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High-resolution core-level spectroscopy of Si(100)c(4 × 2) and some metal-induced Si(111) $\sqrt{3} \times \sqrt{3}$ surfaces

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Received 19 June 2001

Published 23 November 2001

Online at stacks.iop.org/JPhysCM/13/11181

Abstract

High-resolution core-level spectroscopy has been applied to the Si(100)c(4 × 2) surface. A correct decomposition of the Si 2p spectrum of the clean surface is important for studies of adsorption of different species and the formation of various surface reconstructions. A very well-resolved Si 2p spectrum is presented for the Si(100)c(4 × 2) surface. The decomposition of this spectrum verifies the original decomposition scheme introduced by Landemark *et al* (Landemark E, Karlsson C J, Chao Y-C and Uhrberg R I G 1992 *Phys. Rev. Lett.* **69** 1588). Core-level spectra of some metal-induced Si(111) $\sqrt{3} \times \sqrt{3}$ surfaces are also presented. A comparison is made between the $\sqrt{3} \times \sqrt{3}$ reconstructions formed on Si(111) by In, a group III atom, and by Sn, a group IV atom. Both the 4d core levels of the adatoms and the Si 2p core-level spectra are discussed. Different kinds of deviation from an ideal surface may introduce a significant broadening of the core-level spectra. The effect of additional Ag atoms is discussed in the case of the Ag/Si(111) $\sqrt{3} \times \sqrt{3}$ surface. By reducing the surplus of Ag atoms on this surface, a Si 2p spectrum with extremely narrow components has been obtained.

1. Introduction

Core-level spectroscopy is one of the major spectroscopic techniques used to obtain information about the electronic and atomic structure of surfaces. The continuous improvements in terms of energy resolution and intensity have made it possible to obtain more detailed pictures of the surfaces as the development has progressed. With the use of tunable synchrotron radiation, the photon energy can be easily varied. Since the escape depth has a minimum in a certain kinetic energy range, described by the ‘universal’ curve, one can vary the surface sensitivity for a specific core level. Studies focused on the surface properties are often performed at the most surface-sensitive energy. For silicon surfaces the Si 2p core level with a binding energy of ≈ 100 eV relative to the Fermi level is well

suited for such surface-related studies. The highest surface sensitivity is normally obtained in the photon energy range 130–145 eV. Some variation is found between different surfaces, mostly due to diffraction, which will result in a modulation of the intensity of the different components of the core-level spectrum. The combination of the fairly sharp Si 2p core level and the high resolution achieved by many monochromators in the interesting photon energy range have made core-level spectroscopy quite fruitful as a tool for studies of various silicon surfaces.

This paper presents recent results for the clean Si(100) surface and a few examples of $\sqrt{3} \times \sqrt{3}$ reconstructions induced by In, Sn or Ag on Si(111). Detailed decompositions of the Si 2p core-level spectra from both the 2×1 and the $c(4 \times 2)$ surfaces of Si(100) were presented in 1992 by Landemark *et al* [1]. The decomposition scheme presented in that study has been used in many subsequent papers. Since 1992, the experimental energy resolution that can be achieved in a photoemission experiment has become significantly better. New data for the Si(100) $c(4 \times 2)$ surface are presented in order to check whether the decomposition of reference [1] is still valid.

The Sn/Si(111) $\sqrt{3} \times \sqrt{3}$ surface was, until recently, supposed to be well described by the T_4 model which describes a simple reconstruction with 1/3 ML of adatoms on an unreconstructed Si(111) surface [2]. With the discovery of the phase transition between the $\sqrt{3} \times \sqrt{3}$ and a 3×3 phase for Pb/Ge(111) and Sn/Ge(111) [3, 4] the interest in the Sn/Si(111) surface increased significantly. One aspect of the Sn/Ge(111) and Sn/Si(111) surfaces that is discussed here is the presence of two Sn 4d components in the core-level spectra. The two components have a natural explanation for a 3×3 surface but only one component should be present for a simple T_4 representation of the $\sqrt{3} \times \sqrt{3}$ surface. In this paper the Si 2p and the adatom core levels for two closely related $\sqrt{3} \times \sqrt{3}$ surfaces are compared; one is Sn/Si(111), a group IV adatom surface, and the other one is In/Si(111), a group III adatom surface.

Generally, the widths of the different core-level components are significantly broader than what is expected from the experimental resolution. This leads to an uncertainty in the decomposition of the spectra. The T_4 adatom surfaces, such as In/Si(111), are among the simplest surface reconstructions. But, because of different types of imperfection, such as vacancies, substitutional Si atoms and additional In, the surfaces always exhibit some degree of inhomogeneity which may lead to a broadening of the core-level spectra. Both the Sn/Si(111) $\sqrt{3} \times \sqrt{3}$ and In/Si(111) $\sqrt{3} \times \sqrt{3}$ surfaces show rather broad surface-shifted components. Of several different reconstructed Si surfaces, including simple surfaces such as H/Si(111) 1×1 and As/Si(111) 1×1 , we find that Ag/Si(111) $\sqrt{3} \times \sqrt{3}$ exhibits the narrowest Si 2p components with Gaussian widths as small as 65 meV. The interpretation of the surface components is discussed in terms of the HCT [5] model for the Ag/Si(111) $\sqrt{3} \times \sqrt{3}$ surface.

2. Si 2p core-level study of Si(100) $c(4 \times 2)$ surfaces

Si(100) is one of the most studied surfaces by various surface science techniques. The basic reconstruction element on the clean surface has been known for a long time. Cleaning *in situ* results in an apparent 2×1 surface periodicity at room temperature as evidenced by, for instance, LEED. When the temperature is lowered below approximately 220 K a $c(4 \times 2)$ diffraction pattern emerges. The basic 2×1 periodicity is explained by a pairing of the outermost silicon atoms. This leads to the formation of dimer rows along the surface for which the inter-row distance is double the distance between atoms on a hypothetical unreconstructed surface.

The main question that was discussed earlier was that of whether the dimers are symmetric or asymmetric. In the asymmetric version, one of the dimer atoms moves out from the surface and the other moves closer to the surface, resulting in a tilted dimer. Electronically the up-atom has essentially a doubly occupied dangling-bond orbital and the down-atom has a more or less empty dangling-bond orbital. In the symmetric dimer case, the two atoms would be at the same level above the bulk and they would have one dangling-bond electron each in a half-full orbital. The photoemission results from the 2×1 phase and the low-temperature c(4 × 2) phase have played a crucial role in the determination of the structure of the room temperature surface. Quite early theoretical calculations of the surface electronic structure pointed to the asymmetric dimer reconstruction since this model gave a semiconducting band structure in agreement with the results from angle-resolved photoemission studies [6, 7].

Surface-sensitive core-level spectroscopy has been used by several groups to gain information about the clean Si(100) surfaces. Early core-level spectra of the Si(100) 2×1 surface with moderate resolution show a surface-shifted component at approximately 0.5 eV lower binding energy than the bulk component [8]. A second surface component is also present at about 0.2 eV higher binding energy. These components have been interpreted as due to the surface dimers and to the second-layer silicon atoms, respectively. On the basis of intensity arguments, the dimer component has been interpreted as evidence for both symmetric dimers (one monolayer of silicon atoms) [9] and asymmetric dimers (half a monolayer of up-atoms) [8]. The surface component corresponding to the down-atoms is expected to be located at higher binding energies than the up-atom component.

Decompositions of Si 2p spectra obtained from the 2×1 and c(4 × 2) surfaces are shown in figure 1 (from Landemark *et al* [1]). Besides the earlier-identified surface components S and S', two more surface components were identified in these data. The existence of all components but SS can be verified just by an inspection of the raw data. A key observation important for the analysis of these data is that the 2×1 and c(4 × 2) surfaces exhibit very similar Si 2p spectra except that the 2×1 spectrum is broader because of the higher temperature. With silicon dimers as the basic building blocks, the c(4 × 2) surface has to involve asymmetric dimers in order to explain the larger unit cell. Thus one can conclude that the c(4 × 2) spectrum contains the surface components of an asymmetric dimer surface. The decomposition of the 2×1 spectrum is virtually identical to that of the c(4 × 2) surface which is strong evidence that the 2×1 surface also consists of *asymmetric* dimers.

In the original paper by Landemark *et al* [1], the following assignments were made for the different components. The S and SS components correspond to the up- and down-atoms of asymmetric dimers which results in an energy split of ≈ 0.55 eV between these two components. The S' component was assigned to the second-layer atoms in agreement with earlier studies. The origin of the fourth surface component C is more difficult to determine. A possible interpretation as suggested in the original paper is that it corresponds to emission from half of the third silicon layer. The results of a theoretical study of the surface core-level shifts of the S, SS and S' components compared very favourably with the photoemission results under the assumption of an enhanced screening of the down-atom core hole [10].

The fit of spectrum (b) in figure 1 was based on fits of many spectra obtained at different emission angles and photon energies. The presence of the S' component should be evident from the weak shoulder in the raw data. Component C is less evident since it does not lead to any clear shoulder in the spectrum. The presence of the C component is indicated by the shape of the curve near the valley between the S and B components. The existence of the SS component, which is associated with the down-atoms of the asymmetric dimers, was only revealed when all spectra for the different emission angles and the different photon energies were fitted in a consistent way. The decomposition scheme of the Si 2p spectrum from the

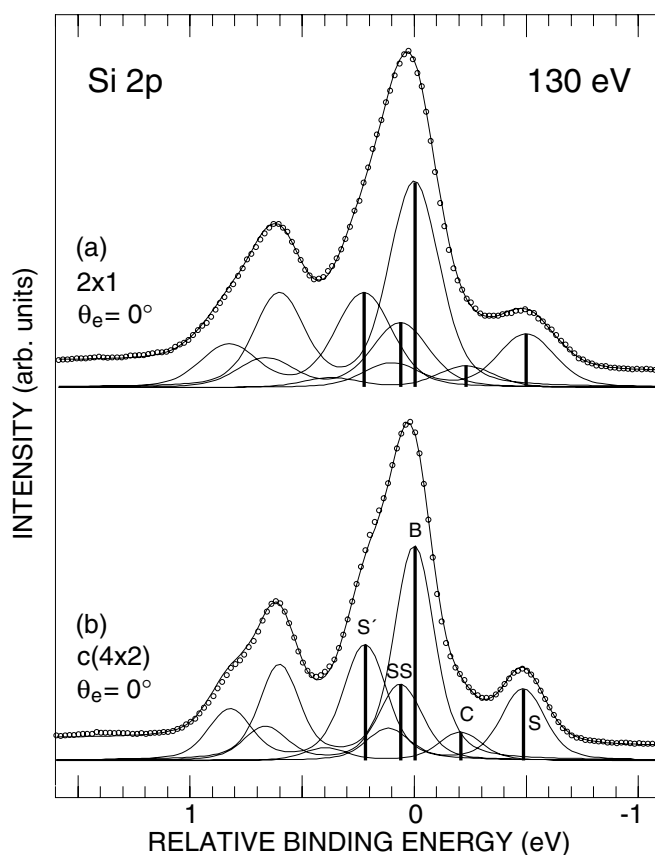


Figure 1. Decompositions of Si 2p photoelectron spectra from the Si(100) 2×1 surface (RT) in (a) and the $c(4 \times 2)$ surface (120 K) in (b) obtained with a photon energy of 130 eV, from reference [1].

Si(100) $c(4 \times 2)$ spectrum introduced by Landemark *et al* [1] is now widely used for the clean Si(100) surface. In many of these studies the experimental resolution is lower than in reference [1] and the shoulder corresponding to S' is not discernible. Starting from spectra that show less structure than spectrum (b) in figure 1, one may arrive at a different set of components when decomposing the Si 2p spectrum. An example of this is the work by Pi *et al* [11] who came to a different conclusion about the S' and SS components. Since decompositions of Si 2p spectra of the clean Si(100) surface are frequently used in the discussion of interaction between adsorbates and the Si(100) surface, it is important to once again check the validity of the decomposition in reference [1]. Does the component assignment survive measurements done with better resolution and/or at lower temperatures? The spectrum in figure 2 was obtained at ≈ 55 K with an energy resolution of ≈ 55 meV. This should be compared to a sample temperature of 120 K and a resolution of about 70 meV for spectrum (b) in figure 1. The spectrum in figure 2 which was recorded at BL 33 at MAX-lab, Sweden, using an angle-resolved analyser ($\pm 2^\circ$)(ARUPS10) is significantly better resolved than spectrum (b) of figure 1. The latter spectrum was measured at BL 22 which was equipped with an analyser with a $\pm 8^\circ$ acceptance angle (Scienta). The weak shoulder due to component S' in figure 1(b) is very clear in figure 2. This verifies the original assignment of a strong S' component. Furthermore, the introduction of the C component is also verified since the spectrum in figure 2 shows a clear shoulder at the corresponding position. Just from the appearance of the raw

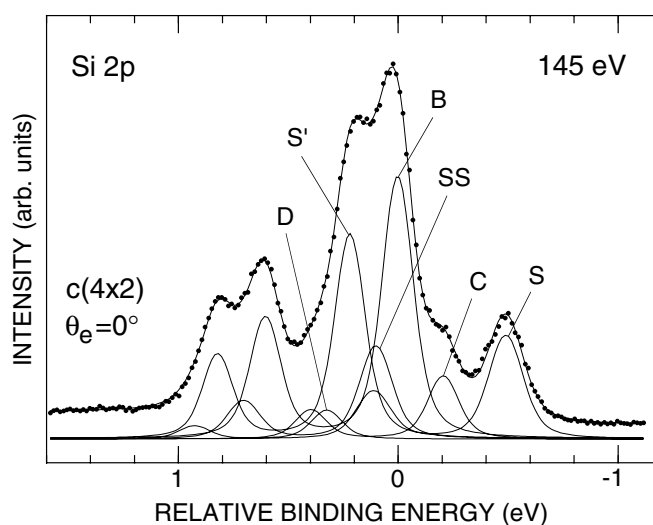


Figure 2. Decomposition of a high-resolution Si(100)c(4 × 2) spectrum measured at 55 K using a photon energy of 145 eV.

spectrum, the components S, C, B and S' are quite well specified, both in terms of energy positions and intensities. It is still not possible to identify the SS component just from the spectrum itself, since it does not give rise to any spectral feature. However, since the other components are quite well specified, the existence of the SS component is obvious after applying the fitting procedure. It turns out that the intensity of the SS component is very similar to that of the S component and that the overall fit to the spectrum in figure 2 is very similar to that of spectrum 1(b). In the original study there was some discrepancy between the fit and the spectrum near the valley around a relative binding energy of 0.4 eV. This tiny deviation between the fit and the spectrum is best observed in the 60° spectrum of reference [1]. A detailed inspection of the spectrum in figure 2 actually reveals a slight break in the curve form near this energy, which motivates the introduction of yet another component, D. The inclusion of this small component results in a very accurate description of the measured spectrum. The energy shifts of the different surface components of the c(4 × 2) surface have the following values (the values from figure 2 are in parentheses): S: -485 meV (-492 meV); C: -205 meV (-207 meV); SS: 62 meV (99 meV); S': 220 meV (217 meV). The energy shift of the D component, which was not identified in the initial study, was determined as ≈ 320 meV.

To conclude the results of the Si 2p study of the Si(100)c(4 × 2) surface, it has been verified that the decomposition introduced by Landemark *et al* [1] gives the proper description of the surface component contributions to the Si 2p line shape. The significantly higher resolution of the spectrum in figure 2 and the excellent fit lend further support to this decomposition scheme.

3. Core-level studies of some $\sqrt{3} \times \sqrt{3}$ surfaces: Sn/Si(111), In/Si(111) and Ag/Si(111)

Phase transitions in low-dimensional systems have recently attracted a lot of experimental and theoretical interest. A recent example is the transition that occurs on the Pb/Ge(111) [3] and Sn/Ge(111) [4] surfaces. The room temperature $\sqrt{3} \times \sqrt{3}$ reconstruction, with 1/3 monolayer of Pb or Sn adatoms, changes gradually to a 3 × 3 phase when the temperature is lowered. As determined from surface x-ray diffraction [12, 13], the transition to the 3 × 3 phase involves

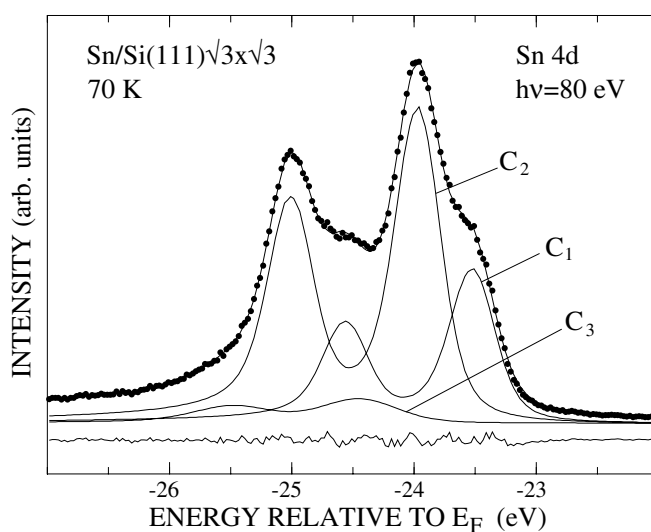


Figure 3. The Sn 4d core-level spectrum from the Sn/Si(111) $\sqrt{3} \times \sqrt{3}$ surface. The spectrum shows two major components, C₁ and C₂, which is inconsistent with a simple T₄ model of the surface.

vertical atomic displacements in the adatom layer which give rise to sharp 3×3 LEED spots. Photoelectron spectroscopy [14–16] exhibits an interesting and rather puzzling result, i.e. the $\sqrt{3} \times \sqrt{3}$ and 3×3 phases both show two Sn 4d components. The two components find a natural explanation in a 3×3 surface phase but are not directly accounted for in a $\sqrt{3} \times \sqrt{3}$ periodicity.

We have studied the Sn/Si(111) $\sqrt{3} \times \sqrt{3}$ surface using photoelectron spectroscopy, LEED and STM [17]. From the STM studies we concluded that the preparation method used for the LEED and photoemission studies results in a surface with a small number of defects. The total defect concentration is $<1.5\%$ with the Si substitutional atom as the most common one ($\approx 1\%$). Because of the strong interest in the $\sqrt{3} \times \sqrt{3}$ -to- 3×3 transition observed in the Sn/Ge(111) system, it is of some interest to study the Sn/Si(111) $\sqrt{3} \times \sqrt{3}$ surface also at low temperature. In contrast to the Sn/Ge(111) case, we were not able to identify any 3×3 diffraction spots despite the enhanced background sensitivity. It was therefore concluded that the Sn/Si(111) surface does not undergo the $\sqrt{3} \times \sqrt{3}$ -to- 3×3 structural transition observed for Sn/Ge(111), at least not for temperatures down to 70 K. Despite this difference, both the Sn 4d core-level and valence band spectra show the features which have been attributed to the 3×3 phase for the Sn/Ge(111) system [14–16]. It is quite intriguing that a second Sn 4d component shows up in the photoemission experiment also for the Sn/Si(111) system, even though there are no signs of a 3×3 phase.

Figure 3 shows a Sn 4d core-level spectrum recorded at 70 K (from reference [17]). The decomposition of the spectrum shows two major components, C₁ and C₂, and a minor component, C₃. The relative intensities of C₁, C₂ and C₃ are 30, 63 and 7%, respectively. Although the LEED pattern shows no sign of any 3×3 periodicity, the Sn 4d spectrum clearly shows two major components. The intensity ratio $63/30 = 2.1$ is close to the expected ratio of 2 for a 3×3 reconstruction. At room temperature the Sn 4d core-level spectrum looks very similar except for a general broadening and it decomposes into the same three components.

Some of the Sn atoms, which form bright hexagons around Si defects in STM images of the occupied states, are obviously different from the other Sn atoms and one might guess that

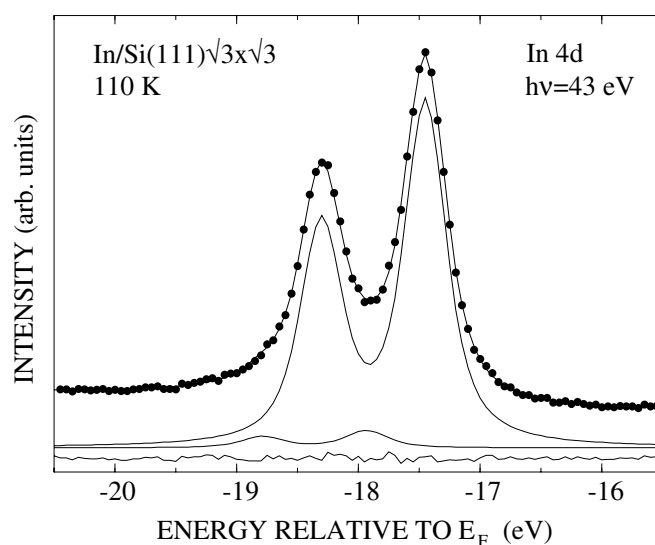


Figure 4. The In 4d core-level spectrum from the In/Si(111) $\sqrt{3} \times \sqrt{3}$ surface. The spectrum exhibits one major component, as expected from the T_4 model.

they give rise to the C_1 component [17]. A quick analysis shows, however, that the intensity of C_1 is far too high for such an assignment. The number of Sn atoms in the bright hexagons constitute less than 6% of the total number of Sn atoms which should be compared to the intensity of C_1 of 30%. With this big discrepancy one will have to look for an explanation of C_1 which involves the Sn atoms that appear to be ordered in a simple $\sqrt{3} \times \sqrt{3}$ periodicity.

Dynamical fluctuations of the Sn-atom positions have been treated theoretically for Sn/Ge(111) in reference [16], where it was concluded that thermal fluctuations could lead to a situation where the Sn atoms are located instantaneously in either of the two vertical positions of a 3×3 phase. This could explain why a ‘time-averaging’ technique like STM shows a $\sqrt{3} \times \sqrt{3}$ periodicity near RT, and why the 3×3 diffraction gradually disappears with increasing temperature. Photoelectron spectroscopy, which works on a much shorter timescale, would however still show the essential features of the 3×3 reconstruction. One merit of the ‘dynamical fluctuation model’ is that it can explain the strong intensity of the extra Sn 4d component at RT and the small difference between low-temperature and RT spectra.

Another example of a simple $\sqrt{3} \times \sqrt{3}$ system is that formed by $1/3$ ML of In. The reconstruction is believed to be accurately described by the T_4 model. In this case the spectrum of the adatoms (In) is completely dominated by one spin-orbit-split 4d component (figure 4). There is just a tiny contribution from a second component which may be attributed to In atoms located on non- T_4 sites, corresponding to about 4% of the total intensity. The conclusion is therefore that In, a group III element, just gives rise to one 4d component as expected for the T_4 model.

Even though the Sn/Si(111) $\sqrt{3} \times \sqrt{3}$ surface does not transform into one with 3×3 periodicity that can be observed by means of LEED, it is quite obvious from the two Sn 4d components that the T_4 model in the simplest form is not applicable. A distortion involving up and down motions of the Sn atoms is most frequently discussed. Beside the adsorbate core levels, it is also of interest to study the Si 2p core levels of these two surfaces. Does the difference in the atomic structure also show up in the substrate core level? Figure 5 shows a Si 2p core-level spectrum from the In/Si(111) $\sqrt{3} \times \sqrt{3}$ surface. The spectrum, obtained

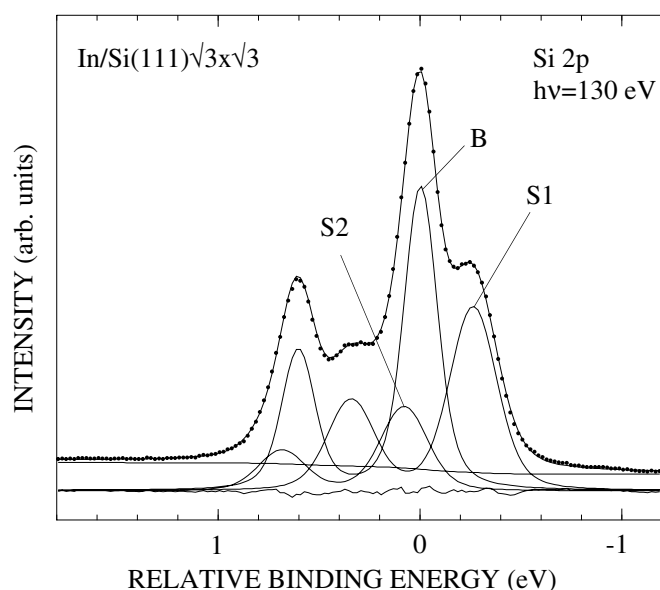


Figure 5. The Si 2p core-level spectrum from the $\text{In/Si(111)}\sqrt{3} \times \sqrt{3}$ surface (110 K). S1 is associated with the Si atoms that bond to the In adatoms. S2 may originate from second-layer silicon atoms.

at 110 K, shows essentially a bulk component, B, and a surface-shifted component, S1. The surface shift is 0.26 eV toward lower binding energy. A third component, S2, is necessary in order to obtain a high-quality fit of the spectrum. The shift of this component is about 0.1 eV to higher binding energy and the intensity corresponds to roughly 17% of the total intensity or $\approx 45\%$ of the intensity of the S1 component. It is quite hard to determine the exact intensity of this component since it is located very close to the bulk. Irrespective of the absolute intensity, we may conclude that there is a contribution from a third component at a binding energy slightly higher than that of the bulk component. If one wishes to guess the origin of this component, the substitutional Si atoms might be one choice. A fair amount of the In adatoms are actually replaced by Si atoms also on a well-prepared $\sqrt{3} \times \sqrt{3}$ -In surface. Of the order of 5–10% of the In atoms might be replaced by Si [18]. Another, more likely explanation for the third component is emission from the second Si layer, since the intensity of S2 is quite strong and since second-layer Si components appear slightly to the left of the bulk component in several cases. The Si 2p spectrum of the $\text{In/Si(111)}\sqrt{3} \times \sqrt{3}$ surface behaves as is expected, since it exhibits one major surface shift which can be attributed to the Si atoms which bond to the In adatoms. Turning to the $\text{Sn/Si(111)}\sqrt{3} \times \sqrt{3}$ surface, we may expect to observe some difference due to the non-equivalence of the Sn adatoms forming the $\sqrt{3} \times \sqrt{3}$ reconstruction. Figure 6 shows a Si 2p core-level spectrum from the Sn-induced $\sqrt{3} \times \sqrt{3}$ surface. Surprisingly, the general line shape is very similar to that for the In case. Except for differences in the intensities of the components, we notice that the decomposition results in two surface contributions similar to those of In/Si(111) . The major surface component is shifted about 0.34 eV toward lower binding energy. The third component is, like for the In case, shifted downwards by in this case ≈ 0.18 eV. It is not meaningful to make a close comparison between the intensities of the different components for the Sn and In cases since analysers of different types were used with different angle acceptances. The In/Si(111) data were recorded at BL 22 with a Scienta analyser and the Sn/Si(111) study was performed at

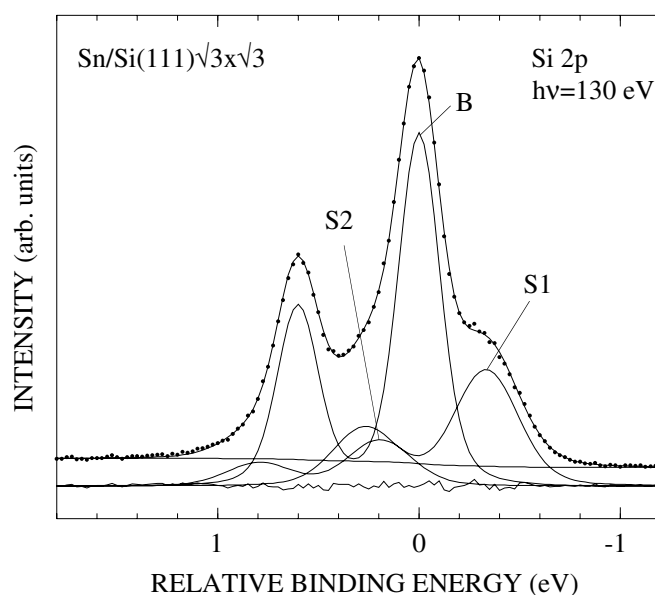


Figure 6. The Si 2p core-level spectrum from the Sn/Si(111) $\sqrt{3} \times \sqrt{3}$ surface (110 K). The surface shows two surface-shifted components S1 and S2. The decomposition is similar to the one for In/Si(111) $\sqrt{3} \times \sqrt{3}$.

BL 33 equipped with an angle-resolved ARUPS10 analyser. Despite this difference, we can conclude that there is no obvious qualitative difference between the Si 2p spectra from the two surfaces, which is in contrast to the result for the adatom core levels. The second surface component, S2, has an intensity which corresponds to about 40% of the S1 component. Since the number of substitutional Si atoms on the Sn/Si surface is quite low, $\approx 1\%$, an interpretation of the third component in terms of these substitutional atoms seems quite unlikely. The S2 component is therefore assigned to the second-layer silicon atoms.

The special character of the Sn/Si(111) $\sqrt{3} \times \sqrt{3}$ surface is not evident from the Si 2p spectrum. It seems that the clear difference observed between the two types of Sn adatom is not transferred down to the substrate or that the effect is too small to be resolved in the spectrum. Having said that, it is interesting to compare the actual widths of the different components. The Gaussian widths (full width at half-maximum) of B, S1 and S2 are 0.20, 0.33 and 0.33 eV, respectively. The corresponding values for the In/Si(111) $\sqrt{3} \times \sqrt{3}$ surface are 0.16, 0.23 and 0.23 eV. A Lorentzian width of 0.08 eV was used in all cases. The measured widths are in all cases significantly larger than the experimental resolution, which was around 70 meV in both cases. This leaves of course some room for a reinterpretation of the core-level data. For instance, should the rather broad S1 component for the Sn/Si surface be decomposed into two or more components? This may be the case, but since there is no indication in the spectrum of more than two surface components, it is reasonable to assume that the decomposition in figure 6 is correct.

The rather large difference between the experimental resolution and the widths of different components makes the decompositions a bit uncertain. Even when simple surfaces are studied there will always be some defects or disordered parts present on the surfaces. In the case of the 'simple' adatom $\sqrt{3} \times \sqrt{3}$ surfaces there are always a number of Si substitutional atoms present, which leads to an inhomogeneous surface, and as a consequence there will be an additional broadening of the core-level spectra. From our studies of different reconstructed

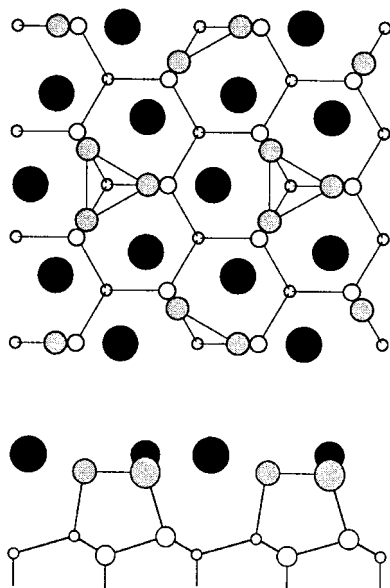


Figure 7. Top and side views of the HCT model of the $\text{Ag/Si(111)}\sqrt{3} \times \sqrt{3}$ surface. The black circles represent the Ag atoms while the other circles show positions of silicon atoms.

Si surfaces we have found that the $\text{Ag/Si(111)}\sqrt{3} \times \sqrt{3}$ surface shows very narrow Si 2p components indicating a high degree of homogeneity. This $\sqrt{3} \times \sqrt{3}$ surface is not described by the T_4 model; instead it seems to be arranged according to the HCT model [5], which is shown in figure 7. In this structure the top Si layer is missing and the Ag atoms as well as Si atoms form trimers on the surface. From this model we can expect to observe one surface-shifted Si 2p component from the outermost Si trimers and one component from the second-layer Si atoms, i.e. the Si atoms which bond to the Si trimer atoms. The third-layer Si atoms are in a bulk-like environment and may not give rise to any significant shift of the Si 2p core level. A high-resolution Si 2p spectrum from the $\text{Ag/Si(111)}\sqrt{3} \times \sqrt{3}$ surface obtained at ≈ 20 meV resolution at BL I311 at MAX-lab is shown in figure 8. This spectrum consists of one bulk component and two major surface contributions, S1 and S2. There are also two very small components at lower binding energy compared to the bulk component. The most striking observation is the very narrow widths of the components. The Gaussian width of the bulk component is only 65 meV and the widths used for the S1 and S2 components are 90 and 95 meV, respectively. A Lorentzian width of 80 meV was used for all components. The surface-shifted components S1 and S2 find a natural explanation in terms of the Si trimer atoms and the second-layer Si atoms, respectively. The two tiny components on the right-hand side of the spectrum may be related to some defect structure on the surface. Whatever is causing the tiny components, it seems to be 'intrinsic' to the $\sqrt{3} \times \sqrt{3}$ surface since another study has reported a similar contribution [19]. Studies of the $\text{Ag/Si(111)}\sqrt{3} \times \sqrt{3}$ surface in the literature show significantly broader Si 2p spectra [19, 20]. This difference is an example of what influence 'defects' may have on the Si 2p line shape. In a recent study of this surface we have shown that a small proportion of extra Ag atoms lead to a significantly broader Si 2p spectrum, which explains some of the differences between the spectrum of figure 8 and spectra in the literature [21]. The presence of a tiny proportion of extra Ag atoms (a few percent of a ML) on top of the $\sqrt{3} \times \sqrt{3}$ surface is well known. It leads to a partial occupation of an intrinsically unoccupied surface band [22]. At low concentrations of additional Ag,

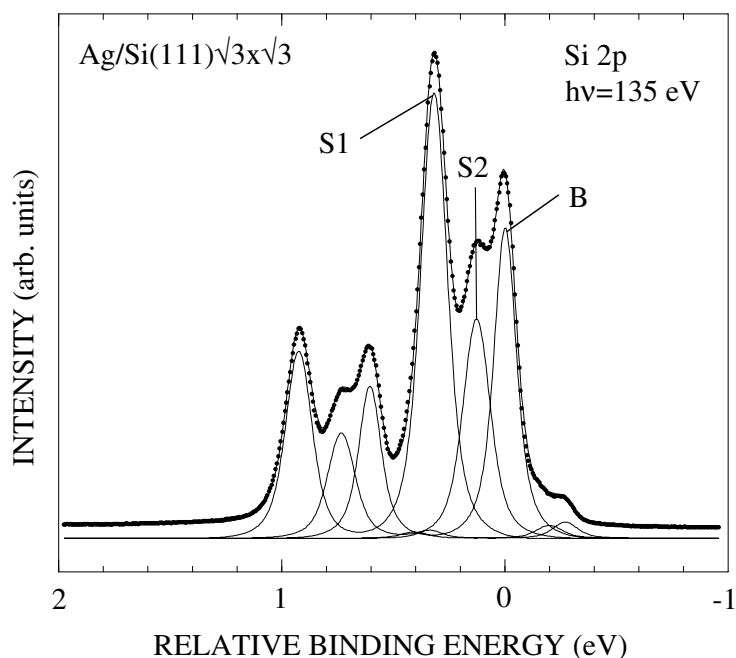


Figure 8. The Si 2p core-level spectrum from the Ag/Si(111) $\sqrt{3} \times \sqrt{3}$ surface. The spectrum was obtained at 100 K from a surface that had been annealed at 600 °C to remove a surplus of Ag adatoms.

the surface still shows a $\sqrt{3} \times \sqrt{3}$ periodicity. With an increasing proportion of Ag on top of the original $\sqrt{3} \times \sqrt{3}$ surface, there is a change of the reconstruction to a $\sqrt{21} \times \sqrt{21}$ and a 6×6 reconstruction provided that the temperature is low enough. To obtain the well-resolved spectrum of figure 8, the surface had to be carefully annealed at around 600 °C in order to remove ‘all’ additional Ag atoms. In this case there was no sign in the valence band spectra of any electrons in the unoccupied band. The Si 2p spectrum therefore represents the intrinsic $\sqrt{3} \times \sqrt{3}$ surface without any interference from extra Ag atoms. As is discussed in reference [21], this is an example which shows the importance of the surface preparation. Just a high-quality LEED pattern is not enough to define the surface quality. A tiny proportion of additional atoms, which are invisible to most surface science techniques, makes a large difference. The detailed preparation and the resulting quality of the surfaces become more and more important as the experimental resolution increases, when the intrinsic properties of different surfaces are studied. Alternatively, high-resolution core-level studies may instead be focused on different defect-induced core-level shifts. Some prior knowledge about the defect structure is of course very important for such studies. A combination of scanning tunnelling microscopy and core-level photoelectron spectroscopy is ideally suited for such studies.

4. Summary

High-resolution core-level spectroscopy has been applied to some of the most studied semiconductor surfaces. In the case of Si(100)c(4 × 2) the decomposition scheme introduced by Landmark *et al* [1] was verified. A highly resolved spectrum was presented which

showed clear shoulders indicating the energy positions of most of the components. A comparison between $\sqrt{3} \times \sqrt{3}$ surfaces induced by group III and group IV adatoms was presented. The In 4d core-level spectrum behaves as is expected, i.e. there is only one major 4d component as predicted by the T_4 model. The Sn 4d spectrum on the other hand shows two 4d components which seem to be related to a '3 × 3 character' of the Sn/Si(111) $\sqrt{3} \times \sqrt{3}$ surface. The influence on the substrate core level from the different behaviours of the adatoms was also investigated. The basic conclusion is that there is no obvious qualitative difference between the Si 2p spectra of these surfaces, i.e. there is no clear indication of the '3 × 3 character' in the Si 2p spectrum of the Sn/Si(111) $\sqrt{3} \times \sqrt{3}$ surface. However, since the components that are used to fit the spectra are quite broad, there might still be some unresolved difference.

Different types of defect result in a broadening of the core-level spectra. The Si 2p spectra are usually significantly broader than what is expected from just the experimental resolution. The Ag/Si(111) $\sqrt{3} \times \sqrt{3}$ surface exhibits the narrowest line shape of any reconstructed Si surface that we have investigated so far. A Gaussian width as small as 65 meV was found for a carefully annealed surface.

Acknowledgments

This paper is based on both published data and data which have not yet appeared in print. I would like to acknowledge my collaborators in the various projects. The Si(100)c(4 × 2) study was performed together with Dr T Kaurila and Dr Y-C Chao, the In/Si(111) studies involved Dr E Landemark and Dr Y-C Chao and finally the investigations of Sn/Si(111) and Ag/Si(111) were done together with H M Zhang and Dr T Balasubramanian. The support of the MAX-lab staff is also acknowledged. All studies were done with financial support from the Swedish Natural Science Research Council.

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