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Surface core-level shifts of Si(111)7×7: A fundamental reassessment

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Extremely well resolved Si $2p$ core-level spectra from the clean Si(111)7×7 surface have been obtained at ~100 K. Surface-shifted components become visible to the naked eye. Contributions from the constitutive entities of the complex 7×7 reconstruction, i.e., rest atoms, adatoms, pedestal atoms, and dimer atoms are clearly identified. This puts into new perspective the spectroscopy and physics (structure and electronics) of this prototypical surface.

I. INTRODUCTION

The physical properties of clean, well-reconstructed silicon low-index surfaces have been extensively studied in the past, in particular with the aim of linking the causal relationships between their geometric and electronic structures. In the last few years high-resolution (HR) synchrotron-radiation photoemission, especially HR photoelectron core-level (CL) spectroscopy, has played a major role to this end. In this respect, particularly well-resolved Si $2p$ core-level spectra from the clean, cold Si(001)$c(4\times2)$ surface have shown surface-shifted components originating from both up and down atoms of asymmetric dimers, the building blocks of this low-temperature $c(4\times2)$ and of the 2×1 room-temperature (RT) reconstruction, as well as second-layer atoms.[1] For the study of the electronic properties of silicon surfaces, chemically prepared, long-range-ordered, ideally hydrogen-terminated Si(111) surfaces are model systems. The perfection of these surfaces leads to remarkably sharp features in both the valence-band and core-level HR spectra. The narrow Si $2p$ lines [0.160 meV full width at half-maximum (FWHM)] have yielded an upper limit of 35 meV for the core-hole lifetime broadening.[2]

The geometrical structure of the Si(111)7×7 reconstructed surface, given by the so-called dimer–adatom–stacking-fault (DAS) model,[3] is widely accepted. However, albeit the Si(111)7×7 surface is one of the most well-studied surfaces and despite the successes of HR CL spectroscopy in recent years at elucidating the geometric and electronic structures of many surfaces, e.g., typically for solving corresponding issues for the related Ge(111)$c(2\times8)$ and Ge(111)7×7-Sn surfaces,[4] there still remains no consensus as to the assignment of the only distinct surface component (so-called $S2$), appearing as a small bump, shifted to lower binding energy (BE) as compared to the bulk component (B), for either rest-atom[5] or adatom emission.[6] Moreover, the standard decomposition scheme with only two surface-shifted components $S1$ and $S2$ used until now, from which these conflicting assignments resulted, has been recently seriously questioned with the crucial consequence that a radical revision of this traditional analysis has to be undertaken.[7]

Having just obtained extremely well-resolved Si $2p$ core-level spectra from a very well-ordered Si(111)7×7 surface we are now in the situation of providing in the present paper an exact deconvolution scheme which gives insights into Si(111)7×7 spectroscopy and opens up new perspectives on the use of Si $2p$ HR CL spectroscopy for surface structural determinations, e.g., typically through chemical-shift low-energy photoelectron diffraction.[8,9]

As mentioned above, Si $2p$ core lines from the 7×7 surface obtained with medium resolution until now were decomposed into only three components: B (bulk), $S1$ (surface component 1, eventually considered as resulting from the adatoms plus the pedestal atoms underneath binding to them[5]), and $S2$, at the center of the controversy.[6]

The Si(111)7×7 surface exhibits the dimer–adatom–stacking-fault reconstruction;[3] it consists of 7 rest atoms, 12 adatoms, 36 pedestal atoms, 18 dimer atoms, and a corner-hole structure in each 7×7 unit cell which is further split into faulted and unfaulted halves. The adatoms are threefold-coordinated atoms bonded above the first Si(111) double layer; the rest atoms are also threefold-coordinated surface atoms, six of which lie in the first double layer plus one lying in each of the corner holes. Indeed, looking at the complexity of the 7×7 reconstruction one would expect more surface-shifted components than just $S1$ and $S2$: in principle, as many as the different surface arrangements, since inequivalent sites may rigorously have slightly different core-level shifts in the photoemission spectra. It is probable that many of them cannot be resolved, but still several contributions should be identified, especially the rest atoms, adatoms, pedestal atoms, and the dimer ones.

II. EXPERIMENT

We show in Fig. 1 a set of high-resolution spectra taken with various photon energies, corresponding to different surface sensitivities, from a well-ordered 7×7 surface. It was prepared at the MAX synchrotron radiation facility in Lund, Sweden using an *n*-type (P-doped) Si(111) wafer preoxidized using an etching method[10] and cleaned *in situ* by resistive heating up to $\sim950\,^\circ$C, which gave rise to a very sharp 7×7 low-energy electron-diffraction (LEED) pattern. The high quality of this surface is further ascertained by the exceptionally sharp surface-state emission (tick marks) observed in the valence-band spectrum of Fig. 2. During this annealing process the pressure was kept below 5×10^{-10} torr, the base pressure in the chamber being 6×10^{-11} torr. All core-level spectra shown in this paper were recorded after cooling to ~100 K, except two of them recorded at RT, presented for comparison. Cleanliness of the sample was checked from the valence band and with photoemission spectra from the O 1*s* and C 1*s* core levels which, as a matter of fact, were never detected. Photoemission experiments were performed using a modified SX700 plane-grating monochromator and a large hemispherical electron energy analyzer with an acceptance angle of $\sim\pm5°$. The angle between the incident photon beam and the direction of the sample normal was 40°. The total energy resolution for all the investigated photon energies was below 80 meV; it was measured from the width of the Fermi edge of a palladium foil in electrical contact with the samples.

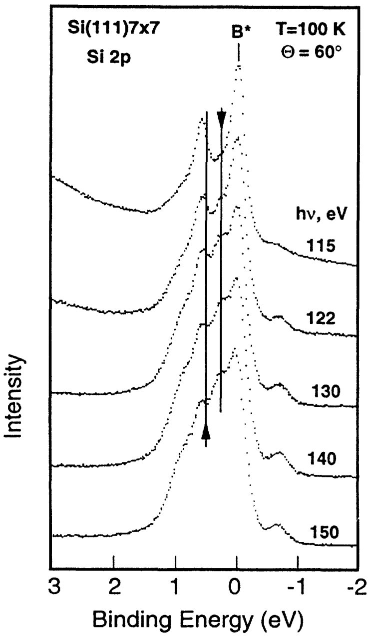

FIG. 1. A set of Si $2p$ core-level spectra acquired from the cold Si(111)7×7 surface at an emission angle of 60° for various photon energies as indicated. The zero of the binding-energy scale is taken at the position of the Si $2p_{3/2}$ line of the bulk component B^*.

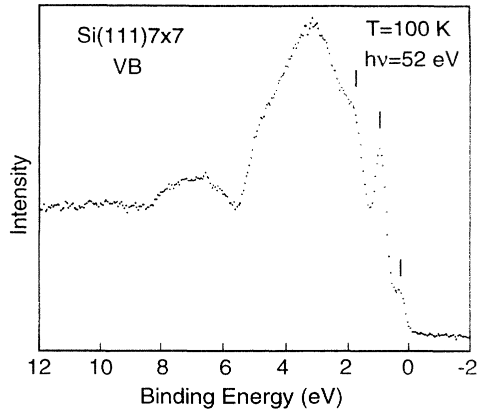

FIG. 2. Normal-emission valence-band photoemission spectrum of the cold Si(111)7×7 surface.

III. SPECTRAL SHAPES

We note that on the same beamline, with the same experimental setup, Landemark *et al.*[1] and Göthelid *et al.*[4] obtained the best resolved spectra ever obtained until now, respectively from the clean Si(100)$c(4\times2)$ and 2×1 and Ge(111)$c(2\times8)$ surfaces. From these spectra they could clearly reveal, respectively, four surface-shifted components derived from the clean Si(100)$c(4\times2)$ and 2×1 surfaces and three surface-shifted components ($S'1$,$S'2$,$S'3$) from the clean Ge(111)$c(2\times8)$ surface. This last result is of particular relevance for our study since the Ge(111)$c(2\times8)$ reconstruction, much simpler than the Si(111)7×7 one, consists also (and only) of rest atoms, adatoms, and pedestal atoms, which were clearly identified in the Ge 3*d* core-level spectra; $S'1$ with the largest intensity, shifted by -0.23 eV (i.e., to lower BE relative to the bulk line) corresponds to the pedestal atoms, $S'2$ seen as a foot at low BE (-0.73 eV) springs from rest-atom emission, while $S'3$ on the high-BE side ($+0.17$ eV) originates from the adatoms. The rest-atom assignment of $S'2$ is supported by a theoretical study[11] [as a matter of fact carried out for the $S2$ component of the Si $2p$ spectra from the Si(111)7×7 surface] which predicts electronic charge transfer from the adatom dangling bonds to the rest-atom dangling bonds, resulting in an electronegative environment at the rest-atom sites, causing the core levels to shift to lower binding energies.

Figure 1 shows unprecedented features. The previous $S2$ bump is now seen as an individual peak at ~-0.70 eV (i.e., at low BE); furthermore, and without any data processing, these 7×7 spectra reveal the presence of several shifted components contributing to the line shape. Most evident is the $2p_{3/2}$ line indicated by the down arrow close to the sharp bulk B^* Si $2p_{3/2}$ line and shifted by $\sim+0.25$ eV (i.e., to higher BE). Another component shifted by $\sim+0.5$ eV indicated by the up arrow is further filling the valley between this last one and the bulk $2p_{1/2}$ line. In addition, the total widths of the spectra, the asymmetry seen on the high-BE side of the bulk B^* $2p_{3/2}$ line especially at $h\nu=115$ and 122 eV as well as the

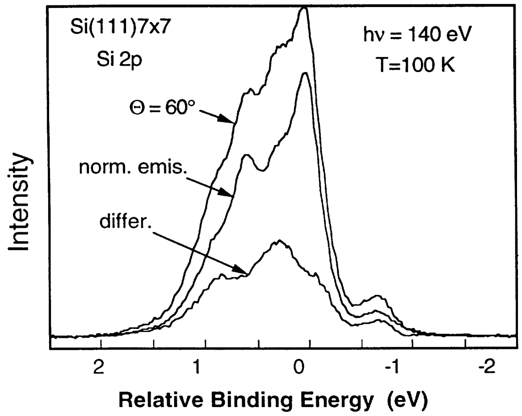

FIG. 3. Si $2p$ core-level spectra acquired from the cold Si(111)7×7 surface with $h\nu = 140$ eV for two different emission angles 0° (normal emission) and 60°, and their difference spectrum. A Shirley-type background has been removed prior to subtraction. Before subtraction the two spectra had been normalized to the same height of their bulk components.

tail noticeable on the low-BE sides indicate the presence of two additional components, one close to B^* and located at lower BE and another one located at high BE (shifted by $\sim +0.8$ eV). The difference spectrum between spectra recorded with $h\nu = 140$ eV, respectively at normal and 60° emission angles, shown in Fig. 3 convincingly confirms these observations.

IV. CURVE SYNTHESIS

More quantitative information is obtained by a least-squares fitting procedure in which the spectra are synthesized with different components consisting of spin-orbit-split Voigt functions. Our philosophy is to impose severe constraints on this curve synthesis by minimizing the number of free parameters involved but sill by utilizing the number of components required by the physics of the reconstruction.

We start with the most bulk-sensitive spectrum recorded at normal emission with a photon energy of 108 eV (Fig. 4). The bulk lines are fitted with a doublet corresponding to a spin-orbit splitting of 0.605 meV and a branching ratio of 2.05, close the statistical value $(l+1)/l = 2$, taking a full width at half maximum of the Lorentzian of $L = 35$ meV as determined earlier by Hricovini *et al.*[2] during their HR study of the ideally H-terminated Si(111) surface. The best fit is then obtained with a Gaussian FWHM $G_B = 210$ meV. This width is three times larger than the experimental resolution but it is ony 50 meV larger than that of the bulk component of the Si $2p$ spectra from the best Si(111):H surfaces at the same temperature measured with the same experimental resolution.[12] This extra broadening may be explained eventually by defects and/or local variations of the Fermi-level position (inhomogeneous band bending). Defects are always observed in scanning tunneling microscopy but we think that this broadening is rather inherent to the 7×7 reconstruction which induces large strains even in deep layers. It has been demonstrated, for instance, that strain could shift the position of Si $2p$ core levels by roughly 20–50 meV per % volume change.[13] Surface contributions are also visible in this spectrum, although acquired in a bulk-sensitive mode, but they can be better examined by analyzing spectra taken in more surface-sensitive conditions.

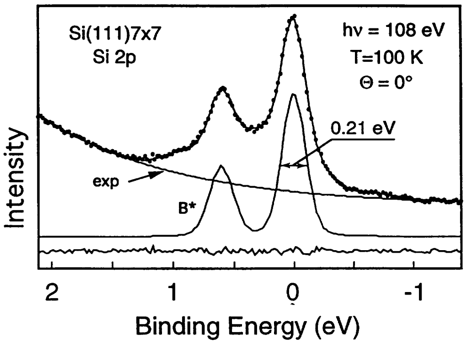

FIG. 4. Normal-emission Si $2p$ core-level spectrum from the cold Si(111)7×7 surface recorded at $h\nu = 108$ eV. The bulk component B^* is represented by a spin-orbit doublet; spin-orbit splitting: 0.605 eV, Lorentzian FWHM: 35 meV, Gaussian FWHM: 210 meV; exponential background.

As examples we show in Fig. 5 the deconvolution of the most surface-sensitive spectra taken at both RT and 100 K with $h\nu = 140$ eV and, respectively, normal and 60° photoemission angle. The position of the bulk component B^*, the binding energy of which was precisely determined from the spectrum recorded previously in bulk-sensitive mode (see Fig. 4) was fixed (we recall that we recorded the Fermi edge from the Pd foil each time the photon energy was changed). The same linewidth (spin-orbit splitting $= 0.605$ eV, $G_B = 210$ meV at 100 K) was imposed. In practice the B^* $2p_{3/2}$ line coincides with the maximum of each spectrum which appears, as a matter of fact, as a spike due to the narrow width of the B^* $2p_{3/2}$ line. Accordingly the spin-orbit splitting of all surface doublets was also fixed at 0.605 eV, while the Lorentzian FWHM of each component was constrained to 35 meV.

The number of these surface contributions and their energy positions relative to the bulk component B^* were inferred from the examination of the overall shapes and of the difference spectra as discussed above. An integrated background of Shirley type was also used. We thus introduced at first five surface-shifted components, three on the high-BE side, two on the low-BE one. Reasonably good fits could be obtained in these conditions with the same Gaussian FWHM $G_S = 310$ meV at 100 K for all surface contributions. However, locally, a poor adjustment, clearly noticed by visual inspection, and especially pronounced in the spectrum of the residuals, systematically present in all spectra just below the well-resolved low-BE component, imposed the presence of a small additional *single* line S^* (with the same values of $L = 35$ meV and $G_S = 310$ meV).

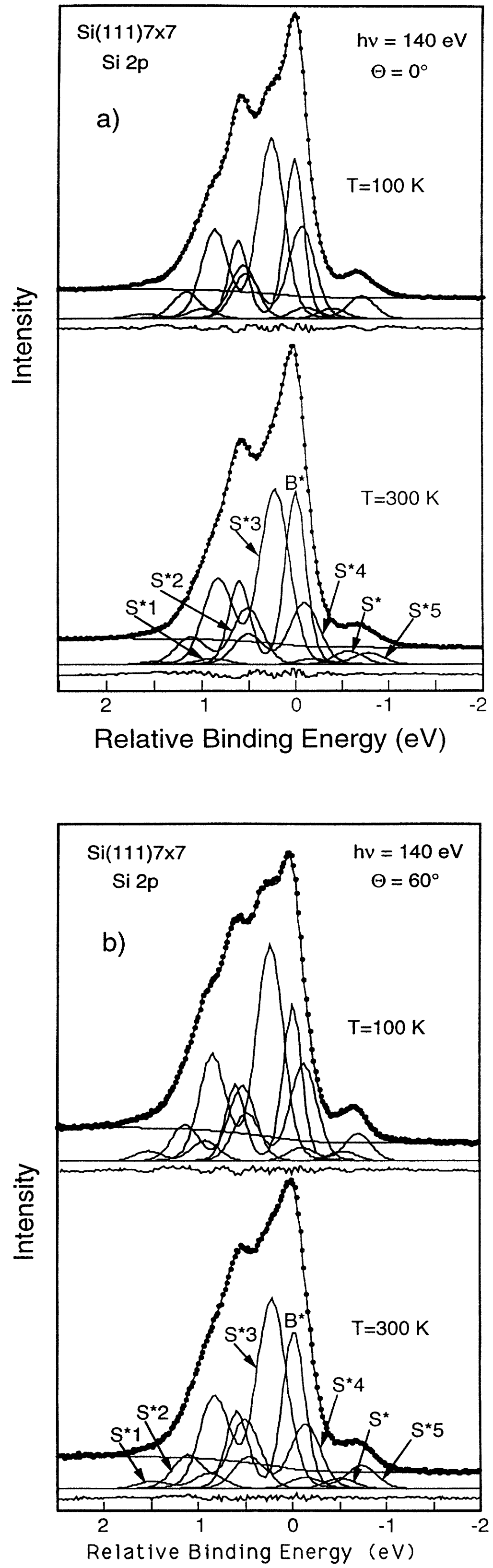

FIG. 5. Normal (a) and 60° (b) emission Si $2p$ surface-sensitive core-level spectra from the cold (top) and RT (bottom) Si(111)7×7 surface taken at $h\nu=140$ eV. The different contributions introduced in the fit are discussed in the text.

TABLE I. Fitting parameters (including an integrating background) for the Si $2p$ spectra. All energies are in eV. The Lorentzian and Gaussian widths refer to the full width at half maximum. Binding-energy shifts are referred to the bulk components. LT indicates low temperature.

Spin-orbit splitting	0.605
Branching ratio	2.05
Lorentzian width L	0.035
Gaussian width G_B	0.21 (LT); 0.31 (RT)
Gaussian width G_S	0.25 (LT); 0.35 (RT)
Surface shifts	S^*1: $+0.90$; S^*4: -0.10
	S^*2: $+0.50$; S^*5: -0.70
	S^*3: $+0.24$; S^*: -0.41

Then all low-temperature spectra taken between $h\nu=108$ and 150 eV, both at normal and 60° emission angle, could be extremely nicely fitted with these six surface contributions consisting of five spin-orbit-split doublets (S^*1–S^*5) and one singlet line S^*. From one spectrum to the other the positions of these surface lines remain practically unchanged, thus assessing the reliability of the decomposition; only their relative intensities varied (the parameters used in the analysis of the spectra are summarized in Table I). The same was true for the spectra measured at RT, the only change being a 40-meV enlargement of each component ($G_B^*=250$ meV; $G_S^*=350$ meV), due to phonon broadening; besides this 40-meV broadening compares fairly well with the values derived by Taleb-Ibrahimi *et al.*[12] for the ideally H-terminated Si(111) surface.

We note indeed the 100-meV extra broadening (at 100 K) of the Gaussian FWHM of the surface-shifted components as compared to the bulk line. Leaving aside defects which give probably some contribution (but unknown) to this extra broadening we may assume that a large part of it stems, for each surface component, from an unresolved shift due to the difference in the electronic structures of the two faulted and unfaulted halves of the 7×7 unit cell and also, as mentioned above, from the larger strain in the first Si double layer as compared to the layers beneath due to the complexity of the reconstruction.

V. SPECTRAL SIGNATURES

Having thus rigorously determined the number of components building the Si $2p$ CL spectra from the Si(111)7×7 surface (six contributions in addition to the bulk one), their assignments now rely on what we know of the physics of the 7×7 reconstruction and on the comparison with the Si $2p$ deconvolution of the ideally H-terminated Si(111) surface on the one hand[2,12] and with the deconvolution of the Ge $3d$ core-level spectra from the closely related Ge(111)$c(2\times8)$ and Ge(111)7×7-Sn surfaces on the other hand.[4]

For the latter Ge(111) surfaces the strongest surface peak $S'1$ at -0.23 eV relative binding energy was attributed to the largest surface atom population, that is, to the second-layer atoms binding the adatoms. For the same reason we can assign S^*3, shifted 0.24 eV to higher BE, to the corresponding pedestal atoms (36) in the Si(111)7×7 structure. The opposite shift of the pedestal-atom contributions for Si(111) and Ge(111) surfaces is not a problem since the two reconstructions, although including the same entities (rest atoms and adatoms), differ nevertheless substantially, and further differences in the charge transfer may be also expected simply because the adatom–to–rest-atom ratios are not similar in the two structures.

The S^*5 component, shifted 0.70 eV to lower binding energy, with an intensity of 0.14 of the S^*3 intensity (N.B., we take as a reference the most surface-sensitive spectrum, recorded with $h\nu = 140$ eV and 60° emission angle), is indeed attributed to the rest atoms as generally agreed[4,5] (except by Carlisle *et al.*;[6] this question will be addressed later) and as supported by a theoretical study,[11] which predicts electronic charge transfer from the adatom dangling bonds to the rest-atom dangling bonds. With simple counting arguments the expected intensity ratio should be $6/36 = 0.16$; the close experimental value we obtain reinforces the rest-atom assignment.

The last argument of Carlisle *et al.* in favor of an adatom (instead of a rest-atom) assignment of this low-BE component relies on a surface extended x-ray-absorption fine-structure (SEXAFS) type of analysis of the oscillations of the $S2$ over B intensity ratio versus photon energy.[6] We note, however, that the very broad component B of the standard decomposition corresponds in fact to several contributions: at least the actual bulk component B^*, the pedestal-atom contribution S^*3, and the dimer-atom contribution S^*4 (discussed next). The intensity ratio of $S2$ to B has thus no clear physical significance and the database on which the EXAFS-like analysis has been carried out is improperly sorted out from the curve-fitting synthesis. Hence the claim that $S2$ corresponds beyond doubt to the adatoms relies on dubious arguments.[7]

The intensity of S^*2 is 0.36 that of S^*3, in fairly good correlation with the occupation ratio $\frac{1}{3}$ corresponding to adatoms; its shift to higher BE, according to the argument on the charge transfer given above, indeed confirms the adatom origin of this contribution as in the case of the Ge(111)$c(2\times8)$ reconstruction [we recall that the corresponding adatom contribution vanished in the case of the Ge(111)7×7-Sn surface when Sn has replaced the Ge adatoms[4]].

The S^*4 component, at -0.10 eV BE, the closest to the bulk line, has an intensity ratio to the S^*3 one of 0.43, in good agreement with the ratio 0.5 of the number of dimer atoms (18) to the number of pedestal atoms (36), taking into account the fact that the dimer atoms lie somewhat deeper than the pedestal atoms, are fourfold coordinated, and are thus expected close to the bulk line.

The tail seen on the spectra at the high-energy side is well adjusted by the introduction of the S^*1 doublet; its intensity is only 0.1 that of the S^*3 one; its binding energy at $+0.90$ eV either indicates a more electropositive environment than that of the adatoms, not so easy to identify in the 7×7 structure, or may eventually reflect a continuum of excitations due to the metallic character of the Si(111)7×7 surface,[5] but indeed, in such a case, a broad feature rather than a surface doublet should give the best adjustment. Hence an alternative suggestion proposed some years ago by Gelius *et al.*[14] to explain the tail seen on the high-energy side in their HR x-ray photoemission spectra (XPS) of Si $2p$ seems to be more appropriate here: this weak S^*1 component would then possibly spring from a shakeup structure.

We are now left with the single small component S^* necessary to fill properly the region intermediate between the S^*4 $2p_{3/2}$ and S^*5 $2p_{3/2}$ lines. Its relative weight is one-third of that of the S^*5 $2p_{3/2}$ line while its intensity dependence follows the same trend as that of the S^*5 component. We will propose its assignment in the light of recent calculations of the Si $2p$ core-level shifts for Si atoms at the ideally H-terminated Si(111) surface by Blase *et al.*[15] These authors found that the $2p_{3/2}$ line of a silicon atom at this surface is split into two peaks [$2p_{3/2}(-)$ and $2p_{3/2}(+)$] due to crystal-field effects (while no splitting is expected for the Si $2p_{1/2}$ line on the grounds of group-theory analysis). Perfect fits were then obtained by Taleb-Ibrahimi *et al.*[12] on the basis of the predicted splitting and relative intensity of the two $+/-$ peaks (calculated to depend strongly on the polarization of the incident photons). In this context we may eventually explain the presence of S^* by crystal-field splitting of the rest-atom core level.

VI. CONCLUSION

To summarize, having obtained with high-resolution synchrotron-radiation spectroscopy extremely well-resolved Si $2p$ spectra from the prototypical Si(111)7×7 surface, we have unambiguously identified the contributions (easily detected by visual inspection of the spectra) of the building entities of this complex reconstruction: the rest atoms at -0.70 eV binding energy, the adatoms at $+0.50$ eV BE, and the pedestal atoms at -0.24 eV BE, as well as the dimer atoms at $+0.10$ eV BE. We have thus put an end to the old controversy about the assignment of the so-called $S2$ component at low BE in the standard deconvolution scheme. With such a fundamental reassessment we give a new insight into the spectroscopy and physics (structure and electronics) of the Si(111)7×7 surface of paramount interest and we open up new routes, typically, for example, to site-resolved adsorption spectroscopic studies on a large scale, as compared to the local STM probe.

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