ELECTRONIC STRUCTURE OF Si(111) SURFACES

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The relation of surface states and surface core levels to the surface geometry is discussed for Si(111) surfaces by comparing photoemission and inverse photoemission results with calculations for different geometries. It is shown that several sets of recent angle-resolved photoemission data for Si(111)-(2×1) and Si(111)-(7×7) are very similar to each other despite the fact that they have been interpreted in terms of different geometries. This indicates that no unique conclusions about the surface geometry can be drawn from the surface electronic structure. At present, only the traditional ionic buckling models can be ruled out rather safely. New information about unoccupied surface states in the gap of Si(111)-(7×7) is obtained from inverse photoemission data. The quenching behavior of occupied surface states under hydrogen exposure shows an unexpected band narrowing which helps identify the origin of surface state bands from the energy level of a localized state at 0.2 eV below the valence band maximum.

1. Introduction

The geometric and electronic structure of Si surfaces has attracted a lot of interest which has been nourished by the fact that models of all Si surfaces have remained controversial. Recently, the widely accepted ionic buckling model [1-7] has been shown to be incompatible with photoemission results [8] for the Si(111)-(2×1) surface and subsequent total energy calculations [9-11] have shown buckling to be unstable. In its traditional form [1-7], the buckling model predicts an ionic surface with almost a full electron per atom charge transfer from the rows of down atoms to the rows of up atoms. This charge transfer should result in a core level shift of 2-3 eV [10,12,13] between up and down atoms whereas only a shift of ≤ 0.6 eV has been observed for low step density Si(111)-(2×1) cleaves [14,15]. The valence states calculated for ionic buckled Si(111)-(2×1) also disagree with angle-resolved photoemission data which exhibit a qualitatively different band dispersion [8] along the high symmetry directions. A recent self-consistent band calculation [11] casts doubt on the earlier calculations by giving a much less ionic surface and different band dispersions. Nevertheless, this calculation stays incompatible with the photoemission results by resulting in a metallic surface and giving a strong
upwards dispersion of the surface state band from $I'$ to $J'$ (i.e., perpendicular to the rows of up and down atoms) while no dispersion (or a small downwards dispersion) is observed \[8,16,17\].

From these discrepancies between band calculations and photoemission results Himpsel et al. concluded \[8\] that either the geometry of Si(111)-(2×1) has not yet been determined unambiguously or that the surface states cannot be described by a band-like model. Both avenues have been pursued. A truncated bulk geometry \[9,10,18-20\] with slight inwards relaxation (∼0.2 Å) of the outermost layer has been shown to exhibit a local energy minimum \[9-11\] which can be lowered by antiferromagnetic arrangement of the dangling bond electrons \[9\]. For such a surface geometry one might expect localization and correlation of the electronic states to become important since surface atoms do not bond to each other directly (only via second layer atoms).

Different approximations for correlation result in different surface state bands some of which are compatible with the data (to be discussed in section 2). In contrast to these models, Pandey proposed a chain model \[21\] where the total energy is lowered by π-bonding beyond the value for the nearly-ideal antiferromagnetic structure \[11\] and showed that the broken bond states agreed with the strongest photoemission features of ref. \[8\]. Subsequently, Uhrberg et al. \[17\] reported that their band dispersions disagree with the band dispersions reported in ref. \[8\] and support the π-bonded chain model. It will be shown in section 2 that the two photoemission data sets are virtually identical and that the main difference lies in the interpretation of the data. In particular, peak positions agree within 0.07 eV and two surface states are seen at the $J$ point with similar intensity ratio. Therefore, no clear cut decision can be made about the geometric structure of Si(111)-(2×1) from the available photoemission data alone. Preferably, more direct probes of the surface geometry such as low-energy electron diffraction (LEED) or high energy ion channeling/blocking should be used to discriminate between the current models of the Si(111)-(2×1) surface. Alternatively, more studies of the surface electronic structure could provide some clues. In section 3, recent results about unoccupied surface states on Si(111) surfaces are presented which are obtained by angle-resolved inverse photoemission (or UV bremsstrahlung spectroscopy). Section 4 shows the effect of localizing the dangling bond states by partially covering the surface with hydrogen.

2. Comparison of photoemission results

Many photoemission studies have been performed for the cleaved Si(111)-(2×1) and the annealed Si(111)-(7×7) surfaces (see refs. \[8,16,17,22,23\] and references therein). Since the (2×1) surface has a simpler unit cell most first principles calculations of the electronic structure have concentrated on this
surface. Experimentally, good cleaves are difficult to prepare and the momentum information in angle-resolved photoemission data is perturbed by momentum transfer at cleavage steps or by the coexistence of several \((2 \times 1)\) domain orientations. Nevertheless, recent data \([8,16,17]\) exhibit a high degree of consistency. Along the \(\overline{1}\) line (the short axis of the surface Brillouin zone) a single surface state is seen \([8,16,17]\) which decreases in intensity going away from \(\overline{1}\). From \(\overline{1}\) to \(\overline{J}\) (i.e., along the long axis) an upwards dispersion of 0.6 eV is seen for the main surface state peak (see fig. 1). Around \(\overline{J}\) a weaker second state appears at the same energy as the \(\overline{1}\) state. The two states at \(\overline{J}\) are marked by ticmarks in fig. 2. Both data sets yield \(E(k)\) dispersions which agree to within 0.07 eV for all \(k\) points if peak positions are used to derive \(E(k)\) (see fig. 1). The discrepancy in band dispersions discussed by Uhrberg et al. \([17]\) is due to the fact that spectra were resolved into two peaks in ref. \([8]\), giving a smaller but perceptible dispersion with the largest \(E(k)\) discrepancy occurring at 0.75\(\overline{1}\), where both data sets show the same (within 30 meV) peak position. Half way between \(\overline{1}\) and \(\overline{J}\) there is room for a discrepancy since there are no data points in ref. \([8]\) near the band minimum observed by Uhrberg et al. \([17]\). However, the angular distribution pictures \([8]\) exhibit an intensity maximum at this point which could be interpreted as a critical point (e.g., a minimum). The two-peak interpretation \([8]\) is triggered by a correlated cluster calculation \([10]\)

SURFACE STATES OF Si(111) - (2x1)

![Surface States of Si(111) - (2x1)](image)

Fig. 1. Comparison of experimental surface state dispersions with theoretical band dispersions along the long axis \(\overline{1}\) of the surface Brillouin zone of Si(111)-(2×1). Full circles are from Himpsel et al. \([8]\) and open circles are from Uhrberg et al. \([17]\) using peak positions of angle-resolved photoelectron spectra. The full curve is a self-consistent band calculation for Pandey's \(\pi\)-bonded chain model \([21]\), where the dot-dash section is degenerate with bulk states. The two dashed curves are for a correlated cluster calculation of a relaxed antiferromagnetic surface by Redondo et al. \([10]\). Note that all data points could shift upwards by up to 0.15 eV using recent values for the Fermi level position \([28]\).
Fig. 2. Comparison of two recent data sets for the surface state at the \( \bar{\mathbf{J}} \) point of Si(111)-(2\( \times \)1) (upper panel from ref. [8], lower panel from ref. [17]). Two surface states (ticmarks) are seen with similar relative areas. The dashed line is for a H-covered surface where surface states are quenched.

(dashed lines in fig. 1) which predicts two surface state bands. This calculation can explain the second state at \( \bar{\mathbf{J}} \). The bandlike states expected from the \( \pi \)-bonded chain model [21] (full line in fig. 1) give qualitatively the correct dispersion but cannot explain a second surface state at \( \bar{\mathbf{J}} \). Uhrberg et al. [17] dismissed this structure by comparing with multidomain cleaves which can cause its intensity to become increased. Previously, we found that such multidomain cleaves resulted in irreproducible intensities for the two peaks in question. Rather than relying on multidomain cleave data, as done in ref. [17], one can use the best single-domain cleave data and come to the opposite conclusion, i.e., the extra lower peak (reproduced in ref. [17]) is an intrinsic feature of the Si(111)-(2\( \times \)1) cleavage surface. Namely, the intensity (i.e., the area) of the weaker peak in ref. [17] is very similar to the intensity of the
shoulder seen in ref. [8] whether normalized to the bulk, or to the lower state at \( \bar{F} \), or to the upper state at \( \bar{J} \) (see fig. 2).

We conclude that the available photoemission data cannot support or eliminate either of the two types of current models for Si(111)-(2 × 1). Both possibilities were used for the discussion of band models in ref. [8]. For example, if the one band interpretation (given originally by Pandey [21]) is correct, then the lower peak at \( \bar{J} \) indicates that the number of defects on the Si(111)-(2 × 1) cleavage plane cannot be reduced below a certain limit, at least in all photoemission experiments to date. This could be an intrinsic property of this metastable surface, e.g., a stabilization by steps [9]. Alternatively, it is quite possible that there are two excited surface state levels. Although correlated antiferromagnetic band calculations [9,19] give nearly flat bands, a fully correlated cluster calculation by Redondo et al. [10] gives two bands, with a strong dispersion of the upper state that is similar to the experimental data in refs. [8] and [17]. From the total energy calculations the \( \pi \)-bonded chain model appears to be most favorable [11]. However, one might argue that the Si(111)-(2 × 1) surface is metastable and does not have to exhibit the lowest total energy. Also, there is a possibility that a fully correlated (see ref. [10]) calculation might turn the energy balance around compared to the local density approximation used in refs. [9] and [11]. For example, the energy gain and the optimum relaxation distance for the relaxed 1 × 1 structure are less than half as large in the correlated cluster calculation [10] relative to the local density band calculations [9,11]. The strongest drawback of the antiferromagnetic model is the lack of atomic reconstruction which is in contrast to the strong second order spots seen with LEED.

3. Inverse photoemission results

Angle-resolved inverse photoemission or UV bremsstrahlung spectroscopy is the most direct experiment for measuring energy and dispersions of unoccupied surface states [24]. These states cannot be seen in photoemission since the interesting range between Fermi level and vacuum level is inaccessible. Other techniques like optical or electron energy loss spectroscopy (EELS) observe transitions from valence to conduction band states, but are hampered by a difficult interpretation which is due to excitonic effects (i.e., electron hole interaction). Inverse photoemission detects the radiation emitted in transitions from free-electron-like states \((\geq 10 \text{ eV above } E_F)\) into conduction band states and is the time reversed process of photoemission and, therefore, can give detailed information on unoccupied states as does photoemission on the occupied states.

The recent improvement of the energy resolution in UV bremsstrahlung spectroscopy [25] down to 0.3 eV enabled us to apply this technique for the
Fig. 3. Inverse photoemission spectra for a clean (line) and hydrogen-covered (dash) Si(111)-(7 × 7) surface taken with an electron beam of 20 eV energy coming in at an angle of 10° relative to the surface normal. Surface states in the band gap are quenched upon hydrogen adsorption. The difference spectrum (lower half of the figure) shows that the surface states extend down to the Fermi level in agreement with other experiments finding a metallic behavior of this surface (ref. [22]). The difference spectrum is broader than the experimental resolution (shown for two δ-functions at $E_F$ and $E_F + 0.4$ eV) indicating several surface states or a surface state band.

For the clean Si(111)-(7 × 7) surface we see clearly intensity between the Fermi level (calibrated relative to a gold sample) and the conduction band minimum $E_c = E_F + 0.53$ eV [28], which is quenched upon hydrogen adsorp-
This evidence of a surface state is seen even better in the difference spectra (fig. 3), where we note that the peak of the surface state lies below the conduction band minimum and emission is seen down to the Fermi level. This agrees favorably with the metallic behavior observed for this surface [22]. In the lower part of fig. 3 we show the resolution function (FWHM = 0.4 eV) for this experiment, which is significantly narrower than the measured surface state. We tentatively explain the measured difference spectrum by two peaks centered at $E_F$ and $E_F + 0.4$ eV, but, regarding the statistics of the data, further experiments are necessary to prove this interpretation. However, the existence of empty surface states below the conduction band minimum extending down to the Fermi level for the Si(111)-(7 × 7) surface is out of question.

4. Quenching of surface states by hydrogen

We have observed an interesting effect when the surface states on Si(111) surfaces are quenched by gradually saturating all dangling bonds with hydrogen. As shown in fig. 4, one sees a single dangling bond surface state for surfaces partially covered with H compared to two dangling bond features for the clean surface (see ticmarks). The double structure narrows gradually upon H adsorption until both features merge into a sharp level at 0.2 eV below the valence band maximum for an isolated dangling bond.

In a band picture, the two ticmarked features on the clean 2 × 1 surface correspond to critical points of a single surface state band [21]. In the limit of an almost full monolayer coverage there are only isolated dangling bonds left with no band dispersion. All features belonging to the same surface state band can be identified because they collapse into the same sharp state upon hydrogen exposure. For the Si(111)-(2 × 1) surface our observations are compatible with the bands derived from the chain model. For the Si(111)-(7 × 7) surface the two uppermost surface states (see fig. 4 ticmarks) could be [27] related to the same energy band if the band picture is correct. This is consistent with the symmetry of these states as determined by polarization selection rules [8,16,22].

In a localized picture the splitting between surface states can be explained either by the fact that there are at least two inequivalent dangling bonds for a reconstructed surface [9,27] or by the existence of different (e.g., symmetric versus antisymmetric) ion states which are split by correlation effects [10]. In the first case, the disappearance of the splitting on the Si(111)-(2 × 1) surface is clear since this surface transforms into a (1 × 1) structure upon hydrogen adsorption. The (7 × 7) surface transforms into a (7 × 1) surface and one might expect a residual splitting. In the second case, one would expect a decrease of the splitting with H coverage, too, since the dangling bonds adjacent to the ionized dangling bond become saturated by H and do not interact with the ion state.
Fig. 4. Transition from interacting bonds to an isolated dangling bond state for Si(111) surfaces. For the clean surfaces the dangling bond states are split (ticmarks) but they collapse into a sharp state (ticmarks) upon saturating neighboring dangling bonds with hydrogen; note refs. [27,28]. Exposures range from 60 to 2000 L of hydrogen activated by a W filament.

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Note added in proof

Recently, Houzay et al. [29] have obtained band dispersions along both symmetry directions of Si(111)-(2 × 1) which are very similar to the results discussed here [8,17] including the second structure at ḟ.
References

[15] S. Brennan, J. Stöhr, R. Jaeger and J.E. Rowe, Phys. Rev. Letters 45 (1980) 1414. These authors report a somewhat larger total splitting of 0.9 eV which could be due to different line shape fitting procedures, to different light polarization, or to higher step density. For high step density cleaves, we find a broader surface core level spectrum.
[28] All energies are measured with respect to the Fermi level $E_F$ and have previously been referenced to the top of the valence band $E_V$ using $E_F - E_V = 0.33$ eV for Si(111)-(2x1) from F.G. Allen and G.W. Gobeli, Phys. Rev. 127 (1962) 150. C. Sebenne et al. (Phys. Rev. B12 (1975) 3280) have obtained $E_F - E_V = 0.48$ eV and recent core level measurements (F.J. Himpsel, G. Hollinger and R.A. Pollak, unpublished) give $E_F - E_V = 0.41$ eV. This value has been used for figs. 3 and 4 whereas figs. 1 and 2 use the value of Allen and Gobeli. Relative to Si(111)-(2x1), $E_F - E_V$ is 0.18 eV larger for Si(111)-(7x7) [14].