

Determination of the Fermi-level pinning position at Si(111) surfaces

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The position of the Fermi level E_F relative to the valence-band maximum E_V has been determined from accurate measurements of the Si $2p$ core-level position relative to E_F . As a reference, we use p -doped samples with a Ga overlayer and n -doped samples with a Cs + O overlayer where E_F is pinned near the valence-band maximum and conduction-band minimum, respectively. We obtain $E_F - E_V = 0.40 \pm 0.03$ eV for low-step-density cleaved Si(111)-(2x1) and $E_F - E_V = 0.63 \pm 0.05$ eV for annealed Si(111)-(7x7). Stepped cleavage surfaces are characterized by $E_F - E_V = 0.46$ eV and exhibit larger surface core-level shifts and a shift of the dangling-bond states towards lower binding energy.

I. INTRODUCTION

At all silicon surfaces and interfaces studied so far the Fermi level E_F is pinned by a large density of surface (interface) states in the gap (typically, one broken-bond electron per atom). The pinning position of E_F determines the Schottky-barrier height¹⁻³ in Si-metal contacts which is given by $\phi_n = E_C^S - E_F$ and $\phi_p = E_F - E_V^S$ for n - and p -type substrates, respectively [E_C^S is the conduction-band minimum, E_V^S is the valence-band maximum at the surface (interface), and $E_C - E_V = 1.12$ eV in the bulk at room temperature²]. Another important motivation to measure $E_F - E_V^S$ is given by the fact that calculations of surface states at semiconductor surfaces reference their energies to E_V^S while most experiments have E_F as a reference level. Consequently, several measurements were performed⁴⁻¹¹ to measure $E_F - E_V^S$ at silicon surfaces, mostly for the cleaved Si(111)-(2x1) surface. However, the reported values differ considerably ranging from the most commonly used value $E_F - E_V^S = 0.32$ eV given by Allen and Gobeli⁴ to $E_F - E_V^S = 0.48$ eV given by Sebenne *et al.*⁹ Surprisingly, both results came from the same type of measurement. The well-known work function $E_{vac} - E_F = 4.85 \pm 0.04$ eV (E_{vac} is the vacuum level) of Si(111)-(2x1) was subtracted from the ionization energy $E_{vac} - E_V^S$ which was obtained from the photoelectric yield near threshold. The difficulty with this measurement is to separate the contributions from bulk and surface states¹² to the photoelectric threshold. This problem is much less serious when the Si $2p$ core levels are used as a reference. They have a constant binding energy relative to the valence band throughout the band-bending region. Compared with the valence-band edge the Si $2p_{1/2,3/2}$ levels are sharp (≈ 0.2 eV intrinsic width) and the emission from surface core levels affects the bulk Si $2p$ line shape much less than surface states affect the valence-band edge.

The measurement method adopted here is illustrated in Fig. 1. Similar ideas have been developed¹³⁻¹⁸ previously and are currently used to determine changes in barrier height by measuring changes in the binding energy (vertical dotted lines in Fig. 1) of the sharp Si $2p_{3/2}$ core level with respect to E_F . However, no accurate absolute mea-

surement has been reported. In order to obtain absolute barrier heights, we have moved the Fermi level very close to the band edges by evaporating Cs + O and Ga overlayers onto cleaved highly doped Si(111) surfaces (see left- and right-hand panels of Fig. 1, respectively). In both cases we create a nearly-flat-band situation where the

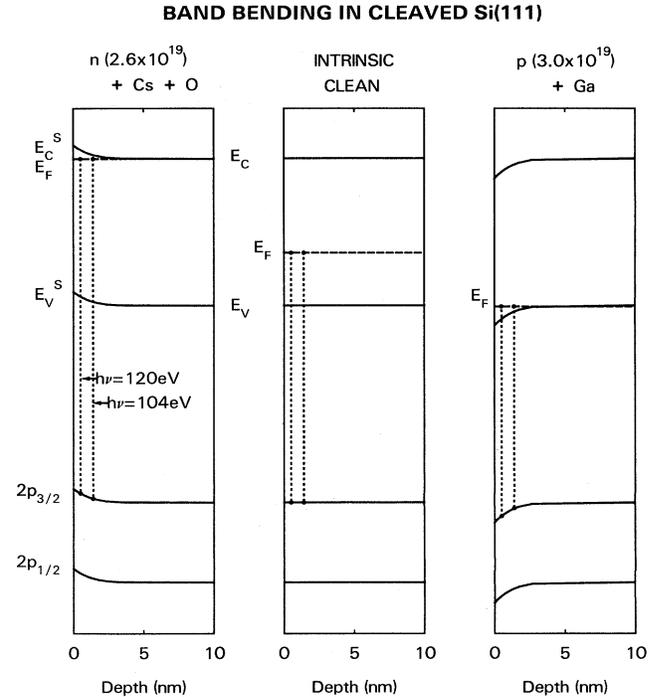


FIG. 1. Energy-vs-position diagram illustrating the measurement method for determining the Fermi-level pinning position at the surface of cleaved silicon. The binding energy of the Si $2p_{3/2}$ level is measured relative to the Fermi level E_F (vertical dotted lines). As a reference, highly doped samples with overlayers are used where the Fermi level is pinned near the bulk position (left- and right-hand panels). The remaining amount of band bending is determined by performing measurements at two different probing depths.

well-known bulk Fermi-level position³ relative to the band edges can be used as a reference for measuring the Fermi-level position at the surface, i.e., the barrier height. The residual band bending is determined by performing two measurements with different surface sensitivity [about 5 Å for $h\nu=120$ eV (Refs. 14 and 15) and 12–25 Å near the photothreshold,^{4,9} i.e., $h\nu\approx 104$ eV] and extrapolating towards the bulk. High doping allows us to see about halfway through the band-bending region in the bulk-sensitive mode (see Fig. 1, $h\nu\approx 104$ eV).

II. EXPERIMENTAL

The measurements were performed with an ellipsoidal-mirror spectrometer in the angle-integrating mode¹⁹ and synchrotron radiation from the storage ring Tantalus I. The total-energy resolution was about 0.25 eV which matches the intrinsic width of the Si $2p$ level [~ 0.2 eV (Ref. 14)]. In order to obtain accurate line shapes (see Fig. 2) the secondary-electron background was measured by lowering the photon energy below the Si $2p$ photothreshold and by matching the background spectrum at the high-kinetic-energy side to the core-level spectrum. Subsequent spin-orbit decomposition is used to select the stronger Si $2p_{3/2}$ level. The spin-orbit splitting was fixed at 0.61 eV and the branching ratio was adjusted since it varies strongly near threshold. For example, the Si $2p_{3/2}$ peak is enhanced relative to the Si $2p_{1/2}$ peak in Fig. 2 due to excitation into an energy region with high density of final states which shows up as a broad maximum in the background of secondary electrons (see the $h\nu=101$ eV

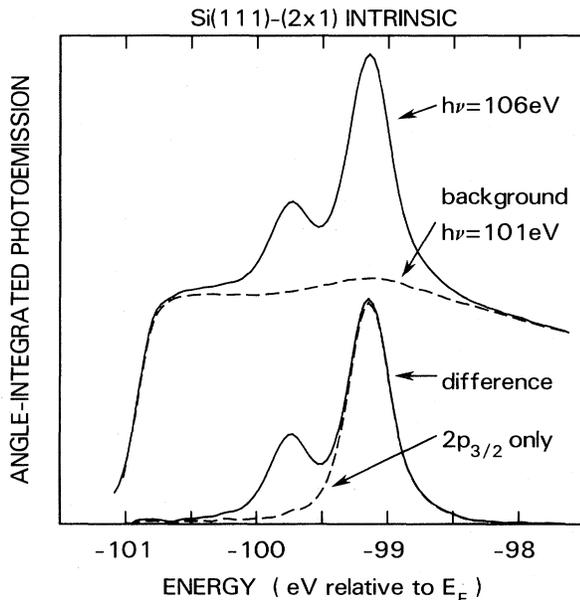


FIG. 2. Raw data are shown for a Si $2p$ core-level photoemission spectrum ($h\nu=106$ eV). Corresponding secondary-electron background was taken at lower photon energy ($h\nu=101$ eV) for the same kinetic-energy range. After background subtraction the spectrum is decomposed into two identical lines ($2p_{1/2}$ and $2p_{3/2}$) with different intensities and a spin-orbit splitting of 0.61 eV.

spectrum). The binding energy of the Si $2p_{3/2}$ level at the surface of low-step-density cleaved Si(111) was found to be 99.14 ± 0.15 eV (below E_F). This absolute measurement is much less accurate than then Fermi-level pinning measurement. The latter uses only differences in binding energies which were reproducible within 0.015 eV.

The samples used for the calibration experiment were intrinsic (B-doped 3×10^{15} cm⁻³) and highly p -type (B-doped 3.0×10^{19} cm⁻³) and n -type (As-doped 2.6×10^{19} cm⁻³) Si(111) surfaces (as measured with a Hall-effect probe). They were cleaved in the $[\bar{2}11]$ direction at 10^{-10} Torr vacuum. Ga and Cs overlayers were evaporated onto fresh cleaves in order to move the Fermi level towards the band edges. This could only be accomplished when about a monolayer was reached and, in the case of Cs only when some oxide was present in the overlayer. In addition, we have prepared clean, intrinsic Si(111)- (7×7) surfaces by stripping the oxide from Si(111) wafers with buffered HF prior to insertion through a vacuum interlock and by subliming residual suboxides from the surface at 900–1000°C *in situ*. Some samples were not etched and heated to higher temperatures (1100–1200°C) in order to evaporate the more stable SiO₂ layer. All evaporations were done in a preparation chamber separated from the spectrometer by a bakable valve. This avoids work-function alterations in the spectrometer.

III. CALIBRATION OF THE Si $2p_{3/2}$ POSITION

In Fig. 3 (top) the Si $2p_{3/2}$ spectra (obtained as in Fig. 2) are shown for a photon energy ($h\nu=106$ eV) near threshold where they are bulk sensitive (≈ 12 -Å escape depth). The band-bending conditions for the clean intrinsic cleaves, for n -type cleaves with a Cs + O overlayer and for p -type cleaves with Ga overlayer are shown in Fig. 1. The Si $2p_{3/2}$ core-level binding energies vary over almost the full gap energy which shows that we were able to move the Fermi level close to the band edges. The distance between the band edges is represented by vertical lines in Fig. 3. The core-level binding energies range between 99.83 eV (n -type Si(111) + Cs + O, $h\nu=103.5$ eV) and 98.78 eV (p -type Si(111) + Ga, $h\nu=104.5$ eV). These values alone are sufficient to derive an upper (lower) limit for $E_F - E_V^S$ of the intrinsic cleavage surface where we measure a core-level binding energy of 99.14 eV. For the n -type + Cs + O sample we conclude (see Fig. 1) that $E_F - E(2p_{3/2}) \geq 99.83$ eV in the bulk. Using the bulk Fermi-level position $E_F - E_V = 1.12$ eV (Refs. 2 and 3) we get $E_V - E(2p_{3/2}) \geq 98.71$ eV and use this result to obtain $E_F - E_V^S \leq 0.43$ eV for the intrinsic cleave. Similarly, one derives $E_F - E_V^S \geq 0.34$ eV for the intrinsic cleave from the p -type + Ga sample.

The accuracy of the measurement is increased by extrapolating the core-level positions towards their bulk value using spectra taken with different surface sensitivity (see pairs of dotted lines in Fig. 1). The tuning of the surface sensitivity has been demonstrated in Ref. 14 for clean highly doped cleaves. For these surfaces the Fermi level is pinned in a position very close to the intrinsic value^{4,9,14} due to the high density of surface states in the gap. Indeed, in surface-sensitive spectra at $h\nu=120$ eV (not shown) we find the Si $2p_{3/2}$ peak positions within ± 0.13

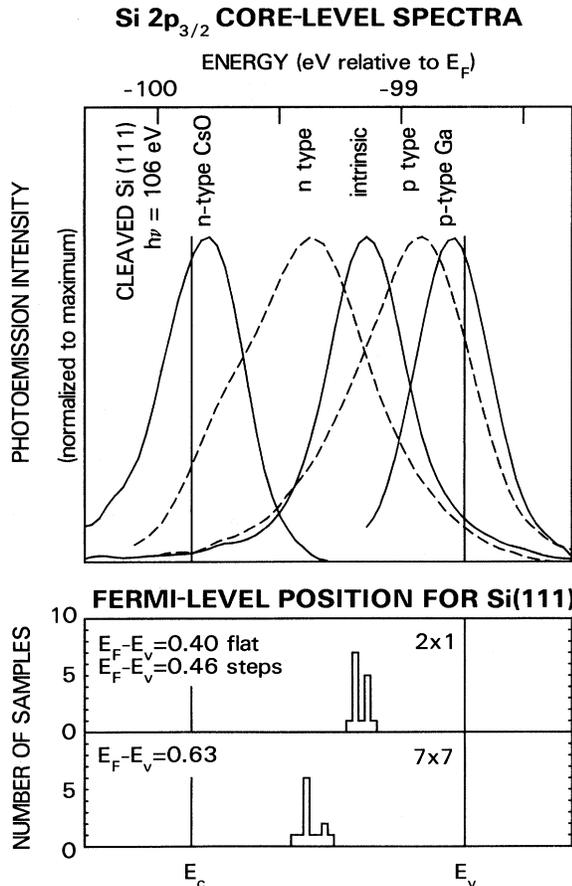


FIG. 3. Bulk-sensitive Si $2p_{3/2}$ core-level spectra (top panel) demonstrate that the Fermi-level E_F can be moved close to the band edges by evaporating overlayers onto highly doped cleaved Si(111) surfaces. As a result the Si $2p_{3/2}$ binding energies relative to E_F span almost the band gap (vertical lines). Bottom panel shows distributions of Fermi-level pinning positions for different intrinsic Si(111) surfaces obtained from their Si $2p_{3/2}$ peak positions.

eV independent of doping.²⁰ At lower photon energies (e.g., dashed lines for $h\nu=106$ eV in Fig. 3) the probing depth is increased and the average core-level positions are about halfway between their value at the surface (intrinsic spectrum in Fig. 3, top) and in the bulk (vertical lines in Fig. 3, top). In addition, the band bending within the sampling depth shows up as broadening of the core-level spectra (compare Ref. 14).

For highly doped cleaves with overlayers a similar dependence of the core-level position on probing depth is observed, only the magnitude of the effect is reduced due to the smaller band bending. Therefore, the extrapolation towards the bulk core-level positions involves only small energies (≈ 0.04 eV) and becomes much more accurate than for cleaves without overlayers. For our extrapolation we have used the band bending obtained from solving Poisson's equation^{2,3} (shown in Fig. 1). For the highly doped samples with overlayers the Fermi level is halfway between its surface and bulk position at a distance of

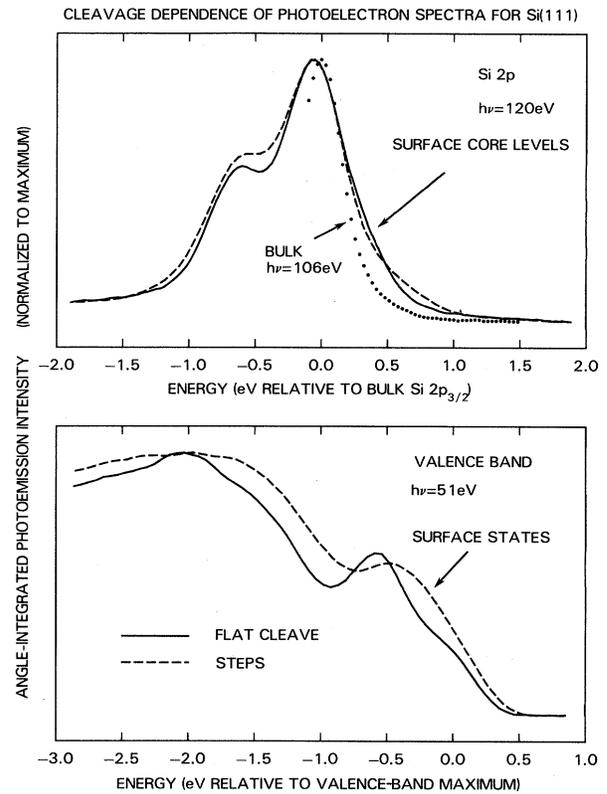


FIG. 4. Photoemission spectra of surface states and surface core levels are shown for two types of cleaves. For the Si $2p$ core levels a bulk-sensitive spectrum at $h\nu=106$ eV (~ 12 -Å depth) is compared with surface-sensitive spectra at $h\nu=120$ eV (~ 5 -Å depth) with the secondary-electron background subtracted.

9 Å from the surface. We have assumed equal probing depths for p - and n -type samples at the same electron energies. Essentially, the five different Si $2p_{3/2}$ binding energies shown in Fig. 1 have been used to determine the following five quantities: The $2p_{3/2}$ binding energy relative to the bulk valence-band maximum $E_V - E(2p_{3/2}) = 98.74$ eV, the Fermi-level pinning at the surface $E_F - E_V^S$ for the three cases shown in Fig. 1 (1.01, 0.40, and 0.15 eV), and the probing depth near threshold (≈ 14 Å). For any other intrinsic sample we obtain directly the position of E_F relative to E_V^S by subtracting 98.74 eV from the measured binding energy of the Si $2p_{3/2}$ level relative to E_F .

IV. RESULTS FOR INTRINSIC SURFACES

After calibrating the core-level binding-energy scale relative to the band edges as described we have determined Fermi-level pinning positions for clean intrinsic Si(111) surfaces. The results are shown in histogram form in the bottom panel of Fig. 3. For the cleaved Si(111)-(2×1) surface we find a distribution of Fermi-level pinnings with two peaks at $E_F - E_V^S = 0.40$ and 0.46 eV which appear to have δ -function character within our reproducibility of ± 0.015 eV. The two pinning positions are correlated with different types of cleaves [flat cleavage planes versus

curved cleavages with high step density and a streaked low-energy electron-diffraction (LEED) pattern]. For the annealed Si(111)-(7×7) surface we find a distribution of pinning positions centered around $E_F - E_V^S = 0.63$ eV which can be resolved into two peaks at $E_F - E_V^S = 0.58$ and 0.66 eV. These two peaks correspond to different sample-preparation methods (subliming SiO₂ at 1100–1200°C and etching-plus-subliming SiO at 900–1000°C, respectively), but the existing amount of data is not sufficient to establish a firm correlation. The Fermi-level position should be rather stable for well-ordered (7×7) surfaces since a surface state close to the Fermi level²¹ (within 0.1 eV) provides a high density of states for pinning. There is a significant difference of about 0.2 eV in the Fermi-level pinning between the cleaved and annealed Si(111) surfaces in agreement with recent measurements [0.30 eV (Ref. 10) and 0.18 eV (Ref. 15)].

The surface electronic structure is correlated with the cleavage type as shown in Fig. 4. The flat cleaves have a characteristic double-surface-state structure with a peak at $E_V - 0.6$ eV and a shoulder at E_V . These features can be assigned to dangling-bond states at the center and at the short boundary of the surface Brillouin zone,²² respectively. The stepped cleaves have a single smeared-out state shifted towards lower binding energy. The stronger tailing into the band gap explains the higher Fermi-level pinning position. The $2p$ core-level spectra exhibit extra surface emission on both sides of the bulk peak when the surface sensitivity is high ($h\nu = 120$ eV). For flat cleaves with $E_F - E_V^S = 0.40$ eV the spectra are reproducible (within two linewidths of the drawing) and exhibit a considerably narrower distribution of surface core-level emission than for stepped cleaves. For example, the difference curve [$h\nu = 120$ eV minus $h\nu = 106$ eV (not shown)] has the main structure at 0.3 eV above the bulk position for low step density and an additional structure at 0.6 eV for the high step density. Also, the valley between the $2p_{3/2}$ and $2p_{1/2}$ spin-orbit partners is filled for stepped cleaves. This finding is able to resolve a discrepancy in previously reported surface core-level shifts for Si(111)-(2×1) which range from 0.37 eV (Ref. 15) to 0.59 eV (Ref. 23) for the surface core levels with lower binding energy (see Fig. 4).

It could be that the latter data were taken on stepped cleaves although different fitting procedures can explain part of the discrepancy for this weakly split off surface core level. The influence of steps on the electronic structure of cleaved Si(111) has been studied previously²⁴ in order to resolve states associated with steps. In view of the observation²⁴ that about 25-Å-wide areas around a step edge are unreconstructed one should expect the principal contribution to come from these (1×1) areas rather than from the step edge itself. Thus, stepped cleavage surfaces might shed some light on the electronic structure of Si(111)-(1×1).²⁵

Our results for cleaved Si(111)-(2×1) can be compared to a variety of previous measurements^{4–10} of $E_F - E_V^S$. Most notable is the low value of $E_F - E_V^S = 0.32$ eV obtained from the difference between the (bulk) photoelectric threshold of 5.15 ± 0.08 eV and the work function of 4.83 ± 0.07 eV in the early work of Allen and Gobel.⁴ Similar values have been used predominantly in the literature despite the fact that Sebenne *et al.*⁹ found $E_F - E_V^S = 0.48$ eV which was based on a different bulk photoelectric threshold (5.35 ± 0.02 eV) but similar work function (4.87 ± 0.02 eV). This higher value is consistent with our determination ($E_F - E_V^S = 0.40$ and 0.46 eV for cleaves with low and high step density, respectively) within our error margin of ± 0.03 eV.²⁶ The use of such a value for $E_F - E_V^S$ improves the agreement between experiment and theory for the surface-state band dispersion^{27,28} on Si(111)-(2×1) using Pandey's chain model. In Schottky-barrier-height measurements the consistency between the core-level-based UHV data from thin films and conventional $I-V$ and $C-V$ measurements on actual junctions can be tested more stringently.^{1,29,30}

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- ³⁰Our Schottky-barrier heights differ from the values reported by J. D. van Otterloo [*Surf. Sci.* **104**, L205 (1981)] for Ga (*p*-type barrier of 0.45–0.52 eV) and for Cs (*n*-type barrier of 0.62–0.67 eV) on cleaved Si. For clean Cs we obtain similar barrier heights and only admixture of impurities such as oxygen provides a low barrier. A previous study of Ga on intrinsic cleaved Si (Ref. 16) gave results very similar to ours if the difference in calibration is taken into account [the Allen and Gobel (Ref. 4) value for the Fermi-level pinning on clean Si(111) was used in Ref. 16].