrt{3}\times\sqrt{3}$ structure occurs in islands, which suggests that the $\sqrt{3}\times\sqrt{3}$ structure has even lower surface energy than Ag metal. Photoemission data have been obtained from highly $n$-doped substrates, where the bottom of the surface conduction band becomes occupied.[5] The distance between this band minimum and the highest of the occupied surface states observed in this experiment is 0.6 eV, which provides an upper limit for a possible band gap. However, the bottom of the surface conduction band is very close to the valence band maximum of the Si substrate, i.e., $\pm0.1$ eV, depending on the time after preparing the surface.[5] Very recent photoemission data[6] point towards a similar band lineup, with the bottom of the surface conduction band at or slightly below the top of the bulk valence band. Consequently, the bulk band gap is filled in by states from the surface conduction band and the combined system surface+bulk becomes metallic.

The nearly metallic nature of the $\sqrt{3}\times\sqrt{3}$ surface shows up in the following results. An early inverse photoemission study[1] shows a weak Fermi edge. Even though this metallic edge is not discussed in the original publication, subsequent theoretical work[9] takes it evidence for an unoccupied surface band predicted by the calculation. Our inverse photoemission data show such an unoccupied surface state band very clearly, starting close to the Fermi level and filling most of the band gap of Si. This surface state has been suggested as

 

being responsible for imaging the $\sqrt{3}\times\sqrt{3}$ honeycomb structure in a scanning tunnel microscope (STM) at positive sample bias.[8] The density of states at the Fermi level can be probed with better energy resolution by observing the Fermi level pinning versus doping of the Si substrate. If there is a band gap at the surface, the Fermi level should jump from the bottom to the top of the gap when switching from $p$ to $n$ doping. Using the Si $2p$ core position and the inverse photoemission spectra, a pinning of the Fermi level comparable to that at the metallic Si(111)$7\times7$ surface is observed.

To clarify the situation, we have combined several techniques that pinpoint the surface band structure. Inverse photoemission maps out unoccupied surface states, the shift of the Si $2p$ core level versus doping reflects the density of pinning states at the Fermi level, and scanning tunneling spectroscopy resolves the fine structure in the density of states around the Fermi level, including a possible band gap. The following picture emerges from these measurements: The ideal Si(111)$\sqrt{3}\times\sqrt{3}$-Ag surface does exhibit a surface band gap, as expected from the electron count and from first principles calculations. However, there are two mechanisms that make the surface nearly metallic. First, the real surface is not perfectly ordered, either due to a finite domain size[12,13] of 10–20 nm, or due to thermal disorder at room temperature, or due to Si adatoms.[6] Consequently, the band edges are smeared out, and the band gap becomes filled in, such that there is a substantial density of states pinning the Fermi level. Scanning tunneling spectroscopy gives a dip in the density of states around the Fermi level of about 0.4 eV full width half maximum, which can be taken as a rough measure of band gap at the ideal surface. The second mechanism for metallicity is based on the band lineup between surface and bulk. The bottom of the surface conduction band lies very close to the top of the bulk valence band,[5,6] which lets the effective $abdn$ gap shrink to zero.

## EXPERIMENT

Angle-resolved inverse photoemission was performed with a spectrograph[18] that provides variable photon energy and the best energy resolution currently achievable ($\approx$0.2 eV). For Si $2p$ core level spectroscopy we used a general user beam line at the Synchrotron Radiation Center (SRC) in Madison. The energy position of the $2p_{1/2}$ and $2p_{3/2}$ lines were determined by least squares fitting. Scanning tunneling microscopy and spectroscopy was performed in a semicommercial version of a low temperature STM[19] that was operated at room temperature. It includes a sample transfer system identical to that in the inverse photoemission apparatus, which facilitates reproducing the exact sample preparation conditions in the two experiments.

The Si(111)$\sqrt{3}\times\sqrt{3}$-Ag surface was prepared according to established methods. Si(111) wafers were cleaned by flashing to 1250 °C and Ag deposited immediately after the flash at a substrate temperature of 500–550 °C. This gave sharp low energy electron diffraction (LEED) patterns. Inverse photoemission, LEED, and scanning tunneling spectroscopy were insensitive to the detailed sample preparation conditions, but Si $2p$ core level spectra changed somewhat with growth temperature and step density of the substrate. At higher growth temperature and step density, the shape of the Si $2p$ spectrum and the Fermi level pinning position were closer to that of the clean Si(111)$7\times7$ surface, indicating incomplete coverage. Therefore, the data presented here are for Ag depositions slightly higher than the nominal amount of 1 monolayer required for the ideal $\sqrt{3}\times\sqrt{3}$ structure, i.e., most likely in the region of sample C in Ref. 6. The misorientation was varied from $\frac{1}{4}°$ to 6°, and the doping of the samples was $7\times10^{18}$ cm$^{-3}$ $p$ type, $1.3\times10^{16}$ cm$^{-3}$ $p$ type, $4.5\times10^{14}$ cm$^{-3}$ $n$ type, $4.5\times10^{15}$ cm$^{-3}$ $n$ type, $1.2\times10^{19}$ cm$^{-3}$ $n$ type, and $5\times10^{17}$ cm$^{-3}$ $n$ type for a stepped Si(9911) surface with 5.6° misorientation towards (1 1 2). Si(111)$\sqrt{3}\times\sqrt{3}$ Ag was found to be not as perfect as the Si(111)$7\times7$ substrate in STM. It exhibited islands with typical diameters of 10–20 nm, in agreement with other recent STM studies.[12,13] Therefore, photoemission and inverse photoemission data contain contributions from a high density of imperfections between the islands. Only scanning tunneling microscopy and spectroscopy are able to zoom in on locally perfect areas. Our spectroscopy data were taken from $10\times10$ nm$^2$ areas that were atomically flat and were averaged over a few thousand $I(V)$ spectra taken in such an area.

## INVERSE PHOTOEMISSION

Unoccupied surface states in the band gap of semiconductors can be detected by inverse photoemission.[18] Since the Fermi level is located close to the valence band maximum in Si(111)$\sqrt{3}\times\sqrt{3}$ Ag, we expect most of the possible gap states to be unoccupied. Inverse photoemission spectra for Ag adsorption on Si(111)$7\times7$ are given in Figs. 1–3. Figure 1 shows the surface states of clean Si(111)$7\times7$ and Si(111)$\sqrt{3}\times\sqrt{3}$ Ag, Fig. 2 displays the coverage dependence, and Fig. 3 the changes with doping and step density. Note that the energy axis in Fig. 1 is referenced to the valence band maximum (VBM), whereas it is referenced to the Fermi level $E_F$ in Figs. 2 and 3. The VBM lies 0.65 eV above $E_F$ for the Si(111)$7\times7$ surface[20] and 0.25 eV above VBM for Si(111)$\sqrt{3}\times\sqrt{3}$ Ag, as we will discuss in detail in the section on Si $2p$ photoemission below.

The characteristic feature of the Si(111)$7\times7$ surface in Fig. 1 is a surface state at an energy of 1.2 eV above the VBM (0.55 eV above $E_F$). This peak has been identified previously with the help of scanning tunneling spectroscopy[18,21] as the mostly empty broken bond orbital located above the adatoms of the $7\times7$ structure. The adatom state becomes quenched at about 1 monolayer Ag coverage (one Ag atom per Si surface atom), where the $\sqrt{3}\times\sqrt{3}$ LEED pattern is fully established (Fig. 2).

For the $\sqrt{3}\times\sqrt{3}$ Ag structure, a continuum of surface states is observed, extending all the way up to the conduction band minimum (CBM) and starting close to $E_F$ (0.25 eV above the VBM). To ensure that these states are not just a remnant of the $7\times7$ surface state, we have added extra Ag coverage up to 34 monolayers (Fig. 2). The inverse photoemission spectrum remains unchanged, which demonstrates that the continuum in the gap is truly a feature of Si(111)$\sqrt{3}\times\sqrt{3}$ Ag. These states are not due to metallic silver, either. Extra silver is known to form thick, three-dimensional Ag(111) islands at our growth temperature of 500–550 °C, which cover a negligible fraction of the surface. This is evidenced by our STM results and by many

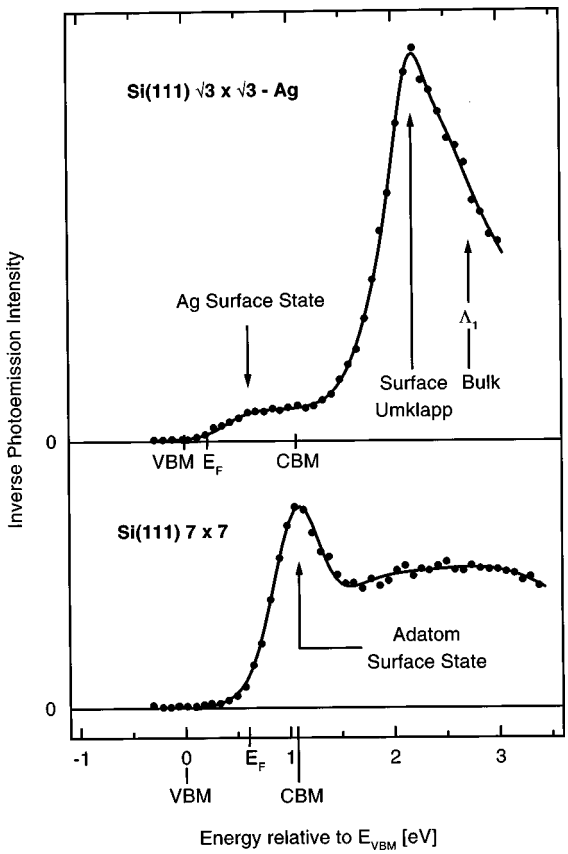


FIG. 1. Comparison between inverse photoemission spectra of clean Si(111)$7\times7$ and Si(111)$\sqrt{3}\times\sqrt{3}$ Ag, taken with electrons incident normal to the surface at an energy of 11 eV above the Fermi level $E_F$. The adatom surface state of Si(111)$7\times7$ at 1.2 eV above the valence band maximum (VBM) is quenched by Ag, but a nearly metallic surface state emission remains in the gap, which is not a remnant of the adatom state (see Fig. 2).

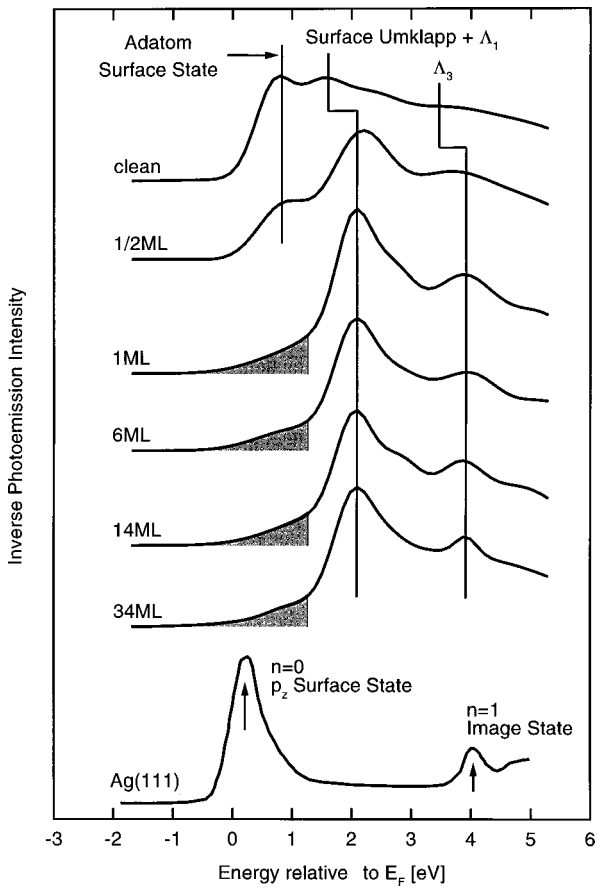


FIG. 2. Coverage dependence of the inverse photoemission spectra, measured at an electron energy of 14.5 eV above $E_F$. The surface state of the Si(111)$7\times7$ substrate is quenched after depositing one monolayer of Ag. The remaining continuum of surface states in the band gap of Si (hatched) is not affected by further adsorption of Ag and, thus, characteristic of Si(111)$\sqrt{3}\times\sqrt{3}$ Ag. It is not caused by metallic bulk Ag, either, since the extra Ag forms thick islands that cover a negligible fraction of the surface (compare the bottom spectrum). 1 monolayer (ML)=1 Ag atom per Si(111) surface atom=1.34 Å of Ag.

previous microscopy studies.[22] If any of these (111)-oriented islands contributed to the spectrum, they would cause a peak to appear at the Fermi level with increasing coverage, due to the $p_z$-like $\Lambda_1$ surface state observed on Ag(111), as shown on the bottom of Fig. 2 for comparison.

A second, intense surface feature is observed for the $\sqrt{3}\times\sqrt{3}$-Ag surface at 2.2 eV above the VBM. It has been reported for several other noble metal overlayers as well.[1] This peak has at least partial surface character, judging from its absence on Si(111)$7\times7$ and Si(111)$2\times1$ and from the fact that it lies just below the $L_1$ point of bulk Si, which defines the top of the Si bulk gap in the [111] direction. Our best assignment of the surface feature at 2.2 eV is a surface umklapp process, whereby the extra reciprocal lattice vectors of the $\sqrt{3}\times\sqrt{3}$ lattice transfer bulk transitions from the corner $K$ of the $1\times1$ surface Brillouin zone to its center $\Gamma$. Such surface umklapp plays a role in detecting the bottom of the $\sqrt{3}\times\sqrt{3}$ gap state by photoemission.[5] The corner $K$ is equivalent to a line in the bulk band structure that passes through points with low symmetry near $K$ and $W$ in the bulk Brillouin zone. Further evidence for the origin of this feature in a bulk band comes from the doping dependence in Figs. 3 and 4. At high $n$ doping, there is a finite band bending within the mean free path of the electrons, which smears bulk-derived features, such as the 2.2 eV peak in inverse photoemission [Fig. 3(a)] and the Si $2p$ level in photoemission (Fig. 4; see the discussion in the Si $2p$ section). Surface states should not be affected by band bending, since they are located outside the band bending region.

In addition to these surface features, one expects to see two bulk interband transitions into the lowest two unoccupied bands $\Lambda_1$ and $\Lambda_3$, which are connected to the $L_1$ and $L_3$ points, respectively (Fig. 2). These have been mapped out at the cleaved Si(111)$2\times1$ surface,[18] where they are least perturbed by surface state emission. The energies of the bulk transitions move down in energy as the initial energy is increased, due to the perpendicular band dispersion of the bulk bands. For example, at an initial energy of 11 eV above $E_F$, the transition into the $\Lambda_1$ band occurs significantly higher than the surface feature at 2.2 eV (see the mark in Fig. 1) and produces an asymmetric, high energy tail. At an initial energy of 14.5 eV above $E_F$ (Fig. 2), the $\Lambda_1$ transition moves closer to the surface feature and merges with it. In addition, the $\Lambda_3$-band transition becomes visible.

The unoccupied surface state band in the band gap of Si agrees well with first principles, local density calculations of

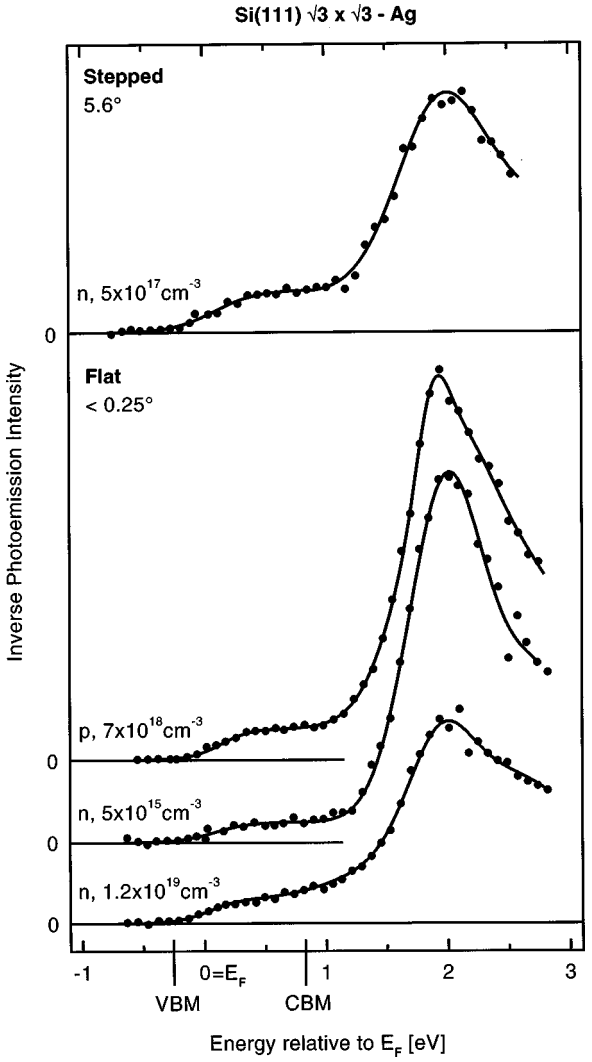


FIG. 3. Inverse photoemission spectra from Si(111)$\sqrt{3}\times\sqrt{3}$ Ag versus doping and versus step density. The broadening of the feature at 2.2 eV in the highly $n$-type sample ($1.2\times10^{19}$ cm$^{-3}$) is due to finite band bending within the probing depth.

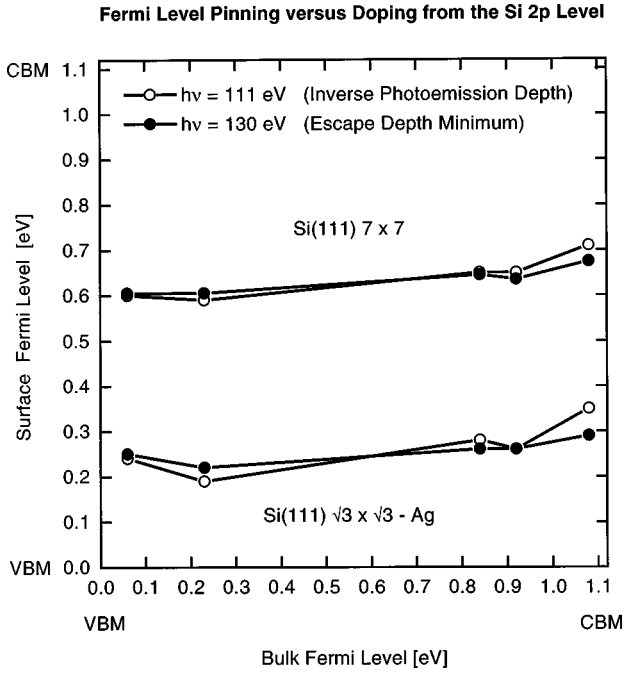


FIG. 4. Position of the Fermi level in the gap versus doping, obtained from Si $2p$ core level shifts. For both Si(111)$\sqrt{3}\times\sqrt{3}$ Ag and Si(111)$7\times7$ the Fermi level is nearly independent of doping, indicating a substantial density of states at the Fermi level. The photon energy $h\nu=130$ eV represent the surface, $h\nu=111$ eV the probing depth of inverse photoemission.

the electronic structure.[8,9] A strongly dispersing surface state band with a minimum at $\bar{\Gamma}$ is predicted,[9] with a minimum at about 0.3 eV above $E_F$. The strong dispersion of about 4 eV/Å$^{-1}$ gives a low density of states and broadens the transition over a wide energy range, due to the finite momentum resolution of the inverse photoemission setup ($\approx0.1$ Å$^{-1}$) and due to scattering of the electrons at the disordered boundaries between the $\sqrt{3}\times\sqrt{3}$ islands (uncertainty in $k\approx2\pi/d\approx0.04$ Å$^{-1}$ for an island diameter $d\approx15$ nm).

### Si $2p$ PHOTOEMISSION

For obtaining the density of states with higher resolution we have measured the doping dependence of the Si $2p$ core level position.[20] If a surface band gap exists, one expects the Fermi level to be pinned at the bottom of the surface gap for $p$-type substrates and at the top of the surface gap for $n$-type substrates. The cleaved Si(111)$2\times1$ surface and Si(100)$2\times1$ display such a behavior.[20] The jump in $E_F$ between $p$ and $n$ doping should be reflected in an equal jump in the energy of the Si $2p$ core level relative to the Fermi level. The shift of the Fermi level can be determined with 0.02 eV accuracy.[20] If there is a finite density of states at $E_F$, instead of a band gap, the Fermi level will shift gradually with doping, as space charge is being transferred to surface states at $E_F$. The higher the density of states at $E_F$, the smaller the shift for a given doping.

The Si $2p$ spectra were obtained at two photon energies, $h\nu=130$ eV and $h\nu=111$ eV, in order to vary the mean free path of the photoelectrons which determines the probing depth. The 130 eV data represent the surface (3.3 Å probing depth),[18] whereas the 111 eV data are selected because they cover the same probing depth as the inverse photoemission data in Figs. 1 and 3. At 111 eV, the energy of the Si $2p$ photoelectrons is identical to that of the electrons in the inverse photoemission spectrum at 11 eV above $E_F$, resulting in an identical probing depth (about 5–10 Å). For converting the binding energy of the Si $2p$ level relative to the $E_F$ into the position of $E_F$ relative to the VBM, as plotted in Fig. 4, we use the Si(111)$7\times7$ surface as reference. Its Fermi level has been determined previously[18] to lie 0.65 eV above the VBM. Any shift in the Si $2p$ spectrum relative to the undoped $7\times7$ surface determines the shift in the Fermi level relative to this reference. On the abscissa of Fig. 4, the various doping levels have been converted to the position of the Fermi level in the bulk. This emphasizes the difference between the Fermi levels at the surface and in the bulk, which is reflected in the band bending. Without surface states, the surface Fermi level would track the bulk Fermi level and give rise to a diagonal line in Fig. 4.

Focusing on the Fermi level position at the surface given by the 130 eV data (full circles in Fig. 4), we find very little variation over the doping levels studied, neither for the 7

$\times 7$ surface, nor for the $\sqrt{3}\times\sqrt{3}$-Ag surface. A small up-and-down movement of the Fermi level position with doping for the $\sqrt{3}\times\sqrt{3}$-Ag surface is attributed to a variation in step density between the samples. In general, we observe a higher Fermi level position (closer to that of the $7\times 7$ surface) for samples with higher step density. For example, the highly $p$-doped sample has a larger miscut than the others (about 10° versus $\frac{1}{4}$°). This explains the nonmonotonic behavior of the data points for the $\sqrt{3}\times\sqrt{3}$-Ag surface at the highest $p$ doping. The data can be summarized by a rigid shift in the Fermi level from 0.65 eV above the VBM for the $7\times 7$ to 0.25 eV above the VBM for the $\sqrt{3}\times\sqrt{3}$-Ag surface. A comparable shift of about 0.4 eV has been observed in previous Si $2p$ measurements,[2–5] which did not study the doping dependence. From the small Fermi level movement over such a wide doping range we conclude that there exists a significant density of states at the Fermi level at the Si(111)$\sqrt{3}\times\sqrt{3}$-Ag surface, which is comparable to that of the metallic Si(111)$7\times 7$ surface.

We also searched for shifts in the valence band spectra due to a movement of the Fermi level across a possible surface band gap. Some of our doping-dependent inverse photoemission spectra are shown in Fig. 3. We do not observe any significant shift within our resolution ($\approx 0.2$ eV), just a broadening for the highly $n$-type substrate which we attribute to the bending of the bulk bands within the probing depth. This is consistent with our Si $2p$ data at a photon energy of 111 eV, which corresponds to the same probing depth. The Si $2p$ spectrum is broadened at 111 eV for the $\sqrt{3}\times\sqrt{3}$-Ag surface with the highest $n$-type doping (not shown). A small shift of 0.06 eV in Fig. 4 between the 130 and 111 eV data points for this surface represents the average band bending within the probing depth.

## SCANNING TUNNELING SPECTROSCOPY

Another high resolution probe of the density of surface states in the gap region is scanning tunneling spectroscopy.[12,21] In planar tunneling, the derivative $dI/dV$ of a current-voltage curve is usually taken as first approximation of the density of states [Fig. 5(d)]. Its normalization strongly depends on the tip distance. In STM, the normalized version $(dI/dV)/(I/V)$ is often used as representation of the surface density of states[12,21] [Fig. 5(a)–(c)]. Operating at room temperature, an energy resolution in the order of $kT = 0.026$ eV can be expected in scanning tunneling spectroscopy. The STM spectrum for Si(111)$7\times 7$ in Fig. 5(c) is similar to previously published results,[18,21] showing a peak in the density of states due to the adatom surface state at $\approx 0.6$ eV above $E_F$ that corresponds to the peak seen by inverse photoemission in Figs. 1 and 2. The detailed line shape depends on the density of states of the tip. The Si(111)$\sqrt{3}\times\sqrt{3}$-Ag surface exhibits a nearly structureless, metallic density of states in the $(dI/dV)/(I/V)$ spectra. Only near the Fermi level ($V=0$) there exists a small dip in the density of states that becomes more pronounced as the tip is retracted [full symbols in Fig. 5(c)]. The dip could be a remnant of the $\approx 0.5$ eV band gap predicted by the calculations.[8,9] It can be fitted by a Gaussian with 0.4 eV full width at half maximum (FWHM), but this value is rather uncertain ($\pm 0.2$ eV) due to the unknown influence of the tip states and the complex nature of tunneling near band edges.[21] The density of states does not go to zero, however, as evidenced by the data with the closer tip spacing (open symbols). They give a larger signal near zero bias and, thus, are more reliable in this region. A previous scanning tunneling spectrum of Si(111)$\sqrt{3}\times\sqrt{3}$ Ag was taken in the $dI/dV$ mode.[12] It is qualitatively similar to our $dI/dV$ data in Fig. 5(d). Possible band edges are difficult to make out in this plot since the strong, exponential increase of the current with voltage simulates band edges that appear to change with tip-sample distance.

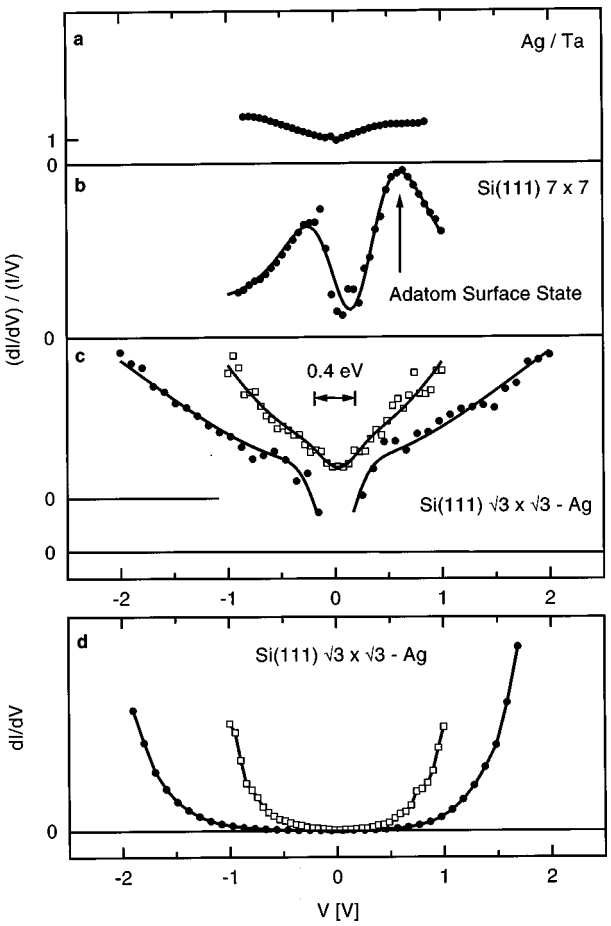


FIG. 5. Scanning tunneling spectra of (a) a metallic surface (Ag on polycrystalline Ta), (b) Si(111)$7\times 7$, (c) and (d) Si(111)$\sqrt{3}\times\sqrt{3}$ Ag. For Si(111)$7\times 7$, the adatom surface state can be seen (compare Fig. 1). The Si(111)$\sqrt{3}\times\sqrt{3}$-Ag surface exhibits a nearly metallic continuum. A $\approx 0.4$ eV wide dip at the Fermi level ($V=0$) indicates the possibility of a filled-in band gap. The two data sets for Si(111)$\sqrt{3}\times\sqrt{3}$ Ag are taken at different tip distances (full and open symbols).

The nearly metallic density of states inferred from the scanning tunneling spectra is consistent with the continuum of states seen by inverse photoemission and the pinning of the Fermi level detected by Si $2p$ photoemission. These results have to be reconciled with the semiconducting band gap suggested by the electron count and predicted by local density calculations. The simplest explanation is based on the band lineup. Photoemission data[5,6] indicate that the bottom of the surface conduction band nearly coincides with the top of the bulk valence band, i.e., the combined system surface+bulk is gapless. This effect alone would give semi-

metallic behavior. However, the Fermi level is pinned 0.25 eV above the bottom of the surface conduction band, which leads to a significant amount of extra charge in a normally empty band and to truly metallic character. Defect states can explain that. The charge might be donated by adsorbed Ag atoms.[6] Other electrically active defects might be generated dynamically due to thermal surface vibrations, or statically by the finite size of the $\sqrt{3}\times\sqrt{3}$-Ag domains. Previous STM work,[12,13] as well as our own observations indicate that ordered regions extend only over 10–20 nm. If we take the fairly steep band dispersion of about 4 eV/nm$^{-1}$ from local density calculations[9] together with the momentum broadening $\delta k \approx 0.04$ nm$^{-1}$ from the finite domain size we obtain an energy broadening of 0.16 eV.

## SUMMARY

In summary, we find clear evidence for an unoccupied surface state band at the Si(111)$\sqrt{3}\times\sqrt{3}$-Ag surface that extends throughout most of the band gap of Si, in agreement with first principles calculations. This is the band that gives rise to the characteristic honeycomb structure seen in STM images at positive sample bias. The surface is metallic, even though a surface band gap is predicted from calculations and from the even number of electrons in the surface unit cell. The metallicity is caused by a combination of two effects, i.e., the surface-to-bulk band lineup and surface doping by defect states.

## ACKNOWLEDGMENTS

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