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Determination of band bending at the Si(113) surface from photovoltage-induced core-level shifts

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The Si 2p core levels were measured by photoelectron spectroscopy with use of synchrotron radiation for the clean Si(113) 3×2 surface. The core levels exhibit shifts of several hundred meV during the change of sample temperature from 300 to 20 K. We interpret these shifts as due to a release of band bending by saturation surface photovoltage. Together with core-level spectroscopy, this turns out to be a new, highly accurate method in determining Fermi-level pinning. For the clean Si(113) 3×2 surface the pinning position coincides within 25 meV for n- and p-type doped samples. At 20 K, a strong reduction of the Si 2p linewidth is found for the p-type sample, which is only to a lesser degree due to band flattening. An intrinsic linewidth of the Si 2p core level of 205 ± 30 meV is derived.

I. INTRODUCTION

For silicon surfaces and interfaces it is well known that the Fermi level E_F is pinned in the energy gap by surface states (SS).[1] The equilibration of E_F in the bulk and at the surface is established through the formation of a depletion layer and through the bending of the bands within this layer. Therefore, the Fermi-level position at the surface cannot simply be derived from its bulk value but has to be measured separately for every surface, each of which may differ by crystallographic orientation and reconstruction. For this purpose, both E_F and E_V (the valence-band maximum) have to be determined separately. E_F can easily be measured by photoemission from any metallic part in contact with the Si sample, e.g., the sample holder. On the other hand, E_V can be determined simply through neither photoemission from valence bands, nor through yield spectroscopy[2,3] nor through surface photovoltage (SPV) measurements,[4–7] since the density of states at E_V is small and the bulk states overlap with SS. Instead of determining E_V directly, the Si 2p core levels have been used for this purpose under the reasonable assumption that valence and core levels move equally with the surface potential. This method turns out to be especially accurate when changes in core-level binding energy are used to determine changes in E_V. An accuracy of ±15 meV has been reached for this mode,[8] which we will confirm in the following.

Here we use the temperature-dependent SPV, which was recently observed with valence-band photoemission by Demuth *et al.*,[9] and combine it for the first time with core-level spectroscopy to increase the accuracy of band-bending determination. The SPV phenomenon has been well-known for years:[10–12] photons, impinging onto a semiconductor surface, generate excess carriers through band-to-band transitions whereby the SS play a role in the trapping and recombination of these excess carriers. At a semiconductor surface, the surface photovoltage (SPV) can be observed,[4–7] and was studied on Si surfaces several years ago.[6,7] There are only very few observations of SPV effects in photoemission.[13,14] For Si surfaces, the effect is too small to be observable at room temperature. Quite obviously, the situation changes when cooling down at 20 K: the SPV becomes several 100 meV large and saturates below 50 K.[9]

In a project on high–Miller-index semiconductor surfaces we are studying the (113) faces of Si and Ge. For Si(113) we have learned to prepare the clean, (3×2)-reconstructed surface.[15] We have also found by photoemission from the valence band with He *I* radiation that an SPV builds up at 20 K, similar to results found by Demuth *et al.*[9] Here we use core-level spectroscopy with synchrotron radiation to increase the accuracy of band-bending determination. We have studied both p-type and n-type samples which have shown core-level shifts into opposite directions. We will confirm that the observed core-level shifts are due to the flattening of the bands, and derive the band bending at the Si(113) surface. At 20 K we observe a remarkable sharpening of the Si 2p spectrum, which leads to the determination of its intrinsic linewidth, and points to some so far unobserved influence of electron-phonon interaction on photoemission linewidth.

Our paper is organized as follows. After some remarks on the experimental setup, we present the temperature-dependent Si 2p core-level spectra and discuss the effect of surface photovoltage in Sec. III A, derive the band-bending and E_F pinning position for both p- and n-type Si(113) surfaces in Sec. III B, and finally discuss the change of linewidth of the Si 2p core level at 20 K in Sec. III C.

II. EXPERIMENT

The experiments were carried out in a UHV μ-Metal chamber with a basic pressure of 3×10^{-11} mbar. The core-level spectra were measured with an angle-resolving spectrometer (VG Scientific ADES-400) in normal emission. Energy and angle resolution were $\Delta E = 100$ meV and $\Delta\theta = \pm 1.5°$. Synchrotron radiation was supplied by the torroidal grating monochromator 3 (TGM 3) at the Berlin synchrotron facility BESSY (Berliner Elektronenspeicherring-Gesellschaft für Synchrotronstrahlung). Sample mounting and preparation have been described elsewhere.[15] Both *p*-type (B-doped, 2.5×10^{17} cm^{-3}) and *n*-type (Sb-doped, 2.3×10^{18} cm^{-3}) samples have been investigated. By using liquid He, the samples could be cooled down to 20 K. The temperature was measured by a Pt-PtRh thermocouple spot welded to the sample holder beneath the sample. Between 800 and 1200 K the readings of the thermovoltage were calibrated using an ir pyrometer. The final temperature of the sample during He cooling is estimated as 20±10 K from our experiments of condensing multilayers of Xe and from other experimental experiences with similar sample holders in our laboratory. The final sample preparation was achieved by repeated cycles of Ar-ion sputtering and annealing to 1200 K.

The clean Si(113) surface is characterized by a 3×2 reconstruction and a strong dangling-bond emission with a mean energy of about 0.35 eV below E_V.[15] The surface cleanliness and structure were controlled by Auger-electron spectroscopy (AES), low-energy electron diffraction (LEED), and valence-band ultraviolet photoemission (UPS).

III. RESULTS AND DISCUSSION

A. Surface-photovoltage-induced core-level shifts

Figures 1 and 2 exhibit typical Si 2*p* core-level spectra measured for the Si(113) surface at 300 and 20 K. The double peak of each curve is due to the Si $2p_{1/2}$ and $2p_{3/2}$ spin-orbit-split components which are separated by 605 meV according to the curve-fitting procedure described below. These measurements have been performed while carefully keeping fixed all settings of the spectrometer and the monochromator of synchrotron radiation during a single filling of the storage ring. The time for cooling the sample from 300 to 20 K was only 30 min., so that it is certain that at a total pressure of 5×10^{-11} mbar no change of band bending due to any adsorbate could occur. Therefore, the changes of the spectra in Figs. 1 and 2 are solely due to the temperature change. Two effects are induced by the change in temperature: (1) a shift of the double peak to higher kinetic energies for the *p*-type sample and to lower kinetic energies for the *n*-type sample, and (2) an essential sharpening of the peaks at 20 K. The change of the shift direction between the *p*- and *n*-type samples points immediately to a band-bending effect.

For the discussion we have schematically sketched the band-gap region for both *p*- and *n*-type samples near the surface, i.e., depicting the depletion layers in Fig. 3. We have assumed a constant SS density throughout the gap and a midgap pinning position. For 300 K we have indicated some band bending typical for Si surfaces. For 20 K we have assumed a flat-band condition. Core levels for the surface atoms are indicated in the lower part of Fig. 3. They are bound in energy to the band edges. Their shift in energy schematically reproduces the experimental results of Figs. 1 and 2.

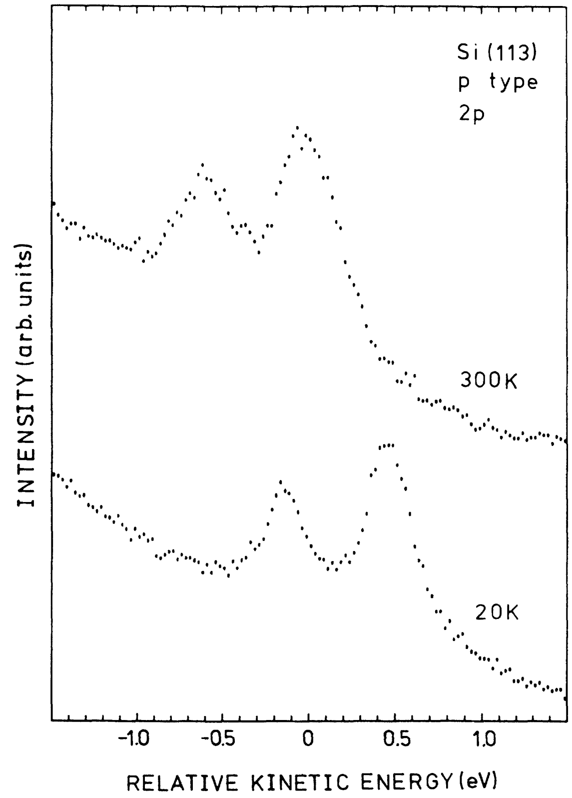

FIG. 1. Si 2*p* core-level spectra for two different sample temperatures of 300 and 20 K. The Si $2p_{1/2}$ and $2p_{3/2}$ spin-orbit components are well resolved in each case. The energy is given relative to the energy for the $2p_{3/2}$ component at 300 K. The spectra are taken at normal emission with the *p*-polarized synchrotron light coming in at 45° with respect to the surface normal. Energy of the light is $\hbar\omega = 108.0$ eV. The measurements are for a *p*-type Si(113) surface.

The 300 K part of Fig. 3 is well understood. E_F is pinned by SS at the surface which has several consequences. For *n*-type material, with E_F (in the bulk) above the midgap position, some negative charge flows into the SS. This charge is then compensated by a space charge of ionized donors. This gives rise to an upward band bending and a depletion of majority carriers (electrons), i.e., to a depletion layer. A completely analogous situation is found for *p*-type material: Some positive charge is left at the surface, which is compensated by a space charge layer of negatively charged acceptor levels. The bands are bent downwards, and no charge carriers (holes) are left in this region. We have sketched a symmetric situation so that the band edges at the surface have the same energy for both the *p*-type and *n*-type surfaces and therefore the (hatched) core levels have the same energy.

Now we briefly introduce the effect of the photovoltage. It has been known for a long time that when light is shining onto a semiconductor, the potential is changed by the photovoltage. In modeling this effect, the following processes have to be taken into account: creation of

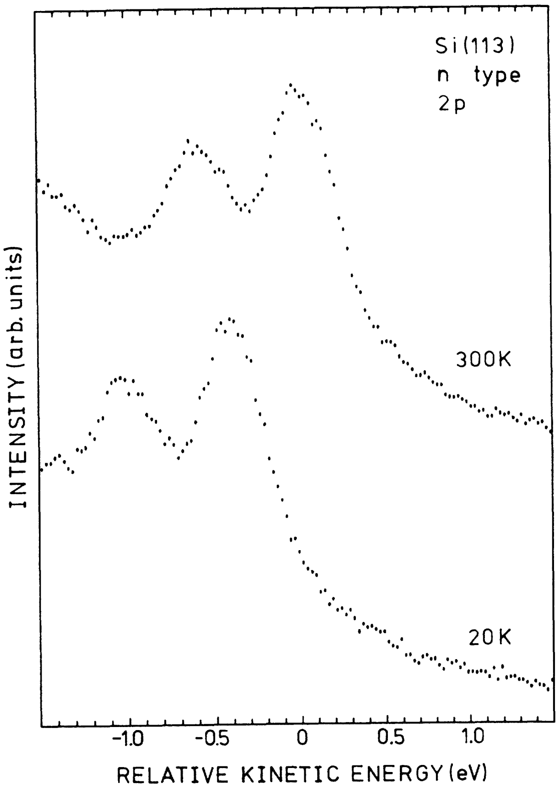

FIG. 2. The measurements are for an *n*-type Si(113) surface. The other parameters are the same as for Fig. 1.

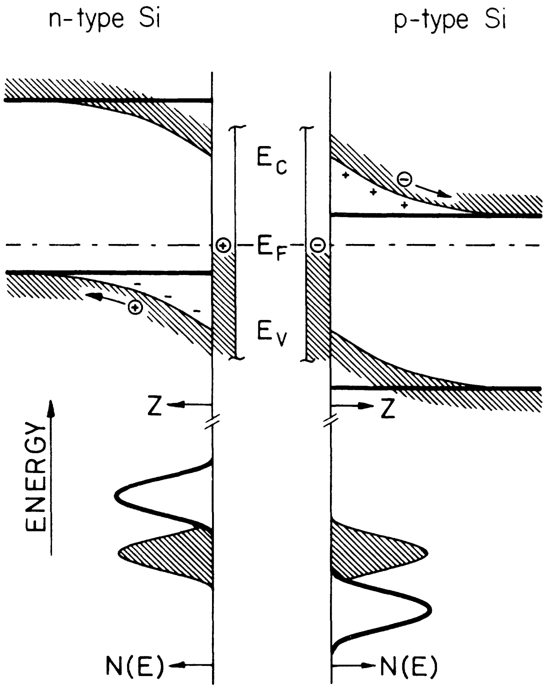

FIG. 3. In the upper part of the figure, schematic sketches of the surface and the depletion layer are depicted for a *p*-type Si sample (left) and an *n*-type Si sample (right). In the lower part of the figure, core-level spectra $N(E)$ from the topmost surface layer are drawn. Hatched bands and spectra are for 300 K and the heavy-lined bands and spectra are for 20 K. Conduction-band minimum E_C, Fermi level E_F, and valence-band maximum E_V are indicated for the 300 K case (see text).

electron-hole pairs in the bulk, in the depletion layer, and at the surface by absorption of photons with an energy larger than the band gap. At the surface, also, the SS get involved, and transitions under the influence of sub-band-gap light become possible. It is quite obvious that this includes a number of different excitation, transport, and recombination processes, which are difficult to separate even for well-defined samples.

The SPV can be understood on a qualitative basis as follows. Considering the *n*-type case, the holes, created in the depletion layer, diffuse to the surface and may accumulate there if the recombination at the surface is frozen out. This accumulation of holes compensates the negative charge in the SS, thus reducing the driving force for the band bending, which is therefore reduced until the bands are flat. This explains why the SPV saturates. For the flat-band situation there is no longer a preferred diffusion of holes towards the surface. Thus, for *n*-doped samples, the SPV shifts the bands at the surface downwards, and for *p*-doped samples, upwards. It is quite clear that the surface is not in electronic equilibrium with the bulk while the photon beam is impinging onto the surface. For a *p*-type sample, one expects photoemission from states above the bulk Fermi level, as was observed by Demuth *et al.*[9] In the case of the Si(113) surface, the density of states around E_F is too small to be observable by UPS. It is to be noted that differences in mobility of excess electrons and holes (Dember voltage) are considered not to influence the SPV.[6]

In conclusion, we believe that size and direction of the observed shifts and the saturation behavior are well explainable by assuming that an SPV is built up. It is interesting to note that the effect is no longer connected with a photon energy only somewhat larger than the band-gap energy, but it also operates at a much higher photon energy of 108 eV, as in our case. Furthermore, also the second effect of the narrowing of the core-level spectra can be explained to some extent in the same model. We will come back to this point after the following discussion of the measured band-bending values for the Si(113) surface.

B. Band bending at the Si(113) surface

For the quantitative determination of the band bending at the Si(113) surface, we did some curve fitting, following a procedure given in the literature.[16] First we subtracted a parabolic background. Then we separated the $2p_{1/2}$ and $2p_{3/2}$ components. A best fit was established for a spin-orbit split of 605 meV and an intensity ratio of the $\frac{1}{2}-\frac{3}{2}$ components of 0.55. The spin-orbit value is close to our recent result[15] and also very close to the literature values of 610 meV,[8] 0.62 ± 0.03,[17] and 611 meV.[18] One example for the decomposition is given in Fig. 4. The peak position could be determined with an accuracy of ±10 meV.

In Table I we have listed the core-level shifts as mea-

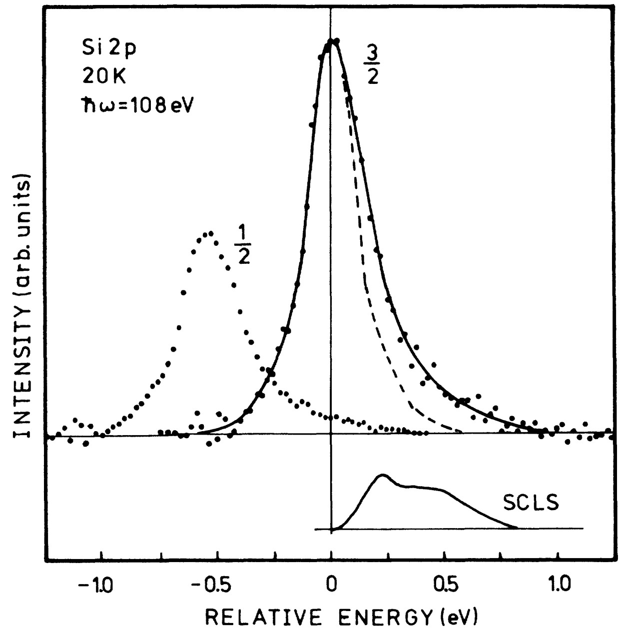

FIG. 4. Si $2p_{1/2}$ and $2p_{3/2}$ spin-orbit split components measured for the p-type Si(113) surface at 20 K. In the lower part, the surface core-level shifted (SCLS) part or the $\frac{3}{2}$ component is depicted.

sured and the band bending. The observed values have been corrected for the escape depth of the photoelectrons. The finite sampling depth for the Si $2p$ core-level photoelectron spectra influences our results as follows. The binding energy with reference to E_V is known to be E_B^{VB} (Si $2p_{3/2}$)$=98.74\pm0.15$ eV.[8,17] We can estimate the kinetic energy of the outgoing photoelectrons to be approximately 4 eV by considering E_B^{VB}, $\hbar\omega=108$ eV, the Si work function Φ_{Si} = 4.8 eV, and the pinning position of about 0.5 eV relative to E_V. The value of 4 eV is in good agreement with the value measured in our spectra. Electrons of this energy escape from several layers below the surface. We take $\lambda=12$ Å as the mean free path for inelastic scattering of the outgoing photoelectron in accordance with values measured for Si.[8] This value is somewhat smaller than the value from data compilations,[19] but is still large enough to recognize that our signal is averaged over several layers near the Si surface, i.e., the contribution from the first atomic layer is rather small. In this sense our measurements are "bulk sensitive." One has to keep in mind, however, that, compared to the Debye length, which is a measure for the width of the depletion layer and is of the order of several hundreds of Å, we still measure core-level binding energies at the surface. We prefer to use a photon energy of 108 eV, compared to the more surface-sensitive value of 120 eV, because in the bulk-sensitive mode the core levels are better resolved in energy, since they consist to more than 90% of one line only. The surface atoms experience a special shift of their binding energy because approximately one out of their four bonds is not saturated. To extrapolate the observed shifts to the first layer, we can assume a linear dependence of the surface potential. In this approximation, the change of potential is given by $\Delta V_S=\lambda(2n\,eV_S/\epsilon\epsilon_0)^{1/2}$, where n is the density of charge carriers and $\epsilon=11.9$ for Si. The correction to the exact value at the topmost surface layer amounts to 37 meV for the n-type sample and 12 meV for the p-type sample, as can be seen from the correction in column 2 of Table I, where the core-level shifts are increased by this amount. We believe that this correction is deduced from well-documented data, so that the uncertainty introduced is not too large. The systematic error is to be on the order of ±30 meV. Compared to these values, our accuracy for the measured values is better, i.e., on the order of ±10 meV. Therefore, the systematic uncertainties determine the overall accuracy of our band-bending values, indicated in Table I.

It may be worth mentioning that we are not taking into account that the width of the indirect gap for Si changes from 1.12 eV at 300 K to 1.17 eV at 0 K.[1] In a first approximation, this change is symmetrically distributed between the conduction and the valence bands. Therefore, the more meaningful reference level for the $2p$ core level is the midgap position. We argue that to first order this level is changed with temperature only by band bending. One further question is not clarified yet. In principle, we would expect that E_F moves with decreasing temperature towards the band edges. This shift would add up to the change in band bending, i.e., the observed core-level shifts would be composed of the changes in band bending and in E_F position. In our case, the deduced band-bending values would be reduced by 120 meV for the p-type sample and by 50 meV for the n-type sample. We believe that this effect is not operating, since otherwise we would have found a gap of 170 meV for the In and Ga

TABLE I. Experimental core-level shifts, corrections, and the band bending derived from it. The minus sign is for a downward move of the level and the plus sign for an upward move. Conduction band (CB). Valence band (VB).

	Experimental core-level shift (meV)	Experimental core-level shift corrected for escape depth (meV)	E_F position in the bulk relative to band edges (meV)	Band bending (meV)	E_F pinning position above VB (meV)
n-type, 2.3×10^{18} cm^{-3}	+413	+450	50 (CB)	+450±30	620
p-type 2.5×10^{17} cm^{-3}	− 463	− 475	120 (VB)	− 475±30	595

Schottky-barrier heights between the *n*-type and *p*-type surfaces in our recent measurements.[20] Demuth *et al.*[9] were led to the same conclusion by the very good agreement between their band-bending data and values from the literature derived with different methods for the Si(111) surface. The question as to why this effect is not observed is not answered at the moment. It may be a result of the nonequilibrium nature of the SPV process.[9]

From the data given in Table I a consistent scheme of band bending and E_F pinning at the Si(113) surface can be drawn. E_F is pinned at 595 meV above E_V for the *p*-type sample and at 620 meV above E_V for the *n*-type sample, so that a difference of 25 meV between these positions exists. This difference is smaller than the above-given accuracy of ±30 meV, so that E_F is pinned at the same position. The small difference may even be meaningful, since we expect some positive charge in these states for the *p*-type sample, and some negative charge for the *n*-type sample, which would shift E_F somewhat downwards or upwards in accordance with the observed difference. We do not know the character of these states, whether they are intrinsic or defect induced. Valence-band photoemission indicates that the density of these states is too small to be seen.[15] We intend to study this question further by high-resolution electron-energy-loss spectroscopy. With this method it was found that a partly filled band of SS leads to a considerable broadening of the elastically reflected beam via electron-hole-pair creation.[21]

C. Line shape and half-width in energy of the Si 2*p* core level

In Fig. 4, we have depicted the result of the curve-fitting procedure described above. This example is especially well resolved in energy. The full width at half maximum (FWHM) is 310 meV, and it is exactly the same value for both components. For the *p*-type sample the FWHM changes from 425 meV at 300 K to 310 meV at 20 K, which is a rather dramatic effect. We interpret this shift in part as due to the lifting of the band bending at 20 K. Under flat-band conditions, no broadening from a change of surface potential through the escape depth is expected. Interestingly, the observed reduction in FWHM is much larger than expected from band bending alone. In our discussion above, we have explained our correction for the surface potential by 12 meV assuming a mean free path of 12 Å for the outgoing photoelectrons. More than 90% of the signal originates from a depth of twice the mean free path. Therefore, we estimate the maximum broadening of the core levels to be of the order of 25 meV due to the band bending at 300 K. Therefore, some interesting freezing out of electron-phonon coupling seems to play a role here. We will answer this question in future studies using an intrinsic sample, for which the band bending- and surface-potential-change part is expected to be small.

There is only one example in the literature for which the FWHM value is similarly small.[17] Interestingly, this was for an intrinsic sample for which no band bending is expected. There is a problem inherent in this very early result in that these authors found the FWHM of the $\frac{1}{2}$ component to be always by 100 meV larger than the value for the $\frac{3}{2}$ component.

The temperature effect on the FWHM is smaller for the *n*-type sample, for which it changes from 475 meV at 300 K to 425 meV at 20 K. At the moment, we do not take this too seriously, since these measurements have been made in a run of the experiments, before we turned to the *p*-type sample and detected the small linewidth there. That means by measuring the *n*-type sample, we concentrated on the core-level shift itself and not so much on energy resolution. Furthermore, a worse resolution can have many trivial reasons; the important fact is the extremely well-resolved spectrum for the *p*-type sample at 20 K, which we have reproduced several times.

The line shapes of the $\frac{1}{2}$ and $\frac{3}{2}$ components are identical, as expected. Both peaks show an asymmetry to lower binding energies, which is indicated for the $\frac{3}{2}$ component. For this purpose, we have mirrored the low-energy half of the peak. Some additional intensity is to be recognized in the actually measured tail. This difference, which is depicted in the lower part of the figure, is due to Si atoms in the topmost layer. They are known to experience some surface core-level shift (SCLS) to smaller binding energy.[18,22] Interestingly, the shift to lower binding energy (noted at S_2) was attributed to the so-called adatoms at the Si(111) 7×7 surface, whereas the atoms in the first Si layer below exhibited a SCLS to higher energies (S_1). At $\hbar\omega = 108$ eV only S_1 was found by these authors.[16] We are in accordance with other authors, who have found that the main part of the SCLS lies at the lower-binding-energy side.[22,23] We will return to this question in a future contribution. The width of our feature points to a distribution of different sites in the topmost layer, what seems not unreasonable with respect to the rather large 3×2 unit cell for the clean Si(113) surface. The distribution of SCLS of the Si(113) surface differs from that of the Si(111) 7×7 surface, which is an important input for any model for the Si(113) surface.

By symmetrization of the $\frac{3}{2}$ peak in Fig. 4, its width is further reduced from 310 to 260 meV. The remaining curve can be fitted by a Lorentzian profile. At this point, it is worth asking for the intrinsic width of the Si 2*p* core level. The energy resolution of our spectrometer is 100 meV for a pass energy of 5 eV, as tested many times at the secondary-electron threshold. If we estimate the resolution of the monochromator to lie between 100 and 150 meV, we arrive at an intrinsic width for the Si $2p_{3/2}$ component of 190–220 meV, in agreement with the early result of Eberhardt *et al.*[17] and of Miller *et al.*[18] Therefore, from our measurement, an intrinsic width of 205 ± 30 meV is deduced.

IV. CONCLUSION

We have measured the E_F pinning position and band bending for the clean Si(113) 3×2 surface for both *n*-type and *p*-type samples. We used the effect of surface photovoltage, which saturates below 50 K, to determine the band bending. This method, combined with the highly accurate core-level spectroscopy, is used here for the first time. We have found that E_F is pinned within 25 meV at the same energy near midgap position for both samples.

We argue that a change of band bending is responsible for the observed core-level shifts. We have observed a strong decrease in energy width for the p-type sample at 20 K. Only 25 meV of the overall effect of 115 meV can be explained by the loss of the gradient in the surface potential at 20 K. The greater remaining part must be due to some freezing out of phonons at 20 K. Finally, we deduce an intrinsic width of the Si $2p$ core level of 205 ± 30 meV at 20 K.

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